PART II
CHEMICAL SCIENCES

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ENVIRONMENTAL POLLUTION CONTROL AND PREVENTION MEASURE

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ABSTRACT

*Pollution **is** an unwanted change in the environment which involves the physical, biological and chemical changes involving air, water and land which affects the human life in one way or the other. Pollution has become a matter of serious concern in many parts of the world. Now a day's results of environmental pollution coming out in the form change in climate etc. Living organism cannot live by itself. Organisms interact among themselves. Every living thing such as plants, animals and human beings, as well as the physical surroundings with whom we interact, form a part of our environment. All these constituents of the environment are dependent upon each other. Thus, they maintain a balance in nature. The imbalance results into environmental problems. The environmental problems may be pollution which includes air, water, soil, extinction of species, instability ecosystems, waste accumulation, deforestation, breaking of ozone layer and global warming. India is facing critical air pollution problems, particularly in its urban centers. The problems as well as solutions are complex due to presence of variety of sources and pollutants. Realizing the intensity of the problems, the Government of India has made strategies for prevention and control of air pollution. The objective of this work is to provide an orientation to the methods that are applied to control and prevent environmental pollution in India.*

Keywords: *Pollution, Pollutants, environment, control, prevention*

INTRODUCTION

Pollution is a severe worldwide problem that urgently requires concepts for monitoring and implementation plans deriving solutions [1]. With the rapid rise of economic development and population, the process of urbanization is accelerating in India. The process of urbanism is accompanied with series of environment problems [2]. Over the course of the twentieth century, growing recognition of the environmental and public health impacts associated with anthropogenic activities has prompted the development and application of methods and technologies to reduce the effects of pollution. The environmental consequences of rapid industrialization have resulted in countless incidents of land, air and water resources sites being contaminated with toxic materials and other pollutants, threatening humans and ecosystems with serious health risks. More extensive and intensive use of materials and energy has created cumulative pressures on the quality of local, regional and global ecosystems [3].

Many options exist for dealing with pollution in the environment. A waste management hierarchy includes prevention, recycling, treatment, and safe disposal [4], with pollution prevention being the optimal choice. Pollution prevention does not include recycling after the pollution or waste has been produced, although it does include measures to avoid its generation and completely eliminating hazardous materials or potential contaminants [5].

METHODS OF POLLUTION PREVENTION

Environmental pollution can be controlled by different way. Some interpretations go further, defining pollution prevention as a means for completely eliminating hazardous materials or potential contaminants [5].

POLLUTION PREVENTION RESEARCH

Reducing environmental pollution requires specialized research, firstly to identify the types of Pollution and how they are being generated, and secondly to identify the most effective method for dealing with them. In Japan, government pollution research institutes at the local and national level are staffed with dedicated researchers engaged in medical and environmental studies on pollution. Examples include a long-term epidemiological tracking study on the effects of environmental pollution on the human body, launched in 1970, and studies of community health management systems for anticipated health problems.

ELIMINATION OR REDUCTION AT SOURCE

Elimination refers to stop or reduce the quantity and toxicity of the materials and products used prior to their generation. Reducing hazardous waste at the source prevents it from entering the waste stream. Hazardous waste can be minimized by eliminating or substituting toxic materials, implementing process modifications such as in-process recycling and segregating waste at the source to avoid the contamination of non-hazardous waste stream [6].

Pollution prevention approaches can be applied to all potential and actual pollution-generating activities, including those found in the energy, agriculture, federal, consumer and industrial sectors. Prevention practices are essential for preserving wetlands, groundwater sources and other critical ecosystems - areas in which we especially want to stop pollution before it begins.
In the energy sector, pollution prevention can reduce environmental damages from extraction, processing, transport and combustion of fuels. Pollution prevention approaches include:

- Increasing efficiency in energy use;
- Use of environmentally benign fuel sources.

In the agricultural sector, pollution prevention approaches include:

- Reducing the use of water and chemical inputs;
- Adoption of less environmentally harmful pesticides or cultivation of crop strains with natural resistance to pests; and
- Protection of sensitive areas.

In the industrial sector, examples of pollution prevention include:

- Modifying a production process to produce less waste
- Using non-toxic or less toxic chemicals as cleaners, degreasers and other maintenance chemicals
- Implementing water and energy conservation practices
- Reusing materials such as drums and pallets rather than disposing of them as waste

In homes and schools examples of pollution control practices include:

- Using reusable water bottles instead of throw-away.
- Automatically turning off lights when not in use.

SUBSTITUTION

This method includes substitutes to toxic materials, without change in product quality, price or customer satisfaction. This method is common in manufacturing processes using solvents or heavy metals. Processes that use toxic metals, such as coating materials, additives in polymers, and processing aids can also benefit from materials substitution. Many chemical industries release substantial amounts of chemicals in the form of waste to the environment during production. People may be exposed to these toxic substances that may cause health or environmental problems. Hence it is important to reduce the risk of damage arising from the hazardous products. This toxic waste can be minimized by substituting hazardous organic solvents by greener solvents.

MODIFICATION

Pollution prevention can also be achieved by modifying production processes. This method includes adopting more advanced technologies or by altering cleaning processes, chemical catalysts, and segregation and separation of hazardous materials. Various technical changes and modifications provide more precise and reliable separation of materials that mixed into a waste stream. The materials are modified or separated by means of different characteristics properties.

RECYCLING

Recycling is the process of converting waste product into new product to prevent energy usage and consumption of raw materials. Recycling involves any process by which reclaimed refuse or other materials that would otherwise become waste are collected, segregated, or processed, and then reused or returned to use in the form of raw materials or products [7]. Inorganic materials like metals, glass and plastic while organic materials like paper can also be recycled. This takes into the account that proven solution to the problem of proper waste management.

WASTE TREATMENT

Waste treatment refers to the activities required to ensure that waste has the least practicable impact on the environment. Various technologies for hazardous waste treatment are available, such as biological, chemical, or physical treatment to reduce the volume or hazard of the waste. Throwing daily waste or garbage in the landfills is the most popularly used method of waste disposal. Incineration or combustion type of disposal

includes the burning of solid waste into the residue and solid products. This method is also known as thermal treatment where solid waste materials are converted incinerators into heat, gas, steam and ash. With the right condition i.e. air and moisture organic waste such as food and plant materials can be decomposed by bacteria, fungi, worms and organisms.

ENVIRONMENTAL POLLUTION LEGISLATION

Environmental pollution has many different causes and affects us in a number of different ways. For this reason, it is important to have a comprehensive legal framework in place to enable the development of effective policy initiatives, backed by a single organization with jurisdiction over environmental pollution control measures and the attendant governmental structures.

FINANCIAL ASSISTANCE FOR PREVENTION OF POLLUTION

Investment in equipment and technology designed to reduce pollution output can pose a significant financial burden in difficult economic circumstances, without providing any direct boost to company revenue. To encourage investment in pollution reduction initiatives, government financial institutions provided preferential taxation and financial measures, low-interest loans for plant and equipment investment, tax exemptions and special depreciation allowances. The Environment Pollution Control Service Corporation, meanwhile, promoted pollution reduction initiatives in industry by setting up green buffer zones and joint facilities

For reducing environmental pollution, building joint-use production facilities and carrying out land reclamation projects.

POLLUTION AWARENESS CAMPAIGNS

The level of commitment to pollution controls and effective outcomes is very much subject to public opinion. The media, particularly television and radio, are constantly working to raise public awareness of pollution and environmental issues.

CONCLUSION

The present study reveals that there are many options to consider in assessing pollution prevention and management for specific processes, products or substances. Due to industrialization, excess use fuels, technological advancement the problem of pollution has been increased in all developed and developing countries. It has become a serious threat to all living and non living things, therefore it is necessary to control and prevent the pollution.

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NEWLY SYNTHESISED GLYCOSYL IMINO-1,2,4 DITHIAZOLIDINES WITH SPECTRAL STUDY

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ABSTRACT

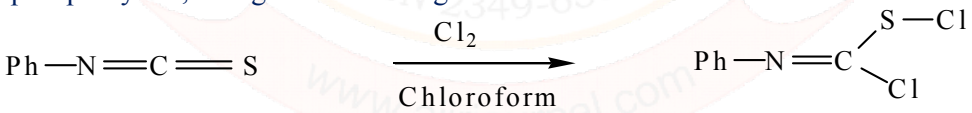
A versatile synthetic procedure is described to prepare various per-O-acetyl and per-O-benzoyl glycosyl imino-1,2,4dithiazolidines which involves interaction of 1-phenyl-(o-benzylidene amino)-3-glycosylthiocarbamides and N-phenyl-S-chloroisothiocarbamoyl chloride. The identities of these newly synthesized compounds were established on the basis of usual chemical transformations, IR, ^{1}H NMR and Mass spectral studies. All the synthesized compounds have been evaluated for their antibacterial and antifungal activity against different bacteria and fungi by agar diffusion method.

KEYWORDS: *N*-phenyl-*S*-chloroisothiocarbamoyl chloride, glycosylthiocarbamides, glycosyl imino-1,2,4 dithiazolidines

INTRODUCTION:

The reaction of amines and aromatic aldehydes to generate imines are well known and extensively studied method to generate these compounds. More than one hundred and fifty years the Schiff bases are an important class of organic compounds in chemical, medical and pharmaceutical areas. Schiff bases have shown a wide range of biological activities.

Glucose derivatives are known to be selective and efficient catalytic inhibitors of human liver glycogen phosphorylase, a target for the design of type 2 diabetes therapeutics[1]. Isothiocyanates are precursors of a wide range of *N*-thiocarbamoyl derivatives; their tendency to undergo nucleophilic additions and cycloadditions make them highly important intermediates in organic synthesis[2] for the preparation of heterocyclic compounds[3,4]. Thus heterocyclic compounds have been used as anti-tumoral[5,6]or antiviral agents, including AIDS[7,8] and hepatitis B[9,10] treatments.The *N*-aryl/alkyl-*S*-chloroisothiocarbamoyl chlorides were prepared by Ottman and Hooks[11] by the controlled chlorination of aryl/alkyl isothiocyanates.



Phenyl isothiocyanate

N-phenyl-S-chloro isothiocarbamoyl chloride

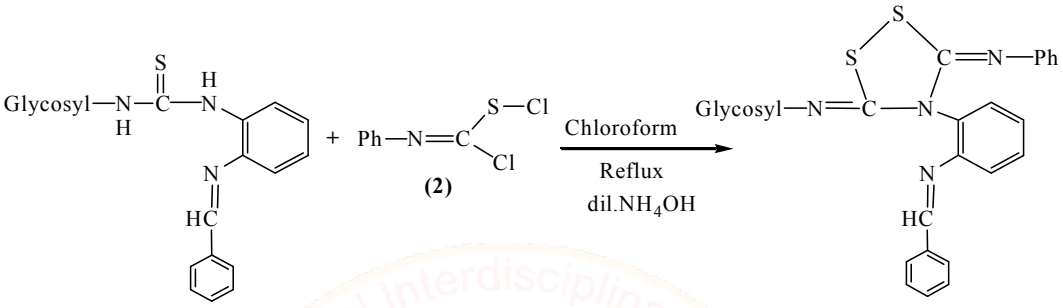
Chemistry of *N*-phenyl-*S*-chloroisothiocarbamoyl chloride with special utility in the synthesis of nitrogen and sulphur containing five and six member heterocyclic compounds have been exhaustively investigated by number of chemists[12-16].

Characterization data of compounds 3(a-f) Table-1

Compound	% yield	M.P. (^{O}C)	Optical Activity $[\alpha]_D^{30}$ (c, 0.01)
3a	70	184-187	+134
3b	89	168	+152
3c	81	170	+196
3d	68	159	+142
3e	76	152-156	+180
3f	80	179	+128
Satisfactory C, H, N and S analysis were found in all compounds			

EXPERIMENTAL

All melting points are uncorrected and were obtained in capillary using paraffin bath. Specific rotations of the newly synthesized compounds were measured on an Equip-Tronic digital polarimeter model no. EQ 801 at 30^0C in $CHCl_3$. IR spectra were recorded on a Shimatzu FTIR spectrophotometer, ^{1}H NMR on a Bruker DRX-300 (300 MHz FT) NMR spectrometer in $CDCl_3$ solution with TMS as an internal reference. The Mass spectra were recorded on a Jeol SX -102 FAB mass spectrometer. Purity of the compound was checked by thin layer chromatography using merck silica gel-coated aluminium plates and petroleum ether: ethyl acetate as eluent and iodine vapours as a visualizing agent.



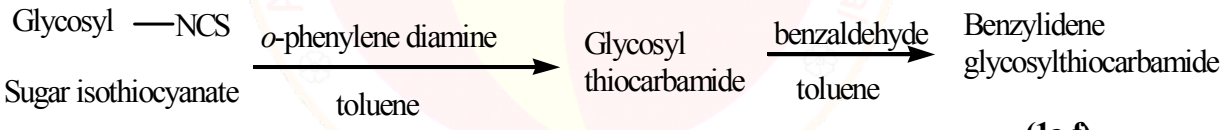
Benzylidene glycosyl thiocarbamide **(1a-f)**

Glycosylimino1,2,4-dithioazolines **(3a-f)**

Where, Glycosyl = a) Tetra-*O*-acetyl-β-D-glucopyranosyl.b) Hepta-*O*-acetyl-β-D-lactosyl.
c) Hepta-*O*-acetyl-β-D-maltosyl.d) Tetra-*O*-benzoyl-β-D-glucopyranosyl.
e) Hepta-*O*-benzoyl-β-D-lactosyl.f) Hepta-*O*-benzoyl-β-D-maltosyl.

Preparation of 1-Phenyl-3-(*o*-benzylidene amino)glycosylthiocarbamides(1a-f):

These have been prepared by the interaction of acetylated/benzoylatedglycosylthiocarbamides and benzaldehyde in boiling toluene medium.



(1a-f)

Preparation of *N*-phenyl-*S*-chloroisothiocarbamoyl chloride (2):

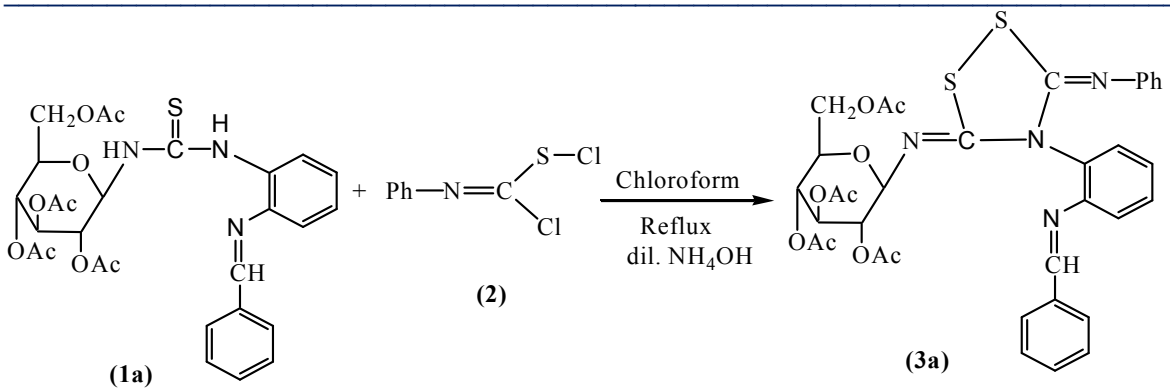
The required *N*-phenyl-*S*-chloroisothiocarbamoyl chloride was prepared by earlier known method[17] by controlled chlorination of phenyl isothiocynate.

RESULT AND DISCUSSION:

Synthesis of 3-phenylimino-4-phenyl-(*o*-benzylidene amino)-5-tetra-*O*-acetyl-β-D-glucopyranosyl imino-1,2,4 dithiazolidine(3a):

To an ice cold chloroformic solution of 1-phenyl-(*o*-benzylideneamino)-3-tetra-*O*-acetyl-β-D-glucopyranosylthiocarbamide **(1a)** ice cold chloroformic solution of *N*-phenyl-*S*-chloroisothiocarbamoyl chloride **(2)** was added and after 1h at room temperature the reaction mixture was gently refluxed for 3h. Reaction was monitored by TLC. After the completion of reaction solvent chloroform was distilled off and the resultant syrupy mass was triturated several times with light petroleum (60-80^{O}C) to afford a pale yellow solid.

This solid was basified with cold dilute ammonium hydroxide solution to afford 3-phenylimino-4-phenyl-(*o*-benzylidene amino)-5-tetra-*O*-acetyl-β-D-glucopyranosyl imino-1,2,4 dithiazolidine**(3a)** as granular solid. This was crystallized from ethanol. The product was found to be non-desulphurizable when boiled with alkaline plumbite solution. m.p. 184-187°C.



All other glycosylimino-1,2,4dithiazolidine**(3b-f)** were prepared in a similar manner.

Spectral Characterizations:

3-phenylimino-4-phenyl-(*o*-benzylidene amino)-5-tetra-*O*-acetyl-β-D-glucopyranosyl imino-1,2,4 dithiazolidine(3a):

$C_{35}H_{33}O_9N_4S_2$; IR (KBr) ν cm^{-1} : 3012 (Ar. C-H str.), 2960 (Ali. C-H str.), 1755 (C=O str.), 1371 (Ar. C-N str.), 1039, 939 (Characteristics of glucose).

3-phenylimino-4-phenyl-(*o*-benzylidene amino)-5-hepta-*O*-acetyl-β-D-lactosyl imino-1,2,4 dithiazolidine(3b):

$C_{47}H_{49}O_{17}N_4S_2$: **IR (KBr) ν cm^{-1}** : 2945 (Ali. C-H str.), 1753 (C=O str.), 1369 (Ar. C-N str.), 1053, 902 (Characteristics of lactose); **^{1}H NMR** in $CDCl_3$ at δ ppm: 2.00-2.17 (21H, s, 7x$COCH_3$), 3.70-5.35 (14H, m, lactosyl-H), 5.45 (1H, s, =CH), 6.98-7.84 (14H, m, Ar-H); **Mass**: 1005 [M^+], 932, 843, 752, 701, 659, 345, 226.

3-phenylimino-4-phenyl-(*o*-benzylidene amino)-5-hepta-*O*-acetyl-β-D-maltosyl imino-1,2,4 dithiazolidine(3c):

$C_{47}H_{49}O_{17}N_4S_2$: **IR (KBr) ν cm^{-1}** : 2935 (Ali. C-H str.), 1753 (C=O str.), 1369 (Ar. C-N str.), 1058, 902 (Characteristics of maltose); **^{1}H NMR** in $CDCl_3$ at δ ppm: 1.91-2.22 (21H, s, 7x$COCH_3$), 3.72-5.49 (14H, m, maltosyl-H), 5.5 (1H, s, =CH), 6.87-7.83 (14H, m, Ar-H); **Mass**: 1005 [M^+], 904, 873, 752, 701, 659, 345, 226, 121

3-phenylimino-4-phenyl-(*o*-benzylidene amino)-5-tetra-*O*-benzoyl-β-D-glucopyranosyl imino-1,2,4 dithiazolidine(3d):

$C_{55}H_{41}O_9N_4S_2$: **IR (KBr) ν cm^{-1}** : 3062 (Ar. C-H str.), 2951 (Ali. C-H str.), 1732 (C=O str.), 1371 (Ar. C-N str.), 1095, 935 (Characteristics of glucose); **^{1}H NMR** in $CDCl_3$ at δ ppm: 3.68-5.88 (7H, m, glucosyl-H), 6.34 (1H, s, =CH), 7.23-8.19 (34H, m, Ar-H). **Mass**: [M^+] not located, 830, 714, 712, 226, 121.

3-phenylimino-4-phenyl-(*o*-benzylidene amino)-5-hepta-*O*-benzoyl-β-D-maltosyl imino-1,2,4 dithiazolidine(3f):

$C_{82}H_{63}O_{17}N_4S_2$**: IR (KBr) ν cm^{-1}** : 3064 (Ar. C-H str.), 2956 (Ali. C-H str.), 1730 (C=O str.), 1097, 933 (Characteristics of maltose); **^{1}H NMR** in $CDCl_3$ at δ ppm: 4.17-5.88 (14H, m, maltosyl-H), 6.13 (1H, s, =CH), 7.01-8.13 (49H, m, Ar-H). **Mass:** [M^+] not located, 1304, 1186, 1185, 1124, 1081, 474, 226.

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EFFICACY OF BIO-PESTICIDE ON *CHICKPEA* CROP

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ABSTRACT

According to World Health Organization (WHO) every year millions of peoples died due to synthetic pesticides poisoning. Use of excess of fertilizers causes paste attach on the different crops. Affect soil fertility and causes water pollution, soil pollution etc Fertilizers and Synthetic pesticides are costly and affect the water cycle, Water Pollution. Touching the fertilizer may cause skin irritation the biggest issue facing the use of chemical fertilizers is groundwater contamination. Nitrogen fertilizers break down into nitrates and travel easily through the soil. Because it is water-soluble and can remain in groundwater for decades, the addition of more nitrogen over the years has an accumulative effect. Pesticides are toxic; they are also potentially hazardous to humans, animals, other organisms, and the environment.

Pesticides can contaminate soil, water, turf, and other vegetation, Insecticides are generally the most acutely toxic class of pesticides, but herbicides can also pose risks to non-target organisms. Many pesticides are "known or probable" carcinogens and, as the President's Panel notes, exposure to these chemicals is widespread. Children are especially at risk of developing cancer from pesticide exposure, and childhood cancer rates continue to rise. They also experience higher rates of a cancer. Some pesticides are more toxic to soil organisms than others. Some pesticides may break down quickly when applied to soils, while others may persist for longer periods. The type of soil and the type of pesticide can also affect pesticide persistence. Very small amounts of pesticides that may remain in or on fruits, vegetables, grains, and other foods decrease considerably as crops are harvested, transported, exposed to light, washed, prepared and cooked. The presence of a detectible pesticide residue does not mean the residue is at an unsafe level. The common diseases affecting the public's health are all too well-known in the 21st century asthma, autism and learning disabilities, birth defects and reproductive dysfunction, diabetes, Parkinson's and Alzheimer's diseases, and several types of cancer. Cramps in your muscles or aches all over your body. Therefore there is a demand of Eco-friendly, effective bio-pesticides as well as bio-fertilizer.

Keyword: *Bio-pesticide, Antifeedant, Anti helicoverpa armigera, repellent, eco-friendly, cost effective.*

Introduction

For the preparation of Bio-pesticides four botanical species *Nerium oleander, Jimsonwead, Azadirachta indica* and *Ricinus commins* are selected. Phytochemical composition of *Nerium oleander* is Saponins, alkaloids, flavanoids, antraquinones, Oleandrin, Nerine, Glycosides,Gentiobiosyl-herigosides, alpha-Tocopherol, triterpenoides, resin, tannins, ursolic acid, vitamin-C, odorosides, adiosides, rosaginosides, neriosides, cortenerosides, pentacyclic triterpene, galacturonic acid, galactose, oxy-triterpenoides, neriucoatraric, isoneriucomaric acids, steroids, olenderoeinoic acid, phenolic compounds, cardiac glycosides, amino acids, carbohydrates, proteins and phenols. It also contains minerals such as potassium (K), sodium (Na), zinc (Zn), Cupper (Cu), Chromium (Cr), Nikhel (Ni), Cobalt (Co), Iron (Fe), Magnase (Mn), Magnesium (Mg) and Calcium (Ca). *Jimsonwead* leaves contains Saponins, alkaloids, flavanoids, Glycosides, alpha-Tocopherol, terpenoids, tannins, triterpene, steroids, amino acids, carbohydrates, proteins, hyocyamine, hyoscine, atropine, scopolamine, stigma sterol, beta-sitosterol, lanosterol,5-avenasterol, sitostanol, gama-tocopherol, crude fiber crude nitrogen, lignin contents and 64 tropanes also contains sodium (Na), zinc (Zn), Cupper (Cu), Magnase (Mn), Magnesium (Mg) and Calcium (Ca), iron (Fe), Nitrogen (N), Nitrates and Vitamin-C. Phytochemical composition of *Azadirachta indica* Vitamins A, E,& C, Saponins, alkaloids, flavanoids, limonoid, isopronoides, Triterpenoides, protomeliacins, azadirine, vilasin, nimbin, salanin, tannins, carbohydrates, proteins, polyphenolic, glycosides, dihydroch alcone, coumarin, nimbidin, steroids, alpha-liolenic acid,9-hexadecenoic acid, margolone-4, margolone-5, Riboflavin, thiamine, niacin, amino acids, acetic acid and pivalic acid and also contains (Zn), Cupper (Cu), Chromium (Cr), Iron (Fe), Magnase (Mn), Magnesium (Mg). Phytochemical composition of *Ricinus Comminus* are Saponins, alkaloids, flavanoids, Glycosides, recinine, N-demethylrecimine, six flavones, gallic acid, querecetin, genetic acid, rutin, epicatechin, ellagic acid, indole-3-acetic acid, ricinoleic acid,

isoricinoleic, steric acid, 8-cineole, alpha-pipnenecamphor,camphene, palmitic acid, arachidic, hexanoic, oleic, linoleic, linolenic, ricinoleic, dihydroxy acid also contains Magnesium (Mg), Calcium (Ca), Nitrogen (N), potassium (K), Phosphorous (P), sulphur (S).

Nerium oleander shows Antimicrobial activity, insecticidal activity, Antifeedant activity, repellent activity, antifungal activity, Antioxidant activity, Larvacidal activity, insecticidal activity and ovicidal activity where as *Jimsonwead* shows antifungal activity, Antioxidant activity Antimicrobial activity, Antifeedant activity, bio-pesticide activity against *Helicoverpa armigera.*

Azadirachta indica shows Antibacterial activity, antifungal activity insecticidal activity, Antifeedant activity, and *Ricinus commins* shows antibacterial activity, Antioxidant activity Antimicrobial activity, Larvacidal activity, insecticidal activity.

MATERIALS AND METHODS

Bio-pesticide is prepared with the help of *Nerium oleander, Jimsonwead, Azadirachta indica* and *Ricinus commins* leaves, steam, flowers and seeds. The contents of above botanical species are extracted in crude soybean oil and emulsifier is used as a mixing agent for its application in *chickpea* crop. Field trials are conducted on *chickpea* crop. Step-I: Add 50 ml Bio-Pesticide in 20 liter water and mixed it properly. Step-II: Foliar spray on crop every 20 days interval. Step-III: Add 1 liter Bio-Pesticide (Fertilizer) in 200 liters water and mixed it properly drenching with pump without nosel at root of the plat every 20 day interval minimum two drenching. Observed their plant growth, pest control, quality of seeds, cost effectiveness and yield compared to control crop which is cultivated conventionally using fertilizers and pesticides.

USE OF BIO-PESTICIDE

Particulars	Treated Plot	Control Plot
Variety	JG-11 (Cost Rs=3000)	JG-11(Cost Rs=3000)
First Dose & Quantity per/Acre	1 Liter/Acre (Bio-Pesticide) (Cost Rs=125)	Trazer (Synthetic Pesticide) 75ml/Acre(Cost Rs=1200)
Second Dose & Quantity per/Acre	500 ml /Acre (Bio-Pesticide) (Cost Rs=63)	Corrasion (Synthetic Pesticide) 100ml/Acre (Cost Rs=1700)
Third Dose & Quantity per/Acre	500 ml/Acre (Bio-Pesticide) (Cost Rs=63)	Corrasion (Synthetic Pesticide) 100ml/Acre (Cost Rs=1700)
Labour Cost	Rs=1200	Rs=1200
Fertilizer Cost	Nil	Rs=1600
Yield /Acre	10 Quintal/Acre	7 Quintal/Acre
Conversion Rate of Chickpea nuts into a Futhane	90%	41%
Market Cost of Chickpeas nuts per Quintal	Rs=7000/-	Rs=4300/-
Total Expenditure	Rs=4451	Rs=10,400
Total Income	Rs=70,000/-	Rs=30,100/-
Net profit	Rs=65,549	Rs=19,700

Growth of Control & Treated *Chickpea* Crop

Control *Chickpea* Crop

Treated *Chickpea* Crop

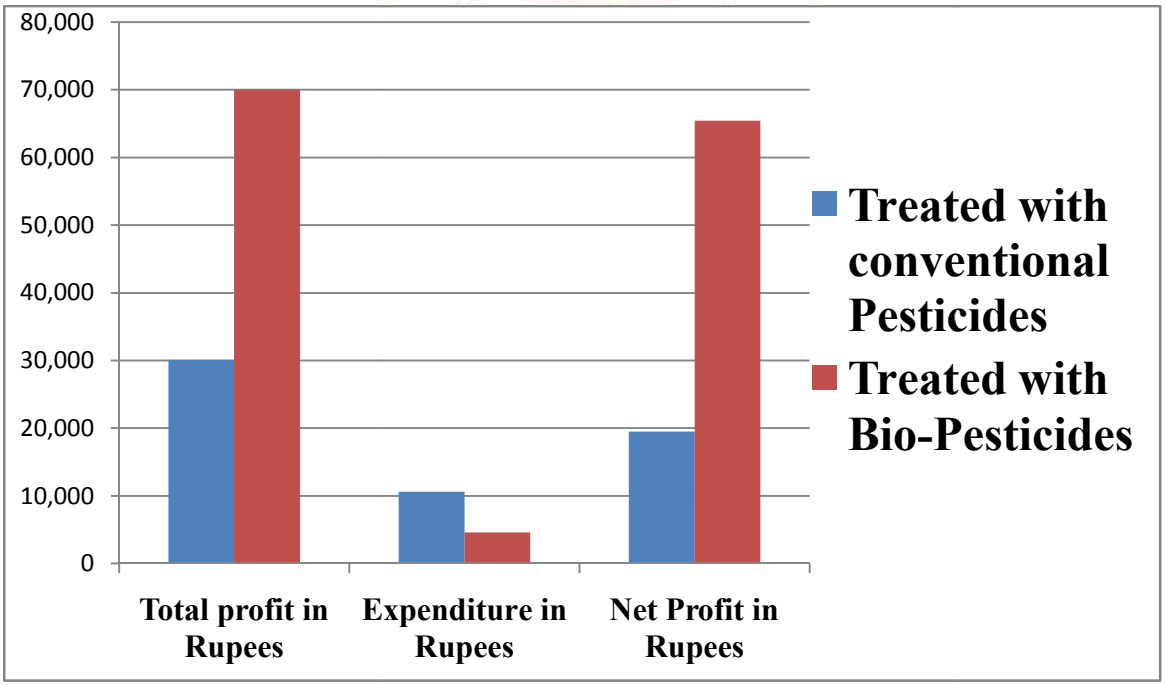
Quality of Control *Chickpea* nut

Quality of Treated *Chickpea* nut

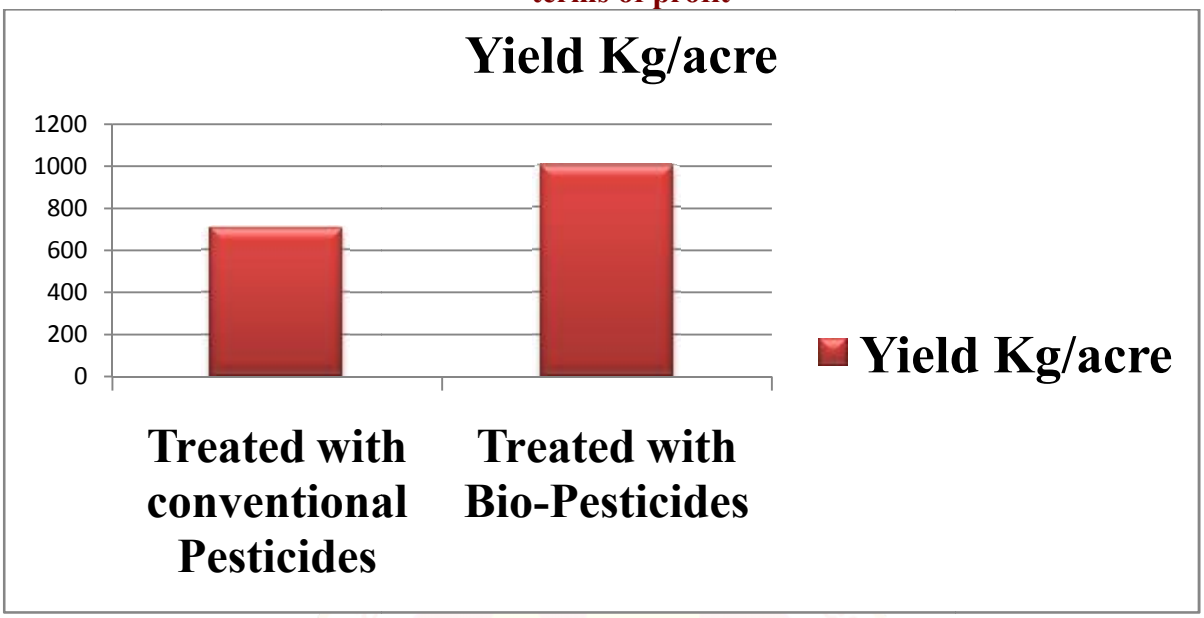
Quality of Control Futhane

Quality of Treated Futhane

Result and discussion:



Graph shows comparison of Bio-pesticide plot with conventionally treated plot results in terms of profit



GRAPH SHOWS COMPARISON OF BIO-PESTICIDE PLOT WITH CONVENTIONALLY TREATED PLOT RESULTS IN TERMS OF YIELD

Total expenditure in treated plot is Rs=4451/- (excluding harvesting) where as Total expenditure in control plot (conventional method) is Rs=10,400/- (excluding harvesting) by using bio-pesticides Net profit is Rs=66,500 per acre where as in control plot (conventional method) Net profit is Rs=22100/- per acre, which is more than tree times as compared to control plot.

CONCLUSION It increases quality of seeds & Yield, Abled to convert *Chickpeas* seeds into Futhane; Useful to society, society gets poison free food. Save the environment from air, water & soil pollution. It is more profitable for the farmers, safe. It is not only cost effective but also yield oriented as well as eco-friendly. Increases the fertility of soil and does not kill useful bacteria of soil.

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SYNTHESIS, SPECTRAL CHARACTERIZATION AND INVESTIGATION OF ANTIBACTERIAL ACTIVITY OF SOME NOVEL AZO DYES DERIVED FROM 4-CHLOROPHENOL.

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ABSTRACT

In this study, four azo derivatives were synthesized in excellent yields via the diazotization of some different substituted primary aromatic amines followed by coupling with p-chlorophenol. These compounds were characterized by FTIR, ^{1}HNMR and MASS spectral techniques. The synthesized compounds have been tested in vitro against human pathogens in order to assess their antibacterial properties using disk diffusion method. The compounds analysed for its antibacterial action were found to be antibacterial against all the tested pathogens.

KEYWORDS *4-chlorophenol, Azo compounds, Antibacterial activity, Human pathogens.*

INTRODUCTION

Azo compounds are mostly used as dyes due to its various applications in the fields such as textile fibers, coloring of different materials, biomedical studies and organic synthesis[1-2]. The azo dyes containing azo linkages have advanced applications in high technology areas like lasers[3], LCD color filters[4]. In addition to this, azo dyes were reported to have variety of biological applications like antineoplastics, antidiabetics, antiseptics, anti-inflammatory and other useful chemotherapeutic agents[5-8]. Scarlet red and diamazon are the most commonly used azo dyes which are antiseptics. Several azo compounds derived from thymol[9], aspirin[10], paracetamol[11], m-cresol[12], resorcinol[13], vanillin[14], tyrosine[15], 2, 4 dinitrophenol[16], and 4-hydroxybenzoic acid[17] moieties have been frequently reported and exhibit excellent biological properties.

In view of the above relevant literature survey, it can be thought that, compounds with azo moiety have been extensively used as dyes due to their utility in colorings functions. But their variety in biological activity potential is less reported and as a consequence one must have vast scope to synthesize new azo compounds and to test their antibacterial activities. So, in the present work, four new azo compounds namely A to D containing 4-chlorophenol moiety are synthesized and characterized by FTIR, ^{1}HNMR and MASS spectral technique. The antibacterial activities of the synthesized azo compounds were reported in *vitro* using disc diffusion method.

EXPERIMENTAL SECTION

MATERIAL AND METHODS

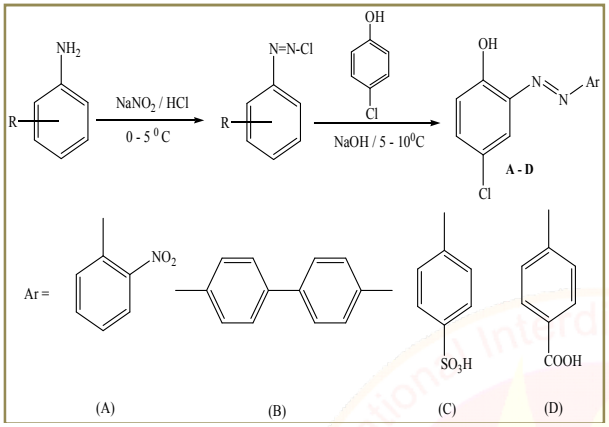
The chemicals used in the present studies are of synthetic grade, Merck company ltd. The products were characterized by IR, ^{1}HNMR and MASS spectral studies. The melting points were determined by open capillary method using digital melting point apparatus model 935/934 by Electronics India and is uncorrected. The IR spectra were recorded on FTIR Spectrophotometer Model RZX (Perkin-Elmer) in the form of KBr pallet. ^{1}HNMR spectra were recorded in $CDCl_3$ on a FT-NMR Cryomagnet Spectrometer 400 MHz (Bruker) using TMS as an internal standard and MASS spectra were recorded on LC-MS Spectrometer Model Q-ToF Micro Waters. The purity of compounds was checked by TLC.

EXPERIMENTAL PROCEDURE FOR SYNTHESIS OF AZO COMPOUNDS

Substituted primary aromatic amines (0.01mole) were mixed with 2.5 ml conc. HCl and 2.5 ml (4N) cold solution of $NaNO_2$ was added with the stirring. The temperature of the reaction was maintained up to 0-5^0 C. Diazonium salt solution so prepared was added drop wise to the alkaline 10% NaOH solution of 4-chlorophenol (0.01mole). The reaction mixture was stirred for 30-45 minutes maintaining the temperature 5-10^0 C. The coloured products obtained was filtered, washed with water and recrystallized from 50% ethanol. The general reaction scheme for synthesis of azo compounds of 4-chlorophenol is shown in figure-(1). Code, chemical name, formulae, mol.

wt. m. p. and % yield of synthesized azo compounds of 4-chlorophenol is shown in table-(1).

FIGURE 1: THE GENERAL REACTION SCHEME FOR SYNTHESIS OF AZO DERIVATIVES OF 4-CHLOROPHENOL



ANTIMICROBIAL ACTIVITY:

Table 1

Code	Name of Compound	Mol. Formula	Mol. Wt.	M. P. ^{0}C	% Yield	Colour
A	4-chloro-2-[(*Z*)-(2-nitrophenyl)diazenyl] phenol	$C_{12}H_8ClN_3O_3$	278.67	106.5	77.54.	Brick Red
B	4-chloro-2-[(*E*)-{4'-[(*Z*)-(5-chloro-2-hydroxyphenyl) diazenyl] biphenyl-4-yl} diazenyl] phenol.	$C_{24}H_{16}Cl_2N_4O_2$	463.31	102.5	81.14	Brown
C	4-[(*Z*)-(5-chloro-2-hydroxyphenyl)diazenyl] benzenesulfonic acid	$C_{12}H_9ClN_2O_4S$	312.73	114.5	76.79	Brown
D	4-[(*Z*)-(5-chloro-2-hydroxyphenyl) diazenyl] benzoic acid.	$C_{13}H_9ClN_2O_3$	276.67	117.5	81.13	Red

RESULT AND DISCUSSION

Spectroscopic study: I.R., ^{1}HNMR and MASS Spectra Showed the expected signals / peaks which correspond to various groups present in each compounds. The I.R. ^{1}HNMR and MASS spectral data are shown in Table (2).

Antibacterial potential of synthesized azo compounds was analysed by employing disc diffusion method [18-19]. All four test pathogens viz. *Escherichia coli, Staphylococcus aureus, Pseudomonas aeroginosa* and *Salmonella typhi* aseptically spreaded over sterile nutrient agar plates by sterile cotton buds separately. Sterile paper discs of diameter 6 mm were dipped in different concentrations viz. 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 mg/mL of all azo compound, and thereafter discs containing azo compounds aseptically placed on nutrient agar plates spread with the test pathogen separately. The plates were further incubated at 37^{0}C for 24 hours. After incubation the antibacterial activity were determined in terms of zone of inhibition around disc. The zones of inhibition were measured using antibiotic zone reader (Hi- Media).

TABLE (2):- IR, ^{1}HNMR AND MASS SPECTRAL DATA

A IR- 3404cm^{-1} (Phenolic –OH stretch), 3101cm^{-1}(Ar–H Stretch), 1598cm^{-1} (N=N Stretch), 1580cm^{-1} (C=C Ring or aromatic stretch), 1384cm^{-1} (C–N Stretch), 1261cm^{-1} (C–O Phenol stretch), 764cm^{-1}(C–H aromatic def), 780 cm^{-1} C□Cl stretching.
NMR- δ 6.9-7.9 (m 7H of Ar-H), δ-8.0 (s 1H of –OH).
MASS- The mass spectrum displayed the m/z molecular ion peak at 278.1

B IR- 3414cm^{-1} (Phenolic –OH stretch), 2922cm^{-1} (C□H Ar stretching), 1610cm^{-1} (N=N Stretch), 1603cm^{-1} (C=C Ring or aromatic stretch), 1492 cm^{-1}(C–H def of CH_3 group), 1384cm^{-1} (C–N Stretch), 1342cm^{-1}(C–O Phenol stretch), 1140cm^{-1}(C–C aliphatic chain stretch), 811cm^{-1} C□Cl stretching.
NMR- δ 6.96 to 7.90 (m 11H of Ar-H), δ-7.9 and 8.0 (s 1H of –OH).

C IR- 3461cm^{-1} (Phenolic –OH stretch), 3066cm^{-1}(Ar–H Stretch, sp^2 plane), 1591 cm^{-1}(N=N Stretch), 1635cm^{-1} (C=C Ring or aromatic stretch), 1218cm^{-1} (C–N Stretch), 1243 cm^{-1}(C–O Phenol stretch),

838cm^{-1}(C–C aliphatic chain stretch), 675cm^{-1}(C–Cl stretching)
NMR- δ 6.70 to 7.80 (m 7H of Ar-H), δ-7.9 (s 1H of –OH), δ3.00 (s 1H of –SO_3H),

D IR- 3463cm^{-1} (Phenolic –OH stretch), 3067cm^{-1}(Ar–H Stretch, sp^2-plane), 1591cm^{-1}(N=N Stretch), 1697cm^{-1} (C=C Ring or aromatic stretch), 1218cm^{-1} (C–N Stretch), 1243cm^{-1}(C–O Phenol stretch), 838cm^{-1}(C–C aliphatic chain stretch), 777cm^{-1}(C–Cl stretching)
NMR- δ 7.00 to 7.90 (m 7H of Ar-H), δ-8.0 (s 1H of –OH), δ-9.90 (s 1H of –COOH).

ANTIMICROBIAL STUDY The experimental data on antibacterial activity for azo compounds viz. A–D against four human pathogens is presented in table (1.1) – (1.4) as follows.

Table (1.1):- Effect of azo compounds of 4-chlorophenol viz. A–D on the growth response of *Escherichia coli*

Conc. (mg/mL)	A	B	C	D
0.5	I (10.2)	I (18.6)	I (10.0)	I (10.0)
1.0	I (10.6)	I (19.0)	I (10.5)	I (10.0)
1.5	I (10.5)	I (18.5)	I (10.2)	I (10.5)
2.0	I (10.5)	I (19.3)	I (10.7)	I (10.3)
2.5	I (10.3)	I (19.5)	I (10.9)	I (10.5)
3.0	I (10.1)	I (18.9)	I (10.5)	I (10.5)

Table (1.2):- Effect of azo compounds of 4-chlorophenol viz. A–D on the growth response of *Staphylococcus aureus*:

Conc. (mg/mL)	A	B	C	D
0.5	I (11.2)	I (14.2)	I (15.0)	I (10.0)
1.0	I (11.3)	I (14.0)	I(15.0)	I(10.0)
1.5	I (11.5)	I (14.5)	I (15.4)	I (10.1)
2.0	I (11.5)	I (14.5)	I (15.7)	I (10.1)
2.5	I (11.7)	I (14.3)	I (15.3)	I (10.4)
3.0	I (11.1)	I (14.1)	I (15.1)	I (10.1)

Table (1.3):- Effect of azo compounds of 4-chlorophenol viz. A–D on the growth response of *Salmonella typhi*:

Conc. (mg/mL)	A	B	C	D
0.5	I (10.2)	I (10.2)	I (11.2)	I (12.2)
1.0	I (10.0)	I (10.0)	I (11.0)	I (12.0)
1.5	I (10.5)	I (10.5)	I (11.3)	I (12.1)
2.0	I (10.3)	I (10.2)	I (11.4)	I (12.6)
2.5	I (10.5)	I (10.7)	I (11.6)	I (12.3)
3.0	I (10.0)	I (10.4)	I (11.1)	I (11.4)

Table (1.4):- Effect of azo compounds of 4-chlorophenol viz. A–D on the growth response of *Pseudomonas aeroginosa*:

Conc. (mg/mL)	A	B	C	D
0.5	I (11.2)	NI	NI	NI
1.0	I (11.6)	NI	NI	NI
1.5	I (11.5)	NI	NI	NI

2.0	I (11.7)	NI	NI	NI
2.5	I (11.9)	NI	NI	NI
3.0	I (11.4)	NI	NI	NI

The results regarding antibacterial activity of four azo compounds of 4-chlorophenol viz A–D against *E.Coli* are presented in table (1.1). The maximum antibacterial activity was observed in case of derivative B for which nearly all six concentrations used were showed significant antibacterial effect against *E.Coli* and the average diameter of zone of inhibition ranges from 18.5–19.5 mm with maximum zone of inhibition recorded 19.5 mm diameter for 2.5 mg/mL over control. This is followed by derivatives A, C and D for which most of the different concentrations showed moderate antibacterial effect with average zone of inhibition ranges from 10 – 10.9 mm with peak zone of inhibition recorded 10.9 mm diameter at 2.5 mg/mL for C over control where antibacterial activity was not observed.

The results on antibacterial activity of four azo compounds of 4-chlorophenol viz A–D against *S.aureus* are tabulated in table (1.2). From the result it was observed that the compounds A, B and C showed prominent antibacterial activity at nearly all the six different concentrations. The peak zone of inhibition recorded 15.7 mm diameter at 2.0 mg/mL for C, 14.5 mm diameter at 2.00 mg/mL for B and 11.7 mm diameter at 2.50 mg/mL for A over control where no activity is recorded against S.aureus. The compound D found to show moderate effect on the growth of *S.aureus* species.

The results regarding antibacterial activity of four azo compounds of 4-chlorophenol viz A–D against *Salmonella typhi* are tabulated in table (1.3). From the result it was observed that the compounds C and D shows major antibacterial properties against *Salmonella typhi* at all the six different concentrations used with average zone of inhibition ranging from 11 – 12.6 mm diameter with peak zone of inhibition 12.6 mm at 2.0 mg/mL for D, 11.6 mm at 2.5 mg/mL for C respectively. The compounds A and B found to exhibit moderate inhibition effect on the growth response of *Salmonella typhi* species.

The results on antibacterial effects of azo compounds viz A-D against *Pseudomonas aeroginosa* is presented in table 1.4. The study indicates that among all azo compounds only A derivative showed antibacterial effect over others. The different conc. of compound A were also analysed for antibacterial activity. From the results it was observed that the maximum antibacterial effect was recorded at 2.5 mg/ml followed by 2.0, 1.0, 1.5, 3.0 and 0.5 mg/ml where zone of inhibition recorded as 11.9 , 11.7 ,11.6 ,11.5 ,11.4 and 11.2 mm respectively.

CONCLUSION

All the four novel azo compounds A–D incorporated with 4-chlorophenol moiety were successfully synthesized in average yield and their structures are elucidated using IR, NMR & MASS spectroscopy. The results on antibacterial evaluation study reveals that all the synthesized compounds viz A-D found to have moderate to significant antibacterial effect against tested pathogens at different concentrations analysed.

Especially azo compound B is extraordinarily effective against *E.Coli*, azo derivative C, B and A are profoundly active against *S. aureus*, D and C are significantly active against *Salmonella typhi* whereas derivative A has remarkable antibacterial effect against *Pseudomonas aeroginosa* at different concentrations used for analysis.

The results revealed, the broad spectrum potential of all the compounds in inhibiting the growth of human pathogens, and this finding enlighten the possible help in drug discovery. However in this course these compounds should be analysed for its hepatic-toxicity and renal toxicity with special interest on drug optimized concentration as well as for pharmaco-kinetic study.

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INVESTIGATION OF ANTIMICROBIAL ACTIVITIES OF 4-TERT-BUTYL-5-ARYL-2,4-DIHYDRO-3H-1,2,4-TRIAZOLE-3-THIONE

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ABSTRACT

Various 4-tert-butyl-5-aryl-2,4-dihydro-3H-1,2,4-triazole-3-thiones (IIIa-g) were synthesized from N-tert-butyl-2-aroyl thiosemicarbazide (IIa-g) and tested for their biological activities. Agar diffusion method was applied for screening antibacterial as well as antifungal activities of all the newly synthesized compounds. The bacterial organisms used included both gram-positive strains like Ecoli and gram negative strain S.aureus. Antifungal activity was performed against the fungus A. niger. The antimicrobial activities including antibacterial and antifungal properties of the synthesized compounds showed poor activity when compared with standard drugs.

Keywords *1, 2, 4-Triazole, Antimicrobial activity, Gentamycin, Amphotericin*

INTRODUCTION

Triazole nucleus is a common feature of variety of natural products and medicinal agents. 1,2,4 and 1,2,3-triazoles derivatives display diverse biological activity, including antimicrobial[1-4], anti-inflammatory[5]. Out of various substituted 1,2,4-triazole, the 4,5-disubstituted 1,2,4-triazole derivatives have gained a lot of interest due to their biological, industrial and agricultural importance. A well known example is of Flucanazole. Although there are antimicrobial agents having different structure are frequently used in the treatment of fungal infections, activity of these drug are based on structure antimicrobial relationship. The different antifungal activity according to antibacterial effect might be postulated as different action in the mechanism of the compounds such as inhibition effect on respiratory systems of fungal cells, rather than cell wall destruction.

Acid hydrazides and hydrazine carbothioamide [6-8] have been in general used as the starting materials in some 1,2,4-triazole. In view of these reports and in continuation of search of new triazole derivatives with better antimicrobial activities herein is reported antimicrobial activites of some newly synthesized triazole derivatives.

MATERIAL AND METHODS

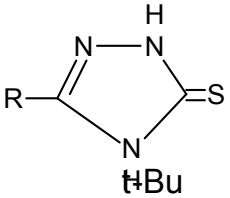
CHEMISTRY

Some new 4-tert-butyl-5-aryl-2,4-dihydro-3H-1,2,4-triazole-3-thiones derivatives were synthesized from various different N-tert-butyl-2-aroylhydrazine carbothioamide.

The synthesis of 4-tert-butyl-5-aryl-2,4-dihydro-3H-1,2,4-triazole-3-thiones derivatives were performed by base catalyzed oxidative cyclisation of various hydrazine carbothioamide according to the known procedure[8-10]. The structure and purity of the compounds synthesized was confirmed by elemental analysis and spectral methods: IR, ^{1}H NMR and TLC.

BIOLOGICAL ACTIVITIES

A series of compounds subjected to antimicrobial screening having general formula are listed below



4-tert-butyl-5-aryl-2,4-dihydro-3H 1,2,4-triazole-3-Thione

Where R= a = -$NO_2C_6H_4$, b = -$CH_2C_6H_5$, c = -C_6H_5, d = O-OHC_6H_4-,

e = O-ClC_6H_4-, f= P-ClC_6H_4-, g = -C_5H_4N

a. 4-tert-butyl-5-(4-nitro phenyl)-2,4-dihydro-3H-1,2,4-triazole-3-thione (IIIa)
b. 4-tert-butyl-5-benzyl-2,4-dihydro-3H-1,2,4-triazole-3-thione (IIIb)
c. 4-tert-butyl -5-phenyl-2,4-dihydro-3H-1,2,4-triazole-3-thione (IIIc)
d. 4-tert-butyl -5-(2-hydroxyphenyl)-2,4-dihydro-3H-1,2,4-triazole-3-thione (IIId)
e. 4-tert-butyl -5-(2-chloro phenyl)-2,4-dihydro-3H-1,2,4-triazole-3-thione (IIIe)
f. 4-tert-butyl -5-(4-chloro phenyl)-2,4-dihydro-3H-1,2,4-triazole-3-thione (IIIf)
g. 4-tert-butyl -5-(pyridin-4-yl)-2,4-dihydro-3H-1,2,4-triazole-3-thione (IIIg)

The microbiological assay was based upon a comparison of inhibition of growth of microorganisms by measured concentrations of test compounds with that produced by known concentration of a standard antibiotic. The antimicrobial activity of a drug/compound is generally expressed as its inhibiting effect toward the growth of the bacterium in nutrient broth or nutrient agar. The agar diffusion method [11-13] was performed using Nutrient broth media for screening antibacterial and antifungal activity.

ANTIBACTERIAL ACTIVITY

The newly synthesized compounds were screened for their antibacterial activity against the bacterial strains: Escherichia coli and Staphylococcus aureus.

PREPARATION OF MEDIUM

The medium used for the study of antibacterial activity of newly synthesized compounds having the following composition.
Media Used (Nutrient broth): Peptone-10 g, NaCl-10g and Yeast extract 5g, Agar 20g in 1000 ml of distilled water.
The antibacterial activities of all the compounds were studied against the bacteria (*Escherichia coli and Staphylococcus aureus*) at a concentration of 20 mg/mL by agar diffusion method. Gentamycin was used as a standard drug for comparison. All the compounds were dissolved in DMSO to give a concentration of 20 mg/ml. Nutrient broth of above composition was used as a growth media. The stock solution was serially diluted to give concentrations of 0.0625, 0.125, 0.25, 0.5, 1.0 and 2.0 mg in nutrient broth. All the plates were incubated at 37^0C for 24 h and the diameter of inhibition zones were noted in mm.

ANTIFUNGAL ACTIVITIES

The antifungal activity of all the synthesized compounds was performed using the fungus - *Aspergillus niger.*
The medium used for the study of antifungal activity of these newly synthesized compounds having following composition, was of fungistatic grade. It was found to be suitable for the growth of fungus, *Aspergillus niger* used in the present study.

PREPARATION OF MEDIUM

Media Used: Czapek-Dox Agar: Composition (g/l) Sucrose-30.0; Sodium nitrate-2.0; K_2HPO_4-1.0, $MgSO_4$. $7H_2O$-0.5; KCl-0.5; $FeSO_4$-0.01; Agar-22; Czapek-Dox agar medium was prepared by dissolving 56.01 g of ingredients in 1000.0 ml of distilled water. Initially, the stock cultures of were revived by inoculating in broth media and grown at 27^0C for 48 hrs.
All the compounds were dissolved in DMSO to give a concentration of 10 mg/ml. The agar plates of the above media were prepared and wells were made in the plate. Each plate was inoculated with 48 h old cultures (100 µl 10^4 CFU) and spread evenly on the plate. After 20 min, the wells were filled with different concentrations 0.0625, 0.125, 0.25, 0.5, 1.0 and 2.0 mg of samples. The control wells were filled with antibiotic Amphotericin used as standard. All the plates were incubated at 27^0C for 72 h and the diameter of inhibition zone were noted in mm.

RESULTS AND DISCUSSION

Investigation of antibaterial screening data of the newly synthesized compounds (a-g) is shown in Table-1. When compared to the standard drug Gentamycin inhibition zone record of the compounds indicated that majority of the compounds were found to be inactive against *E.Coli* whereas few showed weak activity. On the other hand, none of the synthesized compounds showed antibacterial activity against *S. aureus*.
The antifungal activity and inhibition effect of the test compounds on the growth of fungus *A. niger* are summarized in Table -2. Compound (b & c) showed low activity

against *A. niger* whereas others found to be inactive.

TABLE 1: ANTIBACTERIAL ACTIVITY OF 4-TERT-BUTYL-5-ARYL-2,4-DIHYDRO-3H-1,2,4-TRIAZOLE-3-THIONE (A-G)

Organism	Conc.	a	b	c	d	e	f	g
E. Coli	1.0 mg	0	2	0	4	0	0	0
	2.0 mg	0	6	2	8	0	0	0
	MIC mg	NF	1	2	0.5	NF	NF	NF

All the compounds were found to be inactive against *S. aureus*.

TABLE2: ANTIFUNGAL ACTIVITY OF 4-TERT-BUTYL-5-ARYL-2,4-DIHYDRO-3H-1,2,4-TRIAZOLE-3-THIONE (A-G)

Organism	Conc.	a	b	c	d	e	f	g
A. niger	1.0 mg	0	4	0	0	5	0	0
	2.0 mg	3	8	3	4	9	2	3
	MIC mg	2	0.5	2	2	0.5	2	2

CONCLUSIONS

Various 4-tert-butyl-5-aryl-2,4-dihydro-3H-1,2,4-triazole-3-thiones derivatives were synthesized from hydrazine carbothiomides as possible biologically active agents and screened for their antibacterial activity against *E.Coli* (gram negative), *S. aureus* (gram positive) and antifungal activity against *A. niger* .The minimal inhibitory concentrations (MIC) of all the compounds were determined by observing the zones of inhibition formed after 24h of incubation for antibacterial and 48h for antifungal activities. The antimicrobial activities of the synthesized compounds showed a weak activity as compared with standard drugs.

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AN ECOFRIENDLY AND EXPEDIENT SYNTHESIS OFHANTZSCH PYRIDINE DERIVATIVES USING TITANIUM DIOXIDE

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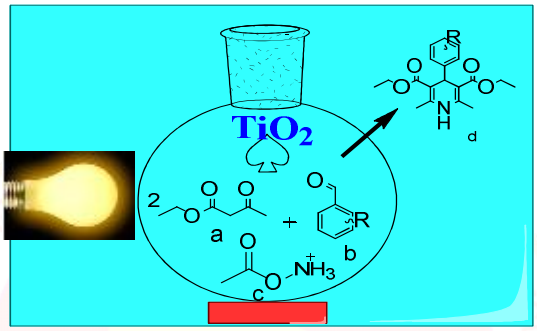
ABSTRACT

Environmental friendly and solvent free method for the synthesis of HantzschPyridine derivatives using Titanium Dioxide(TiO_2)photocatalyst,Ethylacetoacetate, Ammonium acetate and different aldehydes in light cabinet has been described. The present methodology includes inexpensive, ecofriendly, solvent free, easy isolation of product with good to excellent yield.



Graphical abstract

Keywords *Hantzsch pyridine, Titanium dioxide, photocatalyst.*

INTRODUCTION

Introduction 1,4-Dihydropyridines (1,4-DHPs) are important class of compounds in the field of drugs and pharmaceuticals[1-3]. Hantzsch 1,4-dihydropyridines (dialkyl 1,4-dihydro-2,6-dimethylpyridine- 3,5-dicarboxylates) are widely used clinically as calcium channel blockers for the treatment of cardiovascular diseasesnifedipine and nitrendipine are used for the treatment of hypertension and angina pectoris, nislodipine is a potent vasodilator and nimodipine exhibits selectivity for cerebral vasculature[4]. A number of DHP derivatives are employed as potential drug candidates for the treatment of congestive heart failure[5].

They serve asimportant analogues of NADH coenzymes[6] exhibitingneuroprotectant[7] and platelet anticoagulatory activity[8]. These compounds often act as cerebral anti-ischemic[8] agents in the treatments of Alzheimer's disease and as chemosensitizers[9] in tumourtherapy. 1,4-Dihydropyridineskeleton is also present in many,bronchodilator, antiatherosclerotic, antitumor, antidiabetic,geroprotective, and hepatoprotective agents.Moreover, thesecompounds serve as important synthetic intermediates[10-11]for the preparation of various pyridine derivatives throughoxidative aromatization. A number of syntheticprotocols for the construction of the dihydropyridine skeletonare available in the literature using ammonia[12], refluxingammonium hydroxide in a closed vessel microwavesynthesizer[13], urea-silica gel[14], ammonium acetatein ethanol under microwave irradiation[15], ammoniumhydroxide in ethanol[16], 2,4,6-trichloro-1,3,5-triazine[17],magnesium nitride[18] in water at an elevatedtemperaturein a sealed vessel using stoichiometric excess of organic reactants, and many others. Many of the protocolsuse expensive and toxic reagents (often in excessamounts than required for reaction stoichiometry), most of them havecomplicated reaction setup, require long reaction times,and form byproducts due to various side reactions. These reactions when performed in various organic solventsposing a serious threat of fire hazard, especially when theyare carried out under microwave irradiation. Several solventfreeprotocols[14] have been developed, but still they require toxic organic solvents duringproduct isolation. Also the disposal of the left-over inorganicsupports or catalyst remains problematic[14] which is hazardous to the environment. In recent times, ammoniumacetate has been judiciously utilized[19-20] as a

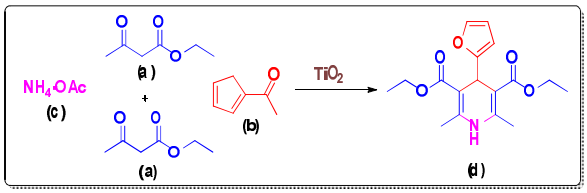
convenientsource of ammonia during the construction of variousimportant heterocyclic skeletons. Its application for the synthesisof 1,4-dihydropyridines in combination with variousreagents like trimethylsilyl iodide[21], tetrabutylammoniumhydrogen sulfate in diethylene glycol[22], baker's yeast[23], *p*-toluenesulfonicacid-sodium dodecyl sulphate[24],phenylboronic acid[25], triphenylphosphine[26], andmanyothers has been reported. Therefore, abetter alternative for the synthesis of 1,4-dihydropyridineskeleton in an ecologically benign medium preventing waste[27] and avoiding auxiliary substances[28] is always in greatdemand in order to improve environmental performance. Nowadays there is an increasing awareness of urgent necessity to limit, as far as possible, any source of pollution. Facing up to these facts, we have carried out the synthesis of 1,4-Dihydropyridine Derivativesusing Titanium Dioxide(TiO_2)photocatalystbecause of its high stability, low cost and safety toward both humans and the environment.

MATERIAL AND METHOD

All the reactions were carried out under in presence of light (100W). The organic materials were purchased from SdFine and Merck and were used without any additional purification. Merck, pre coated Silica gel 60 F_{254}(Aluminum sheet) plates were used for analytical TLC and spots were visualized by exposure to iodine vapours and by ultraviolet light. IR spectra were recorded on FTIR Brucker alpha spectrophotometer, ^{1}H-NMR spectra of all the synthesized compounds were recorded in (DMSO-d^6) on BrukerAvance-2, 400MHz NMR Spectrophotometer using TMS as an internal standard. The melting point was determined in open capillary tubes using Prefit model. The products were purified by column chromatography.

EXPERIMENTAL WORK

*General Synthetic Procedure for Preparation of Substituted Hantzsch 1, 4-dihydropyridine:*A mixture of Furfuraldehyde 1.60mL, ethylacetoacetate 5.30mL and ammonium acetate 1.6gm was placed in 50mL round bottom flask fitted with water condenser, in this mixture TiO_2 about 0.08gm (5%) was added and the reaction mixture was kept in a light cabinet for 18 hrs.The progress of the reaction was monitored by TLC. The reaction mixture was poured in crushed ice and extracted with ethyl acetate and recrystallized from ethanol.



Scheme-1: Synthesis ofHantzsch 1, 4-dihydropyridine

(d)*Diethyl 4-(furan-2-yl)- 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate* : **IR (KBr)** cm^{-1}:3343 (-N-H),2982(-C-H),1844(C=O),1148(C-O);**^{1}HNMR (DMSO–d_6)** 1.24 (m, 6H, 2-CH_3),2.26(s, 6H, -CH_3), 4.27 (m, 4H, 2-CH_2),5.06(s, 1H, -CH), 5.83(d, 1H, -CH), 6.19(q, 1H, -CH), 7.25(d, 1H, -CH), 8.68(s, 1H, -NH)

RESULTS AND DISCUSSIONS

Synthesis of Hantzschdihydropyridine by using TiO_2 as a photocatalyst is an easy, environmentally benign. Very few methods are available in literature for the synthesis of Hantzschdihydropyridine using photocatalyst, it mostly prepared by using acids. In present work synthesis of different derivatives (**Table-1**) of Hantzschdihydropyridine was carried out in presence of light(100W) with satisfactory yield. A probable mechanism for the reaction is proposed in **Scheme-2.**

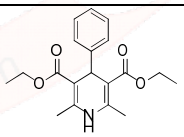
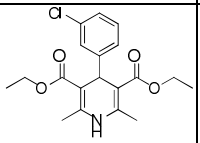
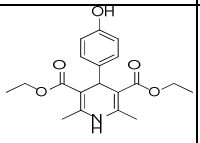
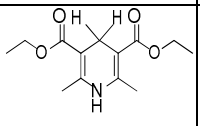
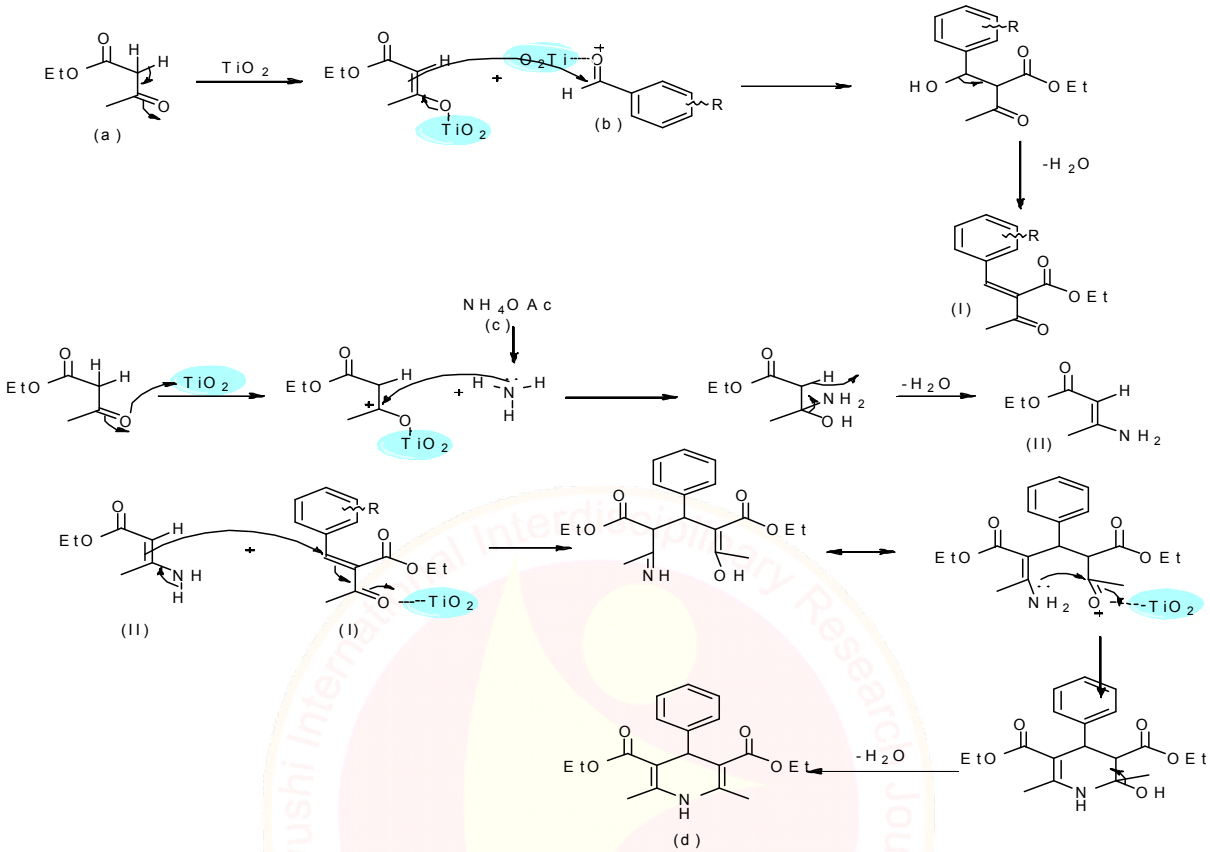
Sr. No.	DHPM Derivative	Reaction time in hr	% yield	Melting point(^{O}C)
1		62	86.85	158
2		40	69.13	203
3		33	69.85	240
4		50	71.08	163

Table-1: Hantzschdihydropyridine derivatives



Scheme-2: Probable mechanism for the synthesis of Hantzschdihydropyridine

CONCLUSION

In this methodology, the uses of hazardous organic solvents have been avoided during the synthesis. This method is satisfactory with respect to yield.This methodology includes the use of TiO_2 as a catalyst in the presence of light (100W). The catalyst has been quantitatively recovered (49.52%). The experimental protocol is simple, mild, affording high yields and represents an attractive alternative to existing methods.

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SYNTHESIS OF 2-IMINO CHLORROSUBSTITUTED-1, 3-THIAZINES AND THEIR PHYSIOCHEMICAL ASPECTS

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ABSTRACT

As a part of systematic investigation of synthesis, spectral analysis of 4-phenyl-2-hydroxy chloro substituted 2-imino-1,3-thiazines with phenyl thiourea and diphenyl thiourea from chalcone gives series, 4-(2-hydroxy-3, 5-dichlorophenyl)-6-(ethyl)-2-iminophenyl-1, 3-thiazines and 4-(2-hydroxy-3, 5-dichlorophenyl)-6-(ethyl)-2-iminophenyl-3-phenyl-1,3-thiazines (3a-6a) from phenyl thiourea and diphenyl thiourea and the interaction of transition metal ion (cobalt II) and (copper II) have been investigated by pH metric technique at 0.1M ionic strength and at 27 ± 0.5 °C in 70% DMF-water medium.

Key words *1,3-Thiazines, proton-ligand ,metal-ligand stability and stability constant.*

INTRODUCTION

Thiazine is the six member ring system which contains two heteroatoms (N & S) placed in the heterocyclic ring at 1,3 positions. Thiazines are very useful units in the field of medicinal and pharmaceutical chemistry. In the present study, various 4-phenyl-2-substituted imino thiazines were synthesized from chalcones by using phenylthiourea and diphenylthiourea[1].Chalcones and their analogues having an α,β-unsaturated carbonyl system are very versatile substrates for the evolution of various reactions[2] and physiologically active compounds[3]. The reaction of phenyl thiourea and diphenylthiourea with brominated chalcone give 1,3 thiazines[4] carried out in presence of ethanol as energy transfer medium in aq. NaOH.

it has been well established that the presence of 4-phenyl (2'-hydroxy-3', 5'-dichloro) moieties shows the m-l stability with the transition metal complexes. Recent studies on complex formation have revealed that the ligand structure plays a critical role in selectivity for metal ions. 4-phenyl-2-imino chloro substituted thiazines are good complexing agents due to electron donor nitrogen. So far meagre work have been carried out on the stability constants of transition metal complexes with the above moiety.[5,6,7]. It was, therefore, thought of interest to study the chelating complexes of 4-pheyl-2-imino chlorosubstituted thiazine under suitable conditions pH metrically. The solutions of ligands were prepared in 70% DMF water medium. The solutions of NaOH, HNO_3, cobalt nitrate and copper nitrate of (Analytical grade) were used. The metal content in its solution was estimated by standard method[8]. The pH measurements were carried out with 335 Systronics pH meter (accuracy ± 0.1 °C. The □ values (pH meter reading) in 70% DMF water mixture were converted to H^+ proposed by Van Uiterts and Hass[8]. The pH meter was calibrated by standard buffer solution (pH 4.00, 7.00, 9.00)

EXPERIMENTAL SECTION

Melting points have been determined in open capillary and are uncorrected. Purity of compound was monitored on silica gel coated TLC plate. The I.R. spectra were recorded on FTIR FTLA 2000 Spectrophotometer in KBr pelates. PMR spectra on spectrometer in $CDCl_3$. U. V. spectra on spectrophotometer (Schimadzu U.V. 1601). The analytical data of compound were highly satisfactory. All the chemicals used were analytical grade. Physical characterization data of all the compounds are given in Table I.

EXPERIMENTAL PROCEDURE INVOLVES THE FOLLOWING THREE SETS OF TITRATIONS:

1. Free acid titration (HNO_3 x 10^{-2} M), (A)
2. Free acid + ligand titration (ligand 20 x 10^{-4} M), (A+L)
3. Free acid ligand + metal ion titration (4 x 10^{-4} M), (A+L+M)

The titrations were carried out with standard NaOH solution (0.12 M) in presence of an inert atmosphere by bubbling a constant flow of nitrogen gas at constant temperature (27 ± 0.5 °C). The pH were recorded for each addition of 0.2 ml.

Ionic strength was kept constant at 0.1 M by adding an appropriate volume of 0.1 M KNO_3 solution.

THE FOLLOWING SYSTEMS WERE STUDIED:

1. pK values of L_1 and L_2 in 70% DMF water medium at 27°C
2. Log k values of Co(II), Cu(II), with ligands L_1 and L_2 were investigated.

Both ligands are monobasic containing only one –OH group; hence its dissociation is represented as below:

$$HL \rightleftharpoons H^+ + L^-$$

The deviation between acid curves and acid ligand curves started at about pH 2.0; it remained constant up to pH 2.8 and it increased continuously up to pH 12. This induced the dissociation of –OH group, which is present in the ligand part of complex structure. For all system this deviation gradually increases up to pH 11.00 to 12.00, which shows dissociation of –OH group of ligands.

Proton-ligand formation number (η_A)

The proton ligand formation numbers η_A were calculated from acid titration curves (A) and (A +L) by Irving and Rossotti's expression[10]. The pK values were estimated from formation curves (η_A vs. pH) by noting the pH at which $\eta_A = 0.5$. The accurate values of pK were determined by half-integral method, which are presented in Table2

2-HYDROXY- 3',5'-DICHLORO ACETOPHENONE (3A)

2'-Hydroxy 5'-chloro acetophenone (3gm) was dissolved in acetic acid (5mL). Sodium acetate (3gm) was added to the reaction mixture and then chlorine in acetic acid reagent (40ml, 7.5 W/V) was added drop wise with stirring. The temperature of the reaction mixture was maintained below 20 °C. The mixture was allowed to stand for 30 minutes. It was then poured into water with stirring. A pale-yellow solid then obtained was filtered, dried and crystallized from ethanol.

I.R. (KBR): 3068 cm^{-1} (-OH phenolic), 1652 cm^{-1} (>C=O in ketone), 1304 cm^{-1} (-OH bending in phenol), 737 cm^{-1} (C-Cl stretching).

PMR: δ 2.65; (s, 3H, $-CH_3$); δ 7.25 -7.63 (m, 2H, ArH); δ 12.71 (s, 1H, Ar-OH).

U. V.: 344 NM

PREPARATION OF 2'-HYDROXY-3',5'-DICHLORO-4-ETHYL CHALCONE (4A):

2'-hydroxy 3',5'-dichloro acetophenone (3a), 0.1M was dissolved in ethanol (50 mL), prpanaldehyde (0.1 M) was added to the above solution and mixture was heated to boiling. Aq. sodium hydroxide solution (50%,40 ml) was added drop wise with constant stirring. The mixture was stirred mechanically at room temperature for about half an hours and kept for overnight. Then it was acidified by hydrochloric acid solution (50 %). The solid separated was filtered, acid washed with sodium bicarbonate 10% followed by water. The crude product was crystallized from ethanol acetic acid mixture (4a).

IR:- (KBR): -3560(-OH phenolic), 2900(aliphatic –CH stretching), 1646(>C=O stretching), 778(C-Cl stretching).

PMR: -δ 2.56 to 2.67(s, 3H, -CH3),δ 7.4to 7.8 (m, 2H,Ar-H),δ 12.6(s, 1H,Ar-OH)

UV: -340.5 NM

PREPARATION OF 4-(2'-HYDROXY-3', 5'-DICHOLOROPHENYL)-6-ETHYL –2-IMINOPHENYL-1,3-THIAZINES (5A):-

2'-hydroxy-3',5'-dicholor-4-ethyl chalcone (4a), (0.01 M) dissolved in ethanol (25 mL), were added phenyl thiourea (0.01M). To this solution aq. KOH solution (0.02 M) was added (prepared from KOH in small amount of distilled water). The reaction mixture was reflux for 2.5 hours, cooled, diluted with water and acidified with conc. HCl. The product was filtered, dried and crystallized from ethanol (5a).

IR (KBR): 3566 (-OH phenolic stretching); 3206 (NH stretching); 1304 (-OH bending in phenol); 1045 (C-S stretching); 697 (C-Cl stretching).

PMR: □ 2.7 (s, 3H, $-CH_3$); □ 7.2 to 7.4 (s, -ArH); □ 4.7 (s, 1H, NH stretching); □ 12.7 (s, 1H, Ar-OH)

UV: -338 nm

PREPARATION OF 4-(2'-HYDROXY-3',5'-DICHLOROPHENYL)-6-(ETHYL)-2-IMINOPHENYL-3-PHENYL-1,3-THIAZINES (6A):

Synthesis of (6a) compound was in similar manner as such (5a), instead of phenylthiourea was used diphenylthiourea.

IR (KBR): 3566 (-OH phenolic stretching); 3209 (NH stretching); 3065 (aliphatic C-H stretching); 1306(OH bending in phenol); 1034 (C-S stretching); 695 (C-Cl stretching).

PMR: □ 2.66 (s, 1H, $-CH_3$); □ 7 to 8 (s, -ArH); □ 2.7 (s, 1H, NH); □ 12.73 (s, 1H, Ar-OH).

UV: 273 NM

SCHEME

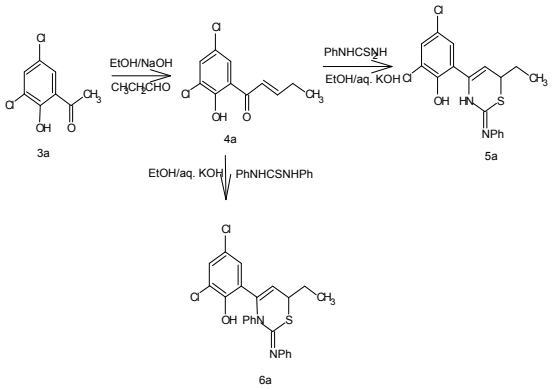

Table I: Characterization data of synthesized new compound:

Compound	Molecular Formula	M.P.	Yield (°C)	R.f. (%)
3a	$C_8H_6O_2Cl_2$	53	75	0.82
4a	$C_{11}H_{10}O_2Cl_2$	103	70	0.84
5a	$C_{18}H_{16}ON_2SCl_2$	114	75	0.77
6a	$C_{24}H_{20}ON_2SCl_2$	110	72	0.82

Table 2

Determination of proton ligand stability constants (pK) of chloro substituted thiazines at 0.1M ionic Strength

System	Constant pK
4-(2'-hydroxy 3', 5' dichlorophenyl)-6(ethyl) 2-iminophenyl –1,3 thiazines(5a)	11.7
4-(2'-hydroxy 3,'5' dichlorophenyl)-6(ethyl) 2-iminophenyl-3 phenyl –1,3-thiazines.(6a).	9.9

From the table, it appears that dissociation of these ligands occurred at higher pH. All ligands showed their dissociation in the pH range 9-12. The pK value of L_1 is found to be greater (i.e., 11.7) as compared to ligand 2. This may be due to the presence of phenyl ring group as an electron-releasing group that there is reduction in pK values.

The pK values are found decrease in the order ligand L_1 >ligand L_2.

Metal ligand stability constant;

The deviation between (acid + ligand) and (acid + ligand+ metal) curves started from pH 2.8 and increased continuously up to pH 12.0. It showed the commencement of complex formation. Intense colouration was observed which also indicated the formation of complex. The formation curves were constructed between η and pH. The metal ligand stability constants were determined by half-integral method at η= 0.5 and 1.5. The values of η are estimated by applying Irving-Rossotti1 expression[10]. The maximum values of ηwas obtained at about of K_1 and log K_2 for complexes are calculated and presented in Table 3.

Table 3

Determination of metal-ligand stability constants (log k) of Co (II), Cu (II) complexes with Chloro substituted -1,3 thiazines at 0.12 M ionic Strength.

Systems	metal ligand stability constant (Log k) (Half-integral method)		Metal ligand stability constant	
	Log k_1	log k_2	logk_1-logk_2	log k_1/ logk_2
Co (II)L_1 complex	9.48	5.99	3.49	1.582
Cu (II)L_1 complex	9.99	7.49	2.50	1.333
C0 (II)L_2 complex	6.74	5.35	1.12	1.259
Cu (II)L_2 complex	7.78	5.75	2.02	1.353

It was observed from Table 3 that log k_1 values are grater than log k_2 values for all metal complexes. The log k_1 and log k_2 values follow the order as Co (II), Cu (II). It could be seen (Table-3) that log k values follow increasing trend. This may be due to phenyl group as electron releasing group.

It could be seen from data in all the cases that the differences between log k_1 and log k_2 are found to be greater which shows formation of stepwise complex. The value of ratio of log k_1 / log k_2 is positive in all the cases (Table3). The implies that

there is no steric hindrance to the addition of secondary ligand molecule.

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SYNTHESIS, CHARACTERIZATION AND BIOLOGICAL EVALUATION OF SUBSTITUTED THIOHYDANTOINS

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ABSTRACT

In ethanol thiourea and aurone derivatives were dissolved then 40% KOH was added . Reflux reaction mixture for 3 hours and after cooling, it was then decomposed in acedified dil HCl. Solid obtained was then washed with sodium bicarbonate, dried and then recrystalised from ethanol to get substituted thiohydantoins. Thin Layer Chromatography was used to check purity of compound. The synthesized substituted thiohydantoins were characterized by 1H NMR Spectroscopy, Infrared Spectroscopy and elemental analysis. All synthesized noval substituted thiohydantoins were tested for their biological study i.e. antimicrobial and antifungal study and synthesized substituted hydantoins compounds shows outstanding antifungal and antimicrobial activities.

KEYWORDS *Antimicrobial Activities, antifungal Activities, biological study, characterization, substituted thiohydantoin, synthesis*

INTRODUCTION

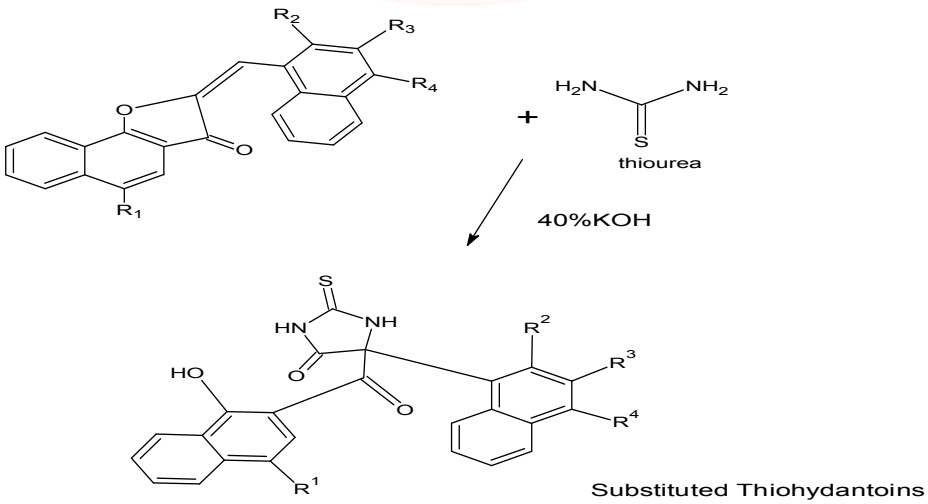
Heterocyclic compounds containing sulphur and nitrogen are not only present in natural products but also artificially synthesized as they are used as a life saving drugs. Heterocyclic compounds shows an excellent biological activities [1-6] Thiohydantoin derivatives provide useful synthetic intermediates with a wide range of applications. These compounds are known to posses wide range of biological activities such as antiepileptic[7], anticonvulsant[8], antiviral[9], antithrombotic[10] antineoplastic[11], hypolipidemic[12], and potential antitumor activities[13] antimicrobial[14]. Most of the derivatives of hydantoin are use in agriculture as a fungicides and herbicides [15-17]. Due to this vital role it was thought to synthesize hydantoin derivatives and study their biological activities

MATERIAL AND METHODS

In ethanol thiourea and aurone derivatives were dissolved then 40% KOH was added . Reflux reaction mixture for 3 hours and after cooling, it was then decomposed in acedified dil HCl. Solid obtained was then washed with sodium bicarbonate, dried and then recrystalised from ethanol to get substituted thiohydantoins.

Melting points of synthesized compounds were noted in a hot paraffin bath. All the chemicals used for the synthesis were purified. 1H NMR spectra was recorded on Bruker-AC-300 F spectrometer using TMS as a standard solvent. The Infrared spectra was recorded with Perkin Elmer spectrometer.

SCHEME



R^1 = H,Br R^2 = OCH_3, CH_3, H R^3 = OCH_3, H R^4= F,OH,H

RESULTS AND DISCUSSION

Compound No	Molecular formula	R1	R2	R3	R4	Melting Point ^{0}C	% Yield	% Nitrogen		R.F. Value
								Found	Calculated	
1	C24H15FN2O3S	H	H	H	F	195^{0}C	47%	6.50	6.51	0.51
2	C24H16N2O4S	H	H	H	OH	145^{0}C	41%	6.52	6.54	0.59
3	C25H18N2O4S	H	OCH3	H	H	212^{0}C	45%	6.33	6.33	0.61
4	C26H20N2O5S	H	OCH3	OCH3	H	167^{0}C	51%	5.92	5.93	0.55
5	C25H18FN2O3S	H	CH3	H	H	173^{0}C	42%	6.28	6.29	0.59
6	C24H14BrFN2O3S	Br	H	H	F	198^{0}C	49%	5.48	5.50	0.63
7	C24H15BrN2O4S	Br	H	H	OH	212^{0}C	53%	5.51	5.52	0.52
8	C25H17BrN2O4S	Br	OCH3	H	H	215^{0}C	44%	5.49	5.50	0.57
9	C26H19BrN2O5S	Br	OCH3	OCH3	H	177^{0}C	47%	5.07	5.08	0.51

Table 1 : Physical Properties

Compound No. 8 : IR Analysis (cm-1): 3362(OH, str) , 3197(NH, str) , 3265 (NH, str) 1703(C=O, str) 1690 (C=O, str) , 1385 (C=S, str).

NMR (δ ppm): 5.55 (s, 1H, OH), 3.85 (s, 3H, OCH_3), 7.10 (s, 1H, NH), 6.51 (s, 1H, NH), 7.54- 8.70 (m, 11Ar-H)

All peaks in Infrared and 1H NMR spectrum were appear at expected values which confirms the formation of hydantoin derivatives. Molecular weight which was determined for the above compounds by Rast's method matches with that of calculated values. The above compounds were Screened for the antimicrobial and antifungal activities against the microbes Bacillus subtilis, Klebsiella pneumoniae, Proteus vulgaris , Pseudomonas aeruginosa , Candida albicans and Aspergillus niger. All of these compounds were found active against all these microbes and fungi.

CONCLUSION

Synthesised hydantoin derivatives can be easily used for the treatment of diseases caused due to test pathogens if they do not have toxic and other side effects.

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GREEN SYNTHESIS OF 2-SUBSTITUTEDIMINO-4-AMINO-6-ALLYL FORMAMIDINO-1,3,5-THIADIAZINES

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ABSTRACT

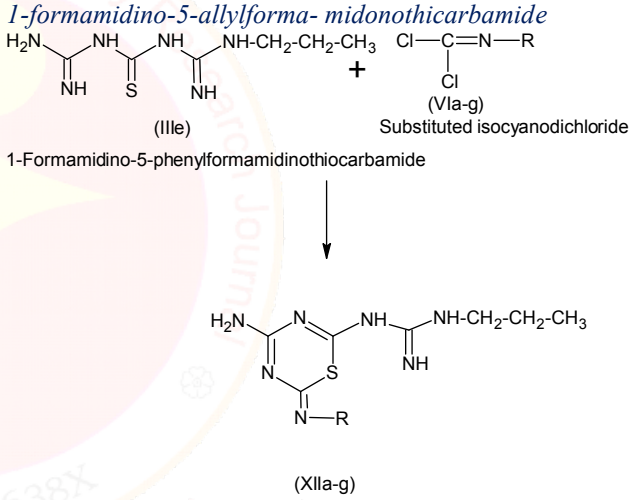
*The non-conventional synthetic method has shown broad applications as a very efficient way to accelerate the course of many organic reactions, producing high yields, higher selectivity and lower quantities of side products and consequently easier work-up and purification of the products. One-pot two component condensation of 1-formamidino-5-formamidonothicarbamide **(IIIa)** with various isocyanodichlorides **(XIa-g)** were carried out in presence of lemon juice as a biocatalyst to synthesize a novel series of 2-substitutedimino-4-amino-6-allylformamidino-1,3,5-thiadiazines **(XIIa-g)**. The structures were confirmed by conventional chemical characterization, elemental analysis and spectral studies.*

Keywords *Green Synthesis, Biocatalyst, isocyanodichlorides, 1-formamidino-5-allylforma- midonothicarbamide*

INTRODUCTION

In recent years the chemical research has been focused on the eco friendly, processes to reduce the impact on environmental pollution. Green Chemistry[1-4] is placed in the frontier areas in this regard which involves the design, development and implementation of the performance criterion. So the 'greening' of conventional reactions is done to meet the ever increasing demands of selectivity in modern synthesis[5]. Biocatalyst methods of synthesis is used for non-classical forms of energy to modify the time duration and product yield by avoiding the undesired side products[6,7]. Microwave heating and sonochemical methods have emerged as a powerful and time saving technique to promote a variety of chemical reactions[8-12]. These reaction methods, under solvent-free conditions are eco-friendly by reducing pollution with low cost, facile, safe and reproducible experimental procedures[13]. Therefore, by using lemon juice as a biocatalyst[14-15] technique has gained popularity in past decade as a powerful tool for rapid, economic and efficient synthesis of variety of compounds.

Many authors have revealed many examples of specific reactions, which do not occur under conventional conditional heating, but could be possible by lemon juice[19] with good product yields. The present study describes suitable, convenient and somewhat direct method for the synthesis of 2-substitutedimino-4-amino-6-allylformamidino-1,3,5-thiadiazines depicted below,



2-Substitutedimino-4-amino-6-allylformamidino-1,3,5-thiadiazines

METHODOLOGY

All reagents were purchased from commercial suppliers and used without further purification. Dry methanol and diethyl ether were purchased and were used as a solvent. All reactions were run in oven-dried round bottom flask or vial containing a teflon-coated stir bar and sealed with septum. Analytical thin layer chromatography was carried out on silica pre-coated glass plates (Silica gel 60 F254, 0.25 mm thickness) and visualized with UV light at 254 nm. ^{1}H NMR spectra were recorded on Bruker 400-MHz Ultrashield Advance II 400 model (400 and 100 MHz, respectively) at ambient temperature with $CDCl_3$ or DMSO-d6 as solvents. $CDCl_3$ (δ 7.26 ppm), DMSO-d6 (δ 2.50 ppm) or with tetramethylsilane (TMS, δ 0.00 ppm) as the internal standard. Chemical shifts (*δ*) were

reported as part per million (ppm) in δ scale downfield from TMS.

Result and Discussion

General procedure for the synthesis of 2-ethylimino-4-amino-6-allylforma-midino-1,3,5-thiadiazine (Xlla)

A mixture of 1-formamidino-5-allylformamidonothiocarbamide (0.1M) **(IIIa),** ethylisocyanodichloride (0.2M) **(Xla)** freshly extracted lemon juice (20 ml.) was taken in round bottom flask. It was tightly sealed and the reaction mixtures were kept in sun light for 50 hours. Then the reaction mixture was poured on ice cubes with vigorous stirring, iveroy crystals were obtained these were washed several times with water. Recrystalised from ethanol. Yield 96%, melting point 174^{0}C.

PROPERTIES OF (XI)

It is brown colour crystalline solid having melting point 210^{0}C. It gave positive test for nitrogen and sulphur. It was desulphurized by alkaline plumbite solution which clearly indicate the presence of C=S group. It was soluble in water, ethanol, DMSO-d_6 while insoluble in carbon tetrachloride, chloroform, benzene, petroleum ether. It formed picrate having melting point 180^{0}C. **Elemental analysis: [**C: 39.37% (found), 40.41% (calculated)], [H: 04.60% (found), 05.50% (calculated)], [N: 41.17% (found), 41.17% (calculated], [S: 13.20% (found), 14.68% (calculated)]. **IR Spectrum**: The IR spectrum was carried out in KBr-pellets The important absorptions are correlated as (cm^{-1}): 3358.29 N–H stretching, 2920.64 C-H stretching, 1665.78 N=C-N stretching, 1150.99 C-N stretching.

NMR SPECTRUM

The NMR spectrum was carried out in DMSO-d_6 and $CDCl_3$ This spectrum distinctly displayed the signals due to Ar-H protons at δ 7.3241-6.0145 ppm, -NH proton at δ 3.6237-3.6582 ppm, -CH_2 protons at δ 2.3251-2.6063 ppm, -CH_3 protons at δ 1.2437 ppm.

Similarly, 2-phenylimino-4-amino-6-allylformamidino-1,3,5-thiadiazine **(Xllb)**, 2-methylimino-4-amino-6-allylformamidino-1,3,5-thiadiazine **(Xllc)**, 2-p-chlorophenylimino-4-amino-6-allylformamidino-1,3,5-thiadiazine **(Xlld)**, 2-o-tolylimino-4-amino-6-allylformamidino-1,3,5-thiadiazine **(Xlle),** 2-m-tolylimino-4-amino-6-allylformamidino-1,3,5-thiadiazine **(Xllf)** and 2-p-tolylimino-4-amino-6-allylformamidino-1,3,5-thiadiazine **(Xllg)** were synthesized by the interaction of 1-formamidino-3-ethylformamidinothiocarbamide (0.1M) **(IIId)** with methyliso- cyanodichloride, (0.2M) **(XIc)**, p-chlorophenylisocyanodichloride (0.2M) (XId), o-tolylisocyanodichloride (0.2M) **(XIe)** m-tolylisocyanodichloride **(XIf)** and p-tolyl isocyanodichloride **(XIg)** lemon juice respectively and enlisted in **Table- VI-7.**

Table-VI-7

Sr. No.	2-**Substituted**imino-4-amino-6-ethylformamidino-1,3,5-thiadiazine	Juice	Yield %	M. P.
1.	2-**methyl**imino----------thiadiazine	Lemon	63	298
2.	2-**phenyl**imino----------thiadiazine	Lemon	96	268
3.	2-**p-chlorophenyl**imino--thiadiazine	Lemon	98	253
4.	2-**o-tolyl**imino----------thiadiazine	Lemon	94	279
5.	2-**m-tolyl**imino----------thiadiazine	Lemon	91	258
6.	2-**p-tolyl**imino----------thiadiazine	Lemon	86	265

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SYNTHESIS, CHARACTERIZATION AND BIOLOGICAL STUDY OF 4-THIAZOLIDINONE DERIVATIVES

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ABSTRACT

This paper sketches the construction of thiazolidin-4-one derivatives. Thiazolidin-4-one derivatives have been the present object of numberless technique, in view of their bioactivity against diverse media. The constructed admixture describes with the support of fulfill testing and spectral (1H NMR, IR) details. The combos were scan for antimicrobial action and they have display unexceptional anti-microbial action.

Keywords *Thiazolidin-4-one derivatives, Bioactivity, Anti-microbial characterization, Synthesis.*

INTRODUCTION

Sulphur and nitrogen incorporated heterocyclic combo display an important properties not only particular for life science industries but also in various another industries linked with chemistry area. 4-Thiazolidinone hereditary forms of thiazolidinone along carbonyl body fix on 4-position. Thiazolidinones which be a part of an important body of heterocyclic combo, have been largely analyze for their value in the area of medicine. Thiazolidinones loop present itself in universe. The nucleus of thiazolidin-4-ones is flexile skeleton which grant to enter structural element in it, to cast worthy transmitted form of source. The transmitted form of 4-thiazolidinone element have take a unique possession in the territory of pharmaceutical chemistry by virtue of broad range of biotic activities such as antiinflammatory[1-2], anticancer[3-4], anticonvulsant[5-7], antitubercular[8-9], antifungal[10-11], antibacterial[12-14], antimicrobial[15-17], anthelmintic[18-19] and antidiabetic[20-21] activity. Several outlines have come into view in the literature, which focus their utility and chemistry. As a result present moment was planned to study and synthesis 4-thiazolidinone by condensation process from naphthalene-1-amine with proper aldehydes and develop intermediates form (1a-10a) which put up with mercaptoacetic acid under cyclization operation effect brought correspondent 4-thiazolidinones hereditary forms of thiazolidinone.

METHODOLOGY

Entire solvents and chemical materials were used of laboratory grade or commercial and were utilize without additionally ablution. The constructed combos are making clean by recyrstallisation utilizing well-suited solvents firstly. The melting points (ºC) were recorded by open capillary tubes technique and were uncorrected. IR spectra's were taped on Shimadzu FTIR using KBr discs. 1H NMR spectra were taped on Bruker Avance II 400 spectrometer in CDCl3 utilizing TMS as a internal standard reference.

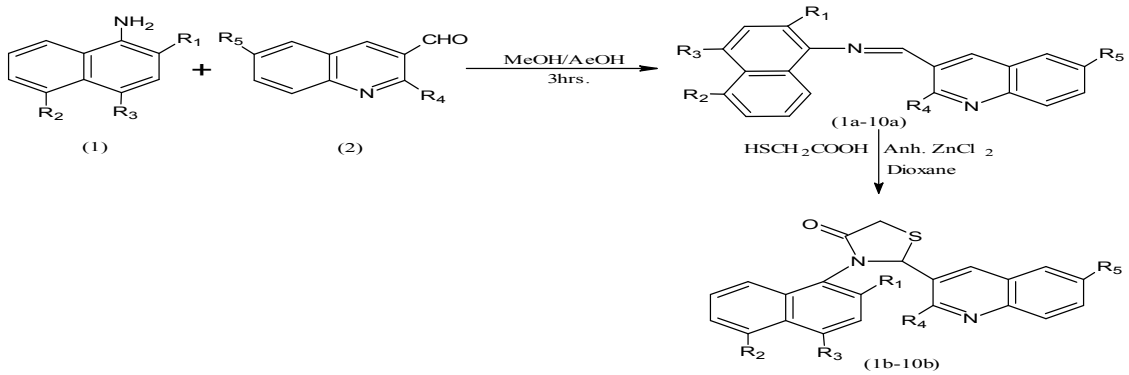
SYNTHESIS OF SCHIFF BASE

An equable admixture of substituted naphthalene-1-amine (1) and substituted quinoline-3-carbaldehyde (2) in methanol including 6-5 drops of acetic acid were refluxed for 3 hrs. Cooled reactionmixture was discharge in chilled water. The solid thus isolated was filtered, dehydrated, dried and crystallized from ethanol to gives substituted quinoline-3yl-azomethines (1a-10a).

SYNTHESIS OF THIAZOLIDINONES

A mixture of substituted quinoline-3yl-azomethines (1a-10a) (0.01 M) in dry dioxane (30 ml) containing pinch of anhydrous ZnCl2 and mercaptoacetic acid (0.01 M) was refluxed for 8 h. The reaction mixture was cooled and discharge into ice cold water. The solid was separated and filtered, dehydrated, dried and crystallized from ethanol solvent to get 4-thiazolidinone derivatives (1b-10b).

SCHEME



Spectral Interpretation: 7b

IR analysis (cm-1): 3054(Ar-H stret.),2985(C-H stret.),1674(C=O stret.),1252(C-N-C stret).

NMR analysis (δ ppm): 2.62 (s, 3H, -CH_3), 3.42 (s, 2H, -CH_2), 6.05 (s, 1H, -CH), 7.55- 8.90 (m, 12Ar-H).

Table1: Analytical and Physical characterization of synthesized compounds

Comp.	Molecular Formula	R_1	R_2	R_3	R_4	R_5	MP °C	%Yield	R.F. Value	N%	
										Found	Calculated
1b	$C_{23}H_{17}ClN_2O_4S_2$	H	SO_3H	H	Cl	CH_3	192	57	0.65	5.75	5.78
2b	$C_{24}H_{19}ClN_2OS$	CH_3	H	H	Cl	CH_3	190	55	0.58	6.67	6.69
3b	$C_{23}H_{16}ClN_3O_3S$	H	NO_2	H	Cl	CH_3	187	58	0.71	9.33	9.34
4b	$C_{23}H_{17}ClN_2OS$	H	H	H	Cl	CH_3	193	51	0.53	6.91	6.92
5b	$C_{23}H_{16}BrClN_2OS$	H	H	Br	Cl	CH_3	263	54	0.70	5.77	5.79
6b	$C_{22}H_{16}N_2O_4S_2$	H	SO_3H	H	H	H	234	59	0.64	6.41	6.42
7b	$C_{23}H_{18}N_2OS$	CH_3	H	H	H	H	218	60	0.57	7.54	7.56
8b	$C_{22}H_{15}N_3O_3S$	H	NO_2	H	H	H	190	58	0.69	10.46	10.47
9b	$C_{22}H_{16}N_2OS$	H	H	H	H	H	203	61	0.54	7.86	7.86
10b	$C_{22}H_{15}BrN_2OS$	H	H	Br	H	H	245	59	0.67	6.43	6.44

BIOACTIVITY

The antimicrobial action of all recently synthesized combo was check out against gram-negative *Escherichia coli, Pseudomonas aeruginosa,* and gram-positive bacteria *Staphylococcus aureus, Bacillus subtilis*. The culture of every pathogen groups was incubated at 37 °C and the zone of inhibition on agar plates (diffusion method) was calculated after 24 hrs. Most of these combos were found effective.

Table 2: Antibacterial Efficacy

Sr.No.	Compounds	Antimicrobial activity (Zone of Inhibition in mm)			
		E. coli	*P. aeruginosa*	*S. Aureus*	*B. subtilis*
1	1b	17	15	17	13
2	2b	7	14	10	17
3	3b	16	16	16	12
4	4b	15	15	13	18
5	5b	14	17	13	14
6	6b	15	18	12	15
7	7b	14	10	10	13
8	8b	19	16	18	17
9	9b	9	11	11	12
10	10b	13	12	13	11

The antimicrobial examination of above synthesized 4-thiazolidinones hereditary forms of thiazolidinone display excellent activity against all pathogen groups (Table-2). With the support of screening information in visible form it was noted that these heterocyclic combo can be easily used against therapy of disease caused by test pathogens.

CONCLUSION

In antimicrobial examination it was observed that the above synthesized 4-thiazolidinones hereditary forms of thiazolidinone were found effective against all the pathogens (Table-2). On the basis of screening data it was observed that these heterocyclic combos have a vast biotic capability can be easily used against treatment of disease caused by test pathogens.

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HIGH PROTEIN POPS

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ABSTRACT

A Lollipop is a type of Confectionary consisting of a sweet meats of hard candy or water ice mounted on a stick & intended for licking. Lollipops are available in many shapes, colours and flavours particularly fruit flavour. Most of the lollipops are eaten at room temperature. Some lollipops contain filling material such as bubble gum or soft candy & most of the lollipops are large boiled sweets mounted on stick.

The pops contain high amount of protein & thus can be used as supplementary foods for preschool & malnourished children. In the present investigation four samples A,B,C, D were formulated with different ingredients such as Sweetened Condensed Milk, Drinking Chocolates, Marie Biscuits and Peanut Butter. These were evaluated chemically, microbiologically as well as by organoleptically by using 9-point hedonic scale. It was found that Sample C containing Marie Biscuits, Sweetened Condensed Milk, Drinking Chocolates, and Peanut Butter in 22 g, 50 g, 23 g and 5 g was better as compared to other samples in terms of chemical analysis and sensory attributes.

KEYWORDS *Lollipops, Confection, High Protein, Drinking Chocolates, Sweeetned Condensed Milk.*

INTRODUCTION

A lollipop is a type of confectionary consisting of a sweet meat of hard candy or water ice mounted on a stick & intended for licking A cake pop is a form of cake styled as a lollipop. These are made primarily of sugar, water, corn syrup & flavouring & are available in number of colours and flavours *(Spangler Candy, 2000)*. Some lollipops contain fillings such as bubble gum or soft candy *(Nancy Bryl, 2000)*. There is also a trend of lollipops with sticks attached to a moisturized device that makes the entire lollipop spin around in one's mouth. *(Spangler Candy, 2000)*. George Smith claimed to be the 1st to invent the modern style of lollipop in 1908. He used the idea of putting candy on stick to make it easier to eat (*Spangler Candy, 2000)*. Most lollipops are eaten at room temperature but ice lollipops are frozen, water based lollipops. Thus the aim of the study was to develop high protein supplementary food in terms of protein pops for malnourished & preschool children.

MATERIALS & METHODS

Following Raw Materials were purchased from Local D-Mart and all the chemicals were of AR Grade.

1) Sweetened Condensed Milk
2) Drinking Chocolate
3) Marie Biscuit
4) Peanut Butter

METHODS

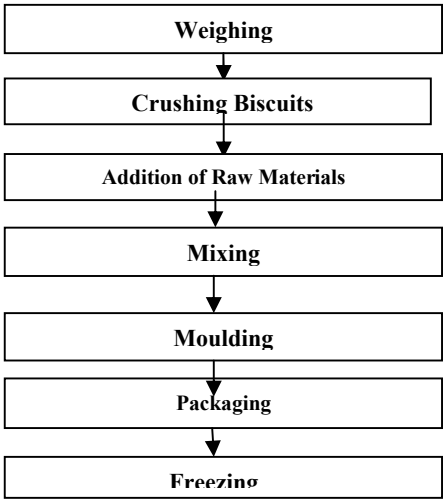
Analytical Method :- Proximate analysis was carried out by standard analytical methods protein by Kjeldahal Method, *(AOAC 1995)*, Fat by soxhlet method *(AOAC 1995*), sugar by lane Eynon's method *Ranganna (1991)*.

Preparation of Lollipop :- The Sample A,B,C,D were formulated by weighing various ingredients as Marie Biscuits, Sweetened Condensed Milk, Drinking Chocolate and Peanut Butter as shown in Table 1. All the Ingredients were mixed and moulded, balls of various sizes were made and packed. They were freezed for further studies. *(Barman, 2007)*.

Samples	Ingredients (g)				Result
	Marie Biscuits	Sweetened condensed milk	Drinking Chocolate	Peanut Butter	
A	20	53	23	5	Pops were very dry.
B	23	52	20	5	Pops were very sticky.
C	22	50	23	5	The product was acceptable.
D	22	48	23	7	Strong flavor of peanut butter.

Table 1. Formulations of the Samples.

Block Diagram of High Protein Pops



C) **Sensory Evaluation** : Sensory Evaluation was carried out to determine which of the Four Samples were better & acceptable *(Larmond, 1977)* by 9-point Hedonic Scale in which 1 = dislike very much to 9 = like very much.

D) **Microbial Analysis** It was determined for E-Coli, Total Plate Count, Yeast and Moulds and Fungal Growth *(Harrigen, 1976, Speck, 1976).*

RESULTS AND DISCUSSION

Table 2 Analysis of The Raw Material

Sr .No	Parameters %	Raw Material/100g			
		Sweetened condensed milk	Drinking Chocolate	Marie Biscuits	Peanut Butter
1	Protein	8.00	6.50	8.00	25.00
2	Fat	9.00	4.80	12.00	52.00
3	Total Sugar	26.00	66.68	22.00	10.00
4	Carbohydrates	55.50	83.08	77.00	19.00
5	Moisture	6.13	2.64	1.29	4.76
6	Ash	0.21	0.16	0.11	0.20
7.	Calories (Kcal)	335.00	405.00	468.75	645.00

Table 3 Analysis of the Sample

		Sample/100g			
Sr. No.	Parameters %	A	B	C	D
1.	Protein	7.25	8.55	9.56	4.57
2.	Fat	6.24	7.78	8.41	14.10
3	Total Sugar	40.41	39.54	41.52	59.84
4	Carbohydrates	61.02	63.53	68.52	62.50
5	Moisture	2.19	2.85	3.47	2.10
6	Ash	0.76	0.86	0.91	0.87
7	Calories (kcal)	328.32	382.34	428.01	394.94
8.	Escherichia Coli	Nil	Nil	Nil	Nil
9.	Total Plate Count	Nil	Nil	Nil	Nil
10.	Yeast and Molds	Nil	Nil	Nil	Nil

Table 4 Sensory Evaluation of the Sample

	Sample A	Sample B	Sample C	Sample D
Colour	6.0	6.4	7.5	6
Aroma	6.4	7.1	8.1	7.0
Texture	7.5	7.5	8.1	7.6
Taste	7.1	7.8	8.3	7.8
Appearance	6.7	6.3	7.7	7.8
Overall liking	6.7	6.9	7.8	7.5

DISCUSSION

Formulations A,B,C,D are given in Table 1. All proximate analysis were determined by AOAC methods (Table 2). Results were comparable with standard product. Pops content 10gm protein per 100 gm since peanut is rich source of protein. Table 3 indicated analysis for sample & market product and also fungal growth which is not appeared in the plate *(Harrigen 1976).*

Organoleptic evaluation showed that Sample 'C' was found to be acceptable compared to market sample which could be used for malnourished and preschool children *(Larmound 1977).*

CONCLUSION

According to all nutritional values High Protein Pops can be use as supplementary food for Preschool childrens and malnourished childrens.

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MICRO AND NANOCRYSTALLINE MICA SKIN CARE PRODUCTS AND THEIR APPLICATIONS

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ABSTRACT

Micas are a group of precious minerals that give the skin a captivating luminous translucency, helping mask imperfections beneath a radiantly sun- kissed appearance. Chemically, micas can be given the general formula $X_2Y_{4-6}Z_8O_{20}(OH,F)_4$ in which X is K, Na, or Ca or less commonly Ba, Rb, or Cs; Y is Al, Mg, or Fe or less commonly Mn, Cr, Ti, Li, etc.; Z is chiefly Si or Al, but also may include Fe^{3+} or Ti. Structurally, micas can be classed as dioctahedral (Y = 4) and trioctahedral (Y = 6). If the Xion is K or Na, the mica is a "common" mica, whereas if the X ion is Ca, the mica is classed as a "brittle" mica.

This review attempts to guide the reader between the various micro and nanocrystalline Mica skin care products and their applications, with a particular focus on Giordani Gold Bronzing Pearls. Paper also deals with Scanning Electron Microscope (SEM) images, Transmission Electron Microscope (TEM) images and FTIR spectra of Giordani Gold Bronzing Pearls. This research, along with better regulation and reporting, will enable consumers to choose products with confidence. This in turn will allow companies to benefit from these novel technologies in the long term while retaining customer confidence.

Morphological graphs of the Giordani Gold Bronzing Pearls sample is provided by scanning electron microscopy (Digital Scanning Electron Microscope - JSM 6100 - JEOL) with a Link analytical system operating at 10 KV (acceleration voltage) and transmission electron microscope (Transmission Electron Microscope, Hitachi H-7500, 120 kV)

Scanning Electron Microscope images of Giordani Gold Bronzing Pearls shows that the material mainly consisted of 1–5 µm size chips, and has a smaller aggregated particle size. Although the majority of material consists of micrometer chips, smaller particles with nanoscale (1–2 nm) are also present in the TEM images.

Transmission Electron Microscope images of Giordani Gold Bronzing Pearls shows that the material mainly consisted of spherical particles with 1–2 nm in diameter, and has a smaller aggregated particle size.

Investigations well confirm the presence of Mica crystals with nanometric size between 1 and 2 nm.

FTIR can be routinely used to identify the functional groups and identification/quality control of raw material/finished products. FTIR spectra of Giordani Gold Bronzing Pearls is obtained at room temperature by using an FTIR Spectrophotometer - Perkin Elmer - Spectrum RX-IFTIR. The spectra is collected in a range from 450 to 4000 cm^{-1}.Interpretation of FTIR Spectra of Giordani Gold Bronzing Pearls shows presence of various functional groups such as Alkane – CH_3– C Methyl, CH_3– (C= O), – CH_2– Methylene, – CH_2– (C= O), – CH_2– (C ≡ N),  *Ethyl, n-propyl; Alkene - Vinyl –CH=CH_2, –CH–CH– (Trans), –CH–CH– (Cis), >CH=CH2, >CH=CH–; Alkyne – C≡C–H; Alcohols - Primary alcohols CH_2–OH, Secondary CH–OH, Tertiary C–OH, Aromatic*  *; Aromatic - Monosustituted Benzene*  *, Para disustituted Benzene*  *; Amides – Amide –CO–NH_2; Amines (Cont) – Hydrochloride C–$NH3^+Cl^-$; Imines – Substituted Imines >C=N–C; Esters – Formates H–CO–O–R, Acetates –CH_2–CO–O–R, Propionates –CH_2–CO–O–R, Butyrates and up –CH_2–CO–O–R, Acrylates =CH–CO–O–R, Fumarates =CH–CO–O–R, Maleates =CH–CO–O–R, Benzoates, phthalates*  *; Aldehydes - Aliphatic Aldehydes – CH_2–CHO; Ketones – Aliph. Ketones CH_2–CO–CH_2; Anhydrides – Normal anhydrides C–CO–O– CO–C, Cyclic anhydrides*  *; Ethers – Aliphatic ethers CH_2–O–CH_2*

Key Words *Mica, Giordani Gold Bronzing Pearls, Scanning Electron Microscope (SEM) images, Transmission Electron Microscope (TEM) images, FTIR spectra.*

INTRODUCTION

Micas are a group of precious minerals that give the skin a captivating luminous translucency, helping mask imperfections beneath a radiantly sun- kissed appearance. Chemically, micas can be given the general formula $X_2Y_{4-6}Z_8O_{20}(OH,F)_4$ in which X is K, Na, or Ca or less commonly Ba, Rb, or Cs; Y is Al, Mg, or Fe or less commonly Mn, Cr, Ti, Li, etc.; Z is chiefly Si or Al, but also may include Fe^{3+} or Ti. Structurally, micas can be classed as dioctahedral (Y = 4) and trioctahedral (Y = 6). If the Xion is K or Na, the mica is a "common" mica, whereas if the X ion is Ca, the mica is classed as a "brittle" mica [1].

Figure 1. Rock with Mica

This review attempts to guide the reader between the various micro and nanocrystalline Mica skin care products and their applications, with a particular focus on Giordani Gold Bronzing Pearls. Paper also deals with Scanning Electron Microscope (SEM) images, Transmission Electron Microscope (TEM) images and FTIR spectra of Giordani Gold Bronzing Pearls. This research, along with better regulation and reporting, will enable consumers to choose products with confidence. This in turn will allow companies to benefit from these novel technologies in the long term while retaining customer confidence.

1. Giordani Gold Bronzing Pearls A simple swirl with the brush and the perfect blend of micro pearls it gives our skin a seamless, natural glow and flawless luminescence. It is Enriched with precious mica and silica minerals for a more radiant look. Its ingredients are Talc, Mica, Octyldodecyl Stearoyl Stearate, Sorbitol, Isostearyl Neopentanoate, Phenoxyethanol, Tocopheryl Acetate, Methylparaben, Propylparaben, Tin Oxide, Sodium Dehydroacetate, BHT, CI 77491, CI 77163, CI 77891, CI 77492, CI 15850, CI 77499, CI 77742, CI 45410, CI 15985, CI 77288 [2]

2. Giordani Gold Age Defying Pressed Powder It is silky powder with instant and long-term age defying results. It instantly hides fine lines and evens out skin tone without settling into creases. Over time, complexion looks brighter and skin becomes softer. With BeautAge Technology it helps to maintain skin's natural moisture and reduce appearance of signs of ageing. Its ingredients are Talc, Mica, Zea Mays Starch, Zinc Stearate, Dimethicone, Octyldodecyl Stearoyl Stearate, Neopentyl Glycol Diheptanoate, Titanium Dioxide, Isononyl Isononanoate, Lauroyl Lysine, Phenoxyethanol, Caprylyl Glycol, Sorbic Acid, Hdi/Trimethylol Hexyllactone Crosspolymer, Caprylic/Capric Triglyceride, Nylon-12, Rosa Canina Fruit Oil, Disodium EDTA, Sodium Hyaluronate, Parfum, Tocopheryl Acetate, Retinyl Palmitate, Paraffinum Liquidum, Silica, Spilanthes Acmella Flower Extract, Ascorbyl Palmitate, Benzyl Benzoate, Hexyl Cinnamal, Benzyl Alcohol, Dehydroacetic Acid, CI 77492, CI 77491, CI 77499 [3]

3. Giordani Gold Sheer Powder SPF 15 Its ingredients are Talc, Silica, Butyrospermum Parkii Butter, Simmondsia Chinensis Seed Oil, Kaolin, Zinc Oxide, Mica, Zeolite, Ethylhexyl Methoxycinnamate, Phenoxyethanol, Ricinus Communis Seed Oil, Caprylyl Glycol, Sorbic Acid, Tocopheryl Acetate, Macadamia Ternifolia Seed Oil, Lecithin, Lauroyl Lysine, Disodium EDTA, Tocopherol, Ascorbyl Palmitate, Citric Acid, BHT, CI 77891, CI 77492, CI 77491, CI 77499, CI 19140, CI 77288 [4]

4. Giordani Gold Mineral Therapy Foundation It is nourishing and hydrating formula that helps to instantly reduce the appearance of fatigue. Skin looks younger over time. Its ingredients are Aqua, Cyclopentasiloxane, Cyclohexasiloxane, Titanium Dioxide, Polyglyceryl-3 Oleate, Butylene Glycol, Cetyl Dimethicone, Cetyl PEG/PPG-10/1 Dimethicone, Mica, Cera Alba, Phenyl Trimethicone, Ethylhexyl Methoxycinnamate, Hydrogenated Castor Oil, Sodium Chloride, Methylparaben, Propylparaben, Trimethoxycaprylylsilane, Disodium EDTA, Alumina, Triethoxycaprylylsilane, Phenoxyethanol, Furcellaria Lumbricalis Extract, BHT, CI 77492, CI 77491, CI 77499 [5]

5. Giordani Gold Age Defying Foundation It is Anti-ageing foundation that visibly improves skin-tone for a younger-looking complexion. It delivers a luminous, flawless finish. It smooth away the appearance of lines and wrinkles and help in maintaining skin's natural moisture balance. It has free radical protection formula with SPF 8. Its ingredients are Aqua, Cyclopentasiloxane, Cyclohexasiloxane, Titanium Dioxide, Butylene Glycol, Cetyl Dimethicone, Cetyl PEG/PPG-10/1 Dimethicone, Polyglyceryl-3 Oleate, Mica, Cera Alba, Phenyl Trimethicone, Ethylhexyl Methoxycinnamate, Hydrogenated Castor Oil, Sodium Chloride, Imidazolidinyl Urea, Methylparaben, Trimethoxycaprylylsilane, Propylparaben, Disodium EDTA, Alumina, Glycerin, Triethoxycaprylylsilane, Parfum, Tuber Aestivum Extract, Benzyl Benzoate, Hexyl Cinnamal, Geraniol, BHT, Phenoxyethanol, Citric Acid, CI 77492, CI 77491, CI 77499 [6]

6. Giordani Gold Eye Shadow Quad Its ingredients are Talc, Mica, Ethylhexyl Palmitate, Polyethylene, Synthetic Fluorphlogopite, Calcium Titanium Borosilicate, Magnesium Stearate, Boron Nitride, Pentaerythrityl Tetraisostearate, Dimethicone, Silica, Methylparaben,

Phenoxyethanol, Lauroyl Lysine, Propylparaben, Tin Oxide, Triethoxycaprylylsilane, CI 77007, CI 77742, CI 77499, CI 77491, CI 77891, CI 77492 [7]

7. Giordani Gold Jewel Lipstick Cashmere-soft lipstick featuring a powerful blend of moisturisers for beautifully conditioned and hydrated lips all day. They are intense colour in classical shades with a lusciously creamy finish and medium coverage that lasts for hours. Its ingredients are Ricinus Communis Seed Oil, Octyldodecanol, Pentaerythrityl Tetracaprylate/Tetracaprate, Lanolin, Pentaerythrityl Tetraisostearate, Cera Microcristallina, Caprylic/Capric Triglyceride, Polyethylene, Paraffin, Bis-Diglyceryl Polyacyladipate-2, Candelilla Cera, Ethylhexyl Methoxycinnamate, Mica, Copernicia Cerifera Cera, Silica, Alumina, Butyl Methoxydibenzoylmethane, Parfum, Talc, Canola Oil, Propylparaben, Rosa Canina Fruit Oil, BHT, Tocopherol, CI 77891, CI 17200, CI 15850, CI 77491, CI 77492, CI 19140, CI 16035, CI 77499, CI 42090 [8]

8. Giordani Gold Baroque Lacque Brilliance It is Long-lasting high-shine nail polish with Fortifying Complex. Its ingredients are Butyl Acetate, Ethyl Acetate, Nitrocellulose, Acetyl Tributyl Citrate, Adipic Acid/Neopentyl Glycol/ Trimellitic Anhydride Copolymer, Isopropyl Alcohol, Styrene/Acrylates Copolymer, Stearalkonium Bentonite, Mica, Synthetic Fluorphlogopite, N-Butyl Alcohol, Benzophenone-1, Silica, Diacetone Alcohol, Aqua, Hexanal, Phosphoric Acid, Tin Oxide, Isomalt, Phospholipids, Rhododendron Ferrugineum Leaf Cell Culture Extract, Sodium Benzoate, Lactic Acid, CI 15880, CI 77891, CI 77491, CI 15850, CI 77266 (NANO), CI 19140 [9]

9. Giordani Gold Lacque Brilliance It is Long-lasting high-shine nail polish enriched with Fortifying Complex to strengthen and protect nails against signs of ageing. Its ingredients are Butyl Acetate, Ethyl Acetate, Nitrocellulose, Acetyl Tributyl Citrate, Adipic Acid/Neopentyl Glycol/ Trimellitic Anhydride Copolymer, Isopropyl Alcohol, Styrene/Acrylates Copolymer, Stearalkonium Bentonite, Mica, Silica, Synthetic Fluorphlogopite, N-Butyl Alcohol, Benzophenone-1, Diacetone Alcohol, Aqua, Hexanal, Phosphoric Acid, Tin Oxide, Isomalt, Phospholipids, Rhododendron Ferrugineum Leaf Cell Culture Extract, Sodium Benzoate, Lactic Acid, CI 15850, CI 77891, CI 15880, CI 77742, CI 19140, CI 77499, CI 77266 (Nano) [10]

METHODOLOGY

The Electron Microscope is an essential component for scientific analysis of a variety of materials. Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM) together comprises a powerful tool in studying (cell and molecular biology, anatomy, microbiology, pathology and forensic science) biological specimens, food stuffs and several other areas of material sciences (electronics, metallurgy, polymer and surface science).

Morphological graphs of the Giordani Gold Bronzing Pearls sample is provided by scanning electron microscopy (Digital Scanning Electron Microscope - JSM 6100 - JEOL) with a Link analytical system operating at 10 KV (acceleration voltage) and transmission electron microscope (Transmission Electron Microscope, Hitachi H-7500, 120 kV)

Scanning Electron Microscope (SEM) - Digital Scanning Electron Microscope - JSM 6100 (JEOL)

SEM facilitates the observation of very fine details (high resolution) of biological materials and good focus over a wide range of specimen surface (large depth of field). It also produces clear image of specimen ranging from object visible to the naked eye to a structure spanning few nanometers. Besides its use in studying soils, sedimentary particles and rock materials, it also helps to elucidate the architecture and evolution of microfossils.

Digital Scanning Electron Microscope - JSM 6100 (JEOL) is used with a digital image processor. It has a large specimen chamber that allows observation of the entire surface of a specimen upto 150 mm and a tilt of -5 to 90°. A special feature of this SEM is a cryostage attached to it to study the low melting point specimens.

The image processing function permits image averaging and storage, filling of acquired still images and comparison of two/four images displayed simultaneously on the 12 inch CRT. This function makes it possible to observe specimens without causing damage to them.

Other features of this microscope are:

Resolution	=	4.0 nm at 8mm working distance
Working distance	=	6 to 48 mm
Accelerating Voltage	=	0.3 to 30 KV
Magnification	=	x10 to x300,000

Image Recording	=	on 120 B&W Roll Film (100 ASA) or 35mm B&W roll (25 ASA)
Instant Print	=	an instant print is also possible on a Thermal Video Printer (8x10.5)

Transmission Electron Microscope (TEM) - Hitachi (H-7500) 120 kV

TEM is analogous to the optical microscope. It provides very high resolution which can reach approximately 0.1 nm in the case of lattice images. Consequently very high magnification (Close to 1 million times) can be obtained. TEM is used to examine very thin sections (<60 nm in thickness) through the cells and tissues or through materials as well as replicas of the surfaces of the samples.

A Transmission Electron Microscope, Hitachi (H-7500) 120 kV is used with CCD Camera This instrument has the resolution of 0.36 nm (point to point) with 40-120 kV operating voltage and can magnify object up to 6 lakh times in High Resolution mode. It has Electron Diffraction, Tungsten Filament, Low Dose Function, High Contrast Mode with ergodynamic look. The specific features of the instrument are: maximum 4000 cm^{-1}.

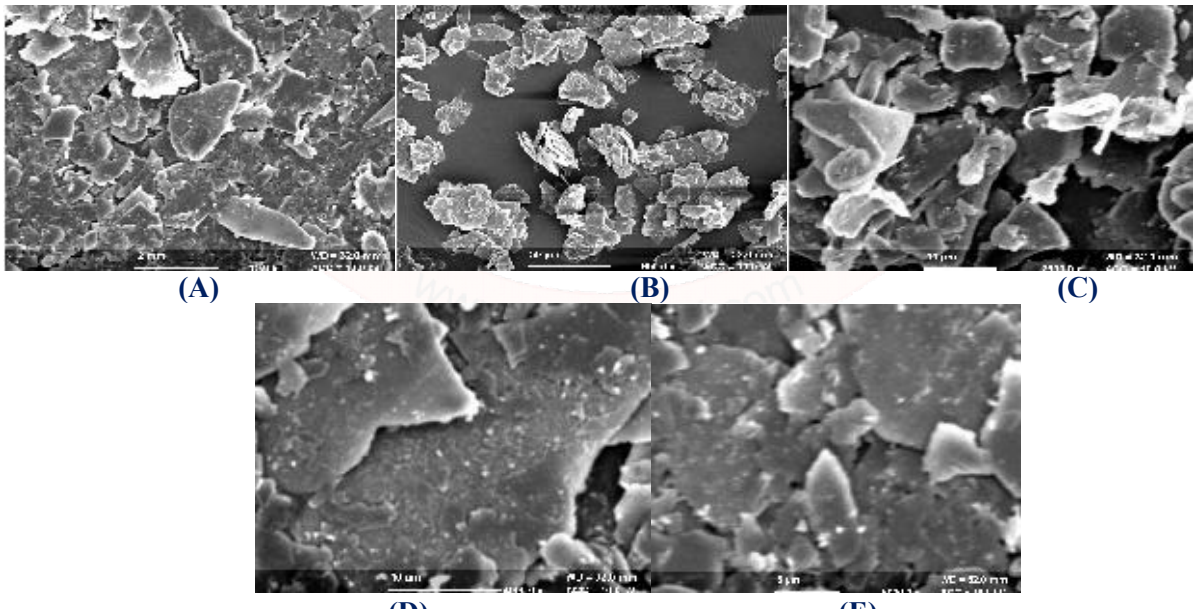
field of views at x700 with dual picture modes, Auto-navigation, Largest possible field with mose contrast, auto pre-irradiation mode (APIS). The equipment has provision for future up-gradation for an analytical system by adding EELS, EDS and STEM attachments.

FTIR Spectrophotometer - Perkin Elmer - Spectrum RX-IFTIR

FTIR can be routinely used to identify the functional groups and identification/quality control of raw material/finished products. Spectrum RX-I offers fast throughput and rapid access to reliable and dependable IR results. High signal to noise ratio makes FTIR more useful for difficult samples. It has resolution of 1 cm^{-1} and scan range of 4000 cm^{-1} to 250 cm^{-1}. In the normal mode around 10 mg sample is required in the form of fine powder. The sample can be analyzed in the form of liquid, solid and thin films also.

FTIR spectra of Giordani Gold Bronzing Pearls is obtained at room temperature by using an FTIR Spectrophotometer - Perkin Elmer - Spectrum RX-IFTIR. The spectra is collected in a range from 450 to

RESULTS AND DISCUSSION



(A) **(B)** **(C)**

(D) **(E)**

Figure 2 (A) – (E) . Scanning Electron Microscope images of Giordani Gold Bronzing Pearls

Figure 2 (A) – (E) shows Scanning Electron Microscope images of Giordani Gold Bronzing Pearls. We can learn from Figure 2 (A) – (E) that the material mainly consisted of 1–5 µm size chips, and has a smaller aggregated particle size. Although the majority of material consists of micrometer chips, smaller particles with nanoscale (1–2 nm) are also present in the TEM images (Fig. 3 H).

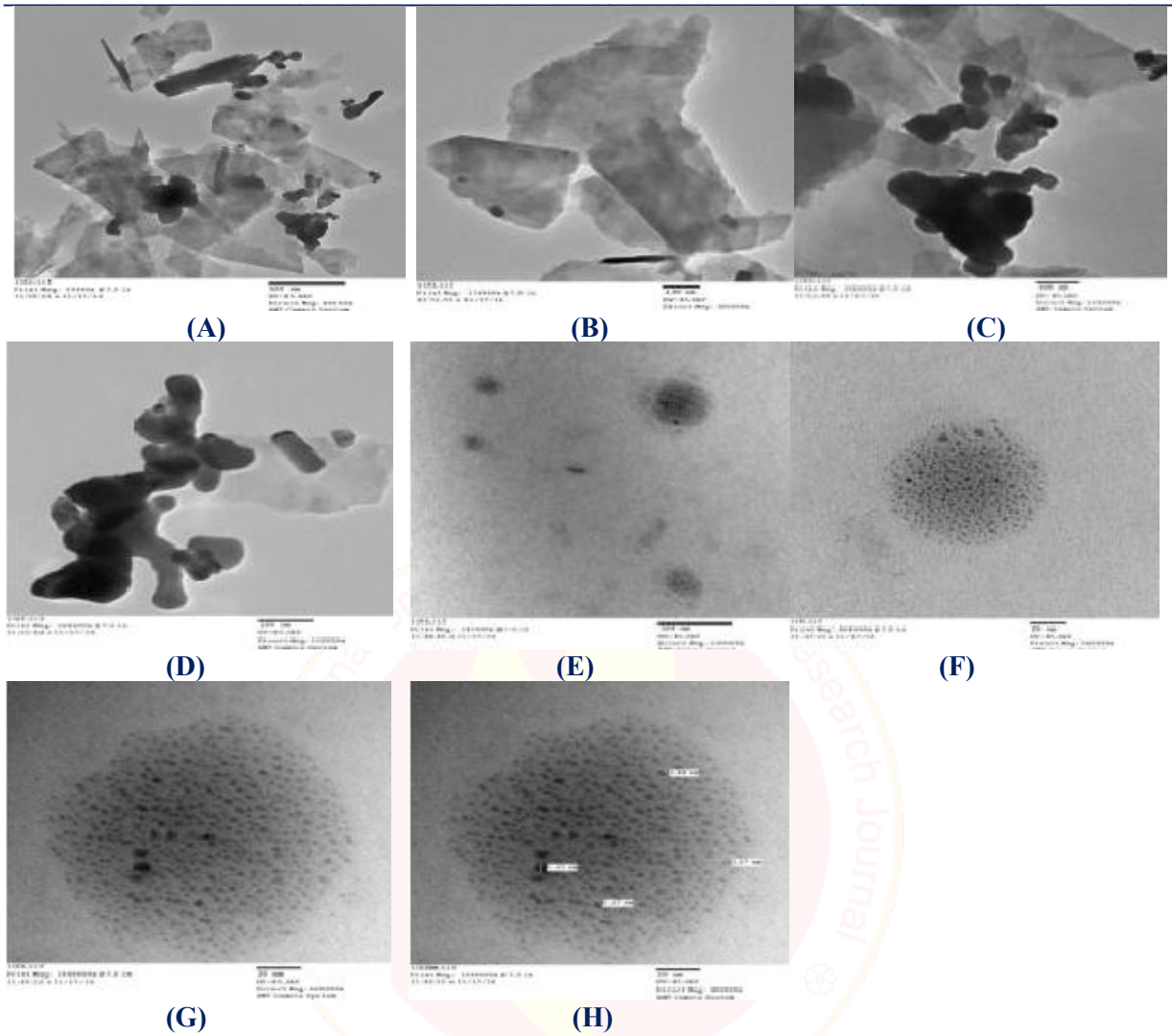


Figure 3 (A) – (H) . Transmission Electron Microscope images of Giordani Gold Bronzing Pearls

Figure 3 (A) – (H) shows Transmission Electron Microscope images of Giordani Gold Bronzing Pearls. These figures shows that the material mainly consisted of spherical particles with 1–2 nm in diameter, and has a smaller aggregated particle size.
Investigations well confirm the presence of Mica crystals with nanometric size between 1 and 2 nm.

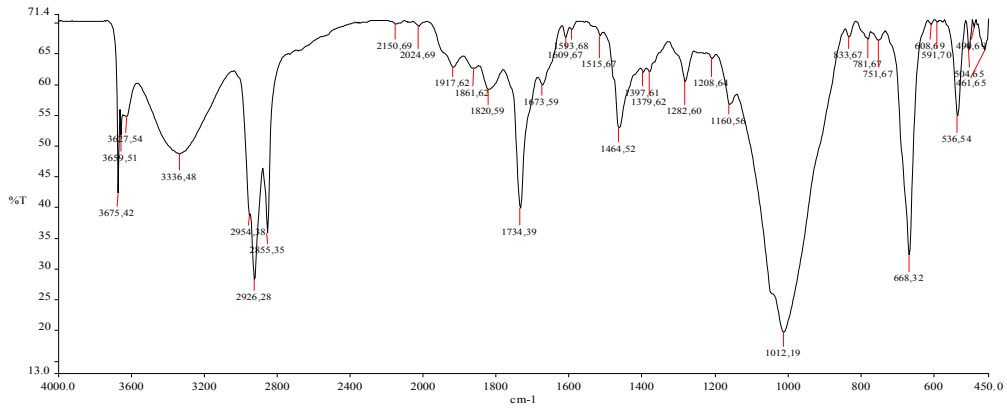


Figure 4. FTIR Spectra of Giordani Gold Bronzing Pearls
Figure 4 shows FTIR Spectra of Giordani Gold Bronzing Pearls. Interpretation of FTIR Spectra of Giordani Gold Bronzing Pearls can be done as follows:

S. N.	Spectral Region Wave number cm^{-1}	Bond causing absorption	Pattern and Intensity of Band
1	3675.42	Alcohols - Primary alcohols CH_2–OH, Tertiary C–OH, Aromatic  -OH	Sharp and Moderate Intensity
2	3659.51	Alcohols - Primary alcohols CH_2–OH, Tertiary C–OH, Aromatic  -OH	Sharp and Moderate Intensity
3	3627.54	Alcohols - Secondary CH–OH	Broad and Moderate Intensity
4	3336.48	Amides – Amide –CO–NH_2	Broad and moderate Intensity
5	2954.38	Alkane – CH_3– C Methyl, CH_3– (C= O), – CH_2– Methylene, – CH_2– (C= O), – CH_2– (C ≡ N), ≥CH, Ethyl, n-propyl	Sharp and Strong Intensity
6	2926.28	Alkane – CH_3– C Methyl, CH_3– (C= O), – CH_2– Methylene, CH_2– (C= O), – CH_2– (C ≡ N), ≥CH, Ethyl, n-propyl	Sharp and Strong Intensity
7	2855.35	Alkane – CH_3– C Methyl, – CH_2– Methylene	Sharp and Strong Intensity
8	2150.69	–	Broad and Low Intensity
9	2024.69	–	Broad and Low Intensity
10	1917.62	–	Broad and Moderate Intensity
11	1861.62	–	Broad and Moderate Intensity
12	1820.59	–	Broad and Moderate Intensity
13	1734.39	Esters – Formates H–CO–O–R, Acetates –CH_2–CO–O–R, Propionates –CH_2–CO–O–R, Butyrates and up –CH_2–CO–O–R, Acrylates =CH–CO–O–R, Fumarates =CH–CO–O–R, Maleates =CH–CO–O–R, Benzoates, phthalates  -CO–O–R ; Aldehydes - Aliphatic Aldehydes –CH_2–CHO; Ketones – Aliph. Ketones CH_2–CO–CH_2; Anhydrides – Normal anhydrides C–CO–  O– CO–C, Cyclic anhydrides	Sharp and Strong Intensity
14	1673.59	Alkene - Vinyl –CH=CH_2, –CH–CH– (Trans), –CH–CH– (Cis), >CH=CH2, >CH=CH–Aromatic - Monosustituted Benzene - Amides – Amide –CO–NH_2Amines (Cont) – Hydrochloride C–$NH3^+Cl^-$Imines – Substituted Imines >C=N–C	Broad and Moderate Intensity
15	1609.67	–	Broad and Low Intensity
16	1593.68	–	Broad and Low Intensity
17	1515.67	–	Broad and Low Intensity
18	1464.52	Alcohols - Primary alcohols CH_2–OH	Broad and Moderate Intensity
19	1397.61	Alcohols - Primary alcohols CH_2–OH	Broad and Low Intensity
20	1379.62	–	Broad and Low Intensity
21	1282.60	Alcohols - Secondary CH–OH	Broad and Moderate Intensity
22	1208.64	–	Broad and Low Intensity
23	1160.56	–	Broad and Moderate Intensity
24	1012.19	Alcohols - Primary alcohols CH_2–OH	Broad and Strong Intensity
25	833.67	Alkane – Ethyl, n-propyl	Broad and Low Intensity
26	781.67	–	Broad and Low Intensity
27	751.67	–	Broad and Low Intensity
28	668.32	Alkene - Vinyl –CH=CH_2, >CH=CH–; Alkyne –C≡C–H	Sharp and Strong Intensity
29	608.69	–	Broad and Low Intensity
30	591.70	–	Broad and Low Intensity
31	536.54	Aromatic - Para disustituted Benzene  ; Ethers – Aliphatic ethers CH_2–O–CH_2	Sharp and Moderate Intensity
32	504.65	–	Broad and Low Intensity
33	490.69	–	Broad and Low Intensity
34	461.65	–	Broad and Low Intensity

Interpretation of FTIR Spectra of Giordani Gold Bronzing Pearls shows presence of various functional groups such as

Alkane – CH_3– C Methyl, CH_3– (C= O), – CH_2– Methylene, – CH_2– (C= O), – CH_2– (C ≡ N), ≥CH, Ethyl, n-propyl

Alkene - Vinyl –CH=CH_2, –CH–CH– (Trans), –CH–CH– (Cis), >CH=CH2, >CH=CH–

Alkyne –C≡C–H

Alcohols - Primary alcohols CH_2–OH, Secondary CH–OH, Tertiary C–OH, Aromatic –OH

Aromatic - Monosustituted Benzene -, Para disustituted Benzene 

Amides – Amide –CO–NH_2

Amines (Cont) – Hydrochloride C–$NH3^+Cl^-$

Imines – Substituted Imines >C=N–C

Esters – Formates H–CO–O–R, Acetates –CH_2–CO–O–R, Propionates –CH_2–CO–O–R, Butyrates and up –CH_2–CO–O–R, Acrylates =CH–CO–O–R, Fumarates =CH–CO–O–R, Maleates =CH–CO–O–R, Benzoates, phthalates –CO–O–R ;

Aldehydes - Aliphatic Aldehydes –CH_2–CHO;

Ketones – Aliph. Ketones CH_2–CO–CH_2;

Anhydrides – Normal anhydrides C–CO–O– CO–C, Cyclic anhydrides 
Ethers – Aliphatic ethers CH_2–O–CH_2

CONCLUSION

Scanning Electron Microscope images of Giordani Gold Bronzing Pearls shows that the material mainly consisted of 1–5 µm size chips, and has a smaller aggregated particle size. Although the majority of material consists of micrometer chips, smaller particles with nanoscale (1–2 nm) are also present in the TEM images.

Transmission Electron Microscope images of Giordani Gold Bronzing Pearls shows that the material mainly consisted of spherical particles with 1–2 nm in diameter, and has a smaller aggregated particle size.

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Interpretation of FTIR Spectra of Giordani Gold Bronzing Pearls shows presence of various functional groups such as

Alkane – CH_3– C Methyl, CH_3– (C= O), – CH_2– Methylene, – CH_2– (C= O), – CH_2– (C ≡ N), , Ethyl, n-propyl
Alkene - Vinyl –CH=CH_2, –CH–CH– (Trans), –CH–CH– (Cis), >CH=CH2, >CH=CH–
Alkyne –C≡C–H
Alcohols - Primary alcohols CH_2–OH, Secondary CH–OH, Tertiary C–OH**,** Aromatic 
Aromatic - Monosustituted Benzene  , Para disustituted Benzene 
Amides – Amide –CO–NH_2
Amines (Cont) – Hydrochloride C–$NH3^+Cl^-$
Imines – Substituted Imines >C=N–C
Esters – Formates H–CO–O–R, Acetates –CH_2–CO–O–R, Propionates –CH_2–CO–O–R, Butyrates and up –CH_2–CO–O–R, Acrylates =CH–CO–O–R, Fumarates =CH–CO–O–R, Maleates =CH–CO–O–R, Benzoates, phthalates  ;
Aldehydes - Aliphatic Aldehydes –CH_2–CHO;
Ketones – Aliph. Ketones CH_2–CO–CH_2;
Anhydrides – Normal anhydrides C–CO–O– CO–C, Cyclic anhydrides 
Ethers – Aliphatic ethers CH_2–O–CH_2

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RELATIVE ASSOCIATION, SPECIFIC RELAXATION TIME AND FREE VOLUMEOF ANTIBIOTIC CEFTRIAXONE SODIUM

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ABSTRACT

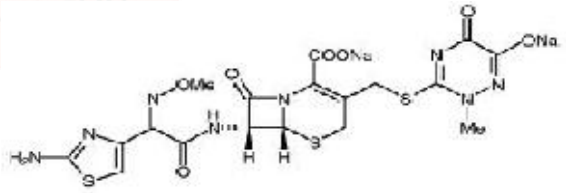
In the recent years ultrasonic is an area of intense scientific research in material science. The ultrasonic technique used to measure speed in liquids, liquid mixtures and solutions has been found useful to study physico-chemical properties of liquid mixtures and solutions. Ultrasonic studies are use for understanding thermodynamic properties of liquid mixtures and solutions. These studies are also useful in understanding the nature and strength of molecular interactions. Antibiotic is a chemical substance derived from a mold or bacterium that can kill micro-organism and cure bacterial infection. Ceftriaxone sodium is an antibiotic used in pharmaceutical. In the present paper ultrasonic velocity, density and viscosity have been measure at different concentrations, temperatures and different frequencies such as 2MHz, 4MHz and 6MHz. The data obtained was used to evaluate relative association, specific acoustic relaxation time and free volume. These data were utilized to explain solute-solvent, solute-solute interaction and molecular association through salvation and hydrogen bonding.

Key words *ultrasonic velocity, molecular interactions, hydrogen bonding, salvation, ceftriaxone sodium*

INTRODUCTION

Measurement of ultrasonic velocity provides qualitative information regarding nature and strength of molecular interaction in the liquid mixtures and solutions. Ultrasonic studies created its own importance in engineering, pharmaceutical, medical, biochemical, chemical sciences, life sciences, various industries like textile industries, process industries, nuclear energy industries and many areas of human endeavor. Ultrasonic waves provide a sensitive probe to sense the intermolecular interactions in liquids and solutions. There has been increasing interest in the use of this probe in the past.[1]Ultrasonic is an area of intense scientific and technological research. Science and technology of ultrasonic widely sought in the recent years for medical applications. A number of researchers[2-6]have investigated the molecular interaction in aqueous solution of different antibiotics. Ceftriaxone sodium is third generation cephalosporin antibiotic used in pharmaceuticals. It is used to prevent or treat certain infections caused by bacteria. It is used to treat infections of lung, urinary track, skin, abdomen, bone, joint and gonorrhea.

A survey of literature reveals that no study on interaction of ceftriaxone sodium in water has been reported from point of view of ultrasonic velocity, density and viscosity measurements.In continuation of our work [7-13]in the present investigation density, viscosity and sound speed of aqueous solution of ceftriaxone sodium were measured at different temperatures, concentrations and frequencies. From this experimental data the parameters such as relative association, specific acoustic relaxation time and free volume have been calculated. These simple parameters are found to be useful in the interpretation of solute-solute, solvent-solvent, solute-solvent interaction and a molecular association in aqueous solution of ceftriaxone sodium not easily obtained by other means.



(Ceftriaxone sodium)

EXPERIMENTAL

Antibiotic drug ceftriaxone sodium obtained from Prosperity 6 pharmaceutics Limited was used.The chemicals used were of analytical grade. Double distilled water was used for preparation of solutions. A special thermostatic water bath arrangement was made for density, ultrasonic velocity and viscosity measurements and temperature variation was maintained within $\pm 0.01^0$C multi frequency interferometer (Mittal

Enterprises, Model F-83) with accuracy of ±0.03% and frequency 2 MHz, 4MHz, 6MHz were used in the present work for measurement of ultrasonic velocities of solutions. Densities of solutions were measured using specific gravity bottle. These values were accurate up to ± 0.1 kg/m^3. All the weighing was made on CA-124 (CB/CA/CT series, Contech) digital electronic balance having an accuracy of ± 0.0001g. Viscosities of the solution were measured by Ostwald's viscometer.

RESULTS AND DISCUSSION

In the present investigation, measurements of densities, viscosities and ultrasonic velocities of solvent water and an antibiotic ceftriaxone sodium solution in water have been made.

Relative association is a function of ultrasonic velocity and is calculated by the equation,

$$R_A = \frac{d_s}{d_0}\left(\frac{v_0}{v_s}\right)^{1/3} \quad \text{--------- (2)}$$

Where, v_0 and v_s are ultrasonic velocities in solvent and solution respectively.

Relaxation time is evaluated by equation

$$\tau = 4/3\beta.\eta$$

Where, β=adiabatic compressibility **η**=viscosity of experimental liquid.

Free volume is calculated by following equation

$$V_f = [Meffv/K\tau]^{3/2} \quad \text{.....(3)}$$

Where, M_{eff} is effective molecular weight, K is a temperature independent constant which is equal to 4.28 x 10^9 for all liquids.

Viscosity of Solution is calculated by equation

$$\eta_2 = \eta_1.t_2.ds/t_1.d_0 \quad \text{... ... (4)}$$

Where, η_1=viscosity of water, η_2= viscosity of experimental liquid, t_1=time flow of water, t_2=time flow of experimental liquid, d_0=density of water and ds=density of experimental liquid.

The values of ultrasonic velocities, densities, viscosities, relative association, specific relaxation time and free volume at different frequencies, concentrations and temperatures are tabulated in table 1, 2 and 3

Table 1: Acoustic parameters of aqueous solution of Ceftriaxone sodium at 2MHz.

Temperature (K)	Concentration (M)	Ultrasonic Velocity (m/s)	Density (Kg/m^3)	Viscosity ηx10^3 (NSm^{-2})	Relative association (R_A)	Specific relaxation time τx10^{-10} (sec)	Free Volume V_fx10^{-8}(m3/mole)
303.15	0.001	1488.09	1025.40	0.8431	1.0321	4.9508	1.2128
	0.01	1488.34	1030.70	0.8736	1.0374	5.1022	1.2873
	0.1	1489.44	1054.37	1.1529	1.0609	6.5722	2.0700
308.15	0.001	1524.32	1020.93	0.7507	1.0297	4.2197	1.0600
	0.01	1525.20	1026.42	0.7794	1.0350	4.3523	1.1300
	0.1	1525.49	1044.61	1.0019	1.0533	5.4956	1.7400
313.15	0.001	1554.55	1015.52	0.6720	1.0183	3.6511	0.9220
	0.01	1563.54	1016.94	0.7208	1.0178	3.8670	1.0400
	0.1	1598.64	1038.52	0.8508	1.0317	4.2745	1.4600

Table 2: Acoustic parameters of aqueous solution of Ceftriaxone sodium at 4MHz.

Temperature (K)	Concentration (M)	Ultrasonic Velocity (m/s)	Density (Kg/m^3)	Viscosity ηx10^3 (NSm^{-2})	Relative association (R_A)	Specific relaxation time τx10^{-10} (sec)	Free VolumeV_fx10^{-8}(m3/mole)
303.15	0.001	1527.62	1025.40	0.8431	1.0477	4.6979	1.2615
	0.01	1524.10	1030.70	0.8736	1.0539	4.8656	1.3340
	0.1	1532.64	1054.37	1.1529	1.0761	6.2069	2.1608
308.15	0.001	1592.98	1020.93	0.7507	1.0343	3.8638	1.1300
	0.01	1594.26	1026.42	0.7794	1.0395	3.9834	1.2000
	0.1	1599.30	1044.61	1.0019	1.0568	5.0000	1.8700
313.15	0.001	1600.16	1015.52	0.6720	1.0410	3.4459	0.9620
	0.01	1600.14	1016.94	0.7208	1.0426	3.6922	1.0800
	0.1	1605.45	1038.52	0.8508	1.0635	4.2383	1.4700

Table 3: Acoustic parameters of aqueous solution of Ceftriaxone sodium at 6MHz.

Temperature (K)	Concentration (M)	Ultrasonic Velocity (m/s)	Density (Kg/m^3)	Viscosity $\eta x10^3$ (NSm^{-2})	Relative association (R_A)	Specific relaxation time $\tau x10^{-10}$ (sec)	Free Volume $V_f x10^{-8}$(m3/mole)
303.15	0.001	1633.57	1025.40	0.8431	1.0477	4.6972	1.2615
	0.01	1634.61	1030.70	0.8736	1.0371	4.2299	1.4817
	0.1	1639.54	1054.37	1.1529	1.0599	5.4239	2.3907
308.15	0.001	1635.90	1020.93	0.7507	1.0497	3.6637	1.1700
	0.01	1636.29	1026.42	0.7794	1.0553	3.7814	1.2500
	0.1	1643.65	1044.61	1.0019	1.0724	4.7338	1.9400
313.15	0.001	1641.51	1015.52	0.6720	1.0435	3.2745	1.0000
	0.01	1642.88	1016.94	0.7208	1.0468	3.5025	1.2200
	0.1	1742.33	1038.52	0.8508	1.0482	3.5985	1.6600

On a keen look at the Tables 1, 2 and 3, it is observed that the values of density and viscosity of aqueous solution of ceftriaxone sodium increases with increase in concentration and the same decreases with increase of temperature. The increasing values of density and viscosity with concentration are mainly due to shrinkage in the volume of solution due to addition of solute whereas, the decreasing values of density and viscosity with temperature are due to decrease of molecular forces which in turn may be due to increasing the thermal energy of the system. Ultrasonic velocity values of aqueous solution of ceftriaxone sodium increases with increase in concentration, temperature and frequency such as 2MHz, 4MHz and 6MHz. A similar effect has been reported by Syal etal.[14-15] The increased values of ultrasonic velocity with the addition of solute is indicative of greater molecular association of molecules due to effective solute-solvent interaction and also due to cohesion brought by the ionic hydration. At 4MHz at 303.15K and 313.15K ultrasonic velocity decreases up to 0.01M and then increases. This may be due to self-association of solvent molecule and very weak dipole-induced dipole interaction between components of molecule, which is concentration dependant. The increasing values of ultrasonic velocity, density and viscosity indicate that there is specific strong attraction between ceftriaxone sodium and water molecules.

Relative association is the measure of extent of association of components in the medium. It is used to assess the association in any solution relative to the association existing in water at 0^{o}C. Relative association is a property of understanding the molecular interaction in liquid mixtures and solutions.From Fig. 1 and Table 1, 2 and 3, it can be easily seen that the $R_A$values increased with increase in concentration and same decreases with increase in temperature. At 4MHz ,R_A values decreases up to 308.15K and then increases whereas, at 6MHz it is reversed that is it increases up to 308.15K and then decreases with increases of temperature. Increase in R_A with increase in concentration suggests that salvation of solute is predominant over the breaking of solvent structure whereas, decrease in R_A with increase in temperature suggests that breaking of solvent structure is predominant over the solution of solute due to polar nature of water. This supports the strengthening of interaction among ceftiaxone sodium and water molecules due to formation of hydrogen bond.

Specific relaxation time is the time taken for the excitation energy to appear as translational energy. It depends on temperature and on impurities. The dispersion of the ultrasonic velocity in liquid mixtures and solutions reveals information about the characteristic time of relaxation process that cause dispersion.From Fig. 2 and Table 1, 2 and 3, it is observed that the values of relaxation time increases with increase in of concentration and same decreases with increase in temperature and frequency, except at 6MHZ at 303.15K it decreases up to 0.01M and then increases. The relaxation time is the order of 10^{-12}sec is due to the structural relaxation process[16] and such situation suggest that the molecules get rearranged due to co-operative process.[17]This indicates the presence of specific molecular interaction among cefriaxone sodium and water.

According to Eyring and Kincaid free volume is defined as the effective volume in which particular molecule of liquid can move and obey perfect gas equation. It is also defined as average available volume between molecules of mixture. From Fig. 3 and Table 1, 2 and 3, it is noted that free volume increases with increase in concentration and frequency. However, with rise in temperature decrease in free volume is noticed. Increase of free volume with increase in concentration and frequency suggests decrease of close packing of molecules inside the shield whereas decrease of free volume with increase in temperature suggests increase of close packing of molecules inside the

shield, which may brought about by increasing magnitude of molecular interaction in aqueous solution of ceftriaxone sodium.

CONCLUSION

Computed acoustical parameters and their values point to presence of specific strong molecular interaction in aqueous solution of ceftriaxone sodium. Hence it is concluded that molecular association in aqueous solution of ceftriaxone sodium is the result of hydrogen bonding .

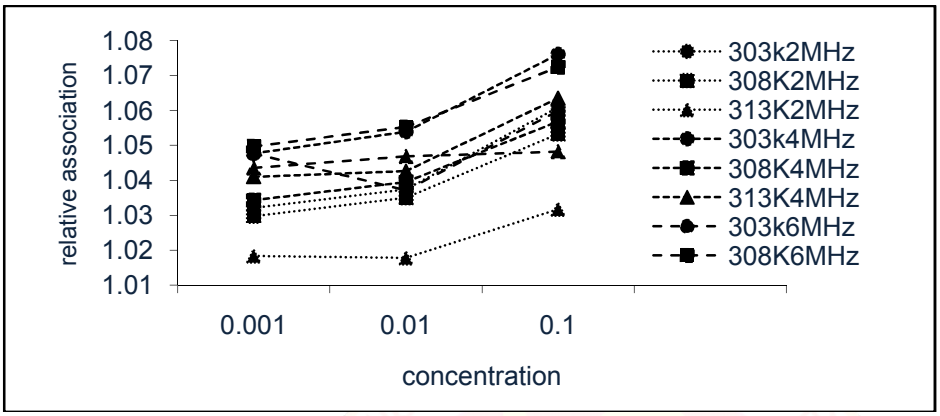


Fig. 1 variation of free volume with concentration, temperature and frequencies.

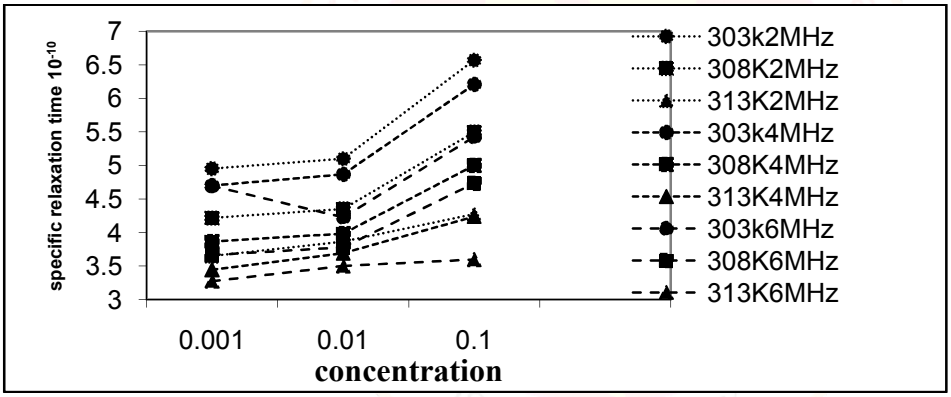


Fig. 2 variation of specific relaxation time with concentration, temperature and frequencies.

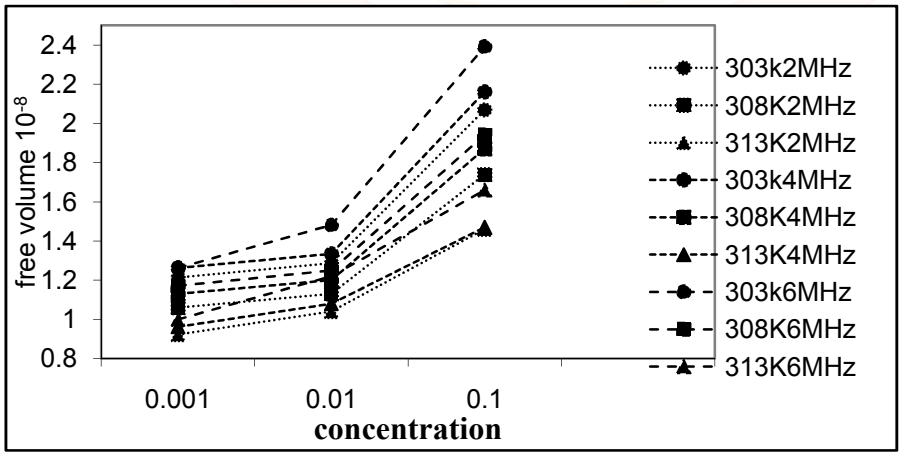


Fig. 3 variation of free volume with concentration, temperature and frequencies.

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A NEW SYNTHESIS OF 4-[5-(4-PHENYL-5-SUBSTITUTED-IMINO-1,2,4-DITHIAZOLO)]IMINO-1,2,4-THIADIAZOLO-PYRIDINES

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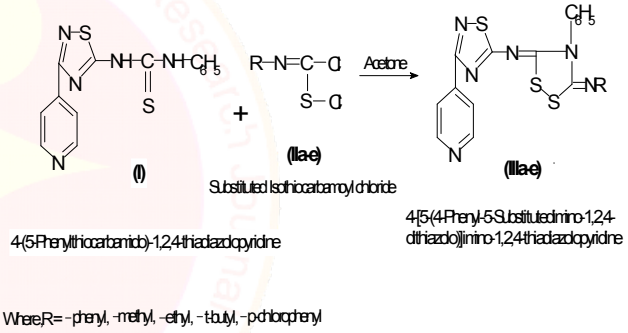
ABSTRACT

*A novel series of 4-[5-(4-phenyl-5-substitutedimino-1,2,4-dithiazolo)]imino-1,2,4-thia-diazolopyridines **(IIIa-e)** was successfully synthesis by the interactions of 4-(5-phenylthio-carbamido)-1,2,4-thiadiazolopyridines **(I)** with various isothiocarbamoylchloride **(IIa-e)** in acetone medium. Synthesized compounds were recrystallised and their structures were justified and established on the basis of elemental analysis, chemical characteristic and through spectral studies.*

INTRODUCTION

When literature survey was carried out it is observed that dithiazolo, thiadiazolo nucleus containing drugs possess an important applications and significances in industrial, medicinal, drug, pharmaceutical, agricultural and biotechnological sciences[1-5]. Dithiazolo nucleus containing drugs are widely used as chemotherapy for cancer[6-7] and anti-HIV drugs[8], they showed various biological activities[9-11] such as anti-tumor[12], anti-tuberculosis[13], antidibetic[14], antiviral[15], anti-fungal[16], anti-hypertensive[17] and anti-histamatic[18]. It was also noticed that this dithizines is used as additive in lubricating oil[19] and possess brightening, finishing properties in textile[20-23].

Some important reactions of substituted isothiocarbamoylchlorides involving nucleophilic displacement of both chlorine atoms have been briefly investigated by Tayade[24], Deohate[25], Pandey[26], Pathe[27], Berad[28] and Aparajit[29]. In the viewed of utility and impotance of these compounds in various fields and as part of wider progrmme in the synthesis of nitrogen, nitrogen and sulphur containing heterocycles and heteroacycles to develop alternative route for the synthesis of five and six membered heterocycles in this labourtory. Hence it appeared sufficiently interesting to explore the synthetic applications of substitutedisothiocarbamoylchlorides by further making use of -phenyl, -methyl, -ethyl, t-butyl, p-chlorophenyl group as a blocking group introducing an isothiocarbamoylchlorides, these interactions were investigated to syntheses the newer type of series which containing dithizole and thiadiazole nucleus in the same molecules. The present work described somewhat suitable and direct method for the synthesis of the novel series of 4-[5-(4-phenyl-5-substitutedimino-1,2,4-dithiazolo)]imino-1,2,4-thiadiazolo pyridines **(IIIa-e).**



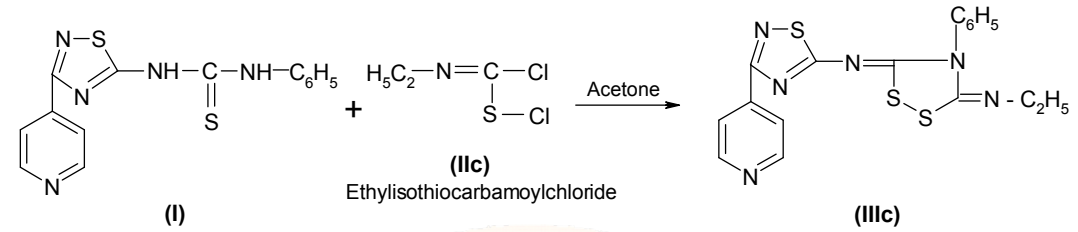
EXPERIMENTAL

Melting points of all the synthesized compounds were recorded using hot paraffin bath and are uncorrected. The carbon and hydrogen analysis was carried out on Carlo-Ebra-1106 analyser, nitrogen estimation was carried out on Colman-N-analyser-29. IR spectra were recorded on Perkin-Elmer spectrometer in the range 4000-400 cm^{-1} in KBr pellets. PMR spectra were recorded on Bruker AC-300F spectrometer with TMS as internal standard using $CDCl_3$ and DMSO-d_6 as solvent. The purity of the compounds was checked on Silica Gel-G plates by TLC with layer thickness of 0.3 mm. All chemicals used were of AR grade (Indian make) except allylthiourea Lancaster (Germany make). Alkyl/Aryl isothiocynates, isothiocarbamoylchloride, isocyanodichlorides and phenylthiourea have been prepared by known literature methods.

RESULT AND DISCUSSION

Synthesis of 4-[5-(4-phenyl-5-ethylimino-1,2,4-dithiazolo)]imino-1,2,4-thiadiazolo-pyridine (IIIc):

4-[5-(4-Phenyl-5-ethylimino-1,2,4-dithiazolo)]imino-1,2,4-thiadiazolo-pyridine **(IIIc)** was synthesized by refluxing the mixture of 4-(5-phenyl-thiocarbamido)-1,2,4-thiadiazolopyridine **(I)** with ethylisothiocarbamoylchloride **(IIc)** in acetone medium on water bath for 4 hours. During boiling the suspended 4-(5-phenylthiocarbamido)-1,2,4-thiadiazolopyridine **(I)** and ethylisothiocarbamoylchloride **(IIc)** went into the solution and new product was found to be gradually separated out. It was filtered in hot conditions, and then on basification with dilute ammonium hydroxide solution gave dark yellow crystalline product. Recrystallized from aqueous ethanolic solution to isolate **(IIIc),** yield 85 %, m.p. 158^{0}C.



Properties

It was dark yellow crystalline solid having melting point 158^{0}C. It gave positive test for nitrogen and sulphur. Desulphurization was not observed when warm with silver nitrate and sodium plumbite solution clearly indicating sulphur is blocked in a ring. The benzene solution of compounds when treated with pure and dry carbon disulphide then colourless solution was obtained indicating =NH (imino) group is not present[30]. It formed picrate having melting point 173^{0}C. **Elemental Analysis: C [**(found 50.8-0%) calculated 51.25%]**, H** [(found 03.10%) calculated 3.51%]**, N [**(found 20.98%) calculated 21.10%], **S** [(found 24.12%) calculated 24.12%]**. IR Spectra:-**The IR spectra was carried out in KBr pellets and the important absorption can be correlated as (cm^{-1}) 2610.43 (C-H stretching), 2194.38 (N-C=S stretching), 1621.70 (N-C=N grouping showing Hexocyclic ring), 1548.21 [C=N stretching (Ring)], 1404.50 (C=N stretching), 1091.35 (C-N stretching), 731.27 (Monosubstituted Benzene), 538.29 (S-S stretching). N**MR Spectra**:-The spectrum was carried out in $CDCl_3$ and DMSO-d_6. This spectrum distinctly displayed the signals due to pyridino proton at δ 8.6805 ppm, Ar-H proton at δ 6.6884-7.9026 ppm, N-CH_2 proton at δ 2.3493-2.8048 ppm, CH_3 proton at δ 1.0545-1.2269 ppm.

Similarly,4-[5-(4-phenyl-5-phenylimino-1,2,4-dithiazolo)]imino-1,2,4-thiadiazolo-pyridine **(IIIa),** 4-[5-(4-phenyl-5-methylimino-1,2,4-dithiazolo)]imino-1,2,4-thiadiazolo -pyridine **(IIIb),** 4-[5-(4-phenyl-5-t-butylimino-1,2,4-dithia-zolo)]imino-1,2,4-thiadia-zolopyridine **(IIId),**4-[5-(4-phenyl-5-p-chlorophenylimino-1,2,4-dithiazolo)]imino-1,2,4- thiadiazolopyridine **(IIIe)** were synthesized by the interactions of 4-(5-phenylthiocarbamido)-1,2,4-thiadiazolopyridine **(I)** with phenylisothiocarbamoyl-chloride **(IIa),** methylisothiocarbamoylchloride **(IIb),** t-butylisothiocarbamoylchloride **(IId),** p-chlorophenylisothiocarbamoylchloride **(IIe)** in acetone medium respectively by the above mentioned method in **Experiment No. 2 to 5** and enlisted in table.

Sr. No.	Expt . No.	4-[5-(4-Phenyl-5-**substituted**imino-1,2,4-dithiazolo)]imino-1,2,4-thiadiazolopyridine **(IIIa-e)**	Yield (%)	M.P. ^{0}C
1.	2	.....**phenyl**.....	84	151
2.	3	.....**methyl**.....	82	152
3.	4	.....**t-butyl**.....	79	160
4.	5	.....**p-chlorophen**y....	82	167

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SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION OF NOVEL THAZINES AND THEIR DERIVATIVE

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ABSTRACT

A Novel heterocyclic derivative such as thazine is synthesized from various chalcones. As the synthesized compound found various electronics environment, in which electron withdrawing and donating moiety explain the 55-85% overall yield formation of the product. The synthesized compound was characterized by elemental analysis, FT – IR and ^1H NMR Spectroscopy. Thin layer chromatography was used to detect the product formation from the chemical reaction and that results were proved to correctness of the chemical structures for the prepared derivatives.

Kew Words *Chalcones, Thiazine, Condensation, aldol reaction.*

INTRODUCTION

Chalcones are prepared by condensing aryl ketone with aromatic aldehydes in presence of suitable condensing agent. They undergo a variety of chemical reactions and are found useful in synthesis of variety of heterocyclic compounds. One of the important classes of reactions of chalcone is the ring closure reactions with hydrazine, phenylhydrazine, urea etc. Producing heterocyclic derivatives of chalcones both chalcones and their heterocyclic derivatives have a number of Pharmacological activities such as antimicrobial, antifungal, antibacterial, antioxidant, anticancer, antitumor etc.

MATERIALS & METHODS

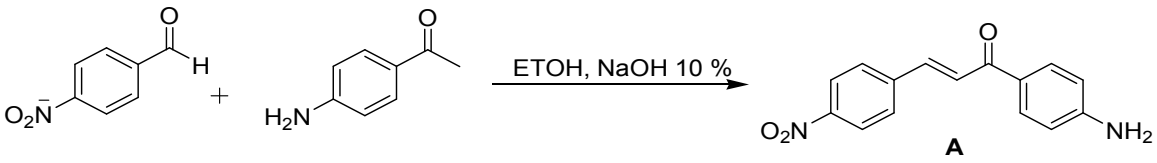
PREPARATION OF CHALCONES

In a round bottom flask containing 4 – Nitro benzaldehyde (0.01 mol) and acetophenone (0.01 mol) were dissolved in minimum amount of alcohol followed by addition of sodium hydroxide solution 3 ml (10%) was added slowly and the mixture was stirred for two hr. until the entire mixture becomes very cloud then the mixture was poured slowly into 20 ml of water with constant stirring and kept in refrigerator for 24 hours. The precipitate thus was obtained by filtration subjected to crystallize from ethanol and the completion of the reaction was monitored by TLC.

PREPARATION OF THIAZINE

A Mixture of chalcone (0.02mol), thiourea (0.02mol) were dissolved in ethanolic sodium hydroxide (30ml) was stirred about 3 – 4 hours with a magnetic stirrer. This was then poured into 20ml cold water with continuous stirring for an hour and then kept in refrigerator for 24 hours. The precipitate obtained was filtered washed & recrystallized from the alcohol. The completion the reaction was monitored by TLC (methanol: Benzene) (1:4).

RESULT & DISCUSSION



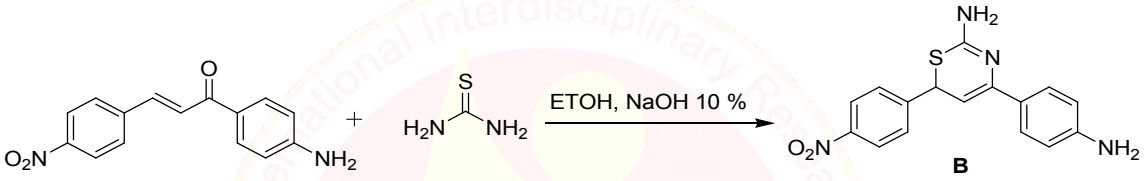
Scheme:1

The present protocol for the synthesis of starting chalcones was done by using literature procedure, in which P-nitrobenzaldehyde was mixture with p – aminioacetophenone in ethanol absolute and sodium hydroxide 10% to produce compound **A** . The different chalcones with electron withdrawing and donating variant shows different product yield. As per literature, number of procedure are available to carry out the reaction with different experiential condition but product utility of these product for different pathological and pharmaceutical in great importance. The structure of the synthesized compound was characterized by different spectroscopic method in which the compound **A** shows good yield i.e. 59 % with m. p. 220-222^O C which is well match with literature

data and in the FT-IR spectrum of **A** compound showed bands at 1635 for C=O, for C=C was observed 1589.The remaining frequency was observed respectively for 1560 C=C, aromatic, 3483 NH_2, 1502 NO_2, bending, 1340 NO_2, stretching. Besides the IR data the elemental analysis calculated (%) for $C_{15}H_{12}N_2O_3$ (268)C,67.16;H,4.47; N,10.44; Found C,67.05 ; H4.33;N,10.21.The ^1H NMR spectrum of compound **A** was characterized and it well matched with spectra in which the peak appeared at 2.68-2.36 doublet for 2H, CH=CH. The delta value at 3.04 correspond to the doublet for 2H, CH=CH. The remaining signals correspond to δ 3.04 for S, 2H, NH2 and δ 7.82-7.10 observed doublet for 4H, Ar,-H.

Table 1. Various Aldehydes for the Aldol Condensation

Entry	Substrate Aldehde	Substrate Acetophenone	Reaction Time (h)	Yield in %
1	C_6H_5	Acetophenone	6	78
2a	2-ClC_6H_4	Acetophenone	10	72
3a	4-ClC_6H_4	Acetophenone	12	75
4a	4-FC_6H_4	Acetophenone	8	70
5a	4-BrC_6H_4	Acetophenone	12	70
6a	4-$MeOC_6H_4$	Acetophenone	12	65
7 (A)	4-$NO_2C_6H_4$	4-NH_2	4	58
8a	2-$NO_2C_6H_4$	Acetophenone	5	78
9a	3-$NO_2C_6H_4$	Acetophenone	6	78
10a	4-CNC_6H_4	Acetophenone	5	84



Scheme:2

The easy preparation of Thiazines was carried out by **A** Mixture of chalcone (0.02mol) and thiourea (0.02mol) was dissolved in ethanolic sodium hydroxide (30ml). The resultant reaction mixture was stirred for about 3 – 4 hours with a magnetic stirrer. This was then poured into 20ml cold water with continuous stirring for an hour and then kept in refrigerator for 24 hours. The precipitate obtained was filtered washed and recrystallized from the alcohol. The completion the reaction was monitored by TLC (methanol: Benzene) (1:4). The product was purified by coloumn chromatography to obtain pure product **B** in quantitative yield. The Structure of the synthesized compound **B** gives 60% yield with m.p.194-196^{0}C. The FT-IR spectrum of **B** compound showed bands at 1610 for C=C in aromatic. The 1645 for C=N, endo cyclic, followed by 3487 for NH_2 group and NO_2 shown bending. The remaining frequency is at 1317 for NO_2 stretching and disappearance of band of C=O ketone, which appeared in 1635 cm^{-1} and the band of C=C, alkene which appeared in 1589 cm^{-1} in compound **A** of spectrum. Finally the ^1H – NMR spectrum of compound **B** is δ 3.33-3.24 for S, 4H, NH_2, δ 5.96 for S, 1H, Thiazine ring. δ 6.81-6.34 for d, 4H, Ar-H. The synthesized product is listed below.

CONCLUSION

The thiazines are synthesized from different chalcones gives 55-85 % yield. The synthesized products are well characterized by all spectroscopic method. The electronic environment of substituted chalcones varies with yield. The scope of this methodology and use of this product are useful in the pharmaceutical drug.

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REVIEW: A CONVENIENT APPROACH FOR THE RECENT SYNTHESIS OF SOME 1, 3, 4 OXADIAZOLE DERIVATIVES BIOLOGICALLY ACTIVE PHARMACOPHORE

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ABSTRACT

To add the knowledge of the medicinal chemistry, different heterocyclic ring showing different biological activity towards the microbes. Five member ring containing N, O shows a good antimicrobial activity. 1, 3, 4-Oxadiazoles are a class of heterocycles that have attracted significant interest in medicinal chemistry. 1, 3, 4 oxadiazole are the five member heterocyclic ring with N, O, N at position 1, 3, 4. Out of four isomer 1, 3, 4 reported novel inhibitors to pathogens. 1, 3, 4-Oxadiazole derivatives are medicinally important science it proved a better pharmacological properties. It is the constituent of several synthetic drugs. Besides pharmacological properties the blue phosphorescent organic light emitting diodes of 1, 3, 4 oxadiazole had been studied, therefore this article aims to review the work reported on some efficient method for the synthesis of 1, 3, 4 oxadiazole.

Keywords *oxadiazole, antibacterial, antiinflametry, antidiabetic anti tubercular.*

INTRODUCTION

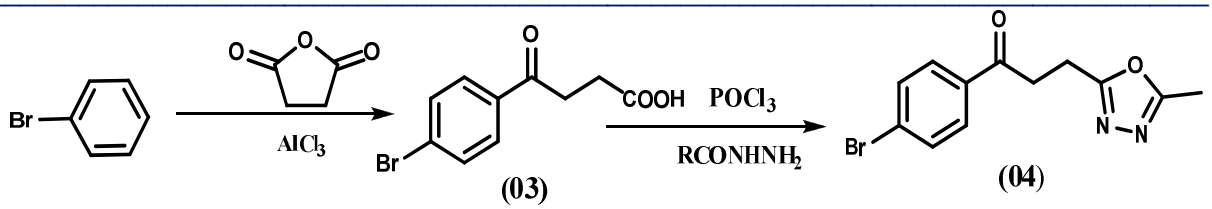
Heterocycles play an important role in biochemical processes. DNA and RNA, essential consistutent of living cells constitutes the heterocyclic ring. During the past few decades interested has been rapidily growing to synthesize the organic aromatic heterocyclic containing oxygen and nitrogen heteroatom which results in significant changes in the cyclic molecular structure due to availability of unshared of electrons and physiochemical properties.

To add the knowledge of the medicinal chemistry, different heterocyclic ring showing different biological activity towards the microbes. Five member ring containing N, O shows a good antimicrobial activity. 1, 3, 4-Oxadiazoles are a class of heterocyclic that have attracted significant interest in medicinal chemistry[1][1]. 1, 3, 4 oxadiazole are the five member heterocyclic ring with N, O, N at position 1, 3, 4. Out of four isomer 1, 3, 4 reported novel inhibitors to pathogens. Oxadiazole is a weak base due to presence of other heteroatom which shows inductive effect. The electroplillic substitution at carbon atom in oxadiazole ring is very difficult due to less electron density since due to electronegative atom oxygen and nitrogen. However electrophillic substitution occurs at nitrogen. Nucleophillic substitution not possible in oxadiazole ring but if one of the carbon is substitute by halogen nucleophillic substitution possible. Oxadiazoles were discovered in 2008, against the schistosomiasis-causing fiuke are effective without any evidence of negative effects on humans[2] .

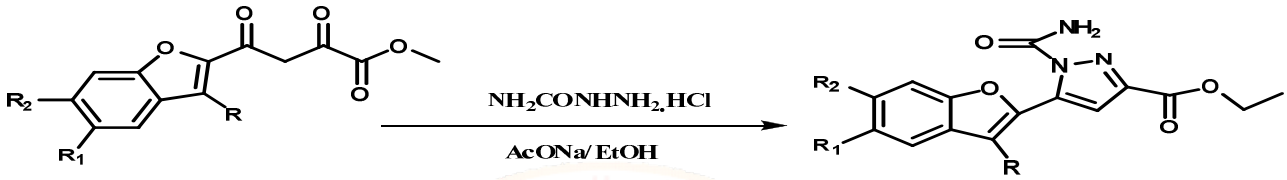
Oxadiazole ring behave as bioesters for amide and esters. Due to the increased hydrolytic and metabolic stability of the oxadiazole ring, improved phar- macokinetic and in vivo performance is often observed, which make this heterocycle an important structural moiety to the pharmaceutical industry.1, 3,4 used as antibacterial[3], [4], antitumour agent[5], antidiabetic, anti- inflammatory and anticancer activities[6], as an dye[7], antioxident[8],[9], antiinflametry[10], inhibitor of E. histolytica [11],antifungal[12] and measomorphic behaviour [13].

Abu-zaied et al reported to synthesized -([1,2,4]Triazolo[3,4-b][1,3,4]thiadiazol-6-ylmethyl)-1,3,4-oxadiazole-2(3H)-thione (02) by coupling between hydrazone (01) and carbon disulphide in HCl and evaluated as a potent anticancer agent[14].

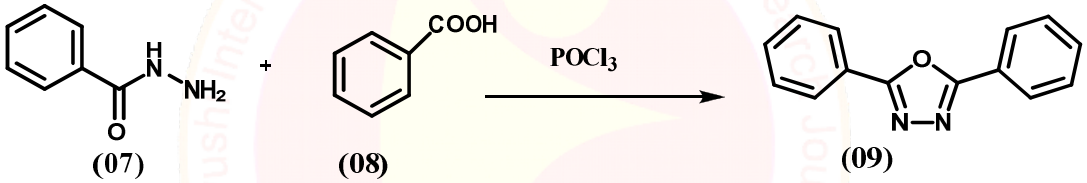
Huasain,A. reported to synthesized A novel series of 2-[3-(4-bromophenyl)propan-3-one]-5- -(substituted phenyl)-1,3,4-oxadiazoles (04) from 3-(4-bromobenzoyl)propionic acid (03) and alkyl acid hydrazides in phosphorous oxychloride and studied their anti-in- flammatory, analgesic activity, antibacterial activity[15].



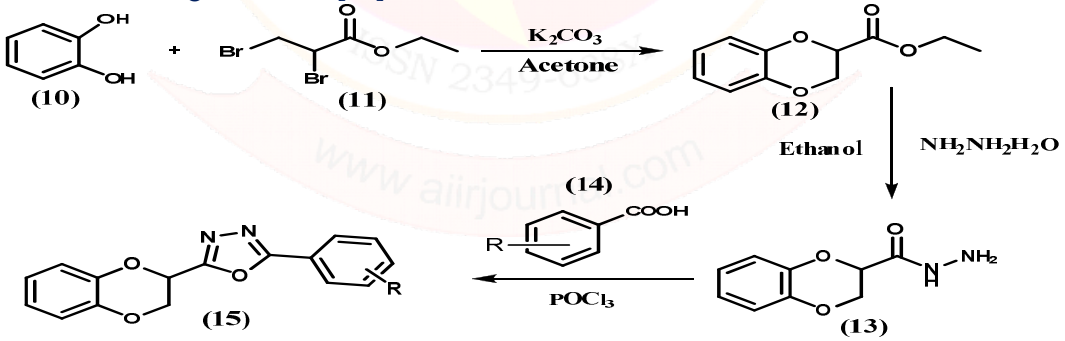
Siddique,N. et al reported to synthesized ethyl 5-(substituted/unsubstituted benzofuran-2-yl)-isoxazole-3-carboxylates (05) by the condensation-cyclodehydration of 2,4-dioxobutanoatesof methyl 4-(substituted/unsubstituted benzofuran-2-yl)-2,4- dioxobutanoates (06)and semicarbazide hydrochloride and evaluated for antimicrobial and antifungal activity[16].



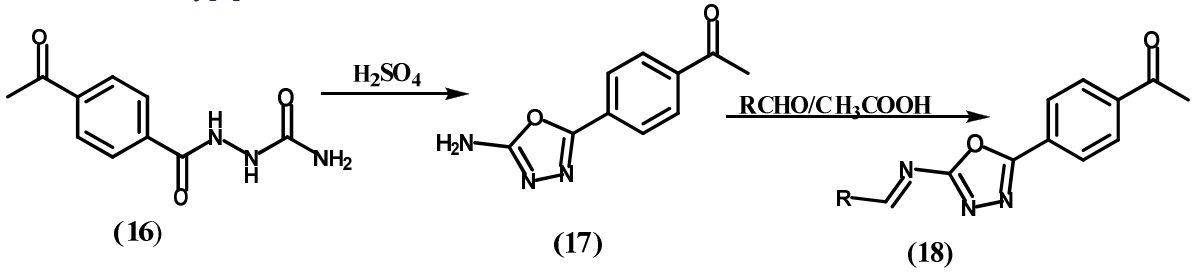
Selvaraj,K. et al reported to synthesized 3-(5-cyclohexyl-1,3,4-oxadiazol-2-yl)-N-substituted aniline (07) by reaction of Benzohydrazide (09) with cyclohexanoic acid (08) was refluxed with phosphorous oxychloride. All synthetic compounds were screened for their antidiabetic, anti- inflammatory and anticancer activities[6].



Khalilullah,H. Et al reported to synthesized 2-(phenyl)-5-(2,3-dihydro-1,4-benzodioxane- 2-yl)-1,3,4-oxadiazole derivatives containing 1,4-benzodioxane ring system (15) were synthesized starting from 2,3-dihydro-1,4-benzodioxane-2-carbohydrazide (13), substitued benzoic acid (14) and $POCl_3$ and tested for antibacterial and antifungal activities[17].

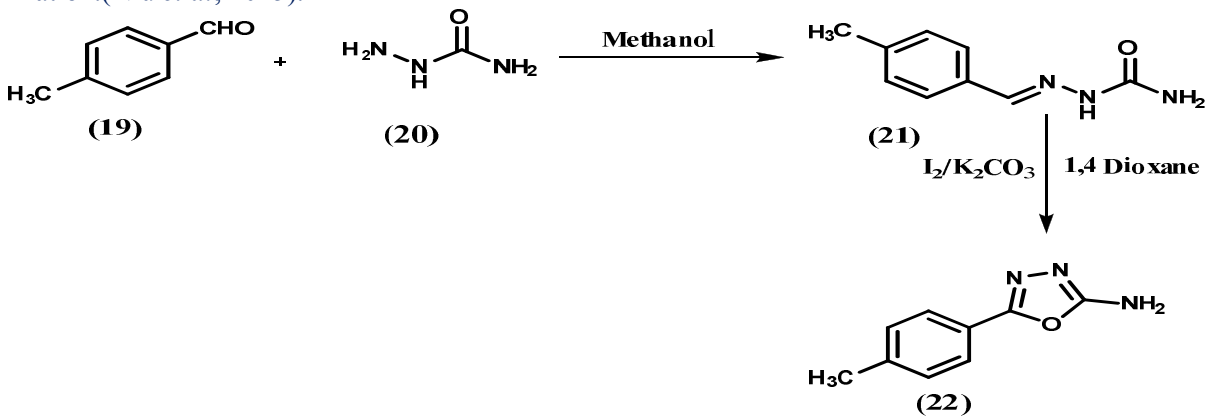


Kumar,V. et al reported to synthesized 2-amino-5- (p-methoxyphenyl)-1,3,4-oxadiazole (17) by the reaction of hydrazine carboxamide (16) treated with concentrated sulphuric acid and evaluated for antibacterial activity[4].

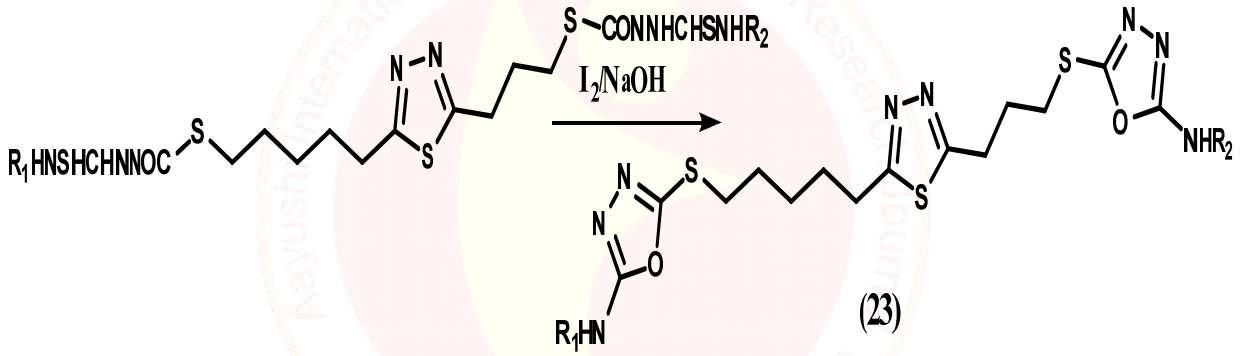


Nilu,P. et al reported to synthesized 2-Amino-substituted 1,3,4-oxadiazoles (22) via condensation of semicarbazide (20) and the corresponding aldehydes (19) followed by I_2-mediated oxidative C–O bond

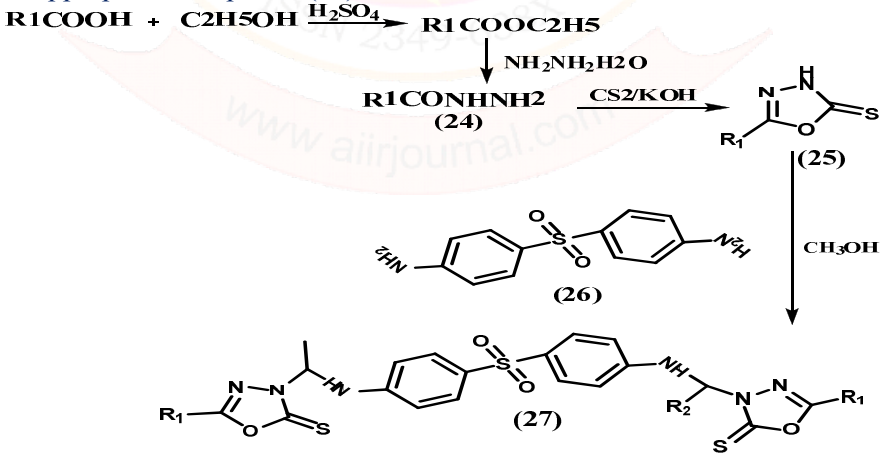
formation.(Niu *et al*, 2015).



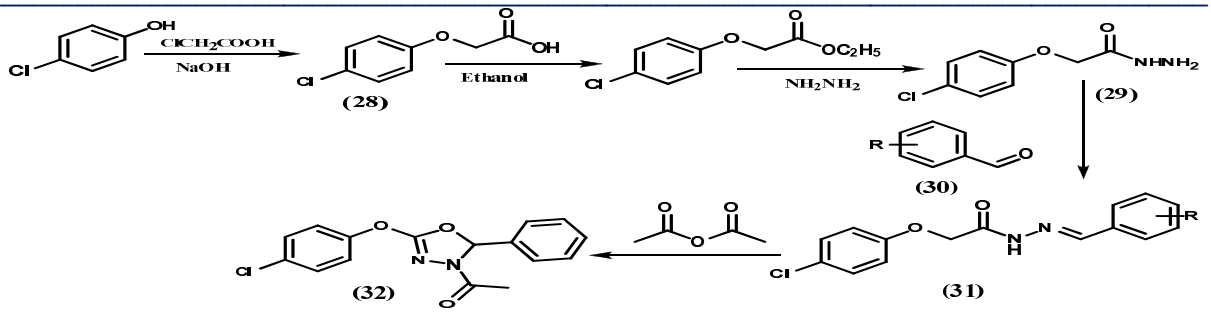
Nadjet, R ,et al synthesized Novel 2,5-disubstituted-1,3,4-thiadiazoles clubbed 1,2,4-triazole, 1,3,4-thiadiazole, 1,3,4-oxadiazole (23) that is 2,5-Bis[(2-(2-chlorophenyl)-1,3,4-oxadiazol-5-yl)propylthio]-1,3,4-thiadiazole from acid hydrazide with benzoyl chloride and phosphorous pentoxide and evaluated as potential antimicrobial and antiproliferative agents[19].



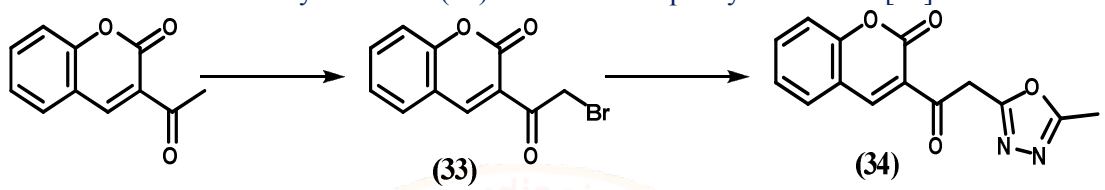
Ashraf, M. et al reported the synthesis of 1, 3, 4-oxadiazole (25) by ring closure reaction of acid hydrazide (24) with carbon disulphide. The mannich (27) base was obtained from synthesized oxadiazole by condensation with appropriate compound (26) in methanol and evaluated for antitubercular activity[20].



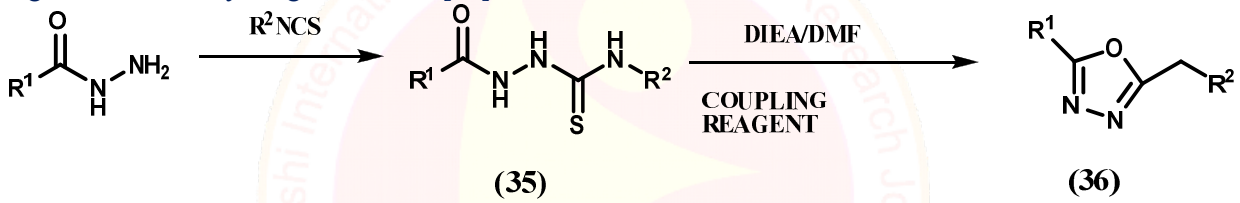
Tiwari, A. et al synthesized 1-{5-[(4-Chlorophenoxy)methyl]-2-(4-methoxyphe- nyl)-1,3,4-oxadiazol-3(2H)-yl}ethanone (32) which was synthesized by the cyclisation of Schiff base (258) in presence of acetic anhydride . Starting from p-Chlorophenoxyacetic (28) acid hydrazide(29) were formed which on reaction with and substituted aromatic aldehyde (30) in ethanol with catalytic amounts of glacial acetic yields Schiff base(31) .The newly synthesized compound were screnned for their cytotoxic activity in vivo anti tumor activity[21].



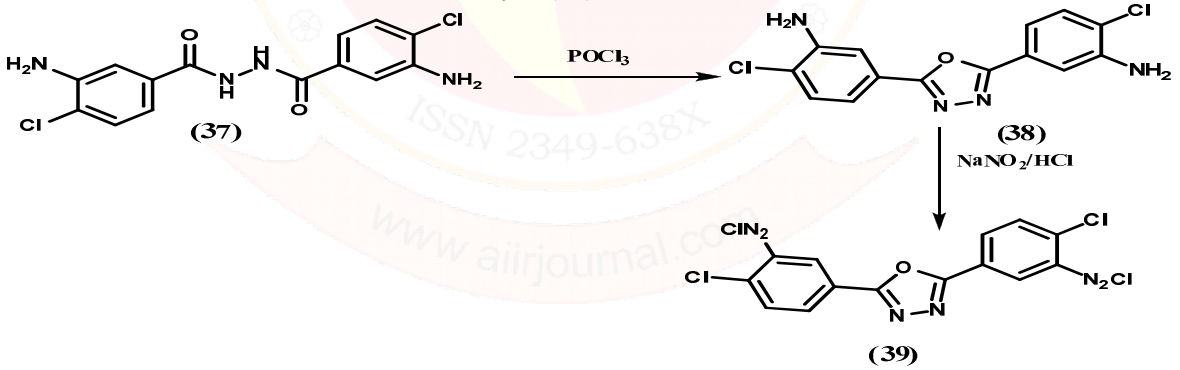
Sahu, S. et al reported to synthesized 3-[N-(5-Phenyloxadiazolyl-2)amino] acetyl coumarin (34)by the condensatation of 3-Bromoacetylcoumarin (33)and 2-amino-4-phenyloxadiazole [22] .



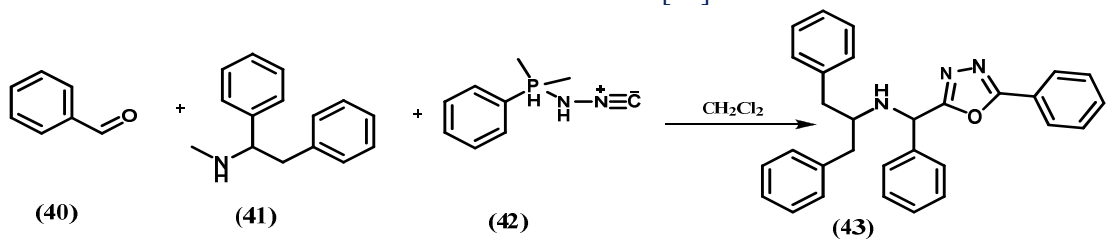
A new efficient synthesisof 2,5 disubstuted 1,3,4 oxadiazole (36) from isothiocyanates and hydrazides (35) via cyclodesulfurisation in the presence of uronium tetrafluoroborate) TBTU as an uronium coupling reagent was done by Maghari, S.et al.[23]



Patel,D. Et al report to synthesized some some novel hetero bisazo reactive dyes, containing a dichloro-s-triazinyl (DCT) reactive group.3-amino chloro benzoic acid on treatment with hydrazine hydrate results hydrazine (37) which treatment with $POCl_3$ results oxadiazole (38) which under goes sandmayer reaction results in some novel hetero bisazo reactive dyes (39) [7].

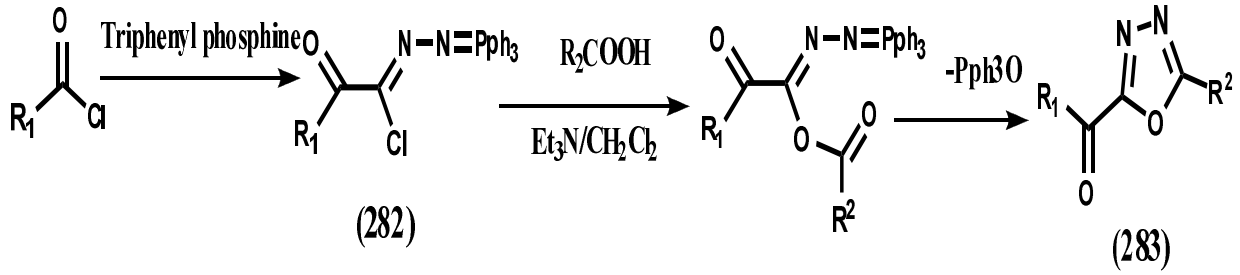


Ramazani,A.et al report the novel method for the synthesis of 2,5-disubstituted 1,3,4-oxadiazole derivatives (43) using (N-isocyanimino)t- riphenylphosphorane (42), a secondary amine (41), and an aromatic aldehyde (40) in CH_2Cl_2 at ambient temperature in high yields without using any catalyst or activation. The procedure provides an alternative method to the synthesis of fully substituted 1,3,4-oxadiazole derivatives[24].



The most commonly used route is the cyclodehydration of diacylhydrazines, which always requires highly toxic and corrosive reagents, such as sulfuric acid, phosphorous oxychloride, and thionyl chloride so one

pot synthesis of various keto-1,3,4-oxadiazole (45) derivatives were reported to synthesized by Bhatt, M. et al via intermolecular dehydrochlorination .Wittig reaction of carboxylic acids and imidoyl chloride intermediates (44), which were generated by isocyanide-Nef reaction of acyl chlorides and (N-isocyanimine) triphenylphosphorane in CH_2Cl_2 at room temperature, the reaction is based on isocyanide-Nef reaction[25].



CONCLUSION

Literature studies revels that five membered heterocyclic 1, 3, 4 oxadiazole and related compound is the major attaraction for researchers in the field of pharmaceutical chemistry. By considering these view researchers focuses on the synthesis of novel 1, 3, 4 oxadiazole and its antimicrobial studies. Derivatives of different oxadiazole with diverse biological activities are reviewed in present article Results of various author diverts the attention of researcher to synthesized more potent oxadiazole containing drugs.

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THERMOGRAVIMETRIC STUDY AND CHARACTERIZATION OF CHEMICALLY SYNTHESIZED CUS NANOPARTICALS

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ABSTRACT

Copper sulfide nanoparticles (CuS) were successfully synthesized by the reaction of copper acetate and thiourea with the addition of sodium hydroxide, by simple chemical precipitation technique at room temperature. Synthesized CuS nanoparticles were characterized by thermogravimetric analysis, powder X-Ray diffraction for finding particle size, optical properties of the product and band gap energy were studied by UV- visible absorption spectroscopy. It was found that the particle size and yield depends on reaction time, amount of reactants, temperature and also on the amount of reducing agent used.

Keywords: *Cus nanoparticals , XRD, UV-Vis spectrum, TGA, Band gap*

INTRODUCTION

Synthesis and characterization of nanoparticles of semiconducting metal sulfides have been an intense field of research due to their interesting properties and potential applications. Recently, transition metal sulfides have claimed substantial response of researchers because of their exciting morphology, electrical, optical and thermal properties [1-3]. From the discovery of photovoltaic behavior of CuS as donor material and its deposition with CuS resulted high rate efficiency. Therefore, CuS is a potential nanocrystals that could be used in the areas of solar energy conversion, gas sensors, IR detectors, electrochemical cells, and catalytic properties [4-11]. Crystals of size in the order of a few nanometers (ranging 1 – 100nm) in at least one dimension are nanocrystals. It has been proved that as particle becomes smaller in size, they may take on different chemical and physical properties. The nanocrystals exhibit higher chemical reactivity than conventionally prepared samples [12-15]. Recently, much attention has been paid to the application of nanoparticles [16]. Copper sulphide is an important p-type semiconductor which belongs to wurtzite structure [17] with copper vacancies within the lattice [18]. Various morphologies of CuS have been prepared such as nanoparticles, nanodisks [19], nanorods [20-22], nanotubes [23] and nanowires [24]. CuS is extensively used in solar cells [25], optical filters, photo electric transformers, sensors and as super ionic materials [26].

MATERIAL AND METHODS

Copper acetate, thiourea, were copper and sulphur precursors. NaOH is used to adjust pH value. All chemicals were analytical reagents. All the reagents used in experiment were analytically pure and used without further purification. 9.965gm of copper acetate was dissolved in 250ml of water with constant stirring. 7.612 gm of thiourea was dissolved in 50ml deionized water. sodium hydroxide was dissolved in 10ml of deionized water. First Cu(ac)2 solution and thiourea solutions were mixed together slowly with constant stirring. Blue colour copper acetate solution turned green by the addition of thiourea solution. Then NaOH solution was added to the original solution. The colour of the solution turned golden brown as the first drop of NaOH solution was added and the colour deepened with more of addition. The solution was left without disturbance for 2 hours at room temperature,(30^0C). The precipitate formed was filtered and rinsed with deionised water several times and repeatedly washed with acetone. Pure CuS nanocrystals were thus synthesized and dried at room temperature. This procedure was again repeated for 4hours, 6hours and 8hours. To improve the ordering the samples were annealed at 60^0C for 30 minutes. When the amount reducing agent (NaOH) added was reduced, the yield also reduced. The synthesis process can be described as follows. Copper acetate reacts with thiourea in the presence of sodium hydroxide gives Copper sulphide precipitate in a pure form with other impurities, which are removed by rinsing with water and acetone. After sufficient drying, the precipitate was crushed to fine powder with the help of mortar and pestle. Four different samples were prepared

by changing the molar concentration. In present work, Cus nanoparticles were prepared by Wet Chemical rout method without using capping agent. Structural properties have been studied by X-raydiffraction and the energy band gap values were calculated by using the UV-visible spectrophotometry.

Results And Discuss

Structural properties

X-ray powder diffractions (XRD) were performed at room temperature on a Miniplex-ii X-ray diffractometer using monochromatic Cu $K_{\alpha 1}$ radiation with λ=1.540562 A^o operated at 40 kV and 40 mA with 2θ ranging from 10^o to 80^o at the speed of 2^o min^{-1}. The diffraction pattern obtained of Cus nanoparticles were prepared with different molar concentration of parent solution. Different sizes of nanoparticles have been prepared by changing the molar concentration of the parent samples. From Fig.(1), XRD patterns obtained in all samples shows three peaks, which shows that the samples have cubic zinc blende structure and the peaks correspond to diffraction at (111), (220) and (311) planes respectively. The lattice parameter has been computed as 5.82 A^o, which is very close to the standard value (5.83 (A^o). It is also seen that peaks are broadened for higher concentration of parent solution of Cus sample. The peak broadening at lower angle is more meaningful for the calculation of particle size, therefore size of nanocrystals has been calculated using Debye-Scherrer formula[27] given as

$$D = \frac{K\lambda}{\beta cos\theta}$$

Where D is the crystallite size, K is constant, λ is the wavelength of x-rays, β is the full width at half maximum (FWHM) after correcting the instrument peak broadening (β expressed in radians), θ is the Bragg's angle.

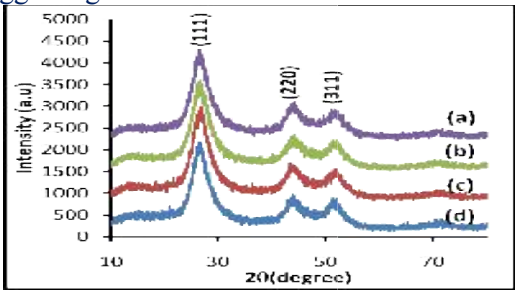

Fig. 1. XRD patterns of Cus nanoparticles.
(a) Cus-I (b) Cus-II (c) Cus-III (d) Cus-IV

OPTICAL ABSORPTION

UV-Visible absorption spectroscopy is an efficient technique to monitor the optical properties of quantum sized particles. The optical absorption spectra of the nanocrystallities were measured using double beam automated UV-Vis spectrophotometer, and absorption spectra have been recorded at room temperature over the range 450 to 550 nm. The most dramatic property of semiconductor nanocrystals were determined, the band gap energy from the optical absorption spectra. The study of optical absorption is important to understand the behavior of semiconductor nanocrystals. A fundamental property of semiconductors is the band gap, the energy separation between the filled valence band and the empty conduction band. Optical excitation of electrons across the band gap is strongly allowed, producing an abrupt increase in absorption at the wavelength corresponding to the band gap energy. This feature in the optical spectrum is known as the optical absorption edge. Fig (2) shows the optical absorption spectra of Cus nanoparticales in the range of 450 to 550 nm . It can be seen that the absorption occurs in visible region, at 486 nm, 484nm, 478nm, 471nm, for Cus-I , Cus-II, Cus-III and Cus-IV samples respectively. This clearly shows that the absorption edge shifts towards shorter wavelength as the molar concentration is increases. The observed blue shift in the absorption edge is reflection of band gap increase owing to quantum confinement effect The energy band gap of material is calculated using the Tauc relation[28]. The relation between the absorption coefficient (α) and the incident photon energy (hν) can be written as $(\alpha h\nu)=A(h\nu - Eg)$ Where, A is a constant, Eg is the band gap of the material and exponent n depend on the type of transition. Here, the transition are direct so we take n=1/2. The value of optical band gap is calculated by extrapolating the straight line portion of $(\alpha h\nu)^2$ vs hν graph (fig. 3.) to hν axis at α=0.. The obtained band gap values for different samples are 2.63, 2.79, 2.81, 2.87 eV respectively.

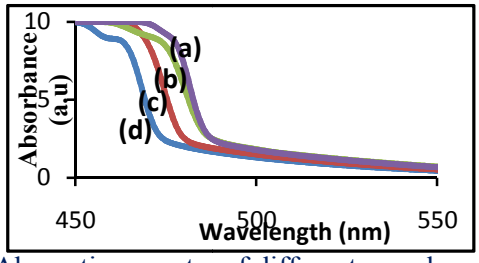

fig .2 Absorption spectra of different samples of Cus nanoparticles.
(a)Cus-I (0.4 M), (b)Cus-II (0.6 M), (c)Cus-III(0.8), (d)Cus-IV(1.0M)

Thermogravimetric Analyses :

TGA study Figure 3 shows a representative thermogram of Cus sample This thermogram is divided into two regions. The first weight loss (region I) is located between 337ºC and 374ºC and second weight loss occurs in (region II) located between 745ºC and 781^{0}C. The first derivative of this thermogram (DTG), clearly reveals the inflection points at 345^{0}C and 750^{0}C. The TGA decomposition patterns of copper sulfide, CuS nanocomposites occurs at 337ºC to 374ºC this is major decomposition step, The first weight loss was mainly contributed by the elimination of impurities, residual water and unreacted monomers. The second step weight loss which is attributed at 745ºC to 781^{0}C is due to the degradation of Cus nanoparticals

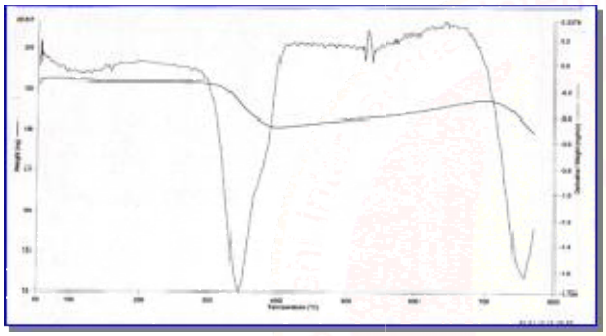

Fig .3 TGA of Cus nanoparticles.

CONCLUSION

The Cus nanoparticles were successfully synthesized through Wet Chemical rout method and X-ray diffraction was employed to study the structural properties, the particle sizes calculated were have zinc blende structure, from optical absorption measurement it is found that as molar concentration varies from 0.4 M to 1.0 M the band gap increases while the wavelength of absorption onset shifts to shorter wavelength. Therefore, the onset wavelength is directly related to nanoparticle size. Chemical reaction rates directly affects the time evolution of the number of nuclei, which determines both nucleation and growth process, nucleation and growth takes place simultaneously. This overlapping of nucleation and growth process, which is more pronounced as the chemical reaction is slower, leads to larger nanoparticle size. Rate of reaction depends on the molar concentration of reactants solution and increases with the increase in molar concentration of reactants solution. In the present study, the molar concentration of reactants solution varies from 0.4 M to 1.0 M, the reaction rate is highest for 1 M solution and hence the particle size obtain smallest for 1 M solution as compare to other material in the series, which is in accordance with the above made argument. TGA results depict that the thermal stability of CuS nanocomposites showing strong interactions between the CuS nanoparticles[29-31], nanocomposites are compared to their respective precursor complexes used in the synthesis of the metal sulfide nanoparticles, it could be noted that the nanocomposites are more thermally stable than their precursor complexes at temperatures below 781^0 C. This confirms strong interaction between metal sulfide nanoparticles

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SYNTHESIS, CHARACTERIZATION AND ANTIBACTERIAL STUDY OF CHLOROSUBSTITUTED THIAZINES

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ABSTRACT

Some new chlorosubstituted 1,3 thiazines have been synthesized by condensation of 2 -hydroxy 3,5 dichloro 4 phenyl chalcone with thiourea and phenyl thiourea in ethanol containing aqueous KOH solution. The structures of newly synthesized chlorosubstituted thiazines have been elucidated on the basis of molecular weight determination, elemental analysis and spectral data. The newly synthesized chlorosubstituted 1,3 thiazines were prepared from chalcone and screened for their antibacterial activity.

Keywords: *Chlorosubstituted 1, 3 thiazines, Chalcone, Antibacterial activity.*

INTRODUCTION

In organic chemistry a series of heterocyclic compounds containing an unsaturated six membered ring which contain two carbons, one nitrogen and one sulphur atom are termed as thiazines. Various methods have been worked out for their synthesis[1-7]. Derivatives of thiazines played a crucial role in the history of heterocyclic chemistry. Thiazine is the important class of heterocyclic compounds being studied by many researchers and possesses a wide variety of biological properties such as antiviral[8], antimicrobial[9], anti HIV[10], antiserotinin[11], antibacterial[12], antifungal[13].The studies also reveal that they can also be used as pesticides[14] and herbicides[15]. Numerous chlorinated compounds have various bioactivities which render them valuable active ingredients of medicine or plant protecting agents. Taking into consideration the widespread use of chlorosubstituted thiazines, it appears worthwhile to synthesize some new chlorosubstituted thiazines. The newly synthesized chlorosubstituted thiazines scheme 1 were assayed for their antimicrobial activity against some bacteria i.e *E. coli*, *Pseudomonas fluorescence*, *Staphylococcus aureus and Enterococcus faccalis*.

EXPERIMENTAL

Synthesis of 2-hydroxy- 3,5-dichloroacetophenone (3a)

2-Hydroxy -5 dichloroacetophenone (3g) was dissolved in acetic acid (5ml), sodium acetate (3g) was added to the reaction mixture and then chlorine in acetic acid reagent (40ml) was added drop wise with constant stirring. allowedstand for half an hour then it was poured into cold water. A pale yellow solid product thus separated was filtered and crystallize from ethanol to get the compound (3a).

Synthesis of 2-hydroxy -3,5 dichloro- 4-phenyl chalcones (4a)

2-Hydroxy 3,5 dichloroacetophenone (3a), (0.1M) was dissolved in ethanol (50ml), salicaldehyde (0.1M) was added to this solution and mixture was heated to boiling. Aqueous sodium hydroxide solution (40%) (40 ml) was added dropwise with constant stirring. The mixture was shaken for half an hour, the product thus obtained then filtered, washed with sodium bicarbonate (10%) and purified by recrystallisation with ethanol to get 2-hydroxy 3,5 dichloro- 4- phenol chalcone (4a).

Synthesis of 4-(2-hydroxy 3,5 dichlorophenyl)-6-phenol-2- imino-3,6- dihydro-1,3 thiazine (5a)

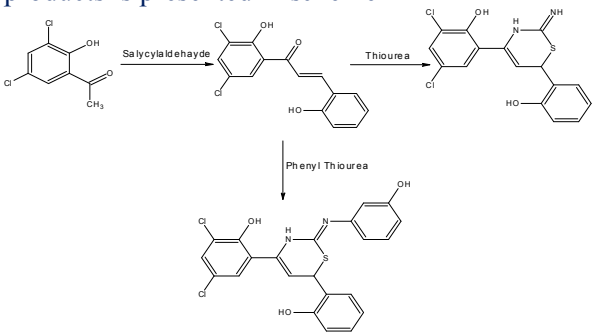
2-Hydroxy 3,5 dichloro 4-phenyl chalcone (4a) (0.01 mol) and thiourea (0.01 mol) were dissolved in ethanol (25 ml), an aqueous potassium hydroxide solution (0.02 mol) was added. The reaction mixture was refluxed for 2.5hours. The reaction mixture was acidified with concentrated HCl. The product thus separated was crystallized from ethanol to get the compound 4-(2-hydroxy 3,5 dichlorophenyl)-6-phenol-2-imino-3,6 dihydro-1,3 thiazine (5a)

Synthesis of 4-(2-hydroxy 3, 5 dichlorophenyl)-6-phenol-2-iminophenyl-3, 6-dihydro 1,3-thiazine (6a)

2-Hydroxy 3,5 dichloro 4-phenyl chalcone (4a) (0.01 mol) and phenylthiourea (0.01 mol) were dissolved in ethanol (25 ml). To this solution an aqueous potassium hydroxide (0.02 mol) was added. The reaction mixture was refluxed for 2.5 hrs. After cooling it was acidified with concentrated HCl. Finally the product was

crystallized from ethanol to get the compound 4-(2-hydroxy 3,5 dichlorophenyl)- 6-phenol- 2-iminophenyl -3,6-dihydro 1,3 thiazine (6a).

The synthetic route for obtaining the final products is presented in scheme 1



Scheme 1

CHARACTERIZATION

Melting points of all synthesized compounds were determined in open capillaries and are uncorrected. IR spectra were recorded on a Perkin-Elmer 1000 spectrophotometer in KBr. The 1H NMR spectra were recorded on a Bruker Advance II 400 NMR spectrometer using TMS as internal standard and chemical shifts were expressed in δ (ppm)

Table No. 1: Physical and analytical characterization data of newly synthesized compounds

Compounds	Mol. Formula	Mol. Wt	Yield%	Melting Point ^{0}C	Found Calculated %			
					C	H	Cl	N
3a	$C_8H_6Cl_2O_2$	205.03	80	53	45.55 (46.86)	2.90 (2.95)	33.90 (34.58)	-
4a	$C_{15}H_{10}Cl_2O_3$	309.14	75	120	57.12 (58.28)	3.10 (3.26)	21.35 (22.44)	-
5a	$C_{16}H_{12}Cl_2N_2O_2S$	167.25	60	110	50.15 (52.33)	2.90 (3.29)	18.54 (19.31)	6.50 (7.63)
6a	$C_{22}H_{16}Cl_2N_2O_3S$	459.34	65	115	56.82 (57.52)	2.85 (3.51)	14.42 (15.44)	5.32 (6.10)

Spectral study of 4-(2-hydroxy 3,5 dichlorophenyl)-6-phenol- 2-imino-3,6-dihydro-1,3 thiazine (5a)and 4-(2-hydroxy 3,5 dichlorophenyl)- 6-phenol-2-iminophenyl -3,6-dihydro-1,3 thiazine (6a) are summarized as

IR (KBr cm-1) of 5a : 3663 (O-H bending), 3500 (-NH stretching), 3085 (Ph stretching), 2980 (C-H stretching), 1654 (-C=N stretching), 1440 (-CH_2 bending), 1345 (-CH_3 bending), 1050 (C-S stretching), 1314 (-OH bending in Ph.), 698 (C-Cl stretching).

^{1}HNMR ($CDCl_3$) of 5a : δ 2.75 (s, 1H, -NH), δ 7.4 to 7.6 (m, 5H, ArH), δ 7.8 to 8.1 (s, 2H, ArH), δ 4.9 (s, 1H, N-Ph), δ 13.01 (s, 1H, ArOH).

IR (KBr cm-1) of 6a : 3665 (O-H bending), 3528 (-NH stretching), 3094 (Ph stretching), 2990 (C-H stretching), 1660 (-C=N stretching), 1445(-CH_2 bending), 1350 (-CH_3 bending), 1320 (-OH bending in Ph), 1065 (C-S stretching), 718 (C-Cl stretching).

^{1}HNMR ($CDCl_3$) of 6a : δ 2.79 (s, 1H, -NH), δ 7.5 to 7.7 (m, 5H, ArH), δ 7.9 to 8.3 (s, 2H, ArH), δ 5.1 (s, 1H, N-Ph), δ 13.20 (s, 1H, ArOH).

RESULT AND DISCUSSION

The synthesized compounds were screened for their antibacterial activity against *E.coli, P. fluroscence, S. aures and E.faecalis*. The compound 5a shows activity against *P. fluorescence* and resists all the other bacteria. Similarly, the compound 6a shows resistivity against all the test bacteria.

CONCLUSION

The newly synthesized chlorosubstituted 1,3 thiazines were characterized for their structure determination. Various chemical and spectral data supported the structures. Antibacterial activities of 1,3-thiazines were screened against gram +ve and gram –ve bacteria and it is concluded that the compound 5a showed significant activity against *P. fluroscence*.

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ANANLYSIS OF DISSOLVED OXYGEN PRESENT IN INDUSTRIAL WATER SAMPLE OF NIPANI TOWN

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ABSTRACT

The Industrial water samples were taken from Halsiddhnath sugar factory from Nipani town and analysed every month throughout the year. We have studied levels of dissolved oxygen (DO) in industrial water. DO content was found higher than the desirable limit of DO (5 mg/ up to 12.56mg / lit). The seasonal analysis indicated that the levels of DO were generally higher in summer and winter than their levels in rainy season.

Keywords: *Industrial water, pollutant, Dissolved Oxygen (DO)*

INTRODUCTION

Due to rapidly increased in industrialisation water pollution problem arises. Industrial waste water directly thrown in to the river and it content lot of toxic chemicals and its adversely affectted on plants, animals and human beings also.

In the present study, the levels of DO were studied from vicinity of Halsiddhanath sugar factory at Nipani [1-2]. The industrial water samples were taken in the twelve glass bottles by following standard procedure. . The samples were collected every month throughout the every year and analysed in the laboratory**.**

MATERIALS AND METHODS

Dissolved oxygen in water was determined with the help of Winklers Iodometric Modified Oxide Method (APHA,1989) . In this method , addition of divalent manganese solution followed by strong alkali to water sample,rapidly oxidize manganese in the form of manganous hydroxide precipitate,giving on ,equivalent amount of dissolved oxygen present in water. In the presence of iodine ions. On acidification , oxides of manganese revert to divalent state , with the liberation of iodine equivalent to original dissolved oxygen content in the sample. The iodine then trapped with standard solution of sodium thiosulphate . The sequence of reactions taking place is given below.

$MnSo_4 \_ Mn^{2+} + SO_4^{2-}$

$Alk.\ KI – K^+ + I^- + OH^-$

$Mn^{2+} + 2OH^- - Mn(OH)_2$ white ppt. (O_2 absent)

$MnO_2 + 2OH - + ½\ O_2 – MnO_2 + H_2O$ Brown ppt (O_2 absent)

$MnO_2 + 4H+ + 2I – I_2 + 2Mn^{2+} + 2H_2O$

$I_2 + 2Na_2S_2O_3 – Na_2S_4O_6 + 2\ NaI$

REAGENTS

a) Sodium Thiosulphate Solution (0.025 N): Dissolved 24.82g of $Na_2S_2O_3, 5H_2O$ in boiled distilled warer and make up the volume to 1 litre. Add) 0.4 g of borax of a pellet of NaOH as a stabilizer . This is 0.1 N stock sodium . Dilute it 4 times with boiled distilled water to prepare 0.025N solution.

b) Alkaline Iodide Oxide Solution
   i) Dissolved 700g of KOH and 150 g of KI in distilled water to make 1 litre of solution.
   ii) Dissolved 10g of NaN_3 in 40ml of distilled Water Mix (i) and (ii) solutions.

c) Manganous Sulphate Solution: Dissolve 100g of $MnSo_4\ 4H_2O$ in 200 ml of distilled water.

d) Starch Solution: It is 1% solution prepared in boiling water and used after cooling to ambient temperature .

e) Conc. Sulfuric Acid: H_2SO_4 (sp. Gravity 1.84).

PROCEDURE

An aliquot of 300 ml water sample was taken in DO bottle to which 2ml of manganese sulphate and 2ml alkaline iodide oxide solution was added , if brown precipitate is observed dissolved oxygen is present , if white precipitate is formed , then dissolved oxygen is absent . The brown precipitate was disc by adding 2ml of concentrated H_2So_4 and the same solution was titrated against 0.025 N. $Na_2S_2O_3$ using starch as an indicator . At the end point, initial dark blue colour turns to colourless.

The dissolved oxygen present in the water sample was determined by using the following formula.

Dissolved Oxygen (mg/Lit) = Normality of $Na_2S_2O_3$ volume of $Na_2S_2O_3$ x 8x 1000

$V_2(V_1\text{-}V)\ V_1$

Where, V_2 = Volume of the part of the content titrated

V_1 = total volume of water sample taken

V = Volume of MnSO4 and KI added

RESULTS AND DISCUSSION

An average concentration of Oxygen in atmosphere is 20 .90% (Whipple and Whipple 1911) The degree of solubility of atmospheric oxygen is a function of temperature and pressure. Dissolved oxygen is a key parameter reflecting the quality of water and hence used in classifying its quality, particularly of water, which receives waste. At site 23, discharge of industrial effluent is responsible for high value of dissolved oxygen.

CONCLUSION

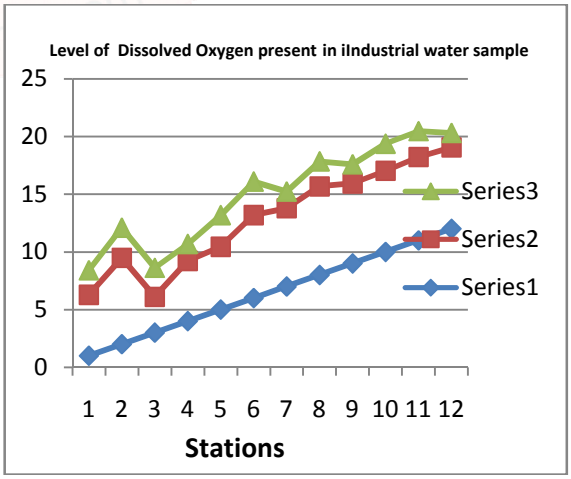
In the present study highest value of DO observed during winter season , Rainy season and further reduction in summer season at various sampling station due to discharge of industrial effluent . The analysis of industrial effluent sample showed an extremely fluctuations in Dissolved oxygen from minimal 2.40 mg/lit in December to maximal 12.46 mg/lit (Table No–63) consideration of seasonal average showed higher average dissolved oxygen in winter season 8.36 mg /lit , followed in rainy season 10.51 mg /lit and less in summer 5.44 mg /lit. (Table No-64). At tvarious site below the minimum expected values prescribed by WHO (1972) Thus finally conclude that the surface water is highly polluted at this site due to discharge of industrial waste water and degradation of waste.

Table 1: Dissolved Oxygen (mg/lit) of Industrial water sample

Stations	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
1	5.60	3.70	6.70	2.30	5.40	5.48	1.73	8.15	8.15	7.20	5.60	3.40
2	12.40	8.40	10.20	7.50	6.70	6.50	1.20	7.50	7.50	7.20	6.40	8.20
3	2.87	2.17	0.94	0.90	0.84	0.47	6.80	6.70	6.40	5.50	2.40	1.30
4	2.20	4.25	4.45	4.65	4.70	5.30	6.30	7.40	7.20	6.70	4.75	4.75
5	8.40	2.20	0.80	2.20	2.70	5.70	6.70	7.50	7.40	6.30	6.25	9.10
6	10.85	9.35	9.45	12.40	6.20	3.70	4.20	7.40	4.20	5.30	4.70	8.50
7	8.78	7.10	7.40	8.40	4.65	6.70	6.30	7.25	4.87	4.75	6.35	8.45
8	11.07	11.94	10.03	8.27	7.25	6.60	4.45	8.50	5.90	5.20	6.50	7.40
9	7.30	6.41	6.03	7.45	6.65	4.45	8.50	5.90	5.67	5.40	8.70	10.40
10	10.80	10.70	3.40	6.75	5.75	5.10	8.70	5.12	5.14	6.17	8.36	8.40
11	5.70	10.40	3.47	10.36	10.50	6.90	6.71	5.80	5.40	5.80	7.75	7.87
12	5.30	4.84	6.40	8.31	8.31	8.40	6.81	7.10	7.13	8.14	7.56	5.90

Fig. 1: Dissolved Oxygen (mg/lit) in Industrial water sample

Stations	Avarage	S.D.
1	5.28	2.13
2	7.48	2.62
3	3.11	2.51
4	5.22	1.47
5	5.44	2.75
6	7.19	2.91
7	6.78	1.45
8	7.68	2.17
9	6.94	1.65
10	7.03	2.35
11	7.22	2.25
12	7.05	1.26



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STUDIES IN STABILITY CONSTANTS OF PR(III),ND(III) & GD(III) METAL IONS COMPLEXES WITH SOME SUBSTITUTED 1,3-THIAZINE IN 70% DIOXANE-WATER MEDIUM PH-METRICALLY

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ABSTRACT

The interaction of Pr(III),Nd(III) & Gd(III) metal ions with ligands, L_1:4-[2-Hydroxy,5-Chlorophenyl]6-phenyl-2-imino,6-H-2,3dihydro,1,3-thiazine. L_2:4-[2-Hydroxy,5-Chlorophenyl]6-(4-anisylphenyl)2-imino-6-H,2,3-dihydro,1,3-thiazine L_3:4-[2-Hydroxy,3-bromo,5-Chloro-phenyl]6-[4-anisyl phenyl]-2-imino-6-H,2,3-diphenyl,1,3-thiazine have been studied at 0.1M ionic strength pH-metrically in 70% dioxane-water mixture by calvin-Bjerrum method.thee obtained were used to estimate & compare the value of proton-ligandstability constant (pK) and metal ligand stability constant (LogK) using half integral & pointwise calculation method.It is observed that metal ions form 1:1 & 1:2 complexes with L_1,L_2 & L_3.

Keywords: *Metal ions Pr(III),Nd(III) & Gd(III),Ligands L_1,L_2 & L_3,Stability Constant &Solvent.*

INTRODUCTION

Substituted 1,3-thiazines are heterocyclic compound and have attracted many researchers due of its application in medicinal field. The stability constant for the metal complex is widely used in many fields such as biological processes, analytical processes, pharmaceuticals, etc. Metal complex play a very important role in nature.

Thile[6] studied complex formation between Cr(III), Nd(III) & Pr(III) metal ions and substituted hydroxyl chalcones at 0.1M ionic strength pH-metrically. Thakur et al[7] have also done some work on stability constant of complexes with Cr(III) metal ions. Meshram et al[8], Studies on formation constant of Co(II), Ni(II), Cr(III) &Fe(III) ion complexes with some heterocycles by pH-metrically, spectrophotometrically & refractometrically.

Rathode et al[9], have studied effect of dielectric constant of dioxane-water mixture on proton-ligand dissociation constant &formation constant of Cu(II) complexes with 1,3-diphenyl thiazines pH-metrically at 0.1M ionic strength.1.3-thiazines possess medicinal properties like anti-inflammatory, anticonvulasant, antibiotic, antitubercular, antifungal and anxiolytic activity. In view of the analytical application of 1,3-thiazine and confirmation of dissosiable hydroxyl group (-OH), it is nessesery to know the physio-chemical properties. So present study deals with complex formation between Pr(III), Nd(III) and Gd(III) metal ions with ligands 1,3-thiazines and determination of stability constants pH-metrically by Calvin-Bjerrum.

In view of the analytical application of 1,3-thiazine and confirmation of dissosiable hydroxyl group (-OH), it is nessesery to know the physio-chemical properties. So present study deals with complex formation between Pr(III), Nd(III) and Gd(III) metal ions with ligands 1,3-thiazines and determination of stability constants pH-metrically by Calvin-Bjerrum.

MATERIAL & METHODS

The solution of ligants L_1, L_2 and L_3 were prepared in 70% dioxane-water mixture. The solution of NaOH,HNO_3, KNO_3 and metal ions $Pr(NO_3)_3$, $Nd(NO_3)_3$, and $Gd(NO_3)_3$ were obtained from BDH grade chemicals. The NaOH solution was standardized with oxalic acid, kept in pyrex vessel and used as a titrant for pH titrations. The 1.0 M KNO_3 solution were prepared to maintain the 0.1 M ionic strength of the solution. The metal nitrates were used to prepare the metal solution and were standardized by usual procedure.

MEASUREMENTS: All measurements were carried out at 30 ± 0.1^{0}C. Systronic microprocessor based pH meter with magnetic stirrer and combined glass and calomel electrode assembly used for pH measurements. The sensitivity of pH is 0.01 units. The instruments could read pH in the range 0.00 to 14.00 in the step of 0.005. The pH meter was switched ON for half an hour before starting the titration for initial warm up of the

instrument. It was calibrated before each titration with an aqueous standard buffer solution of pH 7.00 and 9.20 at (30 ± 0.1^0C) prepared from a 'Qualigens' buffer tablets. The hydrogen ion concentration was measured with combine glass electrode.

PROCEDURE: Experimental procedure involves following three set of titrations carried out with standard NaOH solution (0.1M) in presence of inner atmosphere by bubbling a contant flow of nitrogen gas. Data obtained from the titration was used to plot a graph between volume of NaOH and pH values, they are called acid, ligand and metal titration curves.

1. Free acid titration (HNO_3, 1 x 10^{-2} M)
2.Free acid + ligand titration (20 x 10^{-4}M)
3. Free acid + ligand + metal ion titration (4 x 10^{-4} M)

3. RESULT AND DISCUSSION

Substituted 1,3 thiazines is considered as monobasic acid having only one replaceable H^+ ion from–OH group.

$HL = H^+ + L^-$

It is observed from titration curve for all the system that ligand curves start deviating from free acid (HNO_3) curves at about 2.26 and deviated continuously up to pH 7.00. The deviation shows that dissociation of –OH group in substituted 1,3-thiazines. Proton-ligand formation number $n\bar{}_A$ were calculated from acid titration curve (A) and acid ligand titration curve (A+L) by standard method. It was found that values of $\bar{}_A$ decreases with increased pH of solution due to replacement of H^+ ion from –OH group. The photon ligand formation number were calculated by Irving and Rossotti expression.

$$n\bar{}_A = \gamma - \frac{\{(V_2 - V_1)(E^0 + N)\}}{(V^0 + V_1)T_L^0\}}$$

Where,

$V^0$is the initial volume of solution, E^0 and T_L^0 are initial concentrations of mineral acid and ligand respectively, V_1,V_2 are the volumes of alkali of normality N during acid and ligand titration of given pH, γ is the replaceable protons from the ligand.

Table: 1
Determination of $n\bar{}_A$ Values

pH	V_1 (ml)	V_2 (ml)	$V_2 - V_1$ (ml)	$n\bar{}_A$
1.20	1.05	1.18	0.13	0.8186
1.40	1.19	1.35	0.16	0.7773
1.60	1.45	1.65	0.20	0.7230
1.80	1.60	1.83	0.23	0.6824
2.00	1.78	2.05	0.27	0.6285
2.20	1.82	2.15	0.33	0.5463
2.40	1.90	2.26	0.36	0.5059
2.60	1.98	2.38	0.40	0.4518
2.80	2.02	2.46	0.44	0.3974
3.00	2.06	2.55	0.49	0.3295
3.20	2.10	2.61	0.51	0.2891
3.40	2.11	2.64	0.53	0.2755
3.60	2.12	2.67	0.55	0.2483
3.80	2.13	2.69	0.56	0.2347
4.00	2.15	2.72	0.57	0.2214

System-Ligand (L_1)
T_L^o = 20 x 10^{-4} M
N = 0.10 N

E^0 = 1 x 10^{-2} M
μ = 0.1 M

Medium : 70% Dioxane-water
Temp. = 30 ± 0.1°C
V^0 = 12.5 ml

Table:2
Determination of $n\bar{}_A$ Values

pH	V_1 (ml)	V_2 (ml)	$V_2 - V_1$ (ml)	$n\bar{}_A$
1.60	1.64	1.75	0.11	0.8482
1.80	2.29	2.44	0.15	0.8222
2.00	2.80	2.97	0.17	0.7706
2.20	3.06	3.24	0.18	0.7583
2.40	3.29	3.49	0.20	0.7306
2.60	3.32	3.54	0.22	0.7061
2.80	3.36	3.60	0.24	0.6796
3.00	3.42	3.68	0.26	0.6533
3.20	3.48	3.76	0.28	0.6270
3.40	3.54	3.84	0.30	0.6008
3.60	3.60	3.92	0.32	0.5748
3.80	3.61	3.94	0.33	0.5615
4.00	3.62	3.96	0.34	0.5483
4.20	3.63	3.98	0.35	0.5351
4.40	3.65	4.03	0.39	0.4821
4.60	3.65	4.06	0.41	0.4556
4.80	3.66	4.09	0.43	0.4291
5.00	3.67	4.12	0.45	0.4027

System-Ligand (L_2)
$T_L^o = 20 \times 10^{-4}$ M
N = 0.10 N
$E^0 = 1 \times 10^{-2}$ M
μ = 0.1 M
Medium : 70% Dioxane-water
Temp. = 30 ± 0.1°C
V^0 = 12.5 m

Table:3
Determination of $n\bar{}_A$ Values

pH	V_1 (ml)	V_2 (ml)	$V_2 - V_1$ (ml)	$n\bar{}_A$
1.40	1.18	1.27	0.09	0.8747
1.60	1.35	1.48	0.13	0.8196
1.80	1.51	1.68	0.17	0.7650
2.00	1.70	1.88	0.18	0.7519
2.20	1.82	2.03	0.21	0.7113
2.40	1.94	2.17	0.23	0.6845
2.60	1.98	2.25	0.27	0.6299
2.80	2.01	2.31	0.30	0.5891
3.00	2.05	2.37	0.32	0.5620
3.20	2.08	2.42	0.34	0.5350
3.40	2.12	2.48	0.36	0.5080
3.60	2.13	2.51	0.38	0.4807
3.80	2.13	2.53	0.40	0.4534
4.00	2.15	2.72	0.57	0.2214

System-Ligand (L_3)
$T_L^o = 20 \times 10^{-4}$ M
N = 0.10 N
$E^0 = 1 \times 10^{-2}$ M
μ = 0.1 M
Medium : 70% Dioxane-water
Temp. = 30 ± 0.1°C
V^0 = 12.5 ml

The proton-ligand stability constant pK value of ligand were calculated by algebric method point wise calculation.

Table: 4
Determination of Proton-Ligand Stability Constants (pK)

Ligand	Proton –Ligand Stability Constants (pK)	
	Half Integral Method	Pointwise Calculation
L_1	2.40	2.4022 0.02
L_2	4.20	4.2147 0.02
L_3	3.40	3.4197 0.03

The metal-ligand formation number($n\bar{}$)were calculated by standard method, which increase with increase pH by using the following expression. The metal-ligand stability constant (log K) were determined by half integral method by plotting $n\bar{}$ Vs pH at n=0.5 and 1.5 showing 1:1 & 1:2 formation of complex. The metal-ligand stability constant values are given in table.5.

$$n\bar{} = \frac{\{(V_3-V_2)(E^0+N)\}}{\{(V^0+V_2)_M{}^0\}}$$

Table: 5
Determination of Metal ligand Stability Constants

System	log K_1	log K_2	log K_1 - log K2	log K_1/ log K_2
Pr(III)-L1	3.80	3.78	0.02	1.00
Nd(III)-L1	3.78	3.54	0.24	1.06
Gd(III)-L1	3.48	3.15	0.33	0.33
Pr(III)-L2	5.75	5.55	0.20	1.03
Nd(III)-L2	5.55	5.06	0.49	1.09
Gd(III)-L2	5.25	4.39	0.86	1.19
Pr(III)-L3	4.25	4.06	0.19	1.04
Nd(III)-L3	4.55	4.26	0.29	1.07
Gd(III)-L3	4.64	4.48	0.16	1.03

4. CONCLUSION

It was observed from above table 5 that log K_1 values are greater than log K_2 values for all metal complexes. The difference between log K_1 and K_2 is smaller than 1 then that shows the formation of simultaneous 1:1 & 1:2 complexes. The higher values of ratio ($\log K_1/\log K_2$) indicate the more stable Simultaneous complex formation.

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SYNTHESIS AND ANTIBACTERIAL STUDY OF 3-CARBONYL-(PYRID-4-YL)-5-HEPTA-*O*-ACETYL-β-D-MALTOSYLIMINO-2-ARYLIMINO-1,2,4-THIADIAZOLIDINES

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ABSTRACT

*A series of some 3-Carbonyl-(pyrid-4-yl)-5-hepta-O-acetyl-β-D-maltosylimino-2-arylimino-1, 2, 4-thiadiazolidines **5** have been synthesized by the interaction of various Aryl Isocyanodichlorides **4** with 1-Carbonyl-(pyrid-4-yl)-4-hepta-O-acetyl-β-D-Maltosyl-3-thiosemicarbazide **3** which was prepared by the interaction of Hepta-O-acetyl-β-D-maltosyl isothiocyanate **1** with isonizid **2**. The identities of these new compounds have been established on the basis of chemical transformation and spectral studies. In the present investigation the In-vitro bacterial assay of compounds has been evaluated by using several bacteria such as Escherichia coli, Staphylococcus aureus and Pseudomonas aeruginosa. All compounds studied shows satisfactory bacterial assay.*

Keywords: *Antibacterial study, 1, 2, 4-dithiazolidines, spectral analysis isoniazid, Aryl Isocyanodichlorides, thiosemicarbazide, isothiocyanate, isonizid.*

Section: Organic Synthesis

Introduction

Sugars are ubiquitous in nature much of the cutting edges of synthetic medicinal and biological chemistry meet at the crossroads of carbohydrate science. The sugar science has been extensively studied and many excellent reviews are available N and S – linked derivatives of various sugar[1-6] has revived a great attention because of their vital role in several biological processes. The isoniazid nucleus found in compound has variety of pharmacological activity such as antimicrobial, antifungal, antiinflammatory[7-10].

In view of applications of these compounds in various fields, the current study was related to investigate the following reaction. 3-Carbonyl-(pyrid-4-yl)-5-hepta-*O*-acetyl-β-D-maltosylimino-2-o-tolylimino-1, 2, 4- thiadiazolidine **5a** have been synthesized by the reaction between *o*-tolyl isocyanodichloride **4a** and 1-Carbonyl-(pyrid-4-yl)-4-hepta-*O*-acetyl-β-D-maltosyl-3-thiosemicarbazide **3** in chloroform medium. The compound **3** was synthesized by the interaction of Hepta-*O*-acetyl-β-D-maltosyl isothiocyanate **1** with isonizid **2.**

When the above reaction was extended with other aryl isocyanodichlorids the respective 3-Carbonyl-(pyrid-4-yl)-5-hepta-*O*-acetyl-β-D-maltosylimino-2-arylimino-1, 2, 4- thiadiazolidines **5** were obtained.

Experimental

Melting points were recorded on electro thermal melting point apparatus are uncorrected. Specific rotations were measured on Equip-Tronic digital polarimeter model no. Eq 800 at 30^0c in $CHCl_3$. IR spectra were recorded on a Perkin Elmer spectrometer. ^{1}H NMR were obtained on a Bruker DRX-300 (300 MHz FT NMR) NMR spectrometer in $CDCl_3$ solution with TMS as an internal reference. The mass spectra were recorded on a DART mass spectrometer. Purity of the compounds was checked by thin layer chromatography using Merck silica gel coated aluminum plates and petroleum ether: ethyl acetate as eluent.

Details of the experiment are summarized as follows.

A) Synthesis of Hepta-*O*-acetyl-β-D-maltosyl isothiocyanate 1

The method of preparation of Hepta-*O*-acetyl-β-D-maltosyl isothiocyanate (I) was developed by the interaction of Hepta-*O*-acetyl –α- D-maltosyl bromide and lead thiocyanate.

B) Isoniazid 2

Isoniazid was commercially available was of E-merck grade.

C) Aryl Isocyanodichlorides 4

i) Aryl isothiocyanates[11]

Aryl isothiocyanates were prepared by the oxidative decomposition of ammonium aryl dithiocarbamates with lead nitrate.

ii) Arylisocyanodichlorides[12]

Arylisocyanodichlorides were prepared by passing excess amount of gaseous chlorine into the solution of Aryl isothiocyanates in chloroform. Aryl isocyanodichlorides were obtained as pale yellow oil.

Spectral Analysis[13-20]**:**

The infrared spectrums of synthesized compounds shows the absorption bands :-

Assignment	Absorption observed (KBr cm^{-1}		
	1-Carbonyl-(pyrid-4-yl)-4-hepta-*O*-acetyl-β-D-maltosyl-3-thiosemicarbazide **3**	3-Carbonyl-(pyrid-4-yl)-5-hepta-*O*-acetyl-β-D-maltosylimino-2-*o*-tolylimino-1, 2, 4-thiadiazolidines **5a**	3-Carbonyl-(pyrid-4-yl)-5-hepta-*O*-acetyl-β-D-maltosylimino-2-*p*-methoxy phenylimino-1, 2, 4-thiadiazolidines **5b**
N-H stretching	3468	3473	3473
Aromatic C-H stretching	3142	3184	3184
Aliphatic C-H stretching	2960	2956	2958
C = O Streching	1747	1743	1749
C – N stretching	1535	1508	1525
C = S stretching	1228	1238	1232
Characteristics of Maltose	1039, 941, 900	1035, 940, 900	1039, 941, 900
C - S stretching	758	756	688
C – O stretching	682	790	800
Disubstituted benzene	762	761	775
Monosubstituted benzene	690	688	710

^{1}H NMR spectral analysis: The NMR spectrum of **3-Carbonyl-(pyrid-4-yl)-5-hepta-*O*-acetyl-β-D-maltosylimino-2-*o*-tolylimino-1, 2, 4-thiadiazolidines 5a** showed signals at δ 9.03-7.04 (m, Ar. protons), 5.45-3.83 (m, Maltosyl protons), 2.14 (s, CH_3), 2.30-1.88(m, Acetyl protons), 5.14(s, N-H proton)

Mass spectral analysis: The mass spectrum of **3-Carbonyl-(pyrid-4-yl)-5-hepta-*O*-acetyl-β-D-maltosylimino-2-*o*-tolylimino-1,2,4-thiadiazolidines 5a** displayed molecular ion peak at m/z 858. The other important fragment peaks (m/z) are 945(M^+), 807, 701, 659, 559, 457, 331, 257.

Antibacterial Study[21-22]**:-**

All the compounds have been screened for antibacterial study using Nutrient agar diffusion method by measuring the inhibition zone in mm. The compounds were taken at a concentration of 1 mg/ ml using dimethyl sulphoxide as solvent. Amikacin (100ůrg/ml) was used as a standard for antibacterial activity. The compounds were screened for antibacterial activity against *Escherichia coli, Staphylococcus aureus, Psedomonas aeruginosa* in nutrient agar medium. It has been observed that some of these compound exhibited interesting microbial activities. **3** exhibited most significant activity against *Escherichia coli* **5a, 5b** exhibited most significant activity against *Staphylococcus aureus* and **3, 5a** exhibited most significant activity against *Pseudomonas aeruginosa* respectively. All the other compounds exhibited low to moderate activity.

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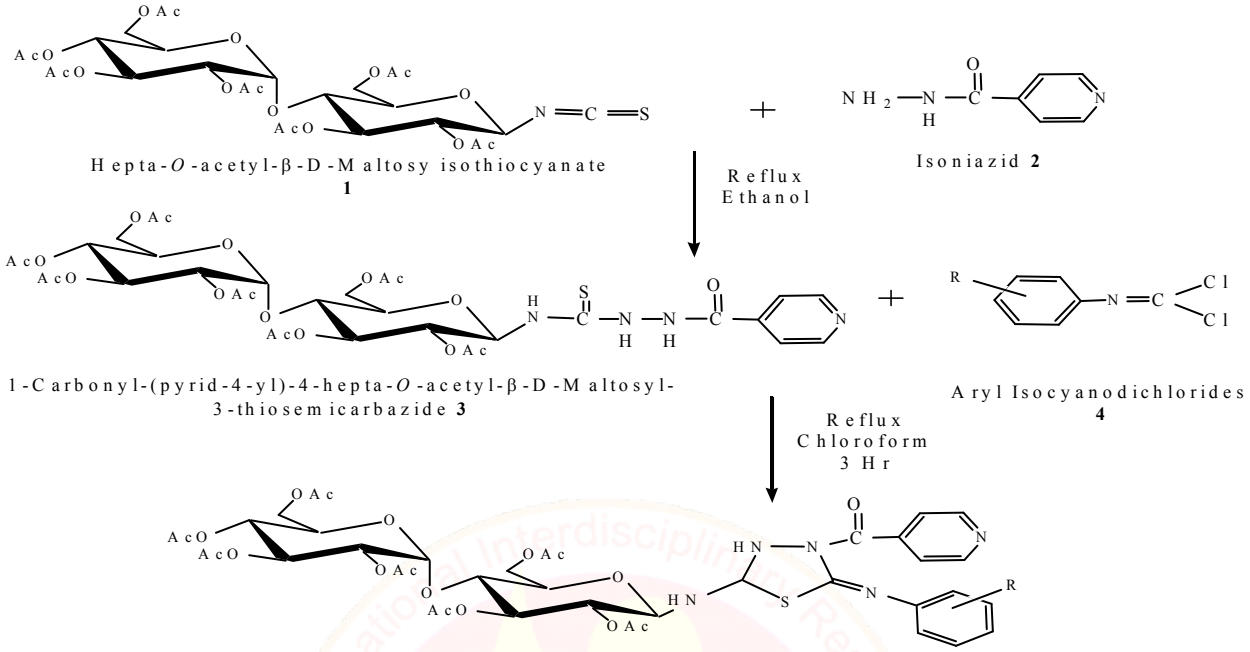
Reaction Scheme:



3-Carbonyl-(pyrid-4-yl)-5-hepta-*O*-acetyl-β-D-maltosylimino-2-arylimino-1,2,4- thiadiazolidines **5**

Where, R =a) *o*-methyl, b) *p*-Methoxy

Table 1: Physical Characterization of synthesized Compounds:

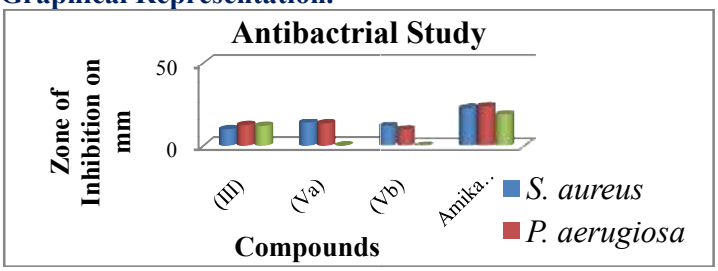
Sr. No	Name of Compounds	M. P. in ^{o}C	Molecular Weight	Molecular Formula	% Yield
1	**1-Carbonyl-(pyrid-4-yl)-4-hepta-*O*-acetyl-β-D-Maltosyl-3-thiosemicarbazide 3**	105	830	$C_{33}H_{43}O_{19}N_4S$	80
2	**Synthesis of 3-Carbonyl-(pyrid-4-yl)-5-hepta-*O*-acetyl-β-D-maltosylimino-2-*o*-tolylimino-1,2,4-thiadiazolidine 5a**	90	945	$C_{41}H_{47}O_{19}N_5S$	75
3	**Synthesis of 3-Carbonyl-(pyrid-4-yl)-5-hepta-*O*-acetyl-β-D-maltosylimino-2-*p*-methoxy phenyl imino-1,2,4-thiadiazolidine 5b**	120	961	$C_{41}H_{47}O_{20}N_5S$	85

Table 2 : Antibacterial study of synthesized Compounds:

Sr. No	**Compounds**	***S. aureus***	***P. aerugiosa***	***E.coli***
1.	1-Carbonyl-(pyrid-4-yl)-4-hepta-*O*-acetyl-β-D-Maltosyl-3-thiosemicarbazide **3**	10	15	12
2.	Synthesis of 3-Carbonyl-(pyrid-4-yl)-5-hepta-*O*-acetyl-β-D-maltosylimino-2-*o*-tolylimino-1,2,4-thiadiazolidine **5a**	14	18	R
3.	Synthesis of 3-Carbonyl-(pyrid-4-yl)-5-hepta-*O*-acetyl-β-D-maltosylimino-2-*p*-methoxy phenyl imino-1,2,4-thiadiazolidine **5b**	12	20	R
4.	Amikacin	23	24	19

**zone of inhibition in mm (15 or less) resistance, (16-20mm) moderate and (more than 20mm) sensitive. *Escherichia coli* (*E. coli*), *Staphalococcus aureus* (*S.* aureus) and *Psudomonas auriginosa* (*P. auriginosa*).

Graphical Representation:



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SYNTHESIS OF *N*-GLUCOPYRANOSYL SUBSTITUTED 1, 3, 4-THIADIAZOLIDINE DERIVATIVES AND ITS APPLICATION AS ANTIMICROBIAL AGENTS

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ABSTRACT

A series of 2-Tetra-O-benzoyl-β-D-glucopyranosyl-4-phenyl-5-substituted benzoylimino-1, 3, 4-thiadiazolidines have been synthesized by the interaction of 1-Tetra-O-benzoyl-β-D-glucopyranosyl-3-phenyl amino thiocarbamide with various substituted benzoyl isocyanodichlorides. The synthesized compounds were structurally confirmed by analytical and IR, ^{1}H NMR and Mass spectral analysis. In the present investigation the In-vitro antimicrobial activity of compounds has been evaluated by using several bacteria and fungi. All compounds studied shows satisfactory antimicrobial activity.

INTRODUCTION

Heterocyclic compounds are found to exhibit anti-inflammatory, anti-parasitic, anti-tubercular, antidiabetic activity[1-3]. In recent years, there has been increasing interest in the synthesis of heterocyclic compounds by cyclization of appropriate linear compounds. Organosulfur compounds play an important role in modern organic synthesis. Recently in our laboratory there are various reports on sugar heterocyclic possessing antimicrobial and antifungal activities [4-6].

In view of applications of these compounds in various fields, we report the synthesis of a series of 2-Tetra-*O*-benzoyl-β-D-glucopyranosyl-4-phenyl-5- substituted benzoylimino imino-1, 3, 4-thiadiazolidines **(3a-h)** have been synthesized by the interaction of 1-Tetra-*O*-benzoyl-β-D-glucopyranosyl-3-phenyl amino thiocarbamide **(1)** with various substituted benzoyl isocyanodichlorides **(2a-h)** .

The structures of the products were confirmed by the spectral (IR, ^{1}H NMR and Mass[8-15]) and elemental analysis (Table 1).

EXPERIMENTAL

Melting points of all synthesized compounds were determined using open capillary tube on Mac digital melting point apparatus and were uncorrected. The IR spectrum was recorded in KBr Disks on SHIMADZU IR affinity – 1 – FTIR spectrometer. The NMR spectrum was recorded in Brucker DRX – 300 instruments operating at 300 MHz using $CDCl_3$ solution with TMS as internal standard. The mass spectrum was recorded on a THERMO Finnigan LCO Advantage max ion trop Mass Spectrometer. Specific rotations were measured on Equip-Tronics EQ-801 Digital Polarimeter. Thin layer chromatography (TLC) was performed on silica gel G for TLC (Merck) and spots were visualized by iodine vapours.

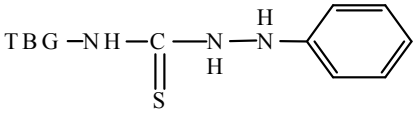
GENERAL METHODS

1. Synthesis of 1-Tetra-*O*-benzoyl-β-D-glucopyranosyl-3-phenyl amino thiocarbamide **(1):**It was prepared by refluxing Tetra-*O*-benzoyl-β-D-glucopyranosyl isothiocyanate and phenyl hydrazine in benzene for 1 hr.
2. Preparation of substituted benzoyl isocyanodichlorides **(2a-h)** [7]: It was prepared by passing excess amount of gaseous chlorine into the solution of substituted benzoyl isothiocyanates in chloroform.
3. 2-Tetra-*O*-benzoyl-β-D-glucopyranosyl-4-phenyl-5- substituted benzoylimino-1, 3, 4-thiadiazolidines **(3a-h)**

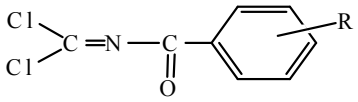
Mixture of 1-Tetra-*O*-benzoyl-β-D-glucopyranosyl-3-phenyl amino thiocarbamide **(1a)** (0.002M, 1.49gm) and benzoyl isocyanodichloride **(2)** (0.002M, 0.268gm) was reflux in chloroform for about 3 hr. The chloroform was distilled off and the sticky mass triturated several times with petroleum ether (60-80 ^oC) to afford solid **(3a)**. It was purified by ethanol-water.

Similarly, when the reaction was extended to other substituted benzoyl isocyanodichlorides **(2b-h)** the corresponding 1, 3, 4-thiadiazolidines **(3b-h)** has been synthesized.

SCHEME:

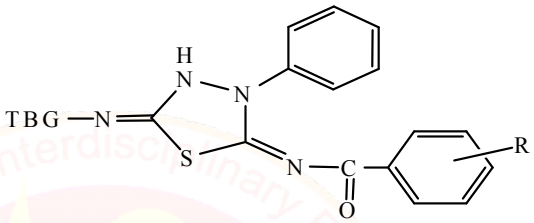


1-Tetra-*O*-benzoyl-β-D-glucopyranosyl 3-phenyl amino thiocarbamide **(1)**



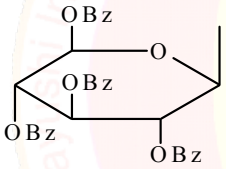
Substituted benzoyl isocyanodichlorides **(2)**

Reflux
Chloroform
3 hr



2-Tetra-*O*-benzoyl-β-D-glucopyranosyl-4-phenyl-5-substituted benzoylimino-1, 3, 4-thiadiazolidines **(3a-h)**

Where,

TBG = 

Bz = COC_6H_5

R = a) H, b) *o*-Cl, c) *m*-Cl, d) *p*-Cl, e) *o*-methyl, f) *m*-methyl, g) *p*-methyl h) *p*-methoxy.

SPECTRAL ANALYSIS

3a:- **IR(KBr cm^{-1}):** 3061 (Aromatic C-H), 2972 (Aliphatic C-H), 1735 (C=O), 1600 (C=N), 1313 (C-N), 1269 (C-O), 1070 (Characteristics of glucose), 713 (C – S); **^{1}H NMR ($CDCl_3$, pm):** δ 7.9-7.2 (35H, m, Aromatic protons), 6.12-4.29 (7H, m, glucopyranosyl protons), 6.57-6.56 (1H, s, hump N-H); **Mass (m/z):** 874, 730, 619, 517, 457, 335, 287, 227, 105.

3d:- **IR(KBr cm^{-1}):** 3059 (Aromatic C-H), 2954 (Aliphatic C-H), 1730 (C=O), 1651 (C=N), 1600 (C=C), 1315 (C-N), 1273 (C-O), 1070 (Characteristics of glucose), 713 (C-S).; **^{1}H NMR ($CDCl_3$, ppm):** δ 7.89-7.40 (34H, m, Aromatic protons), 4.34-6.11 (7H, m, glucopyranosyl protons), 6.34 (1H, s, N-H), 2.39-1.9 (3H, s, CH_3); **Mass (m/z):909** (M^+),745, 729, 667, 579, 335, 231, 108.

3h:- **IR(KBr cm^{-1}):** 3061 (Aromatic C-H), 2960 (Aliphatic C-H), 1735 (C=O), 1620 (C=N), 1600 (C=C), 1313 (C-N), 1278 (C-O), 1070 (Characteristics of glucose); **^{1}H NMR ($CDCl_3$, ppm):** δ 7.89-7.40 (34H, m, Aromatic protons), 5.75-3.74 (7H, m, glucopyranosyl protons), 6.84 (1H, s, N-H), 3.42 (3H, s, O-CH_3); **Mass (m/z):** 905(M^+),723, 619, 579, 457, 257, 231, 105

Table 1: Physical Data of compounds 3(a-g)

Sr. No.	Products	m.p. (°C)	Yield (%)	R_f Value	Elemental Analysis % Found (Required)		$[\alpha]_D^{31}$ (c, in $CHCl_3$]
					N	S	
1.	3a	179	74	0.86	6.39 (6.40)	3.65 (3.66)	+81.2° (0.97 in $CHCl_3$)
2.	3b	185	72.94	0.92	6.08 (6.16)	3.45 (3.52)	+84.1° (0.91 in $CHCl_3$)
3.	3c	174	85.21	0.87	6.07 (6.16)	3.48 (3.52)	+42.2° (0.96 in $CHCl_3$)
4.	3d	178	70.50	0.79	6.18	3.49	+52.6°

					(6.16)	(3.52)	(0.95 in $CHCl_3$)
5.	3e	190	75.25	0.85	6.28 (6.33)	3.60 (3.60)	$+85.1^o$ (0.94 in $CHCl_3$)
6.	3f	181	76.27	0.92	6.29 (6.30)	3.61 (3.60)	$+122.2^o$ (0.9 in $CHCl_3$)
7.	3g	171	80.21	0.81	6.32 (6.30)	3.59 (3.60)	$+52.50^o$ (0.96 in $CHCl_3$)
8.	3h	196	76.57	0.78	6.06 (6.18)	3.52 (3.53)	$+76.2^o$ (0.94 in $CHCl_3$)

ACKNOWLEDGEMENT

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DETECTION OF FOOD ADULTERATION IN PULSES AND SPICES COLLECTED RANDOMLY IN AKOLA REGION

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ABSTRACT

This study was "Detection of food adulteration in selected food items". In this food groups like pulses and spices were selected. Both branded as well as unbranded samples were selected for the study to determine the adulteration levels & the qualitative differences between them. The tests were carried out by chemical analysis in a majority of products and through visual inspection in the few products. After the tests, the products containing adulterants were identified in branded & unbranded food products. This study attempted to bring in awareness to the public on the important subject to food adulteration & various simple methods available to detect food adulteration.

Keywords: *Food Adulteration, pulses, spices, Akola region*

INTRODUCTION

Food is a more basic need of human than shelter and clothing, it provide adequately for the body's growth, maintains, repair and reproduction. Food furnishes the body with the energy required for all human activities –it provide materials required for the building and renewal off body tissues and substances that act to regulate body presses. All the function of food must be served by the diet in order to maintain the body in good health. Most food fulfils more than one function as they are complex mixture of a number of chemical substances.

Adulteration of food means substitution of the genuine food material wholly or in part with any cheaper or inferior substance which or removal of any of its constituents, wholly of in part which affects adversely the nature, substance or quality of the food. Pulses are the edible fruits. They have a high protein content ranging from 20-40 percent and this make them important in human food from the point of views of nutrition pulses can play an important role in bringing the protein gap. India depends greatly on pulses to meet its demand for protein. Spices grown in different part of the word many of them are grown in India. Spices can classified in different ways such as according to their botanical families economic important etc. Each system has its own merits and demerits.

