Ph.D. Thesis

PHYSICOCHEMICAL STUDIES OF SOME COMPOUNDS

ANCHAL A. KULSHRESTHA

DEPARTMENT OF CHEMISTRY

(DST-FIST FUNDED & UGC-SAP SPONSORED)

SAURASHTRA UNIVERSITY

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GUJARAT (INDIA)

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PHYSICOCHEMICAL STUDIES OF SOME COMPOUNDS

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IN

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BY

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UNDER THE GUIDANCE

OF

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Statement under O.Ph.D. 7 of Saurashtra University

The work included in the thesis is my own work under the supervision of **Dr. Shipra Baluja** and leads to some contribution in chemistry subsidized by a number of references.

Date: - - 2009

Place: Rajkot. **(Anchal A. Kulshrestha)**

This is to certify that the present work submitted for the Ph. D. Degree of Saurashtra University by **Anchal A. Kulshrestha** is his own work and leads to advancement in the knowledge of chemistry.

The thesis has been prepared under my supervision.

Date: - - 2009

Place: Rajkot.

Dr. Shipra Baluja
Associate Professor
Department of Chemistry
Saurashtra University
Rajkot - 360 005.

DEDICATED TO MY BELOVED PARENTS

AND

MY BELOVED BROTHER

" You were my strength when I was weak,
You were my voice when I couldn't speak,
You were my eyes when I couldn't see,
You stood by me and I stood tall,
I had your love, I had it all...
You are the one, who held me up and never
let me fall
I am everything. I am, because you love me "

ACKNOWLEDGEMENT

It is a moment of gratification and pride to look back with a sense of contentment at the long traveled path, to be able to recapture some of the fine moments, to be think of the infinite number of people, some who were with me from the beginning, some who joined me at different stages during this journey, whose kindness, love and blessings has brought me to this day. I wish to thank each of them from the bottom of my heart.

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I am thankful to Dr. Kamlesh Joshipura, Vice chancellor, Mr. Kalpak Trivedi, Pro Vice Chacellor, Saurashtra University-Rajkot for providing research as well as hostel facilities.

Finally, each individual creature on this beautiful planet is created by god to fulfill a particular role. Whatever I have achieved in my life is through his help and an expression of his will. He showered his grace on me through some outstanding teachers and colleagues and when I pay my tributes to these fine persons, I am merely praising his glory. All this work is his work through a small person called Anchal.

Anchal A. Kulshrestha
/ 04 / 2009

CONTENTS

Synopsis

SYNOPSIS of the thesis to be submitted to the Saurashtra University for the degree of **Doctor of Philosophy** in Chemistry.

Faculty	:	Science
Subject	:	Chemistry
Title	:	**"PHYSICO CHEMICAL STUDIES OF SOME COMPOUNDS"**
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Heterocyclic compounds have a wide range of applications. They are predominant among the type of compounds used as pharmaceuticals, agrochemicals and veterinary products. Their applications in pharmaceutics is because of their specific chemical reactivity. Further, some of these compounds are known to act as optical brightening agents, antioxidants, corrosion inhibitors and additives with a variety of other functions. One of the reasons for the widespread use of heterocyclic compounds is that their structures can be easily manipulated to achieve a require modification for a particular purpose.

Taking in view of the applicability of heterocyclic compounds, the present work was undertaken to synthesize some new heterocycles bearing 2-amino-benzothiazole and furan nucleus. All the synthesized compounds are characterized by IR, NMR and mass spectra. Further, physicochemical properties such as acoustical properties, density, refractive index, conductance, heat of solution, thermal properties, partition coefficient and dissociation constants of some compounds in different solvents have also been studied. The antibacterial activity of these compounds has also been studied in different solvents.

The present work is divided into four chapters.

CHAPTER-1 **GENERAL INTRODUCTION**

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Part-1 **Synthesis of 2-Amino Benzothiazole Derivatives**

Section-1 Synthesis of Schiff bases

Section-2 Synthesis of 5-Methyl 4-Thiazolidinones

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CHAPTER-1 GENERAL INTRODUCTION

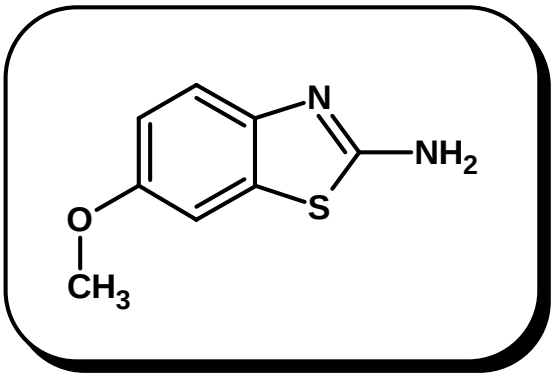
This chapter describes literature survey of synthesis, characterization, applications, physicochemical properties and antibacterial activities of organic heterocyclic compounds.

CHAPTER-2 SYNTHESIS AND CHARACTERIZATION

This chapter deals with synthesis and characterization of some benzothiazole derivatives and furan derivatives.

Part-1 Synthesis of Benzothiazole Derivatives

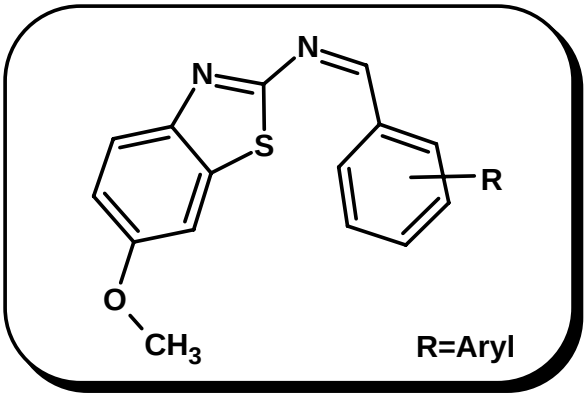
Nitrogen and sulfur containing heterocyclic compounds like benzothiazole has received considerable attention in recent years due to their biological and pharmaceutical activities. The benzothiazole ring system bears phenyl ring fused with thiazole ring.



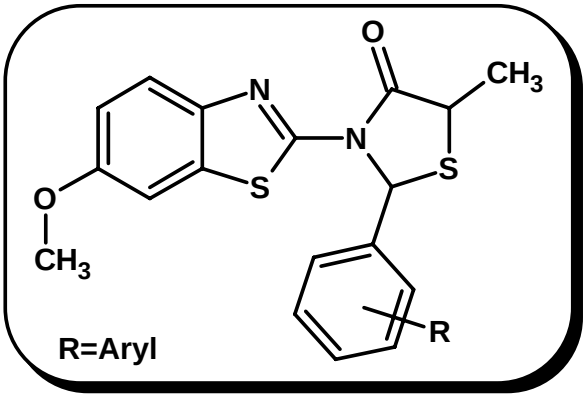
The chemistry of benzothiazole derivatives have been of interest due to its useful application in medicine, agriculture and industry.

Thus the important role displayed by benzothiazole and its derivatives for various therapeutic and biological activities encouraged to synthesize of 6-methoxy 2-amino benzothiazole of some Schiff bases, 4-Thiazolidinones and 5-Methyl 4-Thiazolidinones derivatives which are mentioned in following sections:

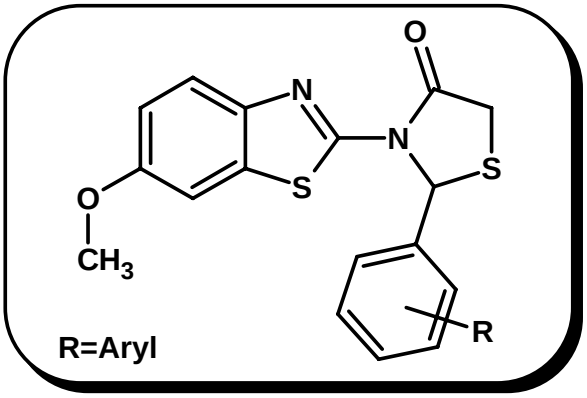
Section-I Synthesis of Schiff bases



Section-II Synthesis of 5-Methyl 4-Thiazolidinones

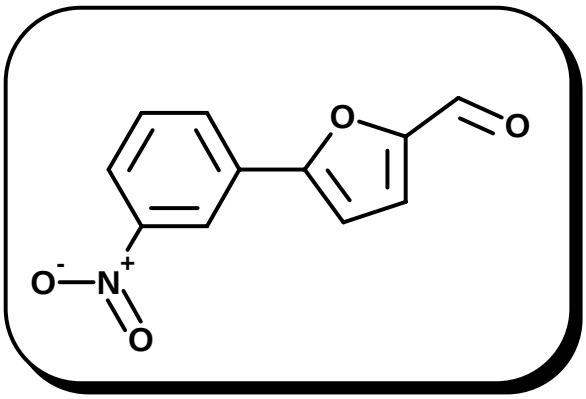


Section-III Synthesis of 4-Thiazolidinones



Part-2 Synthesis of furan Derivatives

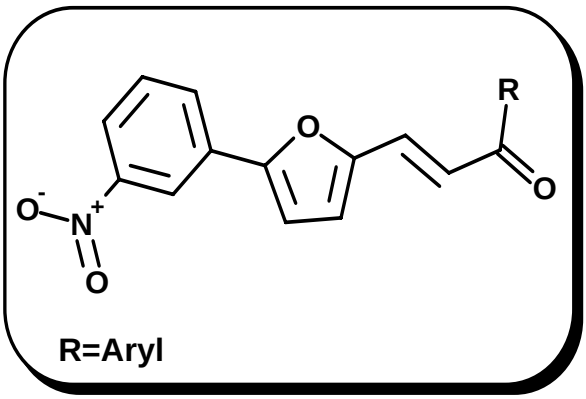
One of the most useful class in heterocyclic compounds is furan. The furan ring consists of a doubly unsaturated five membered ring containing one oxygen atom.



The research on the chemistry of furan has been a focus of attention for chemists for a long time, due to their wide variety of biological activities such as anti-inflammatory, muscle relaxants, antidepressant, antibacterial, antidiabetic, and also used herbicidal and pesticidal etc.

From this furan moiety, various chalcones have been synthesized.

Synthesis of Chalcones



Part-3 Comparison of different methods used for the synthesis of Schiff bases.

In Part -1 synthesis of Schiff bases are reported by the conventional method, which is more time consuming.

In last few years, Microwave-induced Organic Reaction Enhancement (MORE) chemistry has gained popularity as a non-conventional technique for rapid organic synthesis. Many researchers have reported the synthetic utility of MORE chemistry in routine organic synthesis. Compared to traditional processes of organic synthesis, microwave-enhanced chemistry saves significant time and very often improves conversions, clean product formation.

Ultrasound waves are known for their wide applications in various fields like life sciences, medical, cleaning, sonar, electronics, agriculture, oceanography, material science etc. Further, these waves prove to be an important in synthetic organic chemistry by lowering the reaction temperature and reaction time. By using these waves, yield can be increased and one can avoid the use of phase transfer catalysts in chemical reactions.

Thus, in this part, the synthesis of Schiff bases from 2-amino benzothiazole are compared by Microwave assisted method, Ultrasound irradiation and Conventional thermal method.

CHAPTER-3 PHYSICO-CHEMICAL PROPERTIES

Some physicochemical properties of synthesized Schiff bases and Chalcones have also been studied. For chalcones, measurements were done in dimethylformamide and chloroform whereas for Schiff bases, dimethylformamide and dimethylsulfoxide were taken. The choice of different solvents is due to solubility problem.

The various studied properties are given in the following sections:

Section-1 Acoustical Properties

This section deals with the acoustical properties of solutions of Schiff bases and Chalcones over a wide range of concentrations. For this density, viscosity and sound velocities were measured and from these experimental data, various acoustical parameters such as isentropic compressibility, Rao's molar sound function, specific acoustical impedance, internal pressure, Vander Waals constant, free volume etc. were evaluated. The results were discussed in terms of molecular interactions occurring in these solvents

Section-2 Density and Refractive index

In this section, density and refractive index of Chalcones and Schiff bases were measured in different solvents at 308.15 K. From the refractive index measurements, the density and refractive index of synthesized compounds were determined.

Section -3 Conductance

This section deals with the conductance measurement of solutions of Chalcones and Schiff bases in different solvents at various concentrations at 308.15 K. From these experimental values, equivalent conductance at infinite dilution for different compounds were evaluated.

Section -4 Heat of Solutions

The molar heat of solution and melting temperature of a substance can be determined from the solubility measurement at different temperatures. In the present chapter, heat of solution for all the Chalcones and Schiff bases were determined at different temperatures (298.15-318.15K) in dimethylformamide and 1, 4 dioxan.

Section -5 Partition coefficient

This section describes the partition coefficient of Chalcones in Water-Octanol system by UV spectroscopy. From the spectral data, log P values were evaluated.

Section -6 Thermal Properties

This section describes the thermal properties of Chalcones. The Thermo Gravimetric Analysis (TGA) and Differential scanning calorimeter (DSC) measurements were made. From these measurements, various kinetic parameters were evaluated. Further, thermal stability of various compounds are also determined.

Section -7 Dissociation Constants

In this section, the dissociation constant of Chalcones were studied in DMF-water mixtures at 308.15 K.

CHAPTER-4 BIOLOGICAL ACTIVITES

In the present chapter, antibacterial activity of all the synthesized 2-amino benzothiazole and furan derivatives are studied against different microbes in different solvents.

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Chapter-1

General Introduction

GENERAL INTRODUCTION

Organic chemists synthesize hundreds of new heterocyclic compounds every week. In most cases the chemist has specific reasons for synthesizing a particular compound, usually based on theoretical considerations, medicinal chemistry, biological mechanisms or a combination of all three.

The heterocyclic compounds are very widely distributed in nature and are very essential to living organisms. They play a vital role in the metabolism of all the living cells. Among large number of heterocycles found in nature, nitrogen heterocycles are the most abundant specially those containing oxygen or sulphur [(1)] due to their wide distribution in nucleic acid illustration and their involvement in almost every physiological process of plants and animals.

Heterocyclic compounds possess great applicability in industry as well as in our life in various ways. For example most of the sugars and their derivatives, including vitamin C [(2)], exist largely in the form of five membered (Furanosied structure) or six membered (Pyranosied structure) ring containing one oxygen atom. Further, most members of the vitamin B group possess heterocyclic rings containing nitrogen. e.g., vitamin B_6 (Pyridoxine) [(3, 4)], which is a derivative of the pyridine essential in amino acid metabolism.

The heterocyclic compounds also occupy key position in the area of drugs and pharmaceuticals. Almost 80% of the drugs in clinical use are based on heterocyclic constitution because they have specific chemical reactivity. Majority of the large number of drugs being introduced in pharmacopeias in recent year are heterocyclic compounds. A wide variety of modern drugs such as chlordiazepoxide (tranquillizer) [(5, 6)], imipromine (antidepressant) [(7)], guanethidine (antihypertensive) [(8)], indapamide (diuretic and antihypertensive) [(9, 10)], etc. Many non-steroidal drugs such as ketoprofen [(11)], fenoprofen and flurbiprofen [(12)] are well known anti-inflammatory agents; these derivatives were found to more potent with fewer side effects. Many antibiotics including penicillin [(13)], cephalosporin [(14)], norfloxacin [(15)], streptomycin [(16, 17)] etc., also contain heterocyclic ring.

Many veterinary products like pyrantel and morantel are the drug of choice as broad spectrum anthelmintics [(18)]. The herbicides atrazine and

Simazine are well known example of heterocyclic agrochemicals [19, 20]. Plant pigments such as indigo [21], hemoglobin [22] and anthiocyanins [23], chlorophyll [24] has contributed much to colour chemistry and all these contain heterocyclic ring. Further, many other heterocyclic colouring matters are in use since prehistoric times. Further, the heterocyclic tetra selena fulvalene was the first ionic molecular crystal to demonstrate superconductivity [25].

Taking in view of the applicability of heterocyclic compounds, the present work was undertaken to synthesize some new heterocycles bearing benzothiazole and furan nucleus.

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GENERAL REMARKS

1. Melting points were recorded by open capillary method and are uncorrected.
2. Infrared spectra were recorded on SHIMADZU FTIR-8400 (Diffuse reflectance attachment) in the frequency range of 4000-400 cm^{-1} using KBr. Spectra were calibrated against the polystyrene absorption at 1610 cm^{-1}.
3. ^1H NMR spectra were recorded on BRUKER AVANCE II 400 spectrometer. Making a solution of samples in DMSO d_6 and $CDCl_3$ solvents using tetramethylsilane (TMS) as the internal standard unless otherwise mentioned, and are given in the δ scale.
4. Mass spectra were recorded on SHIMADZU GCMS-QP2010 spectrometer operating at 70 eV using direct injection probe technique.
5. Analytical thin layer chromatography (TLC) was performed on Merck-precoated silica gel-G F_{254} aluminium plates. Visualization of the spots on TLC plates was achieved either by exposure to iodine vapor or UV light.
6. The chemicals used for the synthesis of intermediates and end products were purchased from Spectrochem, Sisco Research Laboratories (SRL), Thomas-Baker, Sd fine chemicals and Loba chemie.
7. Microwave assisted reactions were carried out in Qpro-M microwave synthesizer operating at 1000 W.
8. Ultrasonic assisted reactions were carried out in SPINCOTECH-SONIC ultrasonic cleaner operating at 2200 MHz.
9. The structures and names of all the compounds given in the experimental section were generated using ACD Chemsketch version 11.0

Chapter-2

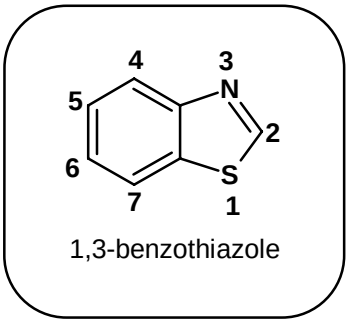
Synthesis and Characterization

Part-1

Synthesis of 2-amino benzothiazole derivatives

INTRODUCTION

The Benzothiazole ring system bears phenyl ring fused with thiazole ring. Thiazole is a five membered heterocyclic ring system having sulfur and nitrogen as heteroatom. The study of benzothiazole derivates is of considerable current interest due to of their important biological and biophysical properties.



1,3-benzothiazole

SYNTHETIC ASPECT

Different methods used for the synthesis of benzthiazole and its derivatives have been reported in literature [1-7].

One of the earliest and most valuable methods for the synthesis of benzothiazole is the reaction of an o-aminothiaphenol, with a carboxylic acid [8-11] or its derivatives or an aldehyde [12-14]. The reaction of aldehyde with o-aminophenols yields either 2, 3-dihydrobenzothiazole, depending on the aldehyde and the thiophenol employed. The reaction of various aldehydes and ketones has been reported [15-20].

2-aminobenzothiazole and some of its derivatives have been synthesized by cyclization of the corresponding arylthioureas with SO_2Cl_2, Br_2 and H_2SO_4 [21-27]. Lau *et. al.* [28] synthesized some novel benzothiazole derivatives by thiourea with excess 1,4-benzoquinones and 1,4-naphthoquinones in the presence of con. HCl offers a convenient route for the synthesis of a variety of 2-amino-6-hydroxybenzothiazoles and 2-amino-5-hydroxynaphtho [1,2-d] thiazoles. Livio *et. al.* [29] synthesized series of novel 2-(substituted-phenyl)-6-aminobenzothiazole as analogous of 2-(4-aminophenyl)benzothiazole prepared as hydrochloride or dihydrochloride salts. o-thiocyanato arylamines undergo spontaneous cyclization to produce

2-aminobenzothiazole in good yields. The required thiocyanatoamines are produced directly by treatment of a p-substituted arylamine with thiocyanogen which is generated in the reaction mixture containing the arylamine [30-32]. In recent years, environmentally benign synthetic methods have received considerable attention and some solvent-free, catalyst-free and microwave promoted reactions have been developed [33-36]

BIOLOGICAL SIGNIFICANCE

A well known drug such as "Riluzole" (Rilutek) [37] having benzothiazole nucleus. Benzthiazole derivatives are known to have wide spectrum of therapeutic activities such as:

- **Antitumor activity**

  Benzothiazole show antitumor activity [38-42], especially the phenyl substituted benzothiazole [43-45]. Some of potent and selective antitumor agents mostly from substituted 2-(4-aminophenyl) benzothiazoles were developed and examined, *in vitro*, their antitumor activity in ovarian, breast, lung, renal and colon carnicoma human cell lines [46-51]. Hutchinson *et al.* [52] have been synthesized fluorinated analogues of 2-(4-aminophenyl) benzothiazole which possessing enhanced efficacy *in vitro* and superior potencies against human breast and ovarian tumor. Pyrimido benzothiazole [53], imidazo benzothiazoles [54] as well as benzothiazole quinoline derivatives [55], also showed antitumor activity.

- **Antimicrobial activity**

  Benzothiazole show a wide spectrum of chemotherapeutic activity and a considerable amount of work has been done on the synthesis of new potent antibacterial [56-59] and antifungal [60-63] benzothiazole. Bhusari *et al* [64], prepared some 2-(substituted phenylsulfonamido)-6-substituted benzothiazoles and screened them for their antibacterial activity against *Bacillus subtilis, Salmonella typhi*, and *S. dysentery*. Sreenivasa *et al* [65]

prepared benzothiazolo triazole derivatives and found to possess good activity against *S. aureus*, *E.Coli* and *C. ablicans*.

- **Anti-inflammatory activity**

  In the last 30 years a number of Benzothiazole derivatives have been synthesized and found to display anti-inflammatory activity [66-68]. Singh *et al.* [69] prepared some new 2-(4-butyl-3, 5-dimethyl pyrazol-1-yl)-6-substituted benzothiazole and 4-butyl-1-(6-substituted-2-benzothiazolyl)-3-methylpyrazol-5-ones and were found to display significant anti-inflammatory activity. Dogruer *et al.* [70] synthesized sixteen (2-benzothiazolone-3-yl and 2-benzoxazolone-3yl) acetic acid derivatives and found to possess good anti-inflammatory activity.

- **Anthelmintic activity**

  In the search of new anthelmintic agents of benzothiazole series, Nargund, [71, 72] synthesized few novel 8-fluoro-9-substituted (1, 3) benzothiazole (5,1-b)-1,3,4-triazole. All these compounds were studied for their anthelmintic activity against earthworm, *perituma posthuma*. The compound with R= o-nitroaniline substituent was found to possess markedly higher anthelmintic activity. Some substituted imidazobenzothiazole were tested for *in vivo* anthelmintic activity against *H. nana* infection and were found to show good to moderate activity [73, 74].

- **Anticonvulsant activity**

  A large number of benzothiazole derivatives were evaluated for anticonvulsant activity and found to possess significant activity against various types of seizures [75-78]. Singh *et al.* [79] synthesized some 2-(4-arylthiosemicarbazidocarbonylthio) benzothiazoles were screened and found to moderate anticonvulsant activity. In the search of new anticonvulsant agents having benzothiazole nucleus, Jimonet *et al.* [80] have synthesized a lot of substituted-2-benzothiazolamines. All these compounds were found to possess significant activity.

- **Antileishmanial activity**

  Leishmaniasis is a protozoal parasitic disease which leads to considerable death. It is a major public health problem particularly in Latin America, Africa and Asia [81]. 2-[(2-Chloro-benzothiazol-6-yl) amino] benzoic acid, demonstrated an interesting antiproliferative activity towards parasites of the species *Trichomonas vaginalis*. Delmas *et al.* [82] has synthesized position 2 substitution-bearing 6-nitro and 6-amino benzothiazoles and their corresponding anthranilic acids and assessed the *in vitro* antiparastic activity of each derivative against the parasites of the genus *leishmania infantum* and *Trichomonas vaginalis* compared to their toxicity towards human monocytes. The antiprotozoal properties depended greatly on the chemical structure of the position 2 substitution-bearing group.

Thus, the important role displayed by benzothiazole and its derivatives for various therapeutic and biological activities encouraged to synthesize some Schiff bases, 4-Thiazolidinones and 5-methyl 4-Thiazolidinones derivatives bearing benzothiazole nucleus in order to achieve compounds having better drug potential.

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Section-I

Synthesis of Schiff bases

INTRODUCTION

The chemistry of >C=N is studied extensively because of its high synthesis flexibility, varied coordinating ability and medicinal utility. The compounds containing >C=N include mainly the products of reaction between aldehyde or ketonic components and primary aliphatic or aromatic amines, ammonia, hydrazine, N-phenylhydrazine, hydroxylamine hydrochloride, semicarbazide, thiosemicarbazide and their substituted derivatives.

These compounds are generally known as Schiff bases to honors Schiff, who first synthesized such compounds [(1)]. These are also known as azomethines. A Lot of works has been done on this class of compounds due to its multi applicability [(2-7)]. They are well known intermediate for the preparation of azetidinone, thiazolidinone, formazone, arylacetamide and many other derivatives.

General account of the summary of reaction of aldehydes with amine (aromatic or aliphatic) has been reviewed by Murray [(8)]. Some Schiff bases from 2-hydroxy benzaldehyde and 3-hydroxy-4-pyridine-carboxaldehyde with various amines were also synthesized and the effect of substituent on Keto-enol equilibria [(9)] and hydrogen bonds [(10)] have also been reported. Some other Schiff bases have also been synthesized from salicyaldehydes with aromatic amines and aliphatic amines and their characterizations were done by using IR, NMR and mass spectra [(11-14)]. Dayagi and Degani [(15)] have reported some methods for the synthesis of Schiff bases. Sampat *et al.* [(16)] gave the detail study report on heterocyclic Schiff bases ligands by condensing pyrrole 2-carboxaldehyde and pyridine 2-carboxaldehyde with aromatic amines. Singh *et al.* [(17)] had synthesized Schiff bases derived from 4-amino antipyrine and studied their IR and thermal properties. A series of new thorium (IV) complexes with a Schiff bases derived from fluoroaniline and p-(N, N'-dicyanoethyl) amino benzaldehyde have been synthesized by Goyal et al. [(18)] Chang and Pan reported some Schiff bases derived from amino phenols and aromatic aldehydes [(19)]. A new one pot procedure for the generation of azomethine via chlorominium salt has been investigated by Anderson and co-workers [(20)]. Amanda J. Gallant *et al.* [(21)] have prepared

Schiff base by condensation of equimolar quantity of 3,6 diformyl catechol and substituted o-phenylenediamine. Pierre L. Beaulieu *et al.* [22] have synthesized (E)-N-phenyl methyleneglycineethyl ester by the cyclocondensation of glycine ethyl ester hydrochloride, t-butylmethyl ether (TBME), benzaldehyde was added followed by anhydrous Na_2SO_4 and triethylamine.

In recent years, environmentally benign synthetic methods have received considerable attention and some solvent-free protocols have been developed [23-28]. Grinding together solid anilines and solid benzaldehydes yielded various kinds of benzylideneanilines [29]. The synthesis of primary imines by condensation of 2-hydroxylaryl ketones with ammonium iodide and piperidine under solvent free conditions [30].

Schiff bases are known to be useful in perfumery [31, 32], as corrosion inhibitor [33, 34], as complexing agents [35-37] and as intermediate in many reactions [38-42]. They are used in optical and electrochemical sensors, as well as in various chromatographic methods, to enable detection of enhance selectivity and sensitivity [43-45]. In literature, some other applications of Schiff bases have also been reported in various fields [46-50]. Some of these compounds and their metal complexes have also been used in the preparation of various medicines [51-55]. Further, many workers [56-63] reported a wide range of biological activities of various Schiff bases. Besides, several Schiff bases have been reported to possess remarkable antibacterial [64-68], antifungal [69-74], anticancer [75-79], anti HIV [80-83], anti-inflammatory [83-86], antiparasitic [87-90] and diuretic [91] activities.

Owing to their characteristic properties like, thermal stabilities, abnormal magnetic properties, relevant biological properties, high synthesis flexibility, varied coordinating ability and medicinal utility [92-100]. Some new Schiff bases have been synthesized in the present work.

EXPERIMENTAL

Synthesis of 4-[(Z)-[(6-methoxy-1,3-benzothiazole-2 yl)imino]methyl] phenol

[A] Synthesis of 6-methoxy 2-amino benzothiazole:

A solution of p-methoxy aniline (1 mole) in chlorobenzene is prepared in a three-necked, round-bottom flask fitted with a stirrer, reflux condenser, thermometer, and dropping funnel. Over a period of 5 minutes, 0.55 mole of concentrated sulfuric acid is added dropwise. To the finely divided suspension of p-methoxy aniline sulfate is added 1.1 moles of sodium thiocyanate, and the mixture is heated for 3 hours at 100° (inside temperature) in an oil bath. The solution, which now contains the thiourea, is cooled to 30°, 1.34 moles of sulfuryl chloride is added over a period of 15 minutes, with care that the temperature does not exceed 50°. The mixture is kept at 50° for 2 hours (no further evolution of hydrogen chloride), after which the chlorobenzene is removed by filtration. The solid residue is then dissolved in hot water, and the remainder of the solvent is removed by a current of steam. The solution is filtered from a little solid and is then made alkaline to litmus by the addition of concentrated ammonium hydroxide (sp. gr. 0.90). The precipitated 6- methoxy 2-aminobenzothiazole is filtered and washed with water. The crude product was isolated and crystallized from absolute ethanol.

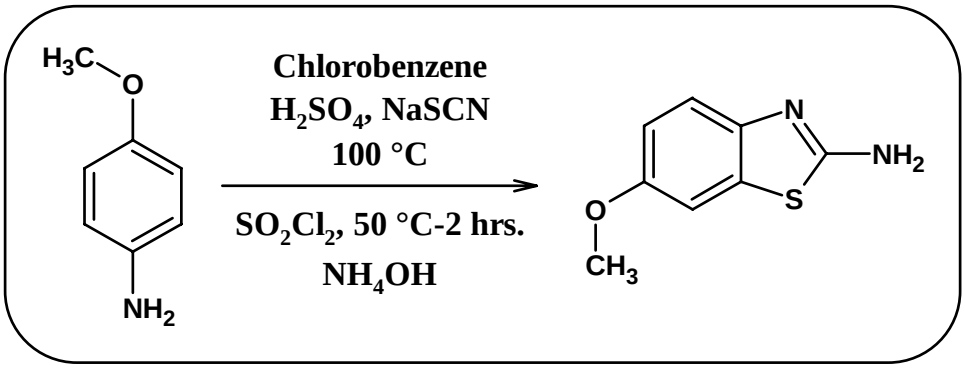
[B] Synthesis of 4-[(Z)-[(6-methoxy-1,3-benzothiazole-2-yl)imino]methyl] phenol

A mixture of 0.01 M 6-methoxy 2-amino benzothiazole and 0.01 M 4-hydroxy benzaldehyde was taken in ethanol using catalytic amount of gla. acetic acid and the reaction mixture was refluxed for 10 hrs. The product was isolated and crystallized from absolute ethanol.

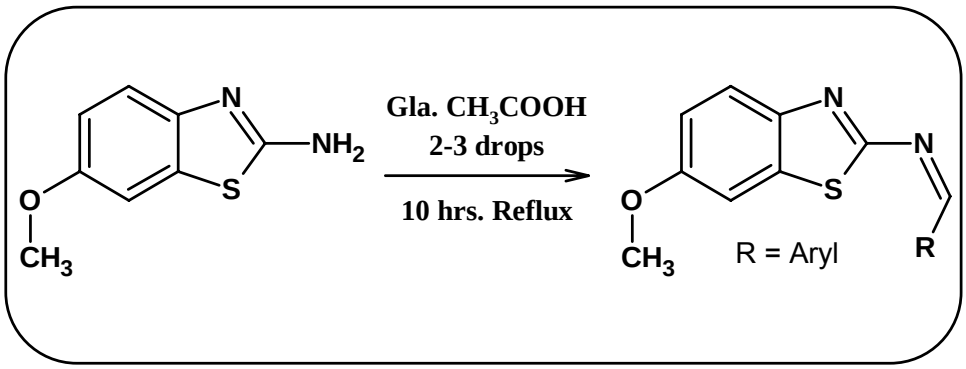
Similarly other Schiff bases were obtained.

REACTION SCHEME

[A] Synthesis of 6-methoxy 2-amino benzothiazole:



[B] Synthesis of 4-[(Z)-[(6-methoxy-1,3-benzothiazole-2-yl)imino]methyl] phenol



The various physical constants such as R_f value, melting point and percentage of yield for all the synthesized Schiff bases are given in Table 1.1.

Table 1.1: Physical constants of Schiff bases.

Sr. No.	Compound Code	R	M.F.	M. Wt. (g/mol)	R_f^* Value	M.P. °C	Yield %
1	AKBS-01	4-OH-C_6H_4	$C_{15}H_{12}N_2O_2S$	284.33	0.53	248	68
2	AKBS-02	2-OH-C_6H_4	$C_{15}H_{12}N_2O_2S$	284.33	0.51	112	65
3	AKBS-03	4-Cl-C_6H_4	$C_{15}H_{11}N_2OSCl$	302.77	0.47	140	57
4	AKBS-04	3-Cl-C_6H_4	$C_{15}H_{11}N_2OSCl$	302.77	0.49	185	60
5	AKBS-05	3-NO_2-C_6H_4	$C_{15}H_{11}N_3O_3S$	313.33	0.52	180	68
6	AKBS-06	2-NO_2-C_6H_4	$C_{15}H_{11}N_3O_3S$	313.33	0.50	156	54
7	AKBS-07	-CH=CH-C_6H_5	$C_{17}H_{14}N_2OS$	294.37	0.58	102	42
8	AKBS-08	4-F-C_6H_4	$C_{15}H_{11}N_2OSF$	286.32	0.46	172	49
9	AKBS-09	1-Naphthalene	$C_{19}H_{14}N_2OS$	318.39	0.54	164	56
10	AKBS-10	9-Anthracene	$C_{23}H_{16}N_2OS$	368.45	0.59	140	70

* Hexane: Ethyl acetate-6:4

The characterization was done by IR, ^{1}H NMR and mass spectra. The IR spectra for AKBS-01 is given in Fig. 1.1. The IR spectral data for this compound and other synthesized compounds are reported in Tables 1.2 and 1.3 respectively. The NMR spectra is shown in Fig. 1.2 for AKBS-01 and the corresponding data is reported in Table 1.4. The mass spectra of the same compound is given in Fig. 1.3 and the proposed mass fragmentation is given in Scheme 1.1.

Figure 1.1: IR spectra of 4-[(Z)-[(6-methoxy-1,3-benzothiazole-2-yl) imino] methyl] phenol (AKBS-01)

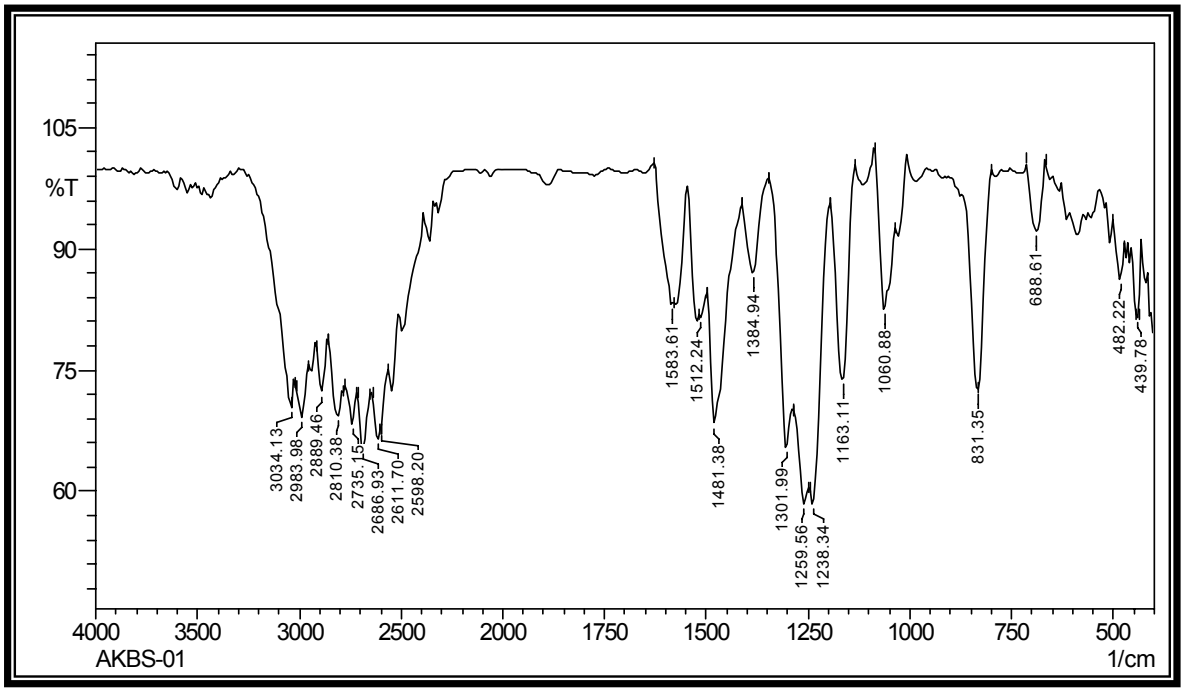


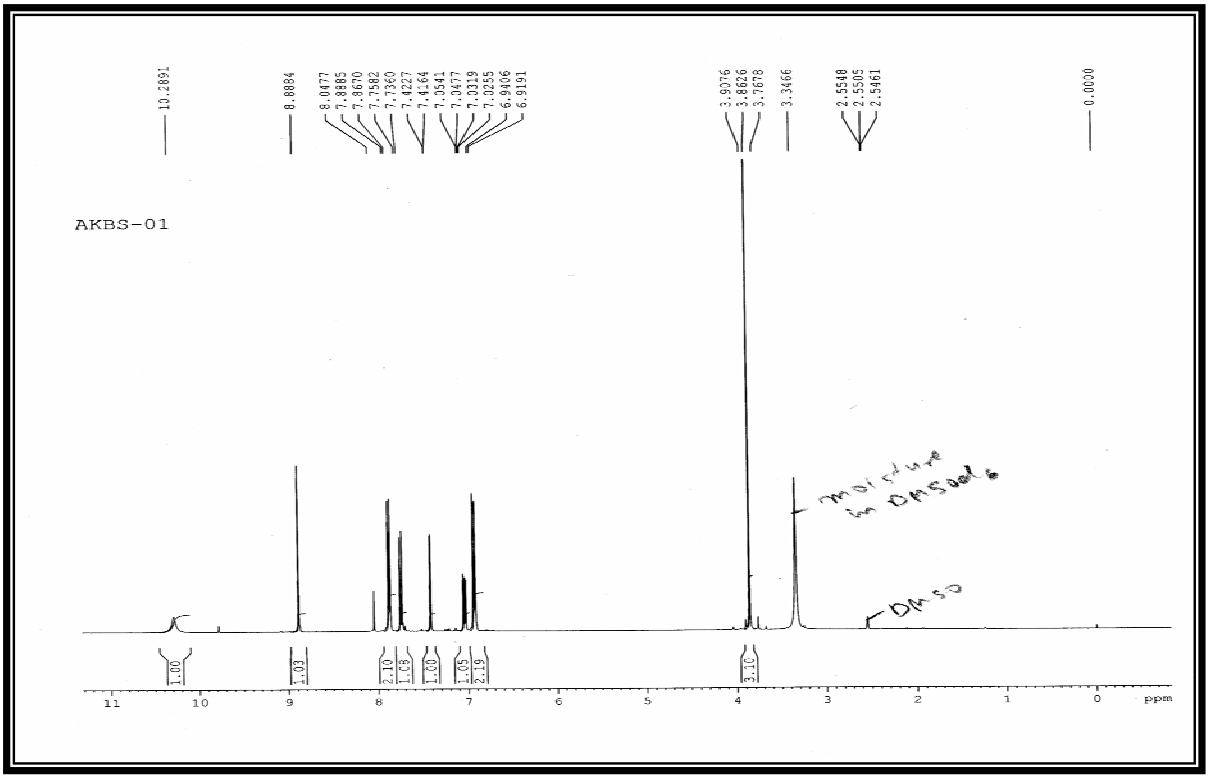
Table 1.2: IR spectral Data of 4-[(Z)-[(6-methoxy-1,3-benzothiazole-2-yl)imino] methyl]phenol (AKBS-01)

Type	Vibration mode	Frequency in cm^{-1}	
		Observed	Reported [101]
Alkane (methyl)	C-H str. (asym.)	2983	2975-2920
	C-H str. (sym.)	2889	2880-2860
	C-H def. (asym.)	1481	1470-1435
	C-H def. (sym.)	1384	1395-1370
Aromatic	C-H str.	2983	3100-3000
	C=C	1481	1585-1480
	C-H i.p. def.	1163	1125-1090
	C-H o.o.p. def.	831	860-810
Azomethine	N=C str.	1583	1650-1580
	C-N str.	1259	1350-1200
Hydroxy	O-H str.	3034	3650-2590
	O-H def.	1301	1410-1310

Table 1.3: IR spectral data of Schiff bases.

Type	Vibration mode	Frequency in cm^{-1}	
		Observed	Reported
AKBS-02			
Azomethine	N=C str.	1584	1650-1580
	C-N str.	1260	1350-1200
AKBS-03			
Azomethine	N=C str.	1588	1650-1580
	C-N str.	1263	1350-1200
AKBS-04			
Azomethine	N=C str.	1584	1650-1580
	C-N str.	1262	1350-1200
AKBS-05			
Azomethine	N=C str.	1582	1650-1580
	C-N str.	1261	1350-1200
AKBS-06			
Azomethine	N=C str.	1586	1650-1580
	C-N str.	1265	1350-1200
AKBS-07			
Azomethine	N=C str.	1583	1650-1580
	C-N str.	1262	1350-1200
AKBS-08			
Azomethine	N=C str.	1589	1650-1580
	C-N str.	1265	1350-1200
AKBS-09			
Azomethine	N=C str.	1586	1650-1580
	C-N str.	1267	1350-1200
AKBS-10			
Azomethine	N=C str.	1584	1650-1580
	C-N str.	1263	1350-1200

Figure 1.2: ^{1}HNMR spectra of 4-[(Z)-[(6-methoxy-1,3-benzothiazole-2-yl) imino] methyl] phenol (AKBS-01)



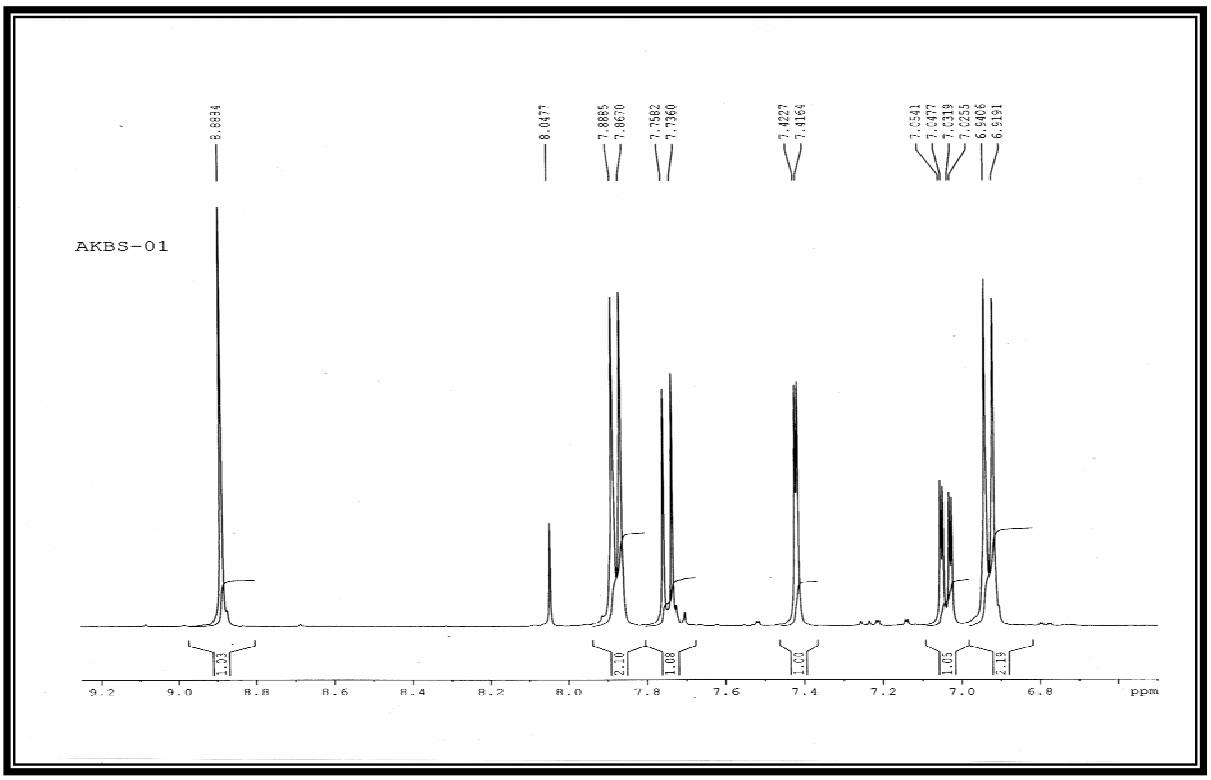
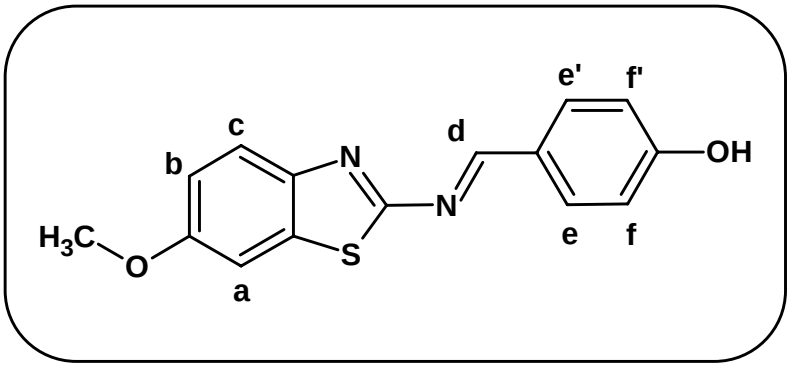
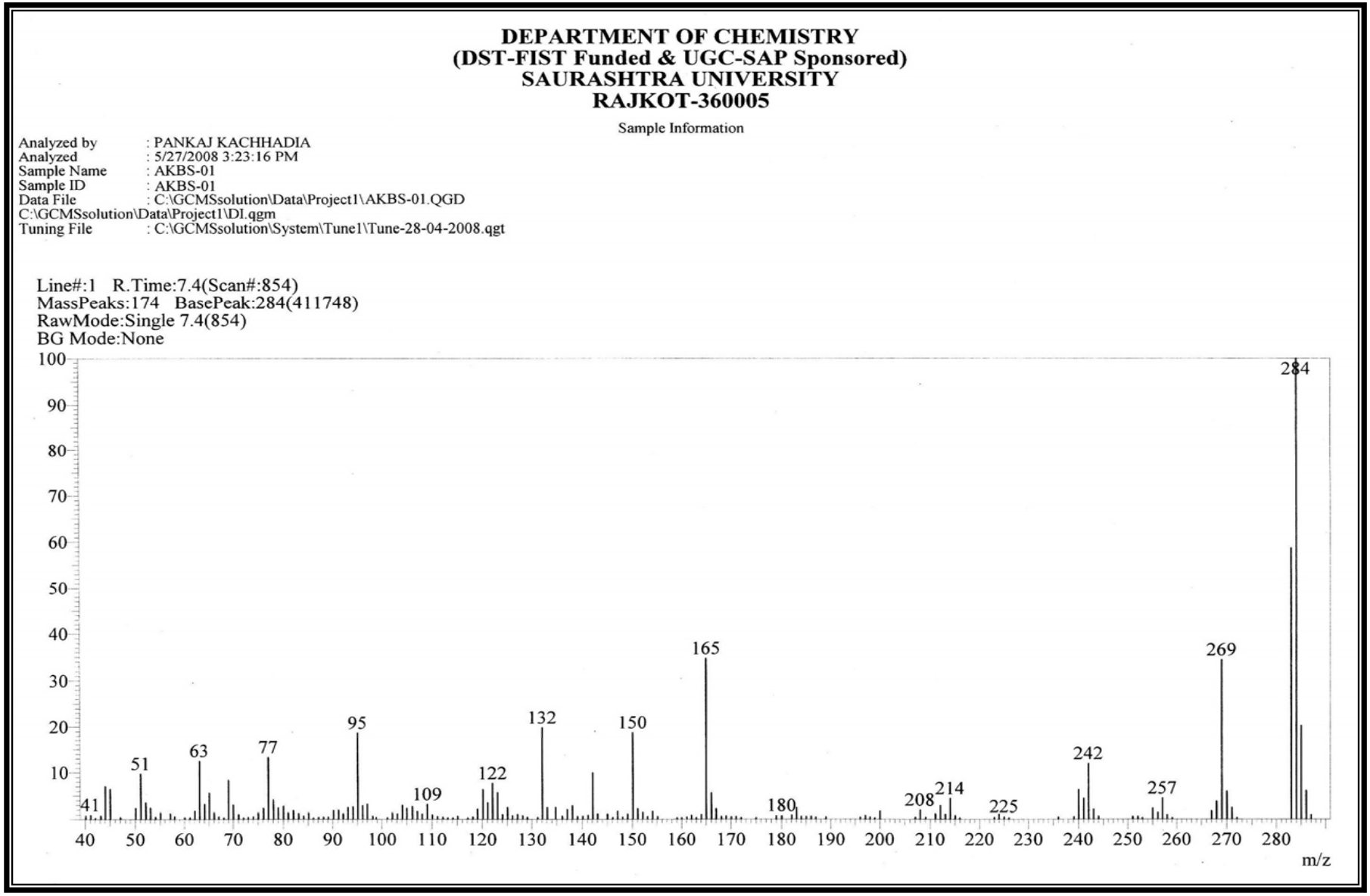


Table 1.4: ^{1}H NMR spectral data of 4-[(Z)-[(6-methoxy-1,3-benzothiazole-2-yl) imino] methyl] phenol (AKBS-01)

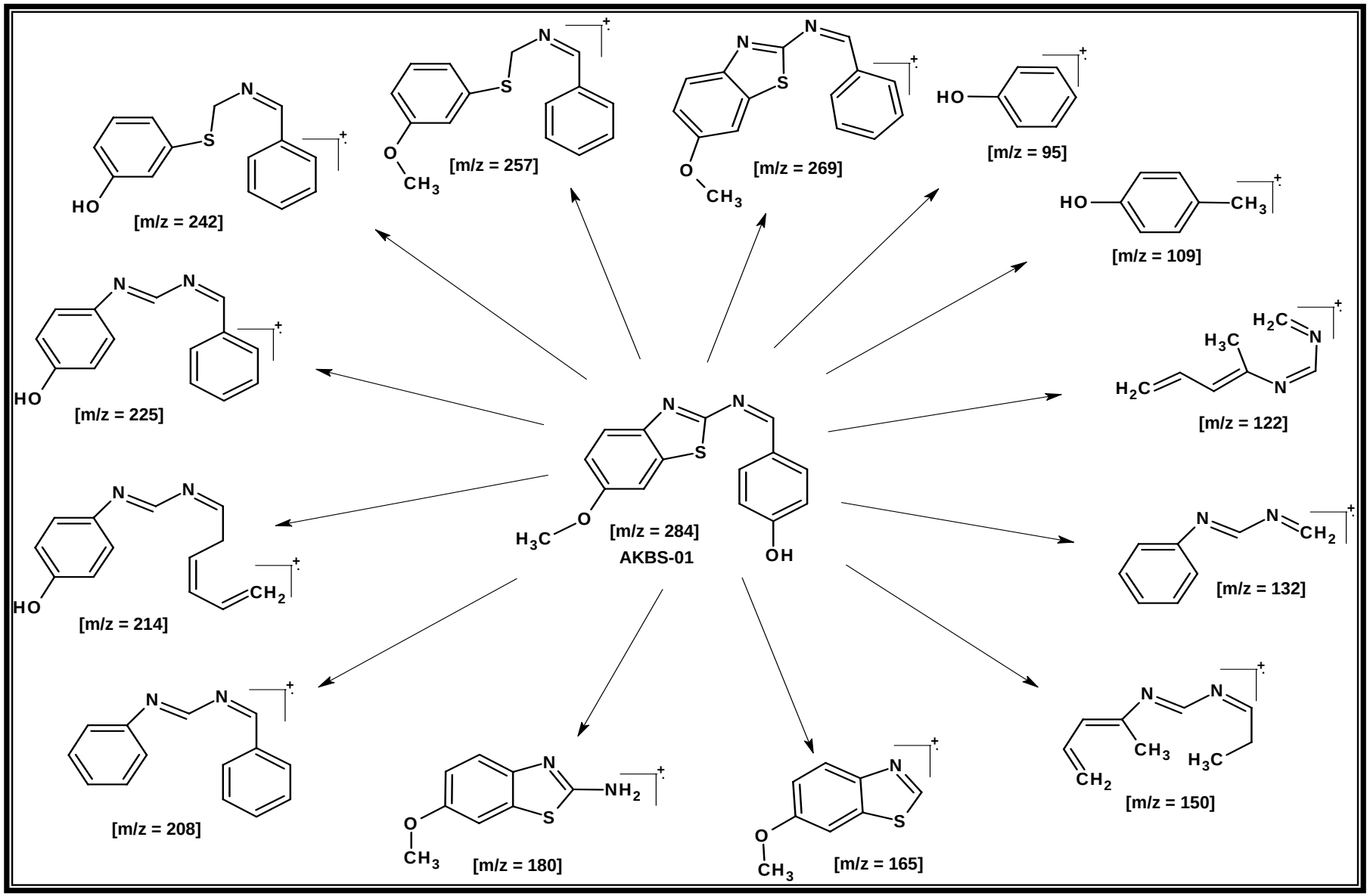


Signal No.	Signal Position (δ ppm)	Relative No. of Protons	Multiplicity	Inference	J (H_z)
1	3.86	3H	Singlet	Ar-OCH_3	-
2	6.91-6.94	2H	Doublet	Ar-H (ff')	8.60
3	7.02-7.05	1H	D-Doublet	Ar-H (b) + H (c)	-
4	7.41-7.42	1H	Doublet	Ar-H (a)	2.52
5	7.73-7.75	1H	Doublet	Ar-H (c)	8.80
6	7.86-7.88	2H	Doublet	Ar-H (ee')	8.60
7	8.88	1H	Singlet	-CH(d)=N	-
8	10.28	1H	Singlet	-OH	-

Figure 1.3: Mass spectra of 4-[(Z)-[(6-methoxy-1,3-benzothiazole-2-yl) imino] methyl] phenol (AKBS-01)



Scheme 1.1: Proposed fragmentation of 4-[(Z)-[(6-methoxy-1,3-benzothiazole-2-yl)imino]methyl]phenol (AKBS-01)



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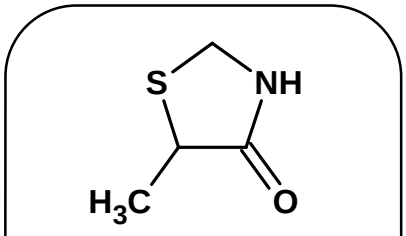
Section-II

Synthesis of 5-Methyl 4-Thiazolidinone

INTRODUCTION

5-methyl 4-thiazolidinones are derivatives of thiazolidine with a carbonyl group at 4-position. Substituents in the 2, 3 position may be varied and 5 position with methyl, but greatest difference in structure and properties is exerted by the groups attached to carbon atom in the 2-position and to nitrogen atom in the 3-position. General structure of 5-methyl 4-thiazolidinones is given below:



5-Methyl 4-Thiazolidinones

Thiazolidinones belong to an important group of heterocyclic compounds. 5-methyl 4-thiazolidinones one of the derivative of 4-Thiazolidinone which are always being an attraction point for researchers because of its efficiency towards various pharmacological usages. Some Thiazolidinones and their derivatives have been long used as precursors for the synthesis of biologically active molecules [1-5].

Various derivatives of thiazolidinone have been synthesized by various researchers [6-12]. Literature survey shows various preparations of thiazolidinones [13-17]. Solankee *et al.* synthesized 5-methyl-4-thiazolidinones by the cyclocondensation of thiolactic acid [18]. Ramsh *et al.* have prepared alkali salts of thiazolidinones [19]. Mukhtar *et al.* have reported the synthesis of some thiazolidinone derivatives from dichlorochalcone [20]. Abbady *et al.* have synthesized some symmetrical and unsymmetrical thiazolidinones using diacetyl diphenyl sulphide [21]. Pardasani *et al.* [22] have also reported the synthesis of some thiazolidinones.

Various worker have applied the Green chemistry approach to the synthesis of thiazolidinone derivatives by using microwave assisted method

and multi component reaction method [23, 24]. The characterization and crystallographic study of various thiazolidinone derivatives have also been reported. [25, 26]

Various 5-methyl 4-thiazolidinone derivatives are known to exhibit biological activities such as antibacterial [27, 28], antimicrobial [29], hypnotic [30], anti diarrhea [31], anti psychotic [32], anti cancer [33-35], antiviral [36, 37], herbicidal [38] etc. Many thiazolidinones are also known to give HIV-inhibitory activity [39, 40].

Lodhi *et al.* [41] have studied antimicrobial, anti-inflammatory and analgesic property of 4-thiazolidinone and arylidine derivatives. Bhawana *et al.* [42] have reported their antiinflammatory and ulcerogenic liability, cardiovascular and CNS effect. Kocabalkani *et al.* [43] also evaluated antimicrobialactivities of some 2,5- di substituted 4- thiazolidinone. Some thiazolidinone have also been reported as as Cystic fibrosis transmembrane conductance regulator (CFTR) inhibitor [44, 45]. Kucukguzel *et al.* [46] have also reported synthesis and biological activity of some 4-thiazolidinones

EXPERIMENTAL

Synthesis of 2-(4-hydroxyphenyl)-3-(6-methoxy-1,3-benzothiazol-2-yl)-5-methyl-1,3-thiazolidin-4-one

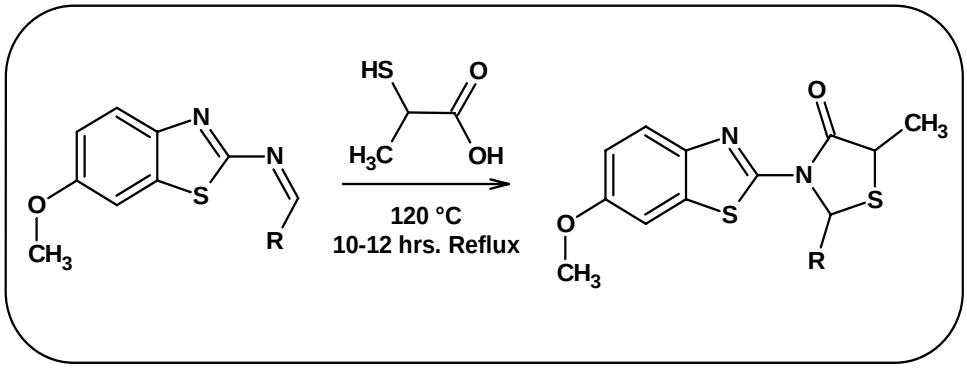
[A] Synthesis of 6-methoxy 2-amino benzothiazole: Section-1 (A)

[B] Synthesis of 4-[(Z)-[(6-methoxy-1,3-benzothiazole-2-yl)imino methyl] phenol : Section-1 (B)

[C] Synthesis of 2-(4-hydroxyphenyl)-3-(6-methoxy-1,3-benzothiazol-2-yl)-5-methyl-1,3-thiazolidin-4-one

A mixture of 4-[(Z)-[(6-methoxy-1,3-benzothiazole-2-yl)imino] methyl] phenol 0.01M and thiolactic acid 0.01M was heated at 120°C for 10-12 hrs. The reaction mixture was cooled and treated with 10% sodium bicarbonate solution. The solid product was than separated, filtered and washed with water and crystallized from absolute ethanol.

Similarly, other Schiff bases were condensed with thiolactic acid.



The various physical constants such as R_f value, melting point and percentage of yield for all the synthesized 5-methyl 4-Thiazolidinones are given in Table 2.1.

Table 2.1: Physical constants of 5-Methyl 4-Thiazolidinones

Sr. No.	Code	R	M.F.	M. Wt. (g/mol)	R_f* Value	M.P. °C	Yield %
1	ABT-01 (a)	4-OH-C_6H_4	$C_{18}H_{16}N_2O_3S_2$	372.46	0.52	192	70
2	ABT-01 (b)	2-OH-C_6H_4	$C_{18}H_{16}N_2O_3S_2$	372.46	0.54	152	72
3	ABT-01 (c)	4-Cl-C_6H_4	$C_{18}H_{15}ClN_2O_2S_2$	390.90	0.52	182	52
4	ABT-01 (d)	3-Cl-C_6H_4	$C_{18}H_{15}ClN_2O_2S_2$	390.90	0.42	177	54
5	ABT-01 (e)	3-NO_2-C_6H_4	$C_{18}H_{15}N_3O_4S_2$	401.45	0.53	180	68
6	ABT-01 (f)	2-NO_2-C_6H_4	$C_{18}H_{15}N_3O_4S_2$	401.45	0.49	151	69
7	ABT-01 (g)	-CH=CH-C_6H_5	$C_{20}H_{18}N_2O_2S_2$	382.49	0.48	126	50
8	ABT-01 (h)	4-F-C_6H_4	$C_{18}H_{15}FN_2O_2S_2$	374.45	0.46	179	53
9	ABT-01 (i)	1-Napthaline	$C_{22}H_{18}N_2O_2S_2$	406.52	0.42	194	71
10	ABT-01 (j)	9-Antracin	$C_{26}H_{22}N_2O_2S_2$	458.59	0.46	198	74

* Hexane: Ethyl acetate-5:5

The characterization was done by IR, ^{1}H NMR and mass spectra.

The IR spectra for ABT-01(a) is given in Fig. 2.1. The IR spectral data for this compound and other synthesized compounds are reported in Tables 2.2 and 2.3 respectively. The NMR spectra is shown in Fig. 2.2 for ABT-01(a) and the corresponding data is reported in table 2.4. The mass spectra of the same compound is given in Fig. 2.3 and the proposed mass fragmentation is given in Scheme 2.1.

Figure 2.1: IR spectra of 2-(4-hydroxyphenyl)-3-(6-methoxy-1,3-benzothiazol-2-yl)-5-methyl-1,3-thiazolidin-4-one (ABT-01(a))

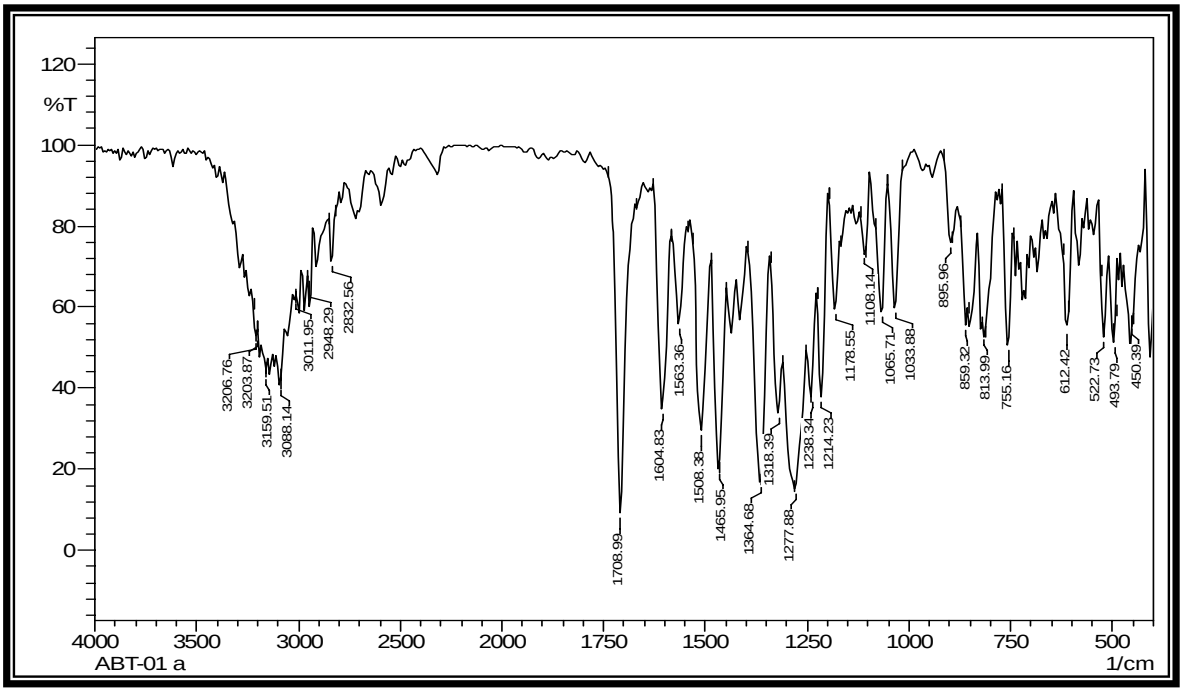


Table 2.2: IR spectra of 2-(4-hydroxyphenyl)-3-(6-methoxy-1,3-benzothiazol-2-yl)-5-methyl-1,3-thiazolidin-4-one (ABT-01(a))

Type	Vibration mode	Frequency in cm^{-1}	
		Observed	Reported [47]
Alkane (methyl)	C-H str. (asym.)	2948	2975-2950
	C-H str. (sym.)	2832	2880-2860
	C-H def. (asym.)	1455	1470-1435
	C-H def. (sym.)	1364	1385-1370
Aromatic	C-H str.	3068	3080-3030
	C=C	1563	1585-1570
	C-H i.p. def.	1108	1125-1090
	C-H o.o.p. def.	859	860-810
Thiazolidinone	C=O str.	1708	1760-1655
	C-N str.	1178	1220-1020
	C-S-N str.	612	700-600
Hydroxy	O-H str.	3203	3650-2590
	O-H def.	1318	1410-1310

Table 2.3: IR spectral data of 5-methyl 4-thiazolidinones.