Among food atom spices and pulses due to their inherent nature great demand and high price become easy substances for gross adulteration. According to the prevention of food adulteration act, 1976 of India, adulteration mean any article of food whose quality or purity falls below the prescribed standards. The seeds of pulses and spices include both edible and inedible type. Even among the edible legumes toxic principle occur and their elimination is important in Order to exploit them for edible purposes. The toxic substances in pulses in kesari dal and metanil yellow causes lathyrim abnormalities anaemia etc. Spices are generally adulterated with less expensive material e.g. papaya seeds and light berry, chalk powder, artificial colour etc.[1]

Table 1: Harmful effect of adulteration in food.[2-6]

Sr. no	Food products	Adulterants	Harmful effect
1.	Pulses	Metanil yellow	Cancer Abnormalities Anaemia etc.
2.	Bengal gram dal arhar dal	Kesaridal	Lahyrim cancer
3.	Black pepper	Papaya seeds and light berry	Stomach, Liver problem.
4.	Termeric powder	Metanil Yellow. Chalk powder.	Carcinogenic Highly carcinogenic
5.	Chilli powder	Brick powder Artificial colour	Stomach problem Cancer

MATERIAL & SAMPLE COLLECTION

The samples were collected for each food products of pulses and spices such as Besan flour, Black pepper, turmeric powder, chilli powder, etc are taken for the detection of adulterants. Three different samples of Besan flour, Black pepper,

turmeric powder, chilli powder collected from different shops of Akola region.

METHODOLOGY

The study methods are given by the following procedure and the tests were done in laboratory with both the chemical & physical analysis. Each item in the food groups were analyzed for various adulterants. The following table show the food items tested in each food groups.

Table 2: Food Groups Food Items

SR.NO	FOOD ITEM	SAMPLES
1.	Pulses	Pigeon pea (Arhar), green gram(moong), chick pea(chana),black gram(urad). Besan flour.
2.	Spices	Black pepper.
3.	Powder spices	Turmeric powder, chilli powder.

Procedure[7-9]

Collected samples were tested as per following tests.

Table 3: Test procedure of selected samples

Food Item	Sample Name	Test	Observation	Inference
Pulses	i)pigeon pea	Take pigeon pea in water and add drops of conc.HCL to it.	If colour of the solution turns pink.	It indicates that the pigeon pea contains metanil yellow.
	ii)green gram	Take green gram in water and add drops of conc.HCL to it	If colour of the solution turns pink.	It indicates that the green gram contain metanil yellow.
	iii)chickpea	Take chickpea in water and add drops of conc.HCL to it	If colour of the solution turns pink.	It indicate that the chickpea contains metanil yellow.
	iv)black gram	Take black gram in water and add drops of conc.HCL to it	If colour of the solution turns pink.	It indicates that the black gram contain metanil yellow.
	Besan flour	Add 50ml of 10% dil HCL to 10grms of besan flour. And keep on simmering water about 15 min.	If the colour of mixture does not turn pink.	It indicates that the besan flour is pure.
Spices	i)black pepper	Add a few corns of pepper to alcohol.	If the corns of pepper will sink.	It shows that the black pepper was adulterated with papaya seeds.
Powder spices	i) Turmeric powder. (metanil yellow).	Take 1/4 tsp of turmeric powder in a test tube, add 3 ml alcohol to it and shake vigorously. Add 10 drops of hydrochloric acid to it.	Colour of the solution turns pink.	It indicates the turmeric powder contains metanil yellow.
	ii)Turmeric powder(Chalk powder or yellow soap stone powder.)	Take a small quantity of turmeric powder add some dilute hydrochloric acid to it.	Solution shows effervesces.	Turmeric powder is adulterated.
	iii)Chilli powder.(brick powder)	Add a spoon full of chilli powder in a glass of water.	Artificial colorant descent as colour streaks.	Chilli powder is adulterated with brick powder.
	iv) Chilli powder (Artificial colours.)	Sprinkle the chilli powder on glass of water.	Water change the colour.	Chilli powder is adulterated.

Table 4 : Observation and Inference of the Selected samples

Food Item	Sample Name	Test	Observation	Inference
Pulses	i)pigeon pea	Take pigeon pea in water and add drops of conc.HCl to it.	Sample1:- Colour of the solution does not turns pink. Sample2:- :-Colour of the solution does not turns pink. Sample3:- :-Colour of the solution turns pink.	I) It indicates that the pigeon pea is pure. II) It indicates that the pigeon pea is pure. III) It indicates that the pigeon pea is adulterated.
	ii)green gram	Take green gram in water and add drops of conc. HCl to it	Sample1:-Colour of the solution does not turns pink. Sample2:-Colour of the solution does not turns pink. Sample3:-Colour of the solution does not turns pink.	I) It indicates that the green gram does not contains metanil yellow. II) It indicates that the green gram does not contains metanil yellow. III) It indicates that the green gram does not contain metanil yellow.
	iii)chickpeas	Take chickpea in water and add drops of conc.HCl to it.	Sample1:-Colour of the solution turns pink. Sample2:-Colour of the solution does not turns pink. Sample3:-Colour of the solution does not turns pink.	I)It indicate that the chickpeas contains metanil yellow. II)It indicate that the chickpeas does not contains metanil yellow. III)It indicate that the chickpeas does not contains metanil yellow.
	iv)black gram	Take black gram in water and add drops of conc.HCL to it	Sample1:-Colour of the solution does not turns pink. Sample2:-Colour of the solution does not turns pink. Sample3:-Colour of the solution does not turns pink.	I)It indicate that the black gram does not contains metanil yellow. II)It indicate that the black gram does not contains metanil yellow. III)It indicate that the black gram does not contains metanil yellow
	Besan flour	Add 50ml of 10% dil HCL to 10grms of besan flour. And keep on simmering water about 15 min.	Sample1:-Colour of mixture does not turn pink. Sample2:-Colour of mixture does not turn pink. Sample3:-Colour of mixture does not turn pink.	I) It indicates that the besan flour is pure. II) It indicates that the besan flour is pure. III) It indicates that the besan flour is pure.
Spices	i)black pepper	Add a few corns of pepper to alcohol.	Sample1:-The corns of pepper will sink Sample2:-The corns of pepper will sink. Sample3:-The corns of pepper will sink.	I) It shows that the black pepper was adulterated with papaya seeds. II) It shows that the black pepper was adulterated with papaya seeds. III) It shows that the black pepper was adulterated with papaya seeds.

Powder spices	i) Turmeric powder. (metanil yellow)	Take 1/4 tsp of turmeric powder in a test tube, add 3 ml alcohol to it and shake vigorously. Add 10 drops of hydrochloric acid to it.	Sample1:-Colour of the solution does not turn pink. Sample2:-Colour of the solution does not turn pink. Sample3:-Colour of the solution does not turn pink.	I) It indicates the turmeric powder is pure. II) It indicates the turmeric powder is pure. III) It indicates the turmeric powder is pure.
	ii) Turmeric powder.(Chalk powder or yellow soap stone powder.)	Take a small quantity of turmeric powder add some dilute hydrochloric acid to it.	Sample 1:-Does not show effervescence. Sample 2:- Shows effervescence. Sample 3:- Does show effervescence.	I) Turmeric powder is pure. II) Turmeric powder is adulterated. III) Turmeric powder is adulterated.
	iii)Chilli powder (brick powder)	Add a spoon full of chilli powder in a glass of water.	Sample1:-Water does not change the colour. Sample2:-Water does not change the colour. Sample3:-Water does not change the colour.	I) Chilli powder is pure. II) Chilli powder is pure III) Chilli powder is pure
	iv) Chilli powder (Artificial colours.)	Sprinkle the chilli powder on glass of water.	Sample1:-Water does not change the colour. Sample2:-Water change the colour Sample3:-Water change the colour	I) Chilli powder is pure. II) Chilli powder is adulterated. III) Chilli powder is pure.

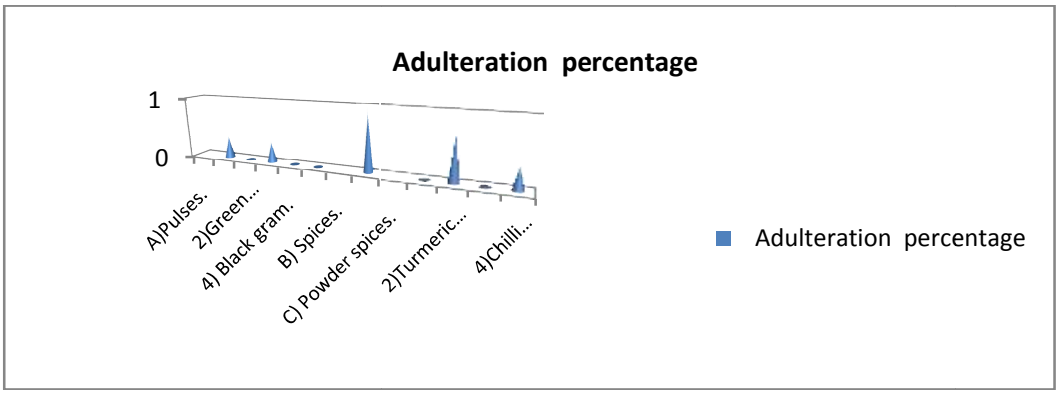
RESULT

On the above observations it is found that the three different samples of each food product show different percentage of adulteration. These three Samples of each food group collected from different places. Pigeon pea(arhar) shows 33.33% adulteration, Green gram shows 0% adulteration, Chickpea shows 33.33% adulteration, Black gram shows 0% adulteration, Besan flour shows 0% adulteration, Black pepper shows100% adulteration, Turmeric powder(metanil yellow) shows 0% adulteration, Turmeric powder(chalk powder) shows 66.66% adulteration, Chilli powder (brick powder)shows 0% adulteration, , Chilli powder(artificial colour) shows 33.33% adulteration. Most of the samples showed higher percentage of adulteration which is the alarming factor for the consumers to be aware about screening of adulteration time to time so that contaminated food should be avoided.

Table 5: Adulteration Percentage

Food Item	Adulteration percentage
A)**Pulses.**	
1)Pigeon pea.(Arhar)	33.33%
2)Green gram.(Moong)	0%
3) Chickpea.	33.33%
4) Black gram.	0%
5)Besan flour	0%
B) **Spices.**	
1) Black pepper.	100%
C) **Powder spices.**	
1) Turmeric powder.(metanil yellow).	0%
2)Turmeric powder.(chalk powder or yellow soap stone)	66.66%
3) Chilli powder.(brick powder).	0%
4)Chilli powder.(artificial colour)	33.33%

Fig. 1 : Graphical representation of Adulteration



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MICROWAVE ASSISTED SYNTHESIS AND CHARACTERIZATION OF 6-DIHYDRO-2,4- DI(SUBSTITUTEDPHENYL)-PYRIMID-5-ONE DERIVETIVES

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ABSTRACT

Microwave irradiation for the synthesis of heterocyclic compounds is rapid, economic, convenient and ecofriendly method for chemical synthesis. Pollution free synthesis, lesser reaction time, easy work up and minimum use of solvent are the major advantages of this technique. Microwave radiation facilitated the polarization of molecule under irradiation causing rapid reaction to occur.in this attempt a novel synthesis of di(substitutedphenyl)-pyrimid-5-one(I_a-I_j) have been carried out from condensation of substituted amide(0.01M), aromatic aldehyde (0.015M)and amino acid(0.01M) in presence of metal salt as a catalyst. The reaction mixture was irradiated under scientific microwave oven for 1-2 minutes. The synthesized compounds were characterized by elemental analysis and IR, NMR, CMR, UV and Mass spectrum. Melting point are uncorrected and carried out on Thieles apparatus.

Keywords: *Condensation, Pyrimidine, microwave irradiation.*

INTRODUCTION

Heterocyclic compounds are widely distributed in nature and are particularly important because of wide variety of physiological activity. Pyrimidine derivatives are important class of heterocyclic compound due to their therapeutic and pharmacological properties like antibiotic[1], antiinflammatory[2], antineoplastic[3-5], antiviral[6-8] and also used as calcium channel blockers and alpha-1α-antogonists. Synthesis of 3, 4-dihydropyrimidine-2-(1H)-ones has been reported By cyclocondensation reaction of ethyl acetoacetate, benzaldehyde and urea under Bronsted acid catalysis, by PietroBiginelli in 1893[9-10] and Aryl substituted 3, 4-dihydropyrimidine-2-(1H)–one[11] and their derivatives are known as an important substance in organic and medicinal chemistry. However this reaction required tedious conditions, high reaction time andlow yields.Marinedihydropyrimidione alkaloids for instance *Batzelladine*[12] shown interesting biological activities, which is to be a potent against HIV group.Conventional method for synthesis of heterocyclic compounds require more time, produce less yield, and need more energy so these techniques are replaced by environmentally benign synthetic methods.

Microwave heating have made it possible to shorten the reactions time significantly, and increase the product yields, which is mainly important in the case of high-temperatureprocesses that take a long time[13].

MATERIALS AND METHODS

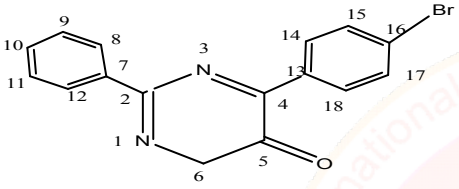
All solvents and reagents are purchased from Merck chemical. All the reactions were carried out in scientific microwave oven (Scientific microwave system model RG311L1, 700w, 2450MHz).Melting ranges of synthesized compounds were determined by open capillary method and are uncorrected. IR spectra were recorded on instrument Perkin Elmer – Spectrum RX- FTIR spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on Advance II 400 NMR spectrometer in $CHCl_3$ using TMS as internal standard. Mass spectra were recorded on a mass spectrometer. The elemental analysis was carried out using Themofinnigan CHNS analyzer. The homogeneity of compound was determined by TLC on silica gel using an eluent acetone. The migrated compounds were visualized by iodine vapours. The physical data of all these compounds are summarized in table.

RESULT AND DISCUSSION

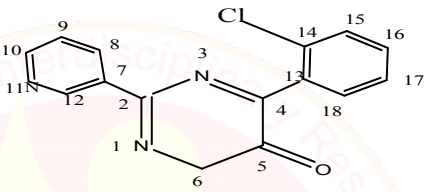
Present work deals with the microwave assisted synthesis of pyrimidine derivatives of high medicinal value to avoid the use of excess of solvent, fuel, water and lesser yield in conventional synthesis. A mixture of substituted amide (0.01M), aromatic aldehyde (0.015M) and glycine (0.01M) in presence of catalytic amount of ferric chloride irradiated in scientific microwave oven on medium power for 1 minutes. On cooling mixture was poured over crushed ice, filtered and crystallized from ethanol to get dirty white crystallized product 2,4-di(substitutedphenyl)-6-dihydropyrimid-5-one (I_a- I_j) in 80-90% yield. Elemental, Spectral analysis like IR, PMR, C[13]

NMR and identified compound I_a as 2,4-diphenyl-6-dihydropyrimid-5-one. It reveals that compound I_a is showing keto-enoltautomerism, in which IR- a strong hydrogen bonded –OH frequency 3285, 3087 (Ar C-H), 2966 (aliphatic C-H), 1652(C=C and C=O) overlap band absorption frequency of C=O group is decreased due to conjugation. Absence of N-H frequency and Presence of stronger Enolic O-H band suggest that enolic form is more stable due to extended conjugation. Since enolic O-**H** appears beyond ∂14 in PMRso it is not visible in PMR spectra. A very weak ∂2.5 singlet due to C**H**$_2$-C=O keto form, ∂7.0-8.9, multipletAr-H for nine Hydrogen in compound are interpreted as 7.9 (d, 2H, $J^3$7.2) 7.5(d, $J^3$7.2, 2H) for paradisubstituted ring and ∂7.0-7.5 multiplet, Ar-H, 5H, monosubstituted ring.

A singlet at ∂9.6 is interpreted as extended –C(OH)=C**H**enolic form highly deshielded due to heteroatom and conjugation. This is also confirmed by C13 NMR signals at 165.53 for enolic carbon**C**(OH)=, 58.5 keto form(**C**H2), and in aromatic regions 126.3, 127.3, 127.4, 128.1, 131.1, 133.7 and 140.3. Spectral data reveals that enolic form is more stable than keto form and stabilized due to presence of extended conjugation and nitrogen atoms in the ring. Similarly compounds I_a- I_j have been synthesized and characterized.



[I_a]

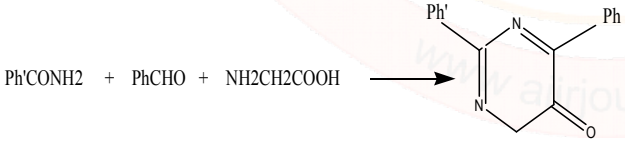


[I_f]

EXPERIMENTAL METHOD

GENERAL METHOD OFPREPARATION

A mixture of substituted amide (0.01M), aldehyde (0.015M), and amino acid (0.01M) in presence of catalyst irradiated in microwave on medium power for appropriate time. After completion, reaction mixture was cooled to room temperature and poured over crushed ice,filtered out and crystallized in ethanol as a solid with maximum yield and appropriate melting point.



Ph' :- C_6H_5 [I_a– I_e], C_6H_4N [I_f – I_j]

Ph :- C_6H_4Br[I_a], $C_6H_4NO_2$ [I_b,I_g], C_6H_5[I_c], C_6H_4Cl [I_d], $C_6H_3Cl_2$[I_e,I_h], C_6H_4Cl [I_f], C_6H_5O[I_i], C_7H_7O[I_j]

4.2. Preparation of 4-(4-bromobenzene)-6-dihydro-2-phenylpyrimid-5-one (I_a) :- (Ph' – C_6H_5 and Ph - C_6H_4Br):A mixture of benzamide(0.01M), 4-bromobenzaldehyde (0.015M), and glycine(0.01M) in presence of $FeCl_3$ as acatalyst irradiated in microwave on medium power for 1 minutes. After completion, reaction mixture was cooled to room temperature and poured on crushed ice, filtered out and crystalized in ethanol as a solid with 76% yield and 250°C melting point. IR(KBr) (□$_{max}$ in cm^{-1}): 3285 (enolic O-H), 3087 (Aromatic C-H), 2966 (Aliphatic C-H), 1652 (C=O of keto form), 1545 (C=C), 1350 (Aromatic C-N), 1048 (C-1272 (C-N), 1048 (C-O), 799 (p-substituted group), 717-696 mono-substituted aromatic bending vibration; ^{1}H NMR 400 MHz, DMSO-d6 (∂ value in PPM) 2.5 (S, 2H, J 5.40), 7.2 (d, 2H, J 7.28), 7.5 (d, 2H, J 7.24), 7-7.5 (m, 5H, J 8.808), 8.9 (d, 1H, J 7.8); C^{13} NMR DMSO d6 (∂ value in PPM) 58.5 (C_4), 126.3 (C_{10},C_{16}), 127.3 (C_{13}),127.4 (C_8,C_{12},C_{14},C_{18}), 128.1 (C_7,C_{11},C_{15},C_{17})131.8 (C_2), 140.3(C_7), 165.3 (C_5). Elemental analysis:- 71.67% Carbon, 5.18% Hydrogen, 7.81% Nitrogen.

Similarly compound I_b–$I_e$have been prepared. Structure, melting point and percentage yield are reported in table.1

Table 1:

Sr.NO.	COMPOUND	% YIELD	MELTING POINT (^{0}C)	MOLECULAR FORMULA
I_a	4-(4-bromobenzene)-6-dihydro-2-phenylpyrimid-5-one	76.21	250^{0}C	$C_{12}N_2OBrH_{11}$
I_b	6-dihydro-4-(4-nitrobenzene)-2-phenyl-pyrimid-5-one	58.02	211^{0}C	$C_{16}N_3O_3H_{11}$
I_c	6-dihydro2,4-diphenylpyrimid-5-one	76.61	225^{0}C	$C_{16}N_2OH_{12}$
I_d	4-(4-chlorobenzene)-6-dihydro-2-phenylpyrimid-5-one	82.14	190^{0}C	$C_{16}N_2OClH_{11}$
I_e	4-(2,4-dichlorobenzene)-6-dihydro-2-phenylpyrimid-5-one	85.17	230^{0}C	$C_{16}N_2OCl_2H_{10}$

4.3. Preparation of 4-(2-chlorobenzene)-6-dihydro-2-pyridinepyrimid-5-one(I_f) (Ph' - C_5H_4N and Ph-C_6H_4Cl):A mixture of nicotinamide(0.01M), 2-chlorobenzaldehyde (0.015M), and glycine (0.01M) in presence of $FeCl_3$ as catalyst irradiated in microwave on medium power for 1 minutes.After completion , the reaction mixture was cooled to room temperature and poured over crushed ice, fltered out and crystalized in ethanol as a solid with 85.7% yield and 255^{o}C melting point**.** IR (KBr) (**ν_{max} value in cm^{-1}**): 3271 (Enolic O-H), 3058 (Aromatic C-H), 2976 (Aliphatic C-H), 1668 (C=C), 1316 (C-N), 1150 (C-O), 767-704(mono-substituted aromatic bending vibration); – ^{1}H NMR 400 MHz, DMSO-d6 (∂ value in PPM) 2.5 (S, C**H**2 of keto form), pyridine Ar-H 8.2 (d, 1H, J7.32), 8.7 (d, 1H, J2.8), 9.0 (S,1H), 9.3 (d, 1H, J6.4), 7.2-7.7 (m, Ar-H) ; ^{13}C NMR 100 MHz, DMSO-d6(∂ value in PPM) 57.20 (C_6), 123.2 (C_8,C_{12}), 126.9 (C_{16},C_{18}), 128.3 (C_{15},C_{17}), 129.30 (C_{14}), 129.39 (C_{13}), 129.57 (C_7), 129.65 (C_6), 135.37 (C_{11}), 136.11 (C_9), 148.7 (C_5), 151.96 (C_4), 164.49 (C_2). Elemental analysis:- 61.06% Carbon, 4.07% Hydrogen, 14.978% Nitrogen

Similarly compound I_g- I_j have been prepared. Structure, melting point and percentage yield are reported in table 2.

Table 2.

Sr.NO.	COMPOUND	% YIELD	MELTING POINT (^{0}C)	MOLECULAR FORMULA
I_f	4-(2-chlorobenzene)-6-dihydro-2-pyridinepyrimid-5-one	85.71	255^{0}C	$C_{15}N_3OClH_{10}$
I_g	.6-dihydro-4-(4-nitrobenzene)-2-pyridinepyrimid-5-one	74.82	221^{0}C	$C_{15}N_4O_3H_{10}$
I_h	4-(2,4dichlorobenzene)-6-dihydro-2-pyridinepyrimid-5-one	84.90	185^{0C}	$C_{15}N_3OCl_2H9$
I_i	6-dihydro-4-(2-hydroxybenzene)-2-pyridinepyrimid-5-one	71.69	295^{0C}	$C_{15}N_3O_2H_{11}$
I_j	6-dihydro-4-(4-methoxybenzene)-2-pyridinepyrimid-5-one	72.41	305^{0}C	$C_{16}N_3O_2H13$

CONCLUSION

The compound 2,4-di(substitutedphenyl)-6-dihydropyrimid-5-one (I_a-I_e) and 4-substitutedphenyl-6-dihydro-2-pyridinepyrimid-5-one (I_f-I_j) of high medicinal value have been synthesized with green protocol under microwave in maximum yield. Spectral data analysis supports the structure of synthesized compounds.

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ESTIMATION OF ANTIOXIDANT ACTIVITY OF HERBAL MEDICINES MADHU VATI AND PUNARNAVADI VATI

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ABSTRACT

Herbal medicines Madhu Vati and Punarnavadi Vati have been evaluated for antioxidant activity using stable free radical 1,1 diphenyl -2- picrylhydrazyl (DDPH). Optical density of the samples were recorded by U. V. Visible spectrophotometer and IC_{50} values have been determined. Both the drugs showed good antioxidant activities.

Keywords: *Madhu Vati, Punarnavadi Vati, Antioxidant activity.*

INTRODUCTION

Ayurveda is an ancient system of life (ayur) knowledge (veda) arising in India thousands of years ago. Ayurveda was first recorded in the Veda, the worlds oldest existing literature. It is a system of medicine with historical roots in the Indian subcontinent. Gobalized and modernized practices derived from Ayurveda are a type of complementary or alternative medicine. In india, Ayurveda therapies and practices have been integrated in general wellness applications. Herbal medicines Madhu vati and Punarnavadi vati are used as Aurvedic medicines for diabetes and vitality respectively.

Madhu Vati contains *Gymnema sylvestre* (Gudmar) which is known as "Destroyer Of Suger" in ancient time. *Gymnema sylvestra* have been used to treat diabetes mellitus in adults[1]. When leaf extract of plant, administered to a diabetic patient, there is stimulation of the pancreas by virtue of which there is an increase in insulin release. These compounds have also been found to increase fecal excretion of cholesterol [2,3]. *G. Sylvestre* is used in folk, Ayurvedic system to treat type 1 and 2 diabetes. It is also used in the treatment of urinary complaints, stomach problems, piles, chronic cough, breathing troubles, asthma, eye complaints, constipation, jaundice, and bronchitis [4,5,6]. It is also used by trials to treat to neutralize the toxin of snake bite [7]. *G. sylvestre* helps in weight loss possibly due to its ability to control blood sugar levels [8]. Punarnavadi vati contains *Boerhavia Diffusa* (Punarnava). It is used in herbal medicine for pain relief and for longevity with age stabilization and retaining youth for longer [9]. These two herbal medicines have been selected for screening of their antioxidant activities in present study.

Study of quantitative antioxidant activity by DPPH

The antioxidant activity of Madhu Vati and Punarnavadi Vati has been assessed for antioxidant activity on the basis of the radical scavenging effect of the stable 1, 1-diphenyl-2-picrylhydrazyl (DPPH). The diluted working solutions of Madhu Vati and Punarnavadi Vati were prepared in water. A solution of 0.004% of DPPH was prepared in ethyl alcohol and 1 ml of this solution was mixed with 1 ml of solution of the Madhu Vati and Punarnavadi Vati separately. This solution mixtures was kept in dark for 30 min and optical density was measured at 517 nm using UV visible spectrophotometer. A mixture of solvent (pure 1 ml) and DPPH solution (0.004%, 1 ml) was used as blank. The optical density was recorded and % inhibition was calculated using the formula given below

Percent inhibition of DPPH

$$(\%AA) = \frac{A - B}{A} \times 100$$

A - O.D. of Blank
B - O.D of sample

RESULTS AND DISCUSSION

Sample preparation: Ten different solutions of each Madhu Vati and Punarnavadi Vati were prepared having different concentration. 1ml of each of this solution was mixed with 1ml of 0.004% DPPH solution and resulting solution was used as sample. Optical density of the sample was recorded by U. V. Visible spectrophotometer and the results obtained are reported in following tables. IC_{50} values have been determined.

Table: 1.1 Otical density and percent antioxidant activity of Punarnavadi Vati

OD of blank DPPH = 0. 570

Concentration mg/ml	1	1.1	1.15	1.25	1.35	1.5	1.7	1.9	1.11
OD	0.536	0.531	0.53	0.529	0.522	0.52	0.516	0.51	0.507
%AA	6.3	7.3	7.5	7.7	9.1	9.6	10.4	10.52	11.05

IC_{50} value = 1.28 mg/ml

Table: 1.2 Optical density and percent antioxidant activity of Madhu Vati

OD of blank DPPH = 0. 570

Concentration mg/ml	1	1.5	2	2.5	3	3.5	4	4.5	5
OD	0.507	0.503	0.501	0.489	0.48	0.476	0.471	0.467	0.453
%AA	11.05	11.75	12.1	14.21	15.78	16.4	17.3	18.07	20.52

IC_{50} value = 3.0 mg/ml

CONCLUSION

Both the herbal medicines Punarnavadi vati and Madu vati showed decrease in OD of DPPH solution indicating free radical scavenging activity.

Percent antioxidant activity increases with concentration in both medicines. IC_{50} value for Punarnavadi vati and Madu vati is found to be 1.28 mg/ml and 3.0 mg/ml respectively.

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SYNTHESIS AND CHARACTERIZATION OF MODIFIED POLYPYRROLE AND TIO_2 DOPED POLYPYRROLE THIN FILMS BY CHEMICAL BATH DEPOSITION

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ABSTRACT

The modified electroluminiscent polypyrrole thin films were deposited by chemical bath deposition technique on precleaned glass substrate by using monomer pyrrole and ammonium persulphate as an oxidant in a ratio of 1:1 with constant stirring at room temperature. The TiO_2 doped polypyrrole thin film was synthesized by using same method. During the polymerization process 1% w/v of TiO_2 was added to the solution. The effect of dopant TiO_2 on the properties of thin films were investigated. The modified undoped and TiO_2 doped polypyrrole thin films were characterized. Chemical composition is investigated by FTIR spectroscopy. Surface morphology of undoped and TiO_2 doped thin films were investigated by SEM, TEM. Thermal properties were investigated by TGA-DTA. Mass spectroscopy is studied. Electrical conductivity by four probe. Finally this study demonstrate that the conducting polymer composite thin film was successfully synthesized. The modification of polypyrrole by doping gives material high thermal stability, modified morphology enables one to avoid the low ability of polypyrrole to processing and to extend the possibilities for the development of new technical devices.

Keywords: *Polypyrrole, TiO_2, Chemical Bath Deposition, SEM, TEM, Electrical Conductivity.*

INTRODUCTION

In the polymer science, the conducting polymers have been studied extensively during the last two decades as an important semiconductor material because of their interesting chemical and physical properties [1-3]. Dopants plays an important role in conjugated polymers because these polymers become conductive when charge carriers generated by dopants are present in their structure [4].

There are lots of conjugated polymers and one of the most widely studied conjugated polymers is polypyrrole, which becomes highly conducive upon doping [5,6]. In polyheterocyclic particularly polypyrrole is one of the extensively studied electronic materials, because it exhibits relatively high electrical conductivity, good environmental stability, low toxicity and versatility of synthesis and ease of tailoring [7] to synthesize functionalized polypyrrole. The properties of polypyrrole are very sensitive to fabrication condition and to the type of preparation technique used. Therefore, study of properties of these conducting polymers with respect to different growing as well as ambient conditions is of high importance. Stability of polypyrrole in air comes from its lower oxidation potential this polypyrrole thin films have been studied by many workers, because of their special electrical properties, considerable thermal stability and oxidation resistance [8].

It has also shown that composite material always has advantages over homogeneous material. Study of polypyrrole has identified over last two decades. It has been found that much of relevant work was carried out in recent year. Many researchers have doped polypyrrole or its derivatives using $LiBF_4$, $NaAsF_6$, $NaPF_6$, Bu_4NClO_4, Et_4NBF_4, Et_4NBF_6 and iodine, LaCl.

Few researchers reported doping of derivatives of polypyrrole by using APS (Ammonium Persulphate) as an oxidant. An optical and electrical properties of polypyrrole are useful for various device applications such as in electronic and electrochromic devices. Light weight batteries, sensors, chromatographic sensory phases [9], microactuators, biosensors [10, 11], electronic windows and displays, antielectrostatic coating [12], electronic devices, packaging and functional membrane [13], optical switching devices, solid electronic capacitor [14, 15].

PPy based polymers can be used to load and release drugs delivery system [14] and biomolecules [15], biomaterials. Poloypyrrole have also been exploited in sensor applications [16].bThere are several routes for synthesis of polypyrrole thin films. The chemical bath deposition method for polypyrrole thin films is important, chemical bath deposition method (CBD) appears most suitable for integration in large scale fabrication process.

In the present research work, we used TiO_2 as a dopant. Present work covers the chemical synthesis of conducting polypyrrole and 1% w/v of TiO_2 doped thin films.

Structural investigation and characterization of the thin films were determined by using TGA-DTA, FTIR analysis, SEM and TEM techniques, Electrical Conductivity.

MATERIAL AND METHODOLOGY

Pyrrole (AR Grade Merk), Iron chloride (sd-fine), Methanol (CH_3OH), TiO_2 and Ammonium persulphate (APS) are used for the synthesis.

TGA-DTA:- Rigakku Thermos Plus EVO_2 instrument at GVISH, Amravati.

FTIR:- Bruker Germany Spectrophotometer at SAIF, Chandigarh.

SEM:- JSM-6380 instrument, VNIT College, Nagpur, SAIF Chandigarh.

TEM:- Chandigarh.

Electrical Conductivity:- At GVISH, Amravati.

EXPERIMENTAL

Synthesis of polypyrrole by chemical bath deposition method

Initially, substrate were washed with deionized water, boiled in chromic acid and washed with detergent, rinsed in acetone and finally ultrasonically cleaned with deionized water before deposition of thin film.

Chemical polymerization can be carried out by mixing monomer and oxidant in a suitable solvent. In this chemical polymerization technique, ammonium peroxydisulphate ($(NH_4)S_2O_8$) is used as oxidizing agent. The oxidant and monomer ratio is taken as 1:1.

The aqueous solution of 0.1 M ammonium peroxydisulphate was prepared. To this solution, 1% w/v of TiO_2 is added. To this solution with a vigorous stirring on magnetic stirrer at 4°C drop by drop 0.1 M solution of monomer pyrrole was added. It was observed that as soon as monomer solution was added, the colour of reaction mixture changes instantaneously and the solution becomes dark green/black in colour. The reaction was carried out at 4°C. There was an increase in temperature of solution during the reaction; this was an indication of exothermic reaction. The reaction was stirred for few hours on magnetic stirrer which gives rise to formation of precipitate of polymer PPy. This reaction mixture was allowed to stand for 24 hours in order to complete polymerization process. The resulting product was vacuum filtered. The precipitate was clear. The polymer composite was dried in dessicator and again dried in an oven at 40-50°C. The precipitate was calcinated at 60°C for 1 hour and grinded to obtained polypyrrole powder.

RESULTS AND DISCUSSION

TG/DTA ANALYSIS

Thermogravimetric and differential thermal analysis of polypyrrole and 1% w/v of TiO_2 composite was carried out in air atmosphere. TGA was performed on Rigaku EVO_2 thermal analyzer with platinum pan in the temperature range room temperature to 555°C. The thermogram of polypyrrole and TiO_2 doped polypyrrole composite is as shown in Fig. 1 and Fig. 2.

Three major weight losses are observed, one around 200-280°C. The weight loss is about 1-3% due to elimination of moisture, evaporation of solvent as well as unreacted monomer. Second weight loss around 280-300°C is due to loss of dopant component of polypyrrole. Third major drop in weight is observed at 350-400°C and beyond the range is due to degradation of polypyrrole itself. In case of DTA, shows exothermic maxima at near about 400-450°C and onwards.

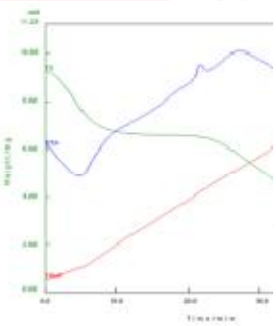

Fig. 1: TG-DTA thermogram of undoped polypyrrole.

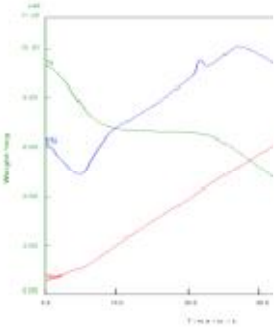

Fig. 2 : TG-DTA thermogram of 1% w/v TiO_2 doped polypyrrole composite.

FTIR INVESTIGATION

FTIR spectroscopy is an important investigation of polymer structure that provides information about the complexation and interactions between the various constituents in the polymeric films. Each type of bond has a different natural frequency of vibration, so the identification of an absorption peak in the vibration portion of the infra-red region will give a specific type of bonding. The IR studies of undoped polypyrrrole and TiO_2 doped polypyrrole composites synthesized in present research work are determined by Bruker Germany Spectrometer in the range of 450-4000 cm^{-1} at SAIF, Chandigarh.

The FTIR spectra for pure polypyrrole and TiO_2 doped polypyrrole composites are shown below.

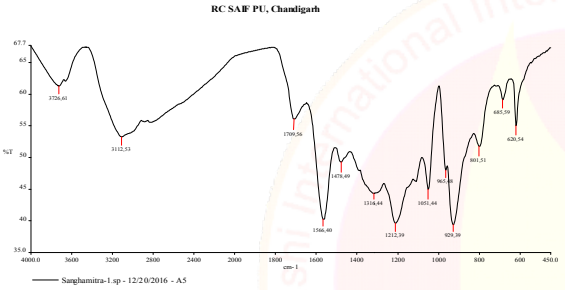

Fig. 3 : FTIR of undoped polypyrrole.

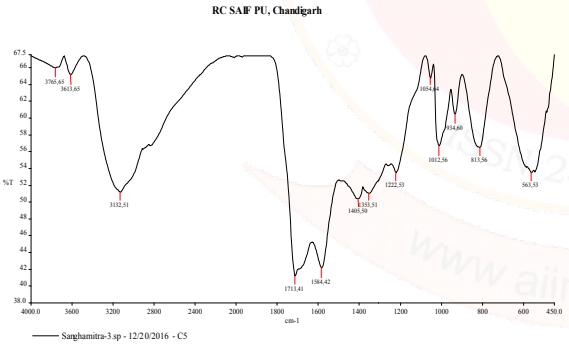

Fig. 4: FTIR of 1% w/v TiO_2 doped polypyrrole composite.

SEM Studies

The SEM images of pure polypyrrole and TiO_2 doped polypyrrole composites thin films are shown in Fig. 5 and Fig. 6, SEM images are obtained from JSM-6380 instrument at VNIT, Nagpur. The images seems to be uniform microporous. The nanometer scale particles are seen. Nanoparticles agglomerated grain structure is observed and are of irregular shape but are well interconnected each other.

SEM image of TiO_2 doped polypyrrole at high resolution seems to have more dense particles. It may be due to successfully doping of TiO_2.

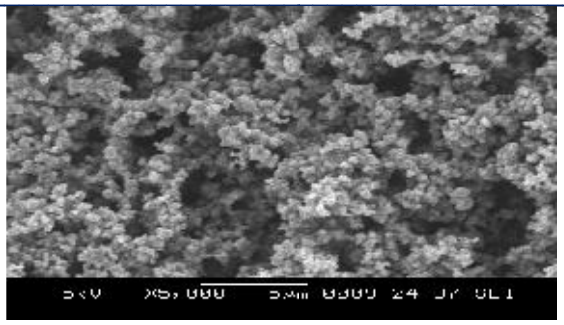

Fig. 5 : SEM image of undoped polypyrrole

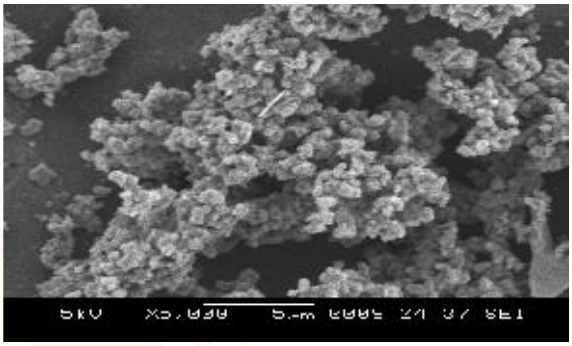

Fig. 6 : SEM image of 1% w/v TiO_2 doped polypyrrole

TEM Studies

TEM images of pure i.e. undoped polypyrrole and TiO_2 doped polypyrrole composite thin films are shown in Fig. 7 and Fig. 8. TEM images are obtained from SAIF, Chandigarh. TEM images of pure polypyrrole shows amorphous in nature while TiO_2 doped polypyrrole shows well developed crystalline structure.

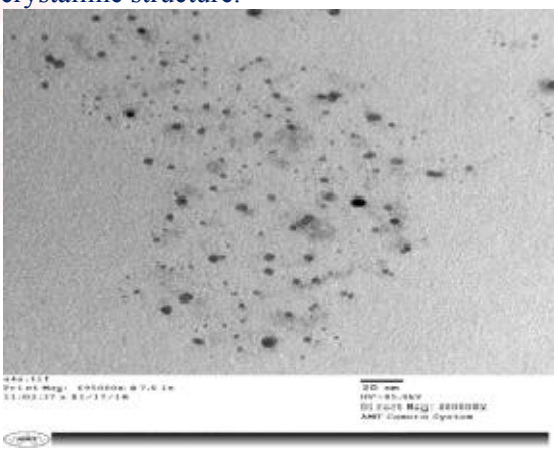

Fig. 7 : TEM image of undoped polypyrrole

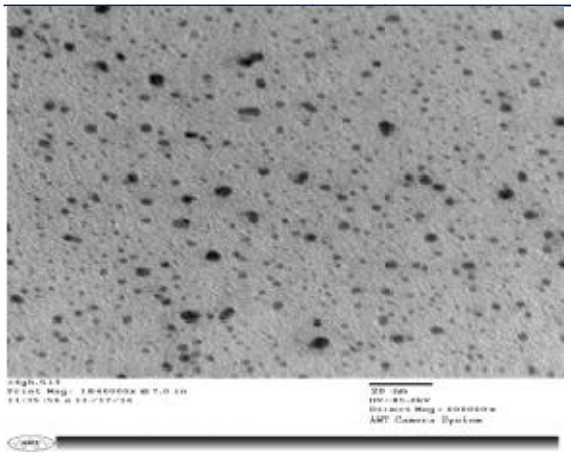

Fig. 8 : TEM image of 1% w/v TiO_2 doped polypyrrole

Electrical Conductivity

The DC conductivity of the synthesized PPy and PPy composite materials was measured by four probe method at constant current with change in temperature, variation of voltage was determined between the temperature range of 35 to 100°C (308 to 373 K). It is observed that the resistance depends upon composition as well as the temperature of the material.

Table 1 : Conductivity and activation energy of PPy/TiO_2 composite

S.N.	Polymer composite	Conductivity at 341°K	Activation Energy (eV)
1.	Undoped PPy	-0.292	12.585 x 10^{21}
2.	PPy+1% w/v TiO_2	-0.236	10.964 x 10^{21}

The temperature dependence of conductivity for polypyrrole and PPy/TiO_2 composites are shown in Fig. 9 and Fig. 10.

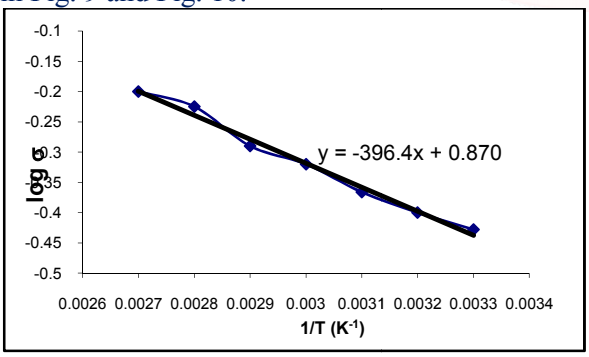

Fig. 9 : Variation of log σ verses 1/T for polypyrrole

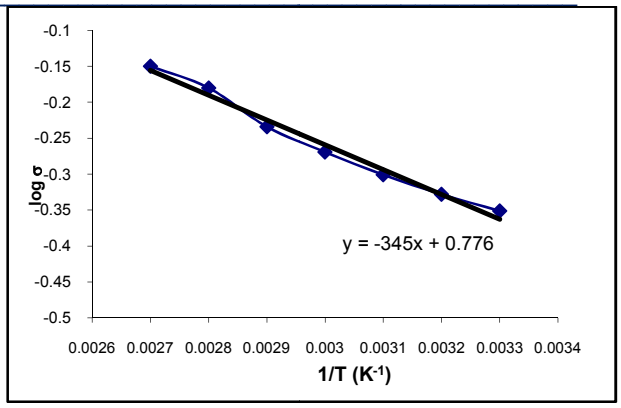

Fig. 10: Variation of log σ verses 1/T for 1% w/v TiO_2 composite

The plot shows linear behaviour. This plot is Arrhenius in nature. The value of conductivity suggests that the composite material synthesized are conductive.

CONCLUSION

We have demonstrated successful synthesis of nanostructure polypyrrole and polypyrrole/Mn composite thin film by chemical bath deposition technique.

The result of FTIR proved the formation of polypyrrole morphology of thin films were analysed by SEM. It shows change in morphology after doping. TEM shows modification from amorphous to the well developed crystalline structure. Thermal properties of nanocomposites were investigated by TG-DTA analysis shows composites of polypyrrole are found to be thermally more stable than pure polypyrrole. From DC conductivity measurements it is observed that conductivity increases with the increasing temperature in PPy and thereafter continuously increases after doping TiO_2.

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AUTHOR'S CONTRIBUTIONS

Authors Sanghamitra J. Dhande designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript.

Authors Dr. V.M. Raut and R.S. Futane managed the analysis of the study. All authors read and approved the final manuscript.

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ANTIMICROBIAL STUDIES OF METAL COMPLEXES WITH TETRADENTATE SCHIFF BASE HAVING N_2O_2 DONOR GROUP

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ABSTRACT

The newly synthesized Schiff base have been prepared by condensation of 2-hydroxy-5-bromo acetophenone with ethylene diamine. The synthesized Tetradentate Schiff base metal complexes are Co (II), Ni (II), Cu (II), Cr (III), Mn (III), Fe (III) VO (IV), Zr (IV) and UO_2 (VI). The Schiff base metal complexes have been characterized on the basis of elemental analysis, infrared, molar conductance and magnetic susceptibilities. The antimicrobial activites of the ligands and their complexes have been examined against the growth of bacteria to assess their antimicrobial potential.

Keywords: *Tetradentate Schiff base, Spectra, Molar conductance, Antimicrobial*

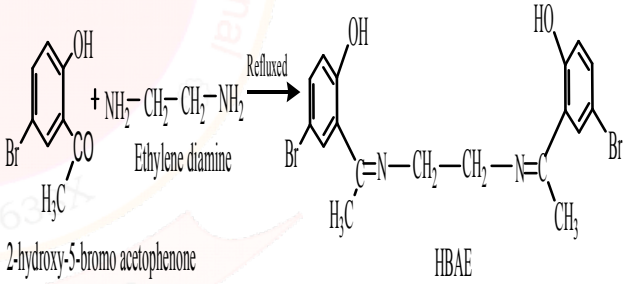
INTRODUCTION

The Schiff bases play a significant role in the area of coordination chemistry. The Schiff base prepared by using variety of aldehydes and amines or any other amines possessed antitubercular, antitumer, anticancer, fungicidal medicinal and agrochemical activities. Schiff base and their metal complexes are becoming increasingly important in recent years due to their biological activity and their used as catalysts photoluminescent, electroluminescent properties Antimicrobial screening, biological great significance of Schiff base metal complexes research. Schiff bases and their complexes have a variety of applications in biological clinical and analytical fields Recently there has been a considerable interest in the chemistry of hydrazine and hydrazone compounds because of their potential pharmacological applications[1,2].This paper discusses the molar conductance, magnetic susceptibilities and biological activity for Schiff base complexes of Co (II), Ni (II), Cu (II), Cr (III), Mn (III), Fe (III) VO (IV), Zr (IV) and UO_2 (VI).

EXPERIMENTAL

All the chemicals were of A.R. grade and used as received ethylene diamine and 2-hydroxy-5-bromo acetophenone (HBA) was prepared by known methods[3]. The solvents were purified by standard methods[4].

Synthesis of 2-Hydroxy-5-bromoacetophenone-N,N'-ethylenediimine (HBAE):
A hot ethanolic solution of ethylene diamine (0.05 mol) was added to an ethanolic solution of respective acetophenone (0.05 mol). The reaction mixture was refluxed in a water-bath for 4-5 h. The colour product was filtered off and recrystallised. Yield 70%. M. P. 270^{0}C



Preparation of complexes:
All the metal complexes were prepared in a similar way by following method. To a hot solution of ligand HBAT (0.02M) in 25ml of ethanol a suspension of respective metal salts was added drop wise with constant stirring. The reaction mixture was refluxed on a water bath for 4-6 h. The precipitated complexes were filtered, washed with ethanol followed by ether and dried over fused calcium chloride. Yield : 45-50%

Table 1. Analytical data and molar conductance of the compounds.

Compounds	Colour	Mol.wt.	Analysis % Found (calc.)					μ_{eff} B.M.	Λ_M (Ω^{-1} cm^2 mol^{-1})
			M	C	H	N	Cl		
$C_{18}H_{18}N_2O_2Br_2$	Yellow	453.8	--	47.83 (47.59)	3.85 (3.96)	6.07 (6.17)	--	--	--
$[CoL(H_2O)_2]$ H_2O	Brown	564.7	10.32 (10.43)	38.12 (38.25)	3.72 (3.89)	4.80 (4.95)	--	4.27	6.1
$[NiL]$ H_2O	Black	528.5	11.02 (11.10)	40.72 (40.87)	3.25 (3.40)	5.17 (5.29)	--	Dia	5.6
$[CuL(H_2O)_2]$ $2H_2O$	Brown	587.3	10.61 (10.81)	36.61 (36.77)	3.95 (4.08)	4.62 (4.76)	--	2.02	18.8
$[CrL(H_2O)Cl]$ $2H_2O$	Yellow	593.3	8.66 (8.76)	36.22 (36.40)	3.52 (3.70)	4.58 (4.71)	5.77 (5.98)	3.86	21.2
$[MnL(OAc)]$ $2H_2O$	Brown	601.7	9.02 (9.12)	39.78 (39.88)	3.62 (3.82)	4.53 (4.65)	--	5.6	12.8
$[FeL(H_2O)Cl]$ H_2O	Green	579.2	9.58 (9.65)	37.13 (37.29)	3.32 (3.45)	4.72 (4.83)	6.02 (6.12)	6.0	18.8
[VOL]	Green	518.8	9.41 (9.83)	41.12 (41.63)	3.01 (3.08)	5.09 (5.39)	--	1.78	14.5
$[ZrL(OH)_2]$ $2H_2O$	Yellow	613.0	14.72 (14.87)	35.08 (35.23)	3.47 (3.58)	4.38 (4.56)	--	Dia	31.9
$[UO_2L]$	Orange	721.9	32.87 (32.98)	29.82 (29.92)	2.08 (2.21)	3.75 (3.87)	--	Dia	23.6

The complexes are soluble in DMSO and DMF but insoluble in water and common organic solvents. The metal chloride content of complexes were analyzed by standard methods.

The ^1H NMR spectra of ligand was recorded and obtained from RSIC Chandigarh. IR spectra of the compounds were recorded on Perkin Elmer 842 spectrophotometer in the region 400-4000cm^{-1}, Carbon, Hydrogen and Nitrogen analysis were carried out at RSIC, Punjab University, Chandigarh. The molar conductance of the complexes at 10^{-3} M dilution in DMF were determined using equiptronic digital conductivity meter EQ-660 with a cell constant 1.00 cm^{-1} at room temperature. The magnetic moment measurement were made on a Gouy balance at room temperature using $[HgCo(SCN)_4]$ as the calibrant. The thermogravimetric analysis were performed on laboratory set up apparatus in air atmosphere at 10^0C min^{-1} heating rate. The molecular weights of the complexes were determined by Rast method.

RESULT AND DISCUSSION

The Schiff base ligand HBAE and its complexes have been characterized on the basis of ^1H NMR, IR spectral data, elemental analysis, molar conductance and magnetic susceptibility. All these values and analytical data are consistent with proposed molecular formula of ligand. All the compounds are coloured solid and stable in air. They are insoluble in water but soluble in coordinating solvents like DMF and DMSO. The molar conductance values in DMF (10^{-3} M) solution at room temperature (Table 1) shows all the complexes are non electrolytes.

The ^1H NMR spectra of ligand HBAE shows signals: □15.97 (1H, s, phenolic OH); 8.06 (1H, s, phenyl); 7.67 and 7.31(2H, m, phenyl), 3.29(4H, s, CH_2CH_2); 2.51 ppm (3H, s, methyl)[5-11]

Table 2. IR spectra of ligand and metal complexes.

Compound	□(OH) hydrogen bonded	□(C=N) imine	□(CO) phenolic	□(MO)	□(MN)	□□□
$C_{18}H_{18}N_2O_2Br_2$	2900	1614	1480	--	--	----------
$[CoL(H_2O)_2]$ H_2O	--	1589	1440	520	455	3400, 1640, 815, 770
$[NiL]$ H_2O	--	1586	1460	510	495	3326, 1630
$[CuL(H_2O)_2]$ $2H_2O$	--	1595	1440	590	490	3406, 1642, 818, 780
$[CrL(H_2O)Cl]$ $2H_2O$	--	1600	1436	570	460	3390, 1635, 830, 745
$[MnL(OAc)]$ $2H_2O$	--	1590	1446	580	495	3330, 1628
$[FeL(H_2O)Cl]$ H_2O	--	1602	1463	530	425	3395, 1638, 845, 740
[VOL]	--	1600	1455	525	480	----------
$[ZrL(OH)_2]$ $2H_2O$	--	1601	1440	565	460	3335, 1628
$[UO_2L]$	--	1590	1420	560	470	----------

ANTIMICROBIAL ACTIVITY:

The ligand HBAE and its complexes[12-18] are found to show considerable bacteriocidal activity against *E. coli, A. aerogenes, S. aureus* and *B. subtilis* and are almost inactive against *B. megatherium, P. vulgaris* and *P. fluorescen*. The ligand inhibits the growth of *S. aureus* more than all its complexes. In contrast, bacteriostatic nature of the ligand is dominated by its complexes against *S. aureus*. All the complexes show moderate to good zone of inhibition against *S. aureus*. The

Cu(II) and Fe(III) complexes are resistant towards *E. coli, B. subtilis, B. megatherium* and *P. fluorescen* but shows moderate activity towards

other bacterial species. The Co(II) and Zr(IV) complexes strongly inhibits the growth of *B. subtilis* and has no activity against *E. coli*. The ligand Cr(III), Mn(III), VO(IV) complexes show considerable activity against *E. coli* and *B. subtilis* and almost inactive towards *P. vulgaris* and *P. fluorescen*. The UO_2(VI) complex exhibits moderate activity against *E. coli, A. aerogenes, S. aureus, B. megatherium* and is almost resistant towards the other bacteria. The results reveals that the sensitivity of the ligand HBAE and its complexes is shows in (Table 3)

Table 3. Antimicrobial activity

Ligand and its complexes	*B. subtilis* (mm)	*P. vulgaris* (mm)	*S. aureus* (mm)	*E. coli* (mm)	*P. fluorescen* (mm)	*A. aerogenes* (mm)	*B. megatherium* (mm)
HBAE	S_8	R	S_{14}	S_{13}	R	R	R
Co- HBAE	S_{15}	S_7	S_{18}	R	S_{16}	R	S_{11}
Ni- HBAE	S_{11}	S_{13}	S_{10}	R	S_{17}	S_{16}	R
Cu- HBAE	R	S_{17}	S_{12}	R	R	S_{11}	R
Cr- HBAE	S_{13}	R	S_{11}	S_{14}	R	S_{12}	R
Mn- HBAE	S_{13}	R	S_{15}	S_9	R	S_8	S_9
Fe- HBAE	R	S_9	S_{14}	R	R	S_{13}	R
VO- HBAE	S_{11}	R	S_{13}	S_9	R	S_{18}	S_9
Zr- HBAE	S_{15}	R	S_{14}	R	R	S_9	R
UO_2- HBAE	R	R	S_{14}	S_{12}	R	S_{12}	S_8

CONCLUSION

The zone of inhibition of ligand varies with organisms as well as metal ions. Thus, it can be concluded that most of our ligands and their complexes possess antimicrobial activities.

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TO STUDY STABILITY CONSTANTS OF COMPLEXES OF DL-ALANYL-DL-ALANINE AND DL-ALANYL-DL-PHENYLALANINE

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ABSTRACT

Peptides of amino acid act as ligands. Protein chemistry is associated with various peptides and consequently amino acids. Various chelates of metal ions like Al(III), Cr(III), Fe(III), Pt(IV) etc. with various chalcones and amino acids were studied for their stability determination. DL-Alanyl-DL-Alanine and DL-Alanyl-DL-Phenylalanine can act as ligand, differing in aromatic phenyl group. Hence in present study it was decided to study effect of this aromatic phenyl group on the stability of complex.
The metal-ligand stability constants of transition metal ions like Cu(II) and Co(II) complexes with peptide; DL- Alanyl-DL- Alanine (L1) and DL-Alanyl-DL-Phenylalanine (L2) at 0.01M ionic strength were studied potentiometrically. The stability was studied from □ (ligand number) values and logK values. It is concluded from results that there is reduction in pK- values for the ligand, Dl-Alanyl-DL-Phenylalanine, which is due to presence of benzene ring which acts as an electron sink.

Keywords: *Complex,Peptides, Stability constant, pH etc.*

INTRODUCTION:

Living cells require thousands of proteins; which are most complex substances known to man. The chemistry of proteins was one of the great chalanges in modern science, since the centuries.
The amino acids are formed by hydrolysis of protein and a certain structural features in common. Each has an acidic carbonyl group (-COOH) and a basic amino group (-NH_2) or imino group (-NH-). Both acidic and basic group are attached to the same carbon atom, called α-carbon. This carbon atom has two other units linked; one is invariably H-atom. In 1820, French chemist, Henry Braconnot isolated the simplest amino acid, glycine. In every protein, amino acid, except glycine can exist in two geometrical forms, L and D, mirror images of each other.
Rossotti and Rossotti have defined a complex as a species formed by the association of two or more simple species, each capable of independent existence, when one of the simple species is a metal ion, the resultant entity is known as 'metal complex'. Some ligands are attached to metal atom by more than one donar atom in such a manner as to form heterocyclic ring, known as Chelation.
The stability of transition metal amino acid complexes in solution has been extensively studied. The thermodynamic stability constants of a species are measures of the extent to which this species will be formed from or be transferred into other species under certain condition s which the system has reached equilibrium. The kinetic stability of species refers to the speed with which transformation leads to the attainment of equilibrium. The complex formation is favoured by negative enthalpy and positive entropy changes. The metal ligand complex formation may be considered due to the displacement of proton from the ligand, causing a change in pH-value of solution. Irving and Rossotti have given a method for calculation of stability constant of complexes by potentiometry.

MATERIALS AND METHOD:

Irving and Rossotti made use of the potentiomtric technique first used by Calvin and Melchior and now generally known as Calvin- Bjerrum titration technique. The method of Irving and Rossotti has been employed in this present investigation.
In method solutions of nitrates of Cu(II) and Co(II) in distilled water, solution of KNO_3 in distilled water, 0.01M solution of HNO_3 in distilled water as free acid, solution of NaOH in water, solution of peptide; DL-Alanyl-DL-Alanine(L1) and DL-Alanyl-Dl-Phenylalanine (L2) in water were used. pH-meter (ELICO- model) with glass-electrode and a saturated calomel electrode was used. For the calibration of pH-meter the standard buffer solutions of pH 4.01, 7.00 and 9.15 were used. Following equations 1 and 2 were used to calculate $\tilde{n}_A$and $\tilde{n}$.

$$\tilde{n}_A = \frac{(V_2-V_1)(N+E^0)}{(\text{ligand no.})\ (V_0+V_1)\ x\ T^0_L} \quad \text{---------- 1}$$

$$\tilde{n} = \frac{(V_3-V_2)(N+E^0)}{(V_0+V_2)\ x\ T^0_L\ x\ \tilde{n}_A} \quad \text{---------- 2}$$

The data obtained for volume of NaOH required for titration of systems with Cu(II) and Co(II) metal ions separately with DL-Alanyl-DL-Alanine (L1) and DL-Alanyl-DL-Phenylalanine (L2) ligands was noted.

RESULT AND DISCUSSION:

Proton – ligand stability constants of the ligand were calculated from acid titration curve and acid+ ligand titration curve. The deviation in the curves for both the systems started at about pH 3.0. These deviations increased continuously upto pH 11.0. This may be due to fact of dissociation of functional groups (-COOH and $-NH_3^+$) of ligands.

The values of $\tilde{n}_A$along with the differences (V_2-V_1) were determined. The formation curve,fig1 ($\tilde{n}_A$vs pH) was plotted and from it pK_1(4.5 for L1 and 3.45 for L2) corresponding to $\tilde{n}_A = 1.5$ and pK_2 (10.2 for L1 and 4.62 for L2) corresponding to $\tilde{n}_A = 0.5$ for were estimated. This is called half integral method.

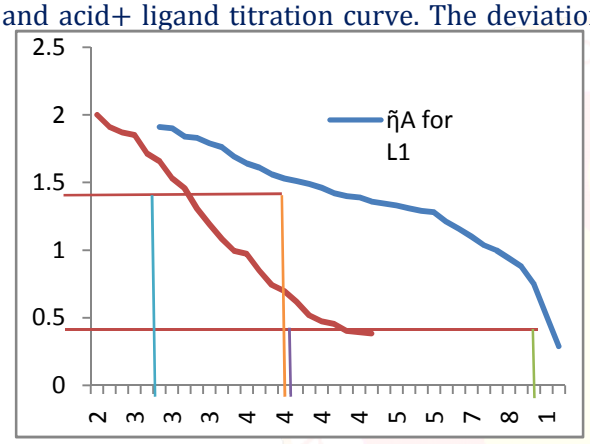


Fig 1 : Plot ofpH vs $\tilde{n}_A$for L1 and L2 ligands.

The formation of chelate of DL-Alanyl-DL-Alanine with Cu(II) and Ni(II) is indicated by –
i) The significant departure starting at pH 2.75 of metal complex titration curve from the ligand curve and
ii) The change in colour from colourless to blue at about pH 5.0 for Cu(II) and from colourless to reddish orange at pH 4.8 for Co(II).

The formation constant ñwas calculated using equation 2. The values of ñwere plotted against pH, fig2 and fig3, to construct formation curve for metal – ligand complexes.

The stability constants were calculated by half integral method.

Log K_1 (9.9447) at ñ= 0.5 logK_2 (8.6958) at ñ= 1.5 for Cu(II) – L1 Log K_1 (9.7847) at ñ= 0.5 logK_2 (7.3959) at ñ= 1.5 for Co(II) – L1
Log K_1 (3.6444) at ñ= 0.5 logK_2 (2.9594) at ñ= 1.5 for Cu(II) – L2 Log K_1 (3.9960) at ñ= 0.5 logK_2 (3.1480) at ñ= 1.5 for Co(II) – L2

Thus it is concluded that complex of Cu(II) is more stable than Co(II) andthere is reduction in pK- values for the ligand, Dl-Alanyl-DL-Phenylalanine, which is due to presence of benzene ring which acts as an electron sink.

Fig 2: Plot of ñ values Vs pH (Formation curve)

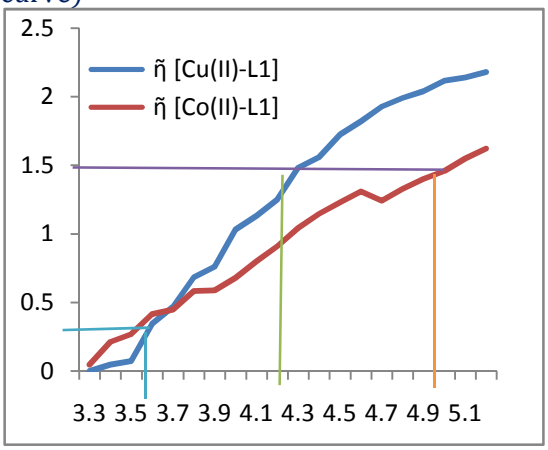
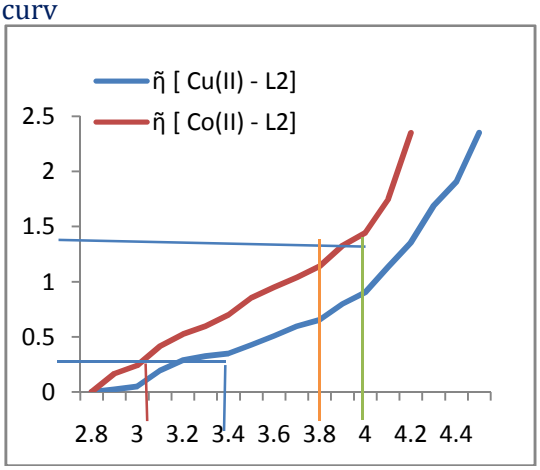


Fig 3: Plot of ñ values Vs pH (Formation curv



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ADSORPTION STUDIES ON WATER HARDNESS REMOVAL BY USING *LIMONIA* ACIDISSIMA *(*KAVATH) SHELL ACTIVATED CARBON AS AN ADSORBENT.

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ABSTRACT

Limonia acidissima(Kavath) Shell Activated Carbon was utilized as an adsorbent to remove water hardness ions from hard water. The effect of pH, contact time, temperature, and adsorbent dosage were investigated using batch adsorption experiments. Characterization of adsorbent was identified by FT-IR and XRD techniques. The pH dependence study of the adsorption process revealed that maximum pH for hardness removal was 10 with efficiency of 96%. However, for the safety of softened water, preferable pH is 7 which yield 92% removal efficiency for water hardness removal respectively. Temperature study reveals that the adsorption is exothermic as efficiency decreases with the increase in temperature. Removal efficiency increases with the increase in contact time. The adsorption of hardness ions on Limonia acidissima(Kavath) shell activated carbon increased as adsorbent dosage increases from 1gm/50ml to 5gm/50ml . The study showed that adsorbent had the potential for hard water softening.

Keywords: *Activated carbon, adsorption, batch adsorption experiments, Limonia acidissima (Kavath) shell, water hardness removal.*

INTRODUCTION

Rapid urbanization, population growth, industrial expansion and waste generation from domestic and industrial sources have released wastewaters which are hazardous to man and other living organisms. Many industries discharge untreated or inadequately treated wastewater into water ways. As water of good quality is a necessary, it has become very important to treat wastewater for removal of pollutants. A number of technologies have been developed over the years to remove pollutants, organic matter, etc. from industrial wastewater. The most important technologies include biological treatment, physical treatment, and chemical treatment and these
Methods are generally expensive and require skilled personnel. Among all the treatment methods, adsorption is one of the more popular methods for the removal of pollutants, metal ions, or dyes from the wastewater. Adsorption process is one of the easiest, safest and more effective methods for metal removal from industrial effluents[1, 2] and this process is already established as a simple operation and an easy-handling process. Activated carbon is a commonly used adsorbent for the water and wastewater treatment. Previous research shows that there is growing interest of searching for a variety of materials as low cost adsorbents including cocoa shell[3], rice husk[4], modified sawdust of walnut[5], papaya wood[6], maize leaf[7], rice husk ash and neem bark[8], fly ash[9] and tea-industry waste[10]. Low cost and non-conventional adsorbents, including agricultural byproducts such as nut shells, wood, bone, peat processed into activated carbons and biomass have been reported to be important adsorbents for the removal of metals and organics from municipal and industrial wastewater. **A**mong the various known forms of water contaminants, Calcium and Magnesium salts are of great apprehension since they lead to water hardness. Water hardness problem is reported to exist in various parts of state, the reason behind is rock type, which is rich in Calcium and Magnesium. These ions dissolve easily in to the groundwater and make them hard. In daily uses, hard water is associated with number of challenges that include scaling in boilers, washing machines and pipes[11], difficult lathering with soap, objectionable spots on sinks and clothes as well as toughening of skin and hair. Hard water is said to cause serious health problems like urolithosis, cardiovascular disorder, kidney problems, anencephaly and cancer[12]. Additionally, WHO reports that excess intake of calcium is associated with kidney stones and that of magnesium leads to diarrhea and laxative effect due to change in bowel habit. Because of the challenges raised by hardness in water, immediate actions to soften water are to be expected. Water softening by adsorption using agricultural wastes based activated carbon as adsorbent seems to be potential in the sense that the agricultural wastes are locally and cheaply available.

Calcium and magnesium play vital roles in the structure and functions of the human body. High intake of calcium and magnesium in drinking water could result in symptoms of toxicity such as a kidney stones, gastric and breast cancer, low blood pressure, muscle weakness, confusion and abnormal cardiac rhythm[13]. Therefore, the need to purify water which is not suitable for human consumption such as hard water cannot be overemphasized. It is obvious that hard water treatment methods required high capital operations. Hence, finding cheap and effective developed processes remains a major concern. For the purpose of removing hardness ions from water, various adsorbent materials have been used such as Moringa oleifera[14], Peanut hull[15], pumice[16] and Phyllanthus emblica[17]. The equilibrium time required for the adsorption of Ca^{2+} is less compared to the time required for Mg^{2+} removal. The reason for that is likely to be due to the smaller hydrated radius of Ca^{2+} ions compared to that of Mg^{2+}ions which leads to Ca^{2+} ions to be adsorbed faster than Mg^{2+} ions[18], Similar finding observed when natural pumice stone used as adsorbent and found it is a better material for removing Ca ions than Mg ions from water[16].

MATERIALS AND METHOD

Limonia acidissima (Kavath)

It is the only species within the monotypic genus Limonia. It is found in the forest of Chandrapur and Gadchiroli district. Common names for the species in English include wood-apple and elephant-apple. It is a large tree growing to 9 metres (30 ft) tall, with rough, spiny bark. The fruit is a berry 5–9 cm diameter, and may be sweet or sour. It has a very hard shell which can be difficult to break, and contains sticky brown pulp and small white seeds. The fruit looks similar in appearance to the Bael fruit *(Aegle marmelos)*. . It is used by the people to make jam and jelly. Kavath shells are wastes that are mainly disposed off after extraction of their inner contents. These wastes can be converted into useful activated carbon which in turn can be used to treat water. Water Treatment by Kavath Shells Activated Carbon (KSAC) is not yet reported to be done.

Fig 1-Limonia acidissima (Kavath)

Preparation of Adsorbent - Limonia acidissima (Kavath) Fruits are collected from nearby forest, after extraction of their inner contents shells were washed to remove soil and other substances and then sun dried for 1-2 days to eliminate moisture. Fruit shells are broken into smaller pieces. . It was then packed in an air tight in a cylindrical container with top completely sealed to prevent the entry of air during the process of charring. The sealed container was heated in furnace for 2hr. The resultant charcoal obtained by above procedure was soaked in 2M KOH overnight. It was followed by washing with distilled water till the attainment of neutral pH, and then dried in the hot air oven at 80±5C temperature for 4 hrs to obtain activated carbon. The KOH saved as activating agent to introduce some functional groups and deepening micro pores.

Adsorbates - Synthetic hard water was prepared as reported by Window on State Government (1996) whereby 1.19g of CaCl2 and 1g of MgSO4 were dissolved in a litre of deionized water to make a water with hardness of 1214.8 mg/L as CaCO3 and this served as a stock solution[19].

Adsorbent Characterization - The adsorbent was characterized by FTIR analysis. In chemical activation, activating agent is expected to significantly affect the properties of substance. X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy analysis performed to determine the structural and surface properties.

Batch Experiments - Batch adsorption experiments were conducted to examine adsorption behavior of different adsorbent on different water hardness removal under different adsorption condition. Adsorption studies were carried in different conditions namely adsorbent dose, initial concentration, contact time, pH and temperature. The adsorption experiments were conducted in 250 ml conical flasks. In each experiment, a known amount of adsorbent was contacted with 50ml of desired contaminated water with known pH and at a regular interval of time of 1 hour. pH of the solution was measured using pH meter and adjusted using 0.1N HCl and 0.1 N NaOH. The solutions were filtered by using

Whattman filters and filtrates were collected for analysis.

RESULTS AND DISCUSSION CHARACTERIZATION OF ADSORBENT

The pH values of Kavath fruit shell charcoal was 6.60 while that of activated charcoal was 8.00. The value of charcoal was less than 7.0 (i.e. acidic) may be due to the presence of acidic groups on the surface. It was found that pH of charcoal increased on activation by KOH. The acidic or basic nature of a charcoal or activated charcoal depends on its preparation, inorganic matter and chemically active oxygen groups on its surface as well as the kind of treatment to which the activated carbon was subjected. The pH of the activated carbon affects the adsorptive property of the carbons, as highly acidic or basic carbons are undesirable for processing.

The FTIR technique is an important tool to identify the characteristic functional groups which are vital in adsorption of hardness ions. Fig.2 is FT-IR spectrum for Limonia acidissima(Kavath) Shell Activated Carbon . Adsorption at 1164.64 and 1115.10cm^{-1} might be due to the vibration of alkoxy group (C−O). Alkane (C−H) stretch is indicated by presence of band at 2906.79 cm-1. The sharp absorption band at 1370.68 cm-1 is ascribed to nitro group (N−O). The region of the spectrum of 1589.97 cm^{-1} is due to primary amine (N−H). A broad adsorption peak appeared at 3416.69cm^{-1} is corresponding to the stretching of O–H functional group. C-H deformation is noticed between 869.93 cm-1. Identified functional groups are likely to account for the adsorption of hardness ions onto the adsorbent surface, hence high efficiency in water softening.

X-ray diffraction pattern of the sample shows many peak, thereby indicating the crystalline nature of the adsorbent.

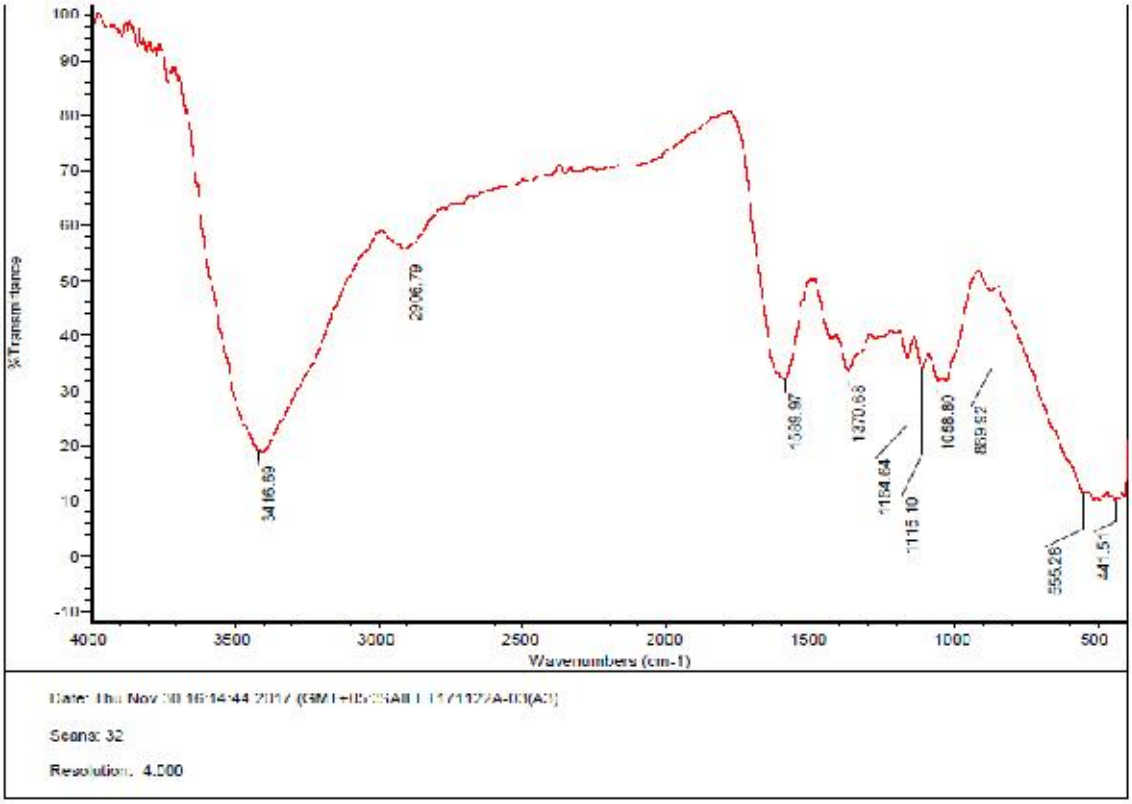

Fig-2 FTIR spectrum of KOH activated **Limonia acidissima(** Kavath) shell charcoal

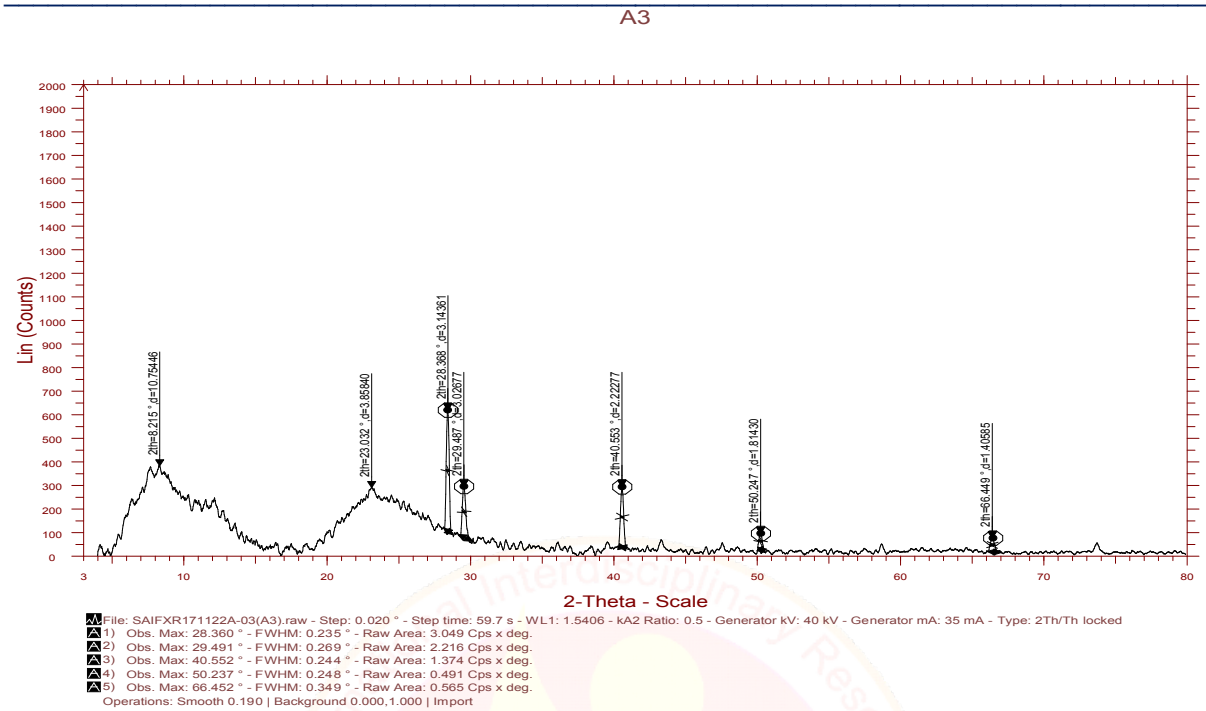

Fig-3 XRD of KOH activated **Limonia acidissima (**Kavath) shell charcoal

Effect of pH on Hardness Removal

Concentration = 820mg/l; Contact time = 60 min,
Adsorbent dose = 1gm/50ml, Temperature = 30°C.

pH	Residual conc. (mg/L)	Amount adsorbed(mg/L)	% Removal
2	344	476	58.04%
4	228	592	72.92%
6	200	620	75.61%
8	148	672	81.95%
10	32	788	96.10%

The removal of water hardness ions was strongly dependent on the pH of the solution. The pH of a solution is an important parameter in the adsorption process. The effect of pH on adsorption was studied by varying initial pH of water samples was from 2 to 10 and keeping all other parameters constant, results shows hardness removal efficiency is very high at all range of pH and there was an increase in efficiency from the pH from 2 to 10. This might be due to that, as pH increases the competition between hydroxonium ions, H_3O and positively charged metal ions on the surface of adsorbent decreases[20]. Highest removal efficiency was 96.10% that was achieved at the pH of 10. For the sake of providing safe water in an economical and safe way, it is important to consider softening efficiency at neutral pH. From the data, it was found that around neutral pH, efficiency was constant with the average removal efficiency of 78%

Effect of initial concentration on Hardness Removal

Contact time = 60min, pH = 7
Adsorbent dose = 1g/50ml, Temperature = 30°C

Initial concentration (mg/L)	Residual concentration (mg/L)	Amount adsorbed (mg/L)	% Removal
280(mg/L)	60	220	78.57%
375(mg/L)	65	310	82.66%
535(mg/L)	85	450	84.11%
825(mg/L)	225	600	72.73%
1150(mg/L)	550	600	52.17%

The effect of initial concentration on adsorption of hardness by Kavath shell activated charcoal was studied by varying the concentration shows that adsorption capacity was found to increase with initial concentration and reaches maximum 84.11% at 535mg/L, increase in the value may be due to the higher concentration difference reduces the mass transfer resistances between adsorbent and adsorption media. On further increase in concentration the percentage of adsorption was observed to decrease. This may be due to saturation of the surface and available active sites of the adsorbent.

Effect of Adsorbent dose on Hardness Removal

Concentration = 840mg/l; Contact time = 60 min,

Temperature = 30°C. pH = 7,

Adsorbent dose	Residual concentration (mg/L)	Amount adsorbed (mg/L)	% Removal
1gm	200	640	76.19%
2gm	100	740	88.09%
3gm	75	765	91.07%
4gm	70	770	91.66%
5gm	69	771	91.78%

Study of effect adsorbent dose on adsorption of hardness ions was indicated that removal efficiency for activated charcoal of kavath shell increases with increase in the adsorbent dose up to 3 gm/50 ml. After a this dose of adsorbent, may be the maximum adsorption is attained and hence the amount of ions remains constant even with further addition of dose of adsorbent. That's why beyond 3gm the adsorption found to be almost constant.

Effect of Temperature on Hardness Removal

Concentration = 675mg/l; pH = 7,
Adsorbent dose = 1g/50ml, Contact time = 1 hr,

Temperature (^{0}C)	Residual concentration (mg/L)	Amount adsorbed (mg/L	% Removal
30^{0}C	150	525	77.77%
40^{0}C	160	515	76.29%
50^{0}C	185	490	72.59%
60^{0}C	250	425	62.96%
70^{0}C	305	367	54.37%

Effect of temperature on adsorption of the hardness ions onto kavath shell activated charcoal shows decreases adsorption of hardness with increase in temperature this may be due to adsorption of Ca^{2+} andMg^{2+} ions on adsorbent surface is exothermic reaction.

Effect of Contact Time on Hardness Removal

Concentration = 900mg/l; pH = 7,
Adsorbent dose = 1g/50ml, Temperature = 30°C.

Contact time	Residual concentration (mg/L)	Amount adsorbed (mg/L)	% Removal
30min	275	625	69.44%
60min	190	710	78.88%
90min	175	725	80.55%
120min	160	740	82.22%
160min	150	750	83.33%

The effect of contact time was studied at 30^{o}C, at intervals of 30 min. Adsorption by activated Kavath shell charcoal initially increased with higher rate and then shows constantly and slowly increased with increase in contact time, This might be due to the fact that, large numbers of vacant surface sites are available for the adsorption during the initial stage. After some times, repulsive forces between solute molecules on solid phase and liquid phase may create difficultness for the solute molecules to occupy remaining vacant surface sites. Equilibrium time is not still reached up to 160min with activated charcoal.

CONCLUSION

Activated Carbon was prepared through pyrolysis followed by chemical activation with KOH and used as an adsorbent for removal of hardness. Removal of hardness (Ca^{2+} and Mg^{2+}) by Application of operational conditions such as contact time, adsorbent dose, pH and concentration of adsorbate led to increase of hardness removal while temperature shows decrease in hardness removal. Result clearly shows that adsorption of Ca^{2+} and Mg^{2+} on to activated materials was favored. The optimal dose was found to be 3gm and the maximum removal was seen within 160 minutes of contact time. Based on the results obtained in the present study, it is clear that it is effective in water softening. Since the Kavath shells are locally available, especially in forest regions of Chandrapur district where hardness problem is prevailing, then, this adsorbent is expected to be economically feasible for removal of hardness from groundwater. Materials we used are reported as an adsorbent very first time.

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INVESTIGATIVE STUDIES ON PHYSICO-CHEMICAL PARAMETERS FOR TESTING OF TAP, WELL AND BOREWELL WATER FROM DIFFERENT STATIONS OF KARANJA LAD DI- WASHIM

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ABSTRACT

The provision of potable water to the rural and urban population is necessary to prevent health hazards. Before water can be described as potable, it has to comply with certain physical, chemical and microbiological standards, which are designed to ensure that the water is safe for all living things. The Karanja Lad is situated about 70 km North-East of Washim city at latitude of 20^0-47'-99". The city lies on 77^0-48'-84" longitude. Source of water to Karanja city is tap, well and bore wells. Water temperature ranges from 20.2^0 to 30.3^0. pH water sample were observed in average range during the study period. The value of conductivity ranges from 292 to 344(µmhos/cm). Total dissolved solids ranges from 214 to 364. Sulphate ranges from 0.008 to 0.310 mg/l during study period. The values of nitrates range from 0.010 to 0.096 mg/l. Phosphorous values range from 0.073mg./l to 0.3251mg./l.

Keywords: *Conductivity, Sulphate, Sarang Talav, pH.*

INTRODUCTION

The water coming from different sources has significant impact on the quality and sustainability of the well, bore well, and taps water. Industrial effluents, direct discharges, percolation as well as precipitation may introduce may introduce a wide variety of pollutants into the various water reservoirs like well, bore well and taps water ranging from agrochemicals, some metals as well as persistent organic pollutants. It is noteworthy that present study discusses about secondary data collected from different spots and determines the water quality parameters of the collected samples. The investigation divided into physico-chemical, chemical, metals, and human contaminating activity effluent. The provision of potable water to the rural and urban population is necessary to prevent health hazards.

Groundwater is an important water resource in both urban and rural areas of Karanja Lad for domestic as well as for agriculture purposes. Protection of groundwater is a major environmental issue for the sake of maintaining the human health and health of the ecosystems. Water is the dominant environment of these ecosystems and has attracted a great deal of interest for maintaining the water quality. Apart from intrusion of sea water into ground water, the addition of various kinds of pollutants and nutrients through the agency sewage, industrial effluents, agricultural runoff etc. can make a series of changes into water bodies in the physico-chemical and characteristics which have been the subject of several investigations.

A vast population in the Karanja Lad rural and urban area utilizes a shallow and deep ground water for drinking, agriculture and other purposes. Regular monitoring of the quality of ground water should be undertaken in view to monitor the quality of ground water by assessing of physico-chemical properties of ground water near the city and its different areas.

REVIEW OF LITERATURE

Assessment and mapping of groundwater is an important quantity because the physical and chemical characteristic of groundwater determines its suitability for agricultural, industrial and domestic usages. Present work deals with the assessment of physico-chemical parameters of ground water samples at industrial, residential and near MSW site of Bhilai city during 2010-2011. [4]

As per investigation getting pure water for drinking and other domestic uses is a fundamental requirement for healthy way of life. However, with the rising soil and water pollution availability of pure water has become a major challenge and polluted water has become a health hazard. With the expansion of city limits, the municipal waste is dumped in surrounding areas and as a result, ground water is getting polluted even in rural areas in the vicinity of big cities. Interestingly most studies on water quality have been focused on quality of water in the cities and generally water in villages is considered pure and safe. The physico-

chemical parameters of water samples collected from various villages in and around Yawatmal district were assess. The physico-chemical parameter like, temperature, pH, electrical conductivity, total dissolved solids, total alkalinity, sulphate, iron, chloride, fluoride, nitrate, was determined. The results were compared with standards prescribed by WHO and ISI. It was found that water samples collected from various villages in and around Yavatmal district was found contaminated by some parameters. All sampling of villages showed physico-chemical parameters above the water quality standards and the quality of water are very bad at some places and it is unfit for drinking purpose.[8] For evaluation of physico-chemical parameters, pond water samples were collected from 27 villages of Bilaspur district, Chhattisgarh (India) in triplicate. Samples were analyzed for physico-chemical parameters including pH, electrical conductivity, total dissolved solids, temperature, salinity and dissolved oxygen. The result of the proposed study will establish some facts about the use of water for various purposes like domestic and agriculture.[3]

Study Area: The Karanja Lad is situated about 70 km North-East of Washim city at latitude of 20^0-47'-99". The city lies on 77^0-48'-84" longitude. Its elevation is 402 meters above sea level; its total area is nearly about 14^2 km square. Yearly average rainfall of the city is 826.3mm. Rural and urban area of Karanja Lad was identifying with its historical value in past, and many temples of different gods and goddess as well as historic water reservoirs are present today also around the city and rural area, like Rishi Lake, Sarang Talav and Lendhi Talav.

MATERIALS AND METHODS

The water samples were collected from different spots like tap, well and bore wells of Karanja Lad during January 2015 to June 2015 for analyzing the various physic-chemical parameters. The samples were collected in plastic container in the morning hours and brought to the laboratory for further analysis. All standard methods of APHA (2005) were used for physico-chemical analysis like pH, Conductivity, TDS were estimated digitally while Sulphates, Phosphates and Nitrates by spectrophotometrically.

RESULT AND DISCUSSION

Rural and urban area of Karanja Lad was depends on water reservoirs like like Rishi Lake, Sarang Talav and Lendhi Talav. But the actual source of water to Karanja city is tap, well and bore wells then the average range of variations in physico-chemical factors of sampling spots during January 2015 to June 2015.

Table - Range of Physico-chemical parameters of Karanja city during January 2015 to June 2015

Sr. No.	Water Parameter	Tap water	Well water	Borewell water
1.	Temperature of water (^{0}C)	20.2^0 to 22.6^0	22.6^0 to 27.1^0	25.1^0 to 30.3^0
2.	pH	6.68 to 7.90	7.12 to 7.48	7.29 to 7.68
3.	uctivity (µmhos/cm)	292 to 310	308 to 333	315 to 344
4.	TDS (mg/l)	214 to 250	222 to 310	242 to 364
5.	Sulphates (mg/l)	0.008 to 0.034	0.028 to 0.152	0.016 to 0.310
6.	Nitrates (mg/l)	0.010 to 0.018	0.021 to 0.083	0.037 to 0.096
7.	Phosphates (mg/l)	0.294 to 0.306	0.073 to 0.322	0.280 to 0.325

Temperature is one of the important physical parameter for the growth of organisms. Atmospheric and water temperature plays an important role in physico-chemical and physiological behaviour of aquatic ecosystem [10] the variations in water temperature ranges from 20.2^0 to 30.3^0. pH water sample were observed in average range during the study period. pH may be associated with increase photosynthesis, similar results were observed by [09].

The conductivity of lake water is a measure of the capacity of substance or a solution to conduct electric flow. It depends upon dissolved solids [01]. The value of conductivity ranges from 292 to 344(µmhos/cm). Similar trends of conductivity were given by [06] while studying certain chemical parameters in soil water phases in a small pond along western India. Water has a large number of dissolved solid, which largely govern its physico-chemical properties and in turn have indirect effect on the organism. Total dissolved solids ranges from 214 to 364. Such results have

also been reported by [05]. Sulphate is the content found in water it ranges from 0.008 to 0.310 mg/l during study period. Nitrate is the most oxidized from the nitrogen and is an important plant nutrient. The values of nitrates range from 0.010 to 0.096 mg/l. respectively, was also noted by [02] during analysis of physico-chemical parameters in Sai Reservoir, Latur District, Maharashtra. Phosphates are prime nutrient for the growth of plant next to the nitrogen and play an important role in metabolism of both plants as well as animals. Phosphorous values range from 0.073mg./l to 0.3251mg./l. in Karanja city. In nature water phosphorous ranges from 0.005mg/l. to 0.020 mg./l [07]. The observed physico-chemical parameters showed that the water from different stations of Karanja city is potable in nature and is suitable for the commercial use.

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SYNTHESIS AND SPECTRAL STUDIES OF ZINC(II) COMPLEXES SUPPORTED BY NO-BIDENTATE SCHIFF-BASE LIGANDS

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ABSTRACT

Complexes of the type $[Zn(phen)_2(L)](OAc)_2(nH_2O)$ (L = ligands derived from 2-chloro ethyl amine and ortho hydroxyl benzaldehyde have been synthesized from the reaction of the metal precursor complex $[Zn(OAc)_2(1,10\text{-}phen)_2](6H_2O)$ with the respective ligands in ethanol and water. The ligands and complexes have been characterized with the aid of elemental analysis and FT-IR, FAB-Mass, UV-Vis., ^{1}H-NMR, ESR spectroscopic methods and further analyzed by powder XRD and thermal studies. Elemental analysis data confirmed that the complexes have a 1:2:1 molar ratio among the metal and ligands. FT-IR and ^{1}H-NMR spectral studies indicate the ligand is bidentate and the binding sites are azomethine nitrogen and carboxylato oxygen atoms. The UV-Vis. studies indicate the presence of Zn(II) in an octahedral environment.

Keywords: *Schiff bases, 1, 10-phenanthroline, Zn(II) complexes.*

INTRODUCTION

Schiff base and their transition and inner-transition metal complexes have been studied extensively due to their unique coordination and biological properties have a variety of applications in clinical, analytical and industrial fields. Schiff bases ligands and their metal complexes containing nitrogen and oxygen donor atoms play an important role in biological and inorganic research. They have significant interest because of their pharmacological properties. They have been studied extensively with the point of interest being their rich and well characterized photophysics. The area of metal complexes with Schiff base investigated intensively during the last years regarding their pharmacological applications such as tuberculostatic, antitumor, antibacterial and antifungal agents. [1-3]

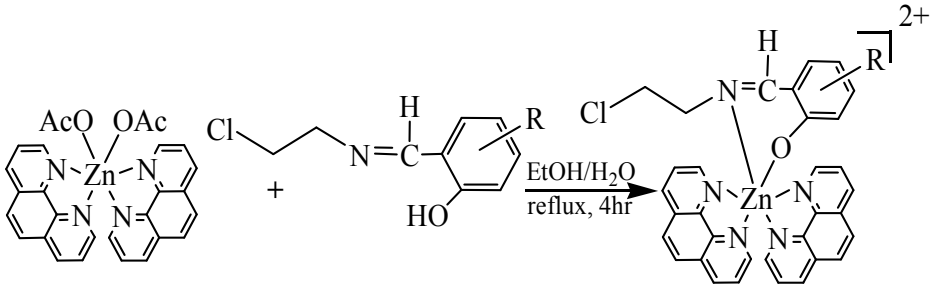
EXPERIMENTAL SECTION

2.1. Materials and Physical measurements

The precursor $[Zn(OAc)_2(1,10\text{-}phen)_2](6H_2O)$ was synthesized according to the published method. All other chemicals were purchased from Aldrich and used as received without further purification. Elemental analyses for C, H and N were done using a Perkin-Elmer elemental analyzer. ^{1}H-NMR spectra were obtained on a Bruker AM400 MHz instrument with Me_4Si as internal reference. The IR spectra were recorded on a JASCO FT/IR-410 spectrometer in the range 4000-400 cm^{-1} using KBr disc method. Electronic spectra were recorded on a Perkin Elmer Lambda-25 UV/Vis spectrometer in the range 200-600 nm.

*2.3. **Synthesis of complexes***

Metal precursors, $[Zn(phen)_2](OAc)_2.6H_2O$ were used as starting material to synthesize all the new complexes (Scheme 1). The synthesis of complexes have been achieved using a similar synthetic procedure by reacting one equivalent of metal precursor and one equivalent of the corresponding ligands in ethanol and water for 4 h (Scheme 1). The solid obtained were filtered, washed with ethanol and then dried.[4]



Scheme 1: Outline the synthesis of complexes

RESULTS AND DISCUSSION

Elemental analysis

Elemental analysis data confirmed that the complexes have a 1:2:1 molar ratio between the metal and ligands. i.e. one mole of Zinc acetate reacted with two moles of 1,10-phenanthroline and one mole of ligands (L^1)/(L^2)/(L^3) to give the corresponding complexes (1)/(2)/(3).Elemental analysis for complex (1) is shown in Fig.1. All the complexes show the analytical results close to the theoretical values indicating the presence of two types of ligands.

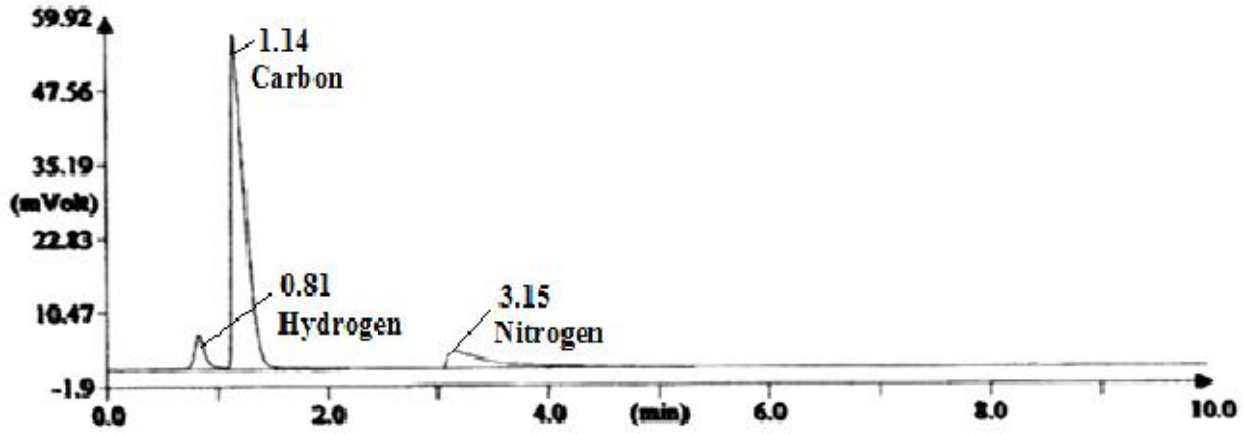


Figure 1 CHN analysis of complex (1).

IR Spectra

The IR spectral data of Schiff base ligands showed the broad bands at 3444 cm^{-1} were due to stretching vibration of phenolic OH. These bands were absent in all the complexes, indicating deprotonation on coordination of the Schiff base to metal ion. In addition, the bands at 1346 cm–^{1} attributed to the phenolic C-O stretching vibration of the free ligands were blue-shifted to 1427 cm^{-1} upon complexation, suggesting the involvement of the phenolic oxygen atom in the coordination. The imine (C=N) functional group of the free ligands was observed as a strong bands between 1670-1643 cm–1, these bands were red-shifted to 1586-1625 cm^{-1} in the spectra of the complexes, indicating coordination of azomethine nitrogen of the Schiff base to metal ion.

The mode of coordination of the Schiff base ligands was further substantiated by the appearance of two new bands in the far infrared spectra of the complexes at 570–520cm–1 and 423–416 cm–^{1}. These bands were assigned to the Zn-N and Zn-O stretches, respectively.[5-8]

UV–vis absorption spectra

The electronic spectra of the ligands and their complexes were recorded in DMSO as a solvent. The electronic spectra of free Schiff base ligandsshowed the bands in the 225–335, 279–430, 285–345 nm range respectively were assigned to π–π* and n–π* transitions. In the Schiff base, the band at 350 nm was attributed to the π–π* of the azomethine. Bands between 334 and 257 nm are associated with phenyl and pyrimidine π-π* transitions. In the spectra of the complexes, the π-π* of the azomethine shifted to 374 nm, indicating that the imino nitrogen was involved in coordination. The electronic spectra of complexes exhibited three well defined bands in the 266–352, 266–428, 267–370 nm range respectively were assigned to intra-ligand charge transfer transitions. The positions of these bands suggested an octahedral environment around zinc atom[9-10]

^{1}H- NMR spectra

The ^{1}H-NMR spectra of ligands and their complexes were recorded in DMSO as a solvent. The assignments of the main NMR signals are given in the experimental section. The ^{1}H-NMR Spectra of ligands displayed broad signal at 12–13 ppm is assigned to OH of phenol. The metal complexes of these ligands did not show any proton signal to the phenolic OH range suggesting the participation of phenolic oxygen in coordination, after complete deprotonation. In the ^{1}H-NMR Spectra of complexes all the protons of ligands absorbed downfield. The signal at 9.3–10.5 ppm is due to OH of the phenol. The chemically equivalent aromatic protons H–1 and H–2, H–3 and H–4, H–5 and H–6, H–9 and H–10 are appeared at 9.1–8.0 ppm. Two additional signals in the spectra of 1–3 at 8.4–7.6 ppm are assigned to phen protons and in the spectra of 4–6 at 7.9–7.1 ppm are assigned to bpy protons. A signal at 2.6 ppm is due to acetate group. The conclusions

drawn from these studies lend further support to the mode of bonding discussed in their IR spectra. The number of protons calculated from the integration curves and those obtained from the values of the expected CHN analyses agree with each other. [5-8]

CONCLUSIONS

Schiff base ligands and their zinc(II) complexes were synthesized and characterized. Based on the above observations of the elemental analysis, UV-Vis., IR, ^{1}H-NMR spectral data it is possible to determine the type of coordination of the ligands in their complexes. The spectral data reveal that all the complexes were six coordinated and possess octahedral geometry around the metal ion.

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SIMULTANEOUS NON-AQUEOUS POTENTIOMETRIC DETERMINATION OF PHARMACEUTICALLY POTENT IBUPROFEN-DIPHENHYDRAMINE HYDROCHLORIDE AND PARACETAMOL-DIPHENHYDRAMINE HYDROCHLORIDE COMBINATION DRUGS

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ABSTRACT

The simultaneous non-aqueous potentiometric determination of pharmaceutically potent combination drugs by using isopropyl alcohol as the solvent and KOH in isopropyl alcohol as the titrant has been established. The two acidic combination drugs ibuprofen-diphenhydramine hydrochloride and paracetamol-diphenhydramine hydrochloride were determined simultaneously in their binary mixtures by the non-aqueous differentiating potentiometric titration methods. These drug combinations are widely used in medicines. Titrations were carried out using a pair of glass and calomel electrodes. The method was found to be precise for assay of double component tablets and results obtained are comparable with those obtained by Indian Pharmacopoeia (I.P.) method.

Keywords: *Non-aqueous, potentiometric determination, combination drugs*

INTRODUCTION

The non-aqueous potentiometric determination has been reported earlier using the pairs of different electrode[1-5]. Different methods were suggested for the estimation of two or more drugs in combination and deals mostly with the separation of components followed by determination of individual component using suitable technique. For the determination of drugs in combination various methods were included in the pharmacopoeias[6-8]. Differentiating potentiometric titrations of mixtures like paracetamol-barbitone[2], paracetamol-salicylamide[9,10], paracetamol-aspirin[11] etc. have also been reported in literature. The literature is enriched with determination of nimesulide-tizanidine[12], nimesulide-chlorzoxazone[13], nimesulide-diclofenac sodium[14] etc. Binary mixture of ibuprofen-paracetamol[15] as well as ternary mixture of ibuprofen-paracetamol-chlorzoxazone[16] has also been determined by spectrophotometric and chromatographic technique. Determination of combination of ibuprofen-diphenhydramine hydrochloride and paracetamol-diphenhydramine hydrochloride drugs by differentiating potentiometric method using acetone or isopropyl alcohol was not reported in literature so far. As these drugs are distinctly acidic, could not be titrated directly with aqueous alkali due to their hydrolysis. The basic titrant is also superior to the alkoxide solvents which are more susceptible to the atmospheric moisture and carbondioxide. The aim of the present work is to find out simple analysis procedure for common drugs which will help the analysis of raw materials and products for quick check of spurious drugs that are feared to penetrate the markets. In this communication, study non-aqueous titrations were carried out to determine one component in presence of other without any prior separation. Determination of ibuprofen and diphenhydramine hydrochloride as well as paracetamol and diphenhydramine hydrochloride in two component tablets has been carried out using isopropyl alcohol as the solvent and KOH in isopropyl alcohol as the titrant by potentiometric titration method.

MATERIAL AND METHODS

The potentiometric titrations were carried out by using a digital potentiometer (Equiptronics, EQ-602). Glass and calomel electrodes were used as indicator and reference electrode respectively. Weighing of all the drugs and chemicals was made on Precisa-310-M (±0.001 g) balance. The chemicals and solvents of AR grade were used. All solvents were purified and made anhydrous by standard methods[17]. Care was taken to protect the titrant from atmospheric moisture and carbon dioxide. The drugs selected for present investigation were obtained from pharmaceutical laboratories. These drugs are of pharmaceutical nature and are included in pharmacopoeias[6-8].

During this analysis, ibuprofen-diphenhydramine hydrochloride and paracetamol-diphenhydramine

hydrochloride drugs containing ten tablets of the same batch were accurately weighed and powdered. The quantity of powder equivalent to about 200 mg of ibuprofen/paracetamol and 25 mg of diphenhydramine hydrochloride was accurately weighed and treated with 50 ml of isopropyl alcohol and stirred vigorously so as to dissolve the active component of the tablets. Binding agents or filler remained insoluble. The additives commonly present in the tablets i.e. calcium carbonate, glucose, lactose, starch, gum etc. are mostly insoluble in acetone and isopropyl alcohol. The solutions were filtered, residues were washed three to four times with small portions of isopropyl alcohol and volumes of solutions were made to 100 ml with isopropyl alcohol. The aliquots of 10 ml of these solutions were diluted with isopropyl alcohol to 20 ml and titrated with 0.1 M solution of KOH in isopropyl alcohol using glass and calomel electrodes by potentiometric method. The titrant was standardized with 0.1 M benzoic acid in isopropyl alcohol by performing potentiometric titration. The end points were found out by plotting the graphs and then amount of drugs present in titrated weights of tablet powder was calculated. The amount of active components (drugs) present in one tablet was calculated by knowing the average weight of the tablet. The same tablets were later on analyzed by the method of pharmacopoeias and the results obtained were compared.

RESULTS AND DISCUSSION

Ibuprofen and diphenhydramine hydrochloride drugs containing ten tablets of the same batch were accurately weighed and powdered. The quantity of powder equivalent to about 200 mg of ibuprofen/paracetamol and 25 mg of diphenhydramine hydrochloride was accurately weighed, it was extracted with isopropyl alcohol and the volume was made to 100 ml. An aliquot of 10 ml of this solution was diluted with isopropyl alcohol to 20 ml and using potentiometer titrated with KOH in isopropyl alcohol. Similarly, the powder of tablets of the same batch having the drugs paracetamol and diphenhydramine hydrochloride was extracted with isopropyl alcohol and using potentiometer titrated with KOH in isopropyl alcohol. The titrant was standardized by performing potentiometric titration using standard benzoic acid in isopropyl alcohol. The weight of drugs ibuprofen and diphenhydramine hydrochloride as well as paracetamol and diphenhydramine hydrochloride present in titrated amount of tablets was calculated. The same tablets were analyzed by I.P. method. The results obtained for two different brands of tablets are tabulated and it is observed that, the present potentiometric method gives fairly accurate and comparable results to those obtained by I.P. method. (**Table 1**) (**Table 2**). It is simple, precise and free from indicator error or interferences. The acidic drugs get hydrolyzed in presence of aqueous alkali but this is avoided in non-aqueous medium. However, in US Pharmacopoeia procedure alcoholic solution of the acidic drugs is titrated with aqueous alkali. Such a titration must be performed quickly so as to minimize hydrolysis. The present method has no such limitations. The most common additives present in the tablets are calcium carbonate, sugars, gum etc. and as these are insoluble in isopropyl alcohol do not affect the results. The solvent isopropyl alcohol can be used as a good differentiating solvent. Using the solvent isopropyl alcohol, potentiometric breaks obtained are quite pronounced and prominent with minimum error (**Graph 1**). The solvent isopropyl alcohol permitted a large change in the solvated proton concentration near the end point. The dielectric constant of isopropyl alcohol is smaller. It can be purified and made anhydrous very easily. This method is simple than the other methods where the components are separated and estimated by chromatographic, spectrophotometric or other techniques.

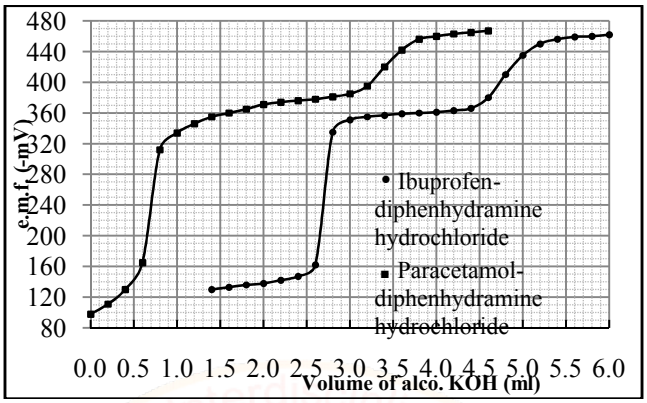
Table 1: Determination of ibuprofen-diphenhydramine hydrochloride (DPHH) in tablets

Sample	Label Claim (mg)		Weight Found by I.P. method (mg)		Weight Found by present method (mg)	
	Ibuprofen	DPHH	Ibuprofen	DPHH	Ibuprofen	DPHH
A	200.0	25.0	201.16	25.06	201.45	25.08
B	200.0	25.0	197.67	24.55	198.63	24.79
C	200.0	25.0	198.11	24.78	198.92	24.93

Table 2: Determination of paracetamol-diphenhydramine hydrochloride (DPHH) in tablets

Sample	**Label Claim (mg)**		**Weight Found by I.P. method (mg)**		**Weight Found by present method (mg)**	
	Paracetamol	**DPHH**	**Paracetamol**	**DPHH**	**Paracetamol**	**DPHH**
A	200.0	25.0	196.44	24.53	197.78	24.66
B	200.0	25.0	198.51	24.61	198.72	24.84
C	200.0	25.0	197.40	24.72	197.68	25.01

Graph 1 : Determination of ibuprofen-diphenhydramine hydrochloride and paracetamol-diphenhydramine hydrochloride in tablets



CONCLUSION

The simultaneous non-aqueous potentiometric determination of pharmaceutically potent ibuprofen-diphenhydramine hydrochloride and paracetamol-diphenhydramine hydrochloride combination drugs is fast, simple, precise method and can be used even in common laboratories without the use of any sophisticated instrument. The pair of glass and calomel electrodes gave stable potentials which were attained quickly. The solvent isopropyl alcohol is found to be more satisfactory for non-aqueous titration of drugs and gave satisfactory results. The potassium hydroxide in solvent isopropyl alcohol was found to be better basic titrant to the alkoxide solvents which are more susceptible to atmospheric moisture and carbondioxide.

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PRELIMINARY WATER SAMPLE ANALYSIS IN KURALI VILLAGE OF WARUD, DIST-AMRAVATI (MAHARASHTRA)

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ABSTRACT

Fourteen physico-chemical parameter of water samples were determined. The samples were collected from Kurali, in first week of February 2016.The temperature of the samples was noted on the spot, during collection. At the same time dissolved oxygen, Chemical oxygen demand, Biological oxygen demand and other parameter like pH, TDS, Alkalinity, Calcium. Magnesium, Chloride, Fluoride, Nitrite were measured within 15 days from sampling, the parameter were analysed by prescribed standard method.It is found that water from all samples can be used for drinking after conventional treatment and disinfection.From the results of physicochemical analysis in the present investigation indicates that the quality of water parameters lye within the maximum permissible limit prescribed by WHO and Indian standards specification for drinking water . It has also been concluded that the water has no hazardous effect on human health.

Keywords: *Water Quality,Physico-Chemical Charectristics, Kurali Village.*

INTRODUCTION

Essential component for lives on the earth is Water, which contains minerals extremely important in human health. It is the basic needthat the Supply of fresh and clean drinking water for all human beings on earth. The quality of groundwater of any area is of great importance for human beings and irrigation, which should be clean and fresh. In India, most of the population is dependent on groundwater as it is the only source of drinking water supply. Water is extremely essential for survival of all living organisms. The quality of water is vital concern for mankind since it is directly linked with human welfare. The quality of public health depends to a greater extent on the quality of ground water, which should be clean and fresh. This ground water has long been considered as one of the purest forms of water available in nature to meet the overall demand of rural and semi urban people. Most of the people in India depend upon fresh water supplies from dug wells, ponds, bore wells, springs and the like.Physico-chemical analysis of surface and ground water of Bargarh district, orissa, India have carried out by M.R.Mahananda et.al. [1]. S.P. Bhalmestudy the analysis of drinking water parameters in an Educational institute situated in Hingna MIDC area, Nagpur[2].Surendra Kumar Yadav,Water pollution parameters viz. pH, conductivity (µ mhos/cm), DO (mg/l), BOD (mg/l), COD (mg/l), faecal coliform (MPN/100 ml) and total coliform (MPN/ 100 ml) are estimated at 5 sites for River Hindon at entering point in Saharanpur (UP, India) and found beyondprescribed limit/ standards. There is need for formulation of plan to control the pollution to improve the water quality of the River[3].H.N. Khare investigated that the quality of the Benisagar dam water system is continuouslydegrading. The source of water pollution in this dam, municipal, domestic and agricultural wastes. Various physical and chemical parameters like temperature, pH, total alkalinity, D.O, C.O.D, and B.O.D. have been observed to either approach or to have exceeded the permissible limits set for drinking water or for human use[4].Analysis of Ground Water of Rural Areas of Wardha-City Using Physico – Chemical and Biological parameters has been reported[5].
Physico-chemical analysis of underground water of HariharaTaluk of Davanagere District, Karnataka, India [6].Analysis of Chloride, Sodium and Potassium in Groundwater Samples of Nanded City in Mahabharata, India have been reported[7].Temperature, pH, electrical conductance, total dissolved solids, fluoride, sodium, potassium, chloride and Hardness calcium hardness, magnesium hardness etc. concentration in ground water was determined in Amdapur in Warudtaluka of Amravati District in Vidarbha region of India[8].Physico-chemical characterization of

groundwater samples are taken from Dindigul Town Tamilnadu, India reported by Mohamed Hanipha and Zahir Hussain[9].Study of Some Physicochemical Parameters of Drinking Water Sources inTembhurkheda and Jarud Region Dist. Amravati, MS, India[10].H. L. Yadav studied the characteristics of mine water in major coal fields by calculating the (WQI) in different sampling location[11].

MATERIAL AND METHOD

Polythene bottles of capacity 1 to 2 litters were sterilised by hot water treatment and sunlight treatment and again washed with alcohol are used as a sample collector. Temperature of water samples were measured when samples were collected.The Conductivity meter ,Spectrophotometer, TDS meter, pH meter, Flame photometer were used to analyse the parameters.

STUDY AREA

The area KURALI is located in Warud Tahsil. Entire samples are Dam water ,well water, Hand Pump samples are of Agriculture and drinking water Water resources chosen for the work are mainly used for the drinking purposes. All the samples were collected in the first weak of Feb. 2016.

ANALYSIS OF WATER SAMPLES

Sr.No	Parameter	A-1	A-2	A-3	A-4
1	Temperature	30^0C	28^0 C	28^0 C	28^0 C
2	P^H	7.87	7.50	7.38	7.39
3	Conductivity	0.30	1.07	1.17	1.24
4	TDS	119	453	539	503
5	Alkalinity (meq/1)HCO_3^-	3.8	7.6	7.6	8.74
6	Calcium	1.4	4.0	4.4	4.8
7	Magnesium	0.4	1.8	1.6	2.4
8	Chloride	1.14	3.04	2.66	3.04
9	Total Hardness(ppm)	17.2	96.32	180.6	177.16
10	SAR	10.46	3.17	2.82	2.64
11	Fluoride	49.213	0.671	0.585	0.618
12	Nitrite	0.567	53.1	67.2	64.1
13	D.O	28.95	29.81	31.38	31.24
14	Sulphate SO_4	6.7	6.63	0.55	0.48

Two samples were collected from Kurali Region, samples were collected from well water, water sample collected from hand pump and one from Dam. These samples were collected from approximately 15-20 cm below the water surface. Care must be taken not to catch any floating material or bed material into the container. Thestandard procedures were adopted for the determination ofphysico-chemical parameters.

At the same time parameter like pH, EC, TDS, Sodium, Calcium, Magnesium, Chloride, Fluoride, Bicarbonate were measured within 15 days from sampling, the parameter were analyzed by prescribed standard method.

RESULT AND DISCUSSION

1) TEMPERATURE

In present investigation water temperature ranging between 28^0C to 30^0C.

2) pH

The $P^H$of water sample A-1,A-2,A-3, & A-4 ranges from 7.38 to 7.87. The P^H of water sample that is A-3 is less then other Samples A-1,A-2,A-3, & A-4 is slightly alkaline. A number bases like carbonate, hydroxide contribute to alkalinity.

3) ELECTRIC CONDUCTIVITY

The Specific conductivity of all water sample varied between 0.30 X 10^{-3}mbo/cm But specific conductivity of water sample A-3 & A-4 is more as compared to sample A-1 & A-2.

4) TOTAL DISSOVED SOLID (TDS)

The total dissolved solid indicates salinity behaviour of ground water. Water containing more than 500 mg/L of TDS is not consider desirable for drinking water supplies but in unavoidable cases 1500 mg/L is also allowed.

The TDS value varies from 393 to 1659 mg/L by ISI. The TDS for water sample A-1 to A-3 ranges from 119 to 539 mg/L.

The TDS of Sample A-3 higher than the other sample due to presence of clay slit, organic matter are present in water.

5) ALKALINITY

Total alkalinity of water sample in terms of HCO_3 varies between 3.8 to 8.74 Mg/L The sample A-4 higher than other sample.

6) CALCIUM

The present of investigation shows the concentration of calcium of the water samples are 1.4 to 4.8 Mg/L water samples A-1 & A-4 containing high concentration of calcium that water sample A-4 as classified as ‘calcium rich’.

7) MAGNESIUM

The observed value ofMagnesium in water sample is varied from 0.4 to 2.4 Mg/L. The observed value of Magnesium for water sample A-4 is higher than sample A-1,A-2,A-3.

8) CHLORIDE

The Stability of Water resources for the irrigational use in agriculture is depending upon salt concentration, especially chloride, content. In water sample reservoir chloride content was in the ranges from 1.14 to 3.04 Meq/L. According to WHO Maximum permissible limit for chloride is 500mg/L.

9) TOTAL HARDNESS

Total hardness of water sample varies between 17.2 to180.6 The sample A-1 lower than other samples A-2,A-3 & A-4.

10)SAR

SAR is an important of parameter of water. The water sample from 2.64 to 10.46 Meg. The water sample A-1 is higher than A-2,A-3 & A-4 sample.

11) FLUORIDE

Fluoride is an also important parameter of water. High concentration of Fluoride is cause dental Fluoride concentration 49.2 Mg/L is higher that sample A-2,A-3,&A-4.

12) NITRIDE

The values of nitride in water sample are varied from 0.567 to 67.2 Mg/L. The sample A-3 is higher than other sample A-1, A-2& A-4.

13) D.O (DISSOLVED OXYGEN)

In the water sample varies from 28.95 to 31.38 Mg/L dissolve Oxygen value of A-3 is higher than other sample A-1,A-2& A-4

14) SULPHATE

Sulphate is an important parameter of water sample the higher value of water sample A-1 & A-2 from 6.63 to 6.7 & other value is lower A-3 & A-4.

CONCLUSION

1) By considering all the data it was concluded that physico – chemical parameters confirmed in water sample after comparing water parameters, it is found that water sample (i.e sample no.A-1)is slightly alkaline, sodium metal present in high concentration. In this sample, chloride present in lower concentration.
2) While in case of sample no.A-2 the p^H of water, is in normal range but magnesium and sulphate present in low concentration. The sample no.A-3 having normal p^H range but having high sodium concentration.
3) It was observed that the main causes high interference of human activities luck of proper sanitation and industrial and domestic waste-water inflow.
4) Present investigation with physico chemical parameter of sample no.A-1&A-3, the concentration of sulphate is medium, so it showed the confirmed organic pollution in some amount.
5) The temperature of water is an important factor which plays an important role in controlling the occurrence and abundance of blue-green algae .the dissolve oxygen content was high in the entire sample.

It is found that water from all samples can be used for drinking after conventional treatment and disinfection. From the results of physicochemical analysis in the present investigation indicates that the quality of water parameters lye within the maximum permissible limit prescribed by WHO and Indian standards specification for drinking water. It has also been concluded that the water has no hazardous effect on human health.

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CHEMICAL ANALYSIS OF WATER IN VILLAGE DEULGAON MAHI, TEHSIL DEULGAONRAJA, DIST BULDANA, STATE MAHARASHTRA

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ABSTRACT

Water samples were collected in sterile containers from various water resources in village Deulgaon Mahi. The water samples were immediately subjected to chemical analysis in order to evaluate the quality of water in circulation within the region and identify its sources of contamination. There is the need for adequate changes to be made at points where water distribution systems integrity appeared compromised.

Keywords: *Chemical Analysis, Water Analysis, Hardness, TDS, Oxygen Demand*

INTRODUCTION

Water is one of the most important of all natural resources known on earth. It is important to all living organisms, most ecological systems, human health, food production and economic development. [1] The safety of drinking water is an ongoing concern within the global village. Traditionally, the safety of potable water supplies has been controlled by disinfection. [2] Understanding the delicate interface between Physics, Chemistry and Biology helps to do the assessment of water quality. The chemical methods measure the concentration of the pollutants. [3] The increase in the electrical conductivity value and chloride concentration in the ground water sources with decreased distance from the drain suggested that these two parameters can be taken as indicators for detecting plumes of contamination from septic system. The main source of drinking water in rural areas of Maharashtra state is groundwater. Groundwater is generally found more cleaner than surface water. Several factors, like agricultural and domestic waste, land use practices, geological formation, infiltration rate etc., are found to affect the quality of groundwater.[4]

MATERIALS & METHODS

In the present study authors tried to give detailed description of chemical quality of groundwater of village Deulgaon Mahi. Ten representative samples were collected during January to April 2017 and analysed for pH, chlorides, conductivity, alkalinity, hardness, sulphate, BOD (Biological Oxygen Demand), COD (Chemical Oxygen Demand), TDS (Total Dissolved Solids) and DO (Dissolved Oxygen). The first and usually the most important step in analytical process is the sampling itself. Mistakes during the sampling process inevitably lead to erroneous results which cannot be corrected afterwards. All parameters like pH, chlorides, conductivity, alkalinity, hardness, sulphates, Biological Oxygen Demand, Chemical Oxygen Demand, Total Dissolved Solids and Dissolved Oxygen are determined as per the standard methods which are used for the physicochemical analysis of water samples.[5-7]

RESULTS & DISCUSSION

Monitoring of water samples from different sources present in the study area were analyzed for the said parameters, which are tabulated as follows.[8]

Parameter	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
pH	8.40	8.00	8.08	8.10	8.23	8.15	8.31	8.12	8.25	8.36
Chlorides (mg/lit)	79.97	124.96	74.97	134.95	69.97	94.97	114.96	209.93	79.97	84.97
Conductivity (Ms/cm)	0.843	1.027	0.792	1.158	0.467	0.946	0.832	1.688	0.633	0.729
Alkalinity (mg/lit)	280	300	290	330	160	350	190	450	150	220
Hardness (mg/lit)	300	370	280	450	250	360	230	630	240	260
Sulphate (mg/lit)	137.2	164.64	129.36	196	117	160.72	109.76	266.56	113.68	121.52
BOD (mg/lit)	6.4	4.8	6.4	8	8	4.8	4.8	4.4	4.8	9.6
COD (mg/lit)	0.032	0.016	0.002	0.0016	0.0032	0.0018	0.0032	0.0128	0.0096	0.0016
TDS (mg/lit)	320	484	366	536	211	446	384	512	290	334
Dissolved Oxygen (ppm)	28.1	21.2	13.3	22.5	14.6	16.6	20.8	23.7	27.0	27.6

pH: No health-based guideline value is proposed for pH. Although pH usually has no direct impact

on consumers, it is one of the most important operational water quality parameters. For effective disinfection with chlorine, the pH should preferably be less than 8; however, lower-pH water (approximately pH 7 or less) is more likely to be corrosive. The pH of the water entering the distribution system must be controlled to minimize the corrosion of water mains and pipes in household water systems. The optimum pH required will vary in different supplies according to the composition of the water and the nature of the construction materials used in the distribution system, but it is usually in the range 6.5–8.5. The pH range for the samples from study area is 8.00 to 8.40

Chlorides: High concentrations of chloride give a salty taste to water and beverages. No health-based guideline value is proposed for chloride in drinking-water. Chlorides were found in the range 69.97 mg/L to 209.93mg/L.

Alkanlinity: Alkalinity also contribute to the stability of water. Alkalinity values for the present study area were found in the range 150 – 350 mg/L.

Hardness: Hardness caused by calcium and magnesium is usually indicated by precipitation of soap scum and the need for excess use of soap to achieve cleaning. Consumers are likely to notice changes in hardness. Hardness values are within range 230-630 mg/L.

Sulphates: The values for the sulphates are in the range 109.76 – 196.00 mg/L.

Oxygen Demands: The oxygen demands for the samples collected from the study area were determined in terms of BOD (Biological Oxygen Demand), COD (Chemical Oxygen Demand) and (Dissolved Oxygen Demand) which were found to be within the range 4.4-9.0mg/L, 0.001-0.003mg/L and 13.3 – 28.0 mg/L respectively.

TDS: The values of Total Dissolved Solids were found within the range 211-536 mg/L.

CONCLUSION

Access to safe drinking-water is important as a health and development issue at national, regional and local levels. In some regions, it has been shown that investments in water supply and sanitation can yield a net economic benefit, because the reductions in adverse health effects and health-care costs outweigh the costs of undertaking the interventions. This is true for investments ranging from major water supply infrastructure through to water treatment in the home. Consumption of water from the water resources within the study region may be done after proper disinfection.

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MICROWAVE ASSISTED SYNTHESIS, CHARACTERISATION AND ANTIFUNGAL ACTIVITIES OF SOME CHLOROSUBSTITUTED IMIDAZOLETHIONES

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ABSTRACT

Chlorosubstituted imidazolethiones have been synthesized in a very good yield under microwave irradiation by a reaction of 2-Bromo-1-(2'-hydroxy-3',5'-dichlorophenyl)ethanone with substituted amides such as thiourea, N-phenyl thiourea using ethanol as a solvent in presence of triethyl benzyl ammonium chloride (TEBA) as a phase transfer catalyst. In these reactions, the products were obtained in short reaction time and easy operation under mild conditions. The newly synthesized titled compounds were screened for their antifungal activities against Aspergillus niger, Penicillium chrysogenum, Fusarium moneliforme, Aspergillus flavus. All these compounds have been characterized on the basis of their IR and NMR spectral results.

Keywords: *Chlorosubstituted imidazolethiones, microwave, TEBA catalyst, antifungal activities.*

INTRODUCTION

The chemistry of nitrogen heterocyclic compounds especially imidazolethiones has attracted more attention during recent years due to their reactivity and novel biological activities. Imidazole-2-thiones are important organic compounds that have gained increased attention because of their pharmacological activities1-6. Its derivatives are used for the treatment of several diseases 1-3. Imidazole-2-thione C-nucleosides are synthetic precursors of azidonucleosides and fluoronucleosides, which possess anti-AIDS activity 4. Imidazole-2-thione moiety is also found in nature. Thus, L-ergothioneine, a rare, essential natural amino acid discovered in the fungus claviceps puprurea, is an antioxidant, known to protect against gamma and UV radiation and in isolated heart against postischemic reperfusion7. Various methods for synthesis of imidazolethiones have been reported8. Lawson prepared imidazole-2-thione and its derivatives from KSCN and the corresponding amino acid ester hydrochloride 9, 10. Fuentes described the reaction of D-fructosamines with different chiral imidazolidine-2-thione N-nucleosides11. Zeng described the synthesis of imidazole-2-thiones in acetone or dichloromethane under the atmosphere of nitrogen12. But these reactions have multiple steps and use of various solvents. Thus, there is a need to develop new methods for the synthesis of imidazolethiones. Therefore, to design the chemical reactions for imidazolethiones in green way is highly desirable. Chemical reactions which are accomplished to get desired chemical transformation with minimized by-products or waste has been classified as greener reactions.

In today's scenario, chemists have been developing new synthetic methods, reaction conditions and uses of chemical that reduces risks to humans and the environment. We have synthesized imidazolethiones using microwave for the synthesis of chlorosubstituted imidazolethiones and also screened titled compounds for antifungal activities.

EXPERIMENTAL

All the synthesized compounds were characterized on the basis of their chemical properties, analytical results and spectral data. The melting points were determined in open capillary tubes using liquid paraffin bath and are uncorrected. IR spectra recorded on F.T.Infra-Red Spectrophotometer in KBr pellets. PMR spectra were recorded on FT-NMR Cryo-magnet Spectrometer 400 MHz (Bruker) in CDCl3/ DMSO solvent. The reactions were carried out in scientific microwave oven (scientific microwave system model RG31L1, 700w, 2450 MHz). The analytical and spectral results were carried out at

SAIF, Panjab University, Punjab. The purity of newly synthesized compounds was tested by TLC.

The synthetic routes which furnished the target compounds are shown below along with their IR and NMR data (Scheme-1)

Preparation of 2'-hydroxy- 3', 5'-dichloroacetophenone (I)

2, 4-Dichlorophenylacetate was mixed with anhydrous aluminum chloride and heated at 120 oC for 45 min. on an oil bath. The reaction mixture was decomposed with ice-cold water containing a little hydrochloric acid to get the crude product. It was then purified by dissolving it in acetic acid and allowing the solution to fall drop by drop into ice cold water with constant stirring. A greenish white solid of the compound (I) was obtained. Yield: 85%, m.p.90oC.

IR (KBr): 3545 (intermolecular –O-H), 1652 (-C=O) cm-1; 1H NMR (DMSO) δ ppm: 12.58 (s, 1H, Ar-OH), 7.91 (s, 1H, Ar-H), 7.73 (s, 1H, Ar-H), 2.70(s, 3H, -COCH3).

Preparation of 4-(3',5'-dichloro-2'-hydroxy)-1H-imidazole-2(5H)-one (II)

2-Bromo-1-(2'-hydroxy-3',5'-dichlorophenyl)ethanone (0.02 M) dissolved in ethanol and aqueous solution of urea (0.02 M) using TEBA (0.05 M) as catalyst was irradiated under microwave for 3.5 min at 700 W. The reaction mixture was allowed to cool and on trituration, it was neutralized in ice cold conditions with sodium acetate. The product thus separated was filtered and crystallized from ethanol to get the compound (II) yield:70%, m.p.950C.

IR(KBr): 3311 (intermolecular –O-H), 1607 (-C=O) cm-1; 1H NMR (DMSO) δ ppm: 11.38 (s, 1H, Ar-OH), 7.86 (s, 1H, Ar-H), 7.76 (s, 1H, Ar-H), 7.67(s, 1H, -C=CH-N), 3.46 (b, 2H, C=C-NH).

Preparation of 2-bromo-1-(2'-hydroxy-3', 5'-dichlorophenyl) ethanone (II)

A solution of 2'-Hydroxy- 3', 5'-dichloroacetophenone (0.25 M) in 100 ml glacial acetic acid was taken in 500 ml flask. To this, {12.5 ml pure, 0.25 M} bromine was added slowly from dropping funnel. The mixture was shaked vigorously during addition and the temperature was maintained below 20 ^{o}C. The product reappeared after about half of the bromine has been introduced. After complete addition of bromine, the mixture was cooled in ice-cold water and the crude product thus separated was filtered and washed with 50% alcohol. Finally it was crystallized from ethanol to yield the compound (II) yield: 90%, m.p.82oC.

IR (KBr): 3060 (intermolecular –O-H), 1655 (-C=O) cm-1; 1H NMR (DMSO) δ ppm: 11.42 (s, 1H, Ar-OH), 7.88 (s, 1H, Ar-H), 7.82 (s, 1H, Ar-H), 7.67(s, 2H, -CH2-Br).

Preparation of 4-(3', 5'-dichloro-2'-hydroxy)-1H-imidazole-2(5H)-thione (III)

2-Bromo-1-(2'-hydroxy-3',5'-dichlorophenyl)ethanone (0.02 M) dissolved in ethanol and aqueous solution of thiourea (0.02 M) using TEBA (0.05 M) as catalyst was irradiated under microwave for 4 min at 700 W. The reaction mixture was allowed to cool and on trituration, it was neutralized in ice cold conditions with sodium acetate. The product thus separated was filtered and crystallized from ethanol to get the compound (III) yield: 75%, m.p.650C.

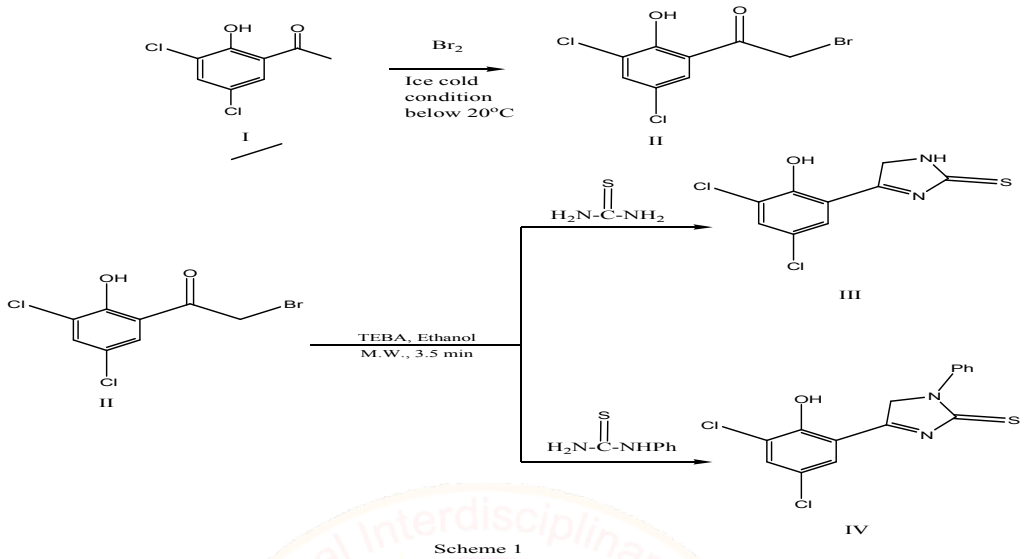
IR (KBr): 3423 (intermolecular –O-H), 1589 (-C=S) cm-1; 1H NMR (DMSO) δ ppm: 13.30 (s, 1H, Ar-OH), 7.24 (s, 1H, Ar-H), 7.64 (s, 1H, Ar-H), 2.54 (s, 2H, -CH2-NH), 3.35 (s, 1H, H-N-C).

Preparation of 4-(3', 5'-dichloro-2'-hydroxyphenyl)-1-phenyl-1H-imidazole-2(5H)-thione (IV)

A mixture of 2-Bromo-1-(2'-hydroxy-3',5'-dichlorophenyl) ethanone (0.02 M) dissolved in ethanol and aqueous solution of N-phenylthiourea (0.02 M) using TEBA (0.05 M) as catalyst was irradiated under microwave for 4 min at 700 W. It was allowed to cool and on trituration, neutralized in ice cold conditions with sodium acetate. The product thus separated was filtered and crystallized from ethanol to get the compound (IV) yield: 70%, m.p. 950C.

IR (KBr): 3093 (intermolecular –O-H), 1593 (-C=S) cm-1; 1H NMR (DMSO) δ ppm: 10.68 (s, 1H, Ar-OH), 7.68 (s, 1H, Ar-H), 7.85 (s, 1H, Ar-H), 3.17 (s, 2H, -CH2-N), 7.31-7.41 (m, 5H, H-Ar).

SCHEME:



Scheme 1

RESULTS AND DISCUSSION

2'-Hydroxy- 3',5'-dichloroacetophenone (I) when treated with bromine below 20 oC, it undergoes substitution at alpha position to yield 2-bromo-1-(2'-hydroxy-3',5'-dichlorophenyl) ethanone (II). The structure of compound (II) was confirmed by its IR and 1H-NMR. IR spectra of compound (II) showed band at 3060 cm-1(-OH) and 1655 cm-1 (-C=O). 1H-NMR spectra revealed the singlet at δ 11.42 corresponding to phenolic –OH group and singlets at δ 7.88 and δ 7.82 to aromatic protons. Compound (II) when treated with thiourea resulted in the formation of 4-(3', 5'-dichloro-2'-hydroxy)-1H-imidazole-2(5H)-thione (III). IR spectrum of compound (III) showed a band at 3423 cm-1(-OH) and 1589 cm-1 (-C=S). Compound (II) on treated with N-phenylthiourea in presence of TEBA yielded 4-(3', 5'-dichloro-2'-hydroxyphenyl)-1-phenyl-1H-imidazole-2(5H)-thione (IV). IR spectrum of compound (IV) showed a band at 3093 cm-1(-OH) and 1593 cm-1 (-C=S). 1H-NMR spectra revealed the singlet at δ 10.68 corresponding to phenolic –OH group and singlet at δ 3.17 corresponds to $-CH_2-$ group and δ 7.31 to δ 7.41 to five aromatic protons. Physical and analytical data of compounds I-IV are shown in Table No. 1.

Table No. 1: Physical and analytical data of compounds I-IV

Compound	Mol. formula	M.P (°C)	Yield (%)	Rf
I	C8H6O2Cl2	90	85	0.84
II	C8H5BrCl2O2	82	90	0.86
III	C9H6Cl2N2OS	65	75	0.44
IV	C15H10Cl2N2OS	95	70	0.65

ANTIFUNGAL AND ANTIMICROBIAL EVALUATION:

The in vitro antifungal activity was performed against *Aspergillus niger, Penicillium chrysogenum, Fusarium moneliforme, Aspergillus flavus*. Griseofulvin was used as negative reference. Synthesized compounds showed the presence of antifungal activity as shown in table no. 2.

Table 2:- Antifungal activities of synthesized compounds II-IV

SN	Compound	A. niger	P. chrysogenum	F. moneliforme	A. flavus
1	II	-ve	-ve	-ve	-ve
2	III	-ve	-ve	-ve	-ve
3	IV	-ve	-ve	-ve	-ve
4	control	-ve	-ve	-ve	-ve

Legends:
+ ve Growth (Antifungal activity absent)
- ve No Growth (Antifungal activity present)

CONCLUSION

All the newly synthesized compounds (II-IV) were found to be active against test pathogens. However, their activity increases from II to IV in accordance with the increase in complexity. Also, benzyl triethyl ammonium chloride work as excellent catalyst and reaction carried in microwave irradiation gives more yield as compare to conventional method.

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EFFICIENT SYNTHESIS OF SUBSTITUTED BENZOTHIAZOLE DERIVATIVE

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ABSTRACT

Bacterial infection often produces inflammation and pain. The compound possessing chemotherapeutic, analgesic and anti-inflammatory activities are not common benzothiazole derivatives. it is reported that thizolidinone derivatives are important for these three activities. hence in the present work thizolidinone and its substituted derivatives were prepared. The substituents used are –N(CH_3)$_2$ and-(OCH_3).Their physical properties were studied and IR Spectra is also obtained to study the structure. These derivaties dimethylamino thizolidinone and p-methoxy thizolidinone were found more effective in chemotherapeutic, analgesic and anti-inflammatory activities.

Keyword: *Synthesis of Thiazolidinone, Schiff base, anti-inflammatory, analgesic, antibacterial etc.*

INTRODUCTION

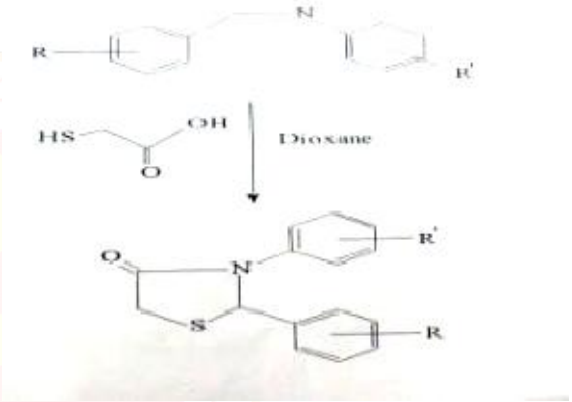
In common, benzothiazole derivatives have attracted great interest due to their pharmaceutical and biological importance. Benzothiazoles are mostly found in medicinal and bio-organic chemistry, with multiple applications in drug discovery[1]. Benzothiazole exhibit diverse and important biological properties. It shows different pharmacological activities such as antibiotic[2], antifungal[3], antiviral[4], anticancer[5], antimicrobial[6], and antiparkinson[7] anti- inflammantory[8], analgesic[9], properties.

Literature survey reveals that thizolidinone derivatives are important for anti-inflammatory[(10,11)] analgesic[(12,13)], antibacterial [14,15], and antipsychotic [(16,17)] activities. Priyanka and co-workers[18] have recently reported the antimicrobial activity of benzothiazoles and their derivatives against Gram positive and negative bacteria. In the present study it was envisaged that a drug molecule possessing the above mentioned the above mentioned the above mentioned pharmacophore could be of advantage since it might possess analgesic, anti-inflammatory and antibacterial activities.

METHODS FOR SYNTHESIS OF 4-THIZOLIDINONE

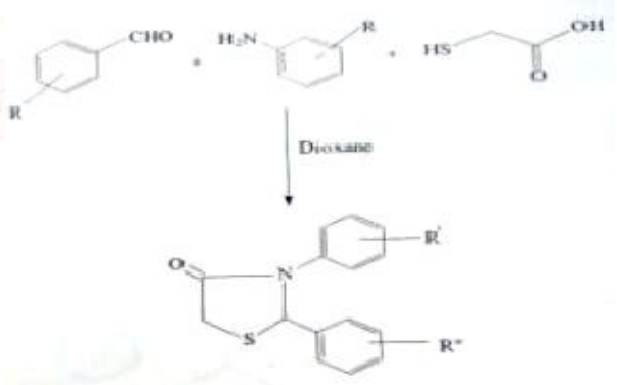
A) Synthesis of 4-thizolidinones from Schiff bases and thioglycolic acid

On condensation a mixture of Schiff bases and thioglycolic acid in dioxane[12] afforded 4-thizolidnone.



B) Synthesis of 4-thizolidinone from thioglycolic acid, aromatic aldehyde and substituted amine:

When a mixture of thioglycolic acid, substituted amine and aromatic aldehyde on condensation, in presence of zinc chloride and dioxane[13] as a solvent, 4-thiazolidinone is obtained as a product.

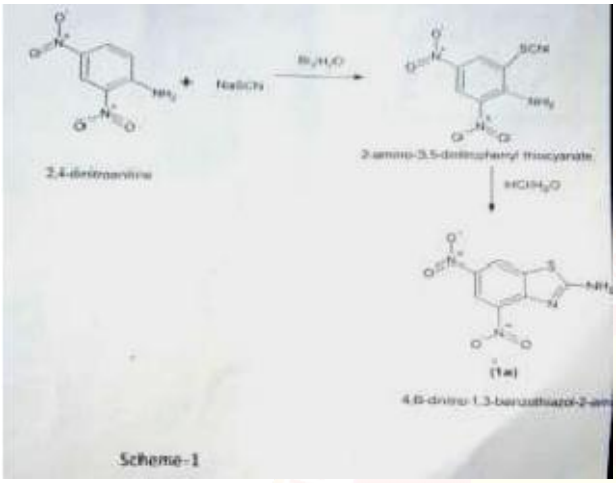


EXPERIMENTAL

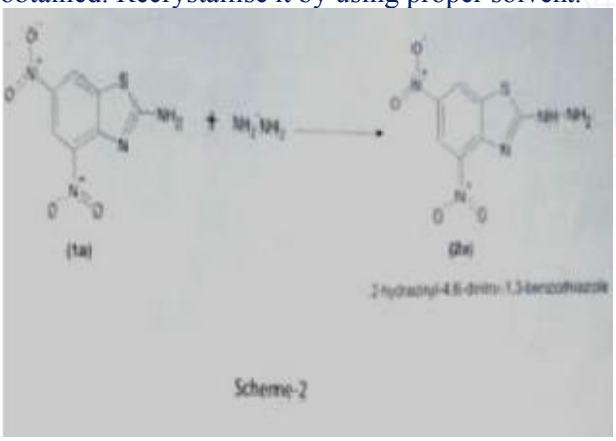
Step 1:- Synthesis of (1a) 4, 6-dinitro-1, 3-benzothiazole-2-amine

Take 9 gm of 2, 4-dinitroaniline in 250 ml conical flask and dissolve in 50 ml glacial acetic acid. In another beaker dissolve 4 gm of sodium thiocynate in minimum quantity of glacial acetic acid.mix

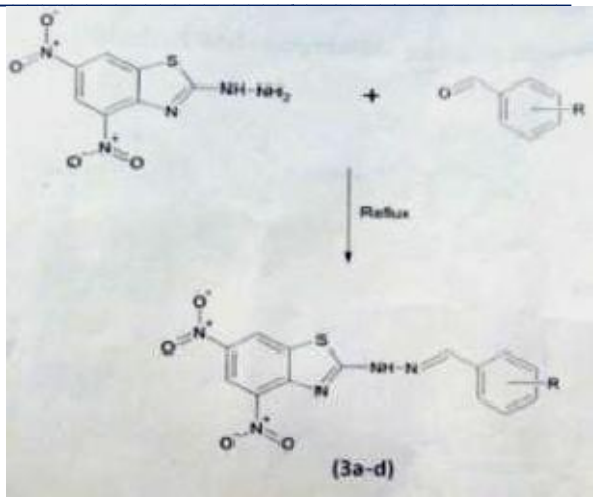
these two solutions and keep this mixture in ice bath by maintaining temperature 0-5^{0}c.
Then in separating funnel take 10 ml bromine in 25 ml glacial acetic acid. Add this bromine solution to reaction mixture drop by drop with constant stirring by maintaining temperature 0-5^{0}c.keep this reaction mixture whole night after complete addition.



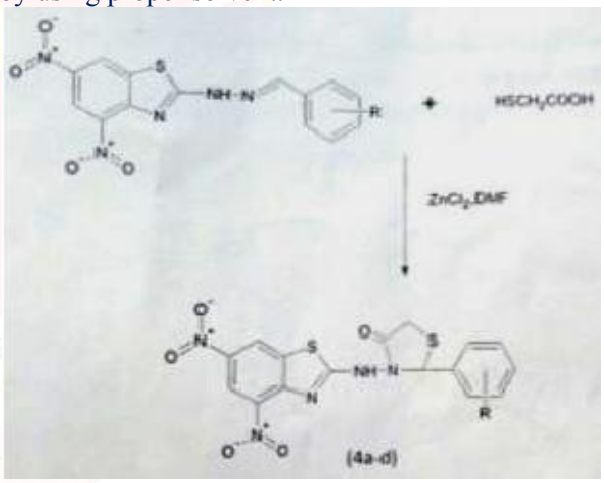
Step 2:- Synthesis of (2a) 2-hydrazinyl-4, 6-dinitro-1, 3-benzothiazole
take 9 ml of hydrazine-hydrate (80%) in a round bottom flask. and keep this round bottom flask in ice bath. then add about 6ml of conc.HCL in drop wise manner. transfer 6ml of yellow crystalline compound and 24 ml ethylene glycol and reflux the content on oil bath at 150-160^{0}c for three hours. cool the reaction mixture and filtrate solid obtained. Recrystallise it by using proper solvent.



Step 3:- Synthesis of Schiff bases (3a-d)
Take hydrazine compound (1.25gm, 0.025m) in ethyl alcohol and aromatic aldehyde (0.025) in ethyl alcohol in separate 100 ml beaker. Mix these two solutions in 100 ml round bottom flask. Attach water condenser and reflux for one and half hours.



Step 4:- Syenthesis of (4a-d) thiozolidinone
Take a mixture of Schiff bases (0.002M) and mercapto acetic acid 3ml and 5ml of DMF solution, now add a pinch of anhydrous Zncl$_2$.
Add a small piece of procelein to it, and reflux directly on wire gauge for six hours. Cool and pour on crushed ice, filter the product and recrystallise by using proper solvent.



Properties of synthesize compound in scheme-4

Sr. No.	Substituents	Molecular formula	Mol. weight	Yield (gm)	M. P.
4a	$N(CH_3)_2$	$C_{19}H_{19}N_6O_5S_2$	475	0.43	145
4b	p-OCH_3	$C_{18}H_{13}N_5O_7S_2$	475	0.76	132

RESULT AND DISCUSSION

The newly synthesized compound is purified by using ethanol. the purity of the compound is checked by the thin layer chromatography and melting point determination on open thisel tube may be uncorrected the compound (thizolidinone)

Schiff base intermediate compound shows absorption peaks at 1600cm^{-1} which gives formation of c=N, while peak at 1715 cm-1 due to aldehydic carbonyl group is disapper which conforms the formation of product Schiff base. the reaction of schiff base with thioglycolic acid of the compound (dimethylamino thizolidinone) shows IR peaks at 1685 cm-1 is due to carbonyl group 3300-3500 cm-1 is due to NH stretching.

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ASSESSMENT OF POTABLE GROUND WATER QUALITY IN HIWARKHED VILLAGE , DIST AMRAVATI

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ABSTRACT

All the water sample were collected from Hiwarkhed region of Morshi Tahsil, of Amravati district (Maharashtra). The people use the water of following sources for drinking as well as for agriculture purposes. Four ground water sample's physico-chemical parameter were determined. The samples were collected from Hiwarkhed region in first week of February 2016. At the same time parameter like pH, EC, TDS, Sodium, Calcium, Magnesium, Chloride, Fluoride,Nitride,Bicarbonate were measured within 15 days from sampling, the parameter were analysed by prescribed standard method. According to Indian Standard Specification it is observed that during the physicochemical analysis drinking water does not crosses the essential and desirable limits.

Keywords: *Potable Ground Water, Physico-Chemical Charectristics, Hiwarkhed Village .*

INTRODUCTION

Nagpur city from Maharashtra state is popularly known as "Orange City" and famous for oranges. All the farmers, stockiest and businessman bring their oranges and distributed through out the world. The actual orange zone begins from Kalmeshwar-Katol-Warud-ShendurjanaGhat-Pusala-Jarud -Morshi-Chandur Bazar-Paratwada -AnjangaoSurji. The agriculture land it is termed as "Orange Belt".In India, most of the population is dependent on groundwater as it is the only source of drinking water supply. The quality of public health depends to a greater extent on the quality of ground water, which should be clean and fresh. This ground water has long been considered as one of the purest forms of water available in nature to meet the overall demand of rural and semi urban people. Most of the people in India depend upon fresh water supplies from dug wells, ponds, bore wells, springs and the like. The consequence of urbanization and industrialization leads to spoil the water. For agricultural purposes ground water is explored in rural areas especially in those areas where other sources of water like dam and river or the canal is available. During last decade, this is observed that the surfacewater get polluted drastically because of increased human activities. [1-3]. KoulNishthaet. al. reported Physico-Chemical analysis of tap water in Millennium city Gurgaon,Haryana, India[4].The source of water pollution in Benisagar dam, municipal, domestic and agricultural wastes. Various physical and chemical parameters like temperature, pH, total alkalinity, D.O, C.O.D, and B.O.D. have been observed to either approach or to have exceeded the permissible limits set for drinking water or for human use have been investigated byH.N. Khare[5].Most of the pH values of the samples were outside therecommended range of 6.5 – 8.5 for drinking water. Predominantly, the ionic dominance patternobserved were Na >Ca> Mg and HCO3 >Cl> SO4, indicating typical cationic characteristics andanionic characteristics of groundwater.Twenty dug wells in each community have studied by B. A. Adelekan[6]. Analysis of Ground Water of Rural Areas of Wardha-City Using Physico – Chemical and Biological parameters has been reported[7].H. L. Yadav studied study assesses the characteristics of mine water in major coal fields by calculating the(WQI) in different sampling location.a quantitative approach of assessment of water quality in coal mines[8].Study of Some Physicochemical Parameters of Drinking Water Sources inTembhurkhedaand Jarud Region Dist. Amravati, MS, India[9].Temperature, pH, electrical conductance, total dissolved solids, fluoride, sodium, potassium, chloride and Hardness calcium hardness, magnesium hardness etc. concentration in ground water was determined in Amdapur in Warudtaluka of Amravati District in Vidarbha region of India[10].

The objective of this study was carried out to assess the quality in terms of physico-chemical

characteristics of potable ground water quality in Hiwarkhed village, Dist-Amravati.

MATERIAL AND METHOD

Polythene bottles of capacity 1 to 2 litters were sterilised by hot water treatment and sunlight treatment and again washed with alcohol are used as a sample collector. Temperature of water samples were measured when samples were collected.The Conductivity meter ,Spectrophotometer, TDS meter, pH meter, Flame photometer were used to analyse the parameters.

STUDY AREA

All the water sample were collected from Hiwarkhed region of MorshiTahsil, of Amravati district (Maharashtra). The people use the water of following sources for drinking as well as for agriculture purposes.

Four water sample's physico-chemical parameter were determined. The samples were collected from Hiwarkhed region in first week of February 2016.

At the same time parameter like pH, EC, TDS, Sodium, Calcium, Magnesium, Chloride, Fluoride, Bicarbonate were measured within 15 days from sampling, the parameter were analysed by prescribed standard method.

Sampling point and place.

Sampling point	**Place**
SAP -1 (Bore Water)	Hiwarkhed
SAP -2 (Well Water)	Hiwarkhed
SAP -3 (Well Water)	Hiwarkhed
SAP -4 (Well Water)	Hiwarkhed

ANALYSIS OF WATER SAMPLES

Sr.No	Parameter	SAP-1	SAP-2	SAP-3	SAP-4
1	Temperature ^0C	31	29	29	29
2	P^H	8.23	7.13	7.49	7.31
3	Conductivity	1.05	1.74	1.77	1.97
4	TDS	478	657	260	387
5	Alkalinity(meq/1) HCO_3^{2-}	1.9	12.54	5.7	9.8
6	Calcium	1.0	5.6	2.0	5.2
7	Magnesium	0.4	2.6	1.0	2.2
8	Chloride	3.8	3.42	1.52	5.7
9	Total Hardness (ppm)	12.04	228.76	67.08	178.88
10	SAR	6.62	1.99	7.71	3.7
11	Fluoride	0.635	0.773	0.437	0.717
12	Nitride	74.1	77.3	53.3	76.1
13	D.O	28.24	31.38	31.52	29.7
14	Sulphate SO_4	1.2	0.9	5.19	3.86

RESULT AND DISCUSSION

1)Temperature :-

Temperature is the important physical parameter which is directly related to chemical reaction in the aquatic ecosystem. In present investigation water temperature ranging between 29^0C to 31^0C.

2) pH:-

The pHof water sample SAP-1,SAP-2,SAP-3, &SAP-4 ranges from 7.13 to 8.23 The P^H of water sample that is S2 is less then other Samples SAP-1,,SAP-3, &SAP-4 is slightly alkaline. A number bases like carbonate, hydroxide contribute to alkalinity.

3) Electric Conductivity

The Specific conductivity of all water sample varied between 1.05 X $10^{-3}$to 1.97 X 10^{-3}mho/cm But specific conductivity of water sample SAP-3 & SAP-4 is more as compared to sample SAP-1 & SAP-2.

4) Total Dissoved Solid :- (TDS)

The total dissolved solid indicates salinity behavior of ground water. Water containing more that 500 mg/L of TDS is not consider desirable for drinking water supplies but in unavoidable cases 1500 mg/L is also allowed.

The TDS value varies from 393 to 1659 mg/L by ISI. The TDS for water sample SAP-1 to SAP-4 ranges from 260 to 657 mg/L.

The TDS of Sample SAP-2 higher than the other sample

5) Alkalinity

Total alkalinity of water sample in terms of HCO_3 varies between 1.9 to 12.54 Mg/L The sample SAP-2 higher than other sample. & other Sample SAP-1,SAP-3& SAP-4 is lower.

6) Calcium

The present of investigation shows the concentration of calcium of the water samples is 18.08 to 29 Mg/L & the water samples is 1.0 to 5.6 Mg/L water samples SAP-2 & SAP-4 containing high concentration of calcium that water sample SAP-1&SAP-3 as classified as 'calcium rich'.

7) Magnesium

The observed value of Magnesium in water sample is varied from 0.4 to 2.6 Mg/L. The observed value of Magnesium for water sample SAP-4 is higher than sample SAP-1,SAP-2 and SAP-3.

8) Chloride

The Stability of Water resources for the irrigational use in agriculture is depending upon salt concentration, especially chloride, content. In water sample reservoir chloride content was in the ranges from 1.52 to 5.7Meq/L. Accordingto WHO

Maximum permissible limit for chloride is 500mg/L.

9) Total Hardness

In the water sample varies from12.4 to 228.76The water samples value of SAP-1&SAP-3 are lower than other samples SAP-2& SAP-4

10)SAR

SAR is an important of parameter of water. The water sample from 1.99 to 7.71 Meg. The water sample SAP-3 is higher than SAP-1,SAP-2& SAP-4 sample.

11) Fluoride

Fluoride is an also important parameter of water. High concentration of Fluoride is cause dental Fluoride the water sample SAP-2 having Fluoride concentration 0.773 Mg/L is higher that sample SAP-1,SAP-3,&SAP-4.

12) Nitride

The values of nitride in water sample is varied from 53.3 to 77.3 Mg/L. The sample SAP-2 is higher that other sample SAP-1,SAP-3& SAP-4.

13) D.O (Dissolved Oxygen)

In the water sample varies from 28.24 to 31.52 Mg/L dissolve Oxygen value of SAP-3 is higher than other samples SAP-1,SAP-2& SAP-4

14) Sulphate

Sulphate is an important parameter of water sample the higher value of water sample SAP-3 & SAP-4 are 5.19 & 3.86 resp.and other value is lower of SAP-1 & SAP-2.

CONCLUSION

From above result and discussion, it is observed that generally all parameters studied do not show undesirable effect on the human being except in few parameters. According to Indian Standard Specificationit is observed that during the physicochemical analysis drinking water does not crosses the essential and desirable limits.

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ACRIDINE SUBSTITUTED [1,2,4]-DITHIAZOLIDINES : A POTENT LARVICIDAL AND SEED GERMINATION PROMOTING AGENT

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ABSTRACT

The series of acridine substituted [1,2,4]-dithiazolidines have been studied for their larvicidal and seed germination promoting activity. The title compounds were prepared by interaction of 1-acridin-9-yl-3-phenyl thiourea with N-phenyl-S-chloroisothiocarbamoyl chloride by grinding method. The structures compounds were confirm on the basis of TLC and IR spectral study.The larvicidal properties were checked against mosquito larvae by taking several dilutions method mortality rate is recorded. Seed germination promoting activity of the test compounds solutions were studied using wheat grains and results clearly revealed that these compounds may acts as a seed germination promoter.

Keywords: *[1,2,4]-dithiazolidines, larvicidal property, seed germination promoting activity.*

INTRODUCTION

Structural properties and various activities of dithiazolidines have been reported[1-3] and enriched with progressive finding about the synthesis of [1,2,4]-dithiazolidines[4-6]. The [1,2,4]-dithiazolidines have been found to possess potent anti-tumour, anti-tuberculosis anti-cancer, and anti-diabetic properties[7-10]. Chemical compounds such as larvicides may acts as insecticides are claimed to be a major factor behind the increase in the agricultural productivity. Nearly all insecticides and larvicides have the potential to significantly alter ecosystems[11].

Many of the major larvicides are inspired by chemical compounds exhibiting bio-activity and one among those is[1,2,4]-dithiazolidine, which has been extensively evaluated in this article[12]. Mosquitoes are one of the deadliest insects in this planet which create biting nuisance and also transmit deadly diseases like malaria, filariasis, yellow fever, dengue, chikungunya and Japanese encephalitis etc. Therefore we made an attempt to utilize these [1,2,4]-dithiazolidines linked with acridine for their larvicidal activity.

The ability of [1,2,4]-dithiazolidines linked with acridine to act as a germination cue in many species has led to widespread interest in this aspect of seed biology. Here, we report the action of these compounds as effective seed germination promoting agents. The purpose of this brief study is an attempt to characterize the regulatory mechanism of seed germination in wheat grains[13].

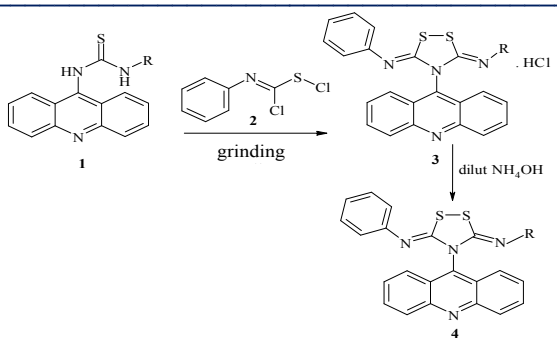
MATERIAL AND METHOD

The melting points of all synthesized compounds were recorded using hot paraffin- bath and are uncorrected. Chemicals used were of A.R. grade. The IR spectra recorded on Perkin-Elmer spectrophotometer in the range 4000-400cm^{-1} in nujol mull and as KBrpellete. Purity of the compounds was checked on silica gel-G plates by TLC.

4-acridin-9-yl-3,5-bis-phenylimino-[1,2,4]-dithiazolidine (**4a**): (Found: C, 68.12; N, 11.28; S, 6.98. Calcd.for $C_{27}H_{18}N_4S_2$: C, 70.12; N, 12.12; S, 7.14%) ;IR : 1550, 1342, 758, 483cm^{-1} (S-S)

4-acridin-9-yl-3-phenylimino-5-o-tolylimino-[1,2,4]-dithiazolidine (**4b**) : (Found: C, 66.91; N, 11.68; S, 12.40. Calcd.for $C_{28}H_{20}N_4S_2$: C, 70.58; N, 11.76; S, 13.44%); IR: 1538, 1332, 763, 458cm^{-1}. 4-acridin-9-yl-3-phenylimino-5-m-tolylimino-[1,2,4]-dithiazolidine (**4c**) : (Found: C, 70.18; N, 11.70 S, 13.21 Calcd for $C_{28}H_{20}N_4S_2$: C, 70.58; N, 11.76; S, 13.44%); IR : 1550, 1338, 755, 470 cm^{-1}.

4-acridin-9-yl-3-phenylimino-5-p-tolylimino-[1,2,4]-dithiazolidine (**4d**) : (Found: C, 66.13; N, 10.89; S, 12.55. Calcd.for $C_{28}H_{20}N_4S_2$: C, 70.58; N, 11.76; S, 13.44%); IR : 1533, 1332, 760, 458 cm^{-1}. 4-acridin-9-yl-3-(2-chlorophenylimino)-5-phenylimino-[1,2,4]-dithiazolidine(**4e**) : (Found: C, 64.93; N, 11.18; S, 13.47. Calcd.for $C_{27}H_{17}N_4S_2Cl$: C, 65.32; N, 11.29; S, 12.90%) ; IR : 1550, 1338, 764, 483 cm^{-1}.



1 2 3 4

LARVICIDAL ACTIVITY

Larvicidal activity for the title compounds was checked by preparing the stock solutions by making up the volume of 0.02M concentration in 100mL distilled water. Slightly warm water was used for preparing the several series of dilutions of 10mL, 30mL, 50mL, 70mL and 100mL to check the toxicity of the compounds in distilled water. 5mL of the dilutions were taken in 50mL of the water containing mosquito larvae used as the test organisms. The setup was kept as it is for a period of 24hrs and the results were recorded the following day. As per the results, the compound 4-acridin-9-yl-3-(2-chlorophenylimino)-5-phenylimino-[1,2,4]-dithiazolidine (**4e**) was found to possess maximum larvicidal activity as compared to the other compounds.

Compounds	**4a**			**4b**			**4c**			**4e**			**4d**		
Dilutions	10	30	50	10	30	50	10	30	50	10	30	50	10	30	50
Mortality Rate %	60	30	20	50	20	20	40	30	10	40	30	20	80	60	50

SEED GERMINATION PROMOTING ACTIVITY

Seed germination promoting activity wasstudied by preparing serial dilutions of the compounds of 10mL, 30mL, 50mL, 70mL,100mL concentrations andwheat grainswere treated with 1mL of test compound solution and then soaked in water for 24 hr. and the result obtained were clearly indicated that 4-acridin-9-yl-3,5-bis-phenylimino-[1,2,4]-dithiazolidine (**4a**) shown maximum promoting activity. Average promoting activity of the compounds (**4a-e**) was also recorded.

Compounds	**Dilutions in ml**					**Promoting Activity %**
	10	30	50	70	100	
4a	+++	++	+	++++	+++++	80
4b	++	+	+	+++	++	50
4c	-	-	-	+	++	40
4d	+++	+	-	-	++	40
4e	++	+	-	+++	+++	60

RESULT AND DISCUSSION

Several 4-acridin-9-yl-3,5-bis-arylimino-[1,2,4]-dithiazolidines (**4a-e**) were studied for their larvicidal and seed germination promoting activity.As a potent larvicidal agent, the compound 4-acridin-9-yl-3-(2-chlorophenylimino)-5-phenylimino-[1,2,4]-dithiazolidine (**4e**) exhibited the maximum mortality rate of 80% and 60% for the 10ml and 30ml dilutions respectively. The compound 4-acridin-9-yl-3,5-bis-phenylimino-[1,2,4]-dithiazolidine (**4a**) was found to posses a remarkable seed germination promoting activity as compared to the other compounds. Beside this, mild reaction conditions, grinding technique, easy work-up procedures and the reaction carried out in catalyst free conditions are the merits of the rout.

CONCLUSION

The larvicidal properties of 4-acridin-9-yl-3,5-bis-arylimino-[1,2,4]-dithiazolidines (**4a-e**)were checked against mosquito larvae by taking several dilutions and some of them found to be highly active with maximum mortality rate of 80%.Seed germination promoting activity of the test compounds solutions were studied against wheat grains and results clearly revealed that these compounds may acts as a good seed germination promoter.

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DEPLETION OF OZONE LAYER CAUSES, EFFECTS & SOLUTIONS

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ABSTRACT

The decrease in Ozone Concentration in the middle layers of the atmosphere mainly in the stratosphere is extremely damaging to life on earth, and is largely caused by emissions of halogenated hydrocarbons produced by man, CFCs, HCFCs, halons Carbon tetrachloride and methyl bromide. For this reason, such substances are commonly referred to as substances that Deplete the Ozone layer (ODS). Effects of the depletion of the Ozone layer on human health cause skin cancer, Infection to immune system effects on aquatic ecosystems, effects on terrestrial ecosystem and finally we see some solutions to Ozone Depletion.

Keywords :*Stratosphere, Chloroflurocarbon, Halons, Hydro-Chloroflurocarbons.*

INTRODUCTION

The first warning voice came from a paper publish in 1974 by scientists Sh. Rowland and M. Molina of the university of California, who showed that chloroflurocarbons (CFCs) used in refrigeration, air conditioning and plastic foam manufacturing were responsible for the rapid destruction of Ozone.

Ozone Destruction Mechanism :-

Substances such as CFCs and other not directly destroy Ozone first they undergo Photolysis, forming hydrogen chloride (HCl) or Chlorine nitrate ($ClONO_2$), molecule that do not react with Ozone directly but slowly decompose, giving among other things a small number of Chlorine atoms (Cl) and of Chlorine monoxide (ClO) molecule that catalyze the destruction of Ozone.

$$Cl + O_3 \rightarrow ClO + O_2$$

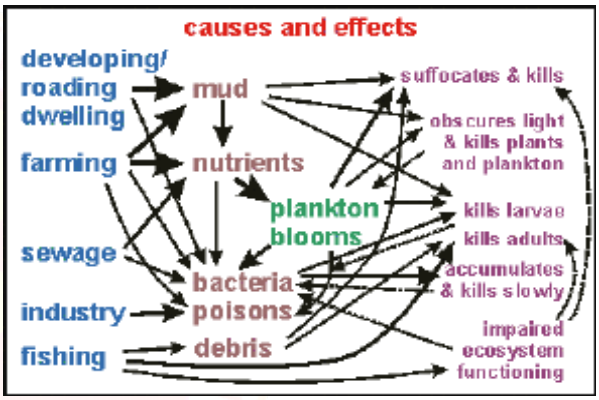
$$ClO + O \rightarrow Cl + O_2$$

Net effect $O_3 + O \rightarrow 2O_2$

The Chlorine atom acts as a catalyst i.e it is not consumed in the reaction, SO_2 it destroyes thousands of Ozone molecule before disappearing. The bromine atom is even more destructive than Chlorine. (about 10 to 100 times more)

Cause of Ozone layers Depletion:

CFCs - They are compounds formed by Chlorine, fluorine and carbon, used as refriger- ants solvents and for the manufacture of spongy plastics. The most common are CFC-11, CFC-12, CFC-113, CFC-114 & CFC-115 which respectively have one Ozone depletion potential of 1, 1, 0.8, 1 and 0.6.

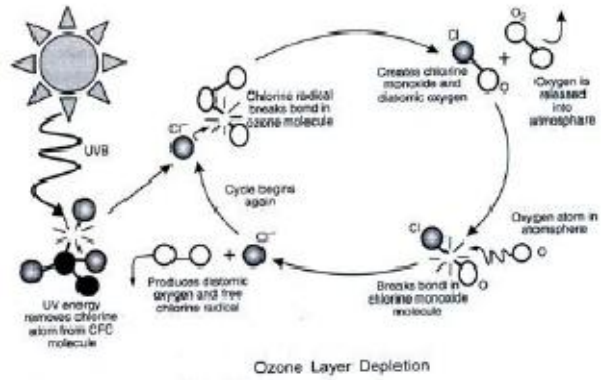


HCFCs - Compounds formed by H, Cl, F & C. They are being used as substitutes for CFCs because many of their properties are similar and are less harmful to Ozone by having a shorter half life and releasing fewer Cl atoms decreases are between 0.01and 0.1. But as they remain harmful to the Ozone layer.

Halons - They are compounds formed by Br, F & C. Because of their ability to put out fires are used in fire extinguishers. Their ability to harm the Ozone layer is very high because they contain Br which is a much more effective atom destroying Ozone than the Cl.

Methyl bromide (CH_3Br) - It is very effective pesticide that is used to fumigate soils and in many crops given its content in Br damages the Ozone layer and has an Ozone depletion potential of 0.6.

Carbon tetra Chloride (CCl_4) - It is a compound that has been widely used as a raw material in many industries. It was no longer used as a solvent when it was found to be caranogenic. Its Ozone depletion potential is 1.2.



Ozone Layer Depletion

Effects of Ozone layers :-

Skin cancer in human -

The most common type of skin cancer called nonmelanoma, is the cause of Expo-sures to UV-B radiation for several years. The increase in skin cancer will be around 250,000 per year.

Effects on the Immune System in human - A persons defenses against infection depends on the strength of his immune system. It is known that exposure to ultraviolet light reduces the effectiveness of the immune system, not only relating to infection to the skin but also to those that can be verifed in other parts of the body.

Effects on aquatic ecosystem -

The loss of phytoplankton, the basic of the marine food chain, has been observed as the cause of the increase in ultraviolet radiation under the Ozone hole in the Antarctic Phytoplankton productivity decreased between 6 and 12 percent mean a loss of 7 million tones of fish production per year.

Effects on terrestrial ecosystem- For some species, an increase in UV-B radiation implies the formation of skin cancer. This has been studied in goats, cows, cats, dogs, sheep and laboratory animal. Also in many plants UV-B radiation alter its shape and damage plant growth, Reduce tree growth, change flowering times, many plants more vulnerable to disease and produce toxic substances. There could even be losses of bio-diversity and species.

Solution to Ozone Depletion :-

1) Desist from using pesticides - Pesticides are great chemicals to rid your farm of pests and weeds, but they contribute enormously to Ozone layer depletion. The sure fire solution toget rid of pests and weeds is to apply natural methods. Just weed your farm manually anduse alternative eco-friendly chemical to alleviate pests.

2) Discourage driving of private vehicles - The easiest technique to minimize Ozone depletion is to limit the number vehicles on the road. These vehicles emit a lot of greenhouse gases that eventually form smog, a catalyst in the depletion of Ozone layer.

3) Utilize environmentally friendly cleaning products - Most household cleaning products are loaded with harsh chemicals that find way to the atmosphere, eventually contributing to degradation of the Ozone layer. Use natural and environmentally friendly cleaning products to arrest this situation.

4) Prohabite the Use of harmful nitrous oxide -

The Monotreal protocol formed in 1989 helped a lot in the limitation of Chloroflurocarbones. However, the protocol never covered Nitrous Oxide, which is a known harmful chemical that can destroy the Ozone layer.

Nitrous Oxide is still in use. Today Government must take action now and out law nitrous Oxide use to reduce the rate of Ozone depletion.

CONCLUSION

The Ozone layer is improving since the Montreal Protocol came into effect to stop and control the use of these chemicals. The Ozone layer depends on UV-C rays from the sun to replenish itself. The Contaminants from chemicals prevents it from getting what it needs to protect the earth from harmful UV-B Rays. The Ozone layer is improving but it will need many years before it the damage is repaired.

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A NOVEL METHOD FOR OXIDATION OF p-BROMO BENZOIC ACID HYDRAZIDE BY THALLIUM(III) IN ACIDIC MEDIUM

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ABSTRACT

The kinetics of oxidation of p-bromo benzoic acid hydrazide by Thaliium(III) in a mixture of perchloric and hydrochloric acid medium at a constant ionic strength has been planned to study iodometrically. The reaction proceeds through formation of complex with reactant, which decomposes in subsequent steps to give product. The increase in $[H^+]$ and $[Cl^-]$ decreases the rate of the reaction. The thermodynamic parameters were also determined and a mechanism is predicted.

Keywords: *kinetics, Thallium (III), Oxidation.*

INTRODUCTION

Aims and Background

During the course of chemical reaction, molecules come closer, atoms change their positions, electron shift takes place and as a result new compounds are formed. A sequence of steps by which the reaction occurs is known as "reaction mechanism". The mechanism of the reaction is known, if the detailed picture of all the individual or elementary processes involving atoms, molecules, radicals, ions and other reactive species are clearly understood.

The mechanism of the reaction gives a detailed picture of the activated complex[1] not only in terms of the constituent molecules but also in terms of geometry.

Thermodynamics is interested only in the initial and final states of a system, the mechanism whereby the system is converted from one state to another and the time is of no importance. Time is not one of the thermodynamic variables. The most important subject in thermodynamics is the state of equilibrium and consequently, thermodynamics is the more powerful tool for investigating the conditions at equilibrium. Kinetics is concerned fundamentally with the details of the process whereby a system gets from one state to another and with the time required for the transition. Equilibrium can also be treated in principle on the basis of kinetics as that situation in which the rates of the forward and reverse reactions are equal. The converse is not true; a reaction rate cannot be understood on the basis of thermodynamics alone.

Therefore, a branch of chemistry, which deals with the study of reaction rates, i.e., chemical kinetics may be considered a more fundamental than thermodynamics.

Literature survey reveals that, although several oxidants are used for oxidation of hydrazides and their mechanisms have been established, there is no report on the oxidation of hydrazides by Thallium(III).

Chemical kinetics, also known as reaction kinetics, is the study of rates of chemical processes. Chemical kinetics includes investigations of how different experimental conditions can influence the speed of a chemical reaction and yield information about the reaction mechanism and transition states, as well as the construction of mathematical models that can describe the characteristics of a chemical reaction.

Thallium oxide is one of the most versatile oxidising agents, reacting with diverse substrates. The oxidation of p-bromo benzoic acid hydrazide (p-BrBAH) continues to be of interest. The oxidant used is a versatile that deserves further investigation. Literature survey reveals that, although several oxidants are used for oxidation of hydrazides and their mechanisms have been established, there is no report on the oxidation of hydrazides by thallium(III).

The hydrazides are pharmaceutically important compounds used as antitubercular[1] and antibacterial[2,3] agents, some of them have been reported to possess anti-inflammatory[4] and diuretic[5] activities. Interest in the use of thallium(III) in the oxidation of organic compounds has increased only recently and research in this regard has not been extensive. The thallium(III) oxidations of several other aliphatic, aryl aliphatic and cyclic ketones have been examined[6]. Some Hydrazides act as antibacterial[7,8]agents, some of them have been reported to possess anti-inflammatory[9] and diuretic[10] activities. An incorporation of

hydrazides[11] has improved applicability in plastics and cable insulators. The small amount of hydrazide is useful in sensitizing electrographic layers made up of polyvinyl carbazole[12] Dihydrazides can be used in cigarrate filters for the selective removal of aldehydes from tobacco smoke.

The objective of the present study is not only to develop method for the oxidation of hydrazides to their corresponding carboxylic acids but also to determine order of reaction and to propose the plausible mechanism of the reaction.

EXPERIMENTAL

Thallium (III) solution was prepared by dissolving Tl_2O_3 (ACROS) in 1.0 moldm^{-3} HCl and the concentration was ascertained by iodometric titration. The benzoic (BAH) and p-Bromo benzoic acid (p-Bromo BAH) hydrazides were prepared from reported[6] procedure and characterized by determining their melting points. Stock solution of benzoic and P-Bromo benzoic acid hydrazides were prepared in 50 % v/v, 1,4-dioxan. Ionic strength was kept constant.

The reactions were carried out in 50 % v/v 1-4 dioxane (s.d.fine.chem) under pseudo first order conditions keeping concentration of hydrazide in large excess over that of the oxidant. The solutions containing the reactants and all other constituents were thermally equilibrated separately, mixed and the reaction mixture was analysed for unreacted thallium (III) iodometrically by titrating against standard thiosulphate. The pseudo-first order rate constants were determined from the slopes of linear log[Tl(III)] versus time plots. The results were reproducible up to ± 5 %. Kinetic runs were followed to about three half-lives of the reactions. Under the experimental condition oxidation of 1,4-dioxan did not occur.

The stoichiometry of the reaction was determined using a known excess of thallium (III) over hydrazide and determining remaining oxidant iodometrically after 24 hrs. The results consistent with equation-(1) were obtained. The corresponding carboxylic acid was characterized by determining it's MP.

$$RCONHNH_2 + 2\,Tl(III) + H_2O \rightarrow R\text{-}COOH + N_2 + 4H^+ + 2\,Tl(I) \quad \ldots (1)$$

RESULTS AND DISCUSSION

The reaction occurs rapidly in perchloric acid medium but in the presence of hydrochloric acid the rate is measurable. Therefore the reaction was carried out in a mixture of both the acids. The effect of reactants on the reaction was studied at constant [HCl] and [$HClO_4$] of 0.1 mol dm^{-3} each and ionic strength of 0.6 mol dm^{-3}. Concentration of oxidant was varied from $6.4x10^{-4}$ to $6.4x10^{-3}$ mol dm^{-3} keeping the [hydrazide] constant at $1x10^{-1}$ mol dm^{-3}.Since,the pseudo first order rate constants were fairly constant ($3.83 \pm 0.1x10^{-4}$ S^{-1} for BAH at 25^{0}C and $1.8 \pm 0.1x10^{-4}$ S^{-1} for P-Br BAH at 25^{0}C), the order with respect to [oxidant] is unity. The effect of [hydrazide] was studied between the concentration range from $1x10^{-2}$ to $1x10^{-1}$ mol dm^{-3} keeping the [oxidant] constant at $3.0x10^{-3}$ mol dm^{-3}.The pseudo first order rate constants increases with increase in concentration($0.62 \pm 0.1x10^{-4}$ S^{-1} for BAH at 25^{0}C and $0.22 \pm 0.1x10^{-4}$ S^{-1} for BAH and p-Br BAH at 25^{0}C) and the order with respect to hydrazide is found to be fractional (0.64 for BAH and 0.42 for p-Bromo BAH).

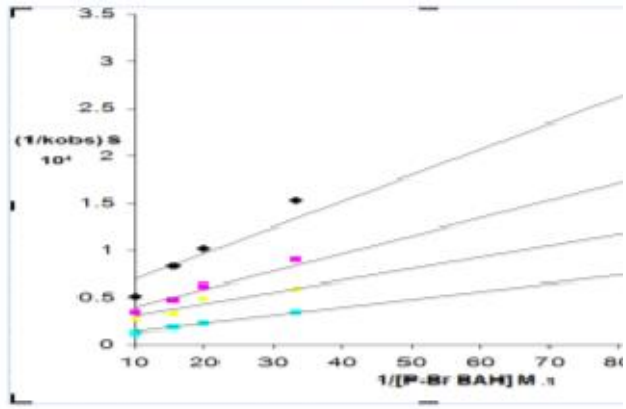
To study the effect of [H^+] and [Cl^-],[oxidant], [hydrazide] and ionic strength were kept as $3.0x10^{-3}$,$1x10^{-1}$ and 0.6 mol dm^{-3} respectively. To vary [H^+] and [Cl^-], $HClO_4$ and NaCl were used. Increase in [H^+] from $7x10^{-2}$ to $5.4x10^{-1}$ mol dm^{-3} decreases 10^{-4} k(S^{-1}) from 4.22 to 0.15 for BAH at 25^{0}C and 1.10 to 0.040 for p-Br BAH at 25^{0}C.Increase in [Cl^-] from $7x10^{-2}$ to $5.4x10^{-1}$ mol dm^{-3} decreases 10^{-4} k(S^{-1}) from 2.80 to 0.095 for BAH at 25^{0}C and 0.60 to 0.035 for p-Br BAH at 25^{0}C. The relative permittivity was varied by changing the 1,4-dioxan content from 5 to 40 % v/v. The rate was found to decrease with decrease in relative permittivity.

Added acrylonitrile in the concentration range 0.5 to 2.5vol.% by keeping concentrations of oxidant,reductant,perchloric acid,hydrochloric acid and ionic strength fixed did not produce any precipitate due to polymerization of the added acrylonitrile on the pseudofirst order rate constants indicating absence of free radicals.

In the present study since there was no effect of added acrylonitrile, a free radical scavenger, rules out the possibility of such free radical formation, therefore the reaction proceeds with two electron transfer.

The order in thallium(III) was found to be unity as evidenced by the linearity of the pseudo-first-order plots of log[Tl(III)] versus time for all the runs studied whereas, the order in the hydrazide were found to be fractional. Such fractional order in substrate concentration is due to the prior complex formation equilibrium between the reactants.

Michaelis-Menten plot for P-Br-BAH



The linearity of Michealis - Menten plots of $1/k_{obs}$ versus 1/[Hydrazide] with an intercept is also in support of the complex formation. Therefore, in agreement with the results obtained, the mechanism of the reaction can be represented as in Scheme 1.

Tl^{III} + Hydrazide $\rightleftharpoons$ Complex K_c

Complex $\rightarrow$ Tl^{I} + Intermediate k_l

Tl^{III}+Intermediate $\rightarrow$ Tl^{I} + Products fast

Scheme 1

The rate according to Scheme1 is given by equation 1. Since, total $[Tl^{III}]$ exists in the form of free $[Tl^{III}]$ and the complex (Equation 2) therefore, the $[Tl^{III}]$ free is given by Equation 4. The overall rate law is now expressed by Equation 5 and the Pseudo-first order rate constant k_{obs}, by Equation 6.

$$\text{Rate} = k_1 [\text{Complex}] = k_1 K_c [\text{Hydrazide}]_{free} [Tl^{III}]_{free} \quad (1)$$

$$[Tl^{III}]_{total} = [T1^{III}]_{free} + [\text{Complex}] \quad (2)$$

$$[Tl^{III}]\ total = [T1^{III}]_{free} + K_c [\text{Hydrazide}] [Tl^{III}]_{free} \quad (3)$$

$$[T1^{III}]_{free} = [Tl^{III}]_{total}/(1 + K_c [\text{Hydrazide}]) \quad (4)$$

$$\text{Rate} = k_1 K_c [\text{Hydrazide}] [Tl^{III}]_{free} \quad (5)$$

$$k_{obs} = k_1 K_c [\text{Hydrazide}]/(1 + K_c [\text{Hydrazide}]) \quad (6)$$

Rate law 6 is verified by plotting $1/k_{obs}$ against 1/[Hydrazide] at four different temperatures and from the slopes and intercepts of these plots the values of k_1 and K_c were calculated and are given in Table no. 01.

The effect of hydrogen and chloride ion concentrations on the reaction is due to the protonation of hydrazides and different chloro – complexes of thallium (III) present in the solution. Hydrazides are known to be protonated in acid medium according to Equation 7.

$RCONHNH_2 + H^+ \rightleftharpoons RCONHNH_3^+$ K_H (7)

Therefore, total [Hydrazide] can be expressed by Equation 8 and the free [Hydrazide] by equation 10.

$$[\text{Hydrazide}]_{total} = [\text{Hydrazide}]_{free} + [\text{Hydrazide}]_{protonated} \quad (8)$$

$$[\text{Hydrazide}]_{total} = [\text{Hydrazide}]_{free} + K_H [\text{Hydrazide}]_{free} \quad (9)$$

$$[\text{Hydrazide}]_{free} = [\text{Hydrazide}]_{total} /(I + K_H [H^+]) \quad (10)$$

Since the rate of reaction decreases as the $[H^+]$ increases, free hydrazide is the active species which is also supported by the fact that there was no effect of ionic strength on the reaction indicating one of the reactant is neutral. Thallium(III) forms strong complexes with chloride ions of the formula $TlCl_n^{3-n}$ where n is the number of chlorides complexes with thallium (III) as represented in equilibrium 11 to 14. The values of respective stability constants are $K_1 = 1.38 \times 10^8$, $K_2 = 3.98 \times 10^{13}$, $K_3 = 6.02 \times 10^{15}$ and $K_4 = 1.0 \times 10^{18}$ $mol^{-1}dm^3$.

$T1^{3+} + C1^- \rightleftharpoons TlCl^{2+}$ K_1 (11)

$TlCl^{2+} + Cl^- \rightleftharpoons TlCl_2^+$ K_2 (12)

$TlCl_2^+ + Cl^- \rightleftharpoons TlCl_3$ K_3 (13)

$TlCl_3 + Cl^- \rightleftharpoons TlCl_4$ K_4 (14)

In presence of 0.03 M chloride ion concentration all the thallium(III) will exists as $TlCl_2^+$ and its concentration can be expressed by Equation 15. The $[TlCl_2]^+_{free}$ can now be given by equation 17 where, $\beta_1 = K_3/K_2 = 151$ and $\beta_2 = K_4/K_3 = 166$. Further, using Equations 16 and 17 the concentrations of $[TlCl_2]^+_{free}$, $TlCl_3$ and $TlCl_4^-$ were calculated at different chloride ion concentrations and compared with the change in rate constant as the chloride ion concentration varies.

$$[\text{TI (III)}]_{total} = [T1Cl_2^+]_{total} = [T1C1_2^+]_{free} + [T1C1_3] + [T1C1_4^-] \quad (15)$$

$$[T1C1_2^+]_{total} = [T1C1_2^+]_{free} (1+\beta_1[Cl^-] + \beta_2[Cl^-]^2) \quad (16)$$

$$[T1C1_2^+]_{free} = [T1Cl_2^+]_{total} / (1 + \beta_1 [Cl^-] + \beta_2[Cl^-]^2) \quad (17)$$

The concentrations of both of $[TlCl_2^+]_{free}$ and $TlCl_3$ parallel the values of rate constants as the

chloride ion concentration changes but the order in chloride ion concentration is – 1.5, which makes $[TlCl_2^+]_{free}$ as the only active species of the oxidant.

$TlC1_2^+ + K_c$ Hydrazide Complex

Complex → RCONNH + $T1C1_2^-$ + H^+ (k_1)

$RCONNH+H_20+T1C1_2^+ \rightarrow RCOOH+N_2+2H^+ + T1C1_2^-$ (fast)

Where R - Alkyl group

Scheme 2

The mechanism considering $TlCl_2^+$ of oxidant and free hydrazide of the substrate as the active species can now be represented by scheme 2 with respective rate law and the expression for the pseudo-first order rate constants by Equations 18and 19. The rate law 19 was verified by plotting $1/k_{obs}$ against 1/[Hydrazide] and $1/k_{obs}$ against $[H^+]$ which were found to be linear. From the slopes and intercepts of these plots the values of K_c and K_H were determined.

$$\text{Rate} = \frac{k_1 K_c [\text{Hydrazide}]_{total} [T1C1_2^+]_{total}}{(1+K_c[\text{Hydrazide}])(1+K_H[H^+])(1+\beta_1[Cl^-]+\beta_2[Cl^-]^2)}$$

$$k_{obs} = \frac{k_1 K_C [\text{Hydrazide}]_{total}}{(1+K_c[\text{Hydrazide}])(1+K_H[H^+])(1+\beta_1[Cl^-]+\beta_2[Cl^-]^2)}$$

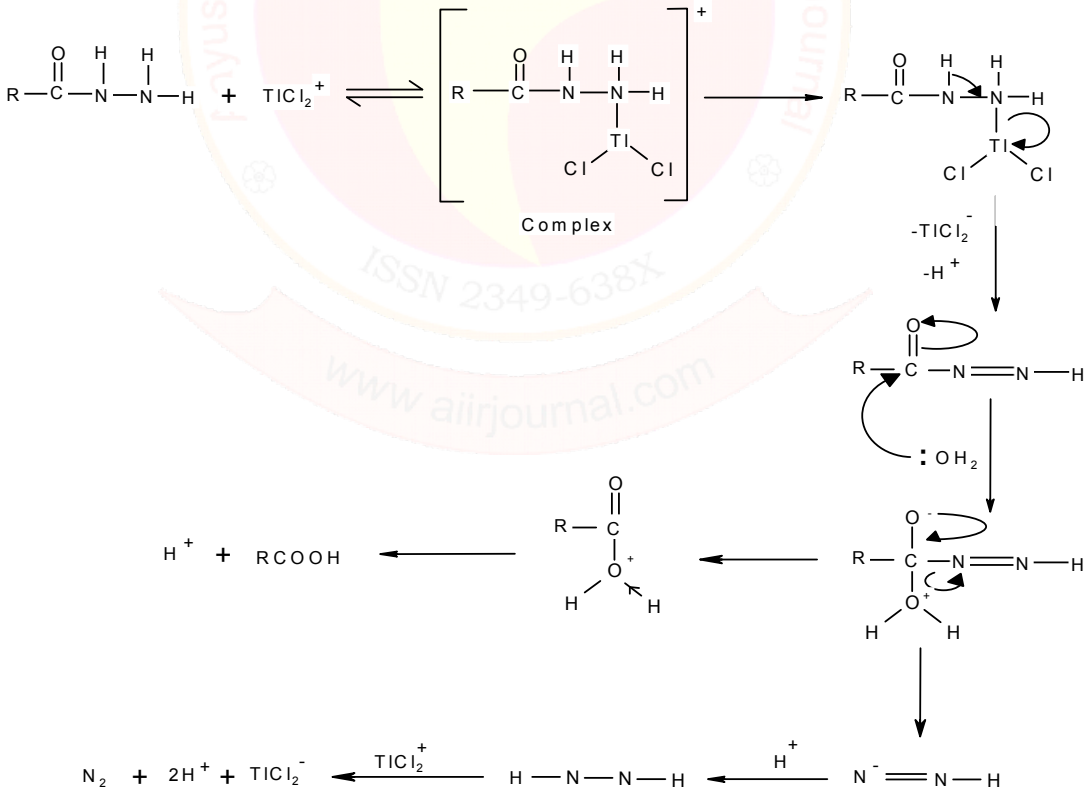
The values of K_c are given in Table The electrophilic character of thallium(III)-chloro cmplex increases as $TlCl_2^+ > TlCl_3 > TlCl_4$ thus making the former species as the reactive ones.

Table No.01 – values of Kc and k_1

[HCl] = 0.1 moldm^{-3}, [$HClO_4$] = 0.1 moldm^{-3},
[Tl^{III}] = 3.0 X 10^{-3} mol dm^{-3}, I = 0.6 mol dm^{-3}

Hydrazide	Kc. (mol dm $^{-3}$)				10^4 x k_1 (s^{-1})			
	15°C	20°C	25°C	30°C	15°C	20°C	25°C	30°C
BAH	58.09	52.50	45.69	38.00	1.20	2.00	2.58	4.42
P-Bromo BAH	9.70	9.50	9.70	9.70	1.15	1.67	2.54	3.36

MECHANISM



Scheme 3

The detailed mechanism involves electrophilic substitution on the nitrogen of the hydrazide with the formation of N-Tl bond which decomposes in the subsequent step with direct two-electron transfer from hydrazide to thallium to give an intermediate followed by fast steps(Scheme 3). Such N-T1 bond formation has been postulated during thallium(III) oxidation of nitrogen containing compounds[13-18].

The activation parameters, with respect to slow step, k_1, $\Delta H^{\#}$ (KJ mol^{-1}), $\Delta G^{\#}$ (KJ mol^{-1}) and $\Delta S^{\#}$ ($JK^{-1}mol^{-1}$) were found to be 27.20,30.11 and –72.38 respectively for benzoic acid hydrazide and 20.70,58.71 and –97.69 for p-Bromo benzoic acid hydrazide. Considerable decrease in the entropy of activation is due to formation of more ordered transition state as shown in scheme 3. The mechanism involves neutral hydrazide as the active substrate thus the reaction is unaffected by the change in the ionic strength. The increase in 1, 4 – dioxan content in the reaction medium decreases; the rate such an effect of the solvent is due to the stabilization of the complex formed between reactants in a medium of low relative permittivity[19-22].

RELATIVE REACTIVITIES OF HYDRAZIDES

The order of reactivities of Benzoic and substituted benzoic acid hydrzides under investigation is –

p-Bromo BAH < BAH

The observed sequence can be attributed to various possibilities and factors. The Slowest rate of oxidation of p-Bromo benzoic acid hydrazide is due to electron withdrawing mesomeric effect of bromo group. Hence, it is evident that the rate of reaction is retarded by electron withdrawing group(s).

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SYNTHESIS AND ANTIBACTERIAL ASSAY OF IMIDAZOLE DERIVATIVES OF ARYL SUBSTITUTED 1,3-THIAZINES

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ABSTRACT

The synthesis, spectral analysis and biological activities of 4-(2'-hydroxy-3',5'-dichlorophenyl)-6-(4''-nitrophenyl)-2-[4-(2-hydroxy-3,5-dichlorophenyl)-2-mercapto-imidazolo]-3-6-dihydro-1,3-thiazine (A'') have been carried out. In this case 4-(2'-hydroxy-3',5'-dichlorophenyl)-6-(4''-nitrophenyl)-2-imino-3,6-dihydro-1,3- thiazine (A), 4-(2'-hydroxy-3',5'-dichlorophenyl)-6-(4''-nitrophenyl)-2-[(2-hydroxy-3,5-dichlorophenyl)ethanonylamino]-3-6-dihydro-1,3-thiazine (A') & 4-(2'-hydroxy-3',5'-dichlorophenyl)-6-(4''-nitrophenyl)-2-[4-(2-hydroxy-3,5-dichlorophenyl)-2-mercapto-imidazolo]-3-6-dihydro-1,3-thiazine (A'') have been screened. The compounds A was synthesized from 2'-hydroxy-3,5-dichlorophenyl-4-(4''-nitrophenyl) chalcone (a) by the action of thiourea, while (A'') was synthesized from (A) by reaction with α-bromo,2-hydroxy-3,5 dichloroacetophenone to get 4-(2'-hydroxy-3',5'-dichlorophenyl)-6-(4''-nitrophenyl)-2-[(2-hydroxy-3,5-dichlorophenyl)ethanonylamino]-3-6-dihydro-1,3-thiazine (A'). Further (A') on treatment with KSCN was dissolved in acetic acid gave (A''). The compound (a) was synthesized from 2'-hydroxy-3',5'-dichloroacetophenone by the action of p-nitrobenzaldehyde in ethanol and 40% NaOH. The newly synthesized imidazole derivatives of aryl Substituted 1,3-thiazines were screened for their antibacterial activities against some Gram positive Staphylococcus aureus and Streptococcus sp. and Gram negative Pseudomonas sp. and Solmonella typhi pathogens. All the newly synthesized compounds were found to be active against test pathogens.

Keywords : *Chalcone, thiazine, thiourea, α-bromo,2-hydroxy-3,5 dichloroacetophenone , KSCN was dissolved in acetic, antibacterial assay.*

INTRODUCTION

Thiazine is a six membered ring system, which contains two hetero atoms [N and S] placed in a heterocyclic ring at 1, 3 positions. Many workers have synthesized different 1,3-thiazines. The researchers have reported the synthesis of several thiazines[1-6] and also their potent biological activities such as blood platelet aggregation inhibitors[7], antibacterial[8-9] antiallergic[10], anticholesterenic[11] and antifungal[12]. Moreover thiazine nucleus is a pharmacophore of cephalosporin that occupy a very important place in the field, of antibiotics and drug chemistry. Chalcones and their analogues having α, β-unsaturated carbonyl system are very versatile substrates for the evolution of various reactions and physiologically active compounds. The reaction of thiourea with α, β-unsaturated ketones also results in the formation of 1,3-thiazines.

Human pathology deals with the cause, etiology, resulting losses and control or management of the human diseases. The chlorosubstituted thiazines with amino group at position 2 in the ring exhibit promising biological activities[13-16], antimicrobial[17], antibacterial activity against gram positive & gram negative bacteria[18],biological activity[19], herbicidal activity[20]

Previous studies confirmed that metal nanoparticles are effective against pathogens & insects. Nanoparticles can be used in the preparation of new formulations like nanomedicines as anticancer drugs like drugs for human breast cancer[21] & liver cancer[22].

Taking into consideration the widespread applications of synthesized Imidazole derivatives of thiazine as antibacterial, antifungal, antiparasitic agents in the field of medicine and agriculture, it was thought interesting to synthesize some new Imidazole derivatives of thiazine and study their antibacterial activity.

The newly synthesized Imidazole Derivatives of thiazines were screened for their antibacterial activities against some *Gram positive Staphylococcus aureus and Streptococcus sp.* and *Gram negative Pseudomonas sp.* and *Solmonella typhi* pathogens. All the newly synthesized compounds were found to be active against test pathogens.

EXPERIMENTAL

All the glassware's used in the present work were of pyrex quality. Melting points were determined in hot paraffin bath and are uncorrected.The purity of compounds was monitored on silica gel coated TLC plate. IR spectra were recorded on Perkin-Elmer spectrophotometer in KBr pelletes, H^1 NMR spectra on spectrophotometer in $CDCl_3$ with TMS as internal standard. UV spectra were recorded in nujol medium. The analytical data of the titled compounds was highly satisfactory. All the chemicals used were of analytical grade. All the solvents used were purified by standard methods. Physical characterisation data of all the compounds is given in Table 1.

Table 1 : Characterisation data of newly synthesized compounds :

Compounds	Molecular formula	M.P. in ^{0}C	% of yield	% of element				
				C	H	N	S	Cl
	$C_8H_6O_2Cl_2$	54	80	47.90/48	2.95/3			34.15/34.58
a	$C_{15}H_9O_4NCl_2$	250	70	53.10/53.25	2.40/2.66	3.98/4.18		21/21.77
A	$C_{16}H_{11}O_3N_3Cl_2S$	120	70	48.50/48.60	2.35/2.53	10.40/10.63	8/8.10	17/17.92
A’	$C_{25}H_{15}O_6N_3Cl_4S$	128	70	56.80/56.25	2.98/2.92	8.25/8.20	6.77/6.82	28/28.73
A”	$C_{26}H_{18}O_5Cl_4N_4S_2$	165	70	46.80/46.42	2.70/2.67	8.40/8.33	9.56/9.52	21.60/21.13

2’-Hydroxy 3’,5’-dichloroacetophenone :

2’-Hydroxy-5-chloroacetophenone (3g) was dissolved in acetic acid (5 ml), and mixed with sodium acetate (3g). To this reaction mixture chlorine in acetic acid reagent (40 ml; 7.5 w/v) was added dropwise with stirring. The temperature of the reaction mixture was maintained below 20^{o}C. The mixture was allowed to stand for 30 minutes and then poured into water. A pale yellow solid thus obtained was filtered, dried and crystallized from ethanol to yield the compound.

Preparation of 2'-hydroxy-3,5-dichlorophenyl-4-(4”-nitrophenyl)-chalcone (a) :

2’-Hydroxy-3',5'-dichloroacetophenone (0.1 mol) was dissolved in ethanol (50 ml) and p-nitrobenzaldehyde (0.1 mol) was added gradually to the solution and the mixture was heated to boiling. Then aquous sodium hydroxide solution [40%; 40 ml] was added dropwise with constant stirring. The mixture was stirred mechanically at room temperature for about half an hour and kept for overnight. It was then acidified by hydrochloric acid (10%) solution . The solid product thus separated, was filtered, and washed with sodium bicarbonate (10%) followed by water. Finally it was crystallized from ethanol acetic acid mixture to get the compound (a).

Preparation of 4-(2'-hydroxy-3',5'-dichlorophenyl)-6-(4''-nitrophenyl)-2-imino-3,6-dihydro-1,3-thiazine (A) :

2'-Hydroxy-3,5-dichlorophenyl-4-(4”-nitrophenyl)-chalcone (a) (0.01 mol) and thiourea (0.02 mol) were dissolved in ethanol (30 ml). To this aquous KOH solution (0.02 mol) was added,. The reaction mixture was refluxed for three hours, cooled and diluted with water then acidified with 1:1 HCl. The product thus obtained was crystallized from ethanol to get the compound (A).

Preparation of 4-(2’-hydroxy-3’,5’-dichlorophenyl)-6-(4”-nitrophenyl)-2-[(2-hydroxy-3,5-dichlorophenyl)ethanonylamino]-3-6-dihydro-1,3-thiazine (A’):

A stoichiometeric mixture of 4-(2’-hydroxy-3’-5'-dichlorophenyl)-6-(4''- nitrophenyl)-2-imino-3-6-dihydro-1,3- thiazine (A) and α-bromo,2-hydroxy-3,5 dichloroacetophenone was dissolved in ethanol and refluxed for one hour. It was then cooled, diluted with water and crystallized from ethanol to get the compound (A’).

Preparation of 4-(2’-hydroxy-3’,5’-dichlorophenyl)-6-(4”-nitrophenyl)-2-[4-(2-hydroxy-3,5-dichlorophenyl)-2-mercapto-imidazolo]-3-6-dihydro-1,3-thiazine (A’’):

A stoichiometeric mixture of 4-(2’-hydroxy-3’,5’-dichlorophenyl)-6-(4”-nitrophenyl)-2-[(2-hydroxy-3,5-dichlorophenyl)ethanonylamino]-3-6-dihydro-1,3-thiazine (A’) and KSCN was dissolved in acetic acid and refluxed for 4.5 hours, cooled and diluted with water. The product thus separated was crystallized from ethanol to get the compound (A’’).

The newly synthesized compounds were characterised on the basis of elemental analysis,

molecular determination, UV, IR, NMR. spectral data.

The UV, IR, and NMR spectral data :-

Compound (A) :

UV : Spectrum No. 1

The UV-Vis spectrum of the compound A reported in dioxane showed λ_{max} value 495 nm corresponding to n→π* transition.

IR (KBr) :- Spectrum No. 2

3365.34 cm^{-1} (-OH phenolic), 2925.2cm^{-1} (aliphatic -C-H stretching), 3068.24cm^{-1} (aromatic -C-H stretching), 3017.30 cm^{-1} (-N-H stretching), 1648.7 cm^{-1} (-C=N stretching), 1342 cm^{-1} [(C-N) (C-NO_2) stretching], 738.13 cm^{-1} (C-Cl stretching in aliphatic), 1177.7 cm^{-1} (C-Cl) stretching in aromatic).

PMR :- Spectrum No. 3

∂ 1.2 (s, 1H, -C-**H**) ; ∂ 2.7 (s, 1H, =N -**H**) ; ∂ 3.6 (s, 1H, =N-**H**) ; ∂ 3.7 (s, 1H, =C-**H**) ; ∂ 7.6 to 8.1 (m, 6H, Ar-**H**) ; ∂ 12.6 (s, 1H, O-**H**)

Compound (A'') :

UV : Spectrum No. 4

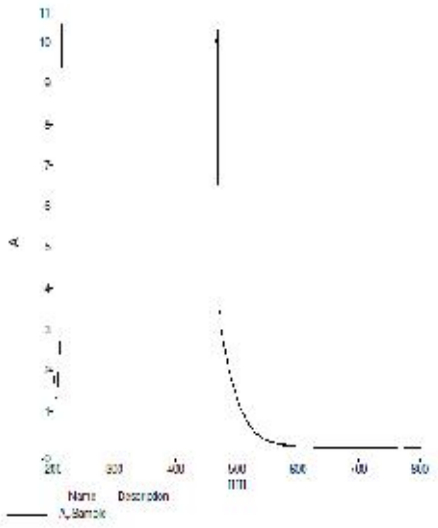
The UV-Vis spectrum of the compound A" reported in dioxane showed λ_{max} value 492 nm corresponding to n→π* transition.

IR (KBr) :- Spectrum No. 5

1605.23 cm^{-1} (=C=O stretching), 3391.39 cm^{-1} (-OH phenolic), 2925.36cm^{-1} (aliphatic -C-H stretching), 3068.24cm^{-1} (aromatic -C-H stretching), 1435 cm^{-1} (-C=N stretching), 1365.14 cm^{-1} [(C-N) (C-NO_2) stretching], 738.15 cm^{-1} (C-Cl stretching in aliphatic), 2547.43 cm^{-1} (-S-H stretching),1605.23 cm^{-1} (=C=O stretching),

PMR :- Spectrum No. 6

∂ 7.7 to 7.9 (m, 8H, Ar-**H**) ; ∂ 12.5 (s, 1H, O-**H**)



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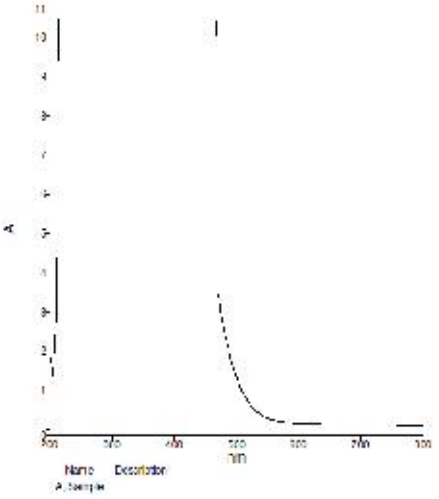

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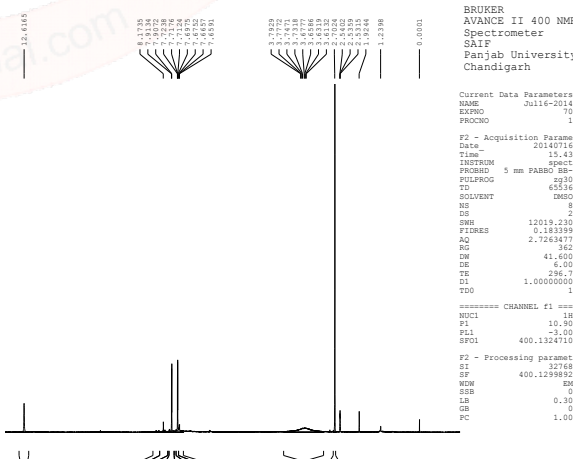

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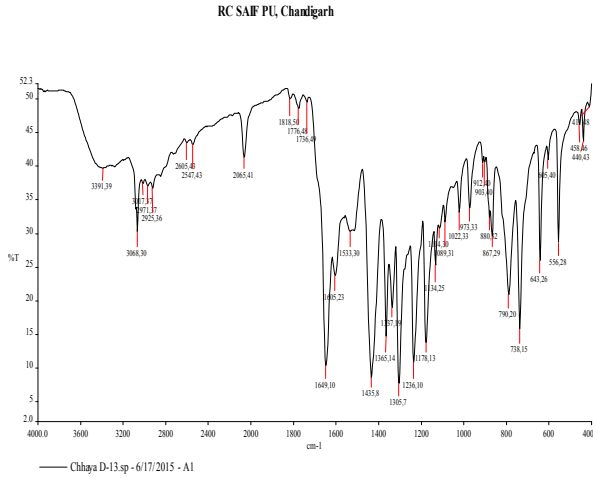

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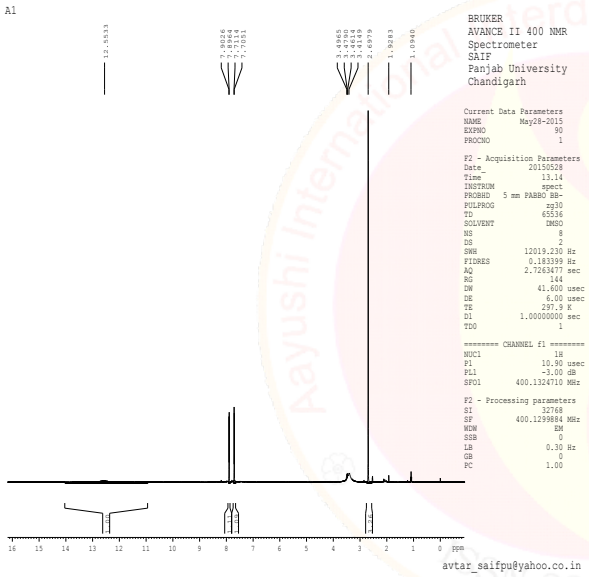

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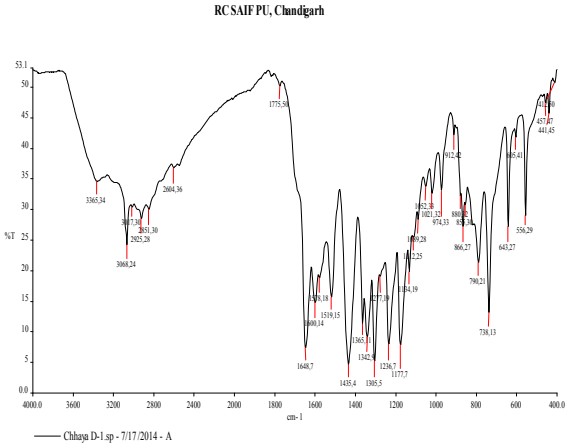

Spectrum No. 06

All the newly synthesised compounds (a, A, A' & A") were screened for their antibacterial activity against some *Gram positive* pathogens viz. *Staphylococcus aureus* and *Streptococcus sp.* and some *Gram negative* pathogens viz. *Pseudomonas sp.* and *Solmonella Typhi.* at conc.of 1000 µm gentamycine as a standard.DMF was used as solvent control using agar plate techniques. The zones of inhibition formed were measured in mm and are shown in table -2.

RESULTS AND DISCUSSION

The newly synthesized compounds (a, A, A' & A") were found to be active against test pathogens. However a further detailed study in the light of Medical sciences is advised.

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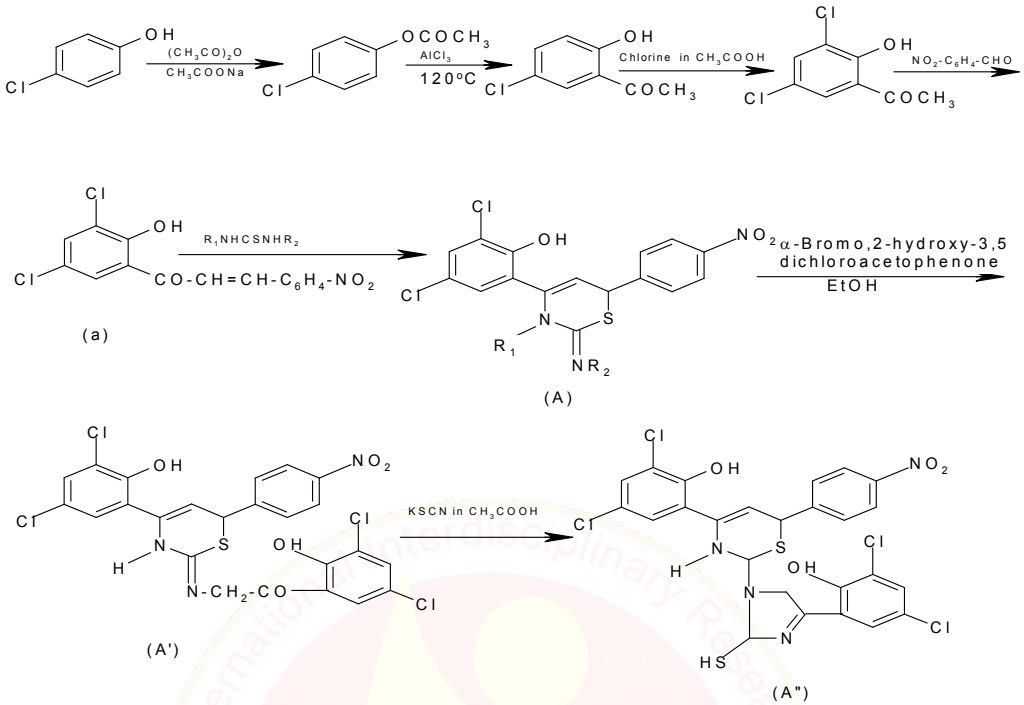
Scheme:



Where :

1) R_1 = -H, -C_6H_5
2) R_2 = -H, -C_6H_5

TABLE-2

ANTIBACTERIAL ACTIVITIES OF SYNTHESISED NEW COMPOUNDS

Zones of inhibition (mm)

Compounds	Staphylococcus aureus	Streptococcus spp.	Pseudomonas spp.	Solmonella typhi	Salmonella paratyphi
a	14	12	14	14	15
A	14	15	15	14	17
A’	14	15	15	16	16
A”	16	17	16	17	16

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"SYNTHESIS AND STUDY OF IMIDAZOLE DERIVATIVES OF ARYL SUBSTITUTED 1,3-THIAZOLES AND THEIR NANOPARTICLES ON PHYTOTIC GROWTH OF SOME VEGETABLE CROPS"

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ABSTRACT

The synthesis, spectral analysis and biological activities of 5-(2'-hydroxy-3',5'-dichlorophenyl)-4-(4''-nitrobenzoyl)-2-[4-(2-hydroxy-3,5-dichlorophenyl)-2-mercapto-imidazolo]-1,3-thiazole (D'') have been carried out. In this case 5-(2'-hydroxy-3',5'-dichlorophenyl)-4-(4''-nitrobenzoyl)-2-amine-1,3-thiazole (D), 5-(2'-hydroxy-3',5'-dichlorophenyl)-4- (4''-nitrobenzoyl)-2- [(2-hydroxy-3,5- dichlorophenyl) ethanonylamino]-1,3-thiazole (D') & 5-(2'-hydroxy-3',5'-dichlorophenyl)-4-(4''-nitrobenzoyl)-2-[4-(2-hydroxy-3,5- dichlorophenyl)-2-mercapto- imidazolo]- 1,3- thiazole (D'') have been screened. The compounds (D), and was synthesized from 1-(2'- hydroxy- 3',5'-dichlorophenyl)- 2- bromo- 3-(4''-nitrophenyl)-1,3 propanedione (a_4) by the action of thiourea, while (D'') was synthesized from (D) by reaction with α-bromo,2-hydroxy-3,5 dichloroaceto phenone to get 5-(2'-hydroxy-3',5'-dichlorophenyl)-4-(4''-nitrobenzoyl)-2-[(2-hydroxy-3,5-dichlorophenyl)ethanonylamino]-1,3-thiazole (D'). Further (D') on treatment with KSCN was dissolved in acetic acid gave (D''). The nanoparticles of the compounds D, D'and D'' have been prepared by using ultrasonic technique. The titled compounds and their nanoparticles were screened for their growth promoting activity on some vegetable crop plants viz.. Momordica charantia-L-Bitter guard (Karela), Lagneria siceraria-snake guard (Lavki), Luffa cylindrica L-sponge guard (Gilke) and Benincasa hispida-Pumpkin (Kohle).

Keywords : *Chalcone, thiazine, thiourea, α-bromo,2-hydroxy-3,5 dichloroacetophenone , KSCN was dissolved in acetic, growth promoting activities.*

INTRODUCTION

Heterocyclic nucleus plays an important role in medicinal chemistry and it is a key template for the growth of various therapeutic agents. Thiazole is a heterocyclic compound featuring both a nitrogen atom and sulfur atom as part of the aromatic five-membered ring. Thiazoles and related compounds are called1,3-azoles (nitrogen and one other hetero atom in a five-membered ring). They are isomeric with the 1,2- azoles, the nitrogen and sulphur containing compound being called isothiazoles. Thiazoles are found naturally in the essential vitamins. Molecules that possess sulfur atoms are important in living organisms. Chalcones and their analogues having α, β - unsaturated carbonyl system are very versatile substrates for the evolution of various reactions and physiologically active compounds. Plant Pathology or Phytopathology deals with the cause, etiology, resulting losses and control or management of the plant diseases.

It is the scientific study of diseases in plants caused by pathogens (infectious organisms) and environmental conditions (physiological factors). Organisms that cause infectious disease include *fungi*, *oomycetes*, *bacteria*, *viruses*,*phytoplasmas*, *protozoa*, *nematod-es* and *parasitic plants*. The researchers[1-6] have reported the synthesis of several thiazoles and also their potent biological activities such as antimicrobial[7], antibacterial[8], antifungal[9], fungicidal[10] and insecticidal agent[11].

Now a days nanotechnology is a promising field of interdisciplinary research It opens up a wide array of opportunities in various fields like medicine, pharmaceuticals, electronics and agriculture. Since the physiochemical properties of nanoforms vary greatly, it becomes important to examine the effect of nanoparticles on microorganisms to harness the benefit of this technology in the plant protection especially against phytopathogens. Previous studies confirmed that metal nanoparticles are effective against pathogens, insects and pests. Hence nanoparticles can be used in the preparation of new formulations like nanomedicines for the diseases like diagnosing & treating cancer[12], enhancing outer membrane of living cells[13], inhibiting tumour growth in human

being[14], brain cancer [15]. Nanotechnology has the potential to revolutionize the different sectors of agriculture and food industry with modern tools for the treatment of diseases by providing the medicines for rapid diseases like malaria[16], cancer & HIV[17], breast cancer[18], localized diseases[19].

In the present study, the chlorosubstituted 1,3-thiazines & their imidazole derivatives (D, D', & D") have been prepared along with their nanoparticles and screened them for their growth promoting activity on some vegetable crop plants viz. *Momordica charantia-L-Bitter guard (Karela), Lagneria siceraria-snake guard (Lavki), Luffa cylindrica L-sponge guard (Gilke) and Benincasa hispida-Pumpkin (Kohle).*

EXPERIMENTAL

All the glasswares used in the present work were of pyrex quality. Melting points were determined in hot paraffin bath and are uncorrected. The purity of compounds was monitored on silica gel coated TLC plate. IR spectra were recorded on Perkin-Elmer spectrophotometer in KBr pelletes, H^1 NMR spectra on spectrophotometer in $CDCl_3$ with TMS as internal standard. UV spectra were recorded in nujol medium. The analytical data of the titled compounds was highly satisfactory. All the chemicals used were of analytical grade. All the solvents used were purified by standard methods. Physical characterisation data of all the compounds is given in Table 1.

2',5'-Dichloroacetophenone:

2-Hydroxy-5-chloroacetophenone was dissolved in acetic acid (5 ml), Sodium acetate (3g) was added to the reaction mixture and then chlorine in acetic acid reagent (40 ml; 7.5 w/v) was added dropwise with stirring. The temperature of the reaction mixture was maintained below 20^0C. The mixture was allowed to stand for 30 minutes. It was poured into cold water with stirring. A pale yellow solid then obtained was filtered, dried and crystallized from ethanol to get the compound 2',5'-dichloroacetophenone.

Preparation of 2'-hydroxy-3',5'-dichlorophenyl-4-(4''-nitrophenyl) chalcone (a):

To the boiling solution of the 2-hydroxy-3,5-dichloroacetophenone (0.01 mol) and p-nitrobenzaldehyde (0.01 mol) in ethanol (20 ml) a 40% solution of NaOH was added gradually. The reaction mixture was stirred mechanically at room temperature for 1 hour and kept steady for 6 to 8 hours, followed by decomposition with ice cold HCl (1:1). The yellow granules thus obtained were filtered, washed with 10% $NaHCO_3$ solution and then crystallized from ethanol-acetic acid mixture to obtain the compound (a).

Preparation of 1-(2'-hydroxy-3',5'-dichlorophenyl)-2,3-dibromo-3-(4"-nitrophenyl)-propan-1-one (a_1):

2'-Hydroxy-3',5'-dichlorophenyl-4-(4"-nitrophenyl)chalcone (a) (0.001 M) was suspended in bromine-glacial acetic acid reagent (25% w/v) (6.4 ml).

The reagent was added dropwise with constant stirring and the reaction mixture was kept at room temperature for about 30 minutes. The solid product, thus separated, was filtered and washed with a little petroleum ether to get the compound (a_1).

Preparation of 2-(4"-nitrophenyl)-6,8-dichloroflavone (a_2):

1-(2'-Hydroxy-3',5'-dichlorophenyl)-2,3-dibromo-3-(4"-nitrophenyl)-propan-1-one (a_1) (0.01 mol) was dissolved in ethanol (25ml). To this, aqueous KOH solution (25 ml) was added. The reaction mixture was refluxed for 1 hour, cooled and diluted with water. The product thus separated was filtered and crystallized from ethanol to get the compound (a_2).

Preparation of 1-(2'-hydroxy-3',5'-dichlorophenyl)-3-(4"-nitrophenyl)-1,3-propandione (a_3):

2-(4"-Nitrophenyl)-6,8-dichloro-flavone (a_2) (0.01 mol) was dissolved in ethanol (25ml). To this, aqueous solution of HCl (25 ml) was added. The reaction mixture was then refluxed for 1 hour, cooled, and diluted with water. The product, thus separated, was filtered, and crystallized from ethanol to get the compound (a_3).

Preparation of 1-(2'-hydroxy-3',5'-dichlorophenyl)-2-bromo-3-(4"-nitrophenyl)-1,3-propanedione (a_4):

1-(2'-Hydroxy-3',5'-dichlorophenyl)-3-(4"-nitrophenyl)-1,3-propandione (a_3) (0.01 mol) was dissolved in a mixture of ethanol and dioxane. To this, calculated amount of liquid bromine was added. The product was not separated even after standing for one hour. It was then diluted with water, washed with water several times and

extracted with ether. The solvent was removed under reduced pressure to get the white solid of the compound (a_4).

Preparation of 5-(2'-hydroxy-3',5'-dichlorophenyl)-4-(4"-nitrobenzoyl)-2-amine-1,3-thiazole (D):

1-(2'-Hydroxy- 3',5'-dichlorophenyl)-2-br omo- 3-(4"-nitrophenyl)-1,3-propandione (a_4) (0.01 mol) and thiourea (0.01 mol) was dissolved in ethanol (25 ml). To this , aqueous KOH solution (0.02 mol) was added. The reaction mixture was then ref luxed for 3 hours, cooled, diluted w ith water and acidif ied w ith conc. HCl. The product thus separated was filtered and crystallized from ethanol to get the compound (D).

Preparation of 5-(2'-hydroxy-3',5'-dichlorophenyl)-4-(4"-nitrobenzoyl)-2-[(2-hydroxy-3,5-dichlorophenyl)ethanonylamino]-1,3-thiazole (D'):

A stoichiometeric mixture of 5-(2'-hydroxy-3',5'-dichlorophenyl)-4-(4"-nitrobenzoyl)-2-amine-1,3-thiazole (D) and α-bromo,2-hydroxy-3,5 dichloroacetophenone was dissolved in ethanol and refluxed for one hour. It was then cooled, diluted with water and crystallized from ethanol to get the compound (D').

Preparation of 5-(2'-hydroxy-3',5'-dichlorophenyl)-4-(4"-nitrobenzoyl)-2-[4-(2-hydroxy-3,5-dichlorophenyl)-2-mercapto-imidazolo]-1,3-thiazole (D"):

A stoichiometeric mixture of 5-(2'-hydroxy-3',5'-dichlorophenyl)-4-(4"-nitrobenzoyl)-2-[(2-hydroxy-3,5-dichlorophenyl)ethanonylamino]-1,3-thiazole (D') and KSCN was dissolved in acetic acid and refluxed for 4.5 hours, cooled and diluted with water. The product, thus separated, was crystallized from ethanol to get the compound (D").

The UV, IR, and NMR spectral data :-

Compound (D) :

UV : Spectrum No. 1

The UV-Vis spectrum of the compound D reported in dioxane showed λ_{max} value **475** nm corresponding to n→π* transition.

IR (KBr) :- Spectrum No. 2

3335.23 cm^{-1} (-OH phenolic), 2923.23cm^{-1} (aliphatic -C-H stretching), 3074.22cm^{-1} (aromatic -C-H stretching), 3788.41 cm^{-1} (-NH_2 stretching), 1566. cm^{-1} (-C=N stretching), 1229 cm^{-1} [(C-N=) stretching], 740.23 cm^{-1} (C-Cl stretching in aliphatic), 1053.26 cm^{-1} (C-Cl) stretching in aromatic).

PMR :- Spectrum No. 3

∂ 3.4 (hump, 2H, -N-**H**) ; ∂ 6.7 (d, 1H, -CH=C-**H**) ; ∂ 6.8 (d, 1H, -C**H**=C-H) ; ∂ 7.1 to 8.3 (m, 6H, Ar-**H**) ; ∂ 12.6 (s, 1H, O-**H**)

Compound (D")

UV : Spectrum No. 4

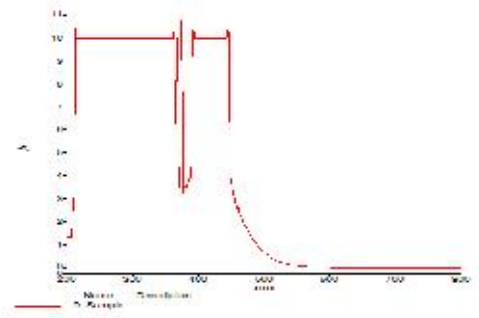
The UV-Vis spectrum of the compound D" reported in dioxane showed λ_{max} value 398 nm corresponding to n→π* transition.

IR (KBr) :- Spectrum No. 5

1650. cm^{-1} (=C=O stretching), 3429 cm^{-1} (-OH phenolic), 2920.20 cm^{-1} (aliphatic -C-H stretching), 3068 cm^{-1} (aromatic -C-H stretching), 1435 cm^{-1} (-C=N stretching), 1365 cm^{-1} [(C-N) (C-NO_2) stretching], 738 cm^{-1} (C-Cl stretching in aliphatic), 2547.38 cm^{-1} (-S-H stretching).

PMR :- Spectrum No. 6

Spectrum No. 01



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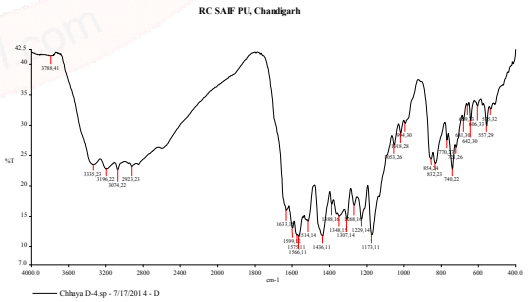

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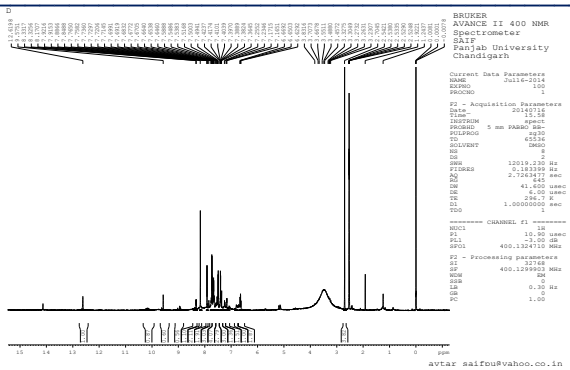

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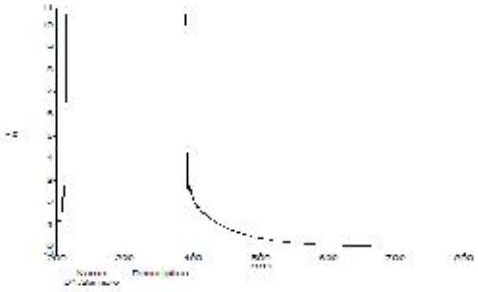

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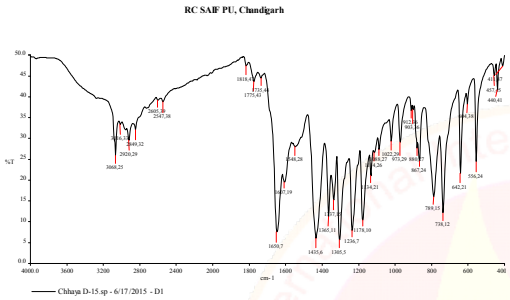


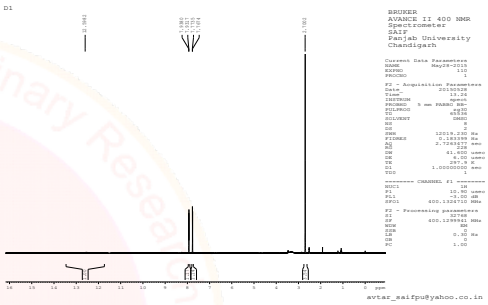
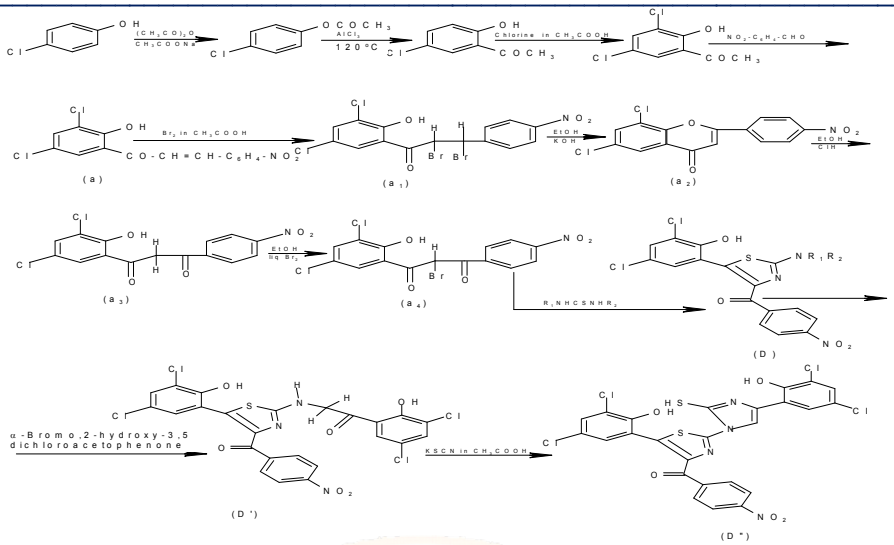


Table 1 : Characterisation data of newly synthesized compounds :

Compounds	Molecular formula	M.P. in ^{0}C	% of yield	% of element					
				C	H	N	S	Cl	Br
	$C_8H_6O_2Cl_2$	54	80	47.90/48	2.95/3			34.15/34.58	
a	$C_{15}H_9O_4NCl_2$	250	70	53.10/53.25	2.40/2.66	3.98/4.18		21/21.77	
a_1	$C_{15}H_9O_4NCl_2Br_2$	72	70	36.01/36.14	1.78/1.80	2.78/2.81		14.20/14.25	32.08/32.12
a_2	$C_{15}H_7O_4NCl_2$	132	60	53.14/53.57	2.07/2.08	4.13/4.16		21.03/21.13	
a_3	$C_{15}H_9O_5NCl_2$	117	50	50.74/50.84	2.45/2.54	3.90/3.95		20.03/20.05	
a_4	$C_{15}H_8O_5NCl_2Br$	78	60	41.12/41.57	1.78/1.84	3.20/3.23		16.08/16.39	18.34/18.47
D	$C_{16}H_{11}O_4N_3Cl_2S$	170	70	46.50/46.60	2.56/2.66	10.05/10.19	7.67/7.76	17.20/17.23	
D’	$C_{24}H_{13}O_6N_3Cl_4S$	105	70	46.90/46.98	2.08/2.12	6.80/6.85	5.2/5.22	23.10/23.16	
D”	$C_{25}H_{12}O_5N_4Cl_4S_2$	115	70	51/51.47	2.00/2.05	9.56/9.60	10.9/10.97	12.00/12.17	



Scheme :

Where :

1. R_1 = -H, -C_6H_5 2. R_2 = -H, -C_6H_5

Growth Promoting Effect on some Vegetable crop Plants :- The experimental set up of the study was devided into two parts: (i) Seed treatment (ii) Field experiment.

(i) Seed treatment :- With a view to safeguard dormant seed's potential from harmful external agencies, the seeds of the test plants were treated by test compounds before sowing.

(ii) Field experiment :- Pregerminated quality seeds of *Momordica charantia L-Bitter guard (Karela), Lagneria siceraria -snake guard (Lavki), Luffa cylindrica L-Sponge guard-(Gilke) and Benincasa hispida -Pumpkin (Kohle)* were procured from Department of Horticulture, Dr. PDKV, Akola. The beds of cotton soil, 2.5 x 2.5 m size were prepared in an open field. The sowing of seeds of all four test vegetable crop plants were done in separate beds and irrigated periodically. The plants from each bed were devided into two groups i.e. A and B and designated as "Control" and "Treated" group plants respectively. The plants from group B were sprayed with the solution of test compounds at weekly intervals. The field experiments were conducted to compare the treated plants of group B with untreated plants of controlled group A. In this context, the observations were recorded on 7, 14, 21, 28, 35, 42, 45, 56, 63, 70, 77, 84, 91 days after sowing corresponding to early vegetative, late vegetative, flowering, pod filing and pod maturation, with special reference to number of leaves and height of shoots. The results of field's experiments are tabulated in the tables 2, 3 and 4.

Table (2) : Activity of the test compounds D,D' and D" :

Table No. (02)

5-(2'-Hydroxy-3',5'-dichlorophenyl)-4-(4"-nitrobenzoyl)-2-amine-1,3-thiazole (D)

Periodicity of Observations [in days]	*Momordica charantia* (Bitter guard) (Karela)				*Lageneria siceraria* (Snake guard) (Lavki)				*Luffa cylindrica* (Sponge guard) (Gilke)				*Benincasa hispida* (Pumpkin) (Kohle)			
	Shoot height		No. of leaves		Shoot height		No. of leaves		Shoot height		No. of leaves		Shoot height		No. of leaves	
	C	T	C	T	C	T	C	T	C	T	C	T	C	T	C	T
7	2.5	1.5	2	2	2.5	1.5	2	2	4.5	6	2	2	20	21	2	3
14	7	2.7	2	2	7.5	10	2	2	10	8	2	2	20	23	2	3
21	25	28	7	9	8	11.2	2	2	15	10	3	5	23	24.5	3	5
28	35	60	9	12	9	15	3	4	16	18	4	6	25	27	4	6
35	47	69	10	16	11	20	4	5	20	24.5	5	8	27	35	5	8
42	51	75	12	14	17	34	5	6	25	32	7	9	30	37	6	9
49	55	81	14	16	25	37	6	7	30	35	8	11	35	40	8	12
56	60	104	16	21	28	47	7	8	35	42	10	13	38	50	10	14
63	67	112	18	24	31	51	8	10	40	46	12	14	42	54	12	16
70	72	120	20	28	34	55	9	11	45	50	14	16	46	60	14	18
77	75	127	22	30	36	58	10	13	50	54	16	20	49	65	16	22
84	80	132	24	32	38	61	11	14	55	59	18	20	53	79	18	24
91	82	175	26	47	40	72	12	17	57	72	20	24	56	83	20	26

Table No. (03)
5-(2'-hydroxy-3',5'-dichlorophenyl)-4-(4"-nitrobenzoyl)-2-[(2-hydroxy-3,5-dichlorophenyl)ethanonylamino]-1,3-thiazole (D')

Periodicity of Observations [in days]	*Momordica charantia* (Bitter guard) (Karela)				*Lageneria siceraria* (Snake guard) (Lavki)				*Luffa cylindrica* (Sponge guard) (Gilke)				*Benincasa hispida* (Pumpkin) (Kohle)			
	Shoot height		No. of leaves		Shoot height		No. of leaves		Shoot height		No. of leaves		Shoot height		No. of leaves	
	C	**T**	**C**	**T**	**C**	**T**	**C**	**T**	**C**	**T**	**C**	**T**	**C**	**T**	**C**	**T**
7	2.5	1.5	2	2	2.5	1.5	2	2	4.5	4	2	2	20	20	2	3
14	7	1.7	2	2	7.5	5	2	2	10	5	2	2	20	22	2	3
21	25	15	7	6	8	8	2	3	15	12	3	7	23	23	3	4
28	35	33	9	10	9	9.5	3	4	16	23	4	7	25	27	4	6
35	47	40	10	12	11	12	4	5	20	30	5	8	27	32	5	8
42	51	60	12	15	17	14	5	6	25	40	7	11	30	37	6	9
49	55	72	14	17	25	17	6	6	30	44	8	13	35	39	8	10
56	60	90	16	21	28	30	7	8	35	52	10	15	38	52	10	14
63	67	96	18	25	31	35	8	9	40	57	12	17	42	60	12	16
70	72	102	20	32	34	38	9	11	45	62	14	19	46	64	14	18
77	75	108	22	34	36	39	10	14	50	66	16	28	49	70	16	19
84	80	123	24	35	38	47	11	17	55	69	18	30	53	76	18	20
91	82	127	26	38	40	49	12	19	57	72	20	32	56	78	20	24

RESULT AND DISCUSSION

The titled compounds and their nanoparticles were screened for their growth promoting activity on test vegetable crop plants viz, *Momordica charantia-L-Bitter guard (Karela), Lagneria siceraria-snake guard (Lavki), Luffa cylindrica L-sponge guard (Gilke) and Benincasa hispida-Pumpkin (Kohle).*

When a comparison of morphological characters was made between those of treated and control group plants, it was interesting to note that all the treated plants exhibited significant shoot growth and considerable increase in the number of leaves as compared to those of untreated ones.

Impact of Compound 5-(2'-Hydroxy-3',5'-dichlorophenyl)-4-(4"-nitrobenzoyl)-2-[4-(2-hydroxy-3,5-dichlorophenyl)-2-mercapto-imidazolo]-1,3-thiazole (D") on phytotic growth of *Momordica charantia*

Control Treated

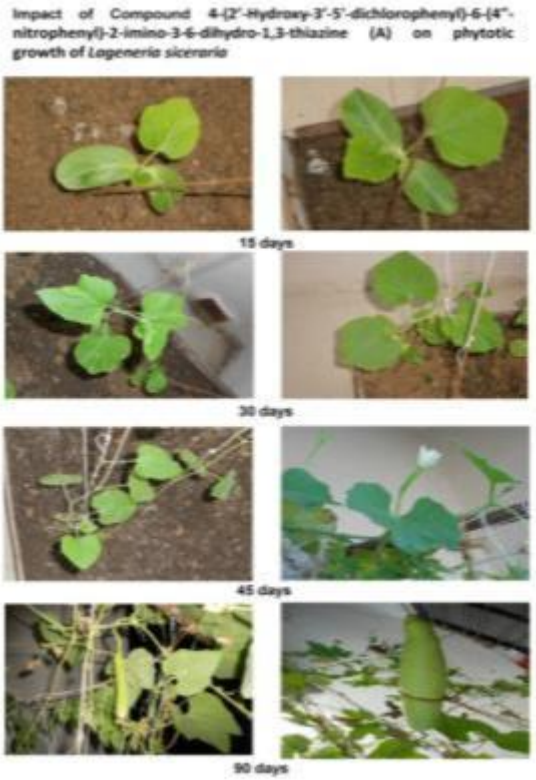
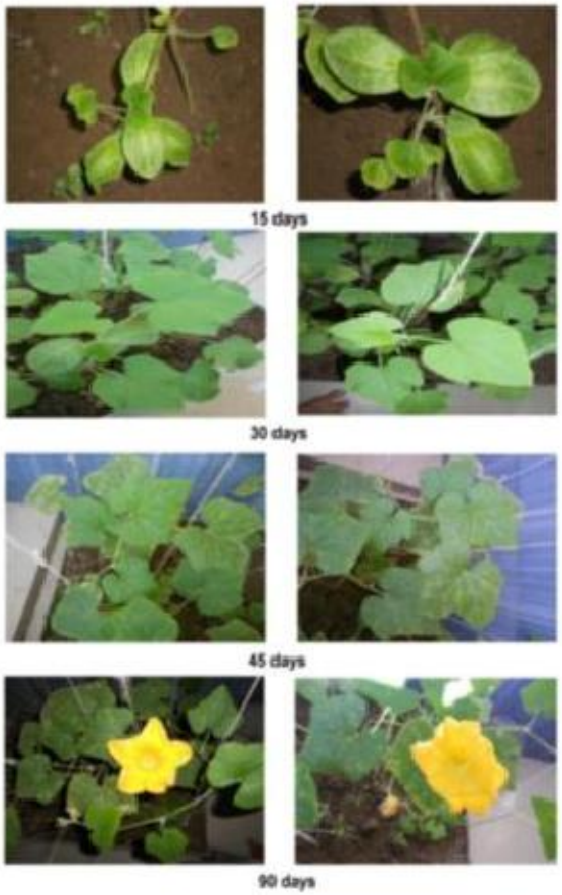


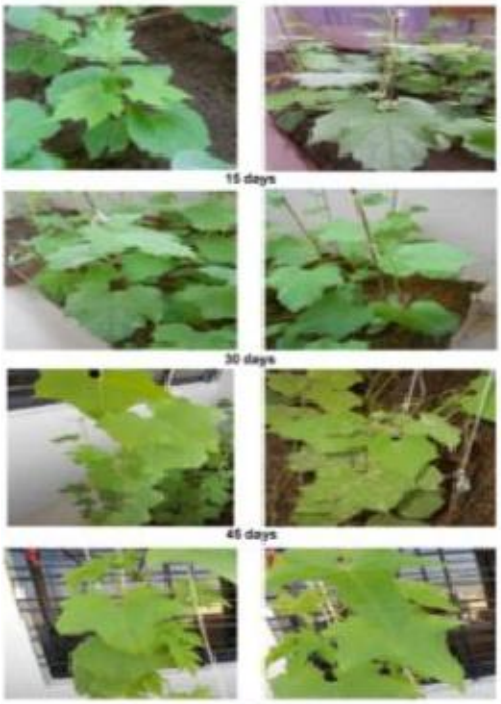
Table No. (0
5-(2'-Hydroxy-3',5'-dichlorophenyl)-4-(4"-nitrobenzoyl)-2-[4-(2-hydroxy-3,5-dichlorophenyl)-2-mercapto-imidazolo]-1,3-thiazole (D")

Periodicity of Observations [in days]	*Momordica charantia* (Bitter guard) (Karela)				*Lageneria siceraria* (Snake guard) (Lavki)				*Luffa cylindrica* (Sponge guard) (Gilke)				*Benincasa hispida* (Pumpkin)(Kohle)			
	Shoot height		No. of leaves		Shoot height		No. of leaves		Shoot height		No. of leaves		Shoot height		No. of leaves	
	C	**T**	**C**	**T**	**C**	**T**	**C**	**T**	**C**	**T**	**C**	**T**	**C**	**T**	**C**	**T**
7	2.5	1.5	2	2	2.5	1.5	2	2	4.4	4	2	2	20	20.5	2	3
14	7	2.7	2	2	7.5	7	2	2	10	8	2	2	20	22.5	2	3
21	25	28	7	10	8	12	2	4	15	11	3	5	23	23.5	3	4
28	35	40	9	11	9	19	3	6	16	25	4	6	25	25	4	5
35	47	47	10	12	11	26	4	7	20	38	5	9	27	30	5	7
42	51	52	12	15	17	42	5	8	25	49	7	12	30	34	6	8
49	55	60	14	18	25	48	6	8	30	53	8	14	35	39	8	9
56	60	81	16	22	28	52	7	9	35	62	10	17	38	45	10	12
63	67	96	18	24	31	55	8	10	40	65	12	18	42	50	12	14
70	72	104	20	28	34	60	9	11	45	70	14	20	46	54	14	16
77	75	108	22	30	36	63	10	13	50	73	16	23	49	59	16	18
84	80	115	24	32	38	65	11	15	55	78	18	25	53	65	18	20
91	82	119	26	36	40	68	12	17	57	82	20	27	56	68	20	22

Impact of Compound 4-(2'-Hydroxy-3'-5'-dichlorophenyl)-6-(4''-nitrophenyl)-2-imino-3-6-dihydro-1,3-thiazine (A) on phytotic growth of *Benincasa hispida*



Impact of Compound 4-(2'-Hydroxy-3'-5'-dichlorophenyl)-6-(4''-nitrophenyl)-2-imino-3-6-dihydro-1,3-thiazine (A) on phytotic growth of *Luffa cylindrica*



Impact of Compound 4-(2'-Hydroxy-3'-5'-dichlorophenyl)-6-(4''-nitrophenyl)-2-imino-3-6-dihydro-1,3-thiazine (A) on phytotic growth of *Momordica charantia*

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PHYSICO-CHEMICAL ANALYSIS OF WATER OF BEMLA DAM BABULGAON, DISTRICT YAVATMAL

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ABSTRACT

The Physico chemical parameter of surface water from Bemla dam of Babhulgaon Dist Yavatmal is determined during may to sep 2016 for 15 locations . The Physico chemical parameters are pH, electrical conductance, DO, BOD, COD, TDS, total hardness, total alkalinity, turbidity; anions includes chlorides, sulphates , nitrates etc. All the parameters are found to be within the permissible limit. The laboratory test of the collected water samples were performed for analysis of various parameters .The methods employed for the analysis as per standard methods recommended by APHA, WHO, ICMR. The obtained values are compared with the standard limits. The results of this study reveal that the physico-chemical parameters are with in the maximum permissible limit of WHO with some slight variations in some parameters. Hence, water is safe and suitable for domestic, irrigation and drinking purposes.

Keywords: *Bembla dam; surface water; physico chemical parameters; water quality.*

INTRODUCTION

Water is an indispensable part of biological life of mankind. Water is liquid of life, as there can be no life without water. Pure water is a real curse for living beings. Man during course of his civilization has settled in places where plenty of water was available. But with increase of population and in exploitation of natural resources for his own benefit, he has behaved in a wild manner by creating problem of pollution hazardous not only to aquatic life but also to his own life Dams are the major part of freshwater resources. All over the water huge reservoirs have been constructed mainly to meet irrigational needs, drinking purposes, industrial, and domestic use etc. Analysis of physico-chemical parameters of water is essential, to assess the quality of water for the best usage like irrigation, drinking, bathing, fishing, industrial processing and so on. Water quality deals with the physical, chemical and biological characteristics in relation to all other hydrological properties. The present investigation has been undertaken to assess the water quality of Babhulgaon dam Tq Babhulgaon district Yavatmal. The Yavatmal district lies between 19^0 26' to 20^0 42' North latitude and 77^0 18' to 79^0 9' East Latitude. It is surrounded by Amravati in the North, Chandrapur and Wardha in the east, Nanded district and Andhra Pradesh in the south and Akola and Prabhani in the west. The Yavatmal district belongs to Balaghat ranges. On the north it extends into Payanghat, and includes a small part of it which is belt of palin from 8 to 22 km in breath along the north of Yavatmal and Dharwha tashil.

MATERIALS AND METHODS

The water samples for physico-chemical analysis were collected from Babhulgaon dam , at 20 different sites with in the water body in morning between 8 am to 11 a.m. in the first week of every month from May 2012 to September 2012 The samples were collected in acid washed five liter plastic container from a depth of 5-10 cm below the surface of water. Separate samples were collected for dissolve oxygen in 250 mL bottles and dissolved oxygen was fixed in the field The samples were analyzed immediately in the laboratory. The physico-chemical characteristics of the dam water like rainfall, temperature, turbidity, transparency, pH, conductivity, total solids (TS), total dissolve solids (TDS), total suspended solids (TSS), dissolved oxygen (DO), chemical oxygen demand (COD), biochemical oxygen demand (BOD), total hardness, alkalinity, chloride, phosphate and nitrate etc. were determined .

MATERIALS AND METHODS

All the chemicals used were of AR grade. Analysis was carried out for various water quality parameters were measured by using Standard methods.

RESULT AND DISCUSSIONS

The physico-chemical characteristics are given in the Table 1 .

Temperature

Temperature is basically important for its affects on certain chemical and biological activities in the organisms attributing in aquatic media. .The temperature ranged between 30^0C to 36^0C. The lowest and highest values of The variation is mainly related with the temperature of atmosphere and weather conditions.

pH

The PH values of water bodies (lakes) was found in alkaline side (PH>7) The PH ranges from 7.5 to 8.10

Electrical conductivity

In present observation the EC varies from 1025 to 1531 µs/cm in pre-monsoo. High EC indicates a large quantity of dissolved minerals, salt thereby making it sour

BOD

BOD is the amount of oxygen required by the bacteria in stabilizing the decomposable organic matter. The aim of BOD test is to determine the amount of bio chemically oxidisable carbonaceous matter vary from 1.1 to 2.0

COD

COD is the amount of oxygen consumed during the chemical oxidation of organic matter using strong oxidizing agent like acidified potassium dichromate. The COD is linked with heavy pollution from paper industries, domestic sewage and industrial effluents .In present study the value vary from 3.1 to 4.1 mg/L .

Total hardness

In most of the fresh water TH is imparted mainly by the calcium and magnesium ions, which apart from Sulphate, Chloride and Nitrates are found in combination with carbonates and bicarbonates. In the present study of Total hardness were found to be 600 to 799 mg/L

Chloride

Chlorides are found in practically all natural waters. This is the most common inorganic anion present in water. Man and animals excrete high quantities of chlorides therefore it indicates sewage contamination. Variation observed is usually associated with the hydrology of the basin In the present study the value ranges from 900 to 1045 mg/L

Nitrates

The results of the Nitrate present in Tables 1 revealed that the higher values recorded (17 -22 mg/L). is may be attributed to the oxidation of ammonia by nitrifying bacteria and biological nitrification . The nitrate concentration could be due to leaching and surface run-off of nitro phosphate fertilizer from nearby farmlands into the water.

sulphates

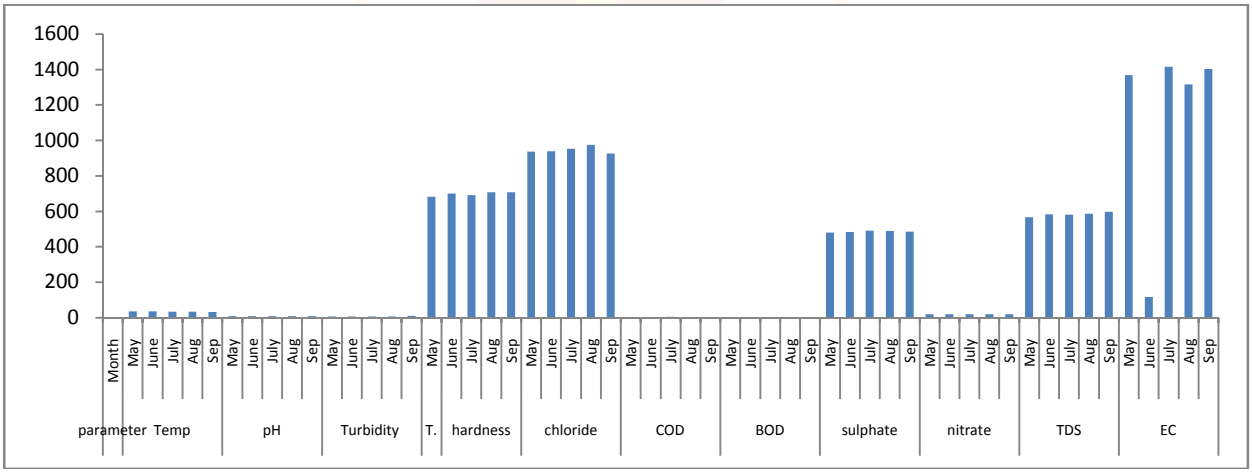
The Sulphate concentration in the dam water were very high 400 to 567 mg/L The source of sulphate could probably be from the mineral rocks antbropogenically added and also enters with rain

Table showing various parameters at different stations

parameter	Month	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	**Av.**
Temp	May	35.1	35.1	36	35.2	35.1	35.1	36.1	36.0	35.9	36.2	35.9	35.8	36.1	36.2	35.8	**35.7**
	June	36.0	36.0	35.9	36.0	35.9	35.8	36.0	36.0	35.8	35.2	35.1	36.0	35.2	35.1	35.3	**35.6**
	July	34.1	33.6	34.0	34.1	34.2	34.0	34.2	34.1	33.9	34.1	33.9	33.9	34.1	34.2	33.8	**34**
	Aug	34.2	34.1	33.9	34.1	33.9	33.9	34.1	34.2	33.8	34.1	34.2	34.0	34.2	34.1	33.1	**33.9**
	Sep	31.5	31.6	30.9	30.8	30.4	31.1	31.2	31.2	31.3	30.9	30.8	30.9	30.7	31.0	31.5	**30.9**
pH	May	7.5	7.5	7.4	7.7	7.8	7.9	7.5	7.8	7.7	8.1	8.1	7.9	8.1	8.0	7.6	**7.8**
	June	8.1	8.1	7.9	8.1	8.0	7.6	7.5	7.5	7.4	7.7	7.8	7.9	7.5	7.8	7.9	**7.7**
	July	7.9	7.5	7.6	7.7	7.5	7.5	7.4	7.7	7.8	7.9	7.5	7.8	7.4	7.6	7.7	**7.6**
	Aug	7.4	7.6	7.7	7.5	7.5	7.4	7.7	7.8	7.9	7.5	7.8	7.7	7.9	7.8	7.7	**7.6**
	Sep	7.6	7.5	7.5	7.4	7.7	7.8	7.9	7.5	7.8	8.1	8.1	7.9	8.1	8.0	7.6	**7.7**
Turbidity (NTU)	May	5	6	6	6	6	7	6	8	7	6	7	6	5	6	7	**6.3**
	June	6	7	8	6	6	7	7	7	7	8	7	6	5	7	8	**6.8**
	July	6	6	6	7	8	7	8	6	5	7	8	7	8	8	9	**7.2**
	Aug	5	6	6	6	6	7	6	8	7	6	7	6	5	6	7	**6.3**
	Sep	7	8	8	9	9	9	10	10	11	12	9	10	11	11	11	**9.9**
Total hardness	May	600	650	625	700	698	666	697	600	650	679	669	700	750	754	700	**683**
	June	634	659	666	697	600	650	679	669	700	750	754	700	700	759	789	**700**

	July	666	697	649	697	666	697	600	650	679	669	700	750	754	700	799	**692**
	Aug	684	679	666	697	600	650	679	669	700	750	754	700	758	785	797	**707**
	Sep	697	666	697	600	650	679	669	700	750	754	700	700	795	746	777	**708**
chloride	May	999	1000	1020	987	894	799	798	954	979	1000	973	900	989	989	900	**937**
	June	981	1031	1027	1000	972	789	970	987	1000	1021	987	894	799	798	954	**938**
	July	987	894	799	798	954	999	1000	1020	987	894	976	976	983	1001	1017	**954**
	Aug	987	1028	1045	978	1027	997	1017	1067	999	1000	1020	987	894	799	846	**975**
	Sep	999	1000	1020	987	894	987	894	799	798	954	936	971	899	897	1000	**926**
COD	May	3.1	3.3	3.5	3.3	4.1	4.1	3.6	3.6	3.9	4.0	3.7	3.7	3.9	4.0	3.7	**3.7**
	June	4.1	3.6	3.6	3.9	4.0	3.7	3.7	3.9	4.0	3.7	3.1	3.3	3.5	3.7	3.6	**3.6**
	July	3.1	3.3	3.5	4.1	3.6	3.6	3.9	4.0	3.7	3.7	3.9	4.0	3.7	4.1	3.7	**3.8**
	Aug	3.9	3.1	3.3	3.5	4.1	3.6	3.6	3.9	4.0	3.7	3.7	3.9	4.0	3.7	3.6	**3.7**
	Sep	4.0	3.5	3.1	3.3	3.5	4.1	3.6	3.6	3.9	4.0	3.7	3.7	3.9	4.0	3.7	**3.7**
BOD	May	1.1	1.0	1.2	1.3	1.1	1.6	1.8	1.9	1.8	1.0	1.6	1.9	2.0	1.5	1.6	**1.5**
	June	1.1	1.6	1.8	1.9	1.8	1.0	1.6	1.9	2.0	1.5	1.6	1.8	1.0	1.1	1.6	**1.5**
	July	1.3	1.0	1.1	1.6	1.8	1.9	1.8	1.0	1.6	1.9	2.0	1.5	1.6	1.2	1.4	**1.5**
	Aug	1.0	1.4	1.7	1.6	1.1	1.6	1.8	1.9	1.8	1.0	1.6	1.9	2.0	1.5	1.6	**1.6**
	Sep	1.1	1.6	1.8	1.9	1.8	1.0	1.6	1.9	2.0	1.5	1.6	1.9	2.0	2.1	1.9	**1.7**
sulphate	May	400	412	419	450	470	500	454	465	437	479	419	500	520	564	567	**479**
	June	454	465	437	479	419	500	520	564	567	454	465	437	444	489	512	**483**
	July	478	496	478	454	465	437	479	419	500	520	564	567	479	497	524	**490**
	Aug	454	465	437	479	499	454	465	437	479	419	500	520	564	567	546	**489**
	Sep	481	454	465	437	479	547	454	465	437	479	419	500	520	564	567	**486**
nitrate	May	20	24	17	19	20	21	17	19	18	17	21	22	20	21	18	**19.2**
	June	17	19	20	21	17	19	18	17	21	22	20	21	18	19	20	**19.4**
	July	15	14	17	19	20	21	17	19	18	17	21	22	20	21	18	**19.1**
	Aug	16	17	19	20	21	17	19	18	17	21	22	20	21	18	17	**19.2**
	Sep	15	17	17	19	20	21	17	19	18	17	21	22	20	21	18	**19.2**
TDS	May	500	524	501	555	601	587	601	597	499	512	547	599	671	555	547	**566**
	June	547	601	587	601	597	499	512	547	599	671	555	547	671	600	597	**583**
	July	547	606	666	601	587	601	597	499	512	547	599	671	555	547	579	**581**
	Aug	597	597	658	649	601	587	601	597	499	512	547	599	671	555	547	**586**
	Sep	601	587	601	597	499	512	547	599	671	555	547	600	647	697	700	**597**
EC	May	1097	1159	1247	1009	1500	1547	1493	1247	1367	1397	1300	1479	1500	1397	1348	**1369**
	June	1497	1500	1547	1493	1247	1367	1397	1300	1479	1500	1397	1348	1564	1497	1267	**116**
	July	1267	1479	1469	1500	1547	1493	1247	1367	1397	1300	1479	1500	1397	1348	1367	**1415**
	Aug	1531	1469	1209	1369	1469	1009	1249	1645	1479	1267	1067	1009	1349	1459	1511	**1316**
	Sep	1025	1099	1249	1469	1500	1547	1493	1247	1367	1397	1300	1479	1500	1397	1348	1403

Graph showing av.values for different months



CONCLUSIONS

Comparing present values of selected parameters with the permissible limits prescribed by bureau of Indian standards (IS 101500) & WHO, it can be concluded that the water of Bembla dam is useful for water supply. But before supplying to urban population this must be treated by water

department to maintain water quality as required for drinking purposes. Results are presented in the graphs.

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PHYTOCHEMICAL, PROXIMATE COMPOSITION AND CHARACTERIZATION OF STEM AND ROOT EXTRACTS IN *CASSIA TORAL.*

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ABSTRACT

Traditionnel médical practices are based on use of plants and plant extracts, as they are playing an important role in protecting health to a large section of people all over the world. In this study Phytochemicals, nutrient analysis and proximate compostion of stem and root extracts of Cassia tora l.. from the campus of Government Vidharbha Institute of Science and Humanity, Amravati had been investigated. Outer surface of stem is greenish brown in color and inner surface is smooth and light yellow colored. Stem and root sample contained tannin, saponin, protein, steroids, carbohydrate, alkaloids, flavonoids and glycosides. Proximate analysis of moisture, ash, fat and mineral analysis of calcium, magnesium, iron, nitrogen and solubility were check. Values of stem is moisture (37%), cold water (16%), hot water (11%), 1%NaOH (21%), 1%HCl (20%), benzene +alcohol (11%), ash content (15%) and the values of root is moisture (60%), cold water (18%), hot water (20%), 1%NaOH (22%), 1%HCl (21%), benzene +alcohol (14%), ash content (4.0%). These results indicate that the stem and root of these Cassia tora l.. contains mineral and nutrients elements that will be useful in nutrition. Also the existence of some phytochemicals like tannin, saponin and steroids illustrated medicinal action of the plant in its therapeutic uses. Result of their phytochemcial screening could justify the observed activities and validate their use in herbal medicine and can also be employed in the treatment of various ailments in modern medicine too.

Keywords *: Proximate composition, Phytochemical , Nutrient analysis, Cassia toral.*

INTRODUCTION

Nature has been a source of medicinal agents since time immemorial. Plants play a significant role in providing primary health care. They serve as therapeutic agents as well as important raw materials for the manufacturing of traditional and modern medicines as well as in mainly due to the current widespread belief that green medicine is a safer and more dependable than the costly synthetic drugs mainly of which have adverse side.[1]

For the treatment of various diseases, globally herbal medicines have been used traditionally. In the last decade, the study of plant extract has attracted attention in curing various challenging diseases. In the indigenous system of medicine *Cassia tora l.* is one of the plants that is use for many centuries. Different parts of the plant root, seeds, leaves and stem have medicinal values.

Exhaustive literature survey reveals that only proximate and phytochemcial analysis of leaves and seeds of *Cassia tora l.* have been investigated but proximate and phytochemical analysis of stem and root is still lacking hence this work had been carried out.[2]

Cassia tora l is an annual foetid herb with a height of 28cm to 100cm. It is found in Asian region but in India it is mainly found in Satpura region in Maharashtra. *Cassia tora l.* is very stress tolerant and is an easy plant to grow in India, it occurs as wasteland rainy season weed. Seeds extract can be used as an energy drink.

Proximate analysis of food is the determination of the major components of food which include moisture, protein, solubility, ash, proximate analysis is a system of analysis of nutrients also termed “conventional analysis” in which the gross components (protein , fat, carbohydrate, ash) of the food material rather than individual nutrients (amino acid, fatty acid, monosaccharide’s) are determined[3].

Phytochemical are chemical compounds derived from plants that are non-nutritive secondary metabolic compounds occurring in different parts of plants. They are important as protective and disease fighting compounds which help the body to prevent of fight against diseases and so are required by the human body to sustain life. Their

therapeutic use in prevention or fighting a number of diseases is the basis of their extensive use in traditional medicine. Some of the phytochemicals are water soluble while others are not[4].

MATERIALS AND METHODS

Plant collection and Preparation:

Stem and root of *Cassia tora l.* were collected from campus of G.V.I.S.H. Amravati, Maharashtra, India from 15th November to 25th December 2015. They were properly shade dried indoors in an airy place, crushed, powdered and stored in dry opaque bottles. Stem and root powder was extracted with ethanol-benzene in a soxhlet apparatus. Solvent was evaporated and the resultant extract was stored at 20□C until use.

Method of extraction for *Cassia tora l.*

Extraction of the stem and root of *Cassia tora l.* was carried out by using ethanol-benzene soxhlet extraction technique. About 5gm of coarsely powdered stem and root were sequentially extracted in a soxhlet extractor using 400ml ethanol-benzene. The extraction time was four hours for each solvent. Resulting extracts were evaporated using rotary evaporator. Filtrates were then combined, concentrated to dryness under controlled temperature and pressure.

Proximate analysis

Moisture, ash and solubility were determined using the Association of official analytical chemists methods[5]. The crude proteins were obtained according to the AOAC(1990). Crude lipid was determined by extracting the samples with petroleum ether in a soxhlet extractor, while crude fiber was estimated from the loss in weight on ignition of dried residue following digestion of fat-free samples. Soluble carbohydrate was obtained by the difference method[6]. Whereas total carbohydrate was calculated by the following equation- Total carbohydrate = 100 – (%Ash + %Moisture + %Crude fiber + %Crude protein)

Nutritive value

Nutritive value of stem and root was expressed in Kilocalories / 100 gm of dry weight of stems and calculated by using the given formula.[7]

Nutritive value = (4 x %Protein) + (9 x %Crude fat) + (4 x %Total carbohydrate)

Phytochemical analysis

Phytochemicals in the stem and root were determined by elemental analysis of magnesium, calcium, sulphur, iron, sodium and chlorine were investigated by color test using appropriate chemicals and reagents and also the filtrate used to test for phenols, tannins, saponins, glycosides, flavonoids, steroids and alkaloids[8,9,10].

Cassia tora l. dry roots

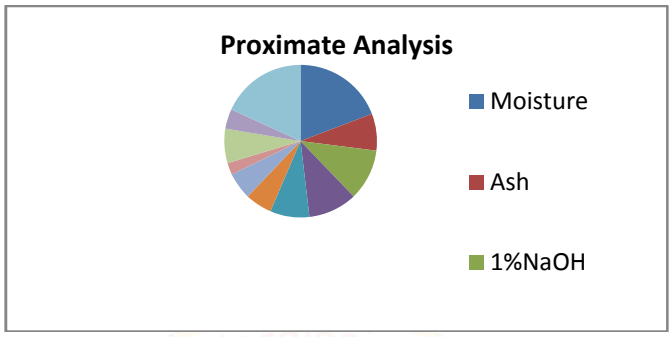
Cassia tora l. dry.stem

RESULT

Proximate analysis of the *Cassia tora l.* stem and root.

		Stem		Root	
Sr.No.	Content	Per 100gm	Percentage	Per 100gm	Percen-tage
1	Moisture	63gm (±2gm)	37%	60gm (±2gm)	40%
2	Ash	85gm (±1gm)	15%	96gm (±1gm)	4%
3	1% NaOH	79gm (±1gm)	21%	78gm (±1gm)	22%
4	1% HCl	80gm (±1gm)	20%	79gm (±1gm)	21%
5	Cold water	84gm (±1gm)	16%	82gm (±1gm)	18%

6	Hot water	89gm (±1gm)	11%	87gm (±1gm)	13%
7	Benzene + alcohol	89gm (±1gm)	11%	86gm (±1gm)	14%
8	Crude Protein	--	4.8%	--	5.0%
9	Crude Lipid	--	14%	--	12%
10	Crude Fiber	--	8.2%	--	8.6%
11	Carbohydrate	--	35%	--	42.4%



Phytochemical analysis of the *Cassia tora l.* stem and root.

Sr.No.	Content	Test	Stem	Root
			Result	
1	Alkaloids	Mayers test	+	+
2	Tannin	Lead acetate test	+	+
3	Saponin	Dist. Water	+	+
4	Flavonoids	Lead acetate test	+	+
5	carbohydrate	Molish test	+	+
6	Protein	Milons test	+	+
7	Steroids	Libarman -burchard reaction	+	+
8	Glycosides	Fehling's reagent	+	+

"+" = present, "-" = absent

Nutrient Analysis of *Cassia tora l.* stem and root

Sr.No.	Content	Stem	Root
		Result	
1	Magnesium	+	+
2	Calcium	+	+
3	Sulphur	+	+
4	Iron	+	+
5	Sodium	+	+
6	Chlorine	+	+
7	Potassium	+	+

"+" = present, "-" = absent

DISCUSSION

Proximate analysis revealed that moisture content is very high so growth of microorganism and life span of stored samples would be less. Ash content was found to be 15% which is a reflection of the good amount of mineral elements are present in samples. *Cassia tora l.* stem and root contains lower fiber content[11]. Proteins are also found in good proportion and they are important and act as enzyme, hormones and antibodies, proteins also helps in the formation of bones, hair and it contributes less energy than 30calories and thus prevents obesity and other related disease. A diet of fat providing 1-2% is sufficient for a human being. High amount of carbohydrates is essential for maintenance of life in plant and animals and also provide raw material for many industries[12].
Presence of flavonoids inferred that the stem and root has the biological functions like antioxidant,

allergies protection, free radical, inflammation, ulcers, hepatotoxins, tumor and viruses[13]. Flavonoids are water soluble free radical and antioxidants which prevent oxidative cell damage, and have strong anti-ulcer and anticancer activity[14]. Saponin content suggest that usefulness of the seeds as a productivity agent. Saponin level is low, either compared with the results from another works. Alkaloids are the most efficient medicinally significant bioactive substances in plants. Alkaloids and the synthetic derivatives are used as medicinal agents because of their bactericidal and analgesic properties. This is water soluble phenolic compounds which precipitate proteins. They exist in all plants. Tannins add to proteins making them bio-unavailable[15,16].

Potassium was the most abundant element. Potassium helps to control body weight and improve water and electrolyte balance in the blood and tissues. The calcium content was determined. It helps in the improvement of muscle contraction required by infants and foetuses for bones and teeth development.[17]The concentration of sodium was low, this vegetable is useful in the treatment of heart related diseases. Excess sodium utilization leads to hypertension. Iron is an important element in the diet of pregnant women, nursing mothers, infants and the elderly to prevent anemia diseases. Magnesium also plays necessary roles in most reaction involving phosphate transfer.[18] It is important in the structural stability of nucleic acids. It plays a powerful role in the internal absorption of electrolyte in the body. Its defect in man includes severe diarrhea and migraines.[19,20]

CONCLUSION

This type of study will be applicable for the pharmaceutical, medicinal, agricultural, industrial and biochemical sciences. This study also showed that proximate, phytochemical, mineral analysis of Cassia tora *l*. setm and root as a balanced and rich source of macro- and micronutrients. The plant was also used by rural people as a vegetable in winter that's mean it was used as heat and energy. So the further study will be carry out on this plant.

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GENERAL TEST FOR PRELIMINARY PHYTOCHEMICAL SCREENING OF COCONUT HUSK FIBERS

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ABSTRACT

The botanical name of coconut is *Cocos nucifera* . The coconut is member of Arecacea family(Palm family). The coconut husk fiber is natural fiber , it is extracted from the outer shell of coconut . This fiber is coarse and durable fiber. Ash of coconut husk fiber, when taken with yoghurt, proves effective against piles. Ash of coconut husk along with honey is used for treating various types of fibroid in uterus and other uterine problems. For this study, extract of coconut husk in n- hexane, ethanol, water is used. It shows positive test for carbohydrate, alkaloid, tannins, essential oil, mucilage.

Keyword: *Coconut husk, phytochemistry, phytochemical screening, preliminary study, ash of husk.*

INTRODUCTION

Since time immemorial, people have been using coconut for variety of reason. Because of its extensive use, it is often called as "KALPATARU". Coconut plays an important part in hindu mythology and festivals. In all over India, any 'Pooja' is not considered to be complete without coconut. Coconut raw oil acts as an excellent lubricant and hence, is highly useful for knee joints and all other joints in human body. As per 'vedas', it is said that ,coconut must be consumed periodically, so it is offered as 'Prasad' in various festive occasions. And it must be taken regular interval period so in all festival of Maharshtra coconut is taken as "Prasad" that is reason to get oil to all body parts and it work smoothly.

MATERIAL AND METHODS

Screening are perform by following method

CARBOHYDRATES

1)Molisch's Test- Mix 1 ml reagent in 2 ml of test Solution. Add 1 ml of concentrated sulphuric acid Red to violet ring depending on amount of sugar appears at the junction of two liquids.
2)Iodine Test- Mix 0.5 ml of iodine solution with 1 ml of the test solution, Starch gives deep blue colour.
3) Fehling's Test - Mix 1 ml of the Fehling's solution 'A' with 1 ml of Fehling's solution 'B' and 1 ml of test solution. Boil. Yellow to red precipitate
4) Benedict's Test- Mix 2 ml of Benedict's reagent With 2 ml test solution. Boil in a water bath
Formation of red, yellow or green precipitate depending on the sugar amount.
5) Barfoed's Test- Mix 2 ml of Barfoed's reagent with 1 ml of test solution. Boil. Wait Brick red precipitate of Monosaccharide.
6)Non reducing sugar- perform Benedict's test, no characteristic coloration.

PROTEINS

1) Millon's test –Mix 2 ml test solution with 2 ml millon's reagent. Red colour formation.
2) Precipitation test- Mix 2 ml test solution with 2 ml 5% HgCl2 or 5% ammonium sulphate. White precipitation.
3) Lead acetate test- Mix 2 ml test solution with 2 ml 40% NaOH, 0.5 ml lead acetate solution. Boil it. Black to brown colour formation.

ALKALOIDS

1)Hager's reagent- Mix 2 ml of reagent with 2 ml of filtrate of plant drug extract. Yellow colour formation.
2) Mayer's reagent- Mix 2 ml of reagent with 2 ml of filtrate of plant drug extract. cream colour precipitate
3) Marme's reagent- Mix 2 ml of reagent with 2 ml of filtrate of plant drug extract. precipitation.

4) Schiebler's reagent (phosphotungustic acid)- Mix 2 ml of reagent with 2 ml of filtrate of plant drug extract. Yellow to orange precipitate
5) Wagner's reagent- Mix 2 ml of reagent with 2 ml of filtrate of plant drug extract. reddish brown precipitate.

FLAVINOIDS

1)Shinoda test- Add magnesium powder and a few drops of concentrated HCl Or H_2SO_4 to 2 ml of sample solution
2)Lead acetate Mix test solution with lead acetate. Yellow precipitate.
3)Alkali test- Treat test solution with increasing amount of NaOH. Yellow colouration.

TANNINS

1)Ferric chloride (5%)- Mix 2 ml of test solution with ferric chloride solution. Blue ,blue black colouration.
2)Gelatin-salt test- Prepare three test tube of extract solution. To the first is added a 1% solution of NaCl. To the second is added a 1% NaCl and 5% gelatin solution,And to the third is added a $FeCl_3$ solution. Precipitate.
3)Lead acetate test- Mix test solution with lead acetate solution. White precipitation.
4)Dilute Iodine test- Mix test solution with lead acetate solution. Red colouration.
5)Potassium dichromate test- Mix test solution with Potassium dichromate solution
6)Dilution HNO_3 test- Mix test solution with Dilute HNO_3 solution. red precipitation.

STEROIDS OR TRITEPENOIDS

Salkowski reaction- Dissolve 1-2 mg of the sample in 1 ml of $CHCl_3$ and add 1 ml conc. H_2SO_4.chloroform layer show red colour ,acid layer show green color.

ANTRAQUINONES

Borntrager's test- Take little quantity of aqueous solution of sample, add H_2SO_4.Then add CCl_4 or ether. Seperate the organic layer and shake with dilute ammonia. rose pink colour of ammonia.

MUCILAGE

Swelling test- Dissolve the powder in water. Powder swell.

ESSENTIAL OILS

Sudan red III test - Treat the test solution with Sudan red III. red colour.

RESULT AND DISCUSSIIIION

PHYTOCHEMICAL ANALYSIS OF COCONUT HUSK FIBERS ARE GIVEN BELOW

Test	Inferences		
Extract	n-Hexane	ethanol	water
CARHYDRATES			
Molish's test	+ ve	+ ve	+ ve
Iodine test	- ve	- ve	- ve
Fehling test	- ve	+ ve	+ ve
Benedict test	- ve	+ ve	+ve
Barford test	- ve	- ve	- ve
Non reducing sugar	+ ve	+ ve	+ ve
PROTEIN			
Millions test	+ ve	+ ve	+ ve
Precipitation test	- ve	- ve	- ve
Lead acetate test	- ve	- ve	- ve
ALKALOIDS			
Hager test	+ ve	+ ve	+ ve
Mayer's reagent	- ve	+ ve	- ve
Wagner's test	- ve	- ve	- ve
Marme's test	- ve	- ve	- ve
Schibler test	- ve	- ve	- ve
FLAVONOIDS			
Shinoda for flavonoids	+ ve	+ ve	+ ve
Lead acetate	- ve	- ve	- ve
Alkali.	- ve	- ve	- ve
TANNINS			
Ferric chloride test	- ve	+ ve	- ve
Gelatin test	+ ve	+ ve	+ ve
Lead acetate	- ve	+ ve	+ ve
Dilute Iodine test	+ ve	+ ve	+ ve
Potassium test	+ ve	+ ve	+ ve
STEROIDS OR TRITEPENOIDS			
Salkowski reaction	+ ve	+ ve	+ ve
ANTHRAQUINONES			
Borntrager's test	+ ve	+ ve	+ ve
MUCILAGE			
Swelling test	powder swell	+ ve	
FATTY OIL			
Sudan red test	+ ve	- ve	- ve

CONCLUSION

Coconut husk fibers contain carbohydrates, proteins alkaloids, flavonoid, tannins, steroids or tritepenoids, anthraquinones, mucilage.

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EFFECT OF BILATERAL EYESTALK ABLATION AND INJECTION OF METHIONINE-ENKEPHALIN *AND SEROTONIN IN FRESHWATER CRABS PARATELLPHUSA* JACQUIMONTTII

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ABSTRACT

The effect bilateral eyestalk ablation and injection of methionine-enkephalin and serotonin are investigated in freshwater crab Paratelphusa Jacquemontii resulted in major hyperglycemia and hyperglucosemia in a dose-dependent behavior. of Result of injection showed a change in hepatopancreas glycogen and TCHO levels was considerably less in Methion-enkephalin injected crab than control crabs and muscle glycogen and TCHO levels decreased. The Phosphorylase (both total and active) activity levels were significantly increased in both hepatopancreas and muscle. The total phosphorylase also increased in the tissues of crabs. After removal of bilateral eyestalk showed significant decrease in hemolymph carbohydrate level. However TCHO level of hepatopancreas and muscle was increased significantly in eyestalk-ablated crabs. Major increase resulted in muscle. The fresh water crabs, Paratelphusa Jacquemontii. were injected with serotonin and hemolymph glucose and CHH levels were determined. Injection of serotonin into intact crabs caused significant hyperglycemia in a dose-dependent manner. In contrast, injection of serotonin did not cause any change in hemolymph glucose level in eyestalk ablated crabs

Keywords: *Bilateral Eyestalk ablation, Carbohrdrate, Phosporylase, hepatopancreas, Muscle, and Protein*

INTRODUCTION

The detailed study of eyestalk hormones on tissue carbohydrate levels and phosphorylase activity are done by (Keller, 1965; Ramamurthi et al., 1968; Sagardia, 1969). In crustaceans, eyestalk factor is responsible for hemolymph glucose level (P S Reddy; M R Basha, 2009), called the crustacean hyperglycemic hormone (CHH) (Bo-MiKim et.al, 2013; Chung JS et.al., 2010; Aquiloni L et.al., 2012). It was first reported as a diabetogenic factor by Abramowitz et al. (1944). The hyperglycemic hormone of eyestalks of the crab *Paratelphusa Jacquemontii* and the prawn Penaeus monodon enhances the activity of the phosphorylase system (Reddy et al., 1982, 1984; Reddy, 1992). In the practical implementation of freshwater crab *Paratelphusa Jacquemontii* investigated that glycogen and TCHO level decreased in normal crabs when exposed to sub lethal concentrations of monocrotophos. In the ablated and pesticide exposed crabs glycogen, protein and TCHO level decreased. In case of ablated and exposed crabs when injected with eyestalk extract, glycogen and TCHO level declined. It was observed that glycogen and TCHO level in eyestalk extract injected crabs were similar to those of normal exposed crabs. This indicates the vital role of eyestalk in the regulation of biochemical contents. Histological studies of the hepatopancreas indicate structural changes such as large number of vacuolated cells and phagocytes when exposed to the pesticide. (Nimgare 1992; Ravindra Paul et al., 2008). The selected specimen i.e. Paratelphusa Jacquemontii represents the natural population in the river or water bodies of the Digras city, Dist Yavatmal and around area.

METHOD AND MATERIAL

The Species which has been selected for the present study is of economic importance and readily available throughout the year and it stands captivity well. This animal belongs to the different levels of the water bodies. The selected specimen i.e. Paratelphusa Jacquemontii represents the natural population in the river or water bodies of the Digras city, Dist Yavatmal and around area.
They were kept in large aquaria with continuous aeration and acclimatized to laboratory conditions for one week under constant salinity (15 ± 1 ppt), pH (7.2 ± 0.1), and temperature (22 ± 2°C). All the animals used were of same size (6.5 x 5.3cm) and weight about (55.65 gm).

RESULT AND DISCUSSION

3.1 Result

Injection of Methionine-enkephalin into Intact Crab resulted in significant hyperglycema and

hyperglucosemia is directly proportional to the dose. Physiological saline injection has not shown any effect on hemolymph carbohydrates for doses from 10^{-9} to 10^{-6}. Doses less than 10^{-9} mol/crab did not extract a sugar level in blood.Hyperglycemia in above 10^{-7} to 10^{-7} where it levels saturating - constant. Significant increase was observered in hemolymph glucose level within half-hours of injection and reached at maximum level after 24 hours and then declined linearly. Hepatopancreas glycogen and TCHO level in crab with injection of Methionine-enkephalin were significantly lower than those of Control Crab. Decrease in muscle glycogen and TCHO levels were also significant after injecting methionine-enkephalin. Decreased hepatopancreas and muscle glycogen indicate/suggesting the possibility of its mobilization of glucose molecule into hemolymph Phophorylase activity levels increased in both hepatopancreas and muscle after injection. After removal of bilateral eyestalk showed significant decrease in hemolymph carbohydrate level (Table 3.1). However TCHO level of hepatopancreas and muscle was increased significantly in eyestalk-ablated crabs (Tables 3.2, 3.3, 3.4 and, 3.5). Major increase resulted in muscle. Also found increase of Glycogen level in hepatopancreas in eyestalk less crabs. The same pattern was found in muscle. But observed decreased in tissue phosphorylase activity of eyestalk-ablated crabs (Tables 3.6, 3.7, 3.8, 3.9 and 3.10). It of observed that hemolymph carbohydrate level did not shown any change compared to control injected eyestalk less crabs (Table 3.1). It is also found there is no significant change in the levels of tissue TCHO and glycogen and activity levels of total and active phosphorylase in eyestalk less crabs after injecting Methionine-enkephalin and Serotonin (Tables 3.3–3.10). Table-3.1: Effect of pesticide (Fenvalerate) impact, addition of Methionine-enkephalin and serotonin injection into intact, eyestalk ablated and eyestalk extract injected crabs on hemolymph and total sugar level in the crab *Paratelphusa Jacquemontii* (Rathban).

Parameters	Intact group	Eyestalk ablated	Eyestalk ablated + pesticide	Eyestalk ablated + Eyestalk extract	methionine-enkephalin	Serotonin
Control	12.11 ± 1.38	9.41 ± 1.19	10.34 ± 0.78	11.02 ± 0.4	11.09 ± 0.8	10.08 ± 0.6
Control with saline	12.73 ± 1.58	9.34 ±1.14	10.88 ±0.78	11.53 ± 0.5	11.88 ± 0.8	11.40 ± 0.33
10^{-9}	16.52 ± 1.54	9.21 ±1.16	12.65 ±0.83	13.26 ± 0.7	14.01 ± 0.76	13.87 ± 0.65
10^{-8}	19.64 ± 1.32	9.43 ±1.03	14.50 ±0.74	15.86 ± 0.23	16.07 ± 0.43	15.78 ± 0.75
10^{-7}	28.80 ± 2.64	9.41 ±1.23	19.62 ±0.64	22.44 ± 0.5	23.08 ± 0.8	22.77 ± 0.45

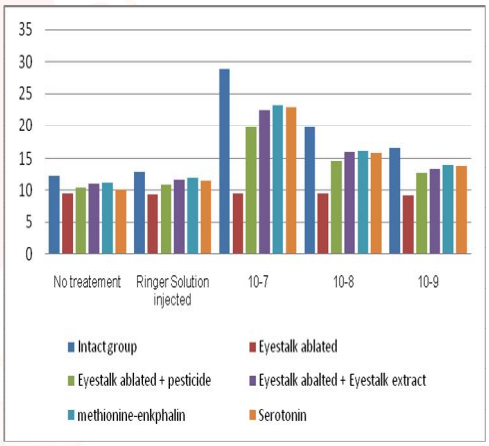

Fig 3.1

Table-3.2**:** Effect of pesticide (Fenvalerate) impact and addition of Methionine-enkephalin and serotonin injection into intact, eyestalk ablated and eyestalk extract injected crabs on hemolymph and glucose level in the crab *Paratelphusa Jacquemontii* (Rathban).

Parameters	Intact group	Eyestalk ablated	Eyestalk ablated + pesticide	Eyestalk ablated + Eyestalk extract	methioninenkephalin	Serotonin
Control	6.41 ± 0.73	5.19 ± 0.77	4.92 ± 0.59	5.76 ± 0.41	6.02± 0.33	5.89 ± 0.42
Control with saline	6.55 ± 0.94	5.52 ± 0.53	5.20 ± 0.53	5.96 ± 0.32	6.12 ± 0.35	6.02 ± 0.42
10^{-9}	9.13 ± 0.97	5.44 ± 0.38	5.14 ± 0.32	5.88 ± 0.41	6.06 ± 0.71	5.65 ± 0.32

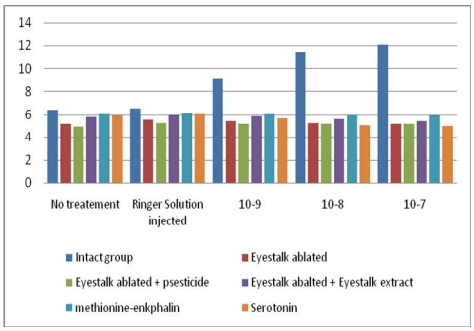

Fig 3.2

10^{-8}	11.44 ± 0.82	5.21 ± 0.70	5.19 ± 0.71	5.56 ± 0.45	5.98 ± 0.82	5.01 ± 0.61
10^{-7}	12.07 ± 0.57	5.19 ± 0.67	5.15 ± 0.98	5.42 ± 0.42	5.92 ± 0.76	4.99 ± 0.73

Table-3.3: Effect of pesticide (Fenvalerate) impact, addition of Methionine-enkephalin and Serotonin injection into intact, eyestalk ablated and eyestalk extract injected crabs on, hepatopancreas and total carbohydrate in the crab *Paratelphusa Jacquemontii* (*Rathban).*

Parameters	Intact group	Eyestalk ablated	Eyestalk ablated + pesticide	Eyestalk ablated + Eyestalk extract	methionine-enkephalin	Serotonin
Control	13.66 ±1.82	17.87 ±1.11	15.28 ±1.75	18.26± 1.02	14.01 ± 1.52	14.03 ± 0.98
Control with saline	13.84 ±1.12	18.01 ±1.45	15.36 ±1.23	18.85± 0.40	14.02 ± 0.45	14.54 ± 0.71
10^{-9}	9.47± 1.45	17.95 ±1.58	15.40 ±1.44	18.65± 1.04	10.13 ± 1.23	10.23 ± 1.06
10^{-8}	9.01 ±1.82	17.81± 1.36	15.11± 1.48	18.45± 0.71	11.02 ± 1.08	10.87 ± 0.98
10^{-7}	8.47 ±0.63	17.44 ±1.10	14.98 ±1.06	18.08± 0.94	09.01 ± 1.05	10.88 ± 0.78

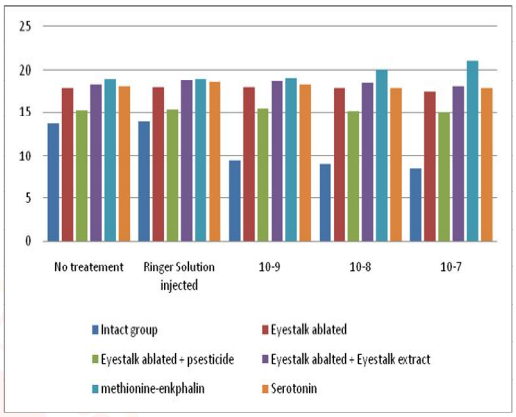

Fig 3.3

Table-3.4 Effect of pesticide (Fenvalerate) impact and addition of [illegible] n injection into intact, eyestalk ablated and eyestalk extract injected crabs on hepatopancreas glycogen level in the crab *Paratelphusa Jacquemontii (Rathban*).

Parameters	Intact group	Eyestalk ablated	Eyestalk ablated + pesticide	Eyestalk ablated + Eyestalk extract	Methionine-enkephalin	Serotonin
Control	1.22 ± 0.39	2.04 ± 0.68	1.80 ± 0.41	2.22 ± 0.35	1.87 ± 0.45	1.95 ± 1.45
Control with saline	1.23 ± 0.30	2.06 ± 0.12	1.75 ± 0.32	2.23 ± 0.44	1.77±1.23	1.83±0.23
10^{-9}	0.64 ±0.10	2.07 ± 0.77	1.80 ± 0.11	2.21 ± 0.80	1.80±0.78	1.88±1.48
10^{-8}	0.61 ± 0.14	2.09 ± 0.61	1.84 ± 0.62	2.24 ± 0.64	1.90±1.43	1.76±0.43
10^{-7}	0.58 ± 0.15	2.11 ± 0.72	1.96 ± 0.54	2.29 ± 0.36	1.67±0.78	1.87±1.28

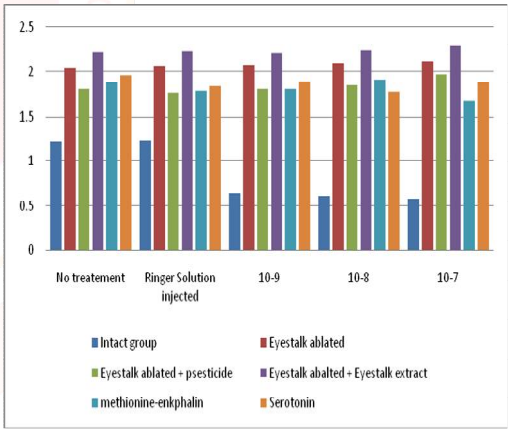

Fig 3.4

Table-3.5 Effect of pesticide (Fenvalerate) impact, addition of Methionine-enkephalin and Serotonin injection into intact, eyestalk ablated and eyestalk extract injected crabs on muscle total carbohydrate level in the crab *Paratelphusa Jacquemontii* (Rathban).

Param	Intact	Eyesta	Eyestal	Eyesta	methio	Seroto

eters	group	lk ablated	k ablated + pesticide	lk ablated + Eyestalk extract	nine-enkephalin	nin
Control	4.39 ± 0.46	6.26 ± 0.65	5.78 ± 0.25	5.96 ± 0.57	6.78 ± 0.52	5.03 ± 0.98
Control with saline	4.41 ± 0.44	6.31 ± 0.47	5.42 ± 0.66	5.72 ± 0.18	6.05 ± 0.75	5.54 ± 0.71
10^{-9}	3.12 ± 0.75	6.33 ± 0.82	5.50 ± 0.30	5.75 ± 0.39	6.13 ± 1.23	5.23 ± 1.06
10^{-8}	3.01 ± 0.67	6.25 ± 0.69	5.32 ± 0.46	5.82 ± 0.37	6.02 ± 1.08	5.37 ± 0.98
10^{-7}	2.94 ± 0.65	6.31 ± 0.47	5.43 ± 0.39	5.91 ± 0.31	6.11 ± 0.55	5.75 ± 0.78

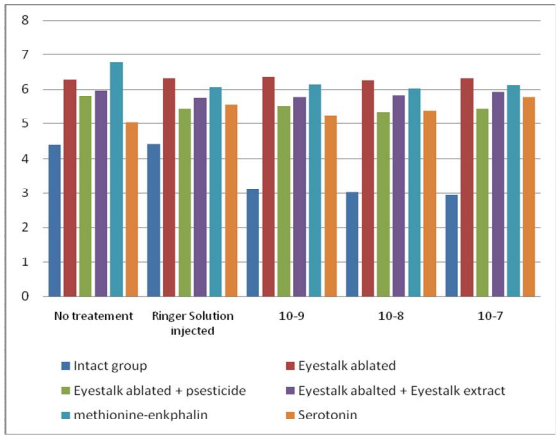

Fig 3.5

Table-3.6 Effect of pesticide (Fenvalerate) impact and addition of Methionine-enkephalin and serotonin injection into intact, eyestalk ablated and eyestalk extract injected crabs on muscle glycogen level in the crab *Paratelphusa Jacquemontii* (Rathban).

Parameters	Intact group	Eyestalk ablated	Eyestalk ablated + pesticide	Eyestalk ablated + Eyestalk extract	methionine-enkephalin	Serotonin
Control	0.66 ± 2.10	1.01 ± 1.08	0.85 ± 0.88	0.90 ± 0.82	0.88 ± 0.52	0.83 ± 0.98
Control with saline	0.64 ± 0.89	1.02 ± 1.06	0.82 ± 0.76	0.92 ± 1.02	0.80 ± 0.75	0.75 ± 0.71
10^{-9}	0.41 ± 1.09	1.03 ± 1.11	0.80 ± 0.23	0.93 ± 0.76	0.67 ± 1.23	0.60 ± 1.06
10^{-8}	0.37 ± 0.89	1.07 ± 1.20	0.83 ± 1.02	0.95 ± 0.89	0.57 ± 1.08	0.50 ± 0.98
10^{-7}	0.34±0.88	0.99±0.98	0.85±0.99	0.96	0.66 ± 0.55	0.55 ± 0.78

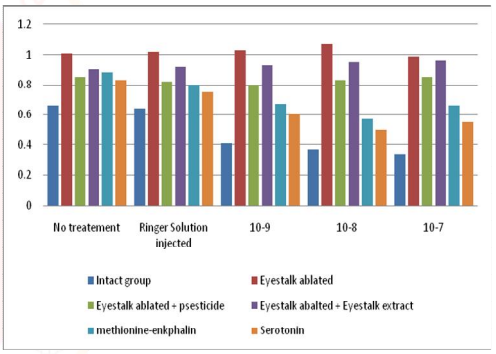

Fig 3.6

Table-3.7 Effect of pesticide (Fenvalerate) impact, addition of Methionine-enkephalin and Serotonin injection into intact, eyestalk ablated and eyestalk extract injected crabs on hepatopancreas and phosphorylase 'A' level in the crab *Paratelphusa Jacquemontii* (Rathban).

Parameters	Intact group	Eyestalk ablated	Eyestalk ablated + pesticide	Eyestalk ablated + Eyestalk extract	methioninneenkephalin	Serotonin
Control	2.62 ± 0.28	1.72 ± 0.19	1.40 ± 0.22	2.17 ± 0.20	2.78 ± 0.32	2.05 ± 0.58
Control with saline	2.67 ± 0.29	1.67 ± 0.17	1.42 ± 0.13	2.20 ± 0.15	3.05 ± 0.75	2.01 ± 0.71
10^{-9}	3.60 ± 0.36	1.84 ± 0.38	1.48 ± .01	2.88 ± 0.03	4.13 ± 1.23	2.23 ± 1.06
10^{-8}	3.63 ±	1.81 ±	1.44 ±	2.93 ±	4.02 ±	2.37 ±

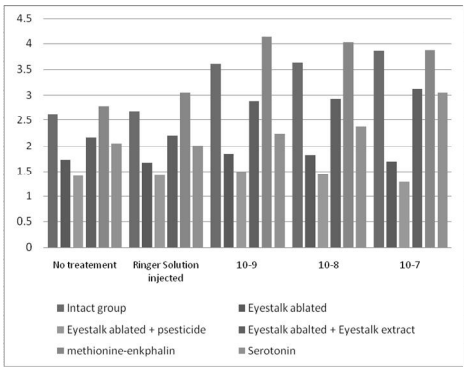

Fig 3.7

	0.42	0.23	0.37	0.51	1.18	0.98
10^{-7}	3.87 ± 0.22	1.69 ± 0.30	1.28 ± 0.34	3.14 ± 0.37	3.88 ± 0.75	3.05 ± 0.58

Table-3.8 Effect of pesticide (Fenvalerate) impact, addition of Methionine-enkephalin and Serotonin injection into intact, eyestalk ablated and eyestalk extract injected crabs on hepatopancreas and phosphorylase 'AB' level in the crab *Paratelphusa Jacquemontii* (Rathban).

Parameters	Intact group	Eyestalk ablated	Eyestalk ablated + pesticide	Eyestalk ablated + Eyestalk extract	methionine-enkephalin	Serotonin
Control	4.52 ±0.85	4.06 ± 0.45	3.11 ± 0.46	.16 ± 0.26	5.78 ±0.32	.03 ± 0.28
Control with saline	4.56 ±0.73	4.08 ± 0.31	3.13 ± 0.50	.18 ± 0.24	5.89 ±0.67	.51 ±0.71
10^{-9}	5.56 ±0.55	4.09 ± 0.21	3.20 ± 0.21	.88 ± 0.39	6.13 ±1.23	.23 ±1.06
10^{-8}	5.69 ±0.48	4.12 ± 0.31	3.31 ± 0.31	.92 ± 0.23	6.57 ±0.38	.37±0.98
10^{-7}	5.81± 0.31	4.10 ± 0.43	3.44 ± 0.57	.14 ± 0.23	6.88 ±0.45	.89 ±0.78

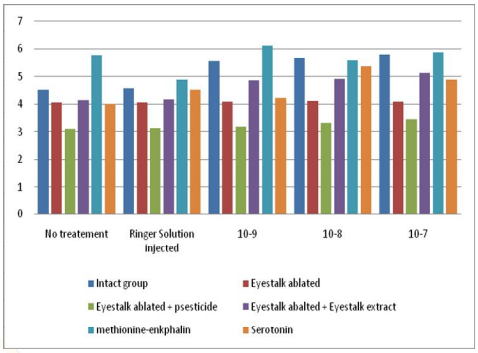

Fig 3.8

Table-3.9 Effect of pesticide (Fenvalerate) impact and addition of Methionine-enkephalin and Serotonin injection into intact, eyestalk ablated and eyestalk extract injected crabs on muscle and phosphorylase 'A' level in the crab *Paratelphusa Jacquemontii* (Rathban).

arameters	Intact group	Eyestalk ablated	Eyestalk ablated + pesticide	Eyestalk ablated + Eyestalk extract	methionine-enkephalin	Serotonin
No treatment	1.92 ± 0.21	0.99 ± 0.22	0.84± 0.23	1.48 ± 0.31	1.08 ± 0.32	1.03 ± 0.28
Ringer Solution injected	1.94 ± 0.11	1.02 ± 0.06	0.82± 0.11	1.52 ± 0.23	1.10 ± 0.67	1.01± 0.71
10^{-9}	3.02 ± 0.22	1.01 ± 0.07	0.84± 0.16	1.63 ± 0.22	2.13 ± 1.23	2.23 ± 1.06
10^{-8}	3.01± 0.12	1.04 ± 0.06	0.86 ± 0.15	1.75 ± 0.13	2.57 ± 0.38	2.37 ± 0.98
10^{-7}	3.26 ±0.45	1.06 ± 0.21	0.88 ±0.16	1.98 ± 0.14	2.88 ± 0.45	2.89 ± 0.78

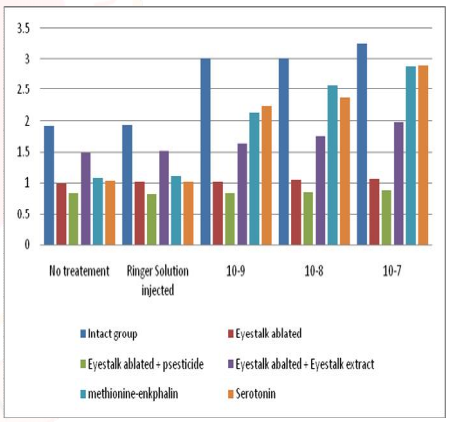

Fig 3.9

Table-3.10 Effect of pesticide (Fenvalerate) impact and addition of Methionine-enkephalin and Serotonin injection into intact, eyestalk ablated and eyestalk extract injected crabs on phosphorylase 'AB' and muscle level in the crab *Paratelphusa Jacquemontii* (Rathban).

Parameters	Intact group	Eyestalk ablated	Eyestalk ablated + pesticide	Eyestalk ablated + Eyestalk extract	methionine-enkephalin	Serotonin
No treatment	2.49 ±0.22	2.22±1.01	1.63±0.92	1.31±0.98	2.08 ± 0.32	1.03 ± 0.28
Ringer Solution injected	2.52±0.45	2.18±1.10	1.61±0.88	1.36±0.67	2.10 ± 0.67	1.01± 0.71
10^{-9}	3.44±0.	2.22±0.	1.64±0.	1.48±0.	2.46±0.	2.40±0.

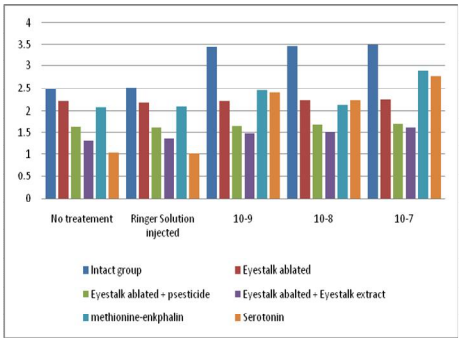

Fig 3.10

	89	98	77	86	78	77
10^{-8}	3.46±0.99	2.24±1.12	1.68±0.78	1.52±0.76	2.13 ± 0.23	2.23 ± 1.06
10^{-7}	3.49±0.87	2.25±0.87	1.70±0.83	1.62±0.57	2.89±0.87	2.78±0.99

3.2 Discussion: Effect of injection of Methionine-enkephalin in Eyestalk ablated Crab.

The role of eyestalks and involvement of Methionine-enkephalin in the regulation of hemolymph sugar level was studied. It is observed that bilateral eyestalk ablation significantly decreased the hemolymph sugar levels; whereas injection of eyestalk extract into ablated crabs significantly increased the hemolymph sugar levels. Total carbohydrate (TCHO) and glycogen levels were significantly increased in hepatopancreas and muscle of eyestalk-ablated crabs, with a decrease in phosphorylase activity. Injection of eyestalk extract into ablated crabs resulted in partial/complete reversal of these changes. Injection of Methionine-enkephalin into intact crabs significantly increased the hemolymph sugar level in a dose-dependent manner.

Effects of injection of Serotonin into Eyestalk ablated Crab.

Injection of serotonin into intact crabs resulted in significant hyperglycemia in a dose-dependent manner when compared to the controls, whereas injection of physiological saline did not cause any significant effect on hemolymph glucose level.

At doses between 10^{-9} mol/crab and 10^{-6} mol/crab, the effect was statistically significant and dose dependent. For doses lower than 10^{-9} mol/crab, however, serotonin did not elicit any hyperglycemic response, whereas doses higher than 10^{-6} mol/crab exhibited a saturated response in inducing hyperglycemia. In the subsequent experiments, 10^{-6} mol/crab was selected as injection dose.

The hemolymph glucose level increased significantly (pb0.001) within 1-h after serotonin injection and reached a highest peak at 2-h. Hemolymph glucose level declined gradually after 2-h and reached control level 6-h post-injection. In the next experiment we determined whether serotonin induced hyperglycemia was mediated by the eyestalk hormone, CHH. Eyestalk less crabs (24-h post ablation) were injected with different doses of serotonin. No elevation in hemolymph glucose concentration was observed 2-h after injection of serotonin in eyestalk ablated crabs. As expected, bilateral eyestalk ablation produced significant hypoglycemia.

CONCLUSION

Injection of Methionine-enkephalin into intact crabs significantly increased the hemolymph sugar level in a dose-dependent manner but in bilateral eyestalk ablation significantly decreased the hemolymph sugar levels; whereas injection of eyestalk extract into ablated crabs significantly increased the hemolymph sugar levels.

The fresh water crabs, *Paratelphusa Jacquemontii* were injected with serotonin, hemolymph glucose and CHH levels were determined. Injection of serotonin into intact crabs caused significant hyperglycemia in a dose-dependent manner. In contrast, injection of serotonin did not cause any change in hemolymph glucose level in eyestalk ablated crabs.

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SYNTHESIS, CHARACTERIZATION AND ACOUSTICAL STUDY OF CHLOROSUSTITUTED CHROMONE IN 70% DIOXANE-WATER MIXTURE

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ABSTRACT

Chromone were synthesized by heating of the mixture of 1-(2-hydroxy-5-chlorophenyl)-3-phenyl-1,3-propanedione and 2,4 dimethoxy benzaldehyde in presence of ethanol and piperidine for 2 min in microwave to give chromanone. chromanone was refluxed in presence of crystal of iodine in DMSO. Characterisation and structural elucidation were done on the basis of chemical, analytical and spectral analysis acoustical properties of chlorosubstituted chromone have been investigated from the ultrasonic velocity, Adiabatic compressibility (β), Apparent molar volume (Φv), Apparent molar compressibility (Φk) at different concentration and 70% dioxane-water mixture values have been calculated from the experimental data. These above parameters are used to discuss the structural and molecular interactions

Keywords: *Synthesis, Acoustical parameters*

INTRODUCTION

Heterocyclic compounds promote the life on earth as they are widely distributed in nature and essential for the sustains of life Chromones are the hetrocyclic compounds with benzopyron network with substituted keto group on pyron ring. It is an isomer of coumarin. The word chromone can be derived from the greek word chroma meaning "color" which indicates that many chromone derivatives exhibit a broad variation of colors. Chromones constitute one of the major classes of naturally occurring compounds, and interest in their chemistry continues unabated because of their usefulness as biologically active agents[1]. The compounds that contain the chromone skeleton (4*H*-benzopyran-4-one) (flavones and chromones) are widely spread in nature, and they are part of the flavonoid family. Chromones and their structural analogues (e.g. flavonoids), in particular, are known to play an important protective role against oxidation processes, either from deleterious radical species or from UV radiation, therefore displaying pharmacologically relevant functions such as antibacterial [2], anticancer[3], antiviral[6] , anti-inflammatory [5] anti-HIV[4]. They have therefore motivated great interest within the medicinal chemistry field, the chromone moiety supposedly being the essential component of pharmacophores of a large number of bioactive molecules.[7] One-pot multicomponent reactions have received considerable attention in synthetic chemistry as they can produce target products from readily available starting materials in one reaction step without isolating the intermediates thus reducing reaction times, labor cost, and waste production.

It is the science of sound waves above the limits of human audibility. Sound is our experience of the propagation of pressure wave through some physical elastics medium such as air or liquids. The pressure waves are generated from some type of mechanical disturb band, generally human hearing cannot go beyond about 18 KHz. The sound beyond this limit is inaudible and is defined an ultrasound. Ultrasound as sound above 20 KHz and up to 100 KHz can generate greater acoustics energy and affect chemical reactivity. The ultrasound range applied in sono- chemistry has been extended upto 2 MHz.[13].

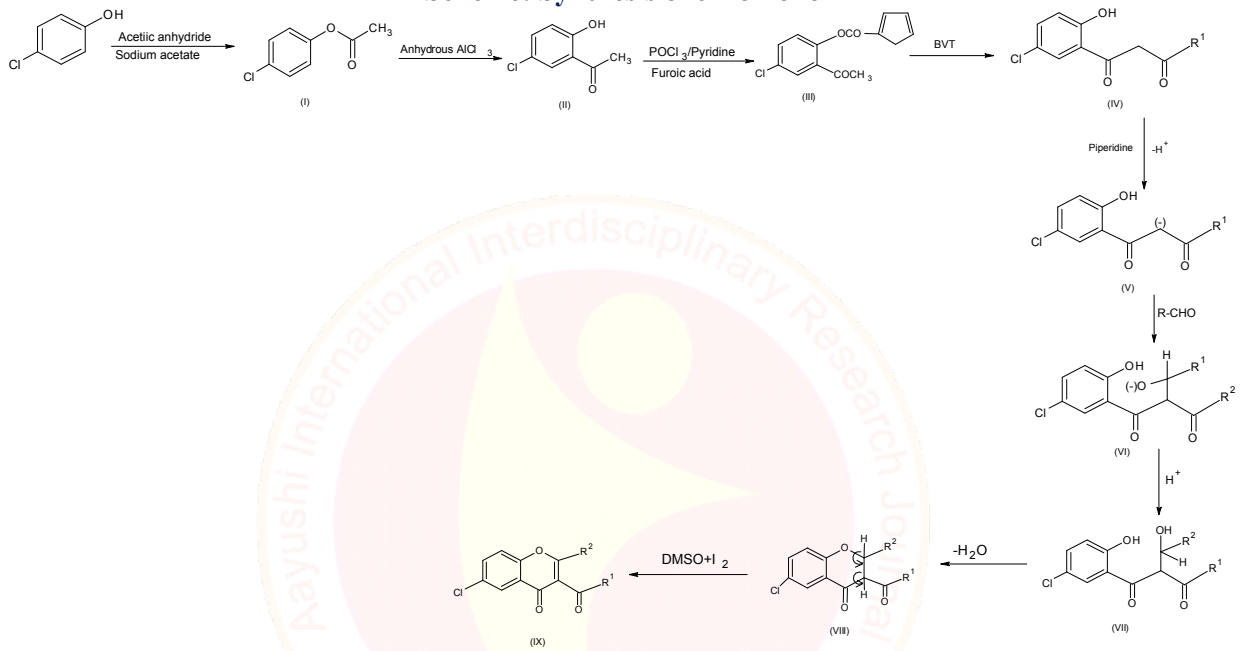
EXPERIMENTAL

Synthesis of 2-(2,4dimethoxy phenyl)-3-furoyl-6-chlorochromone

A mixture of 3-furoyl-2-(2,4 dimethoxy phenyl)-6-chlorochromanone (Vd) (0.01 mol) was refluxed for 1min 45 sec in microwave with a crystal of iodine in DMSO(20ml). After cooling the reaction mixture was diluted with water. the solide product thus separated was filtered, washed with sodium thiosulphate solution and then with water. finally it was crystallized from ethanol to get the compound(VId) Yield: 70%, m.p:171^{0}C.

(VIII) (IX)

Scheme: Synthesis of chromone



Spectral interpretation:

(a) Molecular formula of the (IX)compound $C_{22}H_{15}ClO_6$

(b) The important frequencies observed in the IR spectrum recorded in KBr are correlated as Follows- IR **(υmax)cm^{-1}: 3018(Ar-CH** Stretching); 2934(Ar-OCH_3); 1794(C=O Stretching); 1275(C=O Stretching); 759(C- Cl Stretching)

(c) The PMR spectrum of the compound (IIb) was recorded in $CDCl_3$ with TMS as an internal standard. The observed chemical shifts and their correlations are as follows-
NMR: δ 6.44-6.56 (m,9H,Ar-H); 3.90 (s,3H,OCH_3)

ULTRASONIC INTERFEROMETER

An ultrasonic interferometer is a simple and direct device to determine the ultrasonic velocity in liquids with a high degree of accuracy. Ultrasonic velocity plays an important role in the investigation of intermolecular interactions. The structural arrangements are influenced by the shape of the molecules as well as by their mutual interaction. Velocity measurement combining with other physical quantities provides information of more than 30 parameters. A number of parameters related to ultrasonic velocity are :

Ultrasonic velocities measurements are extensively used to study the intermolecular interactions. The structural arrangements are influenced by the shape of molecules as well as by their mutual interactions. The objective of the study was molecular interactions in the liquid mixtures is very much important to study the structural properties of molecules and great deal of interest in investigating the solute-solute, solute-solvent and solvent-solvent interaction.

i) Ultrasonic velocity:

Ultrasonic velocity $u = n \times \lambda$

ii) Adiabatic compressibility (β):

$$\beta = \frac{1}{v^2.d}$$

iii) Apparent molar volume (Φv) :

$$\Phi v = \frac{1000 (do- ds) I m ds do)}{} + \frac{M}{}$$

C.ds.do ds

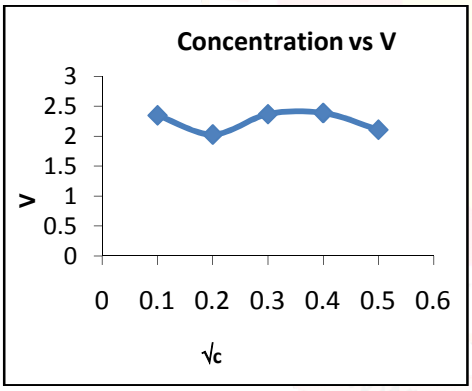
iv) Apparent molar compressibility (Φk) :

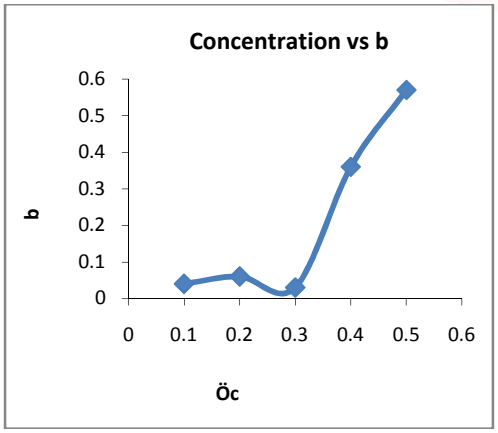
$$\Phi k = \frac{1000\,(\beta s.do - \beta o.ds)}{C.ds.do} + \frac{\beta s\,.m}{ds}$$

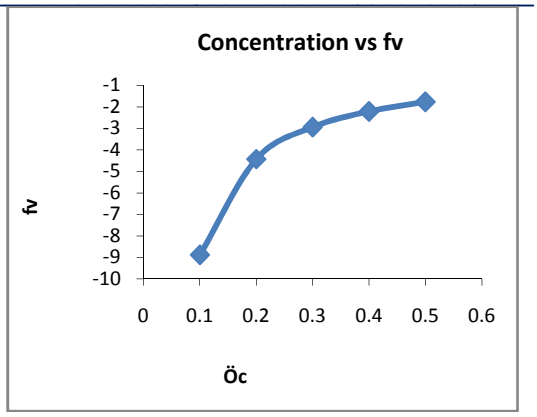
where, do = density of pure solvent
ds = density of solution
m = molarity of solution
M = molecular weight of solute
βo= adiabatic compressibility of pure solvent, and
βs = adiabat ic compressibility of solution.

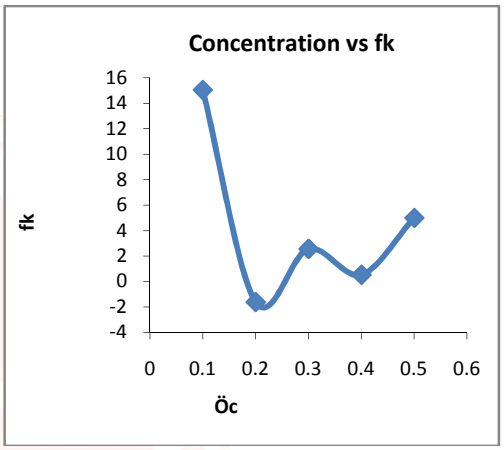
Ultrasonic velocity and related parameters at different concerntration:

Concerntration	Ultrasonic velocity	β	Φv	Φk
0.1	2.35	0.04	-8.89	15.03
0.2	2.03	0.06	-4.43	-1.61
0.3	2.37	0.03	-2.95	2.56
0.4	2.39	0.36	-2.22	0.53
0.5	2.11	0.57	-1.77	4.99









RESULTS AND DISCUSSION

The ultrasonic method is powerful tool for characterizing physico-chemical properties and existence of molecular interaction in the mixture. ultrasonic velocities mixtures of substituted Dioxane-Water Mixture have been experimentally determined over entire concentration range at atmosphere pressure. It indicates that a strong solute-solvent interaction. The graphical data reveals that the molecular interaction in chromone varies with change in molar concerntrations. The change in velocity is always assisted by the functional groups present in structural constitution of the chromones .It has also been observed that halogens help to decrease with increasing velocity and Adiabatic compressibility as compared to others. Apparent molar volume decrease with increasing varies with increasing concentration. Apparent molar compressibility increasing with decrease from the various five concentrations.

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ONE POT SOLVENT FREE SYNTHESIS OF CURCUMIN AND ANALOGUES USING VITAMIN B1 AS AN EFFICIENT CATALYST

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ABSTRACT

A highly efficient, solvent free and simple single protocol is described for the synthesis of curcumin and analogues by grinding method using Thiamine hydrochloride (Vitamin B_1) and Calcium oxide as reagent. Two moles of aromatic substituted aldehydes with acetylacetone presented as starting component. This environmentally benign methodology may prove to be valuable alternatives to traditional curcumin synthesis methods.

Keywords: *Curcumin, synthesis of turmeric, Vitamin B_1, thiamine hydrochloride catalyzed, green reaction*

INTRODUCTION

Curcumin is natural product and isolated from plant *Curcuma longa*, founds with two isomers demothoxy curcumin (DMC) and bisdemethoxy curcumin (BDMC) as yellow colour mixture, collectively called as Curcuminoids. [1] Modern science validate that Curcumin inhibit induction of nitric oxide [2], 5-Chloro curcumin exhibits anti-oxidant [3] properties, due to presence of phenolic unit curcumin exhibits anti-oxidant properties in water [4]. Curcumin found to be excellent inhibitor for various type of cancer [5] such as gastrointestinal cancer [6], breast cancer [7], pancreatic cancer [8], lung cancer [9], blood cancer properties [10], anti-cervical and anti-oral cancer. [11, 12] Curcumin, also reported for possessing anti-inflammatory [13], anti-bacterial [14], anti-diabetic [15], anti-Alzheimer [16] (AD) and anti-HIV [17] properties. Curcumin found useful natural product for treatment of psychiatric disorder like depression [18], many other studies underline pharmacokinetic importance of curcumin. [19, 20]

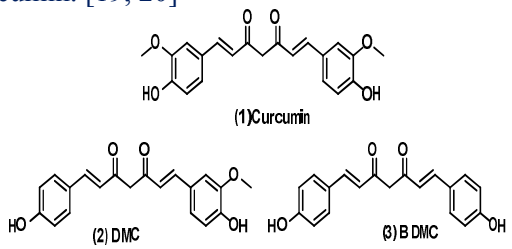


Figure 1.1 Structure of Curcuminoids, (2) Demthoxy curcumin (DMC) and (3) Bisdemethoxy curcumin are differ from Curcumin (1) by absence of methoxy (-OMe) group.

Bioavailability of curcumin [21] is major problem, which prevent curcumin to establish as super drug. Many attempts were made, by synthesizing of curcumin and its analogues in the laboratory, in search of novel pharmacokinetic properties. Majority of such methods involving one mole of Acetylacetone and two moles of vanillin along with suitable base. Conventional synthesis of Curcumin required longer time. [22] Success of the reaction depends upon condensation of terminal methyl groups with aromatic aldehydes. Due to presences of more active methylene moiety at centre, it reacts first and reduce yield of product. Practically, curcumin analogues with non-hydroxyl aromatic aldehydes do react to obtained satisfactory yield. But during the reaction of synthesis of Curcumin or bis-demethoxy curcumin (BDMC) yield of product fall down. One way is to protect hydroxyl groups followed by Claisen-Schmidt reaction. Another way is modification in reaction condition by trial and error basis.

Experimental

All the compounds used in synthesis were of analytical grade; the melting points of the compounds were determined in open head capillary and are uncorrected. The reaction was carried out without further purification of solvent or chemicals. H^1 NMR spectra were recorded on a DRX-300 Bruker FT-NMR spectrophotometer in $CDCl_3$/DMSO-*d6* as solvent using TMS as internal standard. Chemical shifts (δ) are reported in ppm. The IR spectra were recorded using Perkin Elmer

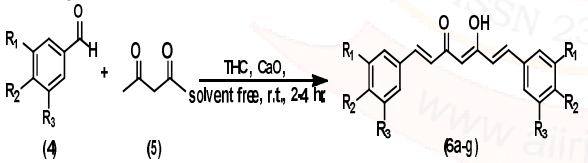
spectrometer (KBr plates). All the compounds were checked for purity by thin layer chromatography (TLC). Mobile phase was used Methanol 3% in DCM. TLC visualization was done with UV chamber and other usual spray reagents.

GENERAL PROCEDURE

In a mortar, aromatic aldehyde (0.02 mol), acetylacetone (0.01 mol, 1gm) and calcium oxide (0.01 mol, 560mg) was added, Thiamine hydrochloride (10mol%, 265mg) was added in single portion, reaction contains was pestle for next few 30 minutes vigorously and further allowed to stand at room temperature for appropriate time (2 hrs.-4 hrs., TLC check) with occasional stirring to offer product. After completion of reaction (TLC) check, distilled water was added to reaction mixture. Yellow mass filter out washed with water and light petroleum repeatedly, dried under high vacuum to offered desired product. During optimization of amount of THC and metal oxide, products were separated by column chromatography using silica gel (60-120 mesh), mobile phase was Methanol (2%) in Chloroform.

Series of sets of reaction were performed to optimized reaction condition. Present work is extended part of our previously reported curcumin and analogues synthesis. [23]

Reaction Scheme 1: Derivative preparation of Curcumin analogues using THC, CaO as catalyst and without solvent



Spectral data of representative compound: (1E,4Z,6E)-5-hydroxy-1,7-bis(4-hydroxy-3-methoxyphenyl)hepta-1,4,6-trien-3-one (6a)

IR (KBr): 3542, 1635, 1622, 1046, 982 cm^{-1}, ^{1}H-NMR (DMSO-*d6*) δ 3.89 (s, 6H, -OCH_3), 6.12 (s, 1H, H-4), 6.73(d, 1H, H-7), 6.75 (d, 2H, Ar), 6.86 (d, 1H, H-6), 7.12(d, 2H, Ar), 7.16(d,1H, H-2), 7.27 (s, 2H, Ar), 7.65 (d,1H, H-1), 9.75 (s, 2H, -OH), 10.11(s, 1H, enol -OH)

RESULTS AND DISCUSSIONS

In our previous report [23 (a)] we synthesized Curcumin analogues using Thiamine hydrochloride as catalyst and PEG as solvent. Vitamin B1 mainly reported in oxidative condensation reactions. Present attempted was to check possibility of THC as catalyst in curcumin synthesis; hence THC and room temperature condition were kept as fixed factors throughout optimization of reaction.

Two molecules of Vanillin and one molecule of acetylacetone, thiamine hydrochloride stirring as room temperature were selected as fixed parameters for model reaction. To minimize byproduct, cheating metal used. Our focus was on simple workup procedure at room temperature, without any catalyst. Model reaction was performed without any metal chelating agent to ensured need of chelating, when THC was introduced without metal obtained result was not satisfactory.

Calcium hydroxide, one of the meritorious substances for this reaction. As previous reports founds its ability to work as base as well as chelating agent (24), obtained yield was good. Calcium oxide (25) was reported with microwave irradiation techniques, which in fact expeditious method, but report was described to offers product after long 12 hours workup.

Table 2. Optimization of Thiamine hydrochloride and metal oxide and yield of model reaction

Sr. No.	THC: CaO	Yield (%)[a]
1)	5mol%:1eq.	13
2)	10mol%:1eq.	59
3)	15mol%:1eq.	63
4)	5mol%:50mol%.	----
5)	10mol%:10mol%	Trace[#]
6)	15mol%:10mol%	----

[a]Isolated yield, [#] TLC check

Calcium oxide (1 eq.) and THC (15mol%) were found most productive and kept constant for further analogues synthesis of curcumin as shown in **Table 3**. It was found that –OCH_3, -Br, -F and methyl substituted benzaldehyde founds more productive. Whereas, Curcumin (6a), BDMC (6b) and other –OH containing curcumin (6d) analogues are less productive in nature. It was observed that –OH containing curcumin analogues are comparatively more water soluble and lost during workup [23].

Table 3. Table showing curcumin and substituent's of analogue and their melting point.

Sr. No.	R_1	R_2	R_3	Time in min.	Yield in %[a]	M.P. (°C) [23 (a)]*
6a	-OCH_3	-OH	-H	240	63	179-180
6b	-H	-OH	-H	240	50	174-176
6c	-H	-OCH_3	-H	90	67	162-163
6d	-H	-Br	-H	90	70	152-145

6e	-H	-$OCOCH_3$	-H	90	45	171-173
6f	-H	-NO_2	-H	300	13	152-153
6g	-H	-Cl	-H	240	46	150-151

[a] Isolated yield, * Literature reports.

Curcumin and analogues obtained as products were determined by Melting point and representative products were scan for IR and ^{1}HNMR. Thus obtained results were compared with reported one and found satisfactory. [24, 26]

CONCLUSIONS

In conclusion, we describe environmentally benign, solvent free, cost effective, mild work-up methodology for the synthesis of curcumin and analogues. Aromatic aldehydes and acetyl acetone are easily available, thiamine hydrochloride and calcium oxide are cheap and non-hazardous, and stirring at room temperature and finally no acid or base workup enhance significant utility of present methodology.

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PHYTOCHEMICAL STUDY OF SOME ANTIDIBETIC MEDICINAL PLANTS IN SATPUDA REGION

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ABSTRACT

The most important traditional medicinal plants having antidiabetic properties occurs in sapuda hills Amravati region. It is popular traditional medicinal plantspresence in warm tropical and subtropical region. It has been used traditionally in local people for treatment to reduce diabetic. The phytochemical analysis of some diabetic controlling plants was evaluated to ascertain some of the secondary metabolites that exhibit medicinal properties. The results of phytochemical screening of ethanol crude leaves extract of some diabetic controlling plants revealed the presence of alkaloids, tannins, saponins and flavonoids. These alkaloids observed by various techniques like solvent extraction ultrasonicator, rotavapour, thin layer chromatography, column separation and hptlc technique.

Keywords: *Phytochemical, Medicinal plant, antidiabetic,antioxidant andhptlc technique etc.*

INTRODUCTION

According to WHO report, globally, approximately 347 million people or 5-8% of the global population is estimated to be affected by this disease (1).Diabetes now is becoming the third "killer" of mankind among another disease, It has also been predicted that by the year 2025, more than 75% of people with diabetes (2).Diabetes is most popular diseases among the people in both developed and developing countries.Diabetes is a disorder of carbohydrate, fat and protein metabolism action tominimize production of insulin or opposed to its action. Diabetes is a chronic disease that occurs either when the pancreas does not produce enough insulin or when the body cannot effectively use the insulin that it produces.Insulin is a hormone that regulates blood sugar (3-4).Hyperglycemia, or raised blood sugar, is a common effect of uncontrolled diabetes andleads to serious damages to many of the body's organs, especially the nerves and blood vessels. Hyperglycemia diabetes can damage the heart, blood vessels, eyes, kidneys and nerves. Diabetes increases the risk of heart disease and 50% of people with diabetes die of cardiovascular disease (5).

In view of its medical importance, the present study was focused to know the traditional medicinal plantsfor their antidiabetic potential in different studies. The present study isinitiated to document the some traditional medicinal plants that are used by natives Amravatidistrict satpuda hills region for the treatment of diabetes.

MATERIALS AND METHODS

Plant material

Some diabetic controlling plants leaves or useful part were collected during the month of January 2015-Octomber 2015, from Amravati region Maharashtra, India. The fresh leaves were separated and kept for shade drying. Dried material was powdered using mechanical grinder and heat in microwave oven to get the powder of desired coarseness. Powdered material was preserved in an air tight container.

Sr no.	Plant name /family /local name	Medicinal use of plant	Plants photographs
1	TribulusTerrestris Lin. Zygophyllaceae. Gokhur/Gokshura Puncture Vine	Seed extract used form Gokhur plants.	
2	Catharanthus roseus (L) Apocyaceae , Sadafully. Sadabahar.	leaf extracts from Sadafully tree.	
3	Aloe barbadensis (L) Liliaceae Gheequar Aloe vera	leaf extracts from Aloe vera.	
4	Gymnemasylvestre Linn Asclepiadaceaegudmar bedakichapala Madhunashini	leaf extracts fromgudmar	

2.1) Preparation of extracts

Dried leavesor useful material plant part powder mixed with ethanol and keep in ultrasonicator for half and hour to mix all chemical constituents in ethanol solvent was subjected to successive extraction in a Soxhlet's extractor using ethanol and water. The extracts were filtered and the filtrates were concentrated under Rota vapour at room temperature to obtain the extracts as solid residues.

2.2. Primary Phytochemical screening

Phyto chemical screening was performed using standard procedures.(6)

Table 1: Qualitative Analysis of Phytochemicals

sr.no	Test	Observation
1	Test of Alkaloids	
	1.0ml of plant extract was taken and then adds 1.0 ml of saturated solution of picric acid was added.	Yellow colour appears
2	Test of Tannins	

	About 0.5 g of the extract was boiled in 10 ml of water in a test tube and then filtered. A few drops of 0.1 fecl3 was added	Brownish green or blue- black coloration.
3	Test of Saponins	
	0.5g of extract was added in 5ml of distilled water in a test tube. The solution was shaken vigorously. The frothing was mixed with 3 drops of olive oil and shaken vigorously.	Stable persistent froth appears. Formation of an emulsion
4	Test for Tarpenoids	
	5 ml of extract was mixed with 2 ml of chloroform and 3 ml of conc. H2SO4 was carefully added to form a layer.	A reddish brown coloration of the interface was formed.
5	Test for Flavonoids	
	5 ml of dil. Ammonia solution were added to a portion of the crude extract followed by addition of conc. H2SO4.	Yellow coloration occurs.
6	Test for Phenol	
	2 ml of extract was taken and add 2 ml of Folin's reagent.	Appearance of violet or brown colour.

2.2) Thin Layer Chromatography (TLC)

TLC analysis was carried out for the plant extracts dissolved in ethanol and water solvent. For the analysis the silica gel sheet was used, fresh leaves extracts were analyzed using TLC. The sheets are kept in TLC Chamber for one hour, depending on the polarity of the eluted fractions to be analyzed. The sheets were treated with 1% ninhydrin diluted to acetone.

2.3) HPTLC Technique

HPTLC analysis was carried out for the plant extracts dissolved in ethanol. The HPTLC characterization perform at Sophisticated Instrumentation Centre For Applied Research & Testing (SICART),Sardar Patel Centre for Science & Technology, Charutar Vidya Mandal **V**allabh Vidyanagar.

3) Results and discussion.

3.1) Phytochemical investigation:

The Phytochemical screening of Dried leaves or useful material plant part showed positive results as the tests like Terpenoids, Flavonoids, Saponins, Tannins and steroids. This data clear that there is presence of various phytochemical in Plant extract diabetic treatment alkaloid has been marketed under the proprietary name Vinculin. Catharanthine is used as antidiabetic drug.

Table-2. The total concentration of phenolic, flavonoids , Alkaloids and steroids.

Sr no	Plant name	phenolic (ug/ml)	Flavonoids (ug/ml)	Alkaloids (ug/ml)	Steroids (ug/ml)
1	TribulusTerrestris	7.232	32.34	14.232	44.232
2	Catharanthus roseus	12.345	4.568	14.987	11.562
3	Aloe barbadensis	47.365	1 3.562	23.123	24.232
4	Gymnemasylvestre	65.236	25.26	12.134	29.562

3.2. Quantitative spectrophotometric analysis for phenolic content and flavonoids:

The total phenolic and flavonoids content of plant aqueous extract were determined spectrophotometrically using the tannic acid and quercetin standard calibration curves, respectively, as per Ranjana sing et al (2015)(7). Both standard curves showed linearity with R_2 value 0.962 and 0.956. The total phenolic and Alkaloids content was found as per given table 3.2. presence of various phytochemical in Plant extract diabetic treatment alkaloid is used as antidiabetic drug.

3.3.TLC purification of the extracts

The TLC of ethanolic extract of plant is shown with their RF values. Hence, further investigations are required to isolate, purify and characterize those compounds which are responsible for the treatment of pharmaceutical disorders like anti-cancer, antitumor, antidiabetic properties.

Table 3: TLC of ethanol extracts in mobile phase petroleum ether: benzene: methanol (16:4:2).

Sr no	Plant name	N0. of Bands	Rf Value	Spraying Regents	Colour of Band appeared	Phytochemical Detected
1	TribulusTerrestris	5	0.08	Vanillin-sulphuric acid reagent	blue	Saponins
			0.42	5% Ferric chloride	Dark grey	Flavonoid
			0.54	5% Ferric chloride	Dark grey	Flavonoid
			0.72	FeCl3	Intense red	Phenol
			0.86	Ethanolic sulphuric acid	brown	Alkaloids
2	Catharanthus roseus	3	0.32	5% Ferric chloride	Dark grey	Flavonoid
			0.54	5% Ferric chloride	Dark grey	Flavonoid
			0.72	FeCl3	Intense red	Phenol
3	Aloe barbadensis	5	0.11	Vanillin-sulphuric acid reagent	blue	Saponins
			0.22	Kedde reagent	blue violet	glycoside
			0.42	5% Ferric chloride	Dark grey	Flavonoid
			0.54	5% Ferric chloride	Dark grey	Flavonoid
			0.78	Ethanolic sulphuric acid	brown	Alkaloids
4	Gymnemasylvestre	4	0.09	Vanillin-sulphuric acid reagent	blue	Saponins
			0.42	5% Ferric chloride	Dark grey	Flavonoid
			0.58	FeCl3	Intense red	Phenol
			0.72	Ethanolic sulphuric acid	brown	Alkaloids

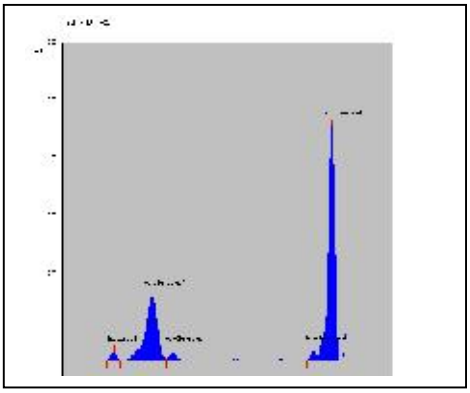
Table (3.1): Phytochemical screening of extracts of medicinal plants

Sr no	**Plant name**	**Plant parts used**	Alkaloids		Tannins		Saponins		Flavonoid's		Steroids		Terpenoids	
			Enol	aq.	Enol	aq.	Enol	aq.	Enol	Aq.	Enol	aq.	Enol	aq.
1	TribulusTerrestris	Fruit	++	+	++	++	++	+	+++	++	+++	++	_	_
2	Catharanthus roseus	Leaves	++	+	+	++	++	++	+	_	++	_	_	+
3	Aloe barbadensis	Leaves	++	_ _	++	++	_	_	+++	_	++	_ _	_ _	+ +
4	Gymnemasylvestre	Leaves	++	_	++	+	+++	+	++	++	_ _	+	_	_

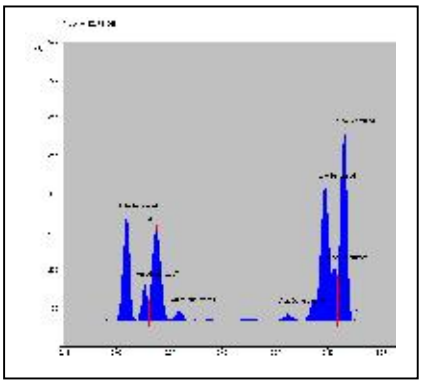
3.4. High Performance Thin Layer Chromatography (HPTLC):

Chromatographic fingerprint profile of ethanol extracts plants were studied by HPTLC. For better resolution and maximum number of spots, and satisfactory resolution was obtained in the solvent Toluene: Ethyl acetate: Formic acid:: 8:4:2. After scanning and visualizing the plates in absorbance mode at both 254nm and 366 nm range.

The results from HPTLC finger print, The Rf values ranged from 0.07 to 0.99. It is also clear from Table 3.4 and the chromatogram as shown in (Fig. 3) that were found to be more predominant as the percentage area is more with respectively. HPTLC plate showed different colour phytoconstituents of ethanol extract. The bands revealed presence of different colour bands showing the presence of steroids, alkaloids and terpenoids etc.



1) Catharanthus roseus



2) TribulusTerrestris

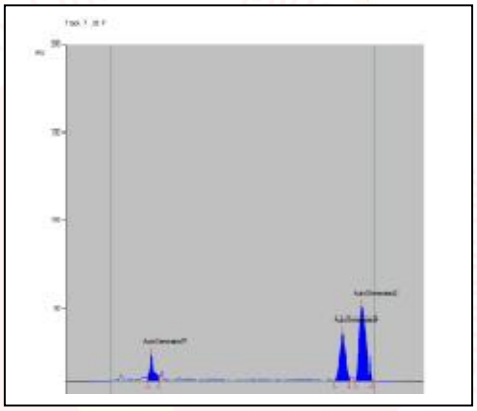


Table 4: HPTLC of ethanol extracts in mobile phase Toluene: Ethyl acetate: Formic acid: (8:4:2)

Sr no	Plant name	N0. of Bands	Rf Value
1	Catharanthus roseus	4	0.19,0.31,0.83,0.92.
2	TribulusTerrestris	8	0.11,0.16,0.23,0.29,0.69,0.79,0.82,0.91
3	Gymnemasylvestre	3	0.22,0.87,0.91.

CONCLUSION

In the present investigation, some diabetic controlling Medicinal plant species which are responsible for the treatment of pharmaceutical disorders like anti-cancer, antitumor, antidiabetic properties. These demand an urgent attention to conserve such vital resources so as to optimize their use in the primary health care system. Now a day, conservation of traditional knowledge is necessary related to modernization of the region and transferring it to next generation. Further advanced spectroscopic studies are required for the structural elucidation and identification of compounds

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SYNTHESIS, CHARACTERIZATION AND BIOLOGICAL STUDIES OF NEWLY SYNTHESIZED 3-ARYL(NITROANILINE)-4-S-BENZYL-6-P-TOLYLIMINO-2-PHENYLIMINO-2,3-DIHYDRO-[1,3,5] THIADIAZINES[HYDROCHLORIDE]

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ABSTRACT

The progress achieved in the synthesis of heterocyclic compounds with biological potential is due to improvement of the methodological study of tested substance. Several five and six membered aromatic systems having three hetero atoms have been studied because of their interesting physiological properties. Serial of 3-Aryl(Nitroaniline)-4-*S*-benzyl-6-*p*-tolylimino-2-phenylimino-2,3-dihydro-[1,3,5] thiadiazine [Hydrochloride] has been synthesized by the interaction of 1-Aryl(Nitroaniline)-5-*p*-tolyl-2-*S*-benzyl-2,4-isodithiobiuretes with phenyl isocyanodichloride in refluxing chloroform medium. Initially evolution of hydrochloric gas to obtain 3-aryl (Nitroaniline)-4-*S*-benzyl-6-*p*-tolylimino-2-phenylimino-2,3-dihydro-1,3,5thiadiazines [hydrochloride]. Constitutions of synthesized compound have been delineated on the basis of chemical transformation, elemental determination, and IR, NMR and Mass spectral studies. These compounds were screened for their antibacterial and antifungal activities against–*Escherichia coli, Proteus vulgaris, Staphylococcus aureus, Salmonella typhimurium, Klebsiella pneumonie, Psudomonas aeruginosa, Aspergillus Niger* and *Candida albicance.* These compounds show appreciable activity towards these microorganisms.

Keywords: *2,4- isodithiobiuretes, phenyl isocyanodichlorides, -1, 3, 5-thiadiazines, Antimicrobial Activity*

INTRODUCTION

Many compounds consisting of 5-membered heterocyclic rings represent important building blocks in organic and medicinal chemistry. In addition, they are interesting in their own right, due to their pharmacological properties[1-3]. The progress achieved in the synthesis of heterocyclic compounds with biological potential is due to improvement of the methodological study of tested substance. Several five and six membered aromatic systems having three hetero atoms have been studied because of their interesting physiological properties. Their analogues have been noted to exert a wide range of clinical applications like antifungal[5-6], antimalerial[7], anticancer[8], anti-HIV-1[9], carbonic ahhydrase inhibitors[10].

Thiadiazine and its derivatives are found as an important pharmacologically[11] and biologically active precursor in the field of heterocyclic chemistry. Some amino derivatives prove useful as herbicides, insecticides, fungicides, diuretics and ant diabetics. Organic thiocyanates [12-14] and sugar thiadiazines [15-17] also posses great potential as carbonic anhydrase inhibitor, PET inhibitor, anti HIV agent, antitumor agent, psychotropic agent and used in treatment of breast cancer.

The heterocyclic compounds having 1, 3, 5-thiadiazine enhanced pharmaceutical [18-19], medicinal, agricultural and industrial activities of the drugs and medicines. So the drugs or medicines containing thiadiazine nucleus are now used extensively in medical, biochemical and biotechnological faculties. The biological importance of the 1, 3, 5-thiadiazine derivatives is further emphasized by showing the presence of 1, 3, 5-thiadiazine ring in therapeutic agent

MATERIALS AND METHODS

All chemicals were research grade. Melting points determined are uncorrected. IR spectra were recorded in KBr on a FT-IR Perkin-Elmer RXI (4000-450cm^{-1}) spectrophotometer. ^{1}H NMR measurements were performed on a Bruker DRX-300 (300 MHz FT NMR) NMR spectrometer in $CDCl_3$ solution with TMS as internal reference. The Mass spectra were recorded on a THERMO Finnigan LCQ Advantage max ion trap Mass spectrometer. Optical rotation $[\alpha]_D^{31}$ measured on

a Equip-Tronics Digital Polarimeter EQ-800 at 31^0C in $CHCl_3$. Thin layer chromatography (TLC) was performed on silica Gel G and spots were visualized by iodine vapour. The compounds describe in this paper were first time synthesized by the multistep reaction protocol

RESULTS AND DISCUSSION

Several 3-Aryl (Nitroaniline)-4-*S*-benzyl-6-*p*-tolylimino-2-phenylimino-2,3-dihydro-[1,3,5] thiadiazine [Hydrochloride] (3a-d) have been synthesized by the interaction of 1-Aryl(Nitroaniline)-5-*p*-tolyl-2-*S*-benzyl-2,4-isodithiobiurets (2a-d) and phenyl isocyanodichloride (1). To the chloroform suspension of Phenyl isothiocyanate chlorinated on chlorination assembly .This chlorinated solution was added to 1-Aryl (Nitroaniline)-5-*p*-tolyl-2-*S*-benzyl-2,4-isodithiobiuret in chloroform medium . Then the reaction mixture was reflux for 3 hrs. and a sticky mass obtained as a residue was triturated several times with petroleum ether (60-80°C).. A product will separate out.

The IR spectra of products shows bands due to Ar-H, N-H, C=N, C-N, C-S stretching and ^{1}HNMR spectra of products distinctly displayed signals due to aromatic protons and aliphatic Protons. The Mass spectrum of product was also observed. The identities of these newly synthesized compounds have been established on the basis of usual chemical transformations and also IR, ^{1}H NMR and Mass spectral studies[20-22].

EXPERIMENTAL

1] Preparation of phenyl isocyanodichloride

a] Preparation of phenyl isothiocyanate: [22]

Place a 500ml conical flask in freezing mixture of ice and salt. Add to it 30 ml of conc. Ammonia solution and 15ml of pure carbon disulphide. Stir the mixture and run in 19 ml of aniline about 15 min. Stir for a further 30min and allow standing for another 30min. A heavy ppt of Ammonium phenyl dithiocarbamate separates. Filter it and dry it.

Transfer the salt to a 2lit R.B. flask. By 2-3 extractions with 100ml portion of distilled water. To this solution of 50gm of lead nitrate in distilled water with constant stirring. Lead sulphide ppt is observed. Steams distill the mixture into a receiver containing 10ml of 0.5ml H_2SO_4 as long as organic material passes over. Separate the oil; dry it over anhydrous Calcium Chloride or Magnesium Sulphate.

b] Preparation of phenyl isocyanodichloride

Through the chloroformic solution of phenyl isothiocyanate, chlorine gas was bubbled maintaining the temperature of the system below 10°C. After the addition of chlorine was completed, the yellow reaction mixture was diluted with 40-50ml petroleum ether (60-80°C). The solvent was then removed by distillation under vacuume. The whole operation was repeated several times with petroleum ether then phenyl isocyanodichloride was obtained as pale yellow oil.

2] Synthesis of 1-Aryl (Nitroaniline)-5-*p*-tolyl-2-*S*-benzyl-2,4-isodithiobiurets (2a-d)

a) Preparation of 1-Aryl (Nitroaniline)-*S*-benzyl isothiocarbamide

To the ethanolic suspension of Nitroaniline thiocarbamide was added benzyl chloride and the reaction mixture was reflux for 90 min. Afterward the reaction mixture was cooled and rendered basic with dil. ice cold NH_4OH and a sticky residue was obtained which on standing for 1 to 2 hrs. Solidifies. It was filtered and washes with petroleum ether.

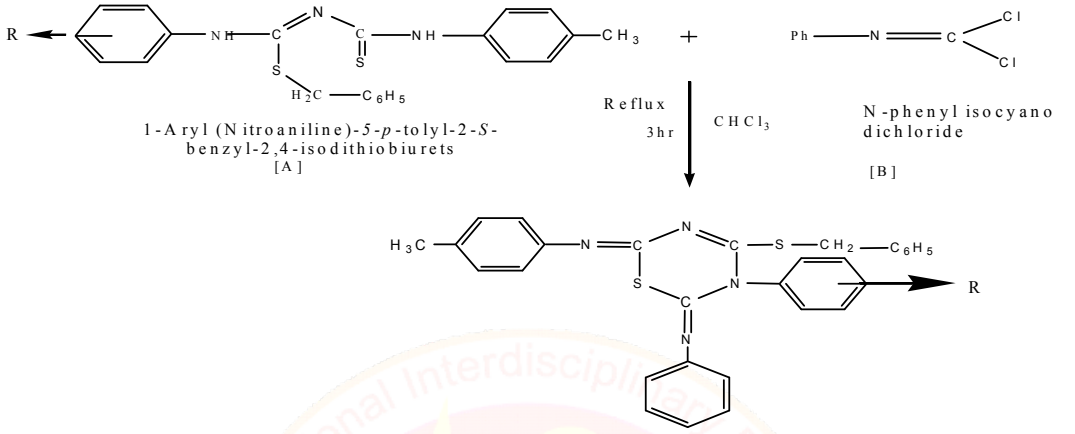
b) Preparation of 1-Aryl (Nitroaniline)-5-*p*-tolyl-2-*S*-benzyl-2,4-isodithiobiurets

Several 1-Aryl (Nitroaniline)-5-*p*-tolyl-2-*S*-benzyl-2,4-isodithiobiurets have been prepared by the interaction of 1-Aryl(Nitroaniline)-*S*-benzyl isothiocarbamide and *p*-tolyl isothiocyanate in benzene medium . To the benzene solution of 1-Aryl (Nitroaniline)-*S*-benzyl isothiocarbamide , *p*-tolyl isothiocyanate was added .This reaction mixture was then reflux over a boiling water bath for 3 hrs. after completion of the reaction, solvent benzene was distilled off and the sticky mass obtained as residue was triturated several times with petroleum ether . A white product separated out crystallised from ethanol.

3] Synthesis of 3-Aryl (o-Nitroaniline)-4-S-benzyl-6-p-tolylimino-2-phenylimino-2,3-dihydro-[1,3,5] thiadiazine[Hydrochloride]

3-Aryl (o-Nitroaniline)-4-*S*-benzyl-6-*p*-tolylimino-2-phenylimino-2,3-dihydro-[1,3,5] thiadiazine[Hydrochloride] was prepared by the interaction of 1-Aryl (o-Nitroaniline)-5-*p*-tolyl-2-*S*-benzyl-2,4-isodithiobiurets and phenyl isocyanodichloride in chloroform medium. A chloroform solution of Phenyl isocyanodichloride was mixed with the chloroform solution of 1-Aryl

(o-Nitroaniline)-5-*p*-tolyl-2-*S*-benzyl-2,4-isodithiobiuret. Then the reaction mixture was reflux on boiling water bath for 3 hr during which evolution of HCl was noticed. The progress of reaction was monitored by TLC. After completion of the reaction, the reaction mixture was brought to room temperature and the solvent removed under reduced pressure to obtain residue. This residue was triturated several times with petroleum ether (60-80°C) to afford a pale yellow solid.



Where, R= (a) Phenyl, (b) *o*-Nitroaniline, (c) *m*-Nitroaniline , (d) *p*- Nitroaniline,

3a: IR (KBr):υ 3201 (Ar-H), 2877 (Ali-H), 1523 (C=N), 1450 (C-C), 1323 (C-N), 694 (C-S). H NMR (δ in ppm, $CDCl_3$): δ 7.63 -6.91 (19H, m, Ar. H), δ 4.27- 2.26 (5H, m, Ali. H) Mass (m/z): 490 (M^+), 477, 387, 300, 91; Anal. Calcd for $C_{29}H_{24}N_4S_2$. C, 70.73; H, 4.87; N, 11.38; S, 13.00; Found: C, 70.70; H, 4.85; N, 11.40; S, 13.04.

On the basis of all above facts the product with m. p. 98°C was assigned the structure 3-Aryl(Phenyl)-4-*S*-benzyl-6-*p*-tolylimino-2-phenylimino 2,3-dihydro- [1,3,5] thiadiazine [Hydrochloride]

When the reaction of phenyl isocyanodichloride was extended to several other 1-Aryl (Nitroaniline)-5-*p*-tolyl-2-*S*-benzyl-2,4-isodithiobiurets corresponding 3-Aryl (Nitroaniline)-4-*S*-benzyl-6-*p*-tolylimino-2-phenylimino 2,3-dihydro- [1,3,5] thiadiazine [Hydrochloride] has been synthesized.

3b: IR (KBr):υ 3082 (Ar-H), 2895 (Ali-H), 1504 (C=N), 1481 (C-C), 1303(C-N), 754 (C-S). H NMR (δ in ppm, $CDCl_3$): δ 8.08 -6.56 (18H, m, Ar. H), δ 4.42- 1.59 (5H, m, Ali. H) Mass (m/z): 537 (M^+), 490, 462, 404, 390, 91; Anal. Calcd for $C_{29}H_{23}N_5S_2O_2$.,: C, 64.80; H, 4.28; O, 5.95; N, 13.03; S, 11.91; Found: C, 64.85; H, 4.32; O, 5.90; N, 13.10; S, 11.89.

Table -1: Physical data for characterization of compounds (3a-d)

Compd	Yield %	R_f	M.P. °C	Analysis (%): Found (calcd)	
				N	S
3a(Aniline)	75.00	0.55	98	11.40(11.38)	13.04(13.00)
3b(o-Nitro-Phenyl)	68.00	0.60	130	13.00(13.03)	11.93(11.91)
3c(m-Nitro-Phenyl)	78.00	0.48	135	13.05 (13.03)	11.98(11.91)
3d(p-Nitro-Phenyl)	80.00	0.55	121	13.10 (13.03)	11.89 (11.91)

C and H analysis was found satisfactory in all cases.

Antimicrobial activity[23]:

All the compounds have been screened for both; antimicrobial and antifungal activity by using disc diffusion assay. For this, sterial filter paper disc (6 mm) impregnated with fixed doses of compounds was placed on pre-innoculated surface. The disc bearing plates were incubated at 37°C for 24 h. After incubation, zone diameters were measured.

The compounds were taken at a concentration or 1 mg/mL using dimethyl sulphoxide as a solvent. Amikacin (100 µg/mL) was used as standard for antibacterial and fluconazole (100µg/mL) as a standard for antifungal activity. The compound were screened for antibacterial activity against *Eschrichia coli, Proteus vulgaris, Staphylococcus aureus, Salmonella typhi, Klebsiella pneumonie* and *Psudomonas aeruginosa* in nutrient agar medium and for, antifungal activity against *Aspergillus niger* and *Candida albicance* in potato dextrose agar medium. It has been observed that all the compounds showed good activity against both; bacteria and fungi.

Compound	*E. coli*	*S. aureus*	*P. vulgaris*	*P. aeruginosa*	*S. typhi*	*K. pneumonie*	*A. niger*	*C. albicance*
1(3a)	15	18	21	19	18	18	19	20
2(3b)	18	15	15	12	20	20	20	21
3(3c)	15	14	19	17	17	19	17	19
4(3d)	11	19	14	18	19	20	20	19
Amikacin	18	21	23	19	20	21		
Fluconazole							24	24

Zone of inhibition in mm. (15 or less) resistance, (16-20 mm) moderate and more than

CONCLUSION

In this research work, the characterizations of newly synthesized products were established on the basis of UV, IR, ^{1}H NMR, & Mass spectral studies. Various 3-Aryl (Nitroaniline)-4-*S*-benzyl-6-*p*-tolylimino-2-phenylimino 2,3-dihydro- [1,3,5] thiadiazine [Hydrochloride] were synthesized and yield of product ranged from 68-82%.

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ONE POT MULTICOMPONENT SYNTHESIS OF COUMARIN DERIVATIVES BY USING ALUM CATALYST IN PEG UNDER MWI TECHNIQUE

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ABSTRACT

*We reported the preparation of **21(a-j)** via a three component, one pot condensation of 4-hydroxy coumarin, aromatic aldehydes and aromatic amine has not been reported in alum catalyst under microwave irradiation method by using a PEG-400 as a green solvent.*

Keywords: *One pot, Multicomponent, Coumarins, Alum Catalyst, PEG-400, MWI method.*

INTRODUCTION

One pot multicomponent reaction (MCR) has attracted considerable attention from the view point of ideal synthesis by virtue of their efficiency facile, implementation and generally high yield of product. [1]This process is rendered green with reduction of waste, time, man power and cost. [2]The multicomponent reactions are powerful synthetic tools which have changed the land scope of organic and medicinal chemistry. Due to their environmental friendliness, atom economy and their ability to generate large library of compounds. [3]

Green synthetic routes are the main concern of the present century and current synthetic efforts are directed to achieve this goal. Reducing or eliminating the use of volatile organic solvents can minimize the generation of waste which is a requirement of one of the principle of green chemistry. [4]

Currently polyethylene glycol (PEG) is finding extensive use in organic synthesis as it is a well known green solvent and more suited to microwave irradiation also. The use of PEG under MWI is reported in several organic reactions including Knoevenagel condensation of formylchromones, [5] green concept for synthesis of organic compounds,[6][7]etc. and use of PEG in synthetic organic chemistry by conventional method is also reported by different scientists. [8]-[18]

Polyethylene glycol (PEG) is a hydrolytic non ionic polymer used in many biochemical and industrial applications. Due to its non ionic and non toxic character, this chemical can be found in cosmetics food and pharmaceuticals products. The mild action of PEG on the biological activity of the cell components, explain the success of this polymer in biotechnological applications. PEG is commonly used for liquid liquid partitioning and precipitation of bio macro molecules. In protein crystallography PEG is considered the most successful precipitating agents for the production of protein crystals. All these applications make PEG by far the most widely used polymer in aqueous solution of biological molecules.

Several organic transformation or reactions suffer from many drawbacks like long reaction time, harsh reaction conditions with product yield, very complex reaction procedure with lengthy workup, formation of undesirable side products which in turn decrease the yield of products, therefore there is still need to search a mild , inexpensive and ecofriendly cheap catalyst for the synthesis of organic molecules, coumarin derivatives under multicomponent one pot without using solvent, Recently alum which is non toxic, inexpensive, house hold, green catalyst has emerged as an efficient alternative catalyst for a verity of prominent organic reactions. [19]-[23].

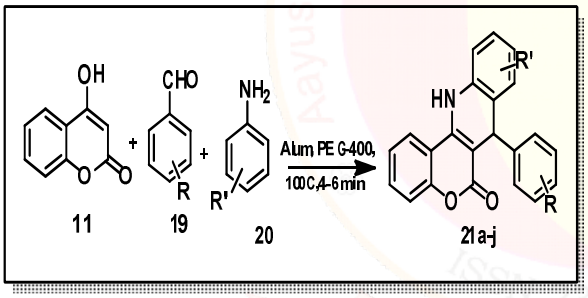
Microwave assisted organic synthesis has been known since 1986.[24] This non conventional synthetic method has shown broad applications as a very efficient way to accelerate the course of many organic reactions. Producing high yields and higher selectivity, lower quantities of side products and consequently easier workup and purification of products. Microwave assisted organic synthesis is considered as a green technology, principally since many organic reactions can be carried out in solvent free condition or used as a green solvent for transformations. [25]

Therefore, the growing interest in academic research and industrial laboratories is not surprising and is reflected in an exponential increase in the productivity of scientific papers,

books, research journals, reviews related to use of this technology.

Microwave heating is a very efficient process, due to the microwave coupling directly with the molecules that are present in the reaction mixture, leading to the fast rise in temperature, faster reaction and cleaner reaction conditions. In synthetic organic chemistry, there is very immense application are found for microwave irradiation technique in organic synthesis.[26]- [32] Synthesis of coumarins and its derivatives has attracted considerable attraction from organic and medicinal chemistry for many years as a large number of natural products contain these heterocyclic nuclei. Coumarin and fused coumarin, polycyclic, heterocyclic molecules, and their derivatives have wide spread application in biological system. [31]-[32]

To the best of our knowledge, herein we report the preparation of **21(a-j)** via a three component, one pot condensation of 4-hydroxy coumarin, aromatic aldehydes and aromatic amine has not been reported in alum catalyst under microwave irradiation method by using a PEG-400 as a green solvent. (**Scheme 1**)



Scheme 1. Synthesis of Coumarin derivatives by using alum catalyst in PEG under MWI.

MATERIAL AND METHODS

GENERAL

All the required chemicals were purchased from Sd fine chemicals and used without further purification. Melting point were determined in open head capillary and are uncorrected montering the reactions and checking. The purity of the final products were carried out by thin layer chromatography (TLC) on alumina coated silica plates. All microwave irradiation experiment was carried out in a Catalysis microwave synthesizer and IR spectra were recorded in KBr on a Perkin Elmer 2400 series IR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on brucker Avance II 400 MHz /100 MHz spectrophotometer using $CDCl_3$/ DMSO-d_6 as a solvent and tetramethylsilane (TMS) as internal reference slandered.

General experimental procedure for the synthesis of fused coumarin derivatives by using alum catalyst under MWI process:

An equimolar mixture of aromatic aldehydes and aromatic amines was taken in a microwave vessel; shake it well for 4-5 min. Then add equimolar amount of 4-hydroxy coumarin in it then dissolve all these contents in minimum quantity of PEG-400 as a solvent. The reaction mixture was irradiated for 2 min under microwave irradiation at 300 Watt (100^{o}C) after completion of reaction (reaction condition was monitored by TLC) the reaction mixture was then poured in cold water and kept for overnight at room temperature to afford the crude product as a solid which was recrystallised from ethyl alcohol to get the analytically pure product.

SPECTRAL CHARACTERIZATION:

21a:7-phenyl-7,12-dihydro-6*H*-chromeno[4,3-*b*]quinolin-6-one :White solid; Yield: 79 %, m.p. 234-236 ^{o}C; IR (KBr): 3312, 3065, 3021, 2918, 1659, 1618, 1528, 1482, 1444, 1389, 1257, 1055 cm^{-1}; ^{1}HNMR (400 MHz, DMSO-*d*6 + CDCl3) δ (ppm) : 9.73 (s, 1H, NH), 8.27 (s, 1H, Ar-H), 7.51-6.61 (m,12H, Ar-H), 5.18 (s, 1H, -CH-); ^{13}C NMR (100 MHz, DMSO-*d*6 + CDCl3) δ (ppm): 160.5, 152.3,147.3, 143.7, 135.5, 131.3, 129.2, 128.1, 127.1, 126.0, 124.2, 123.5, 123.4, 122.7, 116.6, 116.2,113.5, 96.4, 41.1.

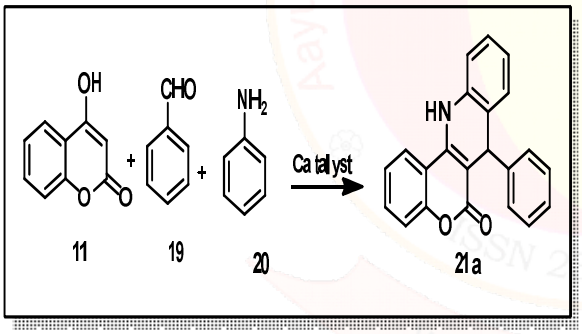
21b:7-(4-methoxyphenyl)-7,12-dihydro-6*H*-chromeno[4,3-*b*]quinolin-6-one:White solid; Yield: 80 %, m.p.236-238 ^{o}C; IR (KBr): 3323, 3077, 2923, 2830, 1657, 1621, 1529, 1488, 1447, 1376, 1258,1176, 1038 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) : 9.93 (s, 1H, NH), 8.35 (dd, J = 8.2, 1.2Hz, 1H, Ar-H), 7.65 (t, J = 8.3 Hz , 1H, Ar-H), 7.46 (t, J = 8.1 Hz, 1H, Ar-H), 7.43-7.36 (m, 4H, Ar-H), 7.25-7.21 (m, 4H, Ar-H), 6.98 (t, J = 7.8 Hz, 1H, Ar-H), 5.27 (s, 1H, -CH-), 3.69 (s, 3H, -OCH3);^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) : 160.4, 152.3, 146.7, 143.8, 135.4, 131.9, 131.2, 129.4,129.3, 127.6, 123.9, 123.7, 123.6, 122.8, 119.3, 116.9, 116.4, 113.3, 95.8, 56.7, 40.3.

21c:7-(4-bromophenyl)-7,12-dihydro-6*H*-chromeno[4,3-*b*]quinolin-6-one:White solid; Yield: 87 %,m.p. 293-295 ^{o}C; IR (KBr): 3324, 3051, 2929, 1665, 1618, 1529, 1482, 1449, 1392, 1294, 1256,1058, 1016 cm^{-1}; ^{1}H NMR (400 MHz,

DMSO-d_6) δ (ppm) : 9.92 (s, 1H, NH), 8.35 (dd, J = 8.1, 1.1Hz, 1H, Ar-H), 7.65 (t, J = 8.4 Hz, 1H, Ar-H), 7.46 (t, J = 8.2 Hz, 1H, Ar-H), 7.42-7.35 (m, 4H, Ar-H), 7.24-7.20 (m, 4H, Ar-H), 6.99 (t, J = 7.7 Hz, 1H, Ar-H), 5.27 (s, 1H, CH); ^{13}C NMR (100 MHz,DMSO-d_6) δ (ppm) : 160.4, 152.3, 146.7, 143.8, 135.4, 131.9, 131.2, 129.4, 129.3, 127.6, 123.9,123.8, 123.7, 122.8, 119.3, 116.9, 116.4, 113.3, 95.8, 40.4.

RESULTS AND DISCUSSION

Nitrogen containing fused coumarin has been well established as biologically interested chemical moiety. Hence, synthesis and synthetic methodology has gained its own importance. By setting goal of introduction of novel methodology for such spectacular useful coumarin derivatives, we planned series of reactions. As Polyethylene glycol has been already introduced as useful and versatile solvent and solvent option we kept PEG as solvent for all sets of reactions. But for fair comparison few reactions were carried out without solvent and compared. By studying mechanistic pathway of reaction and Literature review solvent and temperature combination choice has made final to PEG and 100ºC.



Scheme 2. Model reaction for optimization of reaction condition for synthesis of coumarins derivatives.

As model reaction Benzaldehyde, 4-hydroxy coumarin and Aniline were used in equimolar proportion and PEG as solvent. Various temperature and Watt study performed and 100ºC (300 Watt) were accepted and kept constant for further sets of reactions. As first step involves formation of imines followed by Michael type addition reaction. Along with PEG, for comparison, various solvents were applied (**Table 1; Entry1-7**), as shown below, productivity of reaction dominated by PEG contained reaction. (**Table 1; Entry 5**).

Table 1. Optimization of solvent effect for synthesis of fused coumarin derivatives under MWI method

Entry	Solvents	Time in sec	Yield of Product (%)
1	Neat	120	05
2	AcOH	120	32
3	DCM	120	17
4	Ethanol	120	27
5	PEG-400	120	55
6	Water	120	18
7	DMF	120	36

Reaction Condition: 4-hydroxy Coumarin (0.1mmol), Benzaldehyde (0.1mmol), Aniline (0.1mmol) and Alum (10 mol%) catalyst under MWI method (100 ^{o}C)

Polar protic nature of PEG with extraordinary tendency of association along with active surface of Alum behaves as spectular solvent: catalyst combination. This enhances productivity of reaction practical proof of our perception.

Choice of Alum, based on our previous work done was found correct. Sets of reactions were performed by other catalyst than alum (**Table 2**). Table shown below reflect the appropriate importance of alum in present methodology. Montmorillonite (**Table 2; Entry 7**) gives sensible yield and Alum (**Table 2; Entry 5**) shows excellent productivity. Justification for montmorillonite may be given with respects to its active acid site present on surface like alum. When reaction carried out without any catalyst, as expected starting materials were retained. Lowest yield was obtained in case of Trifluoroacetic acid as catalyst (**Table 2; Entry 3**), in present of TFAA, imines formation takes place readily, but further progress of reaction was not found significant potential consisting conversion of imine into product.

Optimization of amount of catalyst was done by varying mole% of catalyst from 5 mol% to 35 mol% (**Table 3; Entry 1-7**). Increase in amount of catalyst result elevation of percentage of product formation, as expected. Sensible elevation of productivity were observed and may be described mathematically as ‘directly proportional’ to each other.

Table 2. Optimization of effect of catalyst on synthesis of fused coumarin derivatives under MWI method

Entry	Catalyst	Time in sec	Yield of Product (%)
1	L- proline	120	25
2	Boric acid	120	15
3	TFAA	120	12
4	Silica sulphuric acid	120	20
5	Alum	120	55
6	Zinc chloride	120	21
7	Montmorillonite	120	34
8	PMA	120	19
9	AcOH	120	30
10	No catalyst	120	07

Reaction Condition: 4-hydroxy Coumarin (0.1mmol), benzaldehyde (0.1mmol), aniline (0.1mmol) and respective catalyst (10 mol %) by using PEG as a green solvent under MWI method (100 ^{o}C)

Table 3. Optimization of percent of catalyst on synthesis of fused coumarin derivatives under MWI method by using PEG as a solvent.

Entry	Catalyst (mol %)	Time in sec	Yield of Product (%)
1	5	120	34
2	10	120	55
3	15	120	61
4	20	120	70
5	25	100,120,130	68,79,79
6	30	120	80
7	35	120	81

Reaction Condition: 4-hydroxy Coumarin (0.1mmol), benzaldehyde (0.1mmol), aniline (0.1mmol) and PEG as a green solvent under MWI method (100 ^{o}C)

We have reported here, a novel one pot strategy for the synthesis of fused coumarin derivatives by using 4-hydroxycoumarin, aromatic aldehydes and aromatic amines under microwave irradiation technique in presence of 20 % alum as catalyst using poly ethylene glycol-400 as a solvent as shown in **scheme 1**.

Table 4. Physical characteristic data of synthesis of fused coumarin derivatives Under MWI method by using PEG as a solvent.

Sr. No.	Comp	R'	R	Molecular formula	Reaction Time (sec)	Yield (%)
1	21a	H	H	$C_{22}H_{15}NO_2$	120	79
2	21b	H	4-OMe	$C_{23}H_{17}NO_3$	127	80
3	21c	H	4-Br	$C_{22}H_{14}BrNO_2$	110	87
4	21d	4-Br	H	$C_{22}H_{14}BrNO_2$	115	88
5	21e	4-Me	3-NO_2	$C_{23}H_{16}N_2O_4$	128	86
6	21f	4-OMe	4-CN	$C_{24}H_{16}N_2O_3$	129	84
7	21g	4-OMe	4-Br	$C_{23}H_{16}BrNO_3$	111	86
8	21h	4-OMe	3-OMe	$C_{24}H_{19}NO_4$	130	84
9	21i	4-OMe	3-NO_2	$C_{23}H_{16}N_2O_5$	125	89
10	21j	4-Me	4-Br	$C_{23}H_{16}BrNO_2$	119	89

CONCLUSIONS

In conclusion, the present work is described as simple alternative for the synthesis of Fused Coumarin analogues. Importance of present methodology may further elaborate as expeditious in nature of reaction, simple and handy working procedure. Along with use of Green solvent and catalyst concern of this reaction non-conventional energy source MW combination underline as novel strategy for synthesis of fused coumarin compounds. Unlike most of organic transformation strategies, present methodology does not need any hasty work up procedure generally involved toxic solvent or halogenated solvents. Simple water treatment and filtration offers pure product.

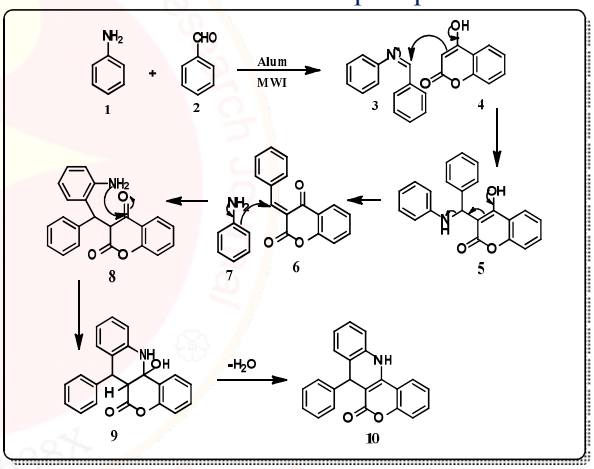


Fig. 1. Possible reaction mechanism for synthesis of fused coumarin derivatives by using alum catalyst in PEG solvent under MWI method.

Analytically pure products were obtained by recrystallization using ethyl alcohol. Hence, until very end of reaction, green impact of present methodology is intact.

Alum used here is easily available, reusable, non toxic, non corrosive, green catalyst. Present methodology and our previously reported work establish Alum as good compatible catalyst along with various non conventional techniques like, microwave irradiation technique.

However, the beauty of this method is its milder reaction condition, reduced reaction time, excellent yields, microwave heating (an alternative and green energy source of energy) and

biodegradable and mild nature of PEG. Among other methodologies, this is one of the best synthetic methods of coumarin derivatives.

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SYNTHESIS AND CHARACTERIZATION OF CHITOSAN BASED PbO_2 NANOBIOCOMPOSITE AS PEROXIDE SENSOR

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ABSTRACT

Lead oxide nanocomposite was synthesized by sol-gel citrate method. As synthesized PbO_2 was structurally characterized by XRD and FT-IR spectroscopy. From XRD analysis, the crystallite size was found to be nearly 35 nm. Synthesis of PbO_2 was confirmed by FT-IR. PbO_2nanocomposite was used for fabrication of Au-CH-PbO_2-HRP bioelectrode. Au-CH-PbO_2-HRP bioelectrode was characterized by Scanning Electron Microscopy (SEM), cyclic voltammetry (CV) and impedence analysis. CV shows defined redox peaks which confirmed immobilization, which was also supported by SEM and Conductivity data.

***Keywords**: peroxide sensor, Au-CH-PbO_2-HRP bioelectrode, XRD, SEM and CV.*

INTRODUCTION

The key issues in developing advanced enzymatic biosensors lie in promoting direct electron transfer between the electrode and the immobilized enzyme. In recent years, there have been many reports about the applications of nanomaterials in bioanalytical detection, biomedical diagnostics and chemical catalysis.

Metal oxide nanomaterials have been demonstrated to have the capability of acting as an electron mediator to facilitate and promote direct electron transfer between electrodes and immobilized redox proteins.

Lead dioxides have been used frequently in industry because of their excellent properties such as good conductivity, low cost, high stability and relatively high service life. A great number of applications have been reported for lead dioxide as positive active material in lead acid batteries [1], oxidation of organic compounds in waste water [2-4], oxidation of glucose[5], ozone evolution [6-7], oxidation of phenol [8-9] and Cr^{3+} [10].

It is well known that PbO_2 has two different crystallographic forms: orthorhombic and tetragonal (α andβ). α-PbO_2 is obtained from alkaline solution and β-PbO_2 from acid solution [11]. α-PbO_2 has a better contact between particles, and a more compact structure than β-PbO_2.Unfortunately, more compact structure leads to bad conductivity compared with β-PbO_2 [12]. Different electro-catalytic activities of α and β forms of PbO_2 were observed in other studies. It was also observed that the structure of crystallization of PbO_2 films influenced the electrocatalytic properties of the material [13].

In this paper we discussed, synthesis of PbO_2nanocomposite by sol-gel method. This material is characterized and further used for the fabrication of Au-CH-PbO_2 and Au-CH-PbO_2-HRP bioelectrode. The fabricated bioelectrode characterized and confirmed the immobilization.

Experimental

Preparation of PbO_2 nanoparticle

The nanocrystalline PbO_2 specimens were prepared by using sol-gelcitrate method. A stoichiometric mixture of Lead nitrate wasmagnetically stirred with citric acid and ethylene glycol at 80°C for 3 hrsto get homogeneous and transparent solution. The solution was furtherheated at about 130°C for 12 hrs in a pressure vessel to form the gelprecursor. The prepared product was subjected to 3 hrs heat treatmentat 350°C in a muffle furnace and then milled to a fine powder. The driedpowder then calcined in the range of 450-750°C in order to improve thecrystallinity of ceramic.

From conductivity data it is found that, PbO_2 nanoparticlesprepared using sol-gel method and calcined at 650°C was found to begood material for the fabrication of bioelectrode.

Preparation of CH-PbO_2 hybrid nanobiocomposite

PbO_2 nanoparticles were dispersed into 10 mL of CH (0.5 mg/mL) solution in acetate buffer of 0.05 M at pH 4.2 under continuous stirring atroom temperature. Finally, viscous solution of CH with uniformlysuspended PbO_2 nanoparticles is obtained. CH-PbO_2 hybridnanocomposite films have been fabricated by uniformly dispersingsolution of CH-PbO_2 composite onto gold surface and allowing it to dryat room

temperature for 12 hrs. These solutions cast CH-PbO_2 hybrid nanocomposite films are washed repeatedly with deionized water to remove any unbound particles.

Immobilization of peroxidase onto CH-PbO_2 hybridnanobiocomposite film

10 µL of bienzyme solution containing peroxidase (10 mg/ml) prepared in Tris buffer (5 mM)] is immobilized onto Au-CH-PbO_2nanobiocomposite electrode. The peroxidase immobilized Au-CH-PbO_2nanobiocomposite was kept undisturbed for about 12 hrs at 4°C. Finally, the dry bioelectrode is immersed in 50 mM PBS (pH 7.0) in order to wash out any unbound enzymes from the electrode surface.

Figure 1 shows the flow chart for the synthesis of PbO_2 nanomaterial and the fabrication of Au-CH-PbO_2-HRP bioelectrode.

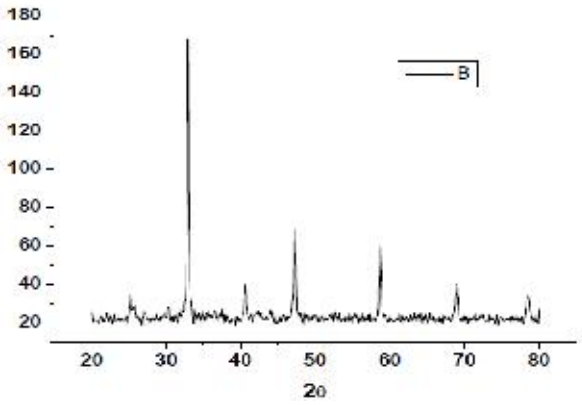
CHARACTERIZATION

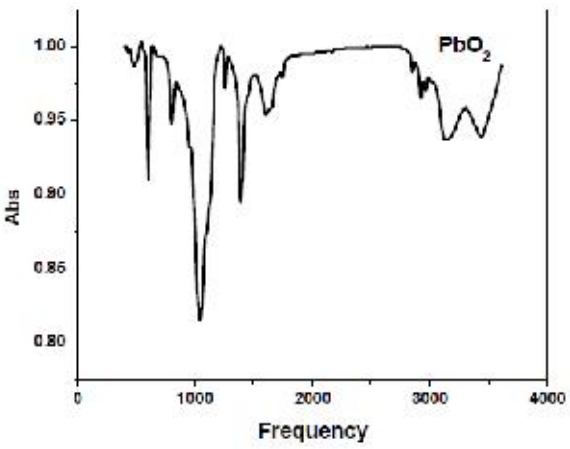
The structure and particle size of PbO_2 nanoparticles have been investigated using X-ray diffraction (XRD) studies. Formation of PbO_2 is further confirmed by FT-IR spectroscopy. The surface morphological studies have been investigated for Au-CH-PbO_2 and Au-CH-PbO_2-HRP bioelectrode by using scanning electron microscopy. The cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) also recorded to confirm the fabrication of Au-CH-PbO_2 and Au-CH-PbO_2-HRP bioelectrode. The electrochemical measurements have been conducted on a three-electrode cell in phosphate buffer (50 mM, pH 7.0, 0.9 % NaCl containing 50 mM $[Fe(CN)_6]^{3-/4-}$electrolyte.

Result and discussion

Structural characterization

X-ray diffraction





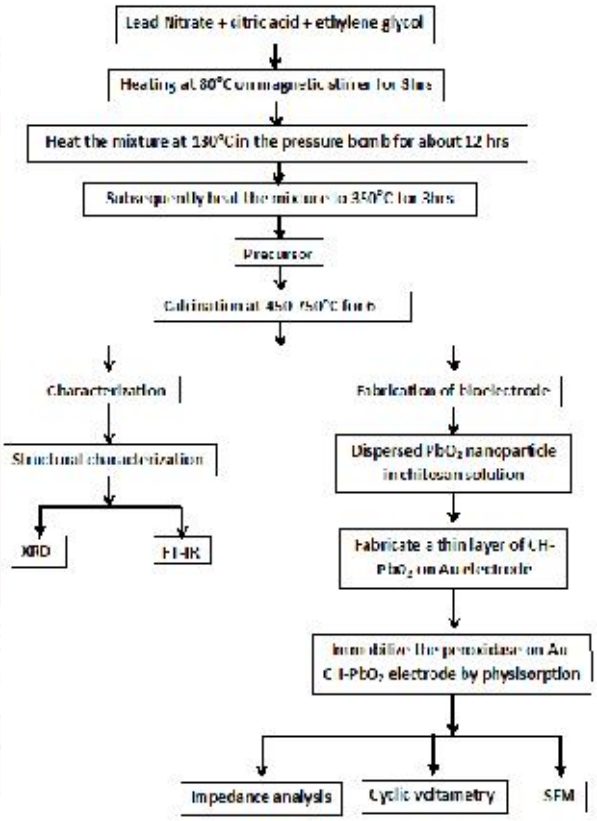


Figure 1: flow chart for the fabrication of CH-PbO2-Au/HRP bioelectrode

Fig 2: XRD plot for the PbO2 nanocomposite prepared by sol gel technique

Sol-gel derived nanostructured PbO_2calcined at 650^{O}C is characterized by XRD. Figure 2 shows results of XRD studies of sol-gel derived nanostructured PbO_2. Three major diffraction peaks were seen which can be assigned to diffraction from 002, 101, 312 planes. This pattern with standard XRD cards shows that the samples include α-PbO_2, β-PbO_2 and small amount of Pb_3O_4. XRD analysis by using of standards showed that the amount of Pb_3O_4 is low. As it is

seen from Figure 2, lead oxide powder has more α and β phases than other samples.

The crystallite size of PbO_2 is estimated using Scherer equation [14].

$$t - \frac{k\lambda}{\beta \cos\theta}$$

Where t is the average size of the crystallite, assuming that the grains are spherical, k is 0.9, λ is the wavelength of X-ray radiation, β is the peak full width at halfmaximum (FWHM) and Φ is the angle of diffraction. The average crystallite size of these samples is found to be ~35 nm.

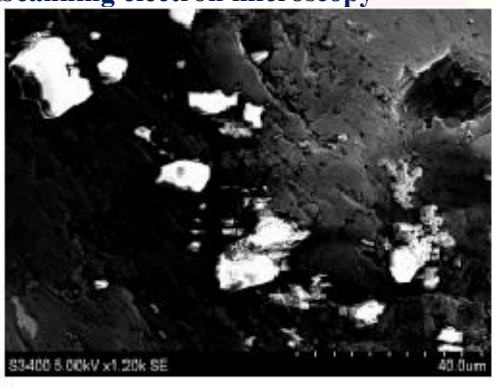
FT-IR

Fig 3: FT-IR plot for the PbO2 nanocomposite prepared by sol gel technique

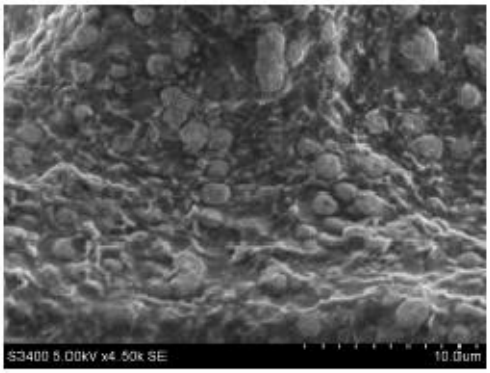
Lead oxide specimen calcined at 650°C was characterized by FTIR spectroscopy. Figure 3 shows the FT-IR spectrum of PbO_2 nanoparticles recorded in the range of 500 to 4000 cm^{-1}.

The absorption peak at 466.74 cm^{-1} indicates the presence of Pb-O Stretching and also the peak at 557.39 cm^{-1} indicates the presence of oxides. These two peaks are very sharp. It is confirmed that the final product is the presence of lead and oxide.

Scanning electron microscopy



(a)



(b)

Fig 4: SEM for (a) CH-PbO2 nanobiocomposite/gold electrode (b) Peroxidase immobilized CH-PbO2 nanobiocomposite/gold Bioelectrode

The surface morphologies of Au-CH-PbO_2nanobiocomposite electrode and peroxidase immobilized Au-Ch-PbO_2nanobiocompositebioelectrode have been investigated using scanning electron microscopy (SEM).

Figure 4a shows SEM images, it shows globular morphology of CH-PbO_2nanobiocomposite, which reveals incorporation of the PbO_2 nanoparticles in chitosan matrix, indicating the formation of CH-PbO_2 hybrid nanobiocomposite. This may be attributed to electrostatic interactions between cationic CH and the surface charged PbO_2 nanoparticles.

However, after the immobilization of peroxidase onto CH-PbO_2nanobiocomposite/gold (figure 4b) electrode, the globular morphology changes to regular form. This suggests that PbO_2 nanoparticles provide a favorable environment for high loading of peroxidase moieties. These results are further supported by electrochemical studies (CV).

Electrical Characterization

Cyclic voltammetry (CV)

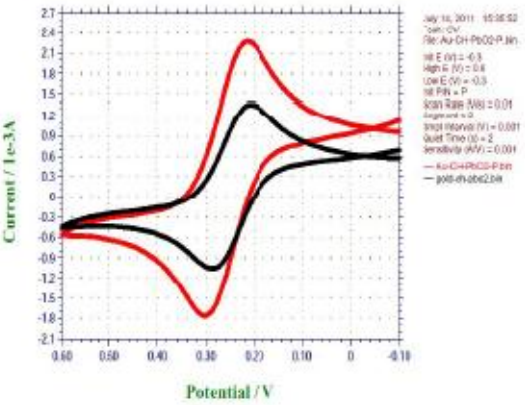


Fig 5: CVs of different electrodes (a) PbO2 nanoparticles chitosan (CH) based nanobiocomposite film deposited onto gold plate, (b) peroxidase immobilized PbO2 nanoparticleschitosan (CH) based nanobiocomposite film deposited onto gold plate in 5.0 mM [Fe(CN)6]4−/3− solution. Scan rate: 0.01V/s.

Cyclic voltammetry is used to investigate the interfacial changes of the electrode. Fig. 5 shows the CVs of differently modified electrodes in 5 mM [Fe (CN) $_6]^{4-/3-}$solution prepared in buffer at the scan rate of 0.01V/s.

As can be seen, a well-defined oxidation and reduction peaks of $[Fe(CN)_6]^{4-/3-}$(curve a) were observed for the PbO_2nanoparticleschitosan (CH)

based nanobiocomposite film deposited onto gold plate with the ip values -1.404x10^{-3}A and 1.359x10^{-3}A. This indicates, the surface was electroactive for the immobilization of enzyme.

After the immobilization of peroxidase on the surface of PbO_2 nanoparticles-chitosan (CH) based nanobiocomposite film deposited onto gold plate, the peak current of the modified electrode increased (curve b) with the ip values -2.263x10^{-3}A and 2.328x10^{-3}A.

This increase in peak current for the Au-CH-PbO2-HRP is for the reason that peroxidase could facilitate electron transfer between biomolecules and electrode surface, indicating that the peroxidase had been successfully immobilized [15-16].

IMPEDANCE ANALYSIS

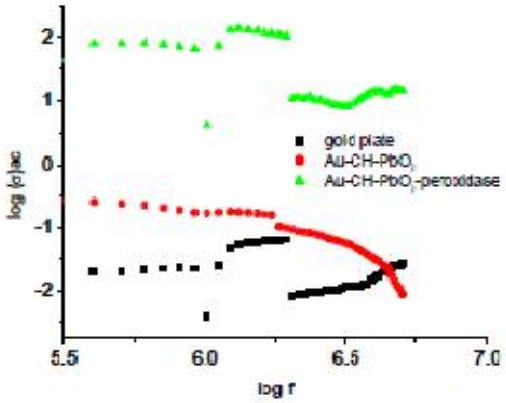


Fig 6: variation of ac conductivity with frequency for (a) gold plate (b) Au-CH-PbO2 nanobiocomposite (c) Peroxidase immobilized Au-CH-PbO2 nanobiocomposite

The electrical properties of the materials have been studied using a complex impedance spectroscopy (CIS) technique with an objective to understand the changes in electrical properties of the materials over a wide range of frequency. The conductivity of the samples was measured by an AC complex impedance method, and the applied frequency range of AC is from 42Hz to 5 MHz. [17-18]

Figure 6 shows the variation of ac conductivity with frequency for gold plate, Au-CH-PbO_2 and Au-CH-PbO_2-HRP. From figure it is observed that conductivity values are increases as the surface of gold plate is modified by forming the thin layer of CH-PbO_2 on it.

Further increase in conductivity was observed for peroxidase immobilized CH-PbO_2 based nanobiocomposite film deposited onto gold plate compare to CH-PbO_2based nanobiocomposite film deposited on gold plate. This also revealed by electrochemical studies. Fig 6 also indicates that, conductivity values are greater at lower frequency compare to higher frequency.

This change in conductivity for Au-CH-PbO_2 and Au-CH-PbO_2-HRP shows the successful immobilization of peroxidase on the surface of Au-CH-PbO_2 electrode, and thus leads to the formation of nanobioelectrode.

CONCLUSION

PbO_2nanocomposite was synthesized by sol-gel citrate method.Formation of PbO_2 is confirmed by FT-IR spectroscopy. The crystals of the as synthesize PbO_2 is characterized by XRD. The crystallite size of the PbO_2 is estimated by using XRD, which is found to be nearly 35nm.

The thin film of the CH-PbO_2 is formed on gold plate by physicaladsorption. Au-CH-PbO_2 was modified by immobilization of peroxidase on its surface. This was carried out by physical adsorption, which results in the Au-CH-PbO_2-Peroxidase nanobioelectrode.

Peroxidase immobilized Au-CH-PbO_2nanobioelectrode was studied by the SEM and electrochemical studied, which shows different redox curve for Au-CH-PbO_2 and Au-CH-PbO_2-HRP, it confirms theimmobilization. Successful immobilization is also supported by the impedance study which shows variation in electrical conductivity with frequency.

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SYNTHESIS, SPECTRAL CHARACTERIZATION AND ANTIBACTERIAL ACTIVITY OF SOME SUBSTITUTED B-DIKETONES CARRYING P-CHLORO-M-CRESOL MOIETY

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ABSTRACT:
An efficient and practical synthesis of some substituted propane-1, 3-diones (β-diketones) containing p-chloro-m-cresol moiety was achieved through Baker-Venkataraman transformation (BVT) of different 2-substituted benzoyloxy acetophenones. The synthesized compounds were characterized by spectral data studies of IR and ^{1}H NMR and were also employed for their antibacterial activity against S. aureus, P. acne and S. typhi by adopting paper disc method.

Keywords: *β-diketones, p-chloro-m-cresol, IR and ^{1}H NMR, antibacterial activity.*

INTRODUCTION

β-diketones are synthetically most important classes of organic compounds. They have gained a lot of interest due to their importance as good ligands for the chelation with metals[1] and as good intermediate in the preparation of heterocyclic compounds like flavanones and flavones[2], pyrimidines[3]. They are also well known for their biological activities such as antibacterial[4], antioxidant[5], systematic insecticidal[6] and prophylactic antitumor[7]. In addition, they have also been used in ultraviolet sunscreen cosmetics as an anti-sunscreen agent that filters ultraviolet rays to protect skin[8]. Further, β-diketones are well known to have a keto-enol tautomerism[9] and recently it is reported that β-ketoenols are the important pharmacophore for the HIV-1 integrase inhibitor[10].

In organic chemistry, the synthesis and characterization of β-diketones is of tremendous importance. With this view here, we have synthesized some substituted β-diketones carrying p-chloro-m-cresol moiety by Baker-Venkataraman transformation of some 2-substituted benzoyloxy acetophenones, characterized them by IR and ^{1}H NMR and determine their antibacterial activity.

MATERIAL AND METHODS

All the chemicals and solvents used for the synthesis of β-diketones were of highest purity obtained from commercial sources. Melting points were determined in open capillary using Thiele tube as melting point apparatus. IR spectra were recorded on Shimadzu IRAffinity-1 FT-IR spectrophotometer in KBr. ^{1}H NMR spectra were recorded on Bruker Avance II NMR spectrometer on 400 MHz in DMSO-d_6 as solvent and TMS as an internal standard. The purity of compounds was checked by TLC on silica gel-G plates.

Synthesis of substituted β-diketones:

Preparation of 5-chloro-2-hydroxy-4-methylacetophenone (1).

p-chloro-m-cresyl acetate (a) was prepared by acetylation of p-chloro-m-cresol. The prepared p-chloro-m-cresyl acetate (a) on Fries rearrangement with anhydrous $AlCl_3$ gives starting compound 5-chloro-2-hydroxy-4-methylacetophenone (1).

Preparation of 2- substituted benzoyloxy acetophenones (3a-d).

5-chloro-2-hydroxy-4-methyl acetophenone (1) (0.04 mol) and appropriate substituted benzoic acids (2) (0.05 mol) were dissolved in dry pyridine and reaction mixture was cooled to 0°C.Then $POCl_3$ was added dropwise with continuous stirring below the temperature of 10°C. The reaction mixture was kept overnight at room temperature, poured over crushed ice and then acidified with 10% HCl. The obtained solid product was filtered, washed with water followed by 10% $NaHCO_3$ washing and finally several times by water. It was recrystallied from ethanol to get corresponding 2- substituted benzoyloxy acetophenones (3a-d).

Preparation of substituted propane-1, 3- diones (4a-d) by Baker-Venkataraman Transformation

2-substituted benzoyloxy acetophenones (3a-d) (0.05 mol) were dissolved in dry pyridine (40 ml). The solution was warmed up to 60°C and pulverized KOH (0.15 mol) was added slowly with constant stirring. After 6-8 hours the reaction mixture was acidified by ice cold dilute HCl (1:1). The coloured solid product thus separated was

filtered, washed with 10% $NaHCO_3$ solution and finally several times by water. It was recrystallized from ethanol- acetic acid mixture to get corresponding substituted propane-1, 3- diones (4a-d). The scheme for synthesis of substituted propane-1, 3- diones is shown in Figure 1.The compound code, substituent, molecular formula, melting point, percentage yield and colour of synthesized compounds are shown in Table 1.

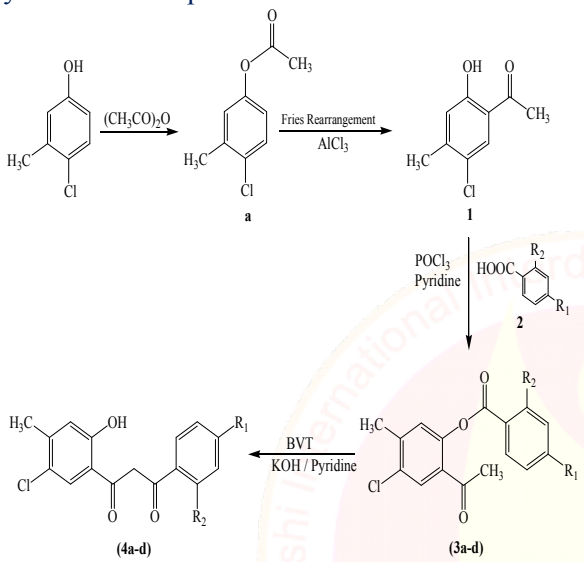

Figure 1: Scheme for the synthesis of substituted propane-1, 3-diones (4a-d)

Table 1: The compound code, substituent, mol. formula, M.P., % yield and colour of synthesized compounds (4a-d)

Comp-ound Code	R_1	R_2	Mol. Formula	M.P. (°C)	% Yield	Colour
4a	4-NO_2	2-H	$C_{16}H_{12}ClNO_5$	218-220	70	Yellow
4b	4-Br	2-H	$C_{16}H_{12}BrClO_3$	112-114	68	Yellow
4c	4-Cl	2-H	$C_{16}H_{12}Cl_2O_3$	140-142	72	Yellow
4d	4-Cl	2-Cl	$C_{16}H_{11}Cl_3O_3$	142-144	75	Yellow

Spectral data of substituted β-diketones:

1-(5'-chloro-2'-hydroxy-4'-methylphenyl)-3-(4'-nitrophenyl)propane-1,3-dione(4a): IR (KBr): 3388 cm^{-1} (Phenolic -OH stretch), 2918 cm^{-1} (Aromatic C-H stretch), 2848 cm^{-1} (Aliphatic C-H stretch), 1695 cm^{-1} (C=O stretch), 1590 cm^{-1} (Aromatic C=C stretch), 1338 cm^{-1} (C-N stretch), 715 cm^{-1} (C-Cl stretch). ^1H NMR (DMSO-d_6): δ 4.2 (S, 1H of OH), δ 2.5 (S, 3H of CH_3), δ 3.34 (S, 2H of CH_2), δ 6.78-8.33 (m, 6H of Ar-H).

1-(4'-bromophenyl)-3-(5'-chloro-2'-hydroxy-4'-methylphenyl)propane-1,3-dione (4b): IR (KBr): 3202 cm^{-1} (Phenolic -OH stretch), 3073 cm^{-1} (Aromatic C-H stretch), 2929 cm^{-1} (Aliphatic C-H stretch), 1709 cm^{-1} (C=O stretch), 1564 cm^{-1} (Aromatic C=C stretch), 707 cm^{-1} (C-Cl stretch), 545 cm^{-1} (C-Br stretch). ^1H NMR (DMSO-d_6): δ 4.75 (S, 1H of OH), δ 2.3 (S, 3H of CH_3), δ 2.5 (S, 2H of CH_2), δ 6.91-8.04 (m, 6H of Ar-H).

1-(5'-chloro-2'-hydroxy-4'-methylphenyl)-3-(4'-chlorophenyl)propane-1,3-dione (4c): IR (KBr): 3413 cm^{-1} (Phenolic -OH stretch), 3136 cm^{-1} (Aromatic C-H stretch), 2950 cm^{-1} (Aliphatic C-H stretch), 1720 cm^{-1} (C=O stretch), 1540 cm^{-1} (Aromatic C=C stretch), 710 cm^{-1} (C-Cl stretch). ^1H NMR (DMSO-d_6): δ 4.54 (S, 1H of OH), δ 1.69 (S, 3H of CH_3), δ 2.28 (S, 2H of CH_2), δ 6.69-7.82 (m, 6H of Ar-H).

1-(5'-chloro-2'-hydroxy-4'-methylphenyl)-3-(2',4'-dichlorophenyl)propane-1,3-dione (4d): IR (KBr): 3734 cm^{-1} (Phenolic -OH stretch), 3096 cm^{-1} (Aromatic C-H stretch), 2919 cm^{-1} (Aliphatic C-H stretch), 1653 cm^{-1} (C=O stretch), 1538 cm^{-1} (Aromatic C=C stretch), 731 cm^{-1} (C-Cl stretch). ^1H NMR (DMSO-d_6): δ 4.75 (S, 1H of OH), δ 2.3 (S, 3H of CH_3), δ 2.5 (S, 2H of CH_2), δ 6.95-8.02 (m, 5H of Ar-H).

ANTIBACTERIAL ACTIVITY

The antibacterial activities of synthesized compounds were determined against *S. aureus, P. acne and S. typhi* by paper disc method[11]. Sterile filter paper discs were dipped in different concentrations of compounds (250, 500, 1000 µg/ml) in methanol-acetic acid (1:1) as solvent, dried and placed on nutrient agar plates spreaded with bacteria. After 24 hr of incubation at 37°C, the diameters of inhibition zone were measured in mm by metric ruler and compared with standard ampicillin (25 µg/ml). The results on antibacterial activity of synthesized compounds and standard are given in Table 2 and shown in Figure 2 to Figure 4.

Table 2- Antibacterial activity of synthesized compounds (4a-d)

Compound code	Diameter of inhibition zone in mm			
	Conc.in µg/ml	*S. aureus*	*P.acne*	*S. typhi*
4a	250	32	22	25
	500	26	27	25
	1000	31	20	25
4b	250	25	21	30
	500	30	21	35
	1000	25	20	35
4c	250	30	22	35
	500	30	23	30
	1000	33	38	35
4d	250	22	26	35
	500	22	22	35
	1000	25	20	32
Standard	25 µg/ml	21	20	22

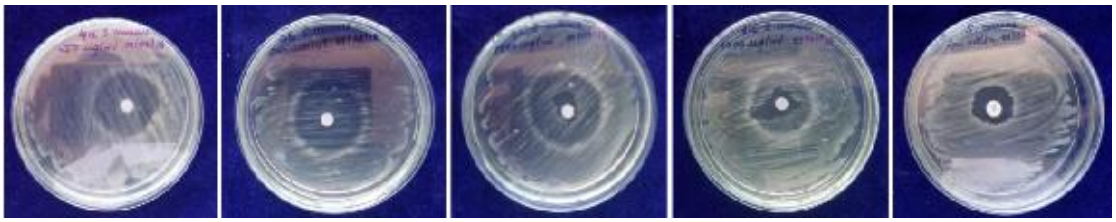

Figure 2: Effect of synthesized compounds (4a-d) and standard against *S. aureus*

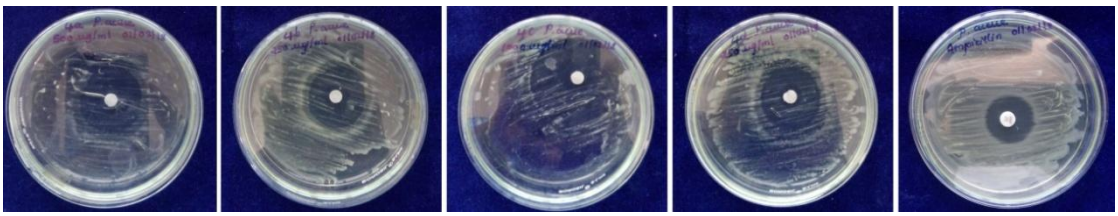

Figure 3: Effect of synthesized compounds (4a-d) and standard against *P. acne*

Figure 4: Effect of synthesized compounds (4a-d) and standard against S. typhi

RESULT AND DISCUSSION

In this work, total four substituted β-diketones namely 4a-d carrying p-chloro-m-cresol moiety have been successfully synthesized by Baker-Venkataraman transformation of different 2-substituted benoyloy acetophenones (3a-d). All the synthesized compounds were recrystallied and five concentrations of each compound were prepared in methanol-acetic acid (1:1) as solvent and used individually to test their antibacterial activity against *S. aureus*, *P. acne* and *S. typhi.* The results of antibacterial activity show that the compound 4a, 4b and 4c showed excellent antibacterial activity against *S.aureus* at all the concentrations except 4d which showed weak activity against *S.aureus*. The maximum 32 mm zone of inhibition was observed at 250 µg/ml and 30 mm for 4b at 500 µg/ml against *S.aureus* .The compound 4c showed 33 mm zone of inhibition at higher concentration of 1000 µg/ml against same pathogen. Standard ampicillin showed 21 mm of diameter against *S.aureus* at 25 µg/ml concentrations. The compounds 4a and 4c showed pronounced antibacterial activity against *P.acne* as compared to 4b and 4d which showed poor activity against *P.acne*. The maximum 27 mm of inhibition zone was recorded for 4a at 500 µg/ml and 38 mm for 4c at 1000 µg/ml concentrations against *P.acne*. The ampicilin showed 20 mm of inhibition zone against *P.acne* bacteria. Also the compounds 4b, 4c and 4d showed excellent antibacterial activity against *S.typhi* at all the concentrations except the compound 4a which showed moderate activity. The maximum 35 mm zone of inhibition was recorded for 4b against *S.typhi* at 500 and 1000 µg/ml of concentrations. The compound 4c showed 35, 30 and 35 mm of inhibition zones and the compound 4d showed 35, 35 and 32 mm of inhibition zones against *S.typhi* at all the concentrations tested with 22 mm for standard ampicilin. The methanol-acetic acid (1:1) solvent was also tested for blank reading against all pathogens by same method and showed 18, 19 and 24 mm of inhibition zones *against S.aureus*, *P.acne* and *S.typhi* respectively.

CONCLUSION

All the four compounds 4a-d containing p-chloro-m-cresol moiety were successfully synthesized and their structure were confirmed by spectral data of IR and 1H NMR.The spectra showed expected signals/peaks due to various groups present in the compounds. The compound 4a at 250 µg/ml against *S.aureus* and 4c at 1000 µg /ml against *P.acne* shows excellent activity. Also the compounds 4b, 4c and 4d show highest activity

against *S.typhi* at all the concentrations. Thus, from the results of antibacterial activity, it is concluded that, these compounds may have medicinal value and finding possible help in the drug discovery.

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DENSITY AND VISCOSITY STUDIES OF GLUCOSE SOLUTION IN WATER AND AQUEOUS ELECTROLYTES AT 298.15, 303.15, 308.15 AND 313.15 K

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ABSTRACT

The densities and viscosities of glucoseare determined in water containing salt such as NaCl, NaBr, KCl and KBrat different temperature. From this density, apparent molar volumes (φ_v) of the electrolytes and ions in these mixtures have been evaluated. The limiting apparent molar volume (φ^0_v) has been interpreted in terms of solute-solvent interaction. The viscosity data have been analyzed with the help of Jones–Dole equation and the viscosity β-coefficients have been determined. Glucose has been found to be structure maker and breaker in aqueous halides from molar volume as well as viscosity studies.

Keywords: *Glucose, Water, Density, Viscosity*

INTRODUCTION

The physical properties of solution such as density, viscosity, refractive index etc. mostly depend on the solvent and solute present in the system. These parameters are related with molecular interactions among the solute and solvent. Drug also interacts with solvent media. These interactions are important to understand mechanism of processes such as drug transport, protein binding, anesthesia [1] diffusion and dissolution rate control [2] of the drug. The binary solvent mixture is used as medium for study of complexation, electrochemical oxidation and ion solvation [3]. The density data of electrolyte has proved to be very useful in elucidating the nature of ion solvent interactions occurring in aqueous and non-aqueous solutions [4]. Measurements of viscosity in solutions provide an excellent method for obtaining data on ion–ion and ion–solvent interactions [5].Therefore, it was decided to study the density and viscosity parameters of glucose in water solvent system in presence of electrolytes.

MATERIALS AND METHODS

The salts KCl, NaCl, KBr, NaBr and nonelectrolyte glucose used were of AR grade. Water used was double distilled over alkaline $KMnO_4$andthe purity of water was checked by comparing their measured densities and viscosities with those reported in the literature[6].Viscosity measurements were performed by using Ostwald's viscometer.

Densities of glucose solution in water and aqueous alkali halides were measured using pycnometer with an accuracy of viscosity ± 1×10^{-4} g/cm^3. Viscosity values were determined using the relation

$$\eta_1/\eta_2 = \rho_1 t_1/\rho_2 t_2$$

The weighing was repeated thrice to ensure the accuracy in weights with a little interval of time. The reproducibility of the result was close to 100%. The viscometer was clamped vertically in a thermostatistically controlled waterbath, whose temperature was maintained constant at 298.15, 303.15, 308.15 and 313.15 K (± 0.02). The measurement of flow time of the solution between the two points on the viscometer was performed at least five times for each solution and the result was averaged.

RESULTS AND DISCUSSION

The measure ρ values of glucose solutions in water and in aqueous NaCl, NaBr, KCl and KBr solutions at 298.15, 303.15, 308.15 and 313.15 K are used to calculate the apparent molar volumes Φ_v using the equation

$$\Phi_v = [1000\,(\rho 0-\rho)/(c\times\rho 0)] + (M/P0) \qquad (1)$$

Where ρ and ρ0 are the densities of solution and solvent respectively, M, is the molecular weight of the solute, c is the concentration in mol L^{-1}. Figure 1 gives representative graphs of Φ_v versus c for glucose in water and in aqueous NaCl at 298.15 K. The limiting partial molar volume of glucose in aqueous electrolyte solutions were obtained by computerized least square fitting of the equation.

$$\Phi_v = \Phi_v + SvC$$

Where Φ_v is the limiting apparent molar volume at infinite dilution and Sv is the experimental slope. The $\Phi_v$and Sv values are presented in Table 1. The value of glucose in water and in aqueous NaCl, NaBr,KCl and KBr solution are large and positive.

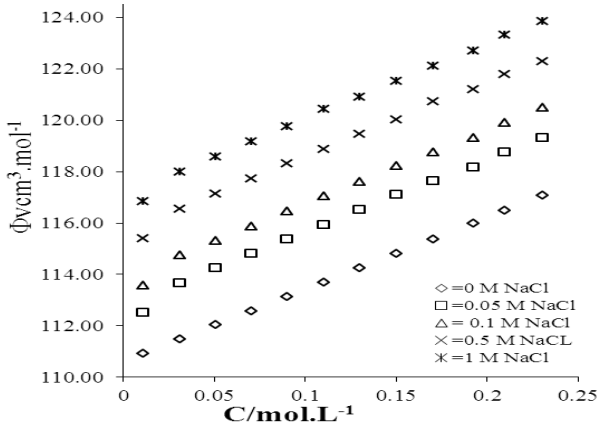

Figure 1.Φ_v vs C for Glucose in water and in aqueous NaCl at 298.15 K

This indicates the presence of strong solute-solvent interactions. It is further observed that Φ_v in all system increase slightly with increase in temperature suggesting decrease in solute-solvent interactions at elevated temperatures. The Φ values of glucose in aqueous solution in the presence of added electrolytes are higher than those for glucose in pure water. The Φ_v are positive and increase in solutions with increasing concentration of each electrolyte.

Table 1. Φ_v and Sv values of glucose in water and in aqueous NaC1, NaBr, KC1 and KBr solution at different temperatures.

	Φv0(cm3mol-1)				**Sv (cm3L ½ mol 3/2)**			
Glucose in Water	298. 15K	303. 15K	308. 15K	313. 15K	298. 15K	303 .15K	308. 15K	313. 15K
	110.6 1	11.07	111.5 6	112.0 2	28.0 1	30.06	31.51	32.15
0.05M NaCl	111.6 6	112.12	112.6 1	113.0 8	28.3 3	30.31	31.72	32.32
0.1M NaCl	112.7 2	113.2	113.6 6	114.1 3	28.7 1	30.72	32.01	32.66
0.5M NaCl	114.4 9	115.36	115.8 5	116.2 9	29.1 6	31.13	32.3 2	32.86
01M NaCl	115.9 4	116.4	116.9 1	117.3 3	29.3 2	31.25	32.4 5	32.92
0.05M NaBr	114.8 5	115.83	116.7 4	117.7 7	30.5 1	32.62	33.73	34.84
0.1M NaBr	116.2	17.15	118.0 5	118.9 6	30.9 3	33.07	34.15	35.24
0.5M NaBr	116.2	17.15	118.0 5	118.9 6	30.9 3	33.07	34.15	35.24
01M NaBr	120.8 6	21.75	122.9 5	123.8 2	31.7 6	33.93	34.85	36.05
0.05MKCl	112.2 1	12.67	113.0 1	113.3 6	29.2 2	31.21	33.71	34.36
0.5M KCl	114.4 2	14.81	115.2 5	115.5 8	31.3 5	33.35	35.83	36.68
0.05M	116.6 1	117.6	118.6 2	119.8 1	31.2 2	33.2 1	35.71	36.3 6
0.5M KBr	121.9 8	122.76	123.6 6	124.3 8	33.3 5	35.3 6	37.84	38.6 8

This suggests that the structure-making tendency of glucose is enhanced in the presence of ions of electrolyte. The Φ_v values of glucose in aqueous NaBr are always higher than those in aqueous NaCl. The $\Phi_v$values of glucose in aqueous KBr are higher than those in aqueous KClpresumably due to introduction of voluminous Br^- ion.

The relative viscosity (ŋ) data of glucose solution in water as well as in aqueous alkali solution are analyzed with the help of equation

$$\eta r = 1 + BC$$

The Figure 2 gives representative graphs of ŋ versus C for glucose in water and in aqueous NaCl at 298.15 K.

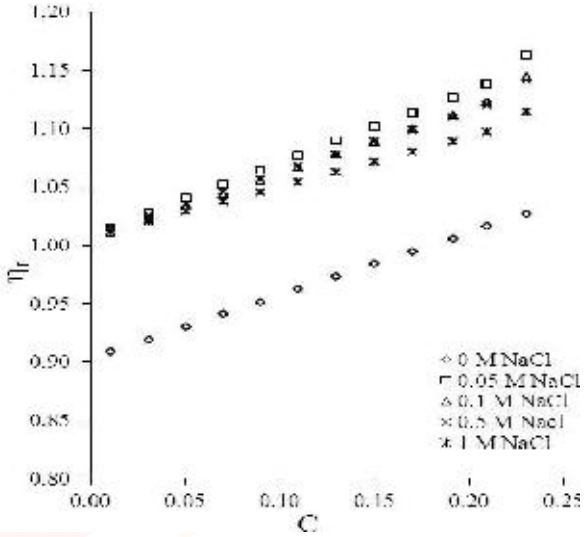

Figure 2 ηr *vs* C of Glucose in water and in aqueous NaCl at 298.15 K

Similar plots have been obtained for other solutions at all temperatures. The values of B obtained from the slopes of these plots are listed in Table 2

Table 2.B Values of glucose in water and in aqueous NaCl, NaBr, KCl and KBr solution at different temperatures

	B(dm^3mol^{-1})			
Glucose inwater	298.15K	303.15K	308.15K	313.15K
	0.603	0.545	0. 494	0.432
0.05M NaCl	0.613	0.557	0.506	0.444
0.1M NaCl	0.554	0.506	0.458	0.413
0.5M NaCl	0.530	0.481	0.435	0.396
01M NaCl	0.425	0.419	0.413	0.406
0.05M NaBr	0.620	0.603	0.581	0.559
0.1M NaBr	0.559	0.486	0.451	0.438
0.5M NaBr	0.470	0.458	0.446	0.437
01M NaBr	0.458	0.446	0.432	0.418
0.05M KCl	0.410	0.395	0.382	0.370
0.5M KCl	0.468	0.441	0.431	0.412
0.05M KBr	0.477	0.469	0.460	0.454
0.5M KBr	0.434	0.420	0.404	0.388

NaCl, NaBr, KCl and KBr at all temperatures which suggest that glucose acts as structure promoter in these solution. The B values of glucose solution in aqueous NaCl, NaBr, KCl, KBr are lower than those in pure water. This could be explained on the basis that electrolyte is the hydrated and reacts with glucose. This leaves less water for sugar molecules for hydration. The positive B and negative dB/dT values in all solutions studies in the present investigation, make glucose as a structure promoter.

CONCLUSION

Glucose has been found to be a structure maker and breaker in aqueous halides from molar volume as well as viscosity studies. Thus glucose as an structure promoter solute and this tendency enhances in presence of electrolytes. The results of density and viscosity measurements of the multicomponent solution are in good agreement with earlier reported work [3].

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SYNTHESIS OF 3-[(4,6-DICHLORO-1,3-BENZOTHIAZOL-2-YL)AMINO]-2-ARYL SUBSTITUTED-1,3-THIAZOLIDIN-4-ONE AND THEIR ANTIBACTERIAL ACTIVITY

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ABSTRACT

4-thiazolidinones are reported to possess significant antitubercular, antibacterial & antifungal activities. 2,4-dichloro aniline (1), which is aniline derivative have been found to be biologically interesting compound for many years. From this aniline derivative first we have synthesized 2-amino-4,6-dichloro benzothiazole (2) which is then treated with hydrazine hydrate to form 2-hydrazino-4,6-dichloro benzothiazole (3). Compound (3) condensed with o-vaniline, p-vaniline, p-methoxy benzaldehyde, p-dimethylamino benzadehyde, o-hydroxy benzaldehyde , p-cyano benzaldehyde , p-hydroxy benzaldehyde, p-bromo benzaldehyde to form corresponding hydrazone (4a-4h). These hydrazone heated with mercapto acetic acid by using DMF as solvent and Pinch of anhydrous ZnCl2 for 5-6 hours, 3-[(4,6-dichloro-1,3-benzothiazol-2-yl)amino]-2-aryl-1,3-thiazolidin-4-one (5a-5h). These newly synthesized 4-thiazolidinone compound screened for their antibacterical activity.

Keywords: *Benzothiazole, hydrazone, thiazolidinone, antibacterial activity*

INTRODUCTION

A survey of literature reveals that large work has been carried out on the synthesis of 4-thiazolidinone and known to exhibits various biological activities as antitubercular[1], antiallergic[2]. Schiff-bases give good antibacterial activity and pharmacological application[3]. 4-thiazolidinone ring are reported to possess various biological activities, as antimicrobial, anti-nflammatory, antiviral, antiparasitic and antituberculosis[4-10]. These Schiff-bases can be prepared by the acid catalysed reaction of amine and aldehyde or ketone which shows good fungicidal acivit[11].

4-thiazolidinone give good pharmacological properties[12] are known to exhibits antitubercular[13], antibacterial[14], anticonvulsant[15], antifungal activity[16]. Large work has been carried out on 4-thiazolidinone but very less information is available about 4-thiazolidinone bearing substituted benzothiazolyl moiety.

The starting compound were prepared by the reaction of 4,6-dichlor aniline and potassium thiocynate to obtained 2-amino-4,6-dichlor benzothiazole. 2-amino-4,6-dichlor benzothiazole treated with hydrazine hydrate which then condensed with aldehydes to obtain the hydrazones. Thease hydrazones then treated with thioglycolic acid to obtain the corresponding 4-thiazolidinone.

EXPERIMENTAL

All the melting points were determined in open capillary tube and may be uncorrected. The purity of compound was checked by TLC on silica gel coated glass plate. Infra-red spectra were monitored in KBr palates on Bomen 104 FT infra-red spectrophotometer. H1 NMR spectra were obtained on a Gemani 200 Mz spectrometer with tetra methyl silane as an internal standard.. Elemental analysis was performed on a Heraeus CHN-O rapid analyzer.

Synthesis of 2-amino-4,6-dichloro benzothiazole

2,4-dichloro aniline (16.2 gm, 0.1 M) and sodium thiocynate (9.7 gm, 0.1 M) were dissolved in glacial acetic acid (150 ml). The solution was cooled in freezing mixture. Bromine (16 gm, 10 ml, 0.1 M) in glacial acetic acid (25 ml) was added with stirring and maintaining temperature below 25°C. The mixture was allowed to stand for one hour at room temp. The resulting hydrobromide was dissolved in hot water and neutralized with 10 % NaOH to obtain base. The amine thus obtained was filtered, washed with water and recrystallized in aq. alcohol to get the product 2-amino-4,6-dichloro benzotiazole.

Yield: 13.5 gm, M.P: 82 °C I.R. (KBr): 3440 cm^{-1} (Asym.stret. of -NH_2), 3340 cm^{-1} (N-H Sym. stret. of -NH_2), 3052 cm^{-1} (Ar-H stret.), 1630 cm^{-1} (-C=N stret.); PMR ($CDCl_3$) δ 6.0 (broad, 2H, NH_2), δ 7.0-7.5 (two singlet, 2H, Ar-H), [Found : C: 37.80 %, H: 1.50%, N: 12.30 %, S: 14.20 %, $C7H4Cl_2N2S$ required : C: 38.37%, H : 1.84%, N : 12.79 %, S: 14.64 %.]

4,6-dichloro-2-hydrazino benzothiazole

Hydrazine hydrate (80%, 17 ml) was taken in a flask cooled to 5°C and concentrated HCl (11 ml) was added to it with stirring. The flask was kept at room temp. for few minutes and then 2, 4-dichloro benzothiazole (11 gm) was added in portions. Ethylene glycol (44 ml) was added into the flask. The contents of the flask were heated at 150°C on an oil bath for three hours. On cooling, the product 4-bromo 2-hydrazino-6-methyl benzothiazole crystallized out. It was filtered at pump, washed with cold water and recrystallized from ethyl alcohol,

Yield: 10.5 gm, M.P: 82 °C I.R. (KBr) : 3452 cm^{-1} (asymmetric N-H stretching in $–NH_2$),3353 cm^{-1} (symmetric N-H stretching in $–NH_2$), 3052 cm^{-1} (Ar-H stretching), 1630 cm^{-1} (-C=N stretching) [Found : C: 35.50 %, H : 1.90%, Cl : 29.90%, N : 17.50 %, S: 13.20 %, C_7H5Cl_2N3S required : C: 35.91 %, H : 2.15%, Cl : 30.29%, N : 17.95 %, S: 13.70 %.]

General procedure for Synthesis of hydrazone of2-hydrazino-4,6-dichlorobenzothiazole amine and substituted aromatic aldehyde

4,6-dichloro-2-hydrazino benzothiazole (0.01 M) was suspended in ethanol (50 ml). To this suspension, ethanolic solution of aromatic substituted benzaldehyde (0.01 M) was add ed. The mixture was refluxed on water bath for three hours, solid separated was allowed to cool. The solid was filtered at pump washed with ethanol and recrystallised from hot benzene.

4a. : Yield: 2.74 gm , M. P. : 112 °C, IR(KBr) : 3185 cm-1 (-OH Stretch), 3160 (N-H) stretch), 1584 (C= N Stretch), 1290, (C-N Stretch), [Found : C: 48.30 %, H : 2.90 %, N : 10.90 %, Cl:18.60 %, S : 8.30 %,$15H11Cl_2N3O2S$ required : C: 48.93 %, H : 3.01 %, N : 11.41 %, Cl : 19.26 %, S : 8.71 %.]

4b. : Yield : 3.05 gm, M. P. : 145 °C. IR (KBr) : 3200 cm-1 (-OH Stretch), 3167 cm-1 (N-H Stretch), [Found : C: 48.30 %, H : 2.90 %, N : 10.90 %, Cl : 18.60 %, S : 8.30 %,$C15H11Cl_2N3O2S$ required : C: 48.93 %, H : 3.01 %, N : 11.41 %, Cl : 19.26 %, S : 8.71 %.]

4c. : Yield : 2.6 gm , M. P. : 115 °C. IR (KBr):3180 cm-1 (-OH Stretch), 3174 cm-1 (N-N Stretch). [Found : C : 50.80%; H : 2.90%; N : 11.34%, Cl : 19.90%, O : 4.30 %, S : 8.90 %, $C15H11Cl_2N3OS$ required : C(51.15%) H(3.15%) Cl(20.13%) N(11.93%) O(4.54%) S(9.10%)

4d. : Yield : 2.68 gm, M. P. : 182 °C. I.R. (KBr) : 3389 (N-H stretching) 3053 (= C-H stretch in aromatic ring), 1541 (C=N stretch), 1290 (C-N stretch), [Found : C : (52.20%); H : (3.30%); Cl : (18.80%) N(14.90%) S(8.20%), C16H14Cl2N4S required C : (52.61%); H : (3.86%); Cl : (19.41%) N(15.34%) S(8.78%)

4e. Yield : 3.0 gm , M. P. 145 °C, IR (KBr):3423 cm-1 (O-H) stretching), 3209 cm-1 (N-H stretching), [Found : C:(49.20%) H : (2.30%); Cl:(20.20%); N:(12.10%); O:(4.20%); S:(9.48%), C14H9Cl2N3OS required:C:(49.72%) H:(2.68%); Cl:(20.96%); N:(12.42%); O:(4.73%); S:(9.20%).

4f. Yield : 3.2 gm , M. P. : 113 °C, IR (KBr) : 3448 cm-1 (O-H) stretching), 3200 cm-1 (N-H stretching), [Found : C:(51.20%); H:(2.10%); Cl:(20.10%); N:(15.90%), S:(9.10%), C15H8Cl2N4S required : C:(51.89%); H:(2.32%); Cl:(20.42%); N:(16.14%), S:(9.23%)

4g. : Yield :- 2.6 gm , M. P. :- 109 °C., IR (KBr) : 3302 (N-H stretching) [Found : C:(49.30%); H:(2.20%); C:l(20.50%); N:(12.10%); O:(4.20%); S:(9.10%), C14H9Cl2N3OS required : C:(49.72%); H:(2.68%); C:l(20.96%); N:(12.42%); O:(4.73%); S:(9.48%)

4h. : Yield :- 2.6 gm , M. P. :- 137 °C., IR (KBr) : 3302 (N-H stretching) [Found : C(41.92%) H(2.01%) Br(19.92%) Cl(17.68%) N(10.48%) S(7.99%), C14H8BrCl2N3S

General Procedure for synthesis of 3-[(4, 6–dichloro-1,3-benzothiazol-2-yl)amino]-2-aryl substituted -1,3-thiazolidin-4-one:

The hydrazone(0.0025M) (4a-4g) is refluxed with mercapto acetic acid (0.005M) by using DMF (15 ml) as solvent in 50 ml RBF containing Pinch of anhydrous ZnCl2 for 5-6 hours. The reaction mixture was cooled and pour it on well crushed ice. The solid product obtained was Filtered and washed with cold water. The obtained product was recrystallised from methanol.

5a. : Yield : 0.77 gm , M. P. : 158 °C, I.R.(KBr) :3400 cm-1 (O-H stretching), 3163 cm-1 (N-H stretching), 1740 cm-1 (C=O) stretching); NMR : 3.8 (s, 3H, O-CH3), _ 6.8 (s, 1H, -OH), _ 7.0 (s, 1H, -CH), _ 7.2- 7.6 (m, 3H, Ar-H), _ 8.4 (s, 1H, N-H), _ 9.5 (s, 1H, enolic O-H), Mass : 465(M+) and base peak at 244. [Found : C:(45.80%); H:(2.30%); Cl: (15.70%); N:(9.10%); O:(10.30%); S:(14.10%)., C17H13Cl2N3O3S2 required : C:(46.16%); H:(2.96%); Cl:(16.03%); N:(9.50%); O:(10.85%); S:(14.50%).]

5b. : Yield : 1.0 gm , M. P. : 185 °C, I.R. (KBr) : 3400 cm-1 (O-H stretching), 3151 cm-1 (N-H stretching), 1716 cm-1 (C=O) stretching[Found : C:(45.80%); H:(2.30%); Cl: (15.70%); N:(9.10%); O:(10.30%); S:(14.10%)., C17H13Cl2N3O3S2

required : C:(46.16%); H:(2.96%); Cl:(16.03%); N:(9.50%); O:(10.85%); S:(14.50%).]

5c. : Yield : 0.72 gm, M. P. : 237 °C, I.R. (KBr) : 3300-3100 cm-1 (broad) due to –OH and N-H stretching, 1701 (C=O stretching). [Found : : C:(47.30%); H:(2.90%); Cl:(16.20%); N:(9.30%); O:(7.10%); S:(14.80%). C17H13Cl2N3O2S2 required : C:(47.89%); H:(3.07%); Cl:(16.63%); N:(9.86%); O:(7.51%); S:(15.04%).]

5d. : Yield : 0.85 gm, M. P.: 116 °C, I.R. (KBr) : 3211 cm-1 due to N-H stretching, 1716 cm-1 (C=O stretching). [Found : C:(48.80%); H:(3.20%); Cl:(15.60%); N:(12.20%), O:(3.30%), S:(14.10%), C18H16Cl2N4OS2 required : C:(49.20%); H:(3.67%); Cl:(16.14%); N:(12.75%), O:(3.64%), S:(14.60%).]

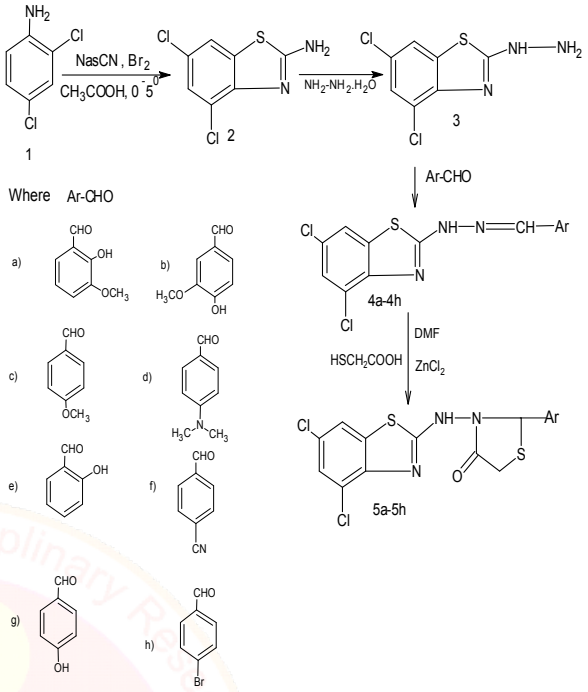
5e. : Yield : 0.89 , M. P. : 175 °C, I. R. (KBr) : 3400 cm-1 broad (O-H stretching), 3103 cm-1 (N-H stretching), 1716 cm-1 (C=O stretching). [Found : C:(46.20%); H:(2.10%); Cl:(16.90%); N:(9.80%), O:(7.20%), S:(15.10%), $C16H11Cl2N3O_2S2$ required : C:(46.61%); H:(2.67%); Cl:(17.20%); N:(10.19%), O:(7.76%), S:(15.55%).]

5f. : Yield : 0.87 gm , M. P. : 193 °C, I. R. (KBr) : 3448 cm-1 broad (O-H stretching), 3277 cm-1 (N-H stretching), 1734 cm-1 (C=O stretching). [Found: C: (48.20%); H:(2.10%); Cl:(16.40%); N:(13.10%),O: (3.20%), S:(14.90%), $C_{17}H_{10}Cl_2N_4OS_2$ required: C:(48.46%); H:(2.39%); Cl:(16.83%); N:(13.30%), O:(3.80%), S:(15.22%).]

5g: Yield : 0.94 , M. P. : 198 °C, I. R. (KBR) : 3178 cm-1 (N-H stretching), 1710 cm-1 (C=O stretching), Mass : 493 (M+. 7%). [Found : C:(46.20%); H:(2.10%); Cl:(16.80%); N:(9.90%), O:(7.20%), S:(15.20%)., $C16H11Cl_2N3O_2S2$ required : C:(46.61%); H:(2.69%); Cl:(17.20%); N:(10.19%), O:(7.76%), S:(15.55%).]

5h. : Yield : 0.94 , M. P. : 203 °C, I. R. (KBR) : 3178 cm-1 (N-H stretching), 1710 cm-1 (C=O stretching), [Found : C:(40.10%); H:(1.90%); Br:(16.40%); Cl:(14.50%); N:(8.30%), O:(3.10%), S:(13.20%), $C16H10BrCl_2N3OS2$ required : C:(40.44%); H:(2.12%); Br:(16.81%); Cl:(14.92%); N:(8.84%), O:(3.37%), S:(13.50%).]

Scheme



ANTIBACTERIAL ACTIVITY

The compound 5a to 5f were tested for their antimicrobial activity by cup plate agar diffusion method against *E.coli* (Gram –ve) *B.subtilis* (Gram +ve), *E. carotovara* and *Xanthomonas citri* using ampicillin, streptomycin. and penicillin as a standard for comparison. The antibacterial screening data of the compounds is presented in table No.1. Dimethyl sulphoxide was used as a control (solvent).

Table : 1

Sr. No.	Comp.	Antimicrobial activity (zone of inhibition in mm)			
		E.coli	*Erwinia*	*Bacillus*	*Xanthom-Onas citri*
1	5a	08	00	04	00
2	5b	16	14	12	13
3	5c	12	04	06	08
4	5d	00	04	03	04
5	5e	14	13	10	12
6	5f	10	10	08	07
7	5g	09	08	11	06
8	5h	12	09	08	10
Ampicillin		16	18	17	15
Streptomycin		20	18	22	18
Penicillin		15	20	18	17
Control		00	00	00	00

RESULT AND DISCUSION

The compounds 5a to 5h were tested for their antimicrobial activity by the cup plate agar diffusion method against *E. Coli, Erwinla carotovara, Bacillus substilis, and Xanthomonas*

citri. The antibacterial screening data of the compound shows compound 5b is more active against *E. Coli, Erwinla carotovara and Xanthomonas citri* while compound 5e is more active against *E. Coli, Erwinla carotovara.*

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Cr(III), Mn(III) AND Fe(III) METAL COMPLEXES WITH DINEGATIVE TRIDENTATE HYDRAZONE SCHIFF BASE: SYNTHESIS AND CHARACTERIZATION

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ABSTRACT

Cr(III), Mn(III) and Fe(III) complexes of 2,4-dihydroxybenzophenone-4-nitrobenzoylhydrazone (H_2L), were prepared, which were structurally characterized by elemental, electronic & infrared spectroscopy, magnetic susceptibility measurements and thermogravimetric analyses. Thermal degradation studies of metal complexes show that the final product is the metal oxide. An octahedral geometry is suggested for the Cr(III) and Fe(III) complexes whereas square pyramidal geometry for Mn(III) complex. Structural analysis reveals that the ligand presents as tridentate ligand with ONO donors and coordinates to the metal center in an enolic form.

Key word: *hydrazone Schiff base, complexes, infrared spectra, thermogravimetric study*

INTRODUCTION

In recent years, considerable attention has been paid to the chemistry of the metal complexes of Schiff bases containing nitrogen and oxygen donors [1–4] because of their stability and biological activity [5–10]. In addition, the presence of nitrogen and oxygen donor atoms in the complexes makes these compound effective and stereospecific catalysts for oxidation, reduction hydrolysis and other transformations of organic and inorganic chemistry [11–13]. Schiff bases of hydrazone moieties have an additional interest, because they also contain the >C=N– structural unit, which forms a strong chelate ring giving possible electron delocalization. It is well known that some drugs have increased activity when administered as hydrazone metal complexes. The present work synthesizes and characterizes new metal complexes of hydrazone Schiff base. The hydrazone Schiff base (H_2L) of *ONO* dibasic ligand is synthesized by condensation of 4-nitrobenzoylhydrazide with 2,4-dihydroxybenzophenone (scheme 1). Three new complexes of H_2L ligand with Cr(III), Mn(III) and Fe(III) are synthesized.

EXPERIMENTAL MATERIALS AND PHYSICAL MEASUREMENTS

All the reagent and solvents (ethanol, methanol and diethyl ether) were of reagent grade and used without purification. Chromium chloride pentahydrate and ferric chloride hexahydrate were of S. D's fine chemicals. $Mn(OAc)_3 2H_2O$ was synthesized by reported method [14]. 2,4-dihydroxybenzophenone and 4-nitrobenzoylhydrazide were prepared by general method [15].

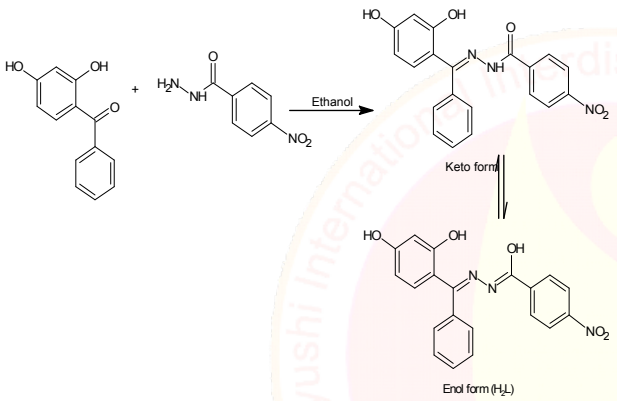
Microanalyses of carbon, hydrogen and nitrogen of the compounds were carried at RSIC, CDRI, Lucknow, India. Metal content in each complex was done gravimetrically by decomposing the complexes with conc. HNO_3 and then igniting to metal oxides [16]. The IR spectra were recorded on a Perkin Elmer infrared spectrophotometer in the range 4000–400 cm^{-1} at CDRI, Lucknow, India. Solid-state electronic spectra of the complexes were recorded on a carry 2300 spectrophotometer at SAIF, Chennai. ^{1}H-NMR spectra of ligand was recorded on a Bruker Ac 250 spectrometer at 250 MHz, using TMS as a reference in *DMSO-d_6*. The magnetic susceptibilities at room temperature were measured on a Gouy balance using $Hg[Co(NCS)_4]$ as the calibrant. Diamagnetic corrections for various atoms and structural units were computed using Pascal's constants. Thermogravimetric curves of the compounds were recorded in the temperature range 30–750^{o}C at the heating rate of 10^{o}C/min.

SYNTHESIS OF HYDRAZONE LIGAND (H_2L)

The hydrazone ligand (H_2L) used in the present work was prepared by following general method (scheme 1). An ethanolic solution (40 ml) of 4-nitrobenzoylhydrazide (50 mmol) was added to an

ethanolic solution (30 ml) of 2,4-dihydroxybenzophenone (50 mmol). The resulting reaction mixture was reflux on a water bath for 4–5 h. On cooling to the room temperature colored solid was obtained. The resulting solid mass was filtered, washed several times with ethanol, diethyl ether and subsequently dried over $CaCl_2$ in a desiccator. The purity of ligand was checked by TLC using silica gel as stationary phase and dimethylformamide as the solvent. Yield: 78%, M.P.- 197°C.

^{1}H-NMR data: 12.46 (s, 1H, OH C_2), 9.14 (s, 1H, OH C_4), 10.60 (s, 1H, NH), 6.34-8.32 (m, 12H, Ar-H).



Scheme 1: Synthesis of ligand (H_2L)

SYNTHESIS OF CR(III), MN(III) AND FE(III) COMPLEXES

An ethanolic solution (20 ml) of the metal salt and alcoholic solution (20 ml) of hydrazone ligand (H_2L) were mixed in 1:1 molar ratio. The resulting reaction mixture was refluxed for about 4–5 h on water bath. The solid product obtained was filtered, wash thoroughly with ethanol and finally with petroleum ether. All these complexes were dried in vacuum over $CaCl_2$.

RESULTS AND DISCUSSION

It appears from the analytical data (Table 1) that the ligand H_2L reacts with metal salts in 1:1 (M:L) molar ratio to form the complexes of general compositions $[CrL(Cl)(H_2O)_2]$, $[CrL(OAc)(H_2O)]$ and $[FeL(Cl)(H_2O)_2]$.

The prepared complexes are coloured and stable in air at room temperature. They are generally insoluble in common organic solvents, *viz*., ethanol, methanol, benzene, chloroform, carbon tetrachloride, ethylene chloride, and diethyl ether, but are soluble in DMF and DMSO.

Table 1: Analytical data of H_2L and its metal complexes.

Compound	Molecular formula	Elemental analysis found (calcd.) (%)			
		C	H	N	M
H_2L	$C_{20}H_{15}N_3O_5$	63.01 (63.66)	3.87 (4.01)	11.93 (11.14)	--
$[CrL(Cl)(H_2O)_2]$	$C_{20}H_{17}ClN_3O_7Cr$	49.02 (48.16)	3.10 (3.44)	8.12 (8.42)	11.23 (10.42)
$[MnL(OAc)(H_2O)]$	$C_{22}H_{18}N_3O_8Mn$	52.44 (52.08)	4.09 (3.58)	8.31 (8.28)	10.02 (10.83)
$[FeL(Cl)(H_2O)_2]$	$C_{20}H_{17}ClN_3O_7Fe$	47.02 (47.79)	3.21 (3.41)	7.94 (8.36)	11.82 (11.11)

IR SPECTROSCOPY

The bonding sites of H_2L ligand involved in the complexes have been determined by careful comparison of the infrared spectra of the complexes with the spectrum of ligand. The IR spectrum of the ligand exhibit bands at 1673 and 3147 cm^{-1} and are due to ν(C=O) and ν(NH) stretches respectively. Both the bands disappear on complexation, indicating the transformation of the carbonyl moiety to the enolic moiety and consequent replacement of the enolic hydrogen by the metal ion. A new band appearing in the 1227–1241 cm^{-1} was assigned to the ν(C–O) (enolate) mode [17]. The ligand show broad band at 3229 cm^{-1} due to intramolecular hydrogen bonding (O–H·····N) this band disappears in all the metal complexes indicating the deprotonation of the phenolic group. The coordination through phenolic oxygen after deprotonation is reveals by a band due to ν(C–O) at higher frequencies (1319–1332cm^{-1}) in all the complexes as compared to that of ligand (1309 cm^{-1}) [18, 19]. The ligand show a weak band at 1624 cm^{-1}, which can be assigned to ν(C=N) vibration of the azomethine linkage. The band due to ν(C=N) appears at a slightly lower wavenumber (5–17 cm^{-1}) in all the complexes suggesting that the nitrogen atom of the azomethine group is coordinated to metal atom [20]. The ligand ν(N-N) band at about 980 cm^{-1} is shifted considerably (16–21 cm^{-1}) to higher wavenumber in all the complexes, further suggesting the coordination through the azomethine nitrogen. The IR spectra of Mn(III) complex show that the ν_{asy} and ν_{sym} bands are assigned at1552 and 1363 cm^{-1}, respectively. The magnitude of difference $[\nu_{asy}(COO) - \nu_{sym}(COO)]$ occurring at 189 cm^{-1} indicates that the carboxylate ion function as monodentate donor [21]. The broad bands at 3312–3402, 1554–1572, and 832–861 cm^{-1} in the IR spectra of the complexes are referred to

m(OH), δ(H_2O), *pr*(H_2O) and *pw*(H_2O) vibrations for the coordinated water molecule [22]. The metal complexes also show a non-ligand bands in the range 509–567 and 439–494 cm^{-1}, which are tentatively assigned to ν(M–O) and ν(M–N), respectively [23].

ELECTRONIC SPECTRA

The electronic spectra of Fe(III) complex shows three bands at 16267, 24519 and 36478 cm^{-1}, which may assigned to $^6A_{1g} \rightarrow {}^4T_{1g}(G)$, $^6A_{1g} \rightarrow {}^4T_{2g}(G)$ and $^6A_{1g} \rightarrow {}^4E_g(G)$ transitions, respectively, indicating an octahedral geometry [24]. The magnetic moment value for Fe(III) complex was found in the range reported for d^5 system containing five unpaired electrons. The electronic spectrum of Cr(III) complex gives three bands at 17211, 23729 and 35731 cm^{-1} attributed to $^4A_{2g} \rightarrow {}^4T_{2g}(F)$, $^4A_{2g} \rightarrow {}^4T_{1g}(F)$ and $^4A_{2g} \rightarrow {}^4T_{1g}(P)$ transitions, respectively. The calculated Dq, B and β values (Table 2) lie in the range reported for octahedral structure [25].

Table 2: Magnetic moment, electronic bands and ligand field parameters of the complexes derived from H_2L.

Compound	Abs. Band (cm^{-1})	Assign-ment	μ_{eff} (B.M.)	B (cm^{-1})	β	Dq (cm^{-1})
[CrL(Cl)$(H_2O)_2$]	17211 23729 35731	$^4A_{2g} \rightarrow {}^4T_{2g}$ (F) $^4A_{2g} \rightarrow {}^4T_{1g}$ (F) $^4A_{2g} \rightarrow {}^4T_{1g}$(P)	3.87	521	0.56	1721
[MnL(OAc)(H_2O)]	12892 14970 20014	$^5B_1 \rightarrow {}^5B_2$ $^5B_1 \rightarrow {}^5A_1$ $^5B_1 \rightarrow {}^5E$	4.12	-	-	-
[FeL(Cl)$(H_2O)_2$]	16267 24519 36478	$^6A_{1g} \rightarrow {}^4T_{1g}(G)$ $^6A_{1g} \rightarrow {}^4T_{2g}(G)$ $^6A_{1g} \rightarrow {}^4E_g(G)$	4.97	-	-	-

The magnetic moment value (3.87 BM) of the Cr(III) lies in the usual range reported for octahedral structure. Mn(III) complex shows three bands at 12892, 14970, 20014 cm^{-1} which may be due to $^5B_1 \rightarrow {}^5B_2$, $^5B_1 \rightarrow {}^5A_1$ and $^5B_1 \rightarrow {}^5E$ transition, respectively, in square pyramidal configuration around the Mn(III) ion [26]. Also, the value of magnetic moment (4.12 BM) lies in the range measured for the high spin d^4 system.

THERMOGRAVIMETRIC ANALYSIS

In order to analyze the number and nature (lattice or coordinated) of water molecules, thermal analysis of the compound was performed on powder samples in the range of 30–750°C. The thermograms of ligand (H_2L) and Fe(III) complex are represented in fig 2 & 3.

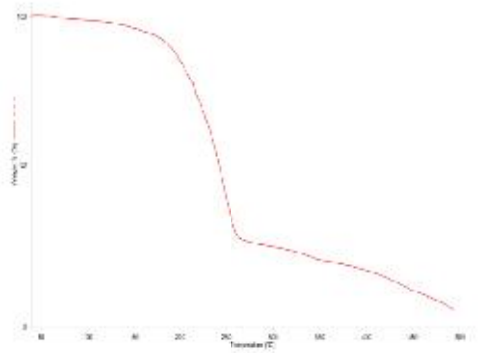


Figure 2: TG curve of Ligand (H_2L)

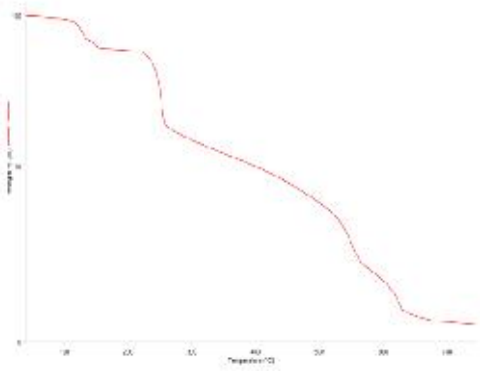


Figure 3: TG curve of [FeL(Cl)$(H_2O)_2$] complex

The assignment of the different decomposition steps are given in table 3. The ligand (H_2L) decomposed in one step whereas its metal complexes undergo decomposition in three different steps. Cr(III), Mn(III) and Fe(III) complexes show mass loss in the temperature range 92–200°C correspond to loss of coordinated water molecules [% mass loss obs/calcd: Cr(III): 7.80/7.22; Mn(III): 4.00/3.54; Fe(III): 7.85/7.16] [27]. The Mn(III), Cr(III) and Fe(III) complexes show mass loss in the temperature 200–275°C which corresponds to loss of one acetate/chloride ion [% mass loss obs/calcd: Mn(III): 11.5/11.63; Cr(III): 6.15/7.12; Fe(III): 7.25/7.07].

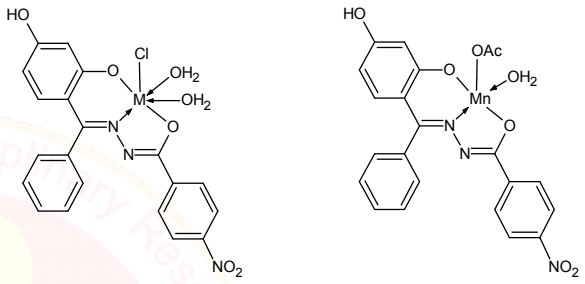
Table 3: Thermal analyses for metal complexes.

Compound	Temp. range (°C)	% mass loss		Decomposition assignment
		Found	Calcd.	
[CrL(Cl)(H_2O)$_2$]	92-190 190-227 227-750	7.80 6.15 -	7.22 7.12 -	Loss of 2 moles of coordinated water molecules Loss of 1 coordinated chloride ion Deligation
[MnL(OAc)(H_2O)]	95-190 190-230 230-750	4.00 11.5	3.54 11.63 -	Loss of 1 moles of coordinated water molecules Loss of 1 coordinated acetate ion Deligation
[FeL(Cl)(H_2O)$_2$]	105-200 200-275 275-700	7.85 7.25 -	7.16 7.07 -	Loss of 2 moles of coordinated water molecules Loss of 1 coordinated chloride ion Deligation

After the loss of water/acetate/chloride molecules the organic part decomposes as further increment of temperature (390–550°C). In this step rapid mass loss is observed in the temperature range 390–550°C, and TG curve attains a constant level above 700°C, finally metal oxide formation takes place.

CONCLUSIONS

On the basis of the physical and spectral data of the hydrazone Schiff Base ligand (H_2L) and its complexes, it can be assumed that the ligand is bonded to the metal ions via azomethine nitrogen, phenolic and enolic oxygen atoms. The probable structure of the complexes is:



M = Cr(III) and Fe(III)

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STUDY OF IMPORTANT ACOUSTICAL PARAMETERS OF SUBSTITUTED PYRAZOLE CARBOXYLIC ACID IN 60% DMF-WATER MIXTURES AT 300K USING ULTRASONIC INTERFEROMETER

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ABSTRACT
Investigation of acoustical molecular interaction of substituted pyrazole carboxylic acid in DMF-water binary liquid mixtures at 300K using ultrasonic interferometer technique is studied. The ultrasonic velocity, density is used to calculate adiabatic compressibility, apparent molal volume, apparent molal compressibility and solvation number. The solute solvent interaction is understood from the magnitude of partial molar volume and partial molar compressibility at infinite dilutions.

Keywords: *substituted pyrazole carboxylic acid, uitrasonic velocity, density, interferometer.*

INTRODUCTION
The most exciting and fascinating field of scientific research among the researchers was ultrasonic study. It provides useful information regarding the structure of molecules, molecular order and packing, inter and intra-molecular interactions. Due to non-destructive nature, ultrasonic investigation has wide range of application in material science, polymer, surface profiling, astronomy, agriculture, medicine, biology, industry and research.

The study of certain physical parameter in science and technology, ultrasonic is widely used in recent years for industrial and medicinal application.[i] Apparent molal volumes of alcohols in aqueous solutions at different temperatures is studied.[ii] Apparent molal compressibility, relative association, apparent molal volume and solvation number of 1-(2'-hydroxy-5' bromophenyl)-3-(4'-chlorophenyl)-1, 3 pronandione in dioxane-water mixture are studied.[iii] The study of acoustical properties of subsitituted thiopyrimidines and substituted oxoimidazoline drugs in 70% (DMF–water) mixture at in different concentrations of ligands are reported.[iv] Ultrasonic technique is utilized for measuring the thickness of skin and biological tissues[v] and to determine the tissue hydration status.[vi] Ultrasonic study of Zwitter-ionic nature of amino acids in water is performed.[vii] Ultrasonic measurements are used to estimate the different elastic properties.[viii] Ultrasonic measurements of some substituted pyrazolines in acetone-water are observed.[ix] Ultrasonic velocity of substituted aminopyrimidine in 70% DMF-water mixture is studied.[x] Acoustical properties of 1-(4-hydroxy-6-methyl)-S-triazino-3-phenylthiocarbamide1-(4-hydroxy-6-methyl)-S-triazinoethylthiocarbamide and 1-(4-hydroxy-6-methyl)-S-triazino-3-methylthiocarbamide are measured at various concentrations.[xi]

Ultrasonic technique is used to determined acoustical property of ternary mixture of toluene in cyclohexane and nitrobenzene at 308K.[xii] Ultrasonic studies of (E)–2-(2-nitrobenzylidene amino) benzoic acid and its Fe(III) complex at different concentration is reported.[xiii] Ultrasonic technique is used to determined the acoustical parameters of chlorosubstituted pyrazole at different concentration and different percentages in dioxane-water mixture at 305K.[xiv] Ultrasonic velocity and density are measured for 1-(4-hydroxy-6-methyl pyrimidino)-3-methyl thiocarbamides in 70% dioxane-water at 302K.[xv] Binary mixtures of 2, 2, 4-trimethylpentane with benzene, toluene, o-xylene, m-xylene and p-xylene at 308K over the entire composition range is studied by ultrasonic technique.[xvi] Ultrasonic study is carried out in n-hexane solutions, containing equimolar concentration from 0.02 to 0.2 M of aromatic ketones and N-methylaniline (NMANI) at 303.15K and atmospheric pressure.[xvii] Apparant molar volume of NaCl in dioxane, glycol, ethanol, propane-2-ol, methanol, glycerol-water mixture at 10, 20 and 30% within the temperature range 303-313K has studied.[xviii] Speed of sound and isentropic compressibility's for binary mixtures of 1, 2-ethanediol with 1-hexanol, 1-butanol and 1-octanol in the temperature range

293.15-313.15K is reported. [xix] Ultrasonic velocity of dilute solutions of caffeine, l-methyl-4-(methylamino) pyrazolo[3,4-d]pyrimidine, adenosine, and deoxyadenosine at a different temperatures has determined.[xx] The ultrasonic investigation of solute-solvent and solute-solute interactions have been reported in aqueous solutions of bases, nucleosides, and nucleotides.[xxi] The ultrasonic velocity, density, viscosity of polyethylene glycol and maltodextrin, β-cyclodextrin and amylase in different concentration ranges are measured at three different temperatures 303,313and 323K.[xxii] Ultrasonic and thermodynamical parameters of cinnamaldehyde with ophenyldiamine in n-hexane at different temperature are studied.[xxiii] Ultrasonic velocity of schiff base (E)–2-(2 chlorobenzylideneamino) benzoic acid and its metal complex with Fe(III) in DMSO are measured at constant temperature 306K and different concentration.[xxiv]

A survey of the literature indicates that no acoustical data on substituted pyrazole carboxylic acid in 60% DMF-water binary liquid mixtures at 300K has been produced. In the present work, different properties such as adiabatic compressibility (β_s), apparent molal volume (ϕ_v), apparent molal compressibility (ϕ_k) and solvation number (Sn) have been evaluated in following Substituted pyrazole carboxylic acid in 60 % (DMF+Water) mixture at different concentrations of ligand at 300K.

1) Ligand A (LA)= 1- phenyl-3-(4'- methyl) phenyl-1H- pyrazol-4-carboxylic acid

2) Ligand B (LB)=1- phenyl-3-(4'- bromo) phenyl-1H- pyrazol-4-carboxylic acid [1]

3) Ligand C (LC)=1- phenyl-3-(4'- ethyl) phenyl-1H- pyrazol-4-carboxylic acid

4) Ligand D (L4)=1,3-diphenyl-1H- pyrazol-4-carboxylic acid

MATERIALS AND METHODS

All the chemicals used are of A. R. grade. The density measurements are done with the precalibrated bicapillary pyknometer. All the weighings are done on one pan digital balance (petit balance AD-50B) having an accuracy of ± 0.001 gm. The speed of sound wave is obtained by using variable path crystal interferrometer (Mittal Enterprises, Model MX-3) with accuracy of ± 0.03% and frequency 1MHz. In the present work, a steel cell fitted with a quartz crystal of variable frequency is employed. The instrument is calibrated by measuring ultrasonic velocity of water at 27° C.

RESULTS AND DISCUSSION

The ultrasonic waves of known frequency produced by a quartz crystal are reflected by a movable metallic plate kept parallel to the quartz plate. When the state of acoustic resonance is reached due to the formation of standing waves, an electrical reaction occurs on the generator driving the quartz plate and its anode current becomes maximum. The micrometer is slowly moved until the anode current meter on a high frequency generator shows a maximum. The distance thus moved by the micrometer gives the values of wavelength.[xxv]

The distance traveled by micrometer screw to get one maximum in ammeter (D) is used to calculate wavelength of ultrasonic wave using following relation:

$$2D = \lambda \qquad (1)$$

Where, λ is wavelength and D is distance in mm.

From the knowledge of the wavelength, the ultrasonic velocity can be obtained by the relation:

rasonic velocity

$$(U) = \lambda \times \text{Frequency} \times 10^3 \qquad (2)$$

Using the measured data some acoustical parameters can be calculated using the standard relations:

The adiabatic compressibility[xxvi] of solvent and solution can be calculated by using equations:

Adiabatic compressibility of solution

$$(\beta s) = 1/ Us^2 \times ds \qquad (3)$$

Adiabatic compressibility of solvent

$$(\beta_0) = 1/ U_0^2 \times d_0 \qquad (4)$$

Where, U_o and Us are ultrasonic velocity in solvent and solution respectively.

d_o and ds are density of solvent and solution respectively.

The apparent molal volume (ϕ_v) and apparent molal compressibility (ϕ_k) are given by following equations.[xxvii]

Apparent molal volume

$$(\phi_v) = \frac{M}{d_s} + \frac{(d_o - d_s)\times 10^3}{(m d_s d_0)} \qquad (5)$$

Apparent molal compressibility

$$(\phi_k) = \frac{1000(\beta_s d_o - \beta_o d_s)}{m d_s d_o} + \frac{\beta_s M}{d_s} \qquad (6)$$

Where, d_o and d_s are the densities of the pure solvent and solution, respectively.

m is the molality and M is the molecular weight of solute.

β_o and β_s are the adiabatic compressibility of pure solvent and solution respectively.

According to the studies intermolecular free length (L_f)[xxviii] is given by:

Solvation number

$$(S_n) = \phi_k / \beta_0 \times (M/ d_0) \quad (7)$$

In present work the measurement of ultrasonic velocity and density at a different concentration of substituted pyrazole carboxylic acid derivatives in 60% DMF+water solvent is carried out at 300K temperature. The data obtained is used to determine adiabatic compressibility (β_s), apparent molal volume (ϕ_v), apparent molal compressibility (ϕ_k) and solvation number (S_n) of Substituted pyrazole carboxylic acid derivatives using equations 3, 5, 6 and 7. From table number 1 it is observed that ultrasonic velocity decreases with decreases in concentration in the system. This is due to association of very strong dipole-induce dipole interaction between the components. In more concentrated solution the possibility of making hydrogen bond increases which gives packed structure due to this ultrasonic velocity increases.

Table number 1 show that the adiabatic compressibility (β_s) increases with decrease in the concentrations. Figure number 2 shows the variation of adiabatic compressibility with concentrations. In more concentrated solution more cohesion is expected and this lead to a decrease in adiabatic compressibility (β_s). The decrease in adiabatic compressibility (β_s) results in an increase in the value of ultrasonic velocity. The increase of adiabatic compressibility with decrease of concentration of solution due to the dispersion of solvent molecules around ions supporting weak ion solvent interactions.

Apparent molal volume (ϕ_v) is very important tool to identify ion-solvent interactions. Table no.1 suggests that the apparent molal volume (ϕ_v) increases with decrease in concentration in all the system. Figure number 3 shows the variation of apparent molal volume with concentrations. The increase in apparent molal volume with decrease in concentration in all systems indicates the existence of strong ion-solvent interaction. Table number 1 shows the variation of apparent molal compressibility (ϕ_k) with concentrations Figure number 4 suggests that apparent molal compressibility (ϕ_k) increases with decreases in concentrations. The increase in value of apparent molal compressibility (ϕ_k) with decrease in concentrations in this systems, shows the weak electrostatic attractive force in the vicinity of ions causing electrostatic salvation of ions.

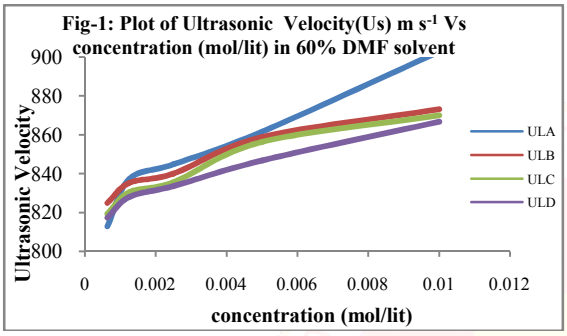
The solvation number (Sn) increases as the concentration decrease as per table number 1. Figure number 5 shows the variation of solvation number with concentrations. When salvation occurs, the solvent molecules of the ion-solvent complex may be assumed to more closely pack than in the pure solvent. The increase in solvation number with decrease in concentration is due to weak solute-solvent interaction in this system.

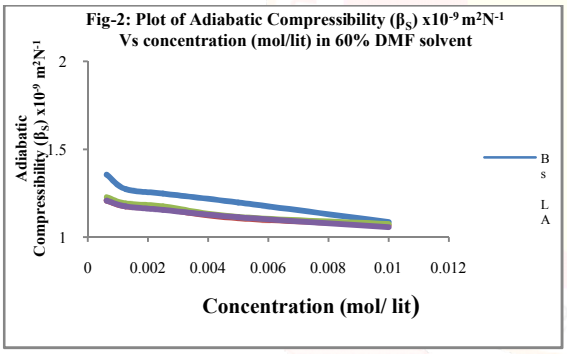
Table 1: Density (d), ultrasonic velocity (U_s), adiabatic compressibility (β_s), apparent molal volume (ϕ_v), apparent molal compressibility (ϕ_k) and solvation number (S_n) in 60% DMF solvent at 300K

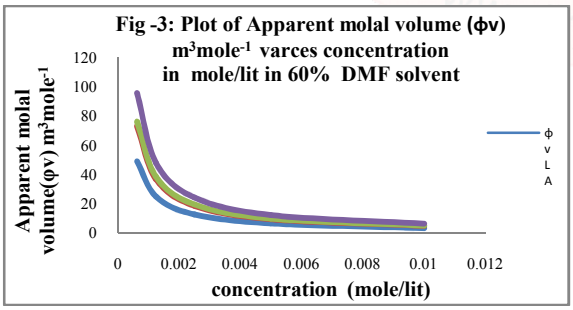
Conc. (m) (mol lit^{-1})	Densiy (d) (kg m^3)	Ultrasonic Velocity (U_s) (m s^{-1})	Adiabatic compressibility (β_S) x 10^{-9}, (m^{2}N^{-1})	Apparentmolal Volume (ϕ_v) (m^{3}mol^{-1})	Apparent molal compressibility (ϕ_k) x 10^{-10} (m^{2}N^{-1})	Solvation Number (S_n)
Ligand LA						
0.01	1129.3	902.8	1.0864	3.2440	2.6547	0.568
0.005	1125.3	861.6	1.1970	6.3721	3.0449	0.651
0.0025	1123.2	844.8	1.2474	12.6215	3.1751	0.679
0.00125	1120.1	837.2	1.2737	24.8754	3.2532	0.696
0.000625	1116.9	812.8	1.3552	48.9838	4.6058	0.985
Ligand LB						
0.01	1227.3	873.2	1.0686	4.6617	2.8555	0.578
0.005	1224.3	858.8	1.1074	9.2670	2.9707	0.601
0.0025	1221.2	840.0	1.1605	18.4030	3.1078	0.629
0.00125	1220.1	835.2	1.1749	36.7122	3.1352	0.635
0.000625	1217.1	824.8	1.2077	72.9089	3.2176	0.651
Ligand LC						
0.01	1228.6	870.0	1.0753	4.9280	3.0323	0.583
0.005	1223.4	856.4	1.1145	9.7424	3.1444	0.604

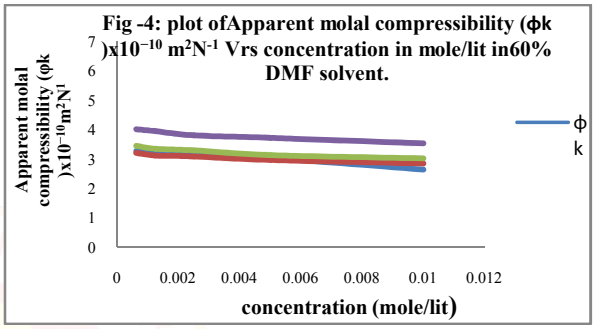
0.0025	1219.2	835.6	1.1747	19.2966	3.3065	0.635
0.00125	1216.5	830.4	1.1921	38.3481	3.3643	0.646
0.000625	1212.9	819.2	1.2285	76.0340	3.4509	0.663
Ligand LD						
0.01	1259.2	866.8	1.0569	6.2074	3.5407	0.574
0.005	1252.2	846.8	1.1136	12.2525	3.7383	0.607
0.0025	1246.3	833.6	1.1546	24.2234	3.8916	0.631
0.00125	1240.2	828.1	1.1761	47.8526	3.9599	0.643
0.000625	1239.6	817.2	1.2079	95.5868	4.0280	0.654

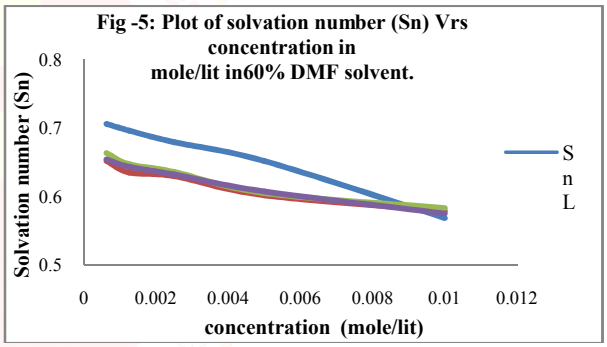
Fig.- 1 to 5: Graphical representation of acoustic parameters in 60% of DMF-water solvent











CONCLUSION

The acoustic parameters are helpful to understand the behavior of solute and solvent molecules in solutions. In more concentrated solution the possibility of making hydrogen bond increases which gives packed structure due to this ultrasonic velocity increases. Adiabatic compressibility (β_s) decreases with increase in concentration which shows ion-solvent interaction. The increase in apparent molal volume (ϕ_v) with decrease in concentration indicates the existence of strong ion-solvent interaction. The increase in value of apparent molal compressibility (ϕ_k) with decrease in concentrations shows the weak electrostatic attractive force in the vicinity of ions causing electrostatic solvation of ions. The increase in solvation number (S_n) with decrease in concentration is due to weak solute-solvent interaction in all the systems.

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EFFICIENT SYNTHESIS OF SOME NEW TRIAZINES AND ITS DERIVATIVES

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ABSTRACT

The 1,3,5-triazines are the oldest known organic compounds. Originally they were called the symmetric triazines. A new series of 4-Chloro-6-Alkoxy-N-alkyl-1,3,5-triazin-2-amine have been synthesized.The promising results are in support of the fact that the compounds are worth to be optimized for some novel drugs in future. The synthetic strategy allows broad structural variation of this new drug-like heterobicyclic scaffold. The newly synthesized compounds were characterized using IR, ^{1}H-NMR and Mass Spectroscopy.

Keyword : *s-triazines and its derivatives,cyanuric chloride and spectral data.*

INTRODUCTION

Cynuric chloride is an inexpensive, commercially available reagent and use for the preparation of variety of s-triazine derivatives. The temperature-dependent displacement of chlorides of cyanuric chloride with various nucleophiles provides a vast array of possible triazine derivatives and applications. 2,4,6-trichloro s-Triazine derivatives preparedreplacement of one chlorine atom of cyanuric chloride at 0-5 ^{0}C, second one chlorine atom at 60-80^{0}Cby amino and alkoxy group.[1]All of the 2,4,6-mono, di,substituted s-triazine derivatives have wide practical applications.[2] Several derivatives of *s*-triazine show herbicidal Pyrimidines and their derivatives posseses several interesting biological activities such as antimicrobial, antitumor and antifungal activities.[3] Many pyrimidine derivatives are used for thyroid drugs and leukemia. Among interest devoted triazine derivatives due to it possess biological activities including biofuel production insulin mimetics, neuroblastoma inhibition,antimicrobial and microtubule inhibition.[4-5]Here we report on the preparation of a series of new 2,4,6-trisubstituted-1,3,5-triazines Via sequential substitution of the three chlorides of cyanuric chloride by N-and -O-centered nucleophiles.They have found wide applications in thedyestuffs and surface active agents, rubber industries pharmaceutical and textile industries.[6-8] Most of the drugs belong to the class of heterogenius compounds. Heterocyclic compounds played a vital role in the metabolism of all living cells.[10]Large number of them are five and six membered heterocyclic compounds having one to three heteroatoms in their nucleus. The compounds may be pyrimidine and purine basis of genetic material DNA, and these heterocyclic compounds may be isolated or fused heterocyclic systems.[13] Substituted s-Triazine derivativesexhibit remarkable Tuberculostatic activity of high therapeutic significance.[14-15]

MATERIAL AND METHOD

General procedure for synthesis of mono-substituted triazine derivative i.e. 4,6-dichloro-N-(4-nitrophenyl)-1,3,5-triazin-2-amine.

Step-I

To a stirred solution of cyanuric chloride (0.02mol) in acetone (10 ml) at 0-5^{0}C.The solution of 4-Nitro aniline (0.02mol) in acetone (10 ml) was added and pH being maintained neutral by the addition of 10% sodium bi-carbonate solution from time to time as per requirement of reaction condition. The stirring was continued at 0-5^{0}C for 2-3 hours. After the completion of reaction the stirring was stopped and the solution was treated with crushed ice. The solid product obtained was filtered and dried. The crude product was purified by crystallization from ether to get title compound. Same material used for next step.

General procedure for preparation of di-substituted triazine derivative i.e. 4-chloro-6-(naphthalen-1-yloxy)-N-(4-nitrophenyl)-1,3,5-triazin-2-amine.

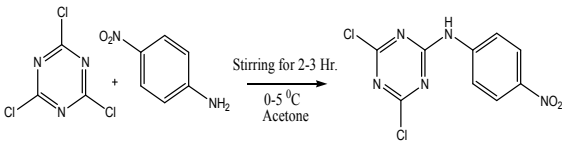
Step-II

To stirred the mixture of4,6-dichloro-N-(4-nitrophenyl)-1,3,5-triazin-2-amine(0.02 mol) 1-naphthol (0.02mol) and K_2CO_3 (0.06 mol) in 25 ml THF or acetone solvent . A solution of 10% $NaHCO_3$ was added and stirred for 6-8 hour at 60–80^{0}C.The progress reaction was observed by TLC using ether:ethyl acetate (8:2) solvent system as an eluent. After the completion of reaction the resultant mixture was poured into crushed ice. The

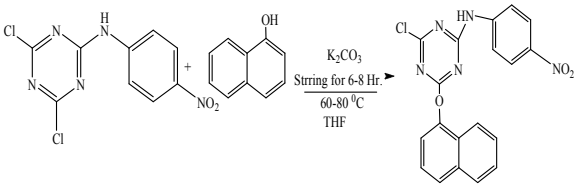
solid product obtained was filtered .Wash with distilled water and dried it.

EXPERIMENTAL SECTION

Scheme 1



Scheme 2



RESULT AND DESCUSSION

The target compounds and respective intermediates were synthesized as outline in scheme.The first step consist of the nucleophilic substitution of first chlorine atom ofcynuric chloride by 4-Nitro aniline give of4,6-dichloro-N-(4-nitrophenyl)-1,3,5-triazin-2-aminewith an efficient yield. Appearance of IR absorption peak at 3353 cm^{-1} shows the attachment of 2^0 aminegroup.4-chloro-6-(naphthalen-1-yloxy)-N-(4-nitrophenyl)-1,3,5-triazin-2-amineobtained by reaction of 4,6-dichloro-N-(4-nitrophenyl)-1,3,5-triazin-2-aminewith 1-naphtol.It displayed absorption band at 2344 cm^{-1} which showed the presence of C-O-linkage.

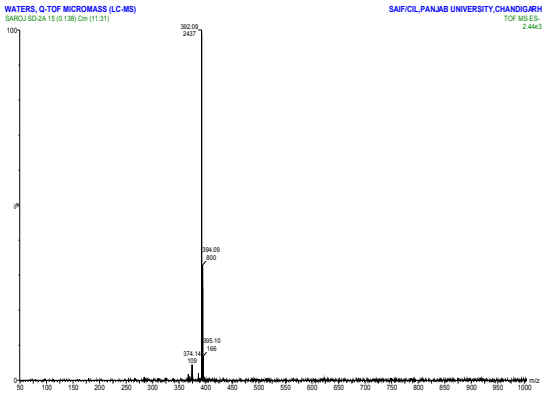
^{1}H NMR signal at δ 3.5 (1H,s,Ar-NH-) and δ 6.8-7.9 (m,aromatic protons). MS: m/z at 392.09 (M+1), at 394 (M+2), at 395 (M+3).

1. 4-chloro-6-(naphthalen-2-yloxy)-N-(4-nitrophenyl)-1,3,5-triazin-2-amine.

Yellow solid, mp 153-160 ^{0}C.1H NMR δppm (DMSO): 6.98-8.12(m,7Ar-H) 7.55-8.23(dd,4H), 4.10 (exchangeable,1H),6.98-7.63(m,Ar-H), IR (cm^{-1}) : 3484, 3119, 3013, 1924, 1542, 1327, 1225, 1111.18, 852, 802, 750. MS (m/z), at 392.09 (M+1), at 394 (M+2), at 395 (M+3).

2. 4-chloro-N-(2,5-dimethylphenyl)-6-(naphthalen-1-yloxy)-1,3,5-triazin-2-amine.

Whitesolid, mp 150-158 ^{0}C.1H NMR δ ppm (DMSO): δ 6.22-8.23 (m,Ar-H), δ 3.5(s,Ar-NH),δ 2.3-2.6(s,6H), 3.8 (exchangeable,1H), IR (cm^{-1}) : 3409.40, 3060.27,1553.1, 652.35, 1225.3, 1363, 1160, 874, 805, 758.1. MS (m/z) at377(M+1).



3. 4-chloro-6-(naphthalen-2-yloxy)-N-p-tolyl-1,3,5-triazin-2-amine.

Brown solid, mp 133-146 ^{0}C.1H NMR δ (DMSO): 6.98-8.12(m,7Ar-H) 7.55-8.23(dd,4H), 4.10 (exchangeable, 1H),6.98-7.63(m, Ar-H), IR (cm^{-1}) : 3484, 3119, 3013, 1924, 1542, 1327, 1225, 1111.18, 852, 802, 750 MS (m/z), 362 (M+1).

CONCLUSION

In summary, we have describe a simple method for synthesis of 4-chloro-6-(naphthalen-2-yloxy)-N-(4-nitrophenyl)-1,3,5-triazin-2-amine.FTIR, ^{1}H NMR and Mass spectroscopic techniques were used for the structural elucidation of the synthesized compounds.The sequential replacement of two chlorine atoms on cyanuric chloride with different nucleophiles provides the synthesis of a variety of substituted s-triazine molecules. In light of its operational simplicity andefficiency, this reliable method is expected to have a broad utility due to the scope of applications of the s-triazines. Antimicrobial activity of the newly compounds were investigated.

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SYNTHESIS OF SOME ISOXAZOLES FROM NITRO SUBSTITUTED ACETOPHENONE AND SUBSTITUTED BENZALDEHYDE VIA CHALCONE INTERMIDIATE AND THEIR ANTIMICROBIAL STUDIES

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ABSTRACT

Isoxazole is five member heterocyclic ring having a broad spectrum of pharmacological activities like anti-tubercular, anti-cancer, anti-bacterial, anti-fungal, anti-HIV, anti-inflammatory and anti-hypertensive activities. In the present research work we reported the synthesis of some new isoxazoles by using various different substituted chalcones and screened for their anti-microbial activity. The structures of the isoxazole derivatives were confirmed by spectral analysis. The derivatives of isoxazoles shows good to moderate activities against number of bacteria and fungus.

Keyword: *Isoxazole, anti-microbial activity.*

INTRODUCTION

In the past few decades, heterocycles play a significant role in the research of agricultural and medicinal chemistry. The isoxazole skeleton, a crucial type of nitrogen-containing heterocycle, has been used in pesticide and drug design because of their various biological activities, such as insecticidal [1-3], herbicidal [4-6], fungicidal [7], antiviral [8-10], and anticancer activities [11]. Recently, Yu et al.obtained a series of 3, 4, 5-trisubstituted isoxazoles that were showing good insecticidal activities [12]. More recently, Sun et al. reported several series of isoxazole compounds carrying benzoylurea moiety displaying perfect insecticidal activities [13]. The wide spread use of isoxazole-based compounds as a scaffold in the field of agriculture and medicine research endows the isoxazole ring as an important structural class. A derivative of Isoxazole has played a crucial role in the history of heterocyclic chemistry and has been used extensively important pharmacophores and synthons in the field of organic chemistry. Owing to their versatile chemotherapeutic importance, a significant amount of research effort has been focused on these Nuclei [14-16]. Such heterocyclic compounds are very widely distributed in nature, and are essential to life in various ways. Depending on the above finding, we decided to synthesize some newly substituted Isoxazole derivatives.

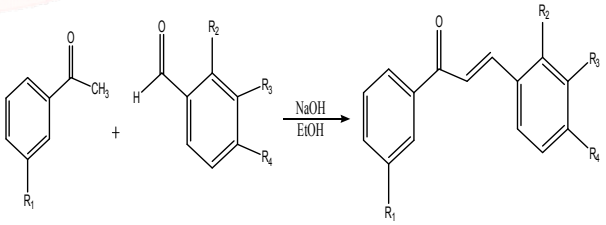
EXPERIMENTAL

(I) Preparation of Substituted Chalcones:

To a cooled solution of NaOH and ethanol, Nitro substituted acetophenone was added followed by addition of substituted benzaldehyde,the reaction mixture was stirred for 2-3 hours till the mixture become viscous and then the mixture was kept overnight in a refrigerator. The separated product was filtered under suction and washed well with cold water. Then it was recrystallized from rectified spirit. Physical characterization and data of synthesized chalcones (I a-g) is given in table 1.

List of chalcones prepared as

Ia (E)-3-(2-chlorophenyl)-1-(3-nitrophenyl) prop-2-en-1-one
Ib (E)-3-(4-chlorophenyl)-1-(3-nitrophenyl) prop-2-en-1-one
Ic (E)-1, 3-bis (3-nitrophenyl) prop-2-en-1-one
Id (E)-1-(3-nitrophenyl)-3-p-tolylprop-2-en-1-one
Ie (E)-3-(2-nitrophenyl)-1-(3-nitrophenyl) prop-2-en-1-one
If (E)-1-(3-nitrophenyl)-3-(4-nitrophenyl) prop-2-en-1-one
Ig (E)-3-(3-chlorophenyl)-1-(3-nitrophenyl) prop-2-en-1-one



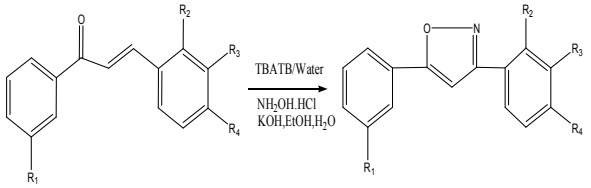
(II) Preparation of Substituted Isoxazoles.

An equimolar mixture of substituted chalcone obtained will be reacted with Tetrabutylammonium Tribromide (TBATB) (Green brominating agent) to obtain dibromo chalcones.The isoxazole will be obtained from dibromo chalcone by the action of $NH_2OH.HCl$ /KOH ($EtOH,H_2O$). The mixture will be concentrated by diluting out solvent under a

reduced pressure and poured into cold water. The precipitate obtained will be recrystallized for purity.Physical characterization and data of synthesized Isoxazoles (II a-g) is given in table 2.

List of Isoxazoles prepared is as

IIa 3-(2-chlorophenyl)-5-(3-nitrophenyl)isoxazole
IIb 3-(4-chlorophenyl)-5-(3-nitrophenyl)isoxazole
IIc 3,5-bis(3-nitrophenyl)isoxazole
IId 5-(3-nitrophenyl)-3-p-tolylisoxazole
IIe 3-(2-nitrophenyl)-5-(3-nitrophenyl)isoxazole
IIf 5-(3-nitrophenyl)-3-(4-nitrophenyl)isoxazole
IIg 3-(3-chlorophenyl)-5-(3-nitrophenyl)isoxazole



RESULT AND DISCUSSION

The Melting points of all compounds were recorded by using Paraffin bath. ^{1}H NMR Spectra and IR Spectra of compound IIb were use for its structural elucidation

Table 1: *Physical Characterization and data of synthesized chalcones.*

Compound	R_1	R_2	R_3	R_4	Mol. Formula	Mol. Wt.	% N Cal. (Found)	MP °C	% Yield
Ia	NO_2	Cl	H	H	$C_{15}H_{10}Cl\ NO_3$	287	4.87 (4.80)	115	75
Ib	NO_2	H	H	Cl	$C_{15}H_{10}Cl\ NO_3$	287	4.87(4.79)	117	75
Ic	NO_2	H	NO_2	H	$C_{15}H_{10}N_2O_5$	298	9.39(9.32)	121	62
Id	NO_2	H	H	CH_3	$C_{16}H_{13}\ NO_3$	267	5.24(5.20)	117	72
Ie	NO_2	NO_2	H	H	$C_{15}H_{10}\ N_2O_5$	298	9.39(9.30)	125	75
If	NO_2	H	H	NO_2	$C_{15}H_{10}\ N_2O_5$	298	9.39(9.30)	132	72
Ig	NO_2	H	Cl	H	$C_{15}H_{10}Cl\ NO_3$	287	4.87(4.80)	128	75

Table 2: *Physical Characterization and data of synthesized Isoxazoles.*

Compound	R_1	R_2	R_3	R_4	Molecular Formula	Molecular weight	%N Cal. (Found)	MP °C	% Yield
IIa	NO_2	Cl	H	H	$C_{15}H_9Cl\ N_2O_3$	301	9.32 (9.25)	181	68
IIb	NO_2	H	H	Cl	$C_{15}H_9Cl\ N_2O_3$	301	9.32 (9.20)	186	70
IIc	NO_2	H	NO_2	H	$C_{15}H_9N_3O_5$	311	13.50 (13.35)	187	65
IId	NO_2	H	H	CH_3	$C_{16}H_{12}\ N_2O_3$	280	9.99 (9.85)	179	65
IIe	NO_2	NO_2	H	H	$C_{15}H_9\ N_3O_5$	311	13.50 (13.40)	183	65
IIf	NO_2	H	H	NO_2	$C_{15}H_9\ N_3O_5$	311	13.50 (13.40)	182	72
IIg	NO_2	H	Cl	H	$C_{15}H_9Cl\ N_2O_3$	301	9.32 (9.30)	179	65

i) Spectral determination of IIb

IR (V_{max}): 1590 cm^{-1}*v*(C-C); 1510 cm^{-1}*v* (N-O); 3000 cm^{-1}*v* (C-H) 560 cm^{-1}*v*(C-Cl); 1480 cm^{-1}*v*(C-C);

^{1}H NMR (δppm**):** δ 8.35 (s, 1H, Ar-H); δ 8.12(d, 1H, -Ar-H); δ 7.75 (d, 1H, Ar-H); δ 7.55 (t, 1H, Ar-H);

δ 7.40 (d, 1H, Ar-H); δ 7.31 (s, 1H, Ar-H).

Further development on this subject to understand their mechanistic interaction and Spectral determination of IIa, IIc-IIg is currently in progress.

ii) Antimicrobial Screening synthesized Isoxazoles

Antimicrobial screening was done by using cup plate method at a concentration of 100µg/ml. The compounds were evaluated for antimicrobial activity against *P. aeruginosa, S. aureus, C. frundii, E. coli, P. mirabilis and S. typhi.*The results of antimicrobial data are summarized in table 3.All compounds show the moderate to good activity. (Zone of inhibitions in mm)

Table 3: *Antimicrobial Screening synthesized Isoxazoles*

Organisms	IIa	IIb	IIc	IId	IIe	IIf	IIg
P. aeruginosa	13	15	11	11	14	13	15
S. aureus	13	14	11	12	15	12	13
C. frundii	14	13	11	10	13	12	12
E. coli	13	14	10	10	13	14	15
P. mirabilis	12	13	12	11	15	14	12
S. typhi	13	12	12	12	14	12	13

CONCLUSIONS

Compounds IIa, IIb and IIg are more active due to presence of more electronegative chloro group as compaired to Nitro substituted isoxazoles against the microorganism mention above. These compounds show the moderate to good antimicrobial activity.

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PREPARATION AND STUDY OF ALCOHOL GAS SENSING BEHAVIOUR OF $CuFe_2O_4$ THICK FILM RESISTORS

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ABSTRACT

In the present work, thick film of nanostructured Mn doped $CuFe_2O_4$ was prepared by sol-gel method and its ethanol gas sensing properties were investigated. The structural and surface morphological characterizations of the sample were analyzed by means of X-ray diffraction (XRD) and scanning electron microscopy (SEM). The minimum crystallite size of Mn doped $CuFe_2O_4$ calculated from Scherrer's formula is found to be in the range ~20–35 nm. SEM images exhibit the porous nature of the sensing material with a number of active sites. The gas sensing properties of the Mn doped $CuFe_2O_4$ film was investigated for different concentration of ethanol. The maximum values of sensitivity and percentage sensor response were found at an operating temperature 180^0C of ethanol. These experimental results show that nanostructured Mn doped $CuFe_2O_4$ is a promising material for ethanol sensor.

Keywords: *Ethanol; sensors; sensitivity; sol-gel*

INTRODUCTION

Gas sensors which can be used in many industries and hospitals are important to environmental monitoring. In order to avoid the toxic gas leaking and endangering the human body, it is necessary to do the detection and examination on different gases. Ethanol vapour has been one of the most extensively studied gases for metal oxide gas sensors, particularly due to the need for small practical devices to detect alcohol on the human breath or even to detect leaks in industrial distribution lines.

Spinel-type metal oxide semiconductors are an alternative for an inexpensive sensors because of good chemical and thermal stability under operating conditions[1-3]. Currently, it is a topic of increasing interest to study the gas sensing properties of ferrites[4-6]. Ferrites show very good surface reactivity and they have temperature dependent surface morphologies[7].

Spinal of the type $M^{2+}M_2^{3+}O_4$ attract the research interest because of their versatile practical application [8]. Spinel ferrites with the general formula AFe_2O_4 (A = Mn, Co, Ni, Mg, or Zn) are very important magnetic materials because of their interesting magnetic and electrical properties with chemical and thermal stabilities [9]. Copper ferrite ($CuFe_2O_4$) is one of the most important ferrites. It has a cubic structure of normal spinel-type. Rezlescu et al [10] reported the high sensitivity of $CuFe_2O_4$ towards LPG, Mn substituted $CuFe_2O_4$ nanoparticles for liquefied petroleum gas sensor [11].$CuFe_2O4$ nanoparticles as a NH_3 gas sensor [12].

In the present study, Mn doped copper ferrite were synthesized by the sol-gel method and tested to sense ethanol gas .The effect of magnese concentration is studied on the sensing response of ethanol gas as compared to pure copper ferrite.

EXPERIMENTAL DETAILS

2.1. Material Synthesis

Four samples with chemical compositions as $CuFe_2O_4$, $Cu_{0.75}Mn_{0.25}Fe_2O_4$, $Cu_{0.50}Mn_{0.50}Fe_2O_4$, and $Cu_{0.25}Mn_{0.75}Fe_2O_4$ were prepared by sol-gel method. The samples are prepared using following analytically pure (AR) grade $Mn(NO_3)_2{\cdot}6H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$, and $Fe(NO_3)_3{\cdot}9H_2O$ as starting materials. Citric acid was used as chelating agent. In order to make ferrite, these reagents in desired stoichiometric ratio were mixed with citric acid in distilled water. Stirring was done on magnetic stirrer for 1 hour at 80^0C to obtain homogeneous solution. Gel was obtained by constant stirring and heating the solution at 120^0C temperature in pressure vessel. The gel was subjected to calcinations at 650^0C for 6 hours in a furnace to obtain the combusted flake form material. By grinding the flakes in mortar and pestle, powdered form of material was obtained.

2.2. Structural Characterization

Structural analysis of synthesized powdered samples was carried out using X-ray diffractometer (Philips 3710, PAN alytical) using Cu-Kα radiation with wavelength (λ = 1.5406 ˚A), and the surface morphology of the samples was investigated with a Scanning Electron Microscope (JEOL-JXA-8100 SEM). The 10mm diameter size of pellet was made using polyvinyl alcohol (PVA) as binder of each sample for ferrite powder. Two-gram powder sample was uniformly mixed with 5 wt% by weight of PVA. The mixture was pressed in a die and punch arrangement using a hand press machine. The prepared pellets were sintered at 300^0C for 3 hours to remove organic PVA. Highly conducting silver paste was applied with the help of n-butyl acetate to make the surface conductive on both sides of each pellet. A gas sensing setup was used for ethanol sensing as shown elsewhere [13]. The gas-sensing characteristics were recorded with reference to time at different operating temperatures and as a function of gas concentration. The

Sensing response was calculated using the given formula [13]:

$$S\ (\%) = [(Ra - Rg)/Ra] \times 100, \qquad (1)$$

where Ra and Rg are the resistance in the air and in the presence of tested gas, respectively.

RESULTS AND DISCUSSION

3.1 Structural analysis

The crystallographic structure of the synthesized $CuFe_2O_4$ and $Cu_{0.50}Mn_{0.50}Fe_2O_4$ nanoparticles were identified by powder X-Ray Diffraction (XRD) measurement. The powder XRD patterns of $CuFe_2O_4$ and $Cu_{0.50}Mn_{0.50}Fe_2O_4$ are presented in Fig.1. All of the main peaks are indexed as the spinel $CuFe_2O_4$ in the standard data (JCPD No: 34-0425). The average crystallite sizes of $CuFe_2O_4$ samples were calculated from X-ray line broadening of the reflections of (112), (211), (213), (105), and (400) using Scherrer's equation (i.e., D = 0.89k/(β cosθ), where k is the wavelength of the X-ray radiation, K is a constant taken as 0.89, h the diffraction angle, and b is the full width at half-maximum. The estimated crystallite size is about 20-35 nm.

The SEM technique was employed for finding morphology of $Cu_{0.50}Mn_{0.50}Fe_2O_4$ as synthesized powder, calcined at 650^0 C shown in Fig.2.

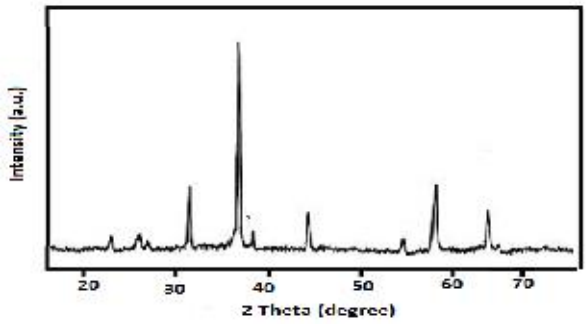

Fig 1 (A):The XRD Pattern of synthesized $CuFe_2O_4$ calcinied at 650^0C

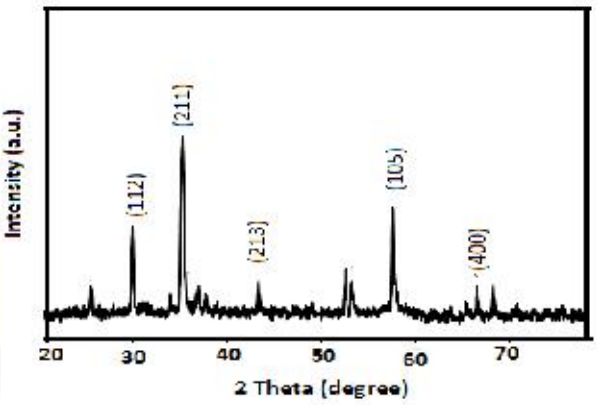

Fig 1 (B): The XRD Pattern of synthesized $Cu_{0.50}Mn_{0.50}Fe_2O_4$ calcinied at 650^0C

One can notice the presence of macro-agglomerations of very fine particles. The particle shapes are not well defined. Many large and small pores are present in the whole material. We assumed that the pores are mainly inter-granular because intra-granular pores are not seen on the SEM photograph.

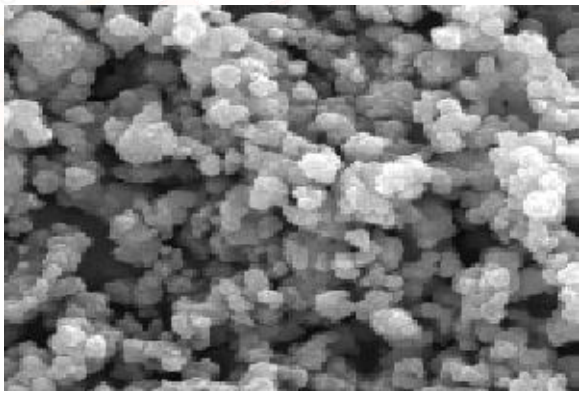

Fig 2 : The SEM Image of $Cu_{0.50}Mn_{0.50}Fe_2O_4$ nanoparticles calcined at 650^0C

3.2. Gas sensing characteristics: Fig. 3 shows the sensitivity of $CuFe_2O_4$ to 200 ppm of ethanol gas as a function of working temperature. As evident, the sensitivity increases with the temperature and reaches a maximum value in an operating temperature 250^0C. If the

temperature increases again, the sensitivity decreases. This behavior can be explained in analogy with the mechanism of gas adsorption and desorption.

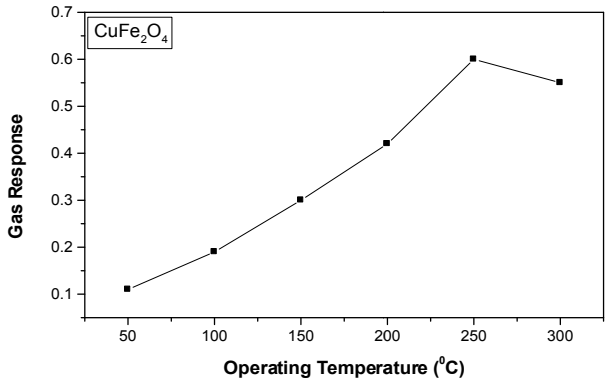

Fig3 : Sensitivity of $CuFe_2O_4$ to 200 ppm of ethanol gas as a function of working temperature.

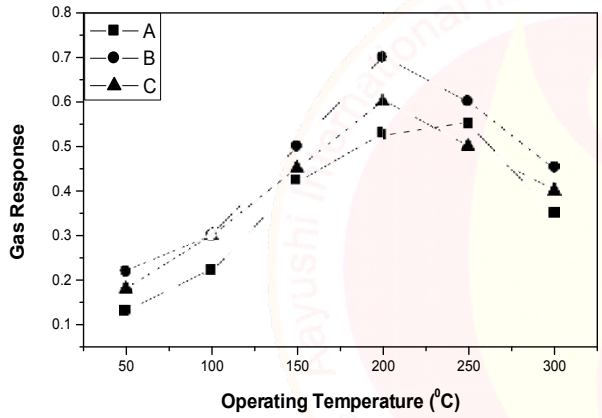

Fig 4: Gas sensitivity of (A) $Cu_{0.75}Mn_{0.25}Fe_2O_4$, (B)$Cu_{0.50}Mn_{0.50}Fe_2O_4$ and (C)$Cu_{0.25}Mn_{0.75}Fe_2O_4$ for 200 ppm ethanol gas

The Gas sensitivity of $Cu_{0.75}Mn_{0.25}Fe_2O_4$, $Cu_{0.50}Mn_{0.50}Fe_2O_4$, and $Cu_{0.25}Mn_{0.75}Fe_2O_4$ as a function of operating temperature range 50 to 300^0C for 200 ppm ethanol gas is displayed in Fig. 4. It is clear from the figure that for $Cu_{0.50}Mn_{0.50}Fe_2O_4$, the gas response increases with operating temperature reaches to the maximum at an operating temperature180 ^{0}C, and falls with further increasing the in operating temperature. The ethanol may burn before reaching the surface of the film at higher temperatures. Hence, the gas response would have been decreased above 180^0C. A larger amount of oxygen-adsorption would have occurred on the surface of the film at 180^0C and have facilitated the sensor to oxidize the ethanol gas immediately, giving faster and larger gas response. Other samples $Cu_{0.75}Mn_{0.25}Fe_2O_4$ and $Cu_{0.25}Mn_{0.75}Fe_2O_4$ shows lower ethanol gas response as compare to $Cu_{0.50}Mn_{0.50}Fe_2O_4$.

Fig. 5 shows the selectivity of $Cu_{0.50}Mn_{0.50}Fe_2O_4$ to 300 ppm of ethanol gas against various gases like NH_3, LPG, H_2S and CO at 180 ^{0}C. It is clear from Figure that, in contrast to pure CuFeO3; the sample shows not only enhanced response towards ethanol but also very high selectivity.

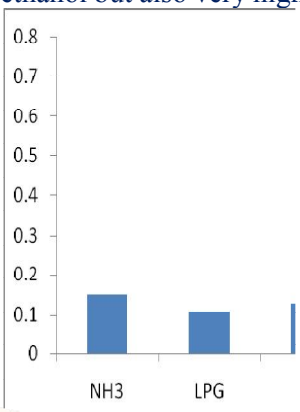

Fig.5: Selectivity of $Cu_{0.50}Mn_{0.50}Fe_2O_4$ for different reducing gases.

Fig. 6 represents the variation of ethanol gas response with the gas concentration of $Cu_{0.50}Mn_{0.50}Fe_2O_4$. For sample $Cu_{0.50}Mn_{0.50}Fe_2O_4$, the response values were observed to increase continuously with increasing the gas concentration up to 200 ppm at 180^0C. The rate of increase in response was relatively larger up to 200 ppm, and then saturated after 200 ppm. Thus, the active region of the sensor would be from 200 ppm.

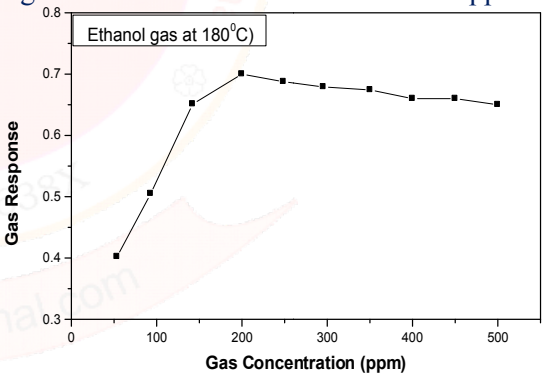

Fig 6: The variation of ethanol gas response with the gas concentration of $Cu_{0.50}Mn_{0.50}Fe_2O_4$

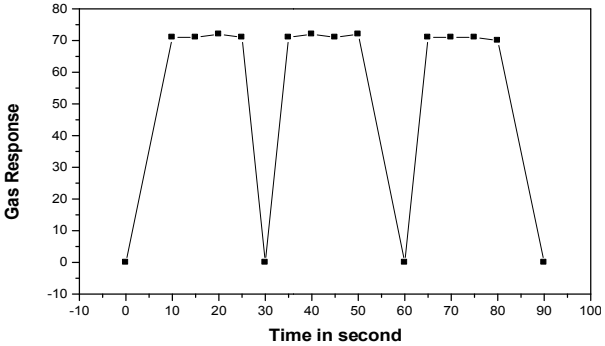

Fig7: Response and recovery time of $Cu_{0.50}Mn_{0.50}Fe_2O_4$

The response and recovery of the $Cu_{0.50}Mn_{0.50}Fe_2O_4$ sensor are represented in Fig. 7. The response was quick (~5 s) to 300 ppm of ethanol. Recovery was also very fast (~35 s). The fast response may be due to the fast oxidation of ethanol into H_2O (gas).

CONCLUSIONS

Mn doped $CuFe_2O_4$ thick films were prepared by a sol-gel technique which is a simple and in expensive method. The XRD patterns also show high degree of crystallinity and complete phase formation with grain size of about ~20–35 nm. SEM images exhibit the porous nature of the sensing material with a number of active sites.

From the results obtained, pure $CuFe_2O_4$ showed low response to Ethanol gas. Mn doped $CuFe_2O_4$ thick films were found to be sensitive for Ethanol gas. Among all other additives $Cu_{0.50}Mn_{0.50}Fe_2O_4$ thick film was found to be optimum and showed highest response to ethanol gas at 180 ^{0}C. The $Cu_{0.50}Mn_{0.50}Fe_2O_4$ thick films sensor has good selectivity to ethanol gas against LPG, NH_3, H_2S & CO at 180 ^{0}C.

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SYNTHESIS AND CHARACTERIZATION OF (2E)-1-(PIPERAZIN-1-YL)-3-SUBSTITUTED PHENYLPROP-2-ONE CINNAMAMIDES

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ABSTRACT

Cinnamamides and their derivatives have a great era of its applications in medicinal as well as pharmaceutical fields. Several cinnamamides were isolated from plants and many of them are prepared in laboratory by different routes. In the present study different cinnamamides were synthesized by convenient witting reaction pathway from Wittig reagent with piperazine heterocyclic moiety and different aromatic aldehydes. All the synthesized compounds were characterized by using IR, ^{1}H-NMR, ^{13}C-NMR and Mass spectral analysis.

Keywords: *Piperazine, aromatic aldehydes, Cinnamamides.*

INTRODUCTION

Several cinnamamides and its derivatives were reported to shows variety of applications in different fields, such as medicinal, pharmaceuticals[1], agricultural and many other fields. Cinnamamides possess broad spectrum of physiological function and biological activities[2] and reported as Sedatives, nervous central system depressant[3], anticonvulsant, muscle relaxant, antiallergic, antioxidant[4], Local anesthetic[5], Antimycobacterial[6], Cytotoxicity[7] and Antioxidant[8]. The *N*-Feruloyl piperazine derivatives showed cytotoxic activity towards cancer cells and they have significant DNA binding activity[9]. In agrochemical field, their avian repellent[10], Antifungicidal, insecticidal and herbicidal activities[11]. This literature survey encourages the author to undertake the present research work and the Wittig reaction is an important method for the synthesis of cimamamides. In the present study, the attempts were made to synthesize the series of (2E)-1-(peperazin-1-yl)-3-substituted phenylprop-2-en-1-one Cinnamamides from Wittig reagent with piperazine moiety**.** Synthesized compounds were characterized by elemental analysis and spectral studies.

MATERIAL AND METHOD

Synthesis of Wittig reagent containing piperazine moiety-

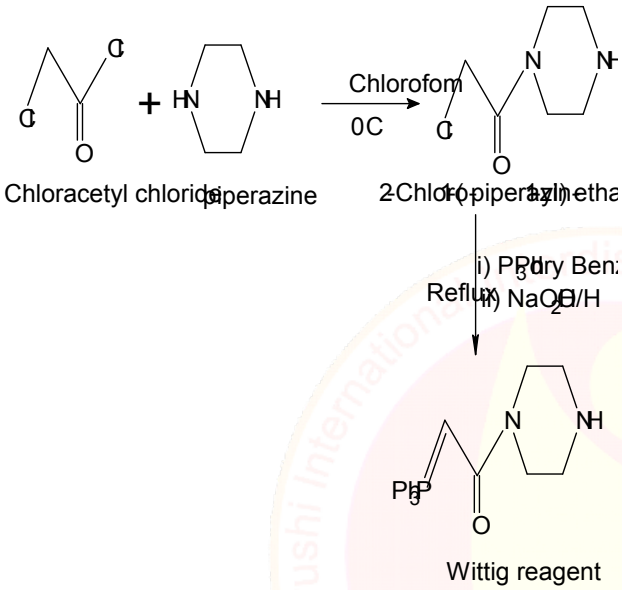
Piperazine chloracetamide were synthesized by using equimolar solution of chloro-acetylchloride and piperazine in chloroform at 0^{o}C with continuous stirring in fuming chamber. When this reaction mixture gives the salt by adding its solution in benzene to the stirred solution of triphenylphosphine and reaction mixture was refluxed for 4-6 hrs. The solid products obtained were filtered and air dried. Thus for Purification obtained salt was dissolved in 100 ml water then 90 ml of dry benzene, add 1-2 drops of phenolphthalein indicator and add NaOH solution in it till pink colour persist this was indicates that the neutralization of present acid from reagent. Then benzene layer was separated and washed with water and concentrated to one third volume. Finally the product scratched with n-Hexane to obtain solid Wittig reagent.

Synthesis of (2E)-1-(peperazin-1-yl)-3-Substituted phenylprop-2-en-1-one cinnamamides –

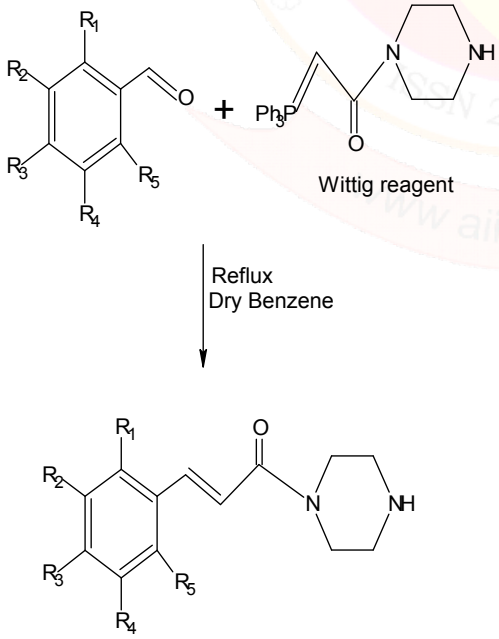
Equimolar solution of Wittig reagent and different aromatic aldehydes were taken in dry benzene and refluxed for 4 to 6 hrs. The progress of reaction was monitored by thin layer chromatography. Melting points were taken by open capillary method. The elemental analysis was calculated for

carbon, hydrogen, nitrogen and chlorine. All Synthesized compounds were purified by coloum chromatography. Obtained compounds were characterized by elemental analysis and spectral studies. All chemicals used were of analytical grade.

Scheme-1



Scheme-2



(2E)-1-(piperazin-1-yl)-3-subtituted phenylprop-2-en-1-one cinnamamides

Spectral Data Studies:-

Ia=(2E)-1-(peperazin-1-yl)-3- phenylprop-2-en-1-one Cinnamamides

^{1}H NMR (300 MHz, CDCl3) δ: 3.62-3.84 m 8H, 6.68 d (*J*= 15.2 Hz) 1H, 6.92d (*J*= 15.2 Hz) 1H, 7.36-7.56m 6H. **^{13}C NMR** (75 MHz, CDCl3) δ: 175, 136, 139, 130, 129, 128, 126, 122, 52, 48; **IR** (KBr, cm-1) :-3040, 1690, 1610; **MS** (ESI): 216.13(M^+). **Ib**=(E)-3-(*p*-Methoxyphenyl)-1-(1-piperazinyl)-2-propen-1-one Cinnamamide

^{1}H NMR-(δ):-3.81(s), (3H); 6.9d, (2H); 7.4d, (2H); 6.7(d), (1H), (CH=CHCO), J=15.8HZ; 7.6d, (1H), (CH=CHC$_6$H$_5$) J=15.8HZ; 7.2(d), (2H); 7.4(d), (2H). **^{13}C NMR** (δ ppm):166, 159, 136, 128, 114, 114, 55, 45. **IR (cm^{-1}):** 3070, 2925, 1475; **MS** (ESI): 246.14 (M^+).

Table-1:-Substituted aromatic aldehydes used in the synthesis of Cinnamamides

Sr. No	Entries	R1	R2	R3	R4	R5
1	**Ia**	H	H	H	H	H
2	**Ib**	H	H	OMe	H	H
3	**Ic**	H	OMe	OMe	H	H
4	**Id**	H	OMe	OMe	OMe	H
5	**Ie**	H	-O-CH$_2$-O-		H	H
6	**If**	NO_2	H	H	H	H
7	**Ig**	H	H	Cl	H	H
8	**Ih**	H	H	NO_2	H	H
9	**Ii**	H	H	$N(Me)_2$	H	H
10	**Ij**	H	H	OH	H	H

Table-2:- Characteristics data for synthesized Cinnamamides

Sr. No.	Entries	Molecular Formula	Molecular weight	Yield %	M.P. ^{0}C
1	**Ia**	$C_{13}H_{16}N_2O$	216	72	90
2	**Ib**	$C_{14}H_{18}N_2O_2$	246	84	136
3	**Ic**	$C_{15}H_{20}N_2O_3$	276	82	181
4	**Id**	$C_{16}H_{22}N_2O_4$	306	74	229
5	**Ie**	$C_{14}H_{16}N_2O_3$	260	70	201
6	**If**	$C_{13}H_{15}N_3O_3$	261	68	248
7	**Ig**	C_{13}H15ClN_2O	251	62	132
8	**Ih**	$C_{13}H_{15}N_3O_3$	261	71	226
9	**Ii**	$C_{15}H_{21}N_3O$	259	74	158
10	**Ij**	$C_{13}H_{16}N_2O_2$	232	80	274

Table-3:- Elemental Analysis of synthesized Cinnamamides

Sr. No.	Entries	Mol. Formula	Analysis (%) Found (Calculated)				
			% C	% H	% O	% N	% Cl
1	Ia	$C_{13}H_{16}N_2O$	72.19 (72.22)	7.46 (7.40)	7.40 (7.40)	12.95 (12.96)	--
2	Ib	$C_{14}H_{18}N_2O_2$	68.27 (68.29)	7.37 (7.32)	12.99 (13.00)	11.37 (11.38)	--
3	Ic	$C_{15}H_{20}N_2O_3$	65.27 (65.22)	7.30 (7.25)	17.37 (17.39)	10.14 (10.14)	--
4	Id	$C_{16}H_{22}N_2O_4$	62.73 (62.75)	7.24 (7.19)	20.89 (20.92)	9.14 (9.15)	--
5	Ie	$C_{14}H_{16}N_2O_3$	64.60 (64.62)	6.20 (6.15)	18.44 (18.46)	10.76 (10.77)	--
6	If	$C_{13}H_{15}N_3O_3$	59.76 (59.77)	5.79 (5.75)	18.37 (18.39)	16.08 (16.09)	--
7	Ig	$C_{13}H15ClN_2O$	62.28 (62.28)	6.03 (5.99)	6.38 (6.39)	11.17 (11.18)	14.14 (14.17)
8	Ih	$C_{13}H_{15}N_3O_3$	59.76 (59.77)	5.79 (5.75)	18.37 (18.39)	16.08 (16.09)	--
9	Ii	$C_{15}H_{21}N_3O$	69.47 (69.50)	8.16 (8.11)	6.17 (6.18)	16.20 (16.22)	--
10	Ij	$C_{13}H_{16}N_2O_2$	67.22 (67.24)	6.94 (6.90)	13.78 (13.79)	12.06 (12.07)	--

RESULT AND DISCUSSION

All synthesized novel cinnamamides compounds contained heterocyclic moiety in the form of Piperazine. The Wittig reaction is an important method for the synthesis of alkenes. By using this method novel cinnamamides containing heterocyclic moiety entitled (2E)-1-(Piperazin-1-yl)-3-substituted phenylprop-2-en-1-one Cinnamamides are synthesized from different aromatic aldehydes and Wittig reagents having good yields. The yields of synthesized compounds were ranging from 62 to 84%. All synthesized compounds were characterized on the basis of melting point, elemental analysis, IR spectra, ^{1}HNMR, ^{13}CNMR and mass spectral analysis.

CONCLUSION

The objective of the present study was to synthesize the novel cinnamamides containing heterocyclic moiety piperazine by using Wittig reagent and different aromatic aldehydes in dry benzene viz. Wittig reaction. The results of synthesized compounds were ranging from 62 to 84%. On the basis of melting point, elemental analysis, IR spectra, ^{1}HNMR, ^{13}CNMR and mass spectral analysis the characterization and yield of synthesized compounds, it was proved that given method is very good for synthesis of heterocyclic Cinnamamides.

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SYNTHESIS AND BIOLOGICAL EVALUATION OF 1,3,4-THIADIAZOLE DERIVATIVES

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ABSTRACT

In the present work, an eco-friendly method has been developed to synthesize 1,3,4-thiadiazole followed by synthesis of a their respective Schiff's bases. The process is economically feasible, eco-benign(solvent-free) and gives moderate to excellent yields. On the basis of qualitative elemental analysis along with spectral and chromatography(TLC) analyses, the structures of the novel compounds have been established. The products were analysed for biological efficacyagainst Escherichia coli and Staphylococcus aureus. The present work suggests that the synthetic procedure is very convenient for the large- scale and commercial preparation of 1,3,4-thiadiazole derivatives.

Keyword : *1,3,4-thiadiazole, Schiff's bases, Green chemistry*

INTRODUCTION

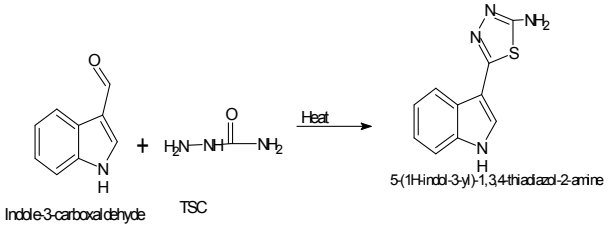
The heterocycles are important and broad class of organic chemistry. These are cyclic compounds (aliphatic or aromatic) having at least one heteroatom and are also called as heterocyclic compounds. Heterocycles are very important in biological activity and in industries [1]. One such important heterocyclic ring is 1,3,4-thiadiazole. It is a 5-membered heterocyclic ring in which nitrogens are at 3rd & 4th position and the sulphur is at 1st position.The general structure of 1,3,4-thiadiazole is shown below:

1,3,4-thiadiazole and its derivatives are widely applied in medicine and agriculture as pesticides. Many derivatives have biological activity, antibacterial, antifungal, tuberculostatic, anti-inflammatory, analgesic, anticancer etc [2-12].Literature reveals that attempt to synthesize the 5-[4-(benzyloxy)phenyl]-1,3,4-thiadiazole-2-amine and its derivatives at room temperature is very difficult. Many methods have been proposed and are effective to synthesize the molecule 1,3,4-thiadiazole with moderate to good yield but are associated with many disadvantages, such as high reaction temperature, prolong reaction time, drastic conditions and use of toxic solvents. Several researchers have executed for the one-step synthesis of 5-[4-9(benzyloxy)phenyl]-1,3,4-thiadiazole-e-amine & its derivatives most of the methods include the use of hazardous & expensive reagents, longer reaction time, extreme drastic reaction conditions & tedious work-up procedures [2-12].

In the present work, we have made an attempt to synthesize the aromatic derivatives of 1,3,4-thiadiazole from aromatic acid using a simple yet very effective one step cyclization reaction. The main emphasis is to develop a green method involving minimum use of toxic chemicals, fuel and solvents.

EXPERIMENTAL METHODOLOGY

In experimental study the melting point were taken in capillary tube at a room temperature and are incorrected. All derivatives were recrystallized and the purity of derivatives confirmed by TLC (solvent system of Glacial acetic acid and Ethylacetate 1:1 ratio using iodine as a visualizing agent). FT-IR (SHIMADAZU) for FT-IR analysis.
Preparation of indole based 1,3,4-thiadiazole: In a 100 ml round bottom flask, a mixture of indole-3-carboxyaldehyde and TSC along with $POCl_3$ as cyclising agent was taken, The mixture was heated for 1 hours at above 100°C. The mixture was cooled and was added into ice cold water followed by addition of dil. NaOH .The solid product was filtered and dried.



It was recrystallized using ethanol. The melting point of crystallized product was determined. Melting Point 145°C.

RESULT & DISCUSSION

THIN LAYER CHROMATOGRAPHY

The development of only single spot on TLC plate confirmed the purity of the product. The high R_f value of the product (0.91) and the high polarity of developing solvent indicates that the product is also highly polar.

ULTRAVIOLET-VISIBLE SPECTROSCOPY

The UV spectrum contains sharps peaks around 300nm. This indicates that the molecule possesses aromatic ring. The sharp peaks are many in number, their by indicating n → π, π→ π* and π→σ*. Hence the molecule possesses many π electron system.

INFRARED SPECTROSCOPY

The FT-IR revealed many peaks of high importance. The peaks have been discussed as following (all values in cm^{-1}): The peaks at 874 and 835 indicate the presence of aromatic ring.The peak at 938 indicate substitute aromatic ring.The peaks at 1612 and 1539 indicate presence of carbon attached to nitrogen, probably as C=N.The peaks at 1432 and 1365 indicate presence of aromatic C=C stretch. The peak at 3042 suggests the presence of aromatic C-H stretch.The peaks at 3143 and 3220 indicate $–NH_2$stretch.The position indicate the $–NH_2$ group is attached to aromatic ring.

BIOLOGICAL EVALUATION

The newly synthesized compounds were screened for activity against *E. Coli* and *S. aureus*, but none of the compound is found to have any significant activity. Hence, future modifications are necessary to achieve better activity profile.

CONCLUSION

The TLC, UV-visible and IR spectra analyses show that the purity of product was quite high. The sharp melting point of 145°C further strengthens the quality. The yield of the product is high(80%) indicating the high scale up ability of the synthesis method. The product was contamination-free. No Solvent was used and hence side reaction could not occur. Thereby, the procedure adopted is as per the green chemistry principle.

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SYNTHESIS AND CHARACTERIZATION OF SCHIFF'S BASE AMALGAMATED WITH 1,3,4-THIADIAZOLES

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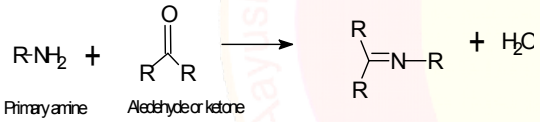
ABSTRACT

In the present work, a green chemistry protocol has been extended to prepare 1,3,4, thiadiazoles, followed bythepreparation of a good number of Schiff's bases. The method is highly efficient, solvent-free and provided good to excellent yields. The structures of the newly synthesized compound were established on the basis of qualitative elements analysis along with spectral analysis. The compound was screened for biological evolution viz. E.coliandS.aureus. The present work indicates that the synthetic protocol is highly useful for large scale and profitable preparation of 1,3,4, thiadiazoles derivatives.

Keywords: *1,3,4,thiadiazoles, Green chemistry, Schiff's bases*

INTRODUCTION

A Schiff's base is a nitrogen analogue of an aldehyde or Ketone in which the C=O group is replaced by C=N-R group [1-5]. It is usually formed by condensation of an aldehyde or Ketone with a primary amine according to the following scheme.

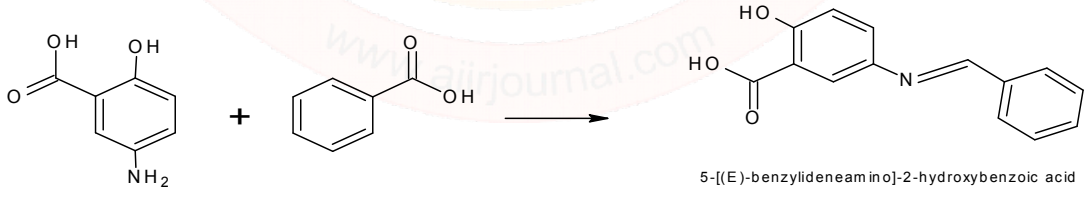


Where R may be an alkyl or an aryl group.Schiff's base that contain aryl substituent are substantiallymore stable and more readily unstable. Schiff's bases of aliphatic aldehyde are relatively unstable and readily polymerizable while those of aromatic aldehyde having effective conjugation are more stable [6-17].

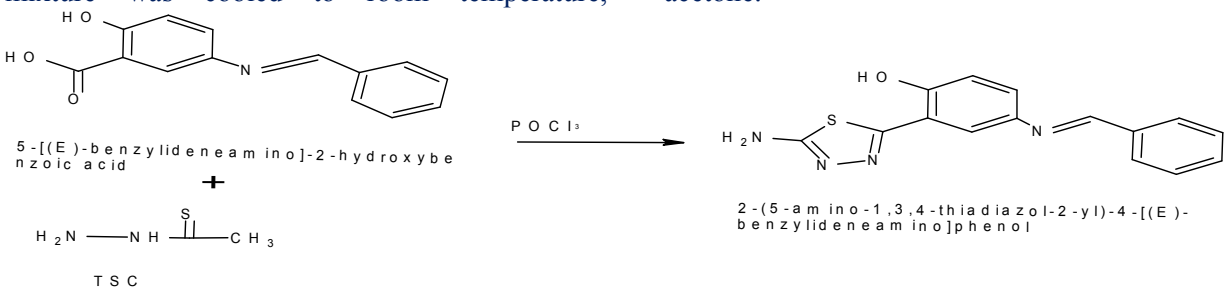
EXPERIMENTAL SECTION

In experimental study the melting point were taken in capillary tube at a room temperature and are incorrected. All derivatives are pure by crystallization process and the purity of derivatives confirmed by TLC (solvent system of Glacial acetic acid and Ethylacetate 1:1 ratio using iodine as a visualizing agent). FT-IR (SHIMADAZU) for FT-IR analysis.

1) Synthesis of ATBAP A mixture of 5-amino salicylic acid, benzaldehyde and glacial acetic acid in a R.B. flask was refluxed for one hour. The content was cooled to room temperature and pour in ice-cold water to get solid product. Recrystallized through ethanol to get pure product.

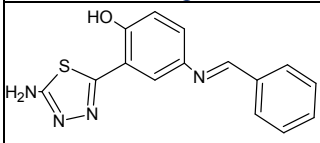
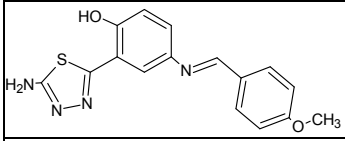
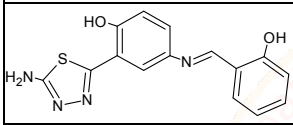
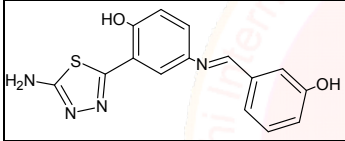
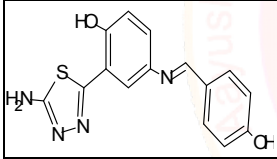
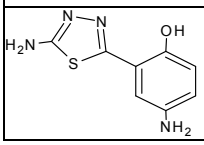


A mixture of Schiff base (ATBAP), TSC and POCl3was refluxed for good time. The reaction mixture was cooled to room temperature, decomposed with ice- cold water to get precipitate of ATBAP. It was dried and recrystallized from acetone.



ELEMENTAL AND FUNCTIONAL GROUP ANALYSIS

The newly synthesised compounds gave satisfactory tests for qualitative elemental analysis for N, S and halogens. Further, investigations revealed the presence of phenolic –OH group (FeCl3 test). The results of elemental analysis, percentage yield and M.P. have been summarized in the following table.

Structure of compound	Molecular formula	% C	% H	% N	% S	%Yield	λmax (nm)
	C15H12N4OS	54.90	4.61	9.15	5.75	65%	--
	C16H15N4O2S	59.61	4.8	11.21	5.13	51%	--
	C15H12N4O2S	58.38	4.39	11.74	5.37	63%	210 & 305
	C15H12N4O2S	59.49	4.57	11.77	5.38	58%	--
	C15H12N4O2S	58.28	4.55	11.72	5.37	67%	220 & 310
	C8H8N4OS	42.47	4.45	24.76	14.17	61%	220 & 300

RESULT AND DISCUSSION

In the present work, various derivative of Schiff's base were synthesized using different starting materials, which are relatively cheap and non hazardous. Aromatic aldehydes with diverse substituent at different position gave moderate to excellent yield especially when the substituent is electron donating group. The o, m, p -hydroxy benzaldehyde gave excellent yield. Thus, the position of –OH group does not influence the yield of final Schiff's base.The method has addition advantage of easy workup, and the compound is obtained with high purity without any tedious separation or work up procedure.

BIOLOGICAL EVALUATION

The newly synthesized compounds were screened for activity against *E. Coli* and *S. aureus*, but none of the compound is found to have any significant activity. Hence, future modifications are necessary to achieve better activity profile.

CONCLUSIONS

The present work involves a solvent-less green chemistry approach for the synthesis of Schiff's bases of substituted 1,3,4-thiadiazole. The protocol is successful with high yield and provides very easy work-up procedure. Future modifications are desired for better biochemical profile.

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SYNTHESIS APPORACH TO BENZIMIDAZOLE FROM O-PHENYLENE DIAMINE BY USING HCl/H_2O_2

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ABSTRACT

It was thought interesting to synthesize benzimidazole. A simple and efficient procedure for the synthesis of substituted benzimidazole through a one-pot condensation of o-phenylene diamines with aryl aldehyde in the presence of H_2O_2 / HCl system in 1,4 Dioxane on magnetic stirrer at room temperature is describe, short reaction time, It gives large scale of synthesis, easy and fast isolation of the products and excellent yield are the advantage of this procedure Benzimidazole nucleus play a very important role as a therapeutic agent. e.g antiulcer and anthemintic drug. Other side benzimidazole derivatives exhibits pharmacological activities such as antimicrobial, antiviral, anticancer, anti-inflammatory and analgesic.

Keywords: *ortho-phenylene diamine, aryl aldehyde, hydrogen peroxide, benzimidazole,*

MATERIALS & METHODS

- ortho-phenylene-diamine
- HCl/H_2O_2
- Aldehyde(Cinnamaldehyde,4-Hydroxyaldehyde,m-nitrobenzaldehyde,2-Hydroxyaldehyde,Anisaldehyde)

S d fine, merk and loba companies' chemicals are used in the synthesis of Benzimidazole.

INTRODUCTION

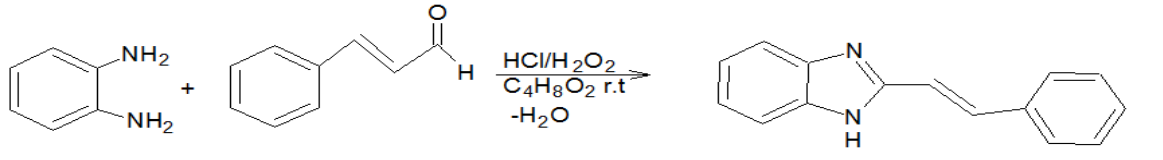
As heterocyclic compound has great importance organic chemistry & they under investigation by no.of chemist hence synthesis of benzimidazole by using o-phenylenediamine in presence of HCl/H_2O_2 by simple economic stirring method. This method of synthesis of benzimidazole gives high yield & atom economy too. Thus, this method is good replacement to other synthesis of benzimidazole.Benzimidazole compound is very useful to in sence of that they are used in various field & synthesis of benzimidazole derivatives by green approach plays a vital role in organic chemistry. The synthetic routes which furnished the target compounds are shown below along with their IR and NMR data.