Type	Vibration mode	Frequency in cm^{-1}	
		Observed	Reported
ABT-01 (b)			
Thiazolidinone	C=O str.	1704	1760-1655
	C-N str.	1172	1220-1020
	C-S-N str.	610	700-600
ABT-01 (c)			
Thiazolidinone	C=O str.	1700	1760-1655
	C-N str.	1164	1220-1020
	C-S-N str.	609	700-600
ABT-01 (d)			
Thiazolidinone	C=O str.	1712	1760-1655
	C-N str.	1176	1220-1020
	C-S-N str.	612	700-600
ABT-01 (e)			
Thiazolidinone	C=O str.	1706	1760-1655
	C-N str.	1172	1220-1020
	C-S-N str.	610	700-600
ABT-01 (f)			
Thiazolidinone	C=O str.	1718	1760-1655
	C-N str.	1180	1220-1020
	C-S-N str.	607	700-600
ABT-01 (g)			
Thiazolidinone	C=O str.	1713	1760-1655
	C-N str.	1176	1220-1020
	C-S-N str.	611	700-600
ABT-01 (h)			
Thiazolidinone	C=O str.	1710	1760-1655
	C-N str.	1170	1220-1020
	C-S-N str.	612	700-600
ABT-01 (i)			
Thiazolidinone	C=O str.	1708	1760-1655
	C-N str.	1176	1220-1020
	C-S-N str.	619	700-600
ABT-01 (j)			
Thiazolidinone	C=O str.	1704	1760-1655
	C-N str.	1178	1220-1020
	C-S-N str.	617	700-600

Figure 2.2: ^{1}HNMR spectra of 2-(4-hydroxyphenyl)-3-(6-methoxy-1,3-benzothiazol-2-yl)-5-methyl-1,3-thiazolidin-4-one (ABT-01(a))

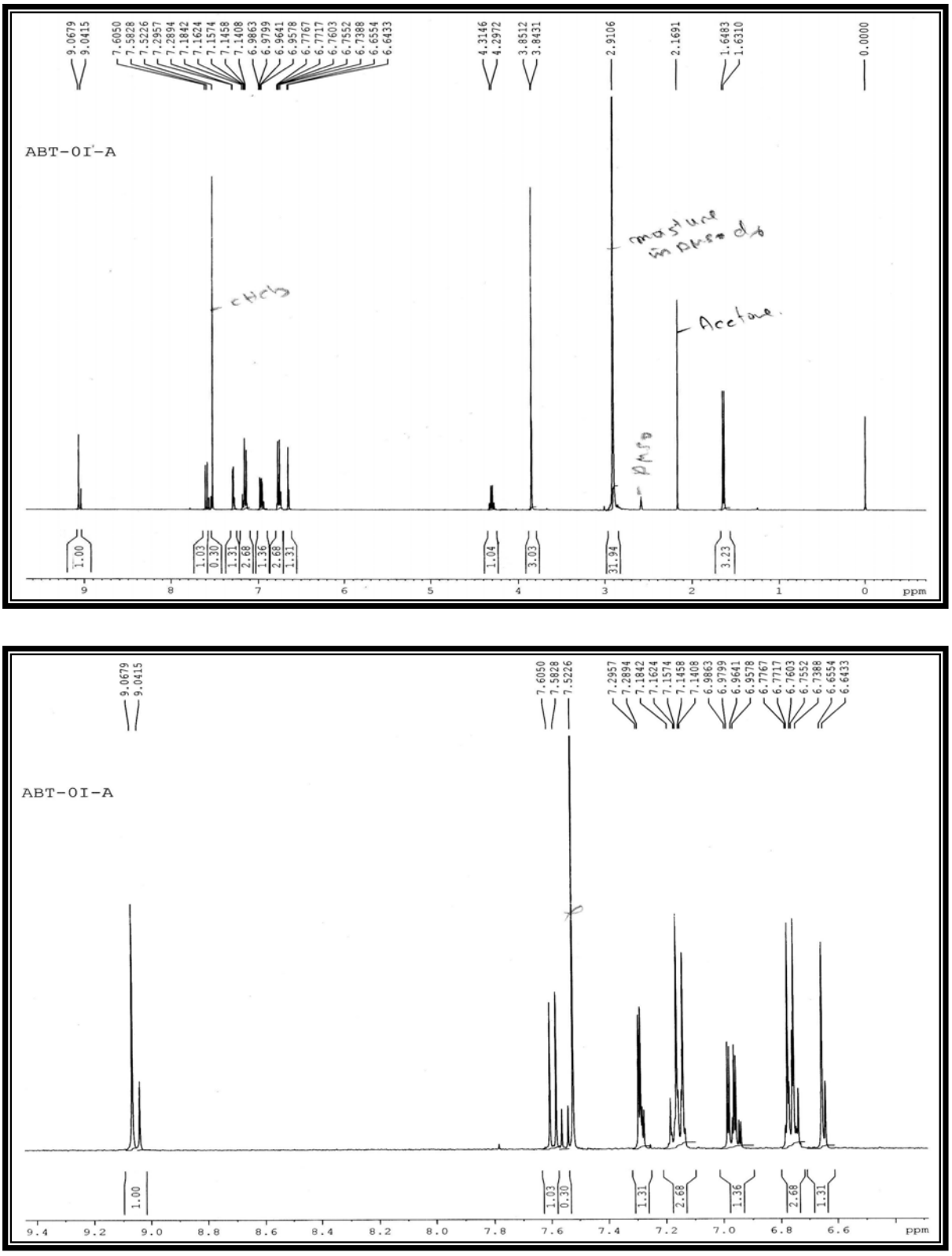
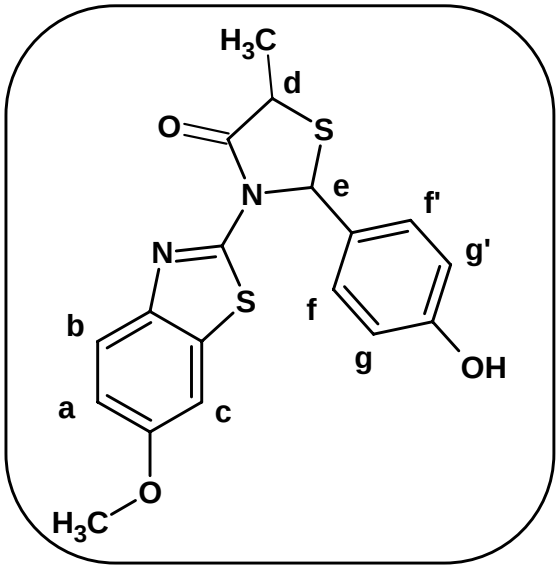
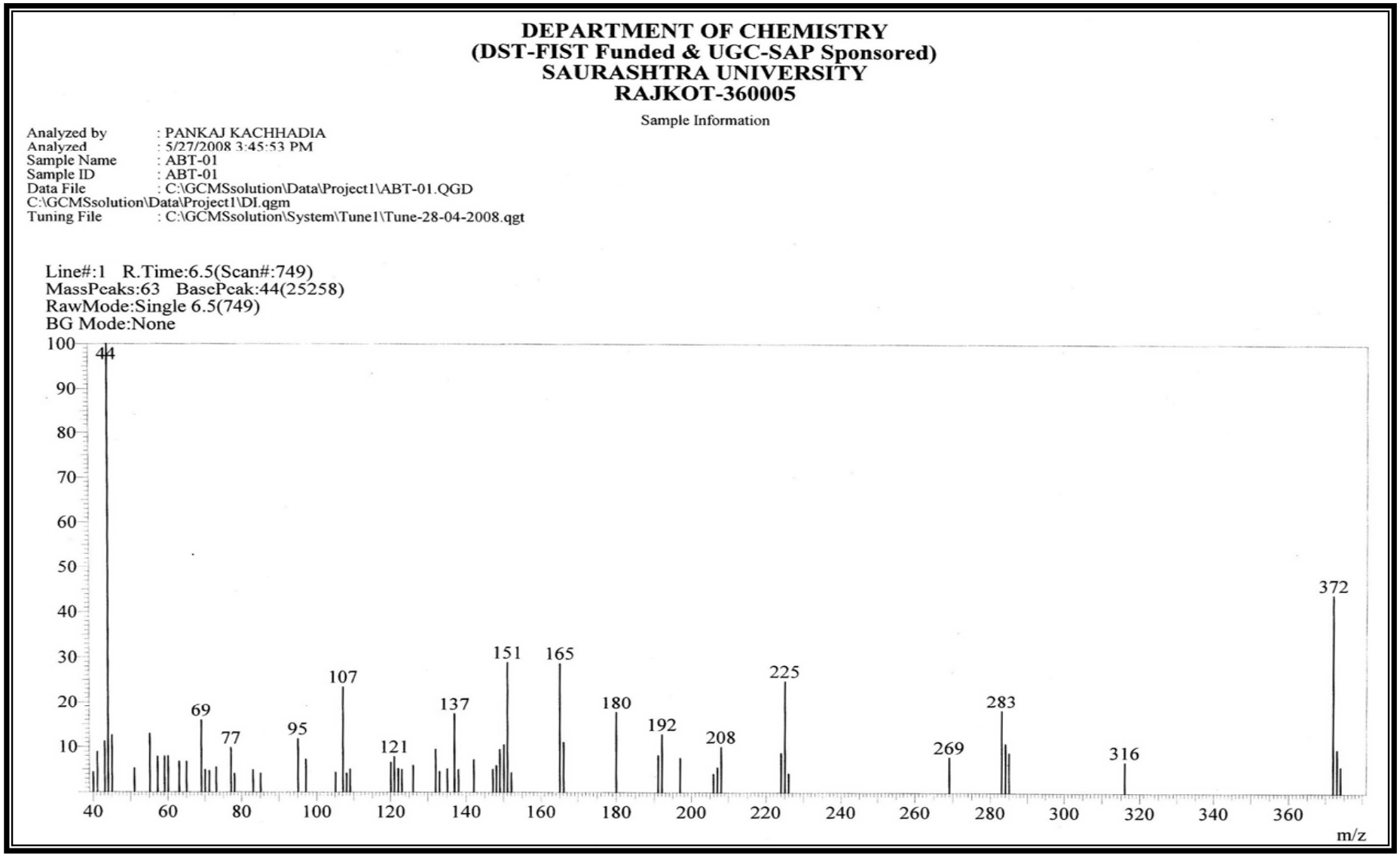


Table 2.4: ^{1}H NMR spectra of 2-(4-hydroxyphenyl)-3-(6-methoxy-1,3-benzothiazol-2-yl)-5-methyl-1,3-thiazolidin-4-one (ABT-01(a))

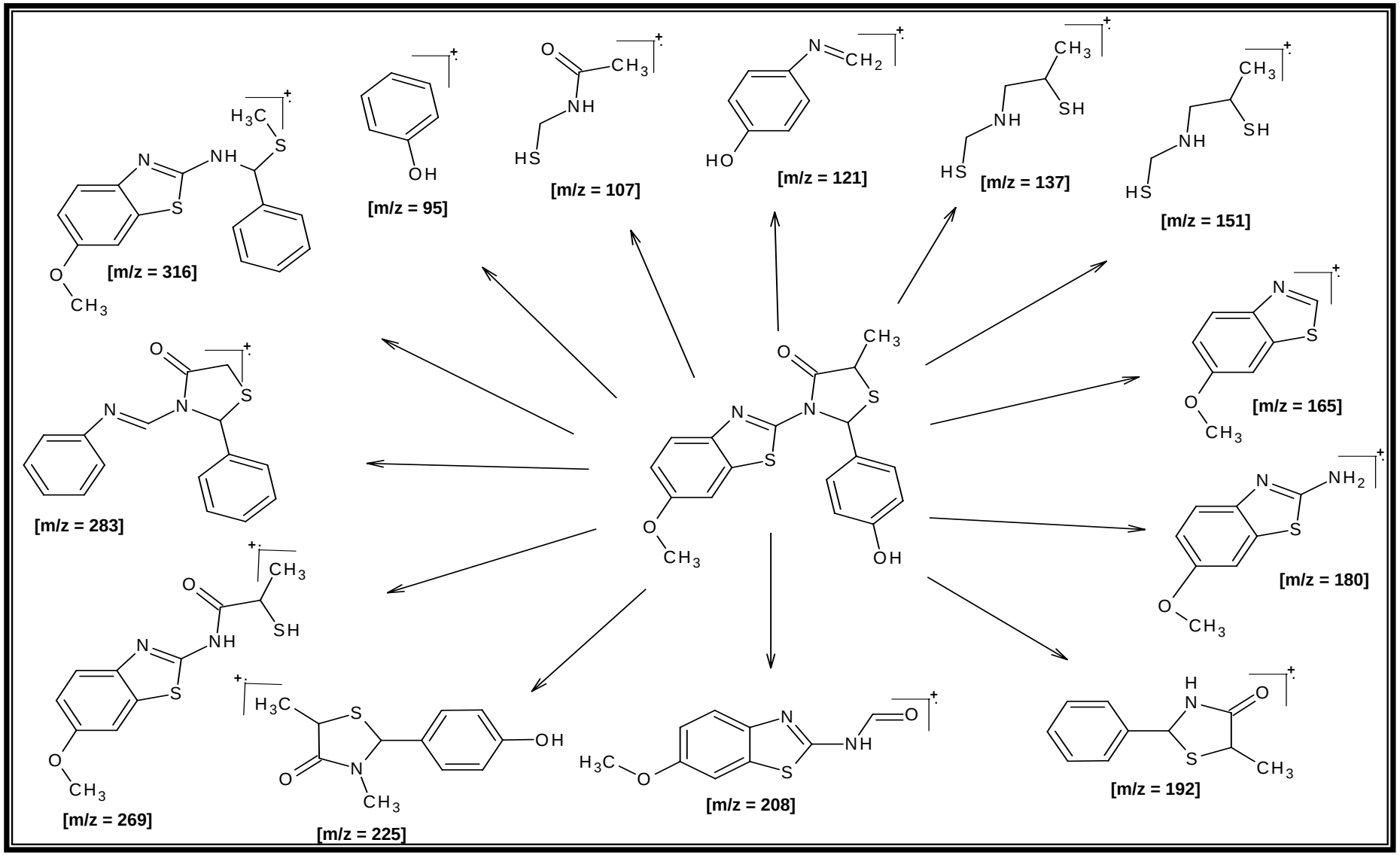


Signal No.	Signal Position (δ ppm)	Relative No. of Protons	Multiplicity	Inference	J (H_z)
1	1.64	3H	Doublet	-CH_3	-
2	3.85	3H	Singlet	Ar- OCH_3	-
3	4.29-4.31	1H	Doublet	-CH (d)	-
4	6.64-6.65	1H	Singlet	-CH (e)	-
5	6.73-6.77	2H	Multiplet	Ar-H (ff')	8.72 2.00
6	6.95-6.98	1H	Doublet	Ar-H (a)	2.56
7	7.14-7.18	2H	Multiplet	Ar-H (gg')	8.72 2.00
8	7.28-7.29	1H	Doublet	Ar-H (c)	2.52
9	7.58-7.60	1H	Doublet	Ar-H (b)	8.88
10	9.06	1H	Singlet	-OH	-

Figure 2.3: Mass spectra of 2-(4-hydroxyphenyl)-3-(6-methoxy-1,3-benzothiazol -2-yl)-5-methyl-1,3-thiazolidin-4-one (ABT-01(a))



Scheme 2.1: Proposed fragmentation of 2-(4-hydroxyphenyl)-3-(6-methoxy-1,3-benzothiazol -2-yl)-5-methyl-1,3-thiazolidin-4-one (ABT-01(a))



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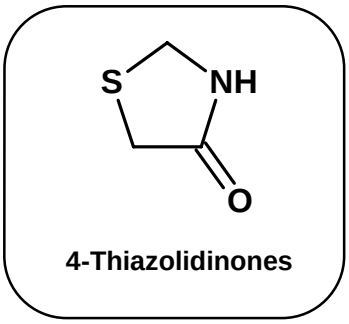
Section-III

Synthesis of 4-Thiazolidinone

INTRODUCTION

4-Thiazolidinones are derivatives of thiazolidine with a carbonyl group at 4-position. Substituents in the 2, 3 and 5 position may be varied, but greatest difference in structure and properties is exerted by the groups attached to carbon atom in the 2-position and to nitrogen atom in the 3-position. General structure of 4-Thiazolidinones is given below:



4-Thiazolidinones

4-Thiazolidinones play a vital role due to their wide range of biological activities and industrial importance. 4-Thiazolidinones are always being an attraction point for researchers because of its efficiency towards various pharmacological usages [1, 2].

A well known antibiotic, actithiazic acid, isolated from a species of streptomyces shows specific *in vitro* activity against *M. tuberculosis*, but it is inactive *in vivo* probably due to antagonisation by biotin, bears the 4-thiazolidinone skeleton.

4-thiazolidinone is synthesized by the cyclisation of acyclic compounds or by the interconversion among appropriately substituted thiazolidinone derivatives. Different methods for the preparation of 4-thiazolidinone are available in literature. [3-6].

Dandia *et al.* [7] have synthesized thiazolidinone derivatives and reported their antifungal activity. Bioactive venlafaxine analogs such as 2,3-disubstituted-1,3-thiazolidinones have been synthesized and reported as antimicrobial agent by Kavitha *et al.* [8]. Denis *et al.* [9] have synthesized 4-thiazolidinones derivatives by the cyclization unsymmetrical thioureas. Some nickel (II) complexes of 4-thiazolidinone has been synthesized by Dave *et al.* [10]. Various worker have applied the Green chemistry approach to the

synthesis of 4-thiazolidinone derivatives by using microwave assisted method and multi component reaction method [11-13]

Various 4-thiazolidinone derivatives are known to exhibit biological cactivities such as antibacterial [14-16], antimicrobial [17-19], anti psychotic [20], anti cancer [21, 22], antiviral [23], anticonvulsant [24, 25], anti HIV [26, 27], antiamebic [28], nematicidal [29], anti-inflammatory [30-32] etc. Sayyed *et al.* [33] synthesized antibacterial 2,3-diaryl-1,3-thiazolidin-4-one derivatives having a antipyrine, 2,6-dichlorophenyl and 1,2,4-triazole moiety. Vagdevi *et al.* [34] synthesized thiazolidinone derivative of naphtha[2,1-b]furan.

EXPERIMENTAL

Synthesis of 2-(4-hydroxyphenyl)-3-(6-methoxy-1,3-benzothiazol-2-yl)-1,3-thiazolidin-4-one

[A] Synthesis of 6-methoxy 2-amino benzothiazole:

Section-1 (A)

[B] Synthesis of 4-[(Z)-[(6-methoxy-1,3-benzothiazole-2-yl)imino] methyl] phenol

Section-1 (B)

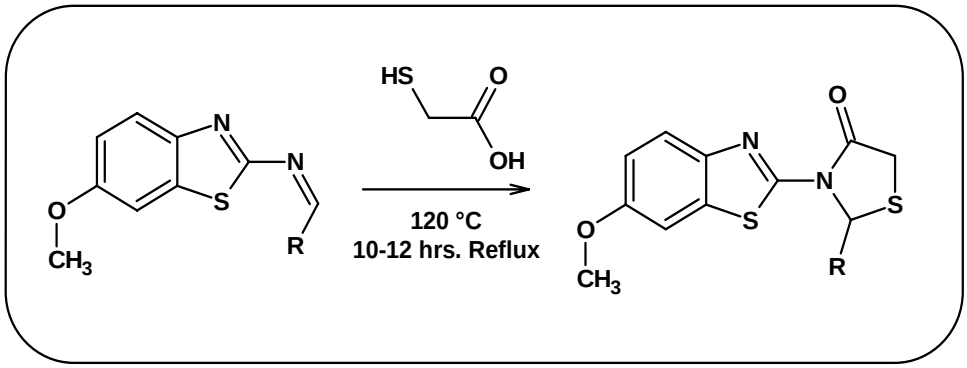
[C] Synthesis of 2-(4-hydroxyphenyl)-3-(6-methoxy-1,3-benzothiazol-2-yl)-1,3-thiazolidin-4-one

A mixture of 4-[(Z)-[(6-methoxy-1,3-benzothiazole-2-yl)imino] methyl] phenol 0.01M and thioglycolic acid 0.01M was heated at 120°C for 10-12 hrs. The reaction mixture was cooled and treated with 10% sodium bicarbonate solution. The solid product was thus separated, filtered and washed with water and crystallized from absolute ethanol.

Similarly other Schiff bases were condensed with thioglycolic acid.

REACTION SCHEME

[A] Synthesis of 2-(4-hydroxyphenyl)-3-(6-methoxy-1,3-benzothiazol-2-yl)-1,3-thiazolidin-4-one



The various physical constants such as R_f value, melting point and percentage of yield for all the synthesized 4-Thiazolidinones are given in Table 3.1.

Table 3.1: Physical constants of 4-Thiazolidinones

Sr. No.	Code	R	M.F.	M. Wt. (g/mol)	R_f^* Value	M.P. °C	Yield %
1	ABT-02 (a)	4-OH-C_6H_4	$C_{17}H_{14}N_2O_3S_2$	358.43	0.42	201	78
2	ABT-02 (b)	2-OH-C_6H_4	$C_{17}H_{14}N_2O_3S_2$	358.43	0.44	167	76
3	ABT-02 (c)	4-Cl-C_6H_4	$C_{17}H_{13}ClN_2O_2S_2$	376.88	0.49	192	61
4	ABT-02 (d)	3-Cl-C_6H_4	$C_{17}H_{13}ClN_2O_2S_2$	376.88	0.47	179	54
5	ABT-02 (e)	3-NO_2-C_6H_4	$C_{17}H_{13}N_3O_4S_2$	387.43	0.53	194	62
6	ABT-02 (f)	2-NO_2-C_6H_4	$C_{17}H_{13}N_3O_4S_2$	387.43	0.56	167	66
7	ABT-02 (g)	-CH=CH-C_6H_5	$C_{19}H_{16}N_2O_2S_2$	368.47	0.56	143	59
8	ABT-02 (h)	4-F-C_6H_4	$C_{17}H_{13}FN_2O_2S_2$	342.60	0.49	176	58
9	ABT-02 (i)	1-Napthaline	$C_{21}H_{16}N_2O_2S_2$	392.49	0.45	189	70
10	ABT-02 (j)	9-Antracin	$C_{25}H_{20}N_2O_2S_2$	444.56	0.46	192	66

* Hexane: Ethyl acetate-5:5

The characterization was done by IR, ^{1}H NMR and mass spectra. The IR spectra for ABT-02 (a) is given in Fig. 3.1. The IR spectral data for this compound and other synthesized compounds are reported in Tables 3.2 and 3.3 respectively. The NMR spectra is shown in Fig. 3.2 for ABT-02 (a) and the corresponding data is reported in Table 3.4. The mass spectra of the same compound is given in Fig. 3.3 and the proposed mass fragmentation is given in Scheme 3.1.

Figure 3.1: IR spectra of 2-(4-hydroxyphenyl)-3-(6-methoxy-1,3-benzothiazol -2-yl)-1,3-thiazolidin-4-one (ABT-02(a))

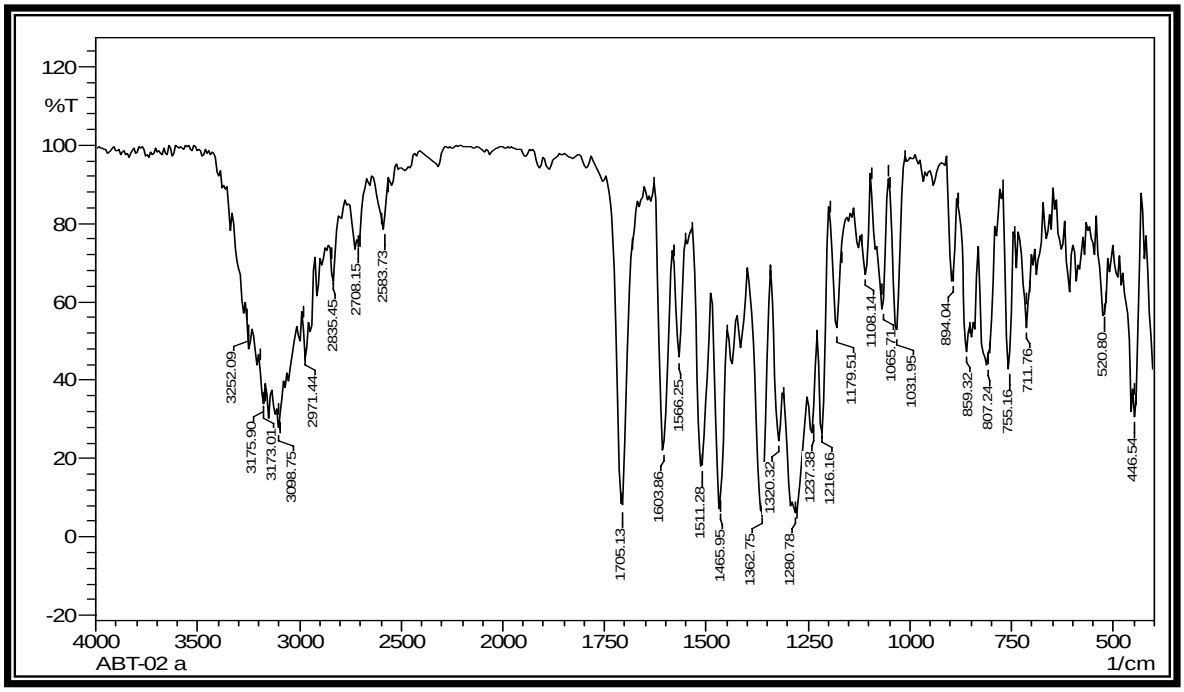


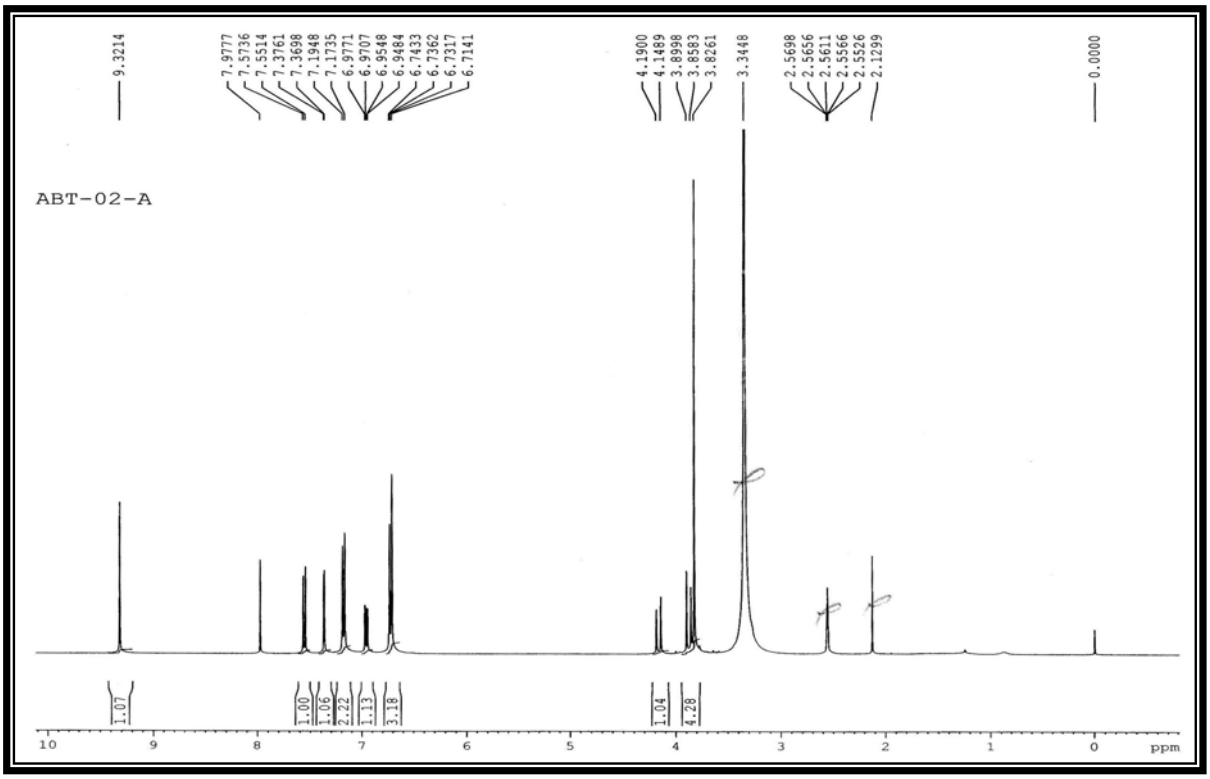
Table 3.2: IR spectra of 2-(4-hydroxyphenyl)-3-(6-methoxy-1,3-benzothiazol-2-yl)-1,3-thiazolidin-4-one (ABT-02(a))

Type	Vibration mode	Frequency in cm^{-1}	
		Observed	Reported [47]
Alkane (methyl)	C-H str. (asym.)	2971	2975-2950
	C-H str. (sym.)	2835	2880-2860
	C-H def. (asym.)	1465	1470-1435
	C-H def. (sym.)	1320	1385-1370
Aromatic	C-H str.	3098	3080-3030
	C=C	1566	1585-1570
	C-H i.p. def.	1108	1125-1090
	C-H o.o.p. def.	859	860-810
Thiazolidinone	C=O str.	1705	1760-1655
	C-N str.	1179	1220-1020
	C-S-N str.	711	700-600
Hydroxy	O-H str.	3252	3650-2590
	O-H def.	1320	1410-1310

Table 3.3: IR spectral data of 4-thiazolidinones.

Type	Vibration mode	Frequency in cm^{-1}	
		Observed	Reported
ABT-02 (b)			
Thiazolidinone	C=O str.	1708	1760-1655
	C-N str.	1170	1220-1020
	C-S-N str.	710	700-600
ABT-02 (c)			
Thiazolidinone	C=O str.	1709	1760-1655
	C-N str.	1168	1220-1020
	C-S-N str.	712	700-600
ABT-02 (d)			
Thiazolidinone	C=O str.	1702	1760-1655
	C-N str.	1177	1220-1020
	C-S-N str.	712	700-600
ABT-02 (e)			
Thiazolidinone	C=O str.	1708	1760-1655
	C-N str.	1172	1220-1020
	C-S-N str.	710	700-600
ABT-02 (f)			
Thiazolidinone	C=O str.	1708	1760-1655
	C-N str.	1180	1220-1020
	C-S-N str.	707	700-600
ABT-02 (g)			
Thiazolidinone	C=O str.	1715	1760-1655
	C-N str.	1178	1220-1020
	C-S-N str.	711	700-600
ABT-02 (h)			
Thiazolidinone	C=O str.	1713	1760-1655
	C-N str.	1173	1220-1020
	C-S-N str.	712	700-600
ABT-02 (i)			
Thiazolidinone	C=O str.	1708	1760-1655
	C-N str.	1174	1220-1020
	C-S-N str.	719	700-600
ABT-02 (j)			
Thiazolidinone	C=O str.	1704	1760-1655
	C-N str.	1175	1220-1020
	C-S-N str.	717	700-600

Figure 3.2: ^{1}HNMR spectra of 2-(4-hydroxyphenyl)-3-(6-methoxy-1,3-benzothiazol-2-yl)-1,3-thiazolidin-4-one (ABT-02(a))



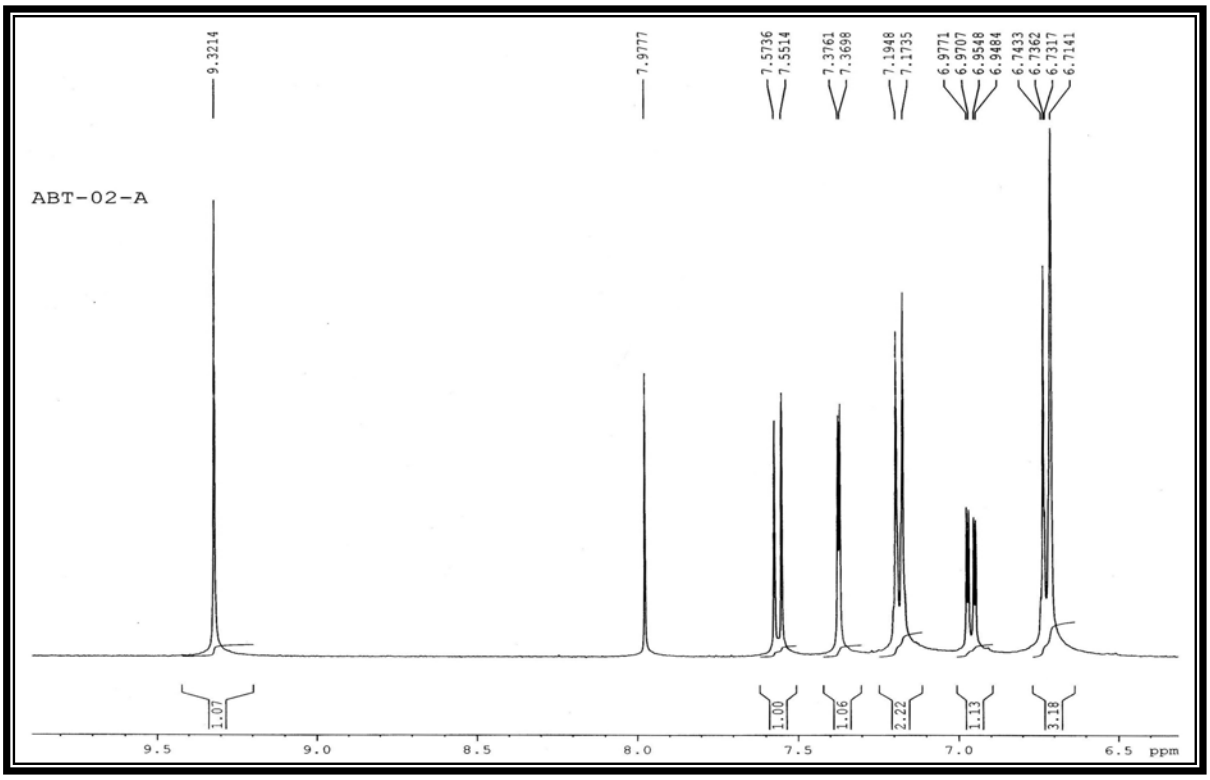
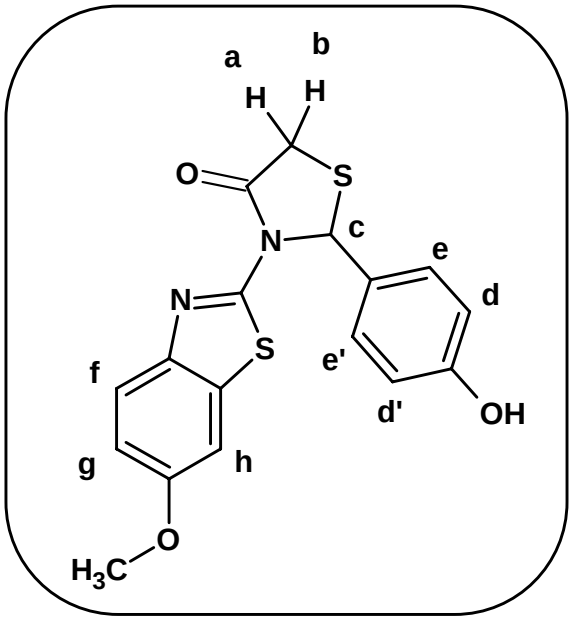
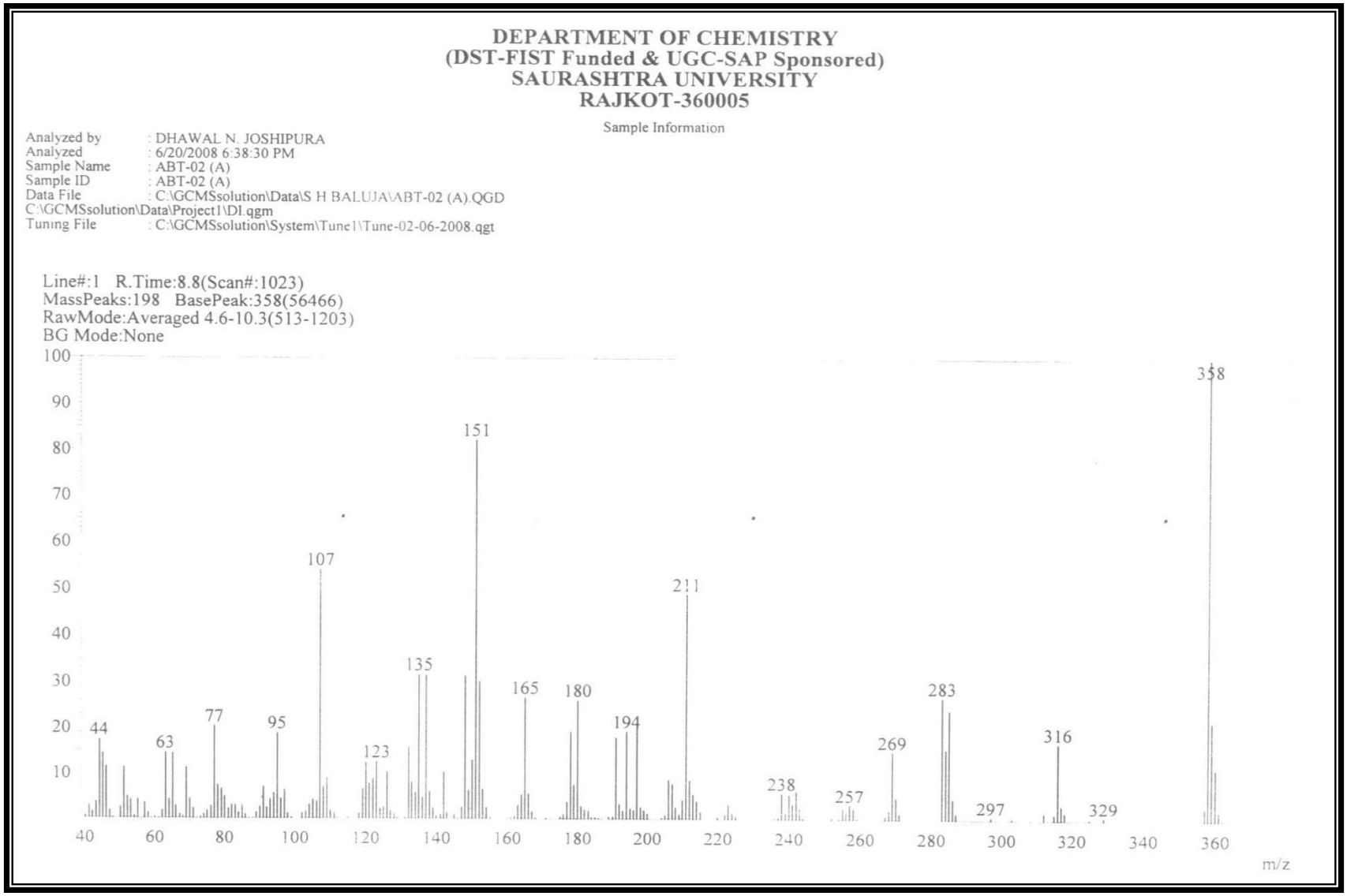