EXPRRIMENTAL WORK

Synthesis of 2-[(E)-2-phenylethenyl]-1H-benz imidazole

In a round-bottomed flask (50 mL) equipped with a magnetic stirrer, a solution of o-phenylene-diamine (1.0 mmol), and cinnam-aldehyde (1.0 mmol) in MeCN (15 mL) was prepared. Aq 30% H_2O_2 (7.0 mmol) and aq 37% HCl (3.5 mmol) were added and the mixture was stirred at r.t. for the time indicated in the table. The progress of the reaction was monitored by TLC (eluent: n-hexane–EtOAc, 7:3). When the starting materials had completely disappeared, the mixture was quenched by adding H_2O (10 mL), extracted with EtOAc (4 × 10 ml), and the combined extracts were dried (MgSO4). The filtrate was evaporated and the corresponding benzimidazole was obtained as the only product (Table 1). An identical procedure was employed using o-phenylenediamine (2.0 mmol) and terephthal-aldehyde (134.1 mg, 1.0 mmol) in the presence of aq 30% H_2O_2 (7.0 mmol) and aq 37% Hcl (3.5 mmol) for the synthesis of bis-benzimidazoles.

REACTION

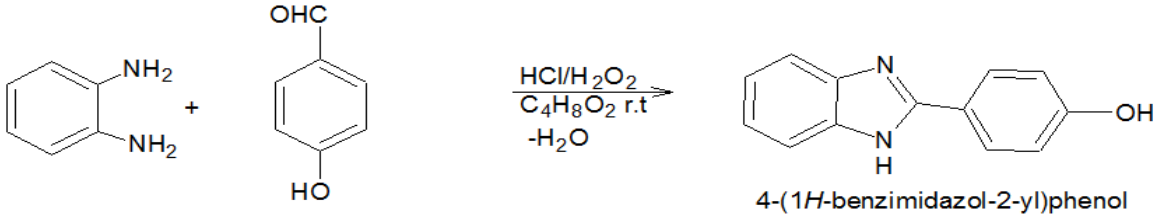


2-[(*E*)-2-phenylethenyl]-1*H*-benzimidazole

Synthesis of 4-(1H-benzimidazole-2-yl) phenol

In a round-bottomed flask (50 mL) equipped with a magnetic stirrer, a solution of o-phenylene-diamine (1.0 mmol), and 4-hydroxy-benzaldehyde (1.0 mmol) in MeCN (15 ml) was prepared. Aq 30% H_2O_2 (7.0 mmol) and aq 37% HCl (3.5 mmol) were added and the mixture was stirred at r.t. for the time indicated in Table 1. The progress of the reaction was monitored by TLC (eluent: n-hexane–EtOAc, 7:3). When the starting materials had completely disappeared, the mixture was quenched by adding H2O (10 mL), extracted with EtOAc(4 × 10 mL), and the combined extracts were dried (MgSO4). The filtrate was evaporated and the corresponding benzimidazole was obtained as the only product (Table 1). An identical procedure was employed using o-phenylenediamine (2.0 mmol) and terephthalaldehyde (134.1 mg, 1.0 mmol) in the presence of aq 30% H_2O_2 (7.0 mmol) and aq 37% HCl (3.5 mmol) for the synthesis of bis-benzimidazoles.

REACTION

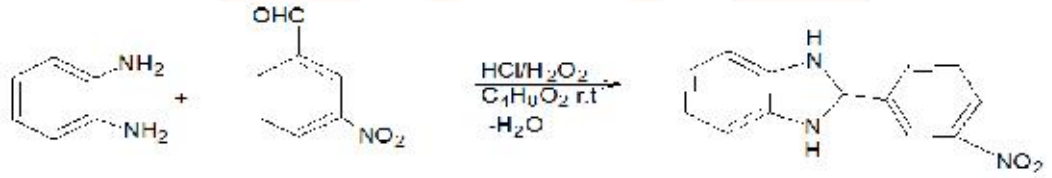


4-(1*H*-benzimidazol-2-yl)phenol

Synyhesis of 2-(3-nitrophenyl)-2,3-dihydro-1H-benzimidazole

In a round-bottomed flask (50 mL) equipped with a magnetic stirrer, a solution of o-phenylene-diamine (1.0 mmol), and meta -nitro benzaldehyde(1.0 mmol) in MeCN (15 mL) was prepared. Aq 30% H_2O_2 (7.0 mmol) and aq 37% HCl (3.5 mmol) were added and the mixture was stirred at r.t. for the time indicated in Table 1. The progress of the reaction was monitored by TLC (eluent: n-hexane–EtOAc, 7:3). When the starting materials had completely disappeared, the mixture was quenched by adding H2O (10 mL), extracted with EtOAc (4 × 10 mL), and the combined extracts were dried (MgSO4). The filtrate was evaporated and the corresponding benzimidazole was obtained as the only product (Table 1). An identical procedure was employed using o-phenylenediamine (2.0 mmol) and terephthalaldehyde (134.1 mg, 1.0 mmol) in the presence of aq 30% H_2O_2 (7.0 mmol) and aq 37% HCl (3.5 mmol) for the synthesis of bis-benzimidazoles.

REACTION

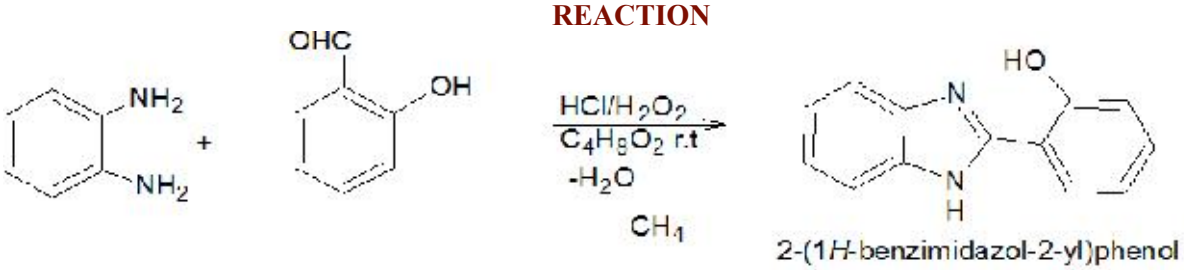


2-(3-nitrophenyl)-2,3-dihydro-1*H*-benzimidazole

Synthesis of 2-(1H-benzimidazole-2-yl)phenol

In a round-bottomed flask (50 mL) equipped with a magnetic stirrer, a solution of o-phenylene-diamine (1.0 mmol), and 2-hydroxy benzaldehyde (1.0 mmol) in MeCN (15 mL) was prepared. Aq 30% H_2O_2 (7.0 mmol) and aq 37% HCl (3.5 mmol) were added and the mixture was stirred at r.t. for the time indicated in Table 1. The progress of the reaction was monitored by TLC (eluent: n-hexane–EtOAc, 7:3). When the starting materials had completely disappeared, the mixture was quenched by adding H2O (10 mL), extracted with EtOAc (4 × 10 mL), and the combined extracts were dried (MgSO4). The filtrate was evaporated and the corresponding benzimidazole was obtained as the only product (Table 1). An identical procedure was employed using o-phenylenediamine (2.0 mmol) and terephthalaldehyde (134.1 mg, 1.0 mmol) in the presence of aq 30% H2O2 (7.0 mmol) and aq 37% HCl (3.5 mmol) for the synthesis of bis-benzimidazoles.

REACTION

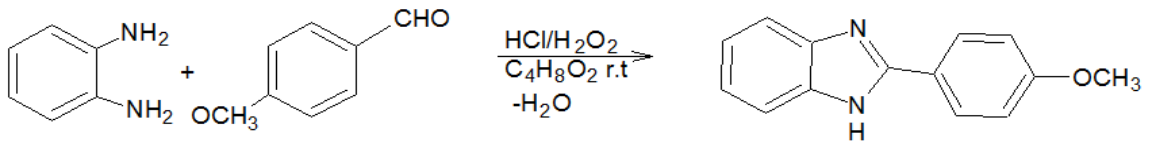


2-(1*H*-benzimidazol-2-yl)phenol

Synthesis of 2-(4-methoxyphenyl)-1H-benz-imidazole

In a round-bottomed flask (50 mL) equipped with a magnetic stirrer, a solution of o-phenylenediamine (1.0 mmol), and Annisaldehyde (1.0 mmol) in MeCN (15 mL) was prepared. Aq 30% H_2O_2 (7.0 mmol) and aq 37% Hcl (3.5 mmol) were added and the mixture was stirred at r.t. for the time indicated in Table 1. The progress of the reaction was monitored by TLC (eluent: n-hexane–EtOAc, 7:3). When the starting materials had completely disappeared, the mixture was quenched by adding H2O (10 mL), extracted with EtOAc (4 × 10 mL), and the combined extracts were dried (MgSO4). The filtrate was evaporated and the corresponding benzimidazole was obtained as the only product (Table 1). An identical procedure was employed using o-phenylenediamine (2.0 mmol) and terephthalaldehyde (134.1 mg, 1.0 mmol) in the presence of aq 30% H2O2 (7.0 mmol) and aq 37% HCl (3.5 mmol) for the synthesis of bis-benzimidazoles.

REACTION



2-(4-methoxyphenyl)-1*H*-benzimidazole

EXPERIMENTAL

Physical characterization data of all the compounds are given in Table-1.

TABLE-1 CHARACTERIZATION DATA OF NEWLY SYNTHESIZED COMPOUNDS ANALYTICAL DATA

SN	COMPOUND	TIME	M.P	% YEILD
1.	Synthesis of 2-[(E)-2-phenylethenyl]-1H-benzimidazole	30 MIN	120 ^{0}C	90%
2.	Synthesis of 4-(1H-benzimidazole-2-yl)phenol	30 MIN	140^{0}C	87%
3.	Synyhesis of 2-(3-nitrophenyl)-2,3-dihydro-1H-benzimidazole	30 MIN	180^{0}C	89%
4.	Synthesis of 2-(1H-benzimidazole-2-yl)phenol	30 MIN	150^{0}C	85%
5.	Synthesis of 2-(4-methoxyphenyl)-1H-benzimidazole	30 MIN	180^{0}C	90%

RESULT & DISCUSSION

- **Synthesis of 2-[(E)-2-phenylethenyl]-1H-benzimidazole**
- NMR : : δ7.3 (d,-Ar- C-H) , δ6.72(m,-C=C-H), δ2.53(s,C-N),
- IR (KBr ν_{max}) (cm^{-1}) 3296 cm^{-1} (O-H w), 3026cm^{-1} (C=C w), 1629cm^{-1} (C-H w), 1309 cm^{-1} (C-N). 1450cm^{-1} (C=N w.), 1219cm^{-1} (C-O strt.)
- **Synthesis of 4-(1H-benzimidazole-2-yl)phenol**
- NMR : : δ6.55 (Ar- O-H) , δ7.3(Ar-H), δ2.53(s,C-N), δ6.72(m,-C=C-H)
- IR (KBr ν_{max})(cm^{-1}) 3360cm^{-1}(O-H w),3194cm^{-1} (C-N),,1606cm^{-1}(C=C w.).1421cm^{-1}(C=N w.),

- **Synyhesis of 2-(3-nitrophenyl)-2,3-dihydro-1H-benzimidazol**
- IR(KBr ν_{max})(cm^{-1}) ,.3450 cm^{-1}(N-H)1560cm^{-1}(C=N w.), 3340cm^{-1}(C-H srt.) 1321cm^{-1} (NO_2), 1072cm^{-1} (C-N).
- **Synthesis of 2-(1H-benzimidazole-2-yl)phenol**
  IR(KBr ν_{max})(cm^{-1}) 3348cm^{-1}(O-H w),,3340cm^{-1}(N-H w),1635cm^{-1}(C=C w.).1321cm^{-1}(C-H w.), 1070cm^{-1}(C-N.)

Synthesis of 2-(4-methoxyphenyl)-1H-benzimidazole

IR(KBr ν_{max})(cm^{-1}) 3317cm^{-1}(N-H w),,2912cm^{-1}(C-H w),1502cm^{-1}(C=C w.).1011cm^{-1}(C=N w.), 1022cm^{-1}(O-CH3 srt.)

CONCLUSION

In conclusion a mild & method has been developed for synthesis of imidazole derivatives with the catalyst is effective and this method of synthesis gives high yield and atom economy too. By simple method of of stirring without expensive reagent, very short reaction period without harsh reaction condition. Thus this method can be used as alternative to other existing methodologies.

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ASSESSMENT OF WATER QUALITY OF RIVER WAINGANGA IN WINTER SEASON FROM GOSEKHURD DAM TO PAUNI TOWN

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ABSTRACT

The water quality of river Wainganga was analysed in winter season to access its suitability for domestic and agricultural purposes. Water samples were collected from the different locations of river during winter season of year 2016 from Gosekhurd dam to Pauni town. The water quality parameters were analyzed using standard methods. The observed values of different physicochemical parameters like pH, total alkalinity, electrical conductivity, total dissolved solids, dissolved oxygen, chemical oxygen demand, biological oxygen demand and total hardness was compared with standard values recommended by WHO. Mean, standard deviation and variance were calculated for different parameters for checking their significance. The maximum parameters are found within the highest desirable limit of WHO. Study indicates that the river stretch was nonpolluted.

Keywords: *Wainganga river, Water quality, Bhandara, Gosekhurd, Pauni.*

INTRODUCTION

"Water" is a prime natural resource and is considered as a precious asset. Water is used for various purposes ranging from domestic, agricultural, industrial & allied purposes. The deterioration of water quality takes place due to untreated disposal of sewage and industrial effluents into natural water resources. Rivers are very important source of water in India. The river Wainganga originates about 12 km from Mundara village of Seoni district in the southern slopes of the Satpura Range of Madhya Pradesh, and flow south through Madhya Pradesh and Maharashtra in a very winding course of approximately 360 miles. After joining the Wardha River, the united stream, known as the Pranahita, ultimately falls into the River Godavari. The river has developed extensive flood plains with sweeping graceful meanders and low alluvial flats and meander terraces. The Wainganga River receives numerous tributaries on either bank and drains the western, central and eastern regions of the Chandrapur, Gadchiroli and Nagpur districts. The chief tributaries of the Wainganga are the Garhavi, Khobragadi, Kathani and Potphondi on the western bank and Andhari on the eastern bank [1].

Balaghat and Bhandara are the major urban hub cities situated just on the bank of Wainganga River while Pauni and Desaiganj are the small urban center situated on the bank of this River. The Government of Maharashtra is developing Protection Wall for Bhandara City to protect the Major City from heavy Flooding of River. The flood protection bund encircles Bhandara City from East and South directions. The river is water lifeline for these towns and primary source of Water. The Balaghat and Bhandara Municipal Council have a water treatment plants and fields pipeline to Wainganga River. A major dam built on the river named Gosekhurd dam about 10 km away from the Pauni in Bhandara district.

Water pollution of becomes the global problem. In India, it is reported that about 70 % of the available water is polluted [2]. The chief source of pollution is identified as sewage constituting 84 to 92 percent of the waste water. Industrial waste water comprised 8 to 16 %. [3]

The physicochemical properties of water determine the health of aquatic ecosystem [4]. There is a naturally occurring dynamic equilibrium between water bodies and biological diversity. This equilibrium is affected drastically by human activities [5].

Water resources are responsible for life on Earth. All great civilizations of the world are evolved around rivers. But, increasing population, indiscriminate urbanization and unplanned industrialization along the rivers as well as in the catchment areas have put tremendous stress on water resources. The indiscriminate discharge of domestic and industrial effluent in to the rivers leads to sever depletion of water quality and aquatic life [6]. The examination of water quality is therefore necessary to assess its quality to find out

source of pollution, which ultimately helps in planning the water quality management [7].

Fig. 1 Satellite view of Gosekhurd dam on Wainganga River showing Sampling locations

This is observed that during last few decade rivers get polluted drastically due to discharge of industrial effluents, domestic sewage and other various sources. Physico-chemical analysis is necessary to assess the quality of water for its best usage say for drinking, bathing, fishing, industrial processing and various other purposes. Therefore, the main objective of this study was to assess the water quality of river Wainganga which is life line for Pauni town.

MATERIAL AND METHOD

Study Area: Pauni is a historical town Bhandara district, in the Nagpur division of the Maharashtra State. The town is situated on the right bank of the Wainganga River. The Gosekhurd dam is a major dam of this area. The river covers about 10 km stretch after Gosekhurd dam reaches up to Pauni.

Sampling and Collection of water samples: The present work was planned to assess the quality of water from different sites of river Wainganga from Gosekhurd dam to Pauni town for physicochemical parameters and the results are compared with the standards given by WHO to determine the extent of pollution. Water samples were collected in the double stoppered polythene containers of two liters capacity in the first week of December, 2016 for analyzing the water quality parameters.

METHODOLOGY

The pH and conductivity of the water samples are determined on the spot using a thermometer, pH meter and conductometer respectively. The dissolved oxygen was fixed on the spot using alkali-iodide-azide method. The physicochemical analysis of collected water samples are carried out according to standard methods of APHA [8].

RESULT AND DISCUSSION

pH: The pH of the Wainganga River was slightly alkaline. In winter season the minimum pH was observed as 7.14 at site W10 and maximum 8.32 at site W1. The average pH was 7.87. The minimum value of pH is discharge of domestic wastes from Pauni town into the river. The water is used for domestic purpose from the residents near the river bank e.g. washing clothes, bathing etc. This decreases the pH of water due to domestic use of water [9].

Total Alkalinity (TA): Total Alkalinity of water is the measure of its capacity to neutralize an acid and it is due to the presence of bicarbonate, carbonate and hydroxide compound of calcium, sodium and potassium [10]. Total alkalinity values for investigated for all samples were found within the range while in samples W1 and W8 it was slightly greater than the value prescribed by WHO.

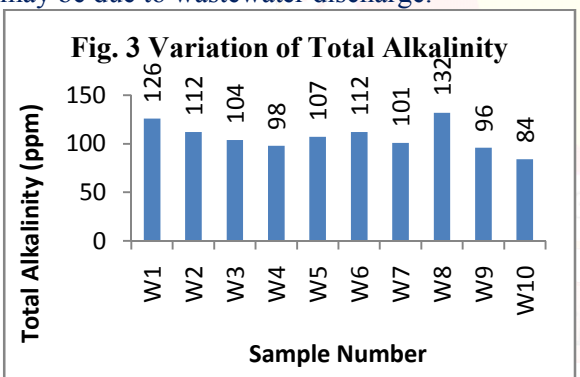
Table 2: Physicochemical Parameters of Wainganga River

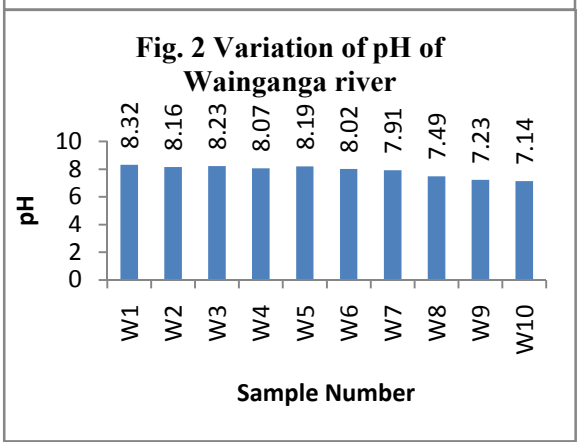
Sr. No.	Parameter	W1	W2	W3	W4	W5	W6	W7	W8	W9	W10	Mean	S.D.(σ)	Var.	WHO
1.	pH	8.32	8.16	8.23	8.07	8.19	8.02	7.91	7.49	7.23	7.14	7.87	0.43	0.185471	7.0-8.5
2.	TA (ppm)	126	112	104	98	107	112	101	132	96	84	107	14.18	201.2889	120
3.	EC (µS/cm)	234	293	253	346	292	241	259	361	433	386	309	68.15	4644.622	1400
4.	TDS (ppm)	160	202	173	234	198	168	179	249	292	260	211	44.85	2011.167	600
5.	DO (ppm)	7.2	6.9	7.1	6.8	7.3	7.0	6.6	7.4	7.1	7.2	7.1	0.24	0.058222	--
6.	COD (ppm)	6.2	5.9	5.5	4.9	5.1	5.3	5.7	6.1	7.0	6.5	5.8	0.65	0.426222	10
7.	BOD (ppm)	1.9	1.8	1.7	1.4	1.5	1.6	1.7	1.8	2.2	2.0	1.7	0.23	0.056	6
8.	TH (ppm)	129.9	121.2	119.2	140.4	131.1	105.5	102.4	98.8	137.4	134.6	122	15.21	231.4228	500

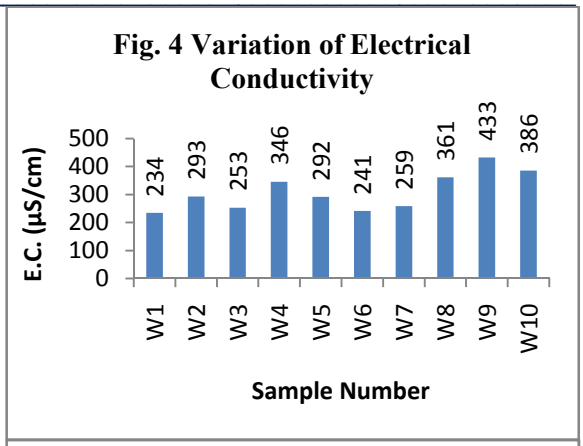
Electrical Conductivity (EC): The higher values of electrical conductivity were related to the abundance of nutrients in the water. In addition to the release from decomposition process of organic matter, increased electrical conductivity is regarded as pollution indicator [11]. The conductivity of collected water samples ranged from 234 to 433µS/cm. The overall electrical conductivity of river stretch indicates low ionic concentration and within the limits of WHO.

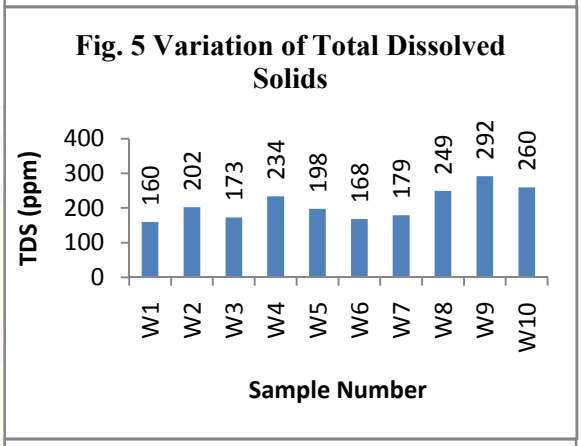
Total Dissolved Solids (TDS): In this study the primary sources of TDS in river water are agricultural runoff, particulate matter, leaching of soil and domestic sewage from villages. The level of TDS in river stretch was found relatively low than the maximum permissible limits of WHO. The reason for the minimum TDS in the river Wainganga is due to the dilution of the sewage and effluents and also more water flow [12].

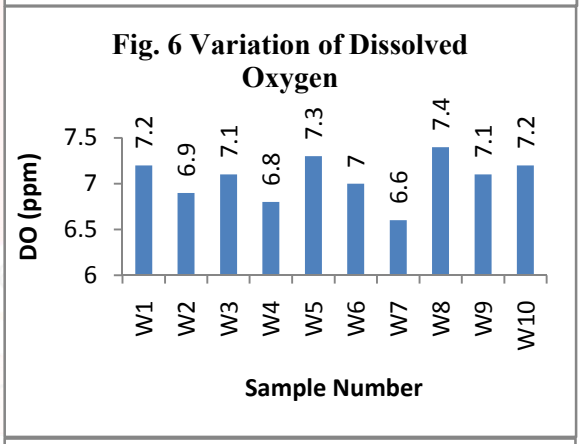
Dissolved Oxygen (DO): The solubility of Oxygen in water depends upon temperature. It decreases with increase of temperature. The higher concentration of dissolved oxygen during winter season is probably due to low water temperature [13]. The minimum DO 6.6 mg/l and maximum 7.4 mg/l was observed at sampling stations W7 and W8 respectively. The minimum DO station W7 may be due to wastewater discharge.

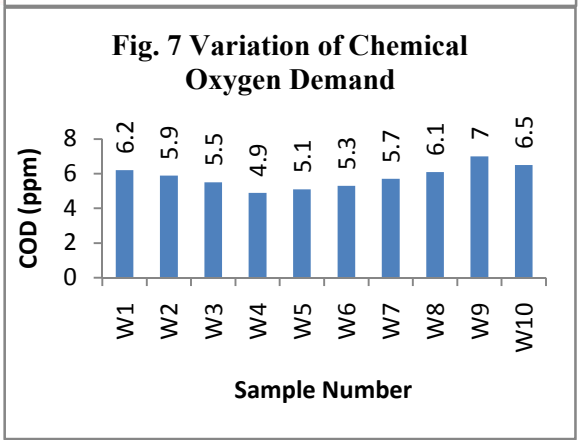












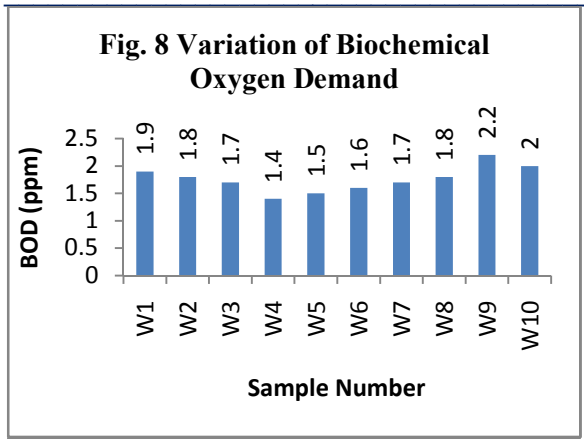


Fig. 8 Variation of Biochemical Oxygen Demand

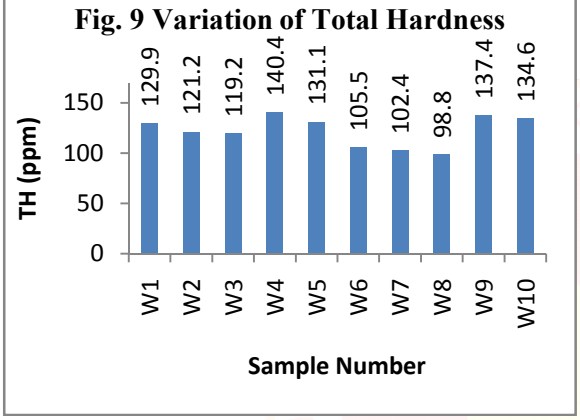


Fig. 9 Variation of Total Hardness

Chemical Oxygen Demand (COD): COD is the measure of amount of oxygen required for chemical oxidation of organic matter. The COD ranges from 4.9 to 7.0 mg/l in the stretch of river Wainganga which is below the maximum permissible limits of WHO. The mean value of COD in the river stretch recorded was 5.8 mg/l with standard deviation of 0.65. The COD is a measure of oxygen equivalent to the chemically degradable organic matter content of the water susceptible to oxidation and become an index of organic pollution in river [14].

Biochemical Oxygen Demand (BOD): It is the amount of oxygen required for biochemical degradation of organic matter by microorganism. BOD is a pollution indicator [15]. The level of BOD in river stretch ranges from 1.4 to 2.2 ppm which is lower than the prescribed norms of WHO. Low BOD content indicated that the river stretch was free from organic pollution. It shows that the river is non-polluted as it does not contain decay of plants and animal matter.

Total Hardness (TH): Total hardness is very important parameter of water for its use. Salts of Calcium and magnesium are important sources for total hardness of water. Excess hardness is undesirable mostly for economic reasons [16]. The TH of water samples from river estimated and found that the high value of 140.4 ppm at location W4 and 99.8 ppm at W8. It is within the maximum permissible level of 600 ppm.

CONCLUSION

The present assessment gives information about the water quality of river stretch of Wainganga from Gosekhurd dam to Pauni town in winter season. The river is recorded comparatively less pollution level at all sampling stations. The chances of pollution in river are by anthropogenic activities, agricultural runoff and discharge of municipal sewage, religious credence etc. The present study indicates that the river water is moderately hard. It requires some water softening treatments before providing for domestic purposes. However, it can be directly used for agricultural purposes.

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A COMPARATIVE SINGLE DOSE BIOEQUIVALENCE STUDY OF EXTENDED RELEASE ANTIHYPERTENSIVE DRUG FORMULATION AMONG HEALTHY HUMAN VOLUNTEERS

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ABSTRACT

The objective of this study was to compare the in vivo characteristics of diltiazem extended release formulations for once daily, which were expected to be bioequivalent. Either two capsules of a test formulation or a 1 of the reference formulation, both containing 360 mg diltiazem were administered to healthy male volunteers after keeping fast for ten hour in a randomized, open label,three period crossover design. Plasma samples obtained over the subsequent period of 72 hours were analyzed using a validated LC-MS/MS method. Safety profile and tolerability of the study medications were assessed by analysis of adverse events obtained by vital sign measurements, electrocardiography, and clinical. The 90% CI for the log transformed data for C_{max}, AUC_{0-t},$AUC_{0-\infty}$ for both the test product fell in the prescribed limits of bioequivalence for narrow therapeutics index drugs i.e. 80 to 120%. This single dose study found that the test and reference products met the regulatory criteria for bioequivalence in healthy, male volunteers under fasting.

Keywords: Diltiazem, bioequivalence, bioavailability

INTRODUCTION

Drug administered orally or parenterally must reach the general circulation in their pharmacological active form to be distributed throughout the body and to exert therapeutic effect. The intensity of therapeutic actions of many drugs correlate well with the concentration of the drug in the biological fluid(1). The rate of absorption is therapeutically important in case of narrow therapeutic index drugs,(2) where relatively small changes in the concentration can lead to marked changes in action of drug.

Diltiazem is a narrow therapeutic index drug and exhibits dose-dependent pharmacokinetics. Diltiazem is a potent vasodilator but does not usually cause reflex tachycardia. It reduces coronary as well as peripheral vascular resistance,(3,4) causing a decrease in blood pressure, and also decreases heart rate and myocardial oxygen demand. In addition, it is extremely well tolerated by patients. These characteristics make diltiazem well suited for the treatment of systemic hypertension. Although the effectiveness of diltiazem for the treatment of patients with hypertension has been well demonstrated in numerous placebo-controlled(5-9) and comparative(10-19) clinical trials, most physicians have had some concern about its efficacy and have used it predominantly in patients with mild hypertension.

Clinical studies compare the diltiazem hydrochloride extended release capsules (Wockhardt Pvt.Ltd.) with the CARDIZEM LA Capsule (Biovail Laboratories, USA). The forms of the drug were shown to have similar trends in half life despite the difference in absorption rate. It was found that 95% of the extended release capsule is absorbed throughout the dosing interval. The capsules takes effect within two to three hour and active effect are detected for 10 to 14 hour.

CARDIZEM® LA (diltiazem hydrochloride) is a calcium ion cellular influx inhibitor (slow channel blocker or calcium antagonist). Chemically, diltiazem hydrochloride is 1,5-benzothiazepin-4 (51-0 one, 3-(acetyloxy)-5-[2- (dimethylamino) ethyl]-2, 3-dihydro-2-(4-methoxyphenyl)-, mono-hydrochloride, (+)-cis-. Diltiazem hydrochloride is a white to off-white crystalline powder with a bitter taste. It is soluble in water, methanol and chloroform. It has a molecular weight of 450.99. It undergoes extensive pre-systemic metabolism (20), and the absolute bioavailability is approximately 40%, showing large inter-individual variation. Diltiazem is a drug with a short half-life, so rapid release diltiazem preparations are required to be administered in multiple daily doses, which may lead to poor patient compliance and hence inadequate therapeutic response. In order to overcome these problems, extended release (SR) preparations of diltiazem have been developed and marketed. Most of the bioequivalence studies on

which the claims of bioequivalence to innovator product do not use confidence intervals (CI) . Determination of CI is a current regulatory requirement of DCGI (Drug Controller General of India) and also of FDA' (http://www.fda.gov/gov/cder/ guidance/ index.htm; April, 2003) to document bioequivalence. Thus, the only way to verify these claims is to do a comparative bioequivalence study with the innovator drug formulation, using confidence intervals. Hence, the present study was undertaken to compare the bioavailability of three brands of 360 mg extended release diltiazem in healthy, adult, male, human subjects under fasting conditions.

MATERIAL AND METHODS

In vitro dissolution characteristics of the study drugs were determined prior to the clinical study to determine a possible lack of robustness of the formulations. Therefore, tablets of each formulation were dissolved in four different buffer media (0.1 M hydrochloric acid, pH 1; acetate buffer, pH 4.5; phosphate buffer, pH 6.8; and phosphate buffer, pH 8) covering the entire pH range of the gastrointestinal tract under the addition of 1% sodium dodecyl sulfate to achieve sink conditions.

Investigations were performed in a standard paddle apparatus 24 with a rotation speed of 100 rpm in vessels of 900 mL over the time range of 24 hours.

Clinical Study

The design of the study was open-label, randomized, and controlled and followed a three period crossover with single oral doses of either one 360-mg capsules of the test formulation (A&B) or one 360-mg capsule of the reference formulation(C) Table.1, with a treatment-three phase of at least seven days to avoid any carry-over effects in the second period. This exploratory trial was performed in 18 healthy volunteers without a formal sample size estimation as the number was considered sufficient to fulfill the objectives of the study. The investigation was performed in healthy males only as there have been no reports of gender-specific differences in diltiazem pharmacokinetics. Subjects were included according to specific inclusion and exclusion criteria, taking into account both participants' safety and optimal standardization of the study. Subjects with any clinically relevant laboratory parameters out of range; clinically relevant findings in ECG or vital signs; existing cardiac, hematologic, hepatic, renal, gastrointestinal diseases or findings; clinically relevant diseases of the internal organs or central nervous system; severe allergies or hypersensitivities or who had undergone a clinically relevant blood donation or participation in a clinical trial during the last months prior to the start of the study were excluded. Any medical disorder, condition, or history of such that would impair the subject's ability to participate or complete this study with a special focus on effect of absorption and metabolism led to exclusion of a subject. Furthermore, subjects were excluded if they had regular intake of alcohol ≥50 g pure ethanol per day or caffeine ≥250 mg/d, were active smokers, and/or had received any systemically available medication within four weeks prior to the intended first study drug administration unless, due to the corresponding terminal elimination t1/2 values, complete elimination from the body for the drug and/or its primary metabolites could be assumed. Finally, drug or alcohol dependence and a positive virologic status (anti-HIV test, HBsAg test, or anti-HCV test) were to be excluded. Prior to the start of administration of the investigational products a pre-study examination was performed to determine the general health status of the subjects. It included an anamnesis for medical history, a physical examination, determination of blood pressure and pulse rate (oscillometry using a manual noninvasive device), a twelve lead ECG, determination of hematologic and clinical chemistry parameters, and a urinalysis (the latter performed by a Good Laboratory Practices–certified central laboratory using common and quality controlled standard methods for determination).

Hospitalizations started twelve hours before study drug administration in each period and lasted for 48 hours post dosing. Drug administration was performed under standardized conditions in an sitting position with 240 ml. tap water by maintaining an overnight fast (at least 10 hours). Standardized meals were served 4, 8, 12, 24, 28, and 32 hours post administration, which had the same standardized composition in three periods. Water restriction one hour predose and two hour post dose except the water given at the time of dosing had maintained Volunteers had to remain in a sitting position for four hours after administration.

Table 1.Randomization

Subject No.	Sequence (hrs)	Time	Period		
			Period-1	Period-2	Period-3
01	CAB	0900	C	A	B
02	BCA	0902	B	C	A
03	ABC	0904	A	B	C
04	ABC	0906	A	B	C
05	CAB	0908	C	A	B
06	BCA	0910	B	C	A
07	ABC	0912	A	B	C
08	BCA	0914	B	C	A
09	CAB	0916	C	A	B
10	CAB	0918	C	A	B
11	BCA	0920	B	C	A
12	ABC	0922	A	B	C
13	CAB	0924	C	A	B
14	ABC	0926	A	B	C
15	BCA	0928	B	C	A
16	CAB	0930	C	A	B
17	BCA	0932	B	C	A
18	ABC	0934	A	B	C

A=Test drug product. B=Test drug product. C= Reference drug product

Venous blood samples were collected immediately before and 0.5, 1, 2, 3, 4, 5, 6, 8, 10, and 12 hours after drug administration. The collected blood samples were immediately chilled; the plasma was separated by centrifugation in a refrigerated centrifuge, and set at 4˚C with a rate of 3500 rpm for 10 minutes. The separated plasma was then immediately shock-frozen using liquid nitrogen and then stored at –70˚C until assay. The stability of these samples at –70˚C is three months [21].

Questioning for general well-being was performed in a non leading manner. In addition to the questioning for general well-being at the pre-study examination and at the time of hospitalization, questioning for general well-being was also performed in the morning prior to the study drug administration as well as 1, 4, 8, 12, 24, 36, and 48 hours post administration and at the post study examination. Blood pressure and pulse rate were measured in the morning prior to the study drug administration as well as 1, 2, 4, 8, 12, 24, 36, and 48 hours post administration. Furthermore, the volunteers were asked to report any adverse events spontaneously, whether or not they occurred during confinement. The entire trial was performed in accordance with the requirements of Good Clinical Practices and the current version of the Declaration of Helsinki [22,23]

Each volunteer provided written informed consent, which could be withdrawn at any time. The design and procedures corresponded to recommendations of international guidelines. The study was approved by the Ethics Committee of the Wockhardt Ltd,Mumbai, India.

Pharmacokinetic Parameters and Statistical Analysis

The pharmacokinetic characteristics of extended release diltiazem were determined from the plasma concentration-time data. Peak plasma concentration (C_{max}) and time to maximum plasma concentration (T_{max}) were determined directly from raw data. The area under the curve (AUC_{0-t}, from 0 to last measured concentration) was calculated.

All the pharmacokinetic parameters statistical values were calculated using LinMax procedures of WinNolin® Version 5.1 (Pharsight Corporation USA) software application and the SAS® system Version 9.1, respectively, at Clinical Pharmacokinetic & Biopharmaceutics Department of Wockhardt Ltd and 95% confidence interval analysis with a minimum level for significant difference set at $P < 0.05$. All data were reported as mean standard deviation.

RESULTS

Study Population

A total of 18 volunteers were enrolled and finished the study according to the protocol without major protocol deviations. The median age was 28.0 years (range, 18–42 years), the mean weight was 70.2 kg (range, 58.5– 80.0 kg), and the mean body mass index was 24.2 kg/m^2 (range, 19.3–27.0 kg/m2) (Table 2).

Table 2. Demographic Characteristics of the 18 Study Participants

	Age (y)	Body weight(kg)	Height(cm)
Mean±standard deviation	21.6±2.9	71±13.3	173±7.9
Minimum	18.0	53.0	162.0
Maximum	40.0	89.0	185.0

Pharmacokinetics and Statistics

The clinical study was completed within four weeks. Extended release diltiazem was well tolerated by subjects, and no adverse events occurred during the study. Mean pharmacokinetic parameters for the 18 subjects for the extended release Diltiazem tested formulations and the reference formulation are shown in Table 3 and 4. The time course of mean Diltiazem concentrations after 360 mg for both formulations is presented in Figure 1.

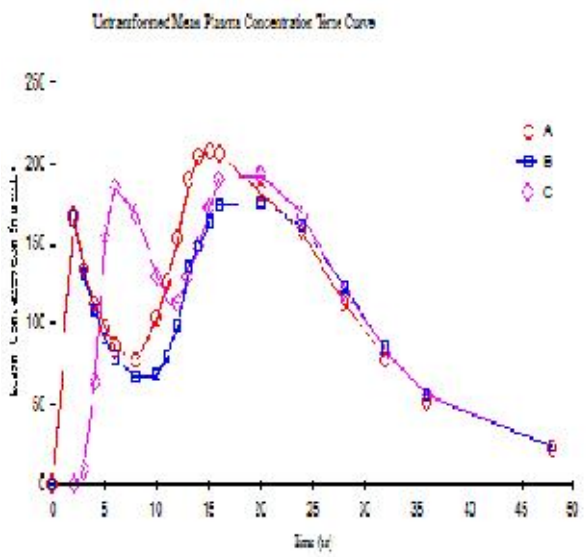

Figure 1. Plasma diltiazem concentration versus time of brand.

Pharmacokinetic Analysis

Parent Drug C_{max}: The C_{max} for test products A ranged from Mean±SD of 443.09±62.389 ng.hr/ml and the AUC_{0-t} for test products B ranged from Mean±SD of 338.85±62.389 ng.hr/ml The AUC_{0-t} for reference product C ranged from Mean ±SD of 307.95±50.038 ng.hr/ ml. The geometric values for the test products A, test products B and reference product C were found to be 211.29 ng.hr/mL& 193.33 ng.hr/mL and 220.58 ng.hr/ mL, respectively.

Time of Peak Concentration (T_{max})

Parent Drug T_{max}: The T_{max} for test products A ranged from Mean ±SD of 20.00±4.78 ng.hr/ml and the AUC_{0-t} for test products B ranged from Mean ±SD of 28.00±8.513 ng.hr/ml The AUC_{0-t} for reference product C ranged from Mean ±SD of 20 ±5.8 ng.hr/ml. The geometric values for the test products A, test products B and reference product C were found to be 15.00 ng.hr/mL and 18.00 ng.hr/ mL and 15.50 ng.hr/mL, respectively.

Area Under the plasma Concentration time curve (AUC_{0-t}, t=72hr) and $AUC_{0-\infty}$

Parent Drug AUC_{0-t}: The AUC_{0-t} for test products A ranged from Mean±SD of 8827.29±1635.529 ng.hr/ml and the AUC_{0-t} for test products B ranged from Mean ±SD of 8303.1900±1370.553 ng.hr/ml The AUC_{0-t} for reference product C ranged from Mean±SD of 8176.60±3029.7850 ng.hr/ml. The geometric values for the test products A, test products B and reference product C were found to be 4844.60ng.hr/mL and 4558.71ng.hr/mL and 4838.91 ng.hr/mL. respectively.

Parent drug $AUC_{0-\infty}$: The AUC0-∞ for test product A and test product B ranged from Mean±SD of 9427.0419±1805.079ng.hr/ml and 8832.9560±1494.748 ng.hr/ml respectively. The $AUC_{0-\infty}$ for reference product C ranged from a Mean±SD of 8894.3815±1660.006 ng.hr/ ml. The geometric values for the test products A and test products B and reference products C were found to be 5082.86ng.hr/mL & 4813.06ng.hr/mL and 5101.52ng. hr/mL.

Elimination Rate Constant (Kel)

Parent Drug: The Mean±SD values of the elimination rate constant (Kel) were found to be 0.1315±0.024 hr-1 and 0.1232±0.016hr-1 for Test Product A and test products B respectively and 0.1297±0.021hr-1 for Reference Product C. The geometric mean values for both the test products A & test products B & Reference Products C were found to be 0.09 hrs-1 and 0.09 hrs-1 and 0.09hrs-1 respectively.

Elimination Half-life ($t_{1/2}$)

Parent Drug: The Mean±SD values of elimination half-life ($t_{1/2}$) were found to be 13.0008±2.487hrs&11.1 026±1.500for Test Product A and test products B and 12.2680±2.010hrs for Reference Product C.

Parent Drug: The Median half-life ($t_{1/2}$) values for the Test A and test products B and Reference Products C were found to be 7.66hrs and 8.01 hrs and 8.07 hrs, respectively.

Residual Area (AUC_%Extrap_obs)

Parent Drug: The Mean ± SD values of the Residual Area (%) were found to be 12.40±3.795& 10.86±2.458 for Test Product A & test products B and 12.01±3.174 for Reference Product C.

Statistical Results

Geometric LSM Ratio and 90 % Confidence Interval

The test by reference geometric least square mean ratio and 90 % confidence interval obtained for Cmax, AUC_{0-t} and $AUC_{0-\infty}$ were as follows:

Parent drug (A): LSM ratio C_{max} 95.79% and CI 88.52% to 103.65%, AUC_{0-t} LSM ratio 92.85% and CI 92.85% to 107.96% and AUC0-∞ ,LSM ratio 99.63% and CI 92.2% to 107.67%, which shows all the values are within the bioequivalence acceptance range 80.00%'to 125.00% .

Parent drug (B): LSM ratio C_{max} 87.65% and CI 81% to 94.84%, AUC0-t LSM ratio 94.21% and CI 87.37% to 101.59% and $AUC_{0-\infty}$ LSM ratio 94.35% and CI 87.31% to 101.95%, which shows

all the values are within the bioequivalence acceptance range 80.00%' to 125.00%

p-values (ANOVA)

The p-value should be greater than 0.05 for C_{max}, AUC_{0-t} and $AUC_{0-\infty}$ for period and formulation effects. For sequence effect it should be greater than 0.01.

The p-values obtained from ANOVA for sequence effect of Drug Diltiazem hydrochloride and metabolite of Drug Diltiazem hydrochloride are greater than 0.05 for C_{max} , AUC_{0-t} and $AUC_{0-\infty}$ which indicates no statistically significant differences were observed for sequence effect on pharmacokinetic parameters C_{max} , AUC_{0-t} and $AUC_{0-\infty}$.

Intra-subject Variability

Parent Drug (A): The coefficients of variation (CV%) corresponding to intra-subject variability for C_{max}, AUC_{0-t} and $AUC_{0-\infty}$ for Drug Diltiazem hydrochloride are 14.03%,13.41%,13.79% respectively which were found to be less than 30%

Parent Drug (B): The coefficients of variation (CV%) corresponding to intra-subject variability for C_{max}, AUC_{0-t} and $AUC_{0-\infty}$ for Diltiazem hydrochloride are 14.03%,13.41%,13.79% respectively, which were found to be less than 30%.

Power

Parent Drug (A): The power values obtained for C_{max}, AUC_{0-t} and $AUC_{0-\infty}$ are 98.84%, 99.86%, 99.74% respectively, which were greater than 80.00% the desired power to support the bioequivalence test, and hence test, and hence considered to be adequate for supporting bio-equivalence conclusions.

Parent Drug (B): The power values obtained for C_{max}, AUC_{0-t} and $AUC_{0-\infty}$ are 98.84%, 99.86%, 99.74% respectively, which were greater than 80.00 % the desired power to support the bioequivalence test, and hence test, and hence considered to be adequate for supporting bio-equivalence conclusions

Safety Results

There was one adverse events reported which was mild fever Subject no. 11 adverse events was resolved. The adverse event was mild and unlikely to study medication administered to the subjects. From the adverse event profile and tolerability of the subjects, it appeared that the test product was equally safe as that of reference product.

DISCUSSION

Proving two drug products (of the same active ingredient) to be therapeutically equivalent entails a similarity in rate and extent to which a drug in a dosage form becomes available for biologic absorption (24). Area-under-the-curve is accepted as a good indicator of extent of absorption, whereas C_{max} and T_{max} are considered estimators of the rate of absorption. Two internationally recognized organizations (U.S. Food and Drug Administration and European Agency for the Evaluation of Medicinal Products) have proposed that bioequivalence can only be assumed when the characteristic parameters of bioavailability show no more than a defined difference (25-26). These differences depend on the nature of the drug, the patient population, and the clinical end point.

The rapid hydrolysis was minimized by working under low temperature at all times using liquid nitrogen to shock-freeze the samples and stop hydrolysis, thawing in chilled ice water, and centrifuging in a refrigerated centrifuge set at 4˚C. Such methods helped us bypass the need to add an enzyme inhibitors (such as potassium fluoride or physostigmine) to plasma to enzymatically inhibit hydrolysis. According to earlier investigations such preservatives are not very efficient, because enzymatic hydrolysis in plasma overlaps with chemical hydrolysis. Therefore, immediate cooling techniques used in this study, including storage at –70˚C after sampling, are the best steps to prevent degradation. Lack of statistical significant differences in AUC values, C_{max} and, T_{max} between the two products indicate that the two formulations are closely similar in terms of their pharmacokinetic properties and bioavailability. This suggests that the in vivo dissolution and the absorption rate are closely identical for the two products. Furthermore, this in vivo finding is consistent with the in vitro release pattern.

Based on the in vitro and in vivo pharmacokinetic results obtained, this study suggests that the two products of extended release diltiazem included in this investigation are bioequivalent. Thus, diltiazem hydrochloride and CARDIZEM LA might be considered interchangeable based on the pharmacokinetic effect.

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REMOVAL OF Cu(II) FROM SOLUTION USING ADSORPTION STUDIES OF ACTIVATED CHARCOAL AND NON ACTIVATED JACKFRUIT POWDER

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ABSTRACT

In India heavy metal pollution is a serious problem today and its treatment is of special concern due to their recalcitrance and persistence in the environment. The method of adsorption is used for removal of Cu(II) by taking non activated jackfruit peel powder and it's activated charcoal.

Keywords: *adsorption, jackfruit peel powder, activated charcoal, Colorimetry*

INTRODUCTION

Due to rapid industrialization and urbanization in developing countries like India heavy metal pollution is a serious problem today. Like organic pollutants, most of these heavy metals do not undergo biological degradation, resulting into harmless end products [1]. Many industries, like metal plating, mining operations, tanneries, radiator manufacturing, smelting, alloy industries and storage batteries industries, etc. release these severely toxic heavy metal ions in their wastewaters contaminating natural streams where in disposed, which is a major concern due to toxicity to many life forms [2].Though there are many treatment methods for removal of heavy metals from wastewater like chemical precipitation, membrane filtration, ion exchange, coagulation and flocculation, floatation, electrochemical treatment, adsorption and co-precipitation followed by adsorption etc. yet various researchers have studied and revealed that physical adsorption is a highly effective and economic technique for the removal of heavy metal from waste stream and from ancient times activated carbon has extensively been used as an adsorbent [3] in the water and wastewater treatment plants, but it is found to be an expensive material. Recently, an idea of the production of safe and low cost alternatives to this expensive and commercially available activated carbon has attracted the researchers towards the low cost agro and horticultural wastes and by-products for the removal of heavy metals from wastewater and it has been investigated successfully [4,5]

Heavy metals are member of a loosely-defined subset of elements that exhibit metallic properties, has high density, which mainly includes the transition metals, some metalloids, lanthanides, and actinides. Certain heavy metals such as iron, copper (Cu), zinc and manganese are required by humans for normal biological functioning. However, heavy metals such as mercury, lead, cadmium are toxic to organisms. Most of the health disorders are linked with specific tendency of heavy metals to bioaccumulate in living tissues and their disruptive integration into normal biochemical processes [6]. Increased use of metals and chemicals in industries has resulted in generation of large quantities of effluent that contains high level of toxic heavy metals and their presence poses environmental-disposal problems due to their non-degradable and persistence nature[7]. Several techniques such as chemical precipitation, oxidation, reduction, coagulation, solvent extraction, ion exchange, filtration, electrochemical treatment, reverse osmosis, membrane technologies, evaporation recovery, and adsorption have been commonly employed for the removal of metal ions [8].

Workers involved in spraying of Bordeaux mixture (an insecticide with Cu) on grapes, other crops develop acute irritation of respiratory tract and metal fume fever characterized by the development of interstitial pulmonary lesions and nodular fibro hyaline scars containing deposits if

copper. Lung cancer may also develop in many cases. An injection of about 50-80 mg of copper causes gastro-intestinal disturbances, nausea, vomiting etc, larger quantities taken accidently or intentionally may cause hemolysis hepatotoxic and nephrotoxic of effects. A higher concentration of copper is injurious to blue green algae since this metal tend to suppress nitrogen fixation.

COLORIMETRIC TECHNIQUE

Colorimetric is the oldest known technique for determining any colour. The intensity of a substance is in direct proportion to its concentration, which is in terms of transmittance (optical density). Concentration of various solution can be determined by colorimetric technique. The absorbance of different concentrated solution without and with prepared non activated and activated adsorbant was recorded. Concentration of unknown solution can be calculated as follows:-

Concentration of solution ---------- x initial concentration

Concentration of solution I

For colour determination of different solution five bottles of different concentration was prepared. Colorimetric technique was used to study for removal of metals from contaminated waste water. The solutions of different concentration were prepared. In a conical flask 50ml solution +0.2 gm activated carbon was shaken for 15 min. the optical density at various wavelengths was recorded before and after adsorption. The pH of the solution was also recorded.

Observation table 1 :- Adsorption of Cu^{2+} on jackfruit peel powder

Initial con.	1M		0.5M		0.25M		0.125M		0.06M	
Wave length	before	after	before	after	before	After	before	after	before	after
400	0.589	0.450	0.350	0.398	0.183	0.121	0.100	0.074	0.082	0.066
420	0.428	0.323	0.250	0.210	0.139	0.102	0.086	0.069	0.072	0.059
440	0.360	0.190	0.205	0.169	0.121	0.096	0.073	0.060	0.070	0.058
460	0.211	0.108	0.167	0.125	0.098	0.069	0.065	0.048	0.062	0.043
480	0.180	0.096	0.123	0.096	0.075	0.056	0.059	0.045	0.055	0.039
500	0.171	0.092	0.111	0.088	0.063	0.050	0.057	0.043	0.050	0.038
520	0.190	0.19	0.138	0.092	0.076	0.054	0.052	0.040	0.046	0.038
540	0.198	0.102	0.157	0.125	0.085	0.060	0.049	0.040	0.046	0.038
560	0.230	0.121	0.243	0.189	0.107	0.069	0.053	0.040	0.047	0.039
580	0.319	0.199	0.289	0.251	0.142	0.103	0.078	0.061	0.067	0.045
600	0.426	0.230	0.327	0.291	0.169	0.117	0.097	0.071	0.081	0.061
pH	2.5	4.9	2.7	5.4	2.9	5.8	3.2	6.1	3.5	6.3

Observation table 2 :-Determination of concentration of Cu^{2}+ after adsorption by using nonactivated jackfruit peels powder

Initial conc	1M	0.5M	0.25M	0.125M	0.0625M
Wave length					
400	0.764007	0.425714	0.165301	0.0925	0.050305
420	0.754673	0.42	0.183453	0.100291	0.051215
440	0.527778	0.412195	0.198347	0.10274	0.051786
460	0.511848	0.374251	0.17602	0.092308	0.043347
480	0.533333	0.390244	0.186667	0.095339	0.044318
500	0.538012	0.396396	0.198413	0.094298	0.0475
520	0.52	0.333333	0.177632	0.096154	0.05163
540	0.515152	0.398089	0.176471	0.102041	0.05163
560	0.526087	0.388889	0.161215	0.09434	0.051862
580	0.623824	0.434256	0.181338	0.097756	0.041978
600	0.539906	0.444954	0.173077	0.091495	0.047068
pH	4.9	5.4	5.8	61	6.3

Observation table 3 :- Adsorption of Cu^{2+} on activated jackfruit charcoal

Initial con.	1M		0.5M		0.25M		0.125M		0.06M	
Wave length	before	after	before	after	before	After	before	after	before	after
400	0.589	0.450	0.350	0.398	0.183	0.121	0.100	0.074	0.082	0.066
420	0.428	0.323	0.250	0.210	0.139	0.102	0.086	0.069	0.072	0.059
440	0.360	0.190	0.205	0.169	0.121	0.096	0.073	0.060	0.070	0.058
460	0.211	0.108	0.167	0.125	0.098	0.069	0.065	0.048	0.062	0.043
480	0.180	0.096	0.123	0.096	0.075	0.056	0.059	0.045	0.055	0.039
500	0.171	0.092	0.111	0.088	0.063	0.050	0.057	0.043	0.050	0.038
520	0.190	0.19	0.138	0.092	0.076	0.054	0.052	0.040	0.046	0.038
540	0.198	0.102	0.157	0.125	0.085	0.060	0.049	0.040	0.046	0.038
560	0.230	0.121	0.243	0.189	0.107	0.069	0.053	0..040	0.047	0.039
580	0.319	0.199	0.289	0.251	0.142	0.103	0.078	0.061	0.067	0.045
600	0.426	0.230	0.327	0.291	0.169	0.117	0.097	0.071	0.081	0.061
pH	2.5	4.9	2.7	5.4	2.9	5.8	3.2	6.1	3.5	6.3

Observation table 4 :-Determination of concentration of Cu^{2}+ after adsorption by using activated jackfruit charcoal

Initial conc	1M	0.5M	0.25M	0.125M	0.0625M
wavelength					
400	0.764007	0.425714	0.165301	0.0925	0.050305
420	0.754673	0.42	0.183453	0.100291	0.051215
440	0.527778	0.412195	0.198347	0.10274	0.051786
460	0.511848	0.374251	0.17602	0.092308	0.043347
480	0.533333	0.390244	0.186667	0.095339	0.044318
500	0.538012	0.396396	0.198413	0.094298	0.0475
520	0.52	0.333333	0.177632	0.096154	0.05163
540	0.515152	0.398089	0.176471	0.102041	0.05163
560	0.526087	0.388889	0.161215	0.09434	0.051862
580	0.623824	0.434256	0.181338	0.097756	0.041978
600	0.539906	0.444954	0.173077	0.091495	0.047068
pH	4.9	5.4	5.8	61	6.3

RESULT AND DISCUSSION

The adsorption study of non activated powder and activated charcoal of jackfruit peel shows that it can act as a good adsorbent for the removal of Cu (II) from the solution. The solution also reveals the change in pH also after adsorption .The adsorbent is more economic and can be prepared from waste material.

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TRANSITION METAL CHELATES WITH ONO DONOR HYDRAZONE LIGAND: SYNTHESIS, CHARACTERIZATION, THERMAL AND ANTIMICROBIAL ACTIVITY

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ABSTRACT

A new ONO donor chelating agent, 1-(1-hydroxynaphthalen-2-yl)ethanone-2-chlorobenzoylhydrazone (H_2L^1), 1-(1-hydroxynaphthalen-2-yl)ethanone-2-iodobenzoylhydrazone (H_2L^2) and its complexes with Fe(III) and Zr(IV) have been prepared by conventional method. The synthesized ligands and its metal complexes have been characterized by elemental analysis, solid reflectance, magnetic moment, IR, ^{1}H-NMR, ^{13}C-NMR and thermal analysis (TGA). Low value of molar conductance of complexes in DMF indicates their non-electrolytic nature. IR spectra suggest that ligands behave monobasic tridentate in Fe(III) complexes and dibasic tridentate in Zr(IV) complexes. TGA study of complexes revealed presence of coordinated and lattice water as well as remaining residue of decomposition. Physicochemical data suggested octahedral geometry for both Fe(III) and Zr(IV) complexes. Ligands and its complexes were screened for antimicrobial activity against some bacteria and fungi. Both ligands and their complexes show higher activity against E. Coli as compared to standard Penicillin. Ligand (H_2L^1) and its complexes show comparatively higher activity than ligand (H_2L^2) and its complexes, against all bacterial and fungal strains.

Keywords: *Tridentate hydrazone Schiff bases, Transition metal complexes, Thermal studies, Antibacterial and Antifungal activity.*

INTRODUCTION

In coordination chemistry hydrazones are versatile class of ligands and studied as multifunctional ligands with different coordination modes [1, 2]. The presence of hydrazine-hydrazone (–CO–NH–N=C–) functional group plays a significant role as pharmaceutical agents, possessing anti-malarial, antimicrobial, anti-leishmanial, anti-tubercular and antitumor activities, anti-inflammatory, anti-convulsant [3]. Transition metal ions with different oxidation state have a strong role in bio-inorganic chemistry and redox enzyme systems and may provide the basis of models for active sites of biological systems [4] .

Iron is an essential element for brain cells and its deficiency or excess causes different brain disorders like restless legs syndrome, Alzeimer disease, Parkinson disease etc [5]. The study of iron hydrazone complexes is important as iron chelating efficiency of hydrazones and their applications in the treatment of iron overload diseases [6, 7]. Zr(IV) complexes posses good antimicrobial activity [8].

The compounds containing halo-substituted hydrazone posses interesting biological and pharmacological activities. In the view of their enormous applications, in this report we describe synthesis and characterization newly synthesized Fe(III) and Zr(IV) complexes. Synthesis and characterization of 1-(1-hydroxynaphthalen-2-yl) ethanone-2-chlorobenzoylhydrazone (H_2L^1) ligand was reported in our previous literature [9], while 1-(1-hydroxynaphthalen-2-yl)ethanone-2-iodo-benzoylhydrazone (H_2L^2) ligand was newly synthesized and characterized. All the synthesized ligands (H_2L^1, H_2L^2) and their metal complexes are screened for antibacterial and antifungal activity.

MATERIAL AND METHODS

Analytical grade (AR) chemicals and solvents are used for starting material of synthesis of ligand and its metal complexes and procured from S. D. fine. The metal salts used for preparation of metal complexes are anhydrous ferric chloride and zirconyloxychloride octahydrate were commercially available. 2-chlorobenzohydrazide [10] and 2-iodobenzohydrazide [11] was synthesized from literature procedure. The metal and chloride contents were determined as per Vogel's procedure [12]. The micro elemental analysis of carbon, hydrogen and nitrogen were done by Elemental Analyser (Thermo Scientific) FLASH- 2000. The infrared spectra of ligands and their metal complexes were recorded on IR Spectrophotometer model RZX (Perkin Elmer) in the 4000-400 cm^{-1} region using KBr pellets. The diffuse reflectance spectra of the metal complexes

were recorded on Jasco UV-Visible Spectrophotometer (V-670) in the range of 1000-200nm. ^{1}H NMR spectra of ligands were recorded in DMSO-d_6 on Bruker 400 MHz spectrophotometer, using TMS as an internal standard. IR, ^{1}H-NMR, ^{13}C-NMR, diffuse reflectance spectra are recorded at (SIF), VIT University, Vellore, Tamil Nadu. Molecular weight measurements were carried out according to Rast's method [13]. The magnetic susceptibility of the metal complexes was measured at room temperature by Gouy's method using mercury (II) tetra thiocyanatocobalt (II), Hg [Co(SCN)4], as a calibrant. Molar conductivity measurements were recorded on a Elico CM-180 conductivity bridge in DMF (10^{-3} M) solution at room temperature. TG analyses of complexes were carried out on TG Instrument, model – SDT Q600 V20.9 Build 20 at a heating rate of 20˚C per minute in an atmosphere of nitrogen, within temperature range from room temperature to 800˚C and recorded at SIF Lab, VIT, Vellore, Tamil Nadu.

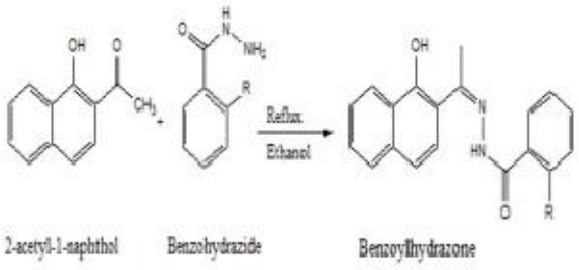
Synthesis of 2-acetyl-1-naphthol by modified Nenchi's method

Freshly fused and powered $ZnCl_2$ (0.24mol) was dissolved in glacial acetic acid (32ml) in beaker on sand bath. Then add 1-naphthol (0.2mol) with stirring. Heat the reaction mixture on sand bath for 1hr, then cool it and pour it slowly in dil HCl (1:1). Solid product1-(1-hydroxynaphthalen-2-yl)ethanone obtained was filtered and washed with acidulated water dry it. Product was recrystallized from ethanol [14].

(Yield = 92-95%; Melting point = 98-100˚C)

SYNTHESIS OF SCHIFF'S BASES

Both ligands H_2L^1 and H_2L^2 are synthesized (Scheme-1) by adding hot ethanolic (25ml) solution of 2-acetyl-1-naphthol (0.001mol) in hot ethanolic (15ml) solution of 2-chloro benzohydrazide (0.001mol) and 2-iodo benzohydrazide (0.001mol) respectively with constant stirring, refluxed on waterbath for 3-4hr. On cooling reaction at room temperature, coloured solid was obtained. Product was then filtered, washed several times with ethanol, dried *in vaccu* over $CaCl_2$. Product was then recrystallized from DMF- ethanol mixture (1:4 v/v).



Where, R = -Cl, -I

Scheme -1: Synthesis of Schiff's base (H_2L^1 and H_2L^2)

Synthesis of Fe(III) complex

To a hot DMF solution (15ml) of ligands (H_2L^1 & H_2L^2) (0.001mol), a hot ethanolic solution of anhydrous $FeCl_3$ (0.001mol) solution was added with continuous stirring. The mixture was then refluxed on sand bath for 6-8hr. The resultant solution was digested to half of its volume, on cooling solid product was obtained. The product was washed several times with water followed by petroleum ether and dried at room temperature and stored in desiccator over $CaCl_2$.

(Yield = 65-68%)

Synthesis of Zr(IV) complex

For the synthesis of Zr(IV) complexes, zirconyl oxychloride octahydrate (0.64 g, 0.002mol was dissolved in methanol (15 mL) and to this, a methanolic solution of anhydrous sodium acetate (0.32 g, 0.004 mL in 15 mL) was added. After stirring for 5 min sodium chloride was separated this then filtered off. The respective ligands (H_2L^1 & H_2L^2) (0.001mol) was dissolved in minimum quantity of hot DMF. To this solution, the solution containing oxozirconium(IV)diacetate was added with continuous stirring and the mixture was refluxed on a sand bath for 6-8 hr. The colored solid Zr(IV) complex obtained was filtered and washed with water, methanol and finally with petroleum ether. The product was dried in air at room temperature and stored in desiccator over $CaCl_2$ [15]. (Yield = 60-75 %)

BIOLOGICAL EVALUATION

Antibacterial activity of synthesized Schiff bases H_2L^1, H_2L^2 and its Fe(III), Zr(IV) complexes are studied by using agar plate method against gram positive bacteria, *Staphylococcus aureus* and *Bacillus subtilis* and gram negative bacteria, *Escherichia coli* and *Salmonella typhi* by using *Penicillin* as standard. Antifungal activity of ligands and complexes are studied by poison plate method against fungal cultures *Aspergillus niger, Penicillium chrysogenum, Fusarium*

moneliforme, Aspergillus flavus by using *Gresiofulvin* as standard.

ANTIBACTERIAL ACTIVITY

Nutrient agar (Hi media) was prepared and sterilized at 15 psi for 15 min. in the autoclave. It was allowed to cool below 45˚C and seeded with turbid suspension of test bacteria separately, prepared from 24 hrs old slant cultures, 3% inocula were used everytime. This seeded preparation was then poured in sterile petri plate under aseptic condition and allowed to solidify. Cups of 10mm diameter were bored in the agar plate with sterile cork borer. 100µl of compound solution prepared in DMSO (1%) was added in the cup under aseptic condition with the help of micropipette. 100µl of DMSO was also placed in one of cup as blank (negative control). Then the plates were shifted to incubator at 37˚C and incubated for 24hrs. Results were recorded by measuring the zone of inhibition in mm using zone reader [16].

ANTIFUNGAL ACTIVITY

The medium used was Potato Dextrose Agar (Hi media). The medium was prepared and sterilized at 10 psi in autoclave for 15min. Then the compound to be tested is added to the sterile medium in aseptic condition so as to get final concentration as 1%. A plate with DMSO was prepared as blank (negative control). All the selected test fungal cultures were allowed to grow on slant for 48 hrs so as to get profuse sporulation. 5ml of 1:100 aqueous solution of Tween 80 was added to the slant and spores were scraped with the help of nicrome wire loop to form suspension. The plates were incubated at room temperature for 48hrs. After inoculation plates were observed for the growth of inoculated fungi. Results were recorded as growth of fungi (No antifungal Activity), reduced growth of fungi (Moderate antifungal Activity) and no growth of inoculated fungi (Antifungal activity) [16].

RESULTS AND DISCUSSION

The analytical and physicochemical data of the ligand and complexes are given in Table 1, which confirm 1:1 metal to ligand stiochiometry in complexes. 8.5 - 25 $ohm^{-1}cm^2mol^{-1}$ molar conductance values of the complexes in DMF at 10^{-3}M indicated the non electrolytic nature of the complexes. All the complexes are completely soluble in DMF and DMSO solvent.

Table 1. Analytical and Physico-Chemical data of the Schiff's base ligands and its Metal Complexes.

Molecular Formula Ligand/ Complexes	Molecu weight	Colour	Elemental Analysis %found (cal.)					μ^{eff} (BM)	Λ^{M*}
			C%	H%	N%	Cl%	M%		
$C_{19}H_{15}ClN_2O_2$ (H_2L^1)	338.78	Yellow	67.03 (67.36)	4.40 (4.46)	8.18 (8.27)	10.38 (10.46)	---	---	---
$[Fe(L^1)Cl_2.H_2O]$	482.54	Burnt green	46.78 (47.29)	3.30 (3.34)	5.43 (5.81)	21.78 (22.04)	11.43 (11.57)	5.95	19
$[Zr(OH)_2(L^1)CH_3OI$	494.05	Signal Yellow	48.32 (48.62)	3.41 (3.88)	5.03 (5.67)	7.02 (7.18)	17.60 (18.46)	---	9
$C_{19}H_{15}IN_2O_2$ (H_2L^2)	430.24	Pale yellow	52.78 (53.04)	3.04 (3.51)	6.31 (6.51)	---	---	---	---
$[Fe(L^2)Cl_2.H_2O]$	573.99	Fern green	39.70 (39.76)	2.30 (2.81)	4.43 (4.88)	12.18 (12.35)	9.34 (9.73)	5.98	20
$[Zr(OH)_2(L^2)CH_3OI$	585.50	Dandelion	40.32 (41.03)	3.11 (3.27)	4.23 (4.78)	--	15.19 (15.58)	---	11

** Molar conductance values in ohm^{-1} cm^2 $mole^{-1}$.*

MAGNETISM AND DIFFUSE REFLECTANCE SPECTRAL STUDY

At room temperature the magnetic moment values of Fe(III) complexes for H_2L^1 and H_2L^2 are found to be 5.95 and 5.97 B.M. respectively, suggest presence of five unpaired and high spin octahedral geometry [17] which are close to 5.92 B.M. shown in table. This indicates that the ground state is sextet with S=1/2. In the ground state of d^5, Iron (III) ion is, ^6S transforms into $^6A_{1g}$ state. The absorption bands and tentative assignments of Fe(III) complexes are given in table 2. The electronic spectra of Fe(III) complexes of both synthesized Schiff's bases, exhibited three bands in the region 15432-15455 cm^{-1}, 19531-19455 cm^{-1} and 25125-25510 cm^{-1} which may be assigned to $^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$, $^6A_{1g}(S) \rightarrow {}^6T_{1g}(G)$

and $^6A_{1g}(S) \rightarrow {}^4E_g$, $^4A_{1g}(G)$ transition respectively. The Zr(IV) complexes of H_2L^1 and H_2L^2 are found to diamagnetic as expected from their electronic configuration with octahedral geometry. Diffuse reflectance spectra for Zr(IV) complexes of H_2L^1 and H_2L^2 shows broad band at 21645 cm^{-1} and 24691cm^{-1} are assigned due to LMCT transitions respectively [18].

Table 2. Diffuse reflectance spectral data of complexes

Compounds	Absorption bands (λmax)		Assignment
	nm	cm^{-1}	
$[Fe(L^1)Cl_2.H_2O]$	648 512 398	15432 19531 25125	$^6A_{1g} \rightarrow {}^4T_{1g}(G)$ $^6A_{1g} \rightarrow {}^6T_{1g}(G)$ $^6A_{1g} \rightarrow {}^4E_g, {}^4A_{1g}(G)$
$[Fe(L^2)Cl_2.H_2O]$	647 514 392	15455 19455 25510	$^6A_{1g} \rightarrow {}^4T_{1g}(G)$ $^6A_{1g} \rightarrow {}^6T_{1g}(G)$ $^6A_{1g} \rightarrow {}^4E_g, {}^4A_{1g}(G)$
$[Zr(OH)_2(L^1)CH_3OH]$	462	21645	LMCT
$[Zr(OH)_2(L^2)CH_3OH]$	405	24691	LMCT

INFRARED SPECTRAL STUDY

The IR spectra of the free Schiff base ligands are compared with spectra of their metal complexes (fig.1,2,3 and 4). The important IR bands with their tentative assignments are depicted in table 3. A medium broad band at 2995-2997 was observed for o-hydroxy schiff's bases due to intramolecular hydrogen bonding (OH----N=C). This band disappeared in the spectra of the complexes, indicate that phenolic oxygen atom undergo coordination via deprotonation [19]. This is further supported by upward shift of phenolic ν(C−O) band at 1301-1330 cm^{-1} and 1296-1292 cm^{-1} in the spectra of complexes as compared to free ligand H_2L^1 and H_2L^2 respectively. The ν(C=N) stretching band in free ligands H_2L^1 and H_2L^2 at 1589 cm^{-1} and 1583 cm^{-1} respectively was generally shifted to a lower frequency in complexes, indicating a coordinate bond formation between the metal and the imine nitrogen lone pair [17]. This was also confirmed on higher shift ν(N-N) band frequency. IR spectrum of the free ligands H_2L^1 and H_2L^2 contains a strong ν(C=O) absorption band at 1653-1654 cm^{-1} and N–H absorption medium band at 3190 -3194cm^{-1} respectively. Both of these bands disappear in Zr(IV) complexes and new C–O (enolic) absorption band appears at 1240-1253 cm^{-1} for complexes providing strong evidence for ligand coordination to the Zr(IV) ion in the enol from by losing its N–H hydrogen. While in Fe(III) complexes of both ligands, downfield shift of ν(C=O) bands (12-7cm^{-1}) was observed, which confirms keto form of ligands during complexation. The strong IR band at 1149-1153 cm^{-1} in Zr(IV) complexes is assigned to Zr−OH vibration. The ν(C−O) of CH_3OH occurs at 1048 cm^{-1} and this band undergoes a negative shift in both Zr(IV) complexes indicating methanol coordination. The absence of a new band in the spectrum of Zr(IV) complex in the range 850-960 cm^{-1} due to the ν(Zr=O) favors the Zr-OH bonding in complexes [20]. The broad band at 3402-3392, 1614-1600, 806-804, and at 732-736 cm^{-1} in the IR spectra of the Fe(III) complexes are referred to ν(OH), ν(H_2O), δ*r*(H_2O) and δ*w*(H_2O) vibrations for the coordinated water molecule. The IR spectra of metal complexes showed new bands in 424-478 cm^{-1} range assigned to (M–N) and 511-538 cm^{-1} range assigned to (M–O) modes [21].

Table 3. Infrared spectral data of ligand and its complexes (cm^{-1})

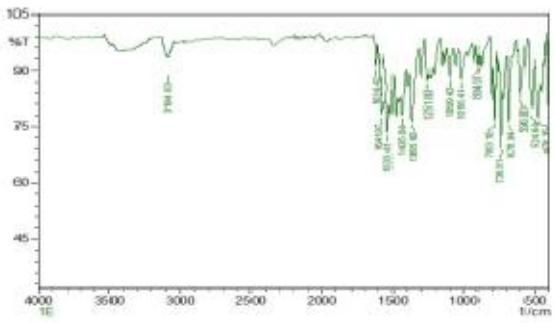


Fig.1. IR spectra of $[Fe(L^1)Cl_2.H_2O]$

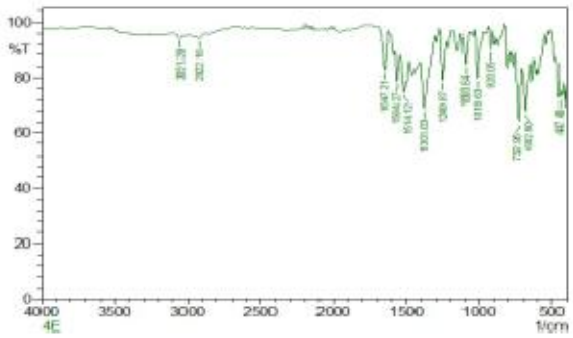


Fig.2. IR spectra of $[Fe(L^2)Cl_2.H_2O]$

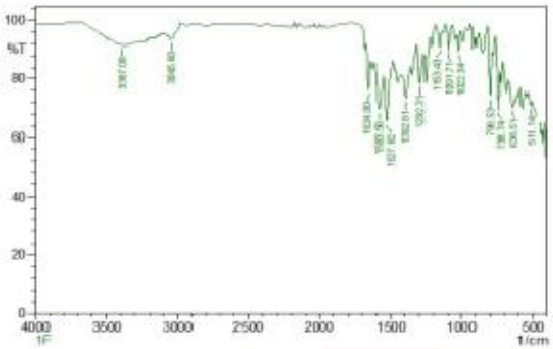


Fig.3.IR spectra of $[Zr(OH)_2(L^1)CH_3OH]$

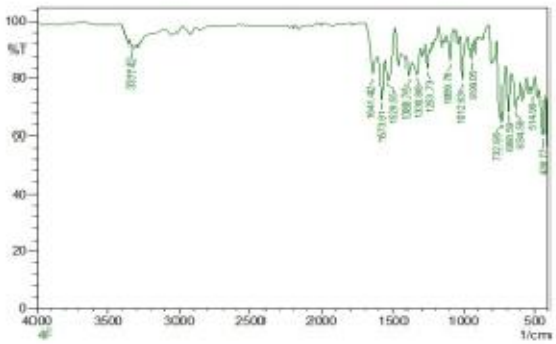


Fig.4.IR spectra of $[Zr(OH)_2(L^2)CH_3OH]$

^{1}H-NMR and ^{13}C-NMR spectral study

^{1}H-NMR spectra of ligands H_2L^1 and H_2L^2 were recorded in DMSO-d_6 presented in table 4. and ^{1}H-NMR spectra of ligand H_2L^2 was given in fig. Schiff base H_2L^1 exhibits, a singlet at δ14.4 ppm due to phenolic proton, a singlet at δ11.6 ppm due to –NH proton, a singlet at δ2.53 ppm due to methyl proton, multiplet of aromatic protons (10H) at δ7.5-δ8.3 ppm. From ^{1}H-NMR spectra of ligand H_2L^2 (fig.5) shows, a singlet at δ14.85 ppm due to phenolic proton, a singlet at δ11.68 ppm due to –NH proton, a singlet at δ2.51 ppm due to methyl proton [22], multiplet of aromatic protons (10H) at δ7.15-δ8.36 ppm.

Additional support for the structure of synthesized ligands was provided by ^{13}C-NMR spectrum given in table 4. In case of H_2L^1 ligand (fig.6) chemical shift values in ppm at δ 167.80, δ 159.74, δ 158.78, δ 135.15 – δ 118.16 and δ 14.95 are observed due to C=O, C-OH, C=N, Ar-C, CH_3 respectively [23]. While for H_2L^2 ligand chemical shift values in ppm are observed at δ 168.10, δ 158.97, δ 157.38, δ 135.11 – δ 117.86 and δ 14.78 are observed due to C=O, C-OH, C=N, Ar-C, CH_3 respectively.

Ligand/ Complexes	ν(OH)+ ν(NH)	ν(NH)	ν(C=O)	ν(C=N)	ν(N−N)	ν(C−O) phe	ν(C−O) enolic	ν(M−O)	ν(M−N)
H_2L^1	2995	3190	1653	1589	1020	1288	---	---	---
Fe(III)	---	3194	1641	1562	1018	1296	---	524	478
Zr(IV)	---	---	---	1583	1022	1292	1240	511	424
H_2L^2	2997	3194	1654	1583	1014	1288	---	---	---
Fe(III)	---	3197	1647	1564	1018	1301	---	538	447
Zr(IV)	---	---	---	1573	1012	1330	1253	514	439

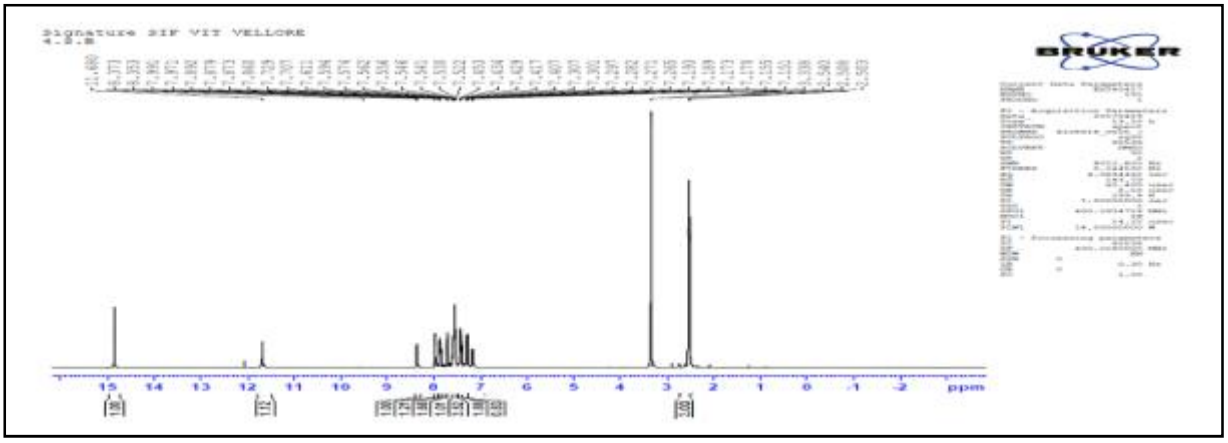


Fig. 5. ^{1}H-NMR spectra of H_2L^2 ligand

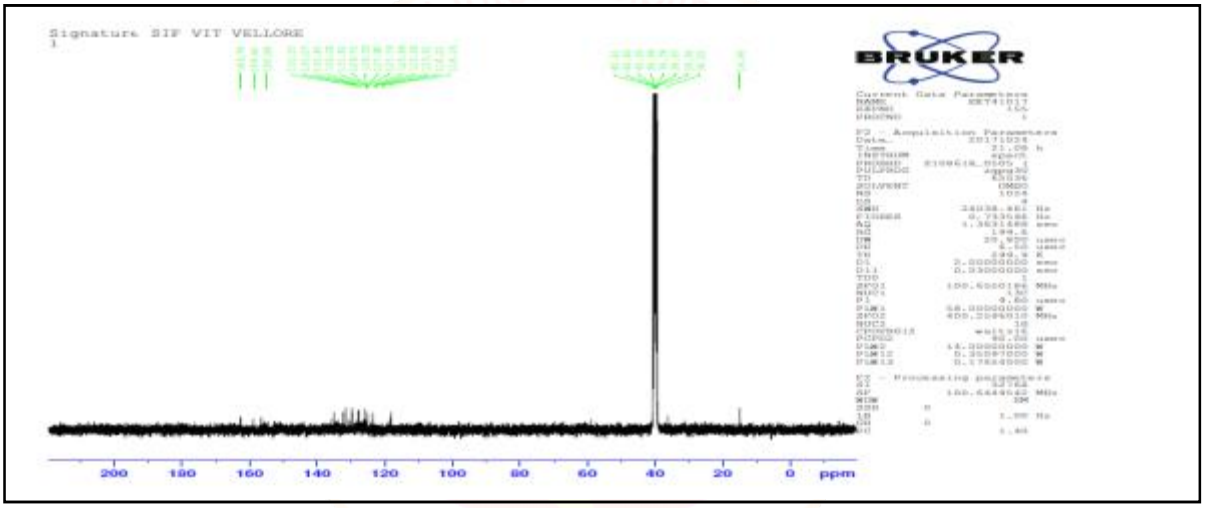


Fig. 6. ^{13}C-NMR of ligand H_2L^1

Table 4. ^{1}H NMR spectral data of ligand H_2L

Compounds	Chemical shift ^{1}H NMR δ ppm	Peak, no. and type of proton	Chemical shift ^{13}C NMR δ ppm	Peak and type of carbon
H_2L^1	δ 14.74	1H (S) -OH (phenolic)	δ 167.80	C=O
	δ 11.62	1H (S) -NH (imino)	δ 159.74	C-OH
	δ7.25-δ8.29	10H (m) Ar-H	δ 158.78	C=N
	δ 2.52	3H (S) -CH_3	δ 135.15 – δ 118.16	Ar-C
			δ 14.95	CH_3
H_2L^2	δ 14.85	1H (S) -OH (phenolic)	δ 168.10	C=O
	δ 11.68	1H (S) -NH (imino)	δ 158.97	C-OH
	δ 7.15- δ 8.36	10H (m) Ar-H	δ 157.38	C=N
	δ 2.51	3H (S) -CH_3	δ 135.11 – δ 117.86	Ar-C
			δ 14.78	CH_3

THEMOGRAVIMETRIC ANALYSIS

Decomposition of H_2L^1 (fig. 7a) and H_2L^2, Fe(III) complexes starts from 148˚C and 150˚C with weight loss 18.28% and 20.82%, corresponds to one coordinated water molecule and two chloride ions respectively [24]. Gradual weight loss for the second step with 42.85% and 46.98% weight loss, in the temperature range 200-480˚C and 210-510˚C represent partial decomposition of ligand H_2L^1 and H_2L^2 moiety respectively. Further

decomposition of remaining part of ligand H_2L^1 and H_2L^2 was continued >600˚C with weight loss 9.25% and 8.67% with high residue about 29.62% and 23.53% respectively was due to some organic part and metal oxide.

For Zr(IV) complex of ligands H_2L^1 and H_2L^2 (fig. 7b) decomposition starts at 165˚C and 160˚C with 7.835% and 8.241% weight loss which could be due to loss of one methanol molecule and at 240˚C and 248˚C the quantitative partial elimination of ligand takes place with 40.73% and 39.87% weight loss, followed by gradual weight loss 13.24% and 12.64% above 500˚C-520˚C respectively. Oxidative thermal decomposition proceeds slowly with a final residue 38.19% and 39.25%. It is clear that, the TG thermograms for the investigated complexes displayed high residual part indicating high stability of the formed chelates [25].

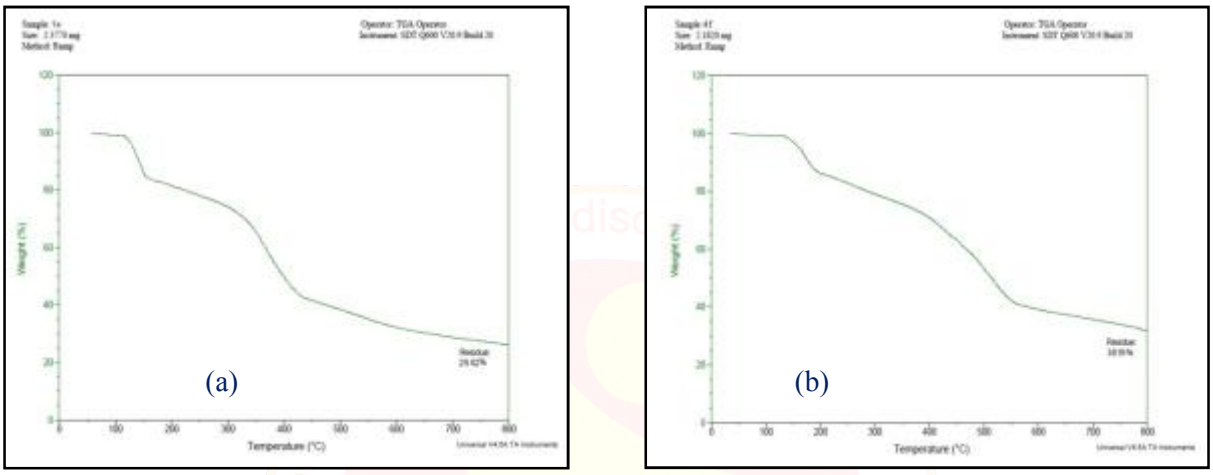


Fig. 7. TGA spectra of (a) $[Fe(L^1)Cl_2.H_2O]$ and (b) $[Zr(OH)_2(L^2)CH_3OH]$

ANTIMICROBIAL STUDY

The antibacterial activity results presented in table 5 reveals that all synthesized ligands H_2L^1 and H_2L^2 and their respective complexes exhibited higher antibacterial activity than standard *Penicillin* when tested against *E. coli* bacteria. Zr(IV) complex of ligand H_2L^2 was inactive against *B. Subtilius*. Antibacterial activity of Zr(IV) complexes was higher than Fe(III) complexes.

In antifungal study of Fe(III) complexes of both ligands, against *F. moneliforms* possess more than 90% reduction in growth. While all ligands and their complexes exhibits reduction in growth of inhibition against all fungal strains. From table it os observed that antimicrobial activity of H_2L^1 complexes are more active than H_2L^2 complexes. This is due to the presence of more electronegative –Cl group present in H_2L^1 ligand [26]. Generally it is indicated that the ligands are less active to entire array of tested microorganism, while complexes have strong antimicrobial activities. This can be well explained due to the chelation according to Tweedy's chelation theory [27].

Table 5. Antibacterial (mm) and antifungal activity of ligand H_2L^1, H_2L^2 and its metal complex
n. a.- No activity

Ligand/ complexes	Antibacterial activity(mm)				Antifungal activity			
	Gram -ve		Gram +ve					
	E. coli	S. typhi	S. aureus	B. subtilius	A. niger	P.chrysogenum	F.moneli forme	A. flavus
H_2L^1	15	n.a.	15	11	RG	RG	RG	+ve
Fe(III)	17	14	16	14	RG	RG	-ve	RG
Zr(IV)	17	15	16	12	RG	RG	RG	RG
H_2L^2	14	n.a.	15	n.a.	RG	RG	-ve	RG
Fe(III)	16	12	14	11	RG	RG	-ve	RG
Zr(IV)	13	15	12	n.a.	RG	RG	RG	RG
Penicillin	11	24	36	30	-	-	-	-
Griseofulvin	-	-	-	-	-ve	-ve	-ve	-ve

+ve – Growth (Antifungal Activity absent)
-ve – No Growth (More than 90% reduction in growth, Antifungal Activity present)
RG – Reduced Growth (More than 50% and less than 90% reduction in growth)

CONCLUSION

From the present investigation it has been observed that Schiff bases H_2L^1 and H_2L^2 was monobasic tridentate towards Fe(III) and dibasic tridentate towards Zr(IV) complexes. It was further confirmed by the analytical, IR, electronic, magnetic and thermal studies. Analytical and physicochemical studies reveals that the octahedral geometry was assigned for Fe(III) and Zr(IV) complexes. All synthesized metal complexes exhibits higher antimicrobial activity than their respective ligands. Generally ligands and its complexes both exhibits higher activity against *E. Coli* bacteria than standard *Pencillin*. From the results it was observed that complexes of ligand H_2L^1 shows higher activity against all tested strains as compared to complexes of H_2L^2 ligand, it shows that presence of more electronegative group (-Cl) enhances antimicrobial activity as compared to less electronegative group (-I).

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SYNTHESIS, CHARACTERIZATION AND BIOLOGICAL ACTIVITY OF NOVEL BIS - DIKETONES

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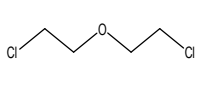
ABSTRACT

4,6- Diacetylresorcinol was obtained by the acylation of resorcinol .The Baker –Venkataramn transformation using NaOH in dimethylsulphoxide (DMSO)77 have been employed for the coversions of ester(o-aroyloxy/heteroaroyloxyacetophenones) into the corresponding bis β-diketones .Bis- β diketones have been synthesized in good to excellent yields. The reaction is carried out regardless of pyridine having unpleasant smell and very difficult to remove it forms the reaction mixture. The structures of these compounds were confirmed by IR, NMR and Mass spectral studies. The titled compounds were screened for qualitative (inhibition zone) and quantitative antimicrobial activity (MIC) by agar well diffusion method . The minimum inhibitory concentration represents the concentration of antimicrobial at which there is complete inhibition of growth of organism. The synthesized compounds were tested for their antibacterial activity against Gram +ve (Bacillus subtilis and Micrococcus albus) and Gram –ve (Escherichia coli and Pseudomonas vulgaris) bacteria.

Keywords: *Bis-β-Diketones, 4,6-Diacetyl resorcinol ,DMSO(Dimethyl sulfoxide), Spectral analysis, Antibacterial activity , Agar well diffusion method.*

INTRODUCTION

Bis compounds are the compounds in which two identical groups are attached to the given atom[1], e.g. bis-(2-chloroethyl) ether **1**, bisphenols **2** and **3.** [2-3]



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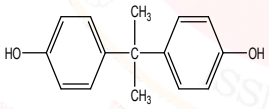

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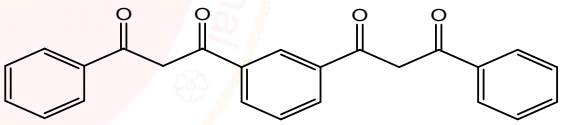
However, molecules containing identical groups in the same structure unit or ring system have also been considered as bis compounds[4-6].The examples are 1,3-bis (3-phenyl-3-oxopropanoyl)benzene **4**,1,4-Bis(3-phenyl-1,3-propanedion) benzene



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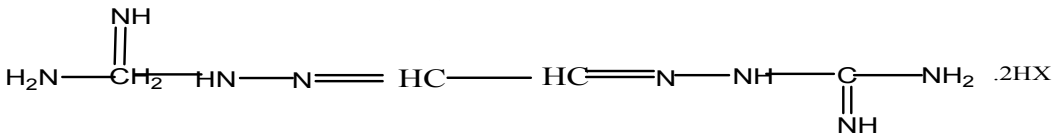
Bis compounds have found to possess numerous applications. Glyoxal bis (guanylhydiazone) **4** an example of Bis(guanylhydrazones) of simple 1,2-dicarbonyl compounds was found to be active against L1210 leukemia [7-12].



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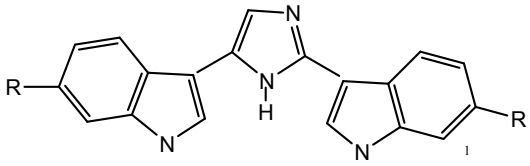
Their N-indolyl methylated derivatives showed significant improvement in [13-15] P388 activity compared with that of the parent compounds. 2,4-Bis(30-indolyl)thiazole analogues **6** exhibited cytotoxicactivities against a wide range of human tumor cell lines at micromolar concentration.

Also 2,5-bis(30-indolyl) pyrazines and 3,6-(30-indolyl)2-(1H)pyrazinone showed inhibitory activity against a variety of human tumor cell lines with GI50 values that reached submicromolar level[17-18.] Bis (3-arylimidazolidinyl-1) methanes **7** and corresponding bis 1,3-azoles reported to posses antimicrobial activity [19-22].



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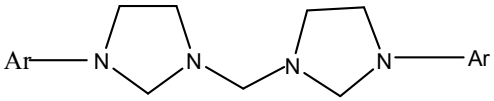
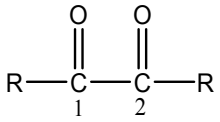


7

β-Diketones are the compounds having two carbonyl (>C=O) groups in their molecule. Depending upon the position of these carbonyl groups; they are designated as α-diketones (1,2-diketone) **1**, β-diketones (1,3-diketone) **2** and γ – Diketones
(1,4-diketone) **3**.



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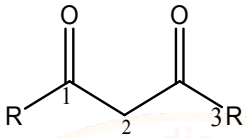

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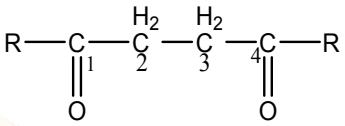
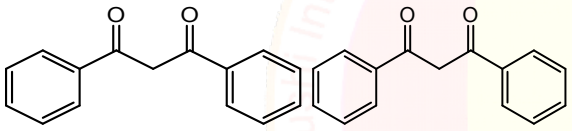


3

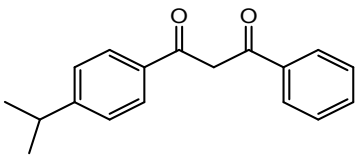
Dibenzoylmethane (DBM, 1,3-diphenyl-propanedione) **8**, has shown to display anti-inflammatory and anti-tumor activities



8 **8**

Dibenzoylmethane (DBM, 1,3-diphenyl-propanedione) **8**, has shown to display anti-inflammatory and anti-tumor activities. In female rats, DBM was an effective inhibitor of in vivo mammary tumors promoted by 7,12-dimethylbenz[a]anthracene and of 7,12-tetradenoylphorbol-13-acetate-induced skin tumors in mice[31]. Recently, the effect of DBM on prostate cancer cell growth has been reported. The sunscreen derivatives from DBM, Eusolex† 8020 **9** and Parsol†1789 **10,** are more efficient in the UVA range because they revent the penetration of the radiation to vital cellcomponents and block over production of oxygen derived free radicals. The use of sunscreen products has been recommended by many health care organizations as a means to reduce skin damage produced by UV radiation from sunlight.

Dibenzoylmethane (DBM) derivatives have been extensively employed in the formulation of UVA sunscreens as well as in cosmetic products photochemistry ofthese compounds involves mainly the formation of transient enol isomers[23-29]. In the ground state, these compounds present keto-enol equilibria where the intramolecularly hydrogen bonded enol ‘‘chelated’’ form is largely favored (EC). This enol form shows a strong absorption band around 340–350 nm, while the keto form (K1) absorbs in the range 260–280 nm. The absorption of UVA light produces the excited enol state (S1) whose main deactivation pathway involves an intramolecular hydrogen bond cleavage and a subsequent formation of a non-chelated enol (Z-isomer)[32].



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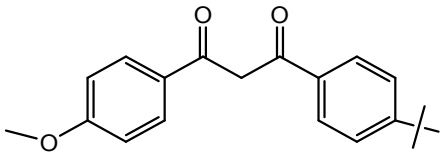

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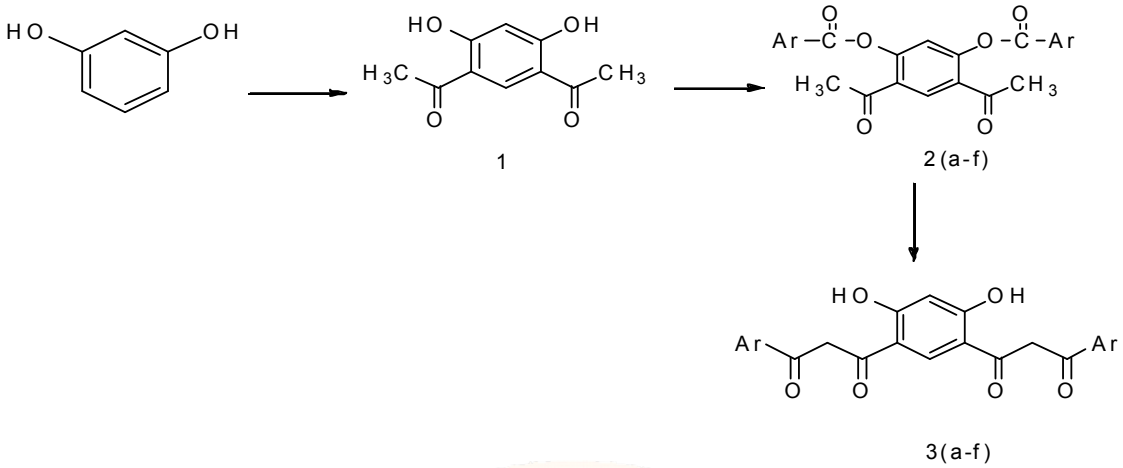
Scheme



Ar = Phenyl, chlorophenyl,methoxyphenyl, touyl, 2-thieny, 3-pyridyl etc.

EXPERIMENTAL METHOD AND MATERIALS

In our preliminary experiment 4,6-Diacetylresorcinol **1** with benzoyl chloride in pyridine furnished the corresponding 1,3-Dibenzoyloxy-4,6-diacetophenones **2** in cold condition, which on further rearrangement affords synthesis of 3,3'-(4,6-dihydroxy-1,3-phenyl)- bis -(1-aryl/heteroaryl propane1,3diones) **3** in 67% yields. The Baker –Venkataramn transformation using NaOH in dimethylsulphoxide (DMSO) have been employed for the conversions of esters (o-aroyloxy/heteroaroyloxyacetophenones) into the corresponding β-diketones . The reaction is carried out regardless of pyridine having unpleasant smell and very difficult to remove it form the reaction mixture (**Scheme1**).

4,6-Diacetyl resorcinol was prepared by acylation from resorcinol and $ZnCl_2$. Resorcinol PoCl3, DMSO, anhydrous $ZnCl_2$ different aromatic acids, solvents and all other chemical used of synthetic grade obtained from local dealer.

METHODS

The following procedures have been adopted for the preparation of 4, 6-Diacetylresorcinol (resdiacetophenones), 1,3-Diaroyloxy / hetero-aroyloxy- 4,6 Diacetophenones, 3,3'-(4,6-dihydroxy-1,3-phenyl) bis (1-aryl/heteroaryl propane-1,3dione)s.

4,6- Diacetylresorcinol (resdiacetophenones)[42]. Resorcinol (20.0g, 0.181mole) was dissolves in (42.65g, 0.4178 mole) of acetic anhydride (63.16g, 0.4644 mole) of ZnCl2 was added and the mixture was heated. After 3hours of the mixture at 150° to 160°C, 4,6-diacetylresorcinol crystallized out. After cooling, 25g of water was added for hydrolyzing the remaining acetic anhydride, then 40g of methanol was added and, for growing crystals, the resulting mixture was heated under reflux for 30 minutes, then cooled and subjected to solid–liquid separation. The solid was washed with 168g of methanol and then dried where by 26.03g (0.1340mole) of 4,6-diacetylresorcinol was obtained. The yield was 73.8 % on the resorcinol basis.

2. **1,3-Dibenzoloxy-4,6-diacetophenone**:4,6-Diacetylresorcinol (resdiacetophenones) (0.1 mole) and dry pyridine (10ml), Benzoyl chloride (0.2 mole) was added slowly maintining the temp. below 20°c. The reaction mixture was kept overnight and poured on a mixture of ice and HCl. Generally a solid compound separated which was washed with water and dilute NaOH solution and crystallized from ethanol.The yield is 70% m.p-90°c. The other 1,3-Diaroyloxy/heteroaroyloxy-4,6-diacetophenone were **2b-f** prepared by adopting the same procedure.The physical and analytical data of the compounds **2a-f** are given in Table-1.
3. **3,3'-(4,6-dihydroxy-1,3-phenyl) bis (1-phenyl propane-1,3dione).** 1,3-Dibenzoyloxy-4,6-diacetophenones (0.005moles) was dissolved in 4ml of DMSO. To that solution powdered NaOH (2g) was added with vigorous stirring for about five minutes. The stirring was continued for about 5 min further. The reaction mixture was then cooled and poured on cold

water. The pale yellow solid product obtained was washed with water dried and crystallized from alcohol.The yield 67% and m.p 121°c

In the same way, the other **3b-f** were prepared by adopting the same procedure. The physical and analytical data of the compounds **3a-f** are given Table-1

RESULT AND DISCUSSION

The products (entry 3**a- 3f**) were characterized based on their IR, ^{1}H NMR, Mass and elemental analysis. The mass spectra of these compounds displayed molecular ion peaks at appropriate m/z values. This synthetic stratagy is more attractive than earlier methods due to easily recoverable and reusable catalyst, easy workup and higher yields of the product.

33,3'-(4,6-dihydroxy-1,3-phenyl) bis (1-phenyl propane-1,3dione):IR(KBr)vmax= : 3568cm^{-1} (OH peak) ,1655cm^{-1} (C=O) , 1589cm^{-1} (C=C), 29261cm^{-1} (aromatic stretching C-H); ^{1}H NMR(CDCL$_3$) : δ: 3.19(s, H,CH$_2$), δ (12.95) (S,1H, phenolic –OH adjacent to carbonyl group), δ 7.42-8.18 (m,12H, Aromatic),EI-MS-m/z403(M+.1); Anal.Calc.for $C_{24}H_{18}O_6$ Found : C, 71.60; H,4.40; requires C, 71.64;H, 4.47 %] In the 1H NMR Spectra it enolic proton and at 12.02 which is gives characteristic peak at 12.72 which corresponds to enolic proton and at), δ 12.02 which is being due to phenolic proton adjacent to carbonyl group. It confirms the formation of -diketones. The compound in enolic form is more stable than that of ketonic one.

Synthesis of 3,3'-(4,6-dihydroxy-1,3-phenyl) bis(1-aryl/heteroaryl propane 1,3dione)3a-h

Compounds	Ar	MP	Time (min)	Yield(%)[c]
3a	C_6H_5	121	50	86
3b	4-OMe- C_6H_5	155	55	90
3c	4-Cl-C_6H_5	135	45	83
3d	4-CH_3-C_6H_5	130	60	88
3e	2-Thienyl	120	45	84
3f	3-pyridyl	125	70	90
3g	4-Br-C_6H_5	128	60	85
3h	4-F- C_6H_5	130	50	80
3i	4-CF_3 C_6H_5	121	60	75

ANTIBACTERIAL ACTIVITY

The preminary antibacterial activity of synthesized compounds **(3a-f)** was studied against two different strain of Gram–negative E.coli, P.vulgaris and Gram positive *Bacillus subtilis* on *Micrococcus albus*. The screening of antimicrobial activity was carried out using the well diffusion method (*Perez etal*[44].,) This method depends on the diffusion of drug from cup through the modified agar layer of a Petri dish to an extent such that growth of the inoculated microorganism is prevented entirely in a circular area “zone” around the cup contining the solution of the compound under test. The most widely used type of assays for identifying antimicrobial activity are the so called diffusion method, which exploits diffusion of antimicrobial compounds through agar media to demonstrate inhibition of bacteria. The use of agar diffusion in the antimicrobial assays recommended by the United States Food and Drugs Administration (USFDA) and the National Committee for Clinical Laboratory Standards (NCCLS).

The basic idea of diffusion assays is as follows: a suspected antimicrobial compound or treatment is presented within a reservoir created on an inoculated plate of agar medium; following diffusion of the compounds (s) through the agar, a “halo” or “zone of inhibition” forms where concentration of the diffused molecules is sufficient to inhibit microbial growth. On the surface theory is quite simple. Diffusion of antimicrobial compounds from a reservoir over time produces an outward gradient of decreasing concentration of the compound. Where concentration of the compound is sufficient to inhibit the growth of the microbes, the growth is blocked; resulting in the observerd zone, which extends outward from the reservoir (with a corresponding decrease in concentration) to the distance from the reservoir at which the minimum concentration required for inhibition exists.

(i) Composition of the media [31,33]. Antibiotic Assay Medium for subculturing (for antibacterial activity) :

Peptone	:	6.0g
Pancreatic digest of casein	:	4.0g
Yeast extract	:	3.0g
Beef extract	:	1.5g
Dextrose	:	1.0g
Agar	:	1.5g
Distilled `	:	Up to 1000 mL(pH 6.6)

The medium was sterilized by autoclaving at 151b pressure for 30 minutes. One loopful of the stock culture was inoculated to 10 mL of agar slant previously in sterilized test tubes , and incubated at 37°C for 24 hours for bacteria[34,35] . About 3ml of distilled water was added to the test tube and a suspension of the culture was obtained by shaking for few minutes.

Stock solution. The test compound (100mg) was dissolved in methanol (10ml), and volume was made upto 100 ml with sterilized distiiled water to produce a concentration of 100 µ/ml. Similarly, the dilutions were prepared for standard drugs i.e., neomycin, erythromycin.

(ii) Control parameters: (a) Media control. Sterilized medium was kept for growth (approx.48h) so as to assure the sterility of the medium. If this control shows growth If any type, then the media were discarded.

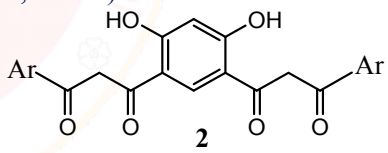
(iii) Culture control. The culture of the organism was inoculated in sterilized medium. If no growth was observed, then the culture was considered to be faulty. The fresh culture was prepared.

(iv) Solvent control. The stock solution was suspended in culture. The organism was inoculated and growth was observed. If the growth i s not observed, it can be concluded that solvent inhibited the growth of the organism and hence, the results were considered invalid.

v) Turbitity control. The turbidity was observed in the media containing different drug dilutions. If turbidity was recorded, the media and stock solution was prepared a fresh.

All the operations were carried out under aseptic conditions. Respective sterile medium was melted on water bath and kept at 37^{0}C in constant temperature water bath. The well diffusion method was used in the antibacterial screening procedure with methanol extract of synthesized compounds. The cultures of above bacterial strains were inoculated in 10mL nutrient agar medium was sterilized by autoclaving. To this sterilized nutrient medium 1 mL of one day old bacterial culture was added and stirred well; this medium was poured into pteri dishes. The well impregnated with 100 µg/mL of newly synthesized 1, 3-diones were introduced aseptically in the nutrient agar plate. The neomycin and erythromycin were used as control. All the nutrient agar plates were incubated at 370C for 24hrs after which the plates were observed for clear zone of inhibition.

Table **2.1** Antibacterial activity of 3, 3'-(4,6-Dihydroxy-1,3-phenyl) bis (1-aryl/ heteroaryl propane 1,3dione) **3a-f**



2

Compd No	Gram-positive			Gram-negative
	M. albus	*B.substilis*	*E.coli*	*P.vulgaris*
3a	15.15	15.78	12.45	13.30
3b	16.12	14.90	11.40	-
3c	14.98	13.23	-	10.99
3d	13.14	16.24	13.75	12.55
3e	14.95	15.54	15.50	14.90
3f	15.67	11.90	16.45	14.25
Std 1	25.78	26.12	26.12	25.29
Std 2	26.11	27.12	27.45	25.10

(i) Minimum Inhibitory Concentration (MIC) 100µgmL^{-1} (ii) Diameter of inhibition zone in mm (iii) **Std 1** Neomycin (iv) **Std 2** Erythromycin – No zone of inhibition

CONCLUSION

The result reveals that novel bis β-diketones were significantly effective against bothGram–positiveand Gram-negative organisms.

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CONDUCTOMETRIC MEASUREMENTS OF SUBSTITUTED THIOCARBAMIDO NAPHTHOL

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ABSTRACT

This is a developing era for various innovations in chemical, industrial and pharmaceutical and medicinal sciences. Recently researchers can be determined the significances and applications of synthesized molecule in various sciences with the help of conductrometric measurements. Conductrometric study provided valuable information regarding to transport properties of drugs. This type of measurements and studies become interdisciplinary bridge in between chemical and biological sciences. Considering all these facts we determined the conductrometric parameters (viz. G, k and μ) and thermodynamic parameters (viz. ΔH; ΔSand ΔG) of 5-phenylthiocarbamido-1-naphthol at different concentration and 308 K in 80% ethanol water mixture.

Keywords: *5-Phenylthiocarbamido-1-naphthol, conductrometric parameter, and thermodynamic parameter.*

INTRODUCTION

Conductivity is a good tool in pharmacodynamics study of drugs. Transport property and permeability of drugs efficiently influence by conductivity of electrolyte, these two are prime biopharmaceutical parameters which are accountable for effective bioavailability and good in vitro and vivo correlation[1]. Nowadays pharmaceutical technologist has a great challenge to raise the solubility and dissolution rate and oral bioavailability of weakly water soluble drugs[2]. Hydrotropic Salisation is considered as one of the sophisticated methods of solubalisation[3]. Enhance the aqueous solubalisation of insoluble drugs by adding hydrotropic agents, number of researchers work on the effect of solubility enhancers[4,5]. The valuable information about solute-solute and solute-solvent interactions obtains from the coductometric measurements[6]. Gomaa and Al-Jahdalli[7] was investigated ionic association of divalent asymmetric electrolyte $Cu(NO_3)_2$ with Kryptofix-22 in mixed (MeOH-DMF) solvents at different temperatures by conductometric measurements. Conductometric measurements of the alkali metal at different proportion of mixed solvents were carried out by Izonfuo and Obunwo[8] and Roy et al[9]. Very few researchers investigated the thermodynamic parameter and Walden product of different complexes and they also examine the comparison of transition metal complexes among the halide group[10-14]. An ion pair formation and thermodynamic parameters of Glycine Bis-1-amidino-O-methylurea cobalt (III) halides in water-methanol mixture at different temperatures was investigated by Singh et al[15]. Recent work deals with determination of thermodynamic parameters viz. ΔH; ΔS and ΔG study of 5-phenylthiocarbamido-1-naphthol by conductometric measurements at different concentrations and constant temperature 308 K in 80% ethanol-water mixture. This study also contributes to solvent-solvent, solute-solvent and solute-solute interactions and the effects of various substituents.

MATERIALS AND METHODS EXPERIMENTAL

Freshly prepared solution used for analysis. The solvents were purified by standard method. 0.01M, 0.005M, 0.0025M and 0.0012M solutions of 5-phenyl thiocarbamido-1-naphthtol 80% ethanol-water mixture were prepared. Maintain Thermal equilibrium at 308K of solution was maintained by using thermostat. After getting thermal equilibrium, conductivity of that electrolyte solution was measured.

RESULT AND DISCUSSION

Firstly 0.01 M concentration of solution was prepared then by serial dilution method solutions of 0.005M, 0.0025M and 0.0012M with 80%

ethanol-water mixture were prepared. Conductance of each solution by using Conductivity Bridge at 308 K was measured. The results obtained are given in Table-1 to Table-2. From the data observed conductance (G), specific conductance (k) and molar conductance (μ) were determined by known literature method.

TABLE – 1 - CONDUCTOMETRIC MEASUREMENTS AT DIFFERENT CONCENTRATIONS OF 5-PHENYLTHIOCARBAMIDO-1-NAPHTHOL

The values of G, k and μ AT DIFFERENT CONCENTRAT AND 308 K

% of solution (Ethanol-water)	Concentration C(M)	Observed conductance (G)	Specific conductance (k)	Molar conductance (μ)
80%	0.01 M	0.0309	0.03684	3.68487
	0.005 M	0.01656	0.02055	4.11067
	0.0025 M	0.01119	0.01021	4.08422
	0.0012 M	0.00904	0.00871	7.25840

From Table 1 it was noted that observed conductance (G) and specific conductance (k) decreases and molar conductance (μ) increases along with decreasing concentrations. The specific conductance increases with increasing temperature. Specific constant (Ksp), log (Ksp) and thermodynamic parameters viz. (ΔG), (ΔS) and (ΔH) of 5-phenylthiocarbamido-1-naphthol were calculated by known literature methods at different concentrations at 308K. Results are computed in **Table 2**.

TABLE – 2 - CONDUCTOMETRIC MEASUREMENTS AT DIFFERENT CONCENTRATION OF 5-PHENYLTHIOCARBAMIDO-1-NAPHTHOL at 308 K

SYSTEM: LIGAND [PTCN] MEDIUM - 80% ETHANOL-WATER

Temp. (K)	Conc. M	Ksp	Log Ksp	ΔG	ΔH	ΔS
308	0.01	0.0970	4.30373	-24968.44	-80244.5	347.237
	0.005	0.0155	4.81081	-27910.3	-89699	388.15
	0.0025	0.00739	5.1311	-29768.49	-95671.5	413.993
	0.0012	0.00486	5.31857	-30856.15	-99166.7	429.118

The change in thermodynamic parameters values closely affected by temperature, molar concentrations and percentage compositions. These parameters shackle by another factors viz. the solute (drug)-solvent interactions, solvent-solvent interactions, solvent-solvent-solute interactions and –solute-solute-solvent interactions. Variation in these parameters affected by the internal geometry as well as internal and intra hydrogen bonding

As observed, μ values increase with decreasing in concentration indicating less solvation or higher mobility of ions. This is due to the fact that increased thermal energy results ingreater bond breaking due to dilution. Also negative values of ΔG indicate that reaction is spontaneous. Negative values of enthalpy change (ΔH) suggest exothermic reaction. Favorable at lower temperature and positive value of (ΔS) revels entropically favorable. The change in thermodynamic parameters values closely affected by molar concentrations and percentage compositions. These parameters shackle by another factors viz. solute (drug)-solvent interactions, solvent-solvent interactions, solvent-solvent-solute interactions and –solute-solute-solvent interactions. Variation in these parameters affected by the internal geometry as well as internal and intra hydrogen bonding

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GREEN SYNTHESIS OF 2-SUBSTITUTEDIMINO-4-AMINO-6-ALLYL FORMAMIDINO-1,3,5-THIADIAZINES

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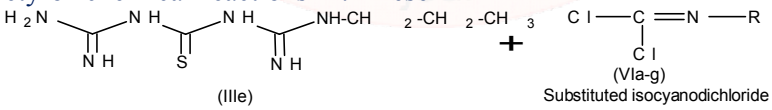
ABSTRACT

Non-conventional synthetic method has shown broad applications and an efficient way to accelerate the course of many organic reactions, producing high yields, higher selectivity and lower quantities of side products consequently easier work-up and purification of the products. One-pot two component condensation of 1-formamidino-5-formamidonothicarbamide with various isocyanodichlorides were carried out in presence of lemon juice as a biocatalyst respectively to synthesize a novel series of 2-substitutedimino-4-amino-6-allylformamidino-1,3,5-thiadiazines which are heither to unknown. The structures were confirmed by conventional chemical characterization, elemental analysis and spectral studies.

Keywords: *Lemon Juice, Various Isocyanodichlorides, 1-Formamidino-5-Allylforma- Midonothicarbamide*

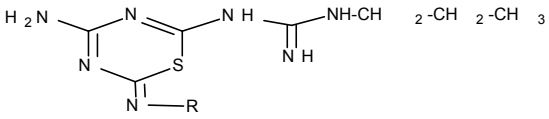
INTRODUCTION

In the recent years chemical research has been focused on an eco-friendly, environmentally benign process to reduce an impact of an environmental pollution. Green Chemistry[1-4] is placed in the frontier areas in this regard which involves design, development and implementation of the performance criterion. So 'greening' of conventional reactions is done to meet the ever increasing demands of selectivity in modern synthesis[5]. In bio-catalyst method of synthesis use of non classical forms of energy is done to modify the time duration and product yield by avoiding the undesired side products[6,7]. Microwave heating and sonochemical methods have emerged as a powerful energy and time saving techniques to promote a variety of chemical reactions[8-12]. These reaction methods, under solvent-free conditions are eco-friendly by reducing pollution and offer low cost, facile, safe and reproducible experimental procedures[13]. Therefore by using lemon juice as a biocatalyst[14-15] technique has gained popularity in past decade as a powerful tool for rapid, economic and efficient synthesis of variety of compounds. Literature survey reveals example of specific reactions, which do not occur under conventional conditional heating, but could be possible by lemon juice with good product yields. The present work describes suitable, convenient and somewhat direct method for the synthesis of 2-substitutedimino-4-amino-6-allylformamidino-1,3,5-thiadiazines as depicted below,



(IIIe)
1-Formamidino-5-phenylformamidinothiocarbamide

(VIa-g)
Substituted isocyanodichloride



(XIIa-g)
2-Substitutedimino-4-amino-6-allylformamidino-1,3,5-thiadiazines

METHOD AND METHODOLOGY

All reagents were purchased from commercial suppliers and were purifide. Dry methanol and diethyl ether were purchased from Aldrich and were used as such. All reactions were run in oven-dried round bottom flask or vial containing a teflon-coated stir bar and sealed with septum. Analytical thin layer chromatography was carried out on silica pre-coated glass plates (Silica gel 60 F254, 0.25 mm thickness) and visualized with UV light at 254 nm. ^{1}H NMR spectra were recorded on Bruker 400-MHz Ultrashield Advance II 400 model (400 and 100 MHz, respectively) at ambient temperature with $CDCl_3$ or DMSO-d6 as solvents. $CDCl_3$ (δ 7.26 ppm), DMSO-d6 (δ 2.50 ppm) or with tetramethylsilane (TMS, δ 0.00 ppm) as the internal standard. Chemical shifts (δ) were reported as part per million (ppm) in δ scale downfield from TMS.

RESULT AND DISCUSSION

Synthesis of 2-ethylimino-4-amino-6-allylformamidino-1,3,5-thiadiazine

Interaction of 1-formamidino-5-allylformamidonothiocarbamide (0.1M), ethyl isocyanodichloride (0.2M) and freshly extracted lemon juice (20 ml) was carried out in presence of sun light, brown crystals were obtained and these were washed several times with water, recrystalised from ethanol. Yield 96%, melting point 210^{0}C. Properties: Gave positive test for nitrogen and sulphur. Desulphurized by alkaline plumbite solution, indicate presence of C=S group. Formed picrate having melting point 180^{0}C. **Elemental analysis: [**C: 39.37% (found), 40.41% (calculated)], [H: 04.60% (found), 05.50% (calculated)], [N: 41.17% (found), 41.17% (calculated], [S: 13.20% (found), 14.68% (calculated)]. **IR Spectrum**: [KBr-pellets (cm^{-1})] : 3358.29 N–H stretching, 2920.64 C-H stretching, 1665.78 N=C-N stretching, 1150.99 C-N stretching. **NMR Spectrum: [**DMSO-d_6 and $CDCl_3$, (δ, ppm)]: Ar-H, 7.3241-6.0145, -NH 3.6237-3.6582, -CH_2, 2.3251-2.6063, -CH_3, 1.2437. Similarly, 2-phenylimino-4-amino-6-allyl formamidino-1,3,5-thiadiazine,2-methylimino-4-amino-6-allylformamidino-1,3,5-thiadiazine, 2-p-chlorophenylimino-4-amino-6-allylformamidino-1,3,5-thiadiazine, 2-o-tolylimino-4-amino-6-allyl forma midino-1,3,5-thiadiazine**,** 2-m-tolylimino-4-amino-6-allylformamidino-1,3,5-thiadiazine and 2-p-tolylimino-4-amino-6-allylformamidino-1,3,5-thiadiazine were synthesized by the interaction of 1-formamidino-3-ethylformamidinothiocarbamide (0.1M) with methylisocyanodichloride, (0.2M), p-chlorophenylisocyanodichloride (0.2M) (XId), o-tolylisocyanodichloride (0.2M), m-tolylisocyano dichloride and p-tolyl isocyanodichloride lemon juice respectively and enlisted in **Table- 1**

Table-1

Sr. No.	2-**Substituted**imino-4-amino-6-ethylformamidino-1,3,5-thiadiazine	Juice	Yield %	M. P.
1.	2-**methyl**imino----------thiadiazine	Lemon	63	298
2.	2-**phenyl**imino----------thiadiazine	Lemon	96	268
3.	2-**p-chlorophenyl**imino--thiadiazine	Lemon	98	253
4.	2-**o-tolyl**imino----------thiadiazine	Lemon	94	279
5.	2-**m-tolyl**imino----------thiadiazine	Lemon	91	258
6.	2-**p-tolyl**imino----------thiadiazine	Lemon	86	265

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THERMODYNAMIC PARAMETERS INVESTIGATION OF SUBSTITUTED THIOCARBAMIDONAPHTHOL

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ABSTRACT

Recently protection of environment and eco systems became a great task for susceptibility of the humanity. The various innovations in chemical and industrial sciences in developing era is a great task to the budding researchers to determine the significances and applications of synthesized drugs can be determined with the help of conductrometric measurements. This type of measurements and studies become interdisciplinary pull between chemical and biological sciences. Considering all this fact we determined the conductrometric parameters and thermodynamics parameters of 5-phenylthiocarbamido-1-naphthol at different concentration and different temperatures in 80% ethanol water mixture.

Keywards:- *5-phenylthiocarbamido-1-naphthol, thermodynamic parameters.*

INTRODUCTION

Conductivity of drug plays a vital role to explain pharmacodynamics of drug. Mobility of ions transmission of ions. Solubility and permeability of drugs efficiently influence by mobility of ions in electrolytic solution, these two are prime biopharmaceutical parameters which are accountable for effective bioavailability and good in vitro and vivo correlation[1]. Nowadays pharmaceutical technologist has a great challenge to rise the solubility and dissolution rate and oral bioavailability of weakly water soluble drugs[2]. Hydrotropic Salisation is considered as one of the sophisticated methods of solubalisation[3]. Enhance the aqueous solubalisation of insoluble drugs by adding hydrotropic agents. number of researchers work on the effect of solubility enhancers[4,5]. The Valuable information about solute-solute and solute-solvent interaction obtain from the coductometric measurements[6]. Gomaa and Al-Jahdalli[7] was investigated ionic association of divalent asymmetric electrolyte $Cu(NO_3)_2$ with Kryptofix-22 in mixed (MeOH-DMF) solvents at different temperatures by conductometric measurements. Conductometric measurements of the alkali metal at different proportion of mixed solvents was carried out by Izonfuo and Obunwo[8] and Roy et al[9]. Very few researcher investigated the thermodynamic parameter and Walden product of different complexes and they also examine the comparison of transition metal complexes among the halide group[10-14]. The ion pair formation and thermodynamic parameters of Glycine Bis-1-amidino-O-methylurea cobalt (III) halides in water-methanol mixture at different temperatures was investigated by Singh et al[15]. Recent work deals with thermodynamic parameters (viz. ΔH; ΔS and ΔG) study of 5-phenylthiocarbamido-1-naphthol by conductometric measurement at different concentrations and different temperatures in 80% ethanol-water mixture. These studies also contribute to solvent-solvent, solute-solvent and solute-solute interactions and the effects of various substituent.

MATERIALS AND METHODS EXPERIMENTAL

All AR grade chemicals used during present investigation. Freshly prepared solution used for analysis. The solvents were purified by standard method. Prepared 0.01M, 0.005M, 0.0025M and 0.0012M concentrations of 5-phenyl thiocarbamido-1-naphthtol 80% ethanol-water mixture. Maintain the thermal equilibrium (293K and 298K) of drugs solution by using thermostat. After getting thermal equilibrium, conductivity of that electrolyte solution was measured.

RESULT AND DISCUSSION

Firstly prepared solution of 0.01 M concentration then by serial dilution method prepared solutions of 0.005M, 0.0025M and 0.0012M with 80% ethanol-water mixture. Measured conductance of each solution by using Conductivity Bridge at 293K and 298 K. The result obtained are given in Table-1 to Table-2. From the data observed conductance (G), specific conductance (k) and

molar conductance (μ) were determined by known literature method.

TABLE – 1 - CONDUCTOMETRIC MEASUREMENTS AT DIFFERENT CONCENTRATIONS OF 5-PHENYLTHIOCARBAMIDO-1-NAPHTHOL

DETERMINATION OF G, k and μ AT DIFFERENT CONCENTRATIONS AND DIFFERENT TEMPERATURES IN 80% E-W MIXTURE

Temp	Concentration C (M)	Observed conductance (G)	Specific conductance (k)	Molar conductance (μ)
293K	0.01	0.0292	0.003023×10^{-3}	0.302376
	0.005	0.01465	0.001806×10^{-3}	0.361379
	0.0025	0.00943	0.001214×10^{-3}	0.485657
	0.0012	0.00739	0.009821×10^{-3}	0.818452
298 K	0.01 M	0.0309	0.003684×10^{-3}	0.368487
	0.005 M	0.01656	0.002055×10^{-3}	0.411067
	0.0025 M	0.01119	0.001421×10^{-3}	0.568588
	0.0012 M	0.00904	0.001145×10^{-3}	0.954592

Table 1 revel that the observed conductance (G), specific conductance (k) decreases and molar conductance (μ) increases along with decreasing concentrations and G, k and μ increasing along increasing temperatures. The specific conductance increases with increasing temperature. Calculated values the specific constant (Ksp), log (Ksp) and thermodynamic parameters viz. (ΔG), (ΔS) and (ΔH) of 5-phenylthiocarbamido-1-naphthol by known literature methods at different concentration with different temperatures. Obtained result computed in.

Table 2.

TABLE – 2 - CONDUCTOMETRIC MEASUREMENTS AT DIFFERENT CONCENTRATION AND DIFFERENTS TEMPERATURES OF 5-PHENYLTHIOCARBAMIDO-1-NAPHTHOL

DETERMINATION OF Ksp, log Ksp, ΔG,ΔH and ΔS AT DIFFERENT CONCENTRATIONS AND DIFFERENT TEMPERATURES

SYSTEM: L_2 [PTCN] **MEDIUM - 80% Ethanol-Water Mixture**

Temp.(K)	Conc. M	Ksp	Log Ksp	ΔG	ΔH	ΔS
293K	0.01	0.02846	-4.54601	-25503.64	-95580	413.255
	0.005	0.01025	-4.99324	-28012.64	-59873.3	299.952
	0.0025	0.004596	-5.33857	-29949.95	-80649.6	377.473
	0.0012	0.003005	-5.52276	-30983.28	-69068.2	341.473
298 K	0.01	0.0970	4.30373	-24968.44	-80244.5	347.237
	0.005	0.0155	4.81081	-27910.3	-89699	388.15
	0.0025	0.00739	5.1311	-29768.49	-95671.5	413.993
	0.0012	0.00486	5.31857	-30856.15	-99166.7	429.118

The change in thermodynamic parameters values closely affected by temperature, molar concentrations and percentage compositions. These parameters shackle by another factors viz. the solute (drug)-solvent interactions, solvent-solvent interactions, solvent-solvent-solute interactions and –solute-solute-solvent interactions. Variation in these parameters affected by the internal geometry as well as internal and intra hydrogen bonding

As observed, the μ values increase with decreasing in concentration and increasing temperature indicating less solvation or higher mobility of ions. This is due to the fact that increased thermal energy results in greater bond breaking due to dilution and increasing temperatures respectivelly.

Also negative values of ΔG indicates that reaction is spontaneous. Negative values of enthalpy change (ΔH) suggests exothermic reaction. Favorable at lower temperature and positive value of (ΔS) revels entropically favorable. The change in thermodynamic parameters values closely affected by molar concentrations and percentage compositions. These parameters shackle by another factors viz. solute (drug)-solvent interactions, solvent-solvent interactions, solvent-solvent-solute interactions and –solute-solute-solvent interactions. Variation in these parameters affected by the internal geometry as well as internal and intra hydrogen bonding

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WATER SAMPLING FROM DIFFERENT REGIONS OF MAHARASHTRA AND ITS ANALYSIS

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ABSTRACT

Different water samples were collected from all over the Maharashtra (Pune, Jalana, Shirdi, Verul, Ojhar,). Brewell Sample intended for chemical analysis was collected during normal operating hours. Samples of reservoir water were collected in the month of November-December & analyzed for physio-chemical parameters like pH, TDS, Total hardness, Density, viscosity, surface tension, refractive index,etc were analyzed. By observing the result it can be concluded that the water quality is below the pollution level for ground water.

Keywords: *Water reservoir, Physico-chemical, ground water, TDS*

INTRODUCTION

Water is often called the universal solvent. Water is the most important in shaping the land and regulating the climate. Once the groundwater is contaminated, its quality cannot be restored back easily and to device ways and means to protect it. The more common soluble constituents include calcium, sodium, bicarbonate and sulphate ions and chloride ion derived from intruded sea water, connate water, and evapotranspiration concentrating salts, and sewage wastes [1]. Earth is the planet having about 70 % of water. But due to increased human population, industrialization, the use of fertilizers in the agriculture and man-made activity, it is highly polluted. In many parts of the country available water is rendered non-potable because of the presence of heavy metal in excess. [2]

Many congenital diseases such as goiter and cancer have been associated with presence of high concentration of a chemical or its inadequate supply in water. About 20% of the world's population lacks access to safe drinking water, and more than 5 million people die annually from illness associated with safe drinking water or inadequate sanitation.[3]. WHO reports that approximately 36% urban 65% of rural Indian were without access to safe drinking water. Human and ecological use of ground water depends upon ambient water quality. During last decade, this is observed that ground water get polluted drastically because of increased human activities. Consequently number of cases of water borne diseases has been seen which a cause of health hazards. An understanding of water chemistry is the basis of the knowledge of the multidimensional aspect of aquatic environmental chemistry which involves the source, composition, reactions and transportation of water. [4]

It is the determination of the exposure of a given organism, human or other species, to a given chemical from the measurement of the concentration of the chemical in samples of water [5]. Water should be free from the various contaminations viz. Organic and Inorganic pollutants, Heavy metals, Pesticides etc. as well as all its parameter like pH, Electrical Conductivity, Calcium, Magnesium, Total Hardness, Carbonate, Bicarbonate, Chloride, Total Dissolved Solid, Alkalinity, Sodium Potassium, Nitrate, DO should be within a permissible limit. Various physicochemical parameters such as water temperature, water colour ,turbidity, free ammonia, total dissolved solid, pH, dissolve oxygen,free CO_2,total hardness ,total alkalinity ,chloride ,BOD ,nitrates, phosphate ,sulphates, were studied On the basis of primarily study.[6-10]

MATERIAL METHOD

Environmental laboratory inside the college department is indentified for this work. Sterilized & disinfected sample bottle were used for sampling purpose. Analysis of various parameters was carried out in the laboratory as per referred literature. Water quality parameters of collected water sample were compared with standards values of water parameter. Analysis of water sample was done to investigate its utility in various sectors.[11]

Parameters included in water quality assessment

Following different physico-chemical parameter are tested regularly for monitoring quality of water.

1. Temperature
2. pH
3. Electrical conductivity
4. Total hardness
5. TDS (Total dissolved solid)
6. Surface tension
7. Viscosity
8. Density
9. Refractive index.

Water sample were collected in sterile bottles from different sources and some preservative agent citric acid was added into it for maintaining the water quality of that environment for the further analysis till the experiment time.

Instruments used for parameter analyzed

S.N.	Studied parameter	Method used
1	Density	Density bottle
2	pH	Potentiometer (Equitronic Mod.No.FQ 601)
3	Electrical conductivity	Conductometer (304 systronic)
4	Surface tension	Stalagmometer
5	Viscosity	Ostwald Viscometer
6	Refractive index	Abbe's Refractometer (Mod.AR-10,mvtex Ind.)
7	Temporary hardness	Volumetric Titration
8	Permanent hardness	Volumetric Titration
9	Total hardness	Volumetric Titration

OBSERVATION TABLE

S.N.	Parameter	Verul	Ojhar	Shirdi	Pune	Jalana	Distilled Water	Mineral Water
1	Density (g/ml)	0.9976	0.9982	0.9981	0.9987	0.9979	0.9967	0.9282
2	pH	7.02	7.177	7.127	7.195	7.121	7	7.122
3	Conductance (mho)	0.7	0.72	1.01	1.09	1.001	0.247	0.324
4	Surface Tension (dyne/cm)	80.111	80.231	83.309	85.218	79.123	72.1	54.457
5	Viscosity (N/m2)	1.008	0.9518	1.009	1.012	1.005	1.008	0.8313
6	Refractive Index	1.368	1.367	1.368	1.369	1.364	1.363	1.333
7	Temporary Hardness (ppm)	564	44	278	589	331	75	62
8	Permanent Hardness (ppm)	336	216	722	591	369	175	168
9	Total Hardness (ppm)	900	260	1100	1180	700	250	230

RESULTS AND DISCUSSION

Different physico-chemical parameters were studied viz. density , pH, electric conductance, surface tension, viscosity, refractive index ,total hardness permanent hardness and temporary hardness.

It was found that the parameter shows slightly different values for each parameter which are as follows

1. DENSITY: For Pune city its density (0.9987) was higher as compared to others. It means that the water of Pune was denser. It was concluded that Pune contains higher amount of dissolved salts. It is also compared with distilled (0.9967) and mineral water (0.9282) values.

2. pH: The pH value of Pune (7.195) is highest. For other samples of water it slightly differs and it was found that nature of water samples is slightly alkaline.

3. ELECTRIC CONDUCTANCE: The conductance of Pune (1.09mho) was higher than others. It was concluded that water from Pune contains higher amount of dissolved salts. It means that if water contains more number of ions higher will be the conductance.

4. SURFACE TENSION: The surface tension of water sample of Pune (85.218 dyne/cm) was highest. It showed that water sample of Pune contains more dissolved salts than other places. It was also compared with distilled (72.1 dyne/cm) and mineral (54.457dyne/cm) water values.

5. VISCOSITY: The viscosity of water sample of Shirdi (1.009 N/m^2) was higher than others. It is shows that water sample of Shirdi contains more dissolved salts which increased viscosity. Higher

the viscosity higher will be the dissolved salts and its inter molecular forces.

6. REFRACTIVE INDEX: The refractive index value of Pune (1.369) was higher than Jalana (1.364). It is shows that water sample of Pune contained more dissolved impurities.

7. TOTAL HARDNESS: It was the main part of our analysis and it was observed that the total hardness of water sample of Pune (1180 ppm) was highest. It showed that water sample of Pune contained more dissolved salts than other places. It was also compared with distilled water (250ppm) and mineral water (230 ppm). From the all the water sample values of total hardness we may determine the purity of water sample.

CONCLUSION

The water sample collected from different locations of Maharashtra i.e.Verul Pune, Jalana, Shirdi , Ojhar. And from the overall conclusion of parameter reading, it finally concludes that the water sample of Pune is not potable for drinking purposes. As its every parameter shows highest reading which are above the standard values of potable water for drinking and other domestic purposes and that of Verul and Ojhar city is most potable water sample for every kind of purposes including drinking.

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GREEN SYNTHESIS AND CHARACTERIZATION OF NEW CONJUGATED ELECTROLUMINESCENT POLYQUINOLINE DERIVATIVE

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ABSTRACT

The synthesis of new conjugated electroluminescent polyquinoline derivative Poly (2,2-(p-phenyl)-6,6-bis(4-phenylquinoline) [PPPQ], which are soluble in organic solvents and its incorporation in light - emitting diodes as the emissive layer are reported. These electroluminescent devices, containing 1, 1- bis (di-4-tolylaminopphenyl) cyclohexane (TAPC) dispersed in polystyrene as the hole-transport layer, emit bright yellow light (λmax =554 nm) with quantum efficiency of 0.26% photons/electron and a luminance of 280 cd/m2 at a current density of 100 mA/cm2. Electroluminescence of moderate brightness was achieved with blue-green, green, yellow, orange, and deep red colors depending on the arylene linkage of the copolymer. The thermal, electrochemical, photophysical, and electroluminescent properties of new polyquinolines varied with the arylene linkage, including p-phenylene, 4, 4-biphenylene, 5, 5-bithienylene. These results also demonstrate that the new polyquinoline is a good electron transport electroluminescent material. Large enhancement in electroluminescence efficiency and brightness of light-emitting diodes fabricated from binary blends of conjugated polyquinolines was observed compared to devices made from the homopolymers. The polymers have thermal properties with glass transitions temperature of 161-339◦C. The electrical properties of the diodes and electric field modulated photoluminescence spectroscopy results confirmed that the enhancement of electroluminescence in the blends originated from spatial confinement of excitons which leads to increased exciton stability and electron hole recombination efficiency. Voltage tunable and composition –tunable multicolor electroluminescence was observed in the polymer blend devices. The observed composition dependent new emission bands and enhanced fluorescence lifetimes in the blends were suggested to originate from exciplex formation and molecular miscibility between the blend components. These results demonstrate new phenomena in the electroluminescence and photophysics of multicomponent conjugated polymers.

Keywords: *Synthesis , characterization, Electroluminescent, Polyquinoline*

INTRODUCTION

Semiconducting polymers with efficient electroluminescence are being developed for various lighting and flat-panel display applications.[1] A better understanding of the relationships of electroluminescence (EL) and photophysical properties of polymers to molecular and supramolecular structures is critical to the rational design of polymers with enhanced EL properties and device performance. Poly (p phenylenevinylene) (PPV),polythiophene (PT), poly(p-phenylene) (PPP), polyfluorene, and their derivatives have been extensively investigated as emissive materials for EL devices. Although a systematic variation of the side group attached to the polythiophene backbone has been shown to tune the EL color from blue to the near-infrared, the materials generally have very low luminescence quantum yield. PPV-based materials have high photoluminescence (PL) and EL efficiencies, and the EL color can be varied by side-chain substitutions and copolymerizations.[1] However, degradation induced by photooxidation,3 which may impede long-term device stability, is a concern with arylenevinylene polymers. Furthermore, all these extensively studied PPV-, PPP-, PT-, and polyfluorene-based EL materials are p-type semiconductors with very good hole transport but very poor electron transport properties.[1-4] Luminescent polymers with efficient electron injection and transport properties are of interest in their own right as well as to complement existing p-type polymers for the development of more efficient EL devices. Such n-type (electrons transport) polymers offer alternative EL device engineering compared to p-type polymers.[5] Here, we focus on the EL and photophysical properties of the polyquinolines which are known to be intrinsic n-type semiconducting polymers. Their n-type characteristics were revealed in previous studies

by chemical doping,6 ion implantation,[7] photoconductivity,[8] and electrochemical redox measurements.[9] The polyquinolines also have excellent mechanical properties and high thermal stability and can be processed into high-quality thin films.[10,11] They were also shown to have interesting electronic, photoconductive,and nonlinear optical properties. Recently, some polyquinolines were demonstrated as promising materials for the fabrication of light-emitting diodes (LEDs). However, their EL and photophysical properties have not been systematically
investigated.[5-6]

EXPERIMENTAL

The synthesis, characterizations, thin filmprocessing, optical absorption, electrochemistry, and nonlinearoptical properties of polymers and were previously reported by our group. The synthesis and characterizations of polymers and were also reported in previous communications.[14]. The polyquinolines used in this study haveintrinsic viscosities of 0.74-31.3 dL/g, which were measuredin 0.1 mol % di-m-cresyl-phosphate/m-cresol at 25 °C or inmethanesulfonic acid at 30 °C.[11,14] The exact molecular weightsof these polymers are unknown. However, light scatteringmeasurements on gave a weight-average molecular weight (Mw) of 370 000 for a sample with an intrinsic viscosity of 20 dL/g.[15] The above intrinsic viscosity values of the polyquinolines used in this study indicate that they are moderate to high
molecular weight polymeric materials. [1-3]

RESULTS AND DISCUSSION

A. Photophysical Properties. Optical Absorption Spectra. The optical absorption spectrum of a thin film of the parent polyquinoline PPQ is shown in Figure 1. The ð-ð* transition has a lowest energy absorption maximum (λmax) at 414 nm and an absorption edge (Egopt) of 2.65 eV. The lowest energy transitions in the absorption spectra and estimated optical gaps of all the polyquinolines investigated are collected in Table 1. The optical absorption spectra revealed that most of the polyquinolines (PPQ,Bu-PQ, PPPQ, Bu-PPQ, PBPQ, PBAPQ, and PSPQ) have similar ð-ð* transitions with ìmax at 399-414 nm (Table 1). The ð-ð* transition showed a gradual small red shift, suggesting increasing electron delocalization along the chain as the linkage changed from phenylene (PPPQ) to biphenylene (PBPQ), ethynylenebiphenylene (PBAPQ), and acetylenebiphenylene (PSPQ). The most striking red shift was observed in PTPQ with the thienylene linkage ,showing the ð-ð* absorption maximum at 471 nm compared to 400nm for PPPQ .On the other hand, PDMPQ in which the conjugation was disrupted by a methylene linkage showed a blue shift (380 nm) in absorption maximum compared to the case of PPPQ.Introduction of tert-butyl substitution on the phenyl side group does not appear to affect the ground-state electronic structure of the polyquinolines as seen by comparing the absorption spectra of PPQ to Bu-PQ ,PPPQ, and Bu-PPQ. Bu-PQ has essentially the same absorption peak (412 nm) as PPQ (414 nm). Bu-PPQ has an identical absorption peak and edge as PPPQ. However, substitution of methyl or nonyl side groups to the bis(quinoline) rings caused large changes in the electronic structure of the polymer. BuMPPQ and BuN-PPQ have absorption ìmax at 358 and 347 nm, respectively, which are substantially blueshifted from the parent Bu-PPQ with absorption peak at 399 nm (Table 1). These effects of methyl and nonyl substitutions indicate that electron delocalization is disrupted along the chain. We can understand these optical absorption spectra and their dependence on main-chain and side-group variations in terms of the effects of geometric structure on the ground-state electronic structure of the polyquinolines. Similar effects of intramolecular and supramolecular interactions on the photophysical properties of oligoquinolines have been found in oligomers investigated by single-crystal X-ray diffraction.[2-4]

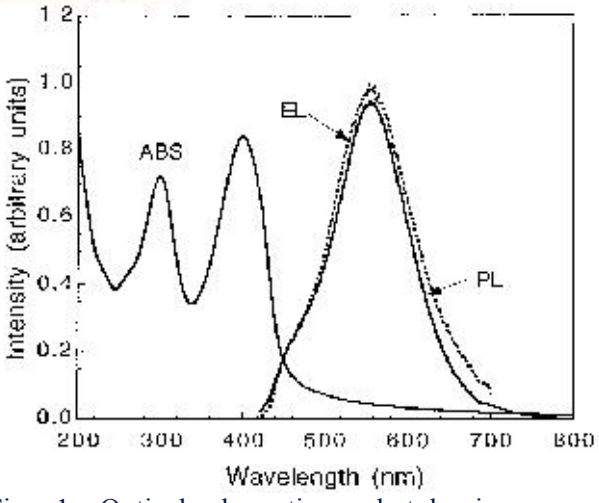

Fig. 1. Optical absorption, photoluminescence (excited at 400 nm) and electroluminescence (10 V) spectra of PPQ.

Table 1. Optical Absorption and Redox Properties of Polyquinoline Thin Films

Polymer	λmax,nm,	α105 cm-1	Egopt,eV	Ered,c V	Eox,c V
1, PPQ	414	1.12	2.65	-1.78	0.95 (0.87)d
2, Bu-PQ	412	0.69	2.65	-1.86	0.78 (0.79)
3a, PPPQ	400	1.31	2.78	-1.90	1.07 (0.88)
3b, PBPQ	405	1.17	2.81	-1.98	1.09 (0.83)
3c, PBAPQ	407	1.12	2.72	-1.93	1.08 (0.79)
3d, PSPQ	414	1.13	2.65	-1.92	0.95 (0.73)
3e, PDMPQ	380	0.67	3.01	-2.04	1.04 (0.97)
3f, PTPQ	471	1.09	2.49	-1.84	0.87 (0.65)
4g, Bu-PPQ	399	0.78	2.78	-1.58	0.99 (1.20)
4h, BuM-PPQ	358	0.47	3.10	-1.95	1.35 (1.15)
4i, BuN-PPQ	347	0.44	3.26	-2.00	1.31 (1.26)

a Data for solid films at absorption λmax. b Optical absorption edge gap (Egopt). c Onset potentials vs SCE from ref 9, except for 2 and 4g-i. d Eox determined from Eox) Egopt - jEredj.

Regulation of the molecular and supramolecular structures of the polyquinolines has allowed both the Current-voltage and luminance-voltage characteristics of LEDs fabricated from PPQ (open marks) and Bu-PPQ (filled marks). Dependence of EL device efficiency on PL quantum yield of the polyquinolines. HOMO/LUMO levels of the polyquinolines (PQs), TAPC, and PVK in relation to the work function of the LED electrodes. Photoluminescence and electroluminescence colors and efficiencies to be tuned over a wide range. Emission fromthin films of the polyquinolines is characterized by primarily excimers with long excited-state lifetimes of 2.4-5.2 ns and fairly good photoluminescence quantum efficiencies of 2-30%. Electroluminescence diodes of the type ITO/HTL/polyquinoline/Al have quantum yields of up to 1% photons/electron and luminance levels of up to 280 cd/m2. The light-emitting diodes fabricated from these emissive n-type conjugated polymers appear to be currently limited largely by hole injection and transport. The efficient electron injection from aluminum into the polyquinolines in these EL devices is proposed to be mediated by a reaction at the aluminum/polyquinoline interface which obviates the otherwise large energetic barrier to electron injection.

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WHEAT GRASS POWDER AND JUICE - AMAZING HEALTH BENEFITS AND ALTERNATIVE FOR THE MANAGEMENT OF VARIOUS DISEASES

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ABSTRACT

Wheat grass is the Young grass of Triticum aestivum .Which is freshly juiced or dried into powder for human consumption. Wheat grass juice and powder contain rich source of chlorophyll, B-complex vitamins, minerals and bioflavonoids,antioxidants which play important role in management of many diseases like various types of cancer,blood pressure,diabetes mellitus, various skin diseases, blood disorder, body rejuvenation, liver detoxification, ulcerative colitis, arthritic disorders, inflammatory disorders, tooth decay disorder and constipation,as well as it neutralizes environmental pollutants, enhances immunity, restore energy and vitality This review article is an attempt to focus on the findings of research studies of wheat grass with regard to its clinical application in various diseased conditions and its therapeutic potential for healthy body.

Key words- *wheat grass powde ,antioxidants,body rejuvenation,detoxification,ulcerative colitis.*

INTRODUCTION

Wheat is used as a source of food all over the world. Wheat grass belongs to *Triticum aestivum* belong to family *Graminae*. Shoot of *Triticum aestium* is called as wheat grass. Wheat grass contain all the nutrients which has been proved powerful health supplement. It contain chlorophyll, vitamins, minerals,antioxidants and enzymes, Wheat grass contain 98 elements and chlorophyll with higher concetntration consider as blood of plant used for healing property which is freshly juiced or dried in powder and used for human consumption[1,2].

wheat grass possess antibacterial, anti oxidant, anti cancer, anti ulcer property. Blood purification, liver detoxification and colon cleansing are the three important effects of wheat grass on human body. It chemically neutralizes environmental pollutants, enhances immunity, restore energy and vitality

Kingdom-Plantae
Subkingdom –Tracheobionta
Superdivision –Spermatophyta
Division Magnoliophyta
Class- Liliopsida
Subclass Commelinidae
Order- Cyperales
Family-Poaceae
Subfamily-Pooideae
Tribe-Triticeae
Genus-Triticum L.
Species: *T. aestivum*

Binomial name: *Triticum aestivum*

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3.Composition of Wheat grass-

Table 1. Nutrients presents in wheat grass juice and powder [4]

Sr.No.	Nutrients	Concentration
1	Chlorophyll	18.5 mg
2	B-carotene	120 IU
3	Vit.B12	0.30 mcg
4	Vit.C	1 mg
5	Vit.E	880 mcg
6	Phosphorus	21 mg
7	Magnesium	8 mg
8	Calcium	7.2 mg
9	Iron	0.66 mg
10	Potassium	42 mg
11	Protein	860 mg
12	Biotin	4 µg
13	Vit B5	36 µg
14	Choline	5 mg
15	Lutein	1 mg
16	Lycopene	29 µg
17	Vit B1	11 µg
18	Vit B2	260 µg
19	Vit B3	252 µg
20	Vit B6	39 µg
21	Vit K	35 µg
22	Cobalt	1.7 µg
23	Copper	17 µg
24	Iodine	8 µg
25	Maganese	240 µg
26	Phosphorus	14 mg
27	Selenium	3.5 µg
28	Sodium	1 mg
29	Sulphur	10.5 mg
30	Zinc	62 µg
31	Alanine	69 mg
32	Arginine	66 mg
33	Cystine	11 mg

- Chlorophyll-is the main constituents present in higher concentration consider as blood of plant. It neutralizes toxin in body,infection, heals the wound, overcome inflammation, and gets rid of parasitic infection,purification of blood, liver detoxification and colon cleansing [5,6,7]
- Proteins -Leucine, iso leucien, threonine, valine, threonine, phenylalanine, tryptophane, metheonine, lysine, arginine aspartic acid, glycein, prolein, glutamic acid, alanine, tyrosine are essential and non essential amino acids present in wheat grass.
- Vitamins- Wheat grass contains carotene,Vit.A, Bcomplex,Vit. E, C and K.
- Minerals- Important minerals like Iron, calcium, phosphorus, megnasium, zinc, copper, sodium, sulfur, boron, molybdenum, iodine are the present in wheat grass.
- Enzymes- Enzymes protease, amylase, lipase, cytochrome oxidase, trans hydrogenase, superoxide dismutase are present in wheat grass. Lipase- Lipase is a highly effective in the digestion of fats. Enhances the digestion of proteins, starch and fat in the gastrointestinal tract. Without lipase fat stagnates and accumulates in the organs, arteries and capillaries. Cytochrome oxidase playmajor role in the body's production of energy. Cytochrome oxidase anchors a chain of enzymes in the mitochondrion; the power plant of the cell enables this by reacting with oxygen to make energy. Catalase serves to protect each individual cell from the toxic effect of hydrogen peroxide. Hydrogen peroxide is caused in the body by bacteria. Malic Dehydorgenase is another Important enzyme which helps in maintaining the body's ability to defeat bacteria and other parasitic hosts in the body.
- Absicic acid Anti-cancer agent. Protease amylaseis Important in supplementing the body's natural digestion of starches, proteins, fats and cellulose. Can help offset the worst aspects of digestive leukocytosis, the immune response to food heated over 118 degrees.
- Bioflavanoids-Apigenin, quercitin, luteonin are found in wheat grass.

PREPARATION OF WHEAT GRASS JUICE AND POWDER-

Wheat grass can be cultivated easily by growing at home mix one part peat moss with three parts planting soil and place in at least 2 inch deep plastic trays. Soak one cup of wheat for 24 hours then rinse. One cup of the seeds will be sufficient for a 25 x 35cm tray. Water the soil mixture first, then spread wheat evenly over the moist soil. Cover the wheatgrass with a paper towel and place it near a window to ensure proper ventilation for three days. However, keep away from direct sunlight. For the first three days, in the morning, water such that seeds are completely soaked in water. In the evening, lightly spray water with a spray bottle. On the fifth day, the young shoots grow above 1 inch. Now, water only once a day but ensure that the soil is damp to keep the roots moist. Around the ninth or 10th day, the wheatgrass is grows to 6 – 7 inch and is ready for

harvesting. At this stage, the wheatgrass is at its nutritional peak. Cut the grass above the soil [8,9]

Place the fresh wheat grass, soon after cutting it, on a platform or in a pounding basic and crush it well.Then wrap them in a clean and thin piece of cloth and strain the juice out of it. A plastic strainer could also be used for this purpose. If the magnetically treated water is added to it while crushing it, the extraction of juice will be in a greater quantity with its effectiveness is also strengthened. This wheat grass can be also crushed in the electric juicer or mixer also.

4.1: Preparation of Wheat grass powder-

- Cut the freshly ordered Wheatgrass evenly
- Pre-heat the oven to 65°C
- Place the freshly cut Wheatgrass on baking sheet and insert it into oven
- Allow the Wheatgrass to dry in oven for approx. 2 hours
- Check if the leaf has turned dry and brittle (if not, heat the oven further)
- Grind entire wheatgrass in a grinder and store it in the container

Mix wheatgrass powder with water for consumption. Ideally, 3 grams of wheatgrass powder should be consumed with 275 ml of water.

THERAPEUTIC APPLICATIONS OF WHEATGRASS IN VARIOUS DISEASES

1. **Anticancer activity**-Wheatgrass juice and powder contain high concentration of chlorophyll as an antioxidants, laetrile and antioxidant enzyme super oxide dismutase which converts dangerous free radical reactive oxygen species (ROS) into hydrogen peroxides (having extra oxygen molecule to kill cancer cells) and an oxygen molecule [10]

Wheat grass juice is used as a alternative medicine for anticancer therapy.Ttetra-pyrroles contain in chlorophyll has the ability to induce mammalian phase 2 proteins that protect cells against oxidants and electrophile[11]

Plant hormone abscisic acid (ABA) is another constituent of wheatgrass act as an anticancer agent,this hormone is 40 times more potent 4 hours after cutting the wheatgrass plant which neutralize the effect of the hormone chorionic gonadotropin and a compound similar to this hormone has been found to be produced by the cancer cells {12,13]

Antioxidant activity of wheat grass juice in preventing oxidative damage to deoxyribonucleic acid (DNA) and lipid peroxidation, stimulation of gap junction communication, effects on cell transformation and differentiation, inhibition of cell proliferation and oncogene (cancer causing gene) expression, effects on immune function and inhibition of endogenous formation of carcinogens.[14] Also Chlorophyll derivatives have been found to be effective in liver, colon, stomach and gastrointestinal cancer cases [15,16,17,18].

2. **Antidandruff activity-** by rubbing wheat grass juice on the scalp for 5 to 10 min. it reduces dandruff and also prevent premature graying of hair and makes them healthy and strong [38].

3. **Ulcer and wheat grass**-antiulcer activity of wheat grass is done in a randomized, double-blind, placebo-controlled study it shows effective and safe as asingle or adjuvant treatment of active distal Ulcerative colitis [19] Most of the results of the study showed that chlorophyll was found effective in treatment of cyst wounds, fistula-in-ano, sarcoma/carcinoma, ulcerative colitis, thoracic empyema, gunshot wound sinus tracts, decubitus ulcer and burns. These clinical studies suggest that chlorophyll may be best agent known for use in the treatment of suppurative diseases, indolent ulcers or wherever stimulation of tissue repair is desired [20,21]

4. **Green blood Therapy**- The structure similarity between chlorophyll and hemoglobin in having a tetrapyrrole ring structure, the only difference between the two being the nature of the central metal atom - magnesium (Mg) in chlorophyll and iron (Fe) in hemoglobin. The apparent resemblance between the two is thus considered to be responsible for the therapeutic effects shown by chlorophyll in conditions involving deficiency of hemoglobin. Hemoglobin and its congeners are protein bodies which act as the oxygen carrier in higher animals by binding two electrons attached to the oxygen molecule, whereas chlorophyll is the active metabolic agent in plants which assimilates carbon from the carbon dioxide of the atmosphere by producing two electrons which are then transmitted through electron transport chain. Due to their structural similarity chlorophyll act as a blood substitute in conditions like chronic anemia, tissue hypoxia, thalassemia and other hemolytic disorders etc.

5. **B- Thalassemia** -B-thalassemia is a genetically inherited disorder that arises due to abnormal beta globin chains which are required for the synthesis of adult hemoglobin (HbA). The characteristic deficiency of beta globin chains, seen in thalassemia results in the production of abnormal red blood cells (RBCs) whis leads to

destruction of such RBCs in the spleen and a decreased number of RBCs in the blood. person with thalassemia may continue to produce gamma globin chains in an effort to increase the amount of fetal hemoglobin (HbF) and compensate for the deficiency of HbA. Reaseacher study show that use of wheat grass juice 3-5 fold increase in the production of HbF [22,23,24].The level and speed of induction of HbF by the wheatgrass extract is significantly greater than any of the pharmaceutical inducers available. During clinical study,the thalassemic patients were administered wheatgrass juice on a daily basis, the following conclusions were drawn - a. 50% patients showed up to 25% reduction in transfusion requirement. b. The mean time interval between transfusions increased to 29.5% c. Hemoglobin levels were not compromised by reducing transfusion volumes. d. The patients reported general well-being, improved appetite and reduced musculo-skeletal aches and pains [25].

6. **Haemolytic anemia** - High nutritional content that includes antioxidant vitamins (C & E) and bioflavonoids. It was seen that wheatgrass juice therapy decreased the total volume of blood transfused and increased the intervals between blood transfusions of the entire study cohort. These analyses suggested that not only is this therapy effective, but also that the benefit is related to the duration of the wheatgrass juice therapy. The beneficial effects of this therapy have been attributed to its rich nutritional content that includes antioxidant vitamins (C & E) and bioflavonoids.

7. **Detoxifying Activity-** Wheat grass containing choline having the lipotropic action is attributed to its in vivo conversion to an active compound which is retained within the hepatic cells and enhances the oxidation of fatty acids and formation of tissue lecithins. The latter effect augments lipoprotein synthesis, which acts as a transport form of fatty acids in plasma and thus helps in removal of lipids from a fatty liver [56]]. Choline promotes the removal of the esters of both cholesterol and glycerol, with the effect on the glyceride fraction preceding that on the cholesterol esters{26,27}.

8. **Anti-arthritic activity-** Many study showed significantly decrease in symptoms of rheumatoid arthritis due to consuptionofwheat grass juice {28,29}

9. **Anti-inflammatory activity**-Chlorophyll in wheat grass juice exhibit anti-inflammatory, wound healing and odor reducing capabilities. Chlorophyllin has bacteriostatic properties due to which it aids in wound healing and stimulates the production of hemoglobin and erythrocytes in anemic animals.wheat grass juice has been used to treat various kinds of skin lesions, burns and ulcers due to its wound healing agent, stimulating granulation tissue and epithelization [30].

10. **Tooth Disorders** –For Pyorrhea and sore throat wheatgrass juice acts as excellent mouth wash. Wheat grass juice destroy toxins and bacteria from gums and teeth. Wheat is valuable in the prevention and cure of pyorrhea[31].

11. **Constipation** –Wheat grass is an excellent laxatives high concentration of cellulose forms bulk mass in the intestine and helps in evacuation by increasing peristalsis.

12. **Skin Diseases**-Chlorophyll act as bacteriostatic it a arrests growth and development of harmful bacteria. Wheat grass therapy can be effectively used for skin diseases and ulcerated wounds as by retarding bacterial growth, chlorophyll also act as sterilizer it applied on infected area, it alsoused in burns, scalds and various itching and burning eruptions.[32]

13. **Digestive System Disorders** -Wheat grass juice used as an enema which helps to detoxify the walls of the colon. The general procedure is to give an enema with lukewarm or Neem water. After waiting for 20 minutes, 90 to 120 ml of wheat grass juice enema is given. It should be retained for 15 minutes. This enema is very helpful in disorders of the colon, mucous and ulcerative colitis, chronic constipation and bleeding piles [33]

14. **Circulatory Disorders**-Wheat grass containing chlorophyll enhances heart and lung functions. Capillary activity also increases while toxemia or blood poisoning is reduced. Due to high content of Iron in the blood and hemoglobin which improve lungs function. Chlorophyll improve oxygenation and the effect of carbon dioxide is minimized. Due to this effect wheatgrass juice is prescribed for circulatory disorders [34].

15. **Internal Rejuvenation** –Wheat grass juice is the rich source of protein, B complex vitamins minerals and antioxidants and as it has eight of the essential amino acids in delicately balanced proportions. When wheat protein is metabolized to health building amino acids which takes place complete internal rejuvenation. These amino acids build a resilient muscle that comes back to its original form after stretching and bending, healthy skin and hair and clearer eyesight

and nourish the heart and lungs, tendons and ligaments, brain, nervous system and glandular network. Wheat grass juice contain B-complex vitamins, especially thiamine, riboflavin and niacin promote youthful energy and nourishment to the skin and blood vessels. It alsocontain minerals which helps to nourish the hormonal system, heal wounds and regulate blood pressure. Wheat juice also contain iron to enrich the bloodstream and phosphorus and potassium to maintain internal water balance along with other nutrients. Thus wheat grass juice helps to restore internal harmony [35,36,37].

CONCLUSION

From the studies it is concluded that wheat grass juice has been widely used to cure number of diseases like cancer due to its high content of antioxidant and chlorophyll, Hypertension, diabetes mellitus, it also to help diminish fatigue, improve sleep, increase strength and stamina, support weight loss, improve digestion and elimination, support healthy skin, teeth, eyes, muscles and joints, improve the function of our heart-lungs and reproductive organs, heal ulcers and skin sores, slow cellular aging, improve mental function, beneficial in arthritic disorders and muscle cramping, B-thalassemia, hemo-lytic anemia, asthma, allergy, inflammatory bowel disease and detoxification. High content of chlorophyll and its strucutral homology with hemoglobin indicates as a blood builder in various clinical conditions involving hemoglobin deficiency as green blood therapy. WGJ content rich source of chlorophyll,vitamins,minerals and antioxidants which aids in clinical application of WGJ in many serious clinical conditions there is lack of substantial in-vivo clinical trials in regards to its clinical application. There is scope for clinical investigation and evolution of new methods for the development of modern medicine for the treatment of other ailments. there is need for further investigation to explore therapeutic potential of WGJ for the treatment of many diseases which is safe and economical .

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SYNTHESIS OF SCHIFF BASES BY CONDENSATION OF AROMATIC AMINES WITH 3-(5-BROMOTHIOPHEN-2-YL)-1-PHENYL-1-H-PYRAZOLE-4-CARBALDEHYDE.

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ABSTRACT

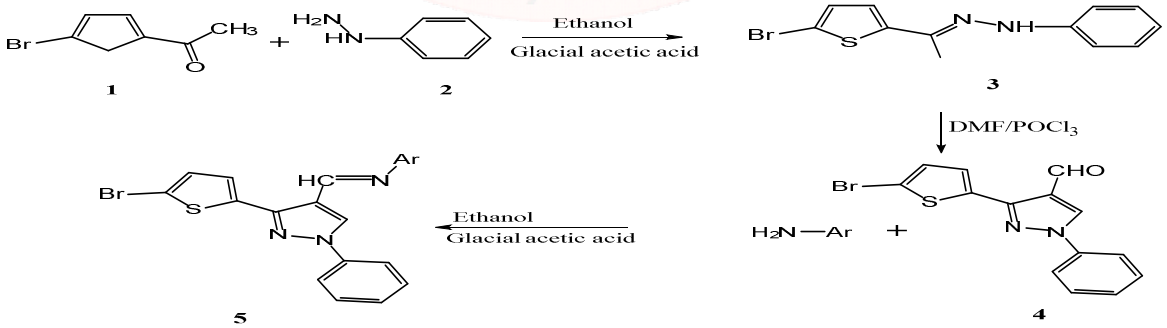
In the present study, novel Schiff bases were synthesized by condensation of 3-(5-bromothiophen-2-yl)-1-phenyl-1-H-pyrazole-4-carbaldehyde with different aromatic amines. 3-(5-bromothiophen-2-yl)-1-phenyl-1-H-pyrazole-4-carbaldehyde was synthesized from 2-acetyl-5-bromothiophene via 1-(1-(5-bromothiophen-2-yl)ethylidiene)-2-phenylhydrazine. The progress of the reaction and purity of the synthesized compounds was monitored by thin layer chromatography with F252 silica gel precoated aluminium sheets using petroleum ether – ethyl acetate (9:1) as a developing solvent and spots were visualized with near UV light and Iodine vapors. The structures of newly synthesized compounds were confirmed on the basis of IR spectroscopy, [1]H-NMR spectroscopy and Mass spectrometry.

Keywords- *Hydrazone, pyrazole shiff bases and spectral characterization.*

INTRODUCTION

Heterocyclic systems containing mainly nitrogen, sulfur and oxygen atom constitute a large class of compounds of biological and medicinal interest. A huge number of heterocyclic systems which include mainly five and six membered compounds represent a diverse group of molecular scaffolds. Several such heterocyclic scaffolds have been successfully incorporated into novel drug leads and therapeutic agents[1]. In recent years Schiff bases are frequently used and studied for the betterment of human welfare, attracting much attention in organic and inorganic synthesis. Schiff bases are the important compounds owing to their wide range of biological activities and industrial applications, they have been found to posses the different pharmacological activities such as antibacterial[2-7], antifungal[8, 9], anticancer[10, 11], antiviral[12, 13], anti-inflammatory[14], anti-HIV[15]and antimalarial[16]. Further more from the literature survey it is observed that Schiff bases with sulfur atom are a class of important compounds in medicinal and pharmaceutical field. Therefore, it seemed interesting to consider the synthesis of new Schiff bases by condensing different aromatic amines with 3-(5-bromothiophen-2-yl)-1-phenyl-1-H-pyrazole-4-carbaldehyde. In this paper we report the synthesis and characterization of Schiff bases derived from 3-(5-bromothiophen-2-yl)-1-phenyl-1-H-pyrazole-4-carbaldehyde.

Scheme-



1 2 3 4 5

5a: Ar = C_6H_5
5b: Ar = C_6H_4-Cl-p
5c: Ar = C_6H_4-Cl-o
5d: Ar = C_6H_4-Br-p
5e: Ar = C_6H_4-OH-p
5f: Ar = C_6H_4-NO_2-p
5g: Ar= C_6H_4-NO_2-m
5h: Ar = C_6H_4-CH_3-p

2. Experimental

MATERIALS AND METHOD

All the chemicals were purchased from Sigma Aldrich and SDFINE chemicals and used further without purification. Melting points were determine in open capillary tube and are uncorrected. The progress of the reactions as well as purity of the compounds was monitored by thin layer chromatography with F252 silica gel precoated aluminium sheets using petroleum ether – ethyl acetate (9:1) as a developing solvent and spots were visualized with near UV light and Iodine vapors. The IR spectra were recorded on FTIR SHIMADZU SPECTOPHOTOMETER using KBr pellets and expressed in cm^{-1}. The NMR spectra were recorded on BRUKER ADVANCE (400 FT-NMR) spectrophotometer in DMSO using tetramethyl silane as an internal standard and chemical shift values are expressed in δ ppm. The MASS spectra were recorded on Waters UPLC-TQC MASS Spectrometer.

2.2. Synthesis of 1-(1-(5-bromothiophen-2-yl)ethylidene)-2-phenylhydrazine 3.

0.01mol of 2-acetyl-5-bromothiophene (1), 0.01 mol phenyl hydrazine (2) and 2ml glacial acetic acid in 20 ml of ethanol. The reaction mixture was stirred on magnetic stirrer at room temperature for two hours. The yellow precipitate thus obtained was separated by filtration, washed with ethanol, dried and purified by recrystallization from ethanol. Yellow solid, Yield – 76.20%. M.p.- 122^{0}c. IR (KBr cm^{-1}): 3347 cm^{-1} (N—H), 3022 cm^{-1}, 3046 cm^{-1} (C—H), 1595 cm^{-1} (C═N), 1452 cm^{-1}(C═C). ^{1}H-NMR (DMSO, δ, ppm): 9.1 (s, 1H, NH), 2.1 (s, 3H, CH_3), 6.7 (m, 1H, Ar—H), 7.1 (m, 4H, Ar—H) 6.8 (d,1H, Ar—H), 6.9 (d,1H, Ar—H). Mass: 295 (M^+), 204, 133, 109. Anal. (%) for $C_{12}H_{11}BrN_2S$, calcd., C, 48.83; H, 3.76; Br, 27.07; N, 9.49; S, 10.86.

2. 3. Synthesis of 3-(5-bromothiophen-2-yl)-1-phenyl-1-H-pyrazole-4-carbaldehyde 4.

0.03 mol of $POCl_3$ was added drop wise to an ice-cold stirred solution of 1-(1-(5-bromothiophen-2-yl)ethylidene)-2-phenylhydrazine (3) (0.01 mol) in 5ml DMF. The reaction mixture was stirred for half hour at room temperature first and then at 70 ^{0}c for about five hours on magnetic stirrer. The resulting mixture was poured onto crushed ice and neutralized with saturated sodium bicarbonate solution. The pale green precipitate obtained was purified by recrystallization with ethanol to yield the product. Pale green solid. Yield- 89.27 %. M. p.- 132^{0}c. IR (KBr, cm^{-1}) 3102 cm^{-1} (Ar—H), 2740 cm^{-1} (CO—H), 1680 cm^{-1} (C═O), 1598 cm^{-1} (C═N), 1467 cm^{-1} (C═C). ^{1}H-NMR (DMSO, δ, ppm): 10 (s, 1H, CHO), 9.2 (s, 1H, C—H, Pyrazole), 8.0 (d, 1H, J=3.92 Hz, Ar—H) 7.1 (d, 1H, J=3.92 Hz, Ar—H), 7.3-7.9 (m, 5H, Ar—H). Mass: 333 (M^+) Anal. (%) for $C_{14}H_9BrN_2OS$, calcd., C, 50.47; H, 2.72; Br, 23.98; N, 8.41; O, 4.80; S, 9.62

2.4. Synthesis of Schiff bases 5a-5h.

0.01 mol of 3-(5-bromothiophen-2-yl)-1-phenyl-1-H-pyrazole-4-carbaldehyde (4), 0.01 mol of aromatic aldehydes were dissolved in 20 ml of ethanol followed by addition of 2-3 drops of glacial acetic acid. The reaction mixture was refluxed for about 1-4 hours and then cools at room temperature. The solid thus obtained separated by filtration, washed with ethanol, dried and purified by recrystallization from ethanol.

2.4.1. 1-(3-(5-bromothiophen-2-yl)-1-phenyl-1H-pyrazol-4-yl)-N-phenylmethanimine 5a.

Pale yellow solid. M. p. - 134^{0}c, Yield-69.48%. IR (KBr, cm^{-1}): 3138 cm^{-1} (Ar—H), 1616 cm^{-1} (C═N), 1484 cm^{-1} (C═C), 758 cm^{-1}(C—Br). ^{1}H-NMR (DMSO, δ, ppm): 9.0 (s, 1H, C—H, Pyrazole), 8.6 (s, H— C═N), 7.2-8.0 (m, 12 H, AR—H). Mass: 408 (M^+). Anal. (%) for $C_{20}H_{14}BrN_3S$, calcd., C, 58.83; H, 3.46; Br, 19.57; N, 10.29; S, 7.85.

2.4.2. 1-(3-(5-bromothiophen-2-yl)-1-phenyl-1H-pyrazol-4-yl)-N-(4-chlorophenyl) methamine 5b.

Pale yellow solid. M. p. -114^{0}c. Yield-78.38% . IR (KBr, cm^{-1}): 3136 cm^{-1} (Ar—H), 1608 cm^{-1} (C═N), 1477 cm^{-1} (C═C), 758 cm^{-1}(C—Br). ^{1}H-NMR (DMSO, δ, ppm): 9.3 (s, 1H, C—H, Pyrazole), 8.5 (s, H— C═N), 6.5-7.9 (m, 11 H, AR—H). Mass: 442 (M^+). Anal. (%) for $C_{20}H_{13}BrClN_3S$, calcd., C, 54.26; H, 2.96; Br, 18.05; Cl, 8.01; N, 9.49; S, 7.24.

Comp-ound	Mol. Formula	Ar	Colour	Yield (%)	M.P. (^{0}c)
3	$C_{12}H_{11}BrN_2S$	--	Yellow	76.20	122
4	$C_{14}H_9BrN_2OS$	--	Pale green	89.27	132
5a	$C_{20}H_{14}BrN_3S$	C_6H_5	Pale yellow	69.48	134
5b	$C_{20}H_{13}BrClN_3S$	C_6H_4-Cl-p	Pale yellow	78.38	114
5c	$C_{20}H_{13}BrClN_3S$	C_6H_4-Cl-o	Pale yellow	84.19	102
5d	$C_{20}H_{13}Br_2N_3S$	C_6H_4-Br-p	Yellow	67.40	118
5e	$C_{20}H_{14}BrN_3OS$	C_6H_4-OH-p	Yellow	68.22	128
5f	$C_{20}H_{13}BrN4O_2S$	C_6H_4-NO_2-p	Yellow	73.76	94
5g	$C_{20}H_{13}BrN4O_2S$	C_6H_4-NO_2-m	Yellow	76.18	124
5h	$C_{21}H_{16}BrN_3S$	$C_6H_4CH_3$-p	Yellow	83.42	122

Table – Physical constant data of synthesized compounds.

RESULTS AND DISCUSSION

The synthetic route to synthesize title compounds is outline in scheme. 1-(1-(5-bromothiophen-2-yl)ethylidene)-2-phenylhydrazine (3) was prepared according to the method reported in literature, using 2-acetyl-5-bromothiophene as a starting material. 3-(5-bromothiophen-2-yl)-1-phenyl-1-H-pyrazole-4-carbaldehyde (4) was prepared by Vilsmeier Haack Reaction. The reaction of 3-(5-bromothiophen-2-yl)-1-phenyl-1-H-pyrazole-4-carbaldehyde (4) with different aromatic amines in ethanol using glacial acetic acid as a catalyst, afforded Schiff bases in good yield.

The structure of prepared compounds was confirmed by Infra Red spectroscopy, ^{1}H-NMR spectroscopy and mass spectrometry. The FTIR spectra of compound (3) showed the band at 3347 cm^{-1} for NH group of hydrazone and then vanished. The bands at 1680 cm^{-1} and 2740 cm^{-1} corresponds to C═O and CO—H groups of pyrazole (4). The band of C═N imine stretching vibration was found in prepared Schiff bases at 1616 cm^{-1} and 1591 cm^{-1}. The ^{1}H-NMR spectrum of compound (3) showed the following characteristic chemical shifts: the singlet signal at δ=9.1ppm suggested the attribution of NH proton, the singlet signal at δ=2.1 ppm suggested the attribution of the protons of CH_3 group. The ^{1}H-NMR spectrum of compound (4) showed the following characteristic chemical shifts: the singlet signal at δ= 10 ppm suggested the attribution of proton of CHO group, the singlet signal at δ= 9.2 ppm suggested the attribution of CH proton of pyrazole ring. Also the ^{1}H-NMR spectrum of Schiff bases showed the following characteristic chemical shifts: the singlet at δ= 9.3 ppm corresponds to CH proton of pyrazole ring and the singlet signal at δ= 8.5 ppm suggested the attribution of H—C═N proton. In the mass spectra of prepared compounds, molecular ion peaks were observed at 295 (M^+), for compound (3), 333 (M^+) for compound (4), 408 (M^+) for compound (5a) and 442 (M^+) for compound (5b), which confirms the proposed structure of prepared compounds.

CONCLUSION

A new series of Schiff bases was prepared and the structure of newly synthesized Schiff bases was confirmed on the basis of IR spectroscopy, 1H-NMR spectroscopy and Mass spectrometry. These newly prepared Schiff bases constitute a family of compounds, of great interest with regards to biological activity.

ACKNOWLEDGEMENT

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PHOTOCHEMISTRY AS IN A SUNNY SIDE OF GREEN CHEMISTRY.

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ABSTRACT

'Nature' – A treasure home for various innovations,where 'green' synthetic methods are used by nature. No doubt it is 'Solar light'. A approach to Photochemistry as a technique to green chemistry is nowadays a key topic of interest. The use of light as an energy source and as an agent of chemical change can surely allow mild chemical reaction. Thus, it is definitely, a sustainable raw material which will be available for millions of years. This paper is just enhancing interest and thought- provoking overview of work of various authors including one of the pioneer in Green Chemistry i.e. Great Scientist, GiacomoCiamician, who confronted the problem.

Keyword: sustainable, Solar energy, green chemistry.

INTRODUCTION

The long history of success in various branches of industry and chemistry have been proved both blessing and a curse. Many of our most reliable strategies for assembling target molecules employ reactions which havethe chronic toxicological properties of chemicals. During these early years, the chronic toxicological properties of chemicals were often completely unknown and many unwittingly became indispensable tools of the trade. Infamously, benzene was widely employed as a solvent, a hand-cleaner and even as an aftershave, decades before its carcinogenicity became appreciated. So the need for Green Chemistry is the realization of the damage to our environment caused due to the man-made pollutants. Thus, the research for more environment friendly and cleaner methods becomes more prominent among researchers.

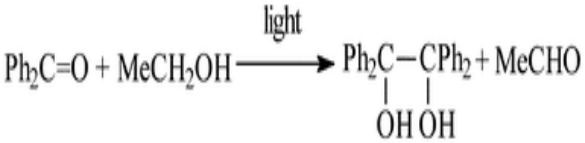
However, the moral imperative of avoiding an irreversible damage to the environment and intellectual motivation to find a cleaner method is the motive behind the research of Green Chemistry. Early pioneers in green chemistry included Trost (who developed the atom economy principle) and Sheldon (who developed the E-Factor).These measures were introduced to encourage the use of more sustainable chemistry and provide some benchmarking data to encourage scientists to aspire to more benign synthesis. Later, green chemistry became formalized by the publication by Warner and Anastas of a holistic set of principles designed to raise awareness of the safe, environmentally sensitive and sustainable practice of chemistry. An unparalleled example of clear-sightedness on this question is offered by the work of GiacomoCiamician at the beginning of the 20th century, he felt some dissatisfaction with this otherwise towering example of ingenuity. Addressing the French Chemical Society on June 8, 1908.

Chemistry in the laboratory differs from chemistry of organisms not in the materials, but also in the reagents used. It is thus, apparent that the further advancement of biology requires all of the compounds present in nature which can be produced by using only reagents present in nature, rather than agents that do not belong to the 'living world.' Thus, a step towards sustainable development. The most widely available reagent is Solar light which is main source of energy for plants to carry out the process of Photosynthesis using Chlorophyll, thus, thereby transforming the solar energy into chemical energy. However, limited source of oil is another need for its use.

Discovering various Photochemical reactions by different researchers are as listed

I. Reductions reactions

Ciamician and Silber found that, aliphatic aldehydes and ketonesabstract hydrogen, but give complex mixtures, aromatic ketones (and, with a lower yield, aldehydes) undergo clean bimolecular reduction to pinacols. In this case not

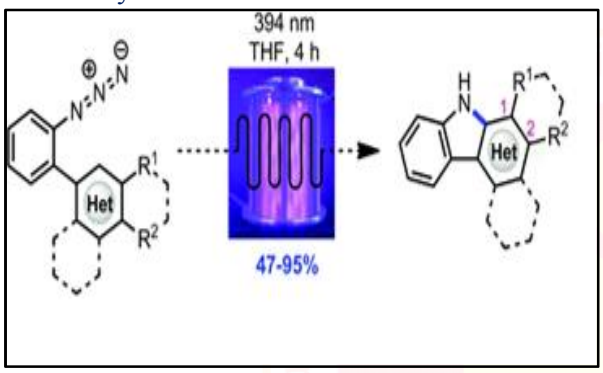


only alcohols, but also alkylaromatics function as reducing agents. Further products containing a C= O bond undergo reductive dimerization, *e.g.* alloxane to alloxantin.

Reductions reactions involves exploitation of hydrogen by abstraction from excited carbonyls whereas photochemistry offers an extremely mild entry for the functionalization of non-activated C–H bonds.[15]

II. Photochemical intramolecularamination for the synthesis of heterocycles

Polycyclic heterocycles can be formed in good to excellent yields *via*photochemical conversion of the corresponding substituted aryl azides under irradiation with purple LEDs in a continuous flow reactor. The photochemical method is presumed to progress through a mechanism differing from the other methods of azide activation involving transition metal catalysis.

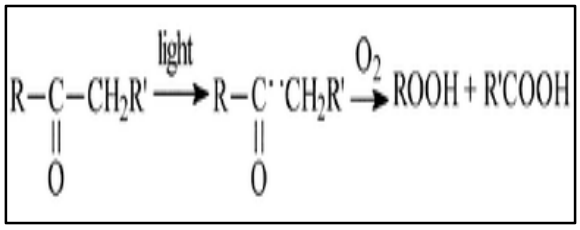


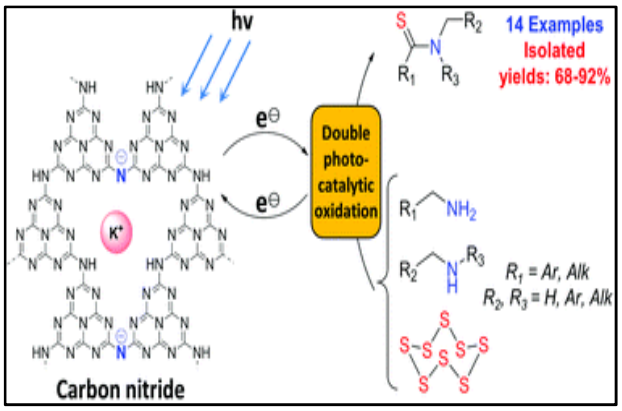
III.Autooxidations

Under this category the Authors considered various processes. One is the α-cleavageof aldehydes and ketones. Under oxygen the radicals are trapped and *e.g.* acetone gives acetic and formic acids, which may be viewed as a mild version of the permanganate cleavage of ketones.

IV. Carbon nitride creates thioamides in high yields by the photocatalytic Kindler reaction

Potassium poly(heptazine imide), a carbon nitride based photocatalyst, effectively promotes the Kindler reaction of thioamide bond formation using amines and elemental sulfur as building blocks under visible light irradiation. The feasibility of the developed methodology was confirmed using 14 different primary and secondary amines, including substituted benzylamines and heterocyclic and aliphatic methylamines, which were successfully converted into thioamides with 68–92% isolated yields.





DISCUSSIONS

The ability of Photochemical reactions of generating highly reactive species with high selectivity and under exceptionally mild (and thus versatile) conditions is nothing but a approach to Green Chemistry. From another perspective Photochemical Process is chemistry of carbon-centered radicals, so need to give stress on its importance in present day synthesis. Hence, it becomes essential from point of view of sustainable development, exploitation of solar energy is required. This is already concerned by Ciamician in his general lecture before the International Conference of Applied Chemistry in New York in 1912,Ciamician was concerned with the contribution of photochemistry as a source of energy. Following recent contributions by Ramsay and Engler, he evaluated the available amount of coal and that mined yearly. He remarked that this was nothing else than a form of fossil Solarenergy.It has been envisaged from work of other chemists that photochemical process is important for industry as it should not wait for apossibleshortage of fossil fuels.

CONCLUSIONS

With no prejudice against the development of advanced agriculture on suitable land, on arid lands a photochemical industry 'without smoke and smokestacks' will flourish. A 'forest of glass tubes' will rise and produce chemicals more abundantly than nature, 'for nature is not in a hurry and mankind is', through clean processes that will not harm the environment. This, will lead the way for mankind to a 'quieter civilization based on the utilization of solar energy', where progress and happiness should not find the drawback that had characterized the 'black and nervous civilization based on coal'.It is appalling how this chemists foresaw the need of finding alternative methods that were economic and non-polluting for giving mankind the chemicals it needed for a more prosperous life without exhausting natural resources or degrading the environment. These are the

principles of present day green chemistry which is more appreciable. Very little has been done in exploiting solar light (an in general really alternative paths for green chemistry) at the industrial level. Thus, a need for setup of photochemical industry.

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SYNTHESIS AND CHARACTERIZATION OF PPy/$LaCl_3$ COMPOSITES

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ABSTRACT

Chemical oxidative polymerization of pyrrole (Py) was carried out by doping it with Lanthanum Chloride ($LaCl_3$) in the presence of oxidizing agent ammonium peroxydisulphate to synthesize polypyrrole/ Lanthanum Chloride (PPY/$LaCl_3$) composites. The PPY/ $LaCl_3$ composites were synthesized with various compositions of viz., O.1 M and 0.02 M $LaCl_3$ in pyrrole. Morphological characterization of synthesized composites was carried out by SEM and powder X-ray diffraction (XRD) analysis. These studies suggest that they exhibit amorphous behavior and also show that $LaCl_3$ particles are embedded in PPy chain to form multiple phases.

Keywords: *Synthesis , characterization, X-ray diffraction, Polypyrrole*

INTRODUCTION

Over the last few decades polymers have attracted considerable interest in research for the development of advanced materials. The organic materials that generally possess an extended conjugation of Π-electron system along a polymer backbone chain are recognized as electroactive conducting polymers. These materials with interesting electron-transport behavior to a material exhibits immense potential in technological applications such as in electrochromic devices, non-linear optical system OLEDs, photoelectrochemical devices, gas sensors, biomechanical sensors.

Among the number of conducting polymers, Polypyrrole (PPy) is profoundly studied material due to its superior conductivity, good thermal and environmental stability, electrochemical reversibility, high polarizability and the ease of preparation through chemical or electrochemical routes. However, PPy is limited in practical use due to its very fragile structure and insolubility. It exhibits poor processability and lacks essential mechanical properties. These properties and applicability of polypyrrole can be improved by some suitable modifications of existing polymers structures. This can be achieved by judicious choice of making composites of PPy by doping it with suitable dopant material in order to prepare multifunctional molecular structures that open possibilities for almost any desired applications.

The association of PPY with $LaCl_3$ in order to prepare its composite which combine the properties of both materials is one very promising way to obtain the specific requirements of physical properties for each type of application.

EXPERIMENTAL

The 0.1 M solution of AR grade pyrrole was contained in a beaker which was placed in a beaker on a magnetic stirrer. 0.1 M ammonium peroxydisulphate solution was continuously added drop-wise with the help of a burette to the above 0.1 M pyrrole solution. The reaction was allowed for 6 hours under continuous stirring by maintaining a temperature of 0°C to 5°C. The precipitated polypyrrole was filtered and dried in hot air oven and subsequently in a muffle furnace at 100 °C. For 0.1 M pyrrole solution, 0.1 M solution of $LaCl_3$ was added and mixed thoroughly, further 0.06 M ammonium persulphate was continuously added drop-wise with the help of a burette to the above solution to get PPy/0.1 M $LaCl_3$ composite.similarly PPy/0.02 M $LaCl_3$ is also prepared by following the above procedure. The pure PPy and PPy/$LaCl_3$ thin films were prepared by bath deposition technique.

The synthesized composite materials were subjected to morphological studies through SEM and X-ray diffraction analysis.

RESULTS AND DISCUSSION

The XRD diffractogram of PPy and PPy/$LaCl_3$ composites is given in fig. From the X-RD analysis of the polypyrrole and PPy/$LaCl_3$ composites, it is observed that the film exhibited broad scattering peaks at 2θ value around 20-30°, which suggests that the polypyrrole and PPy/ $LaCl_3$ composites are amorphous in nature. X-ray scattering studies of polypyrrole films have been

reported to be highly disordered and non-crystalline.

The structural information was deduced from XRD pattern of PPy and PPy/$LaCl_3$ composites which indicates that the peak at 24.67^0 corresponds to basic polymeric chain of PPy. This broad peak at about 2θ= 24.67° is due to the pyrrole intermolecular spacing and the pure PPy is amorphous in nature.

The XRD patterns of PPy/$LaCl_3$ composites show similarity to the pattern of PPy indicated basic polymeric chain pattern is retained in the composite material. The XRD patterns of PPy/$LaCl_3$ composites show similarity to the pattern of PPy indicated basic polymeric chain pattern is retained in the composite material while the peaks are shifted to lower diffraction angle (24.20 and 22.29 in 0.01 M and 0.2 M Rhd-B dopant concentration respectively). The shifting of peak towards lower diffraction angle is attributed to formation of quasi particle polarons and bipolarons which improves and enhances Polypyrrole morphology.

The reflection intensity decreases with increasing concentration of dopant $LaCl_3$ indicates less ordered structure of PPy after doping. This change in XRD pattern in the PPy after doping indicates variation in morphology of PPy. The XRD pattern reveals that the resulting structural and morphological properties of PPy/$LaCl_3$ composite are improved and enhanced.

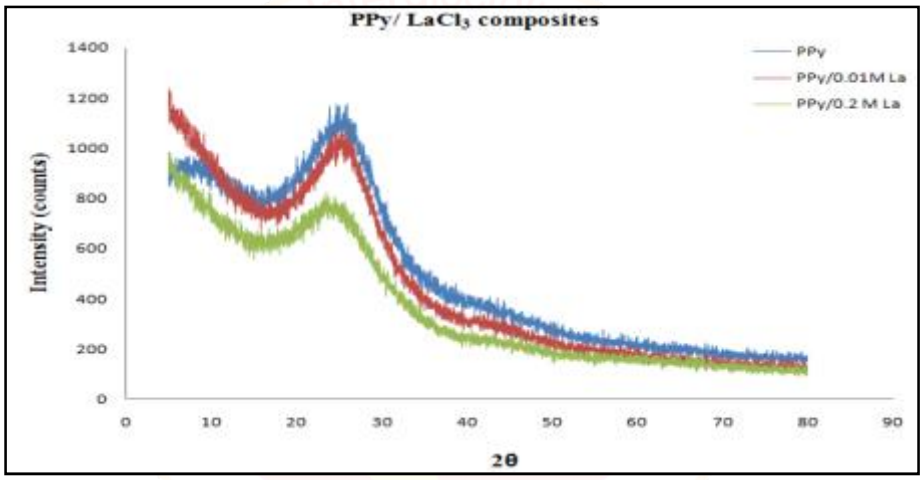

Fig: X-ray diffractogram of PPy/$LaCl_3$ composites

The resulting morphologies of the synthesized polypyrrole and PPy/$LaCl_3$ composites from SEM could be seen from Figure.

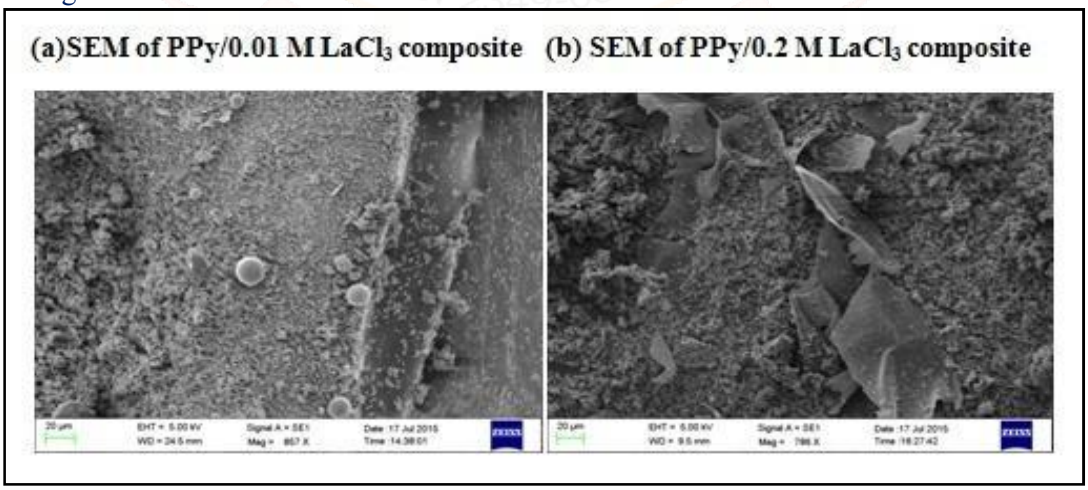

Fig: SEM Analysis of PPy/$LaCl_3$ composites

The resulting morphologies of the synthesized polypyrrole and PPy/$LaCl_3$ composites from SEM could be seen from Figure.

SEM micrograph of PPy and PPy/$LaCl_3$ composites shows polymeric solid structure with granular appearance. There is formation of aggregates of polymeric chains is observed. The aggregation of particles which may be due to the increased interchain interaction showing the crystallinity in coincide with the result of

conductivity. Thus the morphology of the conducting polymers is very much related to the electrical conductivity. PPy structure is more homogeneous than PPy/$LaCl_3$ composites. The doped films of PPy with $LaCl_3$ are having rough, porous surface and having lamellar appearance due to dopant interaction. Uniform, porous and granular surface morphology is shown in each case of the PPY/$LaCl_3$ composite samples preferred for applications like gas sensing promoting the adsorption of gas molecules through the surface, though the size of particles effected by pores varies due to the different mole ratios of PPY in each sample. It can be clearly observed that the surface of polymer has been modified into bulky, porous nature and having globular particles which may be due to adsorption of La^{3+} ions at the surface of PPy, when compared to the SEM images of PPy taken before the treatment of dopant.

Efforts have been made to synthesize the polypyrrole/Lanthanum chloride composites to tailor the structural, morphological, and electrical properties of polypyrrole. Detailed morphological characterizations of the synthesized composites through SEM and XRD studies indicate the incorporation of dopant into the polymeric chain. Comparison of the SEM images of the samples shows no significant change in the shapes of PPy particles. but the porosity increases with the increase in dopant amount. Porosity is directly related to the solubility decreasing with the decrease in the number of pores. Thus the polymer with less number of pores shows less solubility. By the SEM image analysis of the obtained films, the influence of dopant inclusions on the morphology of composite films was shown. The XRD study indicates the amorphous nature of the samples and the presence of hump in the diffractogram indicates the homogeneous nature of the polymer.

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COMPARATIVE STUDIES OF *JONES-DOLE AND STAUARDING* EQUATION OF AQUEOUS SOLUTION OF SOME CARBOHYDRATES AT 298K

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ABSTRACT

Viscosities (η) of aqueous solution of dextrose, fructose and myoinositol have been measured in the concentration range 0.1-0.9 M at 298 K. The viscosity coefficient B and A were calculated from the viscosity data using Jones-Dole equation for all the studied sugars. The data were also analyzed for Stauarding equation. From these parameters, 1results were correlated with solute-solute, salvation of solute and solute-solvent interactions. All the carbohydrates are under studies revealed structure making properties.

Keywords: *Jone-Dole, Stauarding equation, viscosity coefficient, myoinositol, sugar.*

INTRODUCTION

The molecular interactions of dilute as well as concentrate solution of sugars in water play an important role in expressing biophysical and medicinal processes of cellular systems. The viscometric behavior of electrolytes and non-electrolytes give useful information for intermolecular interactions in the solutions [1, 2]. In this regard viscosities were used for investigation of molecular interactions (solute-solvent affinity) [3, 4, 5].

Carbohydrates and their derivatives are most important class of biomolecules and reveal their biological flexibility of different functions such as structure and defensive metabolic recognition. In addition to this, carbohydrate molecules exhibit high receptor affinity and selectivity [6]. It is an essential component for maintaining cell feasibility, natural cell defensive agent as well as energy pool in many organisms [7-8].

Among the cyclic polyols, Myo-inositol ($C_6H_{12}O_6$) is a cyclic sugar alcohol. It is also known as cyclitol. The chemistry of the cell is controlled by myo-inositol. There should be communication between outer and inner environment of a cell. The calcium channels of cell membrane can be opened by the derivative of myo-inositol (inositol-1, 4, 5 triophosphate). It allows the calcium ions to enter into the extracellular fluids [9].

The objective of this work is to work out viscometeric parameters such as viscosity coefficients *A* and *B Jone-Dole* constant and *Staurding* constant of dextrose, fructose and myoinositol in aqueous solution by using viscosity at various concentrations and at 298 K.

EXPERIMENTAL

Dextrose, fructose and myoinositol used in this work were analytical grade with purity of > 99% was procured from Loba Chemie (dextrose and fructose) and SHIMADZU. The water used for the preparation of solution was double distilled. The molar aqueous solutions of solutes were prepared by using digital electronic balance (Model-AJO20, aiwa) with an accuracy of ± 0.1 mg.

Ostwald's viscometer was used for the measurement of viscosity of liquid mixtures with an accuracy of 0.0001Nsm^2. The viscometer was calibrated before used. Time flow of water and liquid solutions were measured respectively.

RESULTS AND DISCUSSION

Relative viscosity of dextrose, fructose and myoinositol solutions at different concentrations was calculated considering solutes as monomer unit of polymer system. Thus, if η is the viscosity of solution and η_o is the viscosity of pure solvent at 298 K. The polymer species follow *Staurding* [10] the Eq .(1) is given by

$$(\eta - \eta_o)/\eta_o = kn\,Cn \qquad (1)$$

Where, *k* is constant for a given solute in a given solvent, C is the molar concentration of solute and n is the number of monomer units in polymer. The observed relative viscosity values for dextrose, fructose and myoinositol are given in the Table 1.

Observed data were used to examine how for the results of viscosities of dextrose, fructose and myoinositol solutions agree with Eq. (1) applicable for polymers. Therefore the relative viscosity

values were plotted against different concentrations of studied sugars and non sugar and for all these molecules plot shows linearity. At zero concentration, intercept value is found to be minimum. The values of slope (*kn*) found for different studied solutes are presented in Table 2.

Table 1. Relative viscosities (η/η_o) for dextrose, fructose and myoinositol at 298 K at different concentration

Concentration (C) (mol dm^{-3})	$\sqrt{C}$	(η/η_o) for sugars		
		Dextrose	Fructose	Myoinositol
0.1	0.3162	1.042	1.021	1.004
0.2	0.4472	1.077	1.052	1.035
0.3	0.5477	1.107	1.074	1.084
0.4	0.6325	1.147	1.123	1.137
0.5	0.7071	1.192	1.164	1.169
0.6	0.7746	1.238	1.222	1.228
0.7	0.8367	1.325	1.292	1.283
0.8	0.8944	1.396	1.360	1.370
0.9	0.9487	1.447	1.459	1.458

Table 2. Values of parameters of *Staurding* and *Jone-Dole* equation for dextrose, fructose and myoinositol at 298 K in aqueous solution

Sugars	(η/η_o-1) *versus* C	(η/η_o-1)/$\sqrt{C}$ *versus* $\sqrt{C}$
Dextrose	kn=0.4959 dm^3mol^{-1}	B = 0.55 dm^3 mol^{-1} A = -0.084 $dm^{3/2}$ $mol^{-1/2}$
Fructose	kn 0.4961 dm^3mol^{-1}	B = 0.64 dm^3 mol^{-1} A = - 0.183 $dm^{3/2}$ $mol^{-1/2}$
Myoinositol	kn=0.5089 dm^3mol^{-1}	B = 0.71 dm^3 mol^{-1} A = - 0.236 $dm^{3/2}$ $mol^{-1/2}$

The structure making and structure breaking properties of solutes is also reported by considering *Jone-Dole* [11] eq. (4), in term of viscosity coefficient B and intercept A

$$\eta/\eta_o = 1+A+B\sqrt{C} \qquad (2)$$

Where, η/η_o is the relative viscosity, C is molar concentration of solute, A and B are constants for the studied solute. A-coefficient atributes the contribution from interionic electrostatic forces and the B- coefficient measures the order or disorder produced by the ions in case of electrolyte and solutes in case of non-electrolyte in the solvent structure [12]. Therefore $(\eta/\eta_o - 1)/\sqrt{C}$ values were plotted against $\sqrt{C}$ shows linearity for all sugar solution with slope B and intercept A. The values of both the constants are reported in Table 2 for dextrose, fructose and myoinositol. The *Jone-Dole* equation is more useful for ionic solute because A gives information about interionic electrostatic forces. In our present study, sugars and myoinositol are covalent (non-electrolytes). Therefore, the values of A for all the studied solutes are very small because the interionic interaction is very poor in case of non-electrolytes. The very small values of intercept A may be due to hydrogen bonding or Vander Waal's forces.

It is observed from the results (Table 2), the values of coefficients B are positive for all the studied molecules in aqueous solutions designating that solute-solvent interactions / solute-solute interaction are more significant and all the sugars behave as "structure maker". The values of coefficient B is in the order of myoinositol > fructose > Dextrose. The trends of variation of coefficient B of aqueous solution of dextrose, fructose and myo-inositol may be explained as follows.

It is observed that strength of molecular interaction of carbohydrates (dextrose, fructose and myo-inositol) depends on molecular ring size and percentage of axial and equatorial hydroxyl groups. It is more favourable when the hydroxyl group is at the equatorial position [13]. It seems that strength of intermolecular interaction of equatorial –OH groups is more. Dextrose has more percentage of equatorial –OH group. It should have strong association with solvent molecules as compared to fructose and myo-inositol. The result shows that the trend of molecular association is in the order of dextrose < fructose < myo-inositol. This can be explained that dextrose is present as a pyranose ring, furanose and straight chain form. But most stable form of dextrose in aqueous medium is pyranose form. Fructose is present as a furanose ring as well as straight chain form which have five hydroxyl (–OH) group, but out of these five; two are attached to $–CH_2$ groups and not to the ring. It is known that the interactions between open chain aliphatic –OH groups and solvent molecules are more extensive than cyclic compounds with solvent [14]. Hence, fructose is somewhat more hydrated than dextrose. Myo-inositol is present as six membered rings and has same number of equatorial –OH groups as like dextrose, but one –OH group is more than in dextrose and fructose and hence forms more number of hydrogen bonds and reveals strong molecular interaction [15].

The observed constant k of dextrose, fructose and myoinositol has values in the same order of coefficient B which are reported in Table 2.

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ASSESSING THE QUALITY AND SUBSEQUENT PHYTOCHEMICAL EVALUATIONOF CALENDULA OFFICINALIS USING HIGH PERFORMANCE THIN LAYER CHROMATOGRAPHY AND GAS CHROMATOGRAPHY-MASS SPECTROMETRY AND THEIR BIOLOGICAL ACTIVITY

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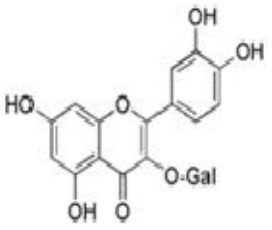
ABSTRACT

In recent years, there has been a growing interest in researching and developing new antimicrobial agents. Therefore, a greater attention has been paid to antimicrobial activity screening and evaluating methods. Several bioassays such as disk-diffusion, well diffusion and broth or agar dilution are well known and commonly used. The primary goal of this study was to develop a simple and reliable High Performance Thin Layer Chromatography method to quantitate active ingredients and the variation in the content and composition of Calendula officinalis essential oils was studied using GC–MS. A total of 22 different compounds were identified in the essential oils. Prevention of food spoilage and food poisoning pathogens is usually achieved by use of chemical preservatives which have negative impacts including: human health hazards of the chemical applications, chemical residues in food & feed chains and acquisition of microbial resistance to the used chemicals. Because of such concerns, the necessity to find a potentially effective, healthy safer and natural alternative preservative is increased.

Keywords: *Calendula officinalis, chlorogenic acid,rutin, hyperoside,essential oils.*

INTRODUCTION

Herbal medicines have stood the test of time for their safety, efficacy, cultural acceptability andlesser side effects and believed to have better compatibility with the human body. Many plants are used as folkmedicines to infectious diseases. Due to the indiscriminate use of antibacterial drugs, the microorganisms havedeveloped resistance to many commercial antibiotics. Therefore, investigation of the chemical compoundswithin medicinal plants has become desirable. Some of the herbal plants traditionally usedin formulations as antimicrobial agents.Calendula officinalis of the family Asteraceae, native to Eastern Europe and the Mediterranean, has long been used in both traditional and clinical medicine in wound healing and to help relieve skin inflammations and irritations. It is commonly known as marigold. The main aim of this study was to separate and compare different polyphenol,glycoside,galactoside and lipophilic extracts from Calendula officinalis flowers usingrutin, hyperoside, chlorogenic acid as a phytochemical marker.Several analytical techniques have been established for the identification and quantification of natural products in herbal preparations. Chlorogenic and caffeic acids are in vitro antioxidants and fight against diabetes and cardiovascular disease. Hyperoside is a flavone found in certain herbs with strong antioxidant activity.[1] Thiscompound has a variety of pharmacological effects, including anti-inflammatory, anti-viral, anti-oxidative. The chemical structures of hyperoside, chlorogenic acid and rutin are shown in(Figure 1, 2 and 3) respectively.



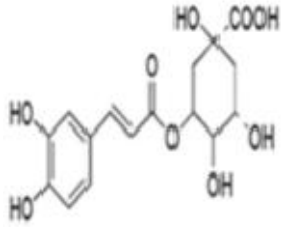


Figure 1.Chemical structure of Hyperoside
Figure 2.Chemical structure of Chlorogenic acid

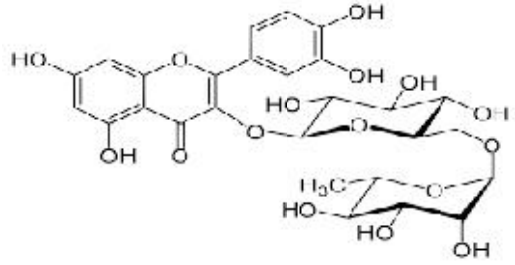


Figure 3.Chemical structure of Rutin

Quantitative Thin Layer Chromatography (TLC) has been used widely for analysis of herbal medicinal extracts due to its simplicity of operation, speed, versatility and reproducibility, and relatively low cost, as a number of samples can be analyzed simultaneously on a single plate using only a small amount of solvent as the mobile phase.

EXPERIMENTAL MATERIALS

Collection of plant: The fresh flower of Calendula officinalis were collected from Lonavala, Pune, in the month of February, 2016 and were identified by the taxonomist, J. Jayanthi,Botanical survey of India,7-Koregaon road, Pune 411001, No. BSI/WRC/IDEN.CER./2017/600.

Chemicals and Reagents: Solvents used in the HPTLC mobile phase were ethyl acetate, anhydrous 99.8% (Sigma Aldrich, Germany), glacial acetic acid 99.8% (Sigma Aldrich, Germany), formic acid (Sigma Aldrich, Germany),HPTLC grade water (Sigma Aldrich, Germany) Extraction solvents used were methanol (Sigma Aldrich, Germany).Chlorogenic acidrutin, hyperoside minimum 95% (Sigma Aldrich, Germany), was used as an external standard.

Equipments: Soxhlet apparatus, digital balance, bunsen burner, pH meter, glass wares, UV spectrophotometer, Magnetic stirrer, hot air oven,HPTLC Silica gel 60 F254 plates (Merck, Switzerland) (10×10 cm) , Nanomat 4 applicator (Serial: 1611, CamagR, Muttenz, Switzerland), 10 µL guided plunger syringe (Serial: 10R-GP, SGE, Australia), TLC-Visualiser (CamagR, Muttenz, Switzerland),Gas chromatography mass spectrometry (Shimadzu).

Plants extraction : The powdered material(10g) was extracted in a Soxhlet extractor with 70% methanol at 40^{0}C for 4 hr. The extract was filtered using Whatman No. 1 filter paper and the residue was removed. Test solution was again filtered and sterilized through 0.22µ micro filters. Finally,the extracts were kept at +4^{0}C.

METHODS

Plate pre-treatment

Parameters	Description
Stationary phase	Silica gel 60 F254pre-coated on aluminium sheet
Mobile phase	Ethyl acetate : glacial acetic acid : formic acid: water (10:1.1:1.1:2.3 v/v).

Plate pre-treatment can be performed for a full plate package in advance. The HPTLCsilica gel plates were washed by pre-development with methanol.The cleaned plate were dried and activated on the TLC Plate Heater III (CAMAG,Muttenz, Switzerland) at 120°C for 20 minutes.The last step is necessary to completely remove all traces of the washing solvent.In a desiccator, the active plate were cooled to room temperature and balanced withthe relative humidity from the laboratory atmosphere. For temporary storage, the pre-washedplates were wrapped in aluminium foil.

STANDARD SOLUTION

For stock solutions preparation (1mg/10mL), chlorogenic acid, hyperoside and rutinwere individually dissolved in 10 ml methanol.For application was prepared a mixture (900µL) from these stock solutions asfollows: 300µL of chlorogenic acid, 300µL of hyperoside and 300µL of rutin.

CHROMATOGRAPHIC CONDITIONS

High Performance Thin Layer Chromatography was performed on a 10 X 10 cm HPTLC Silica gel 60 F254 plates (Merck, Darmstadt, Germany). 10µl of each of the extracts were separately applied on the plate as8mm wide and 6mm apart bands.Different volumes of standard solutions; rutin, chlorogenic acid and hyperoside were also applied as bands. CAMAG Twin Trough Chamber was saturated for 20 minutes with mobile phase consisting of ethyl acetate: glacial acetic acid: formic acid: water (10:1.1:1.1:2.3 v/v). Plate was developed till 8 cm, dried with dryer and heated on TLC plate heater (CAMAG, Switzerland) at 110^{0}C for 5 minutes. Developed plate was observed under UV light at 254nm and 366 nm in TLC visualizer (CAMAG, Switzerland) and scanned using TLC Plate Scanner 3 (CAMAG, Switzerland) for densitometric analysis. rutin, chlorogenic acid and hyperoside were scanned at 254 nm and detected under UV light, TLC plate was derivatized by using natural product reagent, heated on TLC plate heater at 120^{0}C for 5 minutes and scanned.

Table 1. Optimized Chromatographic Condition

Development chamber	CAMAG Twin Trough Chamber
Chamber saturation	20 min.
Sample applicator	CAMAG Automatic TLC Sampler 4 (ATS4)
Band	6mm
Development distance	8cm

Application speed	0.5 µL/sec
Derivatizing reagent	Natural product reagent
Drying of plate	At 110 ^{0}C on TLC plate for 10min
Densitometric scanner	CAMAG TLC SCANNER III
Lamp	Deuterium, Tungsten
Wavelength	254nm
Chromatographic evaluation	CAMAG TLC software winCATS

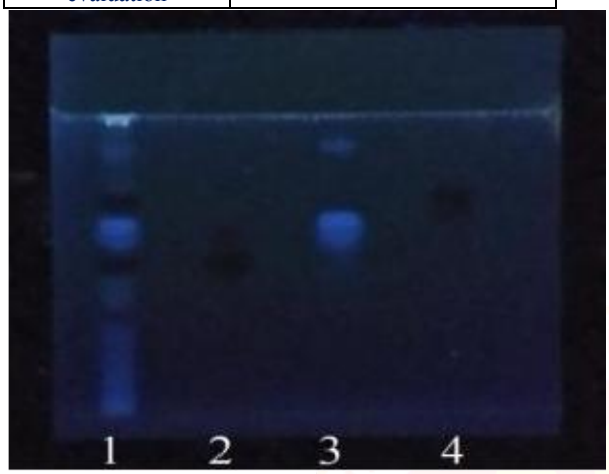


Figure 4. at 254nm

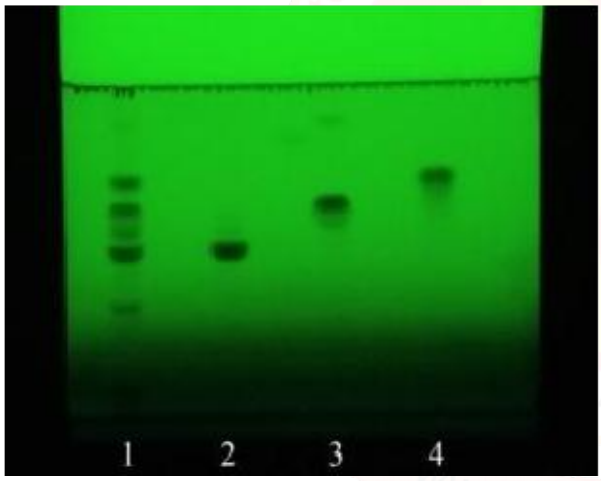


Figure 5. at 366nm

1.Methanolic extract of Calendula officinalis 2.Rutin 3.Chlorogenic acid 4.Hyperoside	1.Methanolic extract of Calendula officinalis 2.Rutin 3.Chlorogenic acid 4.Hyperoside

RESULT ANDDISCUSSION

A normal phase high performance thin layer chromatographic (HPTLC) method for the simultaneous quantification of rutin, chlorogenic acid and hyperoside from Calendula officinalis (Linn) methanolic extract was developed in the present research work.

GAS CHROMATOGRAPHY-MASS SPECTROMETRY

MATERIALS AND METHODS

Collection and storage of the plant and formulation

Collected whole plants were washed with tap water and air-dried thoroughly under shade at room temperature for 2 weeks to avoid direct loss of phytoconstituents from sunlight. The shade dried materials were powdered using grinder and sieved through an ASTM 80 mesh. It was then homogenized to fine powder and stored in an air-tight container for further analysis.

PREPARATION OF THE EXTRACTS

Calendula officinalis (Linn) was extracted using Soxhlet extraction. 5grams of plant powder was weighed in a Extracts were filtered through a syringe filter of pore size 0.45µm before further analysis.

REAGENTS AND STANDARDS

All chemicals and solvents used were of analytical grade and purchased from Merck (Darmstadt, Germany).

PREPARATION OF STANDARD SOLUTIONS

Stock solutions of standards were prepared in methanol immediately before use.

CHROMATOGRAPHIC CONDITIONS

GC-MS analysis of the methanolic extract of Calendula officinalis (Linn) was performed using Shimadzu GCMS-QP2010 system comprising a Gas Chromatograph interfaced to a Mass Spectrometer equipped with Rtx-5ms column (5% diphenyl/ 95% dimethyl polysiloxane) a capillary column having the length of 30 m, internal diameter of 0.25 mm and film thickness of 0.25 µm. For GC-MS detection, an electron ionization system was operated in electron impact mode with ionization energy of 70eV. Helium gas (99.999%) was used as a carrier gas at a constant flow rate of 1.25ml/min, and an injection volume of 1µl was employed (a split ratio of 5:1). The injector temperature was maintained at 250 °C, the ion-source temperature was 200 °C, the oven temperature was programmed from 200 °C (isothermal for 2 min), with an increase of 4 °C/min to 280°C with 10 min isothermal. Total program time was 32 minutes. Mass spectra were taken at and NIST libraries and those described by

Adams as well as on comparison of their retention indices with literature.

Table 2: Optimized Chromatographic Conditions

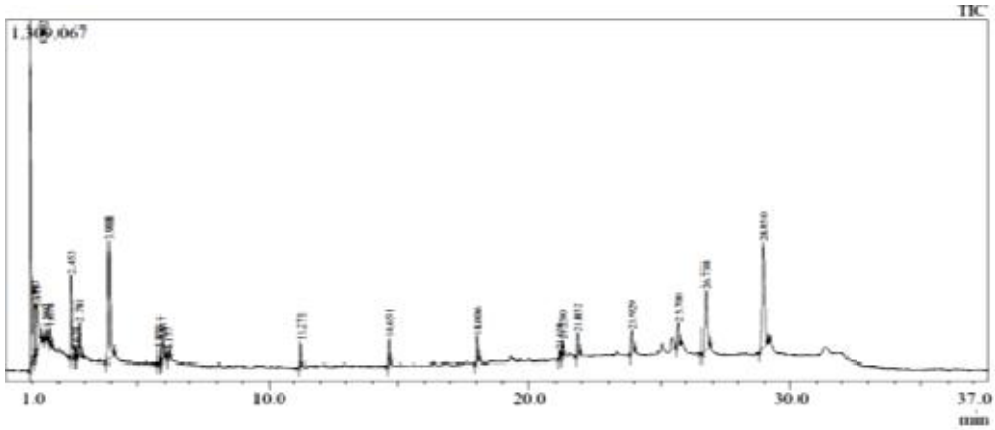
Parameters	Description
Instrument	GC-MS QP 2010 Ultra Shimadzu
Carrier Gas	Helium
Injector Mode	Split
Split Ratio	5:1
Sample Volume	1 µL
Flow Rate	1.5ml/min
Flow control Mode	Linear Velocity
Purge Flow	3ml/min
Interphase Temperature	320ºC
Ion Source Temperature	200 ºC
Run Time	32 min
Start m/z	35
End m/z	600

OBSERVATIONS

Table3: Phytochemicals identified by GC-MS in frond methanolic extract of Calendula officinalis (Linn)

Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Name
1	0.892	4444914	23.87	1262904	Ethane, 1-chloro-1-fluoro-
2	1.093	1099564	5.90	188810	1,2,3,4-Butanetetrol, [S-(R*,R*)]-
3	1.175	1087080	5.84	152900	4H-Pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6-methyl
4	1.507	135173	0.73	38643	Bicyclo[7.2.0]undec-4-ene, 4,11,11-trimethyl-8-methy
5	1.678	222078	1.19	58264	Dodecanoic acid
6	2.453	1174762	6.31	301754	Tetradecanoic acid
7	2.620	133007	0.71	27353	9,10-Dimethyltricyclo[4.2.1.1(2,5)]decane-9,10-diol
8	2.781	538504	2.89	131189	Acetic acid, 2-(2,2,6-trimethyl-7-oxa-bicyclo[4.1.0]he
9	3.908	1825874	9.80	431544	n-Hexadecanoic acid
10	5.830	209482	1.12	48458	9,12-Octadecadienoic acid (Z,Z)-
11	5.917	370123	1.99	77108	9,12,15-Octadecatrienoic acid, (Z,Z,Z)-
12	6.157	109518	0.59	31458	Octadecanoic acid
13	11.271	289457	1.55	88378	Pentacosane
14	14.651	355262	1.91	95939	Pentacosane
15	18.006	366861	1.97	94671	Pentacosane
16	21.130	106679	0.57	25255	N-[1-(2-Adamantan-1-yl-ethylamino)-2,2,2-trifluoro-
17	21.250	200966	1.08	57531	Pentacosane
18	21.852	366773	1.97	83566	dl-.alpha.-Tocopherol
19	23.929	457723	2.46	84768	Stigmasterol
20	25.700	471093	2.53	89087	4,4,6a,6b,8a,11,12,14b-Octamethyl-1,4,4a,5,6,6a,6b,
21	26.738	1704245	9.15	221543	4,4,6a,6b,8a,11,11,14b-Octamethyl-1,4,4a,,5,6,6a,6b,
22	28.950	2955968	15.87	386367	Lup-20(29)-en-3-ol, acetate, (3.beta.)-
		18625106	100.00	3977490	



CHROMATOGRAMS

Figure 6. Chromatogram of Calendula officinalis (Linn)

Table 4: Phytoconstituents with potent biological activity.

Sr. No.	Name of Components	Biological activity
1	Stigmasterol	Antibacterial activity,antihepatotic,anti-inflammatory,antioxidant,antiviral,cancer-preventive,estrogenic,hypocholesterolemic.
2	Pentacosane	Antiviral activityantibacterial activity, acaricidal activity,
3	Lup-20(29)-en-3-ol	Anti-bacterial activity, anti-inflammatory and anti- HIV activity,anti-viral,anti-tumor,anti-peroxidant.
4	Octadecanoic acid	Antibacterial activity,acaricidal activity, cytotoxicity and antiviral activity.
5	dl-.alpha.-Tocopherol	vitamin E activity, antioxidants, anti-bacterial activity
6	n-Hexadecanoic acid	antimicrobial activity, Anti-oxidant, Anti-androgenic

RESULT ANDDISCUSSION

GC-MS analyses of flower extract

GS-MS chromatogram of extracts study showed 22 peaks in C. officinalis flower extract. The fragmentation patterns of the peaks were compared with that of the library of compounds. 22 compounds were identified by GC-MS. Their retention time (RT), molecular formula, molecular weight (MW) and concentration (%) are presented in (Table 3.), (Fig.6). The major components present were Stigmasterol, Pentacosane, Lup-20(29)-en-3-ol, Octadecanoic acid Mass spectra from full scan analysis of components were showed in (Fig.6).

CLINICAL ACTIVITIES OF CALENDULA OFFICINALIS (LINN)

Antimicrobial Activity

Anti-microbial substances derived from plants have received considerable attention in recent years. The plant contains various bioactive compounds with high degree of antimicrobial activity against various pathogens, including pathogens responsible for Urinary Tract Infections. Antibacterial study was carried out on clinically isolated Urinary Tract Infecting (UTI) bacteria by disc diffusion method.Stigmasterol, Pentacosane, Lup-20(29)-en-3-ol, Octadecanoic acid isolated from the methanol extract of dried Calendula officinalis (Linn) showed concentration-dependent broad spectrum of anti-bacterial activity. The used micro-organisms to evaluate the antimicrobial activity are famous pathogens. Bacterial species were Staphylococcus aureus, Bacillus subtilis,Klebsiellapneumonia. The antibacterial of various methanolic extracts was performed by the modified cellulosic disc method .Agar LB and Malt Extract are inoculated with bacterial .The bacterial cultures (OD = 0.4 - 0.6) are homogenized with solid media. Thus, the tested quantities of each extract are deposited on the plate previously sterilized (120°C for 15 min). Times and incubation temperatures were 24 and 48 h for bacterial and fungal strains, respectively at 30 and 37°C. Antimicrobial activity is observed by the presence of an inhibition zone around the disk, impregnated with extract showed in Figure 7, Figure 8,Figure 9.

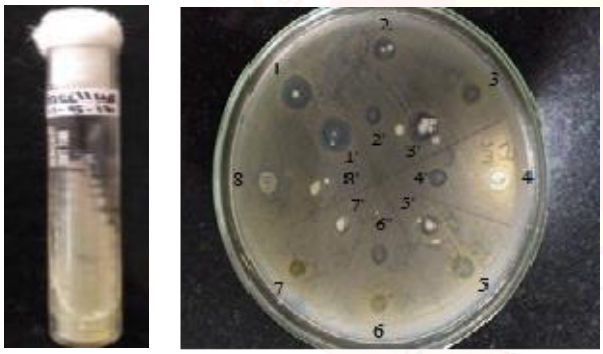


Figure.7

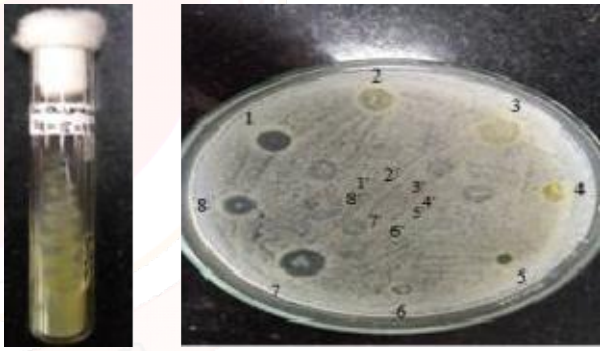


Figure.8

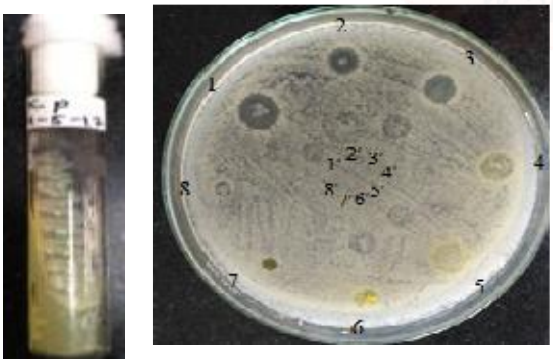


Figure.9

Table 5

Calendula officinalis extracts:		Only pure solvents:	
1-methanol 2-ehtanol 3-water 4-pet ether	5-ethyl acetate 6-toluene 7-ACN 8-n-hexane	1'-methanol 2'-ehtanol 3'-water 4'-pet ether	5'-ethyl acetate 6'-toluene 7'-ACN 8'-n-hexane

CONCLUSION

A normal phase high performance thin layer chromatographic (HPTLC) method is suitable for routine and qualitative analysis of rutin, chlorogenic acid and hyperoside in the methanolic extracts of Calendula officinalis (Linn). Also it can be used as a quality control method for other market formulations or dietary supplements.GC-MS is a powerful practical tool for comprehensive

quality control of plant raw materials and its formulations.Calendula officinalis (Linn) showed a wealth of powerful antimicrobial activities.This plant, mainly its flower, constitutes an excellent source of flavonoids. Indeed, its elevated phenolic compound content makes it a potential source of dietary regime and a protection against numerous diseases and infections. Methanolic flower extract from Calendula officinalis showed significant antimicrobial activities.

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MICROWAVE ASSISTED SYNTHESIS, CHARACTERIZATION & BIOLOGICAL EVALUTION OF SOME NOVEL QUINOXALINE DERIVED CHALCONES

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ABSTRACT

In organic chemistry, compound contain quinoxalins nucleus have been reported for biological activity like, Antibacterial, Antifungal, Anticancer, Hence it was planned to synthesis some novel Quinoxaline derivatives. Orthophenylene diamine was reacted with oxalic acid to form quinoxaling – 2,3 dione was chlorinated by using $POCl_3$ in DMF to form 2,3 dichloro quinoxaline. This dichloro compound reacted with 4 – amino acetophenone gives 1-(4-(3- Chloroquinoxaline – 2 ylamino) ethanone all above compounds were synthesized in Micro oven at 100 watt. 1-(4-(3- Chloroquinoxaline – 2 ylamino)ethanone reacted with substituted aldehyde gives corresponding derivatives. All compound are characterized by IR and ^{1}HNMR and further screened for biological activity like Antifungal and antimicrobial.

Key Words - *Quinoxaline, Micro oven, $POCl_3$, DMF.*

INTRODUCTION

Quinoxaline constitute a useful intermediates in organic synthesis. Its derivatives plays a very important role in medicinal chemistry. Nitrogen containing heterocyclic compounds are indispensable structural unites for both chemist and biochemist. Quinoxaline derivative forms an important class of pharmacologically active compound have an important biological activity like, Anticancer and cytotoxic[1], Antioxidant and Antiinflamatery[2], Antitumer[3] and Antimicrobial[4].

METHODS AND MATERIALS

All chemicals and solvents of AR-grade and LR-grade. All compounds were synthesis in Micro Oven Model CE 1030 CAT (SAMSUNG). Melting points were measure in open capillary tube in paraffin liquid. (IR) spectra were recorded as KBr pallets with FTIR: IRAffinity-1 (SHIMADZU). Spectrophotometer. 1H NMR spectra were recorded in DMSO and CDCL3 in BRUKER ADVANCE II 400 NMR Spectrophotometer. Thin layer Chromatography (TLC) was perform on pre-coated aluminum plates (silica gel 60 F254, Merck). Plates were visualized by UV light.

Synthesis of 1, 4- Dihydro Quinoxaline-2, 3-dione.

A solution of oxalic acid dehydrated (0.283mole) 30 g in H_2O (100 ml) was heated 100 watt & 4.5ml HCI was added, followed by O-phenylenediamine (0.204 mole) 22grm with staring keep the mixture in microwave at 100 watt for 25 minutes. Completion of reaction was confirmed by TLC. The mixture was cooled by addition of ice. The solid thus formed was washed with water and recrystalized by ethanol.

Synthesis of 2, 3 dichloro quinoxaline.

A mixture quinoxaline 2,3 dione (16.2grm) freshly distilled phosphorus oxy trichloride ($POCl_3$) 60 ml & N,N – Dimethyl formamide (DMF) 5ml was kept in microwave for 26 minutes at 100 watt Completion of reaction was confirm by TLC. The mixture was slowly poured into ice water with stirring & resulting solid was filtered wash with water, dried & recrystalized by chloroform and n-Hexane.

Synthesis of 1-(4-(3-Chloroquinoxaline-2-yl amino) phenyl) ethanone.

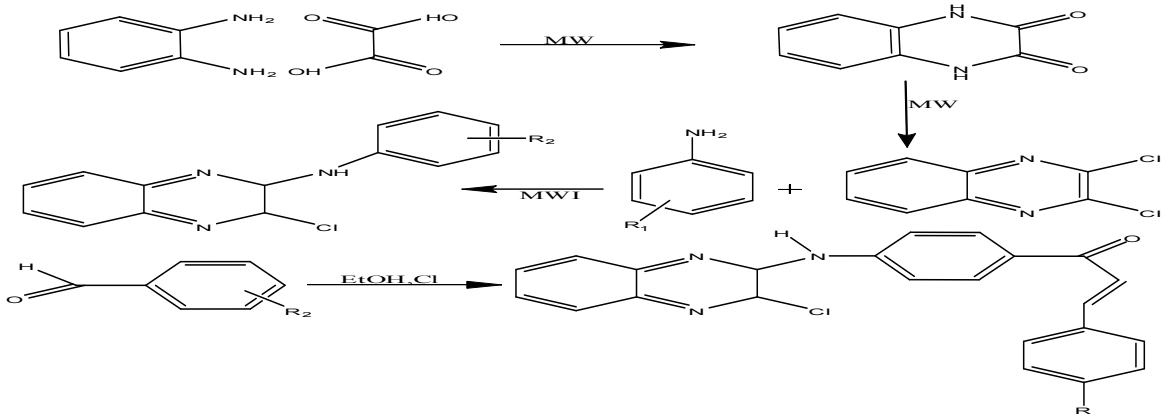
4-Aminoacetophenone (8.2g 0.01 mole) and 2,3 dichloro quinoxaline were dissolved in N, N-Dimethyl formamide (40 ml). Kept this reaction mixture in microwave for 22 min. at 100 watt Cool and poured into crushed ice. Periodically, a sodium carbonate solution (0.005, 0.53g in10 ml water) was added to neutralize HCI evolved during the reaction. The progress of the reaction monitored on TLC plate. The solid separate out was filtered, washed with water, dried and recrystalized from alcohol.

Synthesis of Quinoxaline derivatives.

Equimolar quantities of 1-(4-(3-Chloroquinoxaline-2-yl amino) phenyl) ethanone with substituted aldehyde was dissolve in alcoholic solution and then the solution of NaOH (5 ml of 40%) was added to reaction mixture with constant stirring at room temperature. After 24 h a reaction mixture was neutralized with HCI. The product separated

out was filtered , wash with water, dried and recrystalized from ethanol gives quinoxaline derivative

Scheme



Spectral analysis of synthesized compound:

1, 4-Dihydro Quinoxaline-2, 3-dione

% yield = 80%. Melting point = 360 – 362 ^{o}C . Rf = 0.74 (nHexane & ethyl acetate). IR – KBr Cm^{-1} aromatic C – H = 3040, C=C = 1512, N-H = 3100. ^{1}NHMR (400MHz DMSO) ∂ ppm 11.8 – 12.00 (s 2H, NH). 7.00 – 7.1 (d 4H aromatic).

2,3 dichloro quinoxaline.

% yield = 70%. Melting point = 150 – 152 ^{o}C . Rf = 0.30 (nHexane & ethyl acetate). IR – KBr Cm^{-1} aromatic C – H = 3090, C=C = 1544, C=N = 1649,C-CI = 773, C-N = 1269. ^{1}NHMR (400MHz DMSO) ∂ ppm 7.0 – 8.0 (m 4H, aroma

1-(4-(3-Chloroquinoxaline- 2yl amino) phenyl) ethanone.

% yield = 70%. Melting point = 294 – 296 ^{o}C . Rf = 0.34 (nHexane & ethyl acetate). IR – KBr Cm^{-1} aromatic C – H = 3090, C=C = 1543, C=N = 1693,C-CI = 771, C-N = 1270, C=O =1710, ^{1}NHMR (400MHz DMSO) ∂ ppm 7.0 – 8.0 (m 8H, aromatic). 9.1-9.5 (1H, NH). 3.5-3.8 (d 3H CH_3)

Rg) (E)-1-(4-((3-chloro-2,3-dihydroquinoxalin-2-yl)amino)phenyl)-3-(4-hydroxyphenyl) prop-2-en-1-one

% yield = 64%. Melting point = 200 – 202 ^{o}C . Rf = 0.26 (nHexane & ethyl acetate). IR – KBr Cm^{-1} aromatic C=C = 1523, C=N = 1666,C-CI = 673, C-N = 1276, CH=CH =3062, C-OH =3282, 1NHMR (400MHz DMSO) ∂ ppm 7.0 – 8.1 (m 12H, aromatic). 9.0-9.4 (1H, NH). 6.0-6.5 (d 2H CH=CH). 10.0-10.5 (s 1H OH).

Rh) (E)-1-(4-((3-chloro-2,3-dihydroquinoxalin-2-yl)amino)phenyl)-3-(4-methylphenyl)prop-2-en-1-one

% yield = 72%. Melting point = 255 – 257 ^{o}C . Rf = 0.62 (nHexane & ethyl acetate). IR – KBr Cm^{-1} aromatic C=C = 1512, C=N = 1647, C-CI = 673, C-N = 1226, CH=CH =3047, SP^{3-} C =3145, 1NHMR (400MHz DMSO) ∂ ppm 7.0 – 8.1 (m 12H, aromatic). 9.1-9.5 (1H, NH). 6.0-6.6 (d 2H CH=CH). 3.1-3.8 (d 3H CH_3).

Ri) (E)-1-(4-((3-chloro-2,3-dihydroquinoxalin-2-yl)amino)phenyl)-3-(4-methoxylphenyl)prop-2-en-1-one

% yield = 53%. Melting point = 284 – 286 ^{o}C . Rf = 0.22 (nHexane & ethyl acetate). IR – KBr Cm^{-1} aromatic C=C = 1533, C=N = 1662, C-CI = 675, C-N = 1228, CH=CH =3071, O-CH_3 =3145, 1NHMR (400MHz DMSO) ∂ ppm 7.0 – 8.0 (m 12H, aromatic). 9.0-9.5 (1H, NH). 6.1-6.6 (d 2H CH=CH). 3.0-3.8 (d 3H CH_3).

Rj) (E)-1-(4-((3-chloro-2,3-dihydroquinoxalin-2-yl)amino)phenyl)-3-(2-iodophenyl)prop-2-en-1-one

% yield = 49%. Melting point = 225 – 230 ^{o}C . Rf = 0.10 (nHexane & ethyl acetate). IR – KBr Cm^{-1} aromatic C=C = 1533, C=N = 1662, C-CI = 597, C-N = 1269, CH=CH =3057, C-I =756, 1NHMR (400MHz DMSO) ∂ ppm 7.0 – 8.0 (m 12H, aromatic). 9.0-9.5 (1H, NH). 6.0-6.7 (d 2H CH=CH).

Rk) (E)-1-(4-((3-chloro-2,3-dihydroquinoxalin-2-yl)amino)phenyl)-3-(4-iodophenyl)prop-2-en-1-one

% yield = 45%. Melting point = 224 – 230 ^{o}C . Rf = 0.11 (nHexane & ethyl acetate). IR – KBr Cm^{-1} aromatic C=C = 1521, C=N = 1656 ,C-CI = 673, C-N = 1265, CH=CH =3057, C-I= 756, 1NHMR (400MHz DMSO) ∂ ppm 7.0 – 8.5 (m 12H, aromatic). 9.0-9.5 (1H, NH). 6.0-6.6 (d 2H CH=CH).

Rl) (E)-1-(4-((3-chloro-2,3-dihydroquinoxalin-2-yl)amino)phenyl)-3-(4-flurophenyl)prop-2-en-1-one

% yield = 70%. Melting point = 180 – 185 ^{o}C . Rf = 0.33 (nHexane & ethyl acetate). IR – KBr Cm^{-1} aromatic C=C = 1508, C=N = 1656 ,C-CI =

603, C-N = 1226, CH=CH =3059, C-F= 1336, 1NHMR (400MHz DMSO) ∂ ppm 7.1 – 8.0 (m 12H, aromatic). 9.0-9.6 (1H, NH). 6.1-6.6 (d 2H CH=CH).

Rm) (E)-1-(4-((3-chloro-2,3-dihydroquinoxalin-2-yl)amino)phenyl)-3-(2-flurophenyl) prop-2-en-1-one

% yield = 50%. Melting point = 180 – 185 ^{o}C . Rf = 0.33 (nHexane & ethyl acetate). IR – KBr Cm^{-1} aromatic C=C = 1516, C=N = 1604 , C-CI = 673, C-N = 1224, CH=CH =3062, C-F= 1334, 1NHMR (400MHz DMSO) ∂ ppm 7.0 – 8.0 (m 12H, aromatic). 9.0-9.5 (1H, NH). 6.0-6.6 (d 2H CH=CH).

Determination of antimicrobial and Antifungal activity by disk diffusion method.

The antimicrobial activity of compound was determined by means of disk diffusion method. Each bacteria were inoculated nutrient agar broth and incubated at 37^{0}C for 16 h then adjusted to OD625 ¼ 0.08 – 0.1. The bacterial suspension was placed agar in 60 mm petri dish and spread homogeneously. Solution of compound Ra to Rf in DMSO were placed on agar surface containing bacterium which was incubated at 37^{0}C for h. The inhibition zones were measured with caliper considering total diameter. Compound Ra to Rf were tested for their antifungal activity by disk diffusion method against different fungal strain.

Table- 1- Antimicrobial activity against different bacteria.

Bacteria / Compound	E. coli	S. aureus	Salmonella typhi	Klebsiella pheunoniae	Bacillus cereus
Rg	ND	6mm	ND	6mm	12mm
Rh	ND	ND	3mm	4mm	8mm
Ri	ND	5mm	ND	8mm	6mm
Rj	ND	11mm	14mm	12mm	16mm
Rk	ND	14mm	4mm	8mm	4mm
Rl	ND	6mm	ND	10mm	6mm
Rm	ND	17mm	ND	ND	ND

Table- 1- Antifungal activity against different fungal strain.

Fung.strain / Comp.	Aspergillus Niger	Tricoderma Viride.	Cryptococcus neoform	Phoma
Rg	4mm	ND	4mm	ND
Rh	10mm	11mm	19mm	ND
Ri	6mm	15mm	10mm	ND
Rj	ND	16mm	8mm	ND
Rk	ND	13mm	7mm	ND
Rl	ND	10mm	6mm	ND
Rm	ND	10mm	8mm	ND

RESULT AND DISCUSSION

Microwave assisted synthesis is best method it is time saving and eco friendly also shows better yield than conventional method. Compound Rg, Rh and Rl shows good yield. Compound containing hydroxcy and iodo group shows prominent activity when compared to other compound. Para substituent shows better activity than ortho substituent.

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MOLECULAR INTERACTIONS STUDIES IN SOME TERPOLYMERS USING ULTRASONIC TECHNIQUES

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ABSTRACT

The terpolymer has been synthesized by using the microwave assisted method. The RPF terpolymer have been prepared from Resorcinol (R), Pthalamide (P) and Formaldehyde (F) in 1:1:2 proportions in the presence DMF media. Density (d), ultrasonic velocity (Us) and viscosity (ηs) of terpolymer have been measured in DMSO at different concentrations. The experimental data have been used to calculate the acoustical parameters namely acoustic impedance (z), adiabatic compressibility (βs), intermolecular free length (Lf). The results are discussed in the light of solute-solvent interaction and structural effects on the solvent in solution.

Key words: *Terpolymer, ultrasonic velocity, acoustic impedance, adiabatic compressibility, intermolecular free length.*

INTRODUCTION

The study of intermolecular interaction plays an important role in the development of molecular Sciences. The nature and relative strength of the molecular interaction between the components of the liquid mixtures have been studied by the ultrasonic method [1]. Ultrasonic studies in polymer solutions have been the subject of research in recent years [1-8]. Recently many workers have carried out work on polymer solution using ultrasonic technique. An acoustical study provides a useful technique to understanding the physico-chemical properties of the interacting components in polymer solution. A large number of studies have been made on the molecular interaction in liquid mixtures by various physical methods like Ultraviolent, Infrared [2]. Nuclear Magnetic resonance, Dielectric constant [3], Raman Effect and ultrasonic method. For interpreting solute-solvent, ion-solvent interaction in aqueous and non-aqueous medium was helpful from Ultrasonic velocity measurements in recent year [4].Ultrasonic investigation has been the subject of exhaustive research and finds extensive applications in characterizing physicochemical behaviour and solute-solvent interaction in pure liquids[5], liquid mixtures and electrolytic solutions [6] at various temperatures[7]. In the present investigation, free intermolecular length, acoustic impedance, adiabatic compressibility, relaxation time of terpolymer resin derived from Resorcinol (R), Pthalamide (P) and Formaldehyde (F) in DMF media has been evaluated in DMSO at different concentration using experimentally determined values of ultrasonic velocity, viscosity and density.

MATERIALS & METHODS

All chemicals were AR grade or chemically pure grade; Resorcinol, Pthalamide and Formaldehyde were procured from S.D. fine chemicals, India. Whenever required they were further purified by standard procedure. The solvents and monomers were purified by the conventional methods. The densities of the terpolymer were measured at different concentrations. The viscosities of the terpolymer were measured by using the Ostwald viscometers. To determine the flow time the viscometer was cleaned thoroughly with doubly distilled DMSO, dried and then filled with a fixed amount of DMSO and mounted inside the thermostat vertically. The liquid was then allowed to flow down through the capillary. The stop watch was started as soon the liquid meniscus touched the upper fiducially mark, the stop-watch having an uncertainty of + 0.1s. To measure the flow for given solution, the viscometer was rinsed with given solution and same amount of the solution was introduced in the viscometer and time of flow was measured between same two marks on the capillary. On average, three readings were taken. Ultrasonic velocity measurements were made by variable path single crystal interferometer (Mittal Enterprises, Model F–81) at 2MHz with the accuracy of +0.03 %. Ultrasonic and

thermodynamic parameters have been measured at 310.15 K.

THEORY

The ultrasonic velocity measurement is extensively used to study the physico-chemical behaviour of liquids. With the help of measurements of density and viscosity the following parameters like ultrasonic velocity, adiabatic compressibility, acoustic impedance, relaxation time and ultrasonic attenuation are calculated by using the following expressions

Adiabatic compressibility (β_s):

Adiabatic compressibility (β_s) has been calculated from the ultrasonic velocity (U_s) and the density (d) of the medium using the equation as:

$$\beta_s = 1 / 2\ U_s\ d \ldots\ldots\ldots (1)$$

Acoustic impedance (Z_s):

Acoustic impedance (Z_s) The specific acoustic impedance is related to density and ultrasonic velocity by the relation.

$$Zs = U_s \times d \ldots\ldots\ldots (2)$$

Where U_s and d are the ultrasonic velocity and density of the liquid respectively.

The Intermolecular free length (Lf):

The Intermolecular free length (Lf) is calculated by using the following equations:

$$Lf = K \times \sqrt{\beta_s} \ldots\ldots\ldots\ldots (3)$$

Where K – is a Jacobson's constant.

Relaxation time (τ):

Relaxation time (τ) is the time taken for the excitation energy to appear as translational energy and it depends on temperature and on impurities. The dispersion of ultrasonic velocity in binary mixture reveals information about the characteristic time of the relaxation process that causes dispersion. The relaxation time (τ) can be calculated from the relation as;

$$\tau = 4/3\ \beta s\ \eta_s \ldots\ldots\ldots (4)$$

Where (βs) adiabatic compressibility and (η_s) viscosity of the liquid.

Relative Association (RA):

Relative Association (RA) is calculated by using the following equations:

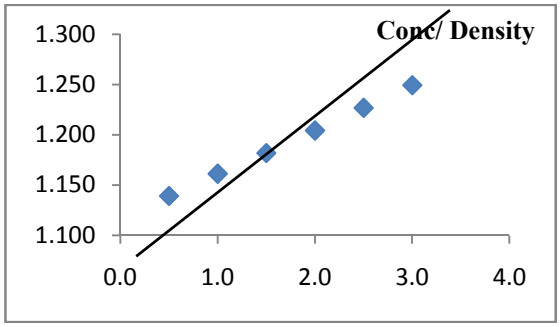
$$RA = (d \times U_s) / (d_s \times U) \ldots\ldots\ldots (5)$$

RESULTS & DISCUSSION

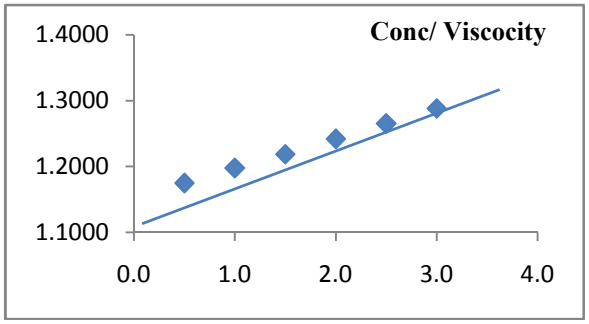
The experimental data of Ultrasonic velocity (U_s), Density (d), Viscosity (ηs), Adibatic Compressibility (βs), Intermolecular free length (Lf), Acoustic impedance (Z_s) and Relative Association (RA) of terpolymer in DMSO is given in table-I.

Sr.No.	Conc	d (Kgm^{-3})	Us (ms^{-1})	η_s	βs ($X10^{-5}m^2N^{-1}$)	Zs ($kgm^{-2}s^{-1}$)	Lf (A^0)	τ (10^{-5})	RA
1	3.0	1.249	1596.40	1.2882	4.9022E-05	1994.41	155.006	8.4199E-05	1.0832
2	2.5	1.227	1532.59	1.2650	5.223E-05	1880.23	156.648	8.8097E-05	1.0771
3	2.0	1.204	1460.33	1.2418	5.6474E-05	1758.744	160.091	9.3507E-05	1.0710
4	1.5	1.182	1402.24	1.2186	6.01066E-05	1657.253	164.424	9.7663E-05	1.0611
5	1.0	1.161	1346.61	1.1975	6.40441E-05	1563.883	168.127	1.0226E-04	1.0531
6	0.5	1.139	1288.82	1.1747	6.85863E-05	1468.298	172.402	1.0742E-04	1.0452

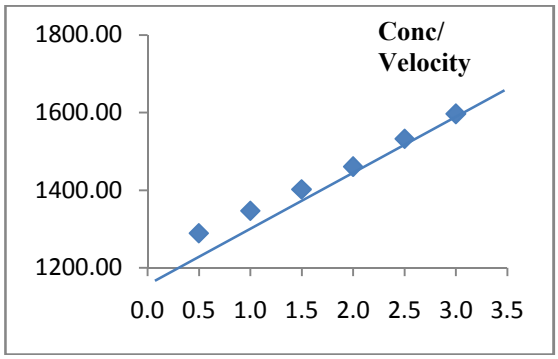
Table-I.



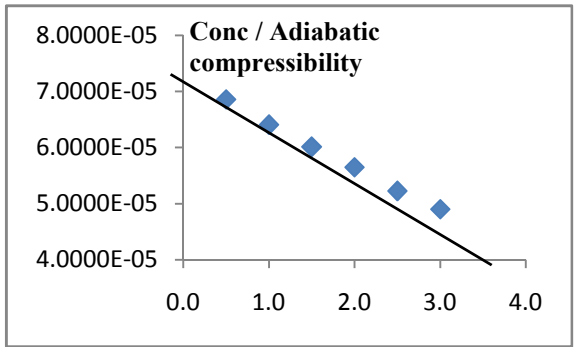
(Figure-1)



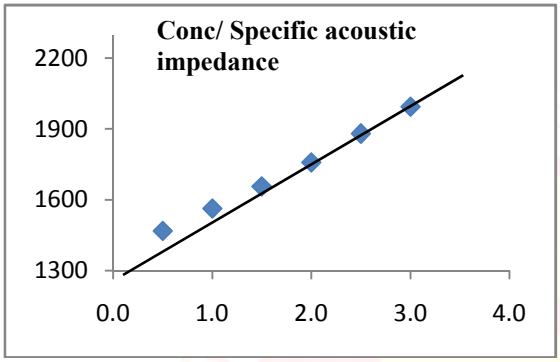
(Figure-2)



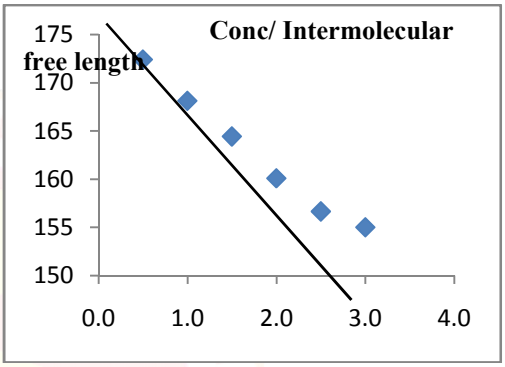
(Figure-3)



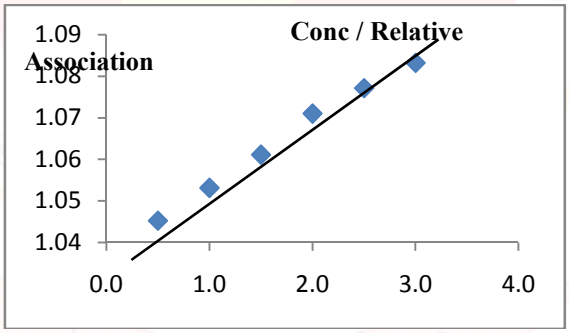
(Figure-4)



(Figure-5)



(Figure-6)



(Figure-7)

Increase in density (Figure-1) with increase in concentration. It is observed from (Figure-2) that the ultrasonic viscosity increases with increase in concentration and this is probably due to solute-solvent interactions. The (Figure 3) depicts that ultrasonic velocity of the liquid increases with the increase in concentration. Ultrasonic velocity and viscosity increase with increase in the concentration of solute. The increase suggests a structure-making capacity of terpolymer in solution. Moreover, the increase in ultrasonic velocity indicates the possibility of H-bond formation between solute and solvent. There is also an indication of greater association among the molecules [9, 10]. The adiabatic compressibility (βs) (Figure-4) decreases with increasing concentration, for terpolymers which further confirms the presence of solute-solvent interactions. From table I, it is evident that, adiabatic compressibility (βs) values of terpolymers solutions show decrease with the increase of solute concentration. This can be explained in terms of the electrostatic effects of terpolymers on the surrounding solvent molecules. Decrease in adiabatic compressibility indicates the formation of large number of tightly bound systems. Acoustic impedance (Zs) (Figure-5) is the product of ultrasonic velocity and density. As density and velocity both increase with increase in concentration of solute. This indicates the complex formation and intermolecular weak association which may be due to hydrogen bonding [11]. Intermolecular free length (Lf) (Figure-6) depends on the intermolecular attractive and repulsive

forces. As concentration increases, number of ions or particles increase in a given volume leading to decrease in the gap (intermolecular free length) between solute-solvent. Also, the decreased compressibility brings the molecules to a closer packing resulting in decrease in intermolecular free length [12]. Relaxation time increases with an increase in concentration. Relative Association (RA) (Figure-7) increase in concentration. It depicts that relative association (RA) increases with increase in concentration. This increase indicates salvation of solute molecules. A similar increase in the value of RA has been found in case of sucrose solution by Syal [12].

CONCLUSION

From the present investigation, it is eventually concluded that existence of solute-solvent interactions in terpolymers but it is more significant in terpolymer as compared to copolymer due to more number of monomeric units.

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ULTRASONIC VELOCITY OF ACRYLATES WITH DECANE-2-OL AT 313.15 K

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ABSTRACT

Thermodynamic data involving ultrasonic velocities of binary liquid mixtures of methyl acrylate, ethyl acrylate andbutyl acrylate with decane-2-ol have been measured at 313.15 K and at atmosphericpressure. Study of thermodynamic properties involves challenges of interpreting the excess quantities as a means of understanding the nature of intermolecular interactions among the mixed components. Experimental values of ultrasonic velocities were correlated with recently proposed Jouyban-Acree model. Deviations inisentropic compressibility were calculated and have been fitted to Redlich-Kisterpolynomial equation. Excess parameters like specific acoustic impendence, intermolecular free length,available volume, intrinsic pressure, molecular association and molar sound velocity were also calculated.Graphical representations of excess derived thermodynamic parameters used to explain the type and extent ofintermolecular interactions.

Keywords: *Intramolecular interactions, isentropic compressibility, specific acoustic impendence, available volume, JouybanAcree model.*

INTRODUCTION

Thermodynamic properties are essential in designing industrial equipments. There has been an increasing interest in the study of molecular interactions and a number of experimental techniques have been used to investigate the interactions between the components of binary liquid mixtures. The knowledge of thermodynamic properties of liquid-liquid systems is of considerable importance due to their wide range of applicability as solvent media in various physicochemical studies, in processing and product formation. Study of thermodynamic properties involves challenges of interpreting the excess quantities as a means of understanding the nature of intermolecular interactions among the mixed components. The knowledge of sound velocity in liquids has been found very helpful in the study of ultra spectrometry for liquids [1], in multiphase flows [2], crystal growth from solutions [3], structural isomerization and molecular motions of liquid n-alkanes [4], sonochemical removal of nitric oxide from flue gases [5], shear impendence spectrometry [6], ultrasonic spectrometry of polystyrene latex suspensions [7]. Density and ultrasonic velocity are important basic data used in process simulation, equipment design, solution theory and molecular dynamics [8, 9].

MATERIALS AND METHODS

Chemicals used in present study were of analytical grade and supplied by S. D. Fine Chemicals Pvt., Mumbai (India) with quoted mass fraction purities: decane-2-ol (> 0.998), methyl acrylate, MA, (> 0.997), ethyl acrylate, EA, (> 0.998) and butyl acrylate, BA, (> 0.995).

Experimental Part

Masses were recorded on a Mettlar one pan balance, which can read up to fifth place of decimal with an accuracy of ± 0.01 mg. Ultrasonic velocities were measured [10] at frequency of 2 MHz by a single crystal ultrasonic interferometer (Model F-81, Mittal Enterprises, New Delhi, India). Temperature was controlled using water bath (GeminiScientific Instruments, Chennai, India) having accuracy ± 0.02 ^{0}C. Ultrasonic velocities of decane-2-ol, methyl acrylate, ethyl acrylate and butyl acrylate at 313.15 K were observed as 1362, 1118, 1123 and1157 m.s^{-1} respectively.

Computational Part

Deviation in isentropic compressibility were calculated using relation,

$$\Box\Box s = \Box s - \Box s^{id} \quad (1)$$

Where$\Box$s is isentropic compressibility and was calculated using Laplace relation,

$$\Box s = (1/ u2\rho) \quad (2)$$

$\Box s^{id}$was calculated from relation,

$$\Box s^{id} = \Sigma \Box i[\Box s,i + TVoi(\alpha oi2) / Cp,i] - [T(\Sigma xiVoi) (\Sigma \Box i\alpha oi)2 / \Sigma xiCp,i] \quad (3)$$

Where$\Box$i is ideal state volume fraction of component i in mixture and is defined by,

□i = xiVoi / (ΣxiVoi) (4)

T is temperature and □s,i, Voi, αoi, and Cp,i are isentropic compressibility, molar volume, coefficient of isobaric thermal expansion and molar heat capacity respectively, for pure component i. αoiis calculated from measured densities by relation,

α = [(ρ1/ ρ2)-1] / (T2-T1) (5)

From ultrasonic velocity different thermodynamic parameters like specific acoustic impendence (Z), intermolecular free length (Lf), available volume (Va), intrinsic pressure (□int), can be calculated, which provides better insight in understanding of molecular interactions in pure and binary liquids mixtures, which are given by relations,

Z = uρ(6)

Lf = K(□s)1/2 (7)

Va = Vm [1-(uexpt /u□)] (8)

Where K is the temperature dependent constant whose values are 1.976×10^{-6} at 313.15 K respectively, u□= 1600 m/s.

For binary liquid mixtures intrinsic pressure can be given as,

□i = bRT (Kη12/u12)1/2(ρ122/3/M127/6) (9)

Where b is packing factor, K is a temperature independent constant having value of 4.28×10^9, R is gas constant andη12, u12, ρ12 are viscosity, ultrasonic velocity and density of mixture.

The excess functions are important to understand molecular interactions between components of liquid mixtures.Excess function Y^E represents excess of a given quantity Y of a real mixture over its value for an ideal mixture Y^{id}at same conditions of temperature, pressure and composition. It is expressed by following relation,

$Y^E = Y - Y^{id}$(10)

Where Y denotes Z, Lf, Va, □int and Y^E represents corresponding excess thermodynamic properties such as excess specific acoustic impedance (Z^E), excess intermolecular free length (L_f^E), excess available volume (Va^E) and excess intrinsic pressure (□int^E).

Molecular association (M_A) and Rao's constant or molar sound velocity (R) for liquid mixtures can be calculated as,

M_A = [(u/□x1u1)2-1] (11)

R = (M/ ρ) u1/3 (12)

Where M is average molecular weight.

Table 1: Ultrasonic Velocities (u), Isentropic Compressibility Deviation (□□s), Excess specific acoustic impendence (Z^E), Excess intermolecular free length (L_f^E), Excess available volume (Va^E), Excess intrinsic pressure (□int^E), Molecular association (M_A) and Rao's constant (R) for Acrylates (1) + Decane-2-ol (2) at 313.15 K.

X_1	u	□□s	Z^E	L_f^E	Va^E	□$_{int}^E$	M_A	R
	($m.s^{-1}$)	(TPa^{-1})	($Kg.m^{-2}.s^{-1}$)	(m)	($m^3.mol^{-1}$)	(atm)		
	Methyl Acrylate + Decane-2-ol							
0	1362	0	0	0	0	0	0	2.171
0.0552	1347	7.36	-4.96	0.001	1.017	-224.10	-0.002	2.101
0.0997	1335	13.08	-8.59	0.002	1.751	-254.20	-0.004	2.045
0.1555	1321	19.04	-12.15	0.002	2.453	-346.15	-0.005	1.976
0.1999	1309	24.54	-15.50	0.003	3.033	-360.40	-0.006	1.920
0.2554	1295	30.09	-18.63	0.004	3.555	-431.51	-0.007	1.851
0.3000	1284	34.01	-20.72	0.004	3.875	-433.76	-0.007	1.796
0.3555	1270	38.85	-23.26	0.005	4.213	-487.36	-0.008	1.728
0.3999	1259	42.17	-24.90	0.005	4.393	-474.87	-0.009	1.674
0.4538	1245	46.47	-27.09	0.006	4.585	-507.88	-0.010	1.608
0.4999	1234	48.37	-27.77	0.006	4.578	-492.04	-0.010	1.552
0.5554	1221	49.66	-28.00	0.006	4.465	-510.55	-0.009	1.485
0.5999	1210	50.69	-28.26	0.006	4.351	-473.90	-0.009	1.432
0.6550	1197	50.18	-27.51	0.006	4.074	-480.36	-0.009	1.366
0.6999	1186	49.30	-26.75	0.006	3.806	-432.72	-0.009	1.312
0.7555	1173	45.94	-24.56	0.006	3.337	-423.18	-0.008	1.247
0.7999	1163	41.39	-21.85	0.005	2.867	-361.27	-0.007	1.194
0.8555	1150	34.41	-17.96	0.005	2.228	-338.55	-0.006	1.129
0.8999	1140	26.41	-13.64	0.003	1.620	-262.39	-0.004	1.077
0.9555	1128	12.84	-6.51	0.002	0.743	-227.48	-0.002	1.013
1	1118	0	0	0	0	0	0	0.962
	Ethyl Acrylate + Decane-2-ol							

0	1362	0	0	0	0	0	0	2.171
0.0554	1348	4.69	-2.58	0.000	0.757	-186.63	-0.001	2.112
0.0999	1336	9.18	-5.23	0.001	1.396	-212.21	-0.003	2.065
0.1553	1322	13.69	-7.61	0.001	2.007	-285.62	-0.004	2.008
0.1998	1310	17.98	-10.00	0.002	2.519	-297.64	-0.006	1.961
0.2556	1296	22.10	-12.03	0.002	2.974	-354.19	-0.008	1.903
0.2999	1285	25.02	-13.39	0.002	3.259	-354.28	-0.008	1.857
0.3554	1272	27.51	-14.28	0.002	3.463	-396.13	-0.008	1.800
0.4000	1261	29.89	-15.30	0.002	3.629	-385.91	-0.009	1.755
0.4555	1247	32.85	-16.62	0.003	3.791	-410.01	-0.010	1.698
0.4999	1237	33.38	-16.50	0.003	3.744	-390.27	-0.009	1.653
0.5554	1224	34.10	-16.48	0.003	3.664	-401.23	-0.008	1.597
0.5999	1213	34.99	-16.76	0.003	3.599	-370.37	-0.009	1.553
0.6555	1200	34.44	-16.20	0.003	3.376	-369.14	-0.009	1.497
0.6999	1190	32.84	-15.16	0.003	3.108	-328.58	-0.008	1.453
0.7556	1177	30.62	-13.93	0.003	2.747	-315.53	-0.007	1.398
0.7999	1167	27.48	-12.30	0.003	2.369	-265.32	-0.006	1.354
0.8555	1155	21.64	-9.41	0.002	1.792	-242.86	-0.004	1.300
0.8999	1145	16.49	-7.07	0.001	1.307	-184.21	-0.003	1.257
0.9555	1133	7.58	-2.99	0.001	0.588	-150.75	-0.001	1.203
1	1123	0	0	0	0	0	0	1.160
	Butyl Acrylate + Decane-2-ol							
0	1362	0	0	0	0	0	0	2.171
0.0555	1350	1.91	-1.24	0.000	0.419	-119.45	-0.001	2.134
0.0998	1340	3.89	-2.63	0.000	0.775	-148.09	-0.002	2.104
0.1556	1328	5.70	-3.78	0.000	1.115	-202.81	-0.003	2.068
0.1998	1318	7.59	-5.05	0.001	1.409	-219.09	-0.005	2.038
0.2554	1306	9.30	-6.08	0.001	1.674	-258.69	-0.006	2.001
0.3000	1297	9.92	-6.35	0.001	1.787	-266.65	-0.005	1.973
0.3556	1285	11.44	-7.24	0.001	1.976	-291.97	-0.006	1.936
0.3998	1276	11.93	-7.42	0.001	2.035	-289.17	-0.006	1.907
0.4555	1264	13.21	-8.13	0.001	2.147	-302.27	-0.007	1.871
0.5000	1255	13.42	-8.15	0.001	2.142	-290.51	-0.007	1.843
0.5555	1244	13.19	-7.83	0.001	2.074	-292.80	-0.007	1.807
0.5999	1235	13.12	-7.69	0.001	2.013	-272.16	-0.006	1.778
0.6555	1224	12.50	-7.18	0.001	1.873	-263.36	-0.006	1.743
0.6999	1215	12.09	-6.88	0.001	1.754	-236.42	-0.006	1.715
0.7554	1204	10.98	-6.15	0.001	1.541	-217.39	-0.005	1.679
0.7999	1195	10.13	-5.63	0.001	1.361	-182.66	-0.005	1.651
0.8545	1185	7.38	-3.98	0.000	1.006	-154.27	-0.003	1.617
0.8999	1176	5.75	-3.08	0.000	0.745	-114.21	-0.003	1.588
0.9550	1166	2.07	-1.01	0.000	0.307	-78.53	0.000	1.554
1	1157	0	0	0	0	0	0	1.526

Deviation in isentropic compressibility were fitted to Redlich-Kister[11]equation,

$$Y = x_1 x_2 \sum_{i}^{n} a_i (x_1 - x_2)^i \qquad (13)$$

Where Y is $\Delta\kappa_s$and n is degree of polynomial. Coefficient $a_i$was obtained by fitting Eq (13) to experimental results using a least-squares regression method. Optimum number of coefficients is ascertained from examination of variation in standard deviation (σ) calculated using relation,

$$\sigma(Y) = \left[\frac{\sum (Y_{expt} - Y_{calc})^2}{N - n} \right]^{1/2} \qquad (14)$$

Where N is number of data points and n is number of coefficients. Calculated values of coefficients $a_i$along with standard deviations are given in Table 2.

Table 2:Parameters of Redlich-Kister Polynomial Equation for deviation in isentropic compressibility for Acrylates (1) + Decane-2-ol (2)at 313.15 K.

Property	a_0	a_1	a_2	a_3	a_4	σ
Δk_s /(TPa^{-1})	Methyl Acrylate + Decane-2-ol					
	53.2667	40.2340	26.3259	-5.7219	-11.7939	0.36265
	Ethyl Acrylate + Decane-2-ol					
	14.6449	16.7048	29.8820	-1.1945	-46.9233	0.33076
	Butyl Acrylate + Decane-2-ol					
	-1.5641	5.8635	19.6866	-5.8184	-37.5566	0.35663

JouybanAcree [12, 13] recently proposed model for correlating ultrasonic velocities of liquid mixtures at various temperatures. The proposed equation is, lnym

$$T = f1\ln y1T + f2\ln y2T + f1f2\ \Sigma\ [Aj\ (f1-f2)\ j/T] \quad (15)$$

Where ymT, y1T and y2T is ultrasonic velocities of mixture, solvents 1 and 2 at temperature T, respectively, f1and f2 are mole fraction and Aj are model constants. The correlating ability of model was tested by calculating the average percentage deviation (APD) between the experimental and calculated values of ultrasonic velocities as,

$$APD = (100/N)\ \Sigma\ [(|\ yexpt - ycal\ |)/\ yexpt)] \quad (16)$$

Where N is number of data points in each set. JouybanAcree model provides reasonably accurate calculations for ultrasonic velocity of binary liquid mixtures and could be used in data modeling. The optimum numbers of constants Aj, in each case, are determined from the examination of the average percentage deviation value which is represented in Table 3.

Table 3:Parameters of Jouyban-Acree Model for ultrasonic velocity for Acrylates (1) + Decane-2-ol (2).

Property	a_0	a_1	a_2	a_3	a_4	σ	APD
u ($m.s^{-1}$)	Methyl Acrylate + Decane-2-ol						
	0.0818	-0.2291	-1.8521	0.5625	3.2343	1313.8158	0.0178
	Ethyl Acrylate + Decane-2-ol						
	0.0988	0.0216	-1.0346	-0.4437	1.2038	1310.0579	0.0201
	Butyl Acrylate + Decane-2-ol						
	-0.0444	-0.2932	-0.9405	0.7343	1.9723	1329.7640	0.0197

RESULTS AND DISCUSSION

Figure 1shows graphical variation of deviation in isentropic compressibility (□□s) of acrylates with decane-2-ol at 313.15 K.

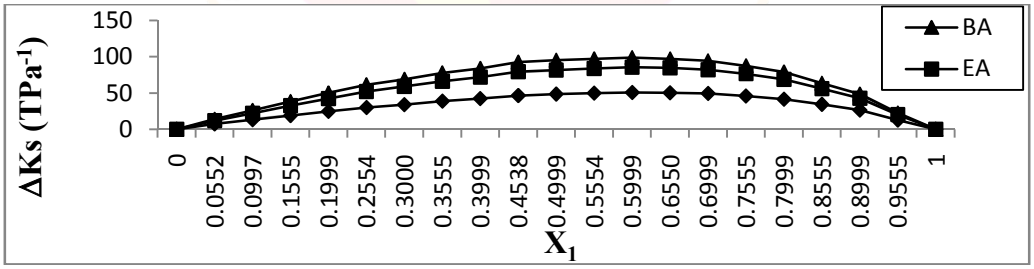

Figure 1 Variation of isentropic compressibility for Acrylates (1) + Decane-2-ol (2).

In present study of binary liquid mixtures, values of □□s are found to be positive for all mixtures. □□s attributed to relative strength of effects which influenced free space, according to which positive □□s arise due to breaking of hydrogen bonds in self associated decane-2-ol and physical dipole-dipole interactions between decane-2-ol monomers and multimers contribute to increase in free space, decrease in sound velocity and positive deviation in □□s.

Figure 2 shows graphical variation of excess specific acoustic impendence (Z^E) with mole fraction acrylates with decane-2-ol at 313.15 K, which clearly indicates exactly reverse graphical variation of □□s.Deviations in Z^E more negative, as length of carbon chain in acrylates increases. Negative values of Z^Ein curves and opposite behavior in □□s curves reinforce that, structure breaking effect and weak interactions between unlike molecules dominates.

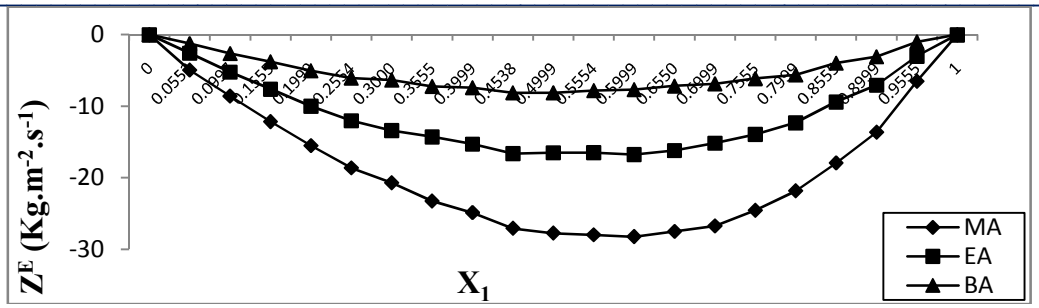

Figure 2 Variation of excess specific acoustic impedance for Acrylates (1) + Decane-2-ol (2).

Table 1 represents variation of excess intermolecular free length (Lf^E) for acrylates with decane-2-ol. Values of $Lf^E$are found to be positive for all systems which suggests that, rupture of hydrogen bonded chain of decane-2-ol and resulting loosening exceeds the interaction i. e. hydrogen bonding and dipole-dipole between unlike molecules. The degree of intermolecular hydrogen bond also decreases as the intermolecular chain length is increased. Positive values of Va^E over entire range of compositionmean strong molecular interactions.Values of □int^E are found to be negative in all binary liquid mixtures. Less magnitude of □int^E suggests that, weaktypes of intermolecular interactions are present with some dispersion due to dissociation of decane-2-ols aggregates with addition of solute (acrylates) in the binary liquid mixtures. Excess internal pressure is used to study intermolecular interactions in liquid mixtures.

Evaluated values of derived thermodynamic parameter such as deviation isentropic compressibility (□□s) were fitted to Redlich-Kister polynomial equation at 313.15 K and are represented as in Table 2 with their standard percentage deviation. The Redlich- Kister equation was originally developed to correlate the excess Gibb's energy function and calculate the values of the activity coefficients. Experimentally measured fundamental values of ultrasonic velocity were correlated using recently proposed Jouyban-Acree model. Constants (Aj) calculated from least square analysis along with average percentage deviation (APD) are presented in Table 3.

CONCLUSION

Positive values of □□s decide compactness due to molecular arrangement. Negative values of Z^E represent the weak interactions are dominant over dispersion forces. Lf^E values increase with increase of chain length in acrylates. Positive values of Va^Emean strong molecular interactions. Negative values of □int^E suggest weak types of intermolecular interactions in liquid mixtures.

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SYNTHESIS AND CHERACTERISATION OF 2-[5-BENZYL–3 (PHENYLAMINO)–1,3-THIOZOL4YL]NAPHTHATEN–1-OL

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ABSTRACT

Thiazole are found in a variety of specialized products often fused with benzene derivative, then so called benzothiazole. It was thought interesting to synthesize of thiozole derivate. The titled compound were pepared by the action of Preparation of (1-1 hydra napthalen 2yl) 3-phenyl prop - 2 en-1one with phenyl thiourea & thiourea. Thizole is one of the important member of the family and use in the comprehensive study of natural products Antioxidant, Synthetic drugs, Insecticdes. It has been observed that chalcones are the best starting compound for the preparation of thiazole derivates. Encouraged by the earlier reports we have designed & synthesized some new substituted of thiazole form chalcone & thiourea & phenyl thiourea.

Keywords : *Phenyl thiourea, thiourea, thiazole*

MATERIALS & METHODS

1) Glacial aceticacid
2) 1 napthol
3) Anhydrous ZnCl2 (Zinc Chloride)
4) Benzaldehyde
5) Pipyridene
6) Thiourea, Phenyl Thiourea
7) NaOH, KOH, ethanol & etc

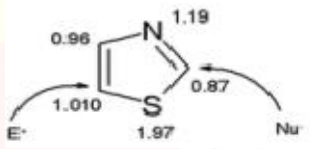
Merk & Loba Companies Chemicals are used in the synthesis of thiozole.

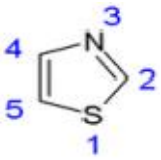
INTROUDCTION

Thiazole

Thiazoles are members of the azoles heterocyclic that includes imidazoles and oxazoles. Thiazole can also be considered a functional group. Oxazoles are related compounds, with sulfur replaced by oxygen. Thiazoles are structurally similar to imidazoles, with the thiazole sulfur replaced by nitrogen. Thiazole, or 1,3-thiazole, is a heterocyclic compound that contains both sulfur and nitrogen; the term 'thiazole' also refers to a large family of derivatives. Thiazole itself is a pale yellow liquid with a pyridine-like odor and the molecular formula C_3H_3NS.[2] The thiazole ring is notable as a component of the vitamin thiamine (B_1).

Thiazole rings are planar and aromatic Thiazoles are characterized by larger pi-electron delocalization than the corresponding oxazoles and have therefore greater aromaticity. This aromaticity is evidenced by the chemical shift of the ring protons in proton NMR spectroscopy (between 7.27 and 8.77 ppm), clearly indicating a strong diamagnetic ring current. The calculated pi-electron density marks C5 as the primary site for electrophilic substitution, and C2 as the site for nucleophilic substitution.





Thiazoles are found in a variety of specialized products, often fused with benzene derivatives, the so-called benzothiazoles. In addition to vitamin B_1, the thiazole ring is found in epothilone. Other important thiazole dervatives are benzothiazoles, for example, the firefly chemical luciferin. Whereas thiazoles are well represented in biomolecules, oxazoles are not.

Commercial significant thiazoles include mainly dyes and fungicides. Thifluzamide, Tricyclazole, and Thiabendazole are marketed for control of various agricultural pests.

Synthesis of 2-acetyl-1-naphthol

Hot glacial acetic acid (15 ml) mixed with 1-naphthol (14.5 gm) and add fused ZnCl2 (13.6 gm) then mixure refluxed for 8 hours . Then cooled and poured in acidulated water. The percentage of solid was obtained . filter and recrystallised with rectified spirit to obtain 2-acetyl-1-naphthol (1).

Yield :- 65 %

Melting Point:- 85˚C

Preparation of 1-(1-hydroxynaphthalen-2–yl)–3-phenylprop-2-en-1-one.

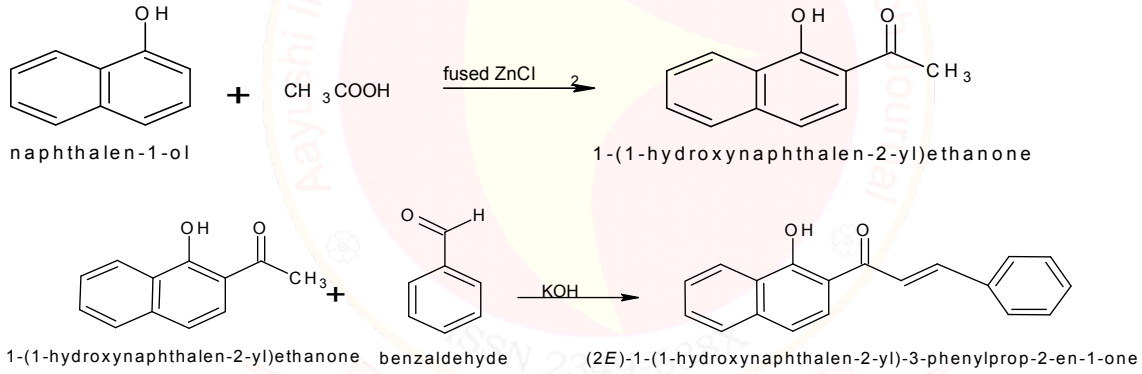
(2 gm) 2- acetyl-1-naphthol(0.01M) add with (2ml) benzadehyde and (10 ml) ethanol with [40%] KOH 7ml and add 1-2 drops of pipyridine. Stir for two hours constantly, kept for over-night. Then reaction mixure poured in crushed ice, then add little HC1. The product was filter and recrystallised by ethanol to obtain compound (2).
Yield :- 70 % Melting Point:- 170˚C

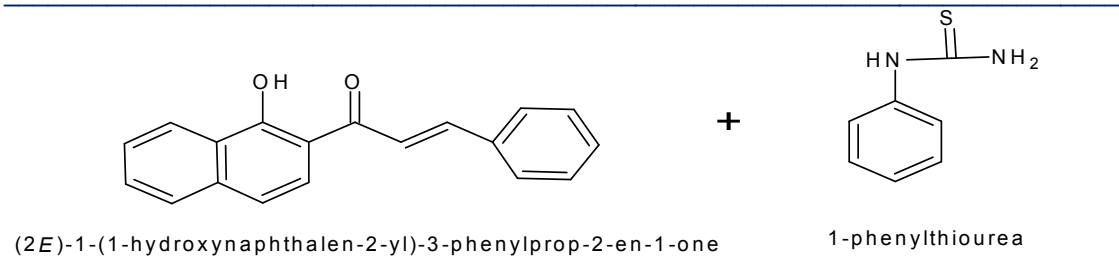
Synthesis of 2-[5-benzyl-2-(phenylamino)-1-3-thiazol-4-yl]naphthalen-1-ol.
Chalcone (2.63 gm) mixed with (1.37gm) phenyl thiourea (0.01 M). Add (25 ml) ethanol and KOH solution (0.02 M).
The reaction mixure was refluxed for 2.5 hours cooled, then diluted with water and acidified with concentrated HCL. Filter the product and recrystallised from ethanol to get the (3).

NMR Spectra :-
The δ values followed by the number of proton, nature of peak and group present in compound.
δ 1.9 (CH3 , NH), δ 2.5 (CH – C), δ 2.7 (CH2 – Ar), δ 3.4 (CH2 – O), δ 7.5 (Ar – H), δ 8.2 (C – OH).

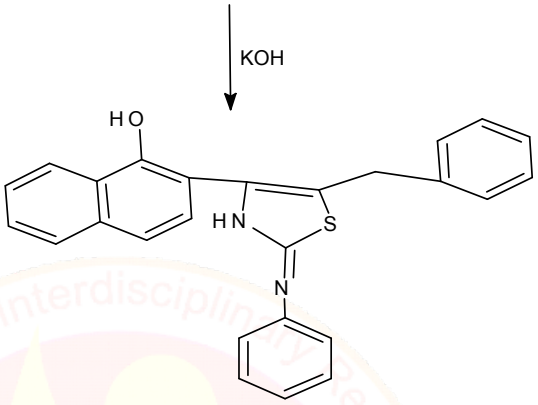
Synthesis of 2-(2-amino-5-benzyl-1-3-thiazol-4-yl) naphalen-1-ol.
Chalcone (2.63 gm) mixed with (1.37gm) thiourea (0.01 M). Add (25 ml) ethanol and KOH solution (0.02 M).
The reaction mixure was refluxed for 2.5 hours cooled, then diluted with water and acidified with concentrated HCL. Filter the product and recrystallised from ethanol to get the compound (4).

NMR Spectra :-
The δ values followed by the number of proton, nature of peak and group present in compound.
δ 2.5 (CH – C), δ 2.8 (CH2 – Ar), δ 3.4 (C – NH2), δ 7.5 (Ar – H), δ 7.9 (Phenolic – OH), δ 8.2 (C – OH)
Reaction Scheme

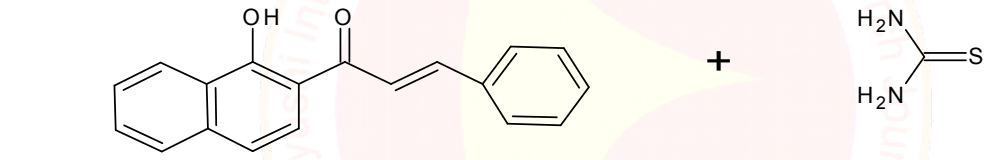




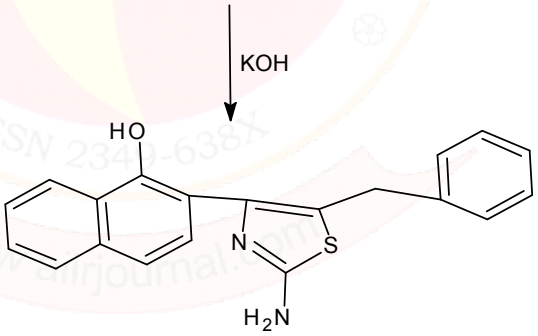
(2*E*)-1-(1-hydroxynaphthalen-2-yl)-3-phenylprop-2-en-1-one 1-phenylthiourea



2-[5-benzyl-2-(phenylamino)-1,3-thiazol-4-yl]naphthalen-1-ol



(2*E*)-1-(1-hydroxynaphthalen-2-yl)-3-phenylprop-2-en-1-one thiourea



2-(2-amino-5-benzyl-1,3-thiazol-4-yl)naphthalen-1-ol

RESULT & DISCUSSION `

EXPERIMENTAL

Physical characterization data of all the compounds are given in Table -1

Table – 1

CHARACTERIZATION DATA OF NEWLY SYNTHESIZED COMPOUNDS

Compound	Mol.Formula	M.P. (^{o}C)	Yield (%)	Rf
2-acetyl-1-naphthol	$C_{12}H_{10}O_2$	85^0C	65%	0.75
1-(1-hydroxynaphthalen-2–yl)–3-phenylprop-2-en-1-one.	$C_{19}H_{14}O_2$	170^0C	70%	0.85
2-[5-benzyl-2-(phenylamino)-1-3-thiazole-4-yl]naphthalen-1-ol.	$C_{26}H_{20}N_2SO$	195^0C	54%	0.89
2-(2-amino-5-benzyl-1-3-thiazole-4-yl)naphalen-1-ol.	$C_{20}H_{16}N_2SO$	182^0C	68%	0.81

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SYNTHESIS AND EVALUATION OF SOME NEW SUBSTITUTED PYRAZOLINE DERIVATIVES AS ANTIMICROBIAL AGENTS

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ABSTRACT

Heterocyclic nitrogenous compounds and their fused analogues represent an important class of heterocyclic compounds. They exist in numerous natural products, display a wide range of biological and pharmaceutical activities. Pyrazolines are well known important nitrogen containing five member heterocyclic compounds Some new pyrazolines have been synthesized by the action of isoniazid on 3-aroyl flavanones in pyridine medium. In this synthesis p-cresol and m-cresol are used as starting material. Isoniazid is use as anti tuberculosis drug. Structures of this compound have been established by spectral and elemental analysis.

Key words: *Chalcones,Isonizid Pyrazolines, Antimicrobial activities*

INTRODUCTION

Heterocyclic compounds are well known for their wide range of biological applications out of which pyrazolines occupy unique position due to dominant applications. Pyrazolines are known to possess antimicrobial, ant tubercular, antiviral, anti HIV, molluscicidal and cerebroprotective properties . Pyrazolines are and important nitrogen-containing five-member ring heterocyclic compounds. Pyrazoline derivatives have been found to possess a broad spectrum of biological activities such as tranquillizing, muscle relaxant, psychoanaleptic, anti-convulsant, antihypertensive, and antidepressant activities[1,2]Pyrazolines derivatives are also used as Anesthetics [3], Analgesic [4],Antitubercular [5], Antitumor [6], Immunosuppressive [7], Antidepressant [8, 9], Cerebroproctive [10], Antidiabetic [11-12], Anticancer [13], Antiviral [14], anticonvulsant [15], molluscicidal [16], Insecticides [17,18], Fungicides[19], Antiinflammatory [20,21], Herbicides [22], Antiimplanatory[23], Antimicrobial and antibacterial [24&19]

One of the important applications of pyrazoline is the use of pyrazolines as a fluorescent brightening agent[25]. They can absorb light of 300-400 nm and emit blue fluorescence. Pyrazolines are also acting as whole transporting material in OELD (organic electroluminescent device) because of formation of p-π conjugated system due to one of the nitrogen atom. Bleaching Agents, Luminescent, Fluorescent [26].

The literature survey clearly indicates that 3,5-diaryl-4-benzoyl-1-pyridoyl-Δ^2- pyrazolines are not yet synthesized. It was, therefore thought of interest to synthesize 3,5-diaryl-4-benzoyl-1-pyridoyl-Δ^2- pyrazolines from 3-aroyl flavanones. Thus the present work deals with synthesis of 3,5-diaryl-4-benzoyl-1-pyridoyl-Δ^2- pyrazolines from 3-aroyl flavanones (scheme) and Isoniazid in pyridine medium . Structures of this compound have been established by spectral and elemental analysis.

EXPERIMENTAL

Melting points are uncorrected. IR spectra in KBr were recorded on PE-983/PE-781IR spectrophotometer. NMR in DMSO on Varian EM 390-cw NMR spectrophotometer and UV on Varian Cary 239 OUV spectrophotometer.

(1) Preparation of 1,3-diaroyl-1,3 propadione (1a – 1f)

2-benzoyloxy acetophenone was dissolved in dry pyridine. The solution was warmed up to 60°C and pulverized KOH was added slowly with constant stirring. After about 4 hours the reaction mixture was acidified by adding ice cold HCl. The brownish yellow product obtained was filtered, wash with sodium bicarbonate solution and sufficient water. The product obtain was crystallized from ethanol-acetic acid mixture.

(2) Preparation of 3-aroyl flavanones (2a-2f)

1,3-diaroyl-1,3 propadione (1a – 1f) and aromatic aldehydes (p-bromobenzaldehyde, m-bromobenzaldehyde and o-bromobenzaldehyde) where reflux for about 1 hours in ethanol containing a few drops of piperidine. The resulting mixture was cool and the product separated was crystallized from ethanol-acetic acid mixture. The

structure of this compound where confirm by spectral analysis.

Spectral interpretation of 3a:

IR (vmax):1750 cm^{-1} ν(C=O); 1630 cm^{-1} ν(C=O);1540-1615 cm^{-1} ν(C=C);1190 cm^{-1} ν(C-O-C).**^{1}H NMR:** □2.30(S, 3H, Ar-CH_3); 3.80(S,3H Ar-O-CH_3);6-7-8.3(m,11HAr-H) **UV(λ max):**322nm.

(3) Preparation of 3,5-diaryl-4-benzoyl-1-pyridoyl-Δ^2- pyrazolines (4a-4f)

3-aroyl flavanones where reflux with isoniazid for 8 to 10 hours in pyridine solvent. The reaction mixture was decomposed by acidified water, filtered and wash with sufficient water. The product obtain was crystallized from ethanol-acetic acid mixture. To obtain a crystalline solid. Yield 60 – 80%.

Spectral interpretation of 4a:

IR (vmax): 1635cm^{-1} ν(C=O);3340cm^{-1} ν(OH);1610 cm^{-1} ν(C=N);1520 cm^{-1} ν(C=C); 1410 cm^{-1} ν(C-N);1070 cm^{-1} ν(C-O)(Phenol)

^{1}H NMR: □1.9(S, 3H,-CH_3); 7.2-7.6(m,17H,-Ar-H); 12(S,1H,-OH). **UV(λ max):**256nm.

TABLE 1

Physical Characterization data of Synthesized Compound

3-Aroyl flavanones (3a-3f)

Compound	R_1	R_2	R_3	R_4	R_5	R_6	Yield (%)	M.P.(°C)	Molecular Formula
3a	H	H	CH_3	H	H	Br	85	132	$C_{23}H_{17}O_3Br$
3b	H	H	CH_3	Br	H	H	85	138	$C_{23}H_{17}O_3Br$
3c	H	H	CH_3	H	Br	H	85	148	$C_{23}H_{17}O_3Br$
3d	H	CH_3	H	H	H	Br	75	135	$C_{23}H_{17}O_3Br$
3e	H	CH_3	H	Br	H	H	90	145	$C_{23}H_{17}O_3Br$
3f	H	CH_3	H	H	Br	H	85	136	$C_{23}H_{17}O_3Br$

TABLE 2

Pyrazolines derivatives (4a-4f)

Compound	R_1	R_2	R_3	R_4	R_5	R_6	Yield (%)	M.P.(°C)	Molecular Formula
4a	H	H	CH_3	H	H	Br	65	252	$C_{29}H_{21}O_3N_3Br$
4b	H	H	CH_3	Br	H	H	75	250	$C_{29}H_{21}O_3N_3Br$
4c	H	H	CH_3	H	Br	H	80	249	$C_{29}H_{21}O_3N_3Br$
4d	H	CH_3	H	H	H	Br	75	254	$C_{29}H_{21}O_3N_3Br$
4e	H	CH_3	H	Br	H	H	80	252	$C_{29}H_{21}O_3N_3Br$
4f	H	CH_3	H	H	Br	H	80	253	$C_{29}H_{21}O_3N_3Br$

SCHEME

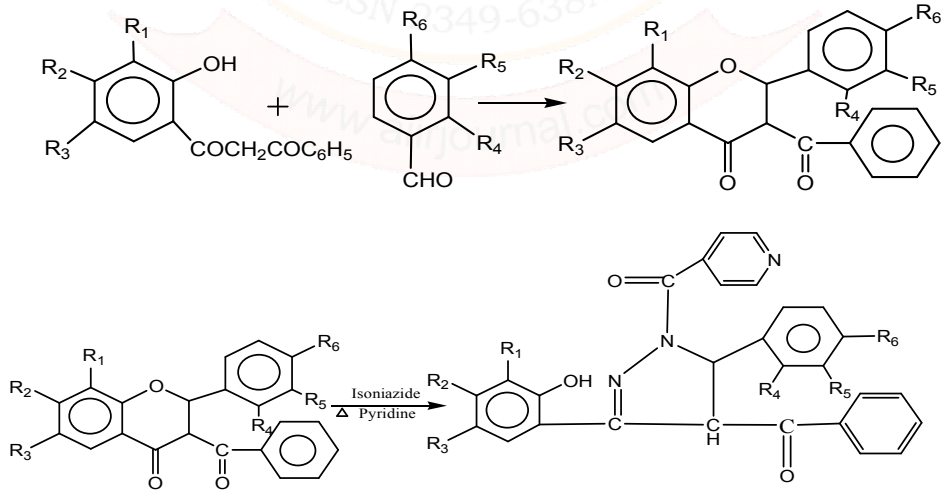

Table:-Antimicrobial activity of synthesized pyrazoline derivatives

Bacteria (zone of inhibition)						Fungi (zone of inhibition)			
Entry	A	B	C	D		A	B	C	D
4a	20	19	22	16		-ve	RG	-ve	-ve
4b	20	15	24	14		RG	RG	-ve	RG
4c	-	24	19	18		RG	-ve	-ve	RG

4d	18	17	18	12		-ve	RG	RG	ve
4e	17	13	21	10		RG	-ve	RG	-ve
4f	14	16	22	11		RG	-ve	-ve	RG

(Zone of Inhibition in mm)
A= Escherichia coli, B=Salmonella typhi, C= Staphylococcus aureus, D=Bacillus subtilis
E= Aspergillusniger F=penicilliumchrysogenum, G=Fusariummoneliforme, H=Aspergillusflavus
- = No Antibacterial activity, RG= Reduced Growth (Moderate Activity)
-ve = Growth (Antifungal Activity Observed)

CONCLUSIONS

In conclusion, we have reported an efficient procedure for the synthesis of pyrazolines in pyridine medium. The major advantage of this method is that the ease of work-up. This method also offers some other merits such as pure synthesis, high yields of products, and use of various substrates, which make it useful and attractive procedure for the synthesis pyrazolines.

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STRUCTURE AND GAS SENSING APPLICATION OF NANOCRYSTALLINE $LACRO_3$ SYNTHESIZED BY SOL – GEL METHOD

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ABSTRACT

In this paper a simple method for the preparation of nanocrystalline undoped and doped $LaCr_{1-x}Zr_xO_3$ is discussed. The compounds were characterized by means of x-ray powder diffraction and transmission electron spectroscopy. These nanostructures have been tested for different reducing gases by depositing the thick film on an alumina substrate as a function of operating temperature. The gas sensitivity tests has demonstrated that the $LaCrO_3$ nanostructure exhibit high sensitivity to CO gas at 220^0C proving their applicability in gas sensors. $LaCr_{0.4}Zr_{0.6}O_3$ powder showed large response to CO gas at an operating temperature 180^0C. The sensitivity, selectivity of $LaCr_{0.4}Zr_{0.6}O_3$ thick films was measured.

Keywords: *Perovskite, Nanoparticles, XRD, Sensitivity, CO.*

INTRODUCTION

Nanostructure metal oxides have been attended in the field of nanotechnology both from a fundamental and industrial point of view. For example, their peculiar electrical properties make them suitable as active sensing materials in resistive sensors, with enhanced performance with respect to bulk materials [1]. The ability to control the particle size of metal oxide nanoparticles is of crucial importance in this respect [2–6]. Great attention is also addressed to the particle morphology and shape. Various shapes can exhibit completely different physical properties and performances; therefore it is often highly desirable to have pure materials with controlled morphology. However, controlling the morphology of materials is not simple as controlling their particle size, yet. As a matter of fact, there is considerable interest in developing novel methods for the preparation of metal oxide nanoparticles possessing particular morphological properties and shape for potential applications in gas sensing [7–9]. Moreover, for practical applications, the main challenge consists in finding cost-effective and scalable synthesis methods for the production of these nanostructures. On the basis of these considerations, syntheses of metal oxide nanostructures by chemical processes are more suited compared to physical ones.

Lanthanum perovskites ($LaMO_3$) containing metals of the first transition series are very appealing functional materials because of their immense technological potential. Some are used as membranes for separation processes or as gas sensors in automobiles, several show magneto-optic or magneto resistant properties.

In the present study, different compositions of $LaCr_{1-x}Zr_xO_3$ (x = 0.2, 0.4, 0.6, 0.8) powders were prepared using sol–gel citrate process and are characterized using XRD and TEM techniques. The nanocrystalline material shows good sensitivity and selectivity to carbon monoxide gas as compared to other reducing gases.

EXPERIMENTAL DETAILS

2.1. Material Synthesis

All reagents of analytical grade were used. Nanostructured undoped and doped $LaCr_{1-x}Zr_xO_3$ were synthesized using chemical route. The precursor was prepared by sol–gel citrate method by using stoichiometric ratio of lanthanum nitrate, chromium nitrate, zirconium nitrate and citric acid. Further it was dissolved in ion-free water at 80^0C for 2 h. Then ethylene glycol was added under constant stirring to obtain a homogeneous and stable sol. The solution was further heated in pressure vessel at about 130^0C for 12 h. During this reaction transparent solution was transform into a gel state with very high viscosity. The material was then heated in a furnace at 350^0C for 3 h and a violent combustion was occurs which spontaneously propagates until all the gel was burnt out to form a loose powder. The powder was then calcined at 650^0C for 6 h in order to improve the crystallinity of materials.

2.2. Characterization techniques

The synthesized samples were characterized for their structure and morphology by X -ray powder diffraction (XRD; Siemens D5000) and transmission electron microscopy (TEM; Hitachi-800). The X-ray diffraction data were recorded by using CuK_α radiation (1.5406 A^0).

2.3. Measurement of sensing properties

The gas-sensing properties of prepared $LaCr_{1-x}Zr_xO_3$ powders were studied for different reducing gases such as hydrogen sulphide (H_2S), ammonia (NH_3), liquefied petroleum gas (LPG) and carbon monoxide (CO) whose concentration were fixed at 500 ppm in air. The gas sensitivity (S) was defined as: $S = (Ra - Rg)/Ra = \Delta R/Ra$; where, Ra and Rg are the resistance of sensor in air and the test gas, respectively. The gas-sensing properties were measured in a temperature range of 50 – 350^{0}C.

RESULTS AND DISCUSSION

3.1. X-ray Diffraction Study

Figure 1 display the XRD pattern of the sample $LaCr_{0.4}Zr_{0.6}O_3$, calcined at 650^{0}C for 6 h. The XRD pattern showed perovskite with tetragonal structure. The XRD pattern indicates that the product has high degree of crystallinity judged from the high and sharp diffraction peaks. The average particle size of the nanocrystalline $LaCrO_3$ according to the scherrer formula were in the range of 30 – 40 nm.

In order to check the effective Zr content in the perovskitic phase, the relative occupancies of both Cr and Zr were refined. No significant variation from the stoichiometric value was detected for oxygen while the cation refinement lead to the effective composition of $La(Cr_{0.4}Zr_{0.6})O_3$. This composition marks the highest degree of Zr-substitution that can be attained at the Cr site in $LaCrO_3$ at the reaction.

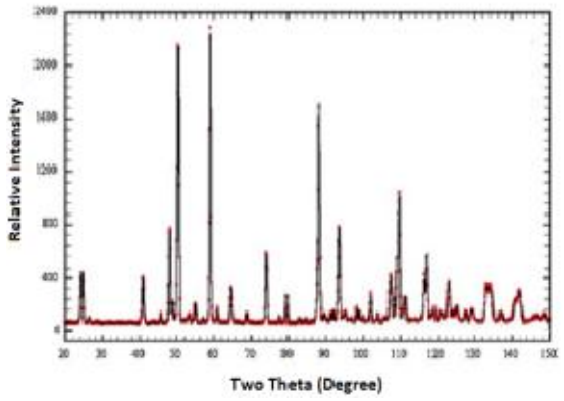

Figure 1: XRD pattern of $LaCr_{0.4}Zr_{0.6}O_3$ calcined at 650^{0}C for 6 h

3.2. Transmission electron microscopy

The morphology of the powder sample has been observed by TEM. Figure 2 shows the TEM micrograph of the $LaCr_{0.4}Zr_{0.6}O_3$ powder with uniform grain size distribution having a small tendency of agglomerates formation**.** Due to the formation of polycrystalline material particle size are formed at 35 nm.

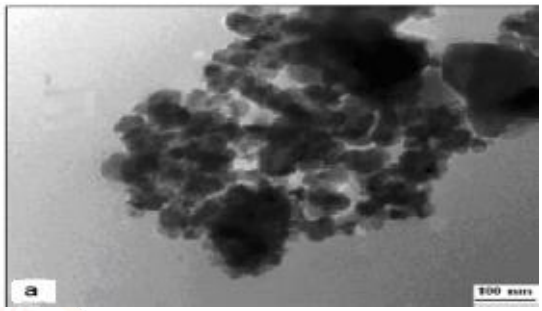

Figure 2: TEM image of the sample $LaCr_{0.4}Zr_{0.6}O_3$, calcined at 650^{0}C for 6 h.

3.3 Gas Sensing Properties

Figure 3 shows the sensor response (S) as a function of operating temperature for undoped $LaCrO_3$ nanopowder calcined at 650^{o}C for 6 h for various reducing gases like NH_3, LPG, CO and H_2S. The sensor characteristic shows higher response for CO gas as compared to LPG, NH_3 and H_2S at an operating temperature 220^{o}C.

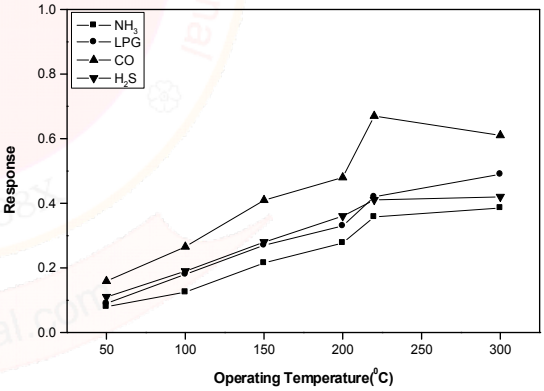

Figure 3: Response as a function of operating temperature for $LaCrO_3$ for different reducing gases.

In order to improve the gas response properties, a great variety of atoms or additives are introduced in the base sensing semiconductor. Figure 4 shows the gas response as a function of different amount of Zr doped $LaCrO_3$ (x = 0.2, 0.4, 0.6 and 0.8). The response to CO gas goes on increasing with increasing amount of Zr. The largest response for $LaCr_{0.4}Zr_{0.6}O_3$ (x = 0.6) was obtained due to more available sites for the oxygen to be adsorbed and in turn to oxidize the test gas. The decrease in response may be due to the insufficient number of sites available on the surface. The partial

replacement of Cr by Zr ion results in decrease in grain size, which results in larger density of grain boundaries, which increases film's effective exposure area to the CO gas. The chemical composition of the semiconductor is also a key parameter that influences their sensing performance. In fact, composition by itself can affect the microstructure and, thus determine the sensing properties.

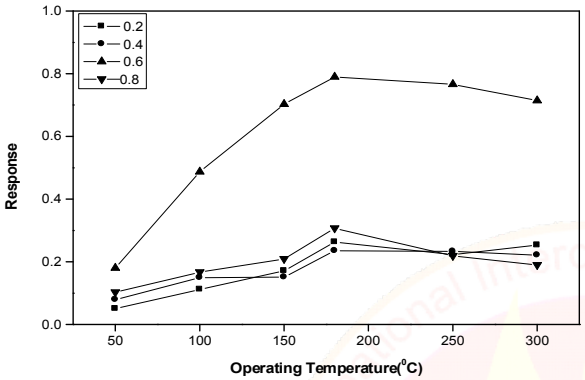

Figure 4: Sensor Response of $LaCrO_3$ doped with different amount of Zr calcined at 650^0C. (a) x=0.2, (b) x=0.4, (c) x=0.6and (d) 0.8

Figure 5 illustrates the gas response of $LaCr_{0.4}Zr_{0.6}O_3$ at different operating temperature. It is observed that the sensor has high response to CO gas as compared to LPG, NH_3 and H_2S at 180^0C. The high response to CO gas can be attributed to the surface modification by Zr over $LaCr_{0.4}Zr_{0.6}O_3$ film.

Figure 6 shows the dependence of gas response of the $LaCr_{0.4}Zr_{0.6}O_3$ sensor on the concentration level of CO at 180°C. It is clear from the graph that with the increase in the concentration, the response increases linearly up to 200 ppm of CO, after that it saturates. After 200 ppm level of CO, the curve flattens because there would not be enough ionosorbed oxygen species to contribute to detecting mechanisms.

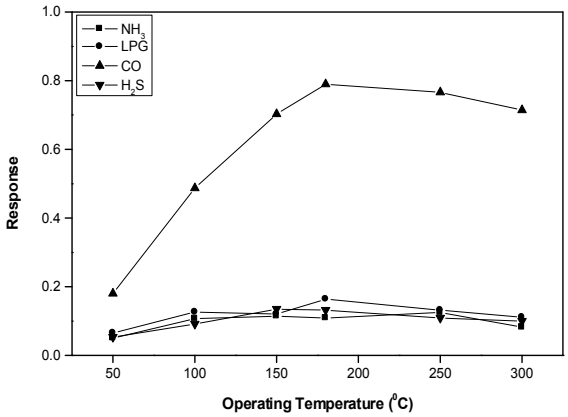

Figure 5: Response to different reducing gases of $LaCr_{0.4}Zr_{0.6}O_3$ as a function of operating temperature.

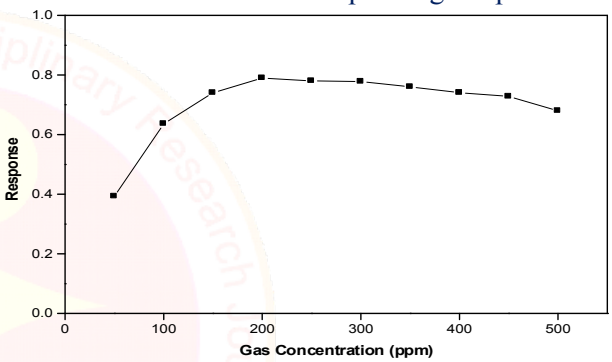

Figure 6: Response of $LaCr_{0.4}Zr_{0.6}O_3$ to CO gas of different concentration at an operating temperature 180°C.

CONCLUSION

Doped and undoped $LaCrO_3$ thick films were prepared by sol-gel citrate method. XRD of $LaCr_{0.4}Zr_{0.6}O_3$ calcined 650^0C for 6 h showed good crystalline quality with a grain size 35 nm. It was also found that $LaCrO_3$ sensor exhibited high response for CO gas at 220^0C. Further improvement $LaCr_{0.4}Zr_{0.6}O_3$ shows response and selectivity for CO gas at an operating temperature of 180°C.

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STUDIES ON SOME PHYSICO-CHEMICAL PROPERTIES OF ACACIA NILOTICA GUM FROM GADCHIROLI DISTRICT

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ABSTRACT

The physico-chemical properties of Acacia Nilitica gum collected from Gadchiroli District are studied. The following results are obtained. The Moisture Contents (9.4%), Water Solubility (49%), Melting Temperature (315 °C), The Relative Density of 20% solution at 30°C (1.245) The Relative Viscosity of 1% solution at 30°c (14.51), Relative Surface Tension of 1% solution at 30°c (75.61), pH of 25% solution (4.61) and Ash (2.64%).

Keywords :*Physico-Chemical properties, Acacia Nilotica, Gum, Gadchiroli District*

INTRODUCTION

The total geographical area of gadchiroli district is 14412 sq. km. out of this area, 11694 sq. km. (78.40%) land is included in the reserved forest category, which consists of various medicinal plants. Acacia Nicotica is a common medium sized tree. Locally known as Babul belonging to the family Mimosaceae. The gums are harvested from the stems and branches of the resource gum trees as dry exudates (FAO, 1995). A gum, in general, is any water-soluable or water swellable polysaccharide that is extractable from marine and land plants, or from microorganisms that possess the ability to contribute viscosity or gelling ability to their dispersions (Abu Baker at al, 2007).

The complex and heterogeneous nature of plant gums in terms of their chemical composition makes it very difficult to predict their properties. Yet, their industrial application has to be based on well characterized gum samples.

The gum varies in colour from very pale yellowish brown depending on the quantity of tannin in the sample. The lighter, more highly valued gums are soluble in water and very viscous, the tannin in the darker gum reduces the solubility (New, 1984).

The use of Acacia gums (in particular) has been widely reported in industrial application notably in the food, pharmaceutical, adhesive, cosmetic, textile, paint and print industries, where they are used variously as food additives, diatary fibres, tackifiers or binders, thickeners, stabilizers, emulsifiers, suspending and surface coating agents, gelling agents etc (yaseen et al., 2005; Al-Assaf et al., 2006; Abu Baker et al, 2007; Elnour et al., 2009). The objective of this study therefore is to determine and compare the physicochemical properties of gum exudates.

MATERIAL AND METHODS

Sample Collection

The samples are obtained from Gadchiroli district (Maharashtra) from the tree barks and dry nodules or lumps. Collection of the sample is done in summer 2017.

PREPARATION OF SAMPLES

The crude samples consisted of mixture of large and small nodules admixed with bark and organic debris. Hand pick select gum (HPSG) method (sabah El-Kheir et al., 2008) was used to separate the neat, quality gum from other constituents. The former was then spread out under room shade until dry. The dried samples (hard nodules) were then ground into fine powder (to pass 0.4 mm mesh screen) the prepared samples were kept in tight containers and stored at room temperature until required for subsequent analysis (Yusuf, 2011).

MOISTURE CONTENTS

Moisture contents of samples was determined by drying 5g of the ground gum sample to constant mass at 80°C using a hot air oven. Dried samples were cooled in a desiccator before weighing. Moisture content was expressed as % of mass loss from the original mass.

WATER SOLUBILITY

Gums are uncrystlizable. The Solubility of Acacia Nilotica gum in water was therefore determined at room temperature (30°C) by adding 10 mg of the sample to 10 cm^3 of distilled water and leaving the mixture overnight. 15 cm^3 of the clear supernatant

was then taken in a small pre weighed evaporating dish and heated to dryness over a water bath. The mass of the solution was determined using a digital top loading balance and expressed as a % solubility of the gum in water (Carter, 2005).

MELTING TEMPERATURE

1 g of the ground gum is taken in a glass capillary tube and melting temperature determined repeatedly until reproducibility.

RELATIVE DENSITY

Density measurements are carried out at 30°C by using density bottle with capacity of 25 cm^3. For this purpose 1 % (w/v) sample in aqueous solution is used.

RELATIVE VISCOSITY

Relative viscosity of gum samples is measured in filtered 1% aqueous solution using U-shaped viscometer (AOAC,1990), A flow time (seconds) stalagmometer which consists of a capillary tube with glass bulb. In this method, liquid is allowed to flow down forming drop at the end of capillary. From the number of drops of standard liquid and sample the relative surface tension be calculated.

p^H: p^H of 25% aqueous gum solution (w/m) is calculated by using glass electrode digital p^H meter.

as a % ratio of the mass of the ash to the oven dry mass (Yebeyen et al. 2009).

RESULTS AND DISCUSSION

Table : The physicochemical properties for the Acacia Nilotica gum samples analyzed.

Sr. No.	Physico-chemical properties	Value
1	Colour	Pale yellow
2	Odour	Odourless
3	Taste	Tasteless
4	Moisture	9.4 %
5	Water Solubility	49 %
6	Melting Temperature	315 °C
7	Relative Density of 20% solution (30°C)	1.245
8	Relative Viscosity of 1% solution (30°C)	14.50
9	Relative Surface Tension of 1% solution (30°C)	75.61
10	p^H (25% solution)	4.61
11	Ash	2.64%

of distilled water was measured by filling the viscometer tube (held at 30°C in water bath) with water and then drawn by suction to the upper mark of the viscometer. The water level was allowed to fall, passing the upper and lower marks of the U shaped tube.

Evaluated thus:

Relative viscosity (30°C) = $(T-T_o)/T_o$ where; T is flow time of gum solution (sec.) T_o is flow time of distilled water (sec.)

RELATIVE SURFACE TENSION

The relative surface tension of gum sample is measured in filtered 1% aqueous solution using

ASH CONTENTS

5 g of gum sample was first heated on a burner in air to remove its smoke. Then it is burned in a furnace at 550°C. The ash content was expressed

CONCLUSION

Acacia Nilotica gum collected from Gadchiroli district form the solution of highest densities Density measures the degree of compact packing of macromolecules in the gums. Present gum sample is water soluble at 30 °C to form viscous solution it indicates that, Acacia Nilotica is natural gum of hydrophilic colloid group. The melting temperature range of 315 °C implies the good thermal stability of the gum sample.

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REFRACTOMETRIC STUDY OF SUBSTITUTED ARYL BISTHIOUREA IN BINARY SOLUTION AT DIFFERENT TEMPERATURES

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ABSTRACT

Refractive indices of substituted aryl bisthiourea have been measured by Abbe's refractometer for the entire range of % composition of dioxane + water binary solution at different temperature. From the data of refractive index and density, molar refraction (Rm) and polarizability constant (α) are calculated. It could be seen that molar refraction (Rm) and polarizability constant (α) of substituted bisthiourea increases with increase in percentage of binary solution. The values of these parameters and their variations have been used to determine molecular solute-solvent, solute-solute interactions in the solution.

Keywords: *Refractive index, molar refraction, polarizability constant, binary solution, Substituted aryl bisthiourea*

INTRODUCTION

Refractometry is a well-established technique for the analysis of gases, liquids and solids. Recently, refractometric analysis is applied for the study of bimolecular interactions. The information regarding the transport property of the ion-solvent interactions can obtained from refractrometric measurements. These measurements provide useful information about solute-solute and solute-solvent interactions.

When a light of beam passes from one substance to another, the beam is bent so that it travels in different direction. If it is passed from less dense to denser medium it is refracted toward normal to form angle of refraction which is less than angle of incident. The refractive index is the ratio of angle of incident to the angle of refraction and it depends on the temperature and wave length of light. The extent of refraction depends on –i) the relative concentration of atom or molecule ii) the structure of atom or molecule. So refractive index gives idea about geometry and structure of molecule. Refraction of light is additive property, but also depends on the structural arrangement of atom in molecule. This can some time be used to determine the structure of an unknown compound whose molecular formula is known.

Sonune et. al. [1] has been studied additive properties such as molar refractivity and molar polarizability constant of allopurinal, acenocoumarol, warfarin and amoxicillin in different media.N. Yadav et. al. [2] has been measured Refractive indices for the binary liquid mixtures of n-butylethanoate and 3-methylethanoate with cyclohexane, benzene, 1,4-dimethylbenzene and 1,3,5-trimethylbenzene over the entire composition range at 308.15K. M. P. Wadekar et. al. [3] have been investigated Molar refraction (Rm) and polarizability constant (α) of some different substituted thiopyrimidine drugs by measuring the densities and refractive index of solution of different percent composition in binary mixture. M. M. Kalaskar et. al. [4] has been studied molar refraction and polarizability constants of some different substituted aminopyrimidine drugs in same concentration of ligand in different percentages of solvent concentration. K. Anil Kumar et.al [5] has been measured the refractive indices of 1, 4-dioxane with 1-butanol over the entire composition at 298.15, 303.15, 308.15, 313.15 and 318.15K using Anton Paar Abbemat. S. Baluja et. al. [6] have been measured the density and refractive index for four binary liquid mixtures: diethyl malonate + dimethylformamide, diethyl malonate + Hexane, diethyl malonate + tetrahydrofuran, diethyl malonate + 1, 4-dioxane. R. Talegaonkar et.al [7] has been studied molar refraction and polarizability constant of substituted thiazolyl Schiff's bases such as 2-[3-phenyl-1-(4-phenyl-thiazol-2-ylimino)-allyl]-methylphenol,2-[-3-(4-methoxy-phenyl)-1-(4 phenylthiazol - 2-ylimino)-allyl]-methyl -phenol and 2-[3-(4-methoxy-phenyl)-1-(4-phenyl-thiazol-2-ylimino)-allyl]-4-methyl-phenolin non aqueous solvent such as 1,4-dioxane, acetone and ethanol with different percentage. P.Krishnamurthi et. al [8] have been measured the refractive index measured for the binary mixtures of n-heptanol with dimethylktone ,

ethyl methyl ketone, methyl methacrylate 301K. The molar refraction, atomic polarization, polarizability and atomic radii andmolar volume evaluated. A.W.Wakode et al [9] measured refractive indices of benzothiazolyl and benzimidazolyl substituted derivatives in different percentage of binary liquid mixture such as acetone-water, dioxane-water and DMSO-water at 35 ± 0.1^{0}C and observed that solvent-solvent interaction was stronger than solute-solvent interaction.

The present work deals with the study of molar refraction and polarizability constants of some different substituted aryl bisthioureas in different percentages of solvent concentration at different percentage.

Substituted aryl bisthioureas used for present work are:

L_1: 1-phenyl Bisthiourea
L_2: p-tolyl Bisthiourea
L_3: p-chlorophenyl Bisthiourea

MATERIAL AND METHOD

The ligands of which physical parameters is to be investigated are synthesized by using microwave induced method with environmentally benign approach. In present investigation, refractive indices of liquid mixtures were measured with the help of Abbe's refractometer. It was specially designed to measure the refractive indices of the small quantities of the transparent liquid ranging from 1.300 to 1.700. The solutions of ligand in different percent composition of binary mixtures were prepared by weight. All the weighing was made on one pan digital balance with an accuracy of (± 0.001gm). The densities of solutions were determined by a pre-calibrated bicapillary pyknometer (± 0.1%). The constant temperature of the prism box is maintained by circulating water from theemostat at (25± 0.1)^{0}C.

RESULT AND DISCUSSION

The refractometric study of L_1 to L_3 ligands at different temperatures determined with different percentage composition to find the specific refraction (r), molar refraction (Rm) and polarizability constant (α) with the help of following equations.

$$r = \frac{(n2-1)}{n2+2} X \frac{1}{d}$$

$$Rm = \frac{n2-1}{n2+2} X \frac{M}{d} = 4/3\ \Pi N\alpha$$

$$\alpha = \frac{Rmx3}{4x3.14xN}$$

Where N = Avogadro's number = 6.023 x 10^{23}These refractometric parameters used to study the intermolecular interactions.The present work deals with the interaction of substituted aryl bisthiourea in different percent composition like 75%, 80%, 85% and 90% of 1,4 Dioxane-water at different temperatures.

Molar Refraction and Polarizability Constant at Different % Of Dioxane – Water (At 298K)

Table 1: L_1: 1-phenyl Bisthiourea **Conc. : 0.01M**

% Dioxane	Density ds X 10^3 (Kg.m^{-3})	Refractive Index (n)	Specific Refraction (r)	Molar refraction (Rm)	α X 10^{-23} (polarizability constant)
75	0.9729	1.435	0.2682	60.6157	2.4038
80	0.9711	1.437	0.2697	60.9711	2.4179
85	0.9723	1.438	0.2699	61.0171	2.4197
90	0.9694	1.439	0.2713	61.3211	2.4318

Table 2: L_2: P-tolyl Bisthiourea **Conc. : 0.01M**

% Dioxane	Density ds X 10^3 (Kg.m^{-3})	Refractive Index (n)	Specific Refraction (r)	Molar refraction (Rm)	α X 10^{-23} (polarizability constant)
75	0.9770	1.433	0.2660	63.8436	2.5318
80	0.9758	1.434	0.2668	64.0508	2.5400
85	0.9752	1.436	0.2681	64.3474	2.5518
90	0.9688	1.438	0.2709	65.0310	2.5789

Table 3: L_3: P- chlorophenyl Bisthiourea **Conc. : 0.01M**

% Dioxane	Density ds X 10^3 (Kg.m^{-3})	Refractive Index (n)	Specific Refraction (r)	Molar refraction (Rm)	α X 10^{-23} (polarizability constant)
75	0.9747	1.434	0.2671	69.6002	2.7601
80	0.9723	1.435	0.2683	69.9121	2.7724
85	0.9735	1.437	0.2691	70.1054	2.7801

9 0	0.9717	1.440	0.2712	70.6544	2.8019	

Molar Refraction and Polarizability Constant at Different % Of Dioxane - Water (At 300K)

Table 4: L_1: 1-phenyl Bisthiourea Conc. : 0.01M

% Dioxane	Density $d_s X 10^3 (Kg.m^{-3})$	Refractive Index (n)	Specific Refraction (r)	Molar refraction (Rm)	$\alpha X 10^{-23}$ (polarizability constant)
75	0.9882	1.433	0.2630	59.4380	2.3571
80	0.9823	1.434	0.2651	59.9154	2.3760
85	0.9823	1.435	0.2656	60.0356	2.3808
90	0.9882	1.438	0.2656	60.0353	2.3808

Table 5: L_2: P-tolyl Bisthiourea Conc. : 0.01M

% Dioxane	Density $d_s X 10^3 (Kg.m^{-3})$	Refractive Index (n)	Specific Refraction (r)	Molar refraction (Rm)	$\alpha X 10^{-23}$ (polarizability constant)
75	0.9776	1.432	0.2653	63.6759	2.5251
80	0.9764	1.433	0.2661	63.8828	2.5333
85	0.9752	1.434	0.2670	64.0902	2.5416
90	0.9711	1.436	0.2692	64.6190	2.5625

Table 6: L_3: P- chlorophenyl Bisthiourea Conc. : 0.01M

% Dioxane	Density $d_s X 10^3 (Kg.m^{-3})$	Refractive Index (n)	Specific Refraction (r)	Molar refraction (Rm)	$\alpha X 10^{-23}$ (polarizability constant)
75	0.9782	1.432	0.2651	69.0725	2.7392
80	0.9735	1.433	0.2669	69.5459	2.7579
85	0.9729	1.434	0.2676	69.7290	2.7652
90	0.9723	1.436	0.2689	70.0520	2.7780

Molar Refraction and Polarizability Constant at Different % Of Dioxane -Water (At 302K)

Table 7: L_1: 1-phenyl Bisthiourea Conc. : 0.01M

% Dioxane	Density $d_s X 10^3 (Kg.m^{-3})$	Refractive Index (n)	Specific Refraction (r)	Molar refraction (Rm)	$\alpha X 10^{-23}$ (polarizability constant)
75	0.9747	1.432	0.2661	60.1399	2.3849
80	0.9752	1.433	0.2665	60.2304	2.3885
85	0.9729	1.434	0.2676	60.4943	2.3990
90	0.9700	1.434	0.2676	60.4943	2.3990

Table 8: L_2: P-tolyl Bisthiourea Conc. : 0.01M

% Dioxane	Density $d_s X 10^3 (Kg.m^{-3})$	Refractive Index (n)	Specific Refraction (r)	Molar refraction (Rm)	$\alpha X 10^{-23}$ (polarizability constant)
75	0.9811	1.430	0.2633	63.1924	2.5060
80	0.9811	1.431	0.2638	63.3206	2.5111
85	0.9805	1.432	0.2645	63.4876	2.5177
90	0.9782	1.433	0.2656	63.7653	2.5287

Table 9: L_3: P- chlorophenyl Bisthiourea Conc. : 0.01M

% Dioxane	Density $d_s X 10^3 (Kg.m^{-3})$	Refractive Index (n)	Specific Refraction (r)	Molar refraction (Rm)	$\alpha X 10^{-23}$ (polarizability constant)
75	0.9800	1.430	0.2635	68.6670	2.7231
80	0.9805	1.431	0.2639	68.7713	2.7272
85	0.9800	1.433	0.2652	69.0848	2.7396
90	0.9770	1.434	0.2665	69.4364	2.7536

Molar Refraction And Polarizability Constant At Different % Of Dioxane- Water At 304K

Table 10: L_1: 1-phenyl Bisthiourea Conc. : 0.01M

% Dioxane	Density ds X 10^3 ($Kg.m^{-3}$)	Refractive Index (n)	Specific Refraction (r)	Molar refraction (Rm)	α X 10^{-23} (polarizability constant)
75	0.9941	1.431	0.2603	58.8471	2.3336
80	0.9882	1.432	0.2624	59.3183	2.3523
85	0.9882	1.432	0.2624	59.3183	2.3523
90	0.9823	1.433	0.2645	59.7950	2.3712

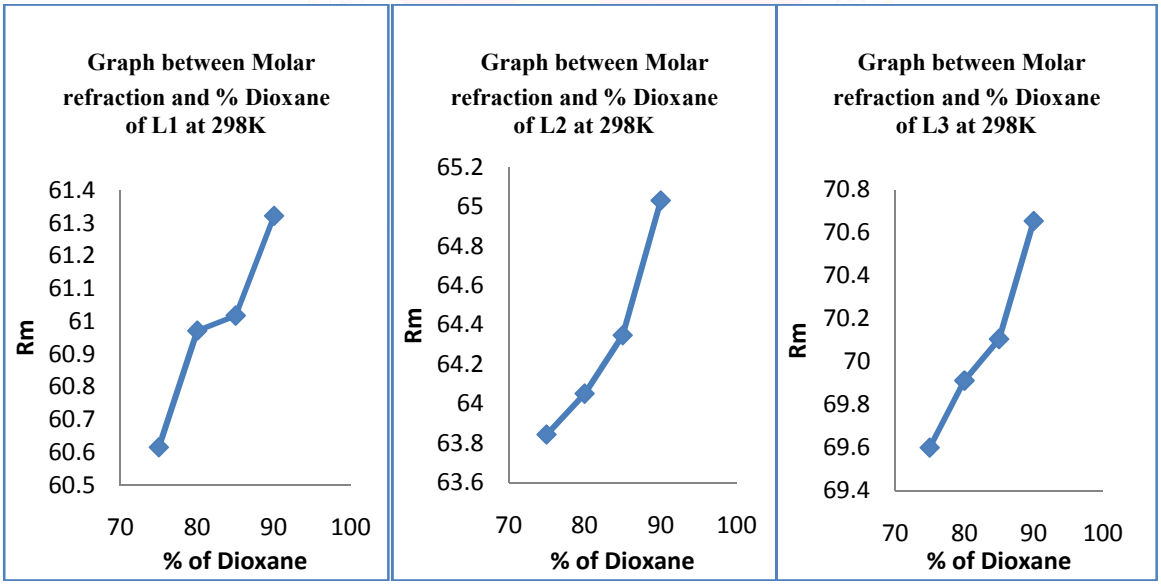
Table 11: L_2: P-tolyl Bisthiourea Conc. : 0.01M

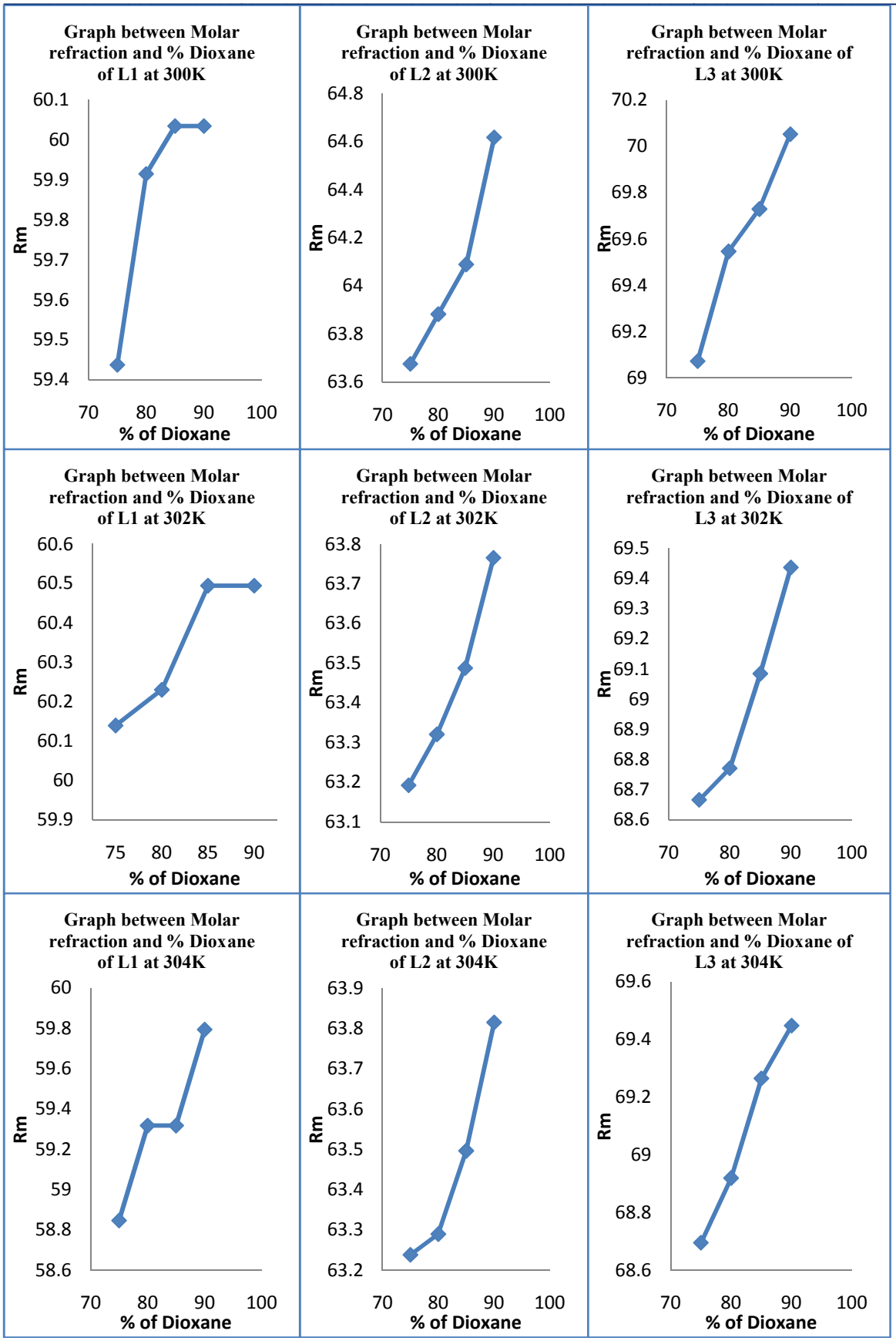
% Dioxane	Density ds X 10^3 ($Kg.m^{-3}$)	Refractive Index (n)	Specific Refraction (r)	Molar refraction (Rm)	α X 10^{-23} (polarizability constant)
75	0.9764	1.428	0.2634	63.2386	2.5078
80	0.9776	1.429	0.2637	63.2898	2.5098
85	0.9764	1.430	0.2645	63.4965	2.5180
90	0.9735	1.431	0.2658	63.8149	2.5307

Table 12: L_3: P- chlorophenyl Bisthiourea Conc. : 0.01M

% Dioxane	Density ds X 10^3 ($Kg.m^{-3}$)	Refractive Index (n)	Specific Refraction (r)	Molar refraction (Rm)	α X 10^{-23} (polarizability constant)
75	0.9776	1.429	0.2637	68.6958	2.7242
80	0.9764	1.430	0.2645	68.9202	2.7331
85	0.9735	1.431	0.2658	69.2658	2.7468
90	0.9729	1.432	0.2665	69.4488	2.7541

Graphical Representation of Molar refraction Vs % composition of Dioxane at 0.01M ligandat 298K, 300K and 302K





From result, it is observed that refractive index increases with the increase in percentage composition of organic solvent. Those solvent having more value of dipole moment shows

greater refractive index and there is same trend for ligands.

Ligand having more dipole moment shows greater value of refractive index. The bulky substituent on the molecule is not only factor in trend of refractive index but the reactivity, stability as well as electron donating and withdrawing nature and also compactness in the molecule will directly hampered results and trend in refractive index.

The value of molar refraction of different percent composition in binary mixture are shown in table-1-12 .From the data it is observed that value of molar refraction goes on increasing with the decrease in amount of water in percent composition.

Table 1-12 shows the comparative data of molar refraction and polarizability constant. These parameters provide important information about structural orientation of ligand in solution.

The trend of ligands L_1, L_2, and L_3 for Molar refraction and Polarizability constant value observed are as follows.

$$L_3 > L_2 > L_1$$

It is due to slight difference in a structure of molecule. In Bisthiourea, there are two S donor atom and N-N linkage in a structure

Molar refraction and Polarizability constant of substituted Bisthioureas

L_3(p-Chloro phenyl) > L_2(p-tolyl)> L_1(Phenyl)

CONCLUSION

- Solvent having more value of dipole moment showed greater refractive index.
- Molar refraction is depends on the reactivity, stability as well as electron donating and withdrawing nature of substituent and also compactness in the molecule.
- Molar refraction is depends on the molecular weight of solute and density.
- The bulky substituent in ligands affects the polarizability value.
- From the results of ligand it is clear that refractive index higher for polarizing group present in ligand.

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SYNTHESIS AND ANTIBACTERIAL ACTIVITY OF 1-H-3-SUBSTITUTED-4,5-(DISUBSTITUTED PHENYL)-2-IMIDAZOLONE.

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ABSTRACT

2-imidazolones are well known for bactericidal as well as insecticidal activity. Though there are several methods for the synthesis of 2-imidazolones, most of them required longer reflux time of 8 to 10 hours. Hence the proposed work was undertaken to workout simple methodology for the synthesis of 2-imidazolones and to improve the yield of the products, by employing Zeolite as a catalyst. The work presented here describes the synthesis of some substituted 2-imidazolones obtained from substituted benzoins and urea in CH_3COOH as a solvent in presence of Zeolite as a catalyst. Substituted benzoins in turn were obtained from aromatic aldehydes by their condensation in presence of aqueous NaCN. The synthesized compounds were characterised on the basis of chemical properties, elemental and spectral analysis. Further these compounds were screened for antibacterial activity against the test organisms E.coli, S.typhi, P.vulgaris, B.subtilis, S.aureus and S.pneumoniae.60% of the total samples tested showed antibacterial activity. The compounds containing –N $(CH_3)_2$ –OCH_3, -OH as a substituents showed antibacterial activity against maximum number of organisms.

Keywords: *Substituted benzoins, Urea, Methyl urea, Phenyl urea, Zeolite catalyst, 2-imidazolones, antibacterial activity.*

INTRODUCTION

Imidazolones are believed to be associated with several pharmacological activities. Many natural products are believed to contain imidazolones. The leucetta and oroidin families of alkaloids [1] have been identified which contain either 2-aminoimidazole or 2-imidazolone moiety[2-3]. Jie-Fei Cheng et al.[4] carried out a traceless solid phase synthesis of 2-imidazolones. Polymer-bound glycerol resin was reacted with bromo acetaldehyde diethyl acetal to give the cyclic acetal bromide on the solid support. Tomokazu Katahira et al.[5] studied stereo selective intermolecular radical addition of polyhaloacyl pendant groups to the 1,3-dihydro-2-imidazolone moiety the chiral, synthesis of threo- diamino carboxylic acids. Marie Pascale[6] synthesized several 2-imidazolone derivatives and screened their fungicidal and herbicidal activities. Xue et al[7] synthesized 2,3-Dihydro-*N*,3-bis(3,4,5-trimethoxyphenyl)-4-(substitutedphenyl)-2-oxo-imidazole-1-carboxamides and 1-acetyl-1,3-dihydro-3-(3,4,5trimethoxyphenyl)-4-(substitutedphenyl)-2*H*-imidazol-2-ones and reported their antitumor activities. Glass D et al[8] reported 4-(4-Guanidinobenzoyl)-2-imidazolones and related compounds having phosphodiesterase inhibitors and novel cardio tonics with combined histamine H_2 receptor agonist and PDE 111 inhibitor activity. Butler and Hussain[9] carried out synthesis of 2- imidazolones by the reaction of benzoins or aliphatic acyloins with urea and methyl urea. Sang-Hyeup Lee and coworkers[10] carried out synthesis of 2-imidazolones by the reaction of substituted urea with 3-hydroxy butanone or 3-iminopentane 2,4-dione in solution or in solid phase. From the review of literature, it was observed that most of the methods of synthesis of 2-imidazolones required longer reflux time of 8-10 hours and the yield of the products was also quite low. Hence, in the context of the above observations, the proposed work was undertaken to reduce the reflux time and to improve the yield of the products by employing Zeolite as a catalyst.Futher in order to know antibacterial activity these compounds, they were screened for antibacterial test against test organisms *E.coli, S.typhi, P.vulgaris, B.subtilis, S.aureus and S.pneumoniae* and their zones of inhibition(mm) were determined.

EXPERIMENTAL

In this work, three substituted benzoins were prepared by the self condensation of 4-dimethyl aminobenzaldehyde, 4-methoxybenzaldehyde and 2-hydroxybenzaldehyde respectively, in presence of aqueous NaCN in ethanolic medium. In the second step, each of above mentioned benzoins was reacted with methyl urea, urea and phenyl urea respectively in CH_3COOH in presence of Zeolite as a catalyst to form 1-H,3-methyl-4-(4-

substituted phenyl)-5-(4-substituted phenyl)-2-imidazolones and their methyl and phenyl derivatives respectively. All the synthesized compounds were characterized on the basis of chemical properties, elemental and spectral analysis.

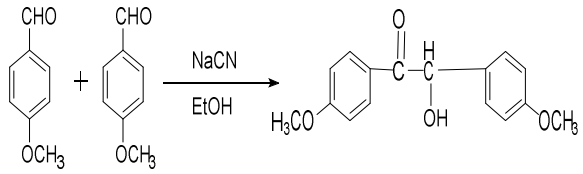
Scheme-1: Preparation of 4, 4'-dimethoxy-benzoin.

Method: In a round bottom flask, took 13.6 gms (0.1 mol) of anisaldehyde, added to it about 50 ml of ethyl alcohol. The mixture was shaken well. To this mixture added 4.9 gms aq. solution of sodium cyanide (0.1 mol). The reaction mixture was refluxed for 30-40 minutes. Cooled reaction mixture and poured it to ice cold water, obtained solid yellow product. Recrystallised it from water-ethanol mixture.

Yield: 65%

Melting point: 113°C

Reaction:



(1a)

IR (KBr,cm-^{1}) : 3427 (O–H Str) 3066 (Ar,C–H str) 2920 (Aliph, C–H) 1653 (C=O str) 1507 (Ar, C=C str) 1310 (C–O str).

^{1}H-NMR (DMSO) (δ): 7.86-7.85 (d,4H,Ar–H); 7.13-7.12 (d,4H,Ar–H); 3.87 (s,1H, CH–OH); 3.37 (s,6H,–OCH_3); 2.50 (s,1H, Aliph, C–H);

Elemental Analysis for $C_{16}H_{16}O_4$ (272.30)

Element (%)	C	H
Calculated	70.58	5.92
Found	70.55	5.90

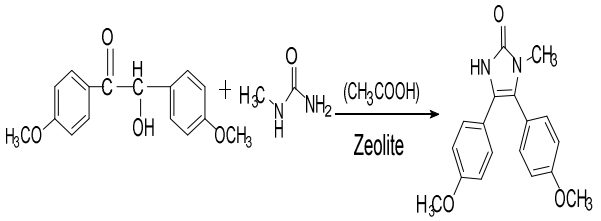
Scheme 2 : Synthesis of 1-H-3-methyl-4(4-methoxyphenyl)-5-(4-methoxyphenyl)-2-imidazolone

Method: To 4,4'-dimethoxybenzoin (2.72 gms) (0.01 mol) added glacial acetic acid (20ml). The mixture was warmed slightly to dissolve the solute. To this solution, added methyl urea 0.74 gm (0.01mol), followed by zeolite (1gm) as a catalyst. The reaction mixture was refluxed for three hours. Allowed it to cool and poured it to ice cold water. The solid yellow product formed was filtered, washed 2, 3 times with cold water and recrystallized from water-ethanol mixture.

Yield: 62%

Melting point: 180°C

Reaction:



(2d)

IR (KBr,cm-^{1}) 3650 (N–H str) 3073 (Ar, C–H str) 2922 (Aliph, C–H str) 1678 (C=O str) 1600 (C=N str) 1507 (Ar, C=C str) 1293 (C–N str) 1245 (C–O str)

^{1}H-NMR (DMSO) (δ): 7.57 (s,1H,N–H) 7.26-7.22 (m,4H,Ar–H) 7.17-7.05 (m,4H,Ar–H) 3.37 (s,6H, –OCH_3) 2.52 (s,3H, –CH_3)

Elemental Analysis for $C_{18}H_{18}N_2O_3$ (310.35)

Element (%)	C	H	N
Calculated	69.66	5.85	9.03
Found	69.62	5.82	9.00

RESULTS AND DISCUSSION

We synthesized variedly substituted -2-imidzolones by the condensation of each of three substituted benzoins with urea, methyl urea and phenyl urea respectively. The target compounds gave positive tests for Nitrogen as well as for C=O linkage (red coloration with 1% solution of m-dinitrobenzene in ethanol) The IR spectrum showed sharp bands at 3650cm^{-1} (N-H str) and 1678 cm^{-1} (C=O str) and 1507 cm^{-1} (Ar, C=C str) similarly, in ^{1}H-NMR spectrum chemical shifts at 7.57 (s,1H,N–H);7.26-7.22 (m,4H,Ar–H);7.17-7.05 (m,4H,Ar–H);3.37(s,6H,–OCH_3);2.52(s,3H,–CH_3); with elemental analysis further confirmed the formation 2-imidazolones. The synthesized compound along with their percent yield and melting point are given in the following table 1.

Table: 1
List of synthesized compounds along with their % yield and melting point

Sr. No	Compound	Percent Yield (%)	Melting point (°C)
1	1-H-3-methyl-4-(4-dimethylaminophenyl)-5-(4-dimethylaminophenyl)-2-imidazolone (2a)	68	160
2	1,3-dihydro-4-(4-dimethylaminophenyl)-5-(4-dimethylaminophenyl)-2-imidazolone (2b)	65	165
3	1-H-3-phenyl-4-(4-dimethylaminophenyl)-5-(4-dimethylaminophenyl)-2-imidazolone (2c)	70	175
4	1-H-3-methyl-4-(4-methoxyphenyl)-5-(4-methoxyphenyl)-2-imidazolone. (2d)	62	180
5	1, 3,dihydro-4-(4-methoxyphenyl)-5-(4-methoxyphenyl)-2-imidazolone. (2e)	66	145
6	1-H-3-phenyl-4-(4-methoxyphenyl)-5-(4-methoxyphenyl)-2-imidazolone. (2f)	58	138
7	1, 3-dihydro-4-(2-hydroxyphenyl)-5-(2-hydroxyphenyl)-2-imidazolone (2g)	66	190
8	1-methyl-3-H-4-(2-hydroxyphenyl)-5-(2-hydroxyphenyl)-2-imidazolone (2h)	62	168
9	1-H-3-phenyl-4-(2-hydroxyphenyl)-5-(2-hydroxyphenyl)-2-imidazolone (2i)	63	185

ANTIBACTERIAL ACTIVITY

Method for the determination of antimicrobial activity

These newly synthesized compounds were assayed for their antimicrobial activities against some organisms, such as *E.coli (gram+ve), S.typhi (gram+ve), P.vulgaris (gram+ve), B.subtilis(gram-ve), S.aureus (gram-ve) and S.pneumoniae(gram-ve)* at a concentration of 100 µg/ml by disk diffusion method[11]. Each standardized test organism (0.1ml) was spread on the solidified sterile agar plates.

Table: 2
Antibacterial activity of compounds

Sr.No.	Compound (100 µg/ml)	Zone of inhibition (mm)					
		E. coli	*S. typhi*	*P. vulgaris*	*B. subtilis*	*S. aureus*	*S. pneumoniae*
1	1,3-dihydro-4-(4-dimethylaminophenyl)-5-(4-dimethylaminophenyl)-2-imidazolone (2a)	S (11)	S (15)	R	R	S (12)	S (14)
2	1-H-3-methyl-4-(4-dimethylaminophenyl)-5-(4-dimethylaminophenyl)-2-imidazolone (2b)	S (14)	R	S (10)	S (12)	R	R
3	1-H-3-phenyl-4-(4zdimethylaminophenyl)-5-(4-dimethylaminophenyl)-2-imidazolone (2c)	R	S (12)	S (12)	S (15)	S (12)	R
4	1,3,dihydro-4-(4-methoxyphenyl)-5-(4-methoxyphenyl)-2-imidazolone. (2d)	S (12)	R	S (10)	S (10)	S (10)	S (10)
5	1-H-3-methyl-4-(4-methoxyphenyl)-5-(4-methoxyphenyl)-2-imidazolone. (2e)	R	S (14)	R	S (14)	S (10m)	S (12)
6	1-H-3-phenyl-4-(4-methoxyphenyl)-5-(4-methoxyphenyl)-2-imidazolone. (2f)	S (10)	S (12)	R	R	R	S (12)
7	1,3-dihydro-4-(2-hydroxyphenyl)-5-(2-hydroxyphenyl)-2-imidazolone (2g)	S (12)	S (15)	S (14)	R	R	R
8	1-methyl-3-H-4-(2-hydroxyphenyl)-5-(2-hydroxyphenyl)-2-imidazolone (2h)	R	R	S (12)	R	S (15)	S (12)
9	1-H-3-phenyl-4-(2-hydroxyphenyl)-5-(2-hydroxyphenyl)-2-imidazolone (2i)	S (12)	R	S (12)	S (15)	S (12)	S (14)

The compounds given in Table-5 (from 2a to 2h), were tested for their antimicrobial activity. In the initial screening processes, the 100ug/ml conc. of compound was taken to screen the activity of these compounds against the microorganisms. In these screening processes, the compounds showing the

zone against the selected organisms were interpreted in their respective diameter of zone of inhibition. While the compounds having resistance towards the selected organisms were interpreted as R (resistant) whose MIC were not calculated. Most of them showed positive results. All the compounds showed maximum zone against *P. vulgaris* bacterium. Many of these compounds have been found to be moderately active against above-mentioned organisms. Statistically, it can said that 60% of the total samples tested showed antimicrobial activity. The compound 2a shows high zone of inhibition that is 15mm against *S.* typhi. In addition, compounds 2g, 2h and 2i showed maximum zone against *S. typhi, S. aureus, B. subtilis, P. vulgaris and S. typhi* respectively.
Among these, the imidazolones synthesized from 4-hydroxy-benzaldehyde,4-dimethylaminobenzaldehyde,salicylaldehyde,4-methoxybenzaldehyde (2a,2b,2c,2d,2h) showed antibacterial activity against maximum number of organisms which can be attributed to the presence of, $-N(CH_3)_2$, $-OCH_3$ and $-OH$, groups as substituents in these compounds.

CONCLUSION

Thus we could succeed in synthesizing variedly substituted-2-imidazolone with simple and easy to workout methodology. Use of Zeolite as a catalyst enabled us rapid route for the synthesis of 2-imidazolones which could reduce reflux time to as low as two and half hours. The catalyst is insoluble in solvent due to which isolation of the product became much easy. Most of the synthesized compounds showed antibacterial activity due to presence of $-N(CH_3)_2$, $-OCH_3$ and –OH etc groups as substituent in these compound.

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IMPACT OF CHLOROSUBSTITUTED HETEROCYCLES ON SEED GERMINATION OF SOME ORNAMENTAL PLANTS

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ABSTRACT

Flowers have a unique place in the life of every human being irrespective of his country, caste and religion. Floriculture is the study of growing and marketing flowers and foliage plants. Indian floriculture which was in the hands of small and marginal farmers but now has developed into a highly professional business. Literature survey reveals that Auxines, Gibberlines, Cytokinins and Indole acetic acid are important growth promoting harmones. Various researchers studied the effect of heterocyclic compounds on seed germination i.e. root and shoot elongation and consequently crop yields. So we decided to undertake the study of some chlorosubstituted heterocycles on tropical ornamental plants viz. Tagetes patula (Zandu), Catharanthus roseus (Sadafuli) and Helianthus annus (Suryaful) with special reference to their growth promoting and disease controlling impact.

Keywords: *chlorosubstituted heterocycles; seed germination; root and shoot elongation; Tagetes patula; Catharanthus roseus; Helianthus annus.*

INTRODUCTION

Horticulture is the branch of agriculture that deals with the art, science, technology and business of garden plants growing and management. Floriculture or flower farming, is a discipline of horticulture concerned with the cultivation of flowering and ornamental plants for gardens and for floristry, comprising the floral industry. In simpler terms floriculture can be defined as the art and knowledge of growing flowers to perfection. The flowers have indispensible place of paramount importance in almost all religious and cultural festivities. This is the only creation of the nature that is equally loved by Gods and Demons. The flowers have a unique soothing effect on mind of human being. As such there is a constantly growing demand of flowers in the current civilized society. Nowadays floriculture has emerged as an important agri-business, providing employment opportunities and entrepreneurship in both urban and rural areas.

Tagetus patula (Zandu) is a common ornamental plant grown in gardens. It is of medicinal use also, a fine paste of *Marigold* leaves is applied to boils. *Vinca rosea* (*Catharanthus roseus*), a native of Madagascar, is commonly called as *Sadabahar, Barmasi, Sadafuli* and *Periwinkle*. In traditional Chinese medicine, extracts of these plants have been used to treat numerous diseases, including diabetes, malaria, and Hodgkin's disease etc. The substances *vinblastine* and *vincristine* extracted from this plant are used in the treatment of leukemia. *Helianthus annus* also called as *sunflower* or *surajmukh*i. Its leaves are emetic and are useful in lumbago, malarial fever, ulcers, wounds, cephalagia and burning sensation.

Heterocycles are predominantly used as pharmaceuticals such as anticancer[1], as agrochemicals[2] and as veterinary products. Heterocycles[3] have shown considerable biological[4,5] actions such as antibiotic, antifungal, anti-inflammatory, antiviral, anticancer, anticonvulsant, anthelmintic, antihistamine, antidepressant activities. Many plant growth promoting[6] compounds are commercially available in the market are mostly heterocycles. Literature survey reveals that Auxines, Gibberlines, Cytokinins and Indole acetic acid are the important growth promoting harmones[7-10]. Various experiments[11-13] reported the application of micronutrients in the field is useful to promote the vegetative growth as well as crop yield. Many workers demonstrated the results of various micronutrients on seed germination[14-20], shoot and root elongation[21-23] and biological[24-27] activities.

MATERIALS AND METHODS

Various chlorosubstituted heterocyclic compounds were synthesized by procedures[28-31] already

published and characterized on the basis of elemental analysis, chemical properties and IR, ^{1}H NMR spectral data.

Table No.1: List of the compounds tested for their effect on seed germination

Sr. No.	Compound	Name of compound
1.	(IVa)	4-(2-Hydroxy-3,5-dichlorophenyl)-6-(2,3-dichlorophenyl)-2-amino-1,3-thiazine
2.	(IVb)	4-(2-Hydroxy-3,5-dichlorophenyl)-6-(2,3-dichlorophenyl)-2-aminophenyl-1,3-thiazine
3.	(VIIIa)	2-Amino-4-(2,3-dichlorobenzoyl) 5-(2-hydroxy-3,5-dichloro-phenyl)-1,3-thiazole
4.	(VIIIb)	2-Aminophenyl-4-(2,3-dichlorobenzoyl) 5-(2-hydroxy-3,5-dichlorophenyl)-1,3-thiazole
5.	(Xa)	1*H*-2-One-4-(2-hydroxy-3,5-dichlorophenyl)-5*H*-imidazole
6.	(Xb)	1*H*-2-Imine-4-(2-hydroxy-3,5-dichlorophenyl)-5*H*-imidazole
7.	(XIIIa)	3-Phenyl-5H-6-(2,3-dichlorophenyl)-4-one-6,7-dihydro-imidazo-1,2-oxazol
8.	(XIIIb)	3-Phenyl-5H-6-(2,6-dichlorophenyl)-4-one-6,7-dihydro-imidazo-1,2-oxazol
9.	(XVa)	3-Phenyl-5H-6-(2,3-dichlorophenyl)-4-one-imidazo-1,2-oxazole
10.	(XVb)	3-Phenyl-5H-6-(2,6-dichlorophenyl)-4-one-imidazo-1,2-oxazole

The synthesized compounds i.e. chlorosubstituted Thiazines, Thiazoles, Imidazoles, Isoxazoline-imidazoles and Isoxazolo-imidazoles were assayed for their growth promoting impact on test plants viz. *Tagetes patula (Zandu)*, *Catharanthus roseus (Sadafuli) and Helianthus annus (Suryaful)*.

In this regard experimental setup of the study was divided into following two parts: Seed Treatment and Field Experiment. The plants were divided into two groups as Controlled and Treated group plants. The seeds from controlled group were soaked in water for 10 h. whereas the seeds from treated group were soaked separately in the suspensions of the titled compounds for 10 h. The concentrations of solutions used for these experiments were 1 mg/ml. Then the seeds were placed in the beds of cocopeat in different sets specially made and labeled for the study. They were periodically irrigated.

The observations were recorded as regard to elongation of roots and increase in shoot heights. Average length of radicles and plumules were observed after every 24 h. upto next10 days. The comparisons were made between controlled and treated group plants with reference to their elongation of roots and increase in shoot heights.

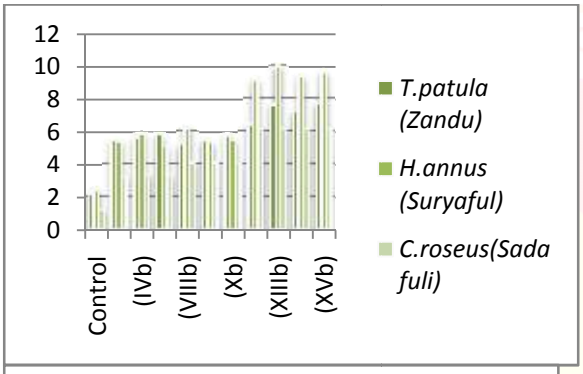
The observed data obtained as on 6^{th} , 8^{th} and 10^{th} day was subjected to analysis of percentage of germination with special reference to growth parameters such as shoot height and root elongation. The observed readings were recorded in Table No.2 and 3.

Table No.2: Effect of titled compounds on seed germination, length of radical and length of plumule of *Zandu*, *Suryaful* and *Sadafuli* on 6^{th} Day.

Sr. No	Comp-ound	*Tagetes patula* (*Zandu*)		*Helianthus annus* (*Suryaful*)		*Catharanthus roseus* (*Sadafuli*)	
		Avg. length of radicle (cm)	Avg. length of plumule (cm)	Avg. length of radicle (cm)	Avg. length of plumule (cm)	Avg. length of radicle (cm)	Avg. length of plumule (cm)
1.	Control	1.61	1.71	1.81	1.85	0.90	0.77
2.	(IVa)	4.76	5.03	4.60	5.26	2.90	2.52
3.	(IVb)	4.72	4.31	5.03	5.31	2.90	2.82
4.	(VIIIa)	4.74	6.02	4.44	5.11	3.91	3.00
5.	(VIIIb)	4.66	5.77	5.27	5.21	3.33	3.81
6.	(Xa)	4.81	5.12	4.30	5.00	3.74	4.61
7.	(Xb)	5.06	5.31	4.51	5.30	3.52	3.72
8.	(XIIIa)	5.71	5.60	7.94	8.04	5.12	5.61
9.	(XIIIb)	7.00	6.04	9.05	8.11	5.42	5.35
10.	(XVa)	6.72	6.11	8.60	8.75	5.11	5.60
11.	(XVb)	7.01	5.73	8.71	8.10	5.71	5.35

Table No.3: Effect of titled compounds on seed germination.

Sr. No	Compound	*T. patula* (*Zandu*)	*H. annus* (*Suryaful*)	*C. roseus* (*Sadafuli*)
1.	Control	45	50	50
2.	(IVa)	80	80	90
3.	(IVb)	86	85	95
4.	(VIIIa)	84	80	90
5.	(VIIIb)	87	90	84
6.	(Xa)	88	85	87
7.	(Xb)	90	90	92
8.	(XIIIa)	91	100	95
9.	(XIIIb)	96	95	97
10.	(XVa)	97	95	96
11.	(XVb)	93	94	92



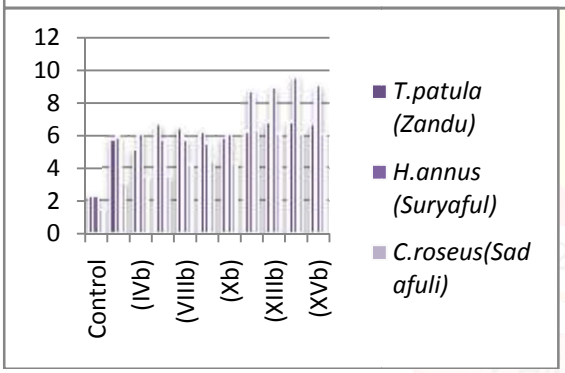


Fig1: Graphical representation of length of radical on 10th day

Fig.2: Graphical representation of length of plumule on 10th day of radical on 10th day

Result and Discussion

In the present study of comparison of morphological characters of controlled and treated group plants, it was interesting to note that the treated group plants exhibit significant improvement in shoot heights and elongation of roots as compared to control group plants. Analysis of seed germination study of synthesised compounds clearly showed that there was good percentage of germination, enhancement in growth of shoot as well as root heights in all treated plants. When all the treated plants were compared among themselves it was distinctly seen that morphological change in *H. annus* (*suryaful*) was dominant than other two test plants. More detailed results showed that the fused ring heterocyclic compounds were found very effective in the enhancement of morphological characters.

While analyzing seed germination results, it was seen that there was a great difference between the percentage germination of control group plants and treated group plants. In general, compounds XIIIa, XIIIb, XVa and XVb showed good effects on percentage germination. Particularly compound IVb showed very good results in case of all the three groups of treated plants. Compound XIIIa showed excellent results in zandu and *H. annus* (*suryaful*) test plants. In case of *T. patula (zandu)* plants compound XVa, while in case of *H. annus* (*suryaful*) compound XIIIa and in *C. roseus* (*sadafuli*) plants compound XIIIb showed excellent results for root and shoot elongation.

CONCLUSION

From the above discussion it was concluded that the effects of titled compounds were significant in all the treated group plants as compared to controlled group plants. However, further detailed study in the light of agricultural sciences especially for their disease controlling activities in plants would certainly prove to be beneficial tool for service to the society.

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SYNTHESIS AND SPECTRAL STUDY OF POLY M-TOLUDINE–LA METAL COMPOSITE

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ABSTRACT

The present work reports the synthesis of Poly m-toludine-La composite via in situ oxidative polymerization by ammonium persulphate.The doped PANI-La composite was characterized by UV,FTIR , XRD and SEM, TEM, and TGA analysis. FTIR of Poly m-toludine-La composite showed its successful synthesis with the presence of some dopant characteristic peaks in its FTIR Spectrum.XRD spectra of composite has revealed its crystalline nature. Electrical conductivity measurements were done by Four probe conductivity meter and the thermal studies have been done by Thermo gravimetric techniques. The results of TGA analysis shows the improvement in the thermal stability of composite and conductivity measurements showed the increase in conductance, together reveal that poly m-toludine –La is a possible material in future for high temperature application purposes. The electronic properties of composite were investigated using UV -Visible spectroscopy which revealed that increase in energy band gap of composite on irradiation. These results revealed the distortion of polymer chains on exposure to irradiations which results into decrease in conjugation and hence increase in energy band gap.

Key words: *Polym-toludine composite, odidative polymerization , ammonium persulphate,*

INTRODUCTION

The conducting organic polymers like polyaniline, poly m-toludine, poly o-toludine, polypyrole, have capacity of conducting electric current and are known as material of 21stcentury. These advance materials are synthesized by controlled addition of dopants. The remarkable change in the electrical, spectral properties of the polymer metal composites are observed with the reduction of metal dopant size to nanoscale. In this direction polyaniline, poly m-toludine, poly o-toludine were investigated extensively with respect to different methods of synthesis, environmental stability, improved conductivity, stability, chemical sensitivity[1]. The conductive organic polymers have drawn much attention due to their applications in microelectronic devices,corrosion capacitors, solar cells, light weight batteries, electrical capacitors, chemical sensors[2-4]. The composites of polyaniline with various dopants like MoO_3, TiO_2, MnO_3, CNTs, and WO_3 have been synthesized and explored for various applications. PANI metal composites are employed for electrical transport and electrification.[5], corrosion resistant protective coating of base metal[6-7] etc, Backbone of PANI consist of two basic groups having different activity with metal ions namely the electron rich benzenoid group and electron deficient quinoid groups hence it can be used as model polymer for study of different interactions.[8-9] The doping of the transition metals in conducting polymers can impart desirable properties to conducting polymers like crystalanity, thermal stability, good mechanical strength etc.These properties when coupled with good electrical conductivity make these nanocomposites as materials having different applications[8-9]. The polyaniline and polythiophene composites with terbium(III) composite posses good thermal stability and fluorescence property which is responsible for their technological application as luminescent probes or light emitting diode materials[10-15] The composites of copper (bisglycinate) are suitable for high temperature applications. The most exciting applications of these polymers are automotive dashboard displays, cellular telephones, light emitting devices, light emitting diodes, light weight batteries, solar cells, polymer actuators, corrosion inhibitors.

MATERIAL AND METHODS

Synthesis of poly m-toludine –La composite

10 ml m-toludine was mixed in 300 ml 1M HCl with 1 hour stirring . O.2 g of Lanthanum oxide was dissolved in m-toludine solution with continuous stirring. 22 g of APS powder was dissolved in 200 ml 1M HCl. Both solutions were kept for 1 hour. The oxidant APS solution was

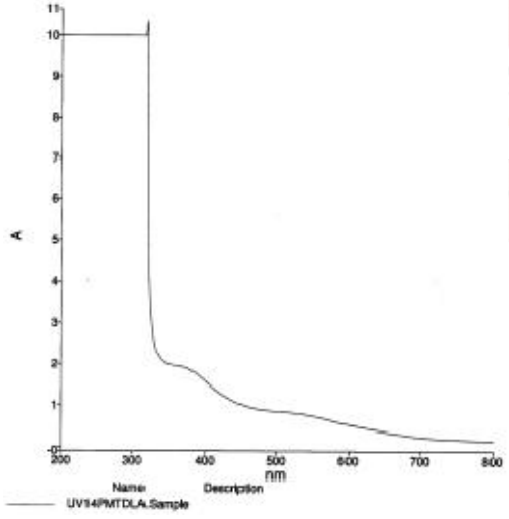
slowly added from burette in to monomer m-toludine-Lanthanum solution within 40 min. The constant stirring was continued for 24 hour with magnetic stirrer. Initially reddish color was developed and later on violet color was obtained, finally greenish colored product obtained was washed with dilute HCl followed by acetone. The dried product was dipped in large excess of 0.5 M NH_4OH overnight. Dark blue colored product was obtained after filtration; it was dried in oven for 8 hours at 50°C.

RESULTS AND DISCUSSIONS

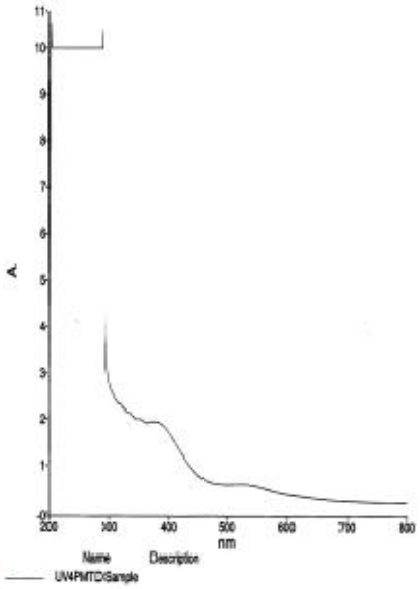
The synthesized composite was analyzed by UV spectroscopy, FTIR spectroscopy, X-ray diffraction method. Thermal stability of composite was analyzed by thermogravimetricanalysis.The morphology of m toludine –La composite was studied by Scanning electron microscopy and Transmission electron microscopy. The electrical conductivity was measured by Four probe conductivity method.

3.1UV –VIS characterization

The UV-visible spectra of Poly m-toludine-Lanthanum composite shows the absorption band at 310 nm it is attributed to π →π transition band. The absorption at wavelength 390 nm correspond to polaron to π* transition band. The shoulder peak at 520 nm indicates the polaron to π* transition which confirm the weak interaction of Lanthanum oxide with polymer chain.*



(a)



(b)

Figure 1.UV spectra of (a) Poly m-toludine(b) Poly m-toludine-Lanthanum composite.

3.2FTIRcharacterization

Figure 2. (a) Shows the FTIR spectra of Poly m-toludine. The broad band observed in spectra at 3182 cm^{-1} is assigned to N–H stretching mode. The characteristic band at 2918 cm^{-1} show vibrations of $–CH_3$ group. The peak at 1595 cm^{-1} and 1493 cm^{-1} are assigned to the stretching vibrations of benzenoid and quinoid ring. The peak appearing at 1402 cm^{-1} indicates the symmetric deformation of $–CH_3$ group. 1301 cm^{-1} and 1230 cm^{-1} corresponds to the C–N vibration. The peak at 1153 cm^{-1} is assigned to C–H stretching of benzenoid ring. The 1108 cm^{-1} peak is assigned to C–C stretching vibrations of methyl substituted benzenoid and quinoid structure. The prominent peaks at 941, 877 and 810 cm^{-1} assigned to an out of plane C–H vibrations, 1, 2, 4- substituted benzenoid ring and in plane C–H vibrations of quinoid ring. The peak at 692 cm^{-1} indicates C–H bending and 615 cm^{-1} indicates aromatic ring deformation. The peaks at 569, 514 and 439 cm^{-1} corresponds C–C stretching in benzenoid ring, C–C stretching and C–N stretching in benzenoid and quinoid structures respectively.

Figure 2. (b) shows The FTIR spectra of Poly m-toludine-La composite. The weak broad absorption band at 3363 cm^{-1} indicates N–H stretching. 2916 cm^{-1} peak indicates stretching in $–CH_3$ group. The intense peaks at 1594 and 1493 cm^{-1} correspond to the quinoid and benzenoid ring stretching vibration. 1300 and 1213 $cm^{-1}$are assigned to C–N stretching. The strong peak at 1152 cm^{-1} indicates the interaction of polymer chain with metal Lanthanum. The FTIR spectrum of poly m-

toludineis very much similar to the spectrum of poly m-toludine –La composite with some shift in the position of peaks and the presence of few new dopant peaks.

(a)

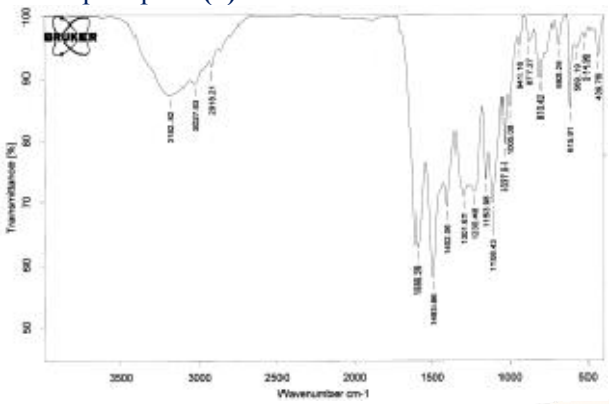


Figure 2. (a) FTIR spectrum of Poly m-toludine.

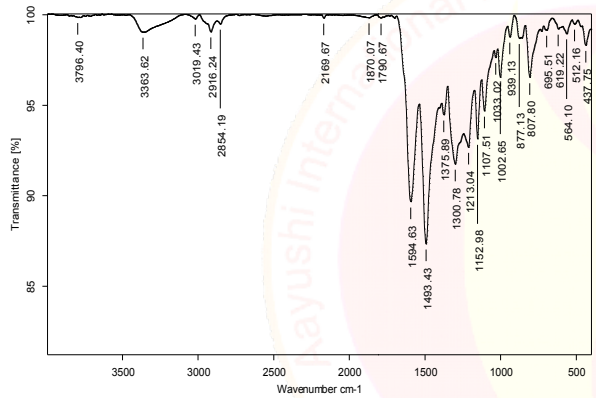


Figure 2. (*b)*: FTIR spectrum of Poly m-toludine-Lanthanum composite.

3.3 X-RAY Diffraction method

The XRD spectrum of Poly m-toludine-Lanthanum oxide composite is shown in Figure 3.The broad peaks at 2θ = 11, 19, 23°, suggesting amorphous morphology of composite. The average particle size in PMTD-La composite was found to be 72.85300873 nm

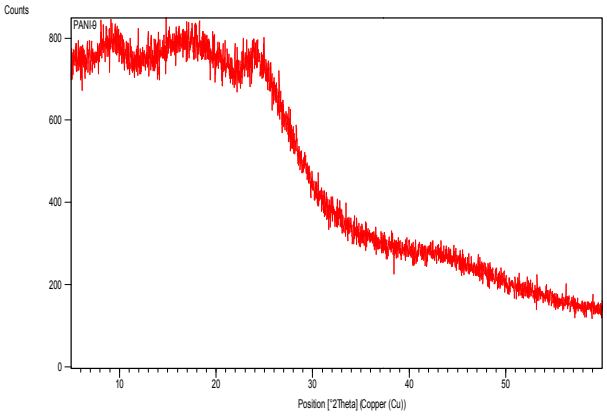
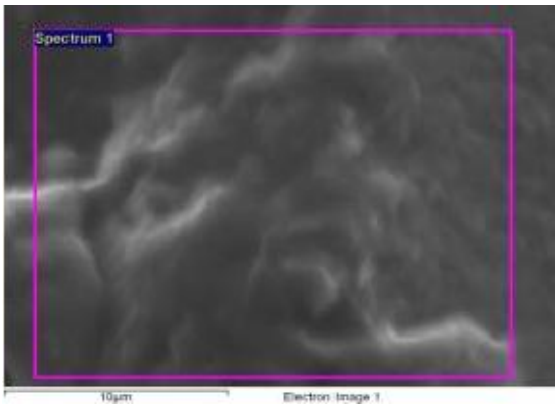
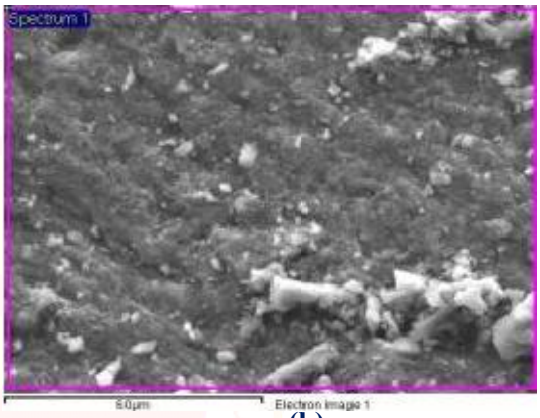


Figure 3.XRD of poly m-toludine-Lanthanum composite.

3.4.Scanning Electron Microscopy



(a)



(b)

Figure 4 SEM micrograph of (a)Poly m-toludine (b) Poly m-toludine-La composite

The surface morphology of pure poly m-toludine and poly m-toludine- La composite have been investigated using SEM analysis and are shown in Figure 4a,b.The SEM picture of poly m-toludineshows uniform morphology with amorphous layer like structure. The poly m-toludine- La doped composite shows compact morphology thereby supporting XRD. The SEM image of polymtoludine composite reveals that dopant metal particles are dispersed in poly m-toludine matrix which also justifies the successful composite formation.

4.5 Transmission Electron Microscopy

Figure 5 shows TEM images of PMTD, PMTD-La.TEM images show the transformation of metal particles in the morphology of PMTD polymer particles. Wide range of particle/cluster size was observed starting from 20 nm to 70 nm.Large number of small scattered grains with the strong spotty patterns observed in TEM images show that La metal particles affect the polyaniline morphology. Metal particles are well adhered on PMTD substrate due to strong affinity of metal to nitrogen.

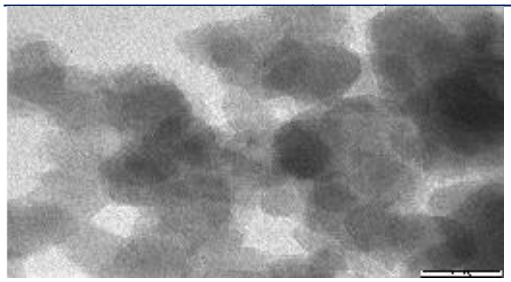


Figure 5 TEM image of (a) Poly m-toludine

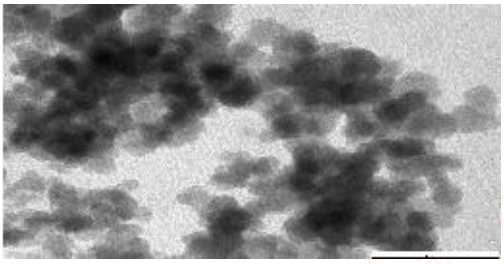


Figure 5 TEM image of (b) poly m-toludine-La composite

Figure 7. TGA curve of PMTD-La composite

3.7 Four-Probe for Conductivity Measurements

The conductivity measurements were carried out by Four-probe method to determine the influence of dopant La metal on polymer electronic properties. The synthesized poly m-toludine and its composite with La,were pressed under pressure into pellets with 0.3 cm radii and approximately 0.05 cm thickness.The temperature dependent DC conductivity is measured at 68 to 122 K. The electrical conductivity of conducting polymers results from mobile charge carriers introduced into carriers - π electronic system through doping. The electrical conductivity of PMTD is found 0.000457 S/cm and that of PMTD-La composite was 0.207507 S/cm..It is observed from the figure----that plot of 1000/T vs log ρ is nearly straight line, indicating the conduction in these samples

3.6 Thermogravimetric Analysis

Figure 6 (a) and (b) shows TGA curve for Poly m-toludine, Poly m-toludine-Lanthanum oxide. TGA curve of Poly m-toludine shows that weight loss occur in two steps. In the first step only 2.544% weight loss is observed upto 150°C. This weight loss is assigned to loss of moisture and low molecular weight oligomers. 29.33% weight loss is observed from 150-500°C, it represent the degradation of PMTD backbone. Two step weight loss is observed in TGA curve of Poly m-toludine-Lanthanum oxide. In the first step 4.205% weight loss is observed in the temperature range 50-100°C, due to loss of moisture and volatile impurities. The maximum 40.65% weight loss is observed in 150-500°C, it can be attributed to polymer composite backbone degradation.

through an activated process having single activation energy in the temperature range 68-122 K. DC conductivity of these polymers increases exponentially with temperature, exhibiting semiconductor characteristics. Thus it was observed that the incorporation of La metal particles into PMTD polymer matrix significantly affect theconductivity of polymer.

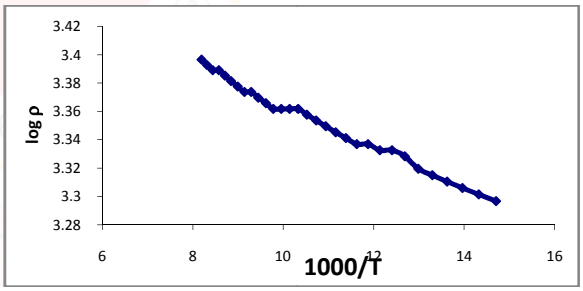


Figure 8. Plot of resistivity log ρ vs. 1000/T for Poly m-toludine

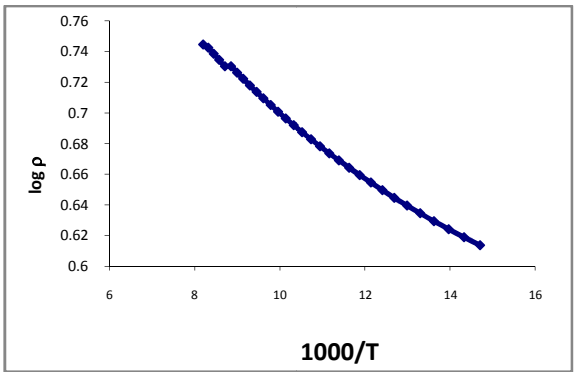


Fig. 5.7 (j) : Plot of resistivity log ρ vs. 1000/T for Poly m-toludine-La composite

CONCLUSION

Poly m-toludine-La composite was prepared successfully by chemical oxidative polymerization method. The presence of La particles in the polymer matrix of poly m-toludine-La composite was confirmed by XRD, UV, FTIR, SEM techniques. The XRD pattern indicated that the poly m-toludine-La composite has amorphous morphology with the particle size of 72.85 nm.TEM images show that La particles are well adhered on poly m toludine substrate because of strong affinity between metal and nitrogen. The Fourprobe conductivity measurements reveals that the poly m-toludine–La composite possesses higher conductivity than the poly m-toludine polymer

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EFFECT OF AILANTHUS EXCELSAAGAINST CYCLOPHOSPHAMIDE INDUCED GENOTOXICITY

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ABSTRACT

The present study was designed to investigate the effect of Ailanthus excelsa on chromosome in bone marrow cells of Swiss albino mice against cyclophosphamide induced genotoxicity. Four groups of mice were assigned for determination of genotoxicity by using chromosomal aberration test. Two test groups were treated with different dose of saponin rich extract of leaves of Ailanthus excelsa 24 hrs before treatment of Cylclophosphamide and positive control group treated only with Cyclophosphamide(50 mg/kg bd.wt). All results were analyzed by One way analysis of variance (ANOVA) and post-hoc analysis was performed with Bonferroni's test. Test results showed that A. excelsa leaves, crude saponinextract (100 and 200, mg/kg) significantly and dose dependently increased incidence of % aberrant cells. The observations suggested that saponin rich extract of A. excelsa has mutagenic activity.

Key words: *Ailanthus excelsa, cyclophosphamide, genotoxicity, chromosomal aberrations, ANOVA*

INTRODUCTION

Mutagenicity refers to the induction of permanent transmissible changes in the amount or structure of the genetic material of cells or organisms. These changes may involve a single gene or gene segment, a block of genes or chromosomes. The term clastogen is used for agents giving rise to structural chromosome aberrations. A clastogen can cause breaks in chromosomes that result in the loss or rearrangements of chromosome segments[1]. In vitro and in vivo tests that measure chromosomal aberrations in metaphase cells can detect a wide spectrum of changes in chromosomal integrity. The assays that detect either chromosomal aberrations or micronuclei are appropriate for detecting clastogens[2].

In somatic cells, Cyclophosphamide produces gene mutations, chromosome aberrations, micronuclei and sister chromatid exchanges in a variety of cultured cells in the presence of metabolic activation as well as sister chromatid exchanges without metabolic activation. It can also produce chromosome damage and micronuclei in rats, mice and Chinese hamsters[3].

Medicinal plants have played a key role in world health. In spite of the great advances observed in modern medicine in recent decades, plant still makes an important contribution tohealth care.

*Ailanthus excelsaRoxb.*belonging to family Simaroubaceae is commonly known asMaharukha. The traditional claims, phytochemical investigation, pharmacological evaluation and some ayurvedic formulations provide the backbone to make this tree, a plant of Heaven[4]. Traditionally or in Indian system of medicine, *AilanthusexcelsaRoxb.*is used in treatment of asthma, cough, colic pain, cancer, diabetes and also used as antispasmodic and bronchodilator[5]. *Ailanthus excelsa*is a large tree originally from China, which is known as the 'Tree of Heaven'. Different parts of this plant are used widely in traditional medicine for a variety of diseases. The bark is used as bitter, refrigerant, astringent, appetizer, antihelmintic, febrifuge, in dysentery, skin disease, troubles of the rectum, and fever due to tridosha andallays thirst. It is also used in gout, rheumatism, dyspepsia, bronchitis and asthma. Ailanthus is used to cure wounds and skin eruptions as mentioned in traditional medicine. Stem bark extracts showed potent antibacterial and antifungal activities[6].

METHOD AND MATERIAL

Collection and preparation of plant extract

Fresh Ailanthus excelsa leaf was obtained from Bhopal and it get authentified by Saifiacollege, Bhopal. The leaves were rinsed with water and dry under shade. Material of known weight was soxheleted using hydrolcoholic solvents. N-butanol soluble fraction was considered for saponins isolation. N-butanol fraction was further treated with chilled diethyl ether, which resulted in formation of saponin precipitate which were further treated with diethyl ether again after separation and then they were dissolved in ethanol and solvent was evaporated in low rate for getting crystallized saponins which were further

confirmed by froth test. These components were considered as crude saponins for further assay.

Phytochemical Screening7

The freshly prepared crude extracts of A. excelsawere qualitatively tested for the presences of alkaloids, Tannins and Phenolic compounds, Flavanoids, Steroids, Glycosides, Saponins, Proteins and Amino acids.

Acute toxicity study

Acute toxicity study was carried out using Swiss albino mice (25 ± 2 gm) according to the OECD 423 guidelines and animals were observed for their mortality and behavioral changes.

Experimental animals

Swiss albino male mice (20-25 g) were separately group housed in ambient room temperature (25±2°C) and relative humidity (50±5%), maintained at 12:12 hr dark–light cycle. Food and water were available ad libitum. All procedures employed in the present study were approved by Institutional Animal Ethics Committee and carried out under strict compliance with Committee for the Purpose of Control and Supervision of Experiments on Animals, Ministry of Environment and Forests, Government of India. Animals were acclimatized to the experimental conditions for a period of one week before actual experimentation.

Chemicals

CP(Cyclophosphamide) and colchicine were purchased from Sigma-Aldrich Co., St. Louis, MO, US.

Experimental design

Four groups of mice are assigned to a different treatment consisting five animals each. One group received control vehicle. Two test groups were treated with different dose of saponin rich extract of leaves of Ailanthus excelsai.e. 100mg/kg and 200mg/kg, 24 hours before treatment of Cyclophasphamide (50 mg/kg bd. wt). Positive control group treated with only Cyclophasphamide (50 mg/kg bd.wt), Colchicines (4 mg/kg b.wt) was administered intraperitoneally 1 hours before the harvest of the cells to every group.

Animals were sacrificed by cervical dislocation and bone marrow cells were excised. Bone marrow cell was aspirated by flushing with normal saline in the centrifuge tube and Flush the suspension in the tube properly to get good cell suspension.Centrifuged for 10 min at 1000 rpm.Supernant discarded and Pellet was treated with pre-warmed (37ºC) KCl on cyclomixer. Left the above suspension in a water bath (37ºC) for 30 min. Again Centrifuged and supernatant discarded. Pellet was treated with freshly prepared cornoy's fixative (methanol: acetic acid = 3:1) on cyclomixer. Once again Centrifuged and supernatant discarded above step of treatment with Cornoy's fixative was repeated 3 times to get debris free white pellet. Cornoy's fixative (quantity sufficient) added to pellet and got a good cell suspension. Slides were made with Air Drop Method. The slides were stained with 5% Giemsa's solution for 15 min and slides rinsed in distilled water blotted. A total of 100 well spread metaphase plates were scored for chromosomal aberrations at a magnification of 1000 × (100×10) for each groups. Different types of chromosomal aberrations such as chromatid breaks/gaps, centromeric association and chromatid fragmentation were scored and expressed as % chromosomal aberrations[8].

Statistical analysis:

Statistical analysis was carried out using primer of Bio-statistical software. All results were analyzed by One way analysis of variance (ANOVA) and post-hoc analysis was performed with Bonferroni□s test. Value of $P<0.05$ was considered to be statistically significant in all the cases.

RESULT

Phytochemical Analysis

The results of the chemical tests performed in the screening, revealed the presences of flavonoids, alkaloids, tannins, glycosides, saponins, carbohydrate in the extract of A. excelsa.

Acute Oral Toxicity

Acute toxicity studies (OECD – 423guideline) of Ailanthusexcelsa revealed that the extract showed no toxicity up to dose of 2000 mg/kg nor any significant variation in behavior of animal was observed. Therefore, for present experimental studies the 1/10th and 1/5th dose of Ailanthus excelsa was selected i.e. 100mg/kg and 200mg/kg.

Chromosomal aberration test

Results are depicted in following table:

Table 1.

Chromosomal aberration test in bone marrow Swiss albino mice:

Separate groups of mice were administered with (1) Saline (p.o) (2) Saline + CP (50 mg/kg, i.p) (3) A.excelsa (100 mg/kg, p.o) + CP (50 mg/kg, i.p) (7) A.excelsa (200 mg/kg, p.o) + CP (50 mg/ kg, i.p). CP (50 mg/kg i.p) was administered after 1 hr. last dose of A.excelsa treatment. Thereafter, 24 the animal was sacrificed and test was performed. All the value expressed as mean ± SD (n=6).

Group	*Break*	Fragmentation	Deletion	Polyploidy	Pulverized	Ring	Total Aberration
I	3.83 ±1.72	*2.83 ± 1.47*	*3.67± 1.63*	*0.00*	*0.00*	*0.00*	*4.83 ± 1.72*
II	31.33±3.01	*24.17 ± 2.56*	*17.33±3.27*	*6.67 ± 1.97*	*6.17 ± 1.47*	*5.83 ± 1.60*	*42.33± 3.50*
III	34.17±2.04	*26.17±2.32*	*19.83±2.32*	*7.17±1.72*	*6.83±1.47*	*7.33±1.63*	*44.17±2.56*
IV	41.33±2.58	*31.33±3.33*	*27.67±2.16*	*10.67±1.21*	*11.33±2.16*	*11.50±2.26*	*49.83±2.32*

DISCUSSION

As depicted in Table 1, CP (50 mg/kg i.p) single dose administration significantly increased in total aberrant cells (%) as compared to control group. Further, comparison by Bonferroni's test showed that A. excelasa leaves, crude saponin extract (100 and 200,mg/kg) significantly and dose dependently increase incidence of % aberrant cells.

CONCLUSION

The observations suggest that saponin rich extract of leaves of Ailanthus excelsa has mutagenic activity.

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ANSLYSIS OF DRINKING WATER QUALITY OF KARANJA TEHSIL, DIST. WASHIM

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ABSTRACT

In the present study, water samples were collected from various villages of Karanja (lad) Tehsil Dist. Washim in Maharashtra state of India for observation of physico-chemical analysis. The invitro test of the collected water samples were performed for analysis of different parameters such as water temperature, pH, dissolved oxygen, total solids, Conductance, Salinity and ORP. The obtained data were compared with standard units. The results of this recent study reveal that physico-chemical parameters are within maximum permissible limit of WHO and BIS. Therefore, water is safe and suitable for domestic and drinking purpose after some treatment.

Key Words: *Physico-chemical analysis, Karanja Tehsil & Drinking water standards.*

INTRODUCTION

Water is one of the most important natural resources. It is essential in the life of all living organisms from the simplest plant and microorganisms to the most complex living system known as human body. Water a combination of hydrogen and oxygen atoms, with a chemical formula, H_2O and known to be the most abundant compound (70%) on earth surface. It is significant due to its unique chemical and physical properties[1, 2]. Many people depend on fresh water supplies from groundwater. It provides water for domestic use for a large part of the Indian population. It is one of the major sources of water for irrigation and drinking purpose. The availability of groundwater depends on the rate at which it is recycled by hydrological cycle than on the amount, which is available for use at any moment in time. In most parts of the country finite supply of fresh water is put of heavy use. Industrial water sewage and agricultural run-off can overload groundwater with chemical wastes and nutrients and make the water-supply toxic. Effective management of water resources and control of pollution are becoming increasingly important for sustainable development and human welfare.

Access to safe drinking water is key to sustainable development and essential to food production, quality health and poverty reduction. Safe drinking water is essential to life and a satisfactory safe supply must be made available to consumers[3]. Water is thus becoming a crucial factor for development and the quality of life in many countries. In individual arid areas it has even become a survival factor[4]. Therefore, water intended for human consumption must not contain pathogen germs or harmful chemicals; because water contaminated with microorganisms is the cause of epidemics[5]. That is good drinking water is not a luxury but one of the most essential requirements of life itself[6]. However, developing countries have suffered from a lack of access to safe drinking water from improved sources and to adequate sanitation services[7]. The WHO[8] revealed that seventy five percent of all diseases in developing countries arise from polluted drinking water.

Therefore; water quality concerns are often the most important component for measuring access to improved water sources. Acceptable quality shows the safety of drinking water in terms of its physical, chemical and bacteriological parameters[9]. International National and local agencies have established parameters to determine biological and physicochemical quality of drinking water[10].

The present work was carried out in the Karanja Tehsil in order to study the Drinking water quality. Karanja Tehsil is located in the Washim district of Maharashtra in Amravati division. It is located between 20°48′33″N & 77°48′33″E Co-ordinates.

MATERIAL AND METHODS

Water samples were collected in pre-cleaned polypropylene bottles with necessary precaution from different Villages. Various physico-chemical parameters were analyses as given in standard manual of water and waste water analysis[11]. Selections of seven different stations were identified and water samples were collected at sites and assign as S1, S2, S3, S4, S5, S6, and S7.

Sample sites are described in Table 1.The main aim of the study was to investigate the physico-chemical characteristics of water samples in Karanja Tehsil. Samples were collected from the sites in between 09:00 a.m. to 10:00 a.m. Sample for the analysis of dissolved oxygen was collected in BOD bottle (250 ml), just below the water surface slowly to avoid any air bubble entering into the bottle. The parameters like temperature, pH, dissolved oxygen, total solids, Conductance, Salinity and ORP was analyzed with the help of thermometer and water analysis kit.

Table 1: Table1. Description of water sampling sites

Sample code	Source	Location
S1	Tap water	Zodga
S2	Tube well	Kinhi
S3	Well	Inza
S4	Tap water	Kajaleshwar
S5	Well	Bhamdevi
S6	Tube well	Sukali
S7	Well	Kamthwada
S8	Tap water	Sohal
S9	Tap warter	Tuljapur
S10	Tube well	Kamragaon

Reagents used for the present investigation were A.R. /G.R. grade and distilled water used for preparing various solutions. All the reagents and calorimetric solution were prepared and purified according to standard method for the examination of water.

RESULT AND DISCUSSION

The values of physico-chemicals parameters of various villages of Karanja (lad) Tehsil are given in Table 2. There is a close relation between the atmospheric temperature and water temperature. Water temperature is one of the most important ecological factor which controls the physiological behavior of aquatic systems and hence the quality of water. In the present investigation, the water temperature in an average for various samples of the Karanja Tehsil was 24.51 ^{0}C. pH is nothing but the measure of the concentration of hydrogen ions, which provides the range of the acidity or alkalinity of a solution. During this study the average value of pH was found to be 7.6.

Table 2: Values of physico-chemicals parameters of various villages of Karanja (lad) Tehsil

Location	Temp.	PH.	DO	EC	Salinity	TDS	ORP
S1	24.3	7.5	7.6	0.3	0.4	519	36
S2	25.3	7.64	6.3	0.4	0.2	479	33
S3	24.4	7.32	5.6	0.5	0.7	970	25
S4	25.5	7.23	5.7	0.3	0.2	367	30
S5	23.6	8.25	7.9	0.3	0.2	283	31
S6	24.5	7.63	6.2	0.2	0.4	453	25
S7	25	7.21	7.3	0.4	0.7	830	32
S8	24.8	7.57	8.2	0.5	0.3	439	29
S9	23	8.15	7.8	0.3	0.4	544	28
S10	24.7	7.35	6.9	0.3	0.6	767	26
Average	24.51	7.585	6.95	0.35	0.41	565.1	29.5

Dissolved Oxygen is the amount of gaseous oxygen (O_2) dissolved in the water. Oxygen enters the water by direct absorption from the atmosphere, by rapid movement, or as a waste product of plant photosynthesis. Water temperature and the volume of moving water can affect dissolved oxygen levels. Dissolved oxygen content indicates the health and ability of water body to purity itself through biochemical processes. During this study average dissolved oxygen recorded was 6.95 mg/L . Conductivity is a measure of water's capability to pass electrical flow. This ability is directly related to the concentration of ions in the water. The conductance in present innvestigation for various samples in an average was found to 0.35 M mhos. And the salinity which is the measure of all the salts dissolved in water was found to be 0.4 ppt.
Total dissolved solids refer to matter suspended and dissolved in water. Waters with high total solids generally are of inferior palatability and may induce an unfavorable physiological reaction in the transient consumer. In present investigation total dissolved solids in an average was found to be 565.1.mg/l. ORP means the Oxidation, reduction potential of water , in the present study in an average it was found to be 29.5 mV.

CONCLUSION

The drinking water quality analysis values of Karanja tehsil showed that most of the values are well within the permissible limits. The result of study reveals that the quality of drinking water is though fit for domestic as well as for drinking purpose after some treatment and need continuous monitoring of physico -chemical parameters to improve the quality of water.

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OVERVIEW OF GREEN CHEMISTRY

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ABSTRACT

At traffic signal, red means "Stop", yellow indicates "Be Ready" and green implies "Go". If somebody crosses during red signal then the cop punishes that person. In the similar fashion the time has come that Regulatory Cops should say "No" or put exorbitant penalty for the Red Chemistry and only give "Go" for "Green Chemistry". But are we geared enough for the "Green Chemistry"?Everybody knows thatGreen chemistry, which is also called as sustainable chemistry, is an area of chemistry and chemical engineering focused on the designing of products and processes that minimize the use and generation of hazardous substances as far as human health and environment is concerned.The challenges for chemistry and chemical engineering, to convert all existing industrial hazardous processes to green one or alternatively innovate products with same applications withnew greenprocesses are extremely tough.The author simplifies the definition of "Green Chemistry", its applications, use in daily life and its future as what more required is to be done.

Keywords: *Green Chemistry, Management, Safety, Environment, Energy.*

PREAMBLE

In the earlier centuries say during "Ramayana", "Mahabharata", "discovery of America" everything was green. Later on with the revolution in science, needs of human being increased, population increased, concrete jungles have taken over natural jungles, and things started changing from Green to Red gradually. Ecological balance disturbed resulting in global warming. Now there is urgent need to change over, to transform from Red to Green.

INTRODUCTION

The last few decades of the 20th century witnessed growing concerns over the impact of industry on the global environment. These concerns included acid rain, increasing levels of greenhouse gases, fertilizers in streams and rivers, polluted city atmospheres, and a hole in the ozone layer. Some of these are directly attributable to power generation and transport, which have caused major problems and lie outside the direct influence of the chemical industry.

However, in spite of an enormous investment over the last 50 years to ensure that the production of chemicals does not have a malign effect on the environment, many of the public, the very consumers of the products, still associate the chemical industry with the worst sorts of pollution. The acceptance that the chemical industry must not adversely affect the environment for future generations has been the driving force behind the development of ***green chemistry***. This is not a separate branch of chemistry, but an approach that permeates every stage of process development.

The term 'Green Chemistry' was invented by Anastas [1] of the US EnvironmentalProtection Agency (EPA). In 1993 the EPA officially adopted the nameUS Green Chemistry Program'Thisdoes not mean that research on green chemistry did not exist before the early 1990s, merely that it did not have the name. It started way back in 1960's when Rachel Carson wrote the mainstream, scientific book, *Silent Spring* in 1962. It outlined the devastation that certain chemicals had on local ecosystems. The book served as a wake-up call for the public and scientists alike, and inspired the

MODERN ENVIRONMENTAL MOVEMENT

In early 1990s both Italyand the United Kingdom have launched major initiatives in green chemistry and, then, the Green and Sustainable Chemistry Network was initiatedin Japan. The inaugural edition of the journal Green Chemistry, sponsored bythe Royal Society of Chemistry, appeared in 1999. Hence, we can say thatGreen Chemistry is here to stay.

As usual, in India the concept of "Green Chemistry" has come recently.

A reasonable working definition of green chemistry can beas[2]: *Green chemistry efficiently utilizes (preferably renewable) raw materials,eliminates waste, avoids the use of toxic*

and/or hazardous reagents and solventsand utilizes energy in efficient way, in the manufacture and application of chemical products.

Green Chemistry is commonly presented as a set of twelve principles as proposed by Anastas and Warner[3], but the author here for better understanding focuses on three major principles of Green Chemistry which most of the people are aware of and i.e Safety Management, Environment Management and Energy Management.

THE ULTIMATEGREEN SYNTHESIS

The UltimateGreen Synthesis as far as green chemistry is concerned is given in fig1.

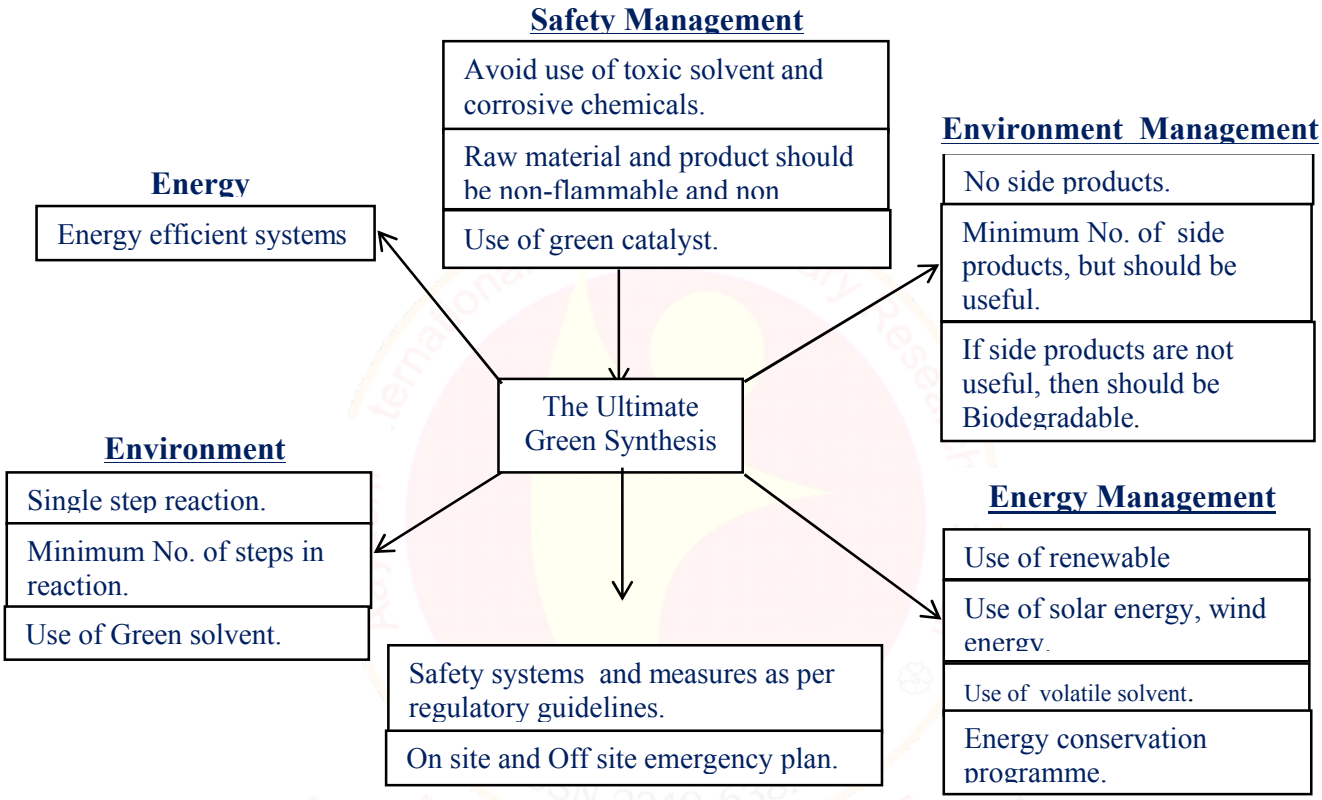

Figure -1: The ultimate green synthesis

It clearly focuses on three parts i.e Environment Management, Safety Management and Energy Management.

ENVIRONMENT MANAGEMENT

As far as Environment Management is concerned, chemists and chemical engineers, during research and synthesis should work for single step reaction. So that there will not be any side products and yield will be 100 %. If single step reaction is not possible, then approach is to have minimum number of side reactions and products generated out of these side reactions should be useful. If not useful should be biodegradable. Chemists should avoid use of toxic solvents and try to use green solvents. But if use of toxic solvent is unavoidable then they should have solution to recover the same from the vents.

SAFETY MANAGEMENT

As far as Safety Management is concerned chemists and chemical engineers, during research and synthesis should avoid use of corrosive chemicals as catalyst, or the catalyst which are going to produce side products which are not useful and also not biodegradable. They should avoid use of raw materials which are hazardous and flammable,also product made should also be non hazardous and non flammable and try to carry out reaction as far as possible at atmospheric conditions. But if it not possible then during technology transfer they should ensure that

companies should have Safety Management Systems as per regulatory guidelines.

ENERGY MANAGEMENT

As far as Energy Management is concerned regulatory authorities have to confirm that each and every industry do have energy conservation programme. Government should give subsidy for solar as well as wind power units. Chemists and chemical engineers while designing process should try to use solvents with less latent of heat of vaporization and try to use renewable feedstock as raw material. We everybody at home shall use energy saving lights, use solar heaters and also should conserve water as water is energy.

UNDERSTANDING OF GREEN CHEMISTRY THROUGH APPLICATIONS

1. Large amounts of adipic acid are used each year for the production of nylon, polyurethane, lubricants and plasticizers. The raw material for the manufacturing of this adipic acid is Benzene, a compound with convinced carcinogenic properties [4].

   Chemists from State University of Michigan developed green synthesis of adipic acid using less toxic, natural and in exhaustive raw material that is Glucose. The glucose can be converted to adipic acid by an enzyme discovered in genetically modified bacteria.

   Red Process : Benzene to Adipic acid
   Green Process : Glucose to Adipic acid
2. From the point of view of Green Chemistry, combustion of fuels obtained from renewable feed stocks is more preferable than combustion of fuels from depleting finite resources. Many vehicles around the world are fueled with diesel oil, which can be replaced by Bio diesel. Combustion of diesel oil generates sulfur compounds and increases the amount of carbon dioxide in the atmosphere where as combustion of Biodiesel does not generates sulfur compound and hence does not pollute environment [4].

   Red Process : Petroleum to Diesel
   Green Process : (Plant Oil + methanol) to (Biodiesel + Glycerine)
3. Disodium amino-di-acetate (DSIDA), is a key intermediate in manufacturing of environmentally friendly herbicide. The traditional manufacturing route of DSIDA uses highly toxic hydrogen cyanide, exothermic and also there is generation of unstable intermediates which requires special care to avoid run away reactions. The process generates 1 Kg of waste per 7 Kg of product and waste comprises of cyanide and formaldehyde which needs treatment prior to disposal. The new manufacturing process of DSIDA is cleaner and safer and is based on catalytic dehydrogenation of di-ethanolamine. The reaction is endothermic, zero waste is produced and after removal of catalyst no further purification is required[5].
4. In conventional method for preparation of 2 cyano,3phenyl,acrylic acid ethyl ester non green solvent toluene is used so also piperdine is toxic and is not ecofriendly. In green process KSF a solid acid catalyst is used, which is renewable[6].
5. In conventional method for nitration of phenol non green component sulfuric acid along with sodium nitrate is used. In green process nitration of phenol can be carried out in presence of calcium nitrate dissolved in warm acetic acid[6].
6. Let us discuss example of manufacturing of phenol. It used to be made from benzene using sulfuric acid and sodium hydroxide in a multi-stage process, which, overall, can be expressed as:

   $$C_6H_6 + H_2SO_4 + 2NaOH \longrightarrow C_6H_5OH + Na_2SO_3 + 2H_2O$$

   The chemical equation shows that 1 mole of benzene (78 g) should yield 1 mole of phenol (94 g). In practice, the quantity of phenol produced is found to be about 77 g, giving a yield of 82%, which may be regarded as quite good.

   However, the calculation obscures the fact that the reaction also generates 1 mole (126 g) of sodium sulfite for each mole of phenol produced. This may be acceptable if there is enough demand for sodium sulfite, but if not, it presents a serious problem of waste management and adds significantly to costs, meaning that this may not be the most suitable reaction for manufacturing phenol.

   In another process of manufacturing of Phenol from benzene and propene, co-product is propanone which is a valuable chemical so the atom economy for this process can be regarded as 100%.

   $$C_6H_6 + CH_3CH{=}CH_2 + O_2 \longrightarrow C_6H_5OH + CH_3COCH_3$$
7. The family of polycarbonates contains very important polymers which are used where high optical properties combined with strength are needed. There are two routes for manufacturing of polycarbonates from bisphenol A. In the first

route polycarbonateis prepared by condensation reaction between bisphenol A and carbonyl chloride where as in second route it is prepared by condensation reaction between bisphenol A and diphenyl carbonate. Carbonyl chloride is a very poisonous gas, manufactured from other hazardous gases, carbon monoxide and chlorine.On the other hand, diphenyl carbonate is produced from dimethyl carbonate, which is readily manufactured from methanol, carbon monoxide and oxygen in the liquid phase, in presence of copper(II) chloride, $CuCl_2$.Dimethyl carbonate, when heated with phenol in the liquid phase, forms the diphenyl carbonate.Overall, the process for the production of polycarbonate that uses diphenyl carbonate is less hazardous than that using carbonyl chloride

Overall, the process for the production of polycarbonate that uses diphenyl carbonate is less hazardous than that using carbonyl chloride.

8. Catalysts have played a huge part in development of more sustainable processes for the manufacturing of chemicals. There are many advantages of using the catalysts such as they enable alternative reactions to be used which have better atom economy and thus reduce waste, with there use it is possible to control reaction pathways more precisely, reducing unwanted side products and making it easier to separate and purify required product, so also reaction can be carried out at lesser temperature and pressure.

   Aluminum chloride was used for many years in the production of alkyl benzene sulfonates an active surfactant in many detergents. The aluminum chloride was needed to effect the reaction between benzene and a long chain alkene. The aluminum chloride could not be recycled and became waste as aluminum hydroxide and oxide. Now a solid zeolite catalyst with acid groups is used and can be reused time and time again with no waste products.

   Similarly, benzene and propene are converted into cumene in the manufacture of phenol. This reaction needs an acid catalyst, such as aluminum chloride. A solid zeolite with acid groups, such as ZMS-5 is now the favored catalyst. The zeolite is more environmentally friendly as the effluent is much cleaner and lower temperatures and pressures can be used.

   Another example is manufacture of one of the most important polymers used to make fabrics, polyamide 6 (sometimes called as nylon 6). In this process cyclohexanone is converted into caprolactam via the oxime. The oxime is isomerized by sulfuric acid to caprolactam, the released sulfuric acid is converted to ammonium sulfate. However ,again a zeolite catalyst, with acidic sites, is now being used to effect this rearrangement. The zeolite is regenerated and saves the use of sulfuric acid and subsequent waste of sulfuric acid i.e ammonium sulfate.

9. Application of Green Chemistry in day to day life is use of a) Organic Vegetables, fruits, grains b) use of Bio gas c) use of paper bags instead of polythene bags d) use of toilet cleaner and floor cleaner based on Cow urine instead of acid base e) use of turmeric powder as antiseptic.

CONCLUSION

After all of the research advancements in green chemistry and engineering, mainstream chemical businesses have not yet fully embraced the technology. Today, more than 98% of all organic chemicals are still derived from petroleum.

Green chemists and engineers are working to take their research and innovations out of the lab and into the board room through the creation of viable industrial products that can be embraced by today's industry leaders.

Western countries are serious about Green Chemistry where as Asian countries are less serious about the same. With the developments in Western countries they havechanged the red processes into green one ,if not then they have closed the units with red chemistry. But in Asian countries plenty of units with red chemistry are still in operation. Hence, now the time has come that the regulatory cops should put heavy fines on Red Plants, cut down the profits, so that Industrieswill become serious and act on changing of Red Plants into Green one. So also researchers at Institutes should work in coordination with industries to convert the Red processes into green one. It is often observed that industries with there own in house talent are solving the red problems and where as the level of research in the institutes is going down.The challenge for chemistry and chemical engineering, to convert all existing industrial hazardous processes to green one or alternatively innovate products with same

applications with new green processes is extremely tough.

To increase the awareness of green chemistry, just as Safety Day/week is celebrated on 4th March, Environment Day is celebrated on 5th June, Energy Conservation day is celebrated on 14th December of every year, in the same fashion some date should be fixed so as to celebrate "Green day and week" On this day it should be made compulsory that everybody should wear Green clothes.

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EFFECT OF METAL-LIGAND COMPLEX ON GROWTH OF SOME VEGETABLES IN SOIL AND SOILLESS MEDIA

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INTRODUCTION

Plant physiology will probably also assume an increasingly important role in agricultural research problems. As world population increases, mankind faces enormously complex problems. One of the primary tasks of the future will be to increase food, forage, fiber and wood production substantially throughout the world. Today the application of various chemical salts to soils is a basic feature of agricultural practice.

In the present work,Chalcone(an α,β-dihydroxy Ketone) for treatment on vegetable plants is selected for study , as they have both nutritional as well as medicinal value. Since organic drugs have intense biological activity and since no work is reported on the biological applications of binary complexes of Fe (III) with ligand(chalcone) and comparing with pure ligand, metal and control solution doubly distilled water to study the effect of complex, metal, ligand and control solution on germination survival, seedling height, root/shoot ratio and chlorophyll content on Methi, Chilly,Spanish&Carrot plants were studed in order to make suggestion whether complex, metal and ligands can be used as plant growth regulators.

The following aspects were studied in laboratory.

1) Estimation of Root / Shoot Ratio in soil & soilless media.

2)Estimation of chlorophyll contents in soil & soilless media.

MATERIAL AND METHOD

The information about the role of metal complexes in biological systems, their concentration and presence in different equilibria is of immense importance. Greshonet. al.[1,2] reported that the activity of metal chelates is considerably increased as compared to that of the free metal and ligand alone on their complexation. The Shelet. al.[3] and Shashindharam et. al.[4] observed the antifungal and antibacterial activities of complexes shows that they are more active as compared to free ligand and metal involved.

Rare earth ions are used as probe in bio-chemistry of calcium. Zielinski et. al.[5] showed that, Lanthanide ion could substitute the calcium ion to produce active enzyme system. Some bivalent metal ions have been reported to be useful in agriculture as plant growth regulators. Such a vast uses of lanthanide necessitate concentrating on the study of lanthanides and ligands for studying the germination pattern.

The complexes of transition metal with bis-alkyl thiourea are prepared and their herbicidal and plant growth regulating activity are tested with wheat and cucumbers by Darnallet. al.[6], Sayedamir et.al.[7] studied effect of some heavy metals on seed germination of canola, wheat, safflower evaluate phytoremedial potential. K. Abraham et. al.[8] also studied effect of heavy metals on seed germination of archishypogeae. L Shivakumar C. K. et. al.[9] also observed the presence of beneficial fungus and effect of copper and zinc metal absorption on growth and metal uptake of legumineous plants as although these metals are required in traces but are important for growth.

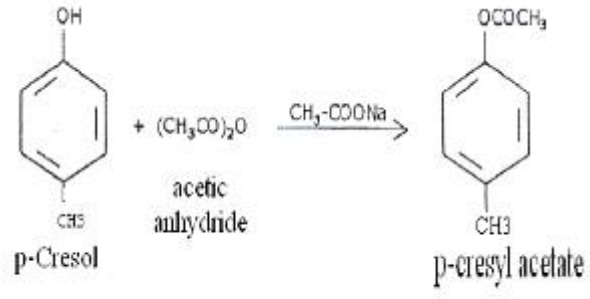
A. A. Ramteke et. al.[10] studied the effect of chlorosubstitutedpyrrazole and their complexes on spinach at different pH.

C. Aydinalp et. al.[11] also studied heavy metal effect on seed germination and plant growth and alfalfa plant (medicago sativa)

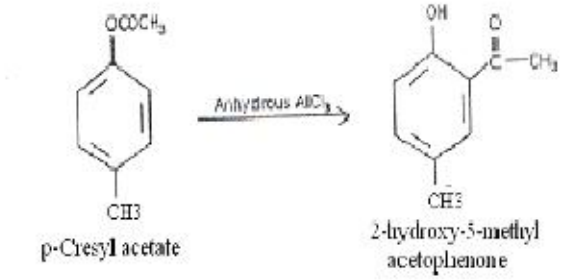
SYNTHESIS OF CHALCONE BY KNOWN METHOD

The chalcone was prepared by known literature method and was confirmed by melting point and also the structure was confirmed by IR spectroscopy as shown in spectra.

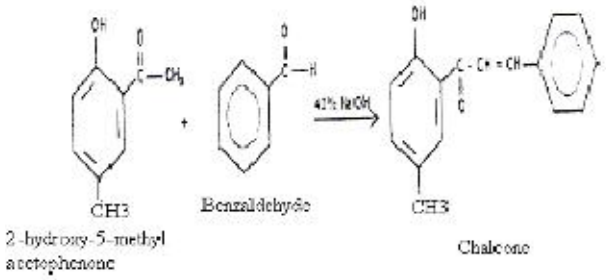
Step I: Preparation of p-cresyl acetate from p-cresol



Step II:Preparation of 2-hydroxy-5–methylacetophenone from p-cresyl acetate



Step III:Preparation of chalcone from 2-hydroxy-5-methyl acetophenone



EXPERIMENTS PERFORMED

- ***Metal ions:-***

The solutions of metal ion in the form of $FeCl_3$ and $MgCl_2$of 0.1 M concentration were prepared using distilled water and the seedsofMethi,Chilly, Spanish&Carrot were soaked in both metal solvents.

- ***Ligand:-***

The organic compound was prepared were dissolved in proper solvent and above seeds are soaked for 2-3 hours.

Metal ion + Ligand:- The mixture of $FeCl_3$ and organic compound (chalcone) and MgCl2 and organic compound (chalcone) were dissolved in the distilled water and seeds are soaked.

Media:-For the germination of the above vegetables seeds, two types of the medias are used.

1)Soil media (media A)
2)Soilless media (media B)

EXPERIMENTS PERFORMED

In general practice, various chemicals are used in agricultural as an important ingredient of various pesticides, insecticides, fertilizers, etc. to improve the crop yield. Amongst several economical important plants Chilly,Methi, Carrot and Spanich are selected as a plants system. These plants are in ideal systems to study the germination and growth pattern. Further, their economical importance is reflected by its wide use for various purposes.

The important uses these plants in daily life are persuasive to study its response against metal ion, ligand and its complex regarding to physiological processes; particularly germination is a vital process for the growth of plants. Therefore, these plants are selected as a plant system.

1]Healthy seeds were takenand thoroughly washed using doubly distilled water. Seedsfrom these healthy seeds of equal size were chosen, immersedin testedsolution. These seeds soaked were taken out of each solution.the seeds are sown in germination trays of all medias.

2]Effect of ligand, metal Fe (III), complex and metal Mg (II), complex on chlorophyll in the leaves of vegetables plants were studied.

After sufficient growth, green fresh leaves were collected, as they contain chlorophyll pigments and chlorophyll content was determined spectrophotometrically given by Jahagirdar D. V.[12]

ESTIMATION OF CHLOROPHYLL IN LEAF PIGMENT

- ***Procedure:-***

Collect the fresh leaves weigh around 1 gm of leaves and cut them into small pieces. Add 5 ml of water and transfer the mixture to a blender. Homogenize the mixture by blending it intermittently for 3-4 minutes.

Take homogenous mixture and add acetone to it. Thoroughly shake the content, centrifuge it. Collect the supernatant liquid and measure its optical density at
645 and 663 nm.

- ***Parameters:-***

Plants growth is decided on the basis of parameters such as percentage of germination survival, seedling height, shoot length, root length (root length / shoot length) and thickness of young leaf having high values compared to control system. The germination was noted after7days ,14 days and 22days for all Plants.

After noting the survival of the plants, they were taken out of the medias. The seedling height (root length / shoot length) was measured. The average values of these parameters are presented in Table 1

RESULT AND DISCUSSION

Some attempts have been made by Beraet. al.[13] to study the effect of tannery effluent on seed germination, seedling growth and chloroplast pigment content in mungbean. Adhikariet. al.[14] have observed the effect of raw savage water on mustard. Recently Farzin M. Parabiaet. al.[15] in their present investigation, effect of ligand, complex and metal ion on percentage seed germination, root length, shoot length (root / shoot ratio) has been studied.

RootLength, Shoot LengthAnd Root / Shootratio

Germination starts when the seed shows emergence phase of growth, which begins, with penetration of embryo from the seed coat and end with development of root and shoot system. The elongation of shoot axis follows emergence of radical.

The rate and extent of elongation is subjected to a variety of controls, including nutrition, hormones and environmental factors. Though the root and shoot development start within a fraction of time but the further developments may vary according to the nutrients required for the development of root and shoot independently.

Therefore, root and shoot length differs from each other.

Table 1:-Effect of Different Treatment on Vegetable Plant in Respect of Parameters in Soil and Soilless Media.

Sr.No.	Parameters	Methi		Chilli		Spanish		Carrot	
		Soil	Soilless	Soil	Soilless	Soil	Soilless	Soil	Soilless
1	% Germination	736%	86%	65.6%	88.6%	88%	90.4%	46%	69.8%
2	Seedling Height(cm)	11.96	12.26	4.38	6.54	9.77	10.6	3.0	2.9
3	Shoot Length(cm)	6.44	6.46	2.84	3.86	6.04	6.29	1.6	1.6
4	Root length(cm)	5.52	5.76	1.54	2.68	3.74	4.28	1.4	1.3
5	Shoot/Root Ratio	1.17	1.15	1.84	1.44	1.68	1.50	1.14	1.23

T

able 1 clearly indicates that percent germination in soilless medium is higher followed soilless media. Similarly the root length and shoot length which is called as seedling height shows a significant development of root / shoot length i.e. height of seedling highest in chalcone + Mg as compaired to over all the treatments and subsequently followed by chalcone + Fe, metal ion Mg, chalcone and control (d/w) respectively in all cases.

When we compare the performance of all the treatments for different parameters in soil and soilless media. The germination & growth parameters are studied in soil and soilless media. Soilless media shows better performance as against soil media in all the treatments.

Mg is a major constituent for the formation of chlorophyll molecule which helps in the process of photosynthesis for the production of food materials in the plant i.e. sugar synthesis.With combination of chalcone + Mg plays a pinnacle role in keeping all the system working properly. This may be the reason for the better performance.

Fe plays major role in energy transfer within the plants and also brings about chlorophyll development and formation. It is also a constituent of certain enzyme and protein. With the combination of chalcone plays a major role in keeping all the plant system working properly may be the reason for a good performance.

The germination of seed and development of the seedling is better in soilless media than the soil media. Because there is less resistance for the root development and shoot development in soilless media than the soil media may be the reason for better, overall development of the plant.

CHLROPHYLLCONTENT

Photosynthesis is the process in which the light energy will be converted into chemical energy. There are some basic requirements for the process of photosynthesis as CO_2, H_2O and light energy besides of course, the structural framework of green plant in the form of chloroplast, which is a unique cell having most important role in all the physiological reactions, starting from the absorption of light energy. Basically, among the smallest group of coordinating pigment molecules necessary to effect a photochemical

act, the most important pigments involved in photosynthesis are chlorophyll and carotenoid.

After performing spectrophotometric experiment, it was observe that for chlorophyll content of plant leaves, absorption is higher at 663 nm in all the treatments. These tables also clearly indicates that the amount of chlorophyll is more in chalcone + Mg. Followed by chalcone + Fe, metal ion Mg,

chalcone and control (d/w) in both soil and soilless media.

Obviously the chlorophyll content is highest in chalcone + Mg in both soil and soilless medias. Because of Mg is major constituent for the formation of chlorophyll.

Table 2:-Effect of different treatment on chlorophyll content in respect to soil media

Sr.No.	Nameof vegetable plants	Treatment with Ligand	Treatment with Ligand+Mg	Treatment with Ligand+Fe	Treatment with Metal ion Mg	Treatment with distilled water
1	Methi	$8.22x10^{-3}$	$10.162x10^{-3}$	$8.363x10^{-3}$	$11x10^{-3}$	$5.64x10^{-3}$
2	Chilli	$7.3x10^{-3}$	$25.83x10^{-3}$	$24.61x10^{-3}$	$12.67x10^{-3}$	$6.22x10^{-3}$
3	Spanich	$4.71x10^{-3}$	$7.65x10^{-3}$	$5.61x10^{-3}$	$8.09x10^{-3}$	$4.50x10^{-3}$
4	Carrot	$12.7x10^{-3}$	$32.22x10^{-3}$	$21.34x10^{-3}$	$37.50x10^{-3}$	$7.095x10^{-3}$

Table 3:-Effect of different treatment on chlorophyll content in respect to soilless media

Sr.No.	Nameof ve getable plants	Treatment with Ligand	Treatment with Ligand+Mg	Treatment with Ligand+Fe	Treatment with Metal ion Mg	Treatment with distilled water
1	Methi	$11.9x10^{-3}$	$14.8x10^{-3}$	$12.5x10^{-3}$	$19.3x10^{-3}$	$10.3x10^{-3}$
2	Chilli	$6.77x10^{-3}$	$16.37x10^{-3}$	$9.94x10^{-3}$	$9.88x10^{-3}$	$6.01x10^{-3}$
3	Spanich	$7.41x10^{-3}$	$8.45x10^{-3}$	$8.31x10^{-3}$	$9.93x10^{-3}$	$5.41x10^{-3}$
4	Carrot	$13.13x10^{-3}$	$36.31x10^{-3}$	$25.35x10^{-3}$	$40.49x10^{-3}$	$7.1x10^{-3}$

CONCLUSION

Result of effect of metal ion Mg, Chalcone, Chalcone+ Mg and control (d/W) and chalcone+ fe, on germination, seedling development clearly revels that, Chalcone +Mg shows significant better performance overall the treatments. All the parameters are considered, while finding out the results. In general order in all the parameters performance wise Chalcone+Mg stood first followed by metal ion Mg, ChalconeChalcone+fe and control (D/W).

Mg is major constituents for the formation of chlorophyll molecule which helps in the process of photosynthesis for the production of food materials in the plants,i.e sugar synthesis.with the combination of Mg chalcone plays a pinnacle role in keeping all the plant system working properly may be the reason for a better performance.

Also Mg is a secondary importance element essential for the plant growth,which is also a constituents of many enzyme the detail information about Mg is already mention in the above para. So, keeping in view of all the characteristics of Mg plays a pivotal role for a good performance against the other treatments.

Germination of seed and development of seedling is better in the soilless media than the soil media, because there is less resistance for the root development and shoot development n the soilless media than the soil media, may be the reason for better overall development of the plant.

The analysis perform for finding out the total chlorophyll in green leaves of the plant. The results of analysis clearly indicates that metal ion Mg is having highest chlorophyll content in both soil and soilless media than the remaining treatment like Chalcone+Mg, Chalcone+fe , Chalcone and control (D/W).

From all above discussion it is observe that accept Carrot , all vegetables show some what better growth in soilless media.

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SYNTHESIS OF SILVER NANOPARTICLES USING NATURAL SURFACTANTS AS A CAPPING AGENT

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ABSTRACT

Experimental studies on the critical role of biological surfactant in the nucleation and growth of silver nanoparticles synthesized by chemical reduction route have been reported. By varying the biological surfactant species, silver nanoparticles (AgNPs) of different morphologies under similar reaction conditions were produced. The synthetic protocol involves the preparation of (AgNPs) derived from three biological surfactants as a capping agents i.e. Balaitis aegyptica (trivial name- Hinganbet), Sapindus emerginatus (trivial name- Ritha) and Acacia concinna (trivial name-Shikekai) by using hydrazine hydrate as a reducing agent. The role of these surfactants in controlling the size and properties of silver nanoparticles has been discussed.

The formation of silver nanoparticles were characterized by transmission electron microscopy (TEM) which shows that the silver nanoparticles are of spherical form and relatively uniform. Wide range of experimental conditions has been adopted in this process and its X-ray diffraction (XRD) pattern has been studied. The average crystalline size was found to be 15.48 nm. The particle size and strain which were calculated using Williamson-Hall equation were 11.46 nm and 0.0025 respectively.

Keywords: *Biosynthesis, silver nanoparticles, Williamson-Hall equation XRD, TEM.*

INTRODUCTION

In recent years, the convergence of nanoscale technologies has created enormous interest amongst the researchers. This relatively new field is focused on experimentation, creation and applications of nanomaterials [1].

Over the past few years, green synthesis of nanoparticles (NPs) using plant extracts has emerged as a promising methodology for the fabrication of metallic NPs, because of its easy, fast, low-cost and ecofriendly bioprocess [2-4]. However, many factors affect the sizes and morphologies of AgNPs synthesized by various methods, including the nature of the plant extract, Ag precursor concentration and temperature etc. Therefore, the green synthesis of metal NPs with defined stability, size and morphology remains under evaluation. Decreasing the particle size to nanoscale may change its intrinsic properties. Thus, the properties of a nanomaterial can be quite different from those of the starting materials, making it suitable for varied applications. The chemical and physical properties of the metal nanoparticles are dependent on their structure, shape and size distribution. Therefore, control over the size and size distribution is crucial and is often achieved by varying the synthesis methods, reducing agents and stabilizers.

Metallic nanoparticles (NPs) have been applied to a wide variety of fields, including agriculture, medicine, bioengineering etc. because they have been proven and recognized as antibacterial and biocide agents (5-10).

AgNPs show effective antimicrobial activity against gram-positive and gram-negative bacteria including highly multiresistant strains such as methicillin resistant *Staphylococcus aureus* [11]. Efforts have been made to use of microorganisms as eco-friendly nanofactories for the synthesis of silver nanoparticles. Various microbes are known to reduce the Ag^+ ions to form silver nanoparticles, most of which are found to be in spherical form [12, 13]. Klaus and coworkers have reported that the bacterium *Pseudomonas stutzeri* AG 259, isolated from a silver mine, when placed in a concentrated aqueous solution of silver nitrate, played a major role in the reduction of the Ag^+ ions and the formation of silver nanoparticles (AgNPs) of well-defined size and distinct topography within the periplasmic space of the bacteria [14].

At present, the nanomaterials field has generated NPs using green synthesis (15-17). Green synthesis involves NPs obtained from the mixing of metal salts and natural agents such as vitamins, sugars, plant extracts, biodegradable polymers, and microorganisms. When plant extracts are used,

they can act as a reducing agent, but also as a stabilizing component for the system (18).

Green synthesis of AgNPs involves two phases, firstly the nucleation phase, where the silver atoms form small nucleuses using high activation energy and the second phase known as growth phase in which these small nucleuses are grouped, giving rise to the creation of NPs (18). Once the AgNPs are formed, stable particles in stabilizer-free aqueous solutions can be obtained. The features of NPs are influenced by several parameters such as temperature, time of reaction, and pH; however, the nature of biomolecules present in the plant extracts could be the most relevant factor in the bioprocess (19).

However, chemical reduction is the most commonly used method, due to its simplicity. The selection of an appropriate reducing agent is also a crucial factor, as the size, shape and particle size distribution strongly depend on the nature of the reducing agent. The introduction of a reducing agent causes the reduction of metal precursor. Reduction of metal salts requires adjustment of the reactivity of the reducing agent to the redox potential of the metal. The choice of the surfactant is critical since it determines the stability, solubility, reactivity, dispersibility and even the size and shape of the nanoparticles during the synthesis [20, 21].

Synthesis and applications of silver nanoparticles using a biosurfactant as a stabilizing agent have been reported in detail. [22-24]. But, use of natural surfactants in the synthesis of AgNPs have not been reported so far. Therefore, in the present study, natural surfactants have been used as capping agents, rather than as a reducing agent, in order to prevent the aggregation of metal particles. The effects of the combined hydrazine hydrate and natural surfactants on the AgNPs produced were characterized by XRD, whilst the particle morphology and size were observed by TEM.

EXPERIMENTAL

***Material and Chemicals*:**

Silver nitrate ($AgNO_3$) (as a metal salt) and hydrazine hydrate ($NH_2NH_2H_2O$) (as reducing agent) have been procured from merck, India. The plant materials i.e. *Balanitis aegyptica [Hingnbet], Sapindus emarginatus [Ritha], Acacia concinna [shikekai]* have been collected from Melghat region, Amravati and used for the preparation of extract.

***Synthesis*:**

I] Preparation of Plant Extract of fruit of *Balanitis aegyptica* (Hingnbet) [$AgNP_1$], nuts of *Sapindus emarginatus* (Ritha) [$AgNP_2$] and pods of *Acacia concinna* (Shikekai) [$AgNP_3$]:-

The respective parts of plant materials was collected, washed and cut into small pieces. It was then crushed with the help of mortar and pestle. It was then dissolved in double distilled water in 100 ml sterilized beaker with continuous stirring. After complete dissolution of the pulp, the extract was filtered with whatman filter paper No. 1 in clean and sterilized conical flask. The filtrate was stored at 4°C for further use.

II] Synthesis of AgNPs

In 100 ml beaker, 50 ml plant extract of *Balanitis aegyptica* (Hingnbet) certain concentration were taken and it was magnetically stirred at 20^0C. Then silver nitrate solution (10 ml, 0.1M) was added followed by addition of reducing agent drop by drop by micropipette under vigorous stirring. After 20 minutes of continuous stirring the change in colour was observed after some time due to addition of the reducing agent. Leafy green colour may indicate the formation of AgNPs which is then cooled at room temperature. This colored solution of Silver Nanoparticals then allowed to evaporate and then kept in muffle furnace which was then used for further characterization analysis. In case of *Sapindus emarginatus* [Ritha] and *Acacia concinna* [Shikekai], light yellow coloured solution and brown red colour solution was obtained respectively which was then cooled at room temperature.

***Characterization techniques*:**

Ultraviolet-visible Spectroscopy (UV-Vis) was performed in a Perkin-Elmer Spectrophotometer. The studies of size, morphology and composition of the nanoparticles were performed by means of transmission electron microscopy (TEM) using Phillips CM200-Ultra twin microscope operating at 200 kv at resolution 2.4 Ao. Samples for TEM studies were prepared by placing drops of the silver nanoparticles solutions on carbon-coated TEM grids. X-ray diffraction (XRD) was carried out to confirm the crystalline nature of the particles. XRD patterns were recorded using powder X-ray diffractometer (Model-D8 Advance, made in BRUKER Germany).

RESULT AND DISCUSSION

A common method to control the size distribution of particles produced by precipitation, particularly in the case of silver powders, is the use of protective agents or capping agents. The main

mechanism by which these protective agents control the particle size is by the suppression of the agglomeration. The most common protective agent used in the production of ultrafine silver powders is the polyvinyl pyrrolidone (PVP), which has proven to reduce the mean particle diameter from several microns to even 100 nm. In the case of PVP, after forming the complex with silver, it favors the reduction of complexed silver over free silver ions, as it allows complexed silver to receive more electronic clouds. Hence, nucleation is favored over crystal growth due to stearic effects. Also for this reason, particle aggregation is avoided. Depending on the conditions of the reaction mixture, hydrazine can act as a reducing agent by releasing either two or four electrons according to the following reactions.

$$N_2H_4 \rightarrow N_2 + 4H^+ + 4e^- \quad (1)$$

$$N_2H_4 \rightarrow N_2H_2 + 2H^+ + 2e^- \quad (2)$$

Depending on which reaction takes place, it can be transformed into either elemental nitrogen (N_2) or an intermediate compound (N_2H_2). For this reason, two or four moles of silver can be reduced with one mole of hydrazine, giving two possibilities for the main reaction stoichiometry.

In the present study, AgNPs were prepared by the chemical reduction method in which the reductant ($NH_2NH_2H_2O$) directly reduced Ag^+ to generate metallic Ag atoms. The produced Ag atoms then acted as nucleation centres and catalysed the reduction of the remaining metal ions present in the solution. The coalescence of atoms led to the formation of metal clusters, which are normally stabilized by ligands, surfactants, or polymers [25]. It is believed that the natural surfactants containing saponin which acted as a surfactant was adsorbed onto the surface of the Ag atoms and thus prevented the nanoparticles from agglomeration.

At the beginning of the process, the newly reduced Ag atoms acted as the nuclei of the nanoparticles. With further processing time, these nuclei grew continuously. Indication of the formation of AgNPs was observed by change in the solution colour.

During this process, the solution went through a number of colour changes before it stabilised. These colour changes indicate the growth of the AgNPs. In this process, the reaction can be expressed as follows [26]:

$$2Ag^+ + N_2H_4 \leftrightarrow 2Ag^0 + N_2H_2 + 2H^+ \quad (3)$$

X-RAY DIFFRACTION SPECTRA

In order to examine the physico-chemical parameters of unknown materials, scientists use primarily X-ray diffraction techniques which are the most important characterization tools used in solid state chemistry and material science. The size, shape, lattice parameters and phase fraction analysis of the unit cell for any compound can be determined by XRD [27-29].

1. Peak Indexing

From the peak positioning, the unit cell dimensions are determined this process is called indexing which is the primary step in diffraction pattern analysis. Miller indices (hkl) are necessary to be assigned for each peak to index [9]. XRD analysis of all the prepared samples of silver nanoparticles was done by a Bruker D8 advanced X-ray diffractometer using CuKα radiation (λ = 1.5418 Å), under 40 kV/30Ma-X-ray, $2\theta/\theta$ Scanning mode, Fixed Monochromator). Data was taken for the 2θ range of 0 to 80 degrees with a step of 0.02 degree. Data for some 2θ range has each peak was assigned in first step. Diffractogram of the entire data is represented in Figure 1. Indexing has been done and data is represented in Table 1. In Table 1, one need to find a dividing constant and values in the 3rd column becomes integers (approximately). Moreover, the high intense peak for cubic materials is generally (111) reflection, which is observed in the sample. Four peaks at 2θ values of 38.32, 44.39, 64.66 and 77.49 degree corresponding to (111), (200), (220) and (311) plane of silver were observed. The XRD study confirms that the resultant particles are (FCC) silver nanoparticles [10]. The ratio between the intensities of the (200) and (111) diffraction peaks and (220) and (111) peaks enumerated in Table 2 is also slightly higher than the conventional value (0.35 versus 0.31) and (0.28 versus 0.22).

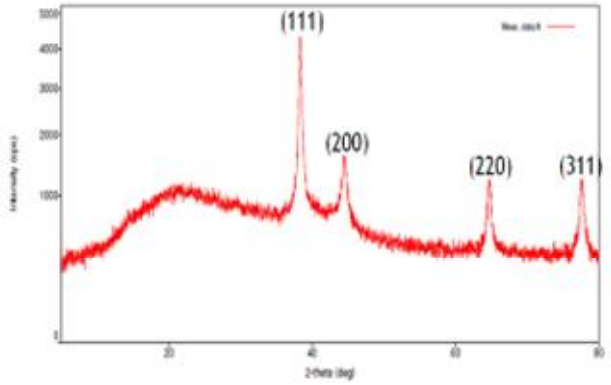


Fig 1: X-Ray diffraction pattern of $AgNP_1$

Table 1: Simple peak indexing

Peak position 2θ	1000× $\sin^2\theta$	1000 × $\sin^2\theta/35$	Reflection	Remarks
38.32	107	3	(111)	$1^2 + 1^2 + 1^2 = 3$
44.39	142	4	(200)	$2^2 + 0^2 + 0^2 = 4$
64.66	286	8	(220)	$2^2 + 2^2 + 0^2 = 8$
77.49	391	11	(311)	$3^2 + 1^2 + 1^2 = 11$

Table 2: Ratio between the intensity of diffraction peaks

Diffraction peaks	Conventional value	Sample value
(200) and (111)	0.31	0.35
(220) and (111)	0.22	0.28

Considering the peak at degree, average particle size has been estimated by using Debye- Scherrer formula.

$$D = 0.9\ \lambda/\beta\ \mathrm{Cos}\theta \qquad (4)$$

Where "λ" is wave length of X-ray (0.1541 nm), "β" is FWHM (full width at half maximum), "θ" is the diffraction angle and "D" is particle diameter size.

The particle size is less than 35 nm and the details are in Table 3. Williamson-Hall equation is another method to calculate particle size and strain. The Williamson-Hall equation is expressed as follows

$$\beta\ \mathrm{Cos}\theta = (k\ \lambda\ /\ D) + 2\varepsilon\ \mathrm{Sin}\theta \qquad (5)$$

where β is the full width at half maximum (FWHM) peak, k is Scherrer constant, λ the wave length of the X-ray, D is the crystalline size, ε the lattice strain and θ the Bragg angle. $\beta\cos\theta$ is plotted against $2\sin\theta$ using a linear extrapolation to this plot where the intercept gives the particle size ($k\lambda/t$) and slope gives the strain (ε).

The value of d (the interplanar spacing between the atoms) is calculated using Bragg's Law

$$2d\mathrm{Sin}\theta = n\lambda \qquad (6)$$

$$d = \lambda\ /\ 2\mathrm{Sin}\theta\ (n = 1)$$

The calculated d-spacing details are in Table 3.

The FCC crystal structure of silver has unit cell edge "a" = 4.0857 Å and this value is Calculated theoretically by using formula,

$$\mathrm{a} = \frac{4}{\sqrt{2}} \times r \qquad (7)$$

For silver r = 144 pm. Following formulas are used in the calculation of the expected 2θ positions of the first four peaks in the diffraction pattern and the inter planar spacing d for each peak.

$$\frac{1}{d^2} = \frac{(h^2 - k^2 + l^2)}{a^2} \qquad (8)$$

Bragg's Law is used to determine the 2θ value: $\lambda = 2d_{hkl}\mathrm{Sin}\theta_{hkl}$

Table 3: The grain size of silver nanoparticle.

2θ of intense peak (deg)	hkl	θ of intense peak (deg)	FWHM of intense peak (β) radians	Size of particle (D) nm	d-spacing nm	Asymmetric factor
38.32	(111)	19.16	0.0088	16.695	0.234	0.94
44.39	(200)	22.195	0.0125	11.925	0.203	0.55
64.66	(220)	32.33	0.0099	16.579	0.144	1.0
77.49	(311)	38.745	0.0106	16.775	0.123	0.55

XRD-INSTRUMENTAL BROADENING

A considerable broadening in X-ray diffraction lines will occur when particle size is less than 100 nm. The broadening is due to the particle size and strain from diffraction pattern. This broadening is used to calculate the average particle size. The sample broadening is described by

$$FW(S)\times\mathrm{Cos}\theta = k\lambda \text{ size} + 4\times\text{Strain} \times 2\varepsilon\ \mathrm{Sin}\theta \qquad (9)$$

The total broadening βt is given by the equation

$$\beta_t^2 \approx \frac{0.9\lambda}{D\mathrm{Cos}\,\theta} + (4\varepsilon\ \tan\theta)^2 + \beta_0^2 \qquad (10)$$

where ε and β_0 are the strain and instrumental broadening respectively. Using least squares method average particle size D and the strain of the experimentally observed broadening of the peaks are calculated. The instrumental broadening is presented in Figure 2. A method for evaluation of size and strain broadening was proposed by Williamson and Hall by looking at the peak width as a function of 2θ. Sinθ on the x-axis and Cosθ on the y-axis (in radians) a Williamson-Hall plot is plotted. A linear fit is drawn to get the data. From y-intercept and slope particle size and strain are extracted respectively. The particle size is 11.46 nm and strain is 0.0025. Figure 3 shows Williamson Hall Plot. Line broadening analysis is one of the most accurate methods as the broadening affects the particle size at least twice the contribution due to instrumental broadening. Therefore the size range is calculated with this technique will lead to most accurate results.

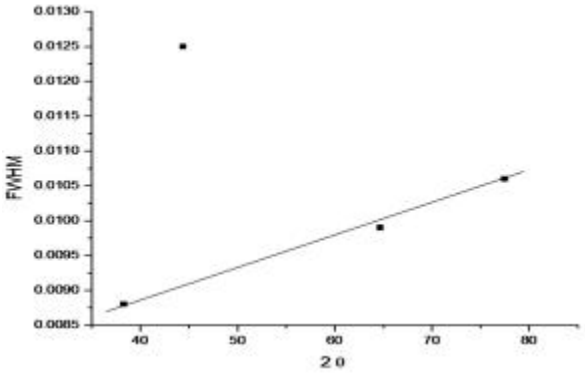


Fig 2: Typical instrumental broadening

SPECIFIC SURFACE AREA

Using Brumauer Emmete Teller (BET) equation the specific surface area of silver nanoparticle are measured.

$$S = \frac{6 \times 10^3}{D_p \times \rho} \qquad (11)$$

where *Dp* is the size of the particles, *S* is the specific surface area, and ρ is the density of silver 10.5 g/cm^3. The particle size is comparable with the crystalline size which is calculated in Debye-Scherrer and Williamson-Hall plot methods (Table 4).

Table 4: Crystalline size calculated from XRD, Particle size calculated from specific surface area

Average crystalline size calculated from XRD (nm)	Particle size calculated from Williamson-Hall plot (nm)	Particle size calculated from s pecific surface area (nm)
15.48	11.46	10.23

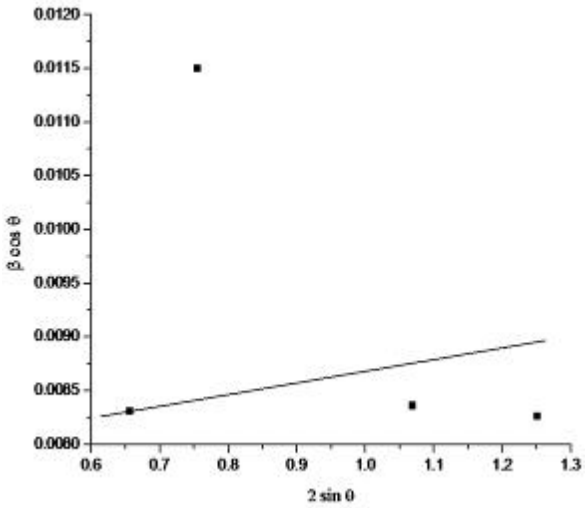


Fig 3- Williamson hall plot

DISLOCATION DENSITY

A dislocation within a crystal structure could be a crystallographic defect, or irregularity. The properties of materials can be influenced by the presence of dislocations which are a type of topological defects mathematically. The intrinsic stress and dislocation density of silver nanoparticles is determined by the X-ray line profile analysis. The dislocation density (δ) in the sample has been determined using expression.

$$\delta = \frac{15\beta Cos\theta}{4aD} \qquad (12)$$

where δ is dislocation density. It is calculated from broadening of diffraction line measured at half of its maximum intensity (radian), θ Bragg's diffraction angle (degree), *a* lattice constant (nm) and *D* particle size (nm). The dislocation density of sample silver nanoparticles is 4.6×10^4 m^{-2}.

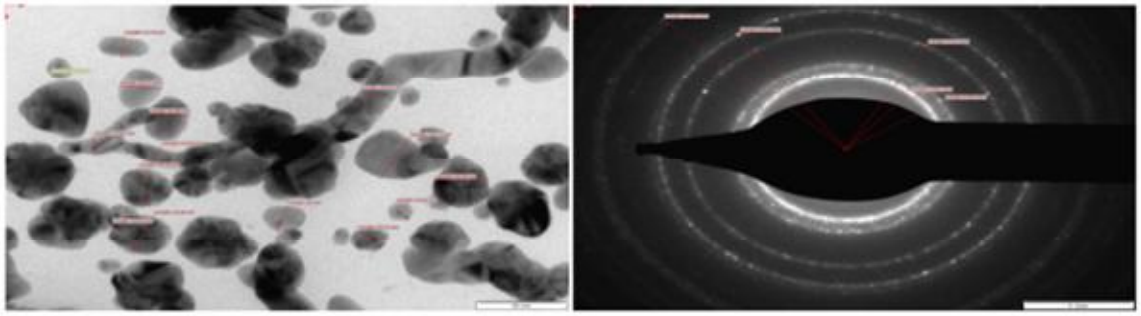
TRANSMISSION ELECTRON MICROSCOPY

TEM analysis was carried out on the $AgNP_1$, $AgNP_2$ and $AgNP_3$ to observe the individual size and shape of the nanoparticles. TEM micrograph and SAED (selected area electron diffraction) pattern of $AgNP_1$, $AgNP_2$ and $AgNP_3$ is shown in Fig. 4 a, b; 5 a, b; 6 a, b respectively. TEM image clearly demonstrates that the AgNPs were spherical or pseudo-spherical, polydispersed with more or less uniform size ranging from 10 to 35 nm. The selected area electron diffraction (SAED) micrograph of all the AgNPs shows ring like diffraction pattern which indicates the crystalline nature of AgNPs [29]. The Debye Scherrer ring patterns are consistent with the plane families {111}, {200}, {220} and {311} of pure face-centered cubic silver structure. Similar SAED patterns have been found for AgNPs synthesized from other kinds of natural surfactants which shows crystalline structure and had been confirmed to FCC [30, 31]. A large number of smaller particles are distributed randomly which indicates that the distribution of silver nanoparticles stabilized by the biosurfactant is rather uniform.

As biosurfactants are natural surfactants have higher biodegradability, lower toxicity, and excellent biological activities. Since the biosurfactants reduce the formation of aggregates due to electrostatic force of attraction they facilitate uniform morphology and stability of nanoparticles.

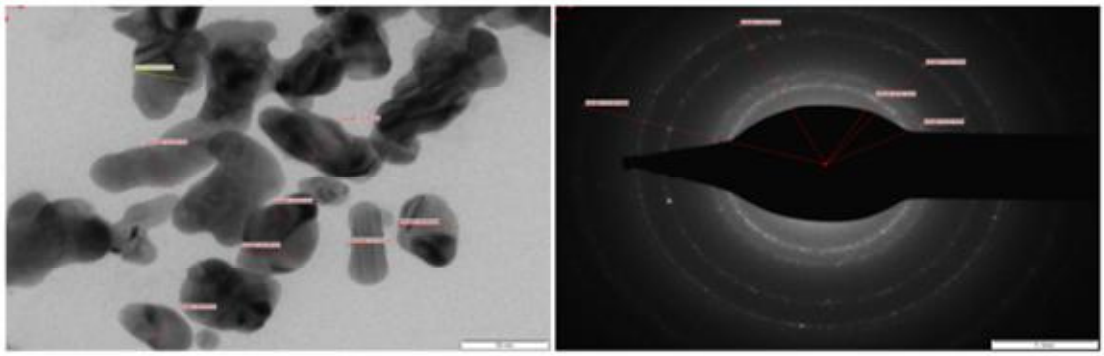
To determine the stability of silver nanoparticles synthesized through the biosurfactant, the prepared silver particles were kept at room temperature for

different day intervals. The results evidenced that nanoparticles were stable for 3 months. The biosurfactant would have acted as stabilization agent and prevented the formation of aggregates and favored the production and stability of the nanoparticles under the experimental conditions.



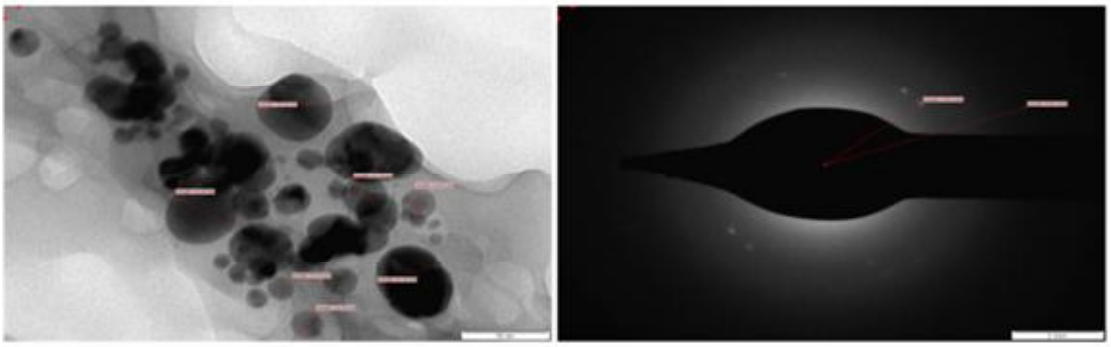
(a) (b)

Fig 4: $AgNPs_1$-(a) TEM and (b) SAED images of Ag-nanoparticles using *Balanitis aegyptica* [$AgNPs_1$]



(a) (b)

Fig 5: $AgNPs_2$-(a) TEM and (b) SAED images of Ag-nanoparticles using *Sapindus emarginatus* [$AgNPs_2$]



(a) (b)

Fig 6: $AgNPs_3$-(a) TEM and (b) SAED images of Ag-nanoparticles using *Acacia concinna* [$AgNPs_3$]

CONCLUSION

Fine dispersion and spherical size distribution of silver nanoparticles can be acquired by a simple and chemical reduction method. The synthesized silver nanoparticles have been characterized and confirmed by XRD and TEM. Different parameters like peak indexing, d-spacing, strain, instrumental broadening, specific surface area, crystallinity index, dislocation density and all other unit cell parameters were studied using XRD. The average crystalline size was calculated to be 15.48 nm and the crystalline structure had been confirmed to FCC. The obtained silver nanoparticles from natural surfactants were well matching with theoretical and experimental 2θ positions and d-spacing values.

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ULTRASONIC VELOCITY,VISCOSITY AND DENSITY OF BINARY LIQUID MIXTURES OF ISOBUTYL ALCOHOLAND ISODECYL ALCOHOL WITH O-NITROTOLUNE AT 298.15 AND 308.15K

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ABSTRACT

The ultrasonic velocities viscosities and densities of Binary Liquid Mixtures of Isobutyl alcohol and Isodecyl alcohol lwith O-nitrotolune are reported at 298.15 and 308.15 K. The Excess molar volume (V^E) viscosity deviation ($\Delta\eta$) have been calculated. The results were interpreted in terms of molecular interaction between the components of the mixtures.

Keyword: *Ultrasonic velocity, viscosity, density, molecular interaction.*

INTRODUCTION

The densities, viscosities and ultrasonic velocity measurements find wide applications in physic-chemical properties of liquids mixtures[(1-3)] and intermoleculaer interaction study. The ultrasonic velocity of liquid is related to biding force between the atoms of molecules .The physico -chemical properties such as densities, viscosities and ultrasonic velocities of pure liquids and of their binary liquid mixtures at different temperature of whole composition are useful for understanding the thermodynamic and transport properties as well as practical chemical engineering purposes. While excess thermodynamic properties are use for types of interaction between components of mixtures [(4-7)] The study of ultrasonic velocities (U) viscosities (η) and densities (ρ) measurements have wide applications in characterzing the physico chemical properties of binary liquid mixtures[(8-11)] .

The change ultrasonic velocity gives information about the bonding between molecules and formation of complexes at various concentration and temperatures through molecular interactions The measurements of Ultrasonic velocity of a liquid and mixtures allows the calculations of compressibility and hence enables to obtain structural information , In turn the data of sound velocity can be subjected to scrutiny by applying Jacobins free length and schaaffs collision factor theory. The deviations observed in free length and other parameters have been attributed to dipole-dipole, dipole-induced dipole and other dispersive force interactions. It is well known that aqueous solutions of hydrocarbons, alcohols, amines, ethers are characterized by H-bonding and hydrophobic interactions. The investigations regarding the molecular association in organic binary mixtures having alkanol group as one of the component is of particular interest, since alkanol group is highly polar and can associate with any other group having some degree of polar attractions.

MATERIALS AND METHODS:

The chemicals used Isobutyl alcohol and Isodecyl alcohol lwith O-nitrotolune were of analytical grade (A.R) minimum assay of 99.9% obtained from s. d. fine chemicals India. Which are used as such without further purification. The densities of pure components and binary mixtures were measured by using a Bi-capillary pycnometer. The purities of the above chemicals were checked density determination.The binary liquid mixtures of different known concentration were prepared in stopper measuring flask. The weight of the sample was measured using electronic digital balance with an accuracy of ± 0.1mg. The viscosity was measured usingubbelohde viscometer (20ml) and the efflux time was determined using a digital clock to within ± 0.015. The ultrasonic velocity (U) in liquid mixtures have been measured using an ultrasonic interferometer (Mittal type, model F-81) working at 2 MHzfrequency The accuracy of sound velocity was ±0.1 ms^{-1}

THEORY AND CALCULATIONS:

Excess volumes of the mixtures have been calculated using density and mole fraction data given by equation:

$$V^E = (M_1X_1+M_2X_2)/\rho_{12} -(M_1X_1) /\rho_1 - (M_2X_2) / \rho_2 \quad \text{-- (1)}$$

Viscosity of Binary Mixtures is calculated by:

$$ln\eta_m=X_1ln\eta_1+X_2ln\eta_2 \quad \text{--(2)}$$

The measured viscosities of the mixtures have been used to obtain deviation in Viscosity parameters on the basis of linearity in following way,

Deviation in Viscosity of Binary Mixtures is calculated by:

$$\Delta\eta_m=\eta_{12}-X_1\eta_1-X_2\,\eta_2 \qquad --(3)$$

Deviation in isentropic compressibility have been evaluated by using the equation

$$\Delta k_S=k_S-(\Phi_1\,k_{S1}+\Phi_2\,k_{S2}) \qquad --(4)$$

where k_{S1}, k_{S2} and K_S are isentropic compressibility of liquid mixtures and Φ is volume fraction of pure i^{th} component in the mixture and is defined as

$$\phi=(xi\ Vi)/(\Sigma\ xi\ Vi) \qquad --(5)$$

where x_1 and V_i are mole fraction and molar volume of ith component in the mixture

RESULTS AND DISCUSSION

The determination of viscosity of alkanols with O-nitrotolune gives reliable information about molecular interaction the pure alcohols get itself association. The association decreases with increase in chain length. When alcohols are mixed with O-nitrotolune then there is interaction between alcohol group and nitro group. The presence of electron donating nitro group increases the electron densities. The polarity of alcohols is less hence degree of association is less.

The experimental values of ultrasonic velocity, viscosity and density for binary liquid system of Isobutyl alcohol and Isodecyl alcohol lwith O-nitrotolune at 298.15 K and 308.15K are given in Tables 1 and 2 respectively.

The calculated value of excess molar volume (V^E), viscosity deviation (Δn) and deviation of isentropic compressibility (Δ ks) for binary liquid system of Isobutyl alcohol and Isodecyl alcohol lwith O-nitrotolune at 298.15 K are also given in Tables 1 and 2. . The variation of ultrasonic velocity gives information about bonding in molecules and formation of complexes at various concentration and tempera

The viscosity deviation of binary mixture gives some reliable information about molecular interaction. The viscosity deviation changes with increase in concentration of O-nitrotolune. The thermodynamic excess properties are found to be more sensitive toward intermolecular interaction between component molecules of binary mixture. The viscosity deviation values are negative with increase in temperature. The negative values in deviations indicates the existence of dispersions and dipolar forces between unlike molecules.

CONCLUSION

The experimental data of density, viscosity and ultrasonic velocity are reported for binary mixtures of Isobutyl alcohol and Isodecyl alcohol lwith O-nitrotolune over entire range of mole fractions at 298.15K and 308.15K are calculated, viscosity deviation, excess molar volume and change in isentropic compressibility are fitted in Redlich Kister type polynomial equation. A good agreement was foundin between Redlich Kister parameters.

Temp. (K)	x_1	ρ (gm/cm^3)	η10^3 (Nsm^{-2})	U (MS^{-1})	V^E x 10^6(m^3 mole^{-1})	Φ	Δη x 10^3 (Kg m^{-1} s^{-1})	Δk_S x 10^{11}(m^2 N^1)
298.15	0.0000	0.85750	12.80620	1584.5	0.0000	0.0000	0.000	
	0.1142	0.88060	10.73480	1629.2	-1.1496	0.0823	-83.056	-19.09
	0.2254	0.91160	8.62750	1649.2	-3.4823	0.1683	-172.837	-25.19
	0.3309	0.92810	6.75690	1661.6	-2.9375	0.2559	-245.148	-19.49
	0.4344	0.95120	5.04190	1664.4	-3.3671	0.3481	-304.074	-10.51
	0.5355	0.98540	3.67280	1664.7	-5.2820	0.4449	-331.021	-3.08
	0.6338	1.01590	3.39130	1668.1	-6.2695	0.5461	-252.253	6.16
	0.7291	1.03970	2.51920	1699.7	-6.1060	0.6517	-235.808	7.94
	0.8221	1.07590	2.43480	1814.5	-7.3206	0.7626	-143.095	-18.95
	0.9128	1.15260	2.18490	1847.6	-12.5922	0.8791	-69.433	-22.14
	1.0000	1.06920	1.92950	1932.8	0.0000	1.0000	0.000	
308.15	0.0000	0.84560	7.89520	1546.7	0.0000	0.0000	0.000	
	0.1142	0.87300	7.66480	1596.0	-2.0320	0.0819	48.686	-30.34
	0.2254	0.90400	5.84310	1597.7	-4.3208	0.1675	-63.567	-31.69
	0.3309	0.92040	4.67200	1598.4	-3.6676	0.2548	-114.342	-24.48
	0.4344	0.94380	3.69300	1600.2	-4.0746	0.3469	-147.166	-19.82
	0.5355	0.97680	2.80820	1601.2	-5.7517	0.4435	-172.078	-17.37
	0.6338	1.00710	2.66070	1629.9	-6.6567	0.5447	-125.021	-25.17
	0.7291	1.03150	2.08260	1633.8	-6.5022	0.6504	-122.910	-17.22
	0.8221	1.06710	1.99230	1647.3	-7.5878	0.7616	-73.465	-15.58
	0.9128	0.14250	1.85440	1683.0	840.7976	0.8785	-30.227	2137.09
	1.0000	1.06030	1.60760	1719.2	0.0000	1.0000	0.000	

Table1: Values of density (ρ) viscosity (η) ultrasonic velocity (U), Excess volume (V^E), viscosity deviations and (Δη), deviation on isentropic compressibility (Δk_S) for Binary System of Isobutyl alcohol(1) with O-nitrotolune(2) at 298.15 and 308.15 K.

Temp. (K)	x_1	ρ (gm/cm^3)	$\eta 10^3$ (Nsm^{-2})	U (MS^{-1})	V^E x 10^6(m^3 mole^{-1})	Φ	Δη x 10^3 (Kg m^{-1} s^{-1})	Δk_S x 10^{11}(m^2 N^1)
298.15	0.0000	0.79910	3.76810	1433.0	0.0000	0.0000	0.000	
	0.0568	0.83640	2.83670	1466.0	-1.8762	0.0769	-82.735	-25.57
	0.1192	0.84990	2.52900	1485.0	-0.9416	0.1576	-102.032	-19.36
	0.1880	0.88960	2.56840	1513.0	-2.7989	0.2424	-85.442	-31.44
	0.2651	0.91440	2.24610	1597.0	-2.8448	0.3327	-103.496	-61.29
	0.3509	0.95040	2.31340	1616.3	-3.9654	0.4276	-80.991	-53.27
	0.4479	0.98760	1.96760	1648.5	-5.0343	0.5286	-97.737	-47.19
	0.5580	1.02560	1.90440	1650.2	-6.0180	0.6357	-83.814	-23.30
	0.6834	1.07350	2.01050	1669.2	-7.8628	0.7489	-50.148	-6.40
	0.8296	1.10780	2.00480	1697.1	-8.1156	0.8706	-23.838	16.36
	1.0000	1.06920	1.92950	1932.0	0.0000	1.0000	0.000	
308.15	0.0000	0.79150	2.63940	1383.2	0.0000	0.0000	0.000	
	0.0568	0.82780	2.22070	1415.2	-1.8123	0.0768	-36.036	-31.05
	0.1192	0.84130	1.94040	1448.2	-0.8726	0.1574	-57.627	-39.96
	0.1880	0.88070	1.89770	1451.1	-2.7480	0.2422	-54.799	-38.54
	0.2651	0.90570	1.81650	1493.3	-2.8307	0.3324	-54.963	-51.86
	0.3509	0.94120	1.80900	1533.2	-3.9316	0.4273	-46.861	-62.63
	0.4479	0.97810	1.56590	1565.2	-5.0018	0.5283	-61.162	-62.81
	0.5580	1.01610	1.52870	1598.1	-6.0162	0.6354	-53.522	-58.24
	0.6834	1.06340	1.56880	1599.0	-7.8438	0.7487	-36.573	-37.13
	0.8296	1.09790	1.61350	1649.1	-8.1317	0.8705	-17.018	-28.44
	1.0000	1.06030	1.60760	1719.2	0.0000	1.0000	0.000	

Table2: Values of density (ρ) viscosity (η) ultrasonic velocity (U), Excess volume (V^E), viscosity deviations and (Δη), deviation on isentropic compressibility (Δk_S) for Binary System of Isodecanol(1) with O-Nitrotolune (2) at 298.15 and 308.15 K.

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DETERMINATION OF THE CONDITIONAL STABILITY CONSTANT REAL STABILITY CONSTANT AND CONFIRMATION OF COMPLEX FORMATION BETWEEN Ni(II), Cu(II), Mg(II), Sr(II) METAL IONS AND SOME PEPTIDES BY SPECTROPHOTOMETRIC TECHNIQUE

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ABSTRACT

The spectrophotometric study has been done with a aim of comparing the result obtained by this technique with those of PH-metric technique. PK & LogK values are determined at 0.10 M ionic strength which is maintained constant by addition of appropriate amount of 1.00M Potassium Nitrate solution. Absorption are maeasured by using UV-VIS spectrophotometer model 108(Systronics). some system are studied for determining the metal legand stability constant and confirmation of complexes spectrophotometrically.

Keywords: *Conditional stability constant, confirmation, complexes, peptides, pK, logK.*

INTRODUCTION

Ionic strength is an electrical current produced by the ions of an inert salt in solution. it affects on proton-ligand stability constants (pK) and metal-ligand stability constants (log K)[1]. Manimekalai et al[2] have determined the metal-ligand stability constants and compositions of the 3-(2-furanyl)-2-propenohydroxamicacid chelates by Job's method of continuous variation in 30% ethanol-water mixture. Sawalakhe[3] has investigated the metal-ligand stability constants of substituted pyroxoline complexes with transition metal ions. Narwade et al[4] have studied the conditional stability constants of some substituted isoxazoline complexes with transition metal ions. Bhargava and Tandon[5] have determined metal-ligand stability constants of Pt(IV) with some substituted thiourea complexes. Metal-ligand stability constants and confirmation of complexes of transition metal ions have been studied by Mc Bryde[6] and Banerjee[7].

EXPERIMENTAL

The spectrophotometric study has been done with a limited aim of comparing the results obtained by this technique with those of pH-metric technique. pK and log K values are determined at 0.10M ionic strength which is maintained constant by addition of appropriate amount of 1.00M potassiumnitrate solution. Absorptions are measured by using UV-VIS Spectrophotometer Model 108 (Systronics). Following systems are arbitrarily chosen for determining the metal-ligand stability constants and confirmation of complexes spectrophotometrically. 1:1 and 1:2 complex formations are also investigated for the same systems pH-metrically.

i) Ni(II) - Glutathione (L_2)
ii) Cu(II) - DL-Phenylalanine (L_3)
iii) Mg(II)- Glutathione (L_2)
iv) Sr(II) - Carnosine (L_1)

Methods Used For Confirmation of Complex Formations and Determination of the Conditional Stability

CONSTANTS

Job's Method of Continuous Variation

The same systems are also investigated for determining metal-ligand conditional stability constants using Job's method of continuous variation.The composition of complexes at different pH were confirmed by Job's method as modified by Vosburgh and Robert Gold[8] at pH 2.70, 2.85 and 3.50. Equimolar solutions of metal ion and ligand (peptide) (1.00×10^{-2}M) were mixed in different ratios to prepare Job's solution. Final volume of each solution was made equal to 10 ml after adjusting the appropriate pH and maintaining constant ionic strength (i.e. □ = 0.10M) (by adding calculated amount of 1.00M potassium nitrate solution). In addition to the wave length of maximum (λ_{max}), some other wavelengths were selected as proposed by Vosburgh and Gold[8]. The percentage composition and the values of D are shown in Tables 1 to 4.

The curves were constructed between the values of D and percentage composition of metal ion as shown in Fig. 1 to 4.

where, D = {(optical density of complex solution)˜ (optical density of ligand solution)

It could be seen from above Figures that the compositions of complexes are 1:1 for Ni(II) - L_2, Cu(II) - L_3, Mg(II) -L_2, Sr(II) - L_1 below pH 3.00

Calculation of Conditional Metal-Ligand Stability Constants for 1:1 and 1:2 Complexes

Conditional metal-ligand stability constants were calculated in the present investigation. The concentration of complex (x) in any metal-ligand solution was obtained from Job's curves. If the initial concentrations of metal and ligand in a particular solution are 'a' and 'b', then the equilibrium constant (K) can be determined by the help of simple law of mass action.

$$K = \frac{x}{(a-x)(b-x)} \quad \ldots. (1)$$

$$\text{or } K = \frac{x}{(a_1-x)(b_1-x)} = \frac{x}{(a_2-x)(b_2-x)} \quad \ldots\ldots. (2)$$

The conditional stability constants are found to be lesser than real stability constants obtained from pH-metric technique. This is because the concentration of free acid at a particular pH was not taken into account. The conditional stability constants are converted into real stability constants by the expression given by Banks and Singh[9-10].

RESULTS AND DISCUSSION

Spectroscopic absorptions data obtain are presented in Table 1 to 4. Real stability constants obtained by pH-metric and spectrophotometric techniques are presented in Table 5.

It could be conclude from above Table that the agreement between the values obtained by both the techniques is fairly good. There is no appreciable change in the log K values. This may be due to the fact of attribution to the simultaneous complex formation. It is also observed from above Table that log K values of Cu(II) -L_3 complexes are much less than that of complexes with other ligands due to the presence of phenyl group.

Table - 1
JOBS METHOD
SYSTEM Ni(II)- L_2
λ max. = 400 n.m. Temp. 27± 0.1°C pH = 3.0

% Composition of Metal ion	Optical Density	
	Before Dilution	After Dilution
10	0.054	0.034
20	0.059	0.039
30	0.063	0.044
40	0.069	0.051
50	0.077	0.058
60	0.071	0.049
70	0.065	0.045
80	0.058	0.037
90	0.051	0.033

Table - 2
JOBS METHOD: SYSTEM Cu(II)- L_3
λ max. = 430 n.m. Temp. 27± 0.1°C pH = 3.0

% Composition of Metal ion	Optical Density	
	Before Dilution	After Dilution
10	0.044	0.038
20	0.055	0.041
30	0.066	0.055
40	0.083	0.060
50	0.097	0.065
60	0.071	0.054
70	0.060	0.040
80	0.041	0.035
90	0.035	0.030

Table - 3
JOBS METHOD: SYSTEM Mg(II)- L_2
λ max. = 360 n.m. Temp. 27± 0.1°C pH = 3.0

% Composition of Metal ion	Optical Density	
	Before Dilution	After Dilution
10	0.048	0.038
20	0.064	0.047
30	0.075	0.057
40	0.084	0.066
50	0.089	0.070
60	0.080	0.063
70	0.068	0.051
80	0.057	0.039
90	0.045	0.030

Table - 4
JOBS METHOD: SYSTEM Sr(II)- L_1
λ max. = 380 n.m. Temp. 27± 0.1°C pH = 3.0

% Composition of Metal ion	Optical Density	
	Before Dilution	After Dilution
10	0.067	0.052
20	0.076	0.060
30	0.088	0.070
40	0.098	0.078
50	0.091	0.070
60	0.081	0.060
70	0.070	0.049
80	0.059	0.039
90	0.045	0.031

Table - 5
Comparison of Metal-ligand stability constants (log K) values obtained by pH-metric and spectrophotometric techniques

System	Techniques			
	pH-metric		Spectrophotometry	
	log K_1	log K_2	log K_1	log K_2
Ni(II) -L_2	9.3188	7.2431	9.1629	7.1300
Cu(II) -L_3	8.5070	3.4049	8.6512	3.2530
Mg(II) -L_2	7.7202	4.6098	7. 9080	4.2870

Sr(II) -L_1	8.6964	4.0110	8.6031	4.0230

Fig . 77
Job's Variation Method
System - Ni(II) - (L_2)

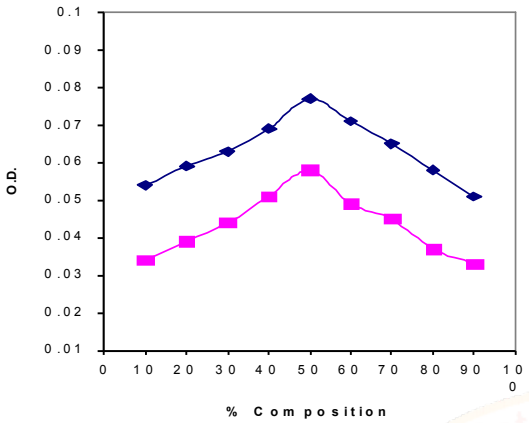


Fig . 78
Job's Variation Method
System - Ni(II) - (L_3)

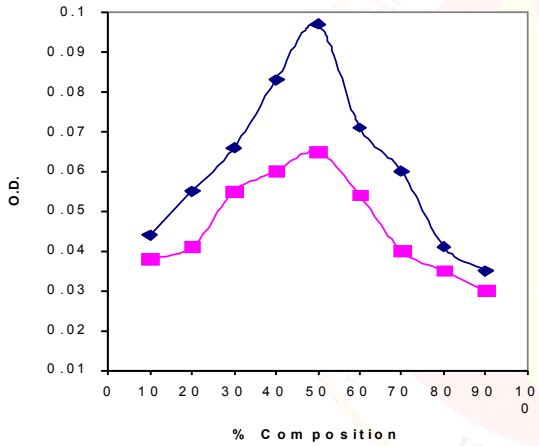


Fig . 79
Job's Variation Method
System - Mg(II) - (L_2)

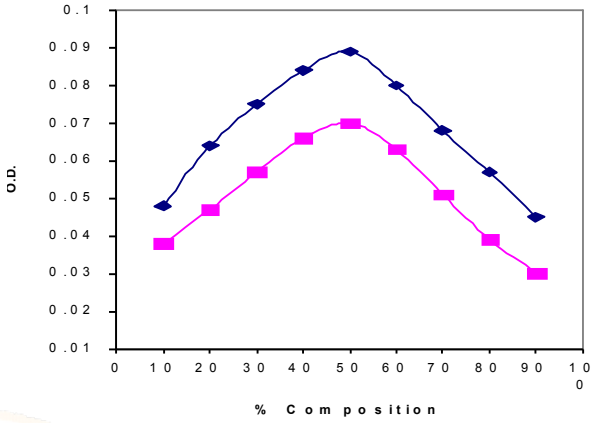
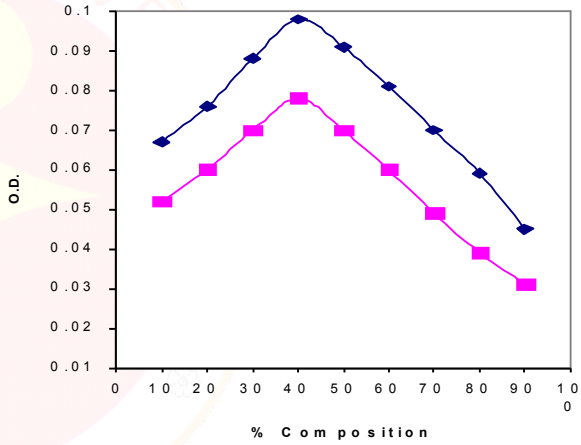


Fig . 80
Job's Variation Method
System - Sr(II) - (L_1)



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ADVENT APPLICATIONS OF NANOMATERIAL AND NANOTECHNOLOGY IN THE VARIOUS SECTOR

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ABSTRACT

Nanoscience and nanotechnology are new emerging fields with great magical applications. Their impacts are on almost every sectors of human life . Nanotechnology is created a revolution in the world performed widespread applications in various areas Nanotechnology encompasses the production and application of physical, chemical, and biological systems . From last many years, researchers, scientists and engineers have succeeded to produced nanoscale materials. Products using nanoscale materials and process are now available in the market and also have been introduced in human life successfully. Though there are few sectors where nanotechnology is not ,almost in every field nanotechnology have performed with great efficiency. In this informative paper, some applications of nanomaterials and nanotechnology have been discussed.

Keywords: *nanotechnology, nanotextiles, nanomedicine, nanofilters ,nanosensors*

INTRODUCTION

The man who lead the whole world towards 'Nano-World' is Nobel Prize-winning physicist Richard Feynman .In 1959 Richard Feynman put the new vision before a world by his words "Plenty of Room at the Bottom" which open the new sector for researchers.. In his talk Feynman reported the unique properties of material at nano level which could lead to new material and new applications in technology.Surface tension and van der Waals interactions contribute major role to be a material at nano level. Nanotechnology has drawn the attention of scientists,researchers, manufacturers,academicians from last many decades. Nanoscience and Nanotechnology is a new and fast growing field that includes the synthesis, processing, and applications of structures, by controlling the shape and size at the nanometer scale with three dimensions of the order of 100 nm or less. It is the nanosize with the chemical composition and surface structure that imparts unique properties as compare to traditional ordinary properties and make it more potential for various applications. Till date there are two ways to synthesize nanomaterials -first is "top down" method, in which nanoscale particles are prepared by breaking up bulk materials, the second one is "bottom up" method in which nanostructures are produced from individual atoms or molecules. At present, there are a number of applications of nanomaterials and nanotechnologies including medicine ,paints, cosmetics,varnishes, coatings, agriculture and food ,information and communication; electronics, environmental protection ,water treatment, solar energy,textile and many more. . As there are various potential uses of nanotechnology in the various fields , only some of the noteworthy applications are highlighted in this paper.

APPLICATION OF NANOTECHNOLOGY IN PHARMACEUTICAL SECTOR

Human health is the topmost priority for effective life processes.Pharmaceutical sector is the leading area where nanotechnology is most beneficial with respect to health as well as researches and industrial development . Although it has increased complexicity yet use of nanomaterial and nanotechnology provide number of advantages specially in drug delivery and diagnosis. Material at nanoscale is more beneficial and provide effective solutions on different physiological, biochemical and pharmaceutical problems and processes. Nanotechnology offers most effective benefits in pharmaceutical field. The most noteworthy advantage of it is to reduction in time consumption in its effectiveness. It has lessen the toxic effects on system. Accurate diagnosis is the prime factor for right treatment.Nanosize devices are now playing a vital role to diagnose the disease speedily and precisely. Target oriented controlled drug delivery is the another equally important for effective result.Nanomedicines are the promising composition to fulfill the requairements.Nanosurgical devices are known for

its successful desired or intended,precised result.Cost effective with less time and large-scale production is also a great feature of nanotechnology. With reference to above mentioned benefits, there are various profitable applicationswhere nanotechnology have gained significant developement in pharmaceutical and biomedical areas.

APPLICATION OF NANOTECHNOLOGY IN TEXTILE SECTOR

The benefits of nanotechnology in the textile market also has become fast growing because of its unique and esteemed properties. There are considerable economical ,value added applications of nanotechnology in textile industries, processing units and products. The nanotechnology has produced multifunctional effect on textiles and designed fabrics with special qualities antimicrobial, anti-odour wrinkle free, UV protection, easy-clean, water and stain repellent,etc.This is possible due to effective use of nanomaterial and nanotechnology than that of traditional methods which are used to since years and years. Traditional methods failed to impart permanent properties to fabric .

Inorganic nanomaterials like metal oxides have proven result oriented potential UV blockers because of its virtuous charecterastics.The reason is nanosize make them more effective for absorption and scattering of UVradiation. Large surface area per unit mass and volume increases UV radiation blocking property of nanomaterial. Nano metal oxides that are mostly use in textile sector are such as titanium oxide, zinc oxide, aluminium oxide etc. because of its unique properties.

Another important charecterastic of smart fabric is it should be free from harmful bacteria. Nanomaterials specially nano silver metal and some metal oxide plays a vital for the same purpose because of its précised properties.Material must have foresaid properties to act as a antibacterial like,resistance to the growth of those bacteria which are responsible for infection,resistance to cellular metabolism and inhibit cell growth, reduces the respiration process.Nano silver is the most result oriented and fulfill the requairements metal so it has been widely used in textile areas.

The water-repellent property of fabric is created by nano-whiskers. Tinywhiskers allineated by counteractant “spines” are fabricated to resist liquids and stick to the fibers with the help of molecular "hooks”. These nanowhiskers and hooks are prominently made up of hydrocarbons and are infinitesimaly small ,in fact no more than 1/1000 of the size of a typical cotton fibre. The spaces between the whiskers on the fabric are smaller than the typical size of drop of water.So water is not absorbed by the top of the whiskers and remain on the surface of the fabric. As the whiskers are of nanosize, they do not create adverse effect on breathability of fabric. However, liquid can still pass through the fabric, if pressure is applied. Wrinkle resistant finishes on cotton fabrics is done generally by moderate use of resin through traditional methods though resin has some disadvantageswise lowering tensile strength of fibre, abrasion resistance, water absorbency and dyeability, as well as breathability. The use of nanometal oxides and nano-silica with resin, elevate the wrinkle resistance of cotton and silk respectively

APPLICATION OF NANOTECHNOLOGY IN CEMENT AND CONCRETE MATERIAL

The nanotechnology to conceive of innovation in infrastructure systems has the ability to alter the civil engineering practices and impart the new vision to civil engineering. civil engineering with design and construction processes is benefited from nano technology. The advanced nano structural materials with impressive properties, stronger and lighter composites, nanocoating, nano-clay filled polymers, self-disinfecting surfaces, water repellents, air cleaners, nano sized sensors, etc. Civil engineering is related with cement, sand, stone and aggregate. Application of Nanomaterials enhance the properties like the compressive strength and ductility of concrete due to the availability of large surface area through filling the nanopores of the cement paste. Nanosilica and nanometaloxide are additives used in concrete. Carbon nanotubes have also been used to intensify strength, modulus and ductility of concretes. Durability of concretes can also be modified through reduced permeability and improved shrinkage properties

APPLICATION OF NANOTECHNOLOGY IN WATER PURIFICATION

Nanotechnology gives a low-cost effective remedies to clean and safe water for millions of people. The nanotechnology provide the potential to curtail the steps, materials and energy require to purify water.Nanomaterials can be modified with specific pore sizes and large enhanced surface areas to filter out pollutants, such as heavy metals or biological toxins.Nanosize titanium oxide is used to

degrade organic pollutants and nanosilver particles are beneficial to degrade biological pollutants such as bacteria. Various membranes and filters of carbon nanotubes, nanoporous ceramics, magnetic nanoparticles and other nanomaterials are employed to abolish water-borne diseases such as typhoid and cholera as well as toxic metal ions, organic and inorganic solutes. Nanofiltration membranes – These are already being applied for removal of dissolved salts from salty water, removal of micro pollutants, water softening, and wastewater treatment. Nanofiltration membranes are specifically use to remove pollutants,as well as to protect nutritious value of water to perform the normal biological life processes of the body. Nanomaterial like Attapulgite clay, zeolite, and polymer filters are useful for filtration of water because of its controlled pore size of filter membranes. Nanocatalysts and magnetic nanoparticles degrade pollutants instead removing them for which available technologies are not proven fruitful.Magnetic nanoparticles coated with different compounds are used to remove pollutants, including arsenic, from water. Nanosensors are used to findout chemical and biochemical parameters in water.

CONCLUSION

Today,in all over the world the most creative researchers, scientists and engineers are toiling to find out new ways to potential use of nanoscience and nanotechnology to modify the world in which human beings live.They tries to provide advanced lifestyle in smart world through new materials, designed at the atomic and molecular level, provide realistic,cost-effective methods for the potential application of nanomaterial. Doctors diagnose the disease at its earliest stages and treating illness such as cancer, heart disease, and diabetes with most effective and safer medicines. They produced new technologies to manufacture smart fabrics loaded with many outstanding qualities . They are successful to impart nanoparticles constructing material and make the structure durable.Amazing success in the field of water purification processes made the billions of people free from water borne diseases.This is not enough as there are many challenges, fields where the scientist have vast scope for researches surely nanotechnology has the strength to find out solution for every problem.

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SYNTHESIS, CHARACTERIZATION AND ANTIMICROBIAL ACTIVITY OF SOME HALO-SUBSTITUTED CHALCONES.

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ABSTRACT

In the present work author reported the synthesis of some halo substituted chalcones.The synthesis was carried out in alcoholic potassium hydroxide at room temperature by ClaisenSchmidt condensation reaction. The compounds were obtained in good yield by using this method. These synthesized compounds were characterized by FT-IR and H-NMR spectral data. These compounds were evaluated for biological activity against the some gram positive and gram negative bacteria and against some fungus. These halo substituted chalcones show good Inhibition activities.

Keywords: *Chalcones synthesis, gram + gram –ve bacteria, biological activity.*

INTRODUCTION

Chalcone is the trivial name given to the α β-unsaturated ketones obtained by condensing an aromatic aldehyde with an aryl methyl ketone in the presence of a base. The chemistry of chalcones has generated intensive scientific interest due to their biological and industrial application. Chalcones are natural biocides and are well known intermediates in the synthesis of heterocyclic compounds exhibiting various biological activities. Chalcones and their derivatives possess some interesting biological properties such as antibacterial, antifungal, insecticidal, anesthetic, anti-inflammatory, analgesic etc.

Renate *et al*[1]. Have reported the synthesis of an acetylenic chalcones. The new acetylenic chalcones were evaluated for antimalarial and antitubercular activity. The antimalarial data for this series suggests that growth inhibition of the W2 strain of *Plasmodium falciparum* can be imparted by the introduction of a methoxy group ortho to the acetylenic group. Most of the compounds were active against *Mycobacterium tuberculosis* H37Rv.

Babasaheb *et al*[2]**.** Have reported synthesis and biological evaluation of β-chlorovinyl chalcones. All these compounds were evaluated for their anti-inflammatory activity and antimicrobial activity. Most of these compounds showed very good antibacterial and antifungal activity.

Anindra *et al*[3]. Have reported synthesis of (2*E*)-1, 1-(3-hydroxy-5-methylbiphenyl-2,6- diyl)-bis(3-pheylprop-2-ene-1-ones. In this case the new chalcones were prepared by the reaction of 1, 3-diacetyl biphenyls with different aldehydes in presence of catalytic amount of solid potassium hydroxide in ethanol with excellent yields. The synthesized compounds were evaluated for anticancer activity against human breast cancer MCF-7 (estrogen responsive proliferative breast cancer model) and MDA-MB-231 (estrogen independent aggressive breast cancer model) cell lines, HeLa (cervical cancer) cell line, and human embryonic kidney (HEK-293) cells. Most of the compounds preferentially inhibited the growth of the aggressive human breast cancer cell lines.

Zohreh *et al*[4]**.** Have reported synthesis of novel chalconoids containing a 6-chloro-2H-chromen-3-yl group. The target compounds were evaluated against the promastigote form of *Leishmania major* using MTT assay. These compounds have shown high *in vitro* antileishmanial activity at concentrations less than 3.0 μM. The results of cytotoxicity assessment against mouse peritoneal macrophage cells showed that these compounds display antileishmanial activity at non-cytotoxic concentrations.

Jen-Hao *et al*[5]. Have reported synthesis of 2, 5-dialkoxylchalcones by Claisen–Schmidt condensation of appropriate acetophenones with suitable aromatic aldehydes. The novel 2,5-dialkoxylchalcones were evaluated for their cytotoxic, anti-inflammatory, and anti-oxidant activities.

Julio *et al*[6]**.** Have reported solution-phase parallel synthesis of substituted chalcones and their antiparasitary activity against *Giardia lamblia.*

Anastasia *et al*[7]**.** have reported synthesis, characterization and evaluation of 2-hydroxy-chalcones and aurones as antioxidant and soybean lipoxygenase, an extensive structure-relationship study was performed and revealed that several chalcones and aurones possess an appealing

pharmacological profile combining high antioxidant and lipid per oxidation activity with potent soybean LOX inhibition.

Kakade *et al*[8]. Have reported synthesis, characterization and biological significance of some substituted novel chalcones.

MATERIAL AND METHODS

4-bromoacetophenone, anisaldehyde, cinnamaldehyde, KOH all taken are of high purity. Instrumental method: IR recorded on Perkin Elmer 237 spectrophotometer and H^1 NMR were recorded on Bruker advance II 400NMR spectrometer. Disc diffusion method for antimicrobial activity. This method applied for screening the synthesized compounds againsed various gram positive and gram negative bacteria.

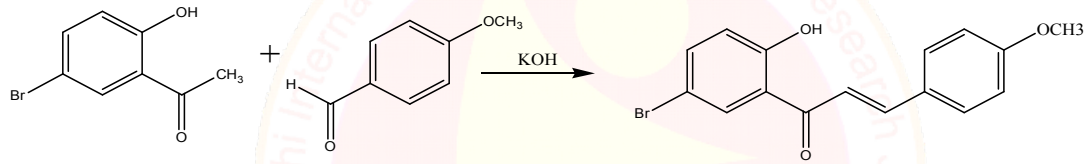
EXPERIMENTAL SECTION

Synthesis of chalcone:

The compound were synthesized by using claisen condensation reaction, the chalcones of 4-bromo acetophenone with substituted aldehydes were prepared. The substituted aldehydes used are anisaldehyde and cinnamldehyde. The synthesized compounds were purified by using alcohol like ethanol. The purity was checked by TLC.

Synthesis of chalcone from Anisaldehyde (L2):

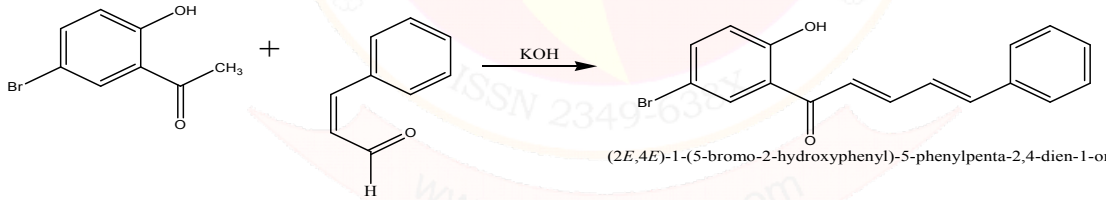
The alcoholic solution of anisaldehyde was added slowly into the alocoholic solution of 4-bromoacetophenone with constant stirring. Then solution of potassium hydroxide (30%) was added with vigorous stirring, the reaction mixture was kept overnight. Then the crude product was obtained by acid workup. The obtained product was crystallized by ethanol (Figure 1)



(*E*)-1-(5-bromo-2-hydroxyphenyl)-3-(4-methoxyphenyl)prop-2-en-1-one

Synthesis of chalcone from Cinnamldehyde (L6):-

The alcoholic solution of cinnamaldehyde was added slowly into the alocoholic solution of 4-bromoacetophenone with constant stirring. Then solution of potassium hydroxide (30%) was added with vigorous stirring, the reaction mixture was kept overnight. Then the crude product was obtained by acid workup. The obtained product was crystallized by ethanol (Figure 2)



(2*E*,4*E*)-1-(5-bromo-2-hydroxyphenyl)-5-phenylpenta-2,4-dien-1-one

Table1: Physical data of compounds

Sr. no	Compounds	Molecular formula	Colour	Melting Point	Nature
1	L2	$C_{16}H_{13}O_3Br$	Yellow	72°C	Crystalline
2	L6	$C_{17}H_{13}O_2Br$	Dark Yellow	80oC	Crystalline

Table 2: The FTIR spectral analysis of compounds (V=cm$^-$)

Sr. no	Compounds	C=C	Ar-OCH_3	C=C conjugation	Ar-Br	C=O	C-H	-OH
1	L2	1610	2560	3600	820	1570	2895	3125
2	L6	1622	-	3640	826	1570	2898	3130

Table 3: The H1 NMR of compounds (σ in ppm)

Sr.no	Compounds	σ in ppm	No of Proton	Assignment
1	L2	7.18	1H	Ar-H
		5.0	1H	Ar-OH
		7.56	1H	CH-H
2	L6	7.21	1H	Ar-H
		6.65	1H	CH-H
		7.81	1H	Ar-OH

Table 4: Analysis of antimicrobial activity of chalcones.

Sr.no	Compounds	staphylococci	E-Coli	candidaalbicans
1	L2	10mm	12mm	12mm
2	L6	14mm	10mm	16mm

CONCLUSION

The synthesized series of chalcone under mild condition and evaluated for their antibacterial and antifungal activity. All synthesized compounds were found to be potent antifungal and antibacterial agents. It is to be noted that chalcone of cinnamaldehyde found to be much more potency with respect to other chalcone.

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USE OF NATURAL FOOD ADDITIVES FROM HYDROCERUS UNDATUS (DRAGON FRUIT) IN FOOD INDUSTRY- A GREEN STEP IN GREEN CHEMISTRY.

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ABSTRACT

Natural food colour in any dye obtained from any vegetable, animal or mineral which is capable of colouring food, drugs, cosmetics or any part of human body. These natural colour or additives come from variety of sources such as seeds, fruits and vegetables, leaves algae and insects.Sometimes due to lack of knowledge the applications of these additives are not widely used.Dragon fruit or pitahya is one of the tropical fruit which has low calories and filled with various nutritive elements ,vitamins and antitoxidants. Dragon fruit is cultivated in India by farmers .In Maharashtra, area like karjat, solapur and Pune and even in certain places of Hydrabad.Dragon fruits is also called as strawberry pear. Dragon fruit colouring powder named (DFCP)as a natural food additive using dragon fruit albedo which is nothing but thin layer of dragon fruit peel. The albedo of dragon fruit is dried and use to colour various food stuffs. In this study, a conventional method was used to access the albedo powder and as a additive in a similar process to saffron as a food colouring .To prepare powder from albedo the dragon fruit was dried on a stove after outer layer was peeled .Heating at low temperature is one of the conventional method for drying dragon fruit albedo . Using DFCP as natural food colourant is healthy for humans and also ecofriendly to society.

Keywords: *Albedo, dragon fruit, peel , conventional.*

INTRODUCTION

Dragon fruit is one of the tropical fruit which has low calories and filled with various nutritious elements, vitamins and antitoxidants. Though the dragon fruit is popular in several American and South Asian countries but due to its delicious taste and health benefits it is becoming popular in India too.

In India the crop is cultivated by formers in areas like, Karjat, Solapur, and Pune in Maharashtra and even in certain places of Hydrabad.

Since this plant is from cactus family it requires less water.

Traditionally people use natural colour which obtained from nature. We use turmeric, saffron, various flower petals, paprika and beet extracts as yellow, orange, red etc. colours into various food stuffs which plays vital role for human health. (Arnell, Need, M. 2011).

In the beginning of 20th Century, numerous synthetic food additives had been produced, however only few synthetic colours approved to be used since the banned items have been identified as being potential cancer – causing chemicals. According to FDA, since 1955, the trend of synthetic food consumption has been stronger. The excessive increase is due to higher consumer on processed food, such as soft drinks, breakfast cereals, candies, \Snacks, food, baked food, frozen desert, pickles, salad dressing. Where synthetic colours being used on large scale. However, it is challenge how we replace synthetic food colouring with natural one.

To overcome such problem using dragon fruit albedo namely Dragon fruit colouring powder (DFCP). It is tremendously healthy and attractive especially for consumers. Developing DFCP as the natural food colorants is not healthy for human body but also eco-friendly to society. It is estimated to cost effective as it is sourced from the only disposable part (peel) of the fruit. The DFCP has several properties compared to the extracted flesh from fruit, which is feasible to carry, packing and less space for storing.

"Red pitaya" or dragon fruit has rich sources of vitamins eg. B1, B2, B3 and C, minerals eg. Potassium sodium, calcium, iron and phosphorous and nutrients eg. fat, protein carbohydrate, flavonoids, crude fiber, thiamin, phytoalbumin, niacin, pyridoxine, glucose, betacyanins, phenolics, carotene and polyphenol (Le Bellec *et al.*, 2006). It has relatively high antoxidant activity in comparison with other subtropical fruits (Davis

et al., 2007). Betalins, for the first time extracted from red beet (Beta vulgaris) and is used largely for food colouring additives and the extract includes red and yellow pigments namely beta cyanins and betaxanthins respectively.

Due to unfavourable earthy favour of geosmin and pyrazine derivatives as well as possibilities of carcinogenic nitrosamines in red beet, there is a high demand to replace this source (Esquivel, Patrica *et al.,* 2007).

Since Betacyanin is the main component (95%) of the red pigment extract, in addition dragon fruit peel includes betacyanin can make contribution to produce beauty and health products (Arrifin AA, Bakar J., *et al*., 2008). Since dragon peel contains betalins and lacks disadvantages of beet root, it can be replaced as a new red dye. The flesh of dargon fruit according to a study of Luders and McMahon, (2006), can be mixed with milk, soft drink, ice used jellies.

MATERIALS AND METHOD

Dragon fruit peel has a high potential to be used as natural dye Harivaindaran *et al.,* (2008). The inner layer of dragon fruit peel i.e. Albedo can have high potential as a colour powder and a natural food additive.

In this study, a conventional method was used to assess the albeda powder as a food additive in a similar process to Saffron as a food colouring.

To prepare powder from albedo, the thick dragon fruit was dried on stove after the outer layers was peeled. Heating method as one of the conventional method for food drying was used to dry dragon fruit albedo. Both the sides of the Albedo were evenly dried for approximately one hour with low temperature. The dried layer was then ground in a mortar and pestle to make a fine powder, which was filtered through a strainer and dissolved in boiling water.

The prepared solution of dragon fruit albedo was then added to milk, yogurt, pastry, juice and rice in order to test dragon fruit albedo has ability to change colour.

RESULTS AND DISCUSSION

DFCP is a natural food additive by using dragon fruit albedo. In the previous study researchers have found that the red peel of dragon fruit contains varieties of vitamins, minerals and nutrients with remarkable amount to antioxidant compounds compared to other subtropical fruits. It has a source of functional ingredients that provide nutrients to prevent nutrition related diseases and improvement and physical well-being of the consumers.

Through a conventional method in this study, different parts of dragon fruit eg. outer layer inner layer (albedo) and flesh were used. However only the albedo part was successful in the preparation of powder.

Concern study revealed that consumer prefer chemical free products especially when it is related to food consumption. The process to prepare dragon fruit powder is also believed to be less time consuming. In the economics of scale of the production, it is also expected that they can produce with less time.

In conclusion, the albedo powder of dragon fruit can be used for food colouring. In order to mass production of DFCP, where would be a need for future research in wider perspective to introduce this new product.

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GREEN APPROACH FOR THE SYNTHESIS OF OXIMES USING SILICA SUPPORTED PERCHLORATE IONIC LIQUID.

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ABSTRACT

The present work deals with the synthesis of Silica supported ionic liquids ($SilprClO_4$) from the Silica gel, 3-chloropropyl triethoxy silane, Imidazole and butane sultone. further perchlorate ion intoduced by reacting chloropropyl silica sultone (SilImps) with perchloroic acid. The synthesized Silica supported imidazolium perchlorate ionic liquid ($SilPrClO_4$) catalyst tested efficasy towards the synthesis of amide derivatives via oxime. The developed catalytic system has shown good activity towards amide Synhesis. The structure of the synthesised catalyst was interpreted by various spectroscopic technique like IR and SEM-EDAX. Also all the Oxime and amide compounds have been confirmed by spectral interpretation as ^{1}H-NMR & ^{13}C NMR, and IR spectroscopy.

Keywords:- *Ionic Liquids, Imidazolium, Perchlorate, Silica Supported, Oximes.*

INTRODUCTION

In recent years, the use of heterogeneous catalysis has received universal attention that offers a clarification for the major drawback of homogeneous catalysis. From both an industrial and an environmental point of view, this method is very interesting, since it allows the upcoming application of heterogeneous catalysts in the synthesis of cost-effective products, leading to rapid, clean and selective green industrial processes. Supported ILs catalysis is an idea which combines the benefits of ILs with those of heterogeneous support materials. The feasibility of this model has been established by several studies which have effectively restrained various ionic phases to the surface of support materials and discovered their prospective catalytic uses. Heterogenisation of catalysts can offer advantages in handling, separation and recycling [1,2]. By supporting ionic liquids, the required amount of the ionic phase can be significantly reduced. In addition, it enables the use of fixed-bed reactor systems [2]. Three main methods of immobilisation of an ionic liquid on a silica support, namely, via an anion, via a cation and physically supported liquid phase (SILP) were described.

Supported ionic liquid phase (SILP) catalysis has been developed to address these issues. SILP materials are prepared by overlaying an IL over a solid support with a high surface area. The resulting material appears as dry solid but up-close contains the active species as a thin liquid film in its pores [3]. SILP catalysts combine the benefits of high activity and selectivity from homogeneous catalysts with that of the recyclability, large surface area and hydrothermal stability of heterogeneous systems [4]. Various organic reactions such as hydroformylation [5], esterification [6], polymerization [7], amination [8], dehydration [9] and metal scavenging systems [10] have already been performed using SILP catalysts. In biomass pretreatment, SILP catalysts bearing Brønsted acidic groups could be more advantageous since they can effectively hydrolyze the biomass and be re-used multiple times. Acidic counter-anions such as HSO_4 anion [3, 10–12] and polyoxometalate species [13,14] have already been employed as SILP catalysts and used in various reactions. However, the use of SILP catalysts in biomass hydrolysis has been scarce. A sulfonic acid functionalized IL supported on silica gel was reported previously for the hydrolysis of cellulose using 1-n-butyl-3-methylimidazolium chloride ([BMIM]Cl) as solvent [15]. But the use of a large amount of IL as solvent during hydrolysis would not make this system economically feasible.

From last two to three decades it was observed that many of the silica supported ionic liquids contain hydrogen sulphate as anion. Majority of the reaction have main disadvantage of solubility for starting materials. Till now no one focus on ionic liquids which having perchlorate anions as it these are of great chemical interest and importance, because they possess several unique properties,

behaving as problem-solving reagents and enabling new and unusual chemistry. They have a large degree of ionic character; the perchlorate ion, in fact, has a very high electronegativity, which corresponds to high solvation energy.

Oximes are vital intermediates for many functional group transformations. These compounds were successfully transformed into amides. Among the numerous methods for the synthesis of oximes involved use of some catalysts which are not entirely environmental friendly. Supported ionic liquids play a vital role as dual catalyst and green solvent having enormous application in synthetic organic chemistry due to their peculiar chemical and physical properties, such as good recyclability and stability in air and moisture. Review of literature tells us that, oxime synthesis can be cared out using protic acid like H_2SO_4 or many other compounds like $POCl_3$, $ZnCl_2$, $AlCl_3$. Due to wide range of application of oxime derivatives precurser for the synthesis of aliphatic and aromatic amide compounds in pharmaceutical industries for the synthesis of drugs. It was thought to synthesize the oxime derivatives using heterogeneous greener $SilPrClO_4$ ionic liquids as a catalyst.

MATERIALS AND METHODS

Silica gel (230-400) mesh, pore size 60A and imidazole was purchased from LOBA chem India. 3-chloropropyl diethoxysilane and 1,4 butane sultone, were, purchased from sigma- Aldrich toloune ethanol, methanol acetone, hydrochloric acid, perchloric acid, ethyl acetate, n-hexane and petroleum ether were purchased from Merck.

A) Characterization techniques

NMR spectra were recorded in $CDCl_3$ on Bruker spectrometer operating at 400 MHz and the chemical shifts are given in ppm downfield from TMS (δ = 0.00). FT-IR spectra of the Silica supported catalysts and oximes derivatives were obtained from IR affinity- 1 Shimadzu FT-IR spectrophotometer using KBr pellet method. The surface morphology of catalyst was observed from FESEM Supra 55-CARL ZEISS, Germany.

B) Procedure for Synthesis of Silica Supported Catalyst:

1) Synthesis of Chloropropyl Silica (SilPrCl)

The silica gel supported acidic ionic liquid was synthesized according to the literature. First the silica gel was activated by immerisation in hydrochloric acid for 24 hr and then washed with deionized water to natural and dried it in oven at 80°c for 24 hr. the activated silica gel (10 g) was suspended in 10 ml of dry toluene in a 250 ml flask and then 3-chloropropyl triethoxy silane 10 g was added. The mixture was refluxed with stirring for 48 hr under dry atmosphere. After the suspension was cooled to room temperature, which was transferred to a Buchner funnels and washed alternately with toluene, ethanol and methanol there times. After drying under vacuum at 70°c for 8 hr, chloropropyl silica (abbreviated as SilPrCl) was obtained as a white powder.

2) Synthesis of Chloropropyl Silica Imidazole (SilPrIm)

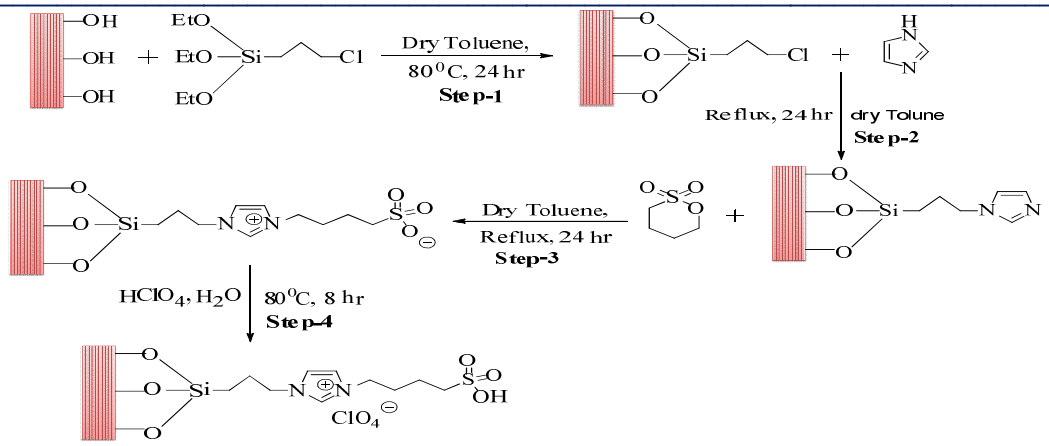
10 g of SliPrCl was added into a flask containing 80 ml of toluene as solvent and an exess of imidazole (10 g) was added subsequently. The suspension was mechanically stirred and refluxed for 24 hr. after cooling to room temperature; the mixure was transferred to a Buchner funnel and alternatively wash with toluene, ethanol, methanol and acetone three times. The silica chemically bonded imidazole abbreviated as SilPrIm was dried at 60°c for 8 hr.

3) Synthesis of Silica Propyl Imidazoilum Sultone (SilImPs)

10 g of SilPrIm and a large excess of 1,4 butane sultone were added in a 250 ml flask containing 80 ml of toluene. The mixture was refluxed with magnetic stirring for another 24 hr to undergo a condensation reaction to from the silica chemically bonded sultone, abbreviated as Si1ImPs, which was dried at 60°C for 8 hr.

4) Synthesis of Silica Propyl Imidazolium Sulphonic perchlorate ($SilPrClO_4$)

Finally, 5 g of Si1ImPs was added into a flask containing 50 ml of double distilled water, and an equimolar amount of perchloric acid was added drop wise. The mixture was refluxed at 80 ºC for 8 hr with mechanically stirring. The solvent then was removed under reduced pressure and a white powder was obtained. The product was dried under vacuum at 70 °C for 8 hr.



Scheme 1: Synthesis of Silica Supported Catalyst

C) General procedure for oxime synthesis

In a round-bottomed flask (25 mL) equipped with a condenser, a solution of Aldehydes (l mmol) NH_2OH•HCl (1.5 mmol) and $SilPrClO_4$ (50 mg) was prepared. The mixture was stirred at 50 ºC conditions for 30 min. The progress of the reaction was monitored by TLC. After completion of the reaction, acidified the reaction mixture with 2 % $HClO_4$ (around 10 mL) and the reaction mixture was continued to stirring for 5 min and filtered to remove $SilPrClO_4$ catalyst. From the filtrate, the product has been extracted with $CHCl_3$ (3 x15 mL). The mixture was dried over anhydrous Na_2SO_4. Evaporation of the solvent and a short column chromatography of the resulting crude material over silica gel (eluent; n-hexane/ethyl acetate: 8:2) afforded the pure oxime.

Spectral data of Oximes:

***o*-Hydroxybenzaldehyde Oxime:** ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.91-6.99 (m,1H), 6.99-7.01 (d,1H), 7.17-7.19 (q, 1H), 7.27-7.31 (m, 1H), 8.23 (s, 1H), 10.1 (bs, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 116, 119, 130, 131, 137, 153, 157. FT-IR (KBr, ν/cm^{-1}): 3419, 3124, 3057, 2933, 2852, 1664, 1558, 1438, 1279, 1195, 1018, 950, 796, 657, 623.

***m*-Nitrobenzaldehyde Oxime:** ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.55-7.59 (t, 1H), 7.89-7.91 (Dd, 1H), 8.21-8.27 (m, 1H), 8.42 (t, 1H),). ^{13}C-NMR (100 MHz, $CDCl_3$): δ.121.9,124.5, 129.9, 132.6, 133.9, 148.3, 148.7. FT-IR (KBr, ν/cm^{-1}): 3410, 3199, 3057, 2875, 1666, 1438, 1359, 1188, 1138, 1029, 843, 656.

***p*-Hydroxybenzaldehyde Oxime:** ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.78 (d, 2H), 7.78 (d, 2H), 9.77 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$; FT-IR (KBr, ν/cm^{-1}): 3414, 3196, 2931, 2875, 1666, 1560,1434, 1263, 1166, 1016, 900, 750, 682.

Anisaldehyde oxime: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.83 (s, 3H), 6.92-6.90 (d, 2H), 7.53-7.50 (d, 2H), 8.1 (s, 1H), 8.6 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 55.4, 114.3, 124.7, 128.6, 150.0, 161.1 FT-IR (KBr, ν/cm^{-1}): 3431, 3223, 3068, 2980, 2050, 1670, 1560, 1448, 1367, 1253, 1197, 1031, 939, 773, 758, 569.

Acetophenone Oxime: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.33-7.27 (m, 2H), 7.39-7.34 (m, 2H), 7.49-7.44 (m, 1H), ^{13}C-NMR (100 MHz, $CDCl_3$): δ 128.4, 129.1, 129.4, 133.5, 137.7, 159.0, 190.0. FT-IR (KBr, ν/cm^{-1}): 3775, 3226, 3070, 2966, 1687, 1562, 1433, 1263, 1193, 1134, 860, 761, 586.

Benzophenone Oxime: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.50-7.46 (m, 5H), 7.59-7.57 (d, 2H), 7.81-7.79 (t, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): 129.9, 130.1, 130.3, 132.5, 137.4, 195.0. FT-IR (KBr, ν/cm^{-1}): 3442, 3388, 3223, 3068, 2951, 1681, 1560, 1485, 1433, 1251, 1188, 1130, 921, 761, 580.

RESULT AND DISCUSSION

In this work, we report the synthesis of a new Silica Propyl Imidazolium Sulphonic perchlorate ($SilPrClO_4$) catalyst and studies their application in operationally simple, safe and fast method for the oxime synthesis for aromatic aldehyde without any additional organic solvent. The FT-IR spectral investigations depicted in Figure 1. FT- IR spectrum (A) SiO_2 shows the mainly contain Si-O-Si bond, the characteristic absorption peaks of Si-O-Si (1058 cm^{-1}) and Aliphatic C-H Strectchng in (B) SilPrCl shows peaks at 2910 cm^{-1}. Compound (C) SilPrIm contain C=C Stretching frequency at 1542 cm^{-1} of imidazole and C=N frequency at 1446 cm^{-1} After reaction with butane sultone the compound (D) SilImPs having various peaks at 1031, 1161 (Si-O stretch), 1643 (Aromatic C=C stretch), 2968 cm^{-1} (aliphatic C-H stretch) indicate butane sultone attached to soild support of silica gel. Finally broad peak at

3441cm^{-1} frequency indicate sulphonic acid O-H strecthing as depicted in figure 1. The surface morphology and the presence of Silcon after the adsorption was confirmed by using SEM and EDX in figure 2.

After synthesis of new Silica Propyl Imidazolium Sulphonic perchlorate ($SilPrClO_4$), We have examined the catalytic activity of our $SilPrClO_4$ towards the solvent free synthesis of different kinds of oxime using different aromatic aldehydes and ketones. Based on the litarature survey, we have carried out reaction of aromatic aldehyde and ketones with hydroxyl amine hydrochloride at 50 °C for for 30 minutes. Intially we have carried out the reaction of *o*-hydroxy benzaldehyde with hydroxyl amine hydrochloride at 50 °C for for 30 minutes got moderate yield of *o*-Hydroxybenzaldehyde Oxime 80% (Table 1 entry 1). Further the present protocol in presence of $SilPrClO_4$ catalyst show moderate to good yield for the preparation of m-nitro benzaldehyde oxime, 90% (Table 1 entry 2) and p-hydroxy benzaldehyde oxime 91% (Table 1 entry 3).

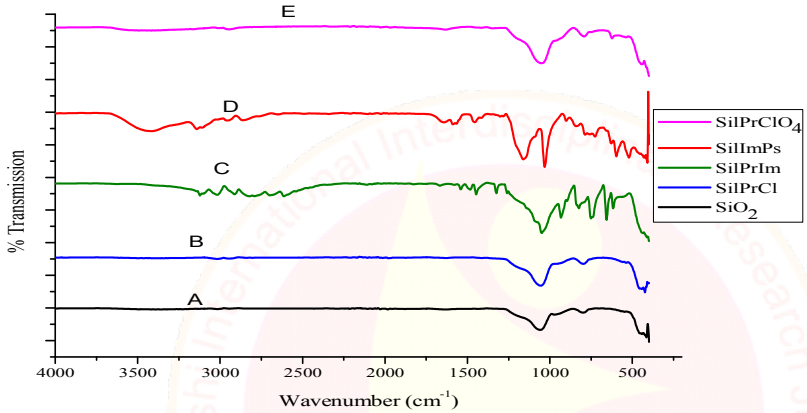


Figure 1. Solid state FT-IR spectra of (A) SiO_2, (B) SilPrCl, (C) SilPrIm, (D) SilmPs and (E) $SilPrClO_4$.

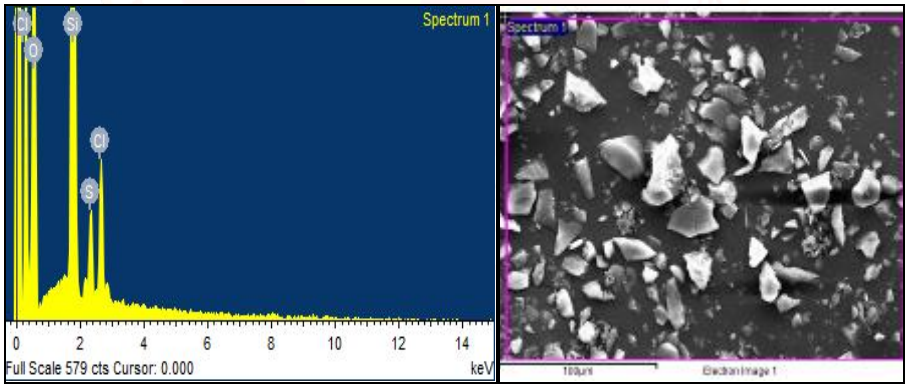
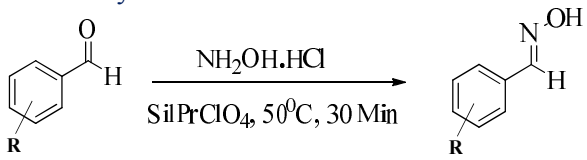
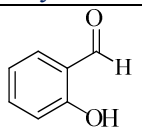
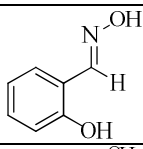
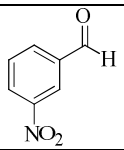
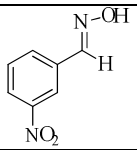
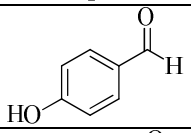
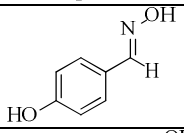
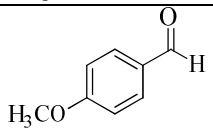
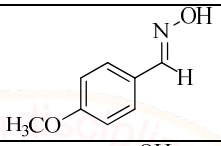
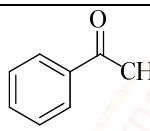
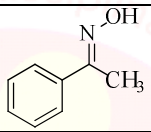
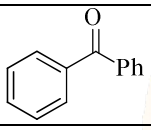
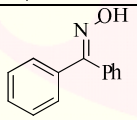


Figure 2. SEM and EDX image of $SilPrClO_4$.

The efficacy of Silica Propyl Imidazolium Sulphonic perchlorate ($SilPrClO_4$) Catalyst tested towards the ketone like Anisaldehyde, Acetopheneone and Benzophenone for oxime synthesis. All the ketones gives good yield (Table 1 entries 4 to 6).

Table 1. Synthesis of Oxime



Entry	Aldehyde/Ketone	Product	Yield (%)	MP (°C)
1			80	62-64
2			91	78-80
3			90	63-65
4			92	61-63
5			89	58-60
6			90	138-143

CONCLUSION

The oximation of aromatic aldehydes and ketones with hydroxyl amine hydrochlorde was accomplished using Silica Propyl Imidazolium Sulphonic perchlorate ($SilPrClO_4$) as catalysts without any solvent. $SilPrClO_4$ has shown the good efficiency for the oximation reactions with maximum yield in less reaction time. In these reactions, sulphonic acid based carrying perchlorate anion $SilPrClO_4$ leading to a decisive role for activating the aldehyde group. Moreover, the present protocol remains an effective and environment friendly alternative for production of oxime. Further, catalytic activity of the $SilPrClO_4$ catalyst is under process in our laboratory for preparation of more derivative of Oximes.

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SYNTHESIS, CHARACTERIZATION AND THERMAL STUDIES OF SYMMETRICAL SCHIFF BASE COMPLEXES OF 1-(2-HYDROXY-5-METHYL-3-NITRO PHENYL) ETHANONE(2S)-2-AMINO-3-(1H-INDOL-3-YL) PROPANOIC ACID

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ABSTRACT

New mono nuclear Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes with Schiff base derived from the condensation of 1-(2-hydroxy-5-methyl-3-nitro phenyl) ethanone and (2S)-2-amino-3-(1H-indol-3-yl) propanoic acid were synthesized. The complexes were characterized by elemental analyses, ^{1}HNMR, IR spectral studies, magnetic moment and thermal analyses. From analytical data, the synthesized complexes have shown 1:2 (metal:ligand) stoichiometry. Free ligands and some new complexes have also been studied for their thermal analysis. All synthesized complexes undergo stepwise decomposition as two, three or multi step and the final products as respective metal oxides.

Keywords: *(2S)-2-amino-3-(1H-indol-3-yl) propanoic acid, IR, Elemental and Thermal analysis.*

INTRODUCTION

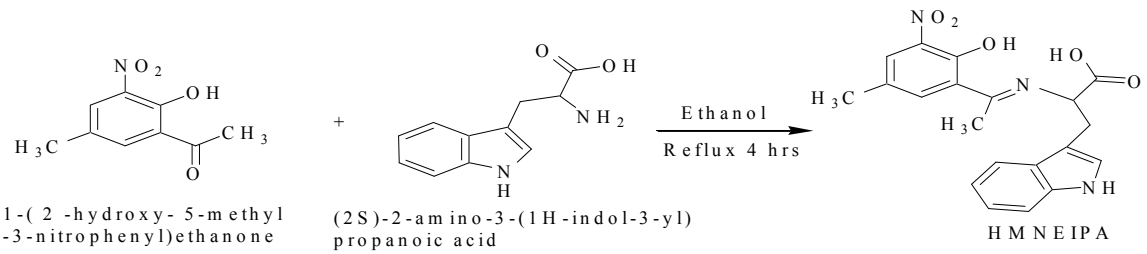
Modern coordination chemistry is the soul of inorganic researchers which deals with interaction between the metal and ligand attracted the researchers because of improved analytical methods and less time consuming preparative techniques. The successful application of spectroscopy and diffraction techniques improved synthesis of simple inorganic complexes used to model or reproduce various aspects of bio-molecules, increased concern about the environmental toxic caused by some metal ions. Use of metal ions or complexes as therapeutic agents and molecular recognition which have importance of an increasing number of trace elements in plant, animal and human diets [1-5].

In the mechanism of Schiff base from an aldehyde or ketone is a reversible process and generally takes place in acidic or basic or in neutral media. In the first part of mechanism, the amine reacts with the aldehyde or ketone to give an unstable addition compound called carbinolamine metal complexes, which can be also use as an ideal candidate for a large variety of useful catalytic transformations. Stereogenic centers or other elements of chirality (planar or axial) can be introduced in the synthetic design and the chiral information can also be transmitted by these complexes through a catalytic process to produce enantio-enriched products. On the industrial scale, they have wide range of applications such as dyes and pigments [6].

MATERIAL AND METHODS

Preparation of [1-(2-hydroxy-5- methyl -3-nitro phenyl) ethanone-(2S)-2-amino-3-(1H-indol-3-yl) propanoic acid] (HMNEIPA)

The Schiff base was synthesized by adding hot ethanolic solution of 1-(2-hydroxy-5-methyl-3-nitro phenyl) ethanone(3.58gm, 0.02M) to a ethanolic solution of (2S)-2-amino-3-(1H-indol-3-yl) propionic acid (4.08gm, 0.02M). The reaction mixture was then refluxed on a water bath for about 4 hours. The condensation product was filtered, washed thoroughly with ethanol and petroleum ether, recrystallized and dried under vacuum. The purity of synthesized compounds was monitored by TLC using silica gel. Yield 68.9%, m.pt. 278°C.



1-(2 -hydroxy- 5-methyl -3-nitrophenyl)ethanone

(2S)-2-amino-3-(1H-indol-3-yl) propanoic acid

HMNEIPA

^{1}HNMR spectrum of HMNEIPA (300MHz, $CDCl_3$ δ in ppm)

The ^{1}HNMR spectrum of ligand HMNEIPA has been recorded in $CDCl_3$ which indicated that different non-equivalent protons resonate at different values of applied field. The δ-values in ppm are given below

δ 12.8 (1H, s, phenolic-OH), 8.01 (2H, d, Ar-H), 7.8 (1H, s, Ar-NH), 4.3 (2H, d, -COOH), 3.0 (2H, d, $-CH_2$), 3.5 (1H, s, -CH).

Preparation of Metal Complexes

Metal complexes were prepared by the reaction by taking metal salts in the form of their respective acetates and ligands in suitable solvent system under suitable conditions. The general method of synthesis of complexes in the present investigation is as described below.bThe metal complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) were prepared by dissolving in 1:2 stoichiometry of metal acetates and ligands in minimum quantity (25 to 50 ml) of hot ethanol, methanol and DMF separately. Both the solutions were filtered and mixed in hot condition with constant stirring. Then the reaction mixture was refluxed on a water bath for a suitable time.

Table No.1: Analytical Data, Color and Synthetic Condition of Complexes of HMNEIPA

S.N.	Compound	Color	Solvent	Time (hrs.)	Elemental analysis % found (calcd.)			
					M	C	H	N
1.	HMNEIPA	Orange	Ethanol	4	-	63.32 (63.18)	4.48 (4.20)	22.16 (22.08)
2.	$[Mn(HMNEIPA)_2].2H_2O$	Yellow	DMF+ Ethanol	6	6.85 (6.78)	59.30 (59.18)	3.57 (3.94)	22.28 (22.16)
3.	$[Co(HMNEIPA)_2].3H_2O$	Light brown	Ethanol	5	7.19 (7.23)	58.70 (58.89)	3.65 (3.92)	20.87 (20.71)
4.	$[Ni(HMNEIPA)_2].2H_2O$	Pale yellow	Ethanol	6	6.96 (7.01)	59.94 (59.04)	3.98 (3.93)	20.27 (20.61)
5.	$[Cu(HMNEIPA)_2].2H_2O$	Olive green	DMF+ Ethanol	7	7.87 (7.80)	58.27 (58.53)	3.45 (3.90)	20.26 (20.66)
6.	$[Zn(HMNEIPA)_2]H_2O$	Brown	Ethanol	6	7.65 (7.91)	58.76 (58.46)	3.97 (3.87)	20.61 (20.46)
7.	$[Cd(HMNEIPA)_2]$	Orange	Ethanol	5	12.47 (12.90)	55.10 (55.29)	3.49 (3.48)	19.44 (19.04)

RESULTS AND DISCUSSION

All compounds gave satisfactory elemental analysis. Values are in the close agreement with the values calculated for expected molecular formulae assigned to these complexes, suggesting 1:2 (M:L) stoichiometry. The IR spectrum of HMNEIPA and its metal complexes are found to be comparable with each other. The informative and diagnostic IR spectra of the ligand and its respective metal complexes are shown in Table 2. The IR spectrum of the Schiff base exhibits slightly sharp band at 3435 cm^{-1} due to intramolecular hydrogen bonded hydroxyl group [7]. This band is absent in all the spectra of complexes indicates the breaking of the hydrogen bond and coordination of oxygen atom to the metal after deprotonation. The coordinated water molecule is observed in Mn(II), Co(II) and Ni(II) complexes in the regions 3350 – 3460 cm^{-1}, 1500 – 1531 cm^{-1} and 817 – 893 cm^{-1} [8]. The strong band at 1651 cm^{-1} is assigned to the υ (C = N) stretching vibration observed in the ligand and this band shifted lower absorption region in the complexes indicates the participation of the azomethine nitrogen in coordination. The presence of a very strong band in the region of 1525 – 1595 cm^{-1} is typical for asymmetric vibration of the coordinated carboxylate group, confirms the coordination of the ligand through the carboxylic oxygen. The band that appears at 1365 – 1367 cm^{-1} can be ascribed to the symmetric vibration of the coordinated carboxylate [9]. The $\upsilon (COO)_{assy}$ of carboxylate group of the transition metal complexes were observed in the range of 1573 – 1730 cm^{-1}. Whereas the $\upsilon (COO)_{sym}$ is attributed around 1365 – 1460 cm^{-1} bands is due to coordination with metal to form as ternary complexes. The separation ($\Delta\upsilon = \upsilon_{assy} - \upsilon_{sym}$) between $\upsilon (COO)_{assy}$ and $\upsilon (COO)_{sym}$ bands of these complexes are consistent with a monodentate coordination of the carboxylate group of ligand [10]. The N-H stretching frequency of indol ring is not altered in the complexes, hence the–COOH group and indol nitrogen of ligand are not involved in the bonding [11]. The coordination through deprotonated phenolic oxygen and nitrogen is further supported by the appearance of new bands at the lower frequency region between 617 cm^{-1}– 626 cm^{-1} attributed to υ (M - N) and those within

the 426 – 472 cm^{-1} are assigned to υ (M – O) [12- 13].

Table No. 2: Infrared Spectral Data (cm^{-1}) of HMNEIPA and its Metal Complexes

S. N.	Compound	υ(O-H)/ υ(OH-N)	υ(COO) assy	υ(COO) sym	υ(C=N)	υ(NH)	υ(M-O)	υ(M-N)	υ(H_2O)
01	HMNEIPA	3435	1573	1365	1651	3172	--	--	--
02	[Mn(HMNEIPA)$_2$].2H_2O	--	1651	1421	1531	3135	624	472	3350
03	[Co(HMNEIPA)$_2$].3H_2O	--	1654	1442	1502	3113	623	418	3442
04	[Ni(HMNEIPA)$_2$].2H_2O	--	1651	1417	1558	3137	624	482	3450
05	[Cu(HMNEIPA)$_2$].2H_2O	--	1730	1460	1525	3164	626	437	3460
06	[Zn(HMNEIPA)$_2$]H_2O	--	1653	1425	1525	3164	617	426	3398
07	[Cd(HMNEIPA)$_2$]	--	1627	1421	1529	3100	621	430	--

Thermogravimetric analysis of HMNEIPA and its Metal Complexes

The thermograms of HMNEIPA and its metal complexes are shown in Fig. 1 and 2. The persual of the thermograms indicates that these complexes (except Cd(II) complex) decomposed at around 90^{0}C-120^{0}C corresponding to three lattice water molecules for Co(II) [% weight loss : obs. (calc.) 11.24 (11:91)] and two lattice water molecules for Mn(II), Ni(II), Cu(II) complexes [% weight loss : obs (calc.) : 7.42(7.88)], [% weight loss : obs.(calc.) 7.59 (7.64)], [% weight loss : obs (calc.) : 8.01 (8.03)] respectively. The Zn(II) complex shows weight loss at around 110-120^{0}C corresponding to one lattice water molecule [% weight loss : obs (calc) : 4.34 (4.68)]. After dehydration of lattice water molecules, these Mn(II), Co(II), Ni(II) Cu(II), Zn(II) and Cd(II) complexes shows no mass loss up to 570^{0}C [14,15]. All the metal complexes indicate oxidation – reduction reaction leading to the formation of metal oxides Mn_3O_4, Co_3O_4, NiO, CuO, ZnO and CdO. The different differential methods of Freeman-Carroll and Sharp-Wentworth were used for evaluating the kinetics and thermodynamic parameters and the comparable values are shown in Table 3.bThe decomposition rate of the metal complexes is faster than that of the ligand and this may be due to catalytic action of metal ion present in them. The relative thermal stability on the basis of half basis decomposition is found to be Mn(II) > Ni(II) > Cu(II) > HMNEIPA > Zn(II) > Cd(II) > Co(II).