Table 3.3: ^{1}H NMR spectra of 2-(4-hydroxyphenyl)-3-(6-methoxy-1,3-benzothiazol-2-yl)-1,3-thiazolidin-4-one (ABT-02(a))

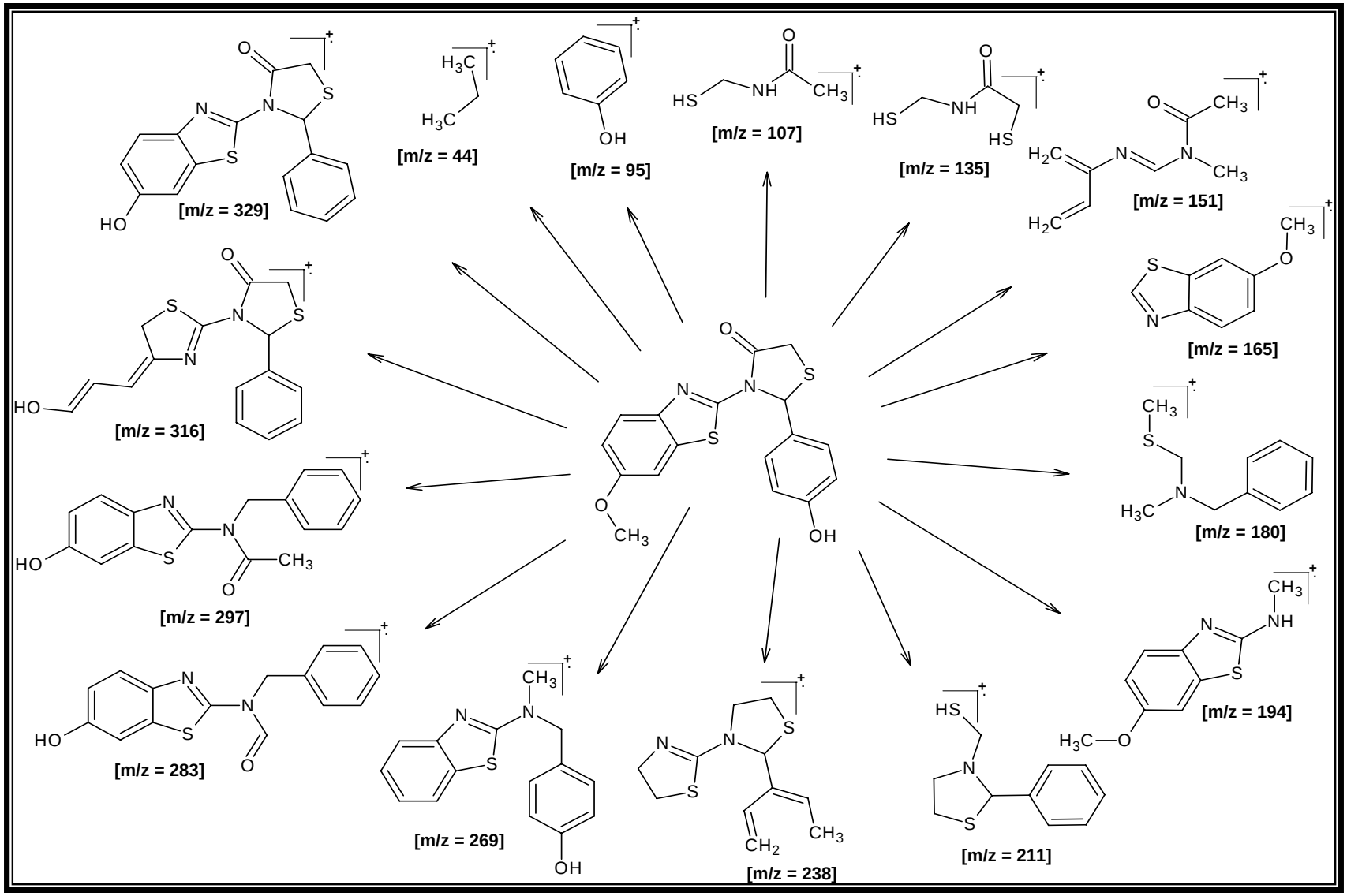


Signal No.	Signal Position (δ ppm)	Relative No. of Protons	Multiplicity	Inference	J (H_z)
1	3.85	3H	Singlet	Ar- OCH_3	-
2	4.14-4.19	2H	Doublet	-CH (a+b)	16.44 16.60
3	6.71-6.74	3H	Multiplet	-CH (c+d)	2.84
4	6.94-6.97	1H	Multiplet	Ar-H (g)	2.80
5	7.17-7.19	2H	Doublet	Ar-H (e)	8.52
6	7.36-7.37	1H	Doublet	Ar-H (h)	2.52
7	7.55-7.57	1H	Doublet	Ar-H (f)	8.88
8	9.32	1H	Singlet	-OH	-

Figure 3.3: Mass spectra of 2-(4-hydroxyphenyl)-3-(6-methoxy-1,3-benzothiazol -2-yl)-1,3-thiazolidin-4-one (ABT-02(a))



Scheme 3.1: Proposed fragmentation of 2-(4-hydroxyphenyl)-3-(6-methoxy-1,3-benzothiazol -2-yl)-1,3-thiazolidin-4-one (ABT-02(a))



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Part-2

Synthesis of Chalcones from furan derivatives

INTORDUCTION

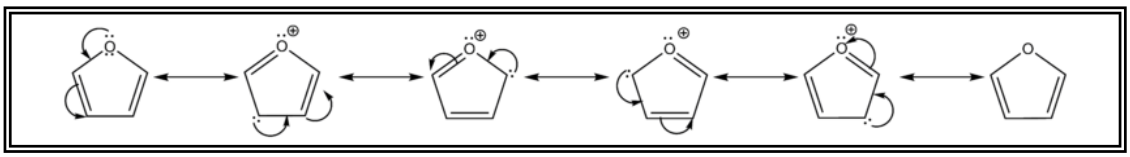
Furan:

Furan derivatives comprise an industrially significant class of heterocyclic compounds. The furan ring system is found in many naturally occurring compounds, either as a fully unsaturated structure or in a reduced or partly reduced form.

Reactivity of the furan nucleus is directly related to the electron density at particular ring atoms.

Furan is aromatic because one of the lone pairs of electrons on the oxygen atom is delocalized into the ring, creating a 4n+2 aromatic system similar to benzene. Because of the aromaticity, the molecule is flat and lacks discrete double bonds. The other lone pair of electrons of the oxygen atom extends in the plane of the flat ring system. The sp^2 hybridization is to allow one of the lone pairs of oxygen to residue in a p orbital and thus allow it to interact within the π system. Due to its aromaticity, furan's behavior is quite dissimilar to that of the more typical heterocyclic ethers such as tetrahydrofuran.

It is considerably more reactive than benzene in electrophilic substitution reactions, due to the electron-donating effects of the oxygen heteroatom. Examination of the resonance contributors shows the increased electron density of the ring, leading to increased rates of electrophilic substitution.



Furans which occur in nature in a reduced or otherwise modified form include pentose sugars such as ribose and deoxyribose, which are components of nucleic acids, and several types of unsaturated lactone such as ascorbic acid.

Furan derivatives have been found to wide range of biological activites such as pesticidal [1], insecticidal [2, 3], antiviral [4, 5], antifungal [6-9], antitumor [10-13], anti-inflammatory [14-15], antidepressant [16] etc.

Chalcones:

The chemistry of chalcones generated intensive scientific studies throughout the world, specially interesting for their biological and industrial applications. Chalcones are coloured compounds because of the presence of the chromophore and auxochromes. They are known as benzalacetophenones or benzylidene acetophenones. Kostanecki and Tambor gave the name Chalcone. The alternative names given to chalcones are phenyl styryl ketones, b-phenyl acrylphenone, g-oxo-a,g-diphenyl-a-propylene and a-phenyl-b-benzoethylene.

Chalcones are characterized by their possession of a structure in which two aromatic rings are linked by an aliphatic three carbon chain.

A considerable variety of methods are available in literature for the synthesis of chalcones [17-23]. The most convenient method is the one which involves the Claisen-Schimidt condensation of equimolar quantities of an aryl methyl ketones with aryl aldehyde in presence of alcoholic alkali [24].

Several condensing agents such as alkali of different strength [24, 25] aluminium chloride [26], anhydrous boron trifluoride [27], hydrochloric acid [28], piperidine[29] etc are used in the synthesis.

The chalcones have been found to be useful for the synthesis of a variety of heterocyclic compounds such as cyanopyridone [30], pyridopyrimidines [31], amino pyrimidines [32], 3-cyanopyridines [33], isoxazoles [34], thiazepines [35], pyrazolines [36], oxirane [37], barbitone [38], oxopyrimidines [39], 1-carboxamide pyrazolines [40], 2-1H-pyrimidines [41], imine derivatives [42].

Chalcones are associated with different biological activities like cardiovascular [43], antispasmodic [44], anthelmintics [45, 46], antiulcer [47, 48], anti-inflammatory [49-51], antiviral [52], antiallergic [53], fungicidal [54-56], bactericidal [57, 58], insecticidal [59-61], antitumor [62-64], antileishmanial [65], herbicidal [66], anticancer [67, 68], antitubercular [69], anti HIV [70] etc.

Mudalir and Joshi [71] reported insecticidal activity of some phenoxy chalcones. Ko et al. [72] have prepared some new chalcones for potent inhibition of platelet aggregation. Ziegler et al. [73] reported some chalcones as antiparasitic. The antimalarial activities of chalcones have also been reported by Xue et al. [74] and Dominguez et al. [75]. Seo et al. [76] have synthesized

chalcones derivatives and reported them as a-glucosidase inhibitors. Larsen and co-worker [77] and Wu et al. [78] have reported anti-plasmodial activity and Boeck and et al. [79] have reported anti leishmanial activity of some chalcones. Analogs containing nitro, fluorine or bromine group respectively displayed increased selectivity against the parasites as compared with natural chalcone.

In the present chapter some new chalcones were synthesized.

EXPERIMENTAL

[A] Synthesis of 5-(3-nitrophenyl) furan-2-carbaldehyde

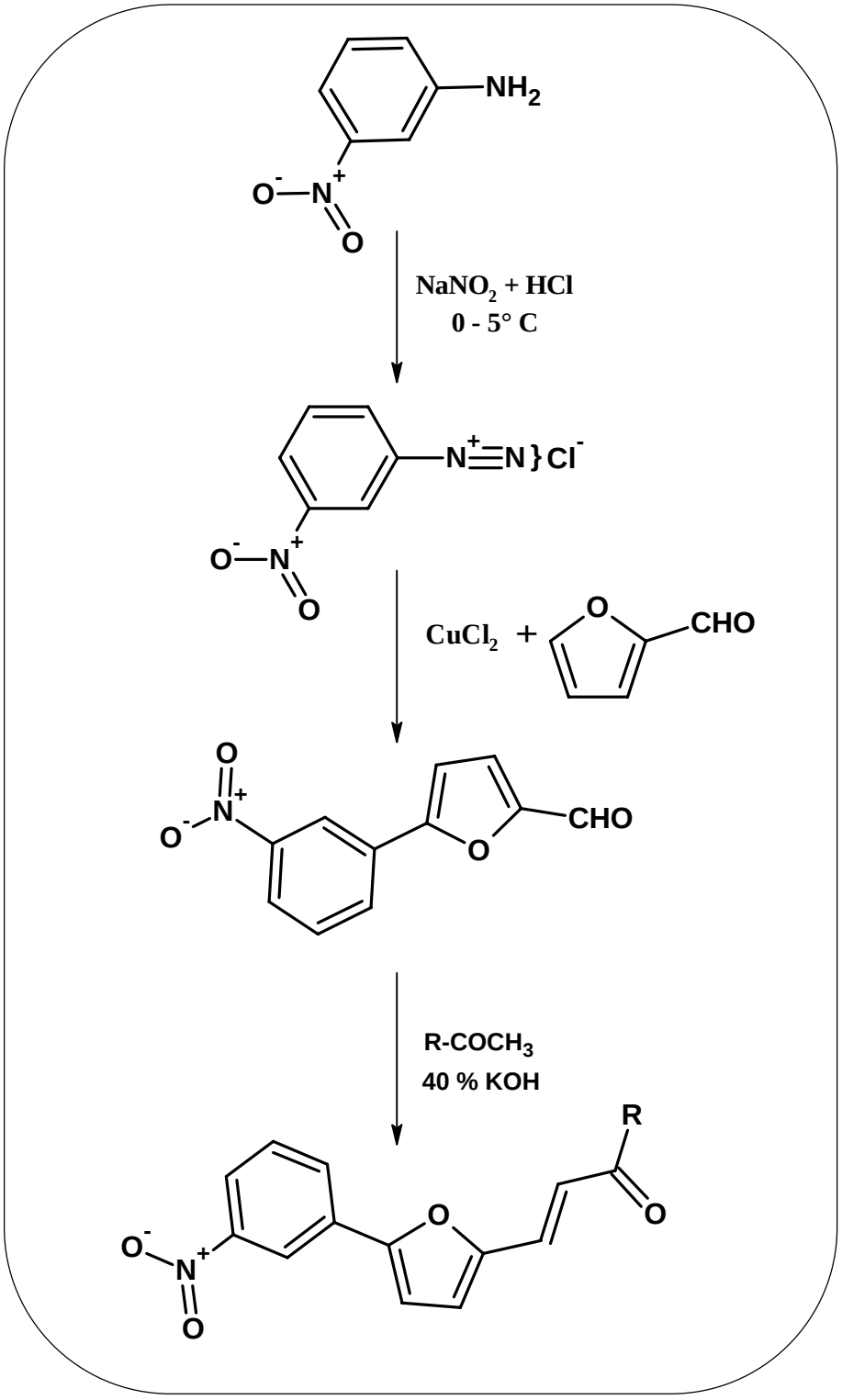
A mixture of 3-nitro aniline (0.01 M), dil. HCl (15%) and water was heated to get a clear solution. The solution was cooled to 0°C and diazotized with $NaNO_2$ solution (30%). The diazonium salt solution was filtered. Water, freshly distilled furfural (0.01 M) and aqueous cupric chloride (2.5 g in water) were added to the filtrate with stirring. The stirring was continued for 4 hrs. and kept overnight. The separated solid was collected by filtration and washed with cold ethanol. The product was crystallized from a mixture of ethanol-DMF. Yield 80%,

[B] Synthesis of (2E)-1-(4-methoxyphenyl)-3-[5-(3-nitrophenyl) furan-2-yl] prop-2-en-1-one

A solution of p-methoxyacetophenone (0.01 M) in minimum quantity of ethanol was added to a mixture of 5-(m-nitro)-2-furaldehyde (0.01 M) in ethanol and 40% NaOH was added to make it alkaline. The reaction mixture was then stirred for 24 hrs. at room temperature. The product was isolated and crystallized from DMF.

Similarly other 1-aryl-3-[5'-(m-nitro)-2'-furyl]-2-propene-1-one were also prepared.

REACTION SCHEME



The various physical constants such as R_f value, melting point and percentage of yield for all the synthesized chalcones are given in Table 2.1.

Table 2.1: Physical constants of Chalcones.

Sr. No.	Compound Code	R	M.F.	M. Wt. (g/mol)	R_f^* Value	M.P. °C	Yield %
1	AKFC-01	4-OCH_3-C_6H_4	$C_{20}H_{15}NO_5$	349.33	0.48	141	58
2	AKFC-02	4-NO_2-C_6H_4	$C_{19}H_{12}N_2O_6$	364.30	0.50	218	54
3	AKFC-03	3-NO_2-C_6H_4	$C_{19}H_{12}N_2O_6$	364.30	0.54	180	62
4	AKFC-04	4-NH_2-C_6H_4	$C_{19}H_{14}N_2O_4$	334.32	0.44	171	58
5	AKFC-05	4-Cl-C_6H_4	$C_{19}H_{12}NO_4Cl$	353.75	0.42	170	60
6	AKFC-06	4-Br-C_6H_4	$C_{19}H_{12}NO_4Br$	398.20	0.48	160	68
7	AKFC-07	-C_6H_5	$C_{19}H_{13}NO_4$	319.31	0.47	142	60
8	AKFC-08	4-OH-C_6H_4	$C_{19}H_{13}NO_5$	335.31	0.51	152	56
9	AKFC-09	2-Furan	$C_{14}H_{11}NO_5$	309.27	0.57	178	55
10	AKFC-10	3-coumarin	$C_{22}H_{13}NO_6$	387.34	0.48	172	62

* Hexane: Ethyl acetate-8:2

The characterization was done by IR, ^{1}H NMR and mass spectra. The IR spectra for AKFC-01 is given in Fig. 2.1. The IR spectral data for this compound and other synthesized compounds are reported in Tables 2.2 and 2.3 respectively. The NMR spectra is shown in Fig. 2.2 for AKFC-01 and the corresponding data is reported in table 2.4. The mass spectra of the same compound is given in Fig. 2.3 and the proposed mass fragmentation is given in Scheme 2.1.

Figure 2.1: IR spectra of (2E)-1-(4-methoxyphenyl)-3-[5-(3-nitrophenyl) furan-2-yl] prop-2-en-1-one (AKFC-01).

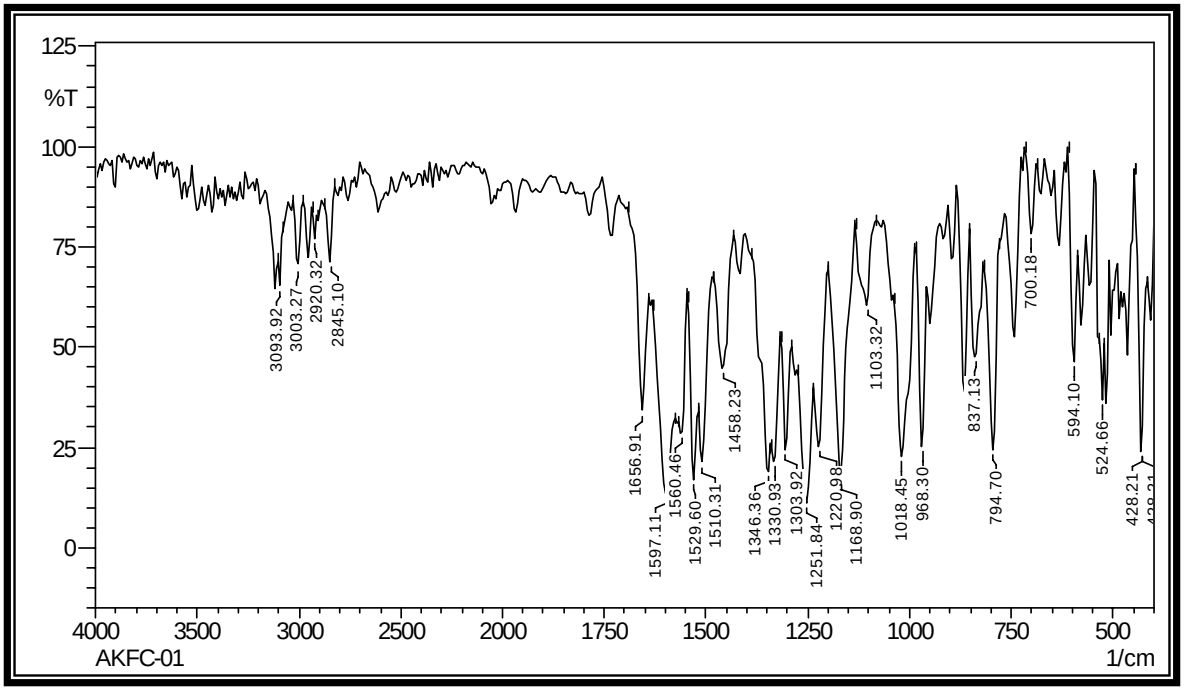


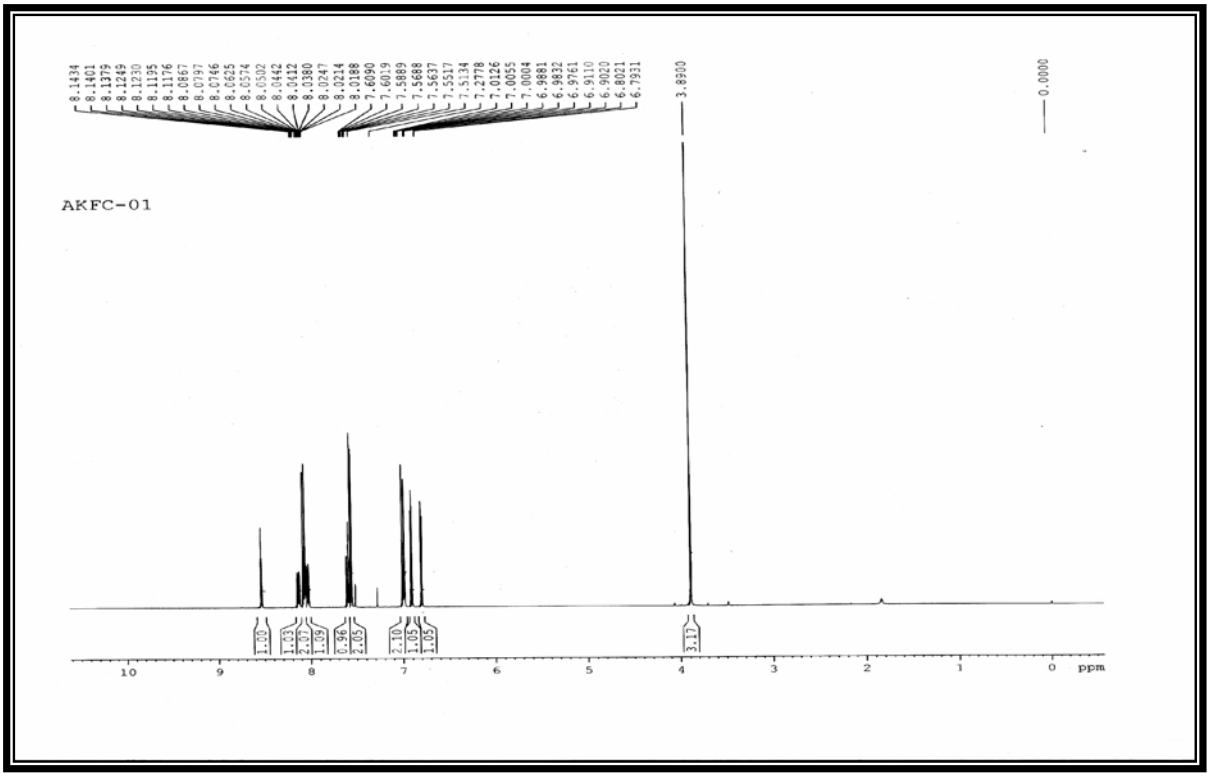
Table 2.2: IR spectral data of (2E)-1-(4-methoxyphenyl)-3-[5-(3-nitrophenyl) furan-2-yl] prop-2-en-1-one (AKFC-01).

Type	Vibration mode	Frequency in cm^{-1}	
		Observed	Reported[80]
Alkane (methyl)	C-H str. (asym.)	2920	2975-2920
	C-H str. (sym.)	2845	2880-2860
	C-H def. (asym.)	1458	1470-1435
	C-H def. (sym.)	1346	1395-1370
Aromatic	C-H str.	3003	3100-3000
	C=C	1510	1585-1480
	C-H i.p. def.	1103	1125-1090
	C-H o.o.p. def.	837	860-810
Furyl moiety	C-O-C str. (sym.)	1251	1275-1200
	C-O-C str. (asym.)	1018	1075-1010
Vinyl	CH=CH str.	3093	3050-3000
Chalcone	C=O str.	1657	1685-1645

Table 2.3: IR spectral data of chalcones.

Type	Vibration mode	Frequency in cm^{-1}	
		Observed	Reported[80]
AKFC-02			
Vinyl	CH=CH str.	3086	3050-3000
Chalcone	C=O str.	1658	1685-1645
AKFC-03			
Vinyl	CH=CH str.	3076	3050-3000
Chalcone	C=O str.	1662	1685-1645
AKFC-04			
Vinyl	CH=CH str.	3082	3050-3000
Chalcone	C=O str.	1654	1685-1645
AKFC-05			
Vinyl	CH=CH str.	3066	3050-3000
Chalcone	C=O str.	1659	1685-1645
AKFC-06			
Vinyl	CH=CH str.	3078	3050-3000
Chalcone	C=O str.	1661	1685-1645
AKFC-07			
Vinyl	CH=CH str.	3088	3050-3000
Chalcone	C=O str.	1659	1685-1645
AKFC-08			
Vinyl	CH=CH str.	3090	3050-3000
Chalcone	C=O str.	1641	1685-1645
AKFC-09			
Vinyl	CH=CH str.	3081	3050-3000
Chalcone	C=O str.	1657	1685-1645
AKFC-10			
Vinyl	CH=CH str.	3070	3050-3000
Chalcone	C=O str.	1662	1685-1645

Figure 2.2: ^{1}HNMR spectra of (2E)-1-(4-methoxyphenyl)-3-[5-(3-nitro phenyl) furan-2-yl] prop-2-en-1-one (AKFC-01)



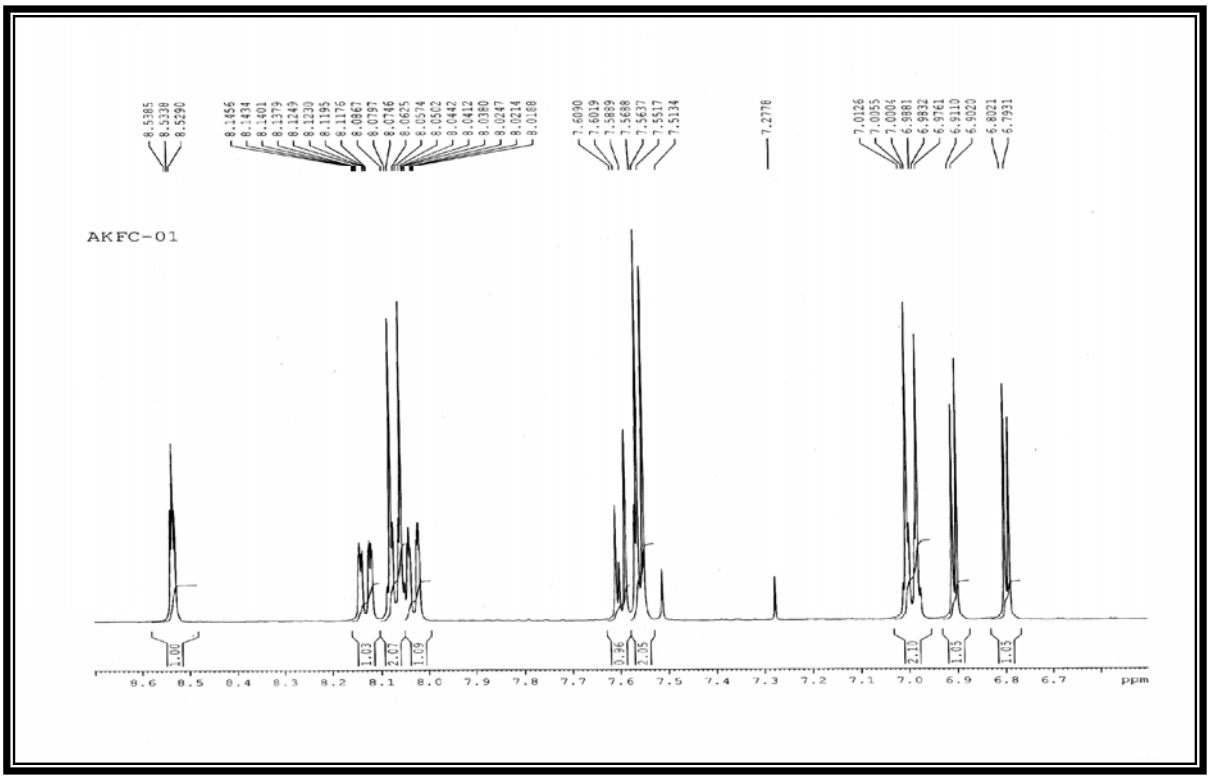
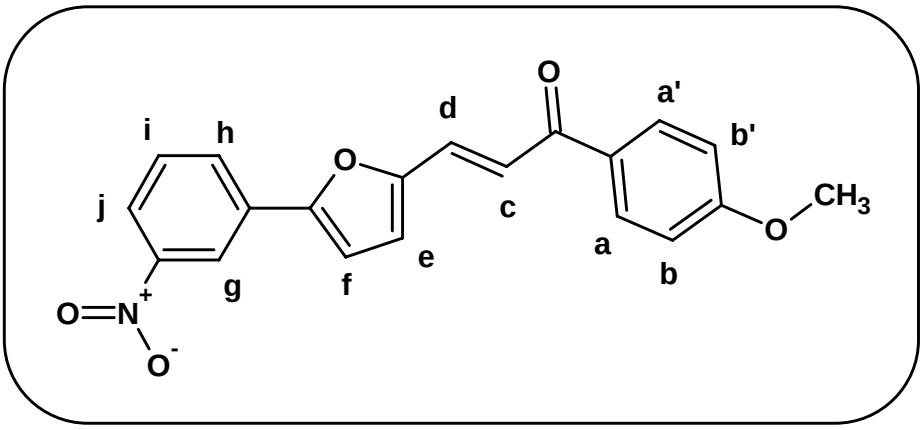
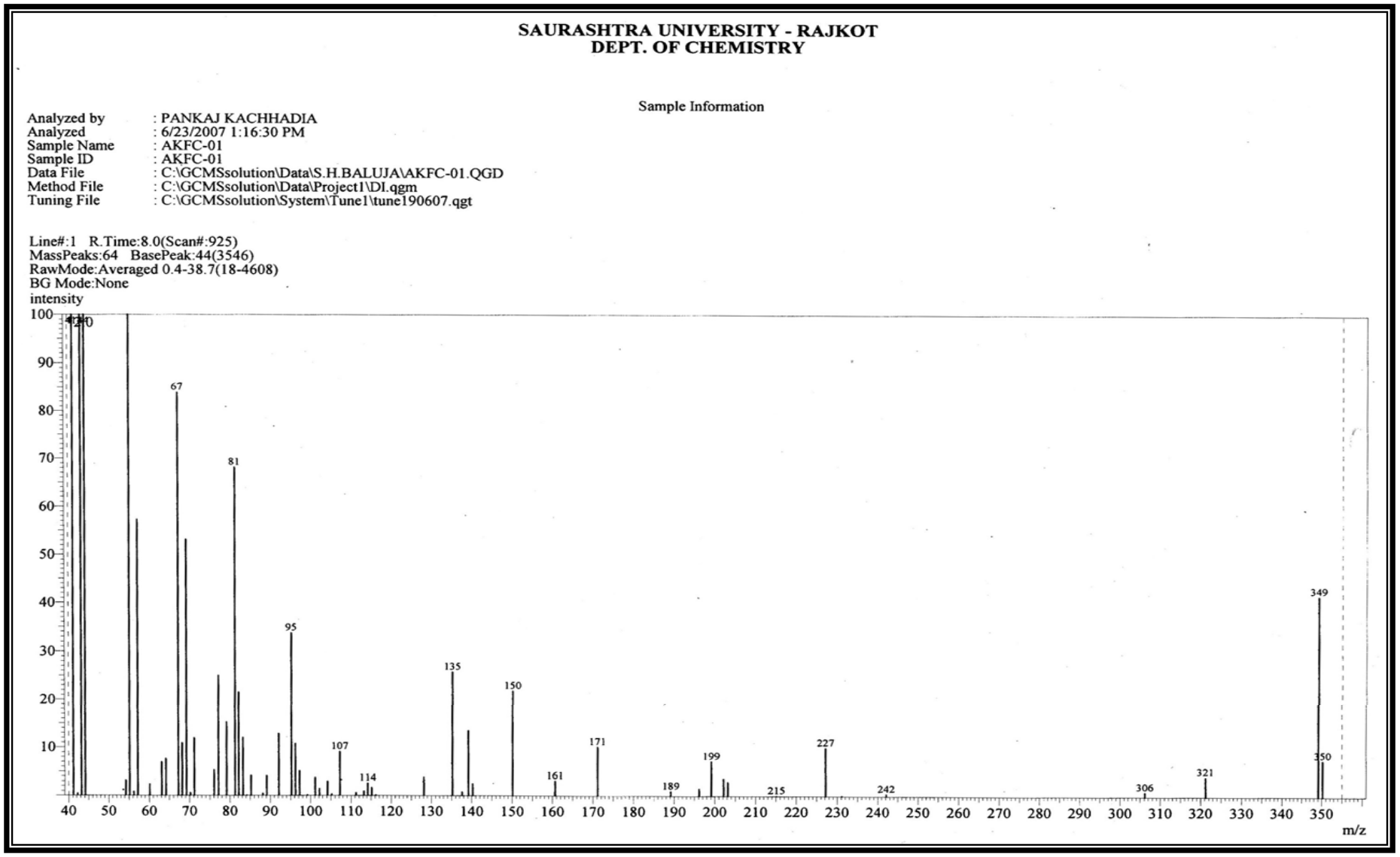


Table 2.4: ^{1}H NMR spectral data of (2E)-1-(4-methoxyphenyl)-3-[5-(3-nitrophenyl) furan-2-yl] prop-2-en-1-one (AKFC-01)

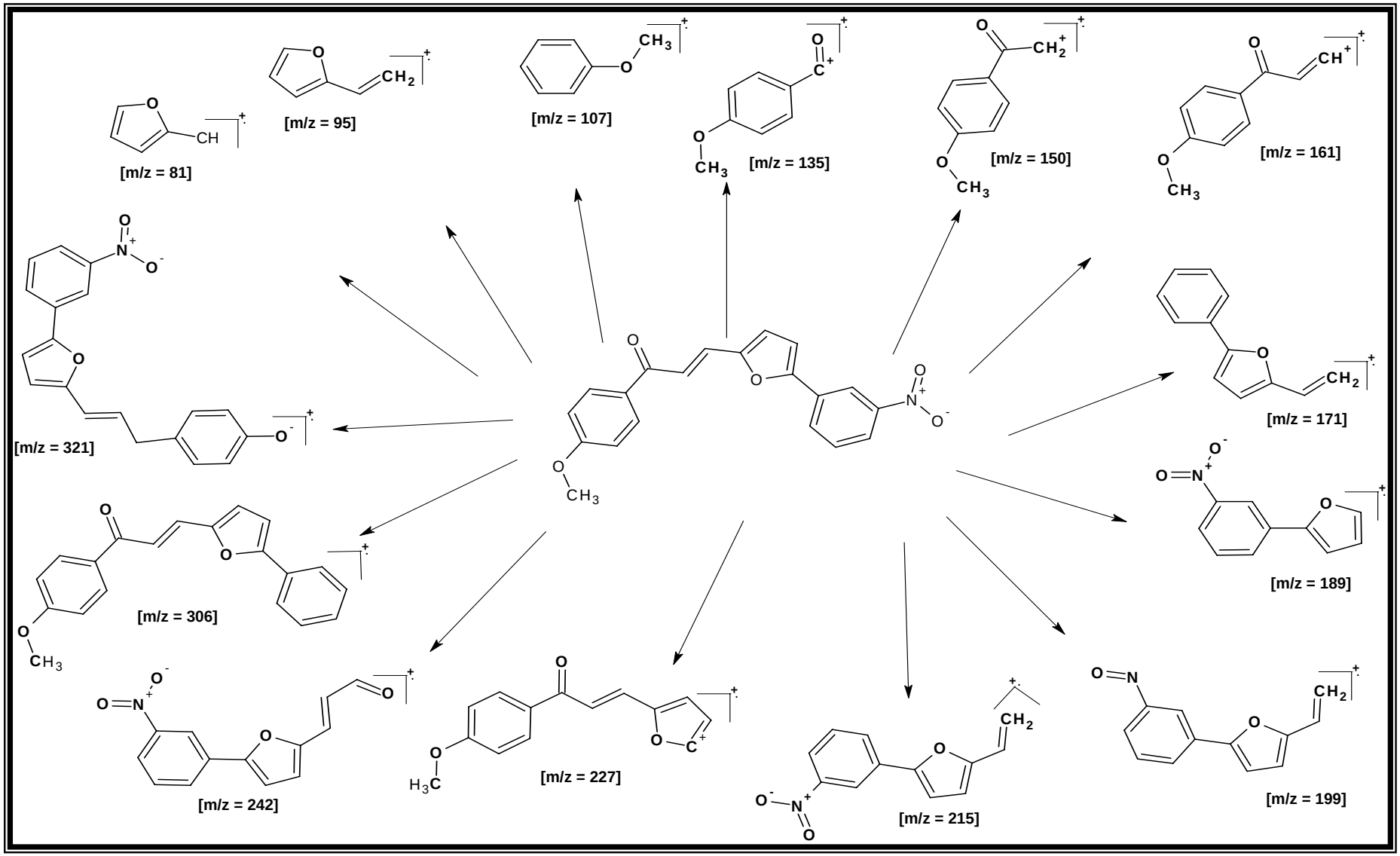


Signal No.	Signal Position (δ ppm)	Relative No. of Protons	Multiplicity	Inference	J (H_z)
1	3.89	3H	Singlet	Ar-OCH_3	-
2	6.79-6.80	1H	Doublet	Furyl-H	3.60
3	6.90-6.91	1H	Doublet	Furyl-H	3.60
4	6.97-7.01	2H	Doublet	Ar-H (bb')	8.60
5	7.55	1H	Doublet	Vin-c	6.84
6	7.56	1H	Doublet	Vin-d	6.84
7	7.58-7.60	1H	D-Doublet	Ar-H (i)	8.04
8	8.01-8.04	1H	Multiplet	Ar-H (h)	-
9	8.05-8.08	2H	Doublet	Ar-H (aa')	8.60
10	8.11-8.14	1H	Multiplet	Ar-H (j)	-
11	8.52-8.53	1H	D-Doublet	Ar-H (g)	1.90

Figure 2.3: Mass spectra of (2E)-1-(4-methoxyphenyl)-3-[5-(3-nitro phenyl) furan-2-yl]prop-2-en-1-one (AKFC-01)



Scheme 2.1: Proposed fragmentation of (2E)-1-(4-methoxyphenyl)-3-[5-(3-nitro phenyl) furan-2-yl] prop-2-en-1-one (AKFC-01).