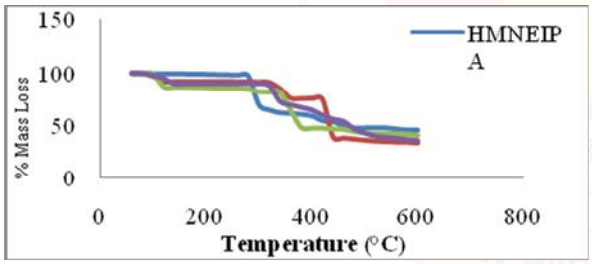


Fig. 1: Thermogravimetric Analysis of HMNEIPA, Mn- HMNEIPA, Co- HMNEIPA, Ni-HMNEIPA

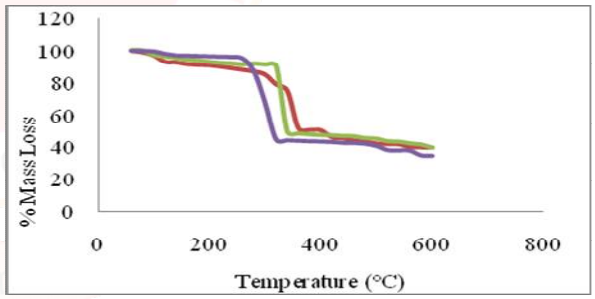


Fig. 2 : Thermogravimetric Analysis of Cu-HMNEIPA, Zn- HMNEIPA, Cd- HMNEIPA

Table No. 3: Thermal and Kinetic Parameters of HMNEIPA and its Complexes

S.N.	Compound	μeff (B.M.)	DH (°C)	Energy of activation (kJmol^{-1})		Z (S^{-1})	-ΔS (J K^{-1} mol^{-1})	ΔF (kJ mol^{-1})
				F-C	S-W			
1	HMNEIPA	-	278	35.12	34.19	-	-	-
2	[Mn(HMNEIPA)$_2$].2H_2O	5.92	328	29.97	33.84	97.41	302.25	124.84
3	[Co(HMNEIPA)$_2$].3H_2O	5.60	255	28.00	24.18	104.26	300.06	122.53
4	[Ni(HMNEIPA)$_2$].2H_2O	2.9	300	31.54	32.35	120.18	301.54	126.35
5	[Cu(HMNEIPA)$_2$].2H_2O	1.84	280	32.20	35.67	91.11	299.89	125.75
6	[Zn(HMNEIPA)$_2$].H_2O	-	275	31.54	32.66	139.57	299.84	124.74
7	[Cd(HMNEIPA)$_2$]	-	290	28.55	30.27	98.16	302.04	123.13

F.-C = Freeman-Carroll, S-W = Sharp-Wentworth, DH = Half Decomposition temp.

CONCLUSOIN

The thermogram of ligand and metal complexes showed that all the complexes comparatively more stable than their respective ligand [16].Thermogravimetric analysis of the synthesized metal complexes of HMNEIPA ligand showed that they are thermally stable to different higher temperatures. They losed weight in a continous manner but at different mode of temperature, means there is no constancy observed in all the metal complexes. After attaining a certain temperature (higher temperature) we observed a constancy to give final product as metal oxide after decomposition.

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ABSTRACT

In the present work we have discussed the effect of annealing temperature on particle size of mixed metal ferrite having compositional formula $Ni_{0.4}Cu_{0.6}Fe_2O_4$. The samples were synthesized via sol-gel auto combustion method at pH = 7and annealed at different temperature 500°C, 600°C, 700°C and 800°C for 2 hrs to study the effect of annealing temperature on particle size. The samples were characterized using XRD and FTIR, SEM and TEM techniques which confirm the formation of nano ferrite with cubic spinel structure. The maximum crystallite size was observed for the ferrite sample annealed at800°C.

Keywords: *Ni-Cu nanoferriets, auto-combustion, XRD, FTIR.*

INTRODUCTION

Nanosized ferrites may have extraordinary electric and magnetic properties that are comparatively different from micro-structured materials, tailoring them to modern technologies, as well as providing novel applications such as ferrofluids, magnetic drug delivery, high density information storage, photocatalysis, gas sensors[1-5], etc. They have gained technological importance by virtue of their high resistivity and negligible eddy current losses[6]. Nickel-copper ferrites are one of them which play significant role among magnetic materials due to their high electrical resistivity, high saturation magnetizationand high magnetic permeability. Ni-Cu ferrites have appealing electrical and magnetic properties, as copper ferrite is one of the most interesting spinel ferrite among all the ferrites[7].Recently, various physical and chemical techniques have been developed to prepare ferrite materials. The chemical techniques for synthesis are advantageous over the physical techniques. In the present work the Citrate-Gel auto combustion technique[8]has been used for the preparation of mixed nanocrystalline spinel ferrites with specific properties, such as controlled stoichiometry and narrow particle size distribution. Further, low cost, simplicity, short time of production, purity and homogeneity of final product are some of its advantages.

MATERIALS AND METHODS

AR grade iron nitrate nonahydrate $Fe(NO_3)_3.9H_2O$, Nickel nitrate hexahydrate $Ni(NO_3)_2.6H_2O$, Copper nitrate hexahydrate $Cu(NO_3)_2.6H_2O$, citric acid, liquor ammonia were purchased from SD fine-chem limited with high purity of 99.99% and used without further purification.

SYNTHESIS OF FERRITE

Ferrite Nanoparticles with compositional formula $Ni_{0.6}Cu_{0.4}Fe_2O_4$ were synthesized by sol gel auto-combustion method. The accurately weighed amount of metal ion precursors and citric acid in desired stoichiometric proportions were dissolved separately in minimum quantity of distilled water. Here citric acid and nitrate ions act as fuel and source of oxygen, respectively. The molar ratio of metal ion precursors to citric acid was kept 1:1. The individual solutions were then mixed together with constant stirring at pH = 7. The solution was then stirred continuously and slowly heated on a hot plate magnetic stirrer at 80°C till gel was formed which was ignited and burnt in a self-propagating combustion manner to obtain loose powder. The powder was finally annealed at temperature 500°C, 600°C, 700°C and 800°C for 2 hrs in a muffle furnace.

Characterization of $Ni_{0.6}Cu_{0.4}Fe_2O_4$ nanoparticles:

Structural characterization of the prepared samples were carried out by X-ray diffraction studies using Bruker AXS, D8 Advance spectrophotometer with Cu-Kα radiation (λ=1.5418A^0) in a wide range of Bragg's angle (20-80°) at room temperature. Infrared spectra of the powder samples were recorded using Fourier Transform Infra-Red Spectrophotometer (FTIR Nicolet, Avatar 370 model) by the KBr pellet method.The SEM studies and elemental analysis was carried out using JEOL

JSM-7600F FEG-SEM model. TEM studies of the ferrites were performed using Transmission Electron MicroscopeJEOL Model JSM - 6390LV.

RESULT & DISCUSSION

Characterization of ferrite:

X-ray diffraction studies:

The synthesized ferrite $Ni_{1-x}Cu_xFe_2O_4$ (x=0.4) at pH= 7 was annealed at different temperatures 500°C, 600°C, 700°C and 800°Cfor 2 hrs to study the effect of annealing temperature on particle size.

X-ray diffraction patterns corresponding to $Ni_{1-x}Cu_XFe_2O_4$ferrite system (x=0.4) annealed at different temperatures 500°C, 600°C, 700°C and 800°Cfor 2 hrs are shown in Fig.1 and corresponding analytical data for the most intense peak at (311) plane is shown in Table 1. For all samples 2θ value for the most intense peak at (311) plane ranges from 35.50°to 35.80°, a characteristic of cubic spinel ferrite. The most intense peak at (311) is used to determine the average crystallite size of nanoparticles. The average crystallite size of the samples was found in the range 41.73nm to 63.05nm which is determined by using the Debye-Scherer's formula Formula[9] given by,

$$D_{hkl} = 0.9\,\lambda / \beta \cos\theta$$

where, D_{hkl} = crystallite size, λ is wavelength of the X-ray radiation, β is the full width at half maximum (FWHM) of the most intense diffraction peak and θ is Bragg's angle.

The lattice constant for each sample was calculated using Le Bail refinement method[10].

$$a = d\sqrt{h^2 + k^2 + l^2}$$

where, a is lattice constant; d is inter planar spacing; (hkl) are Miller Indices.

The lattice parameters of the ferrite nanoparticles are found in the range 8.373A° to 8.401A°, which are close to the standard ferrite samples.

X-ray density is calculated using relation:

$$dx = \frac{8M}{N_A\, X\, a^3}$$

where M is molecular weight of the composition; N_A is Avagadro's number and a is lattice constant.

It is observed that the average crystallite size of nanoparticles fairly increases with increase in annealing temperature. The maximum value of average crystallite size is observed for sample annealed at 800°C, viz. 63.05nm. The lattice parameters of the ferrite nanoparticles are found in the range 8.313A° to 8.381A°, which are close to the standard ferrite samples. Also, the XRD pattern shows that in raw material there are very few and broad peaks but with increase in the annealing temperature the peaks becomes sharper and more peaks generate. Sample annealed at 800°C shows very sharp peaks and maximum crystallite size. The crystallite size was found to increase with higher annealing temperature which is because of the amplification in crystallinity that leads to the increased particle size of the nuclei[11].

Table 1:- Values of 2θ (degrees),*β* (degrees) (FWHM), d-spacing (d), crystallite size, lattice parameter (a) of $Ni_{0.6}Cu_{0.4}Fe_2O_4$ annealed at different temperature

Sr. No.	Annealing temperature (°C)	2θ (degrees)	β (degrees) (FWHW)	d-spacing (Å)	Crystallite size (nm)	Lattice Parameter in Å (a)	X–ray density (dx) (g/cm^3)	Volume of Unit Cell (V) (Å)^3
1.	500	35.50	0.349	2.52704	41.73	8.381	5.347	588.743
2.	600	35.54	0.341	2.52335	42.71	8.369	5.370	586.167
3.	700	35.80	0.376	2.50638	38.76	8.313	5.480	574.420
4.	800	35.53	0.231	2.52446	63.05	8.373	5.363	586.941

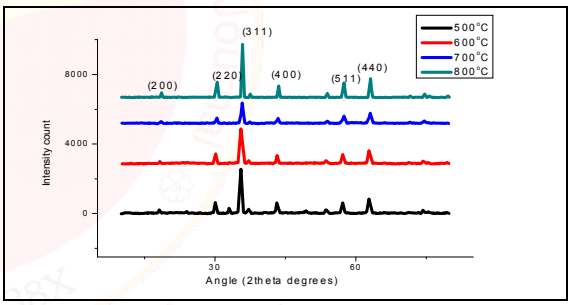

Fig.1: XRD spectra of ferrite sample $Ni_{0.6}Cu_{0.4}Fe_2O_4$ annealed at various temperatures

FTIR studies:

FT-IR spectra of $Ni_{1-x}Cu_xFe_2O_4$ (x=0.4) annealed at various temperatures are shown in Fig.2 and corresponding analytical data is shown in Table 2.The intense broad peaks at 3442.37cm^{-1}, the O-H stretching vibration and 1617.49cm^{-1}, the δ (H-O-H) bending vibration could be attributed to the adsorbed water or humidity which disappears at higher annealing temperatures. The intense peak around 580cm^{-1}can be attributed to intrinsic Fe-O vibration of octahedral Fe^{3+} and another peak near 400 cm^{-1}to that of tetrahedral Fe^{2+} sites which shows the spinel structure of synthesized ferrite samples. Further, with increase in annealing temperature υ_1 band is found to increase from 568.55cm^{-1} to 580.63cm^{-1} which clearly indicates the increase in the size of the particles as the annealing temperature is increased. The result is

consistent with the absorption band of a particular bond is shifted to the higher frequency when the size of the particles is increased[12]. These results strongly support the results of XRD data.

Table 2: Infrared data of $Ni_{1-x}Cu_xFe_2O_4$ (x = 0.4) annealed at different temperatures

Sr. No.	Annealing temperature (^oC)	υ (OH) stretching cm^{-1}	δ(H-O-H) bending cm^{-1}	υ_1 (M-O bond) cm^{-1}
	500	-	-	568.55
	600	-	-	573.16
	700	3442.37	1635.45	573.47
	800	-	-	580.63

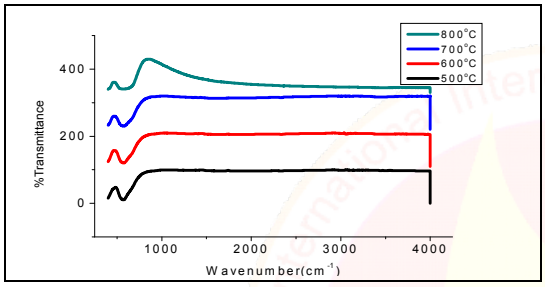

Fig.2:- FTIR spectra of ferrite system $Ni_{0.6}Cu_{0.4}Fe_2O_4$ annealed at various temperatures

Scanning Electron Microscopy (SEM) and EDS Studies:

FE-SEM images of copper substituted nickel nano ferrite $Ni_{1-x}Cu_xFe_2O_4$(x=0.4) synthesized by Sol gel auto combustion method at pH = 7 and annealed at 800^{o}C for 2hrs are shown in Fig. 3a-b. The image suggests the formation of of largely agglomerated well defined nanparticles with irregular shape and morphology.The agglomeration of particles is due to permanent magnetic moment proportional to their volume[13]. It is also evidenced by SEM images that the aggregation of particles lie in nanometric region.The sizes of the particles are in the range of 58-84 nm. The particles were observed as uniform grains confirming the crystalline structure of Ni-Cu Nanoferrites which were detected by XRD studies. The formation of ferrite was chemically favoured by heating during the synthesis whereas final reaction was completed during the annealing where the pores between the particles were removed combined with growth and strong bonds by agglomeration.

The elemental analysis of ferrite system is studied using Energy Dispersive Spectrometer (EDS). Here the elemental analysis of $Ni_{0.6}Cu_{0.4}Fe_2O_4$synthesized at pH = 7 is shownin Fig 3d. The EDS pattern obtained for ferrite gives the elemental and atomic composition in the sample. The compound shows the presence of Ni, Cu, Fe and O without any impurity.

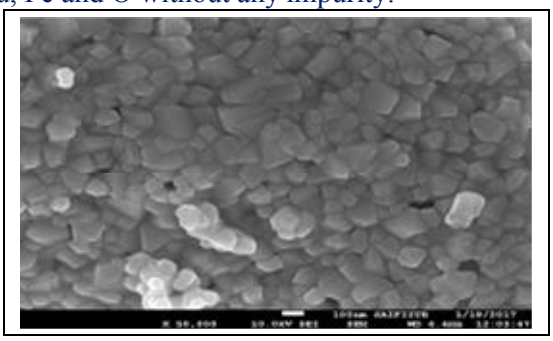

Fig 3a: FE-SEM imagesof ferrite system $Ni_{1-x}Cu_xFe_2O_4$ (x = 0.4)

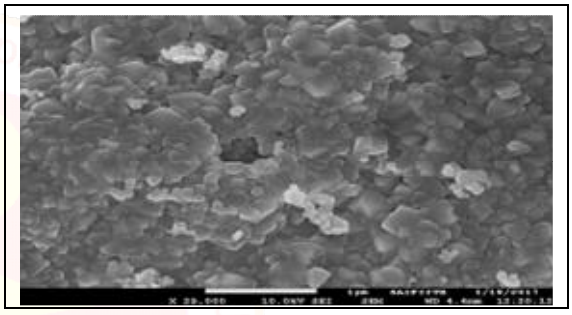

Fig 3b: SEM imageof ferrite system $Ni_{1-x}Cu_xFe_2O_4$ (x = 0.4)

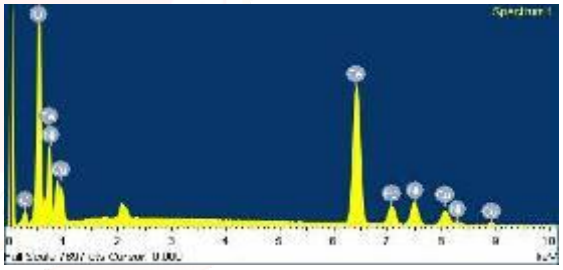

Fig. 3c: EDS pattern of ferrite system $Ni_{1-x}Cu_xFe_2O_4$ (x=0.4)

Transmission Electron Microscopy:

Fig. 4a-c shows the TEM images of $Ni_{0.6}Cu_{0.4}Fe_2O_4$prepared by sol gel auto combustion method at pH = 7 and sample annealed at 800^{o}Cfor 2 hrs.

The direct observations of the lattice image reveal that the particles are elongated spherical shape. The TEM images also reveal that particles are in nano-meter scale andagglomerated. The particle size obtained from TEM is in the range of 100-140 nm whereas the size calculated from peak broadening in X-ray diffractograms is 63.046nm. Also, the selected area electron diffraction pattern (SAED) consists of concentric rings with bright spots over the rings indicating polycrystalline nature of the sample.The rings are consistent with

the cubic spinel structure with an intense ring pattern from (hkl) plane. No secondary phases are found. The observed selected area electron diffraction pattern is consistent with the results.

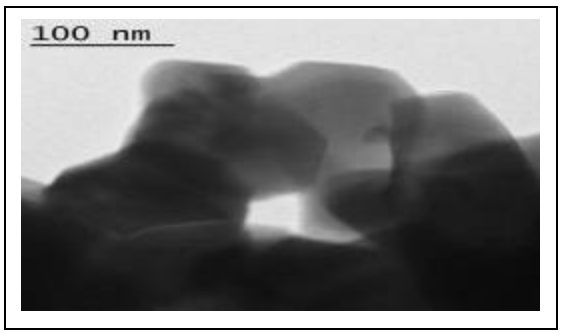

Fig. 4a: TEM image of ferrite system $Ni_{0.6}Cu_{0.4}Fe_2O_4$

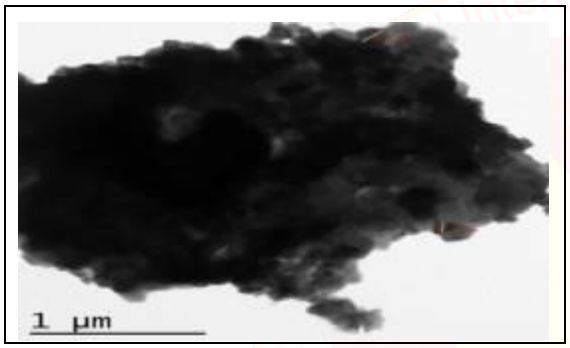

Fig. 4b: TEM image of ferrite system $Ni_{0.6}Cu_{0.4}Fe_2O_4$

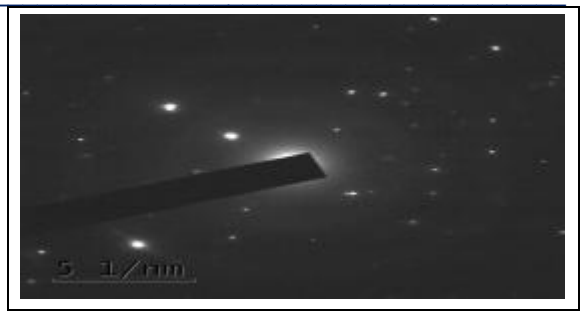

Fig.4c: SAED pattern of ferrite system $Ni_{0.6}Cu_{0.4}Fe_2O_4$

CONCLUSION

Copper substituted nickel ferrite with compositional formula $Ni_{0.6}Cu_{0.4}Fe_2O_4$was synthesized successfully using sol gel auto combustion method of synthesis. The synthesis was carried out at pH =7of reaction mixture and annealed at different temperature 500°C, 600°C, 700°C and 800°C for 2 hrs. Polycrystalline cubic spinel structure of the prepared nanoferrites was confirmed by X-ray diffraction analysis. The average crystallite size of ferrite samples was found in the range 41.73nm to 63.05nm.Maximum crystallite size was observed for sample annealed at temperature 800°C, viz. 63.05nm. FTIR studies also confirm the formation of spinel nanoferrite.SEM - EDX and TEM studies also reveals the formation of Nano ferrites.

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WASTEWATER TREATMENT BY USING NANOMATERIALS AND NANOCOMPOSITES

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ABSTRACT

Water contamination with toxic metal ions and organic dyes represent a serious worldwide problem in the 21st century. A wide range of conventional approaches have been used to remove these contaminants from wastewater. Recently, nanotechnology has been given great scope for the fabrication of desirable nanomaterials with large surface-to-volume ratios and unique surface functionalities to treat these pollutants. Amongst these, oxide-based nanomaterials are promising new materials for Wastewater treatment. We study a broad-spectrum overview of recent developments in the area of oxide-based nanomaterials, such as Fe_3O_4, ZnO and TiO_2, as well as their binary and ternary nanocomposites, for the removal of various toxic metal ions and organic dyes.

Keywords : *Nanomaterials , Metal Oxides, Nanocomposite , Wastewater, Toxic Metal Ions*

INTRODUCTION

Today's world faces alarming challenges in the rising demand for clean drinking water, and conditions are particularly bad in developing countries. The scarcity of water in terms of both quantity and quality has become a significant threat to the well-being of humanity. In particular, the quality of drinking water has become a serious concern, with the rapid escalation of industrialization towards a developed society. The waste products generated from the textiles, chemicals, mining and metallurgical industries are mainly responsible for contaminating the water. This contaminated water contains non-biodegradable effluents, such as heavy metal ions (arsenic, zinc, copper, nickel, mercury, cadmium, lead and chromium, etc.) and organic materials that are carcinogenic to human beings and harmful to the environment. Water contaminated with arsenic (As) causes cancer of the skin, the lungs, the urinary bladder and the kidney, as well as other skin problems such as pigmentation changes and thickening (hyperkeratosis). Another toxic metal pollutant is lead which, if present with a concentration of >70 µg/dL in blood levels (WHO), can damage various bodily systems, including the nervous and reproductive systems and the kidneys, and it can also cause high blood pressure and anaemia. Large amounts of lead (>100 µg/dL) in the body can lead to convulsions, coma and death . However, the presence of nickel at higher levels in the human body can cause serious lung and kidney problems as well as gastrointestinal distress, pulmonary fibrosis and skin dermatitis. A further neurotoxin is mercury, which can cause damage to the central nervous system, and its concentration within the range of 0.12–4.83 mgL−1 may cause the impairment of pulmonary and kidney function, chest pain and dyspnoea. High levels of cadmium exposure (1 mgm−3) may result in several complications leading to death . In addition to heavy metal contaminants, other hazardous contaminants found in the environment are organic dyes, discharged from textile manufacture and other industrial processes into the water. The dyes presently used in industries include methylene blue (MB), Rhodamine B (RhB), methyl orange (MO), Rhodamine 6G (Rh6G) as well as organic chemicals (phenol and toluene), and the release of these into lakes or other water sources has become a serious health concern. Various treatment techniques and processes have been developed for the removal of toxic contaminants from wastewater, such as adsorption, ion exchange, chemical precipitation, membrane-based filtration, photodegradation, evaporation, solvent extraction, reverse osmosis, and so on . Among these, adsorption and photodegradation are conventional but efficient techniques for removing toxic contaminants from water. For this, numerous adsorbents/catalysts have been developed for the removal of such hazardous chemicals from wastewater. However, most of them suffer from certain drawbacks, such as high capital and operational costs for treatment, and the disposal of the residual metal sludge. Thus, there is urgent demand for the development of low-cost materials and better processes for providing clean drinking

water (i.e., free from contaminants such as toxic chemicals and metal ions). Nanotechnology is considered as having the potential to play an important role in shaping our current environment by providing new materials, remediation/treatment techniques and sensors for monitoring purposes. For wastewater treatment, there is a need for technologies that have the ability to remove toxic contaminants from the environment to a safe level and to do so rapidly, efficiently and within a reasonable costs framework. Thus, the development of novel nanomaterials with increased affinity, capacity and selectivity for heavy metals and other contaminants is an active emerging area of research in the field of nanotechnology. The benefits of using nanomaterials are mainly associated with their large specific surface area and high reactivity. A variety of efficient, cost-effective and environmentally friendly nanomaterials have been developed, each possessing unique functionality in their potential application to the detoxification of industrial effluents, groundwater, surface water and drinking water. Among the various kinds of nano-adsorbents, oxide-based nanomaterials such as Fe_3O_4, TiO_2, ZnO and their composites play an important role. These nanomaterials have various applications in many scientific and industrial fields, including wastewater purification, catalysis and magnetic devices. Recently, there have been several reports on magnetic oxides, especially Fe3O4, being used as nano-adsorbents for the removal of various toxic metal ions from wastewater, such as Ni^{2+}, Cr^{3+}, Cu^{2+}, Cd^{2+}, Co^{2+}, Hg^{2+}, Pb^{2+} and As^{3+} [26-31]. These Fe_3O_4 nano-adsorbents are effective and economical for the rapid removal and recovery of metal ions from wastewater effluents due to their large surface area and optimal magnetic properties. They can be reused after magnetic separation in removing the adsorbed toxic contaminants. Further, some semiconductor metal oxides, including ZnO and TiO2, have also received a great deal of attention in the successful photocatalytic degradation of organic contaminants and the adsorption of heavy metals. In particular, these materials have attracted much attention because of theirs high photosensitivity, higher absorption capacity, better quantum efficiency, non toxicity and wide band-gap. Also, numerous oxide-based nanocomposite/hybrid materials have been developed for wastewater treatment. The present paper mainly deals with the development of low-cost, efficient and reusable novel oxide-based nanomaterials for providing wastewater treatment. The importance of the surface engineering/modification of nanomaterials with various functional groups for the capture of toxic metal ions is discussed in this paper. We have also included various oxide-based binary and ternary nanocomposites that have been developed for the removal of pollutants from wastewater.

MATERIALS AND METHODS FOR REMOVAL OF HEAVY METALS AND DYES FROM WASTEWATER

Fe_3O_4 nanoparticles are gaining importance, as they can be used as highly effective, efficient and economically-viable adsorbents, with the additional advantage of their easy separation under a magnetic field for reuse. Many of these reports deal with the influence of different parameters on the removal of metal ions by Fe_3O_4 magnetic nanoparticles. Depending upon the surface functionality (COOH, NH_2 or SH), these magnetic nano-adsorbents capture metal ions either by forming chelate complexes, by ion exchange process or else through electrostatic interaction. It has been observed that these surface engineered Fe_3O_4 nanoparticles have a strong affinity for the simultaneous adsorption of Cr^{3+} , Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+} and As^{3+} from wastewater. In addition, the adsorption process was found to be highly dependent on the amount, surface functionality and pH of the medium, which caused these nanoparticles to selectively adsorb metal ions. An almost 100% removal rate of Cr^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+} and Pb^{2+} ions from water was observed at pH > 8 by these functionalized nanoparticles. The removal efficiency of As^{3+} by carboxyl, amine and thiol-functionalized Fe3O4 was found to be 91%, 95% and 97%, respectively, at pH 8. The adsorption-desorption behaviour of metal ions on amine-functionalized Fe3O4 showed an 85% desorption ratio in the first cycle which indicates their excellent regeneration capacity for their further use. They also prepared ethylenediamine tetraacetic acid-functionalized (EDTA), Fe3O4 nanomagnetic chelators (NMCs), which show a strong tendency towards the adsorption of Cr^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+} and Pb^{2+} from wastewater. They reported a higher removal efficiency of metal ions in acidic pH 5.5 and a lower one in alkaline pH. Based on their results, they have suggested that the polymer-modified Fe3O4 was more efficient than bare Fe_3O_4. All of the above studies clearly suggest that the functional groups present on the surface of magnetic nanoparticles provide a

large number of active sites as well as aqueous stability, which is necessary for the successful adsorption of toxic metal from water. More specifically, these surface-engineered magnetic nanoparticles are highly effective, efficient and economically viable and reusable magnetic nanoadsorbents for the removal of toxic metal ions from water.

TiO2 nanoparticles Titanium dioxide is another highly favourable material for heterogeneous photocatalytic processes due to its high photoactivity, non-toxic nature, large band-gap and stability. There have been numerous reports on the photoabsorption and photocatalytic properties of TiO2 under UV light. They also doped TiO2 with Si and observed that Si doping does not improve the photocatalytic activity of TiO2. However, it has been reported that the photocatalytic activity of TiO2 can be enhanced, either by doping with transition metal ions (Fe, Bi, Ag and V) and rare-earth metal ions (Nd, Gd), or by the surface modification of the crystalline structure, as they could significantly influence charge carrier recombination rates and interfacial electron-transfer rates.

ZnO and TiO2-based oxide nanocomposites were developed for the enhancement of the photocatalytic degradation of organic dyes. For instance, a large number of binary and ternary nanocomposites of ZnO and TiO2, such as ZnO/TiO2, chitosan–polyaniline/ZnO hybrid , ZnO/ TiO2- metal (Ag, Au) composites, N-doped TiO2/C , B-doped Au/TiO2 , Ag@SiO2@TiO2 core shell , TiO2@C/Ag, TiO2/ZnO/Au and TiO2−AgBr−Ag with well-defined structures, have been explored for the photodegradation of organic dyes.

RESULT AND DISCUSSION

Environmental pollution by toxic metal ions and organic contaminants is a global menace and its magnitude is increasing significantly. The recent development of nanotechnology offers great scope for the fabrication of desired nanomaterials with large surface-to-volume ratios and unique surface functionalities in treating these pollutants. Specifically, oxide-based nanomaterials, such as Fe_3O_4, ZnO and TiO_2, as well as their nanocomposites, show great potential for the removal of toxic metal ions and organic pollutants from contaminated water. These nanomaterials are generally modified with different functional groups to improve their catalytic efficiency and lifetime. Further, the use of magnetic nanomaterials or their nanocomposites provides the feasibility of magnetic separation and reusability (not possible with non-magnetic nanomaterials), which are significant for practical application.

CONCLUSSION

This article provides a comprehensive review of these oxide-based nanomaterials for water purification. However, the research in this area is in its nascent stage, and detailed investigations are required to establish the large-scale purification of water in real life. In future, researchers should focus on the development of novel nanomaterials/nanocomposites with a high surface area, sufficient surface functional groups and high sorption ability, for the removal of different heavy metal ions and organic dyes. The microbial threats to human health and safety are also a serious public concern. Thus, further improvements must be made in the direction of the development of materials with greater stability (resistance to pH changes and concentrations of chemicals present in contaminated water) and the capacity for the simultaneous removal of multiple contaminants, such as toxic metal ions, organic dyes and bacterial pathogens. Considering the economics of adsorbents, it is necessary to synthesize low-cost, effective and recyclable adsorbents for their extensive application in our daily life. In addition, a wide range of treatment technologies should be developed for the purification of water in order to meet the demand of increased environmental pollution.

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EFFECT OF SOLVENTS ON THE ULTRASONIC VELOCITY AND ACOUSTIC PARAMETERS OF NALFURAFINEDRUGS AT 308K.

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ABSTRACT

Ultrasonic studies provide information in understanding molecular behavior and intermolecular interactions of Nalfurafine drug solvent mixtures.The measurements of density, viscosity and speed of sound of Nalfurafinedrug have been determined by experimental procedures in different medium. From the experimental data various acoustical parameters such as apparent molar compressibility (ϕ_k), apparent molar volume (ϕ_v), adiabatic compressibility (β_s), specific acoustic impendence (Z), intermolecular free length (L_f) have been evaluated. The concentration range is 0.02 to 0.1 mol dm^{-3} . The measurements are conducted at 308K in different solvents. The variation ofthese acoustic parameters is explained in terms of solute -solvent molecular interaction occurring in a Drug solutions.

INTRODUCTION

The measurement of ultrasonic velocity has been adequately employed in understanding the nature of molecular interactions in pure liquids and liquid mixtures. Ultrasonic propagation parameters yield valuable information regarding the behaviour of liquid systems, because intramolecular and intermolecular association, dipolar interactions, complex formation and related structural changes affect the compressibility of the system which in turnproduces corresponding variations in the ultrasonic velocity. The acoustical and thermo dynamical parameters obtained in ultrasonic study show that the ion solvation is accompanied by the destruction or enhancement of thesolvent structure[1-4]Excess thermodynamic properties of liquid mixtures are of great interest to conveniently design industrial processes and also to provide useful information on the molecular interactions required for optimizing thermodynamic models[3]. When two or more liquids are mixed there occur some changes in physical and thermodynamic properties because of free volume change, change in energy and change in molecular orientations.Derived thermodynamic and acousticalparameters like internal pressure, free volume and acoustic impedance are of considerable interest in understanding the intermolecular orientations in binary liquid mixtures[5-7]. Excess thermomic properties of mixtures are useful in the study of molecular orientations and arrangements[8-9].

Ultrasonic velocity $u = \lambda\upsilon$ -------- 1

Adiabatic compressibility $\beta_s = 1/ u^2{}_s \rho_s$ --- 2

For the present study Nalfurafine[10] drug is selected. This drug is used for the treatments of uremic pruritus in individuals with chronic kidney disease undergoing. The acoustic properties of Nalfurafine have been studied in 20% Methanol-water, 20% Dioxane-water and 20% DMF-water solutions at 308 K.

EXPERIMENTAL

Solvents methanol, dioxane and dimethyl formamide used in the present work were of AR grade and were purified and dried by the usual procedure. Densities, viscosities and ultrasonic velocities were measured at 308 K over a wide range of composition. Densities were determined by using bicapillary pyknometer. The viscosities were measured by precalibrated Ostwald type viscometer. Ultrasonic velocity measurements were made by using an ultrasonic interferometer (Mittal Enterprises, New Delhi) at a frequency of 2MHz with a tolerance of ± 0.005%. All the measurements were carried out at 308 K.

THEORY

Acoustic parameters such as apparent molar compressibility (ϕ_k), apparent molar volume (ϕ_v), adiabatic compressibility (β_s), specific acoustic impendence (Z), intermolecular free length (L_f), Limiting apparent molar volume (ϕ^0_v), Limiting apparent molar compressibility (ϕ^0_k)were determined using following relations.

Apparent molar volume $\phi_v = 10^3(\rho_0-\rho_s)/m-\rho_0\,\rho_s + M/\rho_0$ ---------- 3
Apparent molar compressibility $\phi_k = 10^3(\rho_0\beta_s-\rho_s\beta_0)/m-\rho_s\,\rho_0 + \beta_s M/\rho_s$ ---- 4
Intermolecular free length $L_f = K(\beta_s)^{1/2}$ ---------- 5
Specific acoustic impendence $Z = \rho.u$ --------- 6
Limiting apparent molar volume $\phi_v = \phi^0_v + S_v C^{1/2}$ ----------7
Limiting apparent molar compressibility $\phi_k = \phi^0_k + S_k^{1/2}$----------8

Table no.1: Experimental Data of Density, Ultrasonic Velocity and Viscosity of Nalfurafine in different solvent at 308K

Solvents	Conc. mol.dm^{-3}	Density ρ_s Kgm^{-3}	Ultrasonic Velocity (u)m/s	Viscosity x10^{-3}Nsm^{-2}
20% MeOH-Water Medium	0.02	1076.19	1576.5	1.05148
	0.04	1076.27	1584.0	1.05823
	0.06	1076.48	1587.2	1.05901
	0.08	1076.79	1591.1	1.05921
	0.1	1076.98	1595.1	1.06021
20% Dioxane-Water Medium	0.02	1082.09	1599.5	1.17251
	0.04	1082.16	1601.0	1.18602
	0.06	1082.66	1615.2	1.18856
	0.08	1082.94	1611.1	1.18936
	0.1	1083.15	1689.1	1.19250
20% DMF-Water Medium	0.02	994.19	1548.3	0.92239
	0.04	995.91	1577.4	0.92956
	0.06	997.05	1581.1	0.93278
	0.08	998.29	1582.2	0.93335
	0.1	998.89	1583.3	0.93945

Table no.2 : Variation of some acoustical parameters with concentration of Nalfurafine in different solvents at 308 K

Solvents	**Conc .mol. dm^{-3}**	β_s x10^{-10} Pa^{-1}	Φ_v x10^{-5} m^{3}mol^{-1}	Φ_k x10^{-14} m^{3}mol^{-1} Pa^{-1}	L_f x10^{-11} (m)	Z x 10^5 Kg m^{-2} sec^{-1}
20% MeOH-Water Medium	0.02	3.9658	-81.87	-65.943	3.2158	15.4059
	0.04	3.9569	-43.12	-26.731	3.2069	15.4245
	0.06	3.9458	-7.51	-18.458	3.0126	15.4444
	0.08	3.9163	4.30	-8.0120	3.0102	15.4518
	0.1	3.1825	11.19	-5.0787	3.0036	15.4929
20% Dioxane-Water Medium	0.02	4.8989	-59.5	-79.7945	5.9916	16.2692
	0.04	4.8943	-8.88	-45.6569	5.1058	17.2838
	0.06	4.8836	6.85	-21.6325	5.0945	17.3177
	0.08	4.8755	11.31	-18.5086	5.0656	17.3480
	0.1	4.8342	16.91	-15.5892	5.0584	17.3452
20% DMF-Water Medium	0.02	3.6312	8.82	312.7213	5.4702	13.6382
	0.04	3.6098	20.1	148.5842	5.4628	13.6669
	0.06	3.5902	23.3	122.4264	5.4547	13.7048
	0.08	3.5699	24.4	87.1877	5.4456	13.7456
	0.1	3.5589	25.5	72.4595	5.4385	13.7645

Table-3Limiting values of ϕ^0_v and ϕ^0_k along with slope (S_v & S_k) for Nalfurafinein different medium at 308K temperature

Temp. T (K)	Medium	Parameters			
		ϕ^0_v x 10^{-5} m^{3}mol^{-1}	ϕ^0_k x 10^{-14} m^{3}mol^{-1} pa^{-1}	S_v x 10^{-5} m^{3}mol$^{-3/2}$ dm$^{3/2}$	S_k x 10^{-14} m^{3}mol$^{-3/2}$ dm$^{3/2}$pa^{-1}
308K	20% M-W	-157.6	-85.33	556.3	289.2
	20% D-W	-92.42	-121.6	401.8	342.3
	20% DMF-W	6.760	621.5	64.31	-1653.0

Table-4 A and β, coefficient values at308K in different medium for Nalfurafine

Medium	Coefficient	Temp 308 K
20%Methanol-Water medium	A	0.9801
	β	-0.151
20%Dioxane-Water medium	A	1.425
	β	-0.169
20% DMF-Water medium	A	0.501
	β	-0.059

RESULTS AND DISCUSSION

Table 1 shows that density (ρ), ultrasonic velocity (u) and viscosity (η) increases with increase in concentration for all three systems. The increase in ultrasonic velocity is due to decrease in intermolecular free length (L_f) as shown in table 2. This suggests that there is a strong interaction between Nalfurafine and solvent molecule. Adiabatic compressibility (β_s) is a measure of intermolecular association or repulsion calculated from the measured ultrasonic velocity (u) and density (ρ). Adiabatic compressibility is found to decrease with increase in concentration. Since adiabatic compressibility is inversely related to the product of density and ultrasonic velocity based on this the compressibility is expected to decrease which has observed in the present case. When the sound waves travels through the solution, certain part of it travels through the medium and rest gets reflected by the ion[6] i.e. restriction for flow of sound velocity by the ions. The character that determines the restriction movement of sound waves is known as acoustic impendence (Z). It has been found that acoustic impendence increases with increase in concentration. The apparent molar

compressibility (ϕ_k) explains the solute-solvent and solute- solute interactions in solution and was calculated by using the equation no. 4. The apparent molar volume (ϕ_v) is defined as the change in volume of solution for the added one mole of a particular component at constant temperature and pressure. It is thermodynamic property which helps in elucidating solvation behavior of electrolyte in solution. Apparent molar volume was evaluated from the density of solution and solvent.

It is evident from the table 3 that ϕ^0_k values are negative for 20% MeOH-water and 20% Dioxane-water but for 20%DMF-water ϕ^0_k values are positive. The negative ϕ^0_k values are suggest solute- solvent interaction whereas positive values are due to solute- solute interaction, is further confirmed by ϕ^0_v values which are positive for 20% DMF-water and negative for 20% MeOH-water and 20% Dioxane-water of the drug.S_v is a measure of solute – solvent interaction. It is observed from the table 3 that S_v values are higher in 20% MeOH-water and 20% Dioxane-water and low in 20% DMF-water solution. This confirms that in 20% DMF-water solution solute- solute interactions and in20% MeOH-water and 20% Dioxane-water solute – solvent interaction predominate.

The viscosity B-Co-efficient has been derived from Jones-Dole equation

$$(c > 0.1m)\eta_r\text{-}1 / C^{1/2} = A+B\ C^{1/2}$$

Where η_r is the relative viscosity. A and B are the characteristics of the solute and solvent. A is Falkenhagen coefficient represent the contributor from solute-solute interaction and B is Jones Dole coefficient known to depend on the size of the solute particle and on the interaction between solute and solvent.

They were obtained by a least – squares treatment as intercept and slope of the linear plot of η_r-1 / $C^{1/2}$ Vs $C^{1/2}$.The graph for each system given linear straight line showing validity of Jones-Dole equation. The slope of straight line gives value of B co-efficient.

The viscosity A coefficient represent the ion-ion interactions and negative values have shown some physical significance. However negative A values have also been reported to be in other solvents in some studies.[7-9]

The large and small value of 'A' shows the stronger and weaker solute – solute interactions respectively. When solute is introduced into solvent of organic-water mixture it will interfere with the ordered structure of water in the solutes co-sphere. As only one solute is present so such variation in the values of A can be explained.

In the present study viscosity of liquid solutions increases with increase in concentration of drugs solution in 20% methanol -water, 20% dioxane-water and 20% DMF-water mixture. The increase in viscosity with increase in concentration may be attributed to the increase in solute solvent interactions.

Viscosity B coefficients have been established to arise from ion- solvent interactions and are responsible for introducing order or disorder in the structure of the solvent. Solute with negative B Coefficient is characterized as structure breakers indicating weak solute-solvent interactions. Such type of results is also shown by Reddyet al.[11-12]

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STUDY OF EFFECT OF SOLVENTS ON SOLUTE SOLVENT INTERACTION OF HALOSUBSTITUTED CHALCONEIMINE BY VISCOMETRICALLY

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ABSTRACT

The solute solvent interaction is important physical property of any compound this interaction is usefulness in various field . Therefore in present work the important physical property i.e viscocity of newely synthesized halo substituted chalconeimine are studied. A comparative effect of change of concentration of solvents on viscosity of compounds is studied in dioxane-water and dimethyl fluoride-water system . The experimental viscosity data have been interpreted in terms of the extended Jones–Dole equation for strong electrolyte solutions. The values of viscosity A coefficient , β -coefficients of the extended Jones–Dole equation for the relative viscosity (η/η0) are determined. This derived values of the viscosity A- and β-coefficients were compared with the results predicted by the Falkenhagen–Dole theory of electrolyte solutions and calculated with the ionic β-coefficient data.

Keywords: *Chalconeimine, DMF, Dioxane, solute-solvent interaction*

INTRODUCTION

Viscosity is one of the important physicochemical property. It determines the resistance to flow. The viscosity is one of the key transport properties of electrolyte solutions.Studies of the concentration and temperature dependence of the viscosity coefficient of aqueous electrolyte solutions [1] have provided many useful insights into the extent of ionic hydration [2–4] and into structural interactions [5–9] within the ionic hydration co-spheres [10]. In general, the variation of relative viscosity with the molarity (mol/dm^{-3}) can be represented by the Jones– Dole equation.

The study of viscosity is very important parameter to know the behavior of solute solvent interaction [11].This interaction is useful to describe the properties of micro emulsion and liquid crystal with respect to micellar solution of surfactant system.The viscosity of amine solutions used for post-combustion CO_2 capture is significantly greater than water. The effect of liquid viscosity (μL) on both the effective mass transfer area (ae) and the liquid film mass transfer coefficient (kL) of packings is required to predict mass transfer rate and design the absorber and stripper. Existing correlations are mostly based on water so they do not represent the viscosity of amine solvents [12]

MATERIAL AND METHODS

The halosubstituted chalconeimine are synthesized by using general claisen Schmidt method . For evaluating the viscosity the very pure and analytical grade solvent and extra pure double distilled water is used.The dencities of pure solvent and solutions are determined by using specific gravity bottle.The determination of viscosity is done by using calibrated Ostwald Viscometer ($\pm 0.11\% Kgm^{-1}S^{-1}$)The flow time taken by the solution is measured by using the digital clock (Racer company) having an accuracy up to ±) 0.01 Sec.

OBSERVATIONS AND RESULTS

In the present work determination of Relative and Specific viscosity of different compounds in two different solvent system.

To calculate the Relative and Specific viscosity the equations used are as follows

$$\eta r = ds \times ts / dw \times tw$$

ds = density of solution, dw = density of solvent, ts = flow time of soltuion

tw = flow time of solvent, ηr = relative viscosity of solution

$$\eta s = \eta r - 1$$

The ligands used for viscometric study are -

1] 2 chloro 3 fluro benzaldehyde chalconeimine (CFB)

2] 4 fluro benzaldehyde chalconeimine (FB)

3] 4 fluro 2- chloro benzaldehyde chalconeimine (FC)

4] 2 chloro 3 fluro 2 chlorobenzaldehyde chalconeimine (CFC)

5] 4 fluro NN dimethyl benzaldehyde chalconeimine (FN)

6] 2 chloro 3 fluro NN dimethyl benzaldehyde chalconeimine(CFN)

OBSERVATIONS AND RESULTS

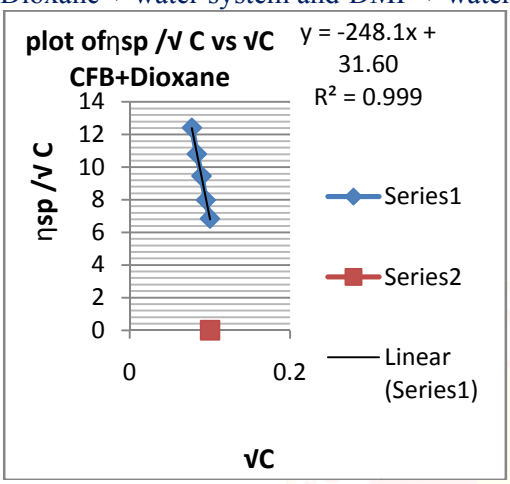
Physical property of ligands in dioxne + water system

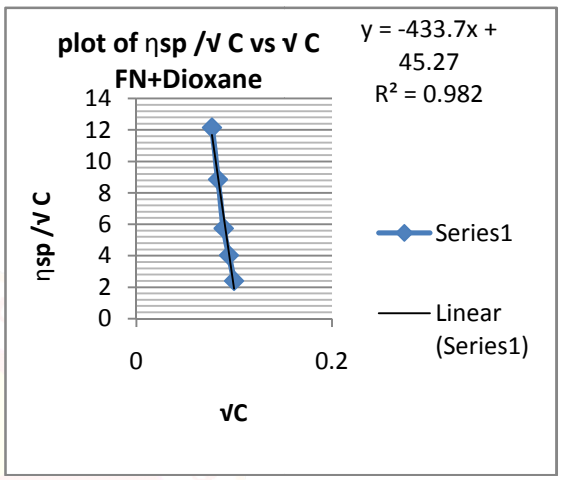
Sr.No	ligand	Conc^n.	Dencity	Relative viscosity	Specific viscosity	A- coefficient	β- coefficient
1	CFB	0.01	1.103	1.685218	0.685218	31.609	-248.1
		0.009	1.1091	1.757298	0.757298		
		0.008	1.111	1.846752	0.846752		
		0.007	1.122	1.904719	0.904719		
		0.006	1.132	1.96173	0.96173		
2	FB	0.01	1.098	1.698238	0.698238	165.86	-1574
		0.009	1.106	2.652049	1.652049		
		0.008	1.1032	3.40226	2.40226		
		0.007	1.118	3.761536	2.761536		
		0.006	1.194	4.377614	3.377614		
3	CFC	0.01	1.11	1.209123	0.209123	16.296	-144.98
		0.009	1.115	1.24838	0.24838		
		0.008	1.121	1.268681	0.268681		
		0.007	1.122	1.293622	0.293622		
		0.006	1.163	1.439609	0.439609		
4	FC	0.01	1.109	1.192345	0.192345	0.1046	-0.0029
		0.009	1.112	1.242764	0.242764		
		0.008	1.113	1.590279	0.590279		
		0.007	1.115	1.618247	0.618247		
		0.006	1.116	1.632571	0.632571		
5	CFN	0.01	1.098	1.328083	0.328083	15.474	-124.97
		0.009	1.106	1.345583	0.345583		
		0.008	1.1032	1.349979	0.349979		
		0.007	1.118	1.383906	0.383906		
		0.006	1.194	1.486428	0.486428		
6	FN	0.01	0.948	1.046067	0.046067	45.275	-433.71
		0.009	1.0184	1.947329	0.947329		
		0.008	1.026	2.798844	1.798844		
		0.007	1.084	4.365361	3.365361		
		0.006	1.0853	4.943818	3.943818		

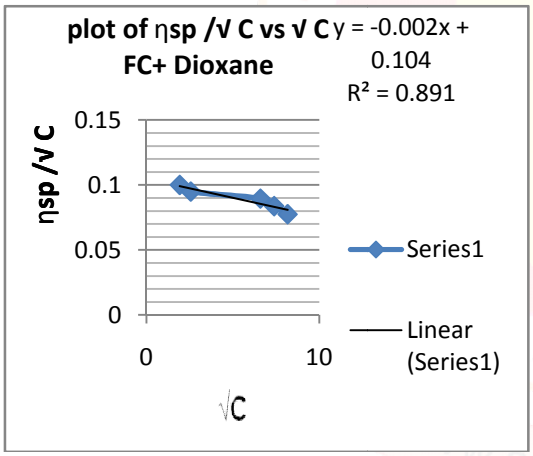
Physical property of ligands in DMF + water system

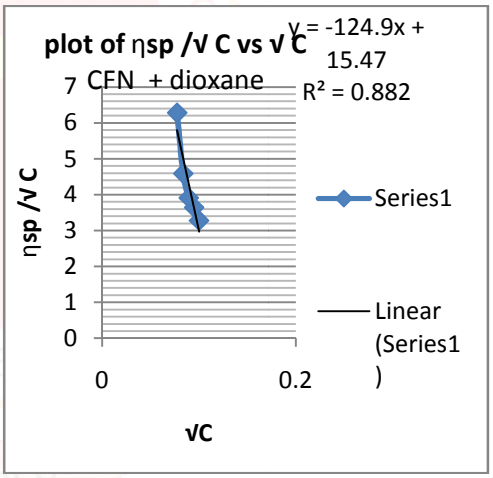
Sr.No	ligand	Conc^n.	Dencity	Relative viscosity	Specific viscosity	A coefficient	β coefficient
1	CFB	0.01	0.9512	1.632664	0.632664	120.86	-1156.6
		0.009	1.035	1.822915	0.822915		
		0.008	1.04	2.488861	1.488861		
		0.007	1.075	3.376123	2.376123		
		0.006	1.086	3.251888	2.251888		
2	FB	0.01	0.963	1.489438	0.489438	198.31	-1905.6
		0.009	1.056	2.532156	1.532156		
		0.008	1.07	4.056723	3.056723		
		0.007	1.087	4.426112	3.426112		
		0.006	1.107	4.606758	3.606758		
3	CFC	0.01	0.945	1.597557	0.597557	151.54	-1477.2
		0.009	1.01	1.671722	0.671722		
		0.008	1.055	3.052127	2.052127		
		0.007	1.057	3.127669	2.127669		
		0.006	1.069	3.692465	2.692465		
S	FC	0.01	0.952	1.535319	0.535319	391.26	-3966.9
		0.009	1.068	2.341853	1.341853		
		0.008	1.075	3.251875	2.251875		
		0.007	1.078	4.697061	3.697061		
		0.006	1.087	8.780564	7.780564		
5	CFN	0.01	1.098	1.258184	0.258184	134.4	-1308.31
		0.009	1.106	1.971435	0.971435		
		0.008	1.1032	2.684352	1.684352		
		0.007	1.118	3.171122	2.171122		
		0.006	1.194	3.454255	2.454255		
		0.01	1.098	1.258184	0.258184		
6	FN	0.01	0.948	1.046067	0.046067	232.21	-233.3
		0.009	1.0184	1.947329	0.947329		
		0.008	1.026	2.798844	1.798844		
		0.007	1.084	4.365361	3.365361		
		0.006	1.0853	4.943818	3.943818		

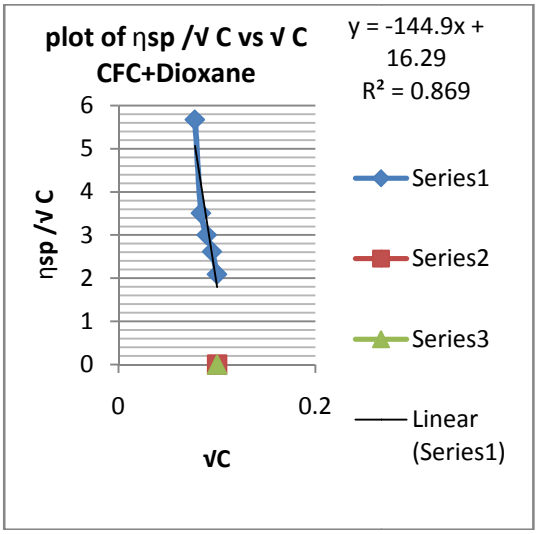
The calculated values of viscosity of ligands in Dioxane + water system and DMF + water system is represented in the following graph.This graph is plotted between ηsp /√ C vs √C.The graph of each ligand system gives a linear straight line showing the validity of Jones –Dole equation. The value of A and β have been determined from the slope & intercept . The plot of ηsp /√ C vs √C for all system are shown in following figures.

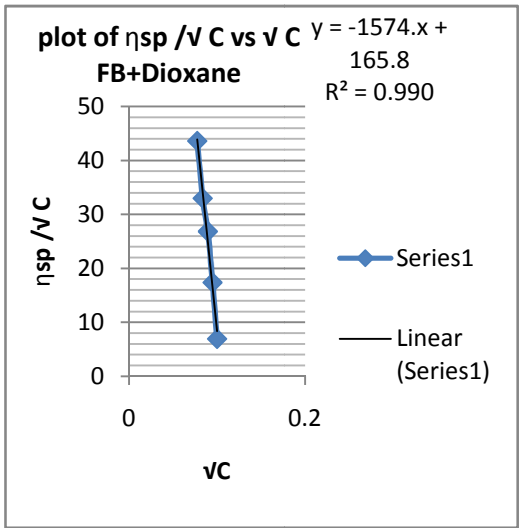


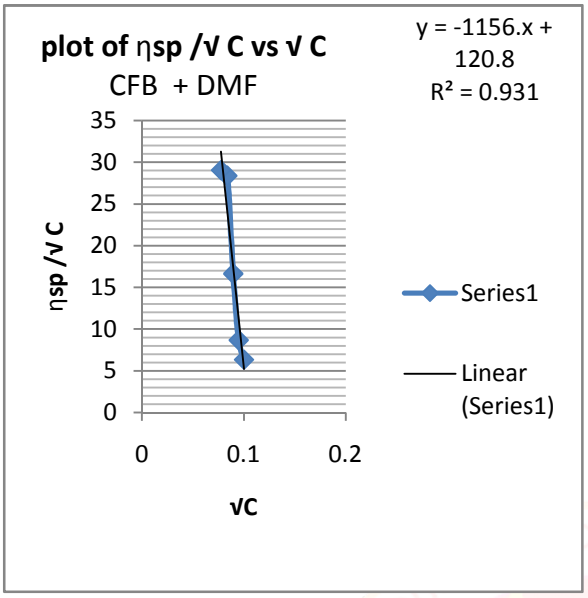


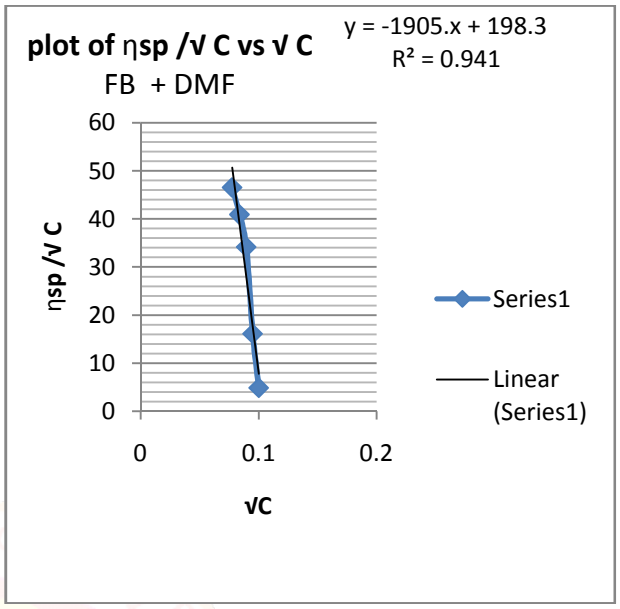









plot of ηsp /√ C vs √ C
CFB + DMF
y = -1156.x + 120.8
R² = 0.931
ηsp /√ C
√C
Series1
Linear (Series1)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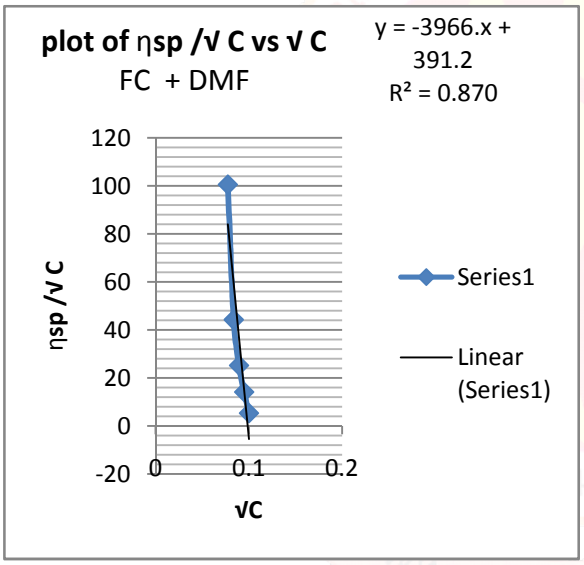
ηsp /√ C
√C
Series1
Linear (Series1)


plot of ηsp /√ C vs √ C
FC + DMF
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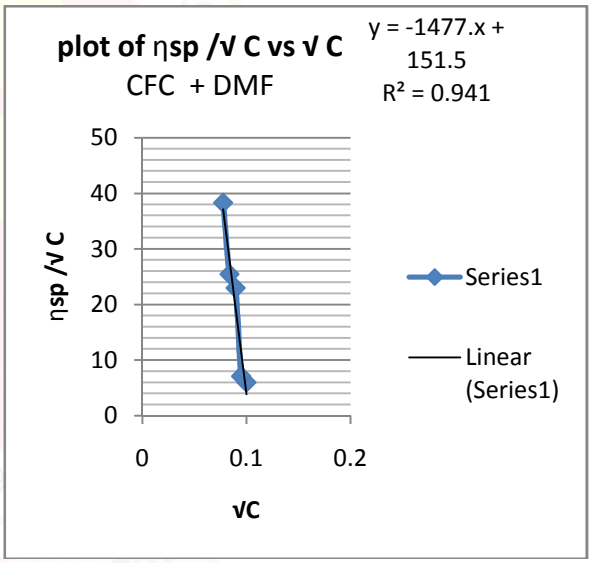
ηsp /√ C
√C
Series1
Linear (Series1)


plot of ηsp /√ C vs √ C
CFC + DMF
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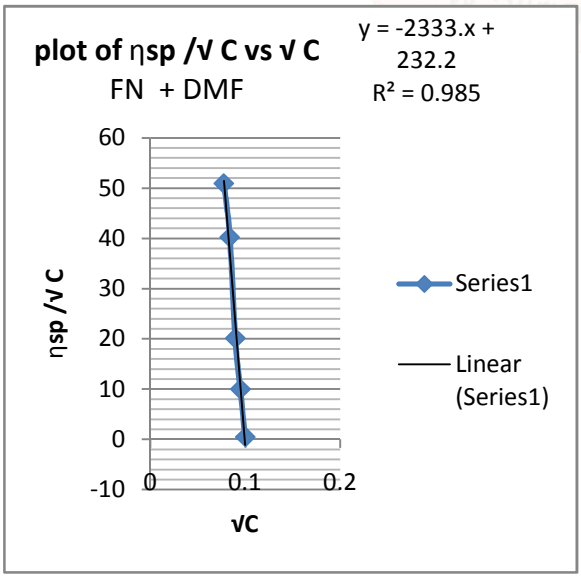
R² = 0.941
ηsp /√ C
√C
Series1
Linear (Series1)


plot of ηsp /√ C vs √ C
FN + DMF
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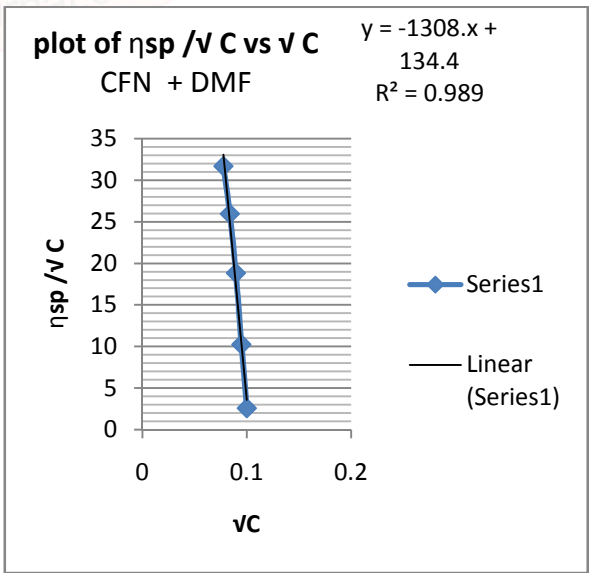
ηsp /√ C
√C
Series1
Linear (Series1)


plot of ηsp /√ C vs √ C
CFN + DMF
y = -1308.x + 134.4
R² = 0.989
ηsp /√ C
√C
Series1
Linear (Series1)

The A-Coefficient (Falkenhagen coefficient) indicate the solute- solute interaction . For all ligands as the value of A is positive indicates the strong solute-solute interaction in all system. The negative value of β-coefficient indicate the good order arrangement with increase of viscosity

Sr.No	compound	solvent-system	A	sβ
1	CFB	Dioxane	31.609	-248.1
		DMF	120.86	-1156.6
2	FB	Dioxane	165.86	-1574
		DMF	198.31	-1905.6
3	FC	Dioxane	0.1046	-0.0029
		DMF	391.26	-3966.9
4	CFC	Dioxane	16.296	-144.98
		DMF	151.54	-1477.2
5	FN	Dioxane	45.275	-433.71
		DMF	232.21	-233.3
6	CFN	Dioxane	15.474	-124.97
		DMF	134.4	-1308.31

CONCLUSION

In present investigation ,viscometric study of halosubstituted chalconeimine are carried out by using their solutions in different solvent (Dioxane and DMF) at different concentration .The relative viscosity of ligands increases with increase in concentration may be attributed to increase in solute – solvent interaction. The value of Falkenhagen coefficient are positive for all system and value and β-Coefficent is negative **.The value of A and β is more in DMF+water system .**

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The author is thankful to dept of Chemistry, Bar. R.D.I. & Ny K.D. college Badnera, dist- Amravati for providing all the necessary facilities.

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MULTICOMPONENT APPROACH SYNTHESIS OF 3-(FURAN-2-YLMETHYLENE)-1-PHENYLQUINOLINE-2,4(1*H*,3*H*)-DIONE CATALYZED BY ZRO_2 NANO PARTICLE

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ABSTRACT

*Multi-component approach synthesis of 3-(furan-2-ylmethylene)-1-phenylquinoline-2,4 (1H,3H)-dione catalyzed by ZrO_2 nano particle starting from easily available reactant molecule such as diphenyl amine **1**, di-ethyl malonate **2**, substituted arylaldehyde or heterocyclic aldehyde**3** in water-ethanol as green solvent. The ZrO_2 NPs gave better yield for the first three to four cycles of reactions. The characterizations of the ZrO_2 NPs were performed by using X-ray diffraction (XRD), Infrared Spectroscopy (IR) and Ultraviolet visible (UV–vis) absorption spectroscopy. The morphological property revealed the formation of nanoscale particles. In addition to developed a greener path for the synthesis of Quinolinone derivatives using ZrO_2 NPs and water-ethanol as catalyst and solvent. The expected results revels the catalytic activity, reaction time and the reusability of catalyst.*

Keywords: *Multi-component; Quinolinone derivatives; ZrO_2 Nano Particles; Green solvent; Conventional method.*

INTRODUCTION

Heteroatoms (Nitrogen and oxygen) containing six member fused heterocyclic compound such as quinolinone and its derivatives are significant for biological with potential medicinal use as anti-microbial [1], anti-tumor [2], anti-trypanosomal agents [3], anti-oxidant [4] and anti-fungal [5], anti-microbial, anti-biofilm activities [6], potential NF-κB inhibitors [7], in molluscicidal activity [8], anti-protozoal activity [9].Multicomponent reactions (MCRs) are well known tool for the organic synthesis and intermediates in medicinal and combinatorial chemistry [10, 11]. By evadelonger time and multistep process [12, 13] an atom economy and high selectivity [14].

Zirconium oxide or zirconia(ZrO_2) nano particles could be more efficient due to their large surface area and reactivity.Zirconia is produced by calcining zirconium compounds, exploiting its high thermal stability [15]. Itestablishes a stable tetragonal phase structure. The conductivity of ZrO_2 material is merely 10^{-7} s/cm at 1000 ºC, which is close to the conductivity of insulating material [16].

In literature survey, it was found that there is lack of effective multi-component procedure for the preparation of benzylidene and or arylidene quinolinone derivatives using ZrO_2 nanoparticle using green solvent (water, water-ethanol) in very short period at room temperature.

Earlier, in organic transformations [17, 18] ZrO_2 (zirconia) nanoparticles were used.

The present work is an effort to multi-component approach, synthesis of 3-(furan-2-ylmethylene)-1-phenylquinoline-2,4 (1*H*,3*H*)-dionecatalyzed by ZrO_2 NPs (Scheme **1**).

EXPERIMENTAL

Materials

The starting chemicals with high purity, playing important role in the present synthesis of quinolinone derivatives starting from easily available diethyl malonate, diphenylamine, various aromatic and heterocyclic aldehyde in water-ethanol as green solvent. The catalyst ZrO_2 NPs were purchased from Alfa Aesar. An appropriate molar proportion of starting materials was taken and the protocols of standard techniques were followed for the multi-component synthesis of quinolinone derivatives. Melting points of synthesized product were recorded on OptiMELT digital melting point apparatus and were uncorrected. The ZrO_2 NPs catalyst was characterized by X-ray diffraction (Figure **1**, **2**), UV-Visible (Figure **3**), FT-IR (Figure **4**) and reusability (Figure **5**) [19]. The IR spectra were recorded on a FT-IR (Bruker). ^{1}H NMR spectra were recorded on a 400 MHz Bruker spectrometer

in solvent $CDCl_3$ as part per million (ppm) downfield from a tetra methyl silane (TMS) internal standard. The elemental analysis was performed on a Perkin Elmer 2400 series II elemental CHNS analyzer. Spectral characterization data for the entire synthesized products (**4a-4k**) as depicted in supplementary data as a supporting data.

General procedure for the synthesis of compounds (4a-k):

A mixture of various aldehyde **1** (1mmol), diphenyl amine **2** (1mmol), diethyl malonate **3** (1mmol) and ZrO_2 NPs (10 mol %) in 8 ml ethanol water (4:1) was stirred temperature at 60-70 ºC for 4-5 min until the reaction mixture solidified. The progress of the reaction was monitored by TLC. After completion of reaction, the solvent was removed under reduced pressure further crude product was stirred with 4-6 ml methyl alcohol at 60-70 ºC for the time of 3-5 min followed by the simple filtration to expel catalyst out by simple filtration. Then methyl alcohol was removed under reduced pressure and the solid compound was purified by recrystallization from ethyl alcohol to give product with an excellent yield (89-98 %).

Reusability of the catalyst (Figure **5**)**:** Procedure: The recovered catalyst from the reaction mixture during the synthesis of N-phenyl 3-arylidene quinolinone derivative washed with methanol (4-6 ml) followed by ethanol (6-8 ml) and finally dried well and reused for subsequent runs. The reusability of catalytic tested and we observed an excellent yield was obtained for the first 4-6th cycles of reaction (Figure **5**) [19].Then yield of the product were decreases even after increases the time of reaction.

CHARACTERIZATION TECHNIQUES

X-ray diffraction (**Figure 1, 2**) [19]**:** The X-ray diffraction (XRD) patterns was characterized by Philips X Pert Pro monochromatized diffractometer Cu-Kα radiation (λ = 1.54056 Å). The size of ZrO_2 nanoparticles, the XRD spectrum of the samples were taken using SSD160 1D Detector (Bruker). By X-ray diffraction pattern, we observed high intensity peak (103) at assigned at 2θ = 30.5. (112) and (101) reflections are present at 2θ = 51.02 and 59.31 respectively. All the reflections are indexed to the characteristic planes of a major tetragonal phase in ZrO_2 crystal system (t-ZrO_2, space group P21/a, JCPDS card No. 37-1484 and 88-1007) no extra peak was observed corresponding to monoclinic plane. A clear broad peak in powder X-ray diffraction confirmed the formation of nano-sized particles of ZrO_2 (Figure **2**) [19]. The crystallite sizes was estimated from the Debye-Scherrer equation

$D = \frac{0.9\lambda}{\beta cos\theta}$; where λ is the wavelength of Cu-Kα radiation (1.54056 Å) and β is the full width of the (h k l) peak at the diffracting angle 2θ. The mean crystallite size was estimated between ~20 and ~30 nm.

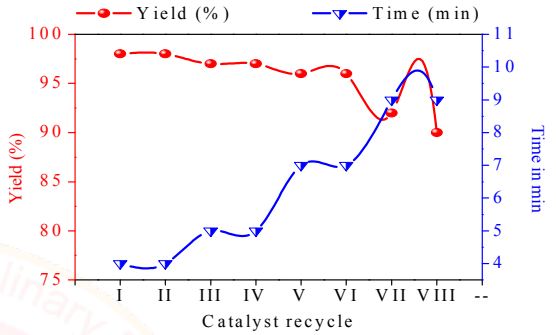
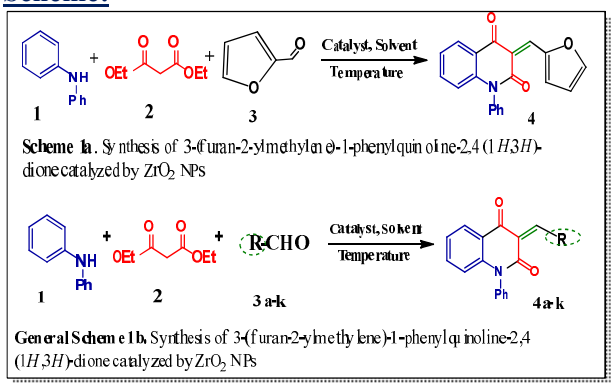


Figure 1(5): Reusability of ZrO_2 NPs for the synthesis of 3-(furan-2-ylmethylene)-1-phenylquinoline-2,4 (1*H*,3*H*)-dione and 3-arylidine Quinolone 2,4-dione (4)

UV-Visible spectroscopy (**Figure 3**) [19]**:** In theUV-Visible spectra of pure ZrO_2 NPs and ZrO_2 NPs after 8th cycle were recorded on Scinco UV–vis scanning spectrometer (Model S-4100) with the wavelength λ= ~260 nm. UV near-band edge (NBE) emission of ZrO_2 was observed at range between 458 nm - 465 nm which was equivalent to band gap of 4.76 eV. Wavelength of pure ZrO_2 NPs; 260 nm and after 8th cycle the wavelength was observed also same. The electronic band structure of ZrO_2 is strongly influenced by the hybridization of Zr-4d orbital and O-2p orbital [18]. The interaction of arylidine quinolinone derivatives with ZrO_2 NPs has perceptible effect in its band structure as revealed by UV–Vis spectroscopy (Figure **3**)[19].

Scheme:

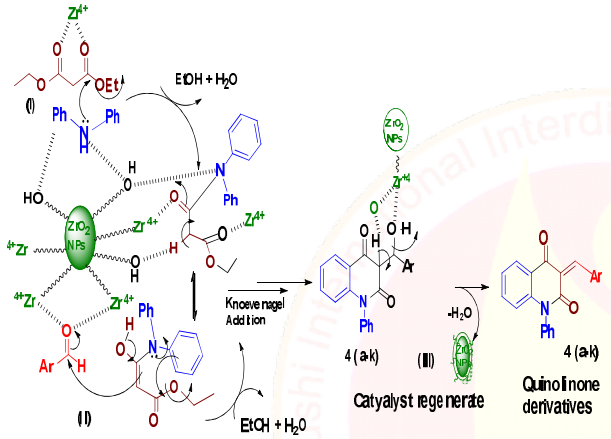


Scheme 1a. Synthesis of 3-(furan-2-ylmethylene)-1-phenylquinoline-2,4 (1*H*3*H*)-dione catalyzed by ZrO_2 NPs

General Scheme 1b. Synthesis of 3-(furan-2-ylmethylene)-1-phenylquinoline-2,4 (1*H*,3*H*)-dione catalyzed by ZrO_2 NPs

Scheme 1. 3-(furan-2-ylmethylene)-1-phenylquinoline-2,4 (1*H*,3*H*)-dione and 3-arylidine Quinolone 2,4-dione

FT-IR (Figure 4) [19]: The FT-IR analysis of ZrO_2 NPs the stretching vibrations can be studied in terms of transmittance % against wavenumbers. The distinctive band around 3300-3425 cm^{-1} can be seen which indicated the transmittance due to O-H absorptions. 930-952 cm^{-1} and a broad band near 1640-1652 cm^{-1} which are associated with the O–H modes of chemisorbed water and/or terminated hydroxides at the surface. The intense absorbance band in FT-IR spectrum were observed in range between 490-498 cm^{-1} and 440-458 cm^{-1} which were attribute to the Zr-O stretching vibrations (Figure **4**) [19].



Scheme 2. Plausible mechanism for the synthesis of 3-(furan-2-ylmethylene)-1-phenylquinoline-2,4 (1*H*,3*H*)-dione and 3-arylidine Quinolone 2,4-dione **(4)**

Tables:

Table 1. Screening of catalyst with solvents, reaction time, and yield for the synthesis **4a.**

Entry	Catalyst	Solvent	Time (min)	Yield[a] (%)
1	Without	Solvent free	120	00
2	ZrO_2 NPs (10 mol %)	Solvent free	60	35
3	ZrO_2 NPs (10 mol %)	H_2O	40	49
4	ZrO_2 NPs (10 mol %)	CH_3CN	30	50
5	ZrO_2 NPs (10 mol %)	DCM	30	40
6	ZrO_2 NPs (10 mol %)	DMF	30	48
7	ZrO_2 NPs (10 mol %)	THF	30	40
8	ZrO_2 NPs (10 mol %)	MeOH	12	59
9	ZrO_2 NPs (10 mol %)	EtOH	7,9	68,70
10	ZrO_2 NPs (10 mol %)	EtOH:H_2O (6:1)	7,9	78,80
11	ZrO_2 NPs (05 mol %)	EtOH:H_2O (4:1)	10	76
12	ZrO_2 NPs (10 mol %)	EtOH:H_2O **(4:1)**	**3,4**	**78, 98**
13	ZrO_2 NPs (15 mol %)	EtOH:H_2O (4:1)	5,6	98,98
14	ZrO_2 NPs (10 mol %)	EtOH:H_2O (2:1)	10	68
15	ZrO_2 NPs (10 mol %)	EtOH:H_2O (1:1)	10	56
16	ZrO_2 (10 mol %)	Solvent free	60	20
17	ZrO_2 (10 mol %)	H_2O	50	38
18	ZrO_2 (10 mol %)	CH_3CN	35	40
19	ZrO_2(10 mol %)	EtOH	15,18	53,55
20	ZrO_2(10 mol %)	EtOH:H_2O (6:1)	12,15	58,60
21	ZrO_2(10 mol %)	EtOH:H_2O (6:1)	12	60

Reaction conditions: diphenyl amine **1** (1mmol), diethyl malonate **2** (1mmol), benzaldehyde **3** (1mmol) and ZrO_2 NPs (10 mol %) in 8 ml of ethanol-water (4-1) was stirred at 60-70 ºC temperature; [a]Isolated yield,

RESULTS AND DISCUSSION

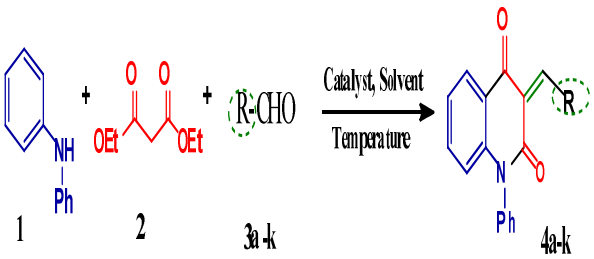
In continuation of our greener approach research work [20-37], keeping focus on multicomponent green approach, the model reaction of diphenyl amine **1** (1mmol), diethyl malonate **2** (1mmol), Benzaldehyde **3** (1mmol) was stirred at 60-70ºC temperature. First, we carry out the reaction without catalyst and solvent, reaction did not detected even after 120 min (Table **1** entry 1). The same reaction was carried out in ZrO_2 NPs, by screening various solvent (Table **1**). A very poor yield was obtained in solvent free condition (Table **1** entry 2). In ethanol, good yield of product was obtained in very less time of reaction (Table **1** Entry 9) but we used water the somewhat yield of products were increased (Table **1**, entry 3). For the nextoptimization we used combination of water and ethanol solvent as ethanol-water (4:1) an excellent yield was obtained in 10 mol% ZrO_2 NPs within 4 min, if we increase the time of reaction more than 4 min there is no more significant effect was observed on the yield of product (Table **1** Entry12). The same yield was obtained even after we increased more than 10 mole % of catalyst (Table **1** Entry13). Further we changed solvent proportion system in set of model reaction, decreasing the amount of ethanol the yield of product were decreases (Table 1 entry 14, 15). For the given set of reaction, we used a common ZrO_2 catalystwith optimizing solvent and solvent free condition (Table 1, entry 16-21). Herein we observed that, good yield was obtained in polar-protic solvent (Table 1, entry 19). The results seem that, yields of products were increases in combination of ethanol-water (6:1) (Table 1, entry 20). If we increase the catalyst more than 10 mole % there is no more significant effect was observed

on the yield of product (Table 1, entry 21).Herein we observed that the ZrO_2 NPs in water-ethanol is found to be the best catalyst-solvent combination.

Thus, all examples were tested reasonably good to the excellent yields in ethanol water (4:1) with 10 mol % of catalyst (Table 2, scheme 1). The ZrO_2 NPs was explored by checking its reusability, after each cycle, the catalyst were recovered by centrifugation process using methanol, dried and reused for continuous reactions. First four to six cycles gave better yield and then gradually decreases (Figure 5)[19], the yield of the product were decreases even after increases the time of reaction and the catalytic activity decreases due to surface area of catalyst reduced, site become inactive due to deposition of electrons on metal from solvent (water and ethanol). The loss of electron from active site of catalyst (Zr^{+} to Zr^{++} and or Zr^{++} to Zr^{+++}) and produced oxygen vacancy of ZrO_2.

The recovered catalyst was characterized by X-ray diffraction, FTIR, UV-Visible spectroscopy (Figure 1-4). The oxygen vacancies in pure tetragonal zirconia were responsible for stability and higher surface activity [38]. The important feature for these catalysts is; surface of catalyst contains active hydroxyl, oxide groups and Zr^{+4} act as Lewis acids and or base which are well reported [39]. The active hydroxide and oxide of NPs plays an important role for cyclization and condensation reaction because of act as both function acid as well as base [40]. The possible mechanistic path for the present work have been described for the synthesis of 3-(furan-2-ylmethylene)-1-phenylquinoline-2,4 (1*H*,3*H*)-dione and 3-benzylidene-1-phenylquinoline-2,4(1*H*,3*H*)-diones *via* Knoevenagel addition reaction using ZrO_2 NPs as catalyst, cyclization followed by Knoevenagel addition reaction between diphenyl amine **1**, diethyl malonate **2**, and substituted aldehyde **3** with the help of active hydroxyl and Zirconium ion of ZrO_2 NPs as catalyst (Scheme **2**).

Table 2. Synthesis of 3-benzylidene-1-phenylquinoline-2,4(1*H*,3*H*)-diones under microwave irradiation:



Entry	Compound	R	Time (min)	Yield[b] (%)	Melting Point (°C)
1 (Q1)	4a	H	4	98	209-210
2 (Q2)	4b	3-NO_2	5	95	257-258
3 (Q3)	4c	4-NO_2	4	97	221-222
4 (Q4)	4d	3-Br	5	90	289-290
5 (Q5)	4e	2-OH	6	89	197-198
6 (Q6)	4f	4-F	5	90	259-260
7 (Q7)	4g	4-OH	6	89	219-220
8 (Q8)	4h	4-Cl	5	92	203-204
9 (Q9)	4i	4-OMe	5	96	215-216
10 (Q10)	4j	4-Br	5	91	188-189
11 (Q10)	4k	furfural	4	93	179-181

Reaction Condition: diphenyl amine **1** (1mmol), diethyl malonate **2** (1mmol), substituted aldehyde **3** (1mmol) and ZrO_2 NPs (10 mol%) in solvent (ethanol-water) 8 ml was stirred at 60-70 ºC.; [b]Isolated yield

Finally the structures of the compounds **4a** were confirmed by spectral characterization data. For example, in the IR spectrum, it gave a peak at 1705 cm^{-1} due to (C=O), 1578 (C=C), 1089 (C-N). The ^{1}HNMR spectrum of compound gave singlet at δ = 8.56 (s, 1H, HC=C-), and three multiplet at δ= 7.18-7.49 (m, 5H, Ar-H), 7.40-8.05 (m, 4H, Ar-H) and 7.30-7.62 (m, 5H, Ar-H) having Mass spectrometry: MS (m/z, %): 326.36 [M^+].

4k (3-(furan-2-ylmethylene)-1-phenylquinoline-2,4(1*H*,3*H*)-dione) were confirmed by spectral characterization data. For example, in the IR spectrum, it gave a peak at 1705 cm^{-1} due to (C=O), 1579 (C=C), 1089 (C-N);^{1}H NMR (300 MHz, DMSOd_6); ^{1}H NMR (300 MHz, $CDCl_3$) δ; 7.16-7.49 (m, 5H, Ar-H); 7.39-8.05 (m, 4H, Ar-H); 6.89 (dd, 1H, furfural); 8.19 (d, 1H, furfural); 8.39(d, 1H, furfural); 8.49(s,1H, HC=C-); MS(m/z %): 315.09 [M^+], Elemental Anal. C=76.18, H=4.16, N=4.44, O=15.22 and having Mass spectrometry: MS (m/z, %): 315.09 [M^+] and Elemental Anal. C=76.18, H=4.16, N=4.44, O=15.22

CONCLUSIONS

In the present research work we developedmulti-component approach for the synthesis of (3-(furan-2-ylmethylene)-1-phenylquinoline-2,4(1*H*,3*H*)-dione) and N-phenyl, 3-arylidine Quinolone 2, 4-dione derivatives by simple conventional method catalyzed by ZrO_2 NPs in combination of water-ethanol as solvent with good to better yield of all product of reaction.

Characterization data of synthesized product (4a-4k):

1 **(*Z*)-3-benzylidene-1-phenylquinoline-2,4 (1*H*, 3*H*)-dione(4a):** Yield: 98%; m.p. 209-210^{0}C; FTIR(KBr,cm^{-1}); 1705(C=O Ketonic), 1578 (C=C), 1089 (C-N).; ^{1}H NMR (300 MHz, $CDCl_3$) δ; 7.18-7.49 (m, 5H, Ar-H); 7.40-8.06 (m, 4H, Ar-H); 7.30-7.62 (m,5H, Ar-H); 8.58(s, 1H, HC=C-); MS (m/z, %): 326.36 [M$^+$], Elemental Anal. C=81.21, H=4.64, N=4.30, O=9.83

2. **(*Z*)-3-(3-nitrobenzylidene)-1-phenylquinoline-2,4(1*H*,3*H*)-dione(4b):** Yield: 95%;m.p.257-258^{0}C; FTIR(KBr,cm^{-1}); 1705(C=O Ketonic), 1578 (C=C), 1089 (C-N) 1340, 1252, 740-850, 1008-1090.; ^{1}H NMR(300 MHz, $CDCl_3$) δ; 7.18-7.48 (m, 5H, Ar-H); 7.40-8.06 (m, 4H, Ar-H); 8.72 (s,1H, HC=C-); 8.32(s, 1H, Ar-H); 7.80-8.16(m,3H, Ar-H); MS(m/z %): 371.095 [M$^+$], Elemental Anal. C=71.34, H=3.80, N=7.55, O=17.28

3. **(*Z*)-3-(4-nitrobenzylidene)-1-phenylquinoline-2,4(1*H*,3*H*)-dione(4c):** Yield: 97%;m.p.221-222^{0}C;FTIR(KBr,cm^{-1}); 1705(C=O Ketonic), 1578 (C=C), 1089 (C-N), 1252, 740-850, 1008-1090, 1374, 740-850, 1010-1090. ^{1}H NMR(300 MHz, $CDCl_3$) δ; 7.18-7.49 (m, 5H, Ar-H); 7.40-8.07 (m, 4H, Ar-H); 8.72 (s,1H, HC=C-); 8.24(d, 2H, Ar-H); 8.02(d, 2H, Ar-H); MS (m/z %): 371.095 [M$^+$], Elemental Anal. C=71.35, H=3.81, N=7.56, O=17.28

4. **(*Z*)-3-(3-bromobenzylidene)-1-phenylquinoline-2,4(1*H*,3*H*)-dione(4d):** Yield: 90%;m.p.289-290^{0}C;FTIR(KBr,cm^{-1}); 1705(C=O Ketonic), 1578 (C=C), 1089 (C-N)1340, 1252, 740-850, 1008-1090.; ^{1}H NMR(300 MHz, $CDCl_3$) δ; 7.18-7.49 (m, 5H, Ar-H); 7.40-8.06 (m, 4H, Ar-H); 8.59 (s,1H, HC=C-); 7.30-7.56(m,3H, Ar-H); 7.59(s, 1H, Ar-H); MS(m/z %): 405.25 [M$^+$], Elemental Anal. C=65.36, H=3.49, Br=19.76, N=3.45, O=7.92

5. **(*Z*)-3-(2-hydroxybenzylidene)-1-phenyl quinoline-2,4(1*H*,3*H*)-dione(4e):** Yield: 89%;m.p.197-198^{0}C; FTIR(KBr,cm^{-1}); 1705(C=O Ketonic), 1578 (C=C), 1089 (C-N), 1252, 740-850, 1008-1090.; ^{1}H NMR(300 MHz, $CDCl_3$) δ; 7.18-7.49 (m, 5H, Ar-H); 7.40-8.06 (m, 4H, Ar-H); 8.74 (s,1H, HC=C-); 5.36(s, 1H, Ar-OH); 6.98-7.72(m,4H, Ar-H) MS(m/z %): 342.35 [M$^+$], Elemental Anal. C=77.41, H=4.42, N=4.11, O=14.06

6. **(*Z*)-3-(4-fluorobenzylidene)-1-phenyl quinoline-2,4(1*H*,3*H*)-dione (4f):** Yield: 90; m.p.259-260; FTIR(KBr,cm^{-1}); 1705(C=O Ketonic), 1578 (C=C), 1089 (C-N), 1252, 740-850, 1008-1090 ^{1}H NMR (300 MHz, $CDCl_3$) δ; 7.18-7.49 (m, 5H, Ar-H); 7.40-8.06 (m, 4H, Ar-H); 7.18 (d, 2H, Ar-H); 7.73(d, 2H, Ar-H); 8.61(s, 1H, HC=C-); MS(m/z %): 344.35 [M$^+$], Elemental Anal. C=76.96, H=4.11, F=5.52, N=4.09, O=9.34

7. **(*Z*)-3-(4-hydroxybenzylidene)-1-phenyl quinoline-2,4(1*H*,3*H*)-dione(4g):** Yield: 89%;m.p.219-220^{0}C; FTIR(KBr,cm^{-1}); 1705(C=O Ketonic), 1578 (C=C), 1089 (C-N), 1252, 740-850, 1008-1090;^{1}H NMR(300 MHz, $CDCl_3$) δ; 7.18-7.48 (m, 5H, Ar-H); 7.40-8.06 (m, 4H,Ar-H); 5.38 (s,1H, Ar-OH); 8.59(s, 1H, HC=C-); 6.68(d, 2H, Ar-H); 7.59(d,2H, Ar-H); MS(m/z %): 342.35 [M$^+$], Elemental Anal. C=77.41, H=4.42, N=4.12, O=14.08

8. **(*Z*)-3-(4-chlorobenzylidene)-1-phenyl quinoline-2,4(1*H*,3*H*)-dione(4h):** Yield: 92%;m.p.203-204^{0}C; FTIR(KBr,cm^{-1}); 1705(C=O Ketonic), 1578 (C=C), 1089 (C-N), 1252, 740-850, 1008-1090 ^{1}H NMR (300 MHz, $CDCl_3$) δ; 7.18-7.49 (m, 5H,Ar-H); 7.40-8.06 (m, 4H, Ar-H); 7.44 (d, 2H, Ar-H); 8.64(s, 1H, HC=C-); 7.69(d, 2H, Ar-H); MS (m/z %): 360.80 [M$^+$], Elemental Anal. C=73.44, H=3.91, Cl=9.85, N=3.87, O=8.88

9. **(*Z*)-3-(4-methoxybenzylidene)-1-phenyl quinoline-2,4(1*H*,3*H*)-dione(4i):** Yield: 96%;m.p.215-216^{0}C; FTIR(KBr,cm^{-1}); 1705(C=O Ketonic), 1578 (C=C), 1089 (C-N), 1252, 740-850, 1008-1090; ^{1}H NMR (300 MHz, $CDCl_3$) δ; 7.18-7.49 (m, 5H,Ar-H); 7.40-8.06 (m, 4H, Ar-H); 3.88(s, 3H, Ar-OMe); 8.58(s, 1H, HC=C-); 6.98(d, 2H, HC=C-); 8.32(d, 2H, HC=C-); MS(m/z %): 356.38 [M$^+$], Elemental Anal. C=77.74, H=4.83, N=3.95, O=13.52

10. **(*Z*)-3-(4-bromobenzylidene)-1-phenyl quinoline-2,4(1*H*,3*H*)-dione (4j):** Yield: 91; m.p.:188-189; FTIR(KBr,cm^{-1}); 1705(C=O Ketonic), 1578 (C=C), 1089 (C-N), 1252, 740-850, 1008-1090^{1}H NMR (300 MHz, DMSOd_6); ^{1}H NMR (300 MHz, $CDCl_3$) δ; 7.16-7.46 (m, 5H, Ar-H); 7.40-8.05 (m, 4H,Ar-H); 7.54 (d, 2H, Ar-H); 7.60(d, 2H, Ar-H); 8.58(s,1H, HC=C-); MS(m/z %): 405.25 [M$^+$], Elemental Anal. C=65.36, H=3.50, Br=19.77, N=3.48, O=7.91

11. **(*Z*)-3-(4-bromobenzylidene)-1-phenyl quinoline-2,4(1*H*,3*H*)-dione (4k):** Yield: 93; m.p.:179-181; FTIR(KBr,cm^{-1}); 1705(C=O Ketonic), 1579 (C=C), 1089 (C-N), 1251, 740-

853, 1006-1092; ^{1}H NMR (300 MHz, DMSOd_6); ^{1}H NMR (300 MHz, $CDCl_3$) δ; 7.16-7.49 (m, 5H, Ar-H); 7.39-8.05 (m, 4H,Ar-H); 6.89 (dd, 1H, furfural); 8.19 (d, 1H, furfural); 8.39(d, 1H, furfural); 8.49(s,1H, HC=C-); MS(m/z %): 315.09 [M^+], Elemental Anal. C=76.18, H=4.16, N=4.44, O=15.22

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SYNTHESIS, CHARACTERIZATION AND ANTIMICROBIAL ACTIVITY OF SOME HALO-SUBSTITUTED CHALCONES.

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ABSTRACT

In the present work author reported the synthesis of some halo substituted chalcones.The synthesis was carried out in alcoholic potassium hydroxide at room temperature by ClaisenSchmidt condensation reaction. The compounds were obtained in good yield by using this method. These synthesized compounds were characterized by FT-IR and H-NMR spectral data. These compounds were evaluated for biological activity against the some gram positive and gram negative bacteria and against some fungus. These halo substituted chalcones show good Inhibition activities.

Keywords: *Chalcones synthesis, gram + gram –ve bacteria, biological activity.*

INTRODUCTION

Chalcone is the trivial name given to the α β-unsaturated ketones obtained by condensing an aromatic aldehyde with an aryl methyl ketone in the presence of a base. The chemistry of chalcones has generated intensive scientific interest due to their biological and industrial application. Chalcones are natural biocides and are well known intermediates in the synthesis of heterocyclic compounds exhibiting various biological activities. Chalcones and their derivatives possess some interesting biological properties such as antibacterial, antifungal, insecticidal, anesthetic, anti-inflammatory, analgesic etc.

Renate *et al*[1]. Have reported the synthesis of an acetylenic chalcones. The new acetylenic chalcones were evaluated for antimalarial and antitubercular activity. The antimalarial data for this series suggests that growth inhibition of the W2 strain of *Plasmodium falciparum* can be imparted by the introduction of a methoxy group ortho to the acetylenic group. Most of the compounds were active against *Mycobacterium tuberculosis* H37Rv.

Babasaheb *et al*[2]**.** Have reported synthesis and biological evaluation of β-chlorovinyl chalcones. All these compounds were evaluated for their anti-inflammatory activity and antimicrobial activity. Most of these compounds showed very good antibacterial and antifungal activity.

Anindra *et al*[3]. Have reported synthesis of (2*E*)-1, 1-(3-hydroxy-5-methylbiphenyl-2,6- diyl)-bis(3-pheylprop-2-ene-1-ones. In this case the new chalcones were prepared by the reaction of 1, 3-diacetyl biphenyls with different aldehydes in presence of catalytic amount of solid potassium hydroxide in ethanol with excellent yields. The synthesized compounds were evaluated for anticancer activity against human breast cancer MCF-7 (estrogen responsive proliferative breast cancer model) and MDA-MB-231 (estrogen independent aggressive breast cancer model) cell lines, HeLa (cervical cancer) cell line, and human embryonic kidney (HEK-293) cells. Most of the compounds preferentially inhibited the growth of the aggressive human breast cancer cell lines.

Zohreh *et al*[4]**.** Have reported synthesis of novel chalconoids containing a 6-chloro-2H-chromen-3-yl group. The target compounds were evaluated against the promastigote form of *Leishmania major* using MTT assay. These compounds have shown high *in vitro* antileishmanial activity at concentrations less than 3.0 μM. The results of cytotoxicity assessment against mouse peritoneal macrophage cells showed that these compounds display antileishmanial activity at non-cytotoxic concentrations.

Jen-Hao *et al*[5]. Have reported synthesis of 2, 5-dialkoxylchalcones by Claisen–Schmidt condensation of appropriate acetophenones with suitable aromatic aldehydes. The novel 2,5-dialkoxylchalcones were evaluated for their cytotoxic, anti-inflammatory, and anti-oxidant activities.

Julio *et al*[6]**.** Have reported solution-phase parallel synthesis of substituted chalcones and their antiparasitary activity against *Giardia lamblia*.

Anastasia *et al*[7]**.** have reported synthesis, characterization and evaluation of 2-hydroxy-chalcones and aurones as antioxidant and soybean lipoxygenase, an extensive structure-relationship study was performed and revealed that several chalcones and aurones possess an appealing

pharmacological profile combining high antioxidant and lipid per oxidation activity with potent soybean LOX inhibition.

Kakade *et al*[8]. Have reported synthesis, characterization and biological significance of some substituted novel chalcones.

MATERIAL AND METHODS

4-bromoacetophenone, anisaldehyde, cinnamaldehyde, KOH all taken are of high purity. Instrumental method: IR recorded on Perkin Elmer 237 spectrophotometer and H^1 NMR were recorded on Bruker advance II 400NMR spectrometer. Disc diffusion method for antimicrobial activity. This method applied for screening the synthesized compounds againsed various gram positive and gram negative bacteria.

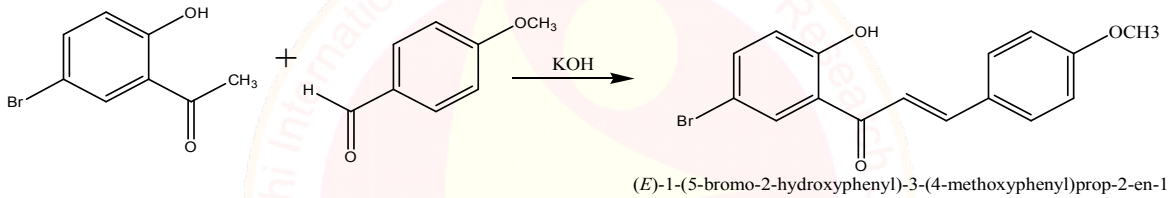
Experimental section

Synthesis of chalcone:

The compound were synthesized by using claisen condensation reaction, the chalcones of 4-bromo acetophenone with substituted aldehydes were prepared. The substituted aldehydes used are anisaldehyde and cinnamldehyde. The synthesized compounds were purified by using alcohol like ethanol. The purity was checked by TLC.

Synthesis of chalcone from Anisaldehyde (L2):

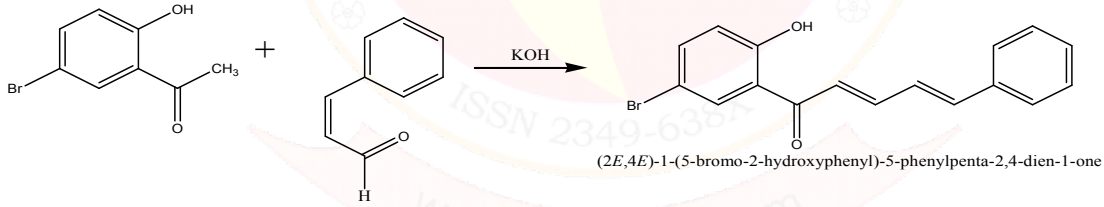
The alcoholic solution of anisaldehyde was added slowly into the alocoholic solution of 4-bromoacetophenone with constant stirring. Then solution of potassium hydroxide (30%) was added with vigorous stirring, the reaction mixture was kept overnight. Then the crude product was obtained by acid workup. The obtained product was crystallized by ethanol (Figure 1)



(*E*)-1-(5-bromo-2-hydroxyphenyl)-3-(4-methoxyphenyl)prop-2-en-1-one

Synthesis of chalcone from Cinnamldehyde (L6):-

The alcoholic solution of cinnamaldehyde was added slowly into the alocoholic solution of 4-bromoacetophenone with constant stirring. Then solution of potassium hydroxide (30%) was added with vigorous stirring, the reaction mixture was kept overnight. Then the crude product was obtained by acid workup. The obtained product was crystallized by ethanol (Figure 2)



(2*E*,4*E*)-1-(5-bromo-2-hydroxyphenyl)-5-phenylpenta-2,4-dien-1-one

Table1: Physical data of compounds

Sr.no	Compounds	Molecular formula	Colour	Melting Point	Nature
1	L2	$C_{16}H_{13}O_3Br$	Yellow	72°C	Crystalline
2	L6	$C_{17}H_{13}O_2Br$	Dark Yellow	80oC	Crystalline

Table 2: The FTIR spectral analysis of compounds (V=cm^-)

Sr.no	**Compounds**	C=C	Ar-OCH_3	C=C conjugation	Ar-Br	C=O	C-H	-OH
1	L2	1610	2560	3600	820	1570	2895	3125
2	L6	1622	-	3640	826	1570	2898	3130

Table 3: The H1 NMR of compounds (σ in ppm)

Sr.no	Compounds	**σ in ppm**	No of Proton	Assignment
1	L2	7.18	1H	Ar-H
		5.0	1H	Ar-OH
		7.56	1H	CH-H
2	L6	7.21	1H	Ar-H
		6.65	1H	CH-H
		7.81	1H	Ar-OH

Table 4: Analysis of antimicrobial activity of chalcones.

Sr.no	Compounds	staphylococci	**E-Coli**	candida albicans
1	L2	10mm	12mm	12mm
2	L6	14mm	10mm	16mm

CONCLUSION

The synthesized series of chalcone under mild condition and evaluated for their antibacterial and antifungal activity. All synthesized compounds were found to be potent antifungal and antibacterial agents. It is to be noted that chalcone of cinnamaldehyde found to be much more potency with respect to other chalcone.

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ASSESSMENT OF PHYSIOCHEMICAL PARAMETERS AND ORGANOCHLORINE PESTICIDES OF DRINKING WATER FROM MANORA TEHSIL DIST. WASHIM

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ABSTRACT

In present investigation study, drinking water was collected from various villages of Manora Tehsil Dist. Washim which is located in Maharashtra state of India for assessment of physio-chemical parameters and organochlorine pesticide residues.Due to increase population, advanced agricultural practices, industrialization, man- made activity, water is being highly polluted with different contaminants.It is necessary to know different parameters of the collected water samples such as water temperature, pH, dissolved oxygen, total solids, Conductance, Salinity and ORP. The result indicate that most of the parameter from this region are within WHO and BIS limit and it is safe and suitable for drinking purpose after some treatment.

Key Words: *Physico-chemical Parameters, Pesticides& Drinking water standards.*

INTRODUCTION

Water is life. No life can exist without water. Water is absolutely essential not only for survival of human beings, but also for animals, plants and all other living beings. It has many beneficial uses such as drinking, irrigation, navigation, propagation of wild life, fisheries, recreation; aesthetics etc. water is one of the most valuable natural resources. It is the basic element of social and economic infrastructure and is essential for healthy society and sustainable development. Water, the matrix of life is exposed to pollution, unhealthy environment, resulting in human affliction and diseases transmission due to rapid industrialization and population[1]. As of now only earth is the planet having about 70 % of water. But due to increased human population, industrialization, the use of fertilizers in the agriculture and man-made activity, it is highly polluted with different harmful contaminants. Therefore, it is necessary that the quality of drinking water should be checked at regular time interval, because due to use of contaminated drinking water, human population suffers from varying of water borne diseases. It is difficult to understand the biological phenomenon fully because the chemistry of water revels much about the metabolism of the ecosystem and explain the general hydro - biological relationship[2]. Fresh water is one of the most important resources crucial for the survival of all the living beings. It is even more important for the human being as they depend upon it for food production, industrial and waste disposal, as well as cultural requirement[3].

Pesticides are broadly classified into two groups viz. A) chemical pesticides and B) biopesticides. A) Chemical pesticides are conventionally synthetic materials that di- rectly kill or inactivate the pest. They are classified according to the type of organisms they act against as for example 1) insecticides, 2) herbicides, 3) fungicides, 4) rodenticide, 5) nematicides. Insecticides include or-ganophosphates (TEPP, parathion. trimesters of phos- phates and phosphoric acids), carbamates (aldicarb), organochlorines (dichlorodiphenyl-trichloroethane, chlor- dane, aldrin, dielrin, lindane, endrin) and botanical insec- ticides (nicotine, rotenoids, pyrethrum). Herbicides are used to destroy other weeds that interfere with productionof the desired crop. Based on their structure they are grouped into chlorophenoxy compounds (e.g.:2,4-D, 2, 4,5-T), dinotrophenols like 2-methyl-4,6-dinitrophenol (DNOC), bipyridyl compounds likeparaquot, carbamate herbicides, substituted urea, triazines and amide herbicides like alanine derivatives.Fungicides include a number of structurally different chemicals like cap tan, folpet,pentachlorophenolziram, nambam etc. Fungicides containing mercury is known to cause nerve disorders[4].

Water is thus becoming a crucial factor for development and the quality of life in many countries. In individual arid areas it has even become a survival factor. Therefore, water intended for human consumption must not contain pathogen germs or harmful chemicals; because water contaminated with microorganisms is the cause of epidemics. That is good drinking water is

not a luxury but one of the most essential requirements of life itself. However, developing countries have suffered from a lack of access to safe drinking water from improved sources and to adequate sanitation services[5]. The WHO revealed that seventy five percent of all diseases in developing countries arise from polluted drinking water.Acceptable quality shows the safety of drinking water in terms of its physical, chemical and bacteriological parameters[6].

All the investigation of drinking water parameters was done in Manora tehsil. Manora tehsil is located in Washim district of Maharashtra in Amravati division. Its Latitude and longitude coordinates are: **20.216112, 77.559074**

MATERIAL AND METHODS

Water samples were taken from 0.3 m below the surface with a pre-cleaned glass bottle. For samplingturbulent midstream position of water bodies were chosen to approximate mean concentration of riverwater. All foreign bodies were removed and the samples were stored in ice during transport and were keptat 40 C in the laboratory until the solid phase extraction.

SAMPLE EXTRACTION

The procedure applied for the extraction of pesticides was similar to those reported by Laabs *et al*[7] and Steinwandter[8]. Water samples were extracted using ultrasonic extraction. Sox let extraction was done with 20 ml of hexane: dichloromethane (3:1) for 30 min. The extract was concentrated with the aid of rotator evaporator. Pre-elution was carried out with the HPLC methanol. The concentration solvent extract was then analyzed for Pesticides. The solvent of the mobile phase of the HPLC is methanol and water (1:1). This was prepared by measuring 250ml of HPLC grade methanol into a 500ml flask and made up with 250ml of distilled water. The HPLC model CECIL 1010 was switched on. The wavelength of the system was determined by using UV visible equipment. Little quantity of stock solution was diluted with methanol and its wavelength determined nu scanning. A peak of 202nm was reached. The system wavelength was then set at 202nm and the sensitivity of the 0.05 nm of the UV detector component set. The flow rate was set at 1ml/min, afterwards, the purging of the system commenced by allowing the system to run for some time. Thepurging was carried out through a washing solution of 30% methanol, 70% water. Bubbling helium gasinto the solution carried out degassing of the mobile phase was then set up and connected with HPLCsystem and allowed to run through the system of 20min.

Each sample residues was dissolved in 1ml methanol. The extracted residues was the loaded and injectedinto the valve of the chromatography system. The resulting chromatograph for each sample was printedout. The various retentions time noted, concentration determined and recorded.

The Water Samples were collected from Different places from different villages in the day time 10:00 a.m. to 11:00 a.m. in Polythene Bottles. Samples were collected from 8 different villages and they assign as W1, W2, W3, W4, W5, W6, W7,& W8. The Water samples were immediately brought in to Laboratory for the Estimation of various Physico-chemical Parameters like Water Temperature, pH were recorded by using Thermometer and Digital pH Meter. Specific conductivities were measured by using digital conductivity meter. The TDS, DO, Salinity and ORP was analysed by water analysis kit.

RESULT AND DISCUSSION

Manora tehsil is surrounded by farm land. Farmers of this region use fertilizers as well as pesticides to control the growth and population of pest for well growth of crops which is useful source of their economy and food. These pesticides can enter in the water by subterranean canal and reservoir and these factor may lead to contaminate the drinking water of this region.

Table 1: Level of organochlorine pesticides in water sample of Manora region.

Sample	DDT	DDE	Lindane	Heptachlore	Endosulpfan
W1	.01	.008	ND	ND	.008
W2	.009	.009	ND	ND	.01
W3	.02	.02	ND	ND	.02
W4	.01	ND	ND	ND	.02
W5	ND	.009	ND	ND	.008
W6	ND	.02	ND	ND	ND

Table 1 is the result of organochlorine pesticide of water sample of Manora region. The concentration of DDT was in the range of 0.009 to 0.02 µg/L. The pesticide Lindane and Heptachlor was ND(not detected) in given water samples. The associate figure of Endosulphon was in the range of 0.008 – 0.02 µg/L.

After investigating the values for the parameters are reported like in given table 2. In present analysis the temperature of the samples in the

range of 23.5 to 26.4^{0}C, pH of most of the samples wasfound to be alkaline and one of it is in acidic in nature. Oxygen is in gaseous form it dissolves in water by rapid movements and by different biological and natural processes. There will be effect of temperature on dissolved oxygen. During this analysis the rage of dissolved oxygen was found to 5.5 to 7.3 mg/lit.

Table 2: Values of physico-chemicals parameters of various villages of Manora Tehsil

Location	Temp. ^{0}C	PH.	DO Mg/lit	EC mhos	Salinity	TDS ppt	ORP mV
W1	23.5	7.1	6.2	0.4	0.4	550	28
W2	26.4	7.5	6.3	0.2	0.2	560	34
W3	25.2	6.9	7.3	0.6	0.7	490	28
W4	24.2	7.8	5.5	0.5	0.2	650	29
W5	26.4	7.2	6.9	0.5	0.2	640	32
W6	23.8	7.9	5.8	0.2	0.4	380	35
W7	23.5	8.0	5.5	0.8	0.7	720	26
W8	25.4	7.5	7.2	0.2	0.3	580	30

Conductance is directly proportional to ions in the water. Conductance of given water sample was reported and average of conductance was found to be 0.3875 M mohs. Salt dissolved in water i.e. salinity of water for investigated sample was in between 0.2 to 0.7 ppt. TDS is used when amount matter dissolve or suspended in water. In present analysis TDS of collected water sample was found to be in range 380 to 720 mg/lit and oxidation reduction potential of water for investigated sample was in range 26 to 35 mV in range.

CONCLUSION

The analyzed water sample which was collected from different villages of Manora tehsil shows the value in the permissible range. The assessment of water confirms that the water of this region is comfortable for drinking as well as domestic purpose after some basic treatments and it also a need of regular monitoring of these parameters after some intervals.

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SYNTHESIS OF SOME HETEROCYCLIC COMPOUNDS DERIVED FROM CHALCONES

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ABSTRACT

Chalcone derivatives were synthesized by reaction of some substituted benzaldehyde derivatives with acetophenone, and then the products obtained were allowed to react with urea, thiourea and hydroxylamine, to give the heterocyclic derivatives of oxazine, thiazine and isoxazole, respectively. The final products have been characterized by elemental analysis, IR and proton NMR spectra. These compounds were also screened for their antibacterial activities.

***Key words**: Synthesis, Heterocyclic compounds, Chalcone, Antibacterial.*

INTRODUCTION

Chalcones were prepared by condensation of acetophenone with aromatic aldehydes in presence of suitable condensing agent [1, 2]. They undergo a variety of chemical reactions that leads to many heterocyclic compounds [3-6]. Chalcones have been used as intermediates for the preparation of compounds having therapeutic value [7,8]. Many reviews reveal that chalcone derivatives exhibit diverse pharmacological activities, such as potential cytotoxic agents, antimicrobial agents, antiviral, anti-inflammatory, anesthetic, etc. [9,10]. In the view of the varied biological and pharmacological applications, we have planned to synthesize some heterocyclic derivatives of chalcone and test their antibacterial activity.

EXPERIMENTAL

Melting points were determined open capillary tube and were uncorrected. IR spectra were recorded on FT IR Perkin-Elmer spectrophotometer using KBr disc method. 1H NMR spectra were recorded on Bruker AMX-300 MHz spectrometer in DMSO. Chemical shifts relative to TMS used as internal standard were obtained in δ unit. The heterocyclic derivatives of chalcone were subjected to antimicrobial screening using nutrient agar medium by well diffusion method [8]. The antibacterial activity was tested against various types of bacteria and compared with standard drugs (Ampicillin and Vibromycin). The chalcones then the heterocyclic derivatives were prepared as shown in the following scheme:

REACTION SCHEME

Synthesis of chalcones (Ia-c)

Benzaldehyde derivative (0.01 mol) and acetophenone (0.01 mol) were dissolved in ethanol (25 mL).Sodium hydroxide solution, 10% (25 ml) was added slowly and the mixture stirred for 4 hrs then it was poured into 400 ml of water with constant stirring and left overnight in Refrigerator. The precipitate obtained was filtered, washed and recrystallized from ethanol.

Preparation of Thiazine/Oxazine derivatives (II a-c; III a-c)

A mixture of chalcone (0.02 mol), thiourea/urea (0.02 mol) were dissolved in ethanolic sodium hydroxide solution (10 ml) was stirred for 3 hrs, then it was poured into 400 ml of cold water with continuous stirring for 1 hr then left overnight. The precipitate formed was filtered, washed and recrystallized from ethanol.

Preparation of Isoxazole derivatives (IV a-c)

A mixture of chalcone (0.02 mol), hydroxylamine hydrochloride (0.02 mol) and sodium acetate in ethanol (25 ml) was refluxed for 6 hrs, and then the reaction mixture was poured into ice water (50 ml). The precipitate obtained was filtered, washed and recrystallized from ethanol.

Table 1: Physical and elemental analysis of synthesized compounds

No.	Mol. Formula	Mol. Wt.	M. P. (o C)	Yield (%)
I a	$C_{15}H_{12}O_2$	224	150	80.35
I b	$C_{17}H_{17}NO$	251	95-98	81.27
I c	$C_{16}H_{14}O_2$	238	40	80.67
II a	$C_{16}H_{14}N_2OS$	282	148-149	68.08
II b	$C_{18}H_{19}N_3S$	309	73-75	69.90
II c	$C_{17}H_{16}N_2OS$	296	40	68.91
III a	$C_{16}H_{14}N_2O_2$	266	144-145	72.18
III b	$C_{18}H_{19}N_3O$	293	65-66	73.72
III c	$C_{17}H_{16}N_2O_2$	280	45	72.85
Iv a	$C_{15}H_{11}NO_2$	237	140-142	75.94

IV b	$C_{17}H_{16}N_2O$	264	76-78	77.27
IV c	$C_{16}H_{13}NO_2$	251	--------	76.49

Table 2: Spectral data of the synthesized compounds

Compd. IR (KBr) ν cm-1 1H NMR (d6-DMSO) δ ppm

Ia 3350 (Ar-OH); 1675 (CH = CH-CO); 1640 (C = C); 1480 (Ar-C = C) 4.4 (d, 2H, 2CH); 5.0 (s,1H,Ar-OH); 7.0-7.8 (m,9H, Ar-H)

Ib 3400 (Ar-I); 1680(CH = CH-CO); 1635 (C = C); 1520 (Ar-C = C) 2.47 (s,6H,I(CH3)2); 4.6 (d,2H,2CH); 7.1-7.8 (m,9H,Ar-H)

Ic 1670 (CH = CH-CO); 1645 (C = C); 1528 (Ar-C = C); 1100 (Ar-OC) 3.4 (s,3H,OCH3); 4.5 (d,2H,2CH); 6.9-7.8 (m,9H,Ar-H)

IIa 3370 (Ar-OH); 2370 (C-S-C); 1655 (C = C); 1624 (C = N); 1610 (NH2) 2.1 (s,2H,NH2); 3.5 (s,1H); 5.2 (s,1H,Ar-OH); 5.7 (s,1H); 6.8-7.9 (m,9H,Ar-H)

IIb 3430 (Ar-N); 2356 (C-S-C); 1650 (C = C); 1620 (C = N); 1590 (NH2) 2.0 (s,2H,NH2); 2.4 (s,6H,N(CH3)2); 3.4 (s,1H); 5.6 (s,1H); 6.9-8.0 (m,9H,Ar-H)

BIOLOGICAL ASSAY OF THE SYNTHESIZED PRODUCTS

Antibacterial activity of the heterocyclic derivatives of chalcone have been carried out against several types of bacteria such as, *E. coli*; *S. aureus*; and *P. aregenosa*, using nutrient agar medium by well diffusion method11. All compounds were suspended in aqueous solutions in different concentrations ranged from 10-100 mg/mL, the results are expressed on MIC (minimal inhibitory concentration), solvent blanks were run against each test organism in all assays and the experimental biological data is given in Table 3.

Table 3: Antibacterial activity data of the heterocyclic derivatives of chalcone

Compound	*E. coli*	*S. aureus*	*P. aregenosa*
IIa	18	19	17
IIb	21	18	20
IIc	22	20	18
IIIa	18	20	22
IIIb	22	21	19
IIIc	23	21	20
IVa	17	19	18
IVb	20	20	19
IVc	22	21	18
Ampicillin	23	20	21
Vibromycin	24	22	20

RESULTS AND DISCUSSION

All synthesized compounds as well as the reactions that carried out were characterized and monitored by TLC, melting points, elemental analysis, IR and 1H NMR, and they all gave satisfactory results.

The compounds were evaluated for their antibacterial activities against various types of bacteria, and they showed comparable activity with that of standard drugs.

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ENVIRONMENTALLY BENIGN ALUM CATALYZED EFFICIENT SYNTHESIS OF 2,3-DIHYDROQUINAZOLINE-4(*1*H)-ONES DERIVATIVES IN WATER

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ABSTRACT

Describe method consist of eco-friendly procedure for the preparation of 2,3-dihydroquinazoline-4(1H)-ones from equimolar 2-aminobenzamide and substituted aromatic aldehydes in presence of 10% aqueous Alum ($KAl(SO_4)_2{\cdot}12H_2O$). Green impact of reaction significantly enhanced due to use of water as solvent and naturally occurring substance as catalyst. Good to excellent yield of products, simple working strategy and easy purification are the advantage of present methodology

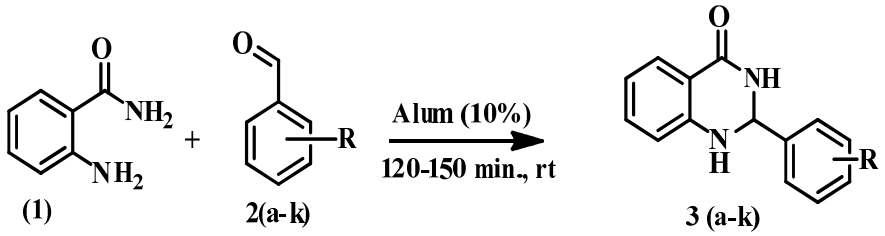
Keywords: *quinazoline, alum catalyzed, water mediated, green methodology*

INTRODUCTION

Search of expeditious and cost-effective methodologies to replace tedious, low productive traditional methodologies gains its own importance. Now a day's green methodologies has attract significant attention and environmentally benign, recyclable, chap solid catalysts get ultimate reputation. Such methodology offers to obtained complex pharmaceutically important molecules or intermediate by possibly viable ways. Such methodologies shine with imminent light when water incorporates as solvent, due to its non-toxic, green, cheap nature and biochemical consequence. [1, 2]

Quinazoline has been occupied distinct position in nitrogen containing heterocycles due to its spectacular wide spectrum of pharmaceutical properties. Various reports of quinazoline underline its widely biopharmaceutical activity like, anticancer [3-5], antibacterial [6-8], antiinflammation [9, 10], antituberculosis [11], antihypertension [12] and antidiabeties [13]. Such wide spectrum of quinazoline strongly demands possible derivatisation to test out for further pharmaceutical possibilities. Various methods have been proposed to obtained quinazoline analogues using catalysts like ammonium bromide[14], Zirconyl chloride [15] Heteropoly acids [16], Gallium (III) triflate [17], Titanium oxide nano-particles [18], Starch solution [19],cyanuric chloride[20]and Cyclodextrin sulphonic acid [21].Most of these methodologies are suffers from long reaction time, high temperature, use of expensive catalyst and tedious work procedures. 'On water' reports [22] ofquinazoline synthesis by using expensive catalyst increase cost of reaction.

Readily accessible Potassium alum sulphate($KAl(SO_4)_2{\cdot}12H_2O$) for the synthesis one pot quinazoline has not attempted. Such catalyst simplifies the reaction procedure and do not pass on unpleasant toxic residue to environment. Potash alum, perhaps most easily available substance and extensively used as support in reactions [23]. In continuation of our previous research work [24] to develop fast, naturally benign, productive methodology for small and fused heterocyclic compounds, we intended to developed facile, efficient, cost-effective and easy workup method for the synthesis of quinazoline derivatives. Here, introduce facile methodology as shown in scheme 1 for syntheses of quinazoline derivatives.



Scheme 1.

EXPERIMENTAL

The reagents and solvents were purchased from Alfa aesarand Aldrich Chemical companies and used without further purification. All compounds obtained were describe for open head capillary tube for their melting point and are uncorrected. The samples were analyzed by FT-IRspectroscopy (JASCO FT/IR-460 plus spectrometer). ^{1}HNMR and ^{13}CNMR spectra ofcompounds were recorded on a Bruker DRX-400Avance instrument in DMSO-*d6*.

General procedure

In a RBF containing 20 ml of 10% Potash alum was added 2-aminobezamide (0.01mol; 1.36gm), substituted aldehyde (0.01mol) with stirring. The reaction mixture was stir at room temperature. Progress of reaction was monitor by thin layer chromatography (TLC) using Ethyl acetate-Hexane. After completion of reaction, reaction mixture was filter off and filtrate neutralized by saturated solution of sodium bicarbonate, brine and extracted with ethyl acetate. Organic layer dried on anhydrous sodium sulphate and evaporated in reduced pressure to afford pure product after recrystallization from ethanol. Representative compounds were scan for spectral data and found satisfactory agreement with reported.

Spectral data of representative compounds

2-phenyl-2,3-dihydroquinazolin-4(1H)-one;

(**1**)m.p.= 219°C,^{1}HNMR (400 MHz,DMSO-*d6*): δ= 8.27 (s, 1H), 7.61 (d, 1H), 7.50 (d, 2H), 7.31-7.41 (m, 3H), 7.22 (t, 1H), 7.06 (s,1H), 6.72 (d, 1H), 6.69 (t, 1H,), 5.75 (s, 1H)ppm;IR (KBr): 3310,3014, 1671, 1630, 1523 cm^{-1}.

Table 1.Quinazoline derivatisation with respect to yield of reaction, time and physical constant of obtained products.

Sr. No.	-R	Compound	Time in min.	Yield[a] %	M.P. (Lit.) in °C	Ref.
1.	-H	**3a**	120	77	219 (218-220)	[25]
2.	*p*-OMe	**3b**	120	86	184 (181-182)	[25]
3.	*p*-OH	**3c**	140	69	177 (183-185)	[25]
4.	*p*-Me	**3d**	120	88	224 (227-229)	[25]
5.	*p*-Br	**3e**	120	90	195 (197-198)	[25]
6.	*p*-Cl	**3f**	150	72	208 (206-208)	[25]
7.	*p*-NO_2	**3g**	150	55	212 (214-216)	[25]
8.	*p*-$N(Me)_2$	**3h**	140	80	224 (227-229)	[25]
9.	*m*-OMe	**3i**	120	90	151 (147-149)	[25]
10.	*m*-OH	**3j**	120	67	204 (209-210)	[25]
11.	*o*-Me	**3k**	120	75	190 (188-189)	[25]

[a]Isolated yields**;** **Reaction condition**: 2-aminobenzamide (0.01 mol), p-methoxy benzaldehyde (0.01 mol), stirred in 10% Potash alum (20 ml) at rt.

RESULTS AND DISCUSSIONS

Series of reactions were performed to optimized reaction condition including amount of catalyst with respect to yield of product. Room temperature and 'on' water was kept as fix reaction parameters. 2-aminobenzamide and p-methoxy benzaldehyde were taken for model reaction and various reaction condition were applied. In continuation with our previous research work [25] silica chloride were successively used as reusable catalyst for the preparation of dihydroquinazoline, using thionly chloride cause serious environmental damage and hence we are eager to replace silica-chloride with green and naturally occurring catalyst. Potash alum is water soluble naturally occurring substance and solubility was found excellent upto 15-16% w/v in water. 10% alum shown pH 3.0-3.2, and by consideration this facts we chose alum as catalyst.

It has been observed that nature of substituent present on aromatic aldehydes has affect on yield of reaction. This correlation was underline by considering yield of product as shown in **Table 1**. Electron donating functionality increase amount of yield of product, whereas withdrawing reduces it.

CONCLUSION

In conclusion, an efficient, green method for thesynthesis of quinazoline analogues has been described using readily Potash alum as naturally occurring catalyst. The green reaction profile and mild reaction conditions are main advantageof this method. Reaction takes place at roomtemperature by simply stirring method, with operational simplicity offers excellentyields.

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SYNTHESIS, SPECTRAL CHARACTERIZATION, THERMAL AND BIOLOGICAL STUDIES OF Co(II), Ni(II) AND Cu(II) COMPLEXES WITH 2-4-DINITROPHENYLHYDRAZONE LIGAND

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ABSTRACT

Schiff base ligand derived from condensation of 2, 4-dinitrophenylhydrazine (0.01mole) and 5-methyl-2-hydroxyacetophenone and its Co(II), Cu(II) and Ni(II) metal complexes were synthesized. The compounds have been characterized using elemental analysis, infrared, thermogravimetric analysis.
The infrared data revealed that the ligand behaved as a bidentate ligand as it coordinating through the O and N atoms of the ligand. The compounds were screened in vitro for antibacterial activity against some pathogenic bacteria: S. aureus, S. epidermis, K. pneumoniae and E. coli. The synthesized Schiff base complexes exhibit higher antibacterial activity.

INTRODUCTION

Schiff base complexes of transition metal are of particular interest to inorganic chemists because of their structural, spectral and chemical properties are often strongly dependant on the nature of ligand structure. Study of compounds of Oxygen, nitrogen and sulphur are extensive as it includes effects of donar sites and electron delocalisation in transition metal complexes. Field of schiff base complexes is fast devloping because the wide veriety of possible structures for the ligands[1-2].

We synthesized Co(II), Cu(II) and Ni(II) metal complexes with the schiff base ligand (E)-2-(1-(2-(2,4-dinitrophenyl)hydrazono)ethyl)-4-methylphenol derived from 2,4-Dinitrophenylhydrazine and 5-Methyl-2-hydroxyacetophenone. The antimicrobial and thermal analysis of compounds was examined in present study[3].

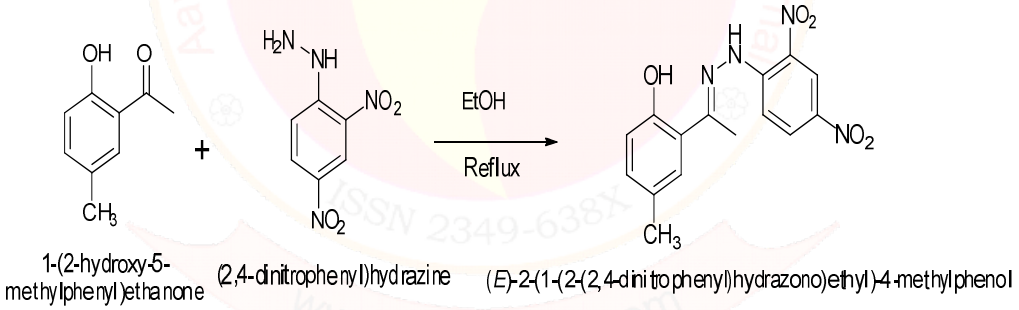

Fig1. Synthesis of the LH ligand

EXPERIMENTAL

***2.1 Reagents and Materials*:**

All the chemicals were obtained from S D Fine and Aldrich and were used without further purification. The solvents were of analytical grade and purified by standard methods. Copper acetate, Cobalt acetate and Nickel acetate were of S.D's fine chemicals.

***2.2 Physical measurements*:**

The IR spectra of the ligand and its complexes were recorded in the 4000-400 cm^{-1} region in KBr disks on a Shimatdzu FT/IR-4100 spectrophotometer. Thermal analysis of complexes was carried out by heating at a rate of 10^0C per minute on a Perkin Elmer thermobalance.

***2.3 Synthesis of the (E)-2-(1-(2-(2,4-dinitrophenyl)hydrazono)ethyl)-4-methylphenol ligand. LH*:**

A mixture of 2, 4-dinitrophenylhydrazine (0.01mole) and 5-methyl-2-hydroxyacetophenone (0.01mole) in absolute ethanol (20 ml) was reflux for 2 to 3 h. The reaction mixture was allowed to cool to room temperature. The precipitate was filtered off and washed. The crystalline yellow solid obtained was purified by recrystalization.

***2.4 Synthesis of Co(II), Ni(II) and Cu(II) complexes*:**

An ethanolic solution of the (E)-2-(1-(2-(2,4-dinitrophenyl)hydrazono)ethyl)-4-methylphenol

ligand was added to an ethanolic solution of $Co(OAc)_2.4H_2O$, $Ni(OAc)_2$ and $Cu(OAc)_2.4H_2O$ in equimolar ratio[5]. The resulting mixture was refluxed for about 3-4 h on a water bath. The solid product obtained on cooling was filtered and washed[4]. Finally dried and stored in vacuum over fused calcium chloride (yield 72-75%).

RESULTS AND DISCUSSION

All the complexes are colored, non-hygroscopic solids and stable in air. They are insoluble in water, but soluble in coordinating solvents like DMF and DMSO. The molar conductance values of 10^{-3}M solutions of complexes lie in the range 5-10 $ohm^{-1}cm^2$ mol^{-1}, indicating the non-electrolytic nature of the complexes.

3.1 *Elemental analysis*

Table1. Analytical and Physical data of LH and its metal complexes

Compounds	Formula Weight	Colour	Yield (%)	M % Found (calc.)	C % Found (calc.)	N % Found (calc.)	H % Found (calc.)
LH	330.14	Yellow	72	-	54.68 (54.55)	16.93 (16.96)	4.25 (4.27)
Co(LH)	771.52	Brown	70	7.58 (7.64)	7.59 (7.64)	14.56 (14.52)	4.21 (4.18)
Ni(LH)	757.10	Pale brown	74	8.41 (8.38)	8.41 (8.38)	14.76 (14.78)	3.95 (3.99)
Cu(LH)]	770.19	Brown	71	7.69 (7.61)	46.68 (46.72)	14.52 (14.53)	. (8.61)

3.2 *Infrared Spectra*

The IR spectra provide valuable information regarding the nature of functional group attached to the metal atom. The IR spectral data of ligand and their metal complexes are listed in table 2.

The band at 3312 cm^{-1} due to intramolecular hydrogen bonded υ(OH) group in the free ligand spectrum disappeared in spectra of all the complexes and the same time υ(C-O phenolic) band at 1512 cm^{-1}, shifted to higher frequency by 12-24 cm^{-1}, confirms the coordination of ligand through phenolic oxygen via deprotonation[5]. The vibrational band at 1621 cm^{-1} assigned to υ(C=N) in the spectrum of ligand show downward shift by 24-47cm^{-1} in the spectra of complexes confirming coordination through azomethine nitrogen[6]. The coordination through the azomethine nitrogen atom is further supported by the shift of υ(N-N) vibration observed at 986 cm^{-1} in the ligand and to higher frequency by 19-33 cm^{-1} in the complexes[7]. Also in addition to above bands all complexes display the bands in the far-infrared region at 516-532 and 469-502 cm^{-1} assigned to υ(M-O) and υ(M-N) vibrations[8].

Table2. Infrared frequencies (in cm^{-1}) of the ligand LH and its metal complexes.

S. N.	Ligand/ complexes	υ(O-H)	υ(N-H)	N-N	υ(C=N)	υ(C-O) phenolic	υ(M-O)	υ(M-N)
1	LH	3312	3235	986	1621	1512	-	-
2	Co(LH)	-	3278	1012	1597	1548	516	469
3	Ni(LH)	-	3179	1005	1574	1539	532	481
4	Cu(LH)]	-	3182	1019	1586	1241	548	502

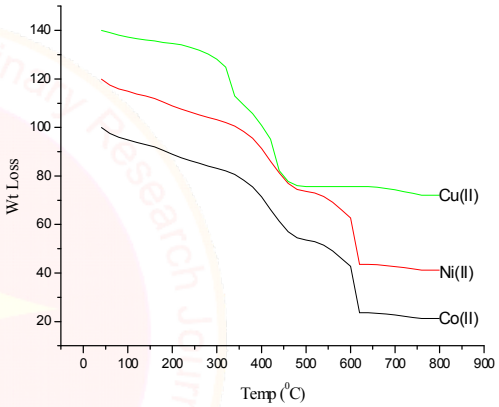

Fig 2. Thermogram of Co(II), Ni(II) and Cu(II) complexes.

3.3 *Thermogravimetric Analysis*

Thermal gravimetric analysis (TGA) for LH_2, [Co(LH), $[Cu(LH)]_2$ [Cr(LH) and [Ni(LH) complexes were obtained to give information concerning the thermal stability of the complex and decide whether the water and solvent molecules are in the sphere or outer coordination sphere o the central metal ion. All the complees are stable upto 80^0c and further decomposed. For Co(II) and Ni(II) complxes loss upto 120^0c indicates the presence of lattice water molecule while in case of Cu(II) complex due to absence of loss at same temperature indicatesd absence of any lattice water molecule[9]. For all three complexes subsequent loss in 120-220^0 C shows the presence of coordinate water molecule. After 350^0 C loss of coordinate part of ligand occurred. All the metal complexes do not decompose completely and finaly converted into their respective metal oxide form.

3.4 Antibacterial Activity

The antibacterial activity of the LH ligand and its metal complexes have been screened against the

four bacteria *E. coli, S. aureus, S. epidermis* and *K. pneumoniae* strains by the cup plate method. The results revealed that (Table 4) the ligand and its complexes show weak to good activity. It is observed that synthesized metal complexes showed good activity than ligand.

Table 3. Thermal analysis data of LH and its metal complexes

Complexes	Half Decomposition Temp (^{0}C)	Ea(kj/mole)		Order of Reaction (n)	ΔS (Kj/mole)	G*
		FC	SW			
LH	352	25.5	25.1	0.99	140.70	38.2
		4	2			8
Co(LH)	455	26.29	25.70	0.99	145.12	42.18
Ni(LH)	490	24.56	24.10	0.98	147.30	41.27
Cu(LH)]	520	28.10	27.56	0.99	145.29	40.78

Table4. Antibacterial activity of the ligand LH and its metal complexes

Ligand and its complexes	*S. aureus*	*S. epidermis*	*K. pneumoniae*	*E. coli*
LH	S12	S10	S11	S09
Co(LH)	S15	S17	S15	S12
Ni(LH)	S16	S14	S12	S10
Cu(LH)]	S14	S12	S14	S13

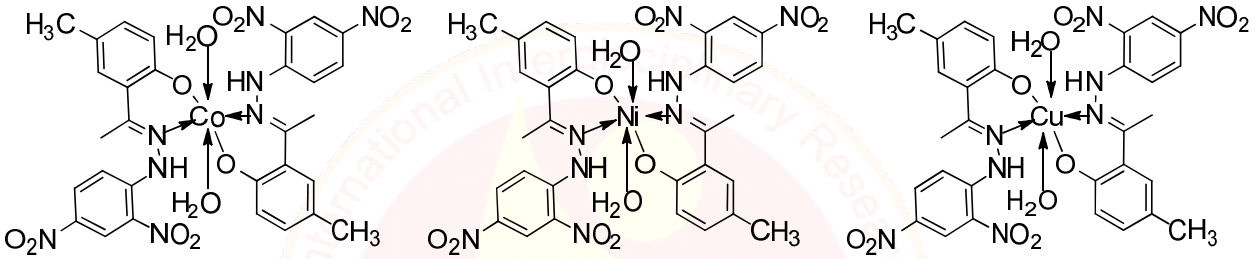

Fig 3 Probable structure of Co(II), Ni(II) and Cu(II) complexes.

CONCLUSION

The complexes are all air stable and are anhydrous. Infrared studies have shown that LH coordinated as a bidentate ligand. Elemental analysis data have revealed the stoichiometric compositions for the complexes as 1:2 molar ratio (metal:ligand). TGA revels the presence of coordinate water molecule in Ni(II) Co(II) complexes and lattice water molecule in Cu(II) complexes. Antibacterial studies have indicated that the complexes show higher activities than the free ligand. The proposed structures of the ligands and their metal(II) complexes are given in Figures 1, 2 & 3 respectively.

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SPECTROPHOTMETRIC MEASUREMENTS OF SOME Cu(II), Cd(II), Cr(II), La(II) AND Nd(II) COMPLEXES IN DIOXANE-WATER SYSTEM

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ABSTRACT

The conditional stability constants of metal-ligand complexes of ligands 2-amno-4-hydroxy-5-benzyl-6-methylpyrimindine (AHBMP)(L1), 1-(4-hydroxy-6-methyl pyrimindino)-3-phenylthiocarbamide (HMPPT)(L2) and 1-(4-hydroxy-6-methyl pyrimindino)-3-methylthicarbaminde (HMPMT) (L3) had been investigated in dioxane-water system at different proportions by Job's method of continuous variation, spectrophotometrically. The stichiometry of complex formation is also determined, which is found to be 1:1.

Keywords: *metal-ligand complexes, spectrophotometric, pyrimindine and thiocarbamide etc.*

INTRODUCTION

Spectrophotometry plays an important role in determination of structure and confirmation of complexes. Usually determination of metal-ligand stability constants and confirmation of complex formation can be justified by pH-metric technique. Never the less intensive research work all over the world is going on for determination and confirmation of complex formation by pectrophotometric measurements nowadays. The formation of co-ordination compounds of metal ions with organic reagents had been extensively used in analytical methods. The metal chelate was formed when proper chelating agent was added to a solution of metal ion. Some properties were changed on complexation, if followed by suitable physiochemical measurements; then it may be of immense importance in elucidating the composition and structure of complexes by spectrophotometric method[14]. The importance of spectrophotometric technique is its significance in measurement of stability constant, confirmation of complex formation in solution and survery of literature.

EXPERIMENTAL METHOD AND STUDY

The metal-ligand stability constants and confirmation of complexes formation of 2-amno-4-hydroxy-5-benzyl-6-methyl pyrimindine (L1), (AHBMP), 1-(4-hydroxy-6-methyl pyrimindino)-3-phenyl thiocarbamide (L2), (HMPPT) and 1-(4-hydroxy-6 methyl pyrimindino)-3-methyl thicarbaminde(L3), (HMPMT) with Cu(II), Cd(II), Cr(II), La(III) and Nd(III), had been investigated respectively by spectrophotometric technique at 0.1M ionic strength using UV-visible spectrophotometer. In this investigation, the effect of solvents, effect of ligands and group as well as effect of metal ions during the formation of complexes were studied by Job's method of continuous variation.

System:

The following systems were arbitrarily selected for determining the metal-ligand stability constants and confirmation of complex formation:

1) Cu(II)-Ligand AHBMP(L1)
   Cu(II)-Ligand HMPPT(L2)
   Cu(II)-Ligand HMPPT(L3)
2) Cd(II)-Ligand AHBMP(L1)
   Cd(II)-Ligand HMPPT(L2)
   Cd(II)-Ligand HMPPT(L3)
3) Cr(II)-Ligand AHBMP(L1)
   La(III)-Ligand HMPPT(L2)
   Nd(II)-Ligand HMPPT(L3)

A) Solvents:

i) Distilled Water:- Carbon dioxide free, double distilled water was used. Distilled water obtained in a steel container was again redistilled over alkaline potassium permanganate in a glass-fit set up and was always used a fresh. (pH=6.85+0.01).

ii) Dioxane:- Extra pure (E.Merck) dioxane was further purified by the prescribed procedure[15] and used for preparation of solutions of ligands.

B) Metal ions

The metal ions Cu(II), Cd(II), Cr(II), La(III) and Nd(III) in the form of their nitrates (to avoid the possibility of complex formation of metal ion with

anion) were used to prepare stock solutions of 0.01 M in requisite quantities in distilled water, The concentration of metal ions in solution was estimated by titrating against sodio salt of EDTA solution, as decribed by schwarzenbach et al[16].

C) Ligands

AHBMP(L1), HMPPT(L2) and HMPPT(L3) were synthesized by literature method[19] and are used as ligands. The 0.01 M solution of each ligand was prepared in dioxane-water mixture. All the solutions of ligands were always used a fresh in the present investigation.

D) Instruments

i) Spectrophotometer:- The optical density of the ligand solutions and their metal complexes have been measured by visible Spectrophotometer model 106, (Systronic make) with an accuracy = + 0.005. This model is a single beam grating Spectrophotometer with a wavelength range of 340nm to 960 nm, at intervals of 5 nm. The display can exhibit transmittance, percentage, absorbance and concentration readings depending upon the selection of parameters. Beer-Lambert's law is of fundamental importance of spectrophotometer analysis.

Metal ion solution (ml)	1	2	3	4	5	6	7	8	9
Ligand solution (ml)	9	8	7	6	5	4	3	2	1
Total volume (ml)	10	10	10	10	10	10	10	10	10

Ionic strength was maintained constant throughout by adding an appropriate volume of potassium nitrate solution. The optical densities were measured.

The graph of percentage composition (1 ml = 10%, 2 ml = 20% ….. etc.) versus absorbance was plotted for each set of solution.

f) Determination of composition complex

Maximum complex formation for each system was determined form the graph which was plotted against percent composition and optical densities of each system. The maximum complex formation is indicated by maximum absorption (maximum optical density) which generally is obtained at 5:5 metal-ligand solutions in the systems studied indicating 1:1 complex formation.

G) Calculation of metal-ligand stability constant

The conditional stability constants of complexes were determined spectrophotometrically. When light falls upon the homogeneous medium, the solution appears coloured due to absorption of light radiation of particular waveleght from visible region. Spectrophotometric analysis is based on the variation of colour intensity of the system with Pyrex glass cells of 1.00 cm path length were used for the study of spectra. One of the cell was filled with reference solvents (ethanol/dioxane) and the other with experimental solution, and the absorbance values were noted. The same cells were used for all the neasurments.

ii) pH Meter :- The pH measurements were carried out on EQ-612 pH-meter (accuracy+ 0.05 units) using combined glass electrode. Before use, the electrode was dipped in distilled water for 24 hrs.

iii) Balance :- Weighing was made on Mechaniki Zaktady Prexcyzyjnej Gdansk Balance, made in Poland (=0.001 gm).

E) Procedure

The determination of conditional stability constant and formation of complex by Job's method of continuous variation was preformed as follows-

1.01 M metal ion solution and 0.01 M ligand solution of (L1), (L2) and (L3) were prepared. Following sets of systems were prepared by mixing the metal ion solution and ligand solution in the following proportions-

changing concentration of the components. It is concerned with the determination of the concentration of the substance present in solution and metal-ligand stability constants of the complexes. The graph of optical density is plotted against percentage compositions. Metal-ligand stability constants can be determined from Eqn. (2).

$$M + L \rightleftharpoons ML \quad .....(1)$$

$$K = \frac{[ML]}{[M]\,[L]} \quad .....(2)$$

The concentration of complex 'x', [ML], in any metal-ligand solution was obtained from Job's curves. If the initial concentrations of metal [M] and ligand [L] in particular solution and 'a' and 'b' then equilibrium constant 'K' can be evaluated by,

$$K = \frac{X}{(a - x)(b - x)} \quad .....(3)$$

or

$$\mathbf{K} = \frac{X}{\quad} = \frac{X}{\quad} \quad \mathbf{(4)}$$

$(a_1 - x)(b_1 - x)$ $(a_2 - x)(b_2 - x)$

And log K gave the conditional stability constant.

RESULTS AND DISCUSSION

The dielectric constant is one of the characteristics of liquid. The stability constants were strongly affected by dielectric constant of medium because one of the constituents was charged and other was either charged or had a dipole moment. Specific variations in relative strengths of acids and bases with changing solvents should be the function of charge, the radii of ions and the dielectric constant of the medium. It is extremely difficult to find out the separate contribution of an individual constituent in mixed solvents, particularly at higher percentage of organic solvents, where it was not known to what extent the metal ions and hydrogen ions are solvated. An understanding of the influence of medium on the reactivity therefore, becomes difficult even at a qualitative level.

Many researchers studied log K values at various percentages in dioxane-water[17], ethanol-water[18], acetone-water[19], DMF-water[20], system. Metal ion and size of metal ion are very important factors because the chelation properties can be related to the properties of metal ions. Mellor and Malley[21] had studied the following order of relative stabilities of complexes of bivalent metal ions,

Pd> Cu> Ni> Pb> Co> Zn> Cd> Fe> Mn> Mg

Irving and Rossotti[22] showed that irrespective of the nature of ligand or steric hindrance, stability of metal complexes always follow the order,

Cu> $U0_2$> Ni> Zn> Mg

Pfeiffer et al[23] showed the order of stabilities as –

Cu> Ni> Fe> Zn> Mg

In the plots of log K_a against atomic number, Irving and Williams[24] observed that the stabilities increase with the increasing atomic number upto the end of transition series and then falls at zine.

Combination of factors viz. charge and size of central metal cation show that it is charge/radius ratio for the central ion which is important. A bigger value of charge/radius ratio for the central ion means that the central ion will be forming more stable complexes[25-27]. the correlation between charge-to-radius ratio and stability of OH complexes of some metal ions in the order.

Be^{2+}> Al^{3+}> Th^{4+}> Y^{3+}> Ni^{2+}> Ca^{2+}> Li^{+}

and it may be noted that charge on the metal ions is somewhat more important than its ionic radius.

In the present investigation that data obtained at maximum wavelength was represented in Table 1 to 9. The curves were construted between the values of optical density (D) and percentage composition of metal ion as show in fig. 1-9.

Table 10
System : Cu(II)- AHBMP(L1)

O.D.	Log K_1	Log K_2
0.30	3.5269	3.5174
0.31	3.5202	3.5130
0.32	3.5150	3.5116
0.33	3.5114	3.5102
0.34	5.5101	3.5086

Table 11
System : Cd(II)- AHBMP(L1)

O.D.	Log K_1	Log K_2
0.78	3.5150	3.5269
0.80	3.5130	3.5202
0.82	3.5114	3.5174
0.84	3.5100	3.5230
0.86	3.5090	3.5114

Table 12
System : Cu(II)- HMPPT(L2)

O.D.	Log K_1	Log K_2
0.30	3.5202	3.5112
0.31	3.7127	3.5174
0.32	3.5401	3.7128
0.33	3.6543	3.6401
0.34	3.8107	3.5521

Table 13
System : Cd(II)- HMPPT(L2)

O.D.	Log K_1	Log K_2
0.86	3.6847	3.5131
0.87	3.5086	3.5150
0.88	3.5010	.35174
0.89	3.5101	3.5202
0.90	3.5120	3.5221

Table 14
System : Cr(II)- HMPPT(L2)

O.D.	Log K_1	Log K_2
0.58	.7128	3.6846
0.59	3.5086	3.7128

0.60	3.5101	3.5141
0.61	3.5114	0.5170
0.62	3.5174	3.5651

Table 15
System : La(III)- HMPPT(L2)

O.D.	Log K_1	Log K_2
0.46	3.8183	3.6403
0.47	3.7128	3.8109
0.48	3.8106	3.5334
0.49	3.5358	3.5112
0.50	3.5210	3.6849

Table 16
System : Na(III)- HMPPT(L2)

O.D.	Log K_1	Log K_2
0.50	3.7128	3.8097
0.51	3.7130	3.5051
0.52	3.5150	3.5101
0.53	3.5114	3.4748

Table 17
System : Cu(II)- HMPPT(L3)

O.D.	Log K_1	Log K_2
0.30	3.7128	3.5150
0.31	3.5101	3.5130
0.32	3.4863	3.5113
0.33	3.5130	3.5102
0.34	3.5101	3.6482

Table 18
System : Cd(III)- HMPPT(L3)

O.D.	Log K_1	Log K_2
0.78	3.5220	3.5164
0.80	3.5201	3.5037
0.82	3.5061	3.5114
0.84	3.5134	3.5101
0.86	3.5014	3.5091

Table 19
Comparison of Results by pH-metry and spectrophotometey.

System	Technique			
	pH-meter		Spectrophotometry	
	Log K_1	Log K_2	Log K_1	Log K_2
Cu(II)- AHBMP(L1)	2.9959	2.4198	3.5269	3.5147
Cd(II)- AHBMP(L1)	3.6970	3.2199	3.5150	3.5269
Cu(II)- HMPPT(L2)	3.6970	2.5198	3.6754	3.5401
Cd(II)- HMPPT(L2)	3.5969	2.5198	3.5101	3.5202
Cr(II)- HMPPT(L2)	3.6969	2.3198	3.7128	3.6846
La(III)- HMPPT(L2)	3.3969	2.5198	3.5358	3.5112
Nd(III)- HMPPT(L2)	3.3936	2.2198	3.5114	3.4748
Cu(II)- HMPPT(L3)	3.9968	2.8197	3.7128	3.5150
Cd(II)- HMPPT(L3)	4.2969	2.3198	3.5220	3.5164

Calculation of conditional and real metal-ligand stability constants for 1:1 complexes:

Conditional metal-ligand stability constants were calculated. The concentration of complex 'x' in any metal-ligand solution was obtained from Job's curves. If the initial concentrations of metal and ligand in a particular solution are 'a' and 'b' then the equilibrium constant 'K' can be determined by eq. (3) & (4).

The conditional stability constants were found to be greater than real stability constants obtained from pH-metric measurements.

The conditional stability constants are found to be slightly greater than real stability constants. This is because the concentration of free acid at a particular pH was not taken in to account, and any may be due to variation in temperature.

If could be concluded from Table No. 19 that, the agreement between the values obtained by both the techniques is fairly good [except in system Cd(II)(L3)]. There is no appreciable change in the log K values. This may be due to the fact of attribution to the simultaneous complex formation.

All the above observations clearly showed that the interactions of solvents with metal ions will directly affect the formation of complex. The dielectric constant, polarity of solvent, protic-oprotic nature and hydrogen bonding in solvent will directly interfere the stability and formation of complexes and hence changes in log K values will occur. These properties of solvents are not prime factors for change in log K values or for conditional stability constants and formation of complexes but nature of metal ions and ligands are other two prime factors which are used during study, will also indirectly affect the change in log K values, formation and stability of complexes. It means that in the case metal ions nuclear change, ionic charge, ionic radius, size of metal ions, oxidation number, effective nuclear change, electroegativity of metal ions will also make direct interaction stability constants. Third important factor which is responsible for conditional stability constant and complex formation is ligand. When we consider ligand, the size of ligand, electron donating capacity of heteroatom present inligand with respect to its resonance, total atoms present in ring, the different substitutions present in the ring, effect of electron donating and accepting groups, satiric hindrance of substituted, resonance stabilization in substituted group must be considered. This study will direct new evolutionary path for pharmaceutical and

medicinal sciences in which most of the drugs which are synthesized and used generally form complexes.

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DENSITES ,REFRACTIVE INDICES AND MOLAR REFRACTION OF SUBSTITUTED AZOMETHINES IN DIFFERENT PERCENT OF VARIOUS SOLVENTS.

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ABSTRACT

Molecular interaction such as solute-solute, solute-solvent and solvent-solvent interactions in the substituted azomethine drug in the different percentage of organic solvent has been pointed out. In the present work refractive index, densities of the substituted azomethine in different percent of various organic solvents were reported. The data thus helps to determines Molar refraction (Rm) and polarizability constant (α) of some different substituted azomethine in binary mixture. Observations showed that the molar refraction and polarizability constant of substituted azomethine drugs increases with increase in percent composition of organic solvents.

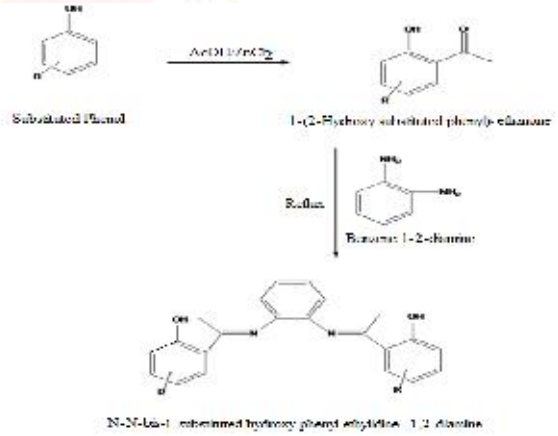
Keyword: *Azomethine, molar refraction (Rm), polarizability constant (α), refractometry. refractive index.*

INTRODUCTION

Refractive index of a liquid is very important property, which gives ideas about geometry and structure of molecule .The refractive index (n) of the medium is the ratio of the velocity of light in vacuum to that in the medium. Its value depends upon the temperature and the wavelength of light used. Generally, the D-line of sodium is used for standard measurements. The refractive index is the ratio of angle of incident to the angle of refraction. Measurement of refractive index shows very interesting applications in pharmaceutical, chemical, agriculture, food, oil and beverage industries.

Many searcher have reported the refractive indices in mixed solvents[1-4]. The properties of liquid such as viscosity, refractive index and ultrasonic velocity of binary mixtures are studied by many workers [5-8]. Refractrometric Study of S-trizinothiocarbamides in Dioxane-water was also reported. [9]. The viscometric,

refractometric and interferometric measurements are very important in medicinal and drug chemistry role [10-12]. Oswal et al[13] have studied dielectric constants and refractive indices of binary mixtures. Dadhichi et al[14] have investigated the measurement of viscosity, refractivity index and metal ligand stability constant of substituted benzofurones in different solvents. Refractive indices of binary, ternary liquid solutions and solutions of biologically important compounds have been studied [15–21].



MATERIAL & METHOD

In the present investigation, refractive indices of liquid mixtures were measured with the help of Abbe's refractometer, specially designed to measure the refractive indices of the small quantities of the transparent liquid by direct reading. The ligands of which physical parameters is to be explore are synthesized by using reported protocol.. The solutions of ligand in different percent composition of binary mixtures were prepared by weight. All the weighing were made on one pan digital balance (petit balance AD_50B) with an accuracy of (±0.001)gm.. The densities of solutions were determined by a precalibrated bicapillary pyknometer (± 0.1%). The constant

temperature of the prism box is maintained by circulating water from thermostat at (27± 0.1)0C.

CALCULATION

The molar refraction of solvent and solution are determined by using Lorentz-Lorentz equation.

The molar refraction of different solvent, mixtures are determined from-

$$R_{DMF\text{-}W} = X_1R_1 + X_2R_2 \quad \ldots\ldots(1)$$

where ,

R_1 and R_2 are molar refractions of DMF and water respectively.

The molar refraction of solutions of ligand in DMF-water mixtures are determined from-

$$RMix = \frac{(n2-1)}{(n2+2)} + \left\{\frac{[X1M1 + X2M2 + X3M3]}{d}\right\} \quad \ldots. (2)$$

where,

n is the refractive index of solution,X_1 is mole fraction of DMF, X_2 is mole fraction of water and X_3 is mole fraction of solute, M_1, M_2 and M_3 are molecular weights of DMF, water and solute respectively. 'd' is the density of solution.

The molar refraction of ligand is calculated as –

$$R_{lig} = R_{mix} - R_{DMF-w} \ldots\ldots\ldots\ldots (3)$$

The polarizability constant (α) of ligand is calculated from following relation-

$$R_{lig} = 4/3\ \pi No\alpha \quad \ldots\ldots. (4)$$

where, No is Avogadro's number.

RESULT AND DISCUSSION

Table 1: Values of Molar Refraction of different composition of solvents.

% of Solvent Mixture	Molar Refraction Rm	
	DMSO	Ethanol
20%	15.0946	19.1123
40%	14.2355	18.5736
60%	12.7632	15.0522
80%	10.8125	12.7245
100%	5.7311	7.0932

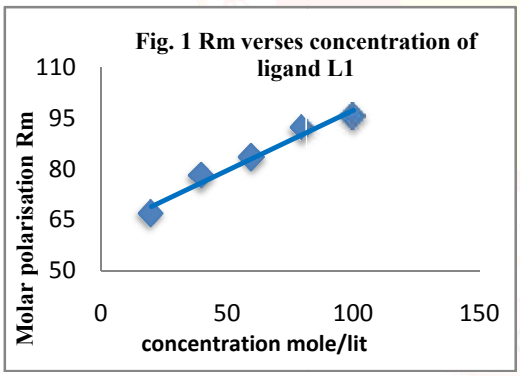
Table 2: The values of refractive index (n) and density(d),molar polarization and polarizability constant of 0.01M solution of ligand in different composition of DMSO, solvent at 300K

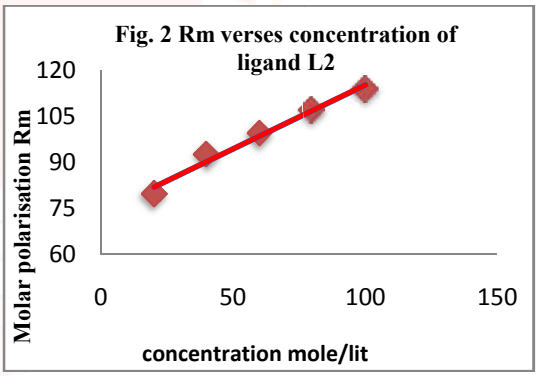
Conc. in %	Constant ligand concentration system (0.01M) with change in DMSO percentage			
	Refractive index (n)	Density (d) gm/cm^3	Rm x10^3 cm^3/mol	α x10^{-23} cm^3
Ligand L1				
20	1.355	1.0150	66.8917	3.4796
40	1.376	1.0156	78.0626	4.0625
60	1.387	1.0166	83.3022	4.5844
80	1.423	1.0176	91.9491	5.1449
100	1.432	1.0213	95.4783	5.6868
Ligand L2				
20	1.367	1.0027	79.5869	3.1331
40	1.387	1.0131	92.5314	3.6445
60	1.401	1.0150	99.3297	4.0136
80	1.432	1.0184	106.918	4.2866
100	1.451	1.0215	113.875	4.6205
Ligand L3				
20	1.384	1.0042	78.7969	3.8283
40	1.405	1.0087	92.1047	4.0812
60	1.423	1.0090	99.6751	4.8935
80	1.446	1.0197	105.5152	5.2259
100	1.465	1.0089	111.9973	5.5646
Ligand L4				
20	1.396	0.9987	103.4741	4.1035
40	1.425	1.0150	117.3996	4.6557
60	1.441	1.0199	125.9359	4.9942
80	1.463	1.0256	133.2286	5.2834
100	1.485	1.0287	139.9505	5.5500

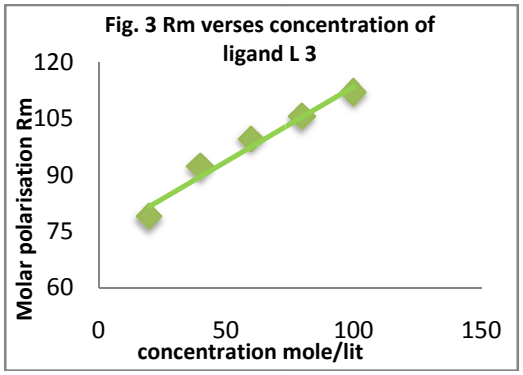
Table3

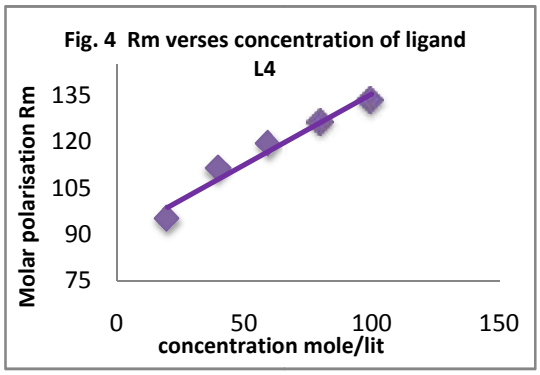
Conc.in %	Constant ligand concentration system(0.01M) with change in Ethanol percentage			
	Refractive index (n)	Density (d) gm/cm^3	Rm x10^3 cm^3/mol	α x10^{-23} cm^3
Ligand L1				
20	1.385	1.0241	70.0866	2.7794
40	1.405	1.0277	81.6871	3.2394
60	1.432	1.0310	89.7373	3.5587
80	1.455	1.0339	95.5928	3.7909
100	1.486	1.0362	102.2347	4.0543
Ligand L2				
20	1.411	1.0072	86.9939	3.4499
40	1.432	1.0176	100.6731	3.9923
60	1.455	1.0237	109.0522	4.3246
80	1.486	1.0278	117.4013	4.6557
100	1.511	1.0313	123.6669	4.9042
Ligand L3				
20	1.432	1.0093	86.3531	3.4245
40	1.459	1.0130	101.4648	4.0237
60	1.486	1.0231	109.8987	4.3582
80	1.509	1.0267	116.3226	4.6129
100	1.532	1.0310	121.7805	4.8294
Ligand L4				
20	1.443	1.0119	102.5996	4.0687
40	1.473	1.0195	120.6784	4.7875
60	1.495	1.0232	130.2451	5.1651
80	1.523	1.0276	138.7619	5.2028
100	1.555	1.0357	146.5556	5.8119

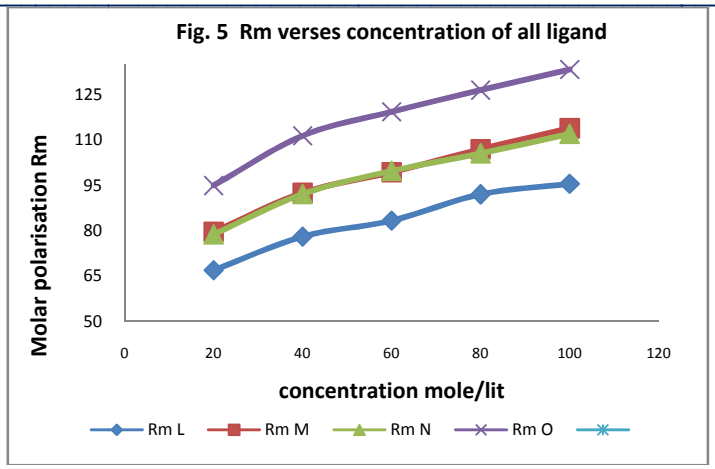
Graphical representation of molar polarization (Rm) of all ligand at 0.01M verses concentration in different percentage of DMSO solvent



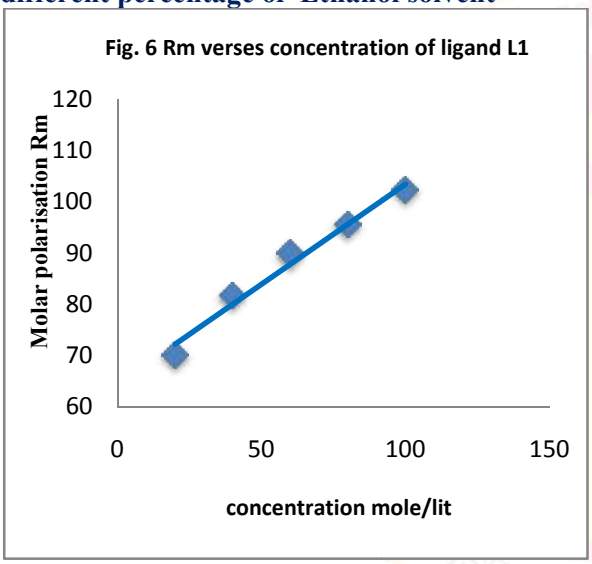


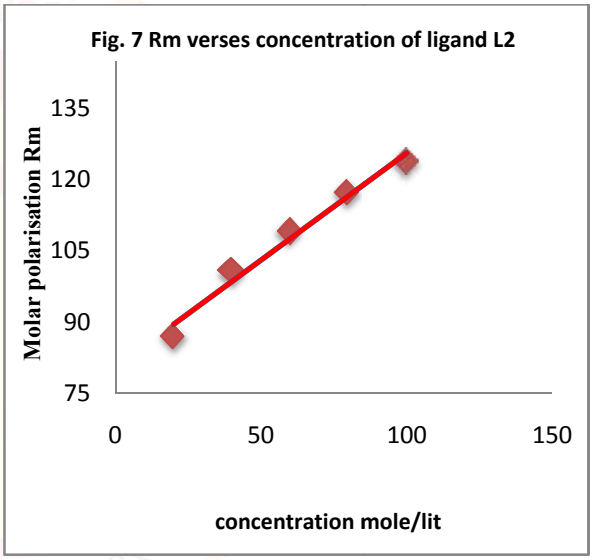


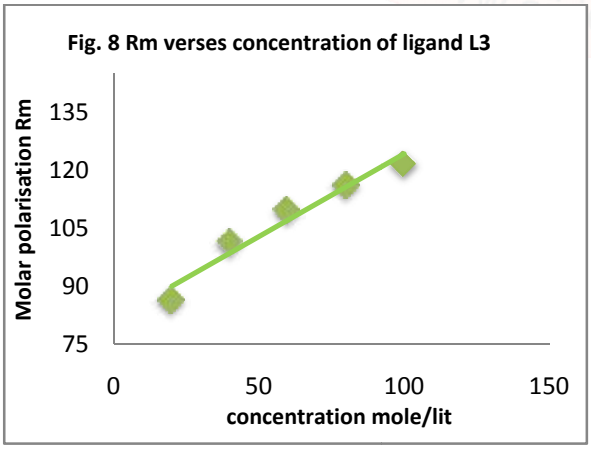


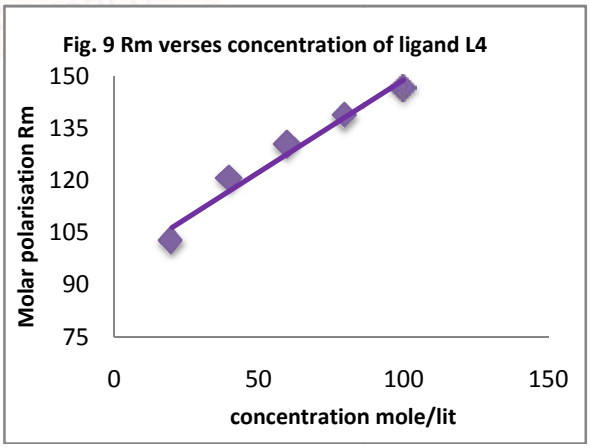


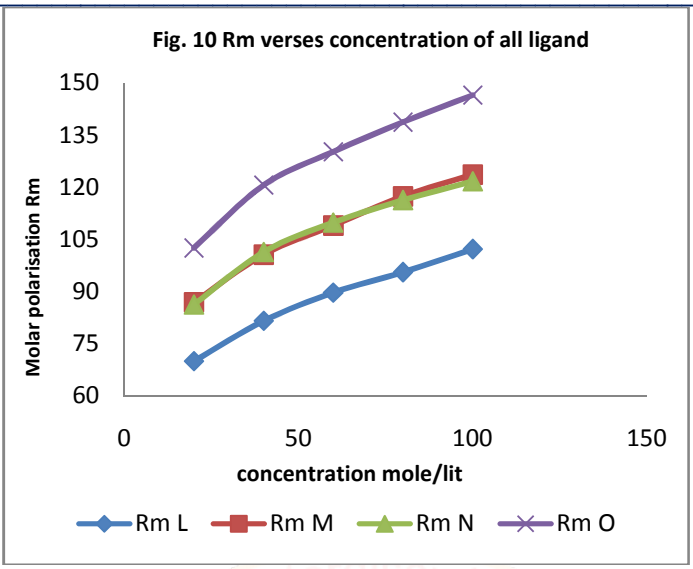
Graphical representation of molar polarization (Rm) of all ligand at 0.01M verses concentration in different percentage of Ethanol solvent











The values of molar refraction of different percent composition in binary mixture are shown in table-1. From the data it is observed that value of molar refraction goes on increasing with the decrease in amount of water in percent composition..

Table-2 and table-3 shows the comparative data of refractive indices, densities ,molar refraction and polarizability constant of DMSO and ethanol respectively, in different percent composition with water. From this, it is observe that, refractive index and density increases with the increase in percent composition of organic solvent. Graphical representation between molar refraction and percent composition of DM SO, Ethanol shows linear relationship. (Fig.1-5 DMSO, fig.6-10 Ethanol)Those solvent having more value of dipole moment shows greater refractive index and density, also there is same trend in case of ligand used. Ligand having more dipole moment shows greater value of refractive index and less value of density.

CONCLUSIONS

The values of molar refraction and polarizability constant of substituted azomethines in binary mixture are examined . It is concluded ,that the molar refraction and polarizability constant increases with increase in the percentage of solvent. This may be due to the increase in percentage of organic solvent which causes decreases in dielectric constant of medium

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STUDY OF PROTON-LIGAND STABILITY CONSTANTS OF Cu(II) AND Mn(II) COMPLEXES WITH (3-(3,5-DICHLORO-2-HYDROXYPHENYL)-1-PHENYL-5-(PYRIDINE-2-YL)-1*H*-PYRAZOL-4-YL)(FURAN-2-YL) METHANONE USING PH-METER IN 80% DMF-WATER SOLVENT.

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ABSTRACT

A stability constant (formation constant, binding constant) is equilibrium constant for the formation of a complex in the solution. It is the measure of the strength of the interaction between the reagents that come together to form the complex. pH meter instrument is also used to find out stability of complexes through titrations. The chlorosubstituted pyrazole acts as complexing agent. The proposed study deals with the proton-ligand stability constant of (3-(3,5-Dichloro-2-hydroxyphenyl)-1-phenyl-5-(pyridin-2-yl)-1H-pyrazol-4-yl)(furan-2-yl) methanone using by Calvin Bjerrum titration on pH-meter with 80% (DMF: water) solvent.

Key Words: *Poton-ligand stability constant, pH-meter, Pyrazole, Calvin Bjerrum titration.*

INTRODUCTION

A coordination compound contains a central metal atom or ion surrounded by a number of oppositely charged ions or neutral molecule known as ligands[1]. Most of the chemist study of proton-ligand stability constants stability constant using pH-meter. The hydrogen-ion activity in water-based solutions, its acidity or alkalinity expressed as pH scientifically is measured on the pH meter.

The chlorosubstituted pyrazoles have received considerable attention during the last few decades, as they are endowed with a wide range of biophysical applications. The most important characteristic of chlorosubstituted pyrazoles have central atom which influence the stability of a complexes compound. The chlorosubstituted pyrazole acts as complexing agent. The conformation of dissociable hydroxyl group their complexes with metals and transition metals were studied by many co-workers. Murhekar[2] *et al* explained stability constants of Pr (III) and Nd (III) with 3(2'-chlorophencyl)-4-pyridoyl-5-(2-hydroxy phenyl)pyrazole. The proposed study deals with the proton-ligand stability constant stability constant of chlorosubstituted pyrazoles by Calvin Bjerrum titration on pH meter.

MATERIALS AND METHODS

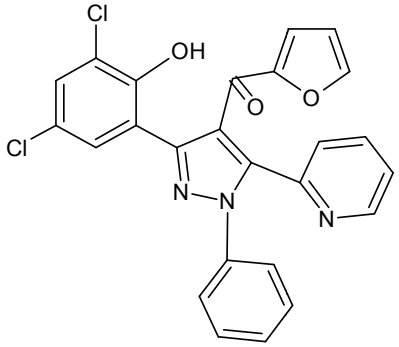
Proton-ligand stability constants and metal-ligand stability constants studied by (3-(3,5-Dichloro-2-hydroxyphenyl)-1-phenyl-5-(pyridin-2-yl)-1*H*-pyrazol-4-yl)(furan-2-yl)methanone (**ligand FP3**). In present study the ligands (FP3) was completely dissolved in 80% DMF-water mixture. The two metals selected for metal-ligand stability constants were: Cu (II) and Mn (II). The Calvin-Bjerrum titration method was used to calculate proton-ligand stability constant and metal-ligand stability constant.

The experimental pH-metric procedure contains the titration of

1. Acid Titration (A): 5 ml ($HNO_3$0.1M) + 5 ml 0.1M (KNO_3) + 35ml DMF + 5 ml water.
2. Acid + Ligand Titration (A + L):
5 ml HNO_3 (0.1M) + 5 ml KNO_3 (0.1M) + 10 ml ligand (in DMF water 80%) + 25ml DMF + 5 ml water.
3. Acid + Ligand + Metal Titration (A + L + M):
5 ml HNO_3 (0.1M) + 5 ml KNO_3 (0.1M) + 10 ml ligand (in DMF-water 80%) + 25ml DMF + 2 ml metal ion solution + 3 ml water.

All the pH measurements and titrations were carried out on ELICO-L1-10 pH meter with accuracy $\pm$ 0.01 by using glass and calomel electrode assembly. 0.1 M KNO_3 solution which was prepared from carbonate free double distilled water. Ionic strength of sodium hydroxide is kept constant as 0.1 M by addition of potassium nitrate solution. The structure and the molecular formula can be determined by UV, IR, NMR and mass spectroscopic techniques. The ligand **(FP3)** was

synthesized by conventional method as well as microwave irradiation.



Calculation of proton-ligand stability constants $\bar{n}_A$:

For the determination of proton-ligand stability constants, $\bar{n}_A$ values (proton-ligand formation number) were determined from the titration curve of acid and (acid + ligand).

$$\bar{n}_A = \gamma - \frac{(V_2 - V_1)(N + \varepsilon_0)}{(V_0 + V_1)T^0_L}$$

Titration data of ligand FP3 with Cu (II):

System: Ligand (BC3), Medium: 80%(DMF: water), N= 0.2N (NaOH), Ionic strength(μ) = 0.1 KNO_3, ε_0 = 0.002 M HNO_3, T^0_m= 0.0004 M

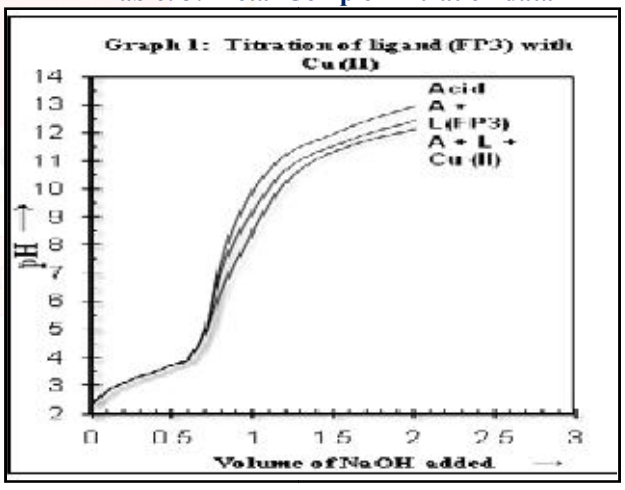
Table: 1: Titration data of ligand FP3 with Cu (II)

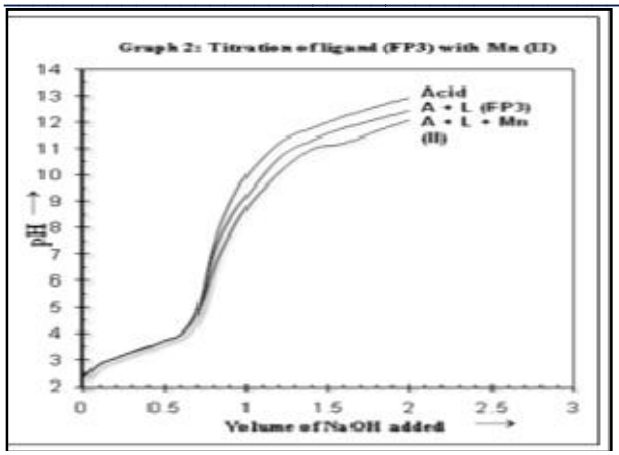
Vol. of NaOH added	Acid	A+ L (FP3)	A+ L+ Cu (II)
0	2.37	2.36	2.36
0.1	2.87	2.86	2.86
0.2	3.11	3.1	3.1
0.3	3.34	3.34	3.34
0.4	3.54	3.54	3.54
0.5	3.78	3.79	3.79
0.6	3.99	3.99	3.99
0.7	4.87	4.88	4.88
0.8	7.44	7.11	6.4
0.9	8.98	8.38	7.54
1.0	9.99	9.22	8.55
1.2	11.23	10.67	10.23
1.4	11.78	11.34	11.11
1.6	12.24	11.78	11.56
1.8	12.62	12.12	11.89
2.0	12.97	12.48	12.15

Table: 2: Titration data of ligand FP3 with Mn (II)

Vol. of NaOH added	Acid	A+ L (FP3)	A+ L+ Mn (II)
0	2.37	2.36	2.36
0.1	2.87	2.86	2.86
0.2	3.11	3.1	3.1
0.3	3.34	3.33	3.33
0.4	3.54	3.53	3.53
0.5	3.78	3.77	3.77
0.6	3.99	3.99	3.99
0.7	4.87	4.88	4.86
0.8	7.44	7.11	6.5
0.9	8.98	8.38	7.76
1.0	9.99	9.22	8.78
1.2	11.23	10.67	10.11
1.4	11.78	11.34	11.01
1.6	12.24	11.78	11.23
1.8	12.62	12.12	11.67
2.0	12.97	12.48	12.1

Table: 3: Metal Complex Titration data





Ligands	Metal ions	pH at Commencement of Hydrolysis (deviation of A + L curve from A acid curve)	pH at Commencement of Hydrolysis (deviation of A + L + M curve from A + L curve)
FP3	Cu (II)	7.01	6.4
	Mn (II)	7.01	6.5

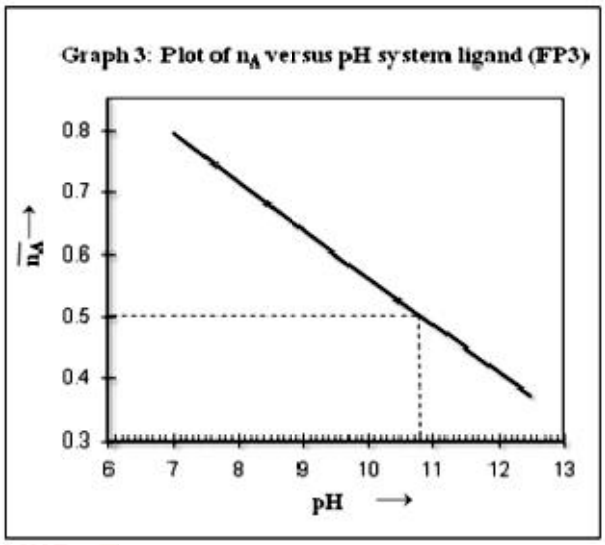
The Pattern of Titration Curves:

The deviation of acid + ligand curve to acid curve at 4.88 and simultaneously increased up to the 12.48. These kinds of deviations show the dissociation of -OH group of ligands.

$HL \rightarrow H^+ + L^-$ H = Acids, L = Ligand.

pH	V_1	V_2	$V_2 - V_1$	$\bar{n}_A$
7.0	1.4	1.5	0.1	0.7957198
7.5	1.6	1.72	0.12	0.755814
8.0	1.8	1.94	0.14	0.7162162
8.5	2.0	2.16	0.16	0.6769231
9.0	2.2	2.38	0.18	0.637931
9.5	2.4	2.6	0.2	0.5992366
10.0	2.6	2.82	0.22	0.5608365
10.5	2.8	3.04	0.24	0.5227273
11.0	3.0	3.26	0.26	0.4849057
11.5	3.2	3.48	0.28	0.4473684
12.0	3.4	3.7	0.3	0.4101124
12.5	3.6	3.92	0.32	0.3731343

Table:3 Titration data of ligand (FP3)



Here we have used the half integral method for determination of pK_1 values. Naik[3] *et al* used half integral method and calculated pK_1 and pK_2 values. The formation curves were constructed by plotting the values of $\bar{n}_A$ against pH of the solution and were represented in graph 3.

RESULT AND DISCUSSION

The pH of hydrolysis for metal ions under investigation was around pH = **7.** The dissociation constants (pK) of ligand are calculated from proton-ligand formation curve. The graphical data (graph 3) shows that pK_1 values for substituted ligand are found at 10.8. This is due to phenolic – OH group dissociating at 9.5 and above it in aqueous medium.

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STUDY OF PHYSICOCHEMICAL PARAMETERS OF DRINKING WATER FROM RURAL REGION OF YAVATMAL DISTRICT (MS)

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ABSTRACT

As water plays vital role in human life, so it is very important to know the quality of water. In view of this, we have collected 10 drinking water sample from different villages of mahagaon tahesil district Yavatmal (MS) having different sources such as bore well, well, hand pump to study it's suitability for drinking purpose. Physico-chemical Parameter such as Temperature(T), P^H, Total Dissolved Solid (TDS), Total Hardness (TH), Salinity of drinking water was determined. Result shows that most of the parameter are within permissible limit given by WHO.

Keywords: *Physico-chemical Parameter, Water Samples, Water quality standards.*

INTRODUCTION

Water is one of the important, abundant & precious compound of earth, Although statistics, the WHO reports that approximately 36% of urban & 65% of rural were without access to safe drinking water [2, 3]. Major source of drinking water is Ground water. Quality of drinking water decreases day by day due to various human activities. As various type of pollutant & several other substances are dissolved in ground water, the concentration of dissolved substances is useful for human body but in specific limit. In this research paper an attempt has been made to evaluate Physico-chemical Parameter of drinking water from different sources & to compare the observed value with standard value of WHO.

MATERIAL & METHOD

Water sample were collected in clean and dry polythene bottle of one liter capacity. Sample are collected from different sources (bore well, well, hand pump) in the month of January 2018. P^H, conductance, TDS, salinity are measured by portable water analysis kit and TH is determined by complexometric titration. Color, odour, temperature were determined at the point of sample collection. Observed value for different parameter is tabulated along with standard specified by world health organization (WHO).

Name of Region	Sample No. & Source	P^H	Total Dissolved Solid(mg/lit)	Total Hardness(mg/lit)	Temperature ^OC
	STANDARD WHO	6.5 to 8.5	2000	600	--
Sawana	S_1 (Bore Well)	7.3	480	460	22
	S_2 (Well)	7.4	520	400	23
Mahagaon	S_3 (Bore Well)	7.8	540	200	24
	S_4 (Bore Well)	8.2	570	550	22.8
Malkhini	S_5(Well)	8.0	460	376	23.9
	S_6(Well)	7.3	700	508	24
Fulsawangi	S_7(Bore Well)	7.8	800	600	23.2
	S_8(Bore Well)	7.0	770	700	22.7
Kalgaon	S_9(Bore Well)	8.2	530	500	22
Veni	S_{10}(Bore Well)	7.6	740	788	23

RESULT AND DISCUSSION

The Value of P^H was within the permissible limit and P^H value fluctuated in between 7.0 to 8.2. Temperature was found to be in the range between 22 to 24 ^OC during study. Temperature was measured using thermometer. Maxima of total dissolved solid (TDS) and total hardness (TH) were found to be 800 mg/lit and 788 mg/lit [7]. Observed value of TDS are within the permissible limit. Hardness of water is due to the Calcium and Magnesium ion, value of total hardness is exceed

the permissible limit in few samples. High concentration of hardness may cause kidney problem [8].

CONCLUSION

The present paper undertaken to account to bring an acute awareness among the people about the quality of water.

The result show that most of the parameter are within the permissible limit. It can be conclude that water is safe for drinking purpose, but requires some purification processes.

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SYNTHESIS AND ASSAY OF CHLOROSUBSTITUTED HETEROCYCLES AGAINST SOME ORNAMENTAL PLANT PATHOGENS

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ABSTRACT

The external diseases in plants were supposed to be the result of attack by microorganisms and insects. Heterocyclic compounds are present in abundance in our surroundings. They are naturally found in nucleic acid, vitamins, antibiotics, hormones etc. Literature survey reveals that many of the heterocycles have remarkable pesticidal, fungicidal, insecticidal and antimicrobial activities in vitro as well as in vivo conditions. So we thought interesting to undertake the synthesis and study of some novel chlorosubstituted heterocyclic compounds against some pathogens viz. Staphylococcus aureus, Staphylococcus epidermis, Pseudomonas aeruginosa and Salmonella typhi which are mainly responsible for the diseases in ornamental plants.

Keywords: *chlorosubstituted heterocycles; antibacterial assay; Staphylococcus aureus, Staphylococcus epidermis, Pseudomonas aeruginosa and Salmonella typhi.*

INTRODUCTION

Plant pathology deals with diseases in plants, their causes, etiology, resulting loss and their control. Plant diseases are caused by some pathogenic living organisms like *fungi, bacteria, viruses* etc or environmental factors. Due to these diseases plant growth reduces or even plant may die. *Fungi* were the first among the various causing agents of plant diseases to be recognized. . Prevost in 1807 described the contagious nature of *wheat smut.*

The growth of plants is regulated by number of organic substances like indole acetic acid (IAA), *auxine*, *gibberline* and chlorosubstituted heterocyclic compounds. Literature survey reveals that much work has been done over many heterocyclic compounds for their diverse pharmacological properties such as antimicrobial[1], pesticidal, fungicidal, antibacterial[2,3], antitumor[4], insecticidal, anti-inflammatory[5,6], antibacterial[7-10], anti- tubercular[11], antifungal[12-14], antiviral, antioxidant[15], anthelmintic, anti-HIV[16] analgesic, anticancer[17-20], anticonvulsant[21], anti-alzheimer[22], antimalarial[23,24] and antidepressant activities. The researchers reported these activities in both *in vitro*[25,26] as well as *in vivo* conditions. *Fungi* were the first among the various causing agents of plant diseases to be recognized. Chalcones[27] and flavones also play important role in plant life and are reported as antimicrobial agents. There are a lot of heterocyclic compounds[28-30] which have applications in many common diseases such as; triazine derivatives have been used as antimicrobial herbicides[31], urinary antiseptics and anti-inflammatory agent. Benzimidazole derivatives have been reported to possess wide range of biological activities such as antibacterial, antifungal, antiviral and anthelmintic etc.

MATERIALS AND METHODS

Various chlorosubstituted heterocyclic compounds were synthesized by the procedures[32-34].

Chlorosubstituted thiazines (Table-1,entry1a and 2a); thiazoles (Table-1,entry 3a and 4a); imidazolo-thiazole (Table-1,entry 5a); Imidazoles (Table-1,entry 6a and 7a) were synthesized and characterized byUV, IR and ^{1}H NMR data as below-

1a:- 2,4-dichloro-6-[6-(2,6-dichlorophenyl)-2-imino-3,6-dihydro-2*H*-1,3-thiazin-4-yl]phenol:

IR(KBr, ν(cm^{-1}): 3393 (Ar-OH), 2918 (N-H stre.), 3100 (Ar C-H stre.), 1664 (C=N stre), 1587 (C=C stre); 811 (C-Cl).

PMR: δ10.2 (s, 1H, Ar-OH), δ7.51-7.54 (m, 5H, Ar-H); δ6.5 (d, 1H, C-H); δ6.2 (s, 1H, N=H), δ4.2 (d, 1H, -S-C-H), δ3.5 (s, 1H, N-H).

UV λmax: 297 nm.

2a:- 2,4-dichloro-6-[6-(4-chlorophenyl)-2-imino-3,6-dihydro-2*H*-1,3-thiazin-4-yl]phenol:

IR (KBr, ν(cm^{-1}): 3390(Ar-OH), 2909(N-Hstre.), 3110(Ar C-Hstre.), 1674(C=Nstre), 1599 (C=Cstre); 813(C-Clstre.).

PMR: δ10.8 (s, 1H, Ar-OH), δ7.5-7.9 (m, 6H, Ar-H); δ6.5 (d, 1H, C-H); δ6.2 (s, 1H, N=H), δ4.2 (d, 1H, -S-C-H), δ3.5 (s, 1H, N-H).
UV λmax: 309 nm.

3a:-[2-amino-5-(3,5-dichloro-2-hydroxyphenyl)-1,3-thiazol-4-yl](2,6-dichlorophenyl) methanone:
IR(KBr, ν(cm^{-1}):3519(Ar-OH), 3330(N-Hstre.), 1660(C=Nstre), 1599(C=Cstre); 805(C-Cl).
PMR: δ10.8 (s, 1H, Ar-OH), δ7.5-7.9 (m, 5H, Ar-H); δ4.0 (s, 2H, N-H).
UV λmax: 415 nm.

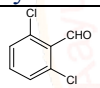
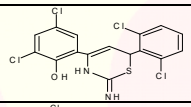
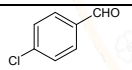
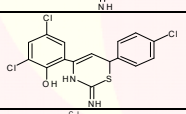
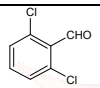
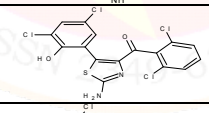
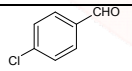
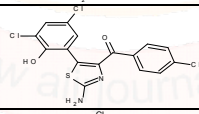
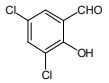
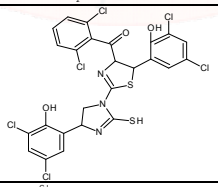
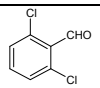
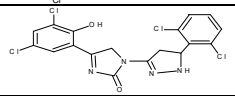
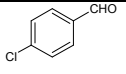
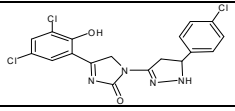
4a:[2-amino-5-(3,5-dichloro-2-hydroxyphenyl)-1,3-thiazol-4-yl](4-chlorophenyl) methanone:
IR(KBr, ν(cm^{-1}):3480(Ar-OH), 3310(N-Hstre.), 1683(C=Nstre), 1621(C=Ostre); 820(C-Cl).
PMR: δ10.9 (s, 1H, Ar-OH), δ7.1-7.9 (m, 6H, Ar-H); δ4.1(s, 2H, N-H).
UV λmax: 420 nm.

5a:2-[2-Mercapto-4-(2-hydroxy-3,5-dichlorophenyl)imidazolo]-4-(2,6-dichlorobenzoyl)-5-(2-hydroxy-2,3-dichlorophenyl)-1,3-thiazol:IR(KBr,ν(cm^{-1}):3341(Ar-OH), 3068(N-Hstre.), 2548(S-Hstre),1662(C=Ostre), 1641(C=Nstre); 825(C-Cl).
PMR: δ12.1-13 (s, 2H, Ar-OH), δ7.0-7.9 (m, 7H, Ar-H); δ3.2 (m, 3H, C-H); δ3.9 (d, 2H, C-H); δ2.5(s, 1H, S-H).
UV λmax: 550 nm.

6a: 4-(3,5-dichloro-2-hydroxyphenyl)-1-[5-(2,6-dichlorophenyl)-4,5-dihydro-1*H*-pyrazol-3-yl]-1,5-dihydro-2*H*-imidazol-2-one:
IR(KBr, ν(cm^{-1}):3490(Ar-OH), 3368(N-Hstre.),1662(C=Ostre), 1622(C=Nstre); 825(C-Cl).
PMR: δ12.4 (s, 1H, Ar-OH), δ7.0-7.9 (m, 5H, Ar-H); δ6.2 (m, 1H, N-H); δ3.9 (d, 1H, N-C-H); δ2.9(s, 2H, CH), δ1.5(dd, 2H, CH).
UV λmax: 450 nm.

7a: 1-[5-(4-chlorophenyl)-4,5-dihydro-1*H*-pyrazol-3-yl]-4-(3,5-dichloro-2-hydroxyphenyl)-1,5-dihydro-2*H*-imidazol-2-one:
IR(KBr, ν(cm^{-1}):3490(Ar-OH), 3368(N-Hstre.), 1662(C=Ostre), 1622(C=Nstre); 785(C-Cl).
PMR: δ12.1 (s, 1H, Ar-OH), δ7.0-7.9 (m, 6H, Ar-H); δ6.1 (m, 1H, N-H); δ3.9 (d, 1H, N-C-H); δ2.9(s, 2H, CH), δ1.5(dd, 2H, CH).

Table:1-Physical constants of newly synthesized heterocycles

Entry	Aldehyde	Product	Melting pt. (^{0}C)	% Yield
1a			168-170	60%
2a			189-191	58%
3a			167-169	51%
4a			180-182	53%
5a			141-143	65%
6a			175-177	57%
7a			193-195	63%

The synthesized chlorosubstituted thiazine, thiazole and imidazole derivatives were screened for their antibacterial assay against some *ornamental plant pathogens* viz. *Staphylococcus aureus, Staphylococcus epidermis, Pseudomonas aeruginosa and Salmonella typhi* by using Agar disc diffusion method.

RESULT AND DISCUSSION

The compounds when assayed against the *ornamental plant pathogens* viz. *Staphylococcus aureus, Staphylococcus epidermis, Pseudomonas aeruginosa and Salmonella typhi* showed moderate to excellent activity. The data of antibacterial activities of the titled compounds is given in Table No.2. In general, compounds 1a, 2a and 3a showed good antibacterial results against all the test organisms viz. *S.aureus, S.typhi*, *P.aeruginosa* and *S.epidermidis.*

Table No.2- Impact of newly synthesized chlorosubstituted heterocycles against plant pathogens:

Diameter of inhibition zone (mm); Values were represented as the mean
AB- Antibiotic Disc (Chloramphenicol-10), SP-Sample, ABSP- Antibiotic+Sample, CL-Control (DMSO)

	Pseudomonas aeruginosa MTCC-424 (Gram Negative)				*Salmonella typhi* ATCC-25812 (Gram Negative)				*Staphylococcus aureus* ATCC-33591 (Gram Positive)				*Staphylococcus epidermidis* MTCC-3086 (Gram Positive)			
Sample Code	AB	SP	ABSP	CL	AB	SP	ABSP	CL	AB	SP	ABSP	CL	AB	SP	ABSP	CL
1a	24	16	26	00	28	20	32	00	16	18	18	00	28	16	28	00
2a	24	16	26	00	27	20	33	00	15	19	17	00	27	15	29	00
3a	24	16	25	00	28	18	32	00	14	20	18	00	28	16	27	00
4a	24	10	24	00	29	15	29	00	18	17	18	00	28	15	28	00
5a	23	09	23	00	28	14	28	00	16	15	16	00	28	12	28	00
6a	23	10	23	00	29	13	27	00	16	14	17	00	27	11	28	00
7a	22	11	22	00	29	11	29	00	15	13	15	00	29	00	27	00

CONCLUSION

While analyzing the antibacterial activities of all the test compounds it was interesting to see that some titled compounds also boosted the activities of standard antibiotic Chloramphenicol especially the compounds 1a, 2a and 3a against *S. typhi* and the compounds 1a and 3a against *S. epidermidis*. Activity against *S. aureus* was boosted by nearly all the compounds. Most of the test compounds were found to be highly active against all the test pathogens. Hence all these heterocycles can be used in the treatment of diseases caused by these pathogens in ornamental plants. However a further detailed study in the light of Agricultural sciences is advised.

ACKNOWLEDGEMENTS

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MOLECULAR INTERACTION STUDIES OF TERNARY MIXTURES OF 2- AMINOBENZOTHIAZOLE IN PROPANOL-WATER AT DIFFERENT TEMPERATURES

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ABSTRACT

The nature and the relative strength of the intermolecular interaction between the components of the liquid mixtures have been successfully investigated by ultrasonic method. In present study, the densities (ρ), ultrasonic velocities (u), in a ternary liquid mixture of 2-aminobenzothiazole with propanol in water have been measured at 303.15, 308.15, 313.15,318.15 and 323.15 K respectively, over the entire composition range by using densitometer, ultrasonic interferometer, respectively. The measured data have been used to compute the various thermo-acoustic parameters using the standard relations namely, adiabatic compressibility (β_s), intermolecular free length (L_f), specific acoustic Impedance (Z),Wada constant (W), molar sound velocity(R), relative association (R_A etc. The results have been analyzed on the basis of variation in thermodynamic parameters. These parameters are useful for explaining the molecular association and interaction between the components of ternary liquid mixtures at different temperatures. The results have been interpreted in terms of solute-solvent and solvent-solvent interaction.

***Keywords*:** Thermo-acoustic, 2-aminobenzothiazole, ultrasonic velocity, density, adiabatic compressibility, ternary mixture, propanol, molecular interaction.

INTRODUCTION

In the historical development of organic chemistry, nitrogen and sulphur heterocyclic compounds have maintained the interest of researchers in the last decades, some most common nitrogen heterocycles are thiazoles and thiadiazoles. The wide spread applications of thiazole in the agrochemical industries and medicinal chemistry proves this moiety is an important bioactive class of heterocycles [1]. Different methods like di-electric, magnetic resonance, infrared and Raman effect are used to study molecular interaction and different solution properties. Like other methods, ultrasonic method has been extensively used by many workers to study the molecular interactions and physicochemical behavior in liquid mixtures[2-3]. The study of thermodynamic properties of mixtures provides good measure of solute –solvent interactions. The experimental data of thermo acoustical properties of liquid and liquid mixtures are fascinating and highly fundamental and practically important in chemical industry and engineering design [4]**.** In continuation of our work, present study reported the results of ultrasonic study of the ternary mixture of 2-aminobenzothiazole with propanol -water solvent in entire composition range, at five different temperatures. 2-aminobenzothiazole is used as an intermediate for dyestuff, in photographic chemicals, in medicinal chemistry and its derivatives can find application for treatment gastric ulcer and cancer etc[5]. An exhaustic survey of literature has shown that a few attempts have been made for ultrasonic velocity data for ternary liquid mixtures in propanol solvent.[12]. However, no effort have been made for the ultrasonic and thermodynamic studies for ternary mixture of 2-aminobenzothiazole with propanol in water. The present study was undertaken in order to have deeper understanding of the intermolecular interaction between the components of ternary liquid mixtures. Using the experimental values of ultrasonic velocity (u), density (ρ), various thermo acoustical parameters have been estimated using standard relations. These thermo-acoustic parameters of pure components and mixtures are being used to investigate the molecular packing, molecular motions and various intermolecular interactions and their strength, influenced by the size in pure components and in the mixtures[13]. The results are interpreted in predicting nature and strength of molecular association between the components of the liquid mixtures.

MATERIALS AND METHODS

Materials

In present study, used solute 2-aminobenzothiazole (Hi-Media) and solvent propanol (Fisher Scientific) were analytical (AR) and spectroscopic reagent (SR) grade. They were used without further purification.

METHOD

The mass of sample was measured using digital electronic balance (Model SHIMADZU AUY-220, Japan,) with precision of ±0.1 mg. The required ternary mixtures were prepared over the entire range of compositions in propanol -water solvent and kept in air tight flask. The densities of pure liquids and ternary mixtures were measured with portable digital densitometer (Anton Paar, DMA-35, Austria).The average uncertainty in measurement in the measured density is ± $5x10^{-3}$ kgm^{-3}. The ultrasonic velocity of pure and liquid mixtures was measured using multi-frequency ultrasonic interferometer (Model: F-81S, Mittal Enterprises, New Delhi,) operating at 2 MHz's frequency at five different temperatures and overall accuracy of ±2 m/s. The instruments was calibrated by measuring the velocity of benzene and carbon tetrachloride. The measured values are agreed closely with literature values.

The density (ρ), ultrasonic velocity (u) of pure liquids and ternary mixtures were measured at 303.15, 308.15, 313.15, 318.15 and 323.15K temperatures. The temperature was controlled through the water circulating around the liquid cell using thermostatically controlled High Precision water bath MSW-274(Macro scientific work pvt. Ltd. Delhi) with an uncertainty of ±0.3°c

THEORY AND CALCULATIONS

Using the measured data, following acoustical parameters are calculated by using standard expressions.

(i) **Adiabatic compressibility:-**

$$\beta_s = \frac{1}{\rho_s u_s^{\,2}} \text{-------(1)}$$

Where ρ_s =density of solution, u_s = sound velocity.

(ii) **Intermolecular free length** (L_f)**:-**

$$L_f = K\sqrt{\beta_s} \text{------(2)}$$

Where 'K' is a temperature dependent constant known as Jacobson constant [m].

(iii) Specific acoustic impedance(Z):-

$$Z = u_s \rho_s \text{--------(3)}$$

(iv) Wada's constant (W) :-

$$W = \left(\frac{M}{\rho_s}\right)\cdot \beta_s^{-\frac{1}{7}} \text{------(4)}$$

Where 'M' molar mass of the solution.

(v) Molar sound velocity or Rao's constant (R) :-

$$R = \left(\frac{M}{\rho_s}\right)\cdot u_s\, 1/3 \text{-------(5)}$$

(vi) Relative association (R_A):-

$$R_A = \left(\frac{d_s}{d_o}\right)\left(\frac{u_o}{u_s}\right)^{1/3} \text{------(6)}$$

Where ρ_o = density of solvent, u_o = velocity of solvent

RESULTS AND DISCUSSION

The experimental values of density, ultrasonic velocity, viscosity and R.I. for 2-aminobenzo-thiazole with propanol in water are presented in Table **1**. The some of the calculated thermo-acoustics parameters are given in Table 2-3.In order to understand reaction kinetics of ternary mixture, tabulated values of thermo-acoustic parameters are graphically represented in Figures 1-8

Table 1: Density (ρ), ultrasonic velocity (u), adiabatic compressibility (β_s), intermolecular free length (L_f), acoustical Impedance (z), Wada's constant (W), Rao's constant (R), relative association (R_A),2-aminobenzothiazole in propanol-Water at different Temperatures

Conc.	(ρ) kg m^{-3}	(u) m s^{-1}	βs x10-^{10} N^{-1} m^{-2}	L_f x10-^{11} m	Z(kg m^2s^{-1}) x 10 ^{6}	W ($m^3Pas^{-8/7}$ mol^{-1})	R(m^3mol^{-1} $(ms^{-1})^{1/3}$)	R_A (m^3mol^{-1})
0.000	883.5	1352.5	6.1876	5.1615	1.1949	3.5152	229.93	0.9901
0.002	869.3	1327.5	6.5277	5.3015	1.1540	3.5454	229.36	0.9901
0.004	869.5	1331.0	6.4919	5.2870	1.1573	3.5470	229.92	0.9894
0.006	871.0	1339.0	6.4035	5.2508	1.1663	3.5482	230.90	0.9892
0.008	872.5	1340.0	6.3830	5.2424	1.1692	3.5438	230.67	0.9906
0.01	873.0	1335.7	6.4205	5.2578	1.1661	3.5388	229.80	0.9922
0.000	877.5	1349.7	6.2557	5.2374	1.1844	3.5337	231.02	0.9917
0.002	864.3	1322.5	6.6152	5.3858	1.1430	3.5592	229.82	0.9917
0.004	865.	1326.4	6.5711	5.3678	1.1473	3.5597	230.31	0.9915
0.006	866.7	1332.5	6.4983	5.3380	1.1549	3.5584	230.92	0.9919
0.008	868.9	1333.6	6.4711	5.3268	1.1588	3.5515	230.52	0.9942
0.01	868.4	1331.7	6.4933	5.3359	1.1564	3.5518	230.33	0.9941
0.000	873.2	1334.2	6.4335	5.3519	1.1650	3.5370	229.49	0.9941
0.002	860.2	1298.4	6.8958	5.5408	1.1169	3.5550	226.71	0.9941
0.004	861.0	1302.5	6.8461	5.5208	1.1215	3.5554	227.21	0.9940
0.006	862.6	1307.5	6.7812	5.4946	1.1278	3.5536	227.66	0.9945
0.008	863.9	1309.0	6.7555	5.4842	1.1308	3.5502	227.58	0.9957
0.01	864.5	1301.4	6.8299	5.5143	1.1251	3.5422	226.10	0.9983
0.000	868.1	1326.7	6.5446	5.44907	1.1517	3.5490	229.54	0.9944
0.002	855.5	1291.4	7.0090	5.63909	1.1048	3.5662	226.73	0.9944
0.004	856.5	1298.5	6.9245	5.60498	1.1122	3.5682	227.71	0.9937
0.006	857.7	1301.5	6.8830	5.58815	1.1163	3.5663	227.91	0.9944
0.008	859.4	1304.0	6.8430	5.57191	1.1207	3.5622	227.90	0.9957
0.01	860.4	1295.4	6.9261	5.60564	1.1146	3.5519	226.13	0.9990
0.000	863.8	1308.0	6.7666	5.5927	1.1299	3.5497	227.43	0.9916
0.002	851.4	1284.4	7.1198	5.7368	1.0935	3.5754	226.58	0.9916
0.004	852.6	1286.5	7.0866	5.7234	1.0969	3.5727	226.63	0.9925
0.006	853.6	1283.2	7.1147	5.7348	1.0953	3.5665	225.79	0.9945
0.008	855.3	1287.0	7.0587	5.7122	1.1008	3.5634	226.01	0.9955
0.01	856.4	1280.3	7.1236	5.7384	1.0964	3.5542	224.54	0.9985

Figs. For ultrasonic properties of 2-aminobenzothiazole with propanol in water

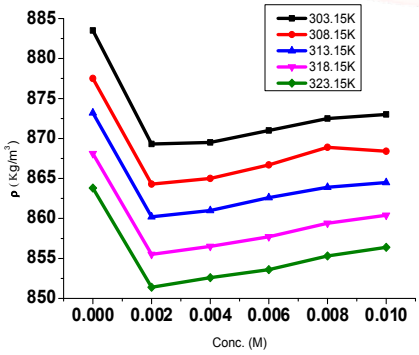


Fig.1. Density Vs conc.

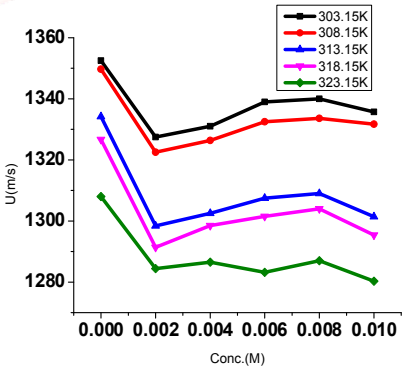


Fig.2. U. Vs conc.

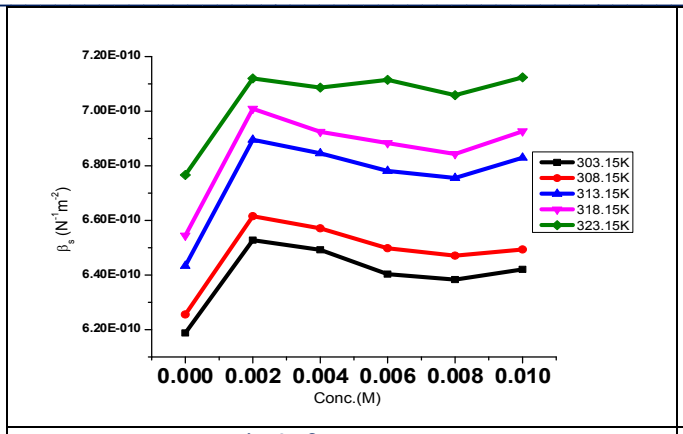


Fig.3. βs. Vs conc.

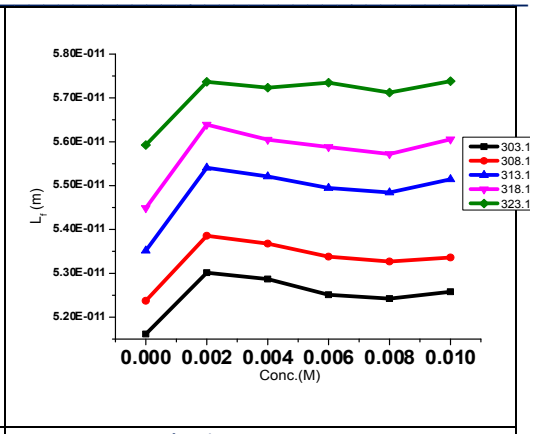
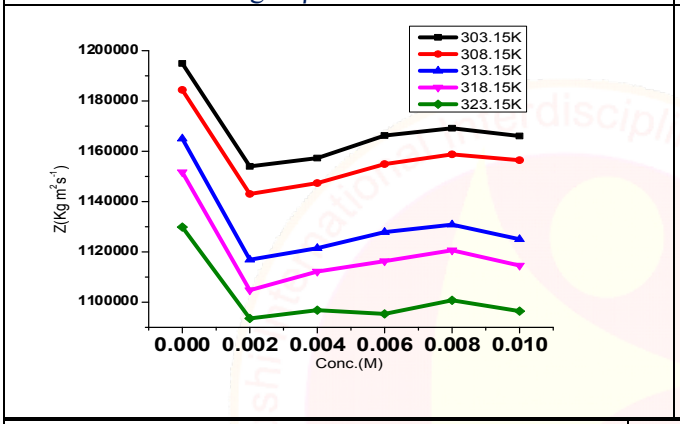
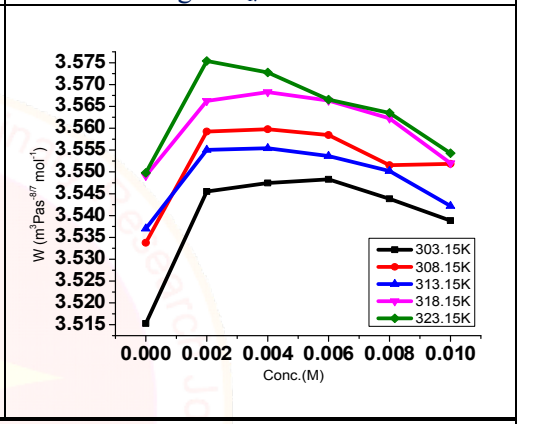


Fig.4. L_f Vs conc.





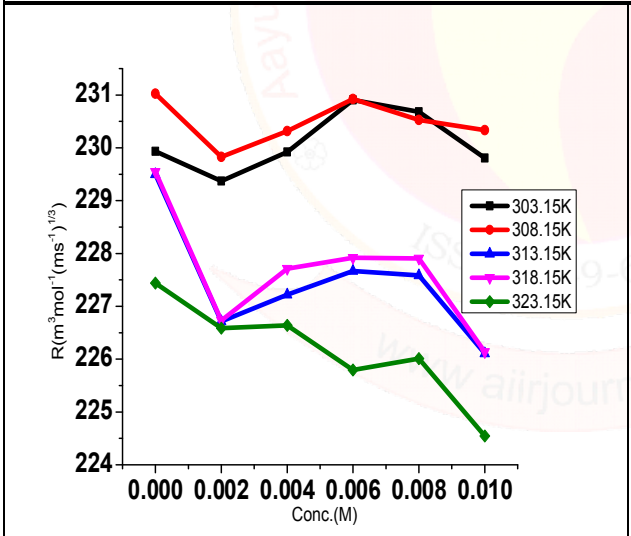


Fig.7. R Vs conc.

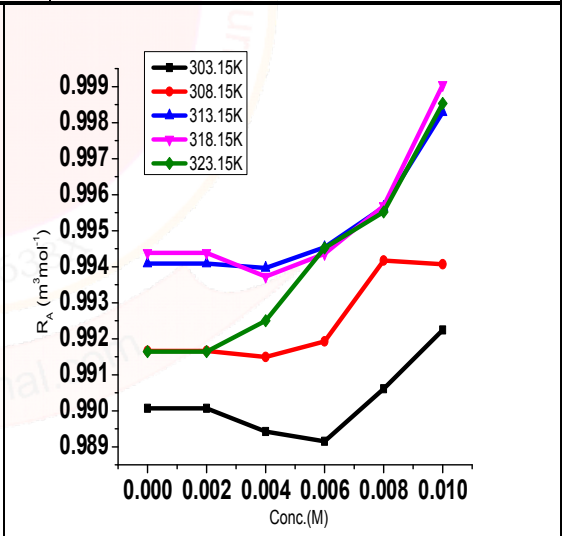


Fig.8. R_A Vs conc.

From the **table 1** and fig. 1and 2 noted that density and ultrasonic velocity increases with increase in concentration of solute. The linear behavior with increase in velocity with concentration indicates the interaction between unlike molecule, which suggests powerful solute-solvent (dipole-dipole) interaction between the component molecules. As density increases number of solute particles in the given region increases, this leads to quick transfer of sound velocity and hence ultrasonic velocity increases with increase in concentration[14]. It shows reverse trends in ultrasonic velocity and density with increase in temperature show molecular forces are weakening at high temperature. The change in ultrasonic velocity can be explained by a model presented by Eyring and Kincaid[15]. The increase in ultrasonic velocity is structure making type.

From **table 1** and fig.3- 4. Increase in concentration of thiazole results the linearly decreases in adiabatic compressibility and free length. This trend supports strong solute-solvent interaction and suggests aggregation of solvent molecules around solute molecules[16-17]. The magnitude of adiabatic compressibility and free length increases with increase in temperature, it clearly reveal that interaction become weaker at higher temperature[18]. The decreases in free length with increase in molar concentration suggest there are good agreements with model of Eyring and Kincaid. The specific acoustic impedance is the parameter related to the elastic properties of the medium. The specific acoustic impedance is the impedance offered to the sound wave by the components of the mixture. In our present investigation (Fig.5), specific acoustic impedance increase with increase in concentration. This trend further supports the possibility of molecular interaction due to H-bonding between solute-solvents and solvent-solvent molecules which restrict the free flow of sound waves[19]. The specific acoustic impedance is directly proportional to density, ultrasonic velocity and inversely proportional adiabatic compressibility [20].
From Fig. 6-7, the molar compressibility (Wada's constant) and Molar sound velocity (Rao's constant) nonlinearly decreases with increase in concentration which indicates that the magnitude of molecular interaction is enhanced in the system, which indicate interaction between solute-solvent molecule increases. This leads to tight packing of the medium by increases the molecular interactions[21].
Relative association is the measure of extent of association of components in the medium. The relative association is depends on either breaking up of the solvent molecules on addition of solute to it or the salvation of present ions. From Fig. 8 the relative association increases with increase in concentration. The increasing trend indicates there is a salvation of present solute ions[22].

CONCLUSIONS

From the present investigation experimental values of density, ultrasonic velocity, and related acoustic parameter values indicate that thermodynamic parameters are sensitive to study molecular interactions for ternary liquid mixtures at different concentrations and at varying temperatures. Thus it is concluding that in mixture of studied compound, both solute-solute and solute-solvent interactions are existing. Some parameters specially, free length and adiabatic compressibility indicate strong interaction between solute-solvent molecules in the studied system.

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VARIATION OF VISCOSITY OF SUBSTITUTED THIAZOLY SCHIFF'S BASES IN 70% OF ACETONE-WATER, ETHANOL-WATER AND DIOXANE- WATER MIXTURES AT VARYING TEMPERATURES.

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ABSTRACT

Viscosity and density of 2-[3-(4-methoxy phenyl) -1-(4 phenyl-thiazol-2-ylimino)-allyl]-4-mehtyl phenol. (I). 2-[3-phenyl-1-(4-phenyl-thiazol-2-ylimino)-allyl]-4-mehtyl phenol (II), 2-[3-(4-chlorophenyl)-1-(4-phenyl-thiazol-2-ylimino)-allyl]-4-mehtyl-phenol (III) in 70% of dioxane-water, ethanol-water and acetone- water mixtures have been measured. The viscosity measurements are carried out at different temperatures (i.e. at 313° k - 338°k). From the data the relative viscosities have been calculated which were used to evaluate the thermodyanamic parameters such as entropy change (ΔS), enthalpy change (ΔH) and free energy change ΔG. The molecular interactions in the solutions in 70 % of solvent-water mixture have been studied.

key words :- *Substituted thiazolyl Schiff's bases, viscosity, Density, Thermodyanamic parameter.*

INTRODUCTION

Every liquid has a property called viscosity, it means resistance which retards the flow of liquid which is developed because of shearing effect.

Viscosity measurement provides useful information about solute-solute and solute-solvent interaction which are related to structure making and breaking properties of liquid. Viscosities of concentrated aqueous electrolytic solutions at various concentrations have been determined by Barry and Irving[1] the solute-solute and solute-solvent interactions have been studied in aqueous and non-aqueous solutions by many workers.[2-4] Densities and viscosities of binary liquid systems of acetonitrile with aromatic ketones have been studied by Savitha Jyostna T & Satyanarayana[5] N for investigating the parameters like excess gibbs free energy of activation of viscous flow, Grunberg – Nissan interaction constant. Pandey and Yasmin[6] have measured viscosities and densities of aqueous binary electrolyte solutions of different molarities. Amalendu pal[7] & Rekha Gaba have been studied the viscosities of binary liquid mixtures of some n-alloxy propanols with n-alkanols as a function of composition using an Ubbelohde viscometer. P.P. Deohate[8], et al Compared the viscosity behavior of some substituted Benzo-(4,5-d)-2-Arylimino-7-Aryl/Alkylimino-1,3,6-Thiadiazepines in different percentages of solvents. P.B Agrawal et.al[9] determined the viscosity and thermodynamic parameters in some substituted 1,3 propanedione. M.E.de Ruiz, et al[10] have studied the viscosities and densities of mixtures containing polyethylene glycol monoethyl ether and 1-propanol have been determined in all concentration ranges between 5° and 45°C. The present work deals with the study of molecular interactions of substituted thiazolyl schiff's bases in 70% of dioxane-water, ethanol-water and acetone-water mixtures at different temperature and also we studied the viscosity behavior on the basis of presence of different substituents.

EXPERIMENTAL

Schiff's Bases I, II, III were prepared by reacting a series of chalcones with 2-aminothiazole. The structures, were confirmed on the basis of IR and NMR spectral data. Weighings was made on contech electronic balance with accuracy (0.01). The densities (□) of solution and solvents were measured with the help of pyknometer and the viscosities were measured by means of ostwald's viscometer (± 0.11% kg $m^{-1}s^{-1}$) which was kept in equilibrium with elite thermostatic water bath (± 0.1°C). solutions were prepared in 70 percentages of dioxane-water, ethanol-water and acetone-water mixtures at (30 ± 0.1°C). The viscometer was kept in water bath and flow time was determined after equilibrating the viscometer with bath temperature. The density and relative viscosity data for binary mixture at different temperatures have been listed in table 1, 2 & 3.

Density, relative viscosity of each of the ligand solutions is determined by using the empirical formula.

$$n_r = \frac{ds \times ts}{dw \times tw} \quad \text{.....(1)}$$

Where $n_r \rightarrow$ relative viscosity of solution.
ds → density of solution.
dw → density of respective solvent.
ts → time flow for solution.
and tw → time flow for respective solvent

$$\Delta G = -2.303 \times R \times \text{Slope} \quad \text{...(2)}$$

$$\log \eta_{r1} - \log \eta_{r2} = \frac{\Delta H}{2.303}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \quad \text{... (3)}$$

$$\Delta S = \frac{\Delta G - \Delta H}{T} \quad \text{...(4)}$$

Table-1 :- Determination of relative viscosities at different temperature in 70% Acetone-water mixture.

Sr. No.	Temp^{0}k	density$\times 10^{-3}$ kg m^{-3}	η_r	Log η_r
System – MPPTMP – I				
1	313	0.9368	1.20788	0.0820
2	318	0.9308	1.19086	0.0758
3	323	0.9192	1.1817	0.0725
4	328	0.916	1.161007	0.0648
5	333	0.9095	1.114825	0.0472
6	338	0.9037	1.10697	0.0441
System – PPTMP – I				
1	313	0.9265	1.20305	0.0802
2	318	0.9235	1.1905	0.0757
3	323	0.915	1.1811	0.0723
4	328	0.9109	1.17318	0.6716
5	333	0.9092	1.153269	0.0619
6	338	0.9068	1.122166	0.0500
System – CPTMP – I				
1	313	0.936	1.420082	0.1523
2	318	0.935	1.395258	0.1446
3	323	0.934	1.3601003	0.1354
4	328	0.933	1.344964	0.1287
5	333	0.932	1.329963	0.1238
6	338	0.931	1.239838	0.0933

Table-2 :- Determination of relative viscosities at different temperature in 70% Dioxane-water mixture.

Sr. No.	Temp^{0}k	density$\times 10^{-3}$ kg m^{-3}	η_r	Log η_r
System – MPPTMP – I				
1	313	0.9277	1.2384	0.0928
2	318	0.9135	1.1955	0.0775
3	323	0.9110	1.1854	0.0738
4	328	0.9099	1.1731	0.0693
5	333	0.8978	1.1661	0.0667
6	338	0.8944	1.1517	0.0613
System – PPTMP – I				
1	313	0.9225	1.1978	0.0784
2	318	0.9206	1.1823	0.0727
3	323	0.9156	1.1723	0.0690
4	328	0.9137	1.1630	0.0656
5	333	0.9112	1.1558	0.0628
6	338	0.9077	1.1346	0.0548
System – CPTMP – I				
1	313	0.9080	1.0176	0.0076
2	318	0.9070	1.0151	0.0065
3	323	0.9660	1.0139	0.0059
4	328	0.9051	1.0092	0.0039
5	333	0.9040	1.0088	0.0038
6	338	0.9030	1.0040	0.0017

Table-3 :- Determination of relative viscosities at different temperature in 70% Ethanol-water mixture.

Sr. No.	Temp^{0}k	density$\times 10^{-3}$ kg m^{-3}	η_r	Log η_r
System – MPPTMP – I				
1	313	0.9520	1.0091	0.0039
2	318	0.9561	1.0040	0.0017
3	323	0.9620	1.0172	0.0074
4	328	0.9681	1.0483	0.0204
5	333	0.9740	1.0938	0.003
6	338	0.9401	1.0578	0.0244
System – PPTMP – I				
1	313	0.9481	1.1522	0.0675
2	318	0.9560	1.2245	0.0879
3	323	0.9640	1.2302	0.0901
4	328	0.9720	1.2589	0.1000
5	333	0.9347	1.2893	0.1103
6	338	0.9362	1.2998	0.1137
System – CPTMP – I				
1	313	0.9372	1.0191	0.0082
2	318	0.9282	1.0221	0.0095
3	323	0.9512	1.0306	0.0130
4	328	0.9639	1.0333	0.0142
5	333	0.9721	0.0856	0.0356
6	338	0.9720	1.1026	0.0424

Table-4 :- Determination of thermodynamic parameters.

System	**β Coefficient**	**ΔG $Jmol^{-3}k^{-1}$**	**ΔH $Jmol^{-3}k^{-1}$**	**ΔS $Jmol^{-3}k^{-1}$**
Medium-Acetone-water (70%)				
MPPTMP-I	4.3470	-117563	159	-35.04
PPTMP-I	7.5314	-4643.1	761	-16.35
CPTMP-I	5.0720	-11679.7	15820	-52.16

Medium-Dioxane-water (70%)				
MPPTMP-I	12.042	-6358.7	5537	-20.69
PPTMP-I	3.7501	-3063.5	415.4	-10.36
CPTMP-I	5.3801	-4578.0	50.5	-14.67

Medium-Ethanol-water (70%)				
MPPTMP-I	5.0970	-8836.40	930	-26.45
PPTMP-I	6.6710	-10946	927	-42.32
CPTMP-I	10.470	-10253.29	1079	-34.28

RESULTS AND DISCUSSION

It would be seen from the table 1, 2 & 3, that relative viscosities and densities decreases with decrease in temperature of dioxane, ethanol and acetone-water mixtures which may be due to interactions between solute-solute and solute-solvent.

The relative viscosity of acetone-water mixture is greater than ethanol-water & dioxane-water-mixture.This may be due to the effect of greater polarity of acetone as compared to the less polar ethanol and non-polar dioxane solvent.

There is no specific trend in viscosity of different solutes. These variations may be due to the varying number of free ions across fluid stream. These ions may carry out change in energy resulting in variable viscosity.

The viscosity measurements are carried out at different temperatures (i.e. at 313° k - 338°k) to evaluate the thermodyanamic parameters such as entropy change (ΔS), enthalpy change (ΔH) and free energy change ΔG. The table no (4) shows relative viscosities at different temperatures. It would be seen from the table that relative viscosities and densities decreases with increase in temperature for all system.

Viscosity is determined by strength of intermolecular force when that force is more, shear strength of liquid will be more and likewise the viscosity. When that force is small shear strength of liquid is small and its viscosity will be low.

The relative viscosity values at different temperature are used to construct the graph between log η_r Vs $1/T$. The slope value of straight line graphs, thermodynamic parameters entropy change ΔS free energy change ΔG and enthalpy change ΔH are calculate by using equations 2, 3 & 4. The values of thermodyanamic parameters are illustrated in table no. (4). It is observed from the table that the values and ΔG, ΔH and ΔS are more more for the system CPTMP-I for acetone-water and ethanol-water mixture. This may be due to the presence of chloro electron withdrawing group..

It would be seen from the relative viscosities and densities with the addition of other solvent intermolecular forces are interrupted and new force intermolecular force developed which again changes on addition for solute. Hence due to variable solvent-solvent and solute-solvent interaction, variable trends are observed in viscosity values.

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SYNTHESIS OF POLYANILINE EFFECT OF TEMPERATURE AND FREQUENCY OF PANI-CDSO4 COMPOSITE

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ABSTRACT

Conduction of polymer is one of example of peculiar family member compounds. This compounds made of monomer unit it have conjugated double bond, After doping it carries electron. Due to this reason from commercial point of view, such polymer can replace metal and semiconductor. This present work show conductivity change of polyaniline after adding $CdSO_4$ at different temp. The electrical properties of polyaniline -$CdSO_4$ composite. Polyaniline prepared by chemical process. $CdSO_4$ dispersed polyaniline composite were prepard by polymerization process. At It observed that electrical properties polyaniline such as conductivity changed by adding $CdSO_4$ with different temp. The adding of $CdSO_4$ in polymerization of polyaniline resulted in increasing molecular weight of polyaniline. Electrical conductivity of polyaniline was increased by adding $CdSO_4$ during polymerization process. Electrical conductivity study of polyaniline is also carried out know its change in properties with respect to temp. At different temperature it show change in electrical conductivity.

Keyword:- *Aniline, electrochemical polymerization, chemical polymerization , ammonium per sulfate*

INTRODUCTION

Electronic conduction and application have been reported in reviewed.[1-4] Conducting polymer is widely used in the electronic and engineering purpose because of its characteristics. It have unique properties such as electrical conductivity, mechanical strength hence it used instead of metal. Polyaniline it is good example of conducting polymer due to it properties it is used solar cell instead of platinum in solar cell. Polyanilne which can be prepared at large scale due to its physiochemical properties.[5-8] polyaniline can be prepared by oxidative and electrochemical method by using suitable oxidant and dc current. Many method available for synthesis of polyaniline .[9] They include oxidation process and Electrochemical process. But chemical oxidation method is more convenient for polymerization because its preparation method easily obtainable. So this reason polyaniline prepared in HCl medium at 0 to 10 °c by using ammonium persulphate .polyaniline composite wildly studies because their dielectric properties, dielectric, electric properties, with environmental friendly qualities polyaniline conduction properties increased 10 time than before adding compositie. [10-16]
.

EXPERIMENTAL

Materials

The A.R. grade aniline , hydrochloric acid, sulfuric acid, ammonium persulfate (APS) , were used, 1000 ml beaker, double distilled water, variable dc power supply were used.

METHOD OF SYNTHESIS

There are various method of preparation of polyaniline such as chemical polymerization, electrochemical polymerization method. But for composite, chemical polymerization is very useful, as compared to electrochemical and chemical polymerization both of them chemical polymerization yield is more obtained than electrochemical . All process carried out below 4°C.

PREPARATION OF POLYANILINE

Polyaniline with $CdSO_4$ was prepared by chemical oxidation method. Whole process were carried out at 4° C. 100 ml cooled solution of 0.2 M ammonium persulphate , 1M sulfuric acid,1M hydrochloric acid were used.During the preparation of polyaniline , Double distilled water were added with sulfuric acid. APS and $CdSO_4$ added with sulphuric acid water mix slowly. Stirred for 120 min. by using magnestic stirrer at below 4° C. After some time a dark green powder was obtained, after it filtered , washed with dilute solution of dilute sulfuric acid .

ELECTRICAL CONDUCTIVITY MEASUREMENT

The conductivity of polymer depend on number of parameter such as temperature, on electrical conductivity . electrical conductivity of semiconductor and metallic conductor is different. In metal when temp increased electrical conductivity decreased but while in semiconductor result increased in conductivity. Because conjugation of double single bond .Electrical conductivity of the prepared polymer were measured by resistively measurement technique.

DC conductivity

DC conductivity of polyaniline and polyaniline Composite were measured by resistively measurement technique. Polyaniline pellet was prepared by Perkin-Elmer hydraulic press using 10 ton pressure machine. And DC conductivity of composite measured by Milli ohm meter, Taiwan.

Observation table

D.C. electrical conductivity at different temp. for polyaniline

1) r=0.134 cm t=0.28cm A= 1.728 v=5 v constant

Temp in k	Current in A	Resistance	Specific resistively	conductivity
293	0.0441	113.05	725.93	0.0011
303	0.0517	95.89	642.12	0.0015
313	0.0598	87.35	563.84	0.0017
323	0.0680	74.22	478.77	0.0022
333	0.0742	68.40	436.41	0.0023
343	0.0784	62.90	401.98	0.0025
353	0.0850	58.13	372.25	0.0026
363	0.0875	56.98	365.56	0.0027
373	0.0932	53.11	339.44	0.0029
383	0.0991	50.32	322.98	0.0032

Table No. 1

D.C.Electrical conductivity at different temp for Polyaniline 10% $CdSO_4$ composite T = 0.37 cm

Temp in k	Current in A	Resistance	Specific resistively	conductivity
293	0.0530	94.566	446.32	0.00224
303	0.0535	92.978	435.88	0.00229
313	0.0543	90.741	427.96	0.00223
323	0.0565	88.859	411.32	0.00242
333	0.0573	85.659	406.55	0.00245
343	0.0604	83.065	409.31	0.00259
353	0.0620	80.358	385.21	0.00269
363	0.0685	79.321	377.96	0.00278
373	0.0755	75.958	330.12	0.00303
383	0.0732	69.475	318.24	0.00329

Table No. 2

D.C.Electrical conductivity at different temp for Polyaniline 10% CdSO4 composite T = 0.43 cm

Temp in k	Current in A	Resistance	Specific resistively	conductivity
293	0.0540	90.665	346.23	0.00286
303	0.0685	82.954	305.63	0.00336
313	0.0786	70.731	272.96	0.00370
323	0.0876	69.899	253.23	0.00412
333	0.0965	57.659	240.65	0.00465
343	0.1365	47.065	255.33	0.00569
353	0.1503	39.358	186.11	0.00732
363	0.1765	30.921	142.36	0.00896
373	0.1932	26.351	112.12	0.00936
383	0.2531	23.754	97.243	0.01237

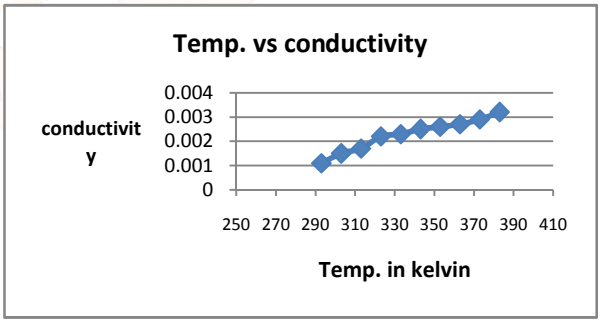
Table No 3

D.C. Electrical conductivity at different temp for Polyaniline 20% CdSO4 composite T = 0.400 cm

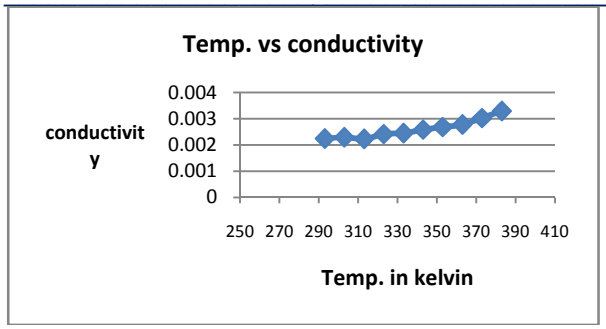
Temp in k	Current in A	Resistance	Specific resistively	conductivity
293	0.1935	29.358	115.357	0.0098
303	0.2047	24.985	108.27	0.0103
313	0.2358	21.655	91.257	0.0107
323	0.2547	17.352	82.784	0.0115
333	0.2936	14.325	76.214	0.0195
343	0.3268	11.414	68.324	0.0234
353	0.4182	10.255	55.32	0.0245
363	0.4465	9.354	42.92	0.0279
373	0.5768	7.368	39.75	0.0295
383	0.6864	6.964	31.81	0.0308

Table No 4

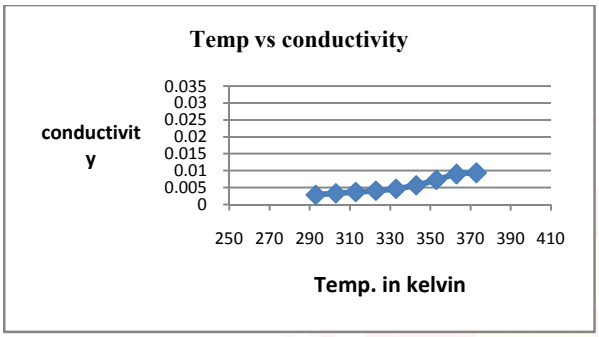
D.C. electrical conductivity at different temp. for polyaniline1) r=0.134 cm t=0.28cm A= 1.728 v=5 v constant



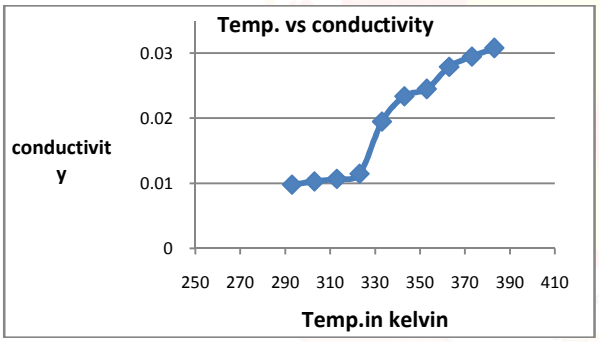
Graph 1



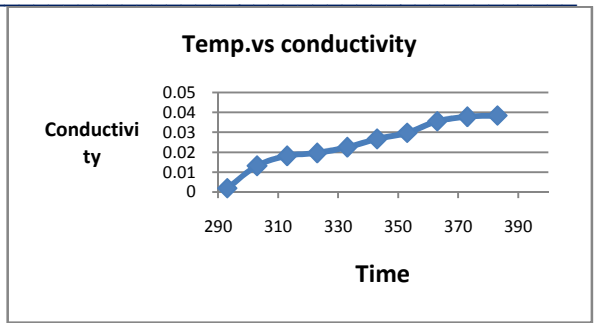
Graph2



Graph 3



Graph 4



D.C. Conductivity vs Temp. of PANI.

RESULT

Solubility

Polyaniline soluble in DMSO and insoluble in methanol , water , chloroform

The electrical conductivity of polyaniline is high than expected, since the polymerization reaction were carried out in highly acidic condition. The conductivity measurement is to observed the effect at CdSO4 on the overall conductivity behavior in these sample. The result behavior in these sample . The result obtained for the conductivity as a function of temperature as shown in graph polyaniline and compositie.

The conductivity of polyaniline at pure PANI obtained was 1.38×10^{-3} s/cm at n303 K while it increase to 2.26×10^{-3} s/cm in the sample of PANI containing 10% CdSO4 for 15% it increase to 2.73×10^{-3} s/cm 8.3×10^{-3} s/cm for 20 % CdSO4 composite.

CONCLUSION

From its interacting that the conductivity values of composites with PANI are significantly higher than PANI itself. The from D.C. conductivity of composites under study, it has been conducted that the room temperature conductivity and value of the activating Energy at all the composites show semi conducting nature.

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ASSESSMENT OF THE ANTIOXIDANT PROPERTIES OF *LAGENARIA SICERARIA* BAGASSE OBTAINED AS A CO-PRODUCT.

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ABSTRACT

The aim of this work was to determine the antioxidant activity of L. siceraria fruit juice extraction bagasses, which were obtained in two different ways viz., direct extraction that involved pulp and peel (WFB) and only from peels (PB). Four different test systems were used, namely the DPPH radical scavenging activity, the ferric reducing antioxidant power (FRAP); the ferrous ion-chelating ability (FIC) and the electrochemical analysis were employed in the determination of antioxidant activity.As regards antioxidant activity, at all concentrations and with all methods, the PB samples showed a higher antioxidant activity than WFB samples. The total phenol contents (TPC), the total flavonoid (TFC), the tannins contents (TC), the total carbohydrate contents (TCC)were also determined and PB presented higher total phenolic, flavonoid and tannins contents (9.85 mg gallic acid equivalent/g sample; 6.36 mg rutin equivalent/g sample and 5.47 mg catechin/g sample) than WFB. The results of this study indicate that L. sicerariabagasse obtained as co-product in the process to obtain juice may be considered a good source of natural compounds with significant antioxidant activity which could be suitable for applications in the pharmaceutical industry as potential remedyfor the treatment of aging disorders.

Keywords: *Lagenaria siceraria, antioxidant properties, bagasse, electrochemical analysis, voltammetry, radical scavenging activity*

INTRODUCTION

Cell damage caused by free radicals appears to be a major contributor to aging and to degenerative diseases of aging such as cancer, cardiovascular disease, cataracts, immune system decline, and brain dysfunction (Dursum et al., 2004; Sies et al., 1992). Free radicals have been implicated in the pathogenesis of at least 50 diseases (Langseth, 1993; Halliwell, 1994). Antioxidants are capable of stabilizing, or deactivating, free radicals before they attack cells (Halliwell B & Gutteridge JMC, 1989). Antioxidants are absolutely critical for maintaining optimal cellular and systemic health and well-being. Vitamin C, vitamin E, and beta carotene are among the most widely studied dietary antioxidants (Halvorsen et al., 2002). These antioxidants are believed to provide antioxidant protection to lipid-rich tissues and are also capable of neutralizing ROS in the aqueous phase before lipid peroxidation is initiated.

Many plant-derived substances, collectively termed phytonutrients are becoming increasingly known for their antioxidant activity (Lindsay & Astley, 2002). Flavonoids have been demonstrated to have anti-inflammatory, antiallergenic, anti-viral, anti-aging, and anti-carcinogenic activity (Kuhnau, 1976). The broad therapeutic effects of flavonoids can be largely attributed to their antioxidant properties. In addition to an antioxidant effect, flavonoid compounds may exert protection against heart disease through the inhibition of cyclooxygenase and lipoxygenase activities in platelets and macrophages (Havsteen, 1983; Middleton, 1984). The best way to ensure an adequate intake of phytonutrients is to eat a diet rich in a wide variety of fresh fruits and vegetables.

Fruit juices, beverages and hot drinks contain high amounts of antioxidants, like polyphenols, flavonoids,proanthocyanidins, stilbenes, coumarins, lignans, and lignins, vitamin C, vitamin E, Maillard reaction products, β-carotene, and lycopene (Halvorsen et al., 2006; Ramadan-Hassanien, 2008; Lindsay & Astley, 2002). The consumption of fruit juices, beverages and hot drinks was found to reduce the morbidity and mortality caused by degenerative diseases(Halvorsen et al., 2002). Many sources of antioxidants of a plant origin have beenstudied in recent years. Among these, *L. siceraria*fruit and its derivate products have been shown to be effective in retarding the process of lipid oxidation in both in vitro and in vivo studies. The antioxidant

activity of *L. siceraria*depends on the part of the fruit used, thus it has been (Deshpande et al., 2007; Erasto, 2009; Dixit et al., 2008), reported that the homogenates prepared from the epicarp of the fruit exhibited higher antioxidant activity than the level found in the whole fruit juice.It has been also reported that an acetone extract of *L. siceraria*peel had much higherantioxidant capacity than that of other parts of the fruits.

L.siceraria(Mol.) Standley (Family Cucurbitaceae) has been extensively used in traditional medicine for a wide range of ailments of the cardiovascular system, immunology, central nervous system, gastrointestinal tract, genitor urinary system, respiratory system, skin and infectious disorders. Recently there has been renewed interest in this plant because of its multimode cardioprotective activity (Upaganlawar & Balaram, 2011; Vijayakumar, 2010; Mali and Bodhankar, 2010). The modern phytochemical screening has revealed that fruits of the sweet variety contain carbohydrates (2.5%), flavonoids, triterpenoids, tannins, glycosides, proteins (0.2%), and fats (0.1%). The fruit is considered a good source of vitamin C, β-carotene, vitamin B-complex, pectin, and also contains the highest level of choline, a lipotropic factor (Prajapati, 2010; Chatterjee, 2009; Baranowska & Cisowaski, 1994; Deshpande et al., 2008; Gangwal et al., 2010; Chen et al., 2008). Generally, the edible parts of *L. siceraria*are used for the preparation of canned beverages, jelly especially, fresh juice which can be obtained from the whole fruit. Once the juice has been extracted, the wastes that remain are composed mainly of pulp and bagasses. Uses for these co-products are scarce and their disposal represents a problem. However, their composition means that they have the potential to be used for other ends, for example to obtain bioactive compounds or dietary fibre which could be used as ingredient in food processing.

Here, the antioxidant activity of *L. siceraria*fruit juice extraction bagasses was determined, which were obtained in two different ways viz., direct extraction that involved pulp and peel (WFB) and only from peels (PB) using 2, 2′-diphenyl-1-picrylhydrazyl (DPPH) radical scavenging activity, the ferric reducing antioxidant power (FRAP); and the ferrous ion-chelating ability (FIC) systems. The total phenol contents (TPC), the total flavonoid (TFC), the tannins contents (TC), the total carbohydrate contents (TCC) were also determined.

MATERIALS AND METHODS

2.1. Chemicals

Analytical reagent grade chemicals and ultrapure water (Millipore, United States) were used to prepare all solutions.2,2-diphenyl-1-picrylhydrazyl (DPPH), ferrozine, Folin–Ciocalteu reagent, gallic acid, iron (III) chloride, iron (II) chloride; trichloroacetic acid (TCA), aluminium chloride and Trolox were from Sigma-Aldrich (Germany). Dibasic potassium phosphate, 2-thiobarbituric acid (TBA), sodium nitrite (II), sodium hydroxide, chloride acid, sodium carbonate and dibasic sodium phosphate were from Merck (Darmstadt, Germany). Potassium hexacyanoferrate was from Fluka BioChemika (Germany). Catechin, rutin and vanillin were from Sigma- Aldrich (Germany). Britton–Robinson (BR) buffers were prepared using phosphoric, acetic and boric acids purchased from Sigma–Aldrich (India). Phosphate buffers were prepared using dibasic sodium phosphate, monobasic potassium phosphate and phosphoric acid purchased from Sigma–Aldrich (India). Sodium hydroxide and hydrochloric acid (Sigma Aldrich, Germany) were used for pH adjustment.

2.2. Plant material

The fruits of *L. siceraria*were collected from Super market,Nagpur, Nagpur District, Maharashtra, India. Further taxonomic identification was conducted at Department of Botany, Rashtrasant Tukdoji Maharaj Nagpur University, Nagpur, Maharashtra, India. A voucher specimen was deposited in the herbarium of our laboratory under the number (Sheet No: 9563).

2.3. Preparation of the extract

To obtain the *L. siceraria*juicepeel bagasse (PB)the *L. siceraria* fruits were peeledmanually and these peels were introduced in a blender Fabio Premia KMF75W6P (Kenstar, Aurangabad, India) to obtain *L. siceraria*juice and the bagasse separately. To obtain the *L. siceraria* juice whole fruit bagasse (WFB), the *L. siceraria*fruits were cut in half and squeezed in a Vitapress 0501N juicer (Kenstar, Aurangabad, India) to obtain *L. siceraria*juice and the bagasse. Both bagasses were triturated for 40 s in a vertical cutter to obtain uniformly sized pieces and so increase the contact time during washing. The mixture was stirred constantly and the water temperature was kept at 75 °C during the 10min that the washing process lasted. The whole co-product was pressed to drain liquid waste and was then lyophilized in Thermo electron corporation, Heto; power dry LL33000, Freeze Dryer overnight in a vacuum flask at 0.125 mbar and – 50ºC for 48 hours in a freeze-dryer. After freeze drying the

process products were packed and stored at – 40ºC until use. A grinder mill and sieves were used to obtain a powder particle size of less than 0.417 mm. The PB and WFB bagasses (1, 2, 5 and 10 g) were extracted with 100 mL of methanol, using an ultrasonic water bath (Selecta S.A. Barcelona, Spain) without temperature control during 2 h. Then, the mixtures were centrifuged at 12,000 rpm for 15 min at 4 °C. The supernatants were stored (4 °C) until antioxidant analysis.

2.4. Determination of total phenolic content

Total soluble phenolics were determined with Folin-Ciocalteu reagent according to the method using gallic acid as a standard phenolic compound (Slinkard and Singleton, 1977). About 10.0 g/L of bagasses solution introduced in a volumetric flask was diluted with 46 mLof distilled water. About 1.0 mL of Folin-Ciocalteu reagent was added and mixed thoroughly. Three minutes later 3.0 mL of 2% sodium carbonate was added and the mixture was allowed to stand for 3 h with intermittent shaking. The absorbance of the blue color that developed was measured at 760 nm. The concentration of total phenols was expressed as mg/g of dry extract (Kim et al., 2003). The concentration of total phenolic compounds in the bagasses was determined as µg of gallic acid equivalent using an equation obtained from the standard gallic acid graph. Each assay was carried out in triplicate.

2.5 Total flavonoid content

For the total flavonoid content (TFC), the method based on Blasa et al. (2005) with some modifications was used. 1 mL of a methanolic solution of *L. siceraria*PB or WFB(30 g/L) were mixed with 0.3 ml $NaNO_2$ (5%), and 0.3 mL $AlCl_3$ (10%) were added after 5 min. The PB&WFBsamples were mixed and after 6 min, were neutralised with 2 mL NaOH solution (1M). For all the samples the absorbance was read on a UV-Vis Shimadzu 1800 spectrophotometer (Shimadzu, Kyoto, Japan) at 510 nm and the quantification was carried out using a calibration curve. Different concentrations of rutin (8.5–170 µg/mL) were used for calibration, giving a linearity of 0.997 (R^2). The results were expressed in mg rutin equivalents (RE)/100 g of sample as mean of three replicates.

2.6 Tannin analysis

Quantitative estimation of tannins (TC) was carried out using the modified vanillin–HCl in methanol method described by Price, Vansoyoc, and Butler (1978). The method is based on the ability of condensed tannins to react with vanillin in the presence of mineral acid to produce a red color. *L. siceraria* fruit peel bagasse or *L. siceraria*whole fruit bagasses (1 g) were extracted with 20mL of 1% HCl in methanol for 20min at 30 °C in a water bath. The samples were centrifuged at 2000 rpm for 4 min. The supernatant (1.0 mL) was reacted with 5 mL vanillin solution (0.5% vanillin + 2% HCl in methanol) for 20min at 30 °C. Blanks were run with 4% HCl in methanol in place of vanillin reagent. Absorbance was read at 500 nm on a UV-Vis Shimadzu 1800 spectrophotometer (Shimadzu, Kyoto, Japan). A standard curve was prepared with catechin. Results were expressed in terms of catechin equivalents (CE). Samples were analyzed in triplicate.

2.7 Total carbohydrate content

Total carbohydrate content was determined by phenol-sulphuric acid method taking D-galactose as standard. One gram of *L. siceraria*PB or WFB was homogenized in 20mL of distilled water and shaken vigorously for 2 minutes and then left 1 hour in a ultrasonic water bath (Selecta S.A. Barcelona, Spain) without temperature control. Extracts were centrifuged at 15,000 rpm for 15min at 4°C. 2 mL of the supernatant were filtered and the absorbance was measured on UV-visible Spectrophotometer Shimadzu 1800 (Shimadzu, Kyoto, Japan) at 490 nm for total carbohydrates (Dubois et al., 1956; Brummer and Cui, 2005).

2.8 Antioxidant activity

2.8.1Determination of2, 2′-diphenyl-1-picrylhydrazyl (DPPH) radical scavenging activity

The antioxidant activity was measured in terms of DPPH free radical scavenging activity and is based on the determination of the concentration of 2, 2-diphenyl-1-picrylhydrazyl (DPPH) at a steady state in a methanol solution, after adding the mixture of antioxidants. UV-Vis Shimadzu 1800 spectrophotometer (Shimadzu, Kyoto, Japan)was used to estimate the antioxidant activity. The extract was prepared at 100 mg/L concentration. DPPH concentration was 50 mg/L. Methanol was used as blank sample and to dissolve DPPH and *to prepare stock solutions of PB and WFB*. Then, 3 mL of DPPH solution was mixed with 2 mL of *PB and WFB*(10, 20, 50 and 100 µg/mL)sample solution and shaken well (quickly). This is because the DPPH and antioxidant reaction begins instantaneously. Then, this solution is quickly moved into cuvette using a pipette. After that, the cuvette was put into the spectrometer and the absorbance was measured at 517 nm. The DPPH radical scavenging in terms of percentage is

calculated (Krishnaiah et al., 2011; Shimada et al., 1992).

$\% I = [(A_B – A_S) / A_S] \times 100$ (1)

Where, I is % DPPH inhibition; A_B is absorbance of control sample (t=0 h); and A_S is the absorbance of a tested sample at the end of the reaction (t =1 hour).

2.8.2 Ferric reducing antioxidant power

Ferric reducing antioxidant power (FRAP) of *L. siceraria*PB or WFB was determined through a method described by Benzie and Strain (1996) with slight modifications. Three reagents were initially prepared: 300 mM acetate buffer (pH 3.6), 10 mM 2,4,6-tripyridyl-*s*-triazine (TPTZ) in 40 mM hydrochloric acid (HCl) and 20 mM Ferric chloride ($FeCl_3$). FRAP reagent was prepared by mixing acetate buffer, TPTZ solution in 40 mM HCl and 20 mM $FeCl_3$ at a ratio of 10:1:1 (v/v/v), respectively. 1 mL of PB and WFB (10, 20, 50 and 100 µg/mL)was added with 2.5 mL of FRAP reagent prior to 30 minutes incubation at 37 °C. Subsequently, the absorbance was measured at 595 nm. The results were calculated, based on a calibration curve plotted using Ferrous sulphate ($FeSO_4$) (0 – 1 mM). The results were expressed as mMol Fe^{2+}/g dried extract.

2.8.3 Ferrous ion-chelating ability assay

The ferrous ion-chelating (FIC) assay was carried out according to the method of Singh and Rajini (2004) with some modifications. Solutions of 2 mM $FeCl_2 \cdot 4H_2O$ and 5 mM ferrozine were diluted 10 times. Briefly, a solution (1mL) of different concentrations of PB or WFB (10, 20, 50 and 100 µg/mL) was mixed with 1 mL $FeCl_2 \cdot 4\ H_2O$. After 5 min incubation, the reaction was initiated by the addition of ferrozine (1 mL). The mixture was shaken vigorously and after a further 10 min incubation period, the absorbance of the solution was measured spectrophotometrically at 562 nm. The inhibition percentage of ferrozine–Fe^{+2} complex formations was calculated by using the formula given below:

Chelating effect (%) = $[(1-A_S) / A_B] \times 100$ (2)

Where A_B the absorbance of control sample; (The control contains $FeCl_2 \cdot 4\ H_2O$ and ferrozine) and $A_S$is the absorbance of a tested sample.

To determine the concentration needed to obtained 50% chelating effect (EC_{50}), the percentage of the chelating effect was plotted against sample concentration. Each assay was carried out in triplicate.

2.9 Electrochemical analysis

2.9.1 Instrumentation

The Voltammetric experiments were performed with CH Instrument, USA (CELL STAND CS – 2, MODEL 680 Amp Booster). A conventional single compartment three- Electrode System consisting of a glassy carbon electrode (GCE) (3 mm diameter) as a working electrode, Ag/AgCl electrode (KCl 3 M) used as a reference electrode and a platinum wire as an auxiliary electrode was used. In order to provide a reproducible active surface and to improve the sensitivity and resolution of the voltammetric peaks, the glassy carbon electrode was polished to as the mirror finish with 0.3 µ alumina on smooth polishing cloth and then rinsed with acetone and Milli-Q water prior to each electrochemical measurement. Examinations of all the solutions were carried out at room temperature 25±2 °C. The pH measurements were made on a Schott Gerate pH meter CG 804 with an accuracy of ± 0.05. For analytical applications, the following parameters were employed: pulse amplitude 50 mV, pulse width 0.005 s; scan rate 0.05 V/s; sample interval 1 mV; &quiet time 2 s.

2.9.2.Analytical procedures

A phosphate buffer in the pH range of 3–12 was prepared using dibasic sodium phosphate, monobasic potassium phosphate and phosphoric acid. Sodium hydroxide and hydrochloric acid were used for pH adjustment. Ascorbic acid was used as a standard. Ascorbic acid was dissolved in 0.1 M phosphate buffer, pH 2.0 to obtain 5 mM stock solutions. This solution was diluted to obtain the ascorbic acid concentration ranging from 0.1-5 mM. The mixture was purged with nitrogen for 10 minutes before analysis. Voltammograms were recorded for standard ascorbic acid. The amount of ascorbic acid was determined by means of a calibration graph. To determine the antioxidant potential, the methanolic extracts of *L. siceraria*WFB&PB were filtered into the beaker of 10 mL; a portion of the filtrate was transferred into an electrochemical cell. The required amount of 0.1 M phosphate buffer, pH 2.0 was added as a supporting electrolyte. For the determination of ascorbic acid in the sample, the standard addition technique was used (Pournaghi & Ojani, 1997).

2.10. 2,6-dichlorophenolindophenol (DCPIP) method

Ascorbic acid content was quantitatively determined according to the modified 2,6-dichlorophenolindophenol (DCPIP) method described by Klein and Perry (1982). Each of bagasse samples (0.5 g) was extracted by 50 mL of 1% metaphosphoric acid (v/v) for 1 h. The extract

was centrifuged at 3000 rpm in a centrifuge (CR22E, Hitachi, Japan) at room temperature for 15 min. One mL of the supernatant was added 9 mL of 0.05 mM DIP and mixed for 15 sec, then measured at 515 nm versus the blank by an UV-Vis Shimadzu 1800 spectrophotometer (Shimadzu, Kyoto, Japan). The standard curve was obtained within the linear range of 0–500 µg ascorbic acid per mL.

2.10 Statistical analysis

Conventional statistical methods were used to calculate means and standard deviations of three simultaneous assays carried out with the different methods. Statistical analysis (ANOVA) was applied to the data to determine differences ($P<0.05$) for the antioxidant activity, ANOVAs with 2 factors (co-product and concentration) were applied for each parameter. The Statistical analyses were made using Sigma Stat 11.0 for Windows. To explore the effect of the AOX in WFB and PB samples, correlation coefficients of the total phenolics and flavonoids with AOX were also determined.

RESULTS AND DISCUSSION

3.1 Total Phenol content, total flavonoid contents and tannin contents

Phenolic compounds such as flavonoids, phenolics, and tannins possess diverse biological activities including anti-inflammatory, anti-carcinogenic, and antiatherosclerotic activities. These activities might be related to their antioxidant activity (Chung et al., 1998). The total phenolic content (TPC), total flavonoid contents (TFC) and tannin contents (TC) of the different methanolic solutions of *L. siceraria*bagasses are presented in Table 1. The PB showed a higher TPC and TFC ($p<0.05$) than WFB. The total phenol content in the extracts was assessed, and their potential contribution to lees surface antioxidant activity was assessed using DPPH, FIC and FRAP assays. The phenolic and flavonoid contents can be used as important indicators of antioxidant capacity which can be used as a preliminary screen for any product intended as a natural source of antioxidants. Phenolics are powerful antioxidants and act in a structure-dependent manner; they can scavenge reactive oxygen species (ROS), and chelate transition metals which play vital roles in the initiation of deleterious free radical reactions (Fresco et al., 2006). Obviously, total phenolic content could be regarded as an important indication of antioxidant properties of plant extracts (Liu et al., 2008) depend on the cultivar, growing region, climate, maturity, cultivation practice, storage conditions (Poyrazoglu, Gokmen, and Artik, 2002) and method used to obtain the juice. The importance of the antioxidant constituents of plant material in the maintenance of health and protection from coronary heart disease and cancer is also raising interest among scientists, food manufacturers, and consumers. There is increasing evidence that consumption of a variety of phenolic compounds present in natural foods may lower the risk of serious health disorders because of the antioxidant activity of these compounds (Surh, 2002). The total condensed tannins presents in the different methanolic solutions of bagasses are presented in Table 1. WFB showed a higher TC ($p<0.05$) than PB. This may be due to the method used to obtain the juice. The group of hydrolysable tannins is found in the peel (husk, rind or pericarp), membranes and piths of the fruit (Deshpande et al., 2007).

Table 1: Total phenol (TPC) total flavonoid (TFC) and tannins contents (TC) PB and WFB (Mean ± SEM).

Sample	TPC (mg GAE/g sample)	TFC (mg RE/g sample)	TC (mg CE/g sample)
WFB	6.32 ± 0.47	5.41 ± 0.68	4.83 ± 0.73
PB	9.85 ± 1.12	6.36 ± 0.21	5.47 ± 0.43

GAE: gallic acid equivalent, RE: Rutin equivalent, CE: Catechin Equivalent; Values are mean of three replicate determinations ($n = 3$) ± standard error of mean

3.2 The carbohydrate content

The first step of carbohydrates characterization is determination of its purity, which is reflected by its chemical composition, including total sugar content, proteins, ash, and moisture (Brummer and Cui, 2005). The total carbohydrate contents of the WFB and PB were found to be 8.67 ± 5.78% and 10.27 ± 2.0% respectively. The high carbohydrate content of the bagasse indicates its purity.The sugar content present in WFB and PB meant that these co-products showed they would be a source of carbon for the microbiota present in such kind of product.

3.3 Antioxidant activity

Evaluation of AOX is becoming increasingly relevant in the field of nutrition as it provides useful information with regard to health promoting and functional quality of raw material without the analysis of each antioxidant compound (Scalfi et al., 2000). In this study we have used three*in vitro*

assays, namely free radical scavenging assay using DPPH, ferric reducing antioxidant power (FRAP), ferrous ion-chelating ability (FIC) assay. The assays were used because they are quick and simple to perform, and reaction is reproducible and linearly related to the molar concentration of the antioxidant(s) present. Moreover they require a spectrophotometer unlike sophisticated equipment in the case of ORAC assay (Awika et al., 2003). There are substantial differences in sample preparation techniques, antioxidants extraction methods (solvent, temperature, etc.), the selection of end-points and the expression of results even within the same method, so that comparison between the values reported by different laboratories can be quite difficult (Perez-jimenez et al., 2008). The PB samples showed ahigher ($p<0.05$) ability to inhibit DPPH radical than the WFB samples (Table 2). Amoderate increase in radical scavenging activity was observed when the concentration of both PB and WFB was increased. Ascorbic acid showed thehighest ($p<0.05$) radical activity at all concentrations (Fig. 1). The DPPH scavenging data suggests that the extract is capable of scavenging free radicals, thus preventing the initiation and propagation of free-radical-mediated chain reactions.

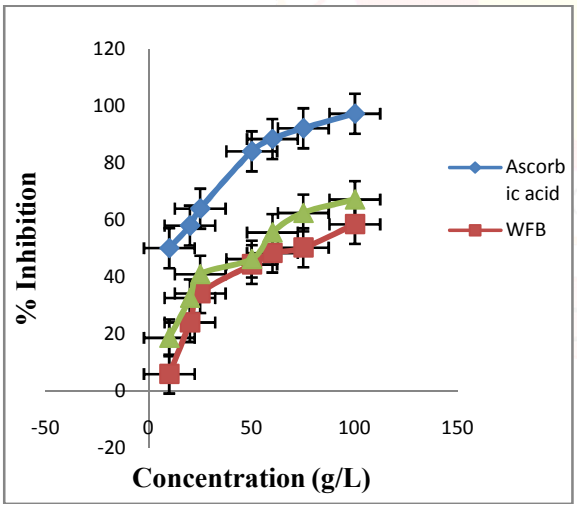


Fig. 1: DPPH radical scavenging effect of polyphenolic extract of *Lagenaria siceraria.* Values are expressed as mean ± SEM. Values are mean of three experiments.