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Part-3

Comparison of different methods used for the Synthesis of Schiff bases of 2-amino benzothiazole

INTORDUCTION

A big challenge facing academia and industry is the relationship of modern societies to the environment that requires reinventing the manufacture and use of materials. Synthetic methodologies now a day should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

In recent years, environmentally benign synthetic methods have received considerable attention and some solvent-free protocols have been developed [1-5]. Grinding together solid anilines and solid benzaldehydes yielded various kinds of benzylideneanilines [6]. The synthesis of primary imines by condensation of 2-hydroxylaryl ketones with ammonium iodide and piperidine under solvent free conditions [7]. Based on these facts, this prompted us to synthesize some Schiff bases of 6-methoxy-1, 3-benzothiazol-2-amine using the microwave-assisted method (MW), ultrasonic irradiation (US) and Conventional thermal method (Con.)

Conventionally Schiff bases have been prepared by refluxing mixtures of the amine and the carbonyl compound in an organic solvent, for example, ethanol or methanol, In general, ketones react more slowly than aldehydes and higher temperatures and longer reaction times are often required as a result. In addition, the equilibrium must often be shifted, usually by removal of the water, either azeotropically by distillation or with suitable drying agents [8].

The microwave region of the electromagnetic spectrum lies between 1 cm and 1 m, most domestic and commercial microwave instruments operate at 2.45 GHz. When a molecule is irradiated with microwaves, it rotates to align itself with the applied field. The frequency of molecular rotation is similar to the frequency of microwave radiation and consequently the molecule continually attempts to realign itself with the changing field and energy is absorbed. It is particularly convenient that qualitatively, the larger the dielectric constant the great the coupling with microwaves. Thus, solvents such as water, methanol, DMF, ethyl acetate, acetone, chloroform, acetic acid and dichloromethane are all heated when irradiated with microwaves.

In the last few years, Microwave-induced Organic Reaction Enhancement (MORE) chemistry has gained popularity as a non-conventional technique for rapid organic synthesis [9]. Many researchers have reported the synthetic utility of MORE chemistry in routine organic synthesis [10, 11]. Compared to traditional processing of organic synthesis, microwave-enhanced chemistry saves significant time and very often improves conversions, clean product formation etc. Further, it offers low cost with simplicity in processing and handling [12]. This technique has been used to promote a variety of chemical reactions such as additions, cycloadditions, substitutions, eliminations, fragmentations etc [13-17]. Recently much has been done in microwave enhanced solvent-free organic synthesis [18-25].

Further, ultrasonic waves have been used for organic synthesis [26-28]. These ultrasonic waves have frequencies greater than 20,000 cycles/sec. The ultrasound waves are known for their wide applications in various fields like life sciences, medical, cleaning, sonar, electronics, agriculture, oceanography, material science etc [29-33]. Literature survey shows that few workers synthesized some compounds using ultrasonic technique [34-43], at lower reaction temperature and in less reaction time [44]. Therefore in the present chapter, some Schiff bases have been synthesized by conventional method, microwave technique and by using ultrasound waves. The reaction scheme for the synthesis is already given in Section-I of Chapter-2 in experimental part.

RESULTS AND DISCUSSIONS

The % yield, reaction time and amount of catalyst used in different techniques are reported in Table 1. It is observed that using microwave and ultrasonic waves, the reaction time is reduced considerably whereas % yield increased markedly.

Further, the amount of catalyst required in these techniques is very less in comparison to conventional method.

Thus, microwave and ultrasonic proved to be better technique than conventional method.

Table 1 Comparison of Microwave-induced (MW), Ultrasonic irradiation (US) and Conventional thermal (Con.) methods.

Code	Yield (%)			Reaction time (min.)			Catalyst amount (ml)		
	MW	US	Con.	MW	US	Con.	MW	US	Con.
AKBS-01	89	86	62	8	120	480	0.1	0.3	0.6
AKBS-02	82	79	65	11	120	480	0.1	0.3	0.6
AKBS-03	86	72	55	12	135	720	0.2	0.3	0.5
AKBS-04	79	68	59	10	130	600	0.2	0.3	0.5
AKBS-05	84	73	45	8	120	540	0.3	0.4	0.4
AKBS-06	89	74	49	12	120	720	0.1	0.2	0.6
AKBS-07	86	69	58	10	120	720	0.2	0.3	0.5
AKBS-08	90	71	69	12	135	600	0.1	0.3	0.5
AKBS-09	87	78	45	10	150	600	0.2	0.4	0.6
AKBS-10	86	76	48	12	120	720	0.2	0.3	0.5

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Chapter-3

Physico Chemical Properties

Section-I

Acoustical Properties

INTRODUCTION

Ultrasonic deals with study and application of high frequency sound waves usually in excess of 20 KHz (20,000 cycles per second). It works on the basis of piezoelectric effect [1-3].

Ultrasound has come to play an important role in our daily life. Due to its non-destructive nature [4-6] it has wide range of application in different fields like chemical industries, consumer industries, medical field, process industries, physics, chemistry, biology etc [7-12]. Further, it is one of the most rapid and reliable technique for the characterization of materials.

In medical field, ultrasound was used to detect gall stones and foreign bodies in soft tissues. It is also used for various diagnosis such as pediatrics [13, 14], vascular diseases [15, 16], brain diseases [17], ophthalmology [18, 19], in urology [20, 21], in cancer cell [22, 23] etc. It is also useful to obtain the information about lung microstructure [24] and biological structures [25]. It is safe for both patient and operator. It is also applied for inactivation of micro-organisms in food [26-28] and dairy industry [29-31].

More recently, a lot of interest has been generated on the use of ultrasound radiation in synthetic organic chemistry, which includes decrease of reaction time, increase of yield, lower reaction temperature, avoidance of phase transfer catalysis etc [32-37].

Another area where ultrasonic is now a day being used, is to obtain the information microstructures [38]. It is reported that these ultrasonic waves provide valuable information about the structure of solids [39, 40]. By ultrasonic velocity measurements, the molecular interactions in pure liquids [41-44], aqueous solutions [45-49] and liquid mixtures [50-53] can also be studied. It provides a powerful, effective and reliable tool to investigate properties of polymers [54-63], carbohydrates [64-66], amino acids [67-70], solution of simple salts [71-76] etc. However, very little work has been done for solid organic compounds [77-81]. In our laboratory, ultrasonic measurements for some Schiff bases in different solvents have been reported [82-84].

Thus, in the present section, ultrasonic studies of Chalcones in dimethylformamide (DMF) and chloroform ($CHCl_3$) and of Schiff bases in

dimethylformamide (DMF) and dimethylsulfoxide (DMSO) have been reported at 308.15 K with a view to understand the molecular interactions in these solutions.

EXPERIMENTAL

Dimethylformamide (DMF) and Chloroform ($CHCl_3$) for chalcones whereas for Schiff bases Dimethylformamide (DMF) and Dimethylsulfoxide (DMSO) have been chosen as solvents in the present study. The choice of different solvents for chalcones and Schiff bases is due to their different solubility in these solvents. These solvents are distilled by the reported procedure [85]. For some compounds, there was solubility problem so measurement for those compounds could not be done.

The synthesized chalcones and Schiff bases are recrystallized before use.

The densities, viscosities and ultrasonic velocities of solvents and solutions of different concentration were measured at 308.15 K by using pyknometer, an Ubbelohde suspended level viscometer and single frequency ultrasonic interferometer operating at 2 MHz, with the uncertainties of 0.0001 g/cm^3, ±0.06 % and 0.01 % respectively.

Density measurements:

The weight of distilled water, pure solvents and solution of chalcones and Schiff bases were measured by using pyknometer. The densities were evaluated by using following equation:

$$\rho(g/cm^3) = \frac{(\text{Wt. of solvent or solution})(\text{density of water})}{(\text{wt.of water})} \quad \ldots\ldots (1.1)$$

Viscosity Measurements:

To determine the viscosity of solution, Ubbelohde viscometer [86] was used, which obeys Stoke's low [87]. The measured quantity of the distilled water / solvent / solution was placed in the viscometer, which was suspended in a thermostat at 308.15 K. The digital stopwatch, with an accuracy of + 0.01 sec was used to determine flow time of solutions. Using the flow times (t) and known viscosity of standard water sample, the viscosity of solvent and solutions were determined according to equation:

$$\frac{\eta_1}{\eta_2} = \frac{t_1\rho_1}{t_2\rho_2} \quad \text{..... (1.2)}$$

Sound velocity measurement:

Ultrasonic interferometer (Mittal Enterprise, New Delhi, Model No. F-81) working at frequency of 2 MHz was used to determine sound velocity.

The solvent / solution were filled in the measuring cell with quartz crystal and then micrometer was fixed. The circulation of water from the thermostat at 308.15 K was started and test solvent / solution in the cell is allowed to thermally equilibrate. The micrometer was rotated very slowly so as to obtain a maximum or minimum of anode current (n). A number of maximum reading of anode current were counted. The total distance (d) travel by the micrometer for n=10, was read. The wave length (λ) was determined according to the equation (1.3).

$$\lambda = \frac{2d}{n} \quad \text{..... (1.3)}$$

The sound velocity (U) of solvent and solutions were calculated from the wavelength and frequency (F) according to equation (1.4).

$$U = \lambda F \quad \text{..... (1.4)}$$

RESULT AND DISCUSSIONS

Tables 1.1 and 1.2 shows the experimental data of data of density (ρ), viscosity (η) and sound velocity (U) of pure solvents and different chalcones and Schiff bases solutions at 308.15 K.

From these experimental data, various acoustical parameters like specific acoustical impendence (Z), isentropic compressibility (κ_s), intermolecular free length (L_f), Roa's molar sound function (R_m), molar compressibility (W), Vander Waals constant (b), relaxation strength (r), internal pressure (π), free volume (V_f), apparent molar volume (ϕ_v), apparent molar compressibility (ϕ_k) etc., were evaluated using the following equations:

1. Specific acoustical impedance:

Specific acoustical impedance (Z) can be calculated as:

$$Z = U\rho \qquad \text{..... (1.5)}$$

2. Isentropic compressibility:

Isentropic compressibility (κ_s) can be evaluated by the equation [88]:

$$\kappa_s = \frac{1}{U^2\rho} \qquad \text{..... (1.6)}$$

3. Intermolecular free path length:

Jacobson [89] proposed an equation to calculate the intermolecular free length (L_f), which is given below:

$$L_f = K_j \kappa_s^{1/2} \qquad \text{..... (1.7)}$$

where K_j is Jacobson constant = 2.0965 X 10^{-6}

4. Molar compressibility:

Molar compressibility (W) can be calculated by the following equation [90]

$$W = \left(\frac{M}{\rho}\right)\kappa_s^{-1/7} \qquad \text{..... (1.8)}$$

The apparent molecular weight (M) of the solution can be calculated according to equation (1.9):

$$M = M_1W_1 + M_2W_2 \qquad \text{..... (1.9)}$$

Table 1.1: The density (ρ), ultrasonic velocity (U) and viscosity (η) of chalcones in DMF and $CHCl_3$ at 308.15K.

Conc. (M)	ρ g. cm^{-3}	U x 10^{-5} cm/s	η x 10^{3} poise	ρ g. cm^{-3}	U x 10^{-5} cm/s	η x 10^{3} poise
AKFC-01		**DMF**			**Chloroform**	
0.00	0.9233	1.4448	7.6367	1.4402	0.9941	6.3929
0.01	0.9240	1.4500	7.6256	1.4404	0.9536	6.4693
0.02	0.9252	1.4504	7.7399	1.4406	0.9554	6.5232
0.04	0.9265	1.4533	7.8505	1.4410	0.9568	6.6310
0.06	0.9272	1.4534	7.9538	1.4413	0.9584	6.6401
0.08	0.9283	1.4540	8.1191	1.4416	0.9608	6.7019
0.10	0.9290	1.4555	8.3740	1.4420	0.9655	6.7490
AKFC-05		**DMF**			**Chloroform**	
0.01	0.9240	1.4446	7.6619	1.4405	0.9518	6.4962
0.02	0.9251	1.4450	7.7026	1.4407	0.9532	6.5087
0.04	0.9263	1.4454	7.7758	1.4412	0.9556	6.5901
0.06	0.9277	1.4457	7.9313	1.4416	0.9592	6.6260
0.08	0.9282	1.4463	8.0159	1.4419	0.9616	6.7413
0.10	0.9288	1.4464	8.0918	1.4422	0.9642	6.7877
AKFC-06		**DMF**			**Chloroform**	
0.01	0.9242	1.4402	7.6587	1.4408	0.9502	6.4637
0.02	0.9250	1.4405	7.6921	1.4413	0.9512	6.5493
0.04	0.9265	1.4407	7.7848	1.4418	0.9539	6.6120
0.06	0.9272	1.4413	7.9197	1.4423	0.9578	6.6674
0.08	0.9280	1.4418	8.0069	1.4428	0.9594	6.7110
0.10	0.9289	1.4430	8.0976	1.4431	0.9622	6.8451
AKFC-07		**DMF**			**Chloroform**	
0.01	0.9244	1.4421	7.6774	1.4423	0.9510	6.4743
0.02	0.9251	1.4448	7.7463	1.4426	0.9531	6.5059
0.04	0.9265	1.4464	7.8432	1.4431	0.9554	6.5610
0.06	0.9275	1.4490	7.9758	1.4435	0.9578	6.5780
0.08	0.9284	1.4498	8.1078	1.4439	0.9604	6.6859
0.10	0.9292	1.4518	8.3148	1.4441	0.9644	6.9144
AKFC-08		**DMF**			**Chloroform**	
0.01	0.9230	1.4404	7.6490	1.4412	0.9504	6.4804
0.02	0.9237	1.4402	7.6964	1.4414	0.9529	6.5536
0.04	0.9240	1.4417	7.7252	1.4419	0.9546	6.6163
0.06	0.9241	1.4434	7.8061	1.4423	0.9571	6.6787
0.08	0.9263	1.4437	7.8854	1.4427	0.9595	6.7182
0.10	0.9287	1.4446	7.9886	1.4429	0.9623	6.7496
AKFC-09		**DMF**			**Chloroform**	
0.01	0.9241	1.4444	7.6628	1.4413	0.9559	6.4733
0.02	0.9246	1.4446	7.6888	1.4416	0.9564	6.5164
0.04	0.9254	1.4455	7.7174	1.4421	0.9577	6.5753
0.06	0.9256	1.4481	7.8186	1.4425	0.9579	6.7252
0.08	0.9276	1.4524	7.9888	1.4430	0.9595	6.7839
0.10	0.9306	1.4526	8.4329	1.4432	0.9609	6.8458
AKFC-10		**DMF**			**Chloroform**	
0.01	0.9245	1.4443	7.6952	1.4414	0.9508	6.4512
0.02	0.9253	1.4446	7.7336	1.4418	0.9510	6.4947
0.04	0.9273	1.4447	7.9109	1.4423	0.9525	6.5347
0.06	0.9284	1.4450	8.1324	1.4428	0.9558	6.5937
0.08	0.9302	1.4480	8.2823	1.4432	0.9567	6.6716
0.10	0.9314	1.4492	8.5326	1.4435	0.9620	6.8735

Table 1.2: The density (ρ), ultrasonic velocity (U) and viscosity (η) of Schiff bases in DMF and DMSO at 308.15K.

Conc. (M)	ρ g. cm^{-3}	U x 10^{-5} cm/s	η x 10^{3} poise	ρ g. cm^{-3}	U x 10^{-5} cm/s	η x 10^{3} poise
AKBS-01		**DMF**			**DMSO**	
0.00	0.9214	1.4136	7.1304	1.0546	1.4660	10.6786
0.01	0.9225	1.4188	7.2726	1.0548	1.4688	10.8684
0.02	0.9237	1.4216	7.4801	1.0556	1.4752	11.1029
0.04	0.9249	1.4296	7.6717	1.0569	1.4808	11.2235
0.06	0.9255	1.4372	7.7688	1.0578	1.4876	11.3879
0.08	0.9267	1.4504	7.9017	1.0585	1.4928	11.5658
0.10	0.9298	1.4588	8.1141	1.0593	1.5016	11.7743
AKBS-02		**DMF**			**DMSO**	
0.01	0.9222	1.4208	7.8079	1.0549	1.4676	11.4215
0.02	0.9236	1.4244	7.9057	1.0556	1.4716	11.4821
0.04	0.9242	1.4308	8.2338	1.0564	1.4732	11.7369
0.06	0.9254	1.4336	8.4017	1.0582	1.4756	11.8288
0.08	0.9275	1.4400	8.5423	1.0587	1.4788	11.9295
0.10	0.9297	1.4464	8.6979	1.0598	1.4848	12.0919
AKBS-03		**DMF**			**DMSO**	
0.01	0.9227	1.4172	7.3486	1.0549	1.4684	10.9846
0.02	0.9239	1.4208	7.4994	1.0558	1.4748	11.1272
0.04	0.9245	1.4260	7.6546	1.0574	1.4820	11.3289
0.06	0.9261	1.4328	7.8192	1.0579	1.4880	11.5165
0.08	0.9282	1.4416	8.0457	1.0584	1.4968	11.7505
0.10	0.9304	1.4568	8.4493	1.0594	1.5016	11.9956
AKBS-04		**DMF**			**DMSO**	
0.01	0.9228	1.4240	7.3262	1.0550	1.4708	10.8858
0.02	0.9246	1.4324	7.5283	1.0557	1.4728	11.1082
0.04	0.9256	1.4448	7.6779	1.0572	1.4824	11.2343
0.06	0.9275	1.4564	7.9188	1.0584	1.4884	11.5827
0.08	0.9293	1.4620	8.1364	1.0593	1.4972	11.7708
0.10	0.9313	1.4648	8.2360	1.0603	1.5124	12.0976
AKBS-05		**DMF**			**DMSO**	
0.01	0.9223	1.4228	7.7931	1.0549	1.4668	10.9889
0.02	0.9238	1.4292	8.0292	1.0556	1.4700	11.1234
0.04	0.9248	1.4368	8.3237	1.0567	1.4716	11.2889
0.06	0.9268	1.4492	8.5209	1.0574	1.4740	11.5085
0.08	0.9285	1.4600	8.7460	1.0579	1.4768	11.6457
0.10	0.9305	1.4756	8.9606	1.0586	1.4824	11.8898
AKBS-06		**DMF**			**DMSO**	
0.01	0.9227	1.4240	7.4815	1.0549	1.4688	11.0546
0.02	0.9244	1.4324	7.6313	1.0557	1.4752	11.1646
0.04	0.9267	1.4448	7.8100	1.0568	1.4836	11.3036
0.06	0.9285	1.4564	7.9829	1.0580	1.4872	11.5920
0.08	0.9293	1.4632	8.1619	1.0594	1.4928	11.7659
0.10	0.9316	1.4664	8.3841	1.0604	1.4984	11.5920
AKBS-07		**DMF**			**DMSO**	
0.01	0.9222	1.4188	7.3752	1.0551	1.4684	10.8860
0.02	0.9237	1.4292	7.4686	1.0558	1.4728	10.9684
0.04	0.9248	1.4368	7.6803	1.0569	1.4780	11.0439
0.06	0.9262	1.4492	7.7339	1.0581	1.4836	11.2593
0.08	0.9284	1.4600	7.8356	1.0594	1.4880	11.3460
0.10	0.9301	1.4756	7.9786	1.0602	1.4952	11.4472

Conc. (M)	ρ g. cm^{-3}	U x 10^{-5} cm/s	η x 10^{3} poise	ρ g. cm^{-3}	U x 10^{-5} cm/s	η x 10^{3} poise
AKBS-08	**DMF**			**DMSO**		
0.01	0.9228	1.4180	7.3852	1.0553	1.4684	10.9572
0.02	0.9239	1.4248	7.5652	1.0559	1.4700	11.1949
0.04	0.9252	1.4340	7.8116	1.0568	1.4728	11.4122
0.06	0.9271	1.4444	8.0646	1.0583	1.4760	11.6030
0.08	0.9288	1.4508	8.3739	1.0594	1.4840	11.7771
0.10	0.9304	1.4592	8.6307	1.0604	1.4892	12.0112
AKBS-09	**DMF**			**DMSO**		
0.01	0.9227	1.4172	7.3941	1.0557	1.4680	10.9776
0.02	0.9240	1.4208	7.5757	1.0565	1.4724	11.0671
0.04	0.9256	1.4260	7.7318	1.0576	1.4768	11.1633
0.06	0.9272	1.4328	7.8907	1.0582	1.4840	11.3443
0.08	0.9289	1.4416	8.0540	1.0594	1.4888	11.4351
0.10	0.9302	1.4568	8.4332	1.0603	1.4960	11.6164

where W_1 and W_2 are weight fractions of solvents and solute, respectively. M_1 and M_2 are the molecular weights of the solvent and compounds respectively.

5. Rao's molar sound function:

Rao's molar sound fraction (R_m) can be evaluated by an equation given by Bagchi *et al.* [91]:

$$R_m = \left(\frac{M}{\rho}\right) U^{1/3} \qquad \text{..... (1.10)}$$

6. Van der Waals Constant:

Van der Waals constant (b) can be evaluated as follows [92]:

$$b = \frac{M}{\rho}\left\{1 - \left(\frac{RT}{MU^2}\right)\left[\sqrt{1 + \frac{MU^2}{3RT}} - 1\right]\right\} \qquad \text{..... (1.11)}$$

where R is the gas constant (8.314 JK^{-1} mol^{-1}) and T is the absolute temperature.

7. Relaxation Strength:

The relaxation strength (r) can be calculated as follows [93]:

$$r = 1 - \left[\frac{U}{U_\infty}\right]^2 \qquad \text{..... (1.12)}$$

where $U_0 = 1.6 \times 10^5$ cm/sec

8. Internal Pressure:

Suryanarayana and Kuppuswamy [94] gave the following equation for evaluating internal pressure:

$$\pi = bRT\left[\frac{K_\eta}{U}\right]^{1/2} \frac{\rho^{2/3}}{M^{7/6}} \qquad \text{..... (1.13)}$$

where b is the packing factor (=2). K is a constant (= 4.28×10^9). The internal pressure (π) depends on temperature, density, ultrasonic velocity and specific heat at constant pressure.

9. Apparent Molar Compressibility (ϕ_k):

The apparent molar compressibility (ϕ_k) of the solution was calculated by the following equation:

$$\phi_k = \frac{(\rho_0\kappa_s - \rho\kappa_s^0)1000}{c\rho_0} + \frac{\kappa_s^0 M_2}{\rho_0} \qquad \text{..... (1.14)}$$

where ρ_0 and κ_s^0 are density and isentropic compressibility of pure solvent respectively, c is the concentration of the solution and M_2 is the molecular weight of the compound.

10. Apparent Molar Volume (ϕ_v):

$$\phi_v = \left[\frac{M}{\rho}\right] - \left[\frac{\left(1000\{\rho - \rho_0\}\right)}{(\rho C)}\right] \quad \text{..... (1.15)}$$

where ρ and ρ_0 are the densities of solutions and solvent respectively and C is the concentration of the solution in molarity.

Some of these calculated parameters are given in Table 1.3 to 1.6.

Figures 1.1 and 1.2 show the variation of ultrasound velocity (U) with concentration for the chalcones and Schiff bases in different solvents respectively. It is observed that ultrasonic velocity (U) increases non linearly with concentration for all the compounds. The velocity depends on intermolecular free length (L_f). The velocity increases with decreases in L_f or vice versa. Figures 1.3 and 1.4 show that L_f decreases continuously which suggest that there is strong interaction between solvent and compound molecules.

This is further supported by isentropic compressibility (κ_s) and relaxation strength (r). The variation of isentropic compressibility (κ_s) with concentration of these compounds are also shown in Fig. 1.5 and Fig. 1.6 for both chalcones and Schiff bases. It is observed from Fig. 1.5 and 1.6 and Tables 1.3 to 1.6 that both isentropic compressibility (κ_s) and relaxation strength (r) are observed to decreases with concentration for studied compounds. The decreases of κ_s with increasing concentration might be due to aggregation of solvent molecules around solute molecules indicating thereby the presence of solute-solvent interactions. The increase of acoustical impedance (Z) (Tables 1.3 to 1.6) further confirms the solute-solvent interactions in these systems.

Further, Tables 1.3 – 1.6 show that Rao's molar sound function (R_m), molar compressibility (W) and Vander Waal's constant (b) are observed to increase linearly (0.9980-1.0000) with concentration for all the chalcones and Schiff bases.

Table 1.3: Some acoustical parameters of chalcones in DMF at 308.15 K.

Conc. (M)	Z. 10^{-5} g.cm^{-2}	r	$R_m.10^{-3}$ cm$^{-8/3}$.s$^{-1/3}$	W.10^{-3} cm^{-1}.dyn^{-1}	b cm^3.mol^{-1}
AKFC-01					
0.00	1.3339	0.1845	4.1538	2.3323	79.1598
0.01	1.3398	0.1787	4.2150	2.3665	80.2301
0.02	1.3419	0.1782	4.2691	2.3973	81.2520
0.04	1.3464	0.1749	4.3840	2.4621	83.3832
0.06	1.3475	0.1747	4.4986	2.5267	85.5619
0.08	1.3497	0.1741	4.6113	2.5904	87.6922
0.10	1.3521	0.1724	4.7266	2.6554	89.8557
AKFC-05					
0.01	1.3348	0.1848	4.2115	2.3650	80.2627
0.02	1.3368	0.1843	4.2677	2.3969	81.3260
0.04	1.3389	0.1838	4.3839	2.4626	83.5318
0.06	1.3411	0.1835	4.4983	2.5274	85.7060
0.08	1.3424	0.1829	4.6172	2.5943	87.9608
0.10	1.3433	0.1828	4.7348	2.6607	90.1998
AKFC-06					
0.01	1.3310	0.1897	4.2248	2.3729	80.5983
0.02	1.3324	0.1894	4.3007	2.4158	82.0403
0.04	1.3347	0.1892	4.4518	2.5012	84.9188
0.06	1.3363	0.1885	4.6067	2.5885	87.8619
0.08	1.3379	0.1879	4.7605	2.6752	90.7848
0.10	1.3404	0.1866	4.9140	2.7617	93.6859
AKFC-07					
0.01	1.3330	0.1876	4.1945	2.3558	79.9856
0.02	1.3365	0.1845	4.2421	2.3826	80.8431
0.04	1.3400	0.1827	4.3333	2.4342	82.5499
0.06	1.3439	0.1797	4.4271	2.4870	84.2848
0.08	1.3460	0.1788	4.5191	2.5390	86.0220
0.10	1.3490	0.1766	4.6127	2.5917	87.7628
AKFC-08					
0.01	1.3295	0.1895	4.2048	2.3612	80.2128
0.02	1.3304	0.1890	4.2551	2.3897	81.1758
0.04	1.3321	0.1881	4.3631	2.4504	83.2085
0.06	1.3338	0.1861	4.4721	2.5115	85.2539
0.08	1.3373	0.1858	4.5683	2.5663	87.0818
0.10	1.3416	0.1847	4.6633	2.6206	88.8723
AKFC-09					
0.01	1.3348	0.1849	4.1947	2.3556	79.9466
0.02	1.3357	0.1847	4.2375	2.3798	80.7573
0.04	1.3376	0.1838	4.3240	2.4286	82.3900
0.06	1.3403	0.1808	4.4153	2.4797	84.0785
0.08	1.3472	0.1759	4.4988	2.5271	85.5840
0.10	1.3518	0.1757	4.5717	2.5692	86.9680
AKFC-10					
0.01	1.3352	0.1851	4.2227	2.3715	80.4812
0.02	1.3367	0.1848	4.2937	2.4116	81.8302
0.04	1.3396	0.1847	4.4328	2.4905	84.4795
0.06	1.3415	0.1843	4.5757	2.5712	87.1960
0.08	1.3469	0.1809	4.7170	2.6511	89.8264
0.10	1.3497	0.1796	4.8588	2.7312	92.5013

Table 1.4: Some acoustical parameters of chalcones in $CHCl_3$ at 308.15 K.

Conc. (M)	Z. 10^{-5} $g.cm^{-2}$	r	$R_m.10^{-3}$ $cm^{-8/3}.s^{-1/3}$	$W.10^{-3}$ $cm^{-1}.dyn^{-1}$	b $cm^3.mol^{-1}$
AKFC-01					
0.00	1.3697	0.6467	3.7873	2.3116	82.9705
0.01	1.3736	0.6448	3.8080	2.3239	83.3471
0.02	1.3764	0.6434	3.8275	2.3357	83.7218
0.04	1.3789	0.6424	3.8636	2.3576	84.4699
0.06	1.3815	0.6412	3.9003	2.3799	85.2237
0.08	1.3852	0.6394	3.9381	2.4028	85.9793
0.10	1.3923	0.6358	3.9789	2.4272	86.7287
AKFC-05					
0.01	1.3711	0.6461	3.8059	2.3229	83.3543
0.02	1.3733	0.6451	3.8253	2.3329	83.7384
0.04	1.3773	0.6433	3.8639	2.3580	84.5105
0.06	1.3828	0.6406	3.9041	2.3822	85.2841
0.08	1.3866	0.6388	3.9428	2.4056	86.0580
0.10	1.3906	0.6368	3.9822	2.4294	86.8412
AKFC-06					
0.01	1.3692	0.6473	3.8090	2.3251	83.4688
0.02	1.3711	0.6465	3.8334	2.3399	83.9727
0.04	1.3754	0.6445	3.8844	2.3709	85.0120
0.06	1.3815	0.6417	3.9370	2.4027	86.0474
0.08	1.3843	0.6404	3.9870	2.4330	87.0877
0.10	1.3885	0.6384	4.0386	2.4643	88.1332
AKFC-07					
0.01	1.3717	0.6467	3.7957	2.3172	83.1532
0.02	1.3750	0.6452	3.8117	2.3268	83.4439
0.04	1.3788	0.6434	3.8416	2.3449	84.0292
0.06	1.3827	0.6416	3.8717	2.3631	84.6179
0.08	1.3867	0.6397	3.9021	2.3814	85.2066
0.10	1.3927	0.6367	3.9350	2.4010	85.8051
AKFC-08					
0.01	1.3698	0.6471	3.7998	2.3195	83.2617
0.02	1.3736	0.6453	3.8183	2.3305	83.5929
0.04	1.3766	0.6440	3.8510	2.3505	84.2598
0.06	1.3805	0.6422	3.8850	2.3710	84.9301
0.08	1.3843	0.6404	3.9190	2.3916	85.6020
0.10	1.3886	0.6383	3.9540	2.4126	86.2820
AKFC-09					
0.01	1.3778	0.6431	3.8039	2.3214	83.1909
0.02	1.3788	0.6427	3.8166	2.3291	83.4547
0.04	1.3811	0.6417	3.8429	2.3452	83.9918
0.06	1.3819	0.6416	3.8677	2.3604	84.5275
0.08	1.3846	0.6404	3.8945	2.3766	85.0661
0.10	1.3868	0.6393	3.9214	2.3930	85.6139
AKFC-10					
0.01	1.3705	0.6469	3.8066	2.3237	83.3996
0.02	1.3713	0.6467	3.8286	2.3372	83.8748
0.04	1.3739	0.6456	3.8749	2.3653	84.8439
0.06	1.3790	0.6431	3.9236	2.3948	85.8117
0.08	1.3808	0.6425	3.9691	2.4226	86.7795
0.10	1.3887	0.6385	4.0213	2.4539	87.7608

Table 1.5: Some acoustical parameters of Schiff bases in DMF at 308.15 K.

Conc. (M)	Z. 10^{-5} g.cm^{-2}	r	$R_m.10^{-3}$ cm$^{-8/3}$.s$^{-1/3}$	W.10^{-3} cm^{-1}.dyn^{-1}	b cm^3.mol^{-1}
AKBS-01					
0.00	1.3025	0.2194	4.1322	2.3219	79.3230
0.01	1.3088	0.2137	4.1691	2.3426	79.9323
0.02	1.3131	0.2106	4.2030	2.3619	80.5296
0.04	1.3222	0.2017	4.2785	2.4042	81.8237
0.06	1.3301	0.1931	4.3565	2.4476	83.1674
0.08	1.3441	0.1783	4.4371	2.4923	84.4493
0.10	1.3564	0.1687	4.5028	2.5297	85.5348
AKBS-02					
0.01	1.3103	0.2115	4.1724	3.442	79.9585
0.02	1.3156	0.2075	4.2062	2.3635	80.5384
0.04	1.3223	0.2003	4.2831	2.4064	81.8878
0.06	1.3267	0.1972	4.3533	2.4461	83.1768
0.08	1.3356	0.1900	4.4224	2.4852	84.3716
0.10	1.3447	0.1828	4.4905	2.5238	85.5448
AKBS-03					
0.01	1.3077	0.2154	4.1722	2.3446	80.0232
0.02	1.3127	0.2115	4.2126	2.3674	80.7281
0.04	1.3183	0.2057	4.2994	2.4160	82.2923
0.06	1.3269	0.1981	4.3829	2.4630	83.7567
0.08	1.3381	0.1882	4.4655	2.5095	85.1610
0.10	1.3554	0.1710	4.5537	2.5587	86.5417
AKBS-04					
0.01	1.3141	0.2079	4.1785	2.3476	80.0145
0.02	1.3244	0.1985	4.2207	2.3714	80.6658
0.04	1.3373	0.1846	4.3129	2.4225	82.1907
0.06	1.3508	0.1714	4.3998	2.4711	83.6230
0.08	1.3586	0.1651	4.4807	2.5168	85.0527
0.10	1.3642	0.1619	4.5572	2.5603	86.4504
AKBS-05					
0.01	1.3122	0.2092	4.1832	2.3502	80.1284
0.02	1.3203	0.2021	4.2286	2.3757	80.8768
0.04	1.3288	0.1936	4.3234	2.4288	82.5434
0.06	1.3431	0.1796	4.4179	2.4816	84.1062
0.08	1.3556	0.1673	4.5119	2.5342	85.6846
0.10	1.3730	0.1495	4.6091	2.5882	87.2201
AKBS-06					
0.01	1.3139	0.2079	4.1826	2.3499	80.0933
0.02	1.3241	0.1985	4.2290	2.3759	80.8231
0.04	1.3389	0.1846	4.3221	2.4281	82.3670
0.06	1.3523	0.1714	4.4166	2.4809	83.9426
0.08	1.3598	0.1637	4.5110	2.5337	85.6049
0.10	1.3661	0.1600	4.5935	2.5807	87.1068
AKBS-07					
0.01	1.3084	0.2137	4.1735	2.3450	80.0179
0.02	1.3202	0.2021	4.2167	2.3690	80.6479
0.04	1.3288	0.1936	4.2985	2.4148	82.0690
0.06	1.3422	0.1796	4.3837	2.4621	83.4545
0.08	1.3555	0.1673	4.4629	2.5066	84.7531
0.10	1.3725	0.1495	4.5493	2.5545	86.0887

Conc. (M)	Z. 10^{-5} $g.cm^{-2}$	r	$R_m.10^{-3}$ $cm^{-8/3}.s^{-1/3}$	$W.10^{-3}$ $cm^{-1}.dyn^{-1}$	b $cm^3.mol^{-1}$
AKBS-08					
0.01	1.3085	0.2146	4.1675	2.3419	79.9177
0.02	1.3164	0.2070	4.2064	2.3637	80.5351
0.04	1.3267	0.1967	4.2839	2.4069	81.8427
0.06	1.3391	0.1850	4.3595	2.4493	83.0860
0.08	1.3475	0.1778	4.4317	2.4900	84.3379
0.10	1.3576	0.1683	4.5061	2.5317	85.5900
AKBS-09					
0.01	1.3077	0.2154	4.1776	2.3476	80.1260
0.02	1.3128	0.2115	4.2228	2.3732	80.9242
0.04	1.3199	0.2057	4.3155	2.4255	82.5993
0.06	1.3285	0.1981	4.4093	2.4783	84.2623
0.08	1.3391	0.1882	4.5044	2.5316	85.9033
0.10	1.3551	0.1710	4.6080	2.5891	87.5734

Table 1.6: Some acoustical parameters of Schiff bases in DMSO at 308.15 K.

Conc. (M)	Z. 10^{-5} g.cm^{-2}	r	$R_m.10^{-3}$ cm$^{-8/3}$.s$^{-1/3}$	W.10^{-3} cm^{-1}.dyn^{-1}	b cm^3.mol^{-1}
AKBS-01					
0.00	1.5460	0.1605	4.7064	2.6914	89.2548
0.01	1.5493	0.1573	4.7340	2.7070	89.7225
0.02	1.5572	0.1499	4.7629	2.7233	90.1390
0.04	1.5651	0.1434	4.8140	2.7525	90.9915
0.06	1.5736	0.1356	4.8683	2.7832	91.8762
0.08	1.5801	0.1295	4.9217	2.8136	92.7761
0.10	1.5906	0.1192	4.9785	2.8456	93.6642
AKBS-02					
0.01	1.5482	0.1587	4.7323	2.7062	89.7139
0.02	1.5534	0.1541	4.7590	5.7214	90.1380
0.04	1.5563	0.1522	4.8081	2.7496	91.0354
0.06	1.5615	0.1495	4.8532	2.7759	91.8404
0.08	1.5656	0.1458	4.9053	2.8055	92.7578
0.10	1.5736	0.1388	4.9574	2.8352	93.6177
AKBS-03					
0.01	1.5490	0.1577	4.7373	2.7090	89.7935
0.02	1.5571	0.1504	4.7699	2.7274	90.2796
0.04	1.5671	0.1421	4.8298	2.7616	91.2643
0.06	1.5742	0.1351	4.8934	2.7976	92.3419
0.08	1.5842	0.1248	4.9601	2.8352	93.4175
0.10	1.5908	0.1192	5.0200	2.8693	94.4438
AKBS-04					
0.01	1.5517	0.1550	4.7395	2.7101	89.7849
0.02	1.5548	0.1527	4.7682	2.7266	90.2883
0.04	1.5672	0.1416	4.8311	2.7623	91.2819
0.06	1.5753	0.1346	4.8914	2.7966	92.2967
0.08	1.5860	0.1244	4.9561	2.8332	93.3343
0.10	1.6036	0.1065	5.0274	2.8730	94.3589
AKBS-05					
0.01	1.5473	0.1596	4.7383	2.7097	89.8450
0.02	1.5517	0.1559	4.7711	2.7284	90.3998
0.04	1.5550	0.1541	4.8325	2.7638	91.5314
0.06	1.5586	0.1513	4.8966	2.8005	92.6946
0.08	1.5623	0.1481	4.9620	2.8379	93.8733
0.10	1.5693	0.1416	5.0295	2.8762	95.0306
AKBS-06					
0.01	1.5494	0.1573	4.7405	2.7108	89.8450
0.02	1.5574	0.1499	4.7762	2.7306	90.3911
0.04	1.5679	0.1402	4.8452	2.7700	91.5226
0.06	1.5735	0.1360	4.9083	2.8062	92.6400
0.08	1.5815	0.1295	4.9725	2.8430	93.7335
0.10	1.5889	0.1230	5.0384	2.8806	94.8590
AKBS-07					
0.01	1.5493	0.1577	4.7345	2.7075	89.7403
0.02	1.5550	0.1527	4.7639	2.7242	90.2076
0.04	1.5621	0.1467	4.8201	2.7563	91.1647
0.06	1.5698	0.1402	4.8762	2.7883	92.1087
0.08	1.5764	0.1351	4.9303	2.8193	93.0389
0.10	1.5852	0.1267	4.9898	2.8530	94.0111

Conc. (M)	Z. 10^{-5} $g.cm^{-2}$	r	$R_m.10^{-3}$ $cm^{-8/3}.s^{-1/3}$	$W.10^{-3}$ $cm^{-1}.dyn^{-1}$	b $cm^3.mol^{-1}$
AKBS-08					
0.01	1.5496	0.1577	4.7318	2.7204	89.6883
0.02	1.5522	0.1559	4.7568	2.7495	90.1292
0.04	1.5565	0.1527	4.8076	2.7495	91.0343
0.06	1.5621	0.1490	4.8559	2.7774	91.8824
0.08	1.5721	0.1397	4.9112	2.8087	92.7618
0.10	1.5791	0.1337	4.9639	2.8387	93.6467
AKBS-09					
0.01	1.5498	0.1582	4.7373	2.7093	89.8005
0.02	1.5556	0.1531	4.7721	2.7291	90.3698
0.04	1.5619	0.1481	4.8391	2.7674	91.5475
0.06	1.5704	0.1397	4.9114	2.8084	92.7656
0.08	1.5772	0.1342	4.9781	2.8466	93.9248
0.10	1.5862	0.1258	5.0489	2.8867	95.1073

Figure 1.1: Variation of ultrasonic velocity (U) of chalcones with concentration in [A] DMF and [B] $CHCl_3$ at 308.15 K.

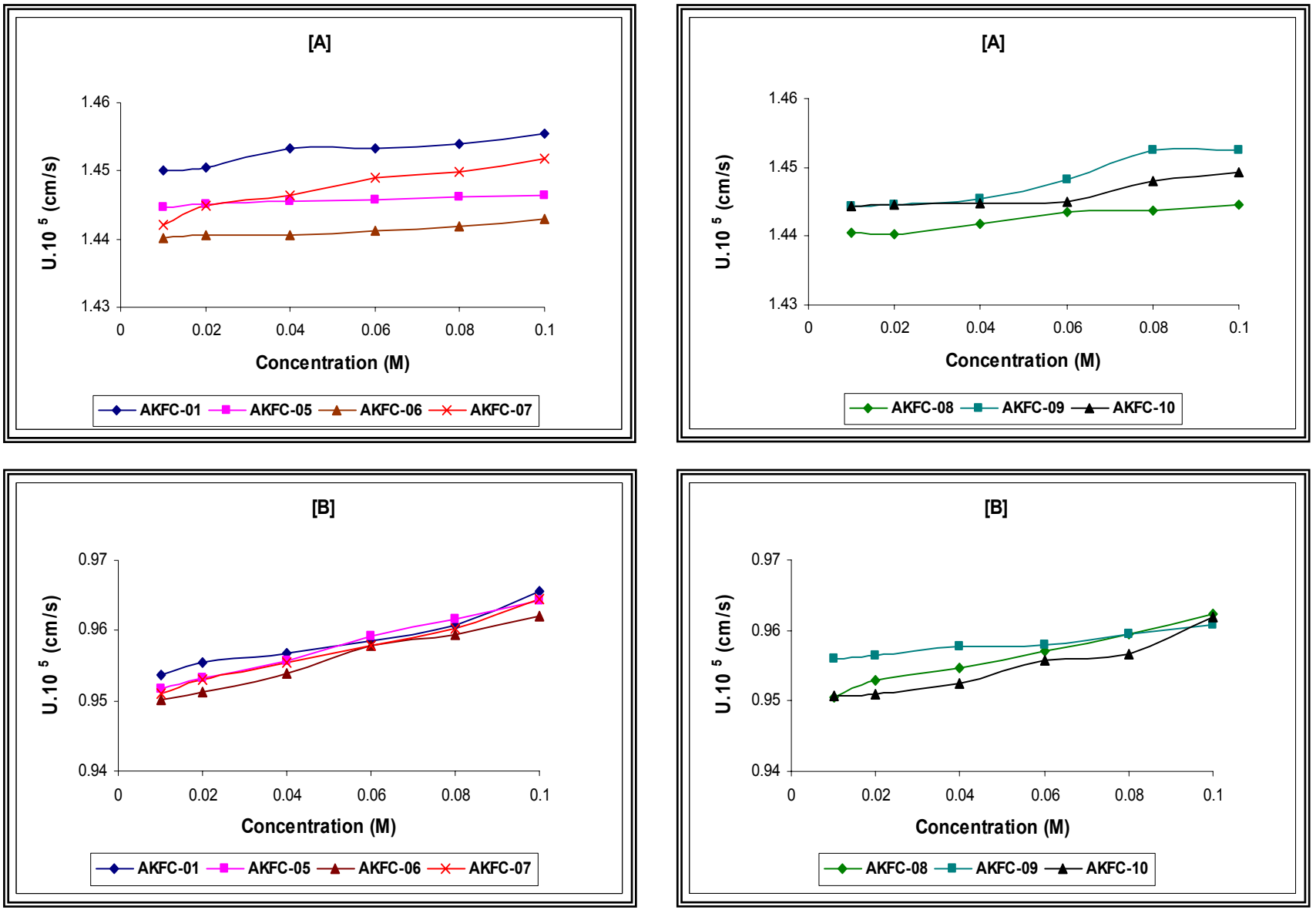


Figure 1.2: Variation of ultrasonic velocity (U) of Schiff bases with concentration in [A] DMF and [B] DMSO at 308.15 K.

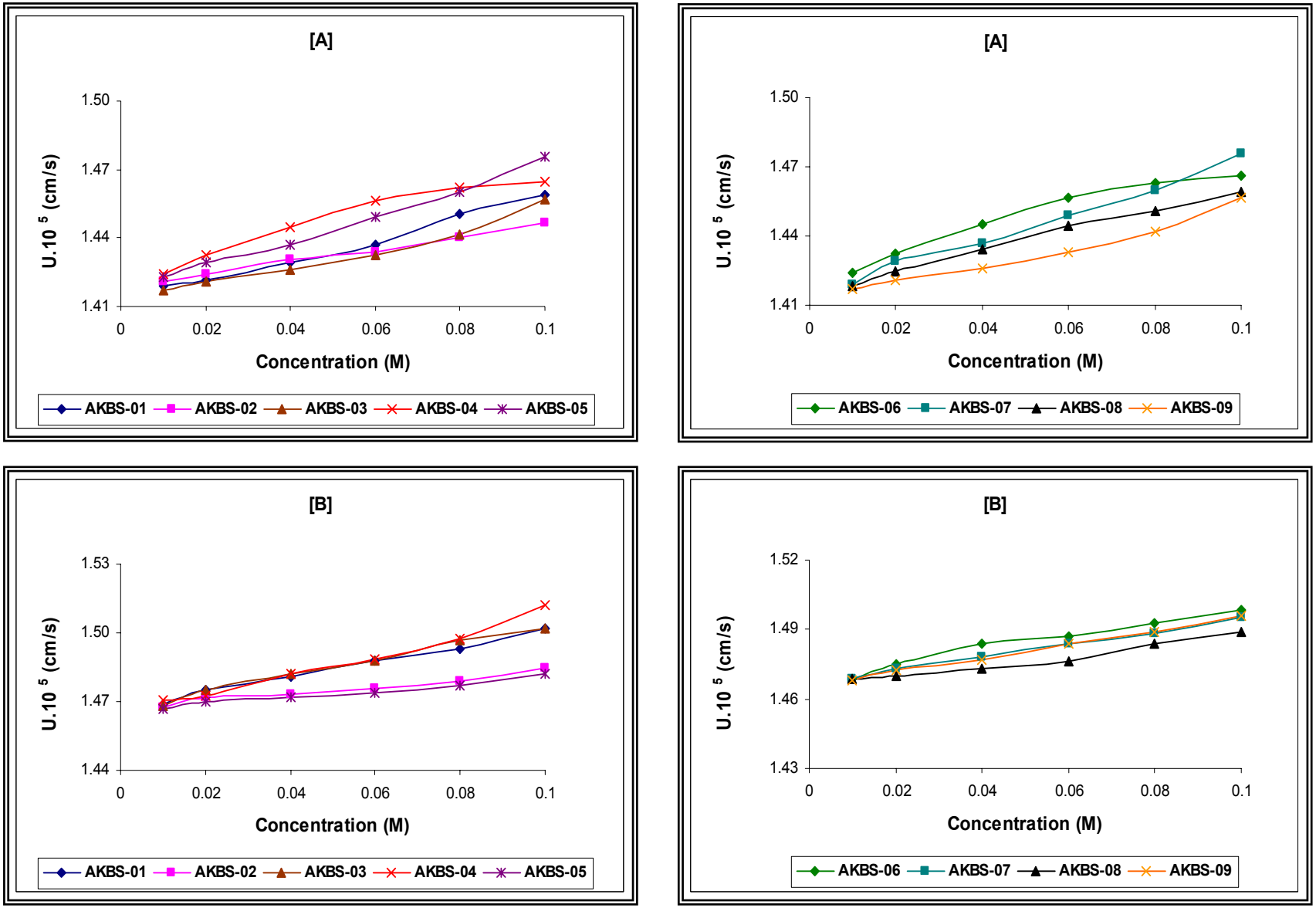


Figure 1.3: Variation of Intermolecular free path length (L_f) of chalcones with concentration in [A] DMF and [B] $CHCl_3$ at 308.15 K.

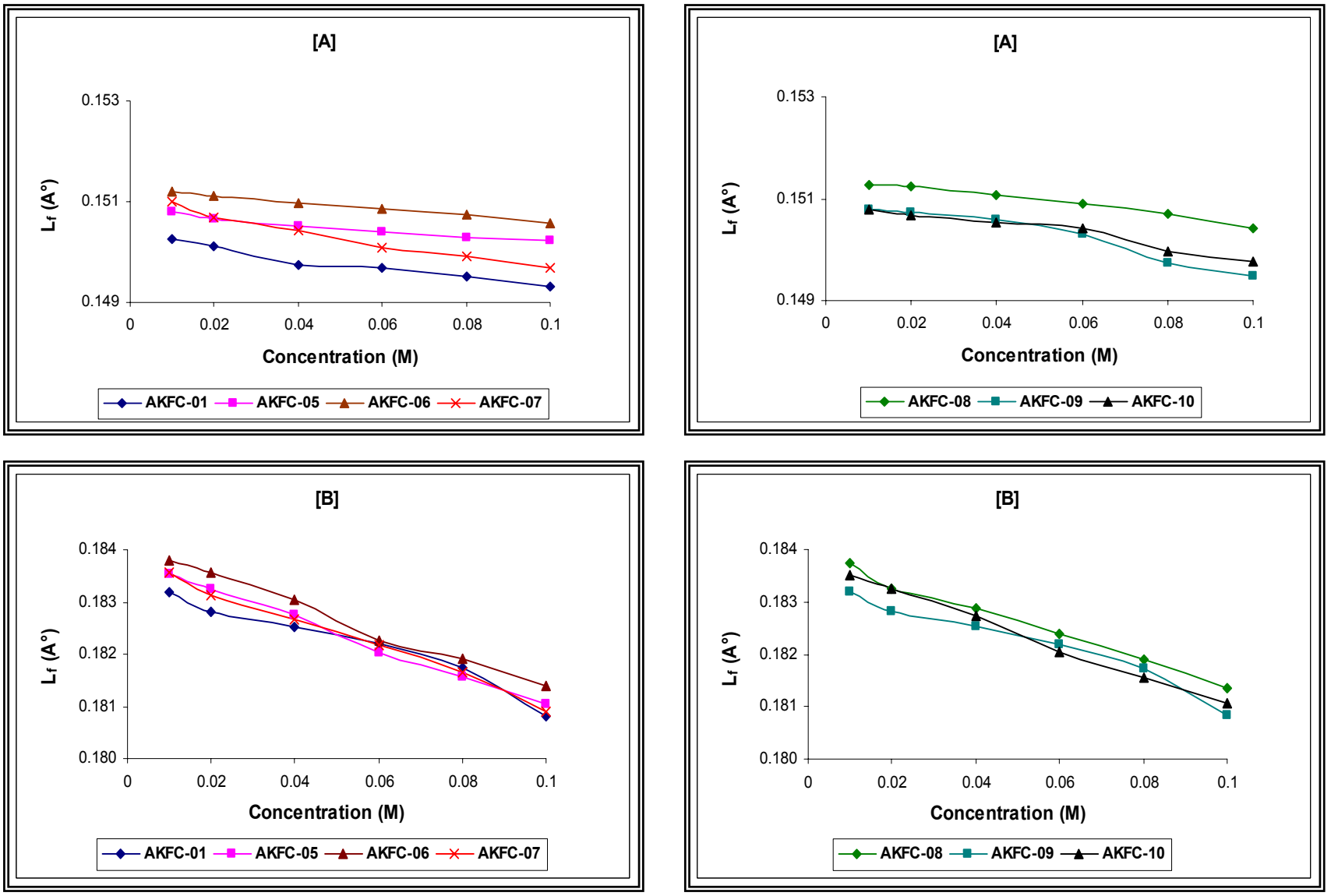


Figure 1.4: Variation of Intermolecular free path length (L_f) of Schiff bases with concentration in [A] DMF and [B] DMSO at 308.15 K.

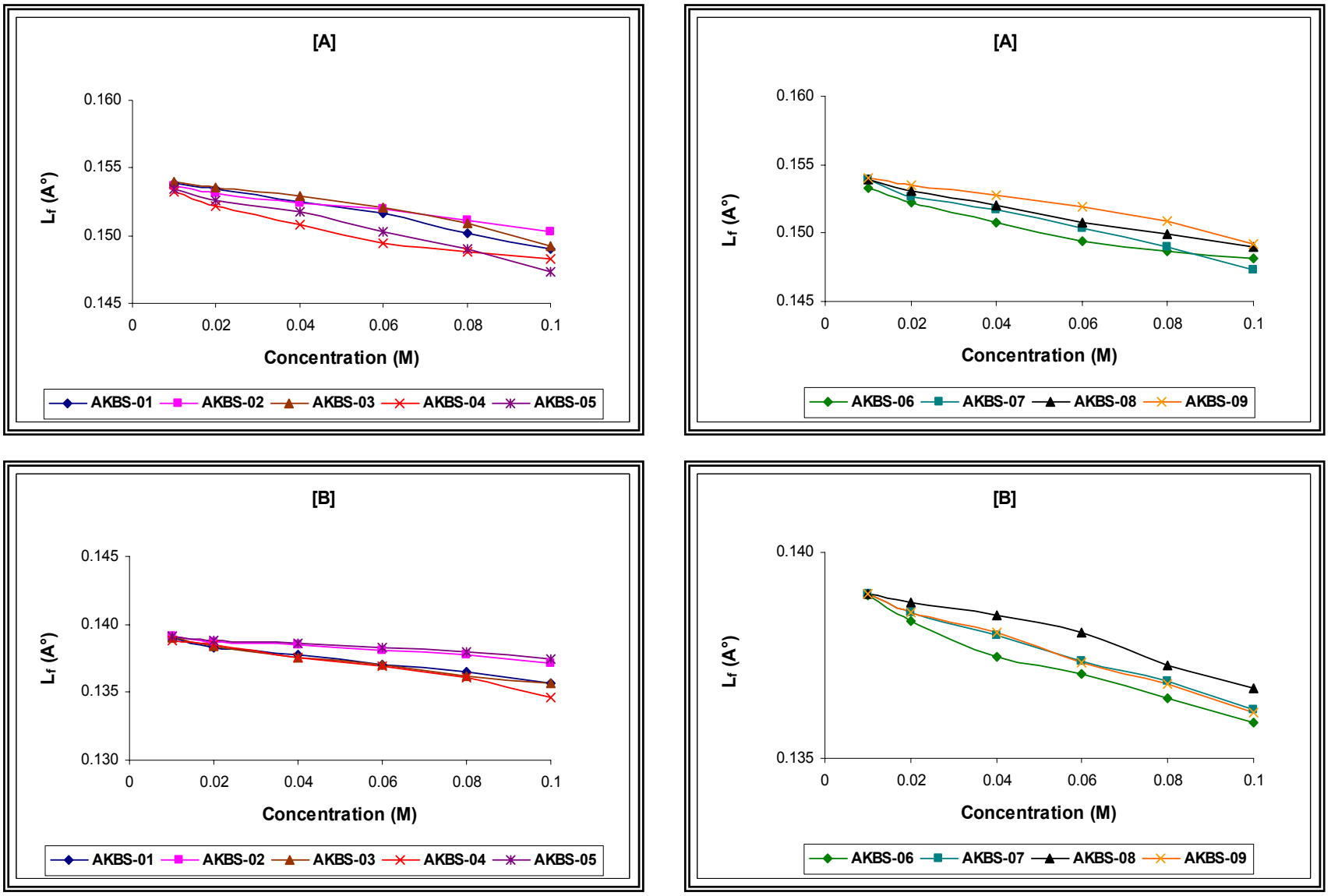


Figure 1.5: Variation of Isentropic Compressibility (κ_s) of chalcones with concentration in [A] DMF and [B] $CHCl_3$ at 308.15 K.

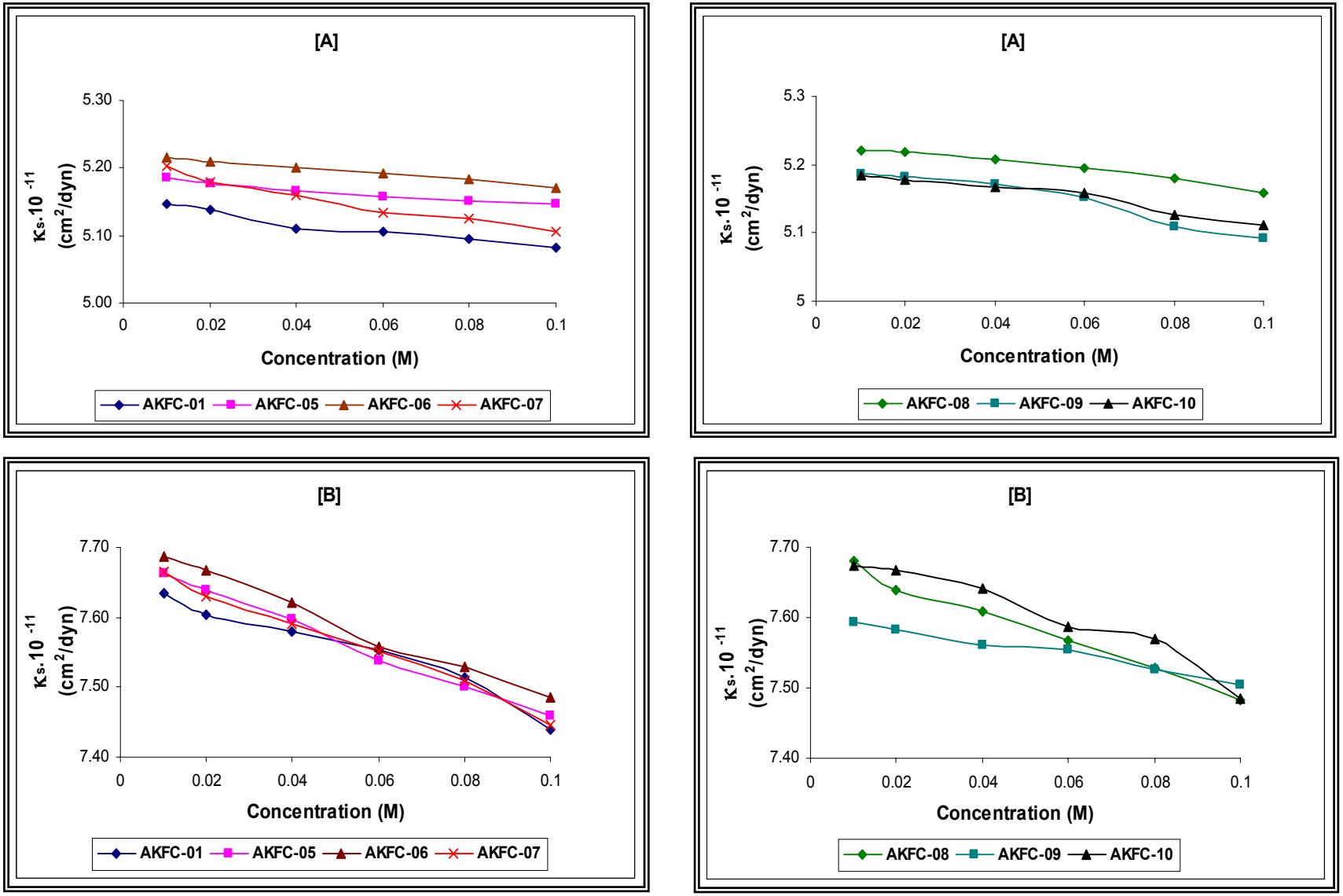


Figure 1.6: Variation of Isentropic Compressibility (κ_s) of Schiff bases with concentration in [A] DMF and [B] DMSO at 308.15 K.

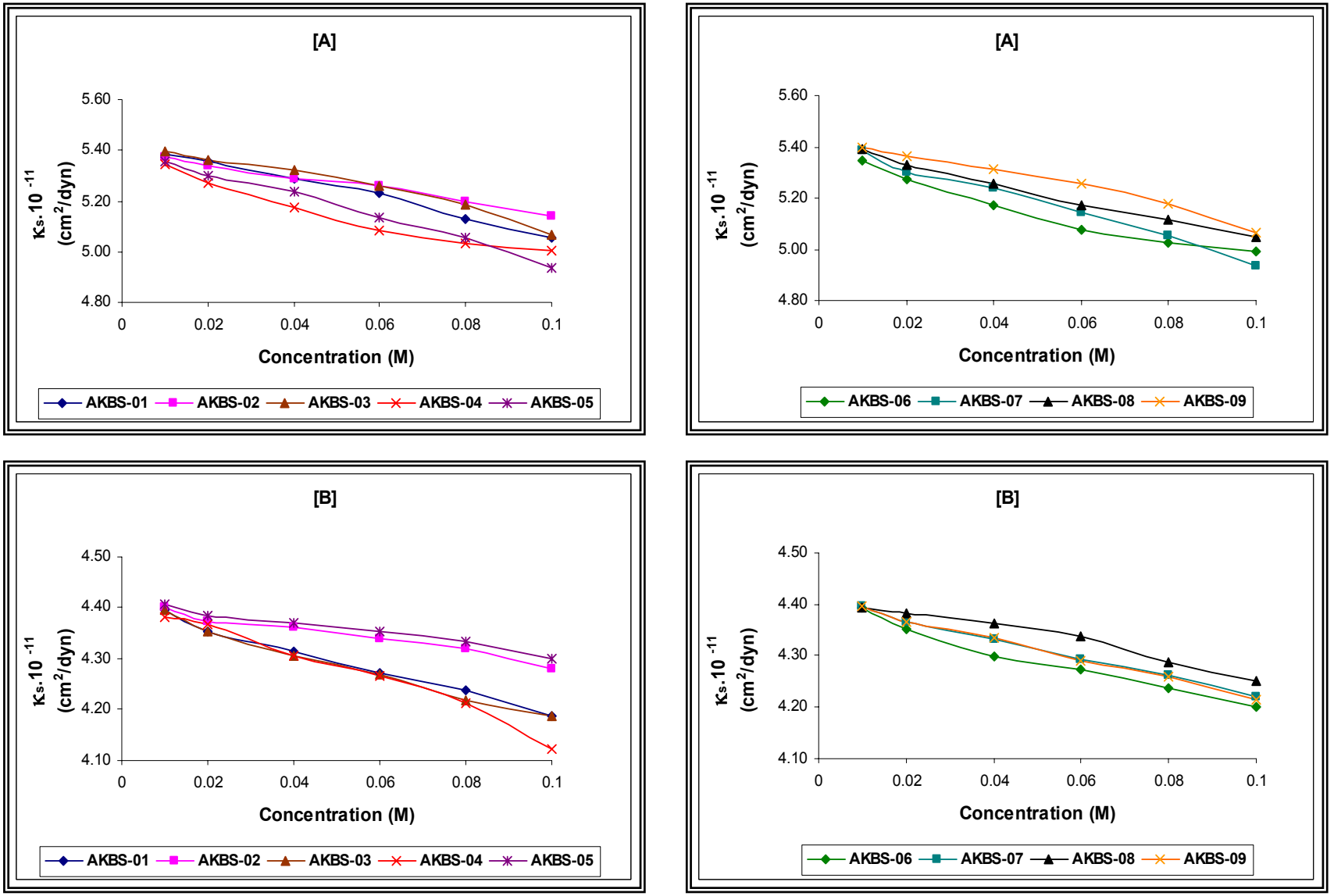


Figure 1.7: Variation of Internal Pressure (π) of chalcones with concentration in [A] DMF and [B] $CHCl_3$ at 308.15 K.