Table 2: Antioxidant activity of at different concentrations (A=10 µg/mL, B=20 µg/mL, C=50 µg/mL,D=100 µg/mL), measured by the DPPH method.

Sample	% DPPH Inhibition				
	A	B	C	D	IC_{50}
PB	18.63 ± 0.68	28.65 ± 0.42	43.31 ± 0.52	65.23 ± 0.75	60
WFB	5.88 ± 0.55	18.01 ± 0.77	39.41 ± 1.01	57.52 ± 0.26	75
Ascorbic acid	50.16 ± 0.78	58.09 ± 0.78	84.19 ± 0.56	97.42 ± 0.64	0.2

Values are mean of three replicate determinations (n = 3) ± standard error of mean

Analysis of the ferrous ion-chelating properties showed that all the PB and WFB concentrations studied were capable of chelating iron (II) and did so in a concentration-dependent manner. PB samples showed a higher ($p<0.05$) ion-chelating capacity than the WFB samples. Both samples presented lower ion-chelating activity than standard ascorbic acid (Table 3).Metal chelating capacity was significant since they reduced the concentration of the catalysing transition metal in lipid peroxidation.

Table 3: Antioxidant activity of at different concentrations (A=10 µg/mL, B=20 µg/mL, C=50 µg/mL,D=100 µg/mL), measured by the FIC method.

Sample	% chelating effect				
	A	B	C	D	EC_{50}
PB	12.11 ± 0.67	18.24 ± 0.48	23.36 ± 0.25	30.12 ± 0.74	45.26
WFB	4.21 ± 0.22	9.32 ± 0.08	19.32 ± 0.83	25.32 ± 0.28	28.83
Ascorbic acid	28.31 ± 0.23	33.45 ± 0.86	39.56 ± 0.37	48.72 ± 0.86	84.36

Values are mean of three replicate determinations (n = 3) ± standard error of mean

According to the on FRAP values; a concentration-dependent reducing capacity was found for all concentrations of PB and WFB samples. The PB samples showed (Table 4) a higher ($p<0.05$) ferric reducing antioxidant capacity than the WFB samples and standard ascorbic acid.The reducing capacity of a compound may serve as a significant indicator of its potential antioxidant activity.

Table 4: Antioxidant activity of at different concentrations (A=10 µg/mL, B=20 µg/mL, C=50 µg/mL, D=100 µg/mL), measured by the FRAP method.

Sample	FRAP (TEAC)			
	A	B	C	D
PB	0.594 ± 0.74	0.644 ± 0.73	0.702 ± 0.42	0.752 ± 0.21
WFB	0.628 ± 0.36	0.657 ± 0.32	0.744 ± 0.22	0.781 ± 0.19
Ascorbic acid	0.376 ± 0.28	0.352 b± 0.11	0.521 ± 0.27	0.586 ± 0.23

Values are mean of three replicate determinations (n = 3) ± standard error of mean.

There was a positive correlation (Table 5)R^2=0.982 in DPPH and R^2=0.948 in FRAP, exceptR^2=0.352 in FIC between total phenolics content and AOX then with flavonoids and ascorbic acid. In all methods used for the determination of antioxidant activity, PB samples showed higher antioxidant activity than WFB samples. This may be explaining because PB samples presented in its composition greater concentration of phenols, flavonoids and tannins than WFBB samples. The phenolic, flavonoid and tannins contents in juices and bagasses are strongly dependent on the processing steps to obtain the juice.

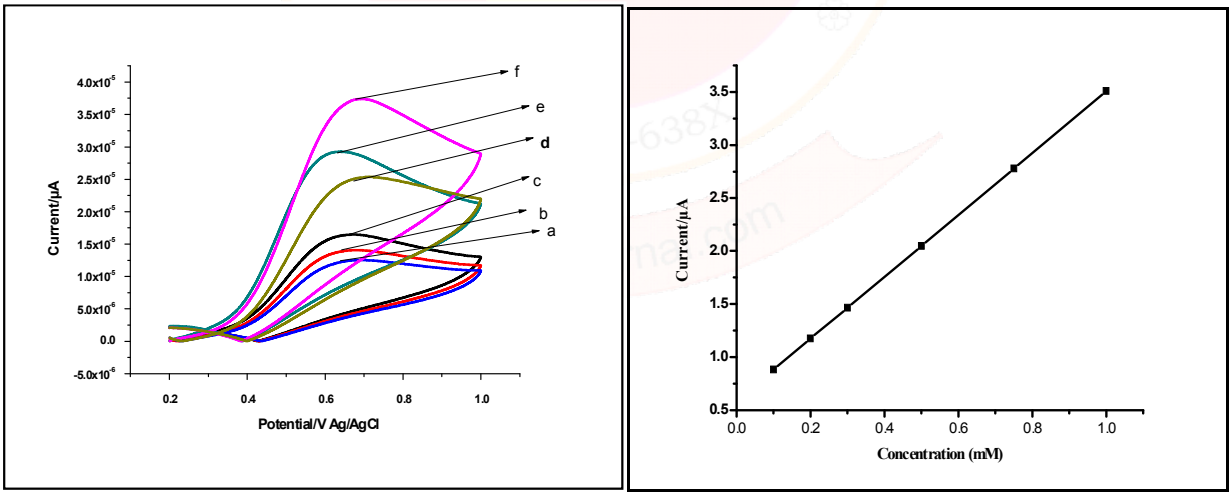
Table 5: correlation coefficients of the contents of total flavonoids and total phenols with the DPPH, FRAP, FIC

Test	T_r = 20 µg/mL		T_r = 50 µg/mL	
	Ascorbic acid	Total flavonoid	Ascorbic acid	Total flavonoid
DPPH	0.982*	0.941*	0.984*	0.532
FRAP	0.943**	0.054	- 0.441	0.948**
FIC	0.352	0.997***	- 0.627	0.724

***, ** and * indicate correlation is significant at the 0.01, 0.05 and 0.1 levels, respectively (2-tailed).

3.4 Electrochemical method

For optimizing the conditions of the experiment, a calibration curve of ascorbic acid was constructed over the concentration range of 0.1 to 5 mM. The relationship between anodic peak current ($I_{p,a}$) and concentration of the ascorbic acid was found to be linear (Fig. 2) with a coefficient of the correlation (R^2) 0.997. The relation of a peak current with ascorbic acid concentration is represented by a straight-line equation $I_{p,a}$ (µA) = 2.92807 + 0.5892. Statistical evaluation of the data was performed through determination of standard error of residuals 0.0131, standard error of intercept 0.0422, and standard error of the slope = 0.07398, and standard error of y is 0.0572. The limit of detection (LD) (0.6 µM) and limit of quantification (LQ) (1.95 µM) were calculated using the equation LD = 3(sd/s), and LQ = 10(sd/s) respectively, where sd is the standard deviation of blank and s is the slope of the calibration curve. The concentration of ascorbic acid was kept fixed, the $I_{p,a}$ was linearly dependent upon the scan rate for a range from 10 – 500 mV/s. Using the slope of this regression and the Randles-Sevick equation, the diffusion coefficient of ascorbic acid was calculated and found to be 2.43 x 10^{-6} cm/s. Over a range of 0.1 mM to 5 mM, ascorbic acid produced a single concentration-dependent peak anodic current ($I_{p,a}$). There was no reversible cathodic peak current.



(a) (b)

Fig. 2: (a) Cyclic voltammograms of different Ascorbic acid concentrations at a) 0.1, b) 0.2, c) 0.3, d) 0.5, e) 1.0, f) 2.0 M respectively, at a glassy carbon electrode in 0.1 M Phosphate buffer, pH 2.0, Scan rate, 0.05 V/s, pulse amplitude 50 mV, pulse width 0.005 s, sample interval 1 mV; quiet time 2 s. (b) Linear plot between current ($I_{p,a}$) and concentration of ascorbic acid.

The developed electroanalytical methodology was applied to the determination of ascorbic acid in *L. siceraria*fruit bagasse. For the analysis procedure, a filtered 0.2 ml aliquot of methanolic extract of WFB & PB were transferred to an electrochemical cell and diluted in 10 ml of pH 2.0 phosphate buffer. The standard addition method was used for quantification and the ascorbic acid content of the

methanolic extract of *L. siceraria*fruit bagasse was determined. The content of ascorbic acid present in WFB and PB was found to be 18.14 ± 0.4 mg/100 cm^3 and 31.7 ± 2.8 mg/100 cm^3 respectively. Degree of recovery was determined in percentages as 97.86% and 100.81% respectively for WFB and PB. Ascorbic acid content in the WFB and PB determined with DCPIP method were found to be 17.58 ± 0.35 mg/100 cm^3 and 30.42 ± 0.58 mg/100 cm^3, respectively. The results of statistical calculation indicate a good precision and good agreement between the repeatability of the voltammetric method and the DCPIP method.

CONCLUSION

In conclusion, the results obtained in the present study has shown that the methanolic extract of *L. siceraria*whole fruit bagasse and *L. siceraria*peel bagasse contain a number of antioxidant compounds which can effectively scavenge reactive free radical species including free oxygen as well as other free radicals under in vitro conditions. Moreover the hydrogen donating ability of all the experimental compounds and the extract has been proven through the assessment of ferric reducing antioxidant power, ferrous ion-chelating ability and DPPH scavenging activity which can be attributed to the high percentages of the main constituents among their different components, especially phenolic acids, flavonoids and tannins. The present electrochemical method has a high degree of specification for determination of ascorbic acid in *L. siceraria*fruit juice bagasse. The results of this study show that the methanolic extract of *L. siceraria*whole fruit bagasse and peel bagasse can be used as an easily accessible source of natural antioxidants or in pharmaceutical industry or in cosmetic industry. It can also be used in stabilizing food against oxidative deterioration.

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STABILITY CONSTANTS OF LANTHANIDES METAL COMPLEXES WITH SUBSTITUTED PYRAZOLES IN DIFFERENT SOLVENTS MEDIUM.

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ABSTRACT

The reaction of Pr (III) and Nd (III) metal ions with L_1 : 3 (2'- chlorophenyl) - 4- benzoyl - 5 (2-hydroxy phenyl) pyrazole, L_2: 3 (2'-chlorophenyl) - 4- pyridoyl -5 (2-hydroxy phenyl) pyrazole , L_3: 3 (2'-aminophenyl)- 4-pyridoyl - 5 (2- hydroxyl phenyl) pyrazole and L_4: 3 (4'-chlorophenyl) -4-Benzoyl -5(2-hydroxy-phyenyl) pyrazole, at 0.1M ionic strength at 28 ± 0.1^{0}C in 70% ethanol -water mixture and 70% dioxane-water mixture have been studied pH-metrically. The data obtained were used to estimate the values of proton-ligand (pK) and metal-ligand (logK) stability constants in different solvents mixture. It is observed that the pK and logK values in 70% dioxane-water mixture are grater than in 70% ethanol - water mixture. Pr (III) and Nd (III) metal ions formed 1:1 and 1:2 complexes with all the ligands in both solvent medium.

Key words *– Substituted pyrazole, solvent effect, stability constants, chelates.*

INTRODUCTION

Pyrazoles are fall in the class of aromatic heterocyclic compounds, and unique structural feature involving pyrazolic nitrogen and make them interesting ligands. Pyrazoles are the good complexing agent [1-3]. The formation constants of transition metal ion complexes with some substituted pyrazoles and pyrazolines have been reported [4]. The influence of ionic strength on the stability constants of transition and lanthanide metal ions complexes with substituted pyrazoles were also reported [5]. Sawalkahe et al [6] have studied the interaction on metal ions with 1,3 diketones, pyrazoles and pyrazoline spectrophotometrcally. Lanthanide (III) metal complexes with nitrogen donor ligands including Schiff bases were reported [7]. The interactions of some lanthanide metal ions with substituted isoxazolines at 0.1M ionic strength have been reported pH metrically [8-11].

Recently ultrasound promoted synthesis of substituted pyrazoles and isoxazoles were studied [12]. The effect of various mixed aqueous solvents on the stability constants of Cu (II) chelates with pperidine-2- carboxylic acid have been studied [13].

The study of proton-ligand stability constants and metal-ligand stability constants of Pr (III) and Nd(III) complexes with some substituted pyrazoles at different solvent medium have been focus due to their wide range application in various field of human interest. In present research work we have undertaken the study of chelating properties of some substituted pyrazoles (mentioned above) with lanthanide metals like Pr(III), Nd(III) under suitable condition, in 70% ethanol-water mixture and 70% dioxane-water mixture pH metrically.

EXPERIMENTAL

Substituted pyrazoles were synthesized in our laboratory by standard method [14]. The substituted pyrazoles are insoluble in water; hence 70% ethanol-water (v/v) and 70% dioxane-water (v/v) mixture was used as solvent. Lanthanide metal nitrates were dissolved in double distilled water and their concentration estimated by standard method [15]. The chemical used in this work where reagent grade including, Sodium hydroxide (Merck, 99.99%), potassium nitrate (Merck, 99.99%) and nitric acid (Merck, 99.98%), were used. Ethanol and dioxane was purified by standard method [16]. pH measurement were carried out with ELICO pH meter (accuracy ± 0.05 units) using combined electrode at 28 ± 0.1^{0}C.

Calvin Bjerrum Titration Technique

The titrations were carried out in an inert atmosphere of nitrogen. The ionic strength of solution was maintained constant by adding an appropriate amount of 1M potassium nitrate solution. The values were recorded by pH meter. These values converted to [H^+] values by applying the correction proposed by Van Uitert and Hass [17]. The contribution of the other ions in addition to K^+ and NO^-_3 also taken into consideration. The

overall 0.1 ionic strength of solution was calculated by expression

$$\mu = \tfrac{1}{2} \sum_{i=1} C_i Z_i^2 \quad \text{---------- (1)}$$

RESULTS AND DISCUSSION

The titration data were used to construct the curve between volumes of *NaOH Vs pH*. They are called as acid titration curve, ligand titration curve and metal titration curve. The pK values of ligand and logK values of Pr (III) and Nd (III) complexes at various ionic strength were calculated by Irving and Rossotti's method [18]. ***(Figure-1and 2)***

i) Proton – ligand stability constants (pK)

Substituted pyrazoles may be considered as monobasic acids having one replaceable H^+ ion from phenolic OH^- group and can therefore be represented as HL

$$HL \rightleftharpoons H^+ + L^-$$

The titrations data in 70% ethanol-water mixture were used to construct the curve between volumes of *NaOH Vs pH*. It is observed from the titration curve that the ligand curves start deviating from free acids curve at about pH – 3.50 for L_1, at about pH 2.80 for L_2 , at about pH 3.45 for L_3 and at about pH 2.88 for L_4. The deviation increased continuously up to pH 12.50. It indicated that OH^- group start to dissociated at about 2.80 and complete its dissociation at about pH 12.50. ***(Table-1)***

The titrations data in 70% dioxane-water mixture were used to construct the curve between volumes of *NaOH Vs pH*. It is observed from the titration curve that the ligand curves start deviating from free acids curve at about pH – 3.55 for L_1, at about pH 2.90 for L_2, at about pH 3.40 for L_3 and at about pH 2.96 for L_4. The deviation increased continuously up to pH 12.56. It indicated that OH^- group start to dissociated at about 2.90 and complete its dissociation at about pH 12.56. ***(Table-2)***

The average number of proton associated with the ligand ($\bar{n}_A$) was determined from ligand titration curves employing the Irving and Rossotti expression [18].

$$\bar{n}_A = \frac{2T_L^0 - \{(V_2 - V_1)(N + E^0)/(V^0 + V_1)\}}{T_L^0} \quad \text{---- (2)}$$

Where,

V^0- is the initial volume of the solution,

E^0 and T^0_L - are initial concentrations of acid and ligand respectively,

V_1 and V_2 -are the volumes of alkali of normality, N -during the acid and ligand titration at given pH and

γ -is the replaceable proton from the ligand.

The pK values were estimated from formation curves ($\bar{n}_A$ *Vs* pH) by noting the pH, at which $\bar{n}_A = 0.5$. The accurate values of pK were estimated by pointwise calculations. The pK values of ligands increases in the following order in both the solvents. ***(Table -1 and 2)***

Ligand- 3 > Ligand-2 > Ligand-1 > Ligand- 4

It could be seen from the values, the more reduction in pK values of ligand L_4 may be due to presence of chlorophenyl and benzoyl groups which act as stronger electron withdrawing groups.

ii) Metal – ligand stability constants (logK) :

Metal ligand stability constants of Pr (III) and Nd (III) complexes with some substituted pyrazoles were determined by employing Calvin-Bjerrum pH-metric titration technique [19-20] as adopted by Irving and Rossotti.

- *The formation of chelates between Pr(III) and Nd(III) with substituted pyrazoles in 70% ethanol-water mixture was indicated by,*

1) The significant departure starting from pH 2.95 for Pr (III) complex systems,
2) The significant departure starting from pH 2.90 for Nd (III) complex systems,
3) The change in colour from, colourless to yellow and then dark yellow as pH increased from 3.50 to 12.50. ***(Figure-1)***

- *The formation of chelates between Pr(III) and Nd (III) with substituted pyrazoles in 70% dioxane-water mixture was indicated by,*

1) The significant departure starting from pH 2.99 for Pr(III) complex system,
2) The significant departure starting from pH 2.92 for Nd(III) complex system,
3) The change in colour from, colorless to yellow and then dark yellow as pH increased from 2.99 to 12.55 ***(Figure-2).***

The logK values were directly read from the formation curves ($\bar{n}$ *Vs PL*) using half integral method. $\bar{n}$ can be calculated by using following expression

$$\bar{n} = \frac{(V_3 - V_2) - \{N + E^0 + T_L^0(\gamma - \bar{n}_A)\}}{(V^0 + V_2)\bar{n}_A T_M^0} \quad \text{------ (3)}$$

Where N, E^0 and T_L^0 have same significance as per the ligand titrations and V_3 represents the volume of alkali required to obtain the same pH as the

ligand and acid titration. The logK values were directly read from the formation curves ($\bar{n}$ *Vs PL*) using half integral method. The most accurate logK values were calculated by pointwise calculation method, for all the systems and in 70% ethanol-water mixture and 70% dioxane-water mixture ***(Table -3 and 4***). The $logK_1$ and $logK_2$ values follow the order as

Pr (III) < Nd (III)

It could be seen that logK values follow increasing trend. This is due to the electron withdrawing group. The values of logK, ($logK_1 - logK_2$), and ($logK_1 / logK_2$) are in good agreement with excepted values. It is observed that the similar difference may be due to" *trans structure*".

The results show that, the ratio $logK_1 / logK_2$ is positive in all cases. This implies that there is little or no steric hindrance to the additions of secondary ligand molecule. The different values of pK and logK in various solvents are due to the solubility of restrictions. The pK values of all the ligands and logK values of Pr(III) and Nd (III) metal ions chelates with L_1 : 3 (2'- chlorophenyl) - 4-benzoyl - 5 (2-hydroxy phenyl) pyrazole, L_2: 3 (2'-chlorophencyl) - 4- pyridoyl -5 (2-hydroxy phenyl) pyrazole , L_3: 3 (2'-aminophenyl)- 4-pyridoyl - 5 (2- hydroxyl phenyl) pyrazole and L_4: 3 (4'-chlorophenyl) - 4- Benzoyl - 5 (2-hydroxy-phyenyl) pyrazole, at 0.1M ionic strength at 28 ± 0.1^0C is grater in 70% dioxane-water mixture than 70% ethanol-water mixture, this is due to the .change in dielectric constants of water in the presence of organic solvent, change in structure and hydrogen bonding in water, relative solvent basicity and proton solvation by organic solvent.

iii) Validity of logK = a pK + b

The linear relationship logK = a pK + b has been found [21], to hold good for transition metal complex of series of closely related ligands. The stability of the metal complexes of substituted pyrazoles follows the order Pr (III) < Nd (III). The plot of $logK_1$ *Vs* pK and $logK_2$ *Vs* pK show satisfactory linear relationship giving slope values of 1.00 and 1.05 respectively. The partial molar free energies of metal ligand and proton ligand complexes exactly compensate with each other. When logK *Vs* pK plot is linear with a slope of unity. Pr (III) and Nd (III) metal ions formed 1:1 and 1:2 complexes with all the ligands. ***(Table-3)***

Table-1 : Determination of proton ligand stability constants (pK) of ligands at 0.1M ionic strength in 70% Ethanol-water mixture .

Ligand	pH of deviation	Proton ligand stability constants (pK)	
		Half integral method	Pointwise method
L_1	3.55	8.40	8.45 ± 0.03
L_2	2.90	10.50	10.20 ± 0.05
L_3	3.40	10.54	10.68 ± 0.03
L_4	2.95	7.00	7.18 ± 0. 04

Table-2: Determination of proton ligand stability constants (pK) of ligands at 0.1M ionic strength in 70% Dioxane-water mixture.

Ligand	pH of deviation	Proton ligand stability constants (pK)	
		Half integral method	Point wise method
L_1	3.50	8.90	8.95 ± 0.03
L_2	2.80	10.85	10.80 ± 0.05
L_3	3.45	10.97	10.95 ± 0.03
L_4	2.88	8.32	8.44 ± 0. 04

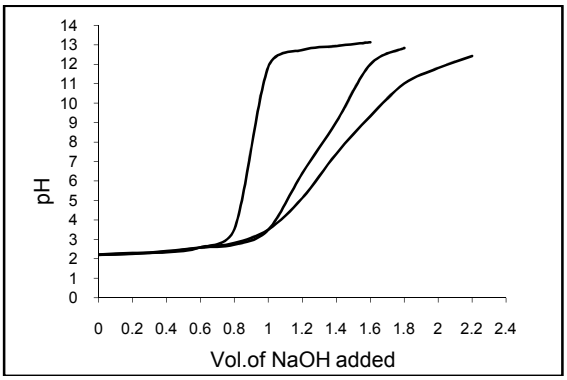
Table-3: Metal ligand stability constants of Pr (III) Nd (III) complexes with ligands at 0.1M ionic strength in 70% ethanol-water mixture

System	M-L stability Constants		$logK_1 - logK_2$	$logK_1 / logK_2$
	$logK_1$	$logK_2$		
Pr(III)-L_1	5.94	0.253	5.68	2.34
-L_2	9.85	2.96	6.89	3.33
-L_3	7.74	2.45	5.29	3.16
-L_4	6.70	2.75	3.95	2.43
Nd(III)-L_1	5.97	0.346	5.62	1.72
-L_2	9.96	6.16	3.80	1.62
-L_3	8.24	4.85	3.39	1.70
-L_4	6.74	2.92	3.82	2.31

Table-4 : Metal ligand stability constants of Pr (III) Nd(III) complexes with ligands at 0.1M ionic strength 70% Dioxane-water mixture

System	M-L stability Constants		$logK_1 - ogK_2$	$logK_1 / logK_2$
	$logK_1$	$logK_2$		
Pr(III)-L_1	6.00	2.54	3.46	2.36
-L_2	9.97	3.00	6.97	3.32
-L_3	8.82	2.64	6.18	3.34
-L_4	6.87	2.83	4.04	2.42
Nd(III)-L_1	6.01	2.79	3.22	2.15
-L_2	10.00	6.27	3.73	1.59
-L_3	8.84	4.92	3.52	1.71
-L_4	7.03	2.86	4.17	2.46

Figure-1 : a) Formation of chelates between Pr (III) with substituted pyrazoles in 70% ethanol-water mixture



b) : Formation of chelates between Nd (III) with substituted pyrazoles in 70% ethanol-water mixture

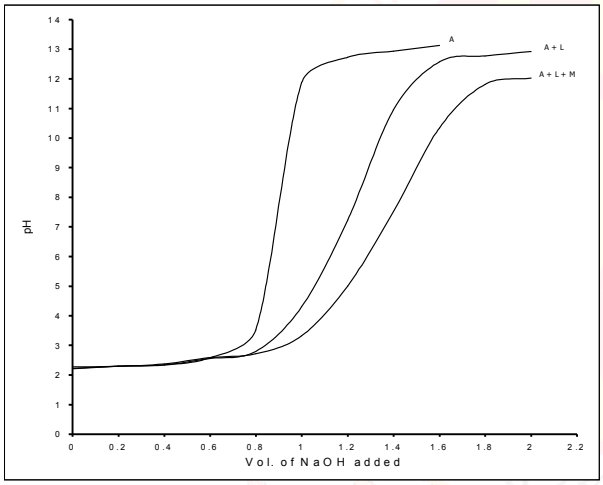
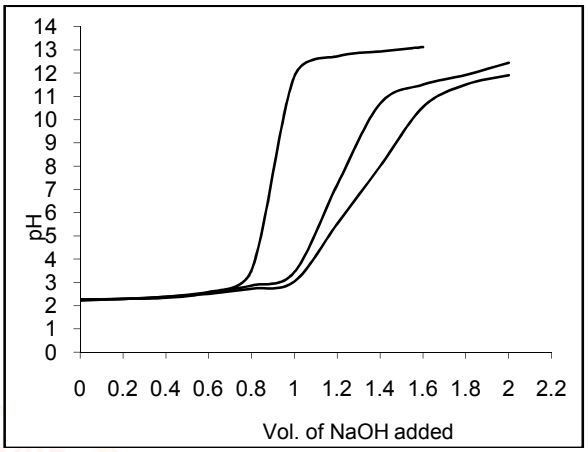
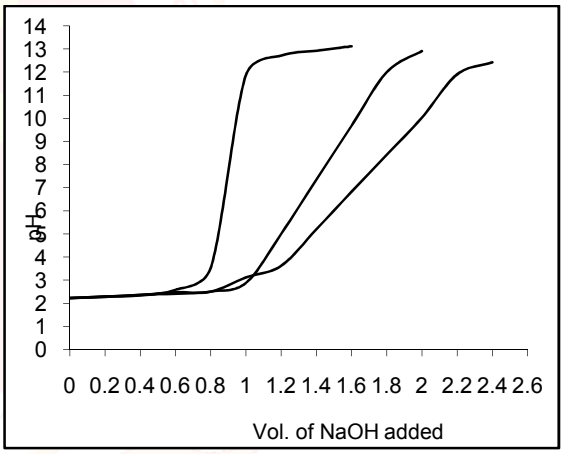


Figure-2 : a) Formation of chelates between Pr (III) with substituted pyrazoles 70% Dioxane- water mixture



b) Formation of chelates between Nd (III) with substituted pyrazoles in 70% Dioxane-water mixture



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SYNTHESIS AND ANTIMICROBIAL SCREENING OF NOVELPYRIMIDINO β-LACTAM

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ABSTRACT

A series of new Novel Pyrimidino β-Lactam compounds such as 5-(4-phenyl,2-azetidinone)-4-(substituted phenyl)-6-methyl-3,4-dihydropyrimidin-2(1H)-ones have been synthesized by a three component (MCR) reaction involving 5-((benzylidene amino)methyl)-4-(substituted phenyl)-6-methyl-3,4-dihydeopyrimidin-2(1H)-ones , haloacetyl chloride, DMF and triethyl amine. The newly synthesized compounds were well characterized by IR, ^{1}H NMR and mass spectral studies. The newly synthesized compounds were also screened for their antibacterial and antifungal activities and have exhibited moderate to excellent growth inhibition of bacteria and fungi. The result of such studies have been discussed in this paper.

KEYWORDS : *β-Lactam, Haloacetyl chloride, DMF, Triethyl amine, antibacterial activity, antifungal activity.*

INTRODUCTION

The four-membered cyclic amides commonly known as β-lactams or 2-azetidinones occupy a prominent place in the realm of organic and medicinal chemistry since the structure elucidation of penicillin showed the presence of β-lactam ring in it and the antibacterial activity of penicillin was attributed to the presence of β-lactam ring. Over the last two decades there has been rapid progress in synthetic organic chemistry associated with the search for new organic compound derivatives with desirable properties. Such compounds are widely used in the pharmaceutical industry[1].

Cycloaddition of monochloroacetyl chloride with imines (Schiff base) result in the formation of β-lactam. The reaction involves direct acylation of imine with monochloroacetylchloride. The reaction is carried out with base as triethylamine gives β-lactam[2].

These studies lead to development of several novel methodologies for construction of the β-lactam ring and discovery of several β-lactam antibiotics such as monobactams, cephalosporins, carbapenams, triems etc[3]. β-lactam antibiotics, since their introduction continue to be chemotherapeutics of incomparable effectiveness, conjugating a broad sprectrum of activity with low toxicity[4]. Several natural and synthetic β-lactam compounds are of clinical importance because of their high antibiotic activity. In addition to their well-recognised antibiotics activity, β-lactam[2] have been shown other biological activities as as potential antifungal[5], antitumor[6], anti-inflammatory[7], antiviral[8], anticonvulsant[9], anticancer[10], analgesic[11], cholesterol absorption[12], thrombin inhibitors[13] and inhibitors of human tryptase[14].The β-lactam antibiotics are still the most prescribed antibiotics used in the medicine. They are considered as an important contribution of science to humanity[15-16]. Moreover they have been studied extensively because of their ready accessibility, diverse chemical reactivity and broad spectrum of biological activity[17]. It process pharmacological activities such as antiviral[18], antihyperlidemic[19], antidepressant[20], anti-parkinsonian[21], tubercular[22] and antithrombotic[23].

The antibacterial and the antifungal agents having the property of inhibiting bacterial or fungal multiplication are called as bacteriostatic or fungistatic. Multiplication resumes upon removal of the agent. The antibacterial or the antifungal agents having the property of killing bacteria and fungi are called as bacteriocidalor fungicidal respectively. Antimicrobial assay can be carried out by different technique [24].On the basis of the action and purpose for which the antimicrobial agents are employed subdivision into different groups are possible. Subdivision can be based upon the group of microorganisms affected like antibacterial, antifungal, antiviral and antineoplastic chemotherapeutic agents, all more or less specific for treatments of disease caused by specific pathogenic agents [25-26].

RESULT AND DISCUSSION

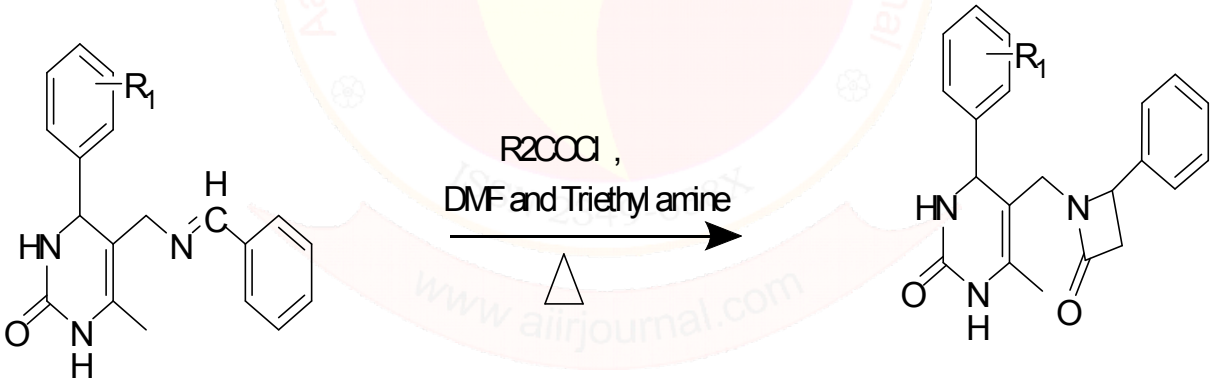
In the present work, the well stirred mixture of 5-((benzylidene amino) methyl)- 4- (substituted phenyl), 6-methyl, 3,4-dihydropyrimidin-2(1H)-ones (1a-1j) (0.01 mol) and haloacetyl chloride (0.01 mol) were taken in round bottom flask with 10 ml DMF and triethyl amine (0.01 mol), then the reaction was subjected to reflux for several hours to give 5-(4-phenyl,2-azetidinone)-4-(substituted phenyl), 6-methyl, 3,4-dihydropyrimidin-2(1H)-one (2a-2j).After refluxed, the product obtained cooled at room temperature and was poured over ice water. The solid separated out was filtered, washed with water and subsequently dried it. The solid product was recrystallized from ethanol to afford 5-(4-phenyl,2-azetidinone)-4-(substituted phenyl), 6-methyl, 3,4-dihydropyrimidin-2(1H)-one (2a-2j). And these results are summarized in Table 1.1. And the study of antimicrobial activity of some newly synthesized compounds in the given series of reation and tested different organism i.e. bacteria as *Escherichia Coli, Staphylococcus aureus* and *Salmonella typhi* and Fungi as *A. nigar*and *T. viride* and these activities are summarized in Table 1.2.The compound synthesized in the Table 1.2 were screened for their antimicrobial activity. Compounds like 2b, 2f against the organism A. nigar and 2e, 2g against T. viride were found to be moderately sensitive. Compounds like 2b, 2e, 2h, 2j against E. Coli, 2a, 2c, 2e, 2h, 2j against S. aureus,2a, 2b, 2d, 2e, 2f, 2h, 2i against B. subtilis, compounds 2b, 2c, 2d, 2e, 2h, 2i, 2j against S. typhi, 2d, 2e, 2h, 2i, 2j against A. nigar and 2a, 2b, 2c, 2i, 2j against T. viride were found to be slightly sensitive , where as compounds like 2a, 2c, 2d, 2f, 2g, 2i against E. coli, 2b, 2d, 2f, 2g, 2i against S. aureus, 2c, 2g, 2j against B. subtilis, 2a against S. typhi, 2c, 2g against A. nigar and 2d, 2f, 2h against T. viride were found to be Resistant.

From the result, it can be found that, some compounds exhibit strong activity against selected microbial species and some compounds show weak to moderate activity.

REACTION

Where, R_1 = a) –H , b) 4-OCH_3 , c) 4-NO_2 , d) 4-Br , e) 4-Cl , f) 4-OC_2H_5 , g) 3-Cl , h) 2-Cl , i) 2-F , j) 2-OC_2H_5

And R_2 = -CH_2Cl



1a-1j **2a-2j**

Scheme 5 :

Synthesis of 5-(4-phenyl,2-azetidinone)-4-(substituted phenyl),6-methyl, 3,4-dihydropyrimidin-2(1H)-one

Table 1.1 :
Analytical data of synthesized 5- (4-phenyl,2-azetidinone) – 4 - (substituted phenyl)- 6-methyl-3,4-dihydropyrimidin-2(1H)-ones (2a-2j)

Sr. No.	Compound	R_1	R_2	Reaction time (hrs)	M.F.	M.W.	Yield	M.Pt (^OC)
1	2a	H	$-CH_2Cl$	1	$C_{21}H_{19}O_2N_3Cl$	380.5	70%	251 ^OC
2	2b	p-OCH_3	$-CH_2Cl$	1.20	$C_{22}H_{21}O_3N_3Cl$	410.5	72%	253 ^OC
3	2c	p-NO_2	$-CH_2Cl$	1.20	$C_{21}H_{18}O_4N_4Cl$	425.5	80%	235 ^OC
4	2d	p-Br	$-CH_2Cl$	1.45	$C_{21}H_{18}O_2N_3BrCl$	459.4	76%	245 ^OC
5	2e	p-Cl	$-CH_2Cl$	1.30	$C_{21}H_{18}O_2N_3Cl_2$	414	85%	255 ^OC
6	2f	p-OC_2H_5	$-CH_2Cl$	1	$C_{23}H_{23}O_3N_3Cl$	424.5	85%	241 ^OC
7	2g	m-Cl	$-CH_2Cl$	1.20	$C_{21}H_{18}O_2N_3Cl_2$	414	70%	257 ^OC
8	2h	o-Cl	$-CH_2Cl$	1.20	$C_{21}H_{18}O_2N_3Cl_2$	414	70%	255^OC
9	2i	o-F	$-CH_2Cl$	1.30	$C_{21}H_{18}O_2N_3FCl$	398.5	74%	252 ^OC
10	2j	o-OC_2H_5	$-CH_2Cl$	1.20	$C_{23}H_{23}O_3N_3Cl$	424.5	80%	260 ^OC

Table 1.2 :
Antimicrobial activity test of 5-(4-phenyl, 2-azetidinone)-4-(substituted phenyl)-6-methyl-3,4-dihydropyrimidin-2(1H)-ones (2a-2j) (Diameter of inhibition zone in mm)

Compound	Antibacterial				Antifungal	
	E. Coli	*S. aureus*	*B. subtilis*	*S.typhi*	*A. niger*	*T. viride*
2a	R	12	13	R	16	14
2b	13	R	12.5	13	15	12
2c	R	12.5	R	12	R	13
2d	R	R	14	14	13	R
2e	11	14	14.5	11	12	16
2f	R	R	13	---	15	R
2g	R	R	R	---	R	17
2h	12	13	12	12	11	R
2i	R	R	13.5	14	14	11
2j	11	12	R	13	13	12
Streptomycin	20	22	18	16	15	17
Penicillin	R	24	19	20	18	16

Where, R : Resistant (10.0 mm and below) **, S** : Sensitive (10.0 mm and above)**,** Slightly Sensitive : (10.0 mm above to 15.0 mm), Moderately Sensitive : (15.0 mm above to 20.0 mm)
Highly Sensitive : (20.0 mm above)

EXPERIMENTAL SECTION

The melting points of all synthesized compounds were recorded using open capillaries and are uncorrected. The IR spectra were recorded on a PERKIN ELMER Spectophotometer in the frequency range 4000-400 cm-′ in Nujol mull and as KBr pellets. ^1H NMR spectra were recorded on BRUKER ADVANCE II 400 spectrometer with TMS as internal standard using DMSO as solvents. All the compounds are synthesized in R. B. Flask by using water condenser and refluxed for several times. Purity of the compounds were checked on pre coated silica-G plates by TLC.
Chemicals (Reagents) used in the synthesis of 5-(4-phenyl,2-azetidinone)-4-(substituted phenyl)- 6-methyl- 3,4-dihydropyrimidin-2(1H)-ones.

GENERAL PROCEDURE

The well stirred mixture of 5-((benzylidene amino) methyl)- 4- (substituted phenyl)- 6-methyl- 3,4-dihydropyrimidin-2(1H)-one (1a-1j) (0.01 mol) and chloroacetyl chloride (0.01 mol) were taken in round bottom flask with 10

ml DMF and triethyl amine (0.01 mol), then the reaction was subjected to reflux for 1 h. After refluxed, the product obtained cooled at room temperature and was poured over ice water. The solid separated out was filtered, washed with water and recrystallized from ethanol to afford pure 5-(4-phenyl,2-azetidinone)-4-(substituted phenyl)- 6-methyl- 3,4-dihydropyrimidin-2(1H)-ones. (2a-2j).In present antimicrobial study of the newly synthesized compounds were screened for their antimicrobial study using "Kirby-Bauer Disc Diffusion Method" OR by Well Method. Kirby-Bauer method is recommended by the National Committee for the clinical laboratory standards and the World Health Organization (WHO).

SPECTROSCOPIC DATA OF DIFFERENT COMPOUNDS

1. **5-(3-chloro-4-phenyl,2-azetidinone)-4-(phenyl)-6-methyl-3,4-dihydropyrimidin-2(1H)-ones (Entry 1) :** Yield 70%, M.P. 251^{O}C, IR(KBr) γ/cm-□ 3580 (N-H), 3067(N-H), 1555 (CO), 1369(C-H), 973(C-N), 671(-Ar), 529(C-Cl) ; ^{1}H NMR (DMSO-d6) 2.5(3H,s,CH_3), 3.34(2H,s,CH_2), 4.2(1H,d,CH), 7.6(4H,m,Ar-H), 7.7(1H,s,NH), 7.9(1H,s,NH).
2. 5-**(3-chloro-4-phenyl,2-azetidinone)-4-(4-methoxy-phenyl)-6-methyl-3,4-dihydropyrimid -in-2(1H)-ones (Entry 2) :** Yield 72%, M.P. 253^{O}C, IR(KBr) γ/cm-□ 3342 (N-H), 2926(N-H), 1679 (CO), 1445(C-H), 1249(C-N), 940(-Ar), 539(C-Cl) ; ^{1}H NMR (DMSO-d6) 1.19(3H,s,CH_3), 5.2(2H,s,CH), 4.2(1H,d,CH), 7.3(4H,m,Ar-H), 8.5(1H,s,NH), 7.6(1H,s,NH) ; MS(m/z,%) 410.5(M^+), 376.33[M-C6H5,CO,β-lactam ring]$^+$.
3. **5-(3-chloro-4-phenyl,2-azetidinone)-4-(4-nitro-phenyl)-6-methyl-3,4-dihydropyrimidin-2(1H)-ones (Entry 3) :** Yield 80%, M.P. 235^{O}C, IR(KBr) γ/cm-□ 33539 (N-H), 3075(N-H), 1641 (CO), 1426(C-H), 1075(C-N), 731(-Ar), 546(C-Cl) ; ^{1}H NMR (DMSO-d6) 2.0(3H,s,CH_3), 5.3(2H,s,CH_2), 4.3(1H,d,CH), 7.5(4H,m,Ar-H), 8.7(1H,s,NH), 7.6(1H,s,NH).
4. **5-(3-chloro-4-phenyl,2-azetidinone)-4-(4-bromo-phenyl)-6-methyl-3,4-dihydropyrimid -in-2(1H)-ones (Entry 4) :** Yield 76%, M.P. 245^{O}C, IR(KBr) γ/cm-□ 3482 (N-H), 3247(N-H), 1672 (CO), 1437(C-H), 1106(C-N), 718(-Ar), 535(C-Cl) ; ^{1}H NMR (DMSO-d6) 1.2(3H,s,CH_3), 3.35(2H,s,CH_2), 4.2(1H,d,CH), 7.6(4H,m,Ar-H), 7.4(1H,s,NH), 7.9(1H,s,NH), MS(m/z,%) 459.4(M^+), 440.48[M-C6H5,NHCONH,β-lactam ring]$^+$.
5. **5-(3-chloro-4-phenyl,2-azetidinone)-4-(4-chloro-phenyl)-6-methyl-3,4-dihydro pyrimid-in-2(1H)-ones (Entry 5) :** Yield 80%, M.P. 255^{O}C, IR(KBr) γ/cm-□ 3749 (N-H), 3427(N-H), 1664 (CO), 1596 (C-H), 1089(C-N), 988(-Ar), 510(C-Cl) ; ^{1}H NMR (DMSO-d6) 1.6(3H,s,CH_3), 5.2(1H,s,CH), 4.26(1H,d,CH), 7.4(4H,m,Ar-H), 7.9(1H,s,NH), 7.2(1H,s,NH).
6. 5-(3-chloro-4-phenyl,2-azetidinone)-4-(4-ethoxy-phenyl)-6-methyl-3,4-dihydropyrimid -in-2(1H)-ones (Entry 6) : Yield 85%, M.P. 241^{O}C, IR(KBr) γ/cm-□ 3752 (N-H), 3469(N-H), 1627 (CO), 1448(C-H), 1049(C-N), 510 (-Ar), 745(C-Cl) ; ^{1}H NMR (DMSO-d6) 1.6(3H,s,CH_3), 5.2(1H,s,CH), 4.2(1H,d,CH), 7.6(4H,m,Ar-H), 7.2(1H,s,NH), 8.5(1H,s,NH).
7. **5-(3-chloro-4-phenyl,2-azetidinone)-4-(3-chloro-phenyl)-6-methyl-3,4-dihydropyrimid -in-2(1H)-ones (Entry 7) :** Yield 70%, M.P. 257^{O}C, IR(KBr) γ/cm-□ 3487 (N-H), 3117(N-H), 1678 (CO), 1436(C-H), 1037(C-N), 907 (-Ar), 745(C-Cl) ; ^{1}H NMR (DMSO-d6) 1.8(3H,s,CH_3), 5.0(1H,s,CH), 4.9(1H,d,CH), 7.0(4H,m,Ar-H), 7.3(1H,s,NH), 8.4(1H,s,NH).
8. 5-(3-chloro-4-phenyl,2-azetidinone)-4-(2-chloro-phenyl)-6-methyl-3,4-dihydropyrimid -in-2(1H)-ones (Entry 8) : Yield 70%, M.P. 255^{O}C, IR(KBr) γ/cm-□ 3500 (N-H), 3168(N-H), 1609 (CO), 1437(C-H), 1127(C-N), 717(-Ar), 622(C-Cl) ; ^{1}H NMR (DMSO-d6) 2.0(3H,s,CH_3), 5.6(1H,s,CH), 4.2(1H,d,CH), 7.3(4H,m,Ar-H), 6.9(1H,s,NH), 8.6(1H,s,NH).
9. **5-(3-chloro-4-phenyl,2-azetidinone)-4-(2-fluoro-phenyl)-6-methyl-3,4-dihydropyrimid -in-2(1H)-ones (Entry 9) :** Yield 74%, M.P. 252^{O}C, IR(KBr) γ/cm-□ 3672(N-H), 3338(N-H), 1608 (CO), 1434(C-H), 1083(C-N), 712(-Ar), 545(C-Cl); ^{1}H NMR (DMSO-d6) 1.6(3H,s,CH_3), 5.3(1H,s,CH), 4.24(1H,d,CH), 7.6(4H,m,Ar-H), 7.1(1H,s,NH), 7.9(1H,s,NH).
10. 5-(3-chloro-4-phenyl,2-azetidinone)-4-(2-ethoxy-phenyl)-6-methyl-3,4-dihydropyrimid -in-2(1H)-ones (Entry 10) : Yield 80%, M.P. 260^{O}C, IR(KBr) γ/cm-□ 3345 (N-H), 3112(N-H), 1672 (CO), 1444(C-H), 997(C-N), 727(-Ar), 632(C-Cl) ; ^{1}H NMR (DMSO-d6) 2.0(3H,s,CH_3), 5.4(1H,s,CH), 4.0(1H,d,CH), 7.1(4H,m,Ar-H), 7.2(1H,s,NH), 8.5(1H,s,NH), MS(m/z,%) 424.5(M^+), 381.29[M-C6H5,NHCONH,β-lactam ring]$^+$.

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IMPACT OF CARBOXYMETHYLATION ON THE PHYSICOCHEMICAL, MORPHOLOGICAL AND THERMAL CHARACTERISTICS OF YELLOW *POINCIANA* SEED POLYSACCHARIDE

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ABSTRACT

In this study, three different carboxymethylated polysaccharides were derived from yellow poinciana seed polysaccharide. The physicochemical, morphological and thermal characteristics of carboxymethylated polysaccharide wereinvestigated. The degree of substitution (DS) and FTIR confirms the formation of carboxymethylated polysaccharide. The DS was found to be in the range of 0.36-1.14. After carboxymethylation, there is a quite increase in solubility power of polysaccharide. The micromeritic properties reveals good flow properties of carboxymethylated polysaccharide. TGA analysis revealed the increased thermal stability with increase in DS. SEM analysis showed a porous microstructure of polysaccharide. Overall results suggest that carboxymethylated yellow poinciana seed polysaccharide can be used as pharmaceutical adjuvant with good thermal stability.

Key words: *Carboxymethylation, yellow poinciana tree, Porous microstructure, FTIR.*

1. INTRODUCTION

Regardless of its key functional roles, native polysaccharide is undesirable for many applications, because of their inability to withstand processing conditions. In order to overcome these, native polysaccharides are usually modified either chemically or physically or using a combination of both which enhance or repress the inherent property of these native polysaccharides or to impact new properties to meet the requirements for specific applications[1].

Among these modifications, chemical modification is one of means to introduce the functional groups resulting in improved functional properties. Chemical modifications like carboxymethylation, acetylation and selenylation are widely reported in the recent studies[2]. Carboxymethylation is a versatile method to improve the solubility and functional properties of polysaccharides.

Yellow poinciana tree (*Peltophorum pterocarpum*), the copper pod, Golden flamboyant, or yellow flame tree, widely grows in tropical regions and having high ornamental value. The seeds of yellow poinciana tree contains 28.6% germ, 29.3% endosperm and 42.1% coat[3]. The rubbery endosperm contains high content of polysaccharide and thereby suggesting a rich source of polysaccharide.

In the present study, the water-soluble polysaccharide of yellow poinciana seed polysaccharide was modified by means of carboxymethylation and to investigate their physicochemical, thermal and morphological characteristics.

2. MATERIALS AND METHODS

2.1. Materials

The dried seeds of yellow poinciana were obtained from the Institute of Forest Productivity, Ranchi, Jharkhand. All the chemicals used were obtained from Spectrochem Pvt. Ltd., Mumbai and RFCL Ltd., Gujarat, India.

2.2. Isolation of water soluble polysaccharide

The extraction of water soluble polysaccharide was performed by the method described by Mandal et al. with slight modifications [4]. The seeds were obtained by crumbling the pods and were subjected for thorough washing to remove unwanted matter. The washed seeds were soaked overnight in water. From the imbibed seeds, the endosperm layer was separated from the hull and germ layer. The separated endosperm layer was subjected for boiling over a period of 8 h. The obtained slurry was kept overnight at 4 oC and filtered through muslin cloth, followed by centrifugation at 4 ^{o}C. The supernatant was collected and precipitated in ethanol (1:4 ratio of supernatant: ethanol). Further, the precipitated material was collected by centrifugation and

dissolved in distilled water, dialyzed through DEAE cellulose using distilled water for 12 h. The resultant solution was lyophilized to yield water soluble polysaccharide (PPSP) and the percentage yield was recorded.

2.3. Carboxymethylation of polysaccharide

To 1 gm of polysaccharide, 5 ml of 10 M NaOHwas added under stirring in an ice bath for 1 h. Then different concentrations (5 ml of 5, 10 & 15%) monochloroacetic acid (MCA)was added dropwise for 1 h under stirring. The prepared solution was maintained at 70 ^{o}C for 1 h with occasional stirring. Further the solution was neutralized with glacial acetic acid and the precipitated in 95 % ethanol. The precipitated matter was dialyzed against Millipore water. The dialyzed solution was lyophilized to get carboxymethylated polysaccharide with different degree of substitution[5].

2.4. Determination of degree of substitution

Degree of substitution (DS) was determined by means of back titration method[6]. The dried carboxymethylated polysaccharide was dispersed in excess of 0.5 N NaOH solutionand stirred for 3 h. Then the solution was back titrated with 0.5 N hydrochloric acid using phenolphthalein indicator.

DS was determined by the equation given below:

% Carbonyl = (S2/W2) − (S1 × M NaOH × 0.045 × 100/W1)

Here, S1 and S2 = the titre of native and polysaccharide sample; W1 and W2 = weight of native and native polysaccharide.

DS = (162 × % carbonyl) / (4500 – 58 × % carbonyl)

2.5. Physicochemical characteristics

2.5.1. Yield, moisture content andpH determination

Determination of moisture content were carried out in accordance with the standard methods of AOAC 2000. Shortly, for moisture contents samples were heated at 105 °C for 3 h in pre-weighed petridish. pH of 1% suspension of each sample was determined by using digital pH meter.

2.5.2. Water holding capacity (WHC), swelling and solubility power

Accurately weighed 0.6 g of starch was taken in 40 mL of water and was heated to 60°C for 30 min. Obtained suspension was centrifuged at 3000 rpm for 15 min. The supernatant liquid after the centrifugation was decanted carefully and the swollen sediment was weighed. An aliquot of 5 mL was taken from decanted solution in pre-weighed petridish and kept for over night drying at 130°C. The residue thus that obtained will be the amount of starch solubilised in the water. Swelling and solubility power can be computed by following equations.

Swelling Power (%) = W_{WT} × 100 / W_P × (100 − % Solubility)

% Solubility = Weight of soluble polysaccharide/ W_{WT} × 100

Here, W_{WT} is weight of wet polysaccharide (g) and W_P weight of polysaccharide on dry weight basis (g).

WHC of carboxymethylated polysaccharide was estimated, using the method described by Deepika et al. (2105) with slight modification[7]. Accurately weighed 0.1 g of polysaccharidewas taken in a 15 mL of water and agitated for 1 h. Then it was centrifuged for 10 minat 3000 rpm. Finally, supernatant water was decanted and wet weight of sample was taken.

WHC (%) = W_{WT} / W_{PS} ×100

Here, W_{WT} = weight of wet polysaccharide (g) and W_{PS} = initial weight of polysaccharide (g).

2.5.3. Elemental analysis

The elements analysis (Carbon, Hydrogen, Nitrogen and Sulphur) were determined by using an Elemental Analyzer (Make- M/s Elementar, Germany; Model-Vario EL III).

2.6. Micromeritic properties

Bulk and tapped densities, Hausner ratio, Carr's index, angle of repose, porosity and true density were determined by the method described by Varma et al. (2014) [8].

2.7. Fourier transform infrared spectroscopy

The FT-IR spectra of carboxymethylated polysaccharide was recorded by using FT-IR spectrophotometer (FTIR-8400S, Shimadzu, Japan) in scale of wave numbers from 4000 to 400 cm−1. The samples were dried at 40 °C and blended with KBr prior to analysis.

2.8. Thermogravimetric analysis

Thermo gravimetric analysis of polysaccharidewas investigated by using TGA- 4000 (Perkin Elmer, United States). Here, the process was done under the nitrogen atmosphere of its flow rate 50 mL/min at a temparature range from 30 °C to 600 °C with heating rate of 10 °C. Approximately 5.0 ± 0.5 mg of sample was taken in platinum crucibles for analyis. From the above analysis, percentage weight loss was known from the onset decomposition temperature.

2.9. Scanning electron microscopy

The morphology ofpolysaccharidewas examined by scanning electron microscope (JEOL-Japan, JSM 6390 LV. Here, the powder starch granules were sprinkled on double sided adhesive tape

mounted on a metal stub and further it was coated with metal platinum in turn to make the sample conductive. Images were taken at an accelerating potential of 10 kv.

3. RESULTS AND DISCUSSION

3.1. Physicochemical characterization

The physicochemical propertied of carboymethylated polysaccharides were presented in Table 1. The % yield of carboxymethylated polysaccharide was found to increase with increase in % MCA. This might be due to theincrease in the interaction between polysaccharide and the etherifying reagent with increased concentration of MCA[2].

To confirm the carboxymethylation reaction, degree of substitution was performed by back titration method. The DS wasfound to increase with increase in the amount of MCA and this due to the more availability of MCA to make sufficient reaction[6]. The slight increase in moisture content was due to increased hydrophilic nature by carboxymethylation.

Table 1. Physicochemical characterization of carboxymethylated polysaccharide

Physicochemical Properties	PPCM1	PPCM2	PPCM3
Yield (%)	100.80	102.28	108.92
Degree of substitution	0.36 ± 0.05	0.58 ± 0.01	1.14 ± 0.03
Moisture (%)	9.87 ± 0.12	10.11 ± 0.22	10.30 ± 0.19
pH	7.34 ± 0.02	7.38 ± 0.01	7.21 ± 0.05
Swelling power (%)	10.85 ± 0.12	9.47 ± 0.08	7.79 ± 0.22
Solubility power (%)	65.09 ± 0.21	72.89 ± 0.09	80.19 ± 0.05
Water binding capacity (WBC) (%)	798 ± 0.23	732 ± 0.17	652 ± 0.20

All values represent the means of triplicate analysis ± standard deviation.

here was significant increase in water holding capacity with the increase in DS. In-corporation of carboxymethyl group to the polysaccharide renders it morehydrophilic and which decreased the water retention.

The swelling power found to decrease with increase in DS. This increase might be due to the weakening of forces polysaccharide chains, which allow the penetration of water and subsequently decrease in swelling power[7]. This was quite opposite in case of solubility power and the reason behind this is dueinclusion of the carboxyl group increases the hydrophilicity, which leads to slight increase in solubility power. The pH of carboxymethylated polysaccharides was found to be neutral.

The elemental analysis confirms the carboxymethylation reaction due to the addition of carboxylic groups.

3.2. Micromeritic properties

The micromeritic properties revealed the good flow properties of carboxymethylated polysaccharide and were presented in table 2. There was no quite significant changes were observed among the carboxymethylated polysaccharides with different DS.

Table. 2. Micromeritic properties of carboxymethylated polysaccharide

Parameter	PPCM1	PPCM2	PPCM3
Bulk density (g/cc)	0.56 ± 0.02	0.39 ± 0.04	0.34 ± 0.01
Tapped density (g/cc)	0.63 ± 0.03	0.48 ± 0.02	0.41 ± 0.02
Hausner ratio	1.90 ± 0.01	1.25 ± 0.01	1.20 ± 0.02
Carr's index (%)	19.51 ± 0.07	18.47 ± 0.05	17.24 ± 0.01
Angle of repose (°)	28.27 ± 0.09	27.59 ± 0.12	25.32 ± 0.01
Porosity	1.07 ± 0.02	1.28 ±0.04	1.62 ± 0.01
True density (g/cc)	0.98 ± 0.05	0.74 ± 0.01	0.65 ± 0.02

All values represent the means of triplicate analysis ± standard deviation.

3.3. FTIR

The FTIR spectra of carboxymethylated polysaccharide were presented in Fig. 1. The broad band near to 3250 $cm^{-1}$is attributed to vibrations of OH stretching. The peak at 2923 $cm^{-1}$is attributed toCH stretching in the CH2 groups. Carboxyl group of modified polysaccharide was confirmed by two strong absorption bands at 1601 cm^{-1} and 1421 cm^{-1}.

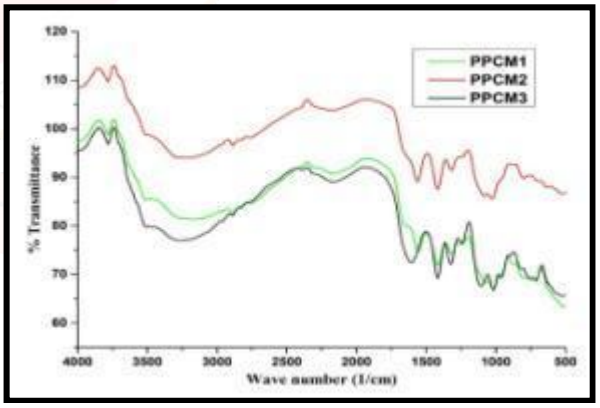

Fig. 1. FTIR spectra of carboxymethylated polysaccharide

3.4. Thermogravimetric analysis

Fig. 2. Shows the thermogravimetric analysis of carboxymethylated polysaccharide. The first stage of weight loss is due to the bound moisture and the second stage is due to the depolymerisation of polysaccharide. The third weight loss contributes to the degradation of polysaccharide. At 500 °C, the percent weight loss for all the carboxymethylated derivatives was

found to be decrease with increase in DS and this data represents that carboxymethylation increased the thermal stability of the samples[9].

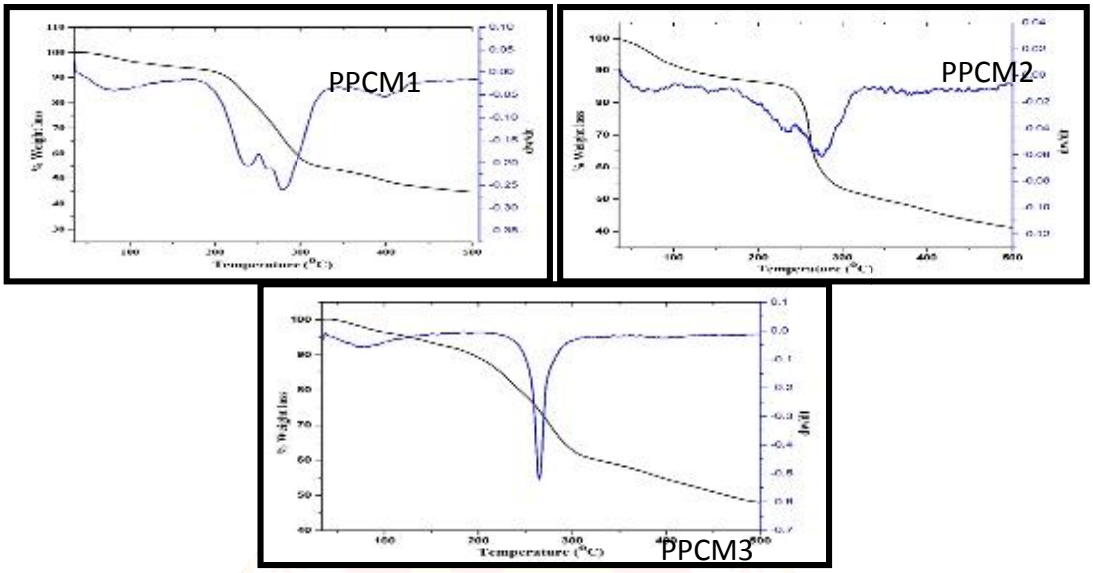

Fig. 2. Thermogravimetric analysis of carboxymethylated polysaccharide

3.5. Morphology of carboxymethylated polysaccharide

The morphology of carboxymethylated polysaccharides were presented Fig. 3. After carboxymethylation, pores were observed on the surface, which are involved in formation of microstructure.This might be due to the chemical treatment resulted in corrosion of surface[10]. Pore formed were comparatively higher in case of polysaccharide (PPCM3) with high DS.

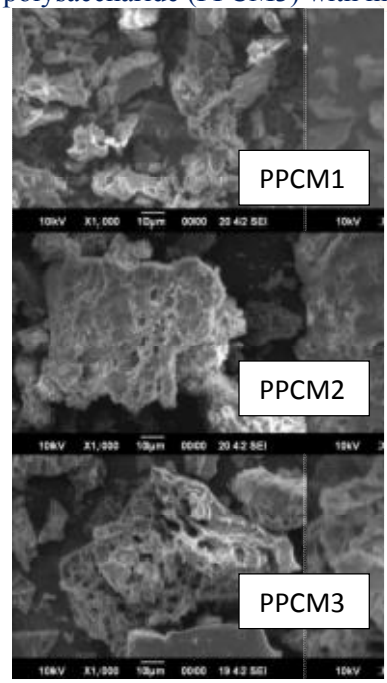

Fig. 22. Scanning electron micrographs of carboxymethylated polysaccharide (PPCM1, PPCM2 & PPCM3)

4. CONCLUSION

Carboxymethylation of yellow poinciana seed polysaccharide was performed and evaluated for its physicochemical, morphological and thermal characteristics. The solubility power of carboxymethylated polysaccharides was found to increase with increase in DS. The micromeritic properties reveals the good flow characteristics. Two new strong absorption bands at 1601 cm-1 and 1421 cm-1, confirmed carboxyl group of modified polysaccharide. The TGA data reveals the improved thermal stability of polysaccharide with increase in DS. SEM reveals the formation of pores in the microstructure of polysaccharide after carboxymethylation.

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PHYSICOCHEMICAL CHARACTERIZATION AND DRUG RELEASE PROFILE OF CARBOXYMETHYLATED STARCHES PREPARED FROM PINK POTATO

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ABSTRACT

Starch isolated from pink potato was carboxymethylated. The influence of degree of substitution on physicochemical and drug release properties were studied. The Amylose content, swelling and solubility power was reduced with increase in degree of substitution. Release profile of paracetamol tablets were reduced with increase in degree of substitution. Carboxymethylated starches can be used as a source of release retardant in sustained release formulations.

Key words: *Starch, carboxymethylation, pink potato*

INTRODUCTION

Synthetic material are readily used in every field of human activity. These synthetic polymers are mainly derived from petroleum sources and can cause serious environmental threats. This drawbacks limit the use of synthetic polymer thus biodegradable polymer may be used as a substitute of synthetic polymers. Starch a natural polymer is widely of interest [1]. Starch can be tailored to obtain desirable properties [2]. Various physical and chemical modification are being carried out to enhance specific functional properties. Among the physical modification pregelatinization, retrogradation, annealing are carried out. Chemical modification comprises of carboxymethylation, acetylation and esterification [3]. The present study mainly focuses on carboxymethylation of starch obtained from pink potato.

MATERIALS AND METHODS

Isolation of starch

Pink potato was collected from the local market in Jharkhand. The starch was isolated from the potato according to the method as described by Deepika, Jayaram Kumar and Anima, 2013. The tubers were washed thoroughly, peeled and cut into pieces. The sliced tubers were then soaked into citric acid (0.3% w/w) for the removal of gummy mucilage layer. Further the pieces of tuber were milled in a blender using distilled water. Paste obtained after blending was washed thoroughly with distilled water until the water becomes clear. The resulting solution obtained after washing was allowed to settle. The supernatant liquid was decanted and crude starch obtained was dried in oven [4].

Preparation of carboxymethylated starch

Carboxymethylation of native starch were carried out by the method of Kulkarni et al. (2013). The solution of 3.2 g of NaOH and 20 ml of water was stirred at 250 rpm until the sodium hydroxide was completely dissolved. Nearly 125 ml of isopropanol was added to the sodium hydroxide solution and the resulting solution was kept for heating at 40º C. The resulting solution was kept at the above temperature and eight grams of starch was added to the above solution. The reaction was continued until the starch solution was completely dissolved. The monochloroacetic acid in different concentrations (1.25, 2.50 and 3.60 g) was added to the starch-NaOH mixture and the reaction was continued for another 4 hours. The product was filtered washed with methanol and neutralized with acetone. The product obtained was dried in hot air oven at about 40º C to obtain the carboxymethylated starch [5].

Determination of the degree of substitution

Back titration method was used for determination of degree of substitution (DS) for carboxymethylated starch. The carboxymethylated starch (0.50 g) was mixed with solution containing 20 ml of 0.2 M NaOH and 50 ml of distilled water. The resulting solution was made upto the volume of 100 ml. 25 ml of solution was taken from the above solution and again diluted to 100 ml. The excess of NaOH present was back titrated using 0.05 M HCl using phenolphthalien solution as indicator. For

comparison native starch was treated with above procedure [5].

Amylose content

10 mg of the starch was weighed and 1 ml of 95% ethanol and 9 ml of 1 N caustic soda solution was added. The resulting mixture was heated for 10 min to gelatinize the starch. The volume of the solution was made upto 100 ml. 1 ml of solution was pipetted out and 1 ml of 1 M acetic acid and 2 ml of iodine solution were added and volume was made upto 10 ml The solution was allowed to stand for 20 mins and the absorbance was determined spectrophotometrically at 620 nm [6].

Water binding capacity

Starch suspension was prepared by taking 1g of starch in 10 ml of distilled water. The resulting solution was agitated for about 1 hour. The solution was centrifuged at 3000 rpm for 10 minutes. Supernatant was decanted and the wet residue was weighed. The water holding capacity was calculated on the dry basis [7].

Swelling and solubility power

The swelling and solubility were determined by the method of Varma et al. (2017). The starch suspension was subjected to heating at 60 ° C. The suspension was stirred continuously so as to prevent lump formation. The suspension was centrifuged at 3000 rpm for 20 minutes. The supernatant was decanted in preweighed petridish. The supernatant portion represent the soluble portion whilst the wet residue represent the swellable portion [8].

W_{sr} is the soluble residue; W_i is the weight of starch on the dry basis; W_{ws} is the weight of wet starch.

Micromeritic properties

The Micromeritic properties like bulk density, tapped density, Carr's index, Hausner ratio and angle of repose were determined by the method of Das et al. (2015) [9].

Preparation and evaluation of tablets

Tablets were prepared by wet granulation method using paracetamol as a model drug. Paracetamol (71.4% w/w), lactose (17.1% w/w), sodium CMC (5% w/w) and starch (4.5% w/w) was mixed until a wet mass is formed. The wet mass was then passed through a #12 mesh. The granules obtained were dried in oven and passed through a #20 mesh. Prior to the compression talc (1%) and magnesium stearate (1%) was added [10].

Tablets were randomly selected and evaluated for determination of weight variation, hardness, friability, disintegration, dissolution. Monsanto hardness tester was used to determine tablet hardness, Roche friabilator was used to determine tablet friability, tablet disintegration test machine of USP standard was used to determine tablet disintegration time [11].

RESULTS AND DISCUSSIONS

Proximate analysis

The percentage yield of starch isolated from tuber was found to be 21.13 %. The percentage yield of carboxymethylated starch 1 (CMC 1) bearing the concentration 1.25 was 70 %. Percentage yield of carboxymethylated starch 2 (CMC 2) bearing the concentration 2.5 was 86.5 %. Percentage yield of carboxymethylated starch 3 (CMC 3) bearing the concentration 3.6 was 87%. Table 1 counts for the values of amylose content, swelling power, solubility power of native as well as modified starches.

The amylose content of native starch was found to be 9.0576%. The amylose content was found to decrease with increase in degree of substitution (**Table 1**). The range of amylose content for carboxymethylated starch was between 20-30 % [12].

The degree of substitution for CMC1, CMC 2 and CMC 3 was fund to be 0.200, 0.572, 0.918 respectively. The increase in degree of substitution with increase in concentration of monochloroacetic acid was observed. The increase in degree of substitution might be due to increase in interaction between etherifying agent and the starch granules [5].

Table 1. Physicochemical characterization of native and carboxymethylated starches of pink potato.

Starch Sample	Amylose content (%)	WHC (%)	Swelling Power (%)				Solubility Power (%)			
			30 ºC	50 ºC	70 ºC	90 ºC	30 ºC	50 ºC	70 ºC	90 ºC
Native	9.0576±0.10	100	16.30±0.02	17.55±0.03	20.02±0.03	22.90±0.01	72.22±0.02	76.67±0.05	79.23±0.02	83.46±0.04
CMC 1	29.6244±0.10	102	15.89±0.01	16.23±0.02	18.98±0.02	22.35±0.04	69.23±0.02	72.95±0.05	75.10±0.05	79.50±0.02
CMC 2	28.8864±0.11	108	14.46±0.01	15.89±0.01	17.89±0.01	19.95±0.01	65.40±0.05	68.01±0.04	71.24±0.01	74.56±0.01
CMC 3	20.7346±0.10	115	11.20±0.02	12.21±0.02	14.01±0.03	15.79±0.01	62.01±0.10	63.95±0.01	66.67±0.01	68.49±0.01

All values represent means of triplicate analysis ± standard deviation.

Table 2. Micromeritic properties of native and carboxymethylated starches of pink potato.

Starch Sample	Bulk density(g/cc)	Tap density(g/cc)	Carr's index (%)	Angle of repose (□)
Native starch	0.7692±0.01	0.8333±0.01	5.69±0.01	45^0
CMS 1	0.3571±0.01	0.3846±0.04	3.83±0.02	30.96^0
CMS 2	0.4166±0.04	0.5555±0.02	3.53±0.01	27.42^0
CMS 3	0.4545±0.01	0.5882±0.01	2.50±0.04	25.01^0

The swelling and solubility power was found to de decrease with increase in concentration of monochloroacetic acid. The increase in heating temperature causes rise in swelling and solubility power [12]. The micromeritic property of carboxymethylated starches showed enhanced flowability. The angle of repose was found to decrease with increase in degree of substitution. Carboxymethylated starches had lower values of carr's index than the native ones [12]

In-vitro **release profile**

In-vitro release profile of the drug suggested that with increase in degree of substitution the % The parameters such as weight variation, hardness and friability meet the criteria specified in the USP [13].

cumulative drug release was lessened. The In-vitro profile of native and carboxymethylated starches is shown in **Figure 1** .The drug release from tablets using CMC1 was 94.40%. and the release steadily decreased to 90.29%. While the drug release of tablets using CMC3 was 87.66%. The dissolution profile of carboxymethylated starches has been supported by their disintegration time (**Table 3).** The tablet matrices exhibited a strong profile for sustained-release delivery for bioactive molecules [12].

Table 3. Physical test of tablets prepared from native and carboxymethylated starches of pink potato.

Starch Sample	Weight variation (mg)	Hardness (kg/cm^2)	Disintegration time	Hardness (kg/cm^2)	Friability (%)
Native	248±0.10	4.42±0.07	1 hr. 04 min±0.12	4.42±0.07	0.90
CMS 1	251±0.12	4.89±0.10	1 hr. 86 min±0.16	4.89±0.09	0.50
CMS 2	247±0.10	5.32±0.09	1 hr. 91 min±0.16	5.32±0.10	0.54
CMS 3	246±0.10	5.12±0.10	1 hr. 97 min±0.14	5.12±0.07	0.59

All values represent means of triplicate analysis ± standard deviation.

Fig.1. *In-vitro* release profile of native and carboxymethylated starches of pink potato

CONCLUSION

In the present study carboxymethylated starches from pink potato was prepared. The physicochemical and drug release properties were evaluated. Degree of substitution has negative correlation with amylose content. Swelling and solubility power increases with rise in temperature. *In-vitro* study exhibited the use for carboxymethylated starches as a source of sustained release excipient.

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STRUCTURAL AND BACTERIAL PROPERTIES OF NANOCRYSTALLINE NICKEL FERRITE SYNTHESIZED BY SOL-GEL METHOD

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ABSTRACT

The magnetic behavior towards biomedical applications of transition metal-ferrite and transition metal-ferrite based nanoparticles is dependent upon the nanoparticles preparation parameters. Nickel ferrites nanoparticles were synthesized chemically by a modified sol-gel method. The structural and biological properties were investigated. The structural characterizations of prepared nanoparticles were characterized by X-ray diffraction (XRD), Fourier transform infrared spectra (FTIR) studies to investigate the formation of crystalline nature of nickle ferrite. The XRD result shows the crystalline inverse spinel structure with particle size 30 nm. The sharp peaks showed all-crystalline nature of single phase ferrite. The antimicrobial activity of the nickle ferrite nanoparticles tested against Gram-positive and Gram-negative bacteria. The results revealed that the Nickle ferrite nanoparticle inhibit the maximum growth of bacteria and the maximum inhibition zone of inhibition was found in Klebsiella pneumonia. Nickle ferrite has high antimicrobial activity and it can be used as good bio- preservater and it can also use for medicinal purpose.

***Keywords**: nanostructures, Spinal ferrites, XRD, FTIR, Bacterial Pathogens.*

INTRODUCTION

For the last few decades, the ferrites nanoparticles have been extensively studied due to their significant different applications such as optical, electrical and magnetic properties which are different from their bulk structure [1,2]. In particular, nickel ferrite has an interesting set of properties making it in a wide range of applications such as in the radio frequency, magnetic resonance imaging contrast agents for biotechnology, and magnetic nano-fluid for hyperthermia cancer treatments [3].

Where, ferrites are one basic but important group of magnetic materials, in which spinel-type ferrites (MFe_2O_4, M = Fe, Co, Ni, etc.) have a considerable attention. [4, 5] Nickel as an essential dopent element in ferrite-based nanoparticles is known to have stimulatory effects on spinal formation [6]. The interesting properties of Spinel ferrites arise from their ability to distribute the cations among the Tetrahedral (A) and Octahedral (B) sites [7].

Magnetic nanoparticles are used in many biological and medical applications due to their interesting properties such as superparamagnetic behavior, high surface-to-volume ratio, and external magnetic force [8]. For instance, their high surface area and ability to bind with suspended antibiotic-resistant bacteria has encouraged environmental researchers to use them in the treatment of polluted waste water [9]. Magnetic nanoparticles also represent a new era of promising applications in counteracting nosocomial infections, where microorganisms tend to attach and subsequently grow on solid surfaces, including medical devices, and form biofilms [10].

Metal nanoparticles (Metal-Nps) have shown copious aspect in biomedical practice as they can be deliver as high-caliber, optically sound bioimaging agents, may be applied in biosensor tool for the early detection of several maladies [11]. These nanosize particles have also established in vivo encouraging effect as therapeutic agents [12]. The studies conducted in past few year, Metal-NPs have been improved for their antimicrobial activity and may locally destroy pathogenic organisms, without being toxic to the surrounding tissue [13].

The application of magnetic nanoparticles as antimicrobial agents is gaining importance due to the fact that they can be easily manipulated by an external magnetic field. The iron oxide nanoparticles have been synthesized and tested for various applications in medicine such as magnetic hyperthermia, targeted drug delivery and bactericides [14].

The biocidal activity was tested on Gram negative (Salmonella typhi, Proteus, *and* Klebsiella pneumoniae) and Gram positive (staphylococcus epidermidis and Bacillus brevis) bacterial strains. Thus the preparation, characterization and fictionalization of nanoparticles open the possibility of formulation of new generation of bactericidal agents.

In general, spinal ferrite can be formed by the traditional methods, which is regarded as simple and suitable for mass production [15, 16]. However, these methods are limited by the evaporation of the volatile component and presence different phases during high-temperature processing. The sol–gel process is an alternative method to preparing ferrite materials that has been widely studied in recent years [17]. The sol–gel process has many advantages are well known such as low temperature process, gives homogeneous mixtures in the final composition, high purity [18, 19].

The present investigation deals with the structural and biological characterization of nickle ferrite nanoparticles synthesized by sol-gel technique and it also aims to detect the activity of these nanoparticles on selected strains of bacteria.

MATERIALS AND METHODS

MATERIAL:

Copper nitrate tetra hydrate ($Ni(NO_3)_2.4H_2O$), Iron nitrate non hydrate ($Fe(NO_3)_2.9H_2O$) and citric acid was obtained of analytical grade. All experiment was done by using ethyl alcohol. $NiFe_2O_4$ were synthesized by sol-gel method.

Synthesis of $NiFe_2O_4$nanoparticle:

Silver doped $NiFe_2O_4$ nanoparticles were synthesis by sol-gel method. All chemicals add in beaker and continuous stirring on magnetic stirrer for 2 hours then form gel and calcinite at temperature 250^0C to form nanoparticles

Antibacterial Study

This work explored the antimicrobial properties of as synthesized nickle ferrite nanoparticles against various microorganisms including Gram negative and Gram positive bacteria.

The Microorganism

Two microbial strains were selected for the experiment on the basis of their pathogenic activity in human being. Bacterial cultures of Salmonella typhi, Proteus, *and* Klebsiella pneumoniae and staphylococcus epidermidis and Bacillus brevis were obtained from the Pathology. These cultures were then sub cultured into nutrient broth according to the standard protocols for sub culturing and allowed to grow in an incubator at 37^0C for 24hours and used for further experiments.

Preparation of Bacterial Culture

The stock culture of each of the bacteria used was sub cultured at 37 ^{0}C for 24 hours

Assay for Antimicrobial Activity

Antimicrobials are agents that kill microorganisms or inhibit their growth. The antimicrobial activity of the obtained compounds was assayed on Gram-negative Salmonella typhi, Proteus,and Klebsillia pneumoniae and Gram-positive staphylococcus epidermidis and Bacillus brevis. Microbial suspensions of 1.5 × 108 $CFUmL^{-1}$ (0.5 McFarland density) obtained from 18 to 24 h bacterial cultures developed on solid media were used. The compounds were suspended in acetone to prepare a stock solution of 10 mg/mL−1 concentration. The qualitative screening was performed by an adapted disk diffusion method. In this purpose, Petri dishes with Mueller Hinton medium were seeded with bacterial inoculum as for the classical antibiotic susceptibility testing (Kirby-Bauer method); subsequently, 20 μL of the stock solution was spotted at 30mm distance. The plates were left at room temperature for 20– 30min and then incubated at 37^0C for 24h. The positive results were read as the occurrence of an inhibition zone of microbial growth around the disk. Positive controls were used. The antimicrobial effects of the NiFe2O4 are sufficient in a way to cater the healing effect. The antimicrobial effect of NiFe2O4 also helps to prevent diseases in many forms. In antimicrobial activity the bacteriostatic and bactericidal effects were determined

RESULT AND DISCUSSION

X-ray Diffraction Analysis (XRD)

The XRD patterns of NiFe2O4 nanoparticles are depicted in Figure 1 The results obtained from XRD data agrees well with the standard values of Nickle ferrite (JCPDS PDF Card No.22-1086). The diffraction peaks corresponding to (220), (311),(222), (400), (422), (511) and (440) reflection planes show that all the samples have attained inverse spinel structure. The study suggests that iron ions change their valence from Fe3+ to Fe2+ to achieve charge neutralization [20]. The crystallite size *D* of the samples has been estimated from the broadening of XRD peaks using the Scherrer equation.

$$D = \frac{0.89\lambda}{\beta\cos\theta}$$

where, λ is the X-ray wave length, β is the full width at half maximum (FWHM) and θ is the

Bragg angle. From this calculation the Nickle ferrite nanoparticle had size approximately 30nm.

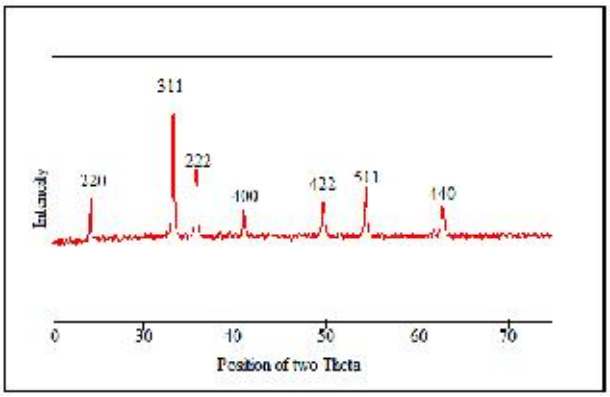

Fig.1. XRD Spectra for $NiFe_2O_4$ powders annealed at 250 ^{0}C.

Fourier Transform Spectroscopy Analysis (FTIR)

Fig.2. shows the FTIR spectra of nickel ferrite. Nickel ferrite belongs to the inverse spinel structure group, so it has a distribution of cations between octahedral and tetrahedral sites and hence the two absorption bands at 667.37 and 451.34 cm^{-1} can be assigned to the stretching vibration frequency of the metal-oxygen at the octahedral site and tetrahedral site respectively. [21, 22] The absorption band at 1020 cm^{-1} may be corresponding to the nitrate traces [23]. The absorption band of symmetric and asymmetric vibrations of CH_2 groups appeared at 2926 and 2853 cm-1, respectively, they can be attributed to organic residues. The band at 3492 cm^{-1} can be assigned to O-H stretching vibration interacting through H bonds that originate from moisture content in the sample [24].

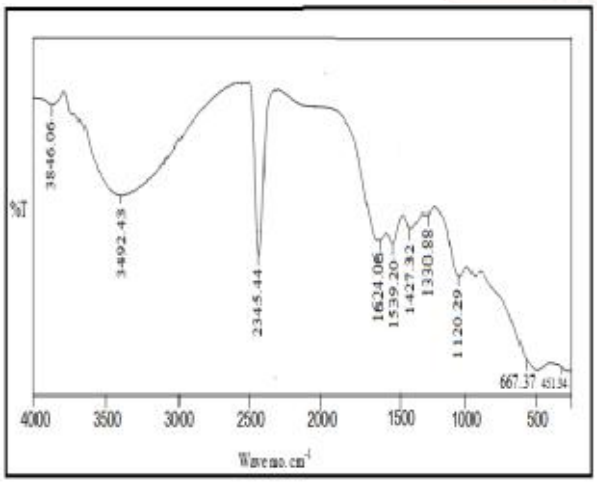

Fig.2. FTIR Spectra for $NiFe_2O_4$powders annealed at 250 ^{0}C.

Antibacterial Activity of $NiFe_2O_4$ Nanoparticles

The bactericidal effect of the nickle ferrite nanoparticles was qualitatively measured by performing agar diffusion test against all microorganisms. The diameters of the ZOI are determined and these are tabulated in Table 1 The absence of growth around the nanoparticles is $_2$an indirect measure of the ability of the material to inhibit the growth. The inhibitory action of $NiFe_2O_4$ against Klebsiella pneumoniae bacterial strains is higher than other samples. This could be due to its small size and the accompanied higher surface area of the nanoparticles. The increase in surface area increases the number of atoms on the surface, which leads to an increase in the biological activity. The ZOI of the nanoparticles produced against the Gram negative microbes Salmonella typhi, Proteus,and Klebsillia pneumoniae are shown in Figures 3. **a, b** and **c** respectively and that against Gram positive bacteria staphylococcus epidermidis and Bacillus brevis is shown in Figure 3. **c and d.** The results obtained from this study revealed that the samples efficiently inhibit the growth of the microbes. From the graph 1 it confirms that the Klebsiella pneumoniae has maximum ZOI. It can be seen that the contact biocidal property of the pure nickel ferrite sample is significant samples. The biocidal activity exhibited by the samples is observed to depend on the particle size. Nickel ferrite shows better activity which can be attributed to its small size and hence better contact with the bacterial cell membrane. It is well known that in the nano-regime, the bactericidal activity exhibited by the smaller particles is higher than bigger particles.

	Zone of inhibition(ZOI) in mm				
Sample	Salmonella typhi	Proteus	Klebsiella pneumoniae	staphylococcus epidermidis	Bacillus brevis
$NiFe_2O_4$	15mm	16 mm	19 mm	18 mm	17 mm
Control	1 mm	3 mm	1 mm	2 mm	1 mm

Table 1. Zone of inhibition of the antibacterial activity of $NiFe_2o_4$ powder for Bacterial pathogens

		Zone of inhibition (ZOI) in mm	
Sample	Bacterial pathogenes	Antibiotic	Antibiotic + NPs
$NiFe_2O_4$	Salmonella typhi	35 mm	37 mm
	Proteus	36 mm	38 mm
	Klebsiella pneumonia	38 mm	40 mm
	staphylococcus epidermidis	34 mm	37 mm
	Bacillus brevis	36 mm	40 mm

Table 2. Zone of inhibition of the antifungal activity of Antibiotic disc for Fungal pathogens

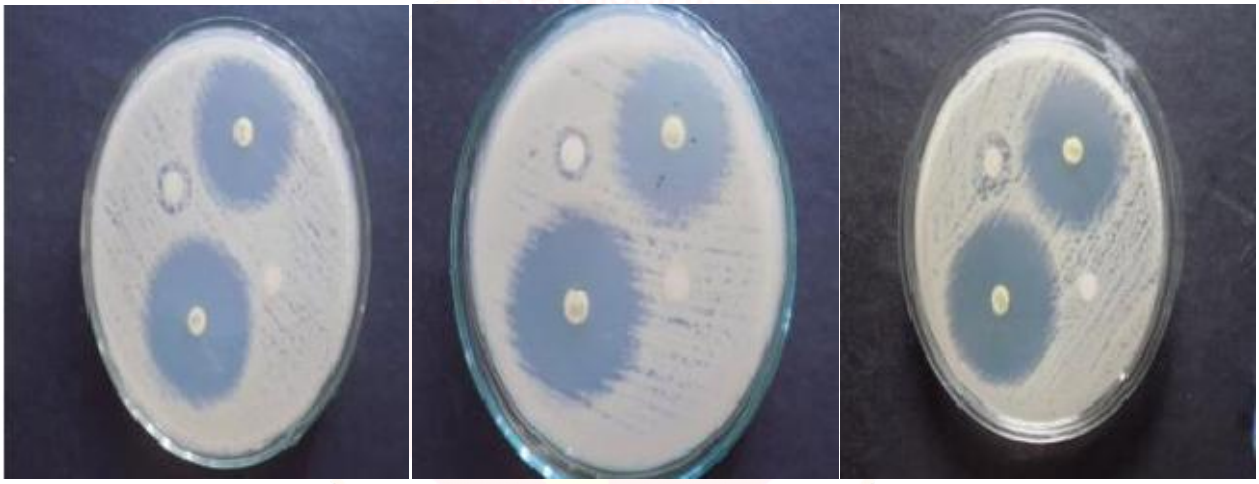

Fig. (a) Salmonella typhi **Fig. (b) Proteus** **Fig. (c) Klebsiella pneumoniae**

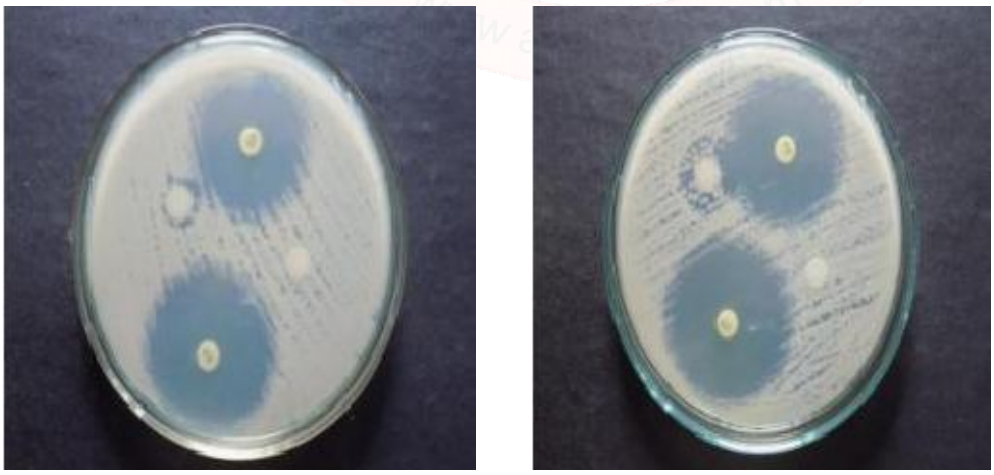

Fig. (d) staphylococcus epidermidis **Fig. (e) Bacillus brevis**

Fig. 3. Zone of inhibition of the antibacterial activity of $NiFe_2o_4$ NPs against (a) Salmonella typhi (b) Proteus (c) Klebsiella pneumoniae (d) staphylococcus epidermidis, (e) Bacillus brevis

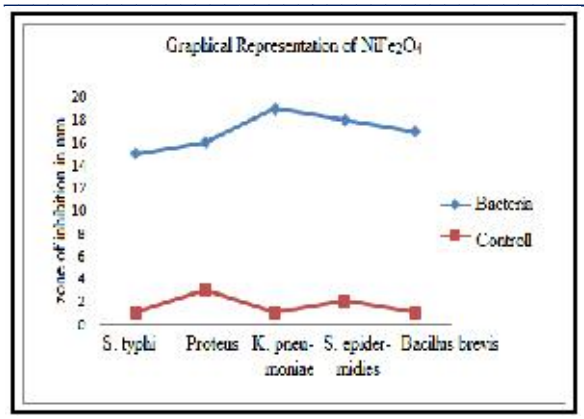

Fig. 4. Graphical representation of $NiFe_2o_4$ against different bacteria

CONCLUSION

Nickle ferrite nanoparticles, have been successfully synthesized by sol-gel technique. The XRD analysis reveals that the prepared samples exhibit a inverse spinel structure with sizes approx 30nm. The FTIR spectra corroborate the formation of spinel ferrite structure in all the samples. The antibacterial efficacy was tested against gram negative and gram positive bacterial strains and the results show an enhancement in the activity of Nickle ferrite. The improvement in the biocidal activity is attributed to the increase in the surface to volume ratio of the nanoparticles which enhances the contact area with the microbes. Thus the Nickle ferrite nanoparticles with good magnetic and antibacterial properties can offer great promises in biomedical and pharmaceutical applications.

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SYNTHESIS AND ANTIMICROBIAL SCREENING OF SOME NEW NITROGEN CONTAINING CHLOROSUBSTITUTED AZOLES AND THEIR GROWTH PROMOTING AND CURATIVE IMPACT ON *OYSTER MUSHROOM* CROP

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ABSTRACTS

The pyrazoles is the one of the mostly studies heterocyclic compounds owing to its applicability as drugs, dyes, anaesthetics and also their use as antioxidant in fuels. They are also well known for their applications in medicinal chemistry and agricultural fields. Some examples are the herbicidal (difenzoquat), fungicidal (raxil), anti-inflammatory (phenylbutazone) and fungal infections inhibitor (fluconazole). Imidazole analogues of pyrazoles were also reported to have herbicidal and pesticidal properties as many pesticides shows their derivatives as a one of the constituents. Some of their derivatives also show plant growth regulatory activities. Considering their curative role in the field of agriculture as a fungal infection inhibitor and plant growth regulator, we have attempted to synthesise some imidazole substituted pyrazoles from substituted flavones. In this context, we have synthesized analogues of 1-phenyl-3-(2-hydroxy-5-chlorophenyl)-4-benzoyl-5-[2-substituted-4-(2'-hydroxy-5'-chlorophenyl)imidazolo] pyrazole from 1-phenyl-3-(2-hydroxy-5-chloro phenyl)-4-benzoyl-5-substitutedpyrazoles. Which was prepared by the reaction of substituted-3-benzoyl-6-chloroflavone with phenylhydrazine hydrochloride in 1,4-dioxane containing a little piperidine. The newly synthesised titled compounds were screened for their antimicrobial efficacy against some mushroom crop damaging organisms like bacteria viz. Burkholderia gladioli, Pseudomonas stutzeri, Pseudomonas fluorescene, Pseudomonas alcaligens and fungi viz. Verticillium fungicola, Gliocladium roseum (Link) Bainier and also studied their impact on phytotic growth of Oyster mushroom crop.

Keywords: *Chlorosubstituted pyrazoles, imidazolopyrazoles, acetylpyrazoles, antimicrobial activity and curative impact on Mushroom spp.*

INTRODUCTION

Synthesis of substituted pyrazoles has been undertaken by many workers using appropriate reaction conditions and solvent mixture owing to their particular applications. The literature survey reveals that, pyrazole derivatives have great importance in the fields of pharmaceutical, agriculture and medicinal chemistry. They are known for their antifungal[1], antibacterial[2-5], antiviral[6], antitumor[7], antipyretic[8], analgesic[9], anticancer[10,11], antileishmanial[12-14], antinociceptive[15], antioxidant[16], antiproliferative[17], anti-inflammatory[18], antipsychotic[19] and anticonvulsant[20] activities. Besides this, they also act as plant growth promoter and showed herbicidal[21, 22] properties.

Nimbalkar *et al.*[23] synthesized pyrazoles from 3-iodoflavanones by treatment of isonicotinic acid and thiosemicarbazide in pyridine medium. Sharshira *et al.*[24] had undertaken the synthesis of pyrazole-1-sulphonamides using p-sulfamylphenylhydrazine in glacial acetic acid. Sridharan *et al.*[25] reported the preparation of 1-pyrazole acid triphenyl imidazole. Cyclization of benzil with appropriate aromatic aldehydes in presence of ammonium acetate and amino pyrazole yields 1-cyanopyrazole 2-substituted phenyl-4,5-diphenyl imidazole.

The present work deals with the synthesis of chlorosubstituted pyrazoles, α-amino ketone derivative of chlorosubstituted pyrazoles, chlorosubstituted 4-benzoyl-imidazolo-Δ^2-pyrazoles and their derivatives by using chlorosubstituted 3-aroyl-6-chloroflavones and phenylhydrazinehydrochloride in 1,4-dioxane containing a little piperidine and their screening for their impact on phytotic growth of *Oyster mushroom* and also against some causative organisms like bacteria *viz. B. gladioli, P. stutzeri, P. fluorescene, P. alcaligens,* and fungi *viz. V. fungicola, G. roseum (Link) Bainier.*

MATERIAL AND METHODS

The structures of all the newly synthesised compounds, reported herein, were confirmed on the basis of their elemental analysis, chemical properties and spectral data such as UV, IR and ^{1}H NMR. The melting points were recorded using Thiele's apparatus and all are uncorrected. The purity of newly synthesized compounds was checked by TLC using solvent combination.

Preparation of 1-phenyl-3-(2-hydroxy-5-chlorophenyl)-4-benzoyl-5-N-substituted-[(2'-hydroxy-5'-chlorophenyl)ethanonylamino] pyrazole (3a-b):

1-Phenyl-3-(2-hydroxy-5-chlorophenyl)-4-benzoyl-5-N-subsituted-aminopyrazole (1a-b) (0.01M) was refluxed with 1-(2-hydroxy-5-chlorophenyl)-2-bromoethanone (2) (0.01M) for 1 hour in absolute ethanol. After cooling, the reaction mixture was decomposed in ice-cold water. The product, thus separated, was filtered and crystallized in ethanol-acetic acid mixture to yield the compound 3(a-b).

Compound (3a) $C_{30}H_{21}N_3O_4Cl_2$: Dark brown amorphous solids, m.p. 103 ^oC, yield 77 %, Elemental analysis (%): **C** 64.49/64.53; **H** 3.74/3.79; **N** 7.44/7.52; **O** 11.40/11.46; **Cl** 12.63/12.70. **UV** (ethanol): λ_{max} 670 nm, n→ π* transition. **IR** (KBr) (cm^{-1}): 3600-2800 (-OH stret.), 3084.72 (Ar. C-H stret.), 2917.72 (Ali. C-H stret.), 1618.54 (C=O stret.), 1601.63 (C=N stret.), 1354.62 (C-N stret.), 771.64 (C-Cl stret.). **^{1}H NMR** (δ ppm): 1.3 (s, 2H, -C**H**$_2$), 6.0 - 6.9 (m, 16H, Ar-**H),** 5.5 (s, 1H, C**H**=C-OH), 10.8 (s, 2H, O-**H**).

Preparation of 1-phenyl-3-(2-hydroxy-5-chlorophenyl)-4-benzoyl-5-[2-substituted-4-(2'-hydroxy-5'-chlorophenyl)imidazolo]pyrazole (4a-b):

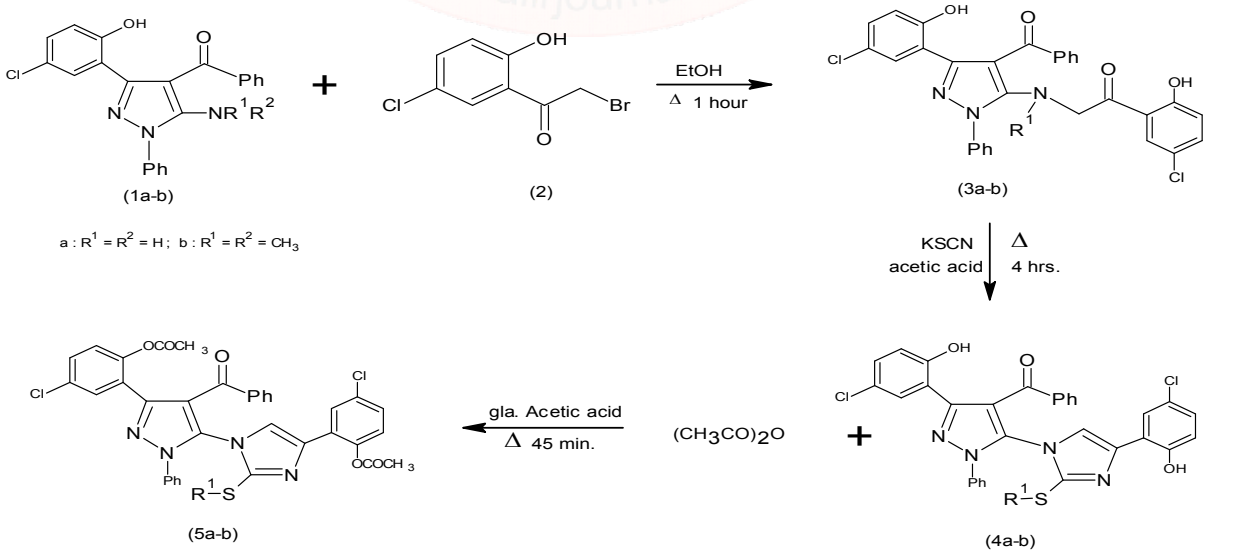
1-Phenyl-3-(2-hydroxy-5-chlorophenyl)-4-benzoyl-5-N-substituted-[(2'-hydroxy-5'-chlorophenyl) ethanonylamino]pyrazole (3a-b) (0.01M) was refluxed with potassium thiocyanate (0.01M) for 4 hours in glacial acetic acid. After cooling, the reaction mixture was poured in ice-cold water. The product thus separated was crystallized from ethanol to get the compound 4(a-b).

Compound (4a) $C_{31}H_{20}N_4O_3SCl_2$: Brown amorphous solid, m.p. 129 ^oC, yield 63 %, Elemental analysis (%): **C** 62.06/62.11; **H** 3.29/3.36; **N** 9.30/9.35; **O** 7.92/8.01; **S** 5.28/5.35; **Cl** 11.77/11.83. **UV** (ethanol): λmax 650 nm nm, n→ π* transition. **IR** (KBr) (cm-1): 3500-2800 (-OH stret.), 2916 (Ar. C-H stret.), 1646.34 (C=O stret.), 1566.37 (C=N stret.), 771.35 (C-Cl stret.), 682.36 (C-Cl stret.). **^{1}H NMR** (δ ppm): 2.6 (s, 1H, -S**H**), 6.8-8.1 (m, 16H, Ar-**H**), 12.13 (s, 1H, H-bonded -O**H**).

Preparation of 1-phenyl-3-(2-acetyloxy-5-chloro phenyl)-4-benzoyl-5-[2-substituted-4-(2'-acetyloxy-5'-chlorophenyl)imidazolo]pyrazole (5a-b):

1-Phenyl-3-(2-hydroxy-5-chlorophenyl)-4-benzoyl-5-[2-substituted-4-(2'-hydroxy-5'-chlorophenyl)imidazolo]pyrazoles (4a-b) (0.01M) was refluxed with acetic anhydride for 45 min. in glacial acetic acid. After cooling, the reaction mixture was decomposed in water and the product thus separated, was filtered and crystallized from ethanol-acetic acid mixture to get the compound 5a-b.

SCHEME:



ANTIMICROBIAL SCREENING

The newly synthesised titled compounds were tested for their efficacy against the pathogens responsible for *Mushroom* crop damage. The cultures of bacterial and fungal species were procured from the NCIM, NCL, Pune and MTCC, Panjab University, Chandigarh. The inhibitory effects of these compounds against some bacteria and fungi were tested using cup plate diffusion method are tabulated in Table-A. The screening results indicate that the compound 1a-b, 3a-b and 4a-b and 5a-b showed good to moderate antibacterial and antifungal activities against bacteria *Burkholderia gladioli, Pseudomonas stutzeri*, *Pseudomonas fluorescene, Pseudomonas alcaligens* and fungi *Verticillium fungicola*, *Gliocladium roseum (Link) Bainier.*

The discs of *Cabendizum* (10mcg/disc) and *Gentamycine* (10mcg/disc) were used as positive controls. The zones of inhibitions were recorded in millimetres by using Himedia Zone Reader Scale. The results obtained in the antimicrobial study are given in table-A.

Table-A: Antimicrobial screening of titled compounds against Oyster mushroom crop pathogens

S.N.	Compounds	Zone of inhibition (mm)					
		Bacterial pathogens				Fungal pathogens	
		B. gladioli	*P. stutzeri*	*P. fluorescene*	*P. alcaligens*	*V. fungicola*	*G. roseum*
1.	1a	15	14	11	14	13	11
3.	3a	18	15	18	14	10	12
5.	4a	22	22	25	19	17	17
7.	5a	16	16	09	11	12	11
9.	*Carbendizium*	--	--	--	--	09	09
10.	*Gentamycine*	08	08	08	08	--	--

GROWTH PROMOTING IMPACT OF TEST COMPOUNDS

The experiment was conducted at the ICAR affiliated Krushi Vidyan Kendra, Durgapur (Badnera) Dist. Amravati. A species of Oyster mushroom *Pleurotus pulmonarius* has been cultivated in the culture house of the centre. The spawns of experimental species were procured form genuine agricultural agencies.

The experimental setup was divided into Part-A (*Control)* and Part-B (*Treated*). In the Part-A, the bed of control experiment, spawns were inoculated and cultivated by the conventional methods. The beds from Group-B were treated with the solutions of test compounds. The spawns of mushroom species were treated with the test compounds solution before inoculation in the respective beds. The uniform size beds of substrate were prepared in polythene bags filled with sterilized soybean straw. The spawns treated with the solutions of titled compounds were inoculated in the beds (packets) and subjected to incubate for mycelium running for 25-30 days in incubation room.

After completion of inoculation period, the spawn packets were transferred to cultivation house and opened and irrigated as per the need. The relative humidity of culture house was maintained. When the first primordial initiation was observed the test compounds were sprayed on the mushroom with specific interval of time. Mushroom crop was harvested before the fruiting body showed any splitting on the edges. The yields of mushroom crop from various bags with different parameters viz length, diameter, weight and colour were recorded and tabulated in table-B.

Table B: Effect of titled compounds on Oyster mushroom: Pleurotus pulmonarius

	Compounds	D(cm)	T(cm)	L(cm)	Weight of Dry Bags (gm) (After Harvesting)	Total Weight (gm)		Colour
						Fresh	Dry	
1.	1a	7.2	0.5	6.1	0.927	211	19.43	White
2.	3a	7.0	0.5	6.2	0.930	207	19.37	Creamy
3.	4a	10.9	0.7	7.0	0.972	232	24.43	White
4.	5a	9.1	0.6	6.6	0.944	221	21.23	Grey
5.	1,4-Dioxane	6.0	0.4	6.1	0.990	176	19.13	White
6.	Control	6.8	0.3	5.5	0.853	204	20.00	White
D = Diameter ; T = Thickness ; L = Length								

ANALYSIS OF MUSHROOM SAMPLES TREATED WITH TEST COMPOUNDS

The samples of *P. pulmonarius* collected during the experiment were sun-dried and immediately analysed with special reference to % crude fibre, % crude protein and elemental detection (N, P, K and S). The analysis of crude fibre percentage of the samples was carried out at Food Testing Laboratory, Krishi Vigyan Kendra, Durgapur (Badnera) Dist. Amravati using Pelicans FBS-06 (P) Laboratory Manuals & AOAC Method, whereas percentage of crude protein and element detection were determined at Analytical Lab, using Leaf method of analysis. The Kjeldahls method, UV spectrophotometer and Flame photometer were used for the analysis of N, P, K and S elements. The results of analysis obtained for treated mushroom samples are tabulated in table no. C:

Table C: Analytical results of dry Oyster mushroom: P. pulmonarius treated with titled compounds.

S.N.	Sample	% of Crude Fibre	% of Crude Protein	% N	% P	% K	% S
1.	1a	9.92	18.03	2.886	0.5371	2.817	0.1328
2.	3a	9.80	12.74	2.039	0.6322	1.984	0.1101
3.	4a	13.28	23.10	3.696	0.4662	2.844	0.1484
4.	5a	11.04	21.43	3.429	0.3840	2.932	0.1388
5.	1,4-Dioxane	8.06	13.29	2.127	0.275	2.346	0.1358
6.	Control	5.64	15.98	2.558	0.367	2.747	0.1412

RESULTS AND DISCUSSION

In the present study newly synthesized 1-phenyl-3-(2-hydroxy-5-chlorophenyl)-4-benzoyl-5-N-sub situted-aminopyrazole (1a-b), 1-phenyl-3-(2-hydroxy-5-chlorophenyl)-4-benzoyl-5-N-substituted- [(2'-hydroxy-5'-chloro phenyl) ethanonyl amino]-pyrazole (3a-b), 1-phenyl-3-(2-hydroxy-5-chlorophenyl)-4-benzoyl-5-[2-substituted-4-(2'-hydroxy-5'-chloro phenyl) imidazolo]-pyrazole (4 a-b) and 1-phenyl-3-(2-acetyloxy-5-chlorophenyl)-4-benzoyl-5-[2-substituted-4-(2'-acetyloxy-5'-chlorophenyl) imidazolo]pyrazole (5a-b) were tested for their antibacterial and antifungal efficacy against some *Mushroom* crop damaging pathogens includes bacteria *viz. B. gladioli, P. stutzeri*, *P. fluorescene, P. alcaligens* and fungi *viz. V. fungicola, G. roseum (Link) Bainier* From the results, it has been observed that the titled compounds showed noticeable antimicrobial activities.

Pleurotus pulmonarius, treated with test compounds. When the treated and control species of mushroom were compared with reference to their morphological characters, it was interesting to note that the treated species exhibited significant growth in diameter and thickness of caps as well as lengthening of stipes. The analytical results obtained for all the treated mushroom samples clearly show the increase in the value of crude fibre percentage as well as the crude protein percentage. The presence of elements like N, P, K and S were also analysed in the treated mushroom samples.

CONCLUSION

On the basis of characterisation, it is concluded that, the synthesis of titled compounds was achieved successfully. The antimicrobial screening of newly synthesised compounds showed these have great potential towards mushroom crop pathogens.

The *Oyster mushroom* species ie. *P. pulmonarius* showed significant growth in diameter, thickness and lengthening of stipe that reveals the curative and growth promoting properties of the titled compounds.

The newly synthesised imidazole blends of azoles also showed noticeable enhancement in the nutritive values. The increase in crude fibre percentage and crude protein percentage indicates titled compounds were found more effective owing to enhancement in the nutritive value.

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THEORY, COMPUTATION AND SIMULATIONS CAN BE STAND ALONE METHODOLOGY AS MUCH AS THE REPRODUCIBLE EXPERIMENTAL DETERMINATION OF PHYSICAL QUANTITIES.

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ABSTRACT

Generally, with references to Chemical Sciences, theory is meant for explaining experimental observations, theoretical calculations are made to sort out experimentally observed anomalous trends and exceptional material characteristics besides in connection with the supportive spectroscopic features. Theory more are less gets validated by the extent to which the calculations and conclusions are helpful in interpreting experimental findings. The perspective in this contribution is to learn how to be consistent within the theoretical frame work and confidently establish trends in calculated results to gain insights into the physical systems under study so that these inferences can be transferred to the experimental domains to design novel experiments.
http://www.ugc-inno-nehu.com/ser-sa/SER-1-Stacking_benzene_dimer.doc
http://ugc-inno-nehu.com/ser-sa/SER-2-BD-HR-BENZ.doc
Three different instances are being enumerated to highlight the points of view as implied in the title of this contributed paper.

The instance of reconciling with the fact that the PMR spectrum of a Polymer chain can become interpretable by invoking a cyclic dimeric structure referred to as the "fictitious spin book keeping" structure.
http://www.ugc-inno-nehu.com/events-2018.html#bhc
(1) The Quantum Mechanical Calculation for Geometry Optimization (G.O.) can handle not only isolated molecules, but also ensemble of structures. I certain cases when the G.O. is applied to an ensemble of molecules, this can conveniently indicate what is the energy optimized equilibrium arrangement of the ensemble of molecules, sometimes even unusual bonding between units or break up of units are possible when there are more number of identical units. Simple example to quote is a cluster of 'n' number of water molecules drawn in structure with arbitrary locations. In such a cluster of material mostly known in liquid state, random diffusions of various degrees of freedom are possible which have to be explicitly taken into account during the energy minimization applying calculus of variations. Such a requirement may be to get results by the G.O. calculations which are apparently much closer to reality.
http://www.ugc-inno-nehu.com/events-2017.html#E09
(2) To this context, two molecules of totally different compounds (which in reality are never considered together for forming useful compounds) can be drawn on structure editor and submitted for a Q.M. calculation of physical properties of the combined system. Certain quantities like the atomic charges, dipole moment and spectroscopic properties (specifically Proton NMR patterns) can reveal the possible nature of interactions which may be revealing certain trends for compounds which really matter in the laboratories.
http://www.ugc-inno-nehu.com/ISC105-OSU/isc105-doc.pdf

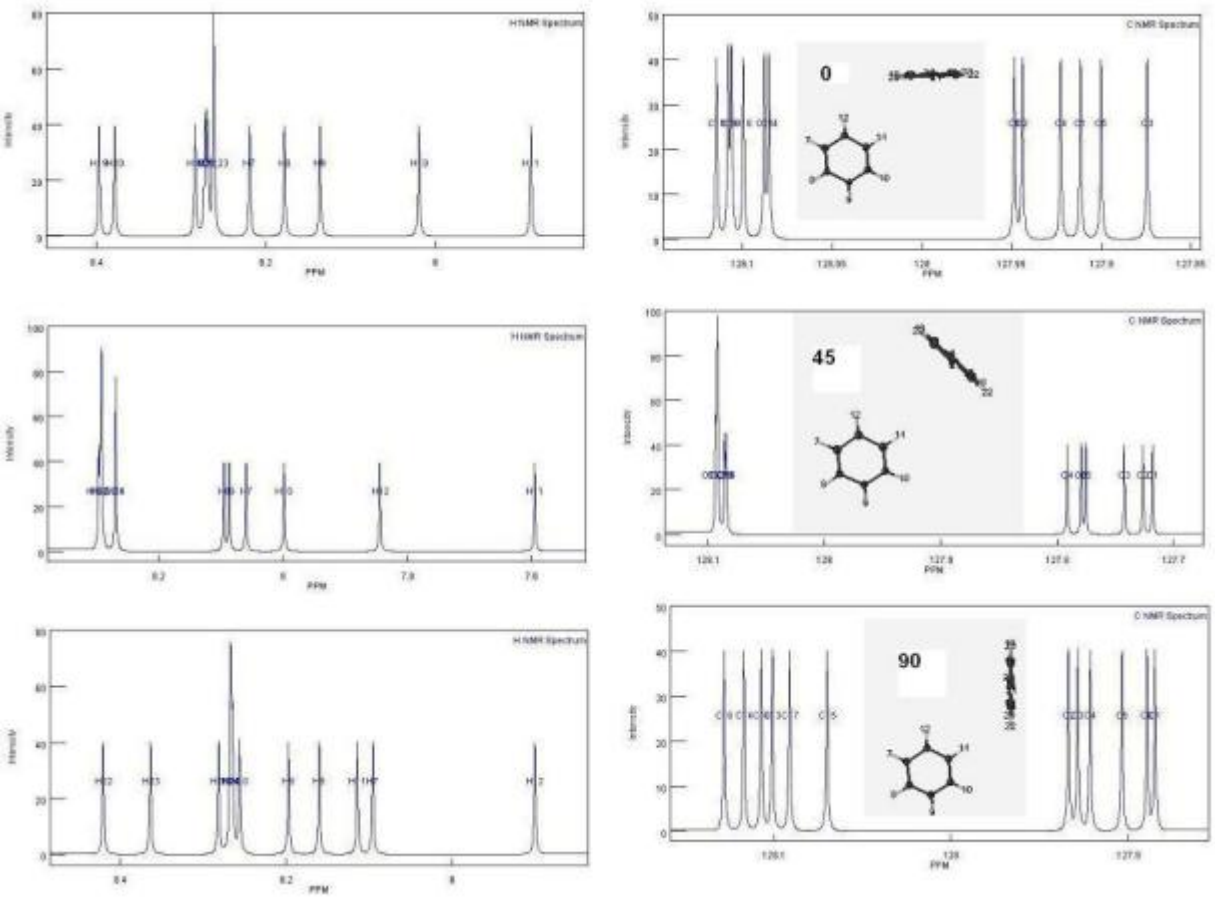
Keywords: *Quantum Theory, Quantum Mechanical Methods, Computational Chemistry, Calculation of Physical Quantities, Theoretical Modelling of Physical Systems, Simulation, Inferences on Trends, Insights into Phenomena and Mechanisms, Spectroscopic Techniques, Determination of Spectral Properties.*

1. AN ELEMENTARY TOPICAL EXPOSURE WITH BENZENE DIMER

A beginning can be made with the simple case of benzene-dimer. The benzene dimer seems to be encountered in vapour state, and certain rotational constants, seems to have been amenable for experimental measurement by microwave pulsed-nozzle FT experiments. However, it is not at all difficult to draw two identical benzene molecules in varying relative disposition and calculate

theoretically molecular properties. Three such dispositions are described and depicted below:

FIG.1 On the Left Hand Side, ^{1}H (proton) NMR is shown, and on the Right Hand Side, the ^{13}C calculated spectrum.



The benzene dimers above were generated by first drawing an optimized benzene structure and then, copying the same, and pasting and placing at the appropriate centroid-separation distance. The inclination of one of the structure is changed with respect to a vertical axis; and thus the three different dispositions above were obtained. Each one of them submitted for NMR calculation without optimizing the dimer.

In the ^{13}C NMR, the two benzene molecules have grouped into two different ranges of Chemical shift. For ^{1}H NMR the pattern is so evident; Obvious changes in the range of chemical shifts of the rings are evidenced for the two rings in case of both nuclei.

Because the dimers are themselves not optimized, the term “motives” may not be applicable. Never the less the results are informative.

The importance of such calculations would be much more evident when non bonded aromatic rings occur in the neighbourhood of each other due to the secondary and tertiary structures of biological macro molecules. Typical contexts are described (1) in connection with occurrence of packing of aromatic rings against tryptophan residues in proteins. Generating patterns of such Calculated NMR spectra and cataloguing might be helpful in identifying relative orientations by using crystallographic data, generating such structures in the structure editors and submitting them for NMR calculations. It may not be necessary to handle any such dimer structures experimentally and obtain NMR spectra from spectrometers.

THE NMR SPECTRA for this structure of DIMER can be simulated (2) using FTNMR Simulation software using the Chemical Shift values obtained from QM Calculations and the tabulated J coupling values for benzene protons at VARIOUS Magnetic Field values corresponding to proton frequency from 100MHz to 2000MHz (2 GHz). Commercial spectrometers currently available have a maximum frequency value 1GHz. Thus the value of simulated spectra is that most of the advantages of obtaining spectra at Higher

fields would be available in frequency ranges in which one cannot obtain experimental spectra for want of spectrometers at such high fields. More over the calculated values of chemical shifts and the J values from tabulations can be used to simulate at higher fields to obtain simplified patterns for recognition of occurrences of aromatic ring stackings / packings. Such set of simulated spectra are depicted in FIG.3. The NMR Simulation software used for the calculations of spectra in FIG.3 is from the link given in the webpage for nehu-saif (3). This illustrates the perspective QM Calculation together with spectral simulation can stand alone without the necessity to refer to experimental values.

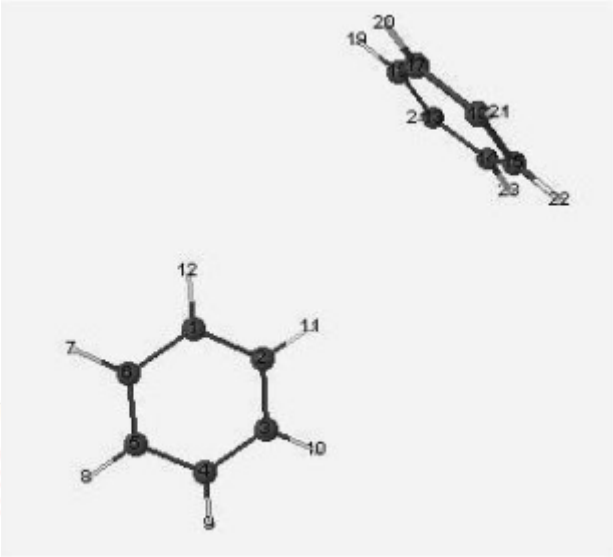


FIG.2 A dimeric structure for NMR Simulation (See Fig.3)

2. A BIT MORE LEAD INTO THE TOPIC OF THE PAPER: POLYMER PMR

Having got an exposure to the theme of this contribution, a bit more lead into the implications of the theme would be possible by considering the case of styrene polymer, where a stand- alone theoretical result can substantiate the practically fictitious conjecture. To explain this case of polymeric styrene further, the PMR spectrum of a polymeric styrene could be explained and simulated convincingly by NMR spectral parameters attributable to a cyclic dimer of styrene. Thus this cyclic dimer structure which seemingly is a much simpler chemical structure as compared to the structure of the polymer is termed as “fictitious spin book keeping structure”. This further sounds as a strange situation when the literature search does not have any record of this particular dimeric isomer as a known compound but another isomer is well known.

Thus an effort could be made by optimizing a styrene isolated molecule to obtain a convincingly stable equilibrium structure and draw two such identical molecules conveniently poised or forming a dimer when the two molecules are subjected to Geometry optimization. If the dimer is more stable than two identical monomers, the variation principle should lead (FIG.4.) to the more stable configuration for the two molecules together. In such a case what is the resulting isomeric conformations and for that resulting stable dimer what are the chemical shift values obtained by QM calculation and how the simulated spectrum would look in comparison to the experimental spectrum (FIG.5.). This also would indicate a reason if anything specific exists, as to why this compound is not known in literature. (4)

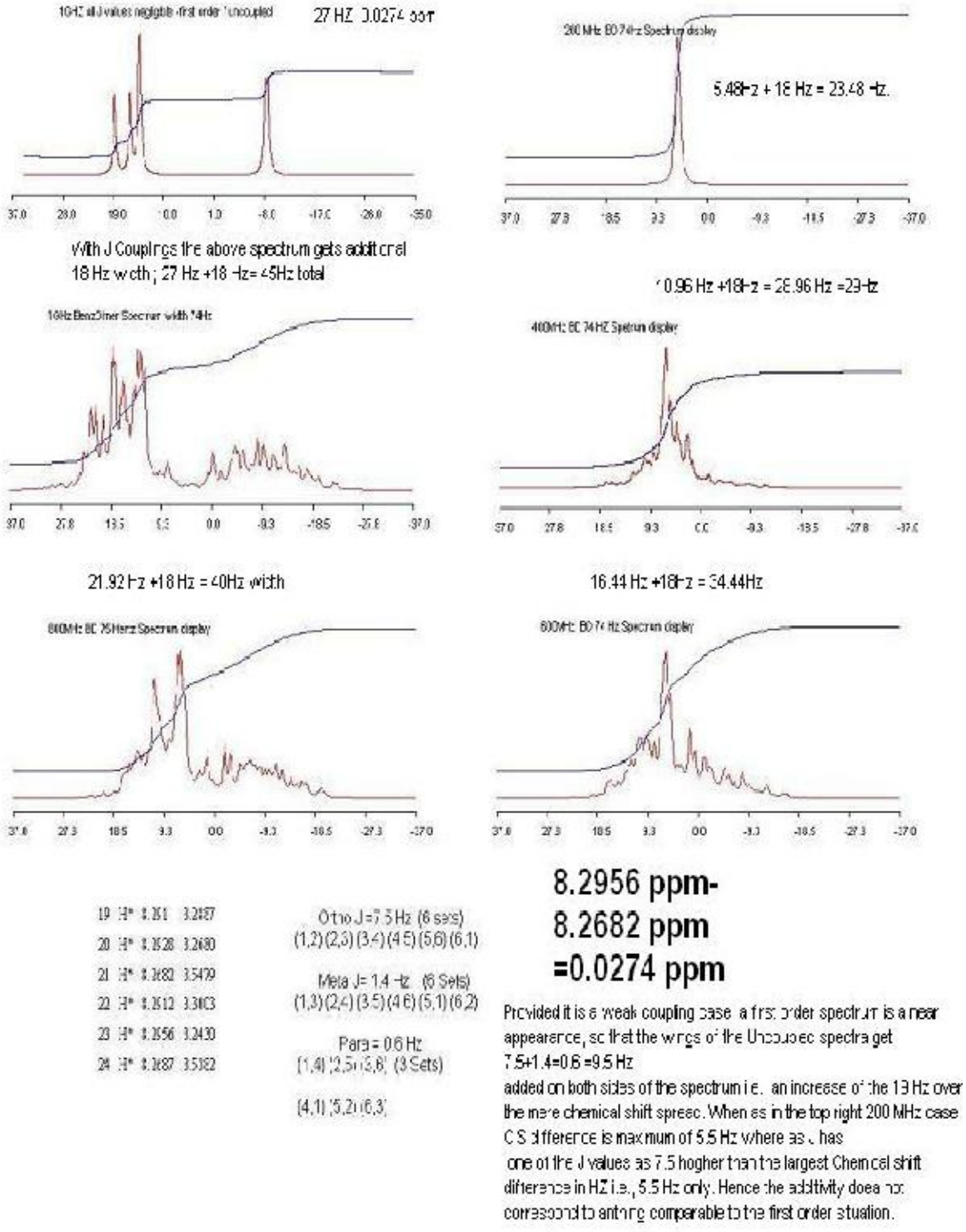


FIG.3: PMR simulation of BENZENE DIMER at several proton NMR frequencies (Spectrometer frequencies).

The simulated spectra beyond 1GHZ is currently not possible to obtain experimentally since spectrometers are not available at these frequencies; benzene dimer itself is such an imaginary compound that it is not possible to get sample to supply for recording any spectra.

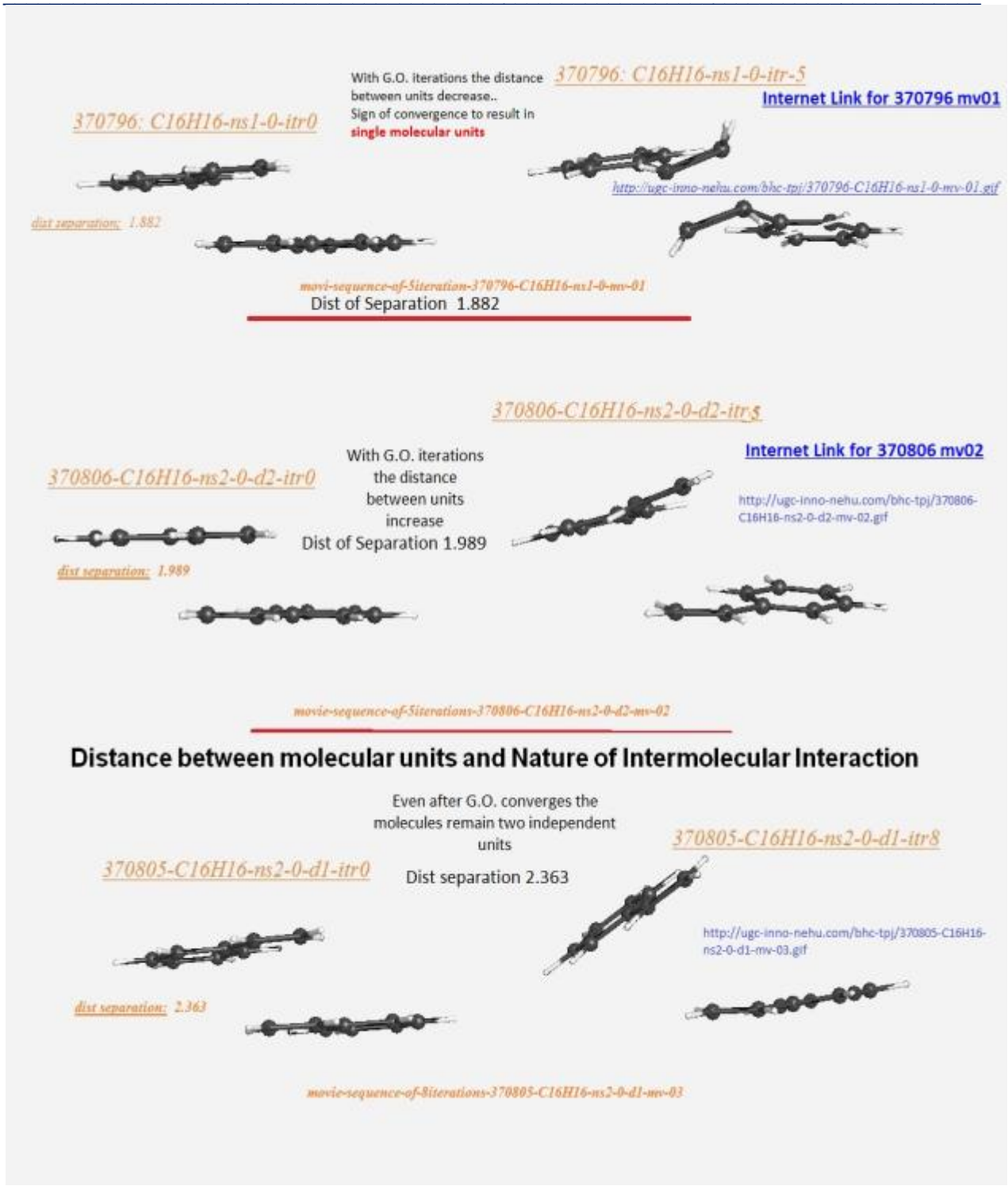


FIG.4. Images of the situation corresponding to visualization of iterative sequences.

The two molecules initially placed at different distances; at a closer distance the propensity for the formation of dimer increases. These details are illustrated elaborately at reference (4). The dimeric structure and the corresponding calculated NMR spectrum are depicted in FIG.5. It could be found that the required conformation does form by such dimerization and the calculated NMR structure also resembles the experimental pattern than the other possible conformations .

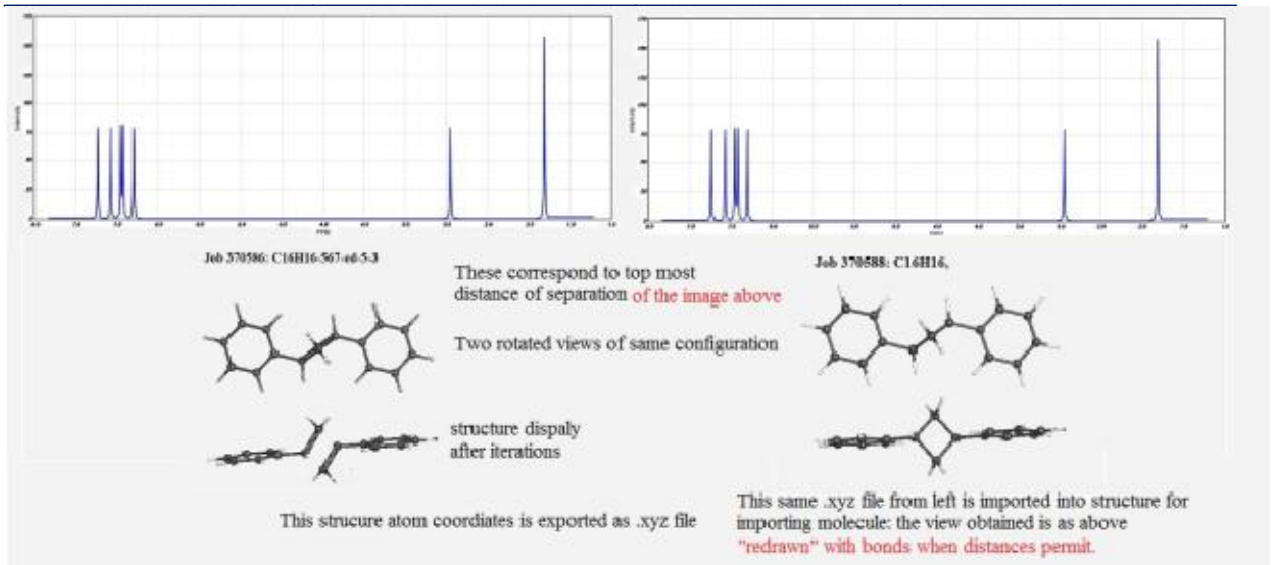


FIG.5. Dimer formed and PMR spectra calculated; different views of resulting dimer structure.

3. TOPICAL APPROACH TO INCREASE EFFICIENCY OF CHEMICAL PLANT

The next illustration would be that of handling an ensemble of water molecules (5). The situation is when small organic dye molecules present in industrial effluents pollute the water and by the AOP process the task is to decompose and degrade these organic pollutants. The TiO_2 semi conductor material with appropriate band gap energies can be irradiated with em radiations to produce electrons and holes. The water molecules from the bulk reach these surfaces and reacting with holes can produce radical products by splitting water and the reacrtive radicals further react with dye molecules at the surface and decompose them. The way QM studies can be made for this context is to consider the radical species, and the dye molecules together and submit the combination for QM investigation of the reaction characteristics. But the production of radical product from water in.situ at the surface of the TiO_2 and the reaction with dye molecule requires a consideration of diffusion phenomena and which is not a simple task, For example the FIG.7 displays a result: That 12 water molecule ensemble is considered as a molecular system to be subjected to Geometry Optimization. And, this system is attributed to have 4 -ve charges and submitted for GO.

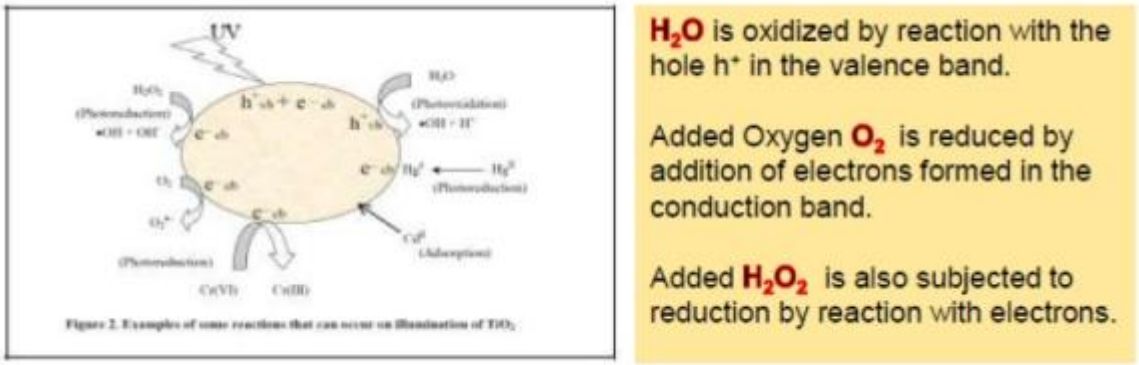


FIG.6. The Solid TiO_2 surface and the reactions envisaged in the polluted water medium.

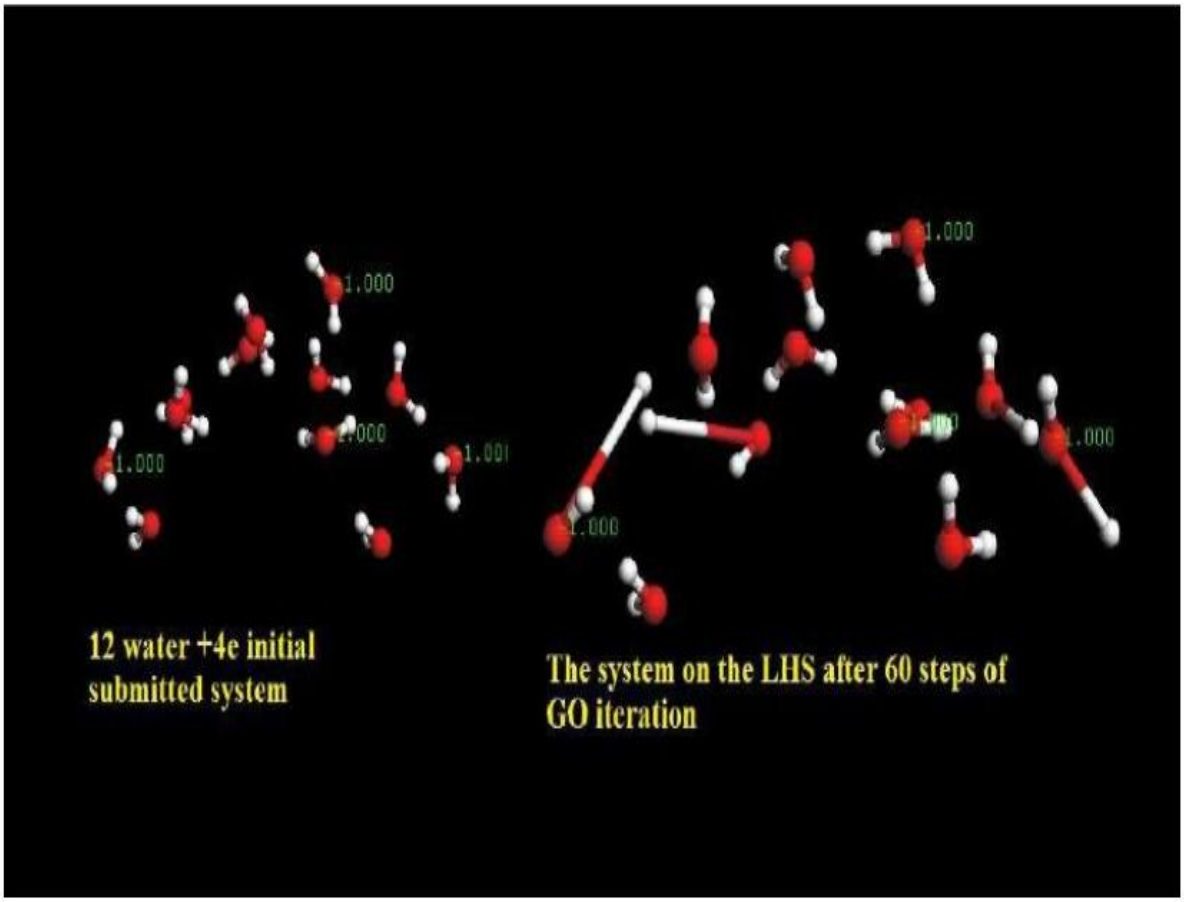


FIG.7. 12 water molecules with +4e added is submitted for G.O. by PM3 semiempirical method at ARGUSLAB computational chemistry portal. On the RHS is the situation of this system which has gone through 60 iterative steps of GO (not yet converged).

The situation on the RHS indicates certain molecules have one or both of their bonds elongated. It was ensured that the intermediate state when the same 12 water system is subjected to GO without adding 4e to it, this peculiarity of bond elongation does not result for the 60 steps or even till the end when the system attains 12 water attains energy minimized equilibrium distribution and GO converges. During this time interval of 60 steps, the evoloution would involve a diffusion process in water which would be rearranging the molecules. Thus at intermittent iterative steps it is necessary to stop the calculation process, edit manually based on chemical intuition and continue the iterative optimization from that stage onwards. These kind of manoeuvres seem to yield some insights as to how exactly to regulate the radical productions and reduce the radical recombination processes to increase the efficiency of AOP. These results can be appropriately translated into experimental conditions while designing water purification plants. These details as the chemists would require to know have been pointed out in reference (5).

FIG. 8. Is a situation that depicts a kind of end result as purportedly what happens in the experiments. Such studies are mostly are theoretical investigations of experimental phenomena, but till the end no comparison with experiment is required and sometimes the results when they are not the same as what experimentally thought off, then calls for additional theoretical studies, finally to be leading to novel experiments

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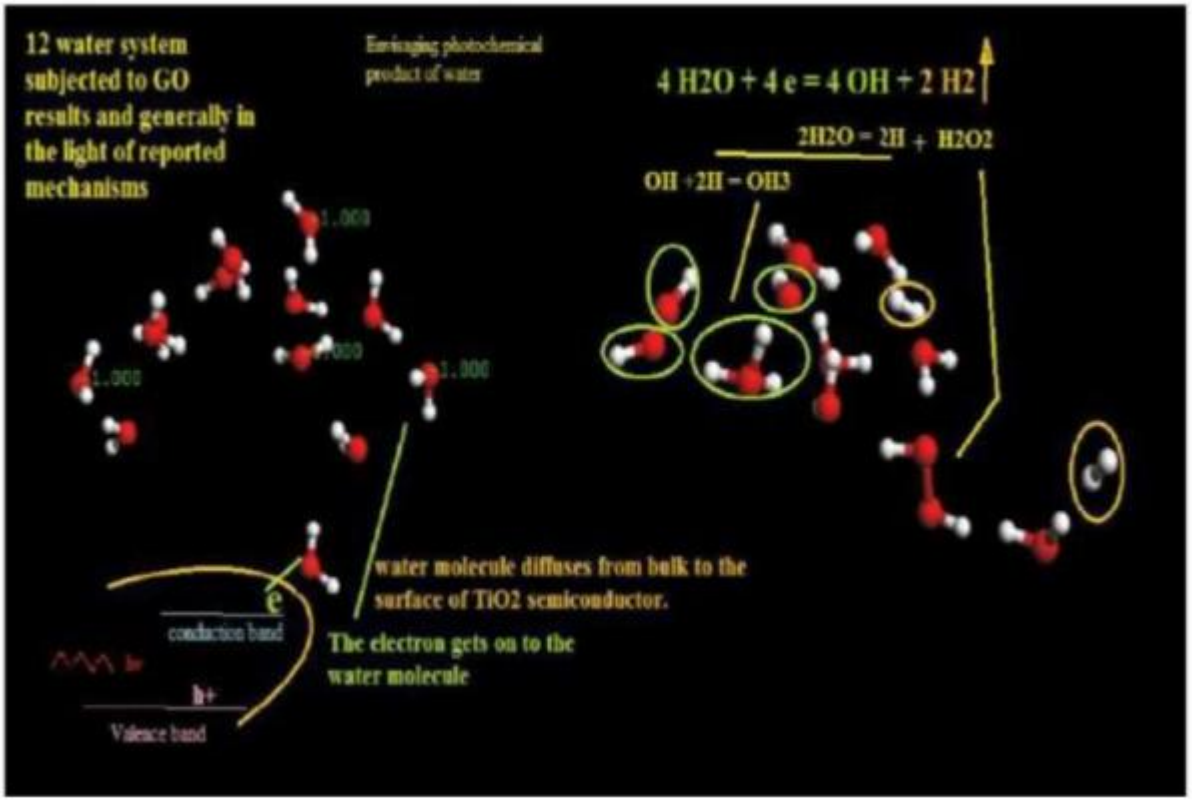

FIG.8. An end convergent result, similar to experimentally envisaged production of radicals, and H_2 evolutions stoichio metrically accounted. From ref (5).

4. FOR THE INTEREST IN CHEMISTRY FROM OUT OF THE LAB INFORMATION

The next system to consider from the stand point of the theme of this paper is the combined molecular system of Methane and Benzene. This combined system (one gaseous and the other liquid in room temp) though experimentally not encountered in Chemical laboratories as any requirement for such a system, can be studied by QM abinitio methods. To consider in an elementary way, the Benzene has D_{6h} point group symmetry and there could be 6 bond dipole moments but net molecular dipole moment is zero. Similarly the Methane molecule ahs a Td symmetry and could have 4 bond dipoles and no net Molecular dipole moment. These molecular dipole moment situations of the two highly symmetric molecules are borne out by QM methods. However, when the two molecules with their individually optimized molecular geometry are drawn together at a distance of separation of about 5 Angstroms there is a non vanishing net dipole moment generated for the combined system and according to the calculation engine such a Dipole Moment is indicated to be located somewhere in the common region for the two molecular system. No GO is carried out only simply single point energy calculation which also calculates the net dipole moment. This raises the question as to how Charge movement occurs to cause a net transfer of charge from one of the molecule to the other there can be net equal and opposite charge separation and a well defined dipole moment. A calculation of NMR spectrum, particularly PMR chemical shifts, results in a varied PMR pattern than the simple two line (one benzene line at aromatic protons vale intensity 6 & one methane proton line at methane chemical shift value with intensity 4) for the non interacting systems. This study gets an elaborate treatment with more involved consideration. Obviously a Benzene+Methane system is not of much relevance to chemical study.

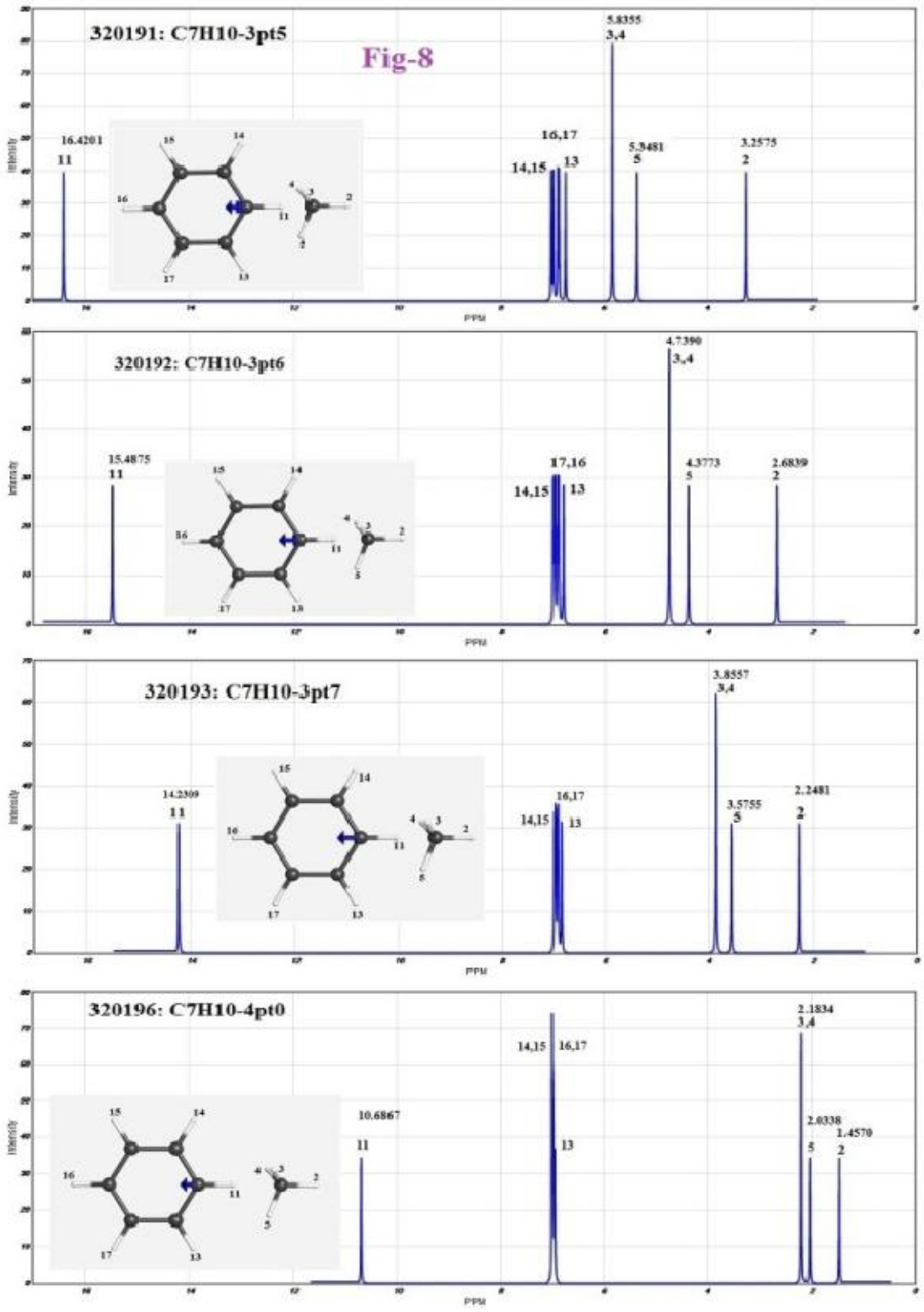

FIG 9. A typical example of the combined Methane & Benzene study, indicating net dipole moment, variation of proton NMR pattern indicating atomic charge variation merely at a farther distance compared to bond lengths.

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5. simulator file can be downloaded to install the simulation software in the computer.
6. Take proper care at the instance of downloading and installing.
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EVALUATION OF SPEED OF SOUND AND ITS ACOUSTICAL PARAMETERS IN LIQUID MIXTURES CONTAINING MAGNESIUM SALICYLATE TETRAHYDRATE AND WATER AT VARIOUS TEMPERATURES

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ABSTRACT

The propagation behavior of ultrasonic waves in solids and liquid systems is now well established as an effective tool for studying certain physical properties of materials. The nature of molecular interactions interms of physical parameters can be well understood from the data obtained by ultrasonic wave propagation parameters such as ultrasonic velocity, adiabatic compressibility, free length, relative association etc. Ultrasonic technique is sensitive technique which is reported as complementary to other techniques like IR, NMR, UV Spectroscopy etc. Owing to the importance of molecular interactions with variation in concentration of one component of medium, the measurement of ultrasonic velocity, density and viscosity has been carried out for liquid mixtures of magnesium salicylate tetrahydrate in water. Present investigation has been undertaken to study the nature of interactions between magnesium salicylate tetrahydrate with water at 298.15K, 303.15K and 308.15K temperatures and 0.1.M, 0.01M and 0.001M concentration. Ultrasonic velocity values show maxima and minima with respect to concentration in the mixture. The origin of maximum in the low concentration region is due to long-range order giving rise to hydrogen bonded structure. The variation in the calculated acoustic parameters shows some molecular interactions between solute and solvent in the binary liquid mixture

Keywords *– Ultrasonic velocity, adiabatic compressibility, density, molecular interactions.*

INTRODUCTION

Ultrasonic wave propagation in liquid has been the subjects of exhaustive research which has been carried out theoretically and practically. When solute is dissolved in solvent, there is interaction which takes place either in between solute-solvent molecules or solvent-solvent molecules. There has been large number of studies done on the molecular interaction in liquid system. There are many approaches and spectroscopic techniques used to determine the structure-function relation of molecules. All these methods are very useful in studying the structures of the compound as well as physicochemical characters. Interactions between atoms, group of atoms, ions and molecules vary widely with respect to their bond strength to differentiate these classes known as bond types. These classes are well suited for understanding and description of the majority of molecular systems. Molecular geometries are not just described by the topology of covalent bonds but as well as weak bonds contribute substantially to the evolution and conservation properties of bimolecular systems. Therefore it is highly desirable to understand the molecular interactions involved in the formation of molecular complexes. Among the techniques used, ultrasonic velocity measurements through liquid medium gain much more importance in assessing the nature of molecular interactions.

Though the numbers of techniques are used to study the molecular structures in mixtures but the complete understanding of the nature of intermolecular and intra-molecular interaction may not be possible by any single method. Ultrasonic methods have the added advantage of being less cost with efficiency comparable to other methods. Many researchers have used ultrasound to study the molecular interactions in aqueous solutions containing electrolytes[1-4]. The study of the propagation behaviors of ultrasonic waves in solids, liquids, liquid mixtures, electrolytes solutions, suspensions, polymers, soaps etc. is now rather well established as an effective means for examining certain physical properties of materials or medium, molecular interactions. Studies on speed of sound, viscosity, acoustic

thermodynamic, excess thermodynamic parameters and their deviations in the binary systems have been the subject of many investigations in the recent years. These investigations on different systems reveal specific interactions between the molecules of the component liquids, it has been reported by several workers[5-10].

EXPERIMENTAL SECTION

Materials : Analytical Range (AR) magnesium salicylate tetrahydrate is used in the present work. The solutions were prepared by using distilled water as solvent. The concentration range selected was 0.1M, 0.01M and 0.001M.

METHODS

All the weighing was done on digital electronic balance Model-CB/CA/CT-Series Contech having accuracy ± 0.0001g. The densities of the solutions were measured accurately using digital densitometer (Model-DMA Anton Paar). Viscosity of the solutions was measured by Ostwald's viscometer which was calibrated with benzene and double distilled water at all three temperatures. The values are accurate to ± 0.001 cp. The ultrasonic velocity was measured by using ultrasonic multi frequency interferometer (Model-M-83) supplied by Mittal Enterprises New Delhi, operating at 4MHz frequency with an accuracy of ± 2 m/s. The principle used in the measurement of ultrasonic velocity through medium is based on the accurate determination of wavelength of ultrasonic waves of known frequency produced by quartz crystal in measuring cell. The temperature of the solution was maintained by circulating water through the jacket of doubled walled cell. Measurements were made using constant temperature bath within ± 0.01K.

RESULTS AND DISCUSSIONS

The experimentally measured values of density, viscosity and sound speed of solutions of magnesium salicylate tetrahydrate at 298.15K, 303.15K and 308.15K are given in **Table-1.**
The acoustical parameters were calculated from v, η and ρ values using standard formulae, and given in **Table - 2 and 3.**

1) Ultrasonic velocity - $v = \lambda \times f$ ----------1
2) Adiabatic Compressibility - $\beta = 1/v2\ \rho$ ----------2
3) Intermolecular free length - $L_f = K\ \beta_S$ ----------3
4) Specific acoustic impedance - $Z = v_s \cdot \rho$ ----------4
5) Relative Association - $R_A = \rho_S / \rho_O [v_o / v_s]^{1/3}$ ----------5
6) Relaxation time - $\tau = 4/3\ \beta \times \eta$ ----------6

Table – 1 : Density, Velocity and Viscosity magnesium salicylate tetrahydrate solution in water as solvent

Sr.No.	Temperature (^{0}K.)	Concentration (M)	Density(ρ_S) (Kg/m^3)	Velocity(v_s) (m/s)	Viscosity(□) (Pa.S.)or Kg m^{-1} s^{-1}
1	298.15	0.1	1010.8	6830.1	5.66E-04
2		0.01	999	8229.68	5.17E-04
3		0.001	997.5	3985.59	2.28E-04
4	303.15	0.1	1009.9	6335.129	5.24E-04
5		0.01	998.7	8376.4156	4.76E-04
6		0.001	997.1	3996.41	2.00E-04
7	308.15	0.1	1009.2	8189.3329	4.69E-04
8		0.01	998.2	8896.8444	4.35E-04
9		0.001	996.8	2970.814	1.79E-04

Table - 2 : Adiabatic Compressibility (β_S), Acoustic impedance (Z) and Free length (L_f) of magnesium salicylate tetrahydrate in water as a solvent.

Sr.No.	Temperature (^{0}K.)	Concentration (M)	Adiabatic Compressibility (β_S)Pa^{-1}	Acoustic Impedance Z (Kgm^{-2}S^{-1})	Free length L_f (m)
1	298.15	0.1	2.121E-11	6.90E+06	9.06E-12
2		0.01	1.478E-11	8.22E+06	7.56E-12
3		0.001	6.3111E-11	3.98E+06	1.56E-11
4	303.15	0.1	2.467E-11	6.40E+06	9.83E-12
5		0.01	1.427E-11	8.37E+06	7.48E-12
6		0.001	6.279E-11	3.98E+06	1.57E-11
7	308.15	0.1	1.477E-11	8.26E+06	7.69E-12
8		0.01	1.266E-11	8.88E+06	7.12E-12
9		0.001	1.137E-10	2.96E+06	2.13E-11

Table - 3 : Relative association (R_A) and relaxation (ι) time of magnesium salicylate tetrahydrate in water as a solvent.

Sr. No.	Temperature (^{0}K.)	Concentration (M)	Relative Association (R_A)	Relaxation Time (τ)
1	298.15	0.1	6.63E-01	1.60E-14
2		0.01	6.16E-01	1.02E-14
3		0.001	7.83E-01	1.92E-14
4	303.15	0.1	6.60E-01	1.72E-14
5		0.01	5.95E-01	9.06E-15
6		0.001	7.60E-01	1.68E-14
7	308.15	0.1	5.79E-01	9.23E-15
8		0.01	5.57E-01	7.34E-15
9		0.001	8.02E-01	2.71E-14

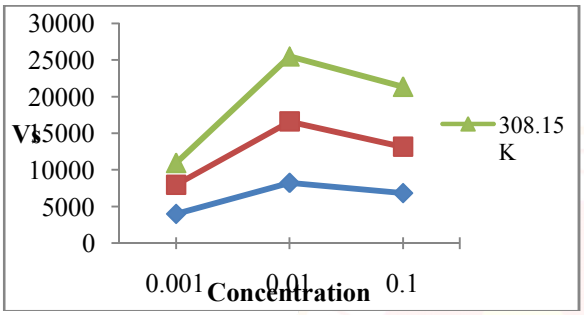

Fig. – 1,Velocity Vs Conc.

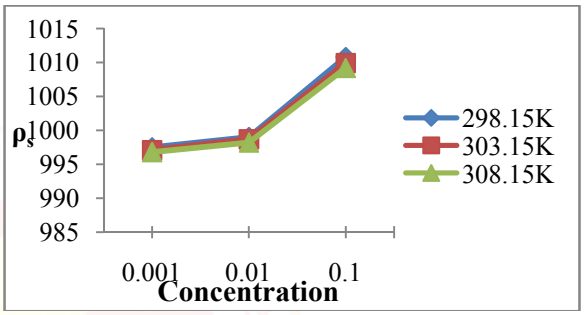

Fig. – 2, Density Vs Conc.

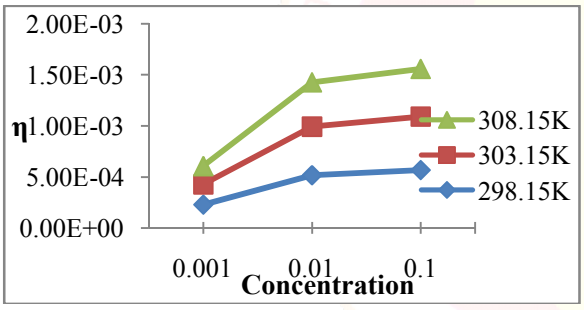

Fig.- 3, Viscosity Vs Conc.

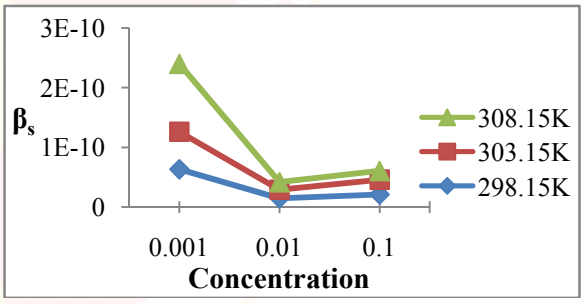

Fig. – 4 Adiabatic compressibility Vs Conc.

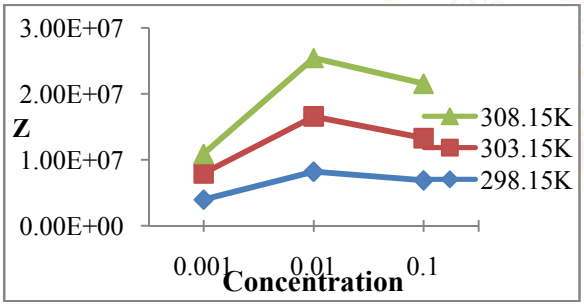

Fig. – 5, Acoustic Impedance Vs Conc.

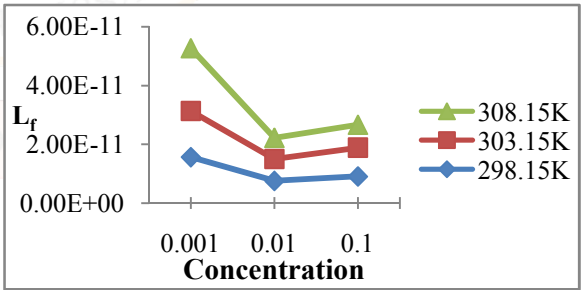

Fig. – 6, Free Length Vs Conc.

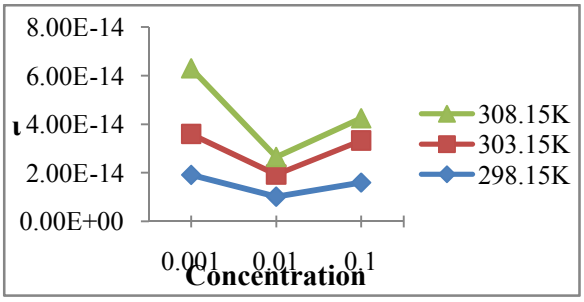

Fig. – 7, Relaxation time Vs Conc.

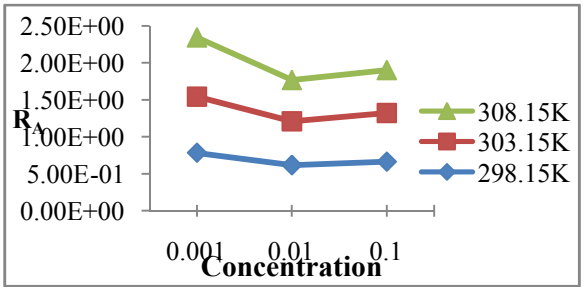

Fig. – 8, Relative association Vs Conc.

This paper describes about the study of molecular interactions that exist between the magnesium salicylate tetrahydrate with solvent water and by using ultrasonic velocity, viscosity, density of the liquid mixture. Magnesium salicylate tetrahydrate is commonly used as Non Steroidal Anti Inflammatory Drug (NSAID) and analgesic drug. It is used to treat mild to moderate muscular pain, headache, general back pain and arthritis. The measurement of ultrasonic velocity in liquid and liquid mixture provides valuable information about the nature of molecular interactions in them[11-13]**.** In the liquid mixture of magnesium salicylate tetrahydrate in water, ultrasonic velocity values show maxima and minima with respect to concentration and variation in the mixture are somewhat irregular. Certain liquid mixtures show unique maxima and minima in their liquid mixtures[14-15]. At all temperatures, ultrasonic velocity suddenly increases at 0.01M concentration and decreases at 0.1M concentration. Viscosity variation is attributed to the structural changes. The structural changes influence the viscosity to a certain extent as compared to density. This indicates solute-solvent interactions[16]. Such type of maxima in ultrasonic velocity is related to the structure in the liquid mixture with many cavities and these cavities can accommodate solute molecules. Adiabatic compressibility values calculated from the values of ultrasonic velocity and density for the system are represented in Table - 2 and Fig.4. The adiabatic compressibility has an inverse relation with ultrasonic velocity. The mixture studied here (magnesium salicylate tetrahydrate + water) shows non linear variation in the values of adiabatic compressibility similar to ultrasonic velocity. For the present system, the variations in the values of β_s show weaker molecular interactions in the system. Specific acoustic impedance (Z) also makes the contribution in explaining the molecular interactions[17]. It can be seen from Table- 2 and Fig. 5 for liquid system magnesium salicylate tetrahydrate + water, the values of acoustic impedance do not show linearity. The acoustic impedance values increase and again decreases with increase in concentration. It shows that there may be weaker molecular interactions and it depends on the structures of the liquid molecules and the molecular packing in the medium. Intermolecular free length is the distance between the surfaces of neighbouring molecules. Variation of values of intermolecular free length are shown in Table - 2 and Fig.6. There is sudden dip in the values of L_f at concentration 0.01M and again increases at 0.1M concentration. It indicates that maximum molecular interactions at 0.01M concentration[18-19]. The relaxation time which is in the order of 10^{-14} s. for the system is due to the structural relaxation process[20]. The values of relaxation time are not linear for the liquid mixtures. It is observed that the relaxation time decreases at 0.01M concentration and again increases with increase in concentration. This is due to aggregation of solvent molecules or ions suggesting strong solute–solvent interactions

CONCLUSION

In the present investigation, ultrasonic parameters are measured for the mixtures of magnesium salicylate tetrahydrate in water. The dependence of densities and viscosities of liquid mixtures on composition is of great interest leads to explain the acoustic parameters. Nonlinear variation in the values of acoustic parameters like adiabatic compressibility, acoustic impedance, relaxation time, shows that there exist solute-solute as well as solute-solvent interactions. It is found out that, the decrease in intermolecular free length shows solute - solvent interactions in the mixture due to which structural arrangement is affected considerably. In the system, weak solute-solute interaction and strong solute-solvent interaction may be present. It may be due to rupture of hydrogen bond in solvent molecules and salvation of solute by solvent molecules.

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PYTOCHEMICAL INVESTIGATION AND ANTIOXIDANT ACTIVITY OF KALONJI (*NIGELLA SATIVA*) AND HONEY

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ABSTRACTS

The phytochemical investigation of aqueous and methanolic extracts of Kalonji was examined and their antioxidant activities were determined. The antioxidant activity of Honey was also determined. The values of O.D. were determined by using U.V. Spectrophotometer. From this investigation it is found that the both Kalonji and honey have good to moderate antioxidant properties. The IC_{50} values of two fractions have been reported in this investigation.

Key Words *: Kalonji, honey, phytochemical investigation, Antioxidant activity, IC_{50}*

INTRODUCTIONS

Seeds and plants are treasure house of potential drugs. In the recent years there has been increasing awareness about the importance of medicinal plants and their seeds. Plants derived substrances have recently become of great interest owing to their versatile application[1]. Spices constitutes an important group of agricultural commodities which are virtually indispensable in the culinary art[2]. Spices are derived from various parts of plants. Spices are not only used for dietry purposes like aroma, test, color but also as a medicine in traditional system of medicine[3].Kalonji is annual flowering plant native and cultivated in south west Asia[4]. Kalonji seeds are used in several diseases like cough, cold, fever skin diseases anticancer and antioxidants[5]. Kalonji sugar powder shows remarkable antidiabetic activity[6]. Kalonji shows meraculous curing ability and used as an analgesic, antilipemic, antihypertensive, bronchodilator, histamine release inhibiter, antifugal, antibacterial, antiviral, anti-inflammatory, anticancer and as an antioxidant[7,8,9,10,11,12,13].

Honey the golden yellow liquid produced by honey bee is valued from ancient times for its medicinal properties. Honey is well known natural sweetener. In recent years there has been increasing interest in determination of antioxidant activity of honey[14]. Nowadays, great attention has been directed to the use of natural antioxidants from honey and honey products. Antioxidant activity and phenolic compounds have most important factors to evaluate the quality and functional properties of honey[15]. Current evidences strongly supports the contribution of polyphenols for the prevention of cardiovascular diseases, cancer, osteoporosis and neurodegenerative diseases[16,17]. Due to this it is recommended to childrens and sportsman. Different types of honey have diverse phenolic content and different antioxidant activity[18]. Depsit phenolic compounds honey contains significant amount of flavanoids and it have remarkably stornger antioxidant activity[19]. Honey has antibacterial property and used in treatment of various diseases like cold, cough, skin wounds, gasterointestinal diseases and has anti – inflammatory action[20]. Present study is undertaken to find out phytochemical study and antioxidant activity of Kalonji and Honey.

MATERIAL AND METHODS

Kalonji seed are collected from Akola market and Honey from honey hives from the farms.

PREPARTION OF SEED EXTRACTS

Seeds of Kalonji were washed under tap water. It was then dried under shade and ground into course powder in the electronic grinder.

SOLVENT EXTRACTION

1) Preparation of Aqueous Extract of Kalonji

The aqueous extract was prepared by boiling method 20 gm of kalonji powder with 100 ml distilled water was continuous boiled for 30 min. Then solution was filtered. The filtrate was evaporated by heating the solution below 60^0C and weight was recorded.

2) Preparation of Methanolic Extract of Kalonji

Methanolic extract of kalonji was prepared by soxhlet extraction method. About 20 gm of kalonji powder was extracted with 100 ml methanol till

the solvent in siphon becomes colourless the temperature was maintained 30^0–40^0C. Then methanol was completely evaporated and weight was recorded.

PHYTOCHEMICAL INVESTIGATION OF KALONJI

Chemical tests were carried out to evaluate the presence of various phytochemicals using procedures described by Sofowora (1993), Trease and Evans (1983).

PHYTOCHEMICAL INVESTIGATION OF KALONJI

Sr. No.	Constituent	Coloration	Aq. extract	Methanolic extract
1)	Alkaloids			
a)	Mayers reagent	Dark brown	+	+
b)	Wagner's reagent	Dark brown	+	+
2)	Flavanoids	Yellow	+	+
3)	Terpenoids	Reddish brown	+	-
4)	Saponins	Foam formation	+	+
5)	Sterols	Red ppt	+	+
6)	Tannins	Bluish green	+	+
7)	Proteins			
a)	Biurete test	Voilet color	+	+
8)	Phenols	Blue green color	+	+

STUDY OF ANTIOXIDANT ACTIVITY OF AQUEOUS, METHANOLIC EXTRACT OF KALONJI AND HONEY

The antioxidant activity of the kalonji extracts and honey were assessed on the basis of radical scavenging effect of stable 2, 2–diphenyl-1-picrylhydrazyl(DPPH). The diluted solutions were prepared and 0.02% solution of DPPH solution was prepared. Then 1 ml each of them is mixed together and optical density was measured at 517 nm using U.V visible spectrophotometer. A blank reading was also recorded. The optical density was recorded and % inhibition was calculated using formulae given below

Percent inhibition of DPPH (% AA) = $\frac{A-B}{A} \times 100$

Where A = Blank O.D of DPPH

B = O.D. of sample solution

From this we can calculate IC_{50} value of each extract

IC_{50} = Max (%AA) – 50% (Max-Min % AA)

RESULT AND DISCUSSION

Eleven different solutions of each extract were prepared as 1 mg/ml, 1.2 mg/ml, 1.4mg/ml …. 3.0 mg/ml and O.D. were recorded.

O.D. of blank DPPH = 0.538

Table No. 1 O.D OF AQUEOUS EXTRACT OF KALONJI

Sr. No	Conc. mg/ml	1	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0
1	O.D.	0.380	0.350	0.342	0.318	0.302	0.279	0.267	0.253	0.227	0.213	0.206
2	%AA	29.36	34.94	36.43	42.37	43.86	38.14	50.47	52.97	57.80	60.40	61.71

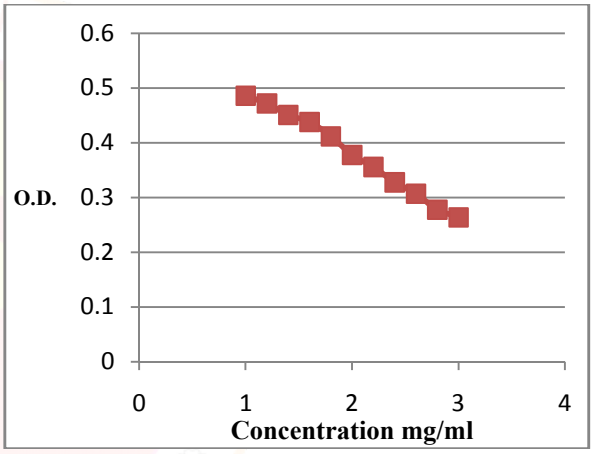


Table No. 2 O.D OF METHANOLIC EXTRACT OF KALONJI

Sr. No	Conc. mg/ml	1	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0
1	O.D.	0.498	0.471	0.456	0.423	0.409	0.387	0.382	0.376	0.347	0.339	0.326
2	%AA	7.43	12.45	15.24	21.37	23.97	28.06	28.99	30.11	35.50	36.98	39.40

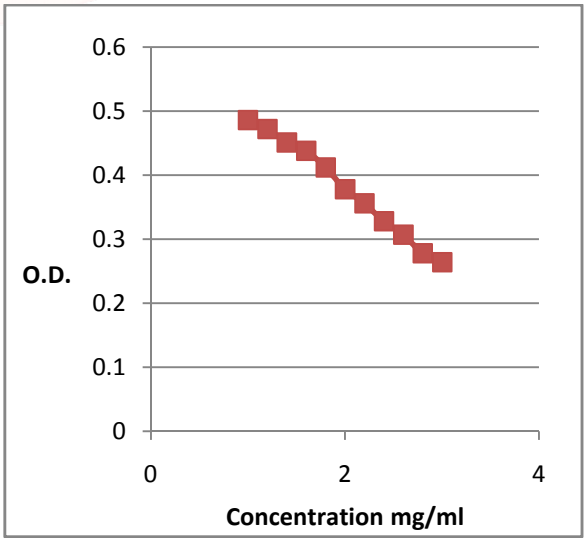
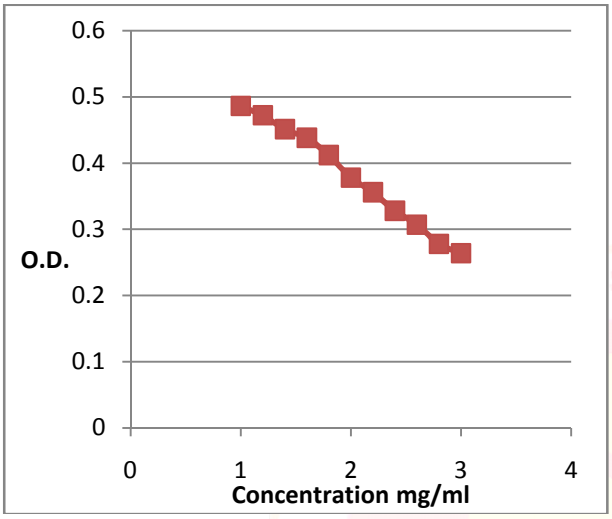


Table No. 3 O.D OF O.D OF HONEY SOLUTION

Sr. No	Conc. mg/ml	1	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0
1	O.D.	0.486	0.472	0.451	0.438	0.412	0.378	0.356	0.328	0.307	0.278	0.264
2	%AA	9.66	12.26	16.37	18.58	23.42	29.73	33.82	39.03	42.93	48.32	50.92



Various phytochemicals were found in kalonji extracts and very good antixodant activity of kalonji and honey were found with their IC50 values are as below.

Sr. No.	Extracts	IC_{50} Values
1	Aqueous extract of kalonji	1.7 mg/ml
2	Methanolic extract of kalonji	1.8 mg/ml
3	Aqueous Solution of Honey	2.2 mg/ml

CONCLUSION

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ULTRASONIC STUDY OF EXTRACT OF BRAYOPHYLLUM LEAVES AT 303 K TEMPERATURE AND 2 MHZ FREQUENCY

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ABSTRACT

Experimental measurement of ultrasonic velocity, density and viscosity have been carried out on solution of Extract of Brayophyllum leaves with Water, Alcohol, Methyl Acetate and Ethyl Acetate at 303 K temperature and 2 MHz frequency. Extraction of leaves were done by Soxhlet extractor. For velocity measurement, Ultrasonic Interferometer (Model No. F-81, Mittal, New Delhi) working at fixed frequency 2 MHz was used. From the experimental data of density (ρ), ultrasonic velocity (U) and viscosity (η), various acoustical parameters such as Adiabatic compressibility (β_a), relaxation time (τ), Gibb's Free Energy (ΔG) and Isothermal Compressibility (β_i) were calculated. Ultrasonic studies may throw more light on the molecular interaction to know the behavior of solute and solvent molecules in liquid mixtures and solutions. Changes in solvent and temperature affect compressibility of solution, which in turn affects molecular interactions in liquid mixtures and solutions. From the acoustic parameters effect of solvent on molecular interaction of extract of Brayophyllum Leaf can be directly predicted.

Keywords: *Acoustical parameters, Molecular interactions, Brayophyllum Leaf, Alcohol, Methyl Acetate and Ethyl Acetate.*

INTRODUCTION

The measurement of ultrasonic velocity in liquid mixtures and solutions has been found to be an important tool to study the physico-chemical properties of liquid mixtures and solutions. The ultrasonic technique is a powerful and effective tool for investigation of molecular interaction in the solutions[1-5].

For healing as well as for curing of human diseases, the medicinal plants are useful because of the presence of phytochemical constituents[6]. Phytochemicals are naturally occurring in the medicinal plants, leaves, vegetables and roots that have defense mechanism and protect from various diseases. Phytochemicals are primary and secondary compounds. Chlorophyll, proteins and common sugars are included in primary constituents and secondary compounds have terpenoid, alkaloids and phenolic compounds[7].Bryophyllum is widely distributed especially in philipines. Components of Brayophyllum leaves possess antibacterial, antitumorous, cancer preventive and insecticidal actions[8].

From the literature, the nature and degree of molecular interactions in different solutions depend upon the nature of solvent, the structure of solute molecule and extent of solutes taking place in the solution[9]. Hydrogen bonding is one of the most important types of intermolecular interactions play an important role in various physicochemical, biological and industrial processes[10]. In the present study we were extracted Bryophyllum leaves using soxhelt extractor in the solvents water, alcohol, methyl acetate and ethyl acetate. The ultrasonic velocity, density and viscosity of each extract is measured. From experimental data acoustic parameters were calculated and effect of solvent on molecular interaction was predicted.

METHODS AND MATERIALS

The leaves of Brayophyllum leaves were collected. The powdered plant samples were extracted successively with water, ethanol, ethyl acetate, and methyl alcohol using Soxhlet apparatus at 55-85 °C for 8-10 hour in order to extract the polar and non-polar compounds[11]. For each solvent extraction, the powdered pack material was air dried and then used.

The ultrasonic velocity (U) in liquid mixtures which prepared by taking purified AR grade samples, have been measured using an ultrasonic interferometer (Mittal type, Model F-81) working at 2MHz frequency and at temperature 303K. The accuracy of sound velocity was ±0.1 ms-1. An

electronically digital operated constant temperature water bath has been used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at the desire temperature. The density of pure liquids and liquid mixtures was determined using pycknometer by relative measurement method with an accuracy of ±0.1Kgm-3.

RESULT AND DISCUSSION

Using the experimental data of ultrasonic velocity (U), density (ρ), viscosity (η), various acoustical parameters such as Adiabatic compressibility (β_a), relaxation time (τ), Gibb's Free Energy (ΔG) andIsothermal Compressibility (β_i) were calculated by the following equations (1-4).

$\beta_a = (U^2\rho)^{-1}$ ….. (1)

$\tau = 4/3\eta\beta_a$….. (2)

$\Delta G^* = - K_B T \ln (h/\tau K_B T)$ …… (3)

$\beta_i = \gamma \beta_a$ …… (4)

K_B is Boltzmann constant (1.3806 x 10^{-23} JK^{-1}), T is the temperature, h is Planck constant (6.626 x 10^{-34}Js) and $\gamma = C_p/C_v$.

Experimental data for density, viscosity, and ultrasonic velocity frequency 2 MHz, for the different extract of Brayophyllum leaves and calculated acoustic parameters have been presented in Table 1.

Ultrasonic velocity in the solutions depends on intermolecular free path length. It is shown that ultrasonic velocity decrease with changing the solvent. In water ultrasonic velocity is highest while it decreases in ethanol, ethyl acetate and methyl acetate gradually. It shows that the there is strong molecular interaction in the extract of Brayophyllum leaves in water solvent as compared to others. More is the ultrasonic velocity more is the cohesive forces in the molecules. This indicates that there is a significant interaction between phytochemicals of Brayophyllum leaves and the solvent.

The decrease of adiabatic compressibility in extract of Brayophyllum leaves shows that there is formation of more hydrogen bonding in water solvent than the extract of ethyl alcohol, ethyl acetate and methyl acetate. Gibb's free energy shows irregularity shows that weak molecular interaction is present in extract of leaves.Longer time is taken for rearrangement of molecules and this suggest a decrease in Gibbs' free energy. Isothermal compressibility is minium in water extract showing strong interaction is present in the water extract.

Table 1: The experimentally measured values of Velocity (U), Density (ρ), Viscosity (η) and the calculated values of Adiabatic compressibility (β_a), relaxation time (τ), Gibb's Free Energy (ΔG) andIsothermal Compressibility (β_i) at 303K and 2MHz frequency.

Extract	Density ρ (kg/m3)	Ultrasonic velocity U (m/s)	Viscosity η*10^{-3} (CP)	Adiabatic Compressibility βa *10^{-10} (Pa^{-1})	Relaxation time τ*10^{-13} (Sec)	Gibb's Free Energy ΔG*10^{-20} ($kJmol^{-1}$)	Isothermal Compressibility β_i*10^{-10} (Pa^{-1})
				T=303K			
Water Extract	1053.1	1715.5	0.9375	3.2252	4.0317	48.7503	4.8410
Alcohol Extract	970.53	1453.50	0.9987	4.8781	6.4957	47.7983	7.3160
Methyl Acetate Extract	991.80	1206.66	0.3443	6.9247	3.0730	49.2260	10.3909
Ethyl Acetate Extract	932.32	1118.00	0.3997	8.5812	4.5730	48.4992	12.8707

CONCLUSION

It is observed that ultrasonic velocity for extract of Brayophyllum leaves in water is high while adiabatic compressibility, intermolecular free length is minimum in the same extract which shows strong molecular interaction of the component of Brayophyllum leaves in water.

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SYNTHESIS CHARACTERIZATION OF SOME BROMO AND NITRO-SUBSTITUTED-1, 3-THIAZINES

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ABSTRACT

some new bromo and nitro substituted 1,3 thiazines have been synthesized by the condensation of 2-hydroxy.3-bromo-5 methyl chalcones and 2-hydroxy.3-nitro-5 methyl chalcones with, phenylthiourea in ethanol containing aqueous KOH soln. The structures of newly synthesized bromo and nitro substituted have been analysed on the basis of their analytical data, molecular weight determination study and UV, IR & NMR spectral results

Keywords: *Thiazines,phenyl thiourea,*

INTRODUCTION

Thiazines are six member heterocyclic compounds containing one nitrogen and one sulphur atom. Nomenclature throughout the literature is varied. The system employed in the ring index[1] is unambiguous but since the majority of known members of thiazines group do not contain unsaturation of their parent compound, this usage has become outdated. Various methods have been worked out for their synthesis[2 - 6].their derivaties have wide variety of biological properties such as antiviral8, antifungal[7], anti HIV[8].

EXPERIMENTAL

Preparation of p-methyl phenyl acetate (1) :
P-cresol (50ml) was mixed with acetic anhydride (60ml) and anhydrous sodium acetate (2g). The mixture was refluxed for about an hour. The mixture was cooled and poured into ice cold water. Acetate layer was separated and washed with water several times. It was finally purified by distillation and distillate was collected at about 220□c. Yield 75.64% and **B**.P. 136^{0}C

Preparation of 2-hydroxy-5 methyl acetophenone(2) :
p-methyl phenyl acetate (50ml) was mixed with anhydrous $AlCl_3$ (120g) and heated at 120□C for 45 minutes on an oil bath. The reaction mixture was decomposed ice- cold water containing a little hydrochloric acid and allowing the solution to fall drop by drop into ice cold water with constant stirring. A yellowish white solid compound (2) was obtained.Yield was 72% andM.P:56℃

Preparation of 2-hydroxy-3-bromo-5- methyl acetophenone (3a)
2-Hydroxy-5-chloroacetophenone (3g) was dissolved in glacial acetic acid (3ml). bromine in acetic acid was added drop wise with constant stirring to this reaction mixture . The temperature of the reaction mixture was maintained below 0°C. The mixture was allowed to stand for 1hour. It was poured into ice cold water with stirring. A yellow solid then obtained was filtered, dried and crystallized from ethanol.

Preparation of 2-hydroxy-3-nitro-5-methyl acetophenone (3b)
2-Hydroxy-5-chloroacetophenone (3g) was dissolved in glacial acetic acid (3ml). bromine in acetic acid was added drop wise with constant stirring to this reaction mixture . The temperature of the reaction mixture was maintained below 0°C. The mixture was allowed to stand for 1hour. It was poured into ice cold water with stirring. A yellow solid then obtained was filtered, dried and crystallized from ethanol.

Preparation of 1-(2-hydroxy-3 bromo-5 methyl phenyl)3-(4-chlorophenyl) - chalcone (4a):
A mixture of 2- hydroxy -3-bromo-5 methyl acetophenone (2a) (0.01 mole and p-chlorobenzaldehyde (0.01 mole) was dissolved in ethanol (20ml) and to this solution 10% potassium hydroxide added gradually with constant stirring. The reaction mixture was kept overnight at room temperature and then it was poured into crushed ice and acidified with dil. HCI. The product precipitates out was filtered washed with NaHCO3 solution and crystallized from ethanol to obtained compound. Yield 72% and M.P: 82℃.

Preparation of 1-(2-hydroxy-3-nitro-5-methylphenyl)-3(4-chloro phenyl)- chalcone (4b):

A mixture of 2-hydroxy -3 nitro-5-methyl acetophenone (3b) (0.01 mole) and p-chlorobenzaldehyde (0.01 mole) was dissolved in ethanol (15 ml) and to this solution 10% potassium hydroxide added gradually with constant stirring. The reaction was kept overnight at room temperature and then it was poured into crushed ice and acidified with dil. HCI. The product precipitates out was filtered washed with $NaHCO_3$ solution and crystallized from ethanol to obtained compoundYield:- 68% and M.P 72℃.

Preparation of 4-(2-hydroxy-3-bromo-5-methylphenyl)-6-p-chlorophenyl-2-iminophenyl-3,6-dihydro-1,3-thiazine(5a) :

1-(2-hydroxy-3 bromo-5 methyl phenyl)3-(4-chlorophenyl) – chalcone (4a) (0.01 mol) and phenyl thiourea (0.02mol) dissolved in ethanol (30 ml). To this aqueous KOH solution (0.02 mol) was added. The reaction mixture was refluxed for three hours, after cooling, diluted with water and acidified with 1:1 HCl. The product thus obtained was crystallized from ethanol to get 4-(2-hydroxy-3-bromo-5-methylphenyl)-6-p-chlorophenyl-2-iminophenyl-3,6-dihydro-1,3-thiazine.Yield: 62%and M.P: 110 ℃

Preparation of 4-(2-hydroxy-3-nitro-5-methylphenyl)-6-p-chlorophenyl-2-iminophenyl-3,6-dihydro-1,3-thiazine(5b) :

1-(2-hydroxy-3 nitro-5 methyl phenyl)3-(4-chlorophenyl) – chalcone (4b) (0.01 mol) and phenyl thiourea (0.02mol) dissolved in ethanol (30 ml). To this aqueous KOH solution (0.02 mol) was added. The reaction mixture was refluxed for three hours, after cooling, diluted with water and acidified with 1:1 HCl. The product thus obtained was crystallized from ethanol to get 4-(2-hydroxy-3-nitro-5-methylphenyl)-6-p-chlorophenyl-2-iminophenyl-3,6-dihydro-1,3-thiazine.Yield: 64% and M.P: 150℃

Charecterization of the compounds :

Melting points of all synthesized compounds were determined in open cappilaries and are uncorrected. IR spectra were recorded on Perkin-Elmer 1000 Spectrophotometer in KBr. NMR spectra were recorded on Bruker advance 400 NMR spectrometer using TMS as internal cal shistandard and chemical shift were expressed in δ ppm.

Compound 5a:

I.R (KBr):cm^{-1} 3422.22 (-OH phenolic), 3365 (N-H stretching); 2950 (Aliphatic C-H stretching);1640.35(-C=N stretching)747.90(Ar-Br stretching); 1640.35 (-CN stretching) 1304 (OH bending in phenol); 690.31 (C-Cl stretching),

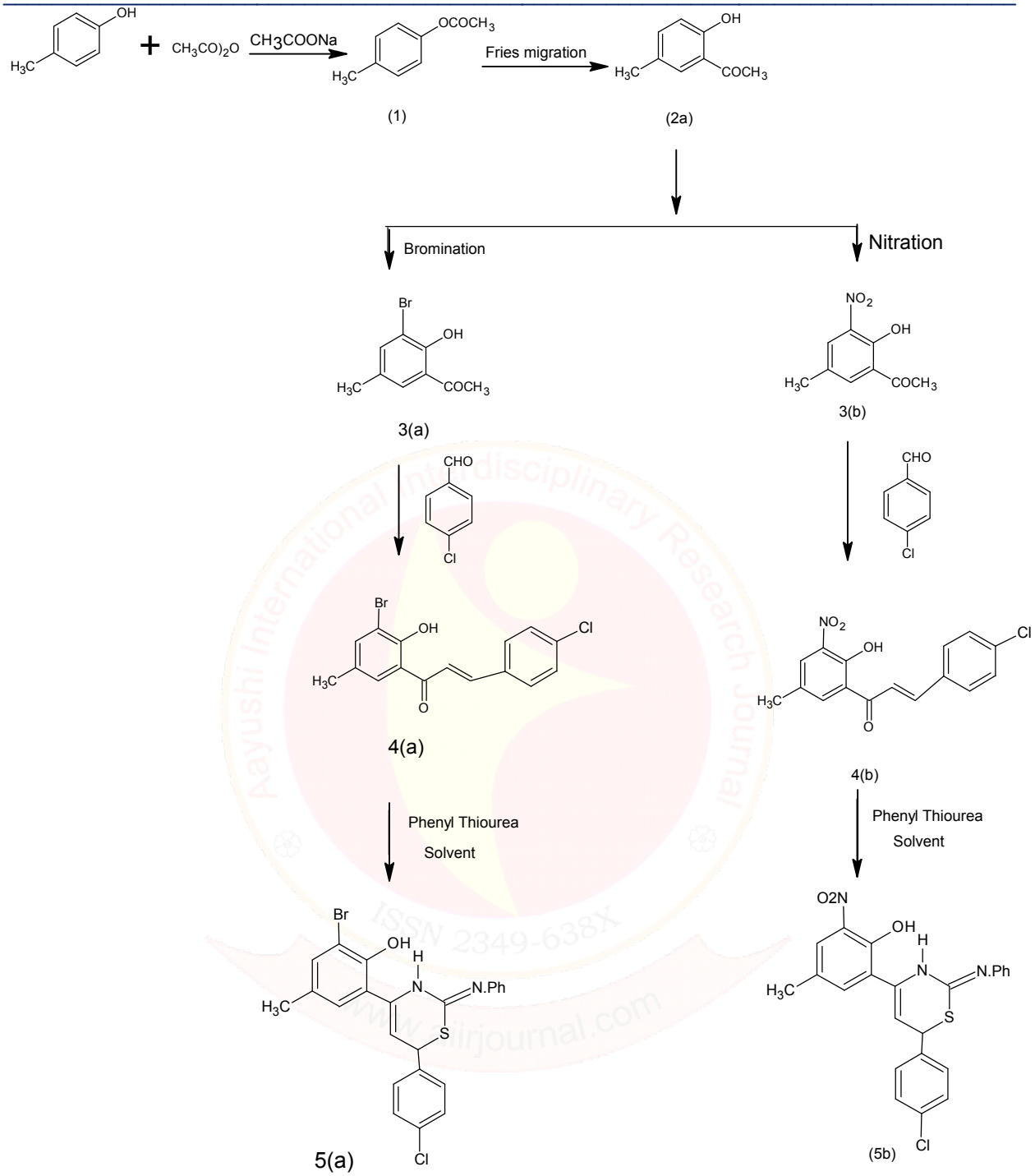
PMR: δ 2.2913 (s, 3H, $-CH_3$); 1.2288 (s, 1H, -S-CH stretching); 3.4305(S,1H,C-NH-C); 5.5351(S,1H,NH-CH); 6.8-7.6(m,11Ar-H); 9.718(S,1H,Ar-OH); 7.1 to7.8 (m,7H, Ar-H).

Compound 5b:

IR (KBr): cm^{-1} 3422.36 (-OH phenolic stretching); 3166.8(-NH stretching) 1649.23 (-C=C stretching); 1522.62(Ar C=C1343.4 (-CN stretching); 748 (C-Cl stretching).

PMR: δ 2.69 (s, 3H,Ar $-CH_3$); 2.33(s,1H S-CH),3.4 (s, 1H, NH stretching); 6.7(s,1H,C=C-H); 6.5(d1,H,C=CH) 6.8 to 8.85(s,11H, Ar-H); 12.83 (s, 1H, ArOH).

Scheme: Synthesis of bromo and nitro substituted 1,3 thiazines



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SYNTHESIS, CHARACTERIZATION AND BIOLOGICAL EVALUATION OF 2-(ALKYLSULFANYL)-1,3,4-OXADIAZOLE BASED ARYLOPYRAZINE-2-ONE AND QUINOXALIN-2-ONE DERIVATIVES .

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ABSTRACT

2-(Alkylsulfanyl)-1,3,4-oxadiazole based arylopyrazine-2-one and quinoxalin-2-one derivatives Synthesised from 1,3,4-oxadiazole -2-thiol based arylopyrazin-2-one derivatives by adding water containing KOH and alkyl halide in methanol dropwise. The mixtures was stirred at for 8 hr.The solid Separated was filtered ,washed with water & recrystallised from appropriate solvent to give the title compound

The compounds thus synthesized have been characterized by physical and spectral data. All of these titled synthesized compounds have been screened for antimicrobial study and are found to possesses excellent antimicrobial activities.

***Key Words** : Synthesis, Characterization, biological evaluation, pyrazine Quinoxaline.*

INTRODUCTION

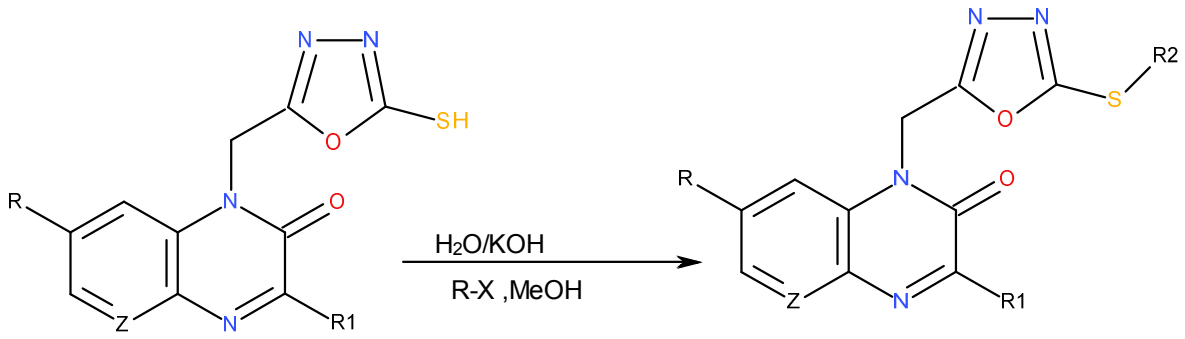
The class of substances known as heteroaromatics is extremely importants in biological activities [1-5].In which context could be mention the nucleus Pyrazine, which posses wide range of biological activities like antibacterial anti-inflammatory[6]. Pyrazine derivatives plays a significant role as anti-tuberculosis [7-8],,antifilarial agents[9], antifungal [10-11], antidepressant [12], vitro anticancer activity[13],antihypertensive agent [14], antiprotiferative [15].

Synthesis characterization and biological evaluation of titled compound becomes most important field for many investigator. Hence, Considering the scope of pyrazine derivatives we have synthesized novel 2-(alkylsulfanyl)-1,3,4-oxadiazole based arylopyrazine-2-one and quinoxalin-2-one derivatives compounds and studied for their biological activities.

MATERIALS AND METHOD

The melting points (ºC) were recorded by open capillary method and are uncorrected. IR spectra (υ max in cm-1) were recorded on a Shimadzu FTIR 8300 spectrophotometer using KBr pellets. The 1H NMR spectra were recorded on DRX-300 (300 MHZ) instrument using $CDCl_3$ as solvent (chemical shift in δppm) and TMS as internal standard. Thin Layer Chromatography on silica gel-G, was used to check the purity of the compounds.

Scheme:



R= Cl, CH_3 Z= C ,N
R1 = CH_3, C_2H_5 , C_6H_5, Cl, R2 = C_2H_5 CH_2- C_6H_5

METHOD AND DISCUSSION OF RESULT

Synthesis of 2-(alkylsulfanyl)-1,3,4-oxadiazole based arylopyrazine-2-one derivatives :
2-(alkylsulfanyl)-1,3,4-oxadiazole based arylopyrazine-2-one and quinoxalin-2-one derivatives Synthesised from 1,3,4-oxadiazole -2-thiol based arylopyrazin-2-one derivatives by adding water containing KOH and alkyl halide in methanol dropwise. The mixtures was stirred at for 8 hr.The solid Separated was filtered ,washed with water & recrystallised from appropriate solvent to give the title compound

RESULT AND DISCUSSION

Table 1. PHYSICAL DATA OF SYNTHESIZED COMPOUNDS

Sr. No.	Compound No.	Z	R	R_1	R2	Molecular formula	Melting Point ^{0}C	% Yield	% Nitrogen		R.F. Value
									Found	Calculated	
1	1	N	Cl	C_6H_5	C_2H_5	$C_{18}H_{14}ClN_5O_2S$	267	39	17.50	17.52	0.52
2	2	N	Cl	C_6H_5	$CH_2\ C_6H_5$	$C_{23}H_{16}ClN_5O_2S$	232	37	15.16	15.17	0.56
3	3	N	Cl	CH_3	C_2H_5	$C_{13}H_{12}ClN_5O_2S$	265	34	20.71	20.74	0.54
4	4	N	Cl	CH_3	$CH_2\ C_6H_5$	$C_{18}H_{14}ClN_5O_2S$	254	38	17.50	17.52	0.53
5	5	N	Cl	C_2H_5	C_2H_5	$C_{14}H_{14}ClN_5O_2S$	279	39	19.90	19.91	0.52
6	6	N	Cl	C_2H_5	$CH_2\ C_6H_5$	$C_{19}H_{16}ClN_5O_2S$	291	38	16.90	16.93	0.54
7	7	N	Cl	Cl	C_2H_5	$C_{12}H_9Cl_2N_5O_2S$	242	35	19.52	19.55	0.58
8	8	N	Cl	Cl	$CH_2\ C_6H_5$	$C_{17}H_{11}Cl_2N_5O_2S$	257	37	16.64	16.67	0.56
9	9	N	CH_3	Cl	C_2H_5	$C_{13}H_{12}ClN_5O_2S$	266	40	20.73	20.74	0.52
10	10	N	CH_3	Cl	$CH_2\ C_6H_5$	$C_{18}H_{14}ClN_5O_2S$	273	41	17.50	17.52	0.60
11	11	N	CH_3	CH_3	C_2H_5	$C_{14}H_{15}ClN_5O_2S$	187	37	22.05	22.08	0.57
12	12	N	CH_3	CH_3	$CH_2\ C_6H_5$	$C_{19}H_{17}ClN_5O_2S$	197	35	18.42	18.47	0.53
13	13	C	Cl	C_6H_5	C_2H_5	$C_{19}H_{15}ClN_4O_2S$	297	40	14.03	14.05	0.62
14	14	C	Cl	C_6H_5	$CH_2\ C_6H_5$	$C_{24}H_{17}ClN_4O_2S$	221	39	12.13	12.16	0.56
15	15	C	Cl	C_2H_5	C_2H_5	$C_{15}H_{15}ClN_4O_2S$	216	36	15.96	15.98	0.58
16	16	C	Cl	C_2H_5	$CH_2\ C_6H_5$	$C_{20}H_{17}ClN_4O_2S$	229	34	13.57	13.58	0.53
17	17	C	Cl	Cl	C_2H_5	$C_{13}H_{10}Cl_2N_4O_2S$	277	39	15.66	15.69	0.52
18	18	C	Cl	Cl	$CH_2\ C_6H_5$	$C_{18}H_{12}Cl_2N_4O_2S$	211	38	13.35	13.37	0.54
19	19	C	CH_3	C_6H_5	C_2H_5	$C_{20}H_{18}ClN_4O_2S$	186	38	14.80	14.81	0.56
20	20	C	CH_3	C_6H_5	$CH_2\ C_6H_5$	$C_{25}H_{20}ClN_4O_2S$	192	33	12.71	12.73	0.53
21	21	C	CH_3	C_2H_5	C_2H_5	$C_{16}H_{18}ClN_4O_2S$	185	34	16.95	16.97	0.50
22	22	C	CH_3	C_2H_5	$CH_2\ C_6H_5$	$C_{21}H_{20}ClN_4O_2S$	168	35	14.27	14.29	0.56

Spectral Analysis : Spectral interpretation of (7)
IR (ν_{max}) (cm^{-1}) :: 3208 (S-R, str) , 3089(Ar-H) ,2966(C-H, str) ,1707 (C=O, str), 1668(C=N,str), 1319(C-N-C,str),1157(C-O, str) , C-O-C (1145& 1036 str), 745(C-Cl ,str) ,740(C-Cl ,str).
NMR : 7.20-8.25(m,2H,Ar-H) 4.11(s,2H,CH_2), 3.05(q,2H,CH_2), 1.31(t,3H ,CH_3)

ANTIMICROBIAL STUDIES

Above synthesized 2-(alkylsulfanyl)-1,3,4-oxadiazole based arylopyrazine-2-one and quinoxalin-2-one derivatives have been studied for their antimicrobial activity against *escherichia coli*, *proteus mirabilis*, *staphylococcus aureas*, *pseudomonas aeruginosa*. The culture of each species was incubated at 37^{0}C and the zone of inhibition was measured after 24 hr. Most of these compounds were found active. Strongly active , range 14-18 Weakly active, range 7-10 mm Moderately active, range 11-13mm
Thus from above results it was observed that these heterocyclic compounds were found effective against *escherichia coli*, *proteus mirabilis*, *staphylococcus aureas*, *pseudomonas aeruginosa* So those compounds can be easily be used for the treatment of diseases caused by test pathogens, only when they does not have toxic and other side effects.

Sr. No.	Compound Number	**Antimicrobial activity**			
		E-coli	Proteus mirabilis	Staphylococcus aureas	Pseudomonas aeruginosa
1	1	15	14	12	14
2	2	13	16	14	14
3	3	17	14	18	18
4	4	15	14	15	17
5	5	10	09	16	10
6	6	14	13	14	11
7	7	17	16	18	16
8	8	15	16	16	18
9	9	17	15	18	18
10	10	15	14	16	17
11	11	11	09	07	10
12	12	14	13	15	07
13	13	15	16	11	14
14	14	14	10	14	15
15	15	17	16	18	13
16	16	18	14	16	15
17	17	16	17	18	17
18	18	15	16	17	18
19	11	13	16	16	10
20	13	10	07	13	09
21	10	14	15	10	14
22	15	13	12	09	11

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METHOD DEVELOPMENT, VALIDATION OF STABILITY INDICATING LIQUID CHROMATOGRAPHIC METHOD AND FORCE DEGRADATION STUDY OF IMIDAZOLE DERIVATIVE OF HIGH PHARMACEUTICAL VALUE

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ABSTRACT

An isocratic reversed phase stability-indicating high-performance liquid chromatographic (HPLC) assay method was developed and validated for quantitative determination of Imidazole Derivative and the simultaneous stability indicating study was carried out by using gradient pump system with the mobile phase Acetonitrile/ Sodium dihydrogen orthophosphate buffer P^H-3 (55/45) was selected to achieve maximum detection. SHIMADZU-HPLC, phenomenex C_{18}, 250×4.6mm, 5µ column was used for the detection having flow rate 1.2 ml/min, at 225 nm. The proposed method was found to be rapid, accurate and robust.

Keywords: *HPLC method development, Stability indicating method, Imidazole Derivative.*

INTRODUCTION

Heterocyclic family has hugely expanded and imidazoles are found today in a myriad of applications. They play an important role in areas such as natural products, medicinal chemistry, material sciences for nonlinear optical application, some imidazole derivatives are used as a catalyst in industrial uses. Since imidazole is biologically active compound it is mostly use in pharmaceutical industry for the preparation of different type of drugs. High performance liquid chromatography is an integral analytical tool in assessing product stability. HPLC method able to separate, detect and quantify the various product that can form on storage or manufacturing and also detect the impurity that may be introduce during synthesis. Stability indicating method on HPLC show the chemical behavior of the molecule which in turn helps in the development of formulation and packaging.

Recently some research had reviewed different studies on Imidazole derivative like the separation possibility of enantiomers of nine active substances belonging to imidazole derivatives: bifonazole, butoconazole, econazole, enilconazole, fenticonazole, isoconazole, miconazole, sertaconazole and tioconazole were studied by Podolska *et. al*[1]. The study developed by Kulik *et. al*[2] shows a versatile HPLC system for identification and determination of four benzimidazole derivatives in the antiparasitic drugs.

Determination of 2-Methylimidazole, 4-Methylimidazole, and 2-Acetyl-4-(1,2,3,4-tetrahydroxybutyl) imidazole in Licorice Using High-Performance Liquid Chromatography was reported by Raters *et. al*[3]. HPLC methods are applied to the analysis of commercial dosage forms (creams) with solid-phase extraction (SPE) procedure, using a diol sorbent, being found to be a convenient technique for the sample preparation giving quantitative drug recovery was reported by DiPietra *et. al*[4]. The catalytic effect of bases (imidazole, pyridine, Tris and triethylamine) on the peroxyoxalate chemiluminescence (PO-CL) reaction for high performance liquid chromatography (HPLC) was investigated by Imai *et. al*[5].

Morin *et. al*[6] investigates the separation and inclusion of a series of weakly polar imidazole derivatives. HPLC analysis of imidazole antifungals in commercial dosage forms was reported by Cavrini *et. al*[7] simillarly HPLC analysis of imidazole antimycotic drugs in pharmaceutical formulations was reported by DiPietra *et. al*[8]. Sawaya *et. al*[9] studied that HPLC method coupled with ESI-MSn was developed for their qualitative and quantitative analysis of imidazole alkaloids. Pande and Chandorkar[10] describe a new rapid, easy Isocratic reversed phase HPLC method for the separation and estimation of intermediate as 2-Methyl 5-Nitro Imidazole and Ornidazole.

So many different types of work were carried out on HPLC. In Kurdi *et. al*[11] study monolithic and fused core stationary phases are compared for fast separation of four fat-soluble vitamins. Hassan *et. al*[12] studied for the separation and quantisation of amlodipine (AML) and atorvastatin (ATV) in the presence of their acidic degradation products. Salmani *et. al*[13] reported an HPLC/UV method developed and validated for determination of wogonin in plasma. Gumieniczek *et. al*[14] introduced and validated new HPLC method for simultaneous determination of perindopril and indapamide. Identification and quantification of benzoic acid from local market beverages of Amravati (M.S.) was investigated by Tidke and Solanki[15].

Salmani *et. al*[16] reported an HPLC/UV method developed and validated for determination of wogonin in plasma. Estimation and forced degradation study of thiazole derivative by HPLC technique was reported by Kamkhede and Solanki[17]. Gumieniczek *et. al*[18] introduced and validated new HPLC method for simultaneous determination of perindopril and indapamide. Development and validation of stability indicating liquid chromatographic method of a semicarbazone derivative was studied by Ughade and Solanki[19].

MATERIAL AND METHODS

In this study high performance liquid chromatography system with LC solution data handling system (SHIMADZU-LCAT) was used for analysis. The system was controlled and data was recorded with spinchrome (RF software). The assays were performed on LC system consisting of SHIMADZU-LC 20 AT pump and SHIMADZU-UV detector. The injection volume was 20µl and it is injected in rhenodyne injector system. The detector was set at 225nm and peak area was integrated automatically by computer using spinchrome CRF software. Detection was carried out by using phenomenex C_{18} column (250mm × 4.6mm, 5µ (micron)) at ambient temperature all the calculation consisting quantitative analysis ware perform with external standardization by the measurement of peak area. The mobile phase was filtered through 0.45µ membrane and solution through 0.25µ, filtered and degassed. The injection volume was 20µl and analysis was performed at ambient temperature.

Preparation of stock solution

Sample preparation is an essential part of analytical cycle in HPLC. The standard solution of concentration 1mg/ml imidazole was prepared by using mobile phase acetonitrile and sodium dihydrogen orthophosphate buffer P^H-3 (55/45). The stock solution was stored at ambient temperature, protected from air and sunlight from the standard stock solution working standard stock solutions were prepared using mobile phase to get 0.005-0.030µg/ml. The solution were stored at ambient temperature and protected from direct sunlight.

RESULT AND DISCUSSION

Method optimization

HPLC analysis was performed by isocratic elution with a series of mobile phase containing acetonitrile and sodium dihydrogen orthophosphate buffer P^H-3. The best results were obtained by the use of mobile phase acetonitrile and sodium dihydrogen orthophosphate buffer P^H-3 at concentration (55/45). The flow rate was determined by testing the effects of flow rate on a pick area and resolution i.e 1.1ml/min, 1.2ml/min, 1.3ml/min. 1.2ml/min was found to be optimum. All experiment carried out at ambient temperature. To determine appropriate wavelength for determination of benzoic acid in mobile phase several trails were carried out. The suitable wavelength selected for monitoring the imidazole derivative was 225nm. All the solutions were filtered, degassed.

It was observed that there was no interference from the mobile phase or baseline disturbance and all the analyte were observed at 225nm. The chromatographic run time was 6 min and column void volume 2.220 min. Through the study the stability of chromatograph i.e. system was monitored by calculating the resolution. Table no-1. Fig - 1

Precision

It can be defined as “response to the repeated injection of the same standard solution under normal operating conditions”. The % RSD value for this method should be ≤ 1.0%. The precision studies were performing by the analysis of five different concentrations i.e 0.005-0.030µg/ml for imidazole derivative six times on same day. The method passed the test for repeatability as determined by %RSD of the peak of six replicate injections at test concentration. The results are shown in following table - 2

Accuracy

Accuracy was determined by the comparison of spike concentration of imidazole derivative with the measured concentration. A standard working solution containing imidazole derivative yielding final concentration of 0.005, 0.010, 0.015, 0.020, 0.025 and 0.030µg/ml respectively were prepared. The prepared standards were injected six times as a test sample. The result for accuracy is given in the table bellow, reviewed that the method was accurate. Table - 3

Linearity, LOD and LOQ

The standard stock solution was further diluted to get imidazole derivative concentration in the range 0.005-0.030µg/ml. Linearity of the method was studied by injecting five concentration of the imidazole derivative prepared in the mobile phase in triplicate in to LC system, keeping the injection volume constant. The peak areas were plotted against corresponding concentration to obtain calibration graph. Table presents the equation of the regression line, correlation coefficient (r^2). Relative standard deviation (RSD) values of the slope and intercept for imidazole derivative. Excellent linearity was obtained for compounds between the peak area and concentration of 0.005-0.030µg/ml with r^2= 0.9996286. Fig - 2

Dilution of imidazole derivative was made from standard stock solution the samples of imidazole derivative were injected in LC system LOD and LOQ were experimentally verified by six injections of at the LOD and LOQ concentration. By using standard deviation of response and slope the LOD was calculated to be 0.0032µg/ml and LOQ was calculated 0.0099 µg/ml for imidazole derivative respectively. Table – 4

Ruggedness

The method ruggedness is defined as the reproducibility of results when then the method is performed under different condition such as different operator in same laboratories, different equipment in same laboratory, different source of reagent and solution, different source of column, etc.

The ruggedness of HPLC method was evaluated by carrying out analysis using standard working solution the same chromatographic system and same column for different days the prepared solution was injected six times as test sample. Small difference in area and good consistency in retention time were obtained. The comparable detector responses obtain on different day indicated that the method is capable of producing result with high precision of different days. Table - 5

Robustness

To evaluate the robustness of HPLC method, few parameters were change. The parameter includes variation of flow rate of mobile phase and solvent from different lots were taken. Robustness of the method was carried out in triplicate only one parameter was change in experiment time. The differentiation of 0.020µg/ml imidazole derivative under various conditions was performed. Each mean value was compared with mean value obtained by optimum condition. The statically comparison was done with the test and no difference was found between result. Therefore the result shows that method is robust to the small change in experimental condition. Table - 6

FORCE DEGRADATION STUDY

ALKALINE HYDROLYSIS

At height temperature

1 mg/ml of imidazole derivative solution was prepared in 10 ml volumetric flask. In a round bottom flask 1 mg/ml of imidazole derivative solution was reflux with 1 ml of 0.1 M NaOH at 80^0 C for 30 minutes. After cooling the reaction mixture was neutralised, diluted, filtered and sonicated. 20 µl of this reaction mixture was injected to HPLC system in triplicate to observe degradation at high temperature.

At room temperature

Equal volume of reactant and 0.1 M NaOH solution was treated in in volumetric flask and kept 24 hrs at room temperature. After 24 hrs reaction mixture was neutralized, diluted, filtered and sonicated. 20 µl of this reaction mixture was injected to HPLC system to analyze the degradation of product. The study was carried out in triplicate. Table - 7

ACID HYDROLYSIS

At height temperature

1 mg/ml of reactant solution was reflux with 1 ml of 0.1 M HCl at 80^0 C for 30 minutes. After cooling the reaction mixture, was processed as above. 20 µl of this reaction mixture was injected to HPLC system in triplicate to observe degradation at high temperature.

At room temperature

Equal volume of drug and 0.1 M HCl solution was kept in volumetric flask at room temperature. After 24 hrs reaction mixture was processed as above and 20 µl of this reaction mixture was

injected to HPLC system to analyze the degradation of product. The study was carried out in triplicate. Table - 8

OXIDATIVE DEGRADATION 3% H_2O_2

At height temperature

1 mg/ml of imidazole derivative solution was reflux with 1 ml of 3% of H_2O_2 at 80^0 C for 30 minutes. After cooling the reaction mixture diluted with mobile phase filtered and sonicated. 20 µl of this reaction mixture was injected to HPLC system in triplicate to observe degradation at high temperature.

At room temperature

1ml of this solution was treated with 1 ml 3% of H_2O_2 solution in volumetric flask and kept 24 hrs at room temperature. After 24 hrs reaction mixture was processed as above.20 µl of this reaction mixture was injected to HPLC system to analyze the degradation of product. The study was carried out in triplicate. Table - 9

OXIDATIVE DEGRADATION 5% H_2O_2

At height temperature

1 mg/ml of imidazole derivative solution was reflux with 1 ml of 5% of H_2O_2 at 80^0 C for 30 minutes. After cooling the reaction mixture diluted with mobile phase, filtered and sonicated. 20 µl of this reaction mixture was injected to HPLC system in triplicate to observe degradation at high temperature.

At room temperature

Equal volume of reactant and 5% of H_2O_2 solution kept in volumetric flask at room temperature. After 24 hrs reaction mixture was diluted with appropriate mobile phase, filtered and sonicateed. 20µl of this reaction mixture was injected to HPLC system to analyze the degradation of product. The study was carried out in triplicate. Table - 10

CONCLUSION

RP-HPLC method was successfully developed for the determination of stability of imidazole derivative. The developed method is selective precise, accurate, linear, robust and rugged. From all the results of method validation of imidazole derivative it is conform that the method is accurate and can be used as standard method to quantify the product in further studies.

The force degradation study under various stress conditions have been shown that the sample is get 80-90% hydrolysed in acidic and alkaline condition at RT 24 hr, on reflux at 80^0C and on oxidising with 3% H_2O_2 and 5% H_2O_2 as well. It shows more percentage of degradation with 5-10% of recovery only. Forced degradation data proved that the method is specific for analysis and free from interference of blank and unknown degradation products. The result indicates the stability of compound under various stress conditions. The method is suitable for the analysis and forced degradation study of imidazole derivatives. Table – 11.This study acquainted us with the degradation pathway of drug in extreme chemical and environmental conditions and chemical behaviour of the molecule which helps in the development of formulation, packaging and stake life of potent drug to researchers and may be beneficial to society.

Table - 1
Optimum chromatographic conditions

Parameter	Optimum condition
Chromatographic column	SHIMADZU-HPLC, phenomenex C_{18}, 250×4.6mm, 5µ
Mobile phase	Acetonitrile/ Sodium dihydrogen orthophosphate buffer P^H-3 (55/45)
Flow rate	1.2 ml/min
Detection	225nm
Injection volume	20 µl
Temperature	Ambient
Retention time imidazole	2.220

Table – 2
Precision

Compound name	Λmax	Peak area	% RSD
Imidazole	225	110.325	0.17

Table – 3
Accuracy

Compound name	Spike concentration	Measured concentration	%RSD	% Deviation
Imidazole	0.020µg/ml	0.019 µg/ml	0.005	5

Table – 4
Linearity, LOD and LOQ

Compund name	Λmax	Equation	R^2	LOQ	LOD
Imidazole	225	Y=4016.20571 X + 30.06173	0.9996286	0.0099 mg/l	0.0032mg/l

Table – 5
Ruggedness

Date	10 Oct	11 Oct	12 Oct
Name	Imidazole	Imidazole	Imidazole
Area	110.125	110.325	110.485
SD	0.047	0.038	0.027
%RSD	0.019	0.014	0.010

Table – 6
Robustness

Flow rate	1.1ml/min	1.2ml/min	1.3ml/min
Mean	2.210	2.234	1.898
SD	0.049	0.071	0.066
%RSD	0.990	1.387	1.527

Table – 7
Alkaline hydrolysis

Sr. No	Reaction condition	Retention time	λmax	Peak area	Concentration	Degradation %	Recovery %
1	T.P 80^{0}C Base	2.297	225	5.697	0.0060	94.83	5.17
2	R.T 24 hr Base	2.167	225	10.858	0.0047	90.15	9.85

Table – 8
Acid hydrolysis

Sr. No	Reaction condition	Retention time	λmax	Peak Area	Concentration	Degradation %	Recovery %
3	T.P 80^{0}C Acid	2.297	225	4.057	0.0064	96.32	3.68
4	R.T 24 hr Acid	2.170	225	15.125	0.0037	86.29	13.71

Table - 9
Oxidative Degradation 3% H_2O_2

Sr. No	Reaction condition	Retention time	λmax	Peak area	Concentration	Degradation %	Recovery %
5	T.P 80^{0}C 3% H_2O_2	2.297	225	6.837	0.0057	93.80	6.2
6	R.T 24 hr 3% H_2O_2	2.173	225	8.949	0.0052	91.88	8.12

Table - 10
Oxidative Degradation 5% H_2O_2

Sr. No	Reaction condition	Retention time	λmax	Peak area	Concentration	Degradation %	Recovery %
7	T.P 80^{0}C 5% H_2O_2	2.293	225	10.568	0.0048	90.42	9.58
8	R.T 24 hr 5% H_2O_2	2.177	225	11.054	0.0047	89.02	10.02

Table – 11
Quantification of imidazole derivative in various stress conditions

Sr.No.	Reaction condition	% Degradation	% Recovery
1	Alkaline hydrolysis		
	T.P 80^0 C	94.83	5.17
	R.T 24 hr	90.15	9.85
2	Acid hydrolysis		
	T.P 80^0 C	96.32	3.68
	R.T 24 hr	86.29	13.71
3	Oxidative degradation 3% H_2O_2		
	T.P 80^0 C	93.80	6.2
	R.T 24 hr	91.88	8.12
4	Oxidative degradation 5% H_2O_2		
	T.P 80^0 C	90.42	9.58
	R.T 24 hr	89.02	10.02

Fig - 1
Standard chromatogram

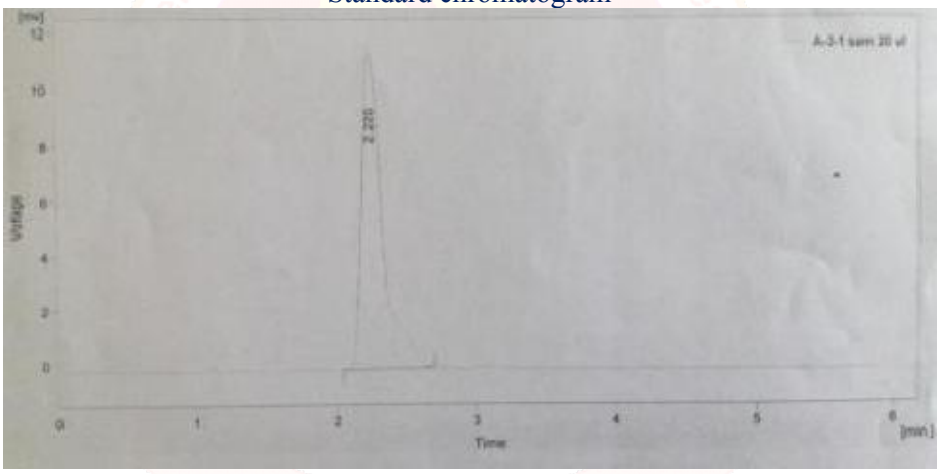
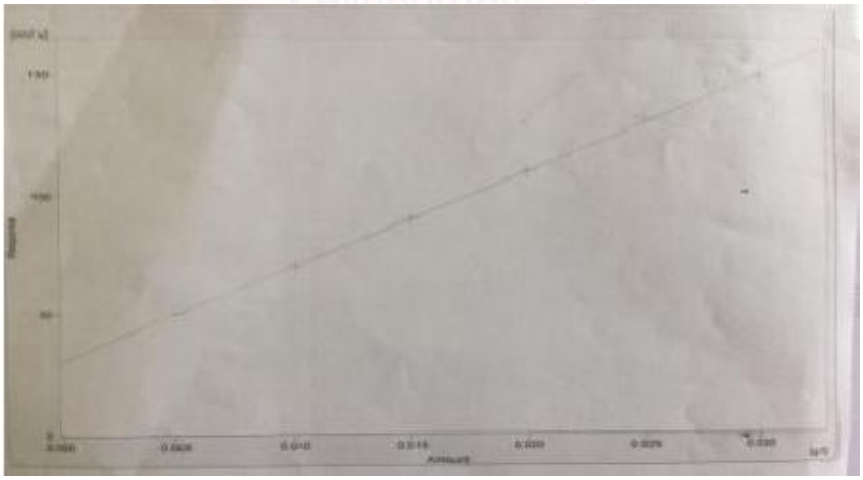


Fig – 2
Calibration curve



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SYNTHESIS OF TETRAHYDROBENZO[B]PYRANS AND DIHYDROPYRANO[2,3-C] PYRAZOLEDERIVATIVES CATALYZED BY MONTMORILLONITE K10: DEVELOPMENT OF NOVEL PROFICIENTMETHODOLOGIES

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ABSTRACT

An proficient and direct protocol for the synthesis of tetrahydrobenzo[b]pyrans (4H-chromenes) and dihydropyrano[2,3-c]pyrazole derivatives employing a multicomponent and one pot condensation reaction of aldehyde, 5,5-dimethyl-1,3-cyclohexanedione, malononitrile, for tetrahydrobenzo[b]pyrans while aldehyde, 3-methyl-1-phenyl -2 -pyrazolin-5-one, malononitrile, for dihydropyrano[2,3-c] pyrazole. In both the cases the reaction catalysed by MontmorilloniteK10 clay is described. The present protocol with Montmorillonite K10 catalyst is superior to therecently reported various catalytic methods. It is noteworthy that both aforesaid synthesized compounds acting as 'drug' having variety of biological activity.

Keywords : *Tetrahydrobenzo[b]pyrans; Dihydropyrano[2,3-c]pyrazole; Montmorillonite K10; Multi-component reaction; Recyclable heterogeneous catalyst.*

INTRODUCTION

Multi component reactions [1] that are performed in heterogeneous catalyst have gained improved interest in synthetic chemistry over the past decade not only for the advantages rendered by avoiding extensive decay of reactants, tough reaction conditions and solvents, but also for the development of environmentally benign methodology.[2]

Furthermore when a heterogeneous catalyst [3] is used, the insoluble catalyst can be separated by simple filtration and the catalyst can be reused. Therefore, the improvement of a heterogeneous catalyst in solvent appears enormously desirable.

Commercially available Montmorillonite K10 (MK10) [4] is one such catalyst that can fulfill these requirements. MK10 are environmentally friendly and economically reasonable solid acid catalysts that offer several advantages, such as simplicity of handling, non-corrosiveness, low cost and regeneration. The replacement of toxic organic solvents is one of the most important goals in Green Chemistry,[5] which inevitably lead to solvent emission and/or waste. The use of MK10 reagents is also an area presently under dynamic research. These not only avoid the usage of toxic acids, high temperature carrying reactions but also rapid significant simplifications to the reaction procedures. The main contributing factors are the high atom economy, extensive application in combinatorial chemistry and diversity oriented synthesis.[6-10]

Recently, the Synthesis of dihydropyrimidin-2(1H)-ones,[11]regioselective addition of Thiols and thiobenzoic acids onto olefins,[12] [1,3] shift reaction of 3-methyl-2-butenyl phenyl ether,[13] E-trisubstituted alkenes,[14] isobenzofuran-1(3H)-ones,[15] chelation mediated intermolecular hydroacylation,[16] Beckmann rearrangement of aldoximes, [17]amidoalkyl naphthols, [18] 5-Substituted 1H-Tetrazoles, [19]quinoxaline derivatives, [20]Pyrrolocoumarins and Pyrroloquinolones, [21]Nucleophilic Addition Reaction to Aldimines,[22] N,N'-Alkylidenebisamide derivatives [23] by Montmorillonite K10 clay are also reported. These approaches offeredremarkably significant improvements in the synthesis of heterocyclic and asymmetric cyclic scaffold with regards to yield of products, operationally simplicity and green aspects of avoiding toxic catalyst and solvents.

In general, the tetrahydrobenzo[b]pyrans known as 4H-chromenes [24] are well-documented heterocyclic compounds for their diverse

important biological activities like anticoagulant, anticancer, spasmolytic, diuretic, and anti-anaphylactic agents.[25-27] Also, 4H-chromenes have been widely used as cosmetics, pigments, and potentially biodegradable agrochemicals.

Similarly, 1,4-dihydropyrano[2,3-c] pyrazoles system acting as another important class of heterocyclic compounds, which constitute vital precursors to promising remedies in the field of medicinal chemistry and exhibit a wide range of biological activities such as antibacterial, anticoagulant, anticancer, diuretic, and insecticidal properties.[29]

A one-pot highly efficient silica-bonded propylpiperazine-N-sulfamic acid [28] as green heterogeneous catalyst under solvent-free conditions and a novel magnetically immobilized organocatalyst fabricated by covalently attaching 2-aminomethylphenol moiety on the surface of hydroxyapatite-encapsulated maghemite nanoparticles[29] has been explored for the preparation of benzo[b]pyrans and dihydropyrano[c]chromenes.

Unfortunately this method led to low to moderate yields of the desired products, difficulties in the synthesis of catalyst, required special protocol for catalyst preparation and required more time [30]. Hence, to overcome this problem, Montmorillonite K10 as heterogeneous catalyst has been utilized.

Thus, in the present study has been established to report the green synthetic procedure for the synthesis of 4H-chromenes and dihydropyrano[2,3-c]pyrazoles derivatives in the presence of MK10 as an efficient catalyst(Scheme 1). To the best of our knowledge and literature survey,there is no report for the synthesis of these new compounds and synthetic methodology has not been previously described.

MATERIALS AND METHODS

Chemicals were procured from Merck Chemical Corporation. The ^{1}H and ^{13}C NMR spectra were documented for samples in $CDCl_3$ or dimethylsulfoxide (DSMO-*d*6) on 90-, 300-, and 400-MHz Bruker spectrometers using Me_4Si as internal standard. Fourier transform infrared (FT-IR) spectra were documented on a Shimadzu 435-U-04 FT spectrophotometer from KBr pellets. Melting points were measured on a Buchi 510 apparatus in open capillary tubes. Reactions were monitored by TLC, performed on silica gel glass plates containing 60GF-254, and visualization on TLC was achieved by UV light or iodine indicator. Column chromatography was performed by Merck 60–120 mesh silica gel.

2.1. General synthetic procedure for the synthesis of 4H-chromenes derivatives

In a typical reaction procedure, Malononitrile (0.066 g, 1 mmol), and Montmorillonite K10 (0.05 g) inEtOH (5 mL) and H_2O (5 mL), and the resulting mixture was refluxed for an appropriate time (Table 3). After completion of the reaction as monitored by thin-layer chromatography (TLC), the resulted reaction mixture was cooled to room temperature, diluted with hot ethanol (5 mL), and stirred for 10 min. Then, the catalyst was isolated by filtration which was recovered later and the remaining supernatant was diluted with water (30 mL) and stirred for 10 min. The precipitated product was filtered, washed with water, and dried in an oven. Recrystallization of the crude product from EtOAc/n-hexane (1:3) provided pure product. All the synthesized products **2a-k**are known compounds, which were characterized based on their melting points and spectral (FT-IR, ^{1}H and ^{13}C NMR) data and compared with the reported corresponding data.

2.2. General synthetic procedure for the synthesis of 1,4-dihydropyrano[2,3-c]pyrazole derivatives

The catalyst Montmorillonite K10 (0.07 g) was added to a mixture of aldehyde (1 mmol), malononitrile (0.066 g, 1 mmol), and 3-methyl-1-phenyl-1H-pyrazol-5(4H)-one (0.174 g, 1 mmol), under stirring at 110 ^{0}C for an appropriate time (Table 4). The progress of the reaction was monitored by thin-layer chromatography (TLC). After completion of the reaction, the mixture was diluted with hot ethanol (10 mL), and stirred for 10 min. The catalyst was isolated by filtration which was recovered later. The remaining supernatant was evaporated to leave the crude product, which was purified by recrystallization from absolute EtOH. All the synthesized products **3a-i** are known compounds, which were characterized by their melting points and spectral (FT-IR, ^{1}H and ^{13}C NMR) analysis and compared with the reported corresponding data.

Spectral Data of 4H-chromenes derivatives

2-Amino-4-(4-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile
(Compound 2f)

FTIR (KBr) ν_{max}: 3358, 3325, 3358, 3185, 3966, 2192, 1683, 1655, 1605, 1488, 1413, 1369, 1252,1215, 1160, 1142, 1091, 1038, 1014, 847, 564, 514 cm^{-1}; ^1H NMR (90 MHz, DMSO-d_6) δ: 0.943 (s, 3H, CH_3), 1.031 (s, 3H, CH_3), 2.156 (s, 2H, CH_2), 2.505 (s, 2H, CH_2), 4.195 (s, 1H, CH), 7.058-7.305 (s, 6H, H-Ar and NH_2) ppm;^{13}C NMR (100 MHz, DMSO-d_6) δ:14.0, 20.7, 26.8, 28.3, 31.8,

Spectral Data of 1,4-dihydropyrano[2,3-c]pyrazole derivatives

6-Amino-4-(4-chlorophenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile

FTIR (KBr) ν_{max}: 3457, 3326, 3198, 2203, 1663, 1594, 1518, 1491, 1393, 1261, 1127, 1066, 1030,804, 752, 686, 650, 510 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ: 1.80 (s, 3H, CH_3), 4.74 (s, 1H,CH), 7.28-7.81 (m, 11H, H–Ar and NH_2) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ: 13.0, 36.5, 58.2, 98.7, 120.3, 120.4, 120.5, 126.7, 129.0, 129.6, 130.2, 132.1, 138.0, 143.1, 144.4, 145.7, 159.9 ppm.

RESULTS AND DISCUSSION

To estimate the quality and the catalytic ability of the Montmorillonite K10 as heterogeneous catalyst in organic reactions, we selected to observe its catalytic activity in a one-pot, three-component synthesis of tetrahydrobenzo[b]pyrans (4H-chromenes) and dihydropyrano[2,3-c]pyrazoles. Primarily, we scrutinized the reaction of 4-chlorobenzaldehyde, malononitrile, and 5,5-dimethyl-1,3-cyclohexanedione (dimedone) as a model reaction. To begin the reaction conditions, the effects of various reaction parameters such as the catalyst charging, solvent, and temperature were screened on the basis of reaction rate and yield of the model reaction. According to the investigational results as summarized in (Table 1), the best results was carried out in the mixture of EtOH and H_2O in equal volumes as the choice of solvent, under reflux conditions with using 0.05 g catalyst loading (entry 11). In addition, the significant role of the catalyst in the reaction was performed by repeating the reaction in the absence of the catalyst under optimized conditions and observing that only a reduced yield of the expected product was formed (entry 16).

In a similar way, the synthesis of 1,4-dihydropyrano[2,3-c]pyrazole from the reaction of 4-chlorobenzaldehyde, 3-methyl-1-phenyl-2-pyrazolin-5-one, and malononitrile as additional model reaction was chosen to further investigate the versatility and catalytic potential of the catalyst. To establish the reaction conditions, we planned the effects of the same green solvents H_2O and EtOH, catalyst charging, and reaction temperature on the reaction. Grounded on the experimental outcomes summarized in (Table 2), the best results for the reaction are acquired under solvent-free condition consuming a catalyst loading of 0.07 g at 110 ^0C (entry 10). Further increasing the quantity of the catalyst had no enlightening effect on the yield (entry 12). The crucial involvement of the catalyst in the reaction was authenticated by performing the reaction in the absence of the catalyst, no detectable amount of the expected product with almost full retrieval of the starting materials (entry 13).

To improve the scope of the reactions, we conducted these reactions with a variety of substituted aldehydes under the optimized conditions, i.e., catalyst loading of 0.05 g, mixed H_2O/EtOH under reflux condition for the synthesis of 4H-chromenes (**2a–k),** versus catalyst loading of 0.07 g, no solvent, and reaction temperature of 110^0C for the synthesis of 1,4-dihydropyrano[2,3-c]pyrazoles (**3a–i**). Altogether the reactions progressed smoothly to afford the products in high yields. The tentative results are summarized in (Tables 3 and 4) individually.

As revealed, the aldehydes containing electron-donating and electron-withdrawing groups undergo these reactions to afford the analogous products in outstanding yields irrespective of the nature of the substituent groups. All the products are identified compounds, characterized by their melting points and spectral (FT-IR, ^1H and ^{13}C NMR) investigation and associated with those stated in the literature.

The recyclability potential of the Montmorillonite K10 catalyst was examined for the model reaction of 4-chlorobenzaldehyde, dimedone, and malononitrile. The recycling procedure involved the separation of the catalyst from the reaction mixture simply by usual filtration. The recovered catalyst was purified by washing with ethyl acetate then by drying in an oven. The results shown in (Table 5) show that the catalyst can be used three successive times without significant loss of its activity.

CONCLUSION

In summary, we have synthesized a highly effective pharmacologically active scaffolds by using Montmorillonite K10 as heterogeneous catalyst, which efficiently activates the one-pot, three-component synthesis of tetrahydrobenzo[b]pyrans (4H-chromenes) and 1,4-dihydropyrano[2,3-c]pyrazole derivatives. The main advantages of the present synthetic methodologies are efficiency, versatility, good yield, short reaction times, cleaner reaction profile, convenient workup, easy catalytic recyclability, and reusability with no loss of catalytic activity, which makes this protocol valuable and attractive in improvement of benign chemical processes and products.

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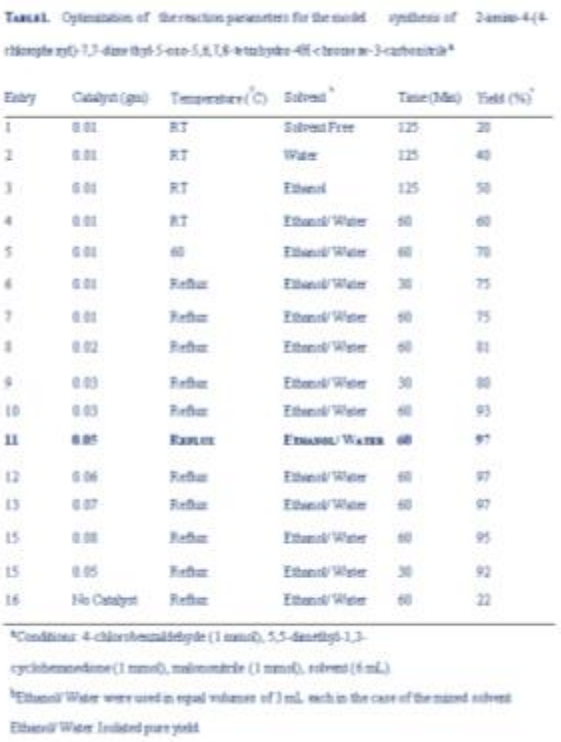
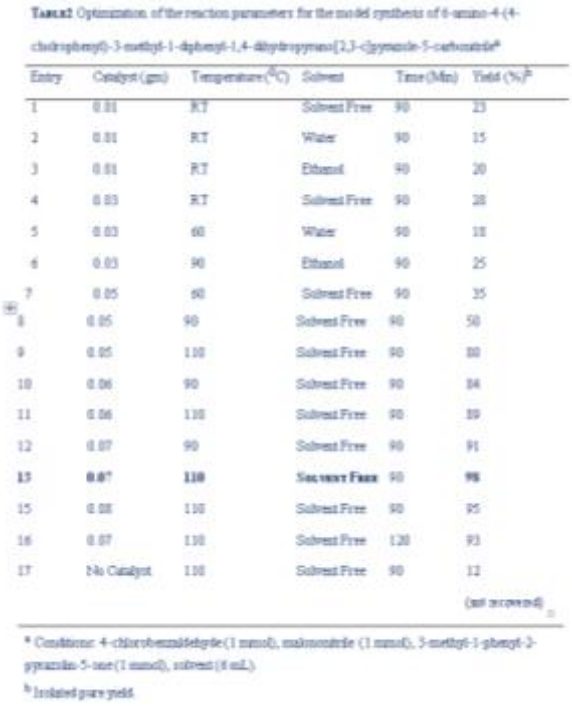


Entry	Catalyst (gm)	Temperature (°C)	Solvent[a]	Time (Min)	Yield (%)[b]
1	0.01	RT	Solvent Free	125	20
2	0.01	RT	Water	125	40
3	0.01	RT	Ethanol	125	50
4	0.01	RT	Ethanol/ Water	60	60
5	0.01	60	Ethanol/ Water	60	70
6	0.01	Reflux	Ethanol/ Water	30	75
7	0.01	Reflux	Ethanol/ Water	60	75
8	0.02	Reflux	Ethanol/ Water	60	81
9	0.03	Reflux	Ethanol/ Water	30	80
10	0.03	Reflux	Ethanol/ Water	60	93
11	**0.05**	**Reflux**	**Ethanol/ Water**	**60**	**97**
12	0.06	Reflux	Ethanol/ Water	60	97
13	0.07	Reflux	Ethanol/ Water	60	97
15	0.08	Reflux	Ethanol/ Water	60	95
15	0.05	Reflux	Ethanol/ Water	30	92
16	No Catalyst	Reflux	Ethanol/ Water	60	22

[a]Conditions: 4-chlorobenzaldehyde (1 mmol), 5,5-dimethyl-1,3-cyclohexanedione (1 mmol), malononitrile (1 mmol), solvent (6 mL).
[b]Ethanol/ Water were used in equal volumes of 3 mL each in the case of the mixed solvent Ethanol/ Water. Isolated pure yield.



Entry	Catalyst (gm)	Temperature (°C)	Solvent	Time (Min)	Yield (%)[b]
1	0.01	RT	Solvent Free	90	25
2	0.01	RT	Water	90	15
3	0.01	RT	Ethanol	90	20
4	0.03	RT	Solvent Free	90	28
5	0.03	60	Water	90	18
6	0.03	90	Ethanol	90	25
7	0.05	60	Solvent Free	90	35
8	0.05	90	Solvent Free	90	50
9	0.05	110	Solvent Free	90	80
10	0.06	90	Solvent Free	90	84
11	0.06	110	Solvent Free	90	89
12	0.07	90	Solvent Free	90	91
13	**0.07**	**110**	**Solvent Free**	**90**	**98**
15	0.08	110	Solvent Free	90	95
16	0.07	110	Solvent Free	120	93
17	No Catalyst	110	Solvent Free	90	12

[a] Conditions: 4-chlorobenzaldehyde (1 mmol), malononitrile (1 mmol), 3-methyl-1-phenyl-2-pyrazolin-5-one (1 mmol), solvent (6 mL).
[b] Isolated pure yield.

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FACILE SYNTHESIS OF CHALCONE DERIVATIVES AND THEIR CHARACTERIZATION

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ABSTRACT

Much research has been carried out with the aim to discover the therapeutic values of chalcone derivatives. The presence of reactive α,β-unsaturated keto group in chalcones is found to be responsible for their biological activity. The derivatives of chalcones were prepared using Claisen-Schmidt condensation scheme with appropriate acetophenone and benzaldehyde derivatives in presence of base and ethanol at room temperature. The yield of the compound was found to be good. The characterizations of the compound have been confirmed by IR spectroscopy, H^1NMR spectroscopy, TLC method and Melting point.

Keywords: *Chalcone derivatives, Claisen-Schmidt condensation*

INTRODUCTION

The chemistry of chalcones has generated intensive scientific studies throughout the world. The name "Chalcones" was given by Kostanecki and Tambor. Chalcones are also known as benzyl acetophenone or benzylideneacetophenone. Chalcones (trans-1, 3-diaryl-2-propen-1-ones) are α, β-unsaturated ketones consisting of two aromatic rings (ring A and B) having diverse array of substituents. Chalcones have been used as intermediate for the preparations of compounds having therapeutic value. Chalcones have been identified as interesting compounds that are associated with several biological activities. The most common chalcones found in foods are phloretin and its glucosidephloridzin (phloretin 2′-0-β-glucopyranoside), and chalconaringenin. Chalcone derivatives shows inhibitory effect against M. Gypsum species of fungus. These are naturally occurring compounds exhibiting broad spectrum biological activity including anticancer through multiple mechanism. Lots of derivatives can be synthesised and were biologically screened for antifungal activity. It also possesses wide range of pharmacological activity such as antibacterial, antituberculosis, antigout, antiinflammatory, antiplasmodic, etc.The chemistry of chalcone remains as a fascination among researchers in 21st century due to large number of replaceable hydrogen atoms that allows a large number of derivatives and a variety of promising biological activity to be generated. The presence of reacting α,β unsaturated keto group in chalcones is found to be responsible for their biological activity. The derivatives of chalcone were prepared using Claisen-Schmidt condensation scheme with appropriate acetophenone and aldehyde derivatives.

EXPERIMENTAL

Determining the melting point of a compound is one way to test if the substance is pure. So, melting point of the compound has been taken in an oil bath using thermometer. IR spectral data were recorded on FTIR-RX1 spectrophotometer. H^1NMR data were measured using $CDCl_3$ solvent on 300 MHz frequency. And their chemical shift values (δ) are in (ppm) units using TMS (Tetramethylsilane) as an internal standard. The reaction progress has been monitored by Thin Layer chromatography (TLC) using 3:1, Hexane :Ethyl acetate solvent system and spots of the compound was visualised using iodine chamber and $KMnO_4$ spray.

METHOD OF PREPARATION

In a 250 ml conical flask placed in an ice bath KOH (1.2 eq.) was dissolved in ethanol (50ml). thenacetophenone derivatives (1 eq.) was added slowly to the reaction mixture with continue stirring using magnetic stirrer. After 20 minutes Benzaldehyde (1 eq.) derivative was added slowly to the reaction mixture. Then reaction mixture was kept for 12-16 hrs with constant stirring at room temperature. Finally work up with water recrystallized it by ethanol. The residue obtained

was purified by column chromatography (Silica gel with 8 % ethyl acetate in hexane).

1-(2-hydroxyphenyl)-3-(phenyl)-prop-2en-1-one (A)

In a mixture of KOH (0.24 g, 4.27 mmol) and ethanol (50 ml) , 2-hydroxy acetophenone (0.5 g, 3.67 mmol) was added slowly. After 15-20 minutes Benzaldehyde (0.38 g, 3.58 mmol) was added dropwise with continue stirring. Further steps will be according to the method of preparation. IR (cm^{-1}) : 1590, 1542 (C=C), 1650 (>C=O conjugated), H^1NMR (300 MHz, $CDCl_3$) δ(ppm) : 12.47 (s, 1H), 8.08 (m, 1H), 8.04 (d, 1H), 7.62 (d, 1H), 7.54 (m, 2H),7.43 (m, 2H), 7.36 (m, 3H), 6.94 (m, 1H)

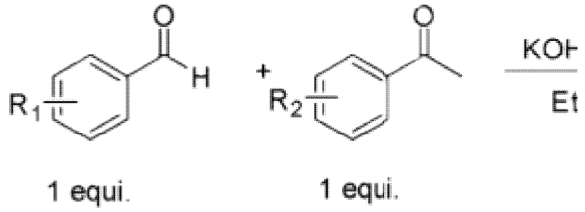
1-(2-hydroxyphenyl)-3-(4-chloro phenyl)-prop-2en-1-one (B)

In a mixture of KOH (0.24 g, 4.27 mmol) and ethanol (50 ml) , 2-hydroxy acetophenone (0.5 g, 3.67 mmol) was added slowly. After 15-20 minutes 4-chloro benzaldehyde (0.51 g, 3.67 mmol) was added dropwise with continue stirring. Further steps will be according to the method of preparation. IR (cm^{-1}) : 1590, 1542 (C=C), 1650 (>C=O conjugated), H^1NMR (300 MHz, $CDCl_3$) δ(ppm) : 12.47 (s, 1H), 8.08 (m, 1H), 8.06 (d, 1H), 7.68 (d, 2H), 7.62 (d, 2H), 7.60 (d, 1H), 7.46 (m, 2H), 6.96 (m, 1H)

1-(2-hydroxyphenyl)-3-(2-chloro phenyl)-prop-2en-1-one (C)

In a mixture of KOH (0.24 g, 4.27 mmol) and ethanol (50 ml) , 2-hydroxy acetophenone (0.5 g, 3.67 mmol) was added slowly. After 15-20 minutes 2-chloro benzaldehyde (0.51 g, 3.67 mmol) was added dropwise with continue stirring. Further steps will be according to the method of preparation. IR (cm^{-1}) : 1590, 1542 (C=C), 1650 (>C=O conjugated), H^1NMR (300 MHz, $CDCl_3$) δ(ppm) : 12.47 (s, 1H), 8.30 (d, 1H), 7.53 (m, 1H), 7.46 (m, 2H), 7.43 (d, 1H), 7.28 (m, 1H), 7.25 (m, 1H), 7.06 (m, 1H), 6.96 (m, 1H)

SCHEME :



1-(3-hydroxyphenyl)-3-(phenyl)-prop-2en-1-one (D)

In a mixture of KOH (0.24 g, 4.27 mmol) and ethanol (50 ml) , 3-hydroxy acetophenone (0.5 g, 3.67 mmol) was added slowly. After 15-20 minutes Benzaldehyde (0.38 g, 3.58 mmol) was added dropwise with continue stirring. Further steps will be according to the method of preparation. IR (cm^{-1}):1590, 1542 (C=C), 1650 (>C=O conjugated), H^1NMR (300 MHz, $CDCl_3$) δ(ppm) : 9.43 (s, 1H), 8.04 (d, 1H), 7.55 (m, 1H), 7.53 (d, 1H), 7.52 (m, 2H), 7.36 (m, 3H), 7.37 (m, 1H), 7.23 (m, 1H), 7.20 (t, 1H)

1-(3-hydroxyphenyl)-3-(4-chloro phenyl)-prop-2en-1-one (E)

In a mixture of KOH (0.24 g, 4.27 mmol) and ethanol (50 ml) , 3-hydroxy acetophenone (0.5 g, 3.67 mmol) was added slowly. After 15-20 minutes 4-chloro benzaldehyde (0.51 g, 3.67 mmol) was added dropwise with continue stirring. Further steps will be according to the method of preparation. IR (cm^{-1}) : 1590, 1542 (C=C), 1650 (>C=O conjugated), H^1NMR (300 MHz, $CDCl_3$) δ(ppm) : 9.43 (s, 1H), 8.03 (d, 1H), 7.68 (d, 2H), 7.62 (d, 2H), 7.60 (d, 1H), 7.55 (m, 1H), 7.37 (m, 1H), 7.23 (m, 1H), 7.20 (t, 1H)

1-(3-hydroxyphenyl)-3-(2-chloro phenyl)-prop-2en-1-one (F)

In a mixture of KOH (0.24 g, 4.27 mmol) and ethanol (50 ml) , 3-hydroxy acetophenone (0.5 g, 3.67 mmol) was added slowly. After 15-20 minutes 2-chloro benzaldehyde (0.51 g, 3.67 mmol) was added dropwise with continue stirring. Further steps will be according to the method of preparation. IR (cm^{-1}) : 1590, 1542 (C=C), 1650 (>C=O conjugated), H^1NMR (300 MHz, $CDCl_3$) δ(ppm) : 9.43 (s, 1H), 8.30 (d, 1H), 7.53 (m, 1H), 7.55 (m, 1H), 7.43 (d, 1H), 7.37 (m, 1H), 7.28 (m, 1H), 7.25 (m, 1H), 7.23 (m, 1H), 7.20 (t, 1H), 7.06 (m, 1H)

RESULT AND DISCUSSION

Code of Compound	R1	R2	Molecular Formula	Molecular weight (g/mol)	Percent Yield (%)	Melting point (^{o}C)
A	-H	2-OH	$C_{15}H_{12}O_2$	224.254	75.80	87-89
B	-4-chloro	2-OH	$C_{15}H_{11}O_2Cl$	258.699	84.22	136-138
C	-2-chloro	2-OH	$C_{15}H_{11}O_2Cl$	258.699	78.00	101
D	-H	3-OH	$C_{15}H_{12}O_2$	224.254	77.20	125
E	-4-chloro	3-OH	$C_{15}H_{11}O_2Cl$	258.699	83.00	---
F	-2-chloro	3-OH	$C_{15}H_{11}O_2Cl$	258.699	76.88	115-117

The characterizations of the compound have been confirmed by IR spectroscopy, H^1NMR spectroscopy, TLC method and Melting point. IR data shows that there is a sharp band observed between 1650-1654 cm^{-1} due to presence of conjugated carbonyl group and second peak 1590, 1542 cm^{-1} due to presence of >C=C< in conjugation with carbonyl group. This is a single step and easy method for the preparation of Chalcone derivatives obtained in good yield.

CONCLUSION

The synthesised product were characterised by IR spectroscopy, H^1NMR spectroscopy, TLC (Thin layer Chromatography), and melting point. On the basis of which the product obtained was confirmed. The yield of the product was good by this method. Preparation of chalconesis beneficial for the medicinal purposes like anti-cancer agents, anti-tuberculosis, anti-hepatic, and have many other pharmacological applications. This will encourage further research related to chalcones.

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ACOUSTICAL STUDIES OF 2-BROMOTHIAZOLE AT DIFFERENT TEMPERATURES

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ABSTRACT

The density and ultrasonic velocity measurements were carried out in organic-aqueous mixture of 2-Bromothiazole at different temperatures to illustrate the molecular bonding. From the experimental data the main acoustic parameters viz. adiabatic compressibility (β_s), intermolecular free length (L_f), acoustic impedance (Z) and relative association (R_A), have also been calculated using standard relations. These parameters have been utilized to study solute-solvent and solvent-solvent interactions.
In present study molecular interactions of ternary liquid mixture namely; 2-Bromothiazole +1,4-Dioxane (Dx)-water have been estimated at T= (303.15, 308.15, 313.15, 318.15 and 323.15) K for the entire range of molar concentrations. The effect of different temperatures on strength of molecular interaction has also been studied.
The result reveals that the density and ultrasonic velocity of liquid mixture decreases with increase in temperature. It is also seen that the formation of linear plot between and respective parameters indicated that the stronger solute-solvent interaction.

Keywords: *Density, ultrasonic velocity, acoustical parameters, solute-solvent interaction.*

INTRODUCTION

Heterocyclic compounds play an important role in synthetic, pharmaceutical and agrochemical industries [1, 2]. Substituted thiazoles are useful in medicinal and pharmaceutical chemistry for the treatment of allergies, hypertension, anti HIV, anti-inflammatory [3-8]. The knowledge of fluid properties is important in many industrial processes specially density [9]. Ultrasonic and density have found wide applications to characterize the physico-chemical behavior of solution [10, 11].
The literature survey reveals that no work is done in ternary liquid mixture that comprises of 2-BT and Dx-water. 2-Bromothaizole is a heterocyclic compound to induce base pair substitution and having mutagenic activity (Sigma-Aldrich). Also used for building blocks of other derivatives. Dioxane (Dx) is a hetero cyclic diethyl ether with each of its two oxygen atoms forming an ether functional group, is an almost apolar, aprotic and protophilic solvent [12]. It has been widely used as a solvent, stabilizer for chlorinated solvent, greasing agents, component of paint, varnish remover in biosciences, pharmaceutical, chemical and textile industries.
The reported work is the continuation of our earlier studies on acoustical and thermodynamical properties of binary and ternary mixtures [12-15]. The temperature dependence of the parameters gives important information about the molecular interaction between the components of liquid mixtures.
Materials: In present study, used solute 2-Bromothiazole (Sigma-Aldrich, USA CAS No 3034-53-5) and solvent Dx (Fisher Scientific) were analytical (AR) and were used without further purification.
Method: The mass of sample was measured using digital electronic balance (SHIMADZU AUY-220, Japan) with precision of ± 0.1 mg. The required ternary mixtures of 2-BT of molar concentration 0.002, 0.004, 0.006, 0.008 and 0.01 were prepared dissolving an accurate quantity in Dx-water solvent and kept in air tight flask. The densities of ternary liquid mixture were measured with portable digital densitometer (Anton Paar, DMA-35, Austria). The average uncertainty in measurement in the measured density is ± 5 x 10^{-3} kgm^{-3}. The ultrasonic velocity of liquid mixture were measured using multi-frequency ultrasonic interferometer (F-81S, Mittal enterprises, India) operating at 2 MHz's frequency with an accuracy of ± 2 m/s. The instruments were calibrated by measuring the velocity and density of distilled water (1505 m/s and 998.1 kgm^{-3}at 300.15K)

respectively. The measured values were agreed closely with literature values [16].

The density (ρ) and ultrasonic velocity (u) of ternary mixtures were measured at 303.15, 308.15, 313.15, 318.15 and 323.15K. The temperature was controlled through the water circulating around the liquid cell using thermostatically controlled High Precision water bath MSW-274 (Macro Scientific work Pvt. Ltd. India) with an uncertainty of ± 0.3°C.

RESULTS AND DISCUSSION

The value of densities, ultrasonic velocities and acoustical parameters at 303.15, 308.15, 313.15, 318.15 and 323.15) K are presented in **Table**.

Conc.	ρ kg m^{-3}	u m s^{-1}	β_s x 10^{-10} N^{-1} m^{-2}	L_f x10^{-11} m	z x10^{6} kgm^{2}s^{-1}	R_A
T=303.15K						
0.000	1033.6	1470.2	4.4217	4.3633	1.5289	0.9994
0.002	1031.5	1472.8	4.4693	4.3867	1.5192	0.9994
0.004	1032.3	1473.6	4.4610	4.3826	1.5212	1.0000
0.006	1032.8	1475.5	4.4474	4.3759	1.5239	1.0001
0.008	1033.2	1478.5	4.4276	4.3662	1.5276	0.9998
0.010	1031.8	1481.5	4.4157	4.3603	1.5286	0.9977
T=308.15K						
0.000	1029.7	1460.2	4.5548	4.4690	1.5036	0.9961
0.002	1027.4	1467.5	4.5196	4.4517	1.5077	0.9961
0.004	1028.0	1470.0	4.5017	4.4429	1.5112	0.9961
0.006	1027.5	1470.8	4.4989	4.4415	1.5112	0.9955
0.008	1027.6	1473.6	4.4814	4.4329	1.5143	0.9949
0.010	1028.4	1474.4	4.4731	4.4287	1.5163	0.9955
T=313.15K						
0.000	1025.2	1442.4	4.6883	4.5687	1.4787	0.9958
0.002	1022.0	1447.0	4.6732	4.5613	1.4788	0.9958
0.004	1023.3	1452.0	4.6352	4.5427	1.4858	0.9959
0.006	1022.8	1457.0	4.6056	4.5282	1.4902	0.9943
0.008	1023.8	1456.8	4.6024	4.5266	1.4915	0.9953
0.010	1024.2	1457.6	4.5956	4.5233	1.4929	0.9955
T=318.15K						
0.000	1019.6	1407.6	4.9501	4.7389	1.4352	0.9900
0.002	1016.6	1438.0	4.7570	4.6456	1.4619	0.9900
0.004	1017.4	1438.3	4.7513	4.6428	1.4633	0.9907
0.006	1018.3	1443.6	4.7123	4.6237	1.4700	0.9904
0.008	1019.7	1443.5	4.7065	4.6209	1.4719	0.9917
0.010	1019.3	1443.7	4.7070	4.6211	1.4716	0.9913
T=323.15K						
0.000	1014.8	1383.6	5.1475	4.8780	1.4041	0.9885
0.002	1012.4	1422.2	4.8834	4.7512	1.4398	0.9885
0.004	1013.3	1422.5	4.8771	4.7481	1.4414	0.9893
0.006	1014.2	1424.2	4.8611	4.7403	1.4444	0.9898
0.008	1014.6	1426.5	4.8435	4.7317	1.4473	0.9897
0.010	1014.4	1426.5	4.8445	4.7322	1.4470	0.9895

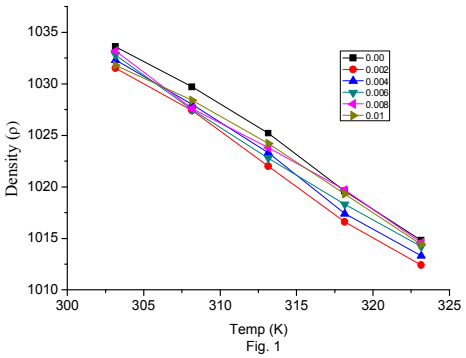

Fig. 1

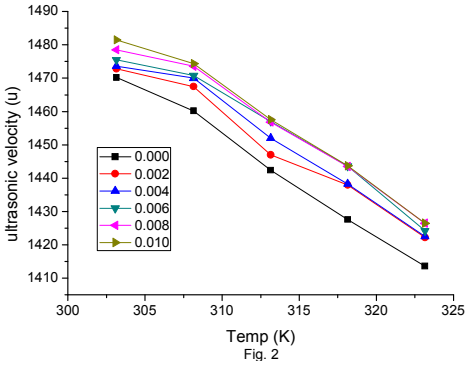

Fig. 2

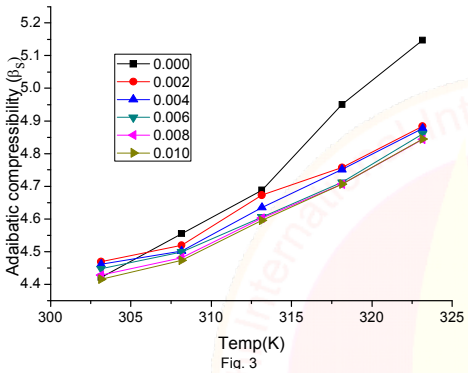

Fig. 3

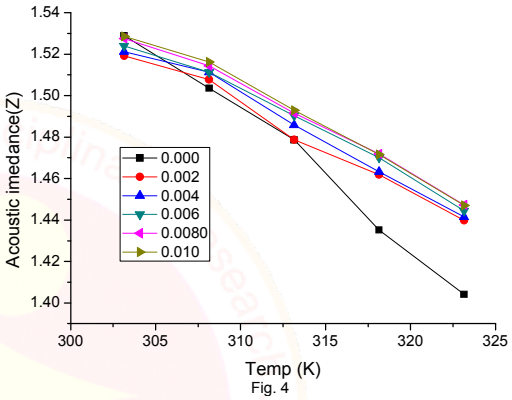

Fig. 4

It is seen from the **Fig. 1** that density of the studied solutes in organic-aqueous solutions decreases linearly with increase in temperature of the solution for the system studied. As the temperature increases, the available thermal energy facilitates the breaking of bonds between the associated molecules. Moreover, rise in thermal energy weaken the molecular forces which tends to decrease the ultrasonic velocity [17].

The ultrasonic velocity of 2-BT solutions **(Fig. 2)** is found to decreases with increasing temperature. As the temperature increases, the hydrogen bonds among water molecules break and more monomeric water molecules are formed. These broken water molecules enter the vacant space present in the cage like water structures and thus get trapped. As a result, the number of close-packed water structure increases with the increase in temperature. These increases in close-packed water structures form the material medium for the propagation of ultrasonic waves [18]. From **Table**, it is also observed that the ultrasonic velocity is found to increases with increase in 2-BT concentration. The increase in ultrasonic velocity in any solution indicates the greater association among the molecules of the solution.

It is seen **Fig.3**, that adiabatic compressibility increases with rise in temperature suggests the aggregation of solvent molecules around the solute molecule indicating strong solute-solvent interactions [19]. It is also reveals that interactions become weaken at higher temperature. Intermolecular free length shows a similar behavior as reflected by the compressibility values. The decreased compressibility brings the molecules to a closer packing resulting in a decrease of intermolecular free length as observed in **Table**. The variations of ultrasonic velocity in a solution rely on the increase or decrease of intermolecular free lengths. According to a model proposed by Erying and Kinkaid [20], ultrasonic velocity decreases with increase in free length and vice versa.

Acoustic impedance (Z) is dependent on both material and its geometry. It is seen from **Fig. 4,** the acoustic impedance decreases with increase temperature [21]. It is also observed from **Table** that the values of acoustic impedance vary linearly with the increase in 2-BT concentrations. The linear variation of acoustic impedance with concentration confirms the presence of strong molecular association between the solute–solvent molecules through intermolecular hydrogen bonding [22].

The values of relative association (R_A) are reported in **Table**. A close examination of relative

association values are found to close to each other which indicated the system under investigation is ideal in nature. It is also influenced by two factors (i) the breaking up of the solvent molecules on addition of solute to it and (ii) the solvation of solute that are simultaneously present [23].

CONCLUSION

Ultrasonic method is a powerful tool for characterizing existence of molecular interaction in the mixture. The result reveals that the density and ultrasonic velocity of solutions decreases with increase temperature. It is also seen that the formation of linear plot between temperature and respective parameters indicated that the stronger solute–solvent interaction.

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LIQUID -LIQUID EXTRACTION OF CD^{2+} BY ETHYL ACETATE DERIVATIVE OF CALIX(4)ARENE IN ACIDIC MEDIUM

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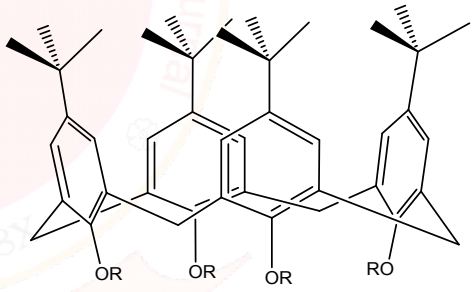
ABSTRACT

In present study extraction of Cd^{2+} has been made by employing calixarene in nitric acid medium. The chromogenic agent PAR was used for determination of cadmium spectrophotometrically at 520nm. The effect of nitric acid molarity 0.1M, metal to ligand ratio 1:5, stoichiometry 1:1 has been established. The interaction between M-L was examined by IR spectra.

Keywords: *Calixarene, Cd^{2+}, PAR*

Cadmium is one of the most concern heavy metal as per the environmental point of view. Owing to its toxicity and its hazardous effect in environment it's important to detect the cadmium from its various sources.Cadmium is also useful metal which finds applications in productionof various materials such as batteries, alloys, metal plating,andpigments.Extraction of cadmium by acetate derivative of calixarene has been reported [1].Solvent extraction has been reported for the extraction of cadmium from chloride, sulfate, nitrate and phosphate solutions using various extracting agents [2,3]. Extraction of cadmium using membrane technique has been extensively studied [4-6]. Solid phase extraction has been used for extraction of cadmium [7, 8]. A carboxylic acid extactant have been reported [9] for the extraction of cadmium.Cadmium extraction from sulphate solution using TOPS99, PC88A and Cynex272organophophorusextractants has been employed by Reddy et al.[10].