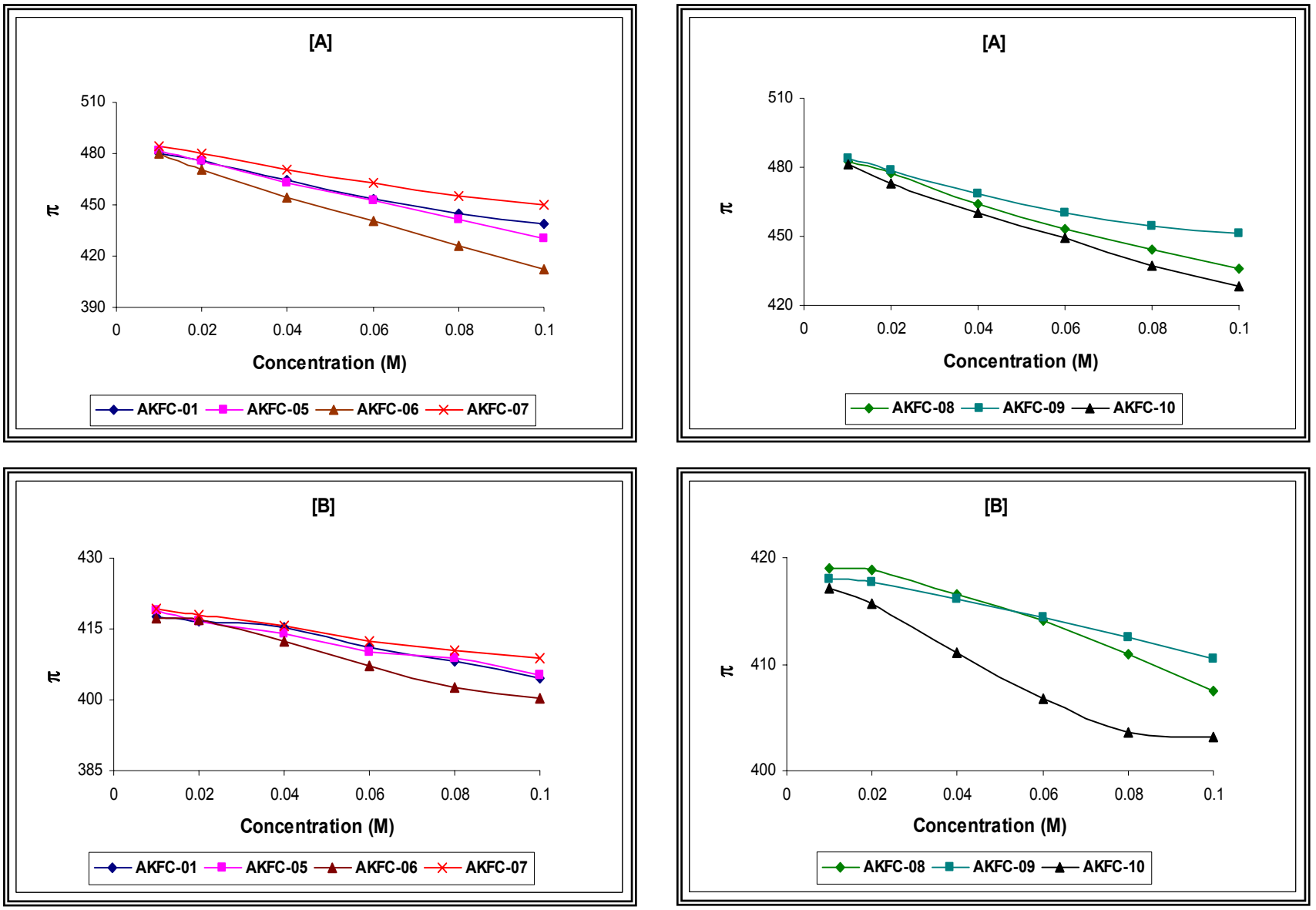
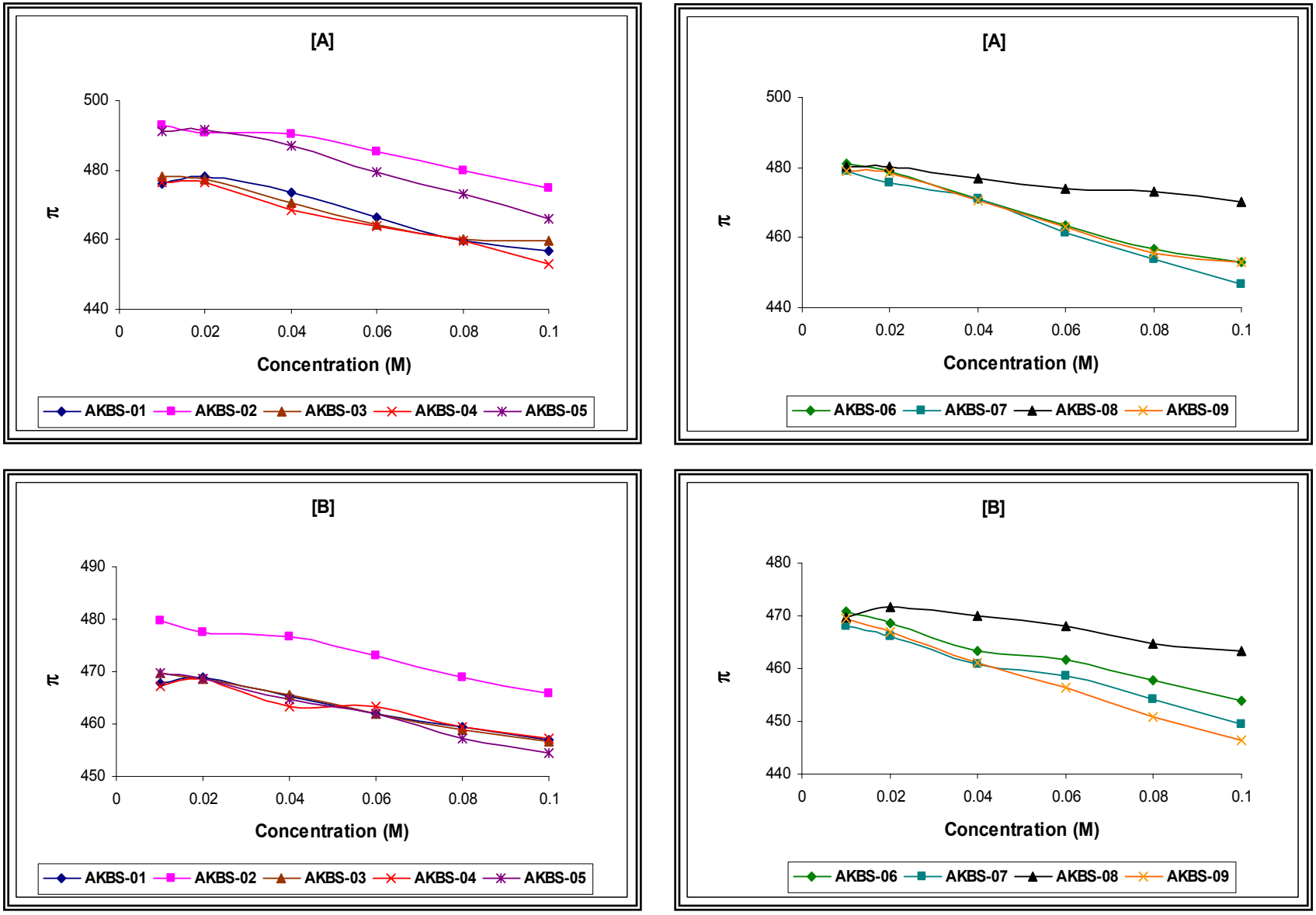


Figure 1.8: Variation of Internal Pressure (π) of Schiff bases with concentration in [A] DMF and [B] DMSO at 308.15 K.



The linear variation of these acoustical properties indicates absence of complex formation in these systems.

The internal pressure (π) is the results of forces of attraction and repulsion between the molecular in a solution. Figures 1.7 and 1.8 show the variation of internal pressure with concentration for the compounds. It is clear from these figures that π decrease with concentration, indicating thereby the decrease in cohesive forces. Although decrease in compressibility (κ_s), intermolecular free length (L_f), relaxation strength (r) and increase of velocity (U), viscosity (η) suggest predominance of solute-solvent interaction, the decrease in internal pressure indicates the existence of solute-solute interactions also in these systems.

Further, the apparent molar compressibilities (ϕ_k) of the solutions is fitted to Gucker's relation [95].

$$\phi_k = \phi_k^0 + S_k\sqrt{C} \qquad \text{..... (1.16)}$$

From the plot of ϕ_k verses C, ϕ°_k and S_k values are evaluated from the intercept and slope. The isentropic compressibility of all the solutions were also fitted to the following Bachem's relations [96]:

$$\kappa_S = \kappa_S^0 + AC + BC^{3/2} \qquad \text{..... (1.17)}$$

and values of A and B were evaluated from the intercept and slope respectively. All these values of the intercepts and slopes are given in Tables 1.7 and 1.8 for chalcones and Schiff bases respectively.

It is evident from Tables 1.7 that for all the chalcones, A values are negative and B values are positive but low. The negative A and low B values indicate solute-solvent interactions in these systems. Further, ϕ°_k values are negative and S_k values are positive. These negative ϕ°_k values and positive S_k confirms the existence of solute-solvent interactions. For Schiff bases (Tables 1.8), A values are again found to be negative and B values are positive. However, B values are higher than those observed for chalcones. The negative A and positive B values confirms the solute-solvent interactions in these systems. These negative ϕ°_k values and positive S_k also confirms the existence of solute-solvent interactions.

Table 1.7: Bechem's, Gucker's and Masson's constants of chalcones in DMF and $CHCl_3$ at 308.15 K

Compounds	$A \times 10^{11}$ $dyn^{-1}.cm^{3}.mol^{-1}$	$B \times 10^{11}$ $dyn^{-1}.cm^{1/2}.mol^{-3/2}$	$\phi_K^o \times 10^8$ $dyn^{-1}.mol^{-1}$	$S_k \times 10^8$ $dyn^{-1}.cm^{-3/2}.mol^{-3/2}$	ϕ_V^o $cm^3.mol^{-1}$	S_V $cm^3.mol^{-1}$
DMF						
AKFC-01	-2.98	2.07	-1.49	25.99	-25.14	580.90
AKFC-05	-0.60	1.84	-0.85	4.01	-20.91	531.46
AKFC-06	-0.29	2.44	-2.30	5.70	-15.91	523.55
AKFC-07	-0.73	1.01	-0.62	0.24	-28.87	582.71
AKFC-08	-1.55	3.91	-0.04	2.50	-53.42	305.05
AKFC-09	-0.02	1.92	-1.27	9.42	-5.15	821.07
AKFC-10	-0.18	1.17	-1.30	12.57	-45.27	529.67
$CHCl_3$						
AKFC-01	-4.58	4.09	-2.81	44.99	-67.72	69.19
AKFC-05	-2.47	2.96	-0.73	3.38	-63.65	94.23
AKFC-06	-0.29	2.44	-0.21	2.60	-39.44	316.36
AKFC-07	-2.20	1.29	-1.35	9.86	-19.53	407.81
AKFC-08	-1.55	3.91	-0.04	2.50	-46.33	217.08
AKFC-09	-2.52	7.97	-2.37	22.39	-43.67	214.16
AKFC-10	-0.18	1.17	-1.30	12.57	-38.22	273.86

Table 1.8: Bechem's, Gucker's and Masson's constants of Schiff bases in DMF and DMSO 308.15 K

Compounds	$A \times 10^{11}$ $dyn^{-1}.cm^{3}.mol^{-1}$	$B \times 10^{11}$ $dyn^{-1}.cm^{1/2}.mol^{-3/2}$	$\phi_K^o \times 10^8$ $dyn^{-1}.mol^{-1}$	$S_k \times 10^8$ $dyn^{-1}.cm^{-3/2}.mol^{-3/2}$	ϕ_V^o $cm^3.mol^{-1}$	S_V $cm^3.mol^{-1}$
DMF						
AKBS-01	-3.90	9.50	-3.06	8.26	-69.10	1332.60
AKBS-02	-5.81	4.71	-4.07	11.71	-56.78	1242.40
AKBS-03	-3.66	1.58	-2.45	3.28	-76.00	1241.60
AKBS-04	-8.86	4.62	-7.66	18.22	-38.21	194.85
AKBS-05	-6.20	1.80	-6.05	15.77	-59.81	900.48
AKBS-06	-8.53	4.87	-7.63	26.69	-99.79	948.53
AKBS-07	-6.18	1.76	-6.08	15.34	-59.80	1023.30
AKBS-08	-4.69	8.12	-3.99	13.68	-66.63	690.75
AKBS-09	-3.30	0.25	-1.99	0.34	-67.67	725.42
DMSO						
AKBS-01	-3.08	1.33	-2.12	12.49	28.33	216.94
AKBS-02	-1.35	2.52	-1.12	12.53	22.52	235.29
AKBS-03	-2.98	7.23	-2.02	8.21	12.63	402.00
AKBS-04	-3.06	8.23	-1.98	7.11	21.94	189.10
AKBS-05	-1.12	2.05	-0.48	10.80	28.88	325.81
AKBS-06	-3.18	1.62	-2.09	11.39	52.97	235.75
AKBS-07	-2.27	4.29	-1.08	1.55	32.36	76.33
AKBS-08	-1.72	9.31	-0.96	17.67	23.60	157.70
AKBS-09	-2.34	4.52	-1.43	6.53	6.34	416.42

Further, the predominance of solvent-solute interactions is indicated by Masson's equation [97].

$$\phi_v = \phi_v^0 + S_v\sqrt{C} \qquad \text{..... (1.18)}$$

From the plot of ϕ_v verses $\sqrt{C}$, ϕ°_v and S_v values are evaluated from the intercept and slope respectively. The ϕ°_v and S_v values are also reported in Tables 1.7 and 1.8 for chalcones and Schiff bases.

Table 1.7 shows that for chalcones, ϕ°_v values are negative and S_v values are positive, which indicate the predominance of solute-solvent interactions in these systems. It is reported by Nikam and Hiray that the negative ϕ°_v and positive S_v suggest electrostrictive solvation of ions [98, 99].

For Schiff bases also (Table 1.8) ϕ°_v values are negative for DMF whereas these values are positive in DMSO, the values of ϕ°_v values are negative, suggesting therby the existence of solute-solute interactions also. S_v values are also found to be positive in DMF and DMSO, which indicates the predominance of solute-solvent interaction in these systems.

Thus, in the studied systems (chalcones and Schiff bases) solute-solvent interactions dominate although solute-solute interactions also exist.

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Section-II

Density and Refractive Index

INTRODUCTION

Refractive index is the measurement of the bending or refraction of light when passing from one medium to another. It is based on Snell's law which is the ratio between the sine of the angle of incidence of light and sine of the angle of refraction of light. It depends upon the temperature and wavelength of the light used. It is constant for pure substances under standard conditions. Refractive Index along with density, molecular mass and specific volume is very useful in the evaluation of various thermodynamics properties of chemical materials. The number of atoms, groups, radicals and bonds present in the compound can also be calculated by refractive index measurement. There are various other applications of refractive index. It is useful for the identification of crystalline substance and to determine isotropic and anisotropic behavior of the crystal [(1)]. It has applications in separation techniques, e.g., in ion exchange chromatography of inorganic and organic ionic species [(2)], for development and test of an integrated micro system for HPLC separation and detection [(3, 4)] etc. Various workers have also used this parameter to determine the film thickness [(5-9)].

Literature survey shows that much work has been done in liquid mixtures [(10-17)]. Solomko and Galadzhii studied refractive index of water-acetone-alcohol systems [(18)]. Refractive index of some aliphatic alcohols with dioxane has also been reported by Sherstneva and Koleboshin [(19)]. Refractive index of methyl isobutyl ketone + pentanols has also been measured by Riggio *et al*. [(20)]. Recently Aal-Wahaibi *et al.* reported refractive index of ternary system: Isopropyl alcohol + Cyclohexane + Water [(21)]. Campos *et al*. determined the refractive index of Formamide + Water system [(22)]. The refractive index of some organic compounds [(23, 24)], inorganic salts [(25, 26)], polymeric materials [(27-29)]. optical fibers [(30-32)] other materials [(33-36)] have also been determined. The most popular use of refractometry is to determine the percentage of sugar [(37-41)].

In the present section, the refractive index and density of solutions of various concentrations of chalcones (in dimethylformamide and chloroform) and Schiff bases (in dimethylformamide and dimethylsulfoxide) have been

measured at 308.15 K. From the experimental data of these solutions, the density and refractive index of the solid compounds have been evaluated.

EXPERIMENTAL

All the solvents used were of LR grade and were distilled by the reported method [42]. For each compound, a series of solutions of different concentrations were prepared in a solvent. For some compounds, there was solubility problem so measurement for those compounds could not be done.

The density and refractive index of pure solvents and solutions were measured by using pycnometer and Abbe refractometer (Modal no. RSR-2) respectively at 308.15 K. The temperature was maintained by circulating water through jacket around the prisms of refractometer from an electronically controlled thermostatic water bath (NOVA NV-8550 E). The uncertainty of temperature was $\pm$ 0.1°C.

RESULTS AND DISCUSSION

The density of solution (ρ_{12}) is related to densities of the solvent, solute and their weight fractions g_1 and g_2 according to the equation:

$$\frac{1}{\rho_{12}} = \frac{g_1}{\rho_1} + \frac{g_2}{\rho_2} \quad \text{..... (2.1)}$$

where ρ_{12} is the density of solution and ρ_1 and ρ_2 are the densities of solvent and solute respectively. Tables 2.1 and 2.2 show the experimental values of densities and refractive index for all the solutions.

The density of these compounds was determined from the slope of the plot of $1/g_1\rho_{12}$ verses g_2/g_1. Figures 2.1 and 2.2 show plot of $1/g_1\rho_{12}$ verses g_2/g_1 for chalcones in DMF and $CHCl_3$ and for Schiff bases in DMF and DMSO respectively. The inverse of slope gives ρ_2 i.e., the density of solid compound. The densities of all the compounds evaluated from such plots are given in Tables 2.3 and 2.4 for both chalcones and Schiff bases respectively. Further, the density of compounds were evaluated by using the following equation,

$$\rho = \frac{KM}{N_A \sum \Delta V_i} \quad \text{..... (2.2)}$$

where ρ is the density of the compound, K is packing fraction (0.599), M is the molecular weight of the compounds, N_A is the Avogadro's number and ΔV_i is the volume increment of the atoms and atomic groups present in the compound. The $\Sigma\Delta V_i$ for various atoms and groups of atoms are given in Table 2.5. These calculated densities for all the compounds from eq. (2.2) are reported in Tables 2.3 and 2.4.

Comparison of densities evaluated from graphs and calculated from eq. (2.2) showed that calculated values are different from those evaluated graphically. Further, for the same compound, density in the two solvents is different. In chalcones, values are much higher in chloroform than in DMF. The different values in different solvents suggest that interactions play an important role. In solutions, molecular interactions exist which differ in different solvents. Further, these interactions differ due to different substitutions in compounds. Due to these interactions, there may be some changes in volume, which affects density.

Table 2.1: The density and refractive index of chalcones in DMF and $CHCl_3$ at 308.15 K.

Conc. (M)		0.00	0.01	0.02	0.04	0.06	0.08	0.10
AKFC-01								
ρ_{12} (g. cm^{-3})	**DMF**	0.9233	0.9238	0.9253	0.9275	0.9281	0.9301	0.9319
	$CHCl_3$	1.4402	1.4404	1.4406	1.4410	1.4413	1.4416	1.4420
n	**DMF**	1.4223	1.4229	1.4234	1.4250	1.4272	1.4288	1.4300
	$CHCl_3$	1.4360	1.4371	1.4392	1.4403	1.4417	1.4429	1.4475
AKFC-05								
ρ_{12} (g. cm^{-3})	**DMF**	0.9233	0.9242	0.9254	0.9262	0.9275	0.9312	0.9338
	$CHCl_3$	1.4402	1.4405	1.4407	1.4412	1.4416	1.4419	1.4422
n	**DMF**	1.4223	1.4231	1.4248	1.4260	1.4280	1.4320	1.4332
	$CHCl_3$	1.4360	1.4386	1.4392	1.4400	1.4428	1.4444	1.4470
AKFC-06								
ρ_{12} (g. cm^{-3})	**DMF**	0.9233	0.9247	0.9253	0.9269	0.9278	0.9317	0.9345
	$CHCl_3$	1.4402	1.4408	1.4413	1.4418	1.4423	1.4428	1.4431
n	**DMF**	1.4223	1.4230	1.4245	1.4268	1.4289	1.4318	1.4333
	$CHCl_3$	1.4360	1.4371	1.4379	1.4408	1.4429	1.4446	1.4462
AKFC-07								
ρ_{12} (g. cm^{-3})	**DMF**	0.9233	0.9248	0.9256	0.9268	0.9285	0.9295	0.9318
	$CHCl_3$	1.4402	1.4423	1.4426	1.4431	1.4435	1.4439	1.4441
n	**DMF**	1.4223	1.4230	1.4250	1.4260	1.4272	1.4289	1.4309
	$CHCl_3$	1.4360	1.4371	1.4379	1.4408	1.4429	1.4446	1.4462
AKFC-08								
ρ_{12} (g. cm^{-3})	**DMF**	0.9233	0.9247	0.9257	0.9269	0.9281	0.9316	0.9335
	$CHCl_3$	1.4402	1.4412	1.4414	1.4419	1.4423	1.4427	1.4429
n	**DMF**	1.4223	1.4230	1.4242	1.4252	1.4281	1.4310	1.4325
	$CHCl_3$	1.4360	1.4384	1.4409	1.4424	1.4431	1.4443	1.4458
AKFC-09								
ρ_{12} (g. cm^{-3})	**DMF**	0.9233	0.9241	0.9246	0.9254	0.9265	0.9279	0.9306
	$CHCl_3$	1.4402	1.4413	1.4416	1.4421	1.4425	1.4430	1.4432
n	**DMF**	1.4223	1.4236	1.4241	1.4251	1.4263	1.4275	1.4296
	$CHCl_3$	1.4360	1.4399	1.4413	1.4425	1.4432	1.4443	1.4449
AKFC-10								
ρ_{12} (g. cm^{-3})	**DMF**	0.9233	0.9245	0.9253	0.9273	0.9284	0.9302	0.9314
	$CHCl_3$	1.4402	1.4414	1.4418	1.4423	1.4428	1.4432	1.4435
n	**DMF**	1.4223	1.4231	1.4241	1.4246	1.4257	1.4261	1.4279
	$CHCl_3$	1.4360	1.4380	1.4392	1.4401	1.4419	1.4427	1.4429

Table 2.2: The density and refractive index of Schiff bases in DMF and DMSO at 308.15 K.

Conc. (M)		0.00	0.01	0.02	0.04	0.06	0.08	0.10
AKBS-01								
ρ_{12} (g. cm^{-3})	**DMF**	0.9214	0.9225	0.9237	0.9249	0.9255	0.9267	0.9298
	DMSO	1.0546	1.0552	1.0558	1.0569	1.0578	1.0585	1.0593
n	**DMF**	1.4225	1.4238	1.4242	1.4262	1.4285	1.4300	1.4333
	DMSO	1.4742	1.4754	1.4772	1.4789	1.4802	1.4819	1.4826
AKBS-02								
ρ_{12} (g. cm^{-3})	**DMF**	0.9214	0.9222	0.9236	0.9242	0.9254	0.9275	0.9297
	DMSO	1.0546	1.0549	1.0556	1.0564	1.0582	1.0587	1.0598
n	**DMF**	1.4225	1.4241	1.4254	1.4269	1.4282	1.4300	1.4312
	DMSO	1.4742	1.4756	1.4770	1.4788	1.4800	1.4815	1.4828
AKBS-03								
ρ_{12} (g. cm^{-3})	**DMF**	0.9214	0.9227	0.9239	0.9245	0.9261	0.9282	0.9304
	DMSO	1.0546	1.0549	1.0558	1.0574	1.0579	1.0584	1.0594
n	**DMF**	1.4225	1.4242	1.4248	1.4262	1.4285	1.4321	1.4335
	DMSO	1.4742	1.4753	1.4769	1.4787	1.4796	1.4809	1.4824
AKBS-04								
ρ_{12} (g. cm^{-3})	**DMF**	0.9214	0.9228	0.9246	0.9256	0.9275	0.9293	0.9313
	DMSO	1.0546	1.0552	1.0559	1.0574	1.0586	1.0592	1.0602
n	**DMF**	1.4225	1.4228	1.4254	1.4263	1.4274	1.4288	1.4302
	DMSO	1.4742	1.4751	1.4767	1.4784	1.4796	1.4812	1.4822
AKBS-05								
ρ_{12} (g. cm^{-3})	**DMF**	0.9214	0.9223	0.9238	0.9248	0.9268	0.9265	0.9305
	DMSO	1.0546	1.0549	1.0556	1.0567	1.0574	1.0579	1.0583
n	**DMF**	1.4225	1.4238	1.4252	1.4264	1.4276	1.4289	1.4305
	DMSO	1.4742	1.4754	1.4765	1.4782	1.4793	1.4810	1.4821
AKBS-06								
ρ_{12} (g. cm^{-3})	**DMF**	0.9214	0.9227	0.9244	0.9267	0.9285	0.9293	0.9316
	DMSO	1.0546	1.0549	1.0557	1.0568	1.0580	1.0594	1.0604
n	**DMF**	1.4225	1.4243	1.4254	1.4262	1.4275	1.4292	1.4309
	DMSO	1.4742	1.4756	1.4762	1.4780	1.4796	1.4808	1.4818
AKBS-07								
ρ_{12} (g. cm^{-3})	**DMF**	0.9214	0.9222	0.9237	0.9248	0.9262	0.9284	0.9301
	DMSO	1.0546	1.0551	1.0558	1.0569	1.0584	1.0594	1.0602
n	**DMF**	1.4225	1.4232	1.4247	1.4258	1.4269	1.4279	1.4291
	DMSO	1.4742	1.4754	1.4763	1.4779	1.4787	1.4796	1.4806

Continue....

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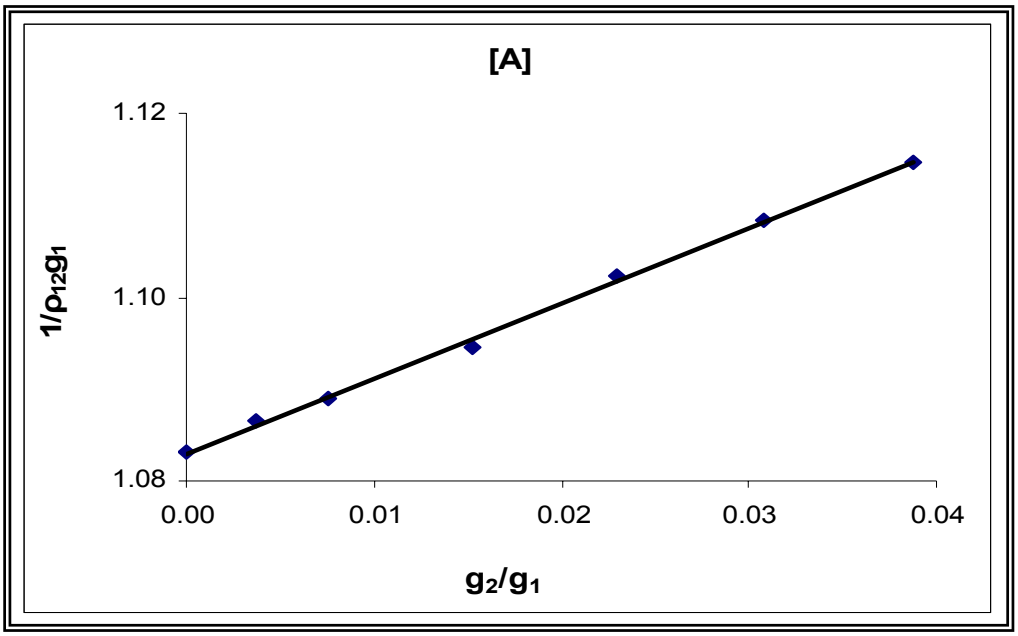
AKBS-08								
ρ_{12} (g. cm^{-3})	**DMF**	0.9214	0.9228	0.9239	0.9252	0.9271	0.9288	0.9304
	DMSO	1.0546	1.0553	1.0559	1.0568	1.0583	1.0594	1.0604
n	**DMF**	1.4225	1.4237	1.4248	1.4260	1.4273	1.4289	1.4301
	DMSO	1.4742	1.4752	1.4759	1.4776	1.4789	1.4797	1.4802
AKBS-09								
ρ_{12} (g. cm^{-3})	**DMF**	0.9214	0.9227	0.9240	0.9256	0.9272	0.9289	0.9302
	DMSO	1.0546	1.0557	1.0565	1.0576	1.0582	1.0594	1.0603
n	**DMF**	1.4225	1.4232	1.4249	1.4260	1.4274	1.4281	1.4282
	DMSO	1.4742	1.4750	1.4758	1.4774	1.4787	1.4794	1.4800

The existence of these interactions has also observed in ultrasonic studies which are discussed in chapter-III of section I.

Figure 2.1: The variation of $1/g_1\rho_{12}$ with g_2/g_1 for chalcones (AKFC-01) in [A] DMF and [B] $CHCl_3$ at 308.15 K.



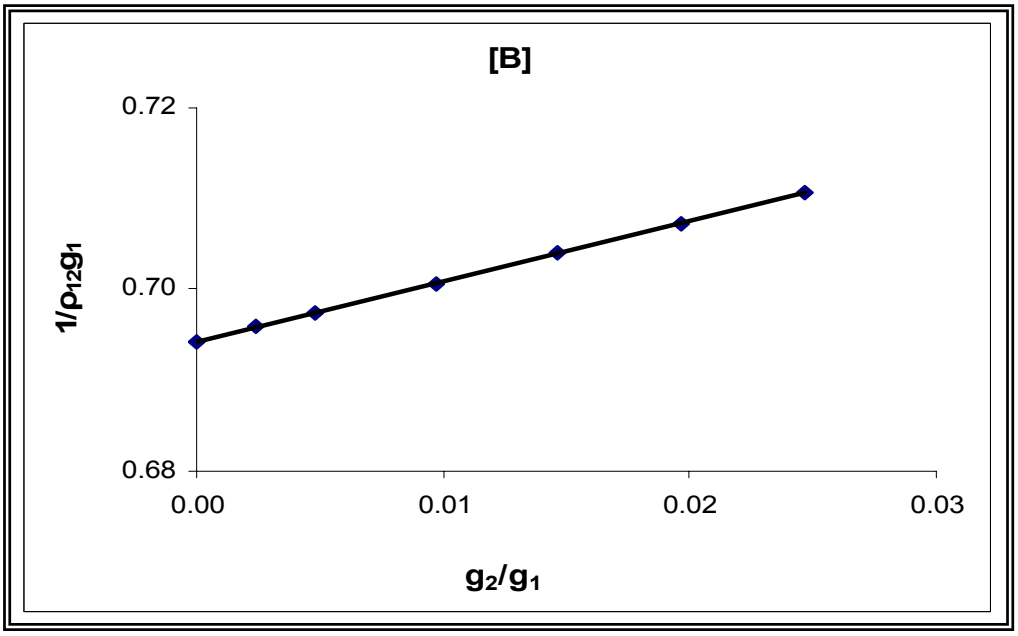
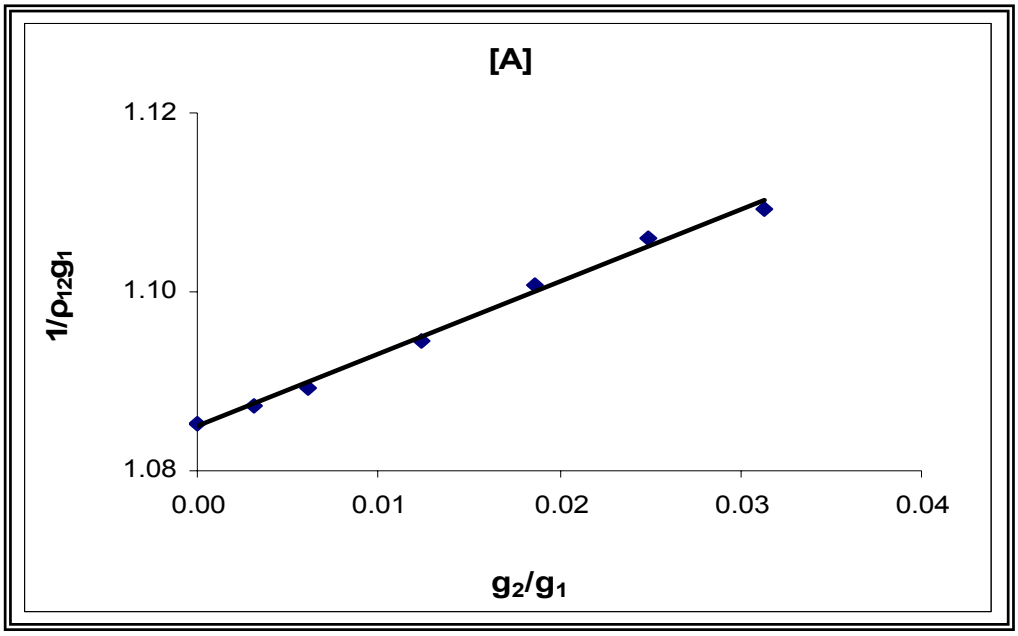


Figure 2.2: The variation of $1/g_1\rho_{12}$ with g_2/g_1 for Schiff bases (AKBS-01) in [A] DMF and [B] DMSO at 308.15 K.



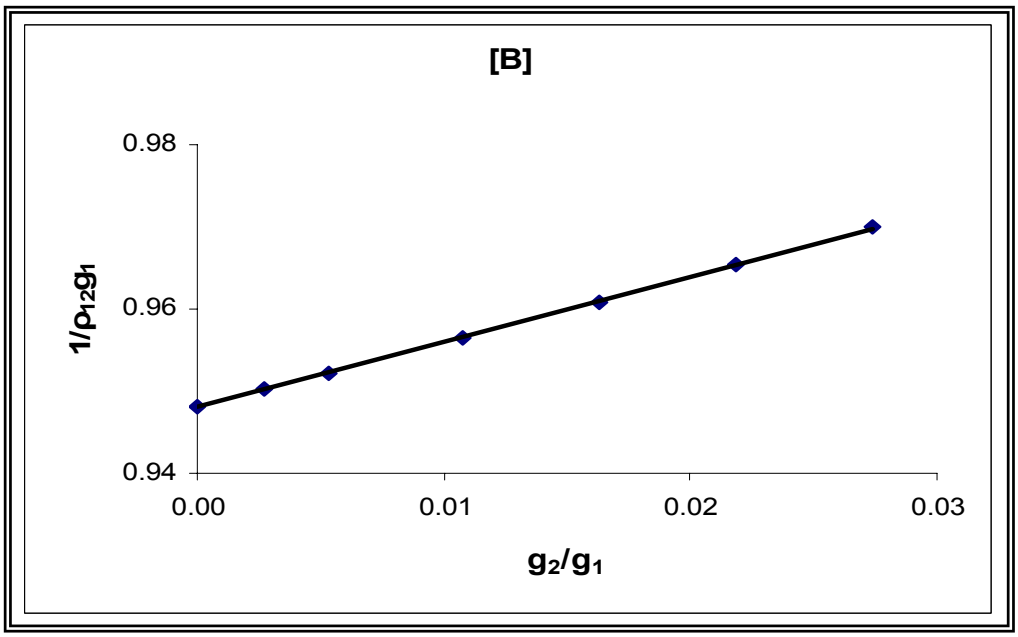


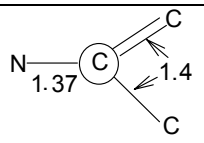
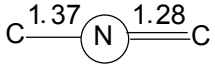
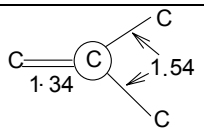
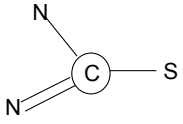
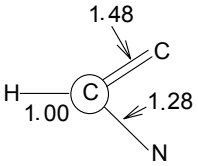
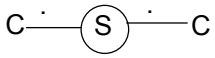
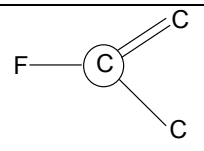
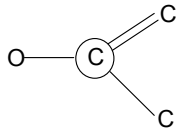
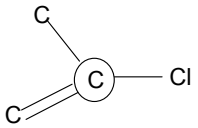
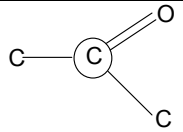
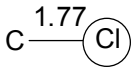
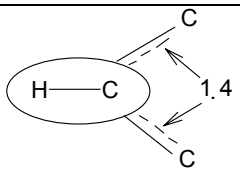
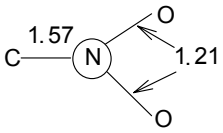
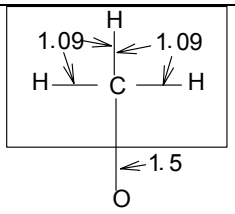
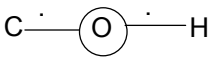
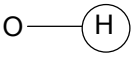
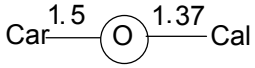
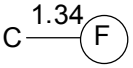
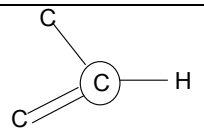
Table 2.3: Experimental and calculated densities of chalcones in DMF and $CHCl_3$ solutions at 308.15 K.

Compounds	Density calculated from slope of Fig. 2.1 in two solvents (g. cm^{-3})		Density (g. cm^{-3}) Calculated from Eq^{n}. 2
	DMF	$CHCl_3$	
AKFC-01	1.2235	1.5172	1.2504
AKFC-05	1.2918	1.5270	1.2628
AKFC-06	1.2593	1.5494	1.4439
AKFC-07	1.2255	1.5962	1.2760
AKFC-08	1.3077	1.5530	1.2314
AKFC-09	1.1766	1.5773	1.3345
AKFC-10	1.1660	1.5579	1.3469

Table 2.4: Experimental and calculated densities of Schiff bases in DMF and DMSO solutions at 308.15 K.