However, the calixarene is one of the studied extractant for the various metal ions. Due to its promising ability of complexing with guest molecules it catches attention of many researchers.Calixarenes have upper and lower rim and can be easily functionalized at upper and lower rim. Calixarene are the classof macro cyclic compound which possess the cavity to accommodate the cation, anion, and neutral molecule [**11-13**]. In present study ethyl acetate derivative (Fig.1) has been synthesized and used for the extraction of cadmium ions.



R= CH3COOC2H5

Fig.1. Ethyl acetate derivative of Calix(4)arene

Apparatus & Chemicals:

Bio-era UV-visible spectrophotometer (model no.EQ820) with matched 10mm quartz cuvette was used. Ethyl acetate calix(4)arene derivative,was prepared according to reported procedure[11,13], $Cd(NO_3)_2$. Of SD Fine Chemical were used.

Procedure for solvent extraction study:

1ml (1250 µM) of calixarene& 1ml (250 µM) of Cd $(NO_3)_2$ were mixed the solution was stirred for 30 min & then allowed to settled down in separating funnel. The aqueous phase was evaporated to dryness & determined spectrophotometrically.

Determination of Cadmium ion

4-(2-Pyridylazo) resorcinol (PAR) [14] reagent was used for determination of cadmium spectrophotometrically.

Result and discussion:

Effect of acid molarity:

The effect of nitric acid molarity on extraction efficiency of cadmium is studied. The extraction efficiency was checked by varying concentration from no acid to 1M. The extraction efficiency was found (Fig.2) to increase by increasing acid morality up to 0.1M and gives highest extraction efficiency about 95% was obtained at 0.1M. On further increasing in acid concentration the extraction efficiency decreases since NO_3^- serves as the counter ion in acidic medium. Therefore the further study was performed at 0.1M acid concentration.

$Cd(II)_{aq} + 2NO_3^- + nCalix_{(org)} \rightarrow Cd(NO_3)_2Calix_{(org)}$

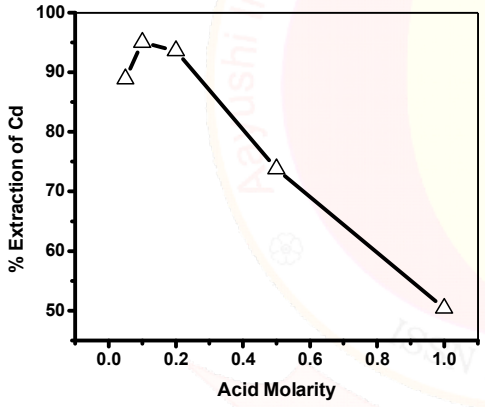


Fig.2. Effect of acid molarity on extraction efficiency

Metal to Ligand Mole Ratio

In order to determine the molar ratio of metal to ligand to obtain the maximum extraction efficiency, metal to ligand mole ratio study was performed. The concentration of Cadmium 250µM was kept constant and ligand concentration changed gradually from 1:250 to 20:250. The extraction efficiency (Fig.3) of cadmium initially increases up to 1:5 ratio and shows the highest percentage of extraction, however afterwards it decreases continuously on increasing concentration of ligand. The decreasing extraction efficiency is may due to the presence of some other competing process like formation of 1:2 metal complexes. Therefore, in further experiments, metal to calixarene mole ratio of 1:5 was selected.

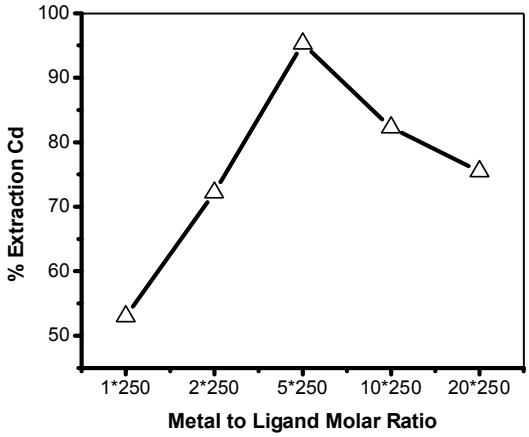


Fig. 3: Effect of metal-ligand molar ratio on the percentage extraction of cadmium

Metal to ligand Stoichiometry:

The stoichiometry of extracted species was determined by slope analysis method, by plotting the graph (Fig.4) of log D versus log [Calix] $_{org}$ The extraction was carried out by taking fixed amount of Cadmium (and nitric acid molarity) with varying amounts of calixarene which shows the formation of 1:1 complex with slope, n = 0.843 The possible structure of the complex can be of the type $[Cd\text{-}Calixarene]^{2+}$

$$Kex = \frac{D}{[NO3]^2[C]^n}$$

Therefore,

$\log D = \log K_{ex} + 2 \log[NO_3^-]_{aq} + n\log[Calix]_{org}$

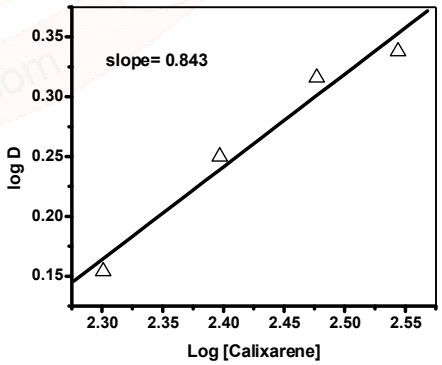
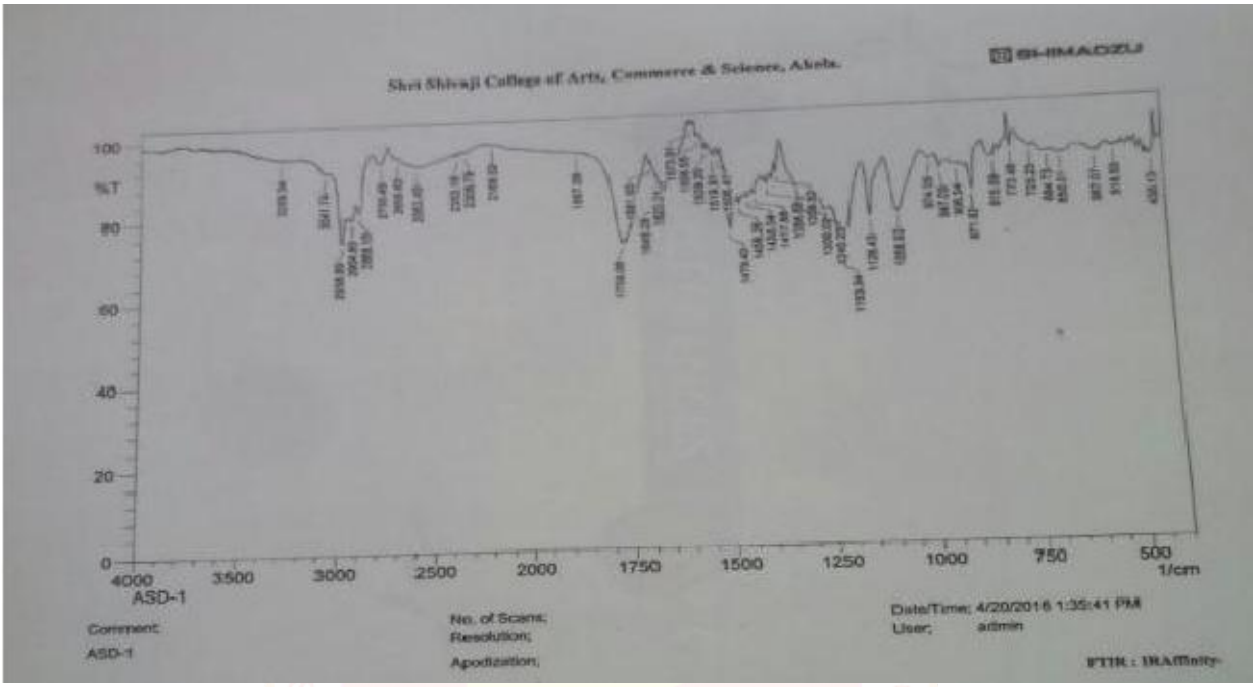


Fig.4. A plot of Log [D] Vs. Log [Q].

IR Spectroscopy study:

FTIR spectroscopic analysis of Cd(II)-calixarene complex collected after extraction was used to study the interaction ofCd(II) with calixarene(Fig.5) The stretching frequency of –

CH_3 group in free ligand was 2958 cm^{-1} which on complexation shifts to 2955 cm^{-1}. Also the stretching frequency of C=O in calixarene and its complex with cadmium are 1758cm^{-1} and 1755cm^{-1} respectively. This decreasing stretching frequency of parent calixarene on complexation with Cd(II) reveals the supportive evidence in formation of Cd(II)-calixarene complex.



(a)

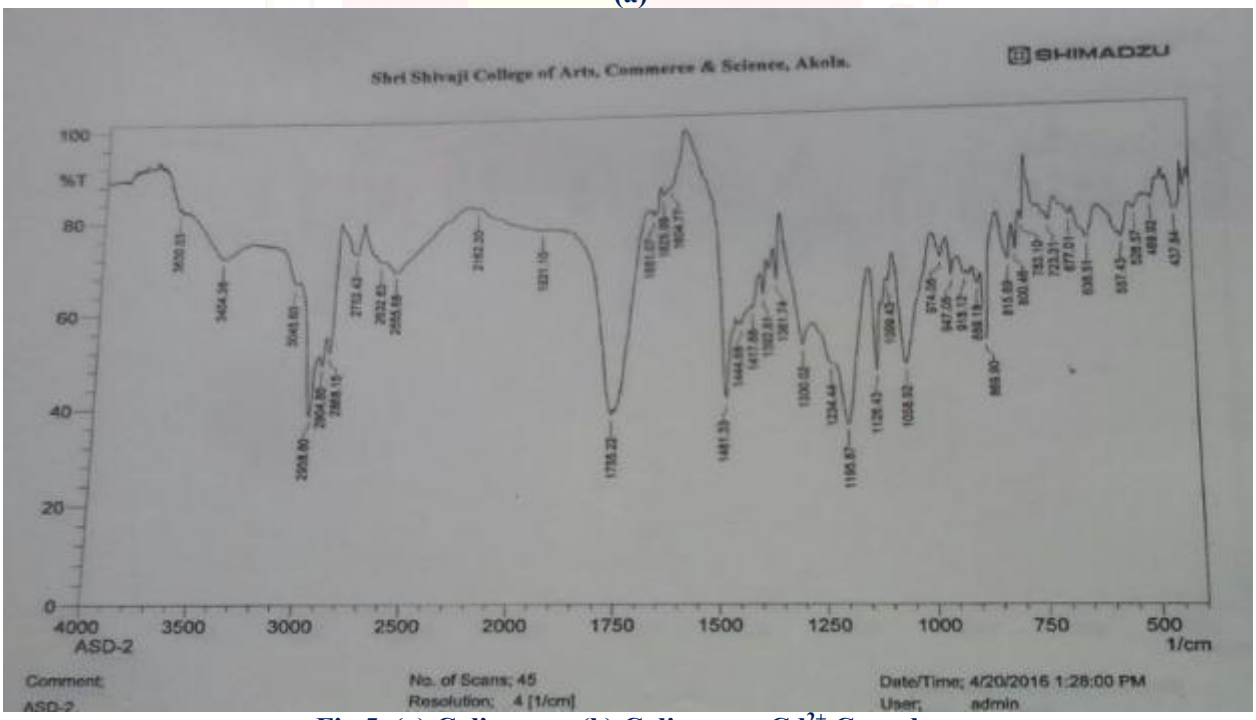


Fig.5. (a) Calixarene (b) Calixarene-Cd^{2+} Complex

CONCLUSION

In summary we have extracted the toxic heavy metal Cd^{2+} by ethylacetate derivative of calix(4)arene. Various parameters were optimized order to get maximum extraction efficiency. M-L mole ratio of 1:5 and HNO_3 molarity of 0.1 M.The M: L stoichiometry is 1:1 indicated the formation

of [Cd-calixarene]$^{2+}$complex. The extracted complex was subjected to IR analysis and supported the complex formation.

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SYNTHESIS AND STUDY OF PHYSICO-CHEMICAL PROPERTIES OF SOME SUBSTITUTED IMINE'S IN DIFFERENT ORGANIC SOLVENT'S BY REFRACTOMETRICALY

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ABSTRACT

The refractive index, Molar refractivity, the polarisibility constant of some substituted imines have studied in DMSO,DMF,THF,Ethanol and Acetone. If the concentration of solution will be decreased the polarisibility constant ,Refractive index,Molar refractivity is decreases. The refractive index is related to the molecular polarisibility because the propogation of light through a medium can be imagined to occur by the incident light inducing an oscillating dipole movement which then radiates light of the same frequency.

Keywords : *- Imine's Solvent's Physico-chemical properties.*

INTRODUCTION

Thomus Yong was presumably the person who first used and invented the of
"Index of Refraction" in 1807. The refractive index is an important physical property of solution. It gives an idea about the aromatic content of liquid using refractive index. The measurement is based on th refraction of light in the process of medium.Lower is the optical density higher is the speed of light. The refractive index of a substanece is depend on the wavelength (λ) at light and concentration of solution (c) structure of an atom or molecule.So refractive index is also used to determine the structure of a molecule. Refractive index is also used to determine the structure of unknown compound whose molecular formula is known.

From literature it was found that much work have been done over many substituted imine's heterocyclic, drugs, chalcones pyrazolines, Ketones, Aldehyde's by refractometricaly and spectrophotometricaly lot of reasearchers are interested to find out binary liquid mixture interactions along with solute[1,2] molar refraction and polarisibility constant of electrolyte and non electrolyte solvents with solute gives various new physical parameters of solvent[3,4].D.R.Nagargoje etal[5] have studied the viscosity and polarisibility of 3-acetyl-6-methyl(2H)-Pyran-2,4(3H)-dione derivative in different phase system and it is observed that percentage of solvent mixture and nature of solute affects viscosity, molar refraction and polarisibility constant.

The physical properties of liquid such as Viscosity,Refractiv Index, Ultrasonic velocity of binary mixture are studied by many works[6-13].Agrawal etal[14] has studied

The molar refraction and polarisibility constant Oswal etal[15] have studied dielectric constant and refractive indices of binary mixtures. The study of refractive indices of binary mixture.The study of refractive indices in mixed solvents is done by Burghate Agrawal[16] and Mhajan[17]. Theorotical study of refractivity of binary and
Ternary solution have been done by J.D.Pande and Etal[18]

The present of work deal's with the study of some substituted Imine's such as –

1) 3,4,5,trihydroxy benzoamido 4-chloro-imine.
2) 3,4,5 trihydroxy benzoamido 4-bromo-imine.
3) 3,4,5,trihydroxy benzoamido 4-methyl-imine.
4) 3,4,5,trihydroxy benzoamido 4-nitro-imine.
5) 3,4,5,trihydroxy benzoamido 4-hydroxy imine.

EXPERIMETAL WORK

The compound 0.1M 3,4,5, trihydroxy benzohydrazide was synthesized in laboratory by reflux method and purity is checked by M.P.,TLC,IR,NMR and after that some substituted Imine's are synthesized from 3,4,5,trihydroxy benzohydrazide in labortary by

microwave method and purity is checked by M.P.TLC, IR,NMR.The solution of Imine's prepared in different solvent like Ethanol, Acetone, DMF, DMSO, THF. by dissolving the appropreate amount by weight.All the weighing were made on mechaniki zaktady precyzying Gdansk Balance made in Poland (+ 0.001gm).

The densities of solution were determined by a bi-capilary pynoometer (+0.2%) having a bulb volume of about 10cm^3 and capillary having an internal diameter of 1 mm and calibrated with deionised doubly distilled water.The Imines's solutions of different concentrations were the refractive indices of solvent mixture and solution were measured by Abbe's refractometer at 27^0 c.The accuracy of Abbe's refractometer was within (+0.001) unit.

instrument.The refractive indices and polarisibility constant can be calculated the equations.

The refractive indices and molar refraction at different molality and polarisibility constant can be calculated the equations.

$Rm = [(n^2+1)/(n^2- 1)]\times(m/d)$---------- (1)

Where

M –is the mass of ligand in gram.

d --is the density of solution of ligand.

N – is the refractive index.

R_m – is the molar refraction.

$R_m = 4/3\ \Delta\ Nc.$ ----------(2)

$\alpha = ¾ \times R_{m/Nc}$ ----------(3)

Where

Nc – is the Avogadro's number having value 6.023×10^{23} per mole.

α – Polarisibility constant.

$Rm(solution) = X_1\ Rm_1 + X_2\ Rm_2$ ----------(4)

Where

Rm – is the Molar refraction

X_1 and X_2 mole fraction of solvent and solute in solution

Rm_1 and Rm_2 be he molar refractivity of solvent and solute.

The molar refraction represent actual or true volume of the substance moleculs in mole.

The molar refraction of solute can be calculated as

Rm(solute) = R(mixture) – R(solvent)

The refractive index of solvent and solutions art different concentrations are measured from prepared in different solvents DMF,DMSO,THF,Ethanol,and Acetone.The refractive index of solvent and solutions art different concentrations are measured from Abbe's refractometer and the values of Rrefractive index ,Molar refraction,Polarisibility constant are evaluated

Table- 1 Refractometry data,system- 3,4,5, trihydroxy benzoamido 4-Bromoimine,
Solvent- D.M.F.

Sr. No	Molality	Refractive Index (n)	Density (d)	Molar Refraction (Rm)	Polarisibility (α)
1	0.01	1.4410	1.7791	10.8524×10^{-3}	1.2197×10^{20}
2	0.05	1.4400	1.7789	5.4043×10^{-3}	0.6729×10^{20}
3	0.0025	1.4390	1.7777	2.6823×10^{-3}	0.3340×10^{20}
4	0.00125	1.4360	1.7769	1.3387×10^{-3}	0.1666×10^{20}
5	0.00063	1.4330	1.7766	0.6579×10^{-3}	0.0819×10^{20}

Table-2 Refractometry data system- 3,4,5,trihydroxy benzoamide 4-Bromoimines
Solvant – EHANOL

Sr No	Molality	Refractive Index(n)	Density (d)	Molar Refraction (Rm)	Polarisibility (α)
1	0.01	1.4870	1.9330	8.9270×10^{-3}	1.1116×10^{20}
2	0.05	1.4810	1.9235	4.4448×10^{-3}	0.5534×10^{20}
3	0.0025	1.4790	1.9155	2.2187×10^{-3}	0.2762×10^{20}
4	0.00125	1.4700	1.9012	1.1073×10^{-3}	0.1378×10^{20}
5	0.00063	1.4690	1.8932	0.5504×10^{-3}	0.0685×10^{20}

Table – 3 Refractometry data 3,4,5,Trihydroxy Benzoamide 4-bromoimine
Solvant – DMSO

Sr. No	Molality	Refractive Index (n)	Density (d)	Molar Refraction Rm	Polarisibility (α)
1	0.01	1.3799	1.3870	12.4532×10^{-3}	1.5507×10^{20}
2	0.05	1.3782	1.3860	6.2184×10^{-3}	0.7743×10^{20}
3	0.0025	1.3762	1.3850	3.0985×10^{-3}	0.3858×10^{20}
4	0.00125	1.3698	1.3820	1.5556×10^{-3}	0.1937×1020
5	0.00063	1.3612	1.3800	0.7656×10^{-3}	0.0953×10^{20}

Table – 4 Refractometry data 3,4,5,Trihydroxy Benzoamide 4-Bromoimine
Solvant – ACETONE.

Sr. No	Molality	Refractive Index (n)	Density (d)	Molar Refraction Rm	Polarisibility (α)
1	0.01	1.3900	1.4752	11.7291×10^{-3}	1.4605×10^{20}
2	0.05	1.3870	1.4736	5.8301×10^{-3}	0.7268×10^{20}
3	0.0025	1.3820	1.4714	2.8783×10^{-3}	0.3584×10^{20}
4	0.00125	1.3700	1.4679	1.4016×10^{-3}	0.1745×1020
5	0.00063	1.3620	1.4649	0.6810×10^{-3}	0.0847×10^{20}

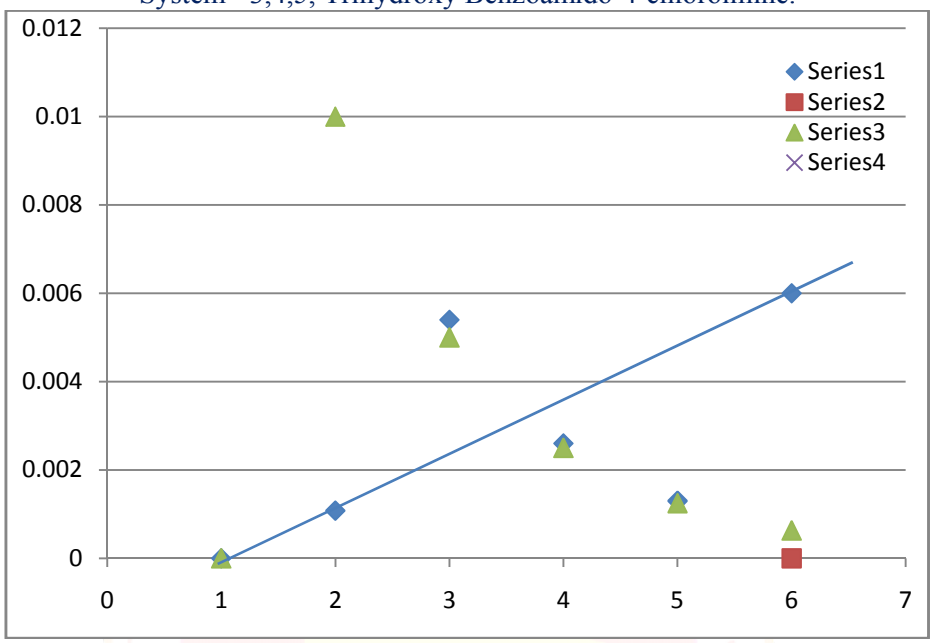
Table – 5 Refractometry data 3,4,5,Trihydroxy Benzoamide 4-Bromoimine
Solvant – THF

Sr. No	Molality	Refractive Index (n)	Density (d)	Molar Refraction Rm	Polarisibility (α)
1	0.01	1.3880	1.4030	12.2738×10^{-3}	1.5283×10^{20}
2	0.05	1.3850	1.4004	6.1067×10^{-3}	0.7604×10^{20}
3	0.0025	1.3820	1.3984	3.0447×10^{-3}	0.3765×10^{20}
4	0.00125	1.3790	1.3909	1.5113×10^{-3}	0.1889×10^{20}

5	0.00063	1.3760	1.3809	0.7473×10^{-3}	0.0935×10^{20}

Graph Between Molar Refraction Vs Molality

Refractometry data
System - 3,4,5, Trihydroxy Benzoamido-4-chloroimine.



Solvent – D.M.F.

Table-2 Refractometry data system-3,4,5,trihydroxy benzoamide 4-Bromoimines
Solvant – ETHANOL.

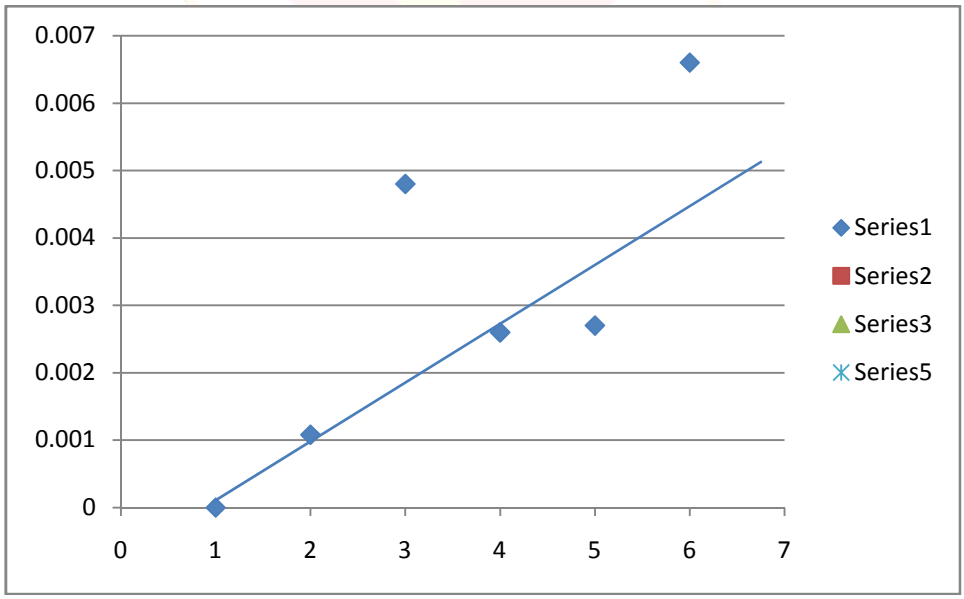


Table III 3,4,5 trihydroxy Benzoamide-4-Bromoimine
Solvent- ACETONE

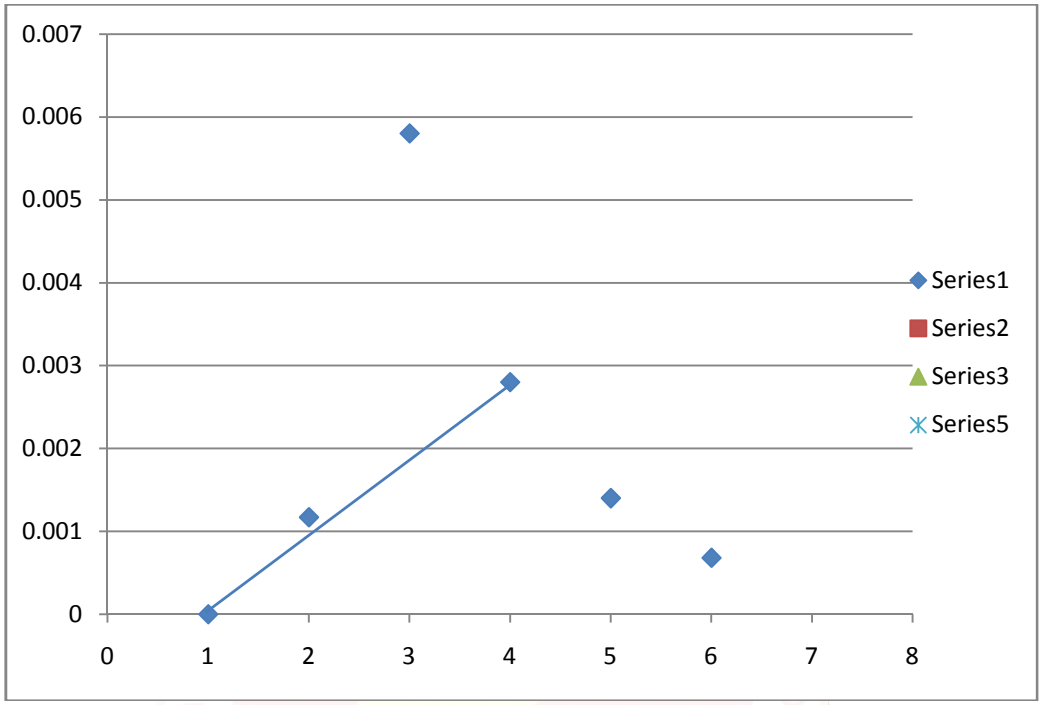


Table IV – 3,4,5,trihydroxy Benzamide -4-Bromoamide
Solvent – THF

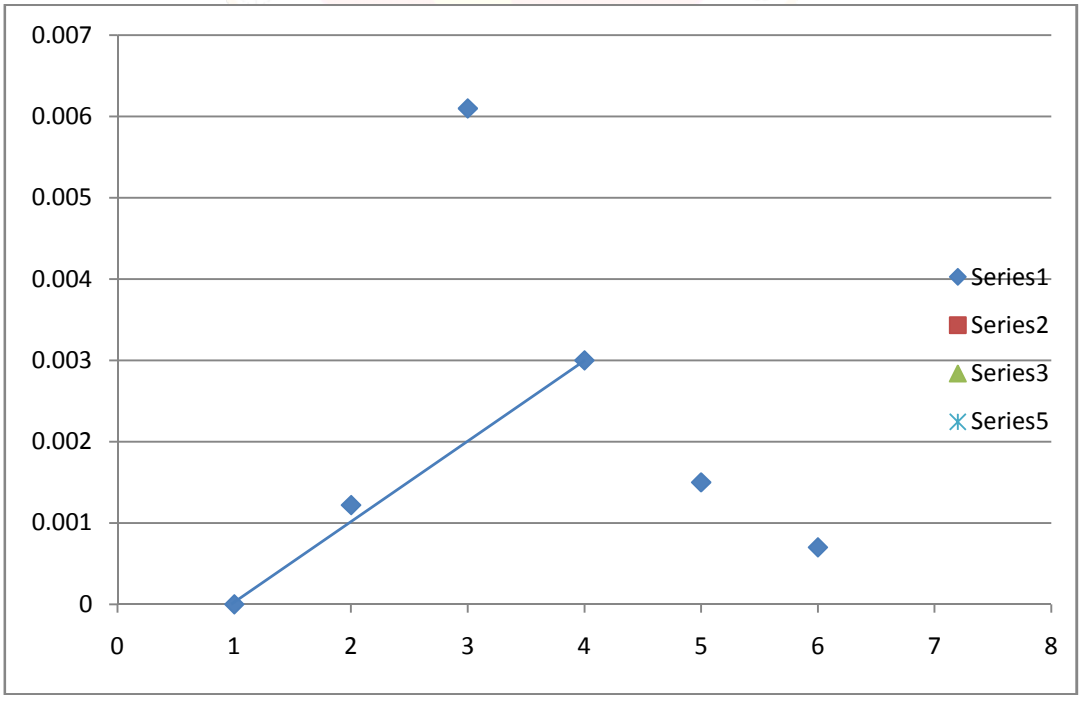
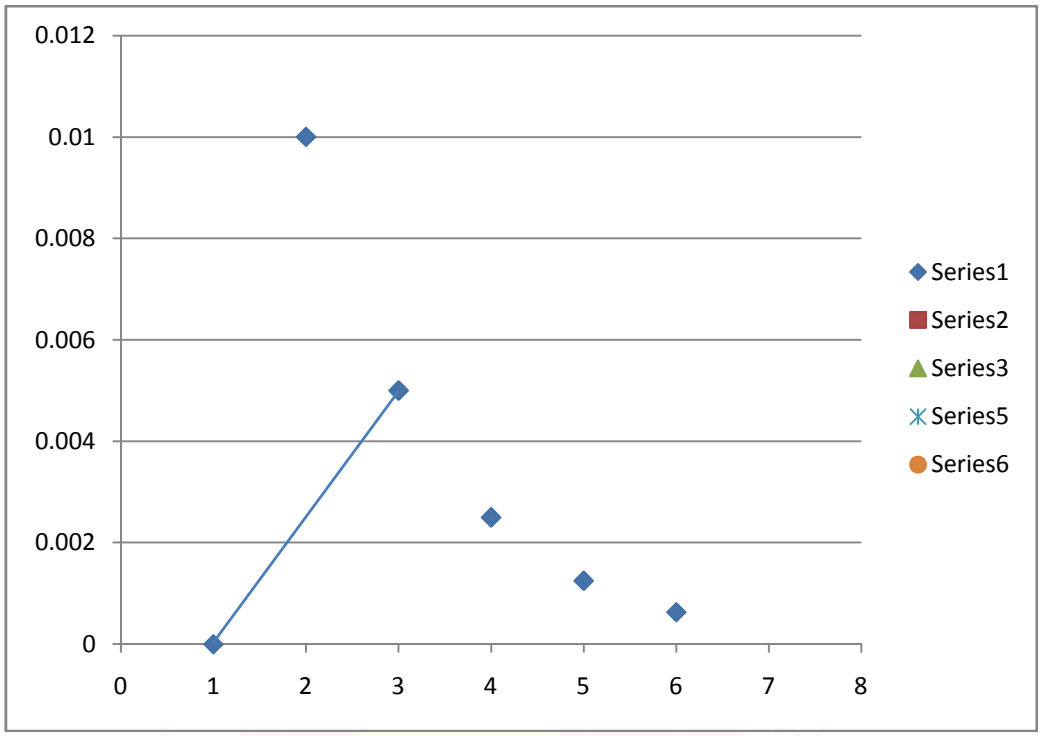


Table V – 3



RESULT AND DISCURSSION

It could be seen that from table I to V the molar refraction and polarisibility constant decreses with decreasing the concentration of solution. The Acetone and Ethanol are found to be lower value of Molar Refraction and Polarisibilty constant than the DMSO,TH F,DMF.Because Polar solvent contains the H-bonding may forms complex with solute,but Non Polar solvent does not contains H-bonding and hence does not forms a complex with solute.

This may also be attributed to the fact that the dipole in the compound , lies perpendicular to longer axis of the molecules.Considerable dipole association (Intermolecular attraction)

Takes place which would be accompanied by increasing polarisibility constant as well as molar refraction with increasing concentration because of mutual compensation of the dipoles

The Graph is Ploted in between the Molar Refraction verses Concentration.It could be seen that linear relation ship between the Molar Refraction and Concentration.From the graph the concentration of unknown solution of ligand can be calculated.

It is also observed the refractive index is also related to the percentage of dissolved solids in solution in different solvents from this the substance containg more polarisible (soft) group will normaly higher

Refractive index than substances containg less polarisible (haed group) .

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PARMAGNETIC OXIDATION OF COPPER (II) METAL COMPLEX IN ACID MEDIUM.

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ABSTRACT

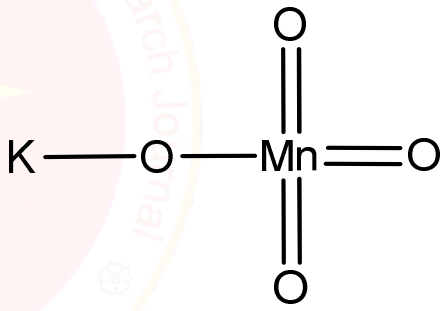
The Kinetic of oxidation of Iron Copper (II) derived from 8-hydroxy quinoline and salicylaldehyde by potassium permanganate has been studied in the presence of acidic medium. The reaction is first order with respect to $KMnO_4$ as well as Metal complex concentration. The reaction rate has been determined at different temperature and different thermodynamic parameters have been calculated which shows that the reaction rate increase with increase in temperature. With increase in the concentration of acid the reaction rate increases. A suitable mechanism has been proposed.

Key words- *Kinetics, Mechanism, Oxidation, Copper (II) Metal Complex, potassium permanganate, thermodynamic parameters, etc.*

INTRODUCTION

The kinetics provides the useful information about the mechanism and rate of chemical reaction, which helps to run a chemical reaction successfully by a way of selecting optimum condition as to get maximum yield.[1] The kinetic study also helps us to study the factors which influence the rate of reaction like temperature, pressure, substrate concentration, oxidant concentration. Composition of reaction mixture and catalyst.[2] The reaction kinetics plays a very important role in the investigation of the reaction mechanism.

In this experiment oxidation of Copper (II) metal complex derived from 8-hydroxy quinoline and salicylaldehyde is done by oxidizing agent.[3] Any oxidizing agent can be used but here permanganate ion is used. An oxidizing agent (also oxidant, oxidizer or oxidiser) is the element or compound in an oxidation-reduction (redox) reaction that accepts an electron from another species.[4] Because the oxidizing agent is gaining electrons (and is thus often called an electron acceptor) it is said to have been reduced. It is a salt consisting of K^+ and MnO^{-4} ions. Formerly known as permanganate of Potash or Condy's crystals, it is a oxidizing agent.[5] It dissolves in water to give intensely pink or purple solutions. It's structure is shown below



Many Zinc and Cadmium complexes with nitrogen containing heterocyclic ligands and pseudo halides are known in the literature. The ring size number of hetero atoms and nature of the substituent in the heterocyclic ring significantly control the chemical and physical properties of complexes.[6]

We recently embarked on a program aimed at exploring and modulating the power the power of $KMnO_4$ in order to transform it into a much more selective and synthetically useful reagent. In this paper, we report on one such successful transformation.

MATERIAL AND METHOD

Chemical which are used in this experiment are highly purified and AR grade, the solutions were used in this study were prepared by using distilled acetic acid[7] and double distilled water. Solution of Copper (II) metal complex were prepared by using double distilled water and this solution was used for kinetic studies. The reaction was carried out in glass stoppered Pyrex boiling tube. The

Kinetics of reaction was followed in the temperature range 30°C to 50°C.

KINETIC MEASUREMENT

The kinetic of reaction were measured by using double beam spectrophotometer model No AU2100 of Systronic Company which is having inbuilt software. The Kinetic of reaction were measured at 520nm wavelength up to the 80% completion of reaction.

STOICHIOMETRY OF REACTION

The Stoichiometry of the reaction were determined by conveying out several sets of experimental with varying amount of oxidising agent potassium permanganate over Cu (II) metal complex in acetic acid using in H_2SO_4. The remaining potassium permanganate was then analysed spectrophotometrically the result indicates that 1 mole of Cu (II) metal complex react with 1 mole of potassium permanganate.

PRODUCT ANALYSIS

Product analysis has been done by chemical test. Solution of each complex after oxidation reaction has been used for the analysis of product. In this it is found that after oxidation reaction M^{2+} is converted in M^{3+}.[8, 9, 10]

$$[Cu(II)(C_9H_6ON)(C_7H_5O_2)(H_2O)]Cl_2 + MnO_4^- + 4H^+ \rightarrow C_9H_6ON + C_7H_5O_2 + MnO_2 + CuO\downarrow + 2HCl + 2H_2O$$

Black ppt.

After completion of oxidation of complex the black coloured precipitate of CuO is formed as the product which confirms the presence of Cu^{2+}.[11]

RESULT AND DISCUSSION

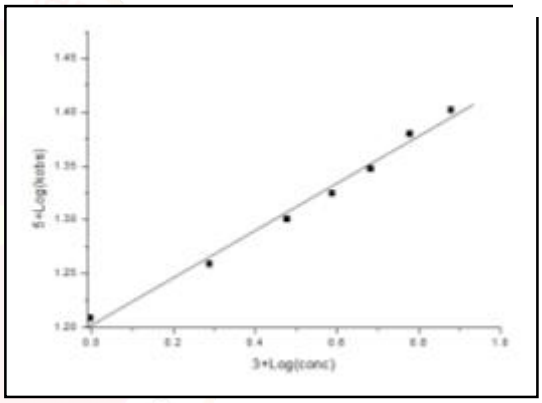
The results of various parameters is given in tabular form and presented with graphs.

1) Effect of variation of concentration of Cu (II) metal complex:-

The oxidation of Cu (II) metal complex with potassium permanganate in acetic acid in presence of sulphuric acid. By keeping constant concentration of potassium permanganate and H_2SO_4 and by changing the concentration of Cu (II) metal complex increases the rate of reaction (Table-1) the plot of log of k_{obs} versus log concentration of Cu (II) metal complex for different initial concentration of metal complex is linear with unit slop, which shows that the first order dependence of rate of reaction on Cu (II) metal complex.[12]

Table-1: Effect of variation of concentration of Cu (II) metal complex.

[Copper complex]	Rate K_{obs}
$1x10^{-3}$	0.00017
$2 x10^{-3}$	0.00018
$3 x10^{-3}$	0.0002
$4 x10^{-3}$	0.00021
$5 x10^{-3}$	0.00022
$6 x10^{-3}$	0.00024
$7 x10^{-3}$	0.00026

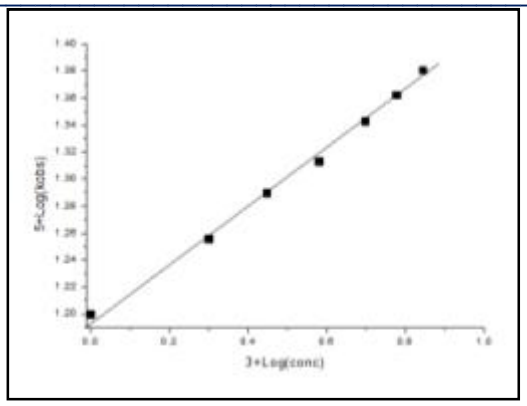


2) Effect of varying oxidising agent potassium permanganate:-

In this parameter studying the effect of variation of oxidising agent potassium permanganate on oxidation reaction of Cu (II) metal complex by keeping constant concentration of Cu (II) metal complex and concentration of H_2SO_4. The Concentration of oxidising agent increases, decreases the rate of reaction Table – 2 the plot of 1/log K_{obs} verses log [$KMnO_4$] for different initial concentration of [$KMnO_4$] is linear with unit slop presents the first order dependence of rate on [$KMnO_4$].[13]

Table-2: Effect of variation of concentration of potassium permanganate.

[$KMnO_4$]	Rate K_{obs}
$1x10^{-4}$	0.00016
$2 x10^{-4}$	0.00018
$3 x10^{-4}$	0.00019
$4 x10^{-4}$	0.0002
$5 x10^{-4}$	0.00022
$6 x10^{-4}$	0.00023
$7 x10^{-4}$	0.00024

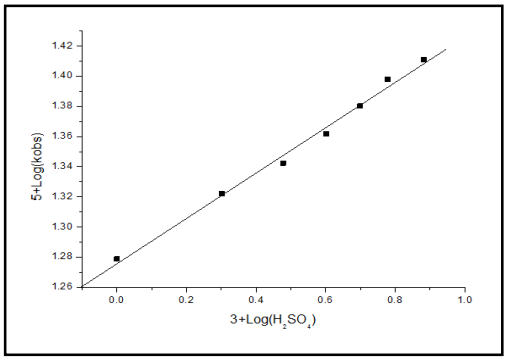


3) Effect of variation of concentration of sulphuric acid:-

In this factor there is study of variation of concentration of sulphuric acid on oxidation of Cu (II) metal complex. By keeping constant concentration of oxidising agent and substrate changing the $[H_2SO_4]$ we find that the rate increases with increase in $[H_2SO_4]$ Table – 3 and plot of log k Vs log $[H^+]$ was linear with a unit slop indicating first order reaction on $[H^+]$.[14] Fig – 3.

Table-3: Effect of variation of concentration of sulphuric acid.

$[H_2SO_4]$	Rate K_{obs}
0.001	0.00019
0.002	0.00021
0.003	0.00022
0.004	0.00023
0.005	0.00024
0.006	0.00025
0.007	0.00026



4) Effect of salts on reaction rate:-

The effect of salts on the reaction rate was studied by adding various concentration by salt. By keeping constant concentration by oxidising agent substrate and acid. It was observed that the rate of oxidation was not altered by the addition of salts.[15]

Table-4: Effect of salts on reaction rate

[KBr]	Rate K_{obs}
$1x10^{-2}$	0.00023
$2\ x10^{-2}$	0.00029
$3\ x10^{-2}$	0.0003
$4\ x10^{-2}$	0.00029
$5\ x10^{-2}$	0.00021
$6\ x10^{-2}$	0.0002
$7\ x10^{-2}$	0.00026

5) Effect of Temperature:-

The study of effect of temperature on rate of oxidation of Cu (II) metal complex by potassium permanganate has been studied at different temperature by keeping all other factors constant concentration with changing temperature from 303K to 323K. The rate constants are given in Table-5 as the temperature increases the values by rate constant also increases that shows rate of reaction depends of temperature the Arrhenius plot 10gk Vs. 1/T were found to be linear fig – 4.[16] The activation energy (Ea) were calculated from the clop of the plots from this values the thermodynamic parameters $\Delta H^{\#}$, $\Delta S^{\#}$, $\Delta G^{\#}$ was calculated Table – 6.

Table-5: Effect of Temperature

Temperature (K)	Rate K_{obs}
293	0.0002
298	0.00023
303	0.00026
308	0.00030
313	0.00033
318	0.00034
323	0.00036

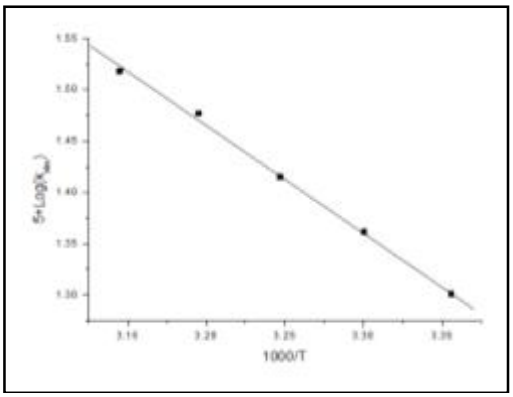


Table –6:

Ea	20956.76
ΔH	18354.17
ΔS	-256.41
ΔG	98611.08

CONCLUSION

The oxidation of Cu (II) metal increases in acetic acid in acid medium shows that the oxidation of Cu (II) metal complex of potassium permanganate is in presence of acidic medium with effect of oxidising agent, substrate an acid and temperature the reaction is first order dependence. The addition of salt does not alter the rate of oxidation reaction. The mechanism of the reaction were given with the activation parameters the negative value of $\Delta S^{\#}$ provides support to the formation of rigid transition state. The overall mechanistic sequence described here is constituent with product and

$$H^+ + Mno_4^- \longrightarrow HMnO_4$$

mechanistic study.

- Mechanism of oxidation of Cu (II) metal complex by potassium permanganate.

This point has been also confirmed by previous researchers. Hence Mn (VII) could be considered as the reactive specie and this probably exists to a certain extent as $HMnO_4$.

As the concentration is increased the formation of $HMnO_4$ is favoured and hence increases the oxidation may be assumed to be taking place by Mn (VII) in the form of either MnO_4 or $HMnO_4$ or both depending on the acid concentration. The linear plot of log k Vs log (H_2SO_4) and log k Vs. Ho indicates that the reactions are acid catalysed, but none of the above plots gives an ideal slope for unity.

Derivation of Rate Law:

Based on the results of kinetic and proposed mechanism, the following rate expression can be derived by applying steady state approximation.

$$[MnO_4] + H^+ \underset{}{\overset{k_1}{\rightleftharpoons}} HMnO_4$$

$$\text{Copper Metal Complex} + HMnO_4 \underset{}{\overset{k_2}{\rightleftharpoons}} C\ (\text{Intermediate Complex})$$

$$C \xrightarrow{k} \text{Product}$$

$$[MnO_4^-] = [MnO_4^-] + [HMnO_4]$$

$$= [MnO_4^-] + k_1[MnO_4^-][H^+]$$

$$= [MnO_4^-] + 1 + k_1[H^+]$$

$$\text{Rate} = \frac{kk_2[MnO_4^-][\text{Cu M.C.}]}{1 + k_1[H^+]}$$

$$\frac{\text{Rate}}{[MnO_4][\text{Cu M.C.}]} = \frac{kk_2}{1 + k_1[H^+]}$$

$$K_{obs} = \frac{kk_2}{1 + k_1[H^+]}$$

$$\frac{1}{K_{obs}} = \frac{1}{kk_2} + \frac{k_1[H^+]}{kk_2}$$

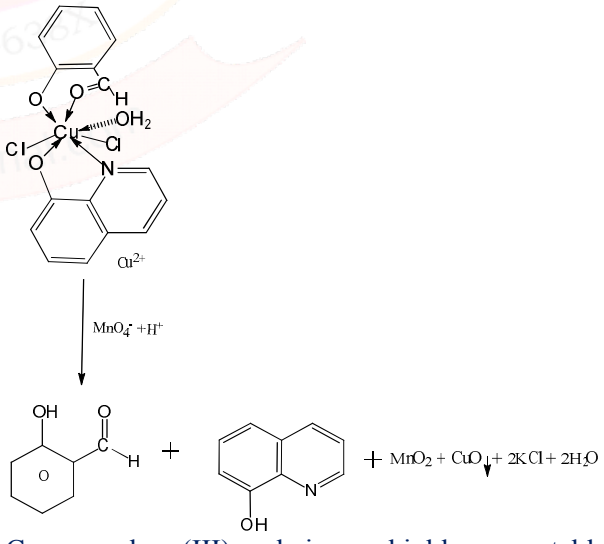
The rate law can be expressed by following equation

$$\frac{-d[Mn(VII)]}{dt} = k[\text{Cu M.C.}][MnO_4]_{Total}$$

Where, Cu M.C. = Copper Metal Complex

This type of hydride ion transfer process has been proposed in the oxidation of aldehyde, formic acid, ethers, alcohols, etc. by permanganate in moderately concentrated acid solutions.[17,18]

Mechanism of oxidation of Copper metal complexes:-



Compound (III) being highly unstable disproportionate to give acid and the corresponding aldehyde. The rate law can be expressed by equation (1).

$$\frac{-d[Mn(VII)]}{dt} = k\,(\text{Copper Metal Complex})[MnO_4]$$

This type of hydride ion transfer process has been proposed in the oxidation of aldehyde, formic acid, ethers, alcohols etc. by permanganate in moderately concentrated acid solutions [20].

The effect of temperature on reaction rate was studied which shows the increase in reaction rate with increase in temperature (Table 4 and 5).

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DENSITY AND VISCOMETRIC STUDIES OF THE SCHIFF BASE LIGANDS AT DIFFERENT TEMPERATURE IN BINARY MIXTURES

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ABSTRACT

In the present work, the density and viscometric study of synthesized Schiff base ligand were carried out in various percentages of binary solvent mixtures of ethanol-dioxane-water. The viscometric study was extended for different concentration of Schiff base ligand in a binary solvent at 308 K, 318 K, and 328 K. From the temperature variation data, thermodynamic parameters like the change in enthalpy, entropy and Gibbs free energy have been evaluated. Further, on the basis of various values of specific viscosity at the different concentration, the molecular interactions of Schiff base ligand with binary solvent mixtures have been explained. It was observed that variation of specific viscosity with concentration is depending upon the type of ligand as well as nature solvents. The results obtained were reproducible and accurate with ≤ 0.5% RSD.

Keywords: *density, viscosity, thermodynamic parameter, Schiff base ligand, molecular interaction.*

INTRODUCTION

Schiff bases are the condensation products of primary amines with carbonyl compounds and were first reported by Hugo Schiff [1]. Schiff bases exhibit useful biological activities such anti-inflammatory, analgesic, antimicrobial, anticonvulsant, antitubercular, anticancer, antioxidant, anthelmintic, antiglycation, and antidepressant activities [2-4]. Schiff bases are also used as catalysts, pigments and dyes intermediates in organic synthesis, polymer stabilizers, and corrosion inhibitors [6-9]. Studies enlightened that metal complexes show greater biological activity than free organic compounds. Augmentation of biological activity was reported by an implementation of transition metals into Schiff bases [10-12].

Viscosity is the measure of the level of resistance to flow of a liquid. It is the stickiness and thickness of a liquid. The viscometric method is simple, inexpensive and sensitive analytical technique and also an attractive to other methods. Absorption, transmission, metabolism, and excretion are also depending on viscosity. Viscometric measurement is a physical parameter and gives primary information about structure, size, shape and molecular weight of compound [13-17]. For natural and industrial processes known significant physicochemical properties are density, viscosity, and surface tension of liquids. The Jones-Dole equation accounts for the observed viscosity concentration dependence of dilute electrolyte solutions [18-19].

Distinct and evident attention had been engrossed on Schiff base polymers, due to their vast applications in many areas especially in their biological features [20-22]. The viscometric and thermodynamic study of Schiff base was carried out to study solute-solvent interaction, drug delivery [23-25] to determine molecular weight [26] and to study antimicrobial viscometric study [27].

Schiff base derivatives in various processes promoted the researchers for designing of novel heterocyclic/aryl Schiff bases for the development of new environmental-friendly technology. Taking all these things into consideration the present work examines the newly synthesis Schiff base derivative and its density, viscometric and thermodynamic study. From the temperature variation, specific viscosity data with the concentration of Schiff base ligands used to calculate thermodynamic parameters like the change in enthalpy, entropy, and Gibbs free energy. The value of coefficient A and β used to interpret solute-solute interaction and solute-solvent interaction.

MATERIALS AND METHODS

All the chemicals used were of analytical grade reagent from *S D* Fine-Chem Limited, Mumbai 400030 and were used without further purification.

Aqueous solutions were prepared with doubly distilled water. The binary mixture of 70% dioxane-water and 70% ethanol-water were prepared gravimetrically in Stoppard bottle. The densities and viscosities of pure liquids and their binary mixtures were measured using single capillary pyknometer and Ostwald's viscometer which was calibrated with double distilled water. The flow time was measure with the digital stop watch, each sample allowed to flow three times and then average flow time was calculated. The thermodynamic measurement was carried out in the thermostat. From the observation density, relative and specific viscosity can be calculated for all the Schiff base ligand in both the solvent.

$$\eta_r = \frac{d_1 \times t_1}{d_w \times t_w}$$

η_r-relative viscosity ($\eta_r = \eta_1/\eta_w$), η_1, d_1, t_1 and η_w, d_w, t_w were viscosity, density and time required to flow for Schiff base ligand and water respectively. Viscosity data were analyzed in the light of Jones-Dole equation.

$$(\eta r - 1) / \sqrt{C} = A + \beta\sqrt{C}$$

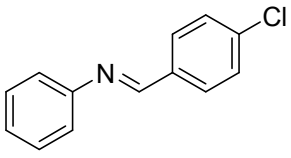
Where A and β are the Falkenhagen and the Jones-Dole coefficients. From the graph of (η_r -1) /√C verses √C, 'A' which is the measure of solute-solute interactions and 'β' which is the measure of solute-solvent interactions has been calculated.

The present study deals with the viscometric measurement of Schiff base ligand 1–(4-chlorophenyl)-N-phenymethanimine (C_1) andN,N-dimethyl-4-(phenylimino)methyl aniline (C_2) and 2-methoxy-5-(phenylimino)methyl phenol (C_3) at 308 K, 318 K and 328 K in prepared binary solvent mixtures. From the thermodynamic study, the value of the change in energy (ΔG), enthalpy (ΔH) and entropy (ΔS) can be calculated.

Synthesis of Schiff Base:-

1) Synthesis 1-(4-chlorophenyl)-N-phenylmethanimine (C_1):-

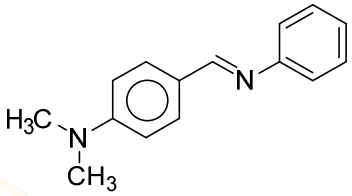
0.01 mole of aniline is added to the solution of 4-chloro benzaldehyde (0.01mole) in ethanol as a solvent. The catalytic amount of nickel nitrate hexahydrate is added to the reaction mixture and stirrer at room temperature. The solid obtained is filter and recrystallized by using ethanol.



(*E*)-1-(4-chlorophenyl)-*N*-phenylmethanimine
Chemical Formula: $C_{13}H_{10}ClN$

2) Synthesis N,N – dimethyl-4-(phenylimino)methyl aniline(C_2):-

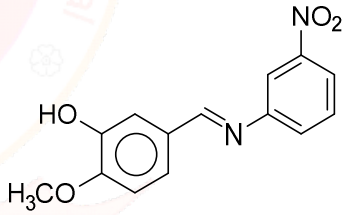
0.01 mole of Aniline is added to the solution of N, N – dimethyl benzaldehyde (0.01mole) in ethanol as a solvent. The catalytic amount of nickel nitrate hexa -hydrate is added to the reaction mixture and stirrer at room temp the solid obtained is filter and recrystallized by using ethanol.



(E)-N,N-dimethyl-4-((phenylimino)methyl)aniline
Chemical Formula: C15H16N2

3) Synthesis of 2 – methoxy- 5-(phenylimino)methyl phenol (C_3):-

0.01 mole of 3- Nitro Aniline is added to the solution of vanillin (0.01mole) in ethanol as a solvent. The catalytic amount of nickel nitrate hexa-hydrate is added to the reaction mixture and stirrer at room temp the solid obtained is filter and recrystallized by using ethanol.



(E)-2-methoxy-5-(((3-nitrophenyl)imino)methyl)phenol
Chemical Formula: C14H12N2O4

IR Spectral Data of Schiff base derivatives

M. F.	ν(C = N)	ν(C–H)	ν(C=C)
$C_{13}H_{10}ClN$	1597	2881	1458
$C_{15}H_{16}N_2$	1605	2890	1464
$C_{14}H_{12}N_2O_4$	1610	2892	1470

RESULT AND DISCUSSION

Viscometric study with variation in concentration:

To explorer the utility of synthesized Schiff base derivatives C_1, C_2 and C_3 its viscosity study was carried out for different concentration in 70%

ethanol-water system and 70% dioxane-water system as a solvent. The data obtained were used to calculate the relative viscosity (η_r) and density of Schiff base derivative. It was observed that relative viscosity decreases in both the solvents. The study was extended to calculate Jones-Dole coefficient A and 'β' which is the measure of solute-solute interaction and solute-solvent interaction respectively. The plot between $(\eta_r - 1)/\sqrt{C}$ verses $\sqrt{C}$ shows a linear graph which shows the validity of Jones–Dole equation for all the tested Schiff base derivative. The slope of this graph shows the value of β –coefficient, and intercept give the value of coefficient A.

Table 1 Viscometric study with variation in concentration

System	Temp (K)	Conc. (M)	*Medium- Dioxane water*					*Medium-Ethanol-water*				
			Density	Relative Viscosity η_r	Specific Viscosity $\eta r - 1/\sqrt{C}$	A	β	Density	Relative Viscosity η_r	Specific Viscosity $\eta r - 1/\sqrt{C}$	A	β
C_1	298	0.1 0.05 0.001	1.0095 1.0038 0.9865	0.7087 0.7047 0.5935	-0.9396 -1.3269 -13.112	-13.87	46.55	0.8375 0.8350 0.8312	1.3667 1.2268 1.0923	1.289 1.017 0.741	0.662	1.8773
C_2	298	0.1 0.05 0.001	0.9996 0.9882 0.9854	0.6683 0.6612 0.5929	-1.07 -1.516 -13.13	-13.96	46.088	0.8466 0.8317 0.7565	1.1130 1.0566 0.9339	3.645 0.182 -0.2964	-1.118	12.28
C_3	298	0.1 0.05 0.001	1.0274 1.0104 0.9841	0.6866 0.6418 0.5592	-1.010 -1.606 -14.21	-15.07	50.364	0.8879 0.8849 0.8743	1.1871 0.8578 0.8148	0.6035 0.637 -5.974	-6.346	25.365

In present work clearly indicates the decrease in density, relative viscosity and specific viscosity with the decrease in concentration ligand in both the solvent because concentration decreases the number of solute particle decreases at the same time number of solvent particle increases which is responsible to increase the solvation effect. It was observed from the table that the values of A are almost negative in both the solvent for C_1, C_2 and C_3 shows weak solute-solute interaction which is also supported by decrease in relative viscosity. Again the values of A are more negative in dioxane-water as compare to ethanol-water medium due to different polarity index of binary solvents. On the other hand value of β -coefficient is positive shows strong solute-solvent interaction which indicates the good drug activity. The value of β-coefficient is more positive in dioxane-water may be due to weak hydrogen bonding. Again it was observed that the value of β -coefficient is more positive for C_3 shows strong solute-solvent interaction due to presence of hydroxyl group.

Table 2Viscometric study with variation in temperature (medium –Dioxane-water)

System	Conc. (M)	Temp (K)	1 / T $(K^{-1}) \times 10^{-3}$	Time flow (sec.)	Relative Viscosity η_r	Log (η_r)
C_1	0.1	308	3.24×10^{-3}	20	0.7158	-0.1452
		318	3.14×10^{-3}	19	0.7865	-0.1043
		328	3.04×10^{-3}	18	0.8411	-0.0751
	0.05	308	3.24×10^{-3}	18	0.6430	-0.1917
		318	3.14×10^{-3}	17	0.7027	-0.1532
		328	3.04×10^{-3}	16	0.7966	-0.0987
	0.001	308	3.24×10^{-3}	18	0.5980	-0.2232
		318	3.14×10^{-3}	17	0.6513	-0.1862
		328	3.04×10^{-3}	16	0.7406	-0.1304
C_2	0.1	308	3.24×10^{-3}	19	0.6770	-0.1694
		318	3.14×10^{-3}	18	0.7429	-0.1290

		328	3.04×10^{-3}	17	0.7962	-0.0989
	0.05	308	3.24×10^{-3}	18	0.6326	-0.1988
		318	3.14×10^{-3}	17	0.6917	-0.1600
		328	3.04×10^{-3}	16	0.7400	-0.1307
	0.001	308	3.24×10^{-3}	17	0.5966	-0.2244
		318	3.14×10^{-3}	16	0.6494	-0.1874
		328	3.04×10^{-3}	15	0.6902	-0.1610
C_3	0.1	308	3.24×10^{-3}	19	0.6961	-0.1573
		318	3.14×10^{-3}	18	0.7880	-0.1032
		328	3.04×10^{-3}	17	0.8165	-0.0880
	0.05	308	3.24×10^{-3}	18	0.6456	-0.1900
		318	3.14×10^{-3}	16	0.6688	-0.1747
		328	3.04×10^{-3}	15	0.7527	-0.1233
	0.001	308	3.24×10^{-3}	16	0.5635	-0.2491
		318	3.14×10^{-3}	15	0.6108	-0.2141
		328	3.04×10^{-3}	14	0.6944	-0.1583

Table 3Viscometric study with variation in temperature (medium –Ethanol-water)

System	Conc. (M)	Temp (K)	1 / T (K^{-1}) × 10^{-3}	Time flow (sec.)	Relative Viscosity η_r	Log (η_r)
C_1	0.1	308	3.24×10^{-3}	46	1.6427	0.2155
		318	3.14×10^{-3}	42	1.3971	0.1452
		328	3.04×10^{-3}	38	1.4217	0.1528
	0.05	308	3.24×10^{-3}	41	1.1950	0.077
		318	3.14×10^{-3}	37	1.235	0.0916
		328	3.04×10^{-3}	35	1.2869	0.1095
	0.001	308	3.24×10^{-3}	36	1.0557	0.0235
		318	3.14×10^{-3}	33	1.1121	0.0461
		328	3.04×10^{-3}	30	1.1300	0.0530
C_2	0.1	308	3.24×10^{-3}	35	1.0221	0.0094
		318	3.14×10^{-3}	31	1.0370	0.00157
		328	3.04×10^{-3}	29	1.0847	0.035
	0.05	308	3.24×10^{-3}	30	0.8928	-0.0492
		318	3.14×10^{-3}	26	0.9113	-0.0403
		328	3.04×10^{-3}	25	0.9396	-0.0270
	0.01	308	3.24×10^{-3}	41	1.1069	0.0440
		318	3.14×10^{-3}	38	1.1079	0.0443
		328	3.04×10^{-3}	36	1.2382	0.0927
C_3	0.1	308	3.24×10^{-3}	38	1.2062	0.0814
		318	3.14×10^{-3}	35	1.2820	0.1078
		328	3.04×10^{-3}	32	1.3361	0.1258
	0.05	308	3.24×10^{-3}	27	0.8487	-0.0712
		318	3.14×10^{-3}	25	0.9054	-0.0431
		328	3.04×10^{-3}	23	0.9263	-0.0332
	0.01	308	3.24×10^{-3}	24	0.7284	-0.1376
		318	3.14×10^{-3}	22	0.8608	-0.0650
		328	3.04×10^{-3}	20	0.7694	-0.1138

Table 4 Value of thermodynamic parameter

System	70%Dioxane-water				70%Ethanol-water		
	Conc. (M)	ΔG (J $mole^{-1}$)	ΔH (J $mole^{-1}$)	ΔS (J $mole^{-1}K^{-1}$)	ΔG (J $mole^{-1}$)	ΔH (J $mole^{-1}$)	ΔS (J $mole^{-1}K^{-1}$)
C_1	0.1M	1.4360	-812.15	2.6415	0.0593	670.05	-2.1752
	0.05M	-0.8807	-1172.75	3.8407	-0.3063	-345.97	1.1222
	0.001M	-0.8807	-6457.55	20.9632	-0.26805	-345.97	1.1224
C_2	0.1M	-0.6701	-812.15	2.6346	-0.2297	-249.51	0.8093
	0.05M	-0.6510	-699.26	2.2684	-0.2106	-257.85	0.8364
	0.001M	-0.5935	-691.96	2.2446	-0.4595	-580.33	1.8826
C_3	0.1M	-0.6510	-804.85	2.6110	-0.4212	-466.17	1.5121
	0.05M	-0.6318	-830.27	2.6959	-0.2106	-571.76	1.8556
	0.001M	-0.8616	-1059.85	3.4382	-0.3637	-153.19	0.4961

Viscometric study with variation in temperature

A liquid molecule needs some energy to move in to hole. As the energy becomes increasingly available at increasing temperature, a liquid can flow more easily at the higher temperature. The coefficient of viscosity thus, falls appreciably with rising temperature. The relationship between of viscosity of liquids and temperature is expressed mathematically as- $\eta = A.e^{\Delta G/RT}$

The viscometric study was extended for different concentration of Schiff base ligand in using 70% dioxane-water system and 70% ethanol-water system at 308K, 318K, and 328K.The graph plotted between log η_r and 1/T for each system was found to linear showing the validity of above equation. From the temperature variation data, thermodynamic parameters like change in enthalpy, entropy, and Gibbs free energy have been evaluated using following equation and are listed in table 2.

ΔG= -2.303 x R x Slope

$$\log\eta_{r_1} - \log\eta_{r_2} = \frac{\Delta H}{2.303}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

ΔS = (ΔH - ΔG)/T

From the above table, it is shown that the value of a change in free energy for different derivative of Schiff base is decreasing using ethanol-water and dioxane-water system. The value of entropy also increases with decreases in the concentration of the compound in both the solvent system. The negative value of enthalpy indicates that the reaction is exothermic.

CONCLUSION

In the present study, the values of A are negative for all Schiff base derivatives in both the solvent shows weak solute-solute interaction. Again the values are more negative in Dioxane-water as compare to ethanol-water medium. On the other hand value of β -coefficient are positive shows strong solute-solvent interaction which indicates the good drug activity. The value of β-coefficient is more positive in dioxane-water may be due to weak hydrogen bonding. The results obtained for present study indicate that the thermodynamic parameters are sensitive to molecular interaction. The negative value of enthalpy shows reaction is exothermic and positive value of entropy shows the randomness of solute molecules in the binary solvent which indicates solute-solvent interaction. Again the values of Gibbs's free energy are negative shows spontaneity of reaction. Also more positive entropy and more negative ΔG in 70% dioxane-water indicate the more hydrophobic nature of Schiff base derivative.

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SYNTHESIS AND CHARACTERIZATION OF NEW UNSYMMETRICAL SCHIFF BASE COMPLEXES OF *N-(2-NAPHTHOL BENZOATE)-N'-(2-HYDROXY ACETOPHENONE)ETHYLENEDIAMINE*AND ITS ELECTRICAL AND CATALYTIC STUDY

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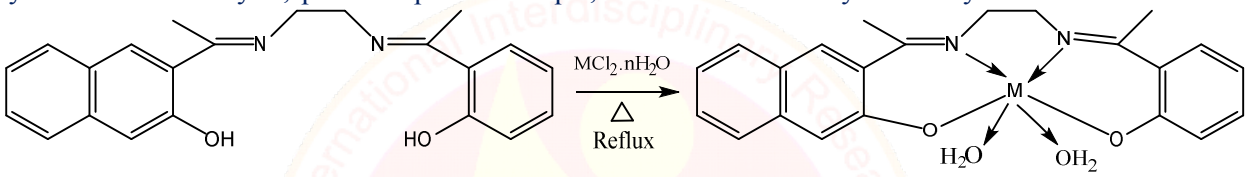
The monomeric Cobalt(II), Manganese (II), Nickel (II), Copper (II) and Zinc (II) chelate series with the general formula of $[M(L)\cdot 2H_2O]$ [L=N-(2-naphthol benzoate)-N'-(2-hydroxy acetophenone) ethylenediaminewere synthesized and recognized by elemental analysis,spectroscopic technique, magnetic moment and thermal analysis; then, their electrical and catalytic activities were studied. The electrical study shows semiconducting behavior of complexes. Catalytic studiesshow the good activity of unsymmetrical Schiff base complexes towards conversion of styrene to styrene oxide.



INTRODUCTION

Schiff bases and their complexes are considered as privileged class of compounds due to their biochemicalsynthesis, electrochemical analysis, anti-fungal, antiviral,anti-malarial, anti-inflammatory, as well as, catalyticactivities.[1,2]. Schiff bases are also of interest in industrialfields and as a corrosion inhibitor, thermo stable materials, as well as, powerful ligands in the formation ofcoordination compounds [3]. Several researchers have reported the synthesis and structuralcharacterization of Schiff bases and their complexesderived from different amines but only few works found on synthesis of unsymmetrical ligand. [4]. Schiff bases continue to occupy as vital ligands in metal co-ordination chemistry, even almost a century since their discovery. Schiff's bases [5] were still regarded as one of the most potential groups of organic compounds for facile preparations of metallo-organic hybrid materials and their role in organic synthesis. Moreover, there is a continued interest in synthesizing unsymmetrical Schiff base ligands [6, 7] because of their potential applications in various fields. In addition, the properties of Schiff base stimulated due to unsymmetrical behavior around metal.

MATERIALS AND METHODS

All the chemicals and solvents were used of analytical grade. All metals salts were use as supplied.

Preparation of N-(2-naphthol benzoate)-N'-(2-hydroxy acetophenone)ethylenediamine

N-(2-naphthol benzoate)-N'-(2-hydroxy acetophenone)ethylenediamine was prepared by reported procedure by condensation of 2-naphthol benzoate and 2-hydroxy acetophenone with ethylenediamine [8]. The yellowish product formed was characterized by spectroscopic techniques and thermal analysis.m.p. $260^{O}C$.

The schematic representation of the synthesis of ligand H_2L is shown in Figure.1

Synthesis of Cobalt (II), Manganese (II), Nickel (II), Copper (II) and Zinc (II) complexes

To a hot DMF-EtOH solution (50:50) (25ml) of ligand (2mmol), a hot ethanolic mixture of the appropriate metal salt (2mmol) was added with continuous stirring. The resulting reaction mixture was heated/reflux for 4-5 h. On cooling to room temperature, the solid complexes were filtered, washed thoroughly with ethanol, DMF and Petroleum ether to remove unreacted ligand and metal salts and dried, (Yield: 65-70%).

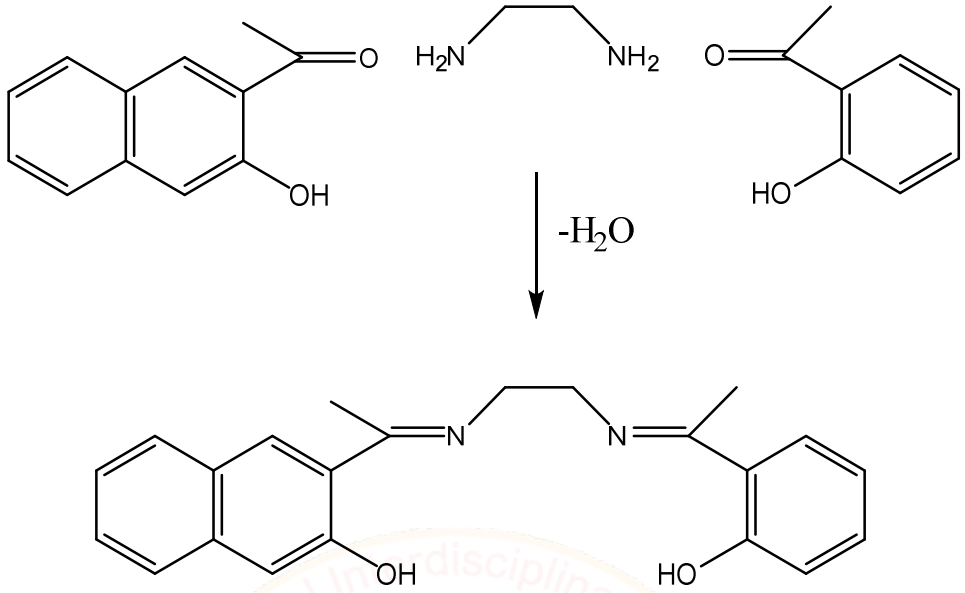


Figure.1: The schematic representation of the synthesis of ligand H_2L.

Physical measurement

Elemental analyses for C, H and N were obtained using Carlo Erba 1108 analyser in micro analytical laboratory, CDRI, Lucknow. IR spectra were recorded on a Bruker alpha IR spectrophotometer. ^{1}H NMR spectrum of ligand was obtained using a BrukerAuance-II 400 NMR spectrophotometer in a mixed solvent (DMSO+$CdCl_3$) at SAIF Punjab University, Chandigarh. The Electronic spectra of the complexes were recorded on Cary-60 UV spectrophotometer.Magnetic susceptibilities were determined on a Gouy balance at room temperature using $Hg[Co(SCN)_4]$ as calibrant; diamagnetic corrections were calculated from Pascal's constants. The solid state D.C. electrical conductivity of compounds was measured by Zentech Electrometer in their compressed pellet form over 313-403 K temperature range. TG analysis of the complexes was carried out on Perkin Elmer TG-2 thermobalance in ambient air with a heating rate of 10°C per minute. Metal contents of the complexes were analyses gravimetrically after decomposing the complexes with a mixture of $HClO_4$, H_2SO_4 and HNO_3 and then igniting to metal oxide. The powder XRD was recorded at VNIT, Nagpur, India.

RESULTS AND DISCUSSION

All the metal complexes are colored solids, non-hygroscopic, air stable and insoluble in common organic solvents but sparingly soluble in DMF and DMSO respectively. The elemental analysis shows 1:1 metal to ligand stoichiometry for all the complexes.

IR spectra

The IR spectra of the complexes have been compared with ligand in order to determine the coordination sites that may involve in complexation. The IR spectrum of the free ligand shows a medium broad band at 3428 cm^{-1} due to intramolecular hydrogen bonding between phenolic H and azomethine nitrogen atom. The absence of this band in the spectra of complexes indicates the breaking of hydrogen bond and coordination of phenolic oxygen to the metal after deprotonation.The ligand shows the ν (C=N) stretching band at 1624 cm^{-1} which shifted to lower frequency 1608-1584 cm^{-1} in the complexes indicating the involvement of the azomethine nitrogen in coordination. This is further supported by the shift of the ν (C-O) (phenolic) band from 1298 cm^{-1} of the free ligand to 1338-1305 cm^{-1}in the spectra of complexes, indicating the coordination of phenolic oxygen atom to the metal ion [9]. This shift to higher frequency is expected due to the main tenure of ring currents arising from electron delocalization in the chelate ring. The bonding through oxygen and nitrogen is further supported by the appearance of new bands in the region 618- 560 cm^{-1} assigned to ν (M-O) and ν (M-N) bending vibrations, respectively [10]. The IR spectra of complexes show a strong band above 3500 cm^{-1}, indicating the presence of coordinated water in these complexes. The presence of coordinated water is further confirmed by the appearance of a non-ligand band in the 840-860 cm^{-1} region, assignable to the rocking mode of water. The presence of coordinated water was also

established and supported by TG analysis of complex. On the basis of these results, it can be concluded that in the complexes, the Schiff base behaves as dibasic tetradentate ligand.

Electronic Spectra

The reflectance spectrum of Mn(II) complex exhibits three bands at 730, 568 and 394 nm, which are assigned to $^6A_{1g} \rightarrow {}^4T_{1g}(4G)$, $^6A_{1g} \rightarrow {}^4T_{2g}$, $^4A_{1g}$ (4G) and $^6A_{1g} \rightarrow {}^4A_{1g}$, ^4E_g (4D) transitions, respectively, in an octahedral symmetry [11]. The Mn(II) complex exhibits magnetic moment 5.68 B.M. is also in consistent with octahedral stereochemistry. The Co(II) complex showed three bands at 785, 556 and 436 nm which may be assigned to the transitions $^4T_{1g}(F) \rightarrow {}^4T2g(F)$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$, respectively expected for an octahedral geometry [12]. The measured value of magnetic moment of 4.92 B.M. for Co(II) complex which lie in the range of octahedral compound. Nickel(II) complex exhibited three absorption bands at 910, 567 and 434nm and may be tentatively assigned as $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$, and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transitions indicating the octahedral geometry of the complex. The magnetic moment value 3.25 B.M. for Ni(II) complex supports the suggested octahedral geometry around the Ni(II) ion [13].The electronic spectrum of Fe(II) complexes exhibited absorption band at range 793 nm which is assigned to $^5T_{2g} \rightarrow {}^5E_g$ transition which may indicate octahedral geometry around Fe(II) ion [14]. The room temperature magnetic moment 4.98 B.M. corresponds to octahedral geometry. The reflectance spectrum of Cu(II) chelates exhibited a broad band centered at 614 nm. The Cu(II) ion(d^9) split under the influence of the tetragonal distortion and the distortion can be such as to cause the three transitions. The Cu(II) complex display absorption bands at 836, 614 and 398 nm corresponding to $^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{1g} \rightarrow {}^2E_g$ and charge transfer transitions, respectively for distorted octahedral geometry around Cu(II) ion [15]. The value of magnetic moment of Cu(II)complex was found to be 2.10 B.M. which lie at the higher end of the range which confirm tetragonally distorted octahedral structure.

Thermogravimetric analysis

Thermal decomposition studies of complex have been carried out as to corroborate the information obtained from the IR spectral studies to know the presence of water molecules in these complexes as well as to know their decomposition pattern. An analysis of the thermogram of the complexes indicated that Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes show two step decomposition. The complexes exhibits weight loss between 140-230^{O}C in the range11.34-11.61% indicates the presence of this water as coordinated water molecule in the complexes.The anhydrous complexes remain stable up to ~ 280^{O}C and thereafter a rapid loss in weight has been observed presumably due to decomposition of organic constituents of the complex molecule as indicated by the step fall in the percentage weight loss in the range 87.43- 88.26%. TG curves attain a horizontal level above 650^{O}C suggesting the formation of final decomposition product as respective stable metal oxides

Electrical conductivity measurements

The temperature dependence of the solid state conductivity (σ) of the synthesized ligand and its complexes in their compressed pellet form (5 ton cm^{-2}) has been measured in the temperature range (313-403 K). The electrical conductivity (σ) was found to vary according to the relation $\sigma = \sigma_0 \exp(-Ea/kT)$. Where: σ_0 is a constant, Ea is the activation energy of electrical conduction, T is the absolute temperature and k is Boltzmann constant. The values of electrical conductivity of the ligand and its complexes increases with increases temperature and plots of logσ vs. 1/T are found to be linear over studied temperature range indicating their semiconducting nature [16, 17]. The value of electrical conductance lies in the range0.565-0.891eV.

Catalytic activity

The catalytic oxidation of organic substrates by transition metal complexes is an area of current interest, in view of this in the present paper the catalytic activity of Cobalt (II), Manganese (II) and Nickel (II) complexes for epoxidation of styrene to corresponding styrene oxide were carried out using H_2O_2 as an oxidant. These oxidation reaction yielded styrene oxide as a major product with minor amount of phenyl acetaldehyde as side product34. Epoxidation of styrene resulted 16.28- 24.70% conversion and 42.63- 74.05% selectivity for complexes, respectively of styrene into styrene oxide. No significant side products were identified.

CONCLUSION

Unsymmetrical Schiff base and its complexes were prepared and characterized using microanalytical, electronic and vibrational spectral analysis. IR spectral data demonstrates the ligand act as dibasic

tetradentate, coordinating via phenolic oxygen and azomethine nitrogen atoms. Magnetic and electronic spectral studies reveal octahedral geometry for all complexes. Thermal study revealed that complexes are thermally stable. The solid- state D.C. conductivity of complexes indicates their semiconducting behavior. The Cobalt (II), Manganese (II) and Nickel (II) complexes are catalytically active toward oxidation of styrene to styrene oxide.

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THERMODYNAMIC STUDY OF SOME SUBSTITUTED SCHIFF'S BASES AT DIFFERENT CONCENTRATION IN 70% (DIOXANE+WATER) SOLVENT BY VISCOMETRICALLY.

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ABSTRACT

Solute-solvent interactions play an important role in a variety of phenomenon.The important information regarding solute-solute and solute-solvent interaction in an aqueous and in non-aqueous solution is obtained by viscometric study.
The present study deals with the study of substituted Schiff Bases at different temperature by preparing the solutions of different concentrations.The themodynamic properties such as free energy change(ΔG), enthalpy change(ΔH) and entropy change (ΔS) of different substituted Schiff Bases have been studied in 70% (Dioxane+water) solvent by the measurement of densities and viscosities at different temperature such as 304K, 306K and 308K. The experimental data obtained used to compute the molecular interaction of different ligands.

Key words *: specific viscosity, Density, thermodynamic parameters,*

INTRODUCTION

The property of liquid by virtue of which it opposes relative motion between its different layers is known as viscosity or internal friction of the liquid. Those liquids flow slowly (glycerin, honey, castor oil etc.) are said to have high viscosity, while those which flow readily are said to have low viscosity. As may be looked upon as the force of friction between two layer layers of liquid moving past one another with different velocities. Viscometricstudy gives valuable information about the solute–solvent interactions in the solution phase. These interactions have been studied in aqueous and non-aqueous solutions by many researchers [1-3]. The molecular interactions of electrolyte in binary mixture of two liquids in terms of viscosity B-coefficients have been studied by Kapadi [4], Mehrotra[5], Das [6], and Nikam [7]. The molecular interactions are also studied by Kalra [8], Yadav[9], Pandey[10], and Raut[11]. The viscosities and densities of an aqueous binary electrolyte having different molar concentrations have been studied by Pandey and Yasmin [12]. The dependence of concentration of viscosity in concentrated electrolyte solution was reported by Breslau Miler [13] and Vand [14]. Rajagopal et al [15] also reported density and viscosity measurements for 4-aminobutyric acid in various composition in aqueous metformin hydrochloride at different temperature.Effects ofconcentration and temperature on viscosity in (l-alanine/l-threonine/glycylglycine + aqueous d-glucose/aqueous sucrose) systems has been reported by Riyazuddeen et al [16]. In the present research work we have performed the viscometric study of following ligands.

1. 2-Hydroxy-5chloro-1-(α phenyl imino) ethyl benzene (L1).
2. 2-Hydroxy-5chloro-1-(α para methyl phenyl imino) ethyl benzene (L2).
3. 2-Hydroxy-3-bromo-5-chloro-1-(α phenyl imino) ethyl benzene (L3).
4. 2-Hydroxy-3-bromo -5-chloro-1-(α para nitro phenyl imino) ethyl benzene (L4).

MATERIAL AND METHOD

The ligands used in the present research work were synthesized by using reported methods. The solvent dioxane of AR grade and freshly prepared doubly distilled water was used. All the weighings were made on ZaktadyPrecyzyjnej Gdansk Balance, made in Poland. The densities of pure solvent and solutions of various concentrations were measured at different temperature using a calibrated pycnometer. Viscosities of the solutions were determined with the help of calibrated Ostwald viscometer thoroughly cleaned and dried. The flow time of solutions were measured by using digital clock of racer company having error (±0.01Sec).for each measurments , sufficient time was allowed to attain thermal equilibrium between viscometer and water bath.

Calculation

To determine the relative and specific viscosity, in the different concentration of the substituted oxoimidazolidone solution were prepared and there viscosities are measured with help of the following mathematical relation

$(\eta r)=(ds \times ts/dw \times tw)\times \eta w$……(1)

Where

ηr = Relative viscosity
ηw = Viscosityof water
ds = Density of solution
dw = Density of water
ts = Flow time for solution
tw = Flow time for water

From the calculated values of relative viscosities (ηr) and the temperature (T),the graph between log (ηr) vs 1/T can be plotted.

The relative viscosities of solutions at different concentration are presented in table 1. The viscosity data have been analyzed by Jones –Dole equation[ ]

$(\eta r -1) /\sqrt{C}= \eta sp/\sqrt{C} = A + B \sqrt{C}$ ---------- (3)

Where

A = Falkenhagen coefficient
B= Jones-Dole coefficient
C = concentration of solutions

The Falkenhagen coefficient (A) measures the solute-solute interation while Jones-Dole coefficient (B) measures the solute-solvent interaction.

The thermodynamic parameters i.e. free energy change(ΔG), enthalpy change(ΔH) and entropy change (ΔS) can be determine by using following relation,

$\Delta G = -2.303\times R\times slope$…… (4)

$\log \eta r1 - \log \eta r2 = (\Delta H/2.303)\times(1/T1 -1/T2)$ .... (5)

$\Delta S = (\Delta G - \Delta H)/T$…… (6)

Table 1

System-Ligand L1

Temp: 31°C±0.1°C Medium: 70% Dioxane-Water

Conc(C) Mole/lit	√ C Mole-1/2 lit-1/2	Density gm/cc	Time Flow (Sec)	Relative Viscosity $\eta r = \eta/\eta 0$	Specific Viscosity $\eta sp= \eta r-1$	$\eta sp/\sqrt{C}$
0.010	0.1000	0.9652	57.7	2.1978	1.1978	11.9785
0.008	0.0894	0.9645	56.2	2.1392	1.1392	12.7423
0.006	0.0774	0.9633	55.8	2.1213	1.1213	14.4869
0.004	0.0632	0.9622	53.7	2.0391	1.0391	16.4419
0.002	0.0447	0.9613	48.5	1.8399	0.8399	18.7897

Table 2

System-Ligand L2

Temp: 31°C±0.1°C Medium: 70% Dioxane-Water

Conc(C) Mole/lit	√ C Mole-1/2 lit-1/2	Density gm/cc	Time Flow (Sec)	Relative Viscosity $\eta r = \eta/\eta 0$	Specific Viscosity $\eta sp= \eta r-1$	$\eta sp/\sqrt{C}$
0.010	0.1000	0.9657	57.4	2.1875	1.1875	11.8755
0.008	0.0894	0.9648	55.5	2.1132	1.1132	12.4616
0.006	0.0774	0.9635	53.1	2.0191	1.0191	13.1662
0.004	0.0632	0.9622	49.3	1.8720	0.8720	13.7982
0.002	0.0447	0.9614	44.4	1.6846	0.6846	15.3149

Table 3

System-Ligand L3

Temp: 31°C±0.1°C Medium: 70% Dioxane-Water

Conc(C) Mole/lit	√ C Mole-1/2 lit-1/2	Density gm/cc	Time Flow (Sec)	Relative Viscosity ŋr = ŋ/ŋ0	Specific Viscosity ŋsp= ŋr-1	ŋsp/√C
0.010	0.1000	0.9660	65.2	2.1425	1.1425	11.4248
0.008	0.0894	0.9652	55.5	2.1140	1.1140	12.4614
0.006	0.0774	0.9645	54.8	2.0859	1.0859	14.0293
0.004	0.0632	0.9636	52.5	1.9965	0.9965	15.7668
0.002	0.0447	0.9628	47.9	1.8200	0.8200	18.3449

Table 4

System-Ligand L4

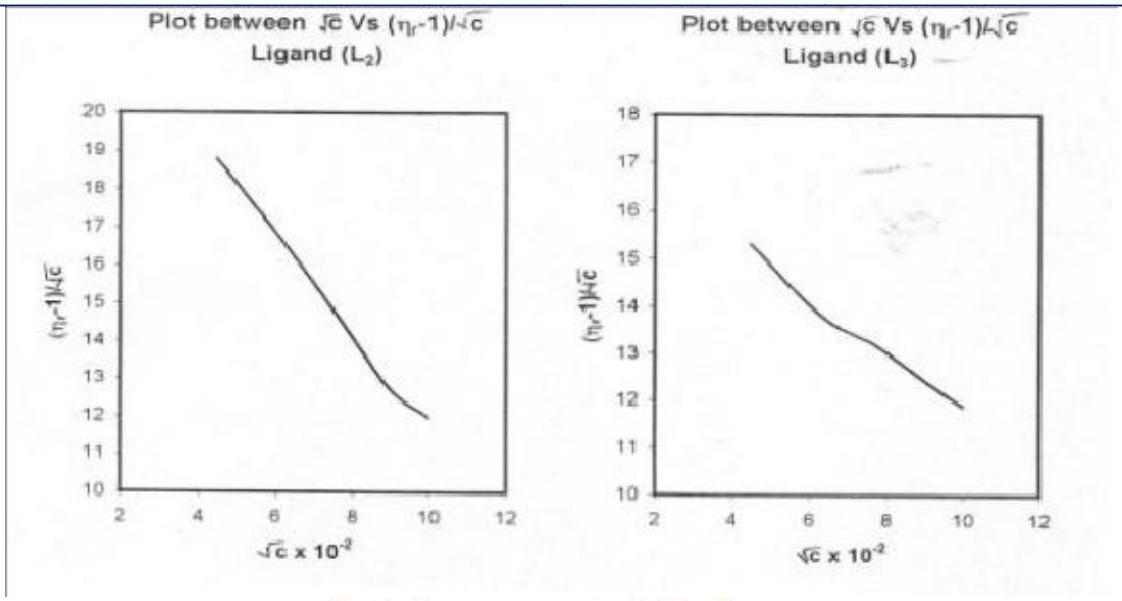
Temp: 31°C±0.1°C Medium: 70% Dioxane-Water

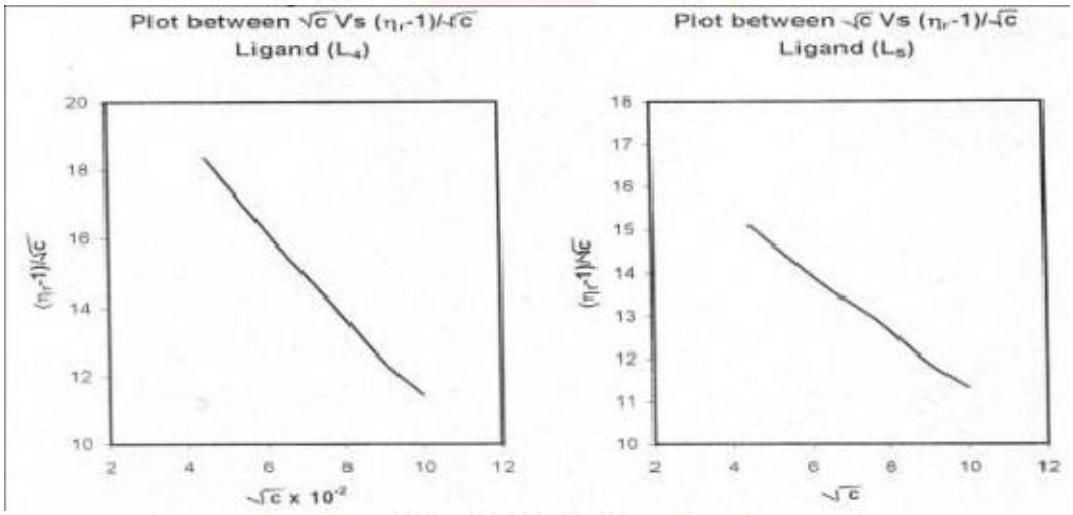
Conc(C) Mole/lit	√ C Mole-1/2 lit-1/2	Density gm/cc	Time Flow (Sec)	Relative Viscosity ŋr = ŋ/ŋ0	Specific Viscosity ŋsp= ŋr-1	ŋsp/√C
0.010	0.1000	0.9665	55.9	2.1322	1.1322	11.3215
0.008	0.0894	0.9653	54.2	2.0647	1.0647	11.9099
0.006	0.0774	0.9644	52.4	1.9943	0.9943	12.8464
0.004	0.0632	0.9632	49.1	1.8664	0.8664	13.7087
0.002	0.0447	0.9619	44.1	1.6741	0.6741	15.0798

Table 5

A = Falkenhagen coefficient, B= Jones-Dole coefficient values

Ligand + 70%Dioxane-Water	**A**	**B (Lit/mol)**
L1	20.60	+125.00
L2	18.10	+62.50
L3	20.20	+123.53
L4	18.30	+72.7273





RESULT AND DISCUSSION

In the present investigation the relative and specific viscosity, of substituted Schiff Bases are measured with help of the following mathematical relation

(ŋr)=(ds ×ts/dw ×tw)× ŋw……(1)

Where

ŋr = Relative viscosity
ŋw = Viscosity of water
ds = Density of solution
dw = Density of water
ts = Flow time for solution
tw = Flow time for water

The relative viscosities of solutions at different concentration are presented in table 1-5. The viscosity datahave been analyzed by Jones –Dole equation .(ŋr -1) /√C= ŋsp/√C = A + B √C --------- (3)

Where

A = Falkenhagen coefficient
B= Jones-Dole coefficient
C = concentration of solutions

The Falkenhagen coefficient (A) measures the solute-solute interation while Jones-Dole coefficient (B) measures the solute-solvent interaction.

In the present investigation, the relative viscosity of solution of synthesized ligands increases with increase in concentration of solutions. The increase in viscosity with increase in concentration is may be ascribed to the increase in the interactions of solute-solvent. The large and small deviations in the values of 'A' give us an idea about the stronger and weaker solute-solvent interaction respectively as shown in table. The increase in relative viscosity of solutions with concentration measures the increase in interaction

of solute and solvent. The relation between viscosity (ηsp/√ C) and concentration of solution (√C) represented by plotting the graph (fig. 1-4). These plotted graphs prove the validity of Jones-Dole equation for all systems by giving linear straight line . The values of Jones-Dole coefficients especially B- coefficients are the slope of graph (ηsp/√C) Vs (√C) while the values of Falkenhagen coefficient i.e. A-Coefficient are the intercept of graph of (ηsp/√C) Vs (√C). The order or disorder introduced by solute in solvent is measured by the values of B coefficient which shows either positive or negative values. B coefficient is in turn measures the effective hydrodynamic volume of solute, which accounts for the ion-solvent interaction.

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SINGLE STEP SYNTHESIS OF 5-(6-CHLORONAPHTHALEN-2-YL)-1,3,4-THIADIAZOL-2-AMINE AND ITS SCHIFF BASES.

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ABSTRACT

5-(6-Chloronaphthalen-2-yl)-1, 3, 4-thiadiazol-2-amine have been synthesized from thiosemicarbazide and $POCl_3$ with single step. Schiff base of 1, 3, 4-thiadiazole prepared with aromatic aldehydes. The purity of synthesized compound and its derivatives was justified by Thin Layer Chromatography. The conformation of structure was done as usual by chemical characteristics, elemental analysis and spectral analysis. Antimicrobial activity against E-coli, S. Aureus and P.seudomonas was tested, and the minimum inhibitory concentrations (MICs) of the tested compounds were determined by the dilution method using Ampicillin, Chloramphenicol, Tetracycline.

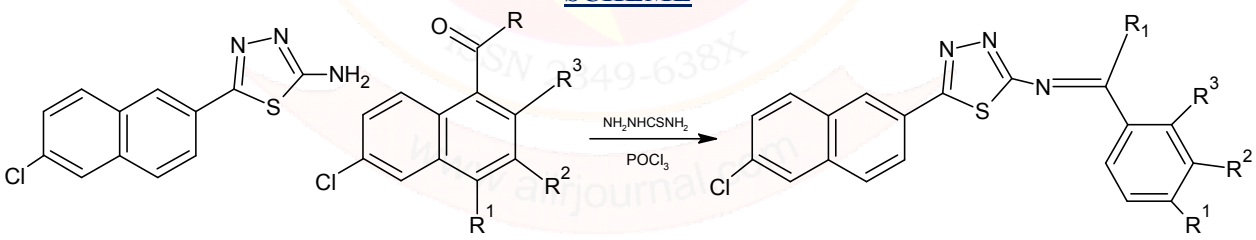
***Key words**: 5-(6-chloronaphthalen-2-yl)-1, 3, 4-thiadiazol-2-amine, synthesis, biological activities, H^1 and C^{13} NMR.*

INTRODUCTION

1,3,4-Thiadiazole and its derivatives are widely applied in medicine[1] and agriculture[2] as pesticides.1,3,4-thiadiazole having biological activity[3], antibacterial[4], antifungal[5], tuberculostatic[6], anti-inflammatory[7], analgesic[8], anticancer[9] etc.

Nowadays, the research field dealing with Schiff base coordination chemistry has expanded enormously. The importance of Schiff base complexes for bioinorganic chemistry[10], biomedical applications[11], supramolecular chemistry, catalysis and material science[12], separation and encapsulation processes. Formation of compounds with unusual properties and structures has been well recognized and reviewed . Schiff bases resulted from aromatic aldehydes Schiff bases have been reported in their biological properties, such as, antibacterial, antifungal activities.

SCHEME



EXPERIMENTAL DATA

Sr.No.	Compo und no.	Molecular formula	M. Pt. 0C	R1	R2	R3	R4	Yield (%)	Mol.wt gm/mole
1	S1	$C_{12}H_8N_3SCl$	128	--	--	--	--	--	261.73
2	N1	$C_{21}H_{17}N_4SCl$	90	H	$N(CH_3)_2$	H	H	30	392.90
3	N2	$C_{19}H_{12}N_3SClO$	219	H	H	H	OH	25	365.83
4	N3	$C_{19}H_{11}N_4O_2SCl_2$	160	H	NO_2Cl	H	H	35	394.83
5	N4	$C_{19}H_{11}N_3SCl_2$	110	CI	CI	H	H	42	384.28

H ^{1} NMR(Compound S1) :
7.3 (d. 1H, J=7.31), 7.5 (d, 1H, J=7.48), 7.9 (d,1H, J=7.93)
6.8 (s, J=6.83).

7.3 (d. 1H, J=7.31), 7.9 (d, 1H, J=7.48), 8.3 (d,1H, J=7.93)
6.9 (s, J=6.83).

H^1 NMR (CompoundN1).
5.9 (cychlohexadiene), 8.36 (benzylidnimin), 3.06 (-N-C-)

C^{13} NMR (Compound N1).
41.3 (-CH_3), 125.9 (-C=N), 153.4 (-C=N-N).

METHEDOLOGY OF SCHIFF BASES.

A mixture of substituted thiadiazole and substituted aromatic aldehyde in glacial acetic acid was refluxed for two hours, cooled and poured cold water

BIOLOGICAL ACTIVITY

The biological assay indicates high antimicrobial activity. For some compounds the activity is better than the reference drugs. This indicates that the molecules are good candidates for lead optimization.

CONCLUSION

In the present work, various derivatives of 1, 3, 4-thiadiazole were synthesized by using substituted aromatic carboxylic acid with moderate to good yield. The method is easy and efficient and less hazardous to environment. The method has advantages of cheaper chemicals and safely too. The method has additional advantage of easy work up and the compounds are obtained in high purity without any special separation techniques. Thus, the method has good number of advantages. The Rf values, determined for two molecules viz. compound number 1 and its derivatives, are close to 0.5. X-ray diffraction studies give the crystalline nature of the compounds.

Newly synthesised thiadiazole compounds and their derivatives are high atom efficiency, increase the biological activity and important thing to resist their E-factor. It will be helpful in theurophatic and biological activities.

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GREENSYNTHESIS OF 3,4-DIHYDROPYRIMIDIN-2(1H)-ONES DERIVATIVES USING CITRIC ACID

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ABSTRACT

Desired product can be prepared which includes the natural and ecofriendly catalyst i.e Dry tomatto which carried out in ethanol as a solvents. In absence of catalyst the yield of reation for the given time is poor while in presence of catalyst it is satisfactory.The present methodology includes inexpensive, ecofriendly,easy work up with good to excellent yield.

Keywords: *3,4-dihydropyrimidin-2 (1H) -ones,Dry Tomatto powder, Ethanol*

INTRODUCTION

DHPMS the reaction was carried out simply by heating a mixture of three components dissolve in ethanol with a catalytical amount of HCl at reflux temperature. The original cyclocondensation reaction was gradually extended by variation of all three building blocks, allowing access to a large number of multifunctionaliseddihydropyrimidines. simple DHPM monastrol as a mitotic kinesin motor protein inhibitor and potential new lead for the development of anti cancer drugs.[1]The synthesis of heterocyclic is thus important, and the most simple and straight forwarding procedure reported by Biginelly in 1813 involve one- pot condensation of 2-keto ether, benzaldehyde and urea under strongly acidic condition. currently, microwave irradiation has a very useful tool in organic synthesis. Microwave technology in organic chemistry has been explored extensively within the last decrease in reaction time increase yields, easier work-up matching with green chemistry protocol.[2] Over the the year, DHPMs and their derivative have displayed a captivating assortment in natural, synthetic, pharmacological, therapeutically and bioorganic chemistry mainly due to their wide range of biological activity [3-5] and they are being studied because of their activity as calcium cannel blockers antihypertensive agent, alpha-la-antagonist and neuropeptide antagonist [6-7] moreover, dihydropyrimidinethiones have been suggest to be useful building block of which batzallidine alkaloids [8,9] have been found to be potent HIV gp-120-CD4 inhibitors. In simple and straight forwording procedure for three component one-pot condensation of bezaldehyde ethyl acetoacetate and urea under strongly acidic condition [10-12] and affords low yields use of expensive reagents, volatile strong acidic conditions, the introduction of milder more efficient method accompanied with higher yield.[13]Acid catalysed elimination of water ultimately lead to DHPM product. In order to promote conditions that would favour the formation and interception of such an iminium ion intermediate[14] in the Biginelli reaction – thereby minimizing side reactions – we have now investigated a variety of reaction conditions more specifically employed in *N*acyliminiumion based amidoalkylations[15]. One of the most efficient reagents tested proved to be polyphosphate ester (PPE), which has been demonstrated to mediate acyliminium ion-based [16-17] condensations in the past such as the somewhat related dihydropyridone formations. The use of PEE in related cyclization reaction [18] In recent decades, the utilization of multicomponent condensations[19] (MCCs) to synthesize novel, drug-like scaffold compounds has permeated in organic transformations. This is due to the fact that products can be prepared directly in a single step and diversity can be achieved simply by varying reaction substrates. Among them, the Biginellireaction[20-21] involving a multicomponent condensation of aldehyde, β-ketoester, and urea ranks as one of the most recognized and widely employed MCCs for the preparation of dihydropyrimidinones[22]

2. EXPERIMENTAL SECTION

2.1 *Materials and Methods*

The organic materials were purchased from SdFine and Merck and were used without any additional purification. Merck, pre coated Silica gel 60

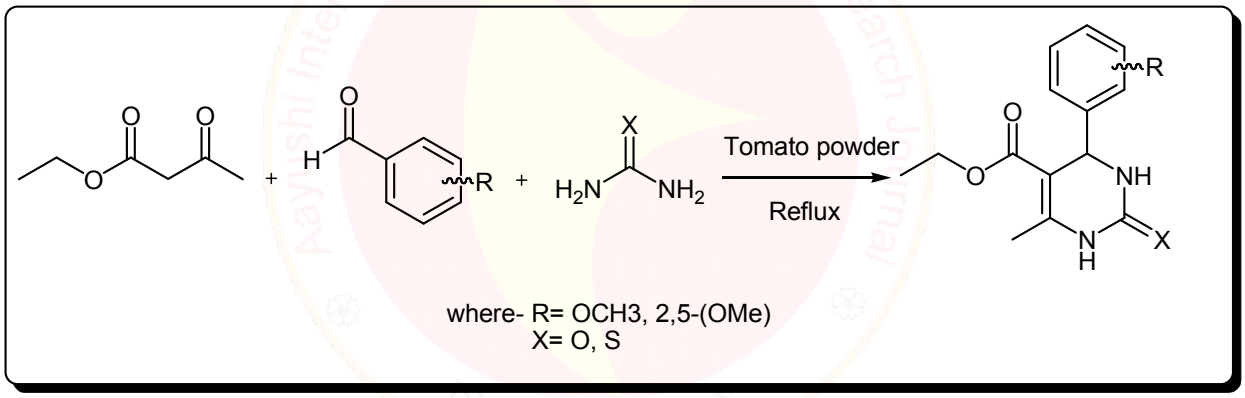
F_{254}(Aluminum sheet) plates were used for analytical TLC.IR spectra were recorded on FTIR spectrophotometer, ^{1}H-NMR spectra of all the synthesized compounds were recorded in ($CDCl_3$\DMSO-d_6) on Bruker Avance-2 400MHz NMR Spectrophotometer using TMS as an internal standard. The melting point was determined in open capillary tubes using Prefit model.

Synthesis of Catalyst:

Tomatoes were collected, clean and cut in small pieces then dried in sun light to remove the water content. Dried tomatoes were crushed in mortar pestle to fine powder. This powder of sundried tomatoes which contain 39.2mg vitamin C, green tomatoes contain 23.4mg vitamin C and yellow tomatoes contain 9mg vitamin C and also contain 2.6g of sugar per 100g for an 'average tomato, the actual amount of sugar is low compared to other fruits.

Synthesis of Dydropyrimidione compounds

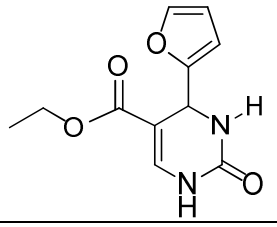
The cyclocondensation reaction of aldehyde (1mol), ethyl acetoacetate (1mol) and urea/thiourea (1mol) was carried out by refluxing with a naturally occurring citric acid (0.49) tomato powder on water bath. The reaction is monitered by TLC. The reaction mixture was poured in crushed ice and extracted with ethyl acetate. The organic layer was washed with water, it was dried over Na_2SO_4 and evaporated. A solid, then obtained was purified by column chromatography.

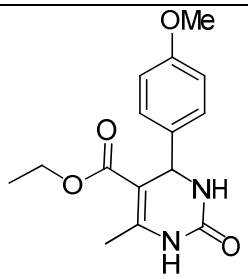
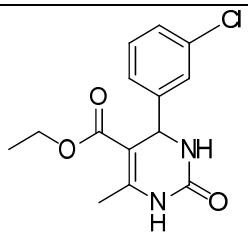
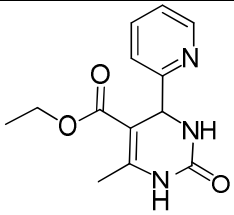
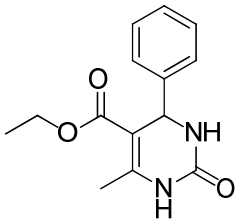


Reaction scheme I

2.1.1 Ethyl-1,2,3,4-tetrahydro-6-methyl-2-oxo-4-phenyl-pyrimidine-5-carboxylate (4a): IR (KBr): 3649(-NH), 2977 (-CH_3), 1897 (-COOR), 1602 (C=C), 1222 (C-N) cm^{-1};^{1}H NMR (400 MHz,DMSO-d_6): δ 8.1 (s, 1H, NH), 7.2 (s, 5H, Ar), 5.7(s, 1H, NH), 5.2(s, 1H, Ar-CH), 4.1(q,2H,CH_2), 2.3 (s, 3H, CH_3), 1.2 (t, 3H, CH_3);^{13}C-NMR (400MHz, DMSO-d_6): δ 15.2, 18.8, 50.7, 52.8, 102.0, 127.5, 128.1, 141.7, 147.8, 152.1, 167.8.

We have synthesised several derivatives of DHP by using our catalyst. Among them the best result I get are as follows.

Sr. No.	DHPM Derivative	MP ^{0}C	% yield
1.		106	82

2.		96	87
3.		90	74
4.		130	78
5		161	91

RESULTS AND DISCUSSION

We were interested in the synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones using dry tomato as an natural catalyst.In order to establish the best reaction condition,the reaction was performed using substrate reaction. benzaldehyde gave excellent yield (90 %)in 2 hr.Experiments were performed using Ethanol as a solvent and dry tomato as a catalyst, but it takes less time than solvent free condition.

To explore thereusability of the catalyst. Thereaction mixture was poured in the crushed ice and product was extracted with ethyl acetate and the catalyst was recovered in aqueous phase, the catalyst was washed with ethyl acetatetwice.

In conclusion,the present procedure for the synthesis of 3,4- dihydropyrimidin-2(1*H*)-ones by three component condensation follows the principle of Green chemistry which provides an efficient and much improved modification of Biginellireaction.From the synthetic point of view,

has been used as potential green, natural, mild catalyst.

4 CONCLUSIONS

In this method, we have carried out the synthesis of different derivatives dihydropyrimidiones. The dihydropyrimidiones were synthesized from ketones such as ethyl acetoacetate and differed aldehydes such as substituted benzaldehyde and urea / thiourea. The reaction was carried out in the presence of naturally occurring citric acid (dry tomotos) under reflux condition for different hour. We have compared this catalyst and without catalyst.

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REVIEW ON LOW ALKALINE PHOSPHATASE (ALP) IN ADULT POPULATION AN INDICATOR OF ZINC (ZN) AND MAGNESIUM (MG) DEFICIENCY

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ABSTRACT

Alkaline Phosphatase (ALP) enzyme activity is usually measured as a part of liver function test (LFT) to detect increases in its activity. Less attention has been put to know the conditions associated with decreases in its activity. Micronutrients like Zinc (Zn) and Magnesium (Mg) are important causes of low ALP activity. Our Objective is to find out Zn and Mg deficiencies as important cause of decrease in ALP activity and to initiate supplementation of these minerals. The study was done to assess Zn and Mg deficiency in 42 persons having low ALP activity and 45 healthy controls. Correlation between minerals and ALP activities were also carried out. It was found that 52.38 % of cases are Mg deficient and 47.62 % cases are Zn deficient.

INTRODUCTION

In this review were deal with simplifying the research topic low alkaline phosphatase (ALP) in adult population an indicator of Zinc (Zn) and Magnesium (Mg) Deficiency. Alkaline phosphatase is a commonly encountered laboratory value that is included in the panel of liver function tests. Although elevated concentrations generally are attributed to either liver or bone sources, the enzyme has been identified as a biomarker for a diverse range of diseases and physiologic processes. Elevated alkaline phosphatase may have implications ranging from indicating periodontal disease to predicting preterm labor.Alkaline phosphatases (ALP) are the metalloenzymes of cell membrane and they are synthesized in intestines, liver, bone, placenta and in the proximal convoluted tubules of kidney[1, 2]. The serum ALP activity is primarily from the liver and 50 % given by bone[3]. Very less attention has been focused on clinical conditions associated with low or decrease ALP activity in humans. Various causes may attribute to low ALP activity such as hypophosphatasia, cardiac surgery and cardiopulmonary bypass, blood collected with EDTA or oxalate anticoagulant, hypothyroidism, vitamin C and B12 deficiency, Milk alkali syndrome, protein/ calorie malnutrition, zinc and magnesium deficiency[4, 5].

Zinc was discovered in 15th century and its role in life processes was first realized many centuries afterwards in 1869. It was found that zinc is imperative for growth of mould *Aspergillus niger*. Experiments on laboratory animals found with conclusive evidence role of zinc in growth and health of animals. Zinc is associated with more than 300 enzymes either as component, activator or cofactor for RNA and DNA polymerases. Some of the important zinc dependent metalloenzymes include alkaline phosphate, a-mannosidase, alcohol dehydrogenase, carboxypeptidase A and B, carbonic anhydrase, D-glyceraldahyde-3phosphate dehydrogenase, glutamic dehydrogenase, and lactic dehydrogenase. Causes of low Zn level such as cirrhosis, lung cancer, and acute myocar dial Infarction (AMI), renal failure, sickle cell anemia, corticosteroids and oral contraceptive therapy. Magnesium is an essential dietary mineral and the second most prevalent electrolyte in the human body. Magnesium deficiencies are common in developed countries. A deficiency increases blood pressure, reduces glucose tolerance and causes neural excitation. Causes of decrease level of Mg such as malabsorption, treatment phase of Diabetic coma, chronic renal disease, chronic alcoholism, pancreatitis and hyperthyroidism are also excluded from the study group.

Divalent ions such as Mg2+, Co2+ and Mn2+ are activators of the ALP and Zn2+ is a constituent metal ion. The accurate ratio of Mg2+/ Zn2+ ions is necessary to avoid displacement of Mg2+ and to obtain optimal activity[3]. Low dietary Magnesium has been associated with low ALP activity and rats fed with Mg deficient diet demonstrated depressed ALP activity that was reversed by adding Mg in their diet[6]. Many studies have also shown that Zn deficiency depressingly affects bone related enzymes and minerals such as ALP and Ca, P and Mg_2. The normal range of ALP is 45-115 Units/Liter (U/L) in an adult population. The

condition in which ALP is below the normal range (45-115) called as LAP (low alkaline phosphatase.).

MATERIALS AND METHODS

The research was conducted in Department of Biochemistry, Institute of Medical Sciences, and Bhubaneswar under the aegis of Siksha 'O' Anusandhan University. In this study they include Outpatients and Inpatients of the hospitals within the age group of 20-50 years. They selected subjects from the patients who give blood for estimation of liver function test (LFT) for any reason. They take detailed history from them and ALP activity in their serum was measured by Roche Cobas Integra 400 plus auto analyzer using International Federation of Clinical Chemistry (IFCC) Gen-2 method[7]. An ALP value of 45-115 Units/Liter (U/L) in an adult population is considered normal[2].they include 42 subjects in one study group with low ALP activity (<45 U/L) as cases and 45 age and sex matched healthy controls with normal ALP as control population. Blood from these persons are subjected to Zn and Mg estimation. They use 2-(5-Nitro-2-pyridylazo)5-(N-n-propyl-N-(3-sulfopropyl)amino)phenol, disodium salt, dehydrate (Nitro-PAPs) method for the estimation of serum zn and for the determination of serum mg they useCalmagite method in semi autoanalyzer (Photometer 5010) using commercially available kits[8,9] .

They use SPSS 20.0 software to analyse data. Continuous data were expressed in terms of mean and standard deviation and proportions in terms of percentages. Means were compared using students'-test. Correlation between continuous variables was done using Pearson's correlation test. They consider a p value of <0.05 as statistically significant.

RESULTS AND DISCUSSION

The studied was showing total of 42 cases and 45 controls within the age group of 20-50 yrs. After the study they found 20 out of 42 cases were Zn deficient, taking 60-120 µg/dl as the normal range. Zn deficiency in control groups was found to be 3 among 45 persons. It has been observed that 22 out of 42 cases were Mg deficient, taking 1.3-2.5 mEq/L as the normal range. Mg deficiency in control groups was found to be 3 out of 45 persons.

Table 1: Details of Zn deficient and Mg deficient percentages

Experimental groups	Zn deficient(in percentage)	Mg deficient(in percentage)
Controls	6.66	13.34
Cases	47.62	52.38

In the above study it was concluded that level ALP is directly proportional to level of another minerals. ALP enzyme has important investigative role to play in liver diseases and bone diseases. It has important role in differentiating parenchymal liver diseases to obstructive liver diseases. The decrease in ALP is also found to have diagnostic role in detecting various diseases. Our study includes the patients within 20-50 yrs of age group. This excludes children having cretinism and achondroplasia and postmenopausal women having osteoporosis. It was found out that 17 out of 42 cases were females suggesting the fact that low ALP is common in female population[6]. They found a significant decrease in Zn and Mg level in our group of cases suggesting the fact that, ALP is a Zn containing metallo enzyme and Mg is an important promoter of ALP which is in concurrence with the authors Naber, *et al*., and Arise, *et al*.,[10, 11]. They found successiveoutput in numbers comes from this study 52.38 % of cases are Magnesium deficient, whereas 47.62 % of cases are Zn deficient which is higher than the percentage found by other authors[6]. They got a positive correlation between Zn and Alkaline phosphatase in these groups signifying the fact that Zn raises the activities of alkaline phosphatases particularly of bone. It also activates osteoblast tyrosine kinase and RNA synthetase suggesting its role in bone formation. This is in concordance with Peretz, et al and yamaguchi *et al*.,[12, 13].Their present study reveals a significant positive correlation between Mg and ALP which suggests the fact that divalent metal ion Mg is a potent stimulator of ALP. Mg occupies the structural site on ALP to convert it to a more active form[11]. Femi J Olorunniji, et al., in their study they showed that Mg and Zn ions interact to activate the non specific tissue alkaline phosphatase[14]. Metal ions participate in catalysis, stabilization of protein structure and regulation of activities of metalloenzymes. The definite binding of Mg to apo-ALP depends on both the cooperative effects of Zn binding and pH. Mg regulates the Zn induced restoration of activity and structural integrity of metal binding loci[14]. In above the study, we can discuss some benefits of this

research. They give co-relationship between ALP and mineral which can help us to give knowledge about the deficiency of mineral after doing liver function test (LST). In some cases, deficiency may be under diagnosed since the obvious signs commonly don't appear until your levels becomes severely low but after this study may be we can identify the level of minerals. After the identification of level of minerals we can take supplement to overcome the normal level.

CONCLUSION

This research will be concluded in our review that not only increase in activity of ALP is important, but also important for decrease in its activity. The co-relation stated that ALP is caused deficiency of zn and mg minerals. During usual check up for Liver function test, the degree of mineral deficiency in different social groups can be obtained. These minerals are much more essential for body to work effectively. Like development of bones, growth, remodeling and various other metabolisms in the body, their replacement in the diet can be set off. The diet containing phosphorus, healthy fats, Zn, vitamin B12 and vitamin A can be started to increase alkaline phosphatase level. A daily intake of zinc is required to maintain a steady state because the body has no specialize zinc storage system.

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PRELIMINARY PHYTOCHEMICAL EVALUATION OF SOME ETHANOMEDICINAL PLANTS OF PAIGANGA WILD LIFE SANCTURY OF UMARKHED OF DISTRICT YAVTMAL

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ABSTRACT

The present study was to evaluate the phytochemical constituents of fruist of Luffa acutangula (Roxb.), pods Plumeria rubra (L.), leaves Indigofera trifoliata (L.) and seeds Psoralea corylifolia (L.) were collected from the local villages of Umarkhed during 2016. The collected seeds were washed thoroughly first in tap water and then rinsed with distilled water. Preliminary of fruist of Luffa acutangula (Roxb.), pods Plumeria rubra (L.), leaves Indigofera trifoliata (L.) and seeds Psoralea corylifolia (L.) revealed the presence of alkaloids, flavonoids, steroids, phenolic, tannins and saponines whereas anthraquinone were not detected. Therefore, the present study is a small effort to gain insight in the knowledge of traditional medicine of this region. Thus present research work will be focuses on the screening of some meaningful medicinal plants from this region and establishing their medicinal values.

Keywords: *Phytochemical, Plumeria rubra, Umarkhed, Medicinal plants.*

INTRODUCTION

The major importance of these bioactive constitute of plants are Steroid, Terpenoids, Tannins, Carotenoids, Flavonoids, Alkaloids and Glycosides. Plants in all aspect of life have served as important material for drug development. Antioxidants and Tyrosinase inhibiting components like Phenolic compounds, Saponins, Glycosides, Flavonoids, Polyphenols and alkaloids are found in plants. Phytochemical screening has revealed that many bioactive agents of plant extract coexist and can thus serve as precursors in the manufacture of drugs. For example, alkaloids which have been known for more than 2000 years to have adverse effect on pregnancy is being used by physician either alone or in combination with oxytocics to induce abortion (Oderinde *et al*., 2002). Preliminary phytochemical studies of some plants indicated the presence of alkaloids, flavonoids, tannin, saponins, steroids, amino acids and carbohydrates. Hiremath *et al*., 1997 studied flavanoids isolated from *Striga lutea* and *striga orobanchiodes* and observed that they possessed antipyretic, analgesic property. The petroleum ether extract of seeds of *Cassia fistula* was screened for the hepatoprotective activity in proven fertile female albino rats at the doses of 100, 200 and 500 mg/kg body weight. The results of the study indicate that the petroleum ether extract of *Cassia fistula* seeds possesses pregnancy terminating effect by virtue of fever protective activity (Gupta, 2000).

Such traditional knowledge form is present in tribal's dominating areas of Yavatmal district of Maharashtra. Some tribals like *Gond, Kolam, Pradhan, Lohar* and *Banjara* of the area have been using various plants and their parts as medicine to on the various diseases. Unfortunately, the ethanobotanical enumerations for various medicinal properties were not recorded for this region. Therefore, the present study is a small effort to gain insight in the knowledge of traditional medicine of this region. Thus present research work will be focuses on the screening of some meaningful medicinal plants from this region and establishing their medicinal values.

MATERIALS AND METHODS

Collection of plant material:

The fruist of *Luffa acutangula* (Roxb.), pods *Plumeria rubra* (L.), leaves *Indigofera trifoliata*

(L.) and seeds *Psoralea corylifolia* (L.) were collected from the local villages of Umarkhed during 2016. The collected seeds were washed thoroughly first in tap water and then rinsed with distilled water. After this, it was sterilized by using absolute alcohol and dried completely in shade at room temperature. The plant seeds were crushed and blended to fine powder in an electronic grinder and stored in polythene bag till further use.

Preparation of extract:

The fruist of *Luffa acutangula* (Roxb.), pods *Plumeria rubra* (L.), leaves *Indigofera trifoliata* (L.) and seeds *Psoralea corylifolia* (L.) were collected, shade dried, powdered and subjected to soxhlet extraction successively with distilled water. The extract was evaporated to near dryness on a water bath, weighed and kept at 4 °C in refrigerator until further use.

Phytochemical screening:

The presence of various plant constituents in the plant extract was determined by preliminary phytochemical screening as per Thimmaiah (2004).

Detection of Alkaloids: Dried plant powder was extracted with 10% acetic acid in aqueous ethanol for about 24 hrs. Extract was further concentrated by boiling in water bath to ¼ of its original volume and cooled. Pigments were removed from extract with chloroform wherever necessary. Pigment free extract was then tested alkaloids with Mayers reagent (cream colour) Wagners reagent (reddish brown colour).

Detection of Anthraquinones: Dry plant powder was extracted with 0.5N KOH and filtered. Extract was diluted with distilled water and acidified with acetic acid. Re-extracted with benzene and filtered. To benzene extract aqueous ammonia was added and shaken gently. red colour to ammonia layer indicated the presence of anthraquinones. The plant powder was extracted with 80% ethanol. Allowed to stand overnight with occasional stirring. Filtered, filtrate collected and evaporated to dryness on water bath. Residue was dissolved in water with vigorous shaking and filtered if necessary 5ml of benzene was added to the solution and benzene layer. Development of red colour indicated the presence of anthraquinones.

Detection of Simple Phenolics: Plant powder was extracted with aqueous ethanol over night. To the extract 1-2 drops of 1% aqueous ferric chloride was added. Development of bluish violet, green, reddish or red violet colour indicates presence of simple phenolics.

Detection of Tannins: Plant material was extracted with rectified spirit. Filtered, evaporated to dryness, dissolved in distilled water and 10% NaOH was added. Filtered and gelatine-salt reagent was added to filtrate, formation of white precipitate indicate the presence of tannins.

Detection of Saponins: One gm of dry plant power was boiled with water for 10 minutes, cooled and shaken vigorously. If stable froth upto 2 cm or more developed, it was recorded as positive test.

Detection of Flavonoids: Dry plant powder was extracted in 70% ethanol overnight. Filtered and 5ml chloroform was added to it. Chloroform layer discarded and chlorophyll-free extract was used for following test. Shinoda Test: To the ethanol extracts a piece of Mg ribbon and HCL was added drop by drop. Formation of purple pink or orange colour indicated positive test. Flavononols: If in Shinoda test deep colour developed, instead of Mg ribbon Zn powder was added with HCL. Flavononols produced deep mangenta colour. Flavonols: To the filtrate a pinch of boric acid and few drops of acetic acid were added. Formation of bright yellow colour with green fluroscence indicated presence of flavonols.

Detection of Steroids: Dry powder was extracted with ethanol. Ethanol extract was dried and defatted with petroleum ether. Defatted extract mixed with chloroform and filtered. To the filtrate 100mg of anhydrous sodium sulphate was added, shaken gently and filtered. To the filtrate Libermann-Burchard reagent was added. Blue or green colour confirmed steroids.

RESULTS AND DISCUSSION

Preliminary phytochemical screening of the pod extract of *Plumeria rubra* revealed the presence of alkaloids, flavonoids, steroids, phenolic, tannins and saponines whereas anthraquinone were not detected. Preliminary phytochemical screening of *Indigofera trifoliata* leaves revealed the presence of alkaloid, steroids, flavanoids, phenolic compounds, saponins, and tannins respectively. Preliminary phytochemical screening of the fruit extract of *L. acutangula* revealed the presence of alkaloids, flavonoids, steroids, tannins, phenols and saponins whereas anthraquinone were not detected. Preliminary phytochemical screening of the seed extract of *Psoralea corylifolia* revealed the presence of alkaloids, flavonoids, steroids, phenolics, tannins and saponines whereas anthraquinone were not detected. Phytochemicals

are known to perform several general and specific functions in plants and may exhibit different biochemical and pharmacological actions in different species of animals when ingested. Their actions range from cell toxicity to cell protective effect (Trease and Evans, 1996). Phytochemical screening has revealed that many bioactive agents of plant extract coexist and can thus serve as precursors in the manufacture of drugs. For example, alkaloid which has been known for more than 2000 years is known to have adverse effect on pregnancy and is being used by physicians either alone or in combination with oxytocics to induce abortion (Oderinde *et al*., 2002). Studies on the phytochemical investigation of the various extract of the stem bark of *Alangium salvifolium* used as an abortifacient, showed the presence of alkaloids, steroids, saponin, tannin and flavonoids (Murugan *et al*., 2000). Similar observation also recorded by Zade *et al*, 2010.

Table 1: Preliminary Phytochemical profile of various plants

Name of the plant	Alkaloids	Anthraquinone	Flavonoids	Simple Phenolics	Steroids	Tannins	Saponins
P. rubra	+	-	+	+	+	+	+
I. trifoliata	+	-	+	+	+	+	+
L. acutangula	+	-	+	+	–	+	+
P. corylifolia	+	-	+	+	+	+	+

+ Present; - Absent

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STUDIES ON PHYSICO-CHEMICAL ANALYSIS OF ADAN RESERVOIR OF WASHIM DISTRICT, MAHARASHTRA, INDIA

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ABSTRACT

The Adan reservoir is one of the fresh water body located within Washim District of Maharashtra state. The present study deals with assessment of the water quality of Adan reservoir, Dist - Washim, (M.S.)India. The physico-chemical characteristics were studied during the period of one year i.e. Feb 2012 to Jan 2013. Seasonal variations at four different sites of the lake were observed. Some parameters like pH, Transparency, Free CO_2, Total Dissolved Solids, Total Alkalinity, Total Hardness, Chlorides, Sulphates, Total Phosphorus and Nitrates were studied throughout year. The results revealed that the condition of this lake in month wise analysis showed fluctuations in physico-chemical parameters.

Key words: *Physico-chemical, Adan reservoir, Washim.*

INTRODUCTION

Water is elixir of the life. Water inevitable is synonymous with life and even though abundantly accessible in nature, fresh water remains a highly sought after natural resource for a gamut of reasons. This is due to the fact that only 0.00192% of the entire water resource available on earth is fit for human consumption (Pawar and Shembekar (2012). Survey and analysis made it clear that 70% of India's water is polluted (Shinde *et al.*, 2010). The main determinants of water quality are its biological, physical and chemical attributes. Generally, anthropogenic activities are responsible for the degradation of the quality of water, biodiversity loss and rapid depletion of other resources of water (Bhawankar *et al*., 2011).

Major part of fresh water resources are Dams. They are formed due to depression on land in which water from all around accumulates. While, Reservoirs are man-made. They are nothing but a body of water confined within an enclosure, created by dam a lotic system, a stream, or river. All over the water huge reservoirs have been constructed mainly to meet irrigational needs, drinking purposes, industrial, and domestic use etc. (Shinde *et al.*, 2010). Dams, rivers and reservoirs are the very important water resources which are used for various purposes. Physico-chemical parameters are the important component of the aquatic system as they indicate the water quality of aquatic ecosystem (Patil, 2012). This present study was conducted at four different sites in the Adan reservoir. Monthly and Seasonal variations in the physico-chemical parameters in Adan reservoir were studied during the study period one year from Feb 2012 to Jan 2013. The present investigation has been undertaken to assess the water quality of Adan reservoir.

MATERIAL AND METHODS

Adan reservoir is 15 Km away from Karanja town as well as on the border of Karanja (Lad) and Manora Tehsil. It is constructed on Adan river and its water acts as drinking water source for Karanja town as well as used for irrigation and fish catching. Co-ordinates of Adan reservoir is ($20^0$25'17.55" N and $77^0$33'47.07" E). Adan Reservior also known as Adan Talav or Adan Lake was constructed as part of irrigation projects by Government of Maharashtra in the year 1977 having net capacity of 1428 MCM..

Water samples were collected for the period of one year i.e. from Feb 2012 to Jan 2013 from the four sites of Adan reservoir and named them as site 1, site 2, site 3 and site 4. Water sample was collected in the morning hours and then brought in suitable polyethylene bottles in the research laboratory for further investigation. The data was recorded in 3 seasons, Summer (February to May), Monsoon (June to September) and Winter (October to January).

Parameters like Transparency and pH were analyzed at Adan reservoir whereas dissolved oxygen, total dissolved solids, chlorides, sulphates and nitrates were analyzed in the laboratory on the same day by titration methods as given in standard methods for the examination of water and sewage (APHA 1998) and Golterman *et al.,* (1978).

RESULT AND DISCUSSION

The physicochemical parameters like pH, Transparency (cm), Free CO_2 (Mg/L), Dissolved Oxygen (Mg/L), Total Dissolved Solids (Mg/L), Total Alkalinity (Mg/L), Total Hardness (Mg/L), Chlorides (Mg/L), Sulphates (Mg/L), Total Phosphorous (Mg/L), Nitrates (Mg/L) were estimated from Adan reservoir. The observations are given in following Table 1.

Table 1: Average Seasonal variation of physicochemical parameter in Adan reservoir, Washim District, Maharashtra (India) during 2014-15

Sr. No.	Physico - Chemical Parameters	Monsoon	Winter	Summer
1	pH	7.80	8.75	9.63
2	Transparency (cm)	11.40	23.20	10.30
3	Free CO_2 (Mg/L)	--	--	--
4	Dissolved Oxygen (Mg/L)	7.90	10.4	6.70
5	Total Dissolved Solids (Mg/L)	256.69	317.54	471.20
6	Total Alkalinity (Mg/L)	82.30	110.62	142.80
7	Total Hardness (Mg/L)	64.70	72.10	86.52
8	Chlorides (Mg/L)	36.48	43.22	56.34
9	Sulphates (Mg/L)	0.13	0.22	0.38
10	Total Phosphorus	0.25	0.31	0.47
11	Nitrates (Mg/L)	0.31	0.39	0.56

pH, total dissolved solids, total alkalinity, total hardness, chloride, sulphate, total phosphorus and nitrate of water increases from monsoon to summer. Such findings were observed by Koli, (2011) and Pandey *et al.,* (2012). DO and Transparency were high during winter than in monsoon and summer. Free CO_2 was completely absent. Sivalingam *et al*., (2013) found same trends for DO and TDS. Total hardness, Sulphate phosphorous and nitrate was lower in monsoon, higher in summer while moderate in winter. Similar findings were made by previous workers (Bhongade and Patil, 2010; Shinde *et al*., 2010; Shinde *et al.,* 2011; Narasimha *et al.,* 2011; Mahajan and Pokale, 2017).

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SELF NANO-EMULSIFYING DRUG DELIVERY SYSTEM FOR HIGH MOLECULAR WEIGHT DRUG

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Self Nano-emulsifying Drug Delivery System For High Molecular Weight Drug

ABSTRACT

Bosentan Hydrochloride (BOS) is poorly water soluble, high molecular weight and eleven hydrogen bond acceptors. Thus, it exhibits poor bioavailability. A new Solid-Self Nanoemulsifying Drug Delivery System (S-SNEDDS) of BOS has been successfully developed to enhance its oral bioavailability by improving its solubility and facilitating high molecular weight of BOS absorption. The primary composition of SNEDDS formulation was selected from solubility, pseudoternary phase diagram, emulsifying efficiency and compatibility test confirmed the suitability of Capmul MCM as oil, Tween 20 as surfactant and Propylene glycol as a co-surfactant for preparation of Liquid-Self Nanoemulsifying Drug Delivery System (L-SNEDDS). The formulation of the BOS loaded L-SNEDDS were prepared in a different concentration of oil, surfactant/co-surfactant and optimized by a various In-vitro evolutionary parameter. The optimized L-SNEDDS converted into free-flowing granules for compression of tablet. In vitro drug release study indicated that significantly increased the dissolution rate of the drug by all S-SNEDDS tablets versus the marketed formulation. In vivo studies in Sprague-Dowley rat for the optimized formulation was performed and compared to Marketed formulation observe significant increase the C_{max} and AUC of BOS compared to Marketed formulation (P>0.05). Thus, the present investigation improved the oral bioavailability of BOS.

Keywords: *Bosentan Hydrochloride (BOS), Self-Nanoemulsifying Drug Delivery System (SNDDS), Nanotechnology, Pharmacokinetics parameters, spray drying technology.*

1. INTRODUCTION

Oral drug delivery continues to be the preferred route of administration [1]. However, most newly discovered and existing drugs administered by oral route, frequently encounter bioavailability problems due to several reasons like poor dissolution, unpredictable absorption, low permeability, the high molecular weight of the drug, intra and inter subject variability and lack of dose proportionality. Lipinski's 'rule of five' predicts that poor absorption or poor permeation is more likely when there are more than five hydrogen bond donors, there are more than ten hydrogen bond acceptors, the molecular weight > 500 and calculated log P more than 5[2].

BOS was selected as a model compound to represent high molecular weight drug (569.64) and having 11 hydrogen bond acceptor exhibits inconsistent bioavailability. BOS belonging to BCS class-II drugs known as Endothelin Receptor Antagonists (ERA's) has slightly higher affinity for ET_A (endothelin-1 type-A and–B) receptor than ET_B[3,4] . It has been used for the treatment of pulmonary hypertension[4]. The bioavailability of BOS is up to 50% [5]. The low bioavailability of BOS is mainly attributed to its poor aqueous solubility, high molecular weight, eleven hydrogen bond acceptors and presystemic metabolism so it is necessary to find a proper approach that will increase solubility, dissolution rate and bioavailability of BOS.

In recent years, much attention has been paid to Self Nano-Emulsifying drug delivery system, which has shown a lot of reasonable success in improving oral bioavailability of poorly aqueous soluble and low permeation drugs[6]. SNEDDS are usually composed of an isotropic mixture of oil, surfactant or co-surfactant and are capable of forming fine oil-in-water nano-emulsion upon gentle agitation provided by the GIT motion (Bio-emulsification process). Above study, had an attempt to develop a novel S-SNEDDS formulation containing BOS employing diverse solidification techniques spray drying[7]. The S-SNEDDS are relatively more robust formulation with high stability, improved patient compliance and simple manufacturing. Therefore, attempts

were made to prepare the S-SNEDDS of BOS using porous carriers like Aerosil 200, Aerosil 300, Maltrin M 108, etc. by spray drying technique to enhance its aqueous solubility and oral bioavailability by possible avoidance of hepatic first pass effect[7], improve membrane permeability by inhibition of P-gp efflux and enhance absorption through lymphatic pathway[8]. Recently, an increased interest in novel analytical methods for pharmaceutical product analysis is observed. In general, the marketing success of any pharmaceutical product depends on stability, bioavailability, cost and patient compliances of the pharmaceutical product. S-SNEDDS complies all the respective parameters which will help to gain market capital.

2. MATERIALS AND METHODS:

2.1. Materials:

BOS was obtained as a gift sample from Lupin Pharma, Mumbai. Diester of caprylic/ capric acid (Captex 200, Captex 355, Captex 500) and mono/diglyceride Capmul MCM C8 were generous gifts from Abitech Corp. USA., Polyoxyethylene 20, sorbitan monolaurate i.e. Tween 20 and Propylene glycol were purchased from Lobachem, Mumbai. Aerosol 200 and 300 was a gift sample from Evonic Degussa, Mumbai. All other reagents were of analytical grade and were used as received.

2.2. Formulation of L-SNEDDS:

Screening and selection of excipients for the BOS L-SNEDDS were done by studying solubility profile of BOS in different oil, surfactant and co-surfactant selected on the basis of ease of emulsification with selected oil by water titration method and drawing ternary phase diagram.

The L-SNEDDS were prepared by admixture of BOS equivalent to 62.5mg with oil and S: Co-s mixtures were facilitated to the solublisation using cyclomixer for 5min, then placed for sonication using probe sonicator till the mixture clear and it could equilibrate for 48hrs in a water bath.

Different L-SNEDDS formulations were prepared by selecting the varied concentration of oil (25% to 65%w/w), surfactant (35% to 75%w/w) and co-surfactant (0 to 25% w/w) from pseudo-ternary phase diagram. The proportion of oil, surfactant and co-surfactant was always kept 100% in all formulations.

2.3. Evaluation of L-SNEDDS:

2.3.1. Droplet size analysis:

Droplet size analysis of resultant emulsion was analyzed by Nano Malvern droplet analyzer (UK). Dynamic light scattering particle size analyzer, wavelength scattering angle 90^0 at 25^0C, the average hydrodynamic diameter of the emulsion was derived from cumulative analysis by the auto measure software[10]. L-SNEDDS were diluted with distilled water in a ratio (1:100).

2.3.2. *In vitro* diffusion study:

Diffusion study was carried out for L-SNEDDS formulations and marketed tablet (Tracleer 156 mg weight of tablet contains equivalent to 62.5mg of anhydrous BOS). The tablet was crushed to fine powder and used for diffusion study. Formulations were filled individually in dialysis membrane bag with one end tied with thread. Each formulation was diluted 10 times with simulated gastric fluid pH 1.2 in the bag for the formation of the nanoemulsion and other end of the bag was tied with thread. The powder of marketed formulation was diluted with 7ml simulated gastric fluid pH 1.2. The bag was held in place with aid of stand in a beaker containing 100ml of pH 7.4 saline phosphate buffer[10]. The medium was stirred at 50rpm with a magnetic bead at 37 ± 0.5^0C. After every 1hr sample was withdrawn and diluted with the same medium. The same volume of fresh medium was transferred to a beaker for maintaining the sink condition. Amount of drug diffused was determined using UV-spectrophotometer at 274nm.

2.4. Preparation of S-SNEDDS:

The optimized L-SNEDDS was converted into free-flowing powder using colloidal porous carriers like colloidal silicon dioxide of different grade (Aerosil 200, Aerosil 300), maltodextrin (Maltrin M 108), etc. in combination and alone. The adsorbent carrier 300mg was suspended in 100ml ethanol at 250rpm using magnetic stirrer with slowly 1g L-SNEDDS added in suspension with constant stirring at room temperature for 15min to obtained good suspension [11]. The suspension was dried using spray drier (Labultima 222 advance, Mumbai, India) under maintained condition inlet temp 60ºC, outlet temp 40ºC. Aspiration rate 40N/m2 and feed rate of the suspension were kept 1.5ml/min [12].

2.4.1. Optimization and Characterization of S-SNEDDS:

The S-SNEDDS prepared using different carriers were optimized based on their micromeritics properties (bulk density, tap density, the angle of repose, carr's index, Hausners ratio, etc.) [13] adsorption capacity, drug content, ease of reconstitution ability into Nano-emulsion, droplet size and solid-state characterization of S-SNEDDS

powder. The solid-state characterizations were done by FTIR, DSC, XRD and SEM [13, 15] .

2.5. Development of S-SNEDDS Tablets:

S-SNEDDS tablets were compressed by using free flowing of S-SNEDDS powder prepared by spray drying technique containing BOS mix with variable concentration of directly compressible excipients. All formulation contains (22%w/w) MCC and lactose anhydrous as a directly compressible excipient [16-19] formulation F1 to F7 contain (1-7%w/w) pregelatinized starch as a superdisintegrents and F8 was a control formulation without superdisintegrants final weight of each tablet was kept 965mg by varying the weight of lactose anhydrous. All formulation studied pre-compression parameter and directly compress using 12mm flat face punches of ten station rotary tablet machine (Cadmach, Germany).

2.6. Evaluation of S-SNEDDS Tablet:

The S-SNEDDS tablets were evaluated for all post compression parameters (Hardness, Thickness, weight variation, Drug content uniformity, Friability, *In-Vitro* Disintegration test, *In-Vitro* Dissolution studies) [20-22]. All the parameters were studied as per the procedure of official book Indian Pharmacopeia.

2.6.1. *In-vitro* Dissolution study:

In-vitro dissolution of S-SNEDDS tablets was carried out using dissolution test apparatus USP XXII in dissolution media SGF pH1.2. The dissolution fluid (900ml) was maintained at 37±0.5ºC, 50rpm. An aliquot of 5ml was withdrawn by means of a pipette at an interval of every 5min for a period of 60min same quantity of fresh fluid equilibrated at 37±0.5ºC was replaced to maintain apparent sink conditions [23-25]. The aliquots were filtered using whatman filter paper no.41 and analyzed UV spectrophotometrically at a λ_{max}274nm. The same procedure was carried out for a marketed tablet.

2.6.2. *In vivo* study:

Male Sprague-Dawley Rats weighing 250±20g could fast for 10-12hrs prior to the experiments also allow for free access water. 24 rats were divided into four groups A, B, C and D groups [26-30]. The groups A, B and C of rats administered with pure drug, Marketed formulation (Tracleer Tablet) and S-SNEDDS formulation respectively. All the above groups of rats administered BOS orally in an aqueous suspension form equivalent to 4mg/kg of BOS and group D was kept as a control group.

Then 0.25ml of blood collected from the tail method using a 1ml needle at predetermined time intervals and 0.1ml of plasma separated by centrifuging blood plasma sample stored at -20^{0}C until further analysis [26, 27] . The blood plasma analyzed by HPLC method using PDA detector, flow rate kept 0.8ml and limit of quantification was 2ug/ml mobile phase developed in house. Mix 100µl plasma with 50µl ACN: 5mM ammonium acetate: acetic acid 10:90:1, add 750µl methanol. Mix the supernatant with 2ml 50mM ammonium acetate buffer (pH 10), wash with 2ml 20mM phosphoric acid and then wash with 2.1ml methanol: water (20:80). Evaporate the elute to dryness, reconstitute the residue with 150µl ACN: 5mM ammonium acetate: acetic acid 10:90:1, inject an aliquot.

3. RESULTS AND DISCUSSION

3.1. Formulation of L-SNEDDS:

The total Thirty Six formulations (LF1 to LF36) were prepared by varying oil, S: Co-S concentration as showed (Table 1). The "%" of oil, S/Co-S used herein was decided on the basis of the requirement for spontaneous formation of Self-nanoemulsifying system [31].

Table no. 1: Formulation and Evaluation of L-SMEDDS of BOS

FC	Oil (Capmul MCM) (%)	Surfactant (Tween 20) (%)	Cosurfactant (Propylene glycol) (%)	Drug Content (%)	No. of Inversions of VF	% Transmittance	Droplet Size (nm)
LF1	25	75	00	99.11	4	89.0	156.0
LF2	25	70	05	100.04	4	89.1	155.8
LF3	25	65	10	99.67	4	86.8	153.0
LF4	25	60	15	99.98	4	87.5	152.6
LF5	25	55	20	97.89	4	86.1	152.2
LF6	30	70	00	98.11	6	89.9	151.0
LF7	30	65	05	98.87	2	92.2	149.5
LF8	30	60	10	98.69	5	89.5	151.2
LF9	30	55	15	99.45	5	86.8	195.7

LF10	30	50	20	99.98	2	92.0	144.8
LF11	35	65	00	97.00	9	85.9	243.2
LF12	35	60	05	97.43	8	88.5	227.2
LF13	35	55	10	97.75	8	86.8	231.9
LF14	35	50	15	96.46	10	88.2	238.1
LF15	35	45	20	96.64	6	89.9	200.4
LF16	40	60	00	95.23	11	83.3	239.5
LF17	40	55	05	95.59	10	84.6	237.7
LF18	40	50	10	95.34	9	88.8	232.4
LF19	40	45	15	94.29	12	78.3	271.4
LF20	40	40	20	94.38	9	78.7	280.3
LF21	45	55	00	94.04	10	83.4	279.9
LF22	45	50	05	94.77	10	75.1	289.9
LF23	45	45	10	93.44	10	82.5	238.0
LF24	45	40	15	91.35	9	81.4	233.0
LF25	45	35	20	91.00	12	64.1	341.6
LF26	50	50	00	90.76	-------	-------	-------
LF27	50	45	05	90.94	-------	-------	-------
LF28	50	40	10	89.40	-------	-------	-------
LF29	50	35	15	88.53	-------	-------	-------
LF30	50	30	20	88.00	-------	-------	-------
LF31	55	45	00	88.12	-------	-------	-------
LF32	55	40	05	87.00	-------	-------	-------
LF33	55	35	10	87.04	-------	-------	-------
LF34	60	40	00	86.29	-------	-------	-------
LF35	60	35	05	86.45	-------	-------	-------
LF36	65	35	00	81.56	-------	-------	-------

FC- Formulation Code, *(n=3), VF- Volumetric Flask,

3.2. Evaluation of L-SNEDDS:

3.2.1. Droplet size determination:

Droplet size of resultant Nano-emulsion was found to be lowest for LF 10 formulation (144.8nm). The results of "%" transmittance were supported by Droplet size evaluation. It observed when "%" transmittance value increased, the droplet size decreased. The effect of drug loading was observed and it was found that droplet size of all formulations was increased upon increasing drug loading [32]. Only two formulations had droplet size, below 150nm which were selected for further study (LF7 and LF10).

3.2.2. *In Vitro* Diffusion Study:

In Vitro diffusion study of L-SNEDDS formulations compared with the marketed formulation. All L-SNEDDS showed drug diffusion more than 97% at the end of 8hr. The formulation LF10 showed 98.06% and marketed formulation showed only 39.28% drug diffusion. The formulation LF10 achieved highest drug diffusion due to smallest droplet size. As the droplet size decreases, the rate of diffusion increases. The droplet size, polarity of droplet, HLB value of surfactant, carbon chain length of oil, level of surfactant and cosurfactant influenced the diffusion of the drug. Based on these studies, optimize LF10 and selected for further preparation of S-SNEDDS depicted in Figure 1.

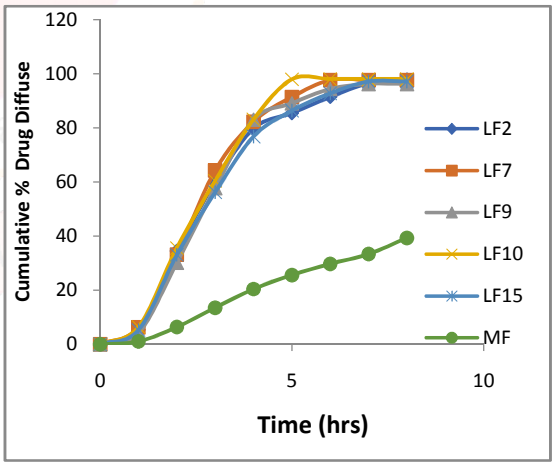

Figure no.1: *In-vitro* Drug Diffusion profile of Marketed formulation (Tab. Tracleer) and L-SMEDDS formulations containing BOS, data represented are Cumulative "%"drug diffuse versus time (hr) interms of mean ± SD (n=3).

3.3. Development of S-SNEDDS:

The S-SNEDDS was prepared by spray drying technology with different carriers to find out the maximum adsorbing capacity and the free-flowing ability of powder SNEDDS. Prepared S-SNEDDS was evaluated by an angle of repose and adsorbing capacity. Maltodextrin (Maltrin M 108), aerosil 300 did not show desired flowing properties and form a semisolid product. Hence, rejected from further study. The aerosil 200 was found to be the best adsorbing carrier for S-SNEDDS.

3.3.1. Characterization of S-SNEDDS:

The highest drug content was found to be 10.21mg/100mg in S-SNEDDS powder prepared by using aerosil 200 (Table 2).

Table no.2: Different composition Carriers for S-SMEDDS powder

Sr. no	Adsorbent	Ratio	Observation of Spray dried Product	Drug Content (mg/ 100mg S-SEDDS)	Droplet Size (nm)	Polydispersity Index
1	Aerosil 200: Maltodextrin	01:01	Powder with slightly viscous nature	4.935	161.2	0.42
2	Aerosil 300: Maltodextrin	01:01	Semisolid nature product	3.87	161.3	0.43
3	Aerosil 300	Alone	Powder with slight Semisolid nature	8.61	160.1	0.41
4	Aerosil 200	Alone	Powder with good flow property	11.21	157	0.32

***(n=3),**

3.4. Development of S-SNEDDS tablets:

The composition of various tablet formulations prepared showed in (Table 3). All the pre-compression parameters were evaluated like bulk density, tapped density, the angle of repose, and Carr's index [13]. All the results were found to be as per the specification of official books required for a compression. It was punched by the 12mm flat punch of 10 station rotary tablet machine. The S-SNEDDS powder batches F4 to F7 were not punched in a comfortable manner thus picking, sticking and lamination problems arose. Hence the post compression study was not executed for these batches. This might be due to the low concentration of anhydrous lactose and more the concentration of pregelatinised starch.

Table no. 3: Development of S-SMEDDS Tablets containing BOS

Formulations code / Ingredients	F1	F2	F3	F4	F5	F6	F7	F8
S-SMEDDS powder (mg)	560	560	560	560	560	560	560	560
Lactose anhydrous (mg)	126.5	117	107.5	98	88.5	79	70.5	136
Pre-gelatinized starch (mg)	9.5	19	28.5	38	47.5	57	66.5	00
Microcrystalline Cellulose (mg)	206	206	206	206	206	206	206	206
Magnesium stearate (mg)	19	19	19	19	19	19	19	19
Talc (mg)	19	19	19	19	19	19	19	19

S-SMEDDS powder contains equivalent to 62.5mg BOS

3.5. Evaluation of S-SNEDDS tablets:

S-SNEDDS tablets (F1 to F3 and F8) were evaluated for various posts compression parameters like hardness, thickness, friability, weight variation, *in-vitro* disintegration time and content of drug uniformity. All the results were complying as per the official book Indian Pharmacopoeia.

3.5.1. *In vitro* Dissolution study:

The execution of BOS from SNEDDS tablet is profitably improved compared with a marketed tablet. F3 formulation showed fastest drug release (98.08%) within the 30min as compared to other S-SNEDDS formulations and marketed formulation showed less than 20% drug release in 30min depicted in (Figure 2). F3 showed better result over the other formulation this might be due to the high concentration of pre-gelatinized starch and disintegration time was found to be least as compared to other. The release pattern of F3 treated with a different kinetic equation to interpret the order of release of BOS. The result indicates that F3 best suited to higuchi followed by zero order kinetics. On the other hand, marketed formulation followed first order kinetics.

In general, the dissolution test was only used to show the advantage of S-SNEDDS formulation compared to a conventional tablet. *In-vitro* dissolution might not predict release behavior of the S-SNEDDS tablet in the gastric environment because the solubilization of SNEDDS might be lost less or more digestion and dilution by GI enzyme and fluid. *In-vitro* dissolution ought to be further correlated with the *in-vivo* performance of S-SNEDDS. Similarity factor calculated by comparing marketed formulation and F3 drug dissolution profile and it was found to be 18.19. Therefore, it confirms the significant difference in release profile between two formulations.

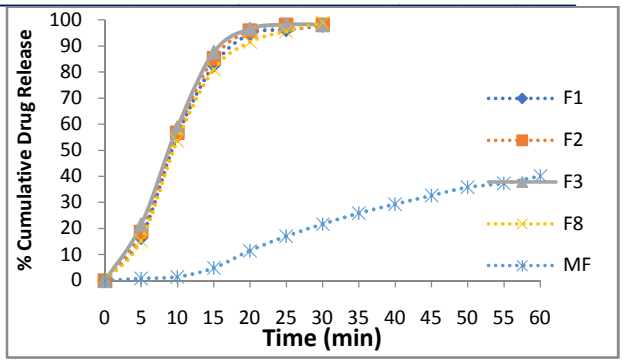

Figure no. 2: Comparative *In-vitro* Dissolution profile of Marketed formulation (Tab. Tracleer) and S-SMEDDS tablets containing BOS. Data represented are cumulative "%"drug release versus time (min) in terms of mean ±SD (n=3).

3.5.2. *In vivo* studies:

The average plasma concentration profile as a function of time obtained during the *in-vivo* pharmacokinetic investigation carried out in Male Sprague-Dawley rats for pure drug BOS, marketed formulation (Tracleer Tablet containing 62.5mg BOS) and optimized (F3) S-SNEDDS Tablet containing 62.5mg BOS. The C_{max} of S-SNEDDS was about 1.76 fold and marketed formulation 1.16 fold higher than pure drug BOS. The values of AUC 0-t of S-SNEDDS were 1.59 fold and marketed formulation showed 1.07 fold higher compared pure drug BOS. T_{max} decreased to 3.44hr for S-SNEDDS and marketed formulation 3.89hr compared to pure drug. Other parameters like MRT 0-t, Ka and $t_{1/2}$ are also found to be higher than pure drug and marketed formulation indicating enhanced bioavailability depicted in (Figure 3 and Table 4). The results of all pharmacokinetic parameters were found to be highly significant ($P<0.05$) for F3 S-SNEDDS tablet compared to pure drug BOS and the marketed formulation. It confirmed that oral absorption of BOS was significantly improved by F3 S-SNEDDS tablet.

Table no.4: Pharmacokinetic parameters of S-SMEDDS and Marketed Formulation (Tab. Tracleer) administered orally in Sprague-Dawley Rats (mean ±SD, n=6)

Sr. No	Parameter	Marketed formulation	S-SMEDDS
1	t_{max} (hr)	3.89	3.44
2	C_{max} (µg/ml)	17.24	26.28
3	$t^{1/2}$ (h)	6.36	6.68
4	Ke (h^{-1})	0.11	0.1036
5	AUC^{t}_{0} (µg.h/ml)	255.7	380.27
6	MRT (hr)	11.61	12.55
7	Ka (hr)	0.497	0.625

All the parameters were determined with statistical significance set at $P<0.05$.

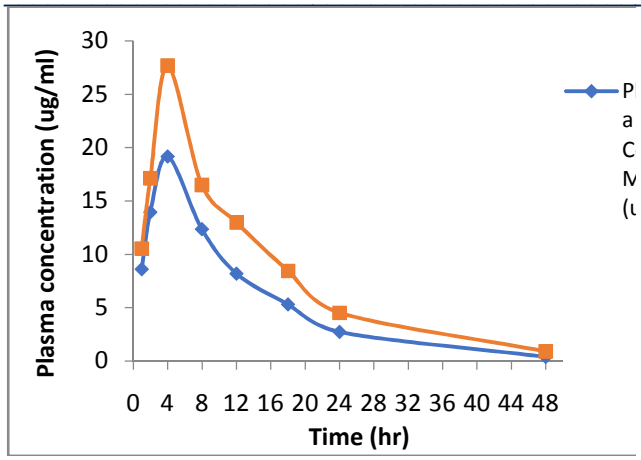

Figure no. 3: Plasma Concentration Time profile of marketed formulation (Tab. Tracleer) and optimized S-SMEDDS tablet containing BOS after oral administration in rat.

4.CONCLUSION:

These current results demonstrated that S-SNEDDS of BOS were successfully developed composing Campul MCM (30%), Tween 20 (50%) and Propylene glycol (20%) for L-SNEDDS. The composition of S-SNEDDS tablet contains L-SNEDDS containing equivalent of 62.5mg BOS and aerosil 200 as an adsorbent carrier (59.57%), anhydrous lactose (11.4%), pregelatinized starch (3%), Microcrystalline cellulose (22%), Magnesium stearate (2%) and Talc (2%) were selected. In this study, the S-SNEDDS of BOS were prepared by spray drying technology. The S-SNEDDS consists of a well separated particle with smooth surface observed from SEM and preserved the self emulsification performance of the L-SNEDDS. Both the DSC and XRD analysis suggest that BOS in S-SNEDDS may be in a molecular dispersion state. *In-vitro* dissolution test shows that S-SNEDDS of BOS tablet has faster release rate. F3formulation released 98.08% BOS within 30 mints. *In-vivo* absorption study in rat showed that S-SNEDDS tablet (F3) increased the significant bioavailability of BOS compared to the pure drug and marketed formulation of BOS with excellent stability. Thus, the S-SNEDDS provide a useful oral solid dosage form for poorly water soluble and higher molecular weight drug BOS.

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MACRONUTRIENTS AND MICRONUTRIENTS FOR DIABETIC MANAGEMENT : A SYSTEMATIC REVIEW

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ABSTRACT

Diabetes millets is a chronic disease where there is a high levels of glucose level in human's blood. Symptoms of diabetes mellitus are frequent urination, depression, increased thirst, hunger, weightloss. It is further classified in two types. Type 1 diabetes and type 2 diabetes. Normally children and young have type 1 diabetes where body does not produce insulin properly and in type 2 diabetes, insulin produce by the body's do not work properly. For the diabetic diet macro nutrients and micro nutrients plays an important role in diabetic patient. Macronutrients are those nutrients which are taken into excess amount which provides calories, energy to human body. Macronutrients are important for functioning of human body, maintaining body's system. These are further classified into three groups' carbohydrate, proteins and fats. Carbohydrate is source of human energy diet, though it is harmful taken in excess amounts. Carbohydrates are mostly present in bread, potatoes rice, banana etc. Proteins are biomolecules consist of large number of amino acids it is essential to regulate body tissues, functioning of immune system and cells. It is present in meat, fish, peanut butter, eggs, milk, tofu, oatmeal etc. A fat plays a major role in our body by supplying energy to our body and protects organs and cells. It is then classified to saturated fatty acids and unsaturated fatty acids. Excess of these fats can increase risk of heart disease, cardiovascular disease, cancer etc. Micronutrients are those nutrients which are required in a small amount i.e. in milligrams and microgram amount. Vitamins and minerals are two types of micronutrients. Vitamins are carbon containing molecules and are classified either as water soluble and fat soluble. They can be affected by heat, light, oxygen and chemical processes. Minerals do not contain carbon and are not destroyed by heat and light. Minerals are simplest compound found in our bodies and foods. These are essential part of human bodies. Mineral deficiencies lead to a major health issue problem including increase chance of risk for diabetes

***KEYWORDS**: Diabetes mellitus, Macronutrient, Micronutrient, carbohydrates, proteins, fats*

INTRODUCTION

Diabetes mellitus

Diabetes mellitus (DM) is a problem or metabolic disease in the body that causes blood glucose (sugar) levels to rise higher than normal for long period of time. This is also called hyperglycemia. It occurs when the pancreas does not secrete enough insulin or when the cells of the body become resistant to insulin. In either case, the blood sugar cannot get into the cells for storage, which then leads to serious complications (Shilpa Arora, 2016).

Diabetes is actually a very popular heath issue. There are 2 major types of diabetes- type 1 and type 2 diabetes. Type 1 diabetes in which the patient's body cannot produce insulin and type 2 diabetes in which the insulin in the patient's body produced cannot work properly or the patient's body cannot produce enough insulin (Lien Nguyen, 2015).

TYPE 1 DIABETES MELLITUS

Type 1 diabetes is usually diagnosed in children and young adults, and was previously known as juvenile diabetes or INSULIN DEPENDANT DIABETES MELLITUS (IDDM). Only 5% of people with diabetes have this form of the disease. In type 1 diabetes, the body does not produce insulin due to pancreas failure. Insulin is a hormone that the body needs to get glucose from the bloodstream into the cells of the body. The body breaks down the sugars and starches you eat into a simple sugar called glucose, which it uses for energy but in diabetes these sugars cannot enters into cells and remains in the blood which

cause high blood sugar levels in the blood, this causes diabetes. With the help of insulin therapy and other treatments, even young children can learn to manage their condition and live long, healthy lives (American Diabetic Associationn, 2015; Glycemic Index, 2017).

TYPE 2 DIABETES MELLITUS

Type 2 diabetes is characterized by insulin resistance which shows reduced insulin secretion. In type 2 diabetes your body does not use insulin properly this defective responsiveness of body tissues to insulin is due to insulin receptor. At first, your pancreas makes extra insulin to make up for it. But, over time it isn't able to keep up and can't make enough insulin to keep your blood glucose at normal levels. So, glucose gets remain in the blood stream cause extra sugar level (glucose) in blood. This is referred as non-insulin dependent diabetes mellitus or adult onset diabetes. Type 2 diabetes is due to lifestyle factor, genetics including obesity, lack of physical activity, poor diet, stress etc (American Diabetic Associationn 2015; Glycemic index 2017).

MACRONUTRIENTS

Macronutrients are a compounds which provides energy or calories to human body and which is taken in greater amount. Macronutrients are necessary for the proper functioning of the body, for their growth and metabolism. The main function of macronutrients is to provide energy, counted as calories. Macronutrients also have specific roles in maintaining the body and contribute to the taste, texture and appearance of foods, which helps to make the diet more varied and enjoyable (Wikipedia.html, 2017; Monique Laberge, 2017).

Macronutrients are further classified in three components

- **Carbohydrates**
- **Proteins**
- **lipids**

CARBOHYDRATE OR CARBOHYDRATES

Carbohydrates gives 50% of human's daily energy requirement but this is not true for diabetic people. Low and high carbohydrates diet have direct effect on blood glucose level. It depends upon glycemic index (Leonie Garden et. al., 2014; Julie Lichty Balay , 2009).

Glycemic Index (GI) is the list of food which are represented by a number from 1-1000. This number shows how the food affects the blood glucose level. If GI is 55 or low is considered as safe whereas 55-69 as moderately and <70 rapidly affects blood glucose level (Julie Lichty Balay, 2009; Glycemic index, 2017).

Carbohydrates are divided in **complex** or **starchy carbohydrate** and **simple** or **sugar carbohydrate**. Simple carbohydrates are not broken down into simple sugar where it has an elevated effect on blood level due to sugar present in it. It is found in white bread, baked products, table sugar; candies etc. Complex carbohydrates are long chain of simple carbohydrate and are less effective on blood glucose than simple carbohydrates due to presence of starch. They are present in green vegetables, apples, lentils etc (Monique Laberge, 2017;Steven Dowshen, 2016) .

After digestion of carbohydrates, sugar gets released which enters to bloods cells so carbohydrates have direct effect on blood glucose, this depends upon the type, quality and quantity of carbohydrates which the body is consuming (franziska Spritzler, 2016). RDA (recommended dietary allowances) for carbohydrates for diabetic patient is 135-230 gms/day (Sandi Busch, 2017).

Fiber is an important because it helps you feel happy and keeps your digestive system working properly. In fact, eating lots of fiber can even help to slow the body's absorption of sugar (glucose) when eaten together with sugar in the same food. Everyone needs fiber, and most people don't get enough. Some experts think that people with diabetes should eat more fiber than people without diabetes to help control blood sugar.

Sugary foods, like soda and candy, don't usually have fiber and typically contain "empty calories." That means they have calories but little nutritional value, and eating too many of them might leave little room for healthy foods. Eating too many empty-calorie foods can also make a person more likely to be overweight or obese. These foods can also cause tooth decay (Steven Dowshen, 2016).

PROTEINS

Proteins are the macromolecules or biomolecules consists of large number of amino acids. Protein is an essential to regulate body tissues, functioning of immune system and cells and for repairing and growth of muscles. Proteins are usually present in a meat or a meat substitute, such as cheese or peanut butter. But most foods that contain proteins also contain fats, and a few also contain carbohydrates. Diabetic people must have an intake of about 80-100 gms/day proteins

In diabetic patient Amino acids are released after breaking down of proteins which encourage insulin to function where as glycogen breaks down into glucose which have adverse effect on blood glucose level (Leonie Garden et. al., 2014 ; Monique Laberge, 2017,; Sheren lehman, 2016).
Some important points about protein

- "Proteins" are foods like meat, meat products, fish, cheese, and peanut butter.
- About 50–60% of protein becomes glucose and enters the bloodstream about 3–4 hours after it's eaten.
- Bedtime snacks should always contain proteins. The proteins will be converted to blood glucose more slowly than carbohydrates and will keep blood glucose levels from dropping too low during the night.
- Treat an insulin reaction with a fast-acting carbohydrate and add proteins to provide a later source of blood glucose. This will prevent the blood glucose from dropping too low again (Marion J. Franz).

FATS

Fats play a major role in our body by supplying energy to our body, protect organs, muscles cells, store some of the vitamins where transfer others. Fatty acids do not have major effect on blood glucose level but its secondary effect is quite dangerous. (Leonie Garden et. al., 2014;Monique Laberge, 2017). Obesity and blood glucose levels are depends upon the low or high fats diet. Egg, meat, white bread, fishes, cheese are high fatty acids diet which can lead to high cholesterol whereas brown bread, vegetables, olive oils, nuts are low fatty acids diet food. Fatty acids are differentiating into saturated fats and unsaturated fats (Leonie Garden et. al., 2014,Alissa Heizler Mendoza et. Al, 2011).
Recent studies have suggested that dietary fat may contribute to delayed increases in blood glucose levels. This is because the presence of fat will slow the rate of gastric emptying. Individuals may be at risk of hypoglycemia (diabetes mellitus) shortly after a high fat meal. The onset time of rapid acting insulin is likely to be faster than the digestion and absorption carbohydrate taken as part of a high fat meal (Leonie Garden et. al., 2014).

FATTY ACIDS

Fatty acids are long hydrocarbon chains that are found in a certain type of lipids (triglycerides and phospholipids). These fatty acids may differ in length of the hydrocarbon chain of 4-24 carbons and in the number of double bonds

SATURATED FATTY ACIDS

Saturated fatty acids are harmful fats which have no double bond between carbon atoms having a general formula of R-COOH in which the R-group is a straight chain hydrocarbon of the form CH_3 $(CH_2)_n$ with varying length ranging from short chain length to length of 30 or more carbon atoms. Most of the fatty acids are found in different plant and animal fats. In human diet most of fatty acids are mysteric,palmitic, stearic acids. These are solid at room temperature. Processed food contains high amount of saturated fats. High amount of these fats in body can lead to high cholesterol, diabetic neuropathy, obesity, heart disease etc. Due to high cholesterol, blood glucose level increases therefore diabetic people are instructed to eat less saturated fatty acids food (American heart association, 2018; Alissa Heizler Mendoza et. Al., 2011) ; AMERICAN DIABETIC ASSOCIATION, 2015;Sarah Smith, 2018).

UNSATURATED FATTY ACIDS

These are simple basic fats (consist of one or more double/triple carbon – carbon bonds in carbon chain) which are healthy fats and are liquid at room temperature. These fats maintain cholesterol, obesity and weight. These fats are digested soon in the body and released during excretion. Unsaturated fatty acids are divided in monounsaturated fats (single double bonded carbon) and polyunsaturated fats (two or more double bonds) (Leonie Garden et. al., 2014; American heart association, 2018; Alissa Heizler Mendoza et. Al, 2011;AMERICAN DIABETIC ASSOCIATION, 2015).

MONOUNSATURATED FATTY ACIDS (MUFAs)

Although 100 MUFAs have been found in nature, they are good fats & are liquid at room temperature. During chilling they turn into solid from liquid form. Common sources are nuts, almonds, avocados, olive oil, cashew nuts. According to American Heart Association consumption of MUFAs improves blood lipid profile. Besides protecting your heart, it decreases your risk cancer; maintain your healthy weight.

POLY UNSATURATED FATTY ACIDS (PUFAs)

IN Human Diet, the consumed PUFAs are almost exclusively linoleic acid (omega-6 fatty acids) and alpha- linolenic acid (omega-3 fatty acids). Linolenic acid, oleic acid and palmitic acid are the three most abundant fatty acids found in fatty tissue. Omega-6 fatty acids are found in sunflower, safflower, corn, groundnut, soya oils whereas fish such as mackerel, sardines, trout are good source of omega-3 fatty acids.

OMEGA-3 FATTY ACIDS are of three types

- Alpha linolenic acid (LNA)
- Eeicosapentaenoic acid (EPA)
- Docosahexaenoic acid (DHA)

LNA is found in vegetable sources where EPA and DHA are in fishes.

Diets rich in **omega-3 fatty acids** may decrease insulin resistance in people with diabetes. Studies show that fish oil supplements may lower triglycerides levels in people with type 2 diabetes which could lower the risk of heart disease. New study in the Lancet diabetes and Endocrinology suggest that **omega-6 poly unsaturated fats** found in vegetable oils reduce the risk of developing type 2 diabetes. The recommended consumption of omega-6 fatty acids are about 5-10 % of total calorie intake (Ginger Vieria, 2017; Robert S Dinsmoor, 2014).

MICRONUTRIENTS

VITAMINS

These are further classified as water soluble, fat soluble vitamins. Water soluble vitamins are vitamins B and vitamins C. These vitamins are soluble in water and can be excreted easily through urine and fat-soluble vitamins are vitamin A, vitamin D, vitamin E, and vitamin K.

Vitamin A

Our bodies require vitamin A for night vision and color vision, but that's not all. We need it for cell differentiation and bone health too. It supports immune function. Vitamin A also aids both male and female reproductive processes. Sources for preformed vitamin A come from animal foods only. They include liver, egg yolks and whole milk. Carotenoids are precursors to vitamin A. Sources of these precursors, referred to as provitamin A, & rich source include broccoli, spinach, carrots, sweet potatoes, cantaloupe, peaches and other dark green and yellow/orange fruits and vegetables.

Vitamin A plays an important role for the development of insulin producing beta-cells in the early stages of life, but also for a proper function during the remaining life especially during path physiological conditions. Beta-cells' resistance to inflammation decreases in the absence of vitamin A. In case of a complete deficiency, the cells die. The RDA for males and females aged 14 years and older is 900 and 700 micrograms, respectively (Jill Weisenberger, 2017).

VITAMIN B

There are eight types of vitamin B Complex Thiamine (Vitamin B1), Riboflavin (Vitamin B2), niacin (Vitamin B3), pantothenic acid (Vitamin B5), pyridoxine (Vitamin B6), biotin (Vitamin B7), folate (Vitamin B9), cyanocobalamin (Vitamin B12).

THIAMINE (Vitamin B1)

Thiamine is also known as vitamin B1 and helps to convert glucose into energy and has a role in nerve function. It assists in carbohydrate and amino acid metabolism & RDA of thiamine is 700-900 mcg. Vitamin B1 is critical for nerve health in diabetes specifically. Thiamine can offer protection from the nerve damage that diabetics face due to excess sugar in the blood. (Best vitamins for diabetes, 2017). Though thiamine is found in most food groups, Americans get most of their thiamine from fortified breakfast cereals and enriched grains such as rice and pasta. Pork, beans and peas are additional sources (Jill Weisenberger, 2017).

VITAMIN B2

Riboflavin assists in carbohydrate, fat metabolism, energy production and helps vision and skin health. It improves the body's metabolic activity, boosts the immune system and promotes the health of the nervous system. Dairy products, fortified cereals and enriched grains are major contributors of dietary riboflavin. Mushrooms and organ meats such as liver are additional sources. Its recommended intake is 1.3 mg (Jill Weisenberger, 2017).

VITAMIN B3 (Niacin, Nicotinic acid)

Niacin assists in carbohydrate and fat metabolism; helps with cell differentiation; and participates in DNA replication and repair. Niacin is essential for the body to convert carbohydrates, fat and alcohol into energy. It helps maintain skin health and supports the nervous and digestive systems. Unlike

other B-group vitamins, niacin is very heat stable and little is lost in cooking. Vitamin B3 also helps to convert food into readily available energy. It is especially helpful for those who suffer from fatigue, indigestion blood pressure and blood cholesterol with diabetes and migraines. Niacin, or Vitamin B3 supplements, helped lower blood sugar, reduce fatty liver and also prevent neuropathy in mice with type 2 diabetes. The study proved that Niacin protected the pre-diabetic and diabetic mice against nerve damage. **Recommended Intakes of Niacin** for adult women and men is 14 and 16 mg (Jill Weisenberger, 2017).

VITAMIN B5 (Pantothenic acid)

Pantothenic acid is needed to metabolize carbohydrates, proteins, fats and alcohol as well as produce red blood cells and steroid hormones. It also helps make lipids and hemoglobin. Deficiency can cause neurological problems and a burning sensation in the feet (both of which are also common in diabetics). Good sources of pantothenic acid are widespread and found in a range of foods, but some good sources include liver, meats, milk, kidneys, eggs, yeast, peanuts and legumes (Vitamin B, 2014).

VITAMIN B6 (Pyridoxine**)**

Pyridoxine is needed for protein and carbohydrate metabolism, the formation of red blood cells and certain brain chemicals. It influences brain processes and development, immune function and steroid hormone activity. It also helps form in hemoglobin which carries blood in the body. One of the best diabetic vitamin supplements, vitamin B6 supports nerve health which is critical in addressing conditions in diabetic neuropathy. Diabetic participants who received B-vitamin therapy had reduced kidney damage caused by diabetes. Their arterial health improved too. Diabetics with kidney issues are often found to have too much of the harmful chemical homocysteine in their blood. B-vitamin therapy – with folic acid, vitamin B6, and vitamin B12 have been shown to lower the blood levels of homocysteine. Good sources of pyridoxine – include cereal grains and legumes, green and leafy vegetables, fish and shellfish, meat and poultry, nuts, liver and fruit. Its recommendation intake is 1.7 mg (Vitamin B, 2014).

VITAMIN B12 (Cynocobolmine)

Vitamin B12 helps to produce and maintain the myelin surrounding nerve cells, mental ability, red blood cell formation and the breaking down of some fatty acids and amino acids to produce energy. Vitamin B12 has a close relationship with folate, as both depend on the other to work properly. Good sources of B12 include liver, meat, milk, cheese and eggs, almost anything of animal origin. It boosts the central nervous system and helps improve body metabolism it is the best vitamin for diabetics for who suffer from neuropathy and a compromised immune system. Diabetic participants who received B-vitamin therapy had reduced kidney damage caused by diabetes. Their arterial health improved too. Issues are often found to have too much of the harmful chemical homocysteine in their blood. B-vitamin therapy – with folic acid, vitamin B6, and vitamin B12 have been shown to lower the blood levels of homocysteine. Its recommended amount is 2.4 mg (Vitamin B, 2014).

VITAMIN C (Ascorbic acid**)**

Vitamin C is important for many reasons. It enhances iron absorption. It helps with collagen synthesis. It acts as an antioxidant and plays a role in immune function. It also regenerates vitamin E and assists in the synthesis of neurotransmitters, DNA and hormones. Vitamin C is present in fruits and vegetables. Rich sources include bell peppers, citrus fruits, strawberries, pineapple, kiwifruit, potatoes, tomatoes, broccoli and leafy greens. It also helps lower levels of sorbitol that sugar can collect in and damage cells in the eyes, kidneys and nerves. All this make vitamin a good vitamin for diabetes. Vitamin C supplements improve widening of arteries to allow sufficient blood flow in patients with non-insulin-dependent diabetes mellitus. The RDA for men and women is 90 and 75 milligrams respectively. Smokers should add an additional 90 milligrams per day (Jill Weisenberger, 2017).

VITAMIN D (Cholecalciferol)

Cholecalciferol regulates blood calcium levels and supports bone health. Vitamin D is essential for good bone health as it plays a crucial role in allowing the body to absorb calcium and phosphorus, making bones and teeth stronger and healthier. It boosts production of antimicrobial peptides called ‘cathelicidins’, which destroy viruses, bacteria and other germs. Since diabetics are highly prone to infections due to diabetic

ulcers and gum diseases, it is important to make sure the body has optimal levels of this fat-soluble vitamin. The best source of vitamin D is sunlight. Ultra violet light triggers the synthesis of vitamin D in your skin. With increased use of sunscreen and fewer work hours and leisure time outdoors, many people do not synthesize adequate vitamin D. There are few food sources of naturally occurring vitamin D. They include fatty fish such as salmon and tuna, egg yolks, beef liver and some mushrooms. Fortified milk, orange juice, breakfast cereals and other foods are additional sources. The RDA for males and females aged 1 to 70 is 600 IU (International Units). After age 70, the RDA jumps to 800 IU (Vitamin B, 2014).

VITAMIN E (Tocopherol**)**

Tocopherol protects cell membranes from oxidation. Seeds, nuts, vegetable oils and fortified breakfast cereals are among the best sources of vitamin E. Vitamin E is relatively nontoxic, but large doses from supplements may interfere with blood clotting. This vitamin improves glucose control and protects blood vessels and nerves from free radical damage which is accelerated by diabetes. This makes tocopherol best vitamin for diabetes. It even may reverse damage to nerve caused by diabetes and protect against diabetes cataracts and atherosclerosis. (Jill Weisenberger, 2017).

MINERALS

CHROMIUM

Chromium enhances the effects of insulin, and may thus, play a role in the development of glucose intolerance and type 2 diabetes. Chromium is a well-documented mineral that can help prevent and help with controlling blood sugar levels in existing diabetes. Chromium is also essential for the population of insulin receptors, for binding insulin to cells, and for increasing the utilization of glucose. While high doses of the mineral can be toxic, small dosage amounts have been shown to help diabetics with type 2 diabetes. Since chromium can boost insulin receptors and lower blood glucose levels, it can be helpful in reducing diabetes symptoms. Some studies have indicated that chromium picolinate may be more effective than other forms of chromium in supplements, as it is easier for the body to absorb and use. According to studies, chromium can enhance the effects of insulin. Deficiencies in chromium impair blood glucose control. In several studies, it was shown that those with diabetes have abnormally low chromium levels. The trace mineral may be able to reduce insulin levels and improve the lipid profile in diabetics. According to the Joslin Diabetes Center, dosages up to 200 mg daily should be safe for most individuals with diabetes. Whole grains, brewer's yeast, Tomatoes, oysters, whole grains, bran onions, Potatoes nuts and dark chocolate are sources of chromium (Jill Weisenberger, 2017).

MAGNESIUM

Magnesium is an essential mineral that is necessary for many of the body's functions from mood-regulating, to hormone health, to fighting insomnia, and even preventing and helping diabetes. Magnesium plays a huge role in the body, according to the National Institute of Health. It develops bones, helps regulate blood sugar, improves mood, controls the nervous system, keeps the heart regulated, and can help lessen PMS symptoms. The biggest role of magnesium for diabetes is its role in controlling blood glucose levels. The RDA for men and women aged 19 to 30 years is 400 and 310 milligrams per day, respectively. For older adults, the RDA bumps up to 420 milligrams and 320 milligrams for men and women, respectively. Leafy greens, potatoes, dairy product, meat, fish rice, whole grains, nuts, seeds and legumes are good sources of magnesium (Jill Weisenberger, 2017).

ZINC

Zinc is an important mineral that provides many benefits for the body. According to the National Institute of Health, the main function of zinc is for energy, cell production, protein synthesis, and development. It is necessary to have a steady dietary or supplement intake of zinc because the body cannot store zinc for future use. Oysters, beef and clams are rich sources of absorble zinc. Whole grains also contain zinc, but it is less available for absorption. Taking more than the recommended daily amount can lead to side effects like nausea, vomiting, headaches, and loss of appetite. Too much zinc may reduce the body's absorption of copper. Dosage Amount the National Institute of Health recommends that healthy adults take about 40 mg of zinc daily for optimal nutrition and health (Jill Weisenberger, 2017).

CALCIUM

Calcium is the most abundant mineral in the body and is beneficial for many processes in the body-from bone health to nerve transmission. Calcium is

a major component of bones and teeth. It is also a mineral that could help reduce diabetes risk. Some studies have indicated that high doses of calcium may actually lead to a higher chance of getting type 2 diabetes. However, other studies have shown that calcium supplements can be beneficial in reducing diabetes risk. A daily intake of around 1,200 mg of calcium was able to reduce a woman's risk of getting type 2 diabetes by about 33 percent (Jill Weisenberger, 2017) .

VANADIUM

Vanadium is a strange metal that is surprisingly beneficial against diabetes in many studies in animals and humans. The use of vanadium as a dietary supplement is highly controversial, as vanadium can be toxic in high doses. Vanadium is actually an essential mineral in the body that helps regulate growth. Vanadium is present naturally in trace amounts in many foods and in water. The researchers found that vanadium supplements can influence regulated blood glucose levels, modulates hepatic glucose output, and enables type 1 diabetic patients to be able to reduce insulin requirements after 2 weeks of supplementing with vanadium. Meat fish chicken eggs beer is the sources of vanadium. In a study where vanadium was able to help reduce the need for insulin in type 1 diabetics, study participants took 125 mg of vanadium daily (Jill Weisenberger, 2017).

SELENIUM

Selenium is a vital mineral that is essential for bodily health. Selenium is present in many foods and is also available in supplement form. Selenium plays a vital role in many functions of the body, including thyroid health, DNA synthesis, protection from infection, and reproduction. It also has a protective effect against diabetes, although researchers have not identified the precise link between selenium levels and diabetes. The National Institute of Health recommends daily selenium dietary and supplement intake of 55 mcg & its sources are beef liver, cheese fish ham lettuce potatoes nuts (Jill Weisenberger, 2017).

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IN-SILICO ANALYSES OF TIPIFARNIB ANALOGUES FOR ANTI-CHAGAS DISEASE

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ABSTRACT

In the present work, extensive SAR analysis was executed for second generation analogues of the cancer drug clinical candidate Tipifarnib for anti-Chagas disease, a neglected disease. The investigation was successful in recognizing the important structural features that control the anti-Chagas profile of Tipifarnib derivatives as a promising agent. The pharmacophoricmodel reveals that the anti-Chagas activity of Tipifarnib analogues has correlation with the inter-relation of nitrogen with lipophilic atoms.

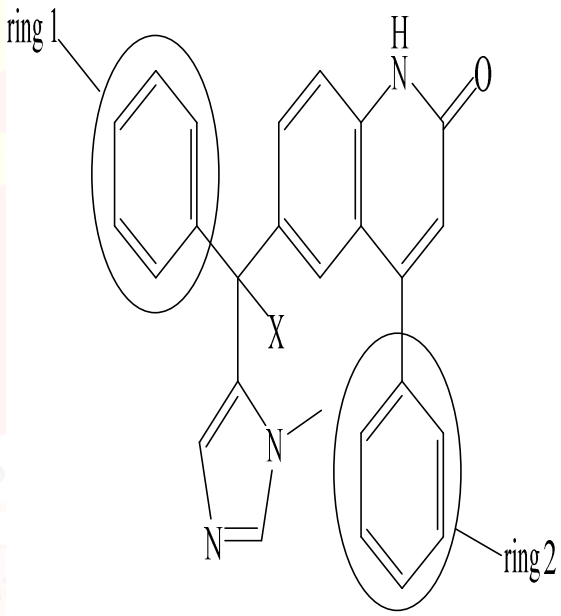
Keywords: *SAR, Pharmacophoric, anti-Chagas, Tipifarnib*

INTRODUCTION

Chagas disease, a disease generally spread by contact with an infected triatomine bug also called "Kissing bug," "Benchuca," "Vinchuca," "Chinche," or "Barbeiro", is one of the most neglected parasitic diseases that can cause serious heart and stomach illnesses.The disease with its major presence in the tropical regions viz. Africa and Latin America, affects more than ten million peoples each year.Kinetoplastidhemoflagellate*Trypanosoma cruzi* (*T. cruzi*), the protozoan parasite, is the causative agent of Chagas disease.

Recently, Tipifarnib, a well-known anti-cancer agent developed by Johnson and Johnson Pharmaceuticals, was found to effectively inhibit *T. cruzi*. But, Tipifarnib binds to human protein farnesyl transferase, thus creating toxic issues for use of Tipifarnib as an effective inhibitor of *T. cruzi*. These issues must be addressed to widen its potential as a drug candidate against *T. cruzi*. Hence, further optimization of Tipifarnib as an effective inhibitor of *T. cruzi* with desired ADMET profile is necessary.For this an attractive idea is to develop pharmacophoricmodel using available data for identification of lead/drug likeness characteristics and thereby continue the optimization.

EXPERIMENTAL METHODOLOGY



Data set and model building: The data set consists of thirty-three Tipifarnib analogues with a variety of substituents at different positions.PyMOL 1.8.4 along with LIQUID plugin were used for developing the model using aligned molecules. The dataset has been tabulated in figure 1 and table 1.

Figure 1. Tipifarnib analogues with a variety of substituents at different positions

Table 1. Experimental EC_{50}, and substituents on Tipifarnib analogues used in the present study

S.N.	*T. cruzi* EC_{50} (nM)	X	ring 2	ring 1	Imidazole
1	4	NH_2	3-chloro	4-chloro	1-methyl-1H-imidazole
2	0.6	OMe	3-chloro-2-methyl	4-chloro	1-methyl-1H-imidazole
3	3.1	OMe	3-chloro	4-chloro	1-methyl-1H-imidazole
4	0.7	OMe	2-methyl	4-chloro	1-methyl-1H-imidazole
5	0.8	OMe	2-trifluoromethyl	4-chloro	1-methyl-1H-imidazole
6	1.1	OMe	3-fluoro	4-chloro	1-methyl-1H-imidazole
7	1.2	OMe	3-methyl	4-chloro	1-methyl-1H-imidazole
8	12	OMe	3-trifluoromethyl	4-chloro	1-methyl-1H-imidazole
9	0.8	OMe	2-fluoro	4-chloro	1-methyl-1H-imidazole
10	0.8	OMe	phenyl	4-chloro	1-methyl-1H-imidazole
11	0.82	OMe	4-chloro	4-chloro	1-methyl-1H-imidazole
12	0.5	OMe	4-fluoro	4-chloro	1-methyl-1H-imidazole
13	2	OMe	4-methyl	4-chloro	1-methyl-1H-imidazole
14	1.8	OMe	2,6-dimethyl	4-chloro	1-methyl-1H-imidazole
15	3.21	OMe	2,6-dichloro	4-chloro	1-methyl-1H-imidazole
16	0.31	OMe	2,6-difluoro	4-chloro	1-methyl-1H-imidazole
17	1.4	OMe	3,5-dimethyl	4-chloro	1-methyl-1H-imidazole
18	2.2	OMe	3-chloro	naphthyl	1-methyl-1H-imidazole
19	17	OH	3-chloro	4-chloro	1-methyl-1H-imidazole
20	112	OH	3-chloro-2-methyl	4-chloro	1-methyl-1H-imidazole
21	27	OEt	3-chloro-2-methyl	4-chloro	1-methyl-1H-imidazole
22	69	OPr	3-chloro-2-methyl	4-chloro	1-methyl-1H-imidazole
23	5	NHMe	3-chloro-2-methyl	4-chloro	1-methyl-1H-imidazole
24	118	NH_2	3-chloro	4-chloro	1-ethyl-1H-imidazole
25	100	NHMe	3-chloro	4-chloro	1-ethyl-1H-imidazole
26	3	OMe	3-chloro	4-chloro	1-ethyl-1H-imidazole
27	228	OH	3-chloro	4-chloro	1-ethyl-1H-imidazole
28	3	OMe	3-chloro	4-methyl	1-methyl-1H-imidazole
29	5	OMe	3-chloro	4-trifluoromethyl	1-methyl-1H-imidazole
30	10	OMe	3-chloro	4-ethyl	1-methyl-1H-imidazole
31	33	OMe	3-chloro	4-cumene	1-methyl-1H-imidazole
32	320	OMe	3-phenyl	4-chloro	1-methyl-1H-imidazole
33	83	OMe	3-benzene	4-chloro	1-methyl-1H-imidazole

RESULTS AND DISCUSSIONS

The pharmacophoric model revealed that the activity has good correlation with molecular surface area of negatively charged acceptor atoms. The same has been depicted in figure 2

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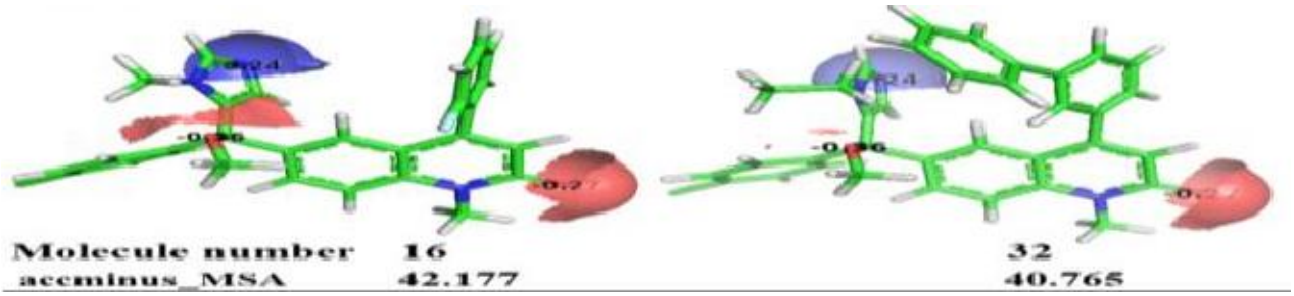

Figure 2. Representation of accminus_MSA, using molecule number 16 (most active) and 32 (least active) as the representatives only

CONCLUSIONS

In conclusion, the robust pharmacophoric model and SAR analysis indicates that activity has good relation with -OCH_3 group, lipophilic atoms within five bonds from Nitrogen atoms, presence of less negatively charged donor atom from oxygen atom of quinolinone ring and molecular surface area of negatively charged H-bond acceptor atoms.

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SYNTHESIS, SPECTRAL CHARACTERIZATION AND ANTIMICROBIAL ACTIVITIES OF AZO COMPOUNDS CONTAINING 4-HYDROXY PHENOL (HYDROQUINONE)

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ABSTRACT

In describe paper, a series of eight azo compounds were synthesized with excellent yield by the process of diazotization of different aromatic amines which is followed by the coupling with hydroquinone (4-hydroxy phenol).The structures of synthesized compounds were characterized by using FTIR, ^{1}HNMR and MASS spectral techniques. These compounds were screened in vitro against human pathogens Escherichia coli, Staphylococcus aureus, Pseudomonas aeruginosa, Salmonella typhi in order to assess their antimicrobial activities using disc diffusion method. The compounds which are screened for their antimicrobial activities exhibited excellent and remarkable inhibitory effect at most of the concentrations against all the tested pathogens.

Keywords: *Azo compounds, Antimicrobial activity, diazotization, Hydroquinone.*

INTRODUCTION

Azo dyes are the largest and the most popular group of dyes showing the full palette of colours. Azo dyes compounds are containing –N=N– group as a characteristic chromophore, and mainly obtained in diazotization and coupling reaction. As per literature survey, it was found that azo dyes have been most widely used in different application fields, such as dying textile fibres, biomedical studies and advanced in organic synthesis as well as shows variety of interesting biological activities including antibacterial and pesticide activities[1-5] and high technology areas like lasers, liquid crystalline displays, electro-optical devices and ink jet printer[6-8]. Synthesis of azo dyes involves diazotization of a primary aromatic amine followed by coupling with one or more nucleophiles. Amino, hydroxy and active methylene groups are commonly used coupling compounds [9]. The chemistry of derivatives of hydroquinone have great interest to medicinal chemistry because of its derivative possess various biological activity[10-15].The above observations prompted us to synthesize the title compounds with the presumption that introduction of Azo group in hydroquinone would produce new compounds with significant antibacterial activity.

MATERIAL AND METHOD

The chemicals used in the present studies are of synthetic grade, Merck company Ltd. The products were characterized by ^{1}H NMR & IR. The melting points were determined by open capillary method and uncorrected. The IR spectra were recorded on Perkin-Elmer spectrum FTIR instrument in the form of KBr pellet. The ^{1}H NMR spectra were measured in DMSO solutions on a Brucker 400 MHz NMR spectrometer using TMS as an internal reference (δ ppm). The purity of compounds was checked by TLC. The crude products were recrystallized from 70% ethanol.

General procedure for synthesis of azo compounds[16-25]

Eight substituted aromatic amines (0.01 M) were mixed with 2.5 mL conc. HCl & 2.5 mL (4 N) cold solution of $NaNO_2$ was added with the stirring. The temperature of the reaction was maintained up to 0-5 ^{0}C. Diazonium salt solution prepared above was added drop wise to the alkaline solution of hydroquinone. The reaction mixture stirred for 10-20 miniutes maintaining the temperature 5-10 ^{0}C. The coloured products obtained is filtered and washed with water dry the product and recrystallised from 70% ethanol.

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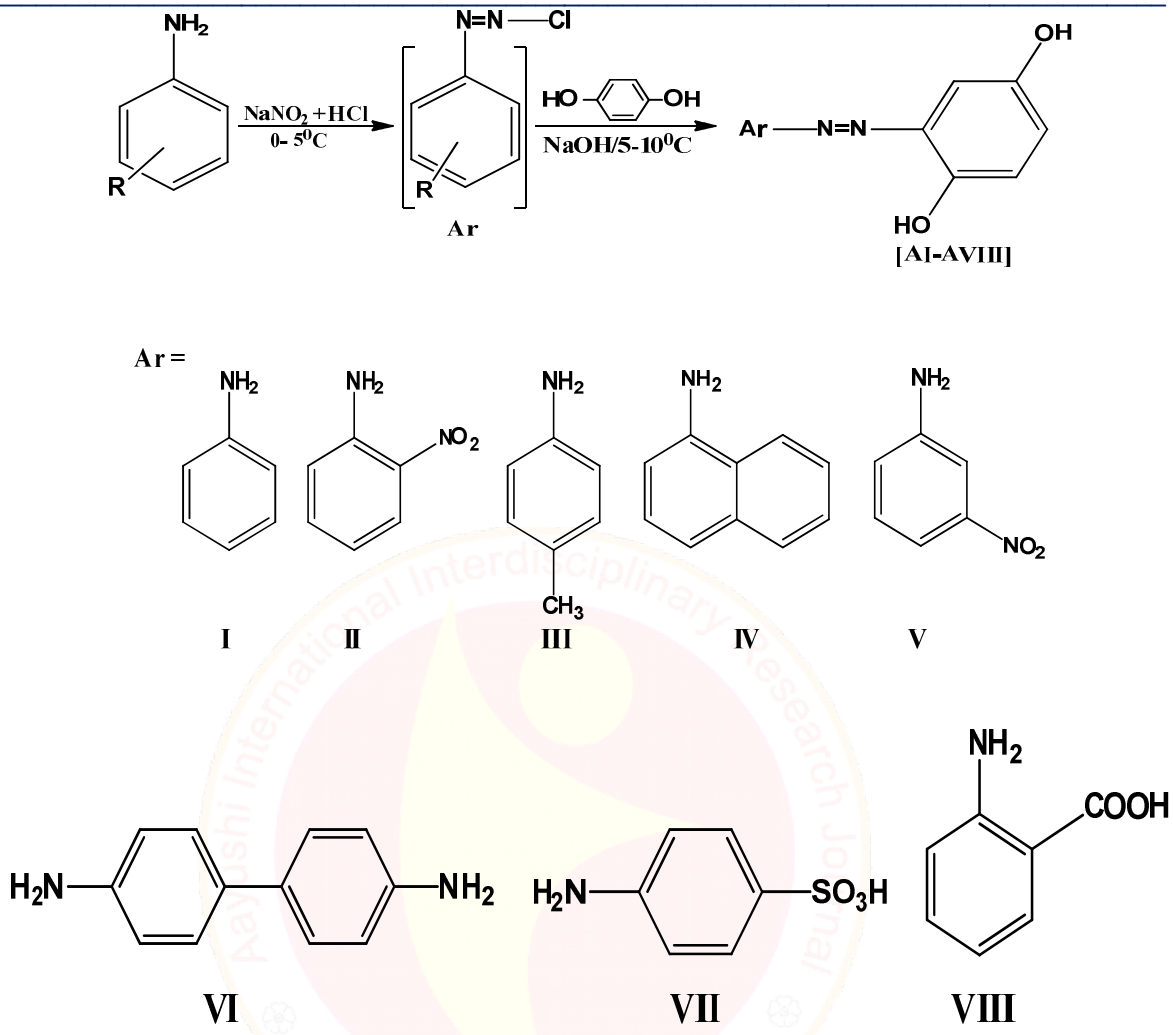


Figure-1. The general reaction scheme for synthesis of azo compounds of hydroquinone.

RESULT AND DISCUSSION

I.R. and ^{1}H NMR spectra show the expected signals which corresponds to various groups present in each compounds (Figure 1). The I.R. and ^{1}H NMR spectral data are shown in Table 2. The azo compounds AI – AVIII containing hydroquinone moiety were successfully synthesized with good yield (Table 1). A total of eight derivatives of hydroquinone have been synthesized, purified and further used individually to analyze its antimicrobial activity at different concentrations against four human pathogens *viz*: *E.coli, S.aureus, S. typhi* and *P.aeruginosa* species as shown in the figure 2 to figure 5. From the results it was observed that the azo compounds of hydroquinone have showed miraculous antibacterial potential against all four pathogens.

The data obtained after screening the synthesized azo compounds AI – AVIII containing hydroquinone moiety against four human pathogens is plotted and discussed in graph 1 to graph 3 at different concentrations

.

Table-1

The symbols, compounds name, molecular formulae, molecular weights, melting points and percentage yield of synthesized azo compounds of hydroquinone.

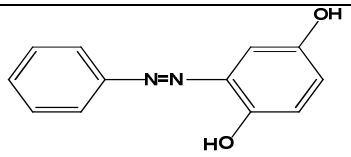
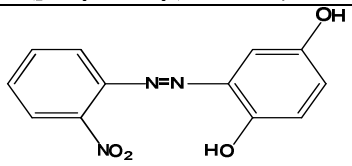
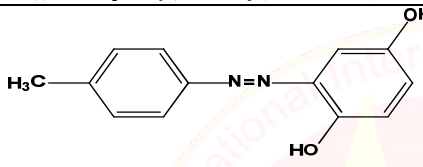
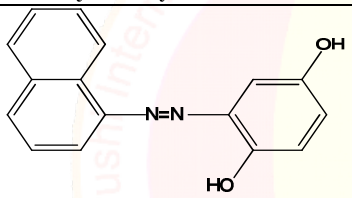
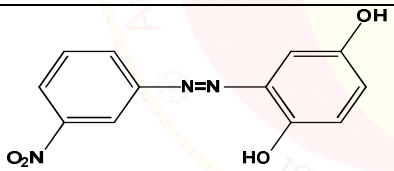
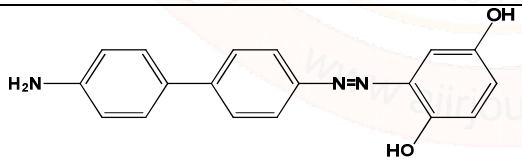
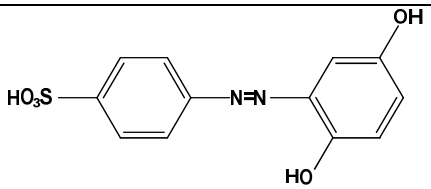
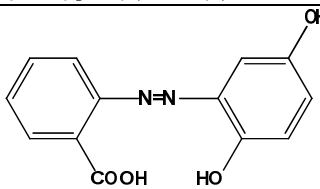
S.N.	Structure	Mol. formula	Mol.Wt.	Melting point.	Yield
AI	 2-(phenyldiazenyl)benzene-1,4-diol	$C_{12}H_{10}N_2O_2$	214	149^{0}C	52%
AII	 2-((2-nitrophenyl)diazenyl)benzene-1,4-diol	$C_{12}H_9N_3O_4$	259	138^{0}C	54%
AIII	 2-(p-tolyldiazenyl)benzene-1,4-diol	$C_{13}H_{12}N_2O_2$	228	148^{0}C	64%
AIV	 2-(naphthalen-1-yldiazenyl)benzene-1,4-diol	$C_{16}H_{12}N_2O_2$	264	136^{0}C	58%
AV	 2-((3-nitrophenyl)diazenyl)benzene-1,4-diol	$C_{12}H_9N_3O_4$	259	139^{0}C	55%
AVI	 2-((4'-amino-[1,1'-biphenyl]-4-yl)diazenyl)benzene-1,4-diol	$C_{18}H_{15}N_3O_2$	305	147^{0}C	61%
AVII	 4-((2,5-dihydroxyphenyl)diazenyl)benzenesulfonic acid	$C_{12}H_{10}N_2O_5S$	294	218^{0}C	51%
AVIII	 2-((2,5-dihydroxyphenyl)diazenyl)benzoic acid	$C_{13}H_{10}N_2O_4$	258	176^{0}C	59%

Table 2:-IR, ^{1}HNMR and Mass Spectral Data

Compunds	Spectra	IR, ^{1}HNMR and Mass Spectral Data/peak
AI	IR (KBr, cm^{-1}) ^{1}HNMR(□ppm) MASS (m/z,%)	3604.71 (Phenolic -OH stretch), 2973.07 (C-H stretch), 1478.34 – 1651.92 (C=C stretch), 1246.89 (C-O stretch), 827.14 (p-position). 5.3 s (2H), 7.1 d (2H), 7.2 s (1H), 7.3 d (2H), 7.4 t (2H), 7.9 t (1H). 214.0460 (M+, $C_{12}H_9N_3O_3$, 70), 215.0103 (M+, $C_{12}H_9N_3O_3$, 9.2)
AII	IR (KBr, cm^{-1}) ^{1}HNMR(□ppm)	3586.51 (Phenolic -OH stretch), 2973.07 (C-H stretch), 1467.1 – 1604.66 (C=C stretch), 1341.2 & 1548.56 (-NO_2 stretch), 1220.58 (C-O) stretch) 822.58 (p-position) 5.4 s (2H), 7.2 s (1H), 7.4 d (2H), 7.8 d (1H), 7.9 t (1H), 8.0 t (1H), 8.1 s (1H).
AIII	IR (KBr, cm^{-1}) ^{1}HNMR(□ppm)	3611.46 (Phenolic -OH stretch), 3025.14 (C-H stretch), 1470.12 – 1603.7 (C=C stretch), 1229.54 (C-O stretch), 1363.58 & 1511.03 (-NO_2 stretch), 2920.08 (-CH_3 stretch). 2.4 t (3H), 5.3 s (2H), 7.1 s (1H), 7.4 d (2H), 7.6 d (2H), 7.9 d (2H).
AIV	IR (KBr, cm^{-1}) ^{1}HNMR(□ppm)	3566.14 (Phenolic -OH stretch), 2946.78 (C-H stretch), 1449.13 – 1652.8 (C=C stretch), 1199.64 (C-O stretch), 774.3 (p-position). 5.3 s (2H), 7.3 d (2H), 7.6 s (1H), 8.0 d (1H), 8.2 d (3H), 7.9 t (3H).
AV	IR (KBr, cm^{-1}) ^{1}HNMR(□ppm)	3544.92 (Phenolic -OH stretch), 2946.78 (C-H stretch), 1471.3 – 1657.92 (C=C stretch), 1349.11 & 1524.62 (-NO_2) stretch), 1196.75 (C-O stretch) 5.3 s (2H), 6.9 s (1H), 7.2 d (2H), 7.8 t (1H), 7.9 d (1H), 7.9 s (1H), 8.2 d (1H).
AVI	IR (KBr, cm^{-1}) ^{1}HNMR(□ppm)	3388.14 (Phenolic -OH stretch), 3429.82 (N-H stretch), 3012.30 (C-H stretch), 1457.12 – 1652.88 (C=C stretch), 1383.83 (C-N stretch), 1215.07 (C-O stretch). 6.2 s (2H), 5.3 s (2H), 6.8 s (1H), 7.1 d (2H), 7.2 d (2H), 7.3 d (2H), 8.0 d (2H), 8.4 d (1H).
AVII	IR (KBr, cm^{-1}) ^{1}HNMR(□ppm)	3352.28 cm-1(Phenolic -OH stretch), 2976.16 (C-H stretch), 1473.6 - 1650 (C=C stretch), 1255 (C-N) stretch), 1265.30 (S=O) stretch), 840.96 (S-O stretch). 5.3 s (2H), 2.0 s (1H), 6.9 s (1H), 7.3 d (2H), 7.3 d (2H), 7.6 d (2H), 8.0 d (2H).
AVIII	IR (KBr, cm^{-1}) ^{1}HNMR(□ppm)	3354.39 (Phenolic -OH stretch), 3095.70 (C-H stretch), 1695.43 (C=O stretch), 1469.8 – 1647.21 (C=C stretch), 1255.66 (C-O stretch). 5.3 s (2H), 7.0 s (1H), 7.4 d (2H), 7.9 d (1H), 8.0 t (1H), 8.2 t (1H), 8.3 d (1H), 10.4 s (1H)

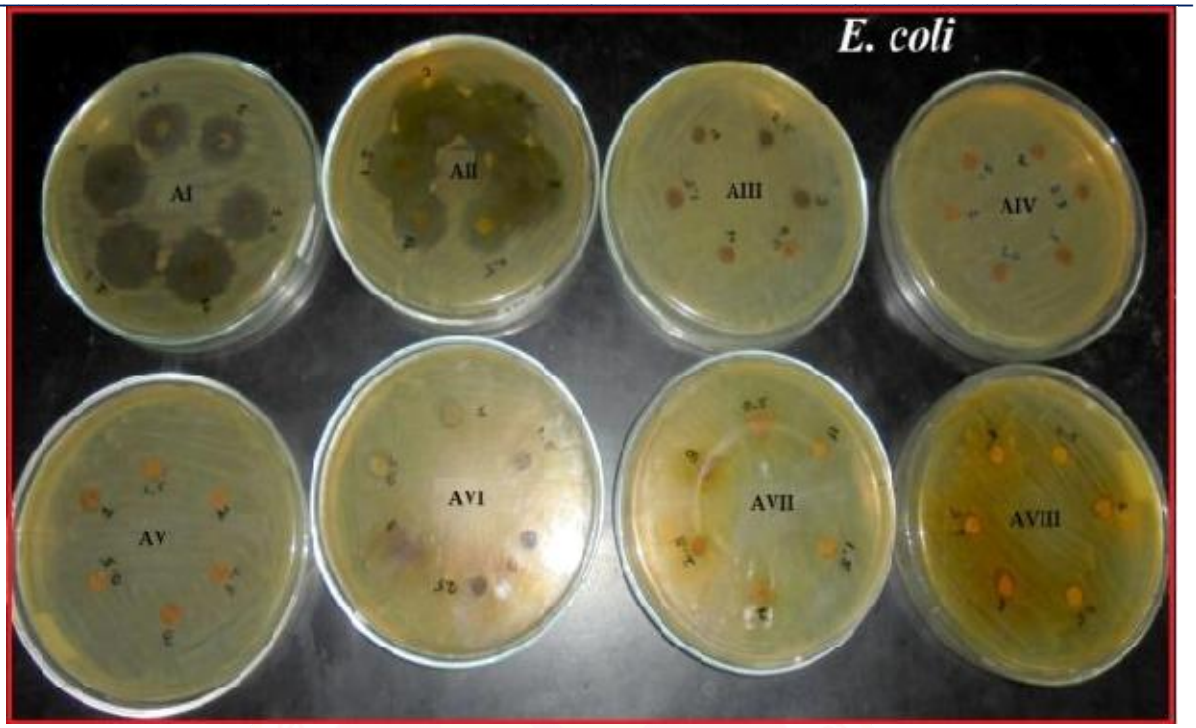


Fig.2. Effect of azo compounds of hydroquinone viz. AI – AVIII on the growth response of *Escherichia coli.*

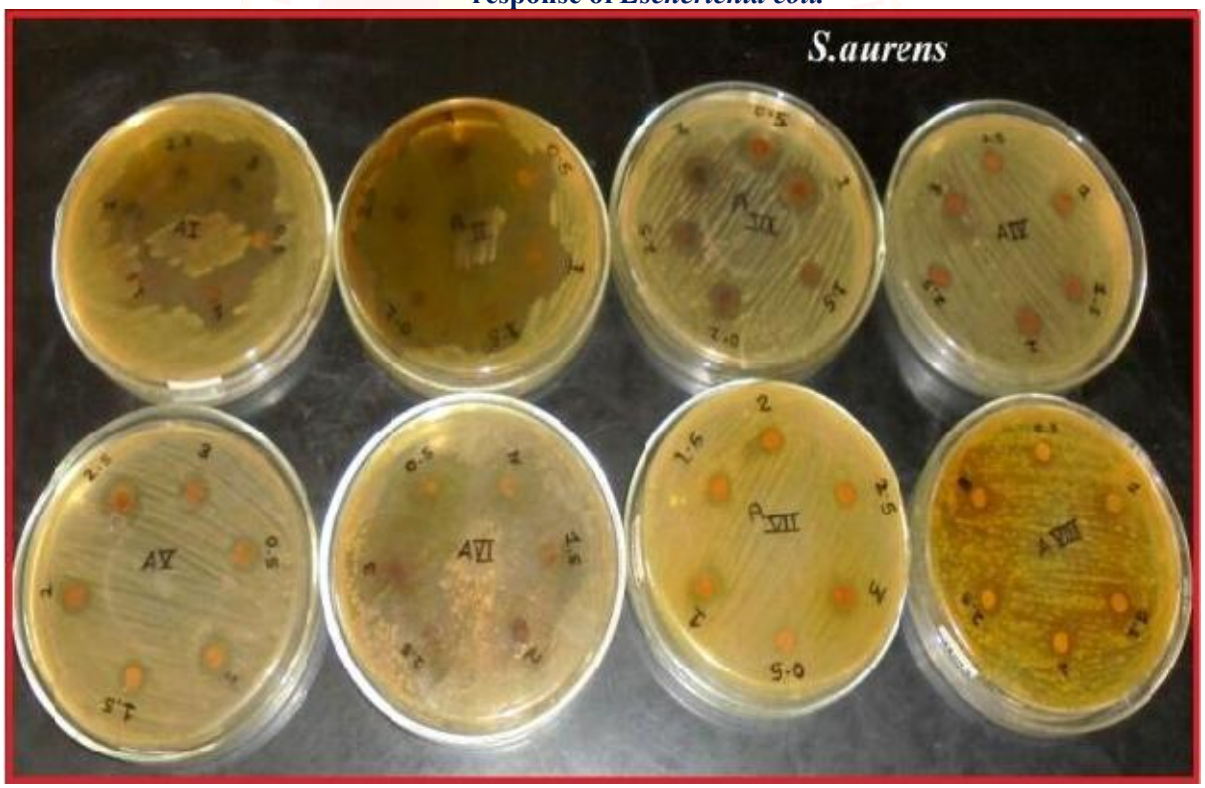


Fig.3. Effect of azo compounds of hydroquinone viz. AI – AVIII on the growth response of *Staphylococcus aureus.*

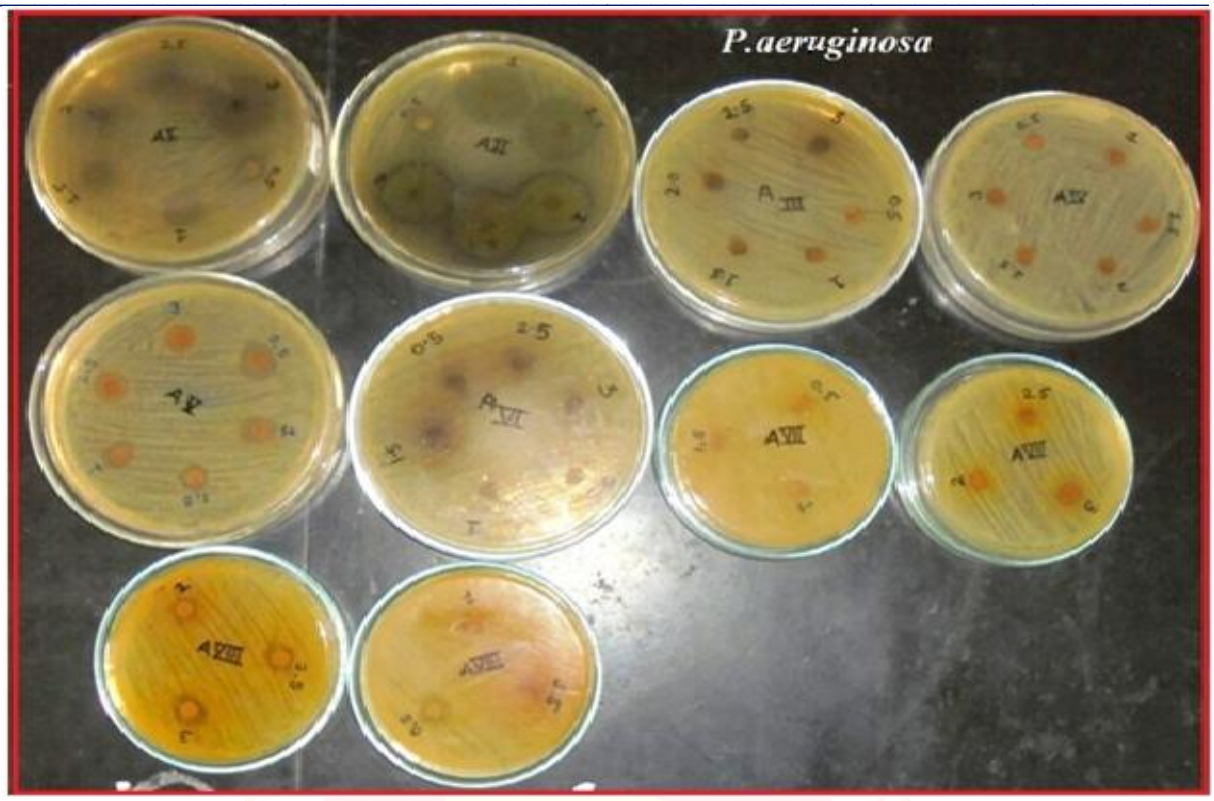


Fig.4. Effect of azo compounds of hydroquinone viz. AI – AVIII on the growth response of *Pseudomonas aeruginosa.*

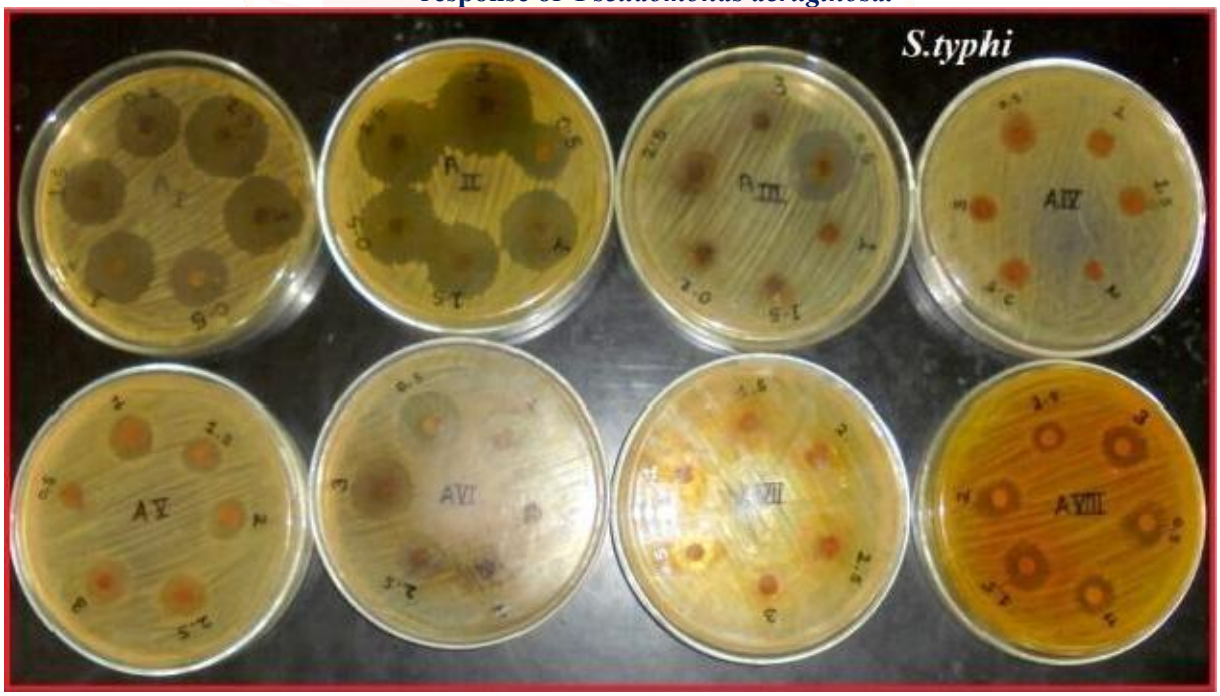
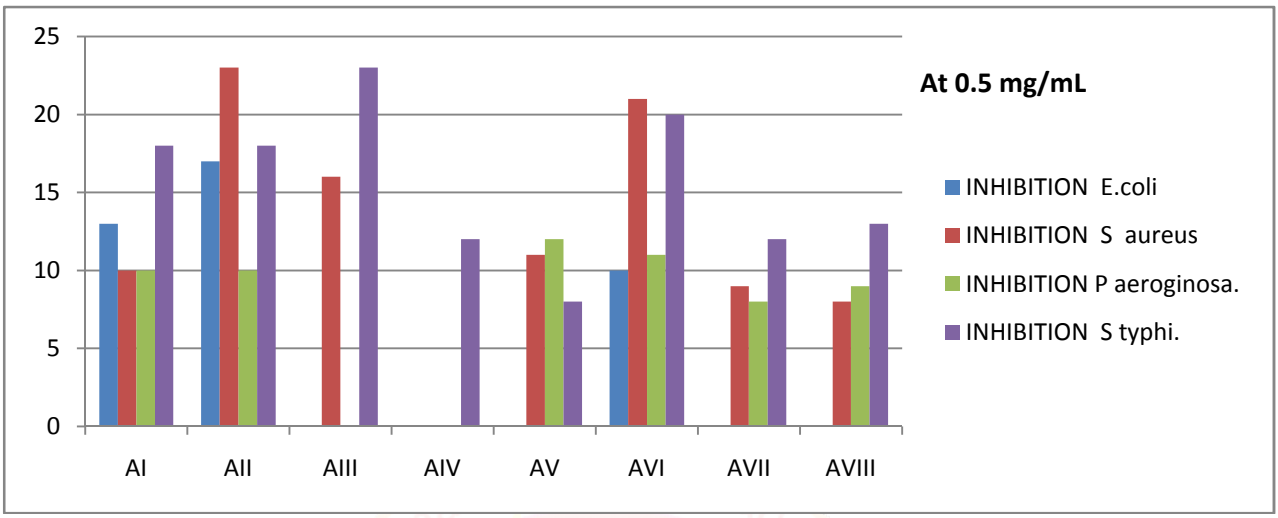


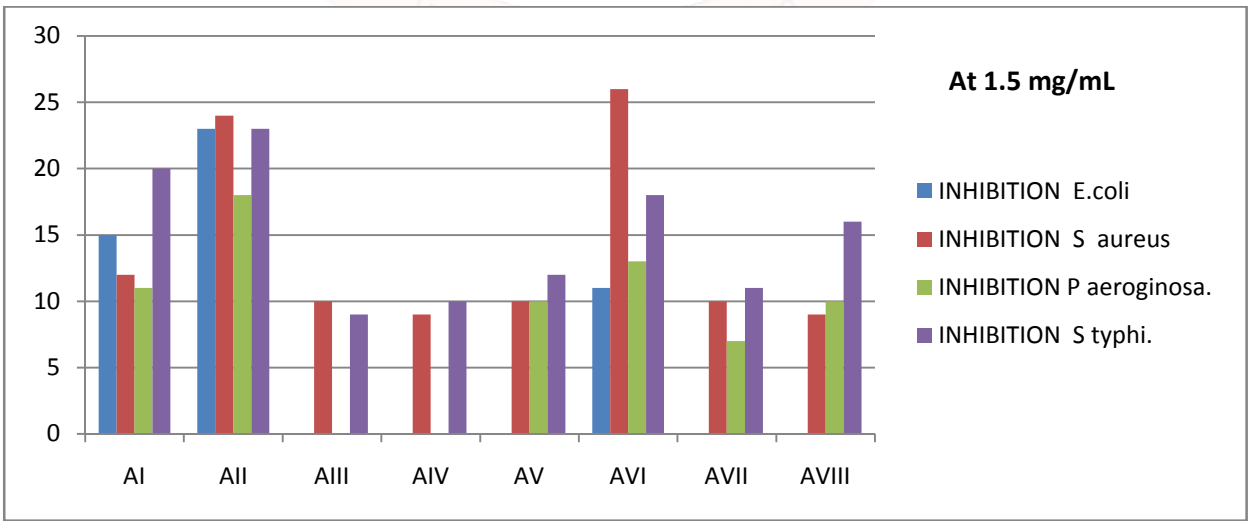
Fig.5. Effect of azo compounds of hydroquinone viz.AI – AVIII on the growth response of *Salmonella typhi.*

Graph No.1. Effect of azo compounds of hydroquinone viz. AI –AVIII on the growth response of *Escherichia coli, Staphylococcus aureus, Pseudomonas aeruginosa* and *Salmonella typhi* at 0.5 mg/mL concentration.



From the above Graph number-1, it is clear that, all the compounds of the series from AI to AVIII shows excellent antimicrobial activity against all four pathogens at concentration 0.5 mg/mL. Diameter of zone of inhibition of compound AII is maximum and it is measure to be 23 mm against *S.aureus*. Similarly, compound AIII also shows maximum zone of inhibition and it is measure to be 23 mm against *S.typhi*. The zone of inhibition of compound AVI is measure to be 21 mm and 20 mm against *S.aureus* and *S.typhi* respectively. Compounds AI, AII and AVI show antimicrobial activity against all four pathogens and it is ranging between 10 mm to 23 mm. The compound AIV shows activity against *S.typhi* only, while the activity against other three pathogens is nil. Compound AV, AVII and AVIII show antimicrobial activity against *S.aureus*, *P.aeruginosa*, *S.typhi* and not against *E.coli*. In this series
compound AII and compounds AIII are the most promising antimicrobial azo compounds against *S.aureus* and *S.typhi*.

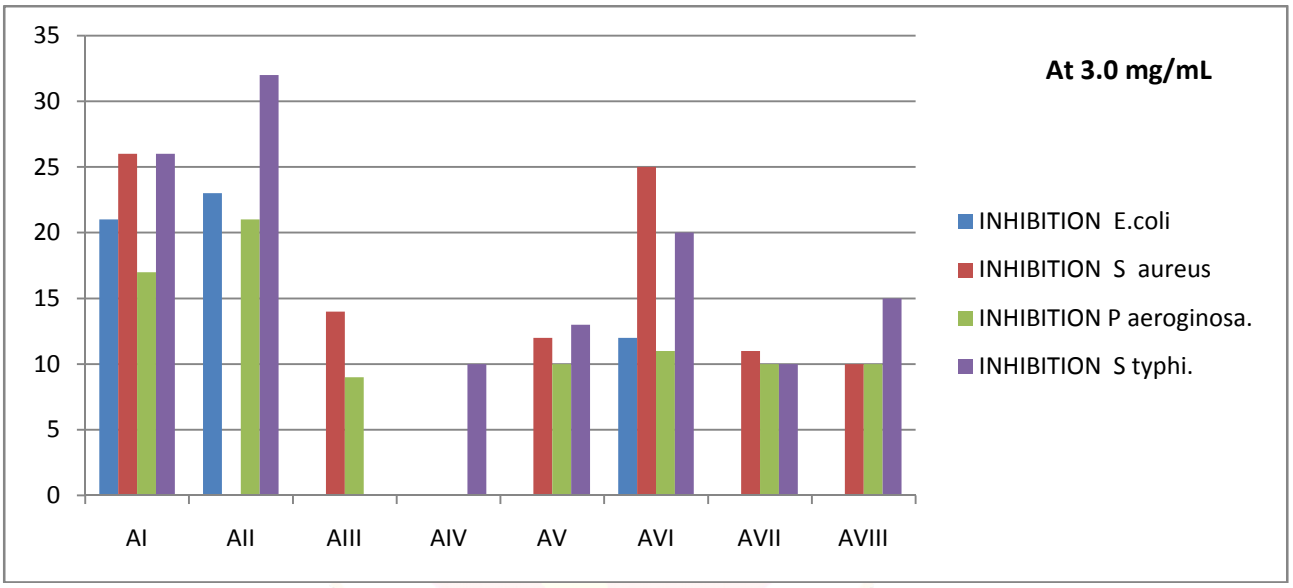
Graph No.2. Effect of azo compounds of hydroquinone viz. AI –AVIII on the growth response of *Escherichia coli, Staphylococcus aureus, Pseudomonas aeruginosa* and *Salmonella typhi* at 1.5 mg/mL concentration.



Graph number-2 shows, all the compounds of the series from AI to AVIII remarkable antimicrobial activity against all four pathogens at concentration 1.5 mg/mL. Maximum diameter of zone of

inhibition is recorded for the compound AVI against *S.aureus* and it is measure to be 26 mm. Similarly, other compounds like AI shows maximum antimicrobial activity (20 mm) against *S.typhi* and azo compound AII exhibit considerable antimicrobial activities against *E.coli*, *S.aureus* and *S.typhi* which is measure to be 23 mm, 24 mm, 23 mm respectively. The azo compounds AIII and AIV shows antimicrobial activity against *S.aureus* and *S.typhi* only and the activity against other two pathogens such as *E.coli* and *P.aeruginosa* is found to be zero. The azo compounds AV, AVII and AVIII grows zone of inhibition against *S.aureus, P.aeruginosa* and *S.typhi* only but not against *E.coli*. Compound AVI is the more efficient antimicrobial azo compound against all four pathogens. So, it is clear that the compound AVI is pharmaceutically most important compound for the research in future

Graph No.3. Effect of azo compounds of hydroquinone viz. AI –AVIII on the growth response of *Escherichia coli, Staphylococcus aureus, Pseudomonas aeruginosa* and *Salmonella typhi* at 3.0 mg/mL concentration.



Graph number-3 indicates that, all the compounds of the series from AI to AVIII exhibit considerable antimicrobial activity against all four pathogens at concentration 3.0 mg/mL. Maximum diameter of zone of inhibition is measured for the compound AII against *S. typhi* and it is 32 mm. Next to this compound other compounds like AI also shows similar growth of inhibition against *S.aureus* and *S.typhi* which is measure to be 26 mm and azo compound AVI exhibit antimicrobial activity against all pathogens but the maximum zone of inhibition is recorded (25 mm) against *S.aureus*. Compound AIII develops a zone of inhibition against *S.aureus* and *P.aeruginosa* only. Azo compound AIV is nil in showing antimicrobial property against *E. coli*, *S.aureus* and *P.aeruginosa* and exhibit antimicrobial activity against *S.typhi* only. The azo compounds AV, AVII and AVIII exhibit antimicrobial activity against *S.aureus* , *P.aeruginosa* and *S.typhi* but unable to develops a zone of inhibition against *E. coli*. At concentration 3.0 mg/mL it is highlighted that, azo compound AII is most powerful antimicrobial compound against *S.typhi*.

CONCLUSION

From the result it was clear that, all eight synthesized azo compounds AI – AVIII containing hydroquinone moiety are found to be more antibacterial in nature against *S.aureus, P.aeruginosa* and *S.typhi* at all different concentrations. But it was also found that, the azo compounds of these series such as AIII, AIV, AV and AVII do not show inhibitory action against *E.coli*.

As most of the azo compounds of these series were found to be more potent and showed superior antibacterial activity against entire test organisms as compare to other compounds which are under study. Hence, these compounds may be further exploited for drug discovery research in pharmaceutical industries.

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SYNTHESIS OF METAL COMPLEX OF AMMONIUM P-TOTYL DITHIOCARBAMATE AND ITS BIOLOGICAL ACTIVITY

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ABSTRACT

The synthesis of sulphur and nitrogen containing dithiocarbamato ligand derived from diisobutylamine as well as its coordination compounds with 3d series transition metals is presented. These synthesized compounds were characterized on the basis of elemental analysis, conductometric measurements and IR spectral studies. The analytical data showed the stoichiometry 1:2 and 1:3 for the compounds of the types ML2 {M=Mn(II), Co(II), Ni(II), Cu(II) and Zn(II)} and M'L3{M'=Cr(III) and Fe(III)} respectively. The conductometric measurements proved the non-electrolytic behaviour of all the compounds. The bidentate nature of dithiocarbamato moiety was confirmed on the basis of IR spectral data.

Keywords: *Coordination complexes, Dithiocarbamates, Transition metals*

INTRODUCTION

Organic dithiocarbamates have attracted a great deal of importance due to their interesting chemistry and wide utility.[1-7] Dithiocarbamates have a wide range of uses and applications and are produced in great quantities throughout the world. Dithiocarbamate acid ester **(1)** is a common class of organic molecules. They exhibit valuable biological effects, including antibacterial activity, antifungal activity, antioxidant activity,[8] inhibition of cardiac hypertrophy,[9] etc. Dithiocarbamic acid ester represents a new kind of compound with a novel structure, significant anticancer activity and very low toxicity. A Dithiocarbamate is a functional group in organic chemistry. It is the analogue of carbamate in which both oxygen atoms are replaced by sulfur atoms (figure 1).
atoms (figure 1).

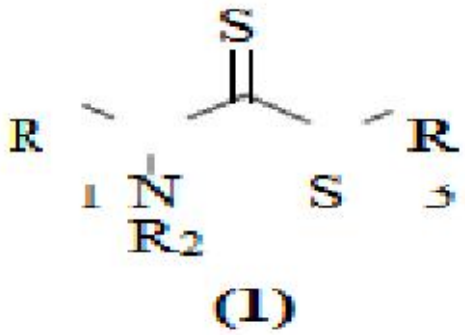


Figure 1: General formula of the dithiocarbamate
The dithiocarbamate containing two donor sulfur atoms, which it is prepared from the reaction of primary amine or secondary amine with base and carbon disulfide.
Sodium diethyl dithiocarbamate is a common ligand in inorganic chemistry. Lots of primary and secondary amines react with carbon sulfide and sodium hydroxide to form dithiocarbamates; they
Are used as ligand when metal salts are added to it. It readily reacts with many metal salts such as Cu, ferrous, ferric, cobaltous, Ni salts.
They are mostly octahedral complexes.Despite major breakthroughs in many areas of modern medicine over the past 100 years, the successful treatment of cancer remains a significant challenge at the start of the 21st century. Because it is difficult to discover novel agents that selectively kill tumor cells or inhibit their proliferation without the general toxicity, the use of traditional cancer chemotherapy is still very limited. Besides being widely used as fungicides to protect crops from fungal diseases,[10] dithiocarbamic acid esters have a number of other applications such as in photochemistry,[11] catalysis in the sulfur vulcanization of rubber,[12] detection and analysis of biological NO produced endogenously from NO synthases,[13] and polymerization.[14]
Furthermore, functionalized carbamates are an important class of compounds and their medicinal and biological properties warrant study.[15] Dithiocarbamic acid esters were recently reported as potent anticancer agents[16] and cell apoptosis inhibitors.[17]
Organic dithiocarbamates are valuable synthetic intermediates,[18] which are ubiquitously found in a variety of biologically active compounds. Functionalization of the carbamate moiety offers an attractive method for the generation of derivatives, which may constitute interesting medicinal and boilogical properties.[19]

Dithiocarbamates (DTCs) are a group of organosulfur compounds that have extensively been used as pesticides in agriculture for more than 50 years with some products being already introduced in the 1930s. Today, the yearly consumption is between 25,000 and 35,000 metric tones.[20] Most of the DTCs are applied as fungicides and some are classified by the World Health Organization as being hazardous.[21] As a consequence, an array of various methods has been developed for the analysis of DTCs and their potential degradation products in environmental samples and in food stuff.

The carbamate moiety is an important structural element in numerous biologically active compounds[22] and has played a crucial role in the area of synthetic organic chemistry primarily as a novel protecting group.[23] Therefore; functionalization of organic carbamates offers great potential in the generation of large combinatorial libraries for rapid screening[24] and drug design.[25]

Dithiocarbamates have received considerable attention due to their numerous biological activities[26] and their pivotal role in agriculture[27] and as linkers in solid phase organic synthesis.[28] They are also used in the rubber industry as vulcanization accelerators[29] and in controlled radical polymerization techniques.[30] Because they have a strong metal binding capacity, they can also act as inhibitors of enzymes and have a profound effect on biological systems.

Dithiocarbamates are also widely used in medicinal chemistry and have found application in the treatment of cancer[31] and have been tested in clinical trials for various indications including HIV.[32-35] Furthermore; dithiocarbamates are versatile classes of ligands with the ability to stabilize transition metals in a wide range of oxidation states,[36] the ability to chelate heavy metals,[37-38] to function as NO scavengers,[39] radical chain transfer agents in the reversible addition fragmentation chain transfer polymerizations,[40] for the protection of amino groups in peptide synthesis,[41] as radical precursors [42] and recently in the synthesis of ionic liquids.[43] They have also been widely used in the synthesis of trifluoromethylamines,[44] thioureas,[45] aminobenzimidazoles,[46] isothiocyanates,[47] alkoxyamines,[48] 2-imino-1,3-dithiolane,[49] and total synthesis of (-)-aphanorphine.[50]

On the other hand, dithiocarbamates are of growing interest due to their biological potencies,[51] such as antihistaminic,[52] antibacterial,[53] and anticancer activties.[54] Owing to their strong metal-binding capacity, they can also act as enzyme inhibitors, such as indoleamine 2,3-dioxygenase, which plays an important role in tumor growth.[55] For these reasons, the synthesis of dithiocarbamate derivatives with different substitution patterns at the thiol chain by a convenient and safe method has become a field of increasing interest in synthetic organic chemistry during the past few years. Traditional methods for the synthesis of dithiocarbamates involve the use of costly and toxic reagents, such as thiophosgene, chlorothioformates, and isothiocyanates.

A number of methodologies have been developed; the standard preparation of carbamates/dithiocarbamates generally involves the use of toxic and highly reactive phosgene/thiophosgene[56] and its derivatives[57], thereby posing environmental and safety problems. As a result, considerable effort has been made to develop a phosgene/thiophosgene free route[58] for the preparation of carbamates and thiocarbamates. However, many of these methods suffer from limitations, such as long reaction times, use of expensive and strongly basic reagents, use of volatile solvents, tedious work-up, and low yields.[59]

Therefore, the synthesis of this type of molecule has received considerable attention. Furthermore, a one pot reaction of amine with carbonyl sulfide and alkyl halides in organic solvents in the presence of a catalyst also has been developed.[60] However, there are several disadvantages to these methods: many isothiocyanates are hazardous and tedious to prepare and display poor long-term stability with the formation of side products such as urethane in alcoholic media. Such intermediates also require high reaction temperatures, give low or moderate yields of products, and usually entail multistep procedures.

Furthermore, these reactions require very toxic reagents and harmful organic solvents in the presence of a catalyst.

Structure modification of folic acid led to the discovery of a number of antifolates as efficient anticancer agents. For example,

Methotrexate **(2)** (figure 2), an inhibitor of dihydrofolate reductase, has been used clinically for the treatment of leukemia and solid tumors in children and adults for several decades.[61] Raltitrexed **(3)**[62-63] (figure 2), which is an inhibitor of thymidylate synthase has been registered widely for the first-line treatment of advanced colorectal

cancer. However, these so-called classical antifolates containing L-glutamic acid moiety in the molecule have shortcomings such as drug resistance, which have originated from the defective cell transport by mutation, and toxicity to the host, which is due to unnecessarily long retention inside normal cells.[64] One strategy to overcome these shortcomings is to design nonclassical lipophilic inhibitors of folate requiring enzymes by deleting or modifying L-glutamic acid component from the folate analogues.[65-66]

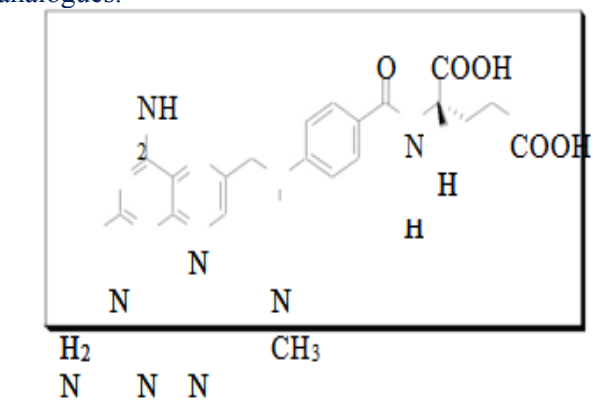


Figure 2: Structures of Methotrexate **(2)** and Raltitrexed **(3)**

Recently, Brassinin **(4)**[67] (figure 3), a dithiocarbamate isolated from cabbage, was reported to have cancer chemopreventive activity, and its structural modification led to the design and synthesis of a potential cancer chemopreventive agent (4-methanesulfinyl-butyl)-dithiocarbamic acid methyl ester **(5)**[68] (figure 2). A steadily increasing number of studies have been published on dithiocarbamates and their anticancer activity. 4-Methanesulfinylbutyl dithiocarbamic acid methyl ester has proved to be a potential cancer chemopreventive compound as a phase II enzyme inducer.[68] More recently, a series of dithiocarbamate compounds have been synthesized and found to possess in vitro and in vivo antitumor activity.[69-70]

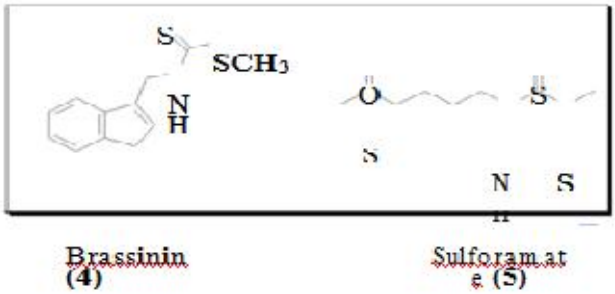


Figure 3: Structures of Brasinin **(4)** and Sulforamate **(5)**

Furthermore, diarylalkyl thioureas have merged as one of the promising nonvanilloid TRPV1 antagonists, possessing excellent therapeutic potentials in pain regulation[71] and human CB1 and CB2 cannabinoid receptor affinity.[72] For these reasons, the synthesis of dithiocarbamate derivatives with different substitution patterns at the thiol chain has become a field of increasing interest in synthetic organic chemistry during the past few years.

Thiocarbamates[73] have received much attention due to their interesting technological,[74] biological,[75] and synthetic applications.[76] Typically, the thiocarbonyl moiety has been utilized ubiquitously as a protecting group,[77] and as an intermediate in further synthesis.[78]

Their formation employs harsh reaction conditions such as the use of strong bases, high temperatures, and long reaction times.[79] In addition, modifications have been reported to use chlorothioformates, which are costly and toxic reagents. Recently, reported a highly efficient cesium base promoted solution phase synthesis of alkyl carbonates and carbamates,[80] which utilizes non-toxic reagents under mild conditions. This protocol has been successfully applied to peptidomimetic synthesis as well as solid phase synthesis.[81] As a complementary approach, this procedure has been extended to the formation of thiocarbonates and thiocarbamates using carbon disulfide.

Direct thiocarboxylation of amines with carbon monoxide and sulfur to form urea derivatives has also been reported.[82] Recently, a one-pot reaction of amines with carbonyl sulfide, alkyl halides, or

α, β-unsaturated compounds also has been developed.[83]

Recently, it was found by Hirschelman□s group that and 5-oxohexyl dithiocarbamic acid methyl ester **(6)** (figure 4) are potent phase II enzyme inducers which could be used as cancer

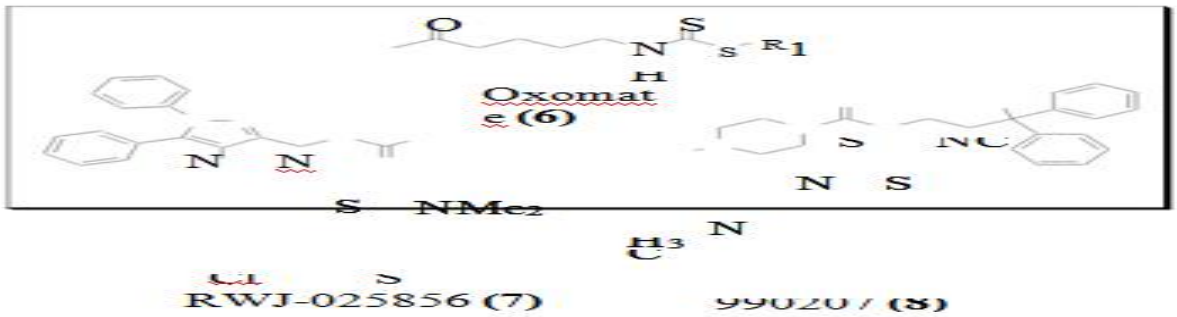


Figure 4. Structures of oxomate **(6),** RWJ-025856 **(7)** and 990207 **(8)**

chemopreventive agents.[84-86] Another group from Italy also found that the metal complex of dithiocarbamic acid esters exhibited anticancer activity. For example, the platinum complexes have similar activity but less toxicity than the cisplatin.[87-89] However, little systematic research has been reported about anticancer activity of this class of compounds, although compound RWJ-025856 **(7)** (figure 4) was unexpectedly found to have attenuating effects on tumor necrosis factor a (TNFa)-induced apoptosis in murine fibrosarcoma WEHI 164 cells.[90] One of the best compounds is 4-methyl-piperazine-1-carbodithioic acid 3-cyano-3,3-diphenyl-propyl ester **(8)** (figure 4) with 79% and 75% inhibition rates against HL-60 and Bel-7402 cell lines at 33 lM in vitro, respectively. A further in vivo test of its hydrochloride salt (4.HCl), which has better solubility, indicated that the inhibition rates against tumor growth of sarcoma 180 (S180), hepatocyte carcinoma 22 (H22), and implanted human gastric carcinoma in nude mice were 46.4–59.6% ($P < 0.01$), 39.3–51.6% ($P < 0.05$ _ 0.01), and 18.1–59.0% ($P < 0.01$) at different doses from 50 to 200 mg/kg, respectively. Taking it orally at a dose of 10 g/kg continuously for 10 days, the rats are neither dead nor damage of organs observed by visual examination. Furthermore, the body weight of tested group is similar to that of control group.[91] To the best of our knowledge, dithiocarbamic acid ester **(8)** represents a new kind of compound with a novel structure, significant anticancer activity, and very low toxicity. Compound **(8)** as a lead compound to further explore the structure–activity relationships with the aim of optimizing potency and anticancer activity.

A series of alkyl/arylsulfonyl-*N,N*-diethyldithiocarbamates display moderate to powerful tumour growth-inhibitory properties against several cancer cell lines in vitro.[92] 4(3*H*)-Quinazolinone derivatives with a dithiocarbamate side chain exhibit antitumour activity against human myelogenous leukaemia K562 cells. Pyrrolidine dithiocarbamate stimulates apoptosis by suppressing the activation of nuclear factor Jb (NF-jB) in various cancer cells (e.g., acute myelogenous leukaemia[95] and pancreatic adenocarcinoma[96]). A variety of 4-substituted-piperazine-1-carbodithioic acid 3-cyano-3,3-diphenylpropyl esters have been found to be effective against the HL-60 and Bel-7402 cell lines.[97] Different metal [Pt(II), Pd(II), Au(III), Cu(II)] complexes of dithiocarbamate derivatives (methyl- and ethylsarcosinedithiocarbamate, *N,N*-dimethyldithiocarbamate, *S*-methyl-*N,N*-dimethyldithiocarbamate and diethyldithiocarbamate) have been prepared and their cytotoxicities were studied.[98-100] The Pt(II) complexes of these sulfur-containing molecules can act as chemoprotectants in platinum-based chemotherapy, modulating cisplatin nephrotoxicity.[101] Besides the compounds mentioned above, probably the most interesting group of dithiocarbamates exhibiting antitumour activity are the phytoalexins from cruciferous plants. The phytoalexins are a group of structurally diverse, low molecular weight, generally lipophilic antimicrobial substances formed in plants. They are not present in healthy plant tissue, but are synthesized in response to pathogen attack or physical or chemical stress; probably as a result of the de novo synthesis of enzymes.[102] Some of the cruciferae species that have been examined

accumulate a series of specific indole-sulfur compounds. The basic structures are characterized by an indole ring variably substituted at positions 2 and/or 3 with nitrogen and sulfur containing substituents.[103] Typical representatives of dithiocarbamate and thiazino[6,5-b]indole-type phytoalexins from cruciferous plants are brassinin **(4)**,1-methoxybrassinin **(9)**, 4-methoxybrassinin **(10)**, cyclobrassinin **(11)** and sinalbin B **(12)** (figure 5). Among these compounds, brassinin **(4)** and cyclobrassinin **(11)** proved active in inhibiting the formation of preneoplastic mammary lesions in culture.[104] The former also exerts an antiproliferative effect in human acute T-lymphoblastic leukaemia cells.[105] Brassinin and its derivatives are inhibitors of indolamine 2,3-dioxygenase, a new cancer immunosuppression target.[106] These compounds can serve as lead compounds for the generation of more efficient analogues.[107]

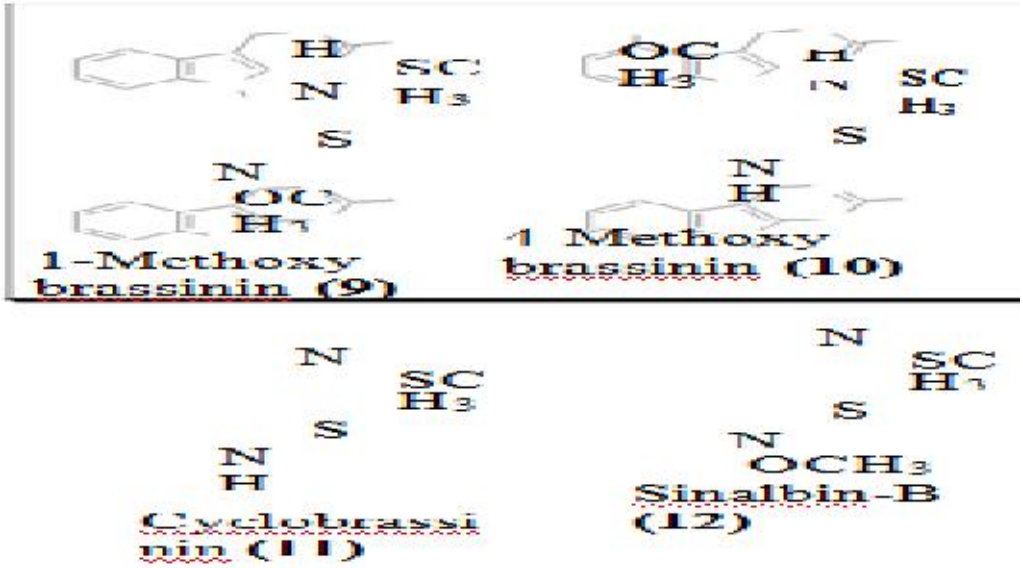
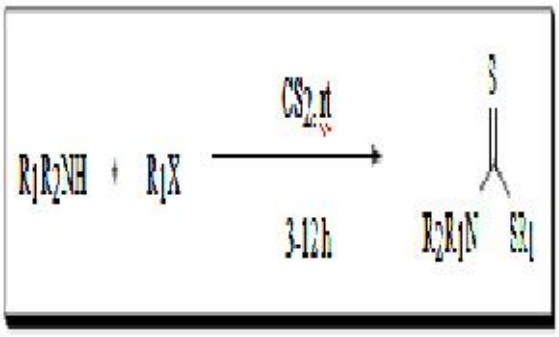


Figure 5: Dithiocarbamate and 1,3-thiazino[6,5-b]indole phytoalexins from cruciferous plants

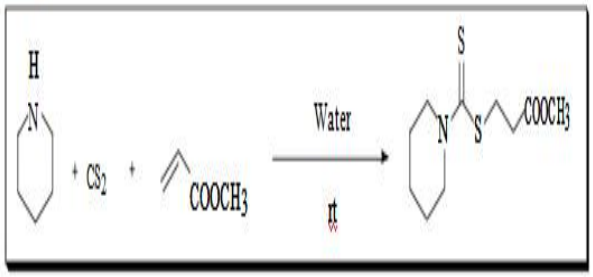
Literature Survey

A). Synthesis of dithiocarbamates

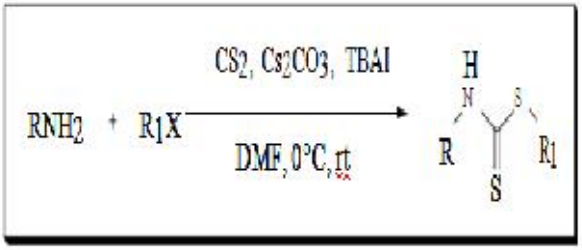
Saidi et al., have been reported one pot synthesis of dithiocarbamates based upon amines, CS2, and alkyl halides without using a catalyst under solvent-free conditions.



Mohammad Reza Saidi et al., have been synthesized dithiocarbamates using amines and carbon disulfide with α,β-unsaturated compounds were carried out in water.

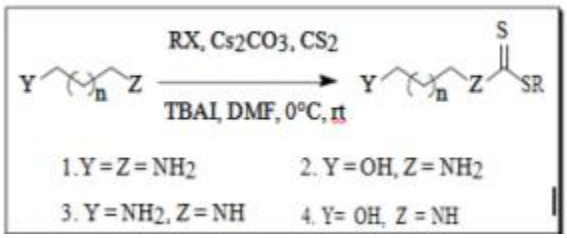


Kyung Woong Jung et al. have been developed a protocol for a one-pot, three-component coupling of various amines with an alkyl halide via a carbon disulfide bridge using Cs2CO3 and TBAI.

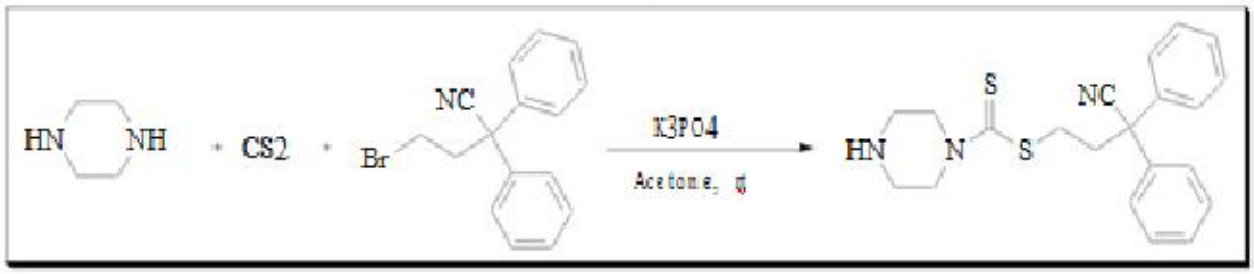


Kyung Woon Jung et al. were developed a three way coupling was performed to combine diols, diamines, and amino alcohols with carbon

disulfide and halides in the presence of a cesium base and TBAI, leading to the synthesis of dithio derivatives.

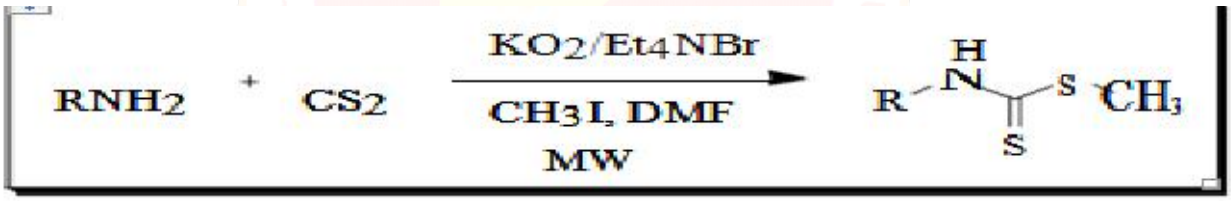


Runtao Li et al. have been synthesized a variety of 4-*N* atom substituted derivatives with a variety of 1-*N*-substituted piperazines, were reacted with carbon disulfide and 3-cyano-3,3-diphenyl-propyl bromide in the presence of anhydrous potassium phosphate at room temperature.

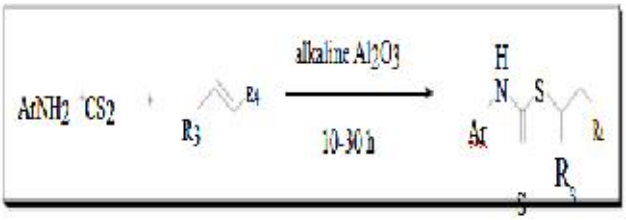


Krishna Nand Singh et al. have been exploited the combined role of microwave superoxide and the synthesis of organic dithiocarbamates under .

non-aqueous medium employing amines, carbon disulfide and methyl iodide



Weiliang Bao et al. have been reported a method for the synthesis of aryl and vinyl dithiocarbamates under Ullmann coupling reaction of sodium dithiocarbamates with aryl iodides and vinyl bromides catalyzed by CuI/*N*,*N*-dimethylglycine proceeds in DMF at110 ºC to give corresponding dithiocarbamates.



Run-tao Li et al., have been developed a method for the preparation of dithiocarbamic acid esters by Michael addition of electron-deficient alkenes with amines and CS2 in solid media alkaline Al2O3.

Aim of work or origin of problem

The synthesis of dithio-carbamate based upon amines, cs_2 and alkyl halides without using a catalyst under solvent free condition[16] dithiocabamate have been synthesis by amine and CS_2 with α- β unsaturated compound were carried out in water[17]. Three component coupling of various amine with on alkyl halide via. CS_2 Bridge using CS_2CO_3 and TBAI [18]. Kyung Woon Jung et.al ,[19] were developed a three way coupling was performed to combine diols diamines and amino alcohol with carbon disulfides and halide in the

presence of cesium base and TBAI leading to the synthesis of dithio derivatives.

Runtoo Li et al[20], have been synthesized a variety of 4-N at on substituted derivative with a variety of 1-N subtracted.

Piperazines were reacted with CS_2 & 3-cyano 3,3-diphenyl propyl bromide in the presence of an hydrous potassium phosphate at room Temperature. Krishna Nand singh et al[21] have been exploited the combined role of microwave super oxide and synthesis of organic dithiocarbamate under non-aqueous medium exploying amines carbon disulfide & methyl iodide.

Above literature surrey reveals that the aryl dithiocarbamate have not been synthesis by involving the use of para-toulidine , CS_2 and ammonium hydroxide.

Hence it was thought to prepared ammonium aryl(p-totyl) dithiocarbmate from p-toulidine , CS_2 and ammonium hydroxide, O^0 C temperature and formation of it complexes with metal ion, Mn^{2+}, Fe^{2+}

Synthesis of ammonium totyl dithiocarbamate :-

The required chemical used in synthesis of ammonium p-totyl dithiocarbamate and its complexes were prepared as follows.

4)

Preparation of ammonium p-totyl dithiocarbamate and its complexes with Mn and Fe.

- **Preparation of ammonium p-totyl dithiocarbamate :-**

These have been prepared by shaking NH_3, CS_2 and p-toulidine in ice – cold water for ½ hour.

Experiment No1:

Formation of ammonium p-totyl dithiocarbamate :-

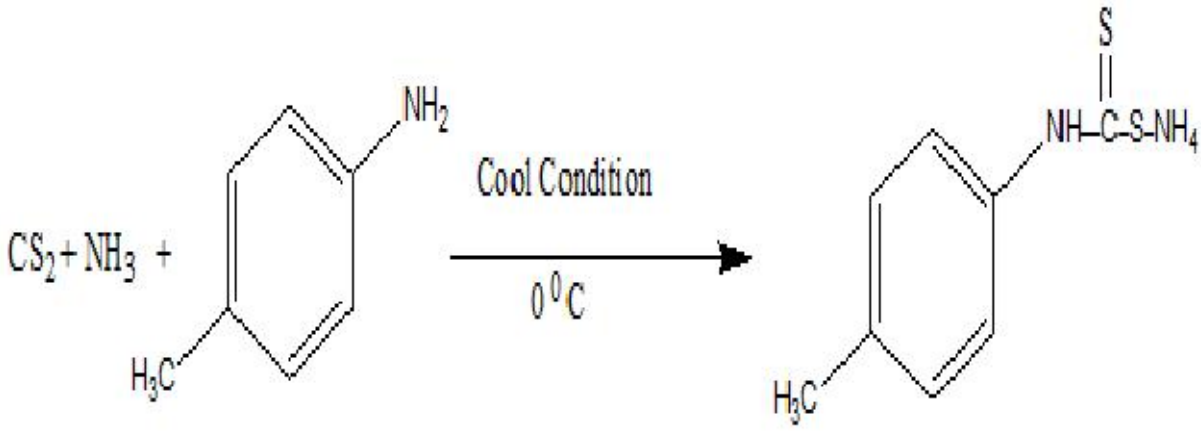
A 250ml conical flask with a powerful mechanical stirrer and separating funnel was equipped. Conical flask was kept loosely stoppered.A flak is coated in a freezing mixture of ice and salt.

A mixture of CS_2 25 ml, ammonia 51ml was introduced into it. The 10.77ml p-toulidine was run into mixture and continues shaking the mixture unto 30 minute. The mixture was allowed to stand for 1 hour. A heavy precipitate of ammonium p-totyl dithiocarbamate was formed.

Detail examination of compound:-

1) Compound is solid .
2) It gave possible test for N and S element.
3) Analytical result show that the molecular formula as C_8 H_{13} N_2 S_2.

REACTION



- Crystallize with alcohol.
- Colour – white
- Melting point – 80^0 c
- Nature after crystallization crystalline
- Weight – 19.5 gm.
- Solubility – acetone , DMSO, $CHCl_3$
- Insoluble – ether, CCl_4.

Material and Experimental methods

{4.1} Metal ion:-

The solution of metal ion in the Magnese chloride, Ferric chloride, in ethanol.

{4.2} ligand:-

Ammonium p-totyl dithiocarbamate from CS_2, Ammonia and p-toulidine.

{4.3} preparation of complex – Magnese chloride :

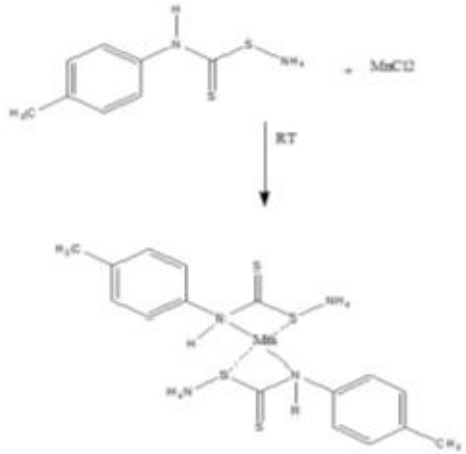
Magnese Choride metal ion with ligand ammonium p-totyl dithiocarbamates :- (ligand 2: Magnese chloride 1)

3.6gm ligand soluble in ethanol & 1.97gm Magnese chloride is also soluble in ethanol. Take the 0.01M solution of ligand in ethanol in 50ml beaker & added to in 0.01M solution of Magnese chloride in ethanol. The Brown color complex is form.

Details of complex:-

1) Colour – Brown
2) M.P – 140 ^{0}C.
3) Nature – amorphous
4) Solubility – soluble in –acetone
   Hot Ethanol, CHCl3

Complex of Ammonium paratotyl dithiocarbamate with Mn metal ion



II) **Preparation of complex Ferric Chloride**:-

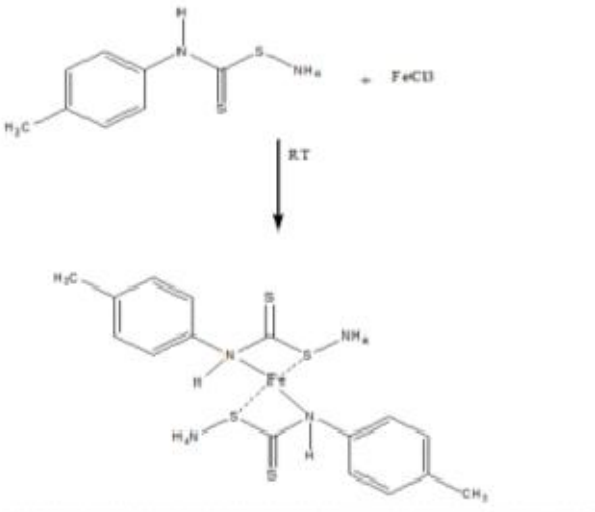
Ferric chloride metal ion with ligand ammonium p-totyl dithiocarbamate (Ligand 2: Ferric Chloride 1)

3.6gm ligand soluble in ethanol and 1.67gm copper sulphate is also soluble in ethanol. Take the 0.01M solution of ligand in ethanol in 50ml beaker & added to 0.01M solution of Ferric Chloride in ethanol. The Red colour complex is formed.

Detail of complex:-

	Nature	Amorphous
1	Colour of complex	Red
1	Melting point –	120°c
2	Molecular formula	C_{14} H_{20} N_4 S_4
3	Solubility-	1. Hot Acetone 2. Hot Ethanol

Complex of Ammonium paratotyl dithiocarbamate with Fe metal ion



RESULT AND DISCUSSION

Properties of ammonium p- totyl dithiocarbamate

Properties of Ammonium phenyl dithiocarbamate:-			
1	Melting point –	144°c	
2	Molecular formula	C_{14} H_{20} N_4 S_4	
3	Solubility-	1	Acetone
		2	Ethanol

1) Melting point – 55^o C
2) Molecular formula – C_{16} H_{26} N_4 S_4
3) Solubility acetone, DMSO, $CHCl_3$
4) IR Spectrum of ammonium p- totyl dithiocarbamate

From the chemical properties, analytical data & the spectral analysis the ammonium p-totyl dithiocarbamat

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