Compounds	Density calculated from slope of Fig. 2.1 in two solvents (g. cm^{-3})		Density (g. cm^{-3}) Calculated from Eq^{n}. 2
	DMF	DMSO	
AKBS-01	1.2447	1.2642	1.1363
AKBS -02	1.2804	1.3028	1.1363
AKBS-03	1.2775	1.2561	1.1733
AKBS-04	1.3410	1.3002	1.1733
AKBS-05	1.2885	1.2133	1.2742
AKBS-06	1.3461	1.3060	1.2742
AKBS-07	1.3001	1.3165	1.0803
AKBS-08	1.3296	1.3264	1.1505
AKBS-09	1.2682	1.2703	1.2679

Table 2.5: Volume increments of some atoms and groups of atoms.

Atoms or Atomic group	Volume Increments $(A°)^3$	Atoms or Atomic group	Volume Increments $(A°)^3$
	10.2		5.62
	9.0		13.46
	3.61		23.43
	11.4		11.65
	10.39		5.85
	19.35		14.7
	7.46		26.3
	5.6		4.7
	2.67		9.2
	11.36		

Further, the molar refraction of a pure liquid $(MRD)_1$ were calculated by the following equation:

$$(MRD)_1 = \left[\frac{n^2-1}{n^2+1}\right]\frac{M}{\rho} \quad \text{..... (2.3)}$$

where n, M and ρ are refractive index, molecular weight and density of pure liquid respectively.

For solutions, the following equation was used to determining molar refraction.

$$(MRD)_{12} = \left[\frac{n_{12}^2-1}{n_{12}^2+1}\right]\left[\frac{X_1M_1 + X_2M_2}{\rho_{12}}\right] \quad \text{..... (2.4)}$$

where n_{12} and ρ_{12} are refractive index and density of solution respectively. X_1 and X_2 are the mole fractions and M_1 and M_2 are the molecular weight of the solvent and solute respectively.

The plots of $(MRD)_{12}$ verses concentration for chalcones and Schiff bases are given in Figures 2.3 and 2.4 respectively. it is evident from these figures that $(MRD)_{12}$ values increase with increase in concentration. From the values of the molar refraction of solution and pure solvent, molar refraction of solid compounds were determined by following equation:

$$(MRD)_{12} = X_1(MRD)_1 + X_2(MRD)_2 \quad \text{..... (2.5)}$$

From the density and molar refraction data, the refractive indexes of all the compounds were calculated for 0.1 M solution from eq. (2.3). The molar refraction $(MRD)_2$ and refractive index of all the compounds are reported in Tables 2.6 and 2.7. It is evident from these Tables that both $(MRD)_2$ and refractive index of compounds are different in each solvent. This again proves that in different solvents, intermolecular interactions are different, which affect these parameters. The values are much different in DMF and chloroform for chalcones than in DMF and DMSO for Schiff bases. In some solvents, aggregation or hydrogen bonding takes place whereas in others, breakage of bonds takes place. As refractive index and molar refraction depends not only upon atomic refraction but also upon single, double or triple bonds, these parameters are affected by the type of interactions taking place in solution. However, it is reported that bond refraction is more effective than atomic refraction. Further, bond polarity also causes change in molar refraction.

Figure 2.3: The plots of molar refraction $(MRD)_{12}$ against concentration of chalcones in [A] DMF and [B] $CHCl_3$ solutions at 308.15 K.

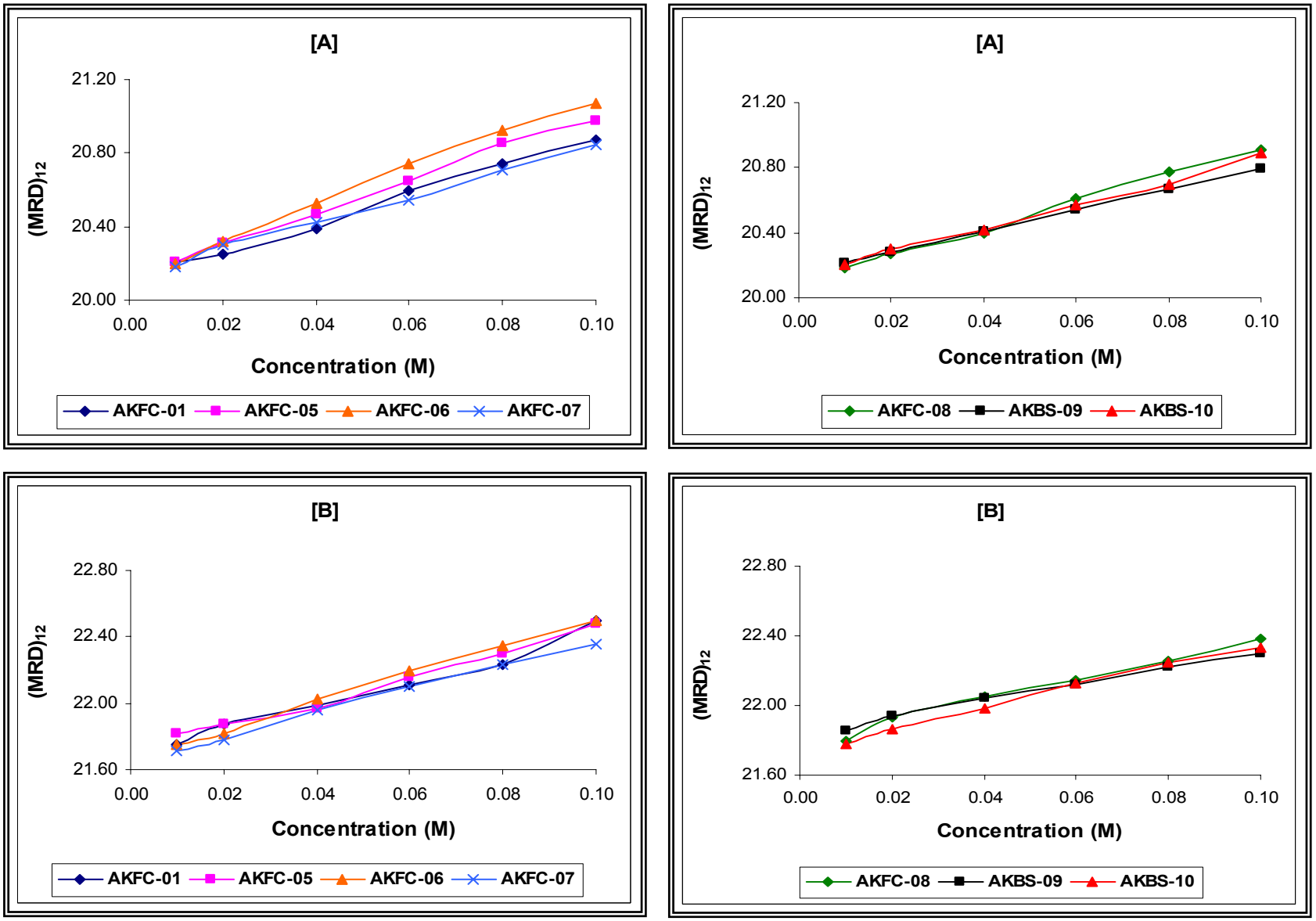
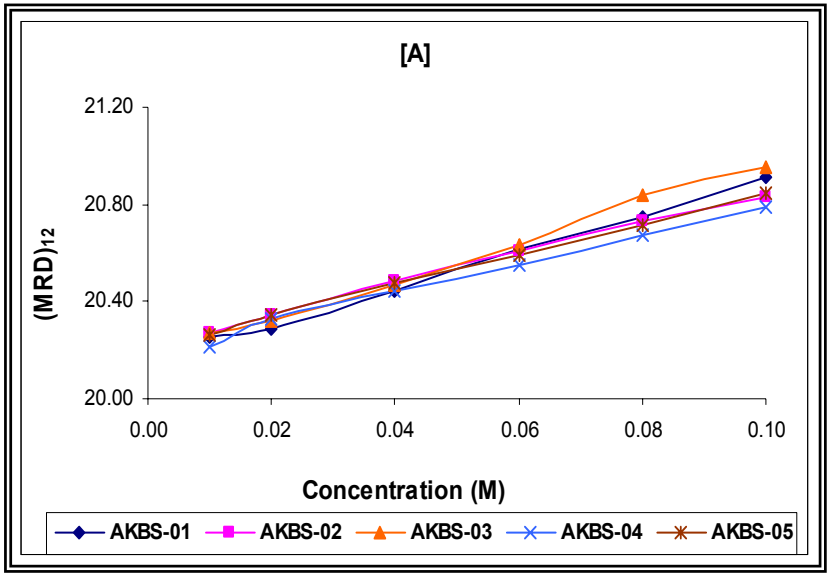
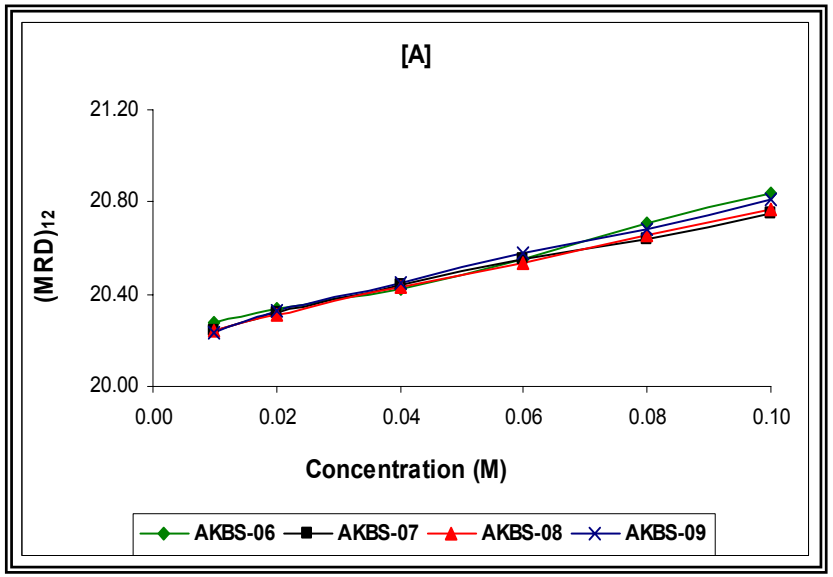
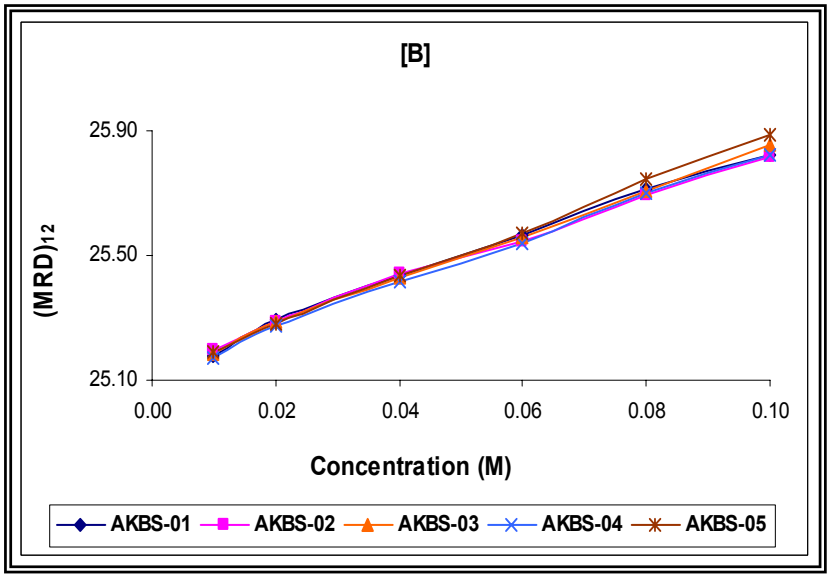


Figure 2.4: The plots of molar refraction $(MRD)_{12}$ against concentration of Schiff bases in [A] DMF and [B] DMSO solutions at 308.15 K.







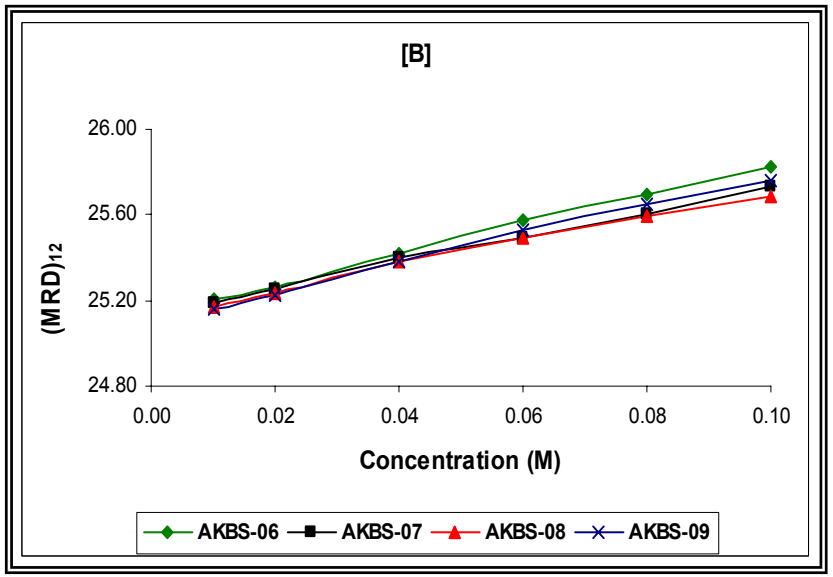


Table 2.6: Calculated molar refraction $(MRD)_2$ and refractive index (η) of 0.1 M solution of chalcones in DMF and $CHCl_3$ at 308.15 K.

Compounds	Solvents			
	DMF		$CHCl_3$	
	$(MRD)_2$	η	$(MRD)_2$	η
AKFC-01	113.11	1.3653	120.29	1.7241
AKFC-05	125.92	1.4125	118.12	1.6905
AKFC-06	142.11	1.4145	120.37	1.5961
AKFC-07	115.25	1.4190	104.22	1.6662
AKFC-08	117.90	1.4066	107.18	1.6477
AKFC-09	103.57	1.3803	97.26	1.3745
AKFC-10	118.15	1.3393	100.44	1.4822

Table 2.7: Calculated molar refraction $(MRD)_2$ and refractive index (η) of 0.1 M solution of Schiff bases in DMF and DMSO at 308.15 K.

Compounds	Solvents			
	DMF		DMSO	
	$(MRD)_2$	η	$(MRD)_2$	η
AKBS-01	112.13	1.4697	105.88	1.5184
AKBS-02	101.35	1.4121	105.56	1.5165
AKBS-03	116.49	1.4558	109.40	1.4985
AKBS-04	96.60	1.3596	106.24	1.4797
AKBS-05	103.44	1.3741	112.95	1.4954
AKBS-06	102.50	1.3704	106.60	1.4596
AKBS-07	91.92	1.3491	95.97	1.4347
AKBS-08	94.16	1.3722	91.27	1.4223
AKBS-09	98.80	1.3464	99.05	1.4093

Thus, type of solvent affects the density, refractive index and molar refraction of a solute due to interactions in solution.

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Section-III

Conductance

INTRODUCTION

Electrical conductance is a property of ionic solutions. Conductometry is one of most important electroanalytical technique which is widely applicable for titration reactions involving ions, from which one can calculate the dissociation constant of weak electrolytes, solubility of sparingly soluble salt and rate of reactions that proceed with the formation or disappearance of ions. In acid-base titrations, this technique is useful to determine relative strength of the two weak acids or bases, degree of hydrolysis, basicity of organic acid etc.

Further, conductometry method is useful to various biological processes [1-4], micro amounts of carbon in aqueous phase [5], ascorbic acid in vitamin C tablet [6], carbon in uranium carbide and its solution in nitric acid [7], enzymatic degradation of microbial biofilm [8], dye-surfactant ion pair formation in aqueous solutions [9] etc. Morita *et al* reported ionic conductance of polymeric electrolytes and of polymeric composite solid electrolytes [10]. The antibiotic residues in bovin kidneys have also been detected by conductometry [11]. Stanisz used conductometric technique to determine electrolyte and osmotic permeability coefficients [12]. Mehta *et al* used this method to study interactions between diclofenac sodium and cyclodextrin molecules in aqueous media [13].

Literature survey shows that conductance of various many inorganic and organic compounds have been measured in aqueous [14-25] and non-aqueous solvents [26-35].

Recently, conductance of some Schiff bases in DMF and DMSO has been measured at different temperatures by Grzeszcuk and Bator [36]. Further, in our laboratory, some conductance measurements have been done for some Schiff bases in different solvents [37, 38].

Thus, in present work, conductance of some new Schiff bases and chalcones derivatives are measured in different solvent at 308.15 K.

EXPERIMENTAL

All the solvents used were distilled prior to use. The solutions of different concentrations were prepared for each compound in a solvent.

The conductance of each solution was measured by using SYSTRONICS CONDUCTIVITY METER (Model No. 306) having cell constant 0.88 cm^{-1} at 308.15 K. The measured conductance was corrected by subtracting the conductance of pure solvent.

For Schiff bases, solution were prepared in DMF and DMSO and for chalcones, DMF and $CHCl_3$ were selected. The choice of different solvents for these compounds is due to their solubility in these solvents. However, due to insolubility of some compounds, it was not possible to measure their conductances in the selected solvents.

RESULTS AND DISCUSSION

The measured conductance (k) of each solution after correction was used to determine the specific conductance (κ), which is then used for the calculation of equivalent conductance (λ_C).

The equations used for calculating specific conductance (κ) and equivalent conductance (λ_C) are:

$$\kappa = k\theta \quad \text{..... (3.1)}$$

$$\lambda_C = 1000\frac{\kappa}{C} \quad \text{..... (3.2)}$$

where θ is the cell constant (= 0.88) and c is the concentration (g.equi./lit) of solution.

These equivalent conductance values of all chalcones and Schiff bases at 308.15 K are reported in Tables 3.1 to 3.4 along with measured conductance (k). It is observed that for all the systems studied, conductance increases with concentration. For chalcones and Schiff bases, conductivities are less in $CHCl_3$ and DMSO respectively. The variations of conductance with concentration are shown in figures 3.1 and 3.2.

The equivalent conductance (λ_c) is plotted against $\sqrt{c}$ for all chalcones and Schiff bases and are shown in figures 3.3 and 3.4 respectively. It is evident from these figures that the compounds exhibit different nature in different solvents. In figure 3.3, some chalcones (AKFC-05, AKFC-06 and AKFC-10) exhibit weak electrolytic in nature in DMF whereas in $CHCl_3$, they show strong electrolytic behavior. In case of Schiff bases (fig. 3.4) AKBS-07 exhibit weak electrolytic in nature in DMF whereas in DMSO all the compounds show weak electrolytic nature except AKBS-01

For weak electrolytes, it is difficult to determine λ_0. However, in the studied solutions of compounds, λ_0 values are evaluated approximately by extrapolation method and are given in Table 3.5 and 3.6. In some compounds, λ_0 values could not be evaluated by extrapolation due to weak electrolytic nature of compound.

Table 3.1: The Conductance (k) and equivalent conductance (λ_C) of Chalcones in DMF at 308.15 K.

Compounds	Conc. (g/lit)	0.000	0.001	0.002	0.004	0.006	0.008	0.010	0.020	0.040	0.060	0.080	0.100
AKFC-01	$k.10^5$ (mho)	2.82	2.92	2.98	3.02	3.08	3.12	3.18	3.32	3.63	3.75	3.83	3.86
	λ_C (mho.cm^2/equi.)	----	0.8800	0.7040	0.4400	0.3813	0.3300	0.3168	0.2200	0.1782	0.1364	0.1111	0.0915
AKFC-05	$k.10^5$ (mho)	2.82	3.08	3.17	3.31	3.49	3.52	3.67	3.86	4.26	4.57	4.88	4.92
	λ_C (mho.cm^2/equi.)	----	2.2880	1.5400	1.0780	0.9827	0.7700	0.7480	0.4576	0.3168	0.2567	0.2266	0.1848
AKFC-06	$k.10^5$ (mho)	2.82	3.12	3.26	3.38	3.45	3.54	3.66	4.00	4.35	4.63	4.82	4.90
	λ_C (mho.cm^2/equi.)	----	0.2600	1.9360	1.2320	0.9181	0.7920	0.7392	0.5192	0.3366	0.2655	0.2200	0.1830
AKFC-07	$k.10^5$ (mho)	2.82	2.91	2.99	3.04	3.09	3.16	3.22	3.41	3.77	4.15	4.36	4.57
	λ_C (mho.cm^2/equi.)	----	0.7920	0.7480	0.4840	0.3960	0.3740	0.3520	0.2596	0.2090	0.1951	0.1694	0.1540
AKFC-08	$k.10^5$ (mho)	2.82	2.86	2.89	2.94	2.98	3.02	3.10	3.28	3.34	3.42	3.53	3.60
	λ_C (mho.cm^2/equi.)	----	0.3520	0.3080	0.2640	0.2347	0.2200	0.2464	0.2024	0.1144	0.0880	0.0781	0.0686
AKFC-09	$k.10^5$ (mho)	2.82	2.88	2.94	3.02	3.09	3.12	3.18	3.48	3.62	3.80	3.97	4.29
	λ_C (mho.cm^2/equi.)	----	0.5280	0.5280	0.4400	0.3960	0.3300	0.3168	0.2904	0.1760	0.1437	0.1265	0.1294
AKFC-10	$k.10^5$ (mho)	2.82	2.93	3.01	3.08	3.12	3.15	3.23	3.38	3.58	3.72	3.90	4.20
	λ_C (mho.cm^2/equi.)	----	0.9680	0.8360	0.5720	0.4400	0.3630	0.3608	0.2464	0.1672	0.1320	0.1188	0.1214

Table 3.2: The Conductance (k) and equivalent conductance (λ_C) of Chalcones in $CHCl_3$ at 308.15 K.

Compounds	Conc. (g/lit)	0.000	0.001	0.002	0.004	0.006	0.008	0.010	0.020	0.040	0.060	0.080	0.100
AKFC-01	$k.10^5$ (mho)	0.12	0.15	0.18	0.22	0.25	0.28	0.30	0.35	0.38	0.39	0.42	0.42
	λ_C (mho.cm^2/equi.)	----	0.2992	0.2728	0.2112	0.1833	0.1738	0.1593	0.1003	0.0568	0.0400	0.0325	0.0267
AKFC-05	$k.10^5$ (mho)	0.12	0.14	0.15	0.16	0.17	0.18	0.20	0.22	0.24	0.25	0.27	0.28
	λ_C (mho.cm^2/equi.)	----	0.1584	0.1100	0.0792	0.0660	0.0627	0.0660	0.0449	0.0264	0.0194	0.0160	0.0141
AKFC-06	$k.10^5$ (mho)	0.12	0.14	0.15	0.17	0.18	0.19	0.21	0.25	0.29	0.32	0.35	0.38
	λ_C (mho.cm^2/equi.)	----	0.1584	0.1408	0.0990	0.0836	0.0792	0.0766	0.0563	0.0370	0.0290	0.0248	0.0229
AKFC-07	$k.10^5$ (mho)	0.12	0.14	0.16	0.19	0.21	0.23	0.25	0.29	0.32	0.34	0.38	0.40
	λ_C (mho.cm^2/equi.)	----	0.1760	0.1628	0.1540	0.1349	0.1254	0.1162	0.0726	0.0436	0.0326	0.0284	0.0247
AKFC-08	$k.10^5$ (mho)	0.12	0.13	0.14	0.15	0.16	0.18	0.19	0.22	0.24	0.27	0.30	0.32
	λ_C (mho.cm^2/equi.)	----	0.0704	0.0660	0.0638	0.0616	0.0638	0.0634	0.0440	0.0268	0.0219	0.0196	0.0177
AKFC-09	$k.10^5$ (mho)	0.12	0.13	0.14	0.16	0.17	0.19	0.20	0.23	0.26	0.30	0.33	0.35
	λ_C (mho.cm^2/equi.)	----	0.1056	0.0968	0.0836	0.0792	0.0770	0.0704	0.0475	0.0304	0.0260	0.0233	0.0204
AKFC-10	$k.10^5$ (mho)	0.12	0.13	0.14	0.15	0.16	0.17	0.18	0.23	0.26	0.29	0.31	0.31
	λ_C (mho.cm^2/equi.)	----	0.0792	0.0704	0.0638	0.0631	0.0561	0.0528	0.0475	0.0304	0.0246	0.0205	0.0170

Table 3.3: The Conductance (k) and equivalent conductance (λ_C) of Schiff bases in DMF at 308.15 K.

Compounds	Conc. (g/lit)	0.000	0.001	0.002	0.004	0.006	0.008	0.010	0.020	0.040	0.060	0.080	0.100
AKBS-01	$k.10^5$ (mho)	3.04	3.18	3.27	3.39	3.49	3.60	3.75	3.92	4.19	4.35	4.48	4.67
	λ_C (mho.cm^2/equi.)	----	1.2320	1.0120	0.7700	0.6600	0.6160	0.6248	0.3872	0.2530	0.1921	0.1548	0.1434
AKBS-02	$k.10^5$ (mho)	3.04	3.29	3.49	3.72	3.87	4.08	4.27	4.49	4.63	4.87	5.02	5.25
	λ_C (mho.cm^2/equi.)	----	2.2000	1.9800	1.4960	1.2173	1.1440	1.0824	0.6380	0.3498	0.2684	0.2178	0.1945
AKBS-03	$k.10^5$ (mho)	3.04	3.22	3.35	3.57	3.72	3.80	3.98	4.21	4.40	4.58	4.72	4.99
	λ_C (mho.cm^2/equi.)	----	1.5840	1.3640	1.1660	0.9973	0.8360	0.8272	0.5148	0.2992	0.2259	0.1848	0.1716
AKBS-04	$k.10^5$ (mho)	3.04	3.20	3.32	3.48	3.65	3.80	3.92	4.17	4.39	4.62	4.87	5.09
	λ_C (mho.cm^2/equi.)	----	1.4080	1.2320	0.9680	0.8947	0.8360	0.7744	0.4972	0.2970	0.2317	0.2013	0.1804
AKBS-05	$k.10^5$ (mho)	3.04	3.26	3.43	3.51	3.62	3.73	3.89	3.95	4.08	4.21	4.38	4.52
	λ_C (mho.cm^2/equi.)	----	1.9360	1.7160	1.0340	0.8507	0.7590	0.7480	0.4004	0.2288	0.1716	0.1474	0.1302
AKBS-06	$k.10^5$ (mho)	3.04	3.22	3.33	3.48	3.64	3.79	3.92	4.22	4.31	4.48	4.68	4.82
	λ_C (mho.cm^2/equi.)	----	1.5840	1.2760	0.9680	0.8800	0.8250	0.7744	0.5192	0.2794	0.2112	0.1804	0.1566
AKBS-07	$k.10^5$ (mho)	3.04	3.40	3.61	3.82	4.12	4.29	4.41	4.59	4.79	4.91	5.01	5.13
	λ_C (mho.cm^2/equi.)	----	3.1680	2.5080	1.7160	1.5840	1.3750	1.2056	0.6820	0.3850	0.2743	0.2167	0.1839
AKBS-08	$k.10^5$ (mho)	3.04	3.28	3.46	3.63	3.72	3.89	4.02	4.32	4.55	4.78	5.08	5.32
	λ_C (mho.cm^2/equi.)	----	2.1120	1.8480	1.2980	0.9973	0.9350	0.8624	0.5632	0.3322	0.2552	0.2244	0.2006
AKBS-09	$k.10^5$ (mho)	3.04	3.19	3.32	3.51	3.77	3.98	4.21	4.46	4.62	4.85	5.02	5.25
	λ_C (mho.cm^2/equ.)	----	1.3200	1.2320	1.0340	1.0707	1.0340	1.0296	0.6248	0.3476	0.2655	0.2178	0.1945

Table 3.4: The Conductance (k) and equivalent conductance (λ_C) of Schiff bases in DMSO at 308.15 K.

Compounds	Conc. (g/lit)	0.000	0.001	0.002	0.004	0.006	0.008	0.010	0.020	0.040	0.060	0.080	0.100
AKBS-01	$k.10^5$ (mho)	1.00	1.29	1.49	1.87	2.08	2.41	2.67	2.98	3.21	3.46	3.72	4.00
	λ_C (mho.cm^2/equi.)	----	2.5520	2.1560	1.9140	1.5840	1.5510	1.4696	0.8712	0.4862	0.3608	0.2992	0.2640
AKBS-02	$k.10^5$ (mho)	1.00	1.83	2.39	2.61	2.86	3.29	3.44	3.83	4.12	4.39	4.67	4.82
	λ_C (mho.cm^2/equi.)	----	7.3040	6.1160	3.5420	2.7280	2.5190	2.1472	1.2452	0.6864	0.4972	0.4037	0.3362
AKBS-03	$k.10^5$ (mho)	1.00	1.89	2.23	2.59	2.84	3.19	3.43	3.79	3.93	4.11	4.36	4.57
	λ_C (mho.cm^2/equi.)	----	7.8320	5.4120	3.4980	2.6987	2.4090	2.1384	1.2276	0.6446	0.4561	0.3696	0.3142
AKBS-04	$k.10^5$ (mho)	1.00	2.27	2.41	2.62	3.29	3.44	3.69	3.98	4.19	4.35	4.53	4.76
	λ_C (mho.cm^2/equi.)	----	11.1760	6.2040	3.5640	3.3587	2.6840	2.3672	1.3112	0.7018	0.4913	0.3883	0.3309
AKBS-05	$k.10^5$ (mho)	1.00	2.29	2.45	2.64	2.91	3.17	3.38	3.69	3.88	4.06	4.29	4.40
	λ_C (mho.cm^2/equi.)	----	11.3520	6.3800	3.6080	2.8013	2.3870	2.0944	1.1836	0.6336	0.4488	0.3619	0.3010
AKBS-06	$k.10^5$ (mho)	1.00	2.11	2.37	2.52	2.78	2.98	3.17	3.32	3.61	3.91	4.12	4.32
	λ_C (mho.cm^2/equi.)	----	9.7680	6.0280	3.3440	2.6107	2.1780	1.9096	1.0208	05742	0.4268	0.3432	0.2922
AKBS-07	$k.10^5$ (mho)	1.00	2.13	2.35	2.61	2.89	3.09	3.22	3.48	3.59	3.81	4.06	4.24
	λ_C (mho.cm^2/equi.)	----	0.9440	5.9400	3.5420	2.7720	2.2990	1.9536	1.0912	0.5698	0.4121	0.3366	0.2851
AKBS-08	$k.10^5$ (mho)	1.00	1.65	1.96	2.32	2.69	3.20	3.48	3.69	3.96	4.29	4.47	4.67
	λ_C (mho.cm^2/equi.)	----	5.7200	4.2240	2.9040	2.4787	2.4200	2.1824	1.1836	0.6512	0.4825	0.3817	0.3230
AKBS-09	$k.10^5$ (mho)	1.00	1.60	2.12	2.48	2.70	2.89	3.20	3.47	3.75	4.05	4.38	4.52
	λ_C (mho.cm^2/equi.)	----	5.2800	4.9280	3.2560	2.4933	2.0790	1.9360	1.0868	0.6050	0.4473	0.3718	0.3098

Figure 3.1: The variation of Conductance with concentration for Chalcones in [A] DMF and [B] $CHCl_3$ at 308.15 K.

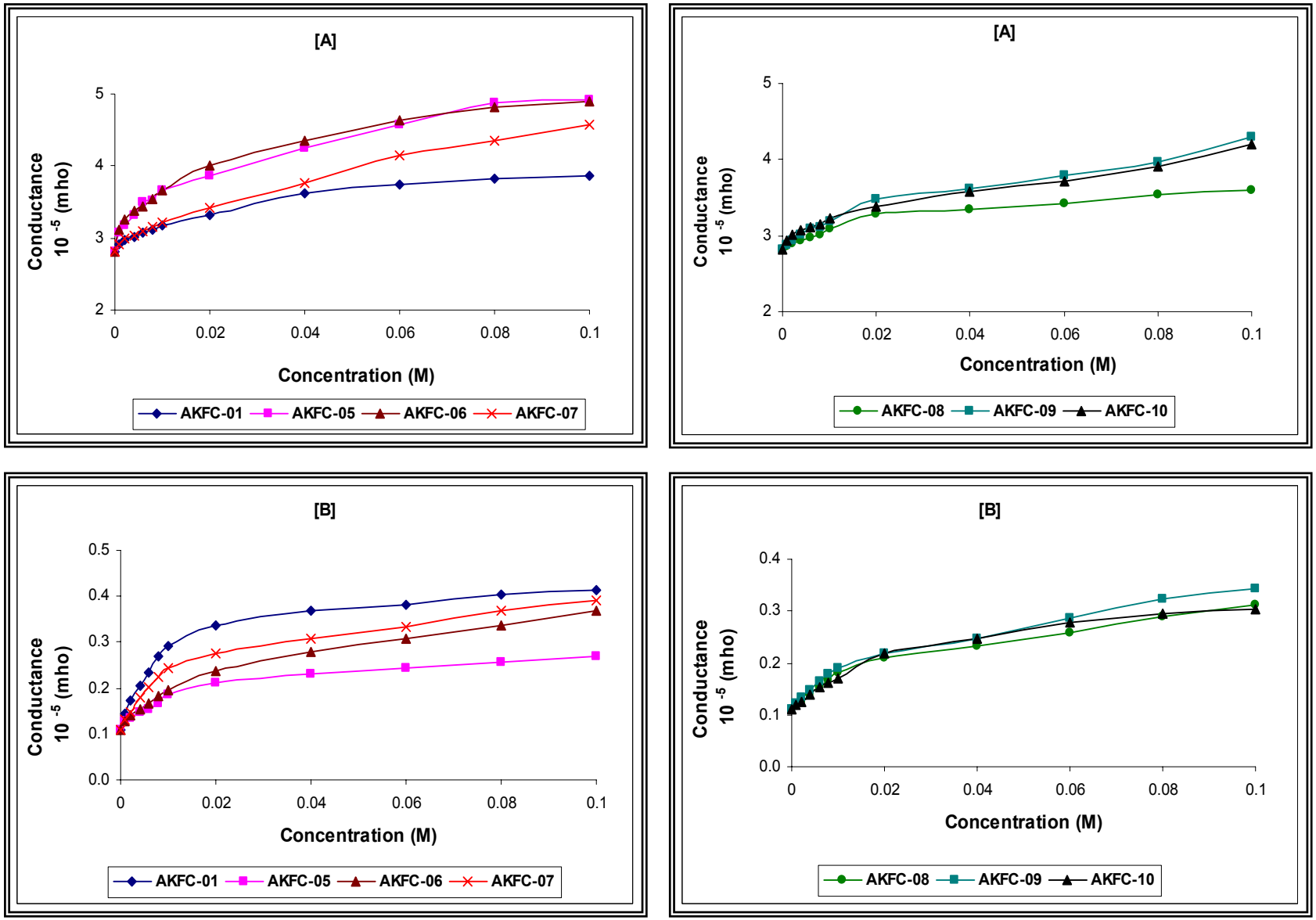

Figure 3.2: The variation of Conductance with concentration for Schiff bases in [A] DMF and [B] DMSO at 308.15 K.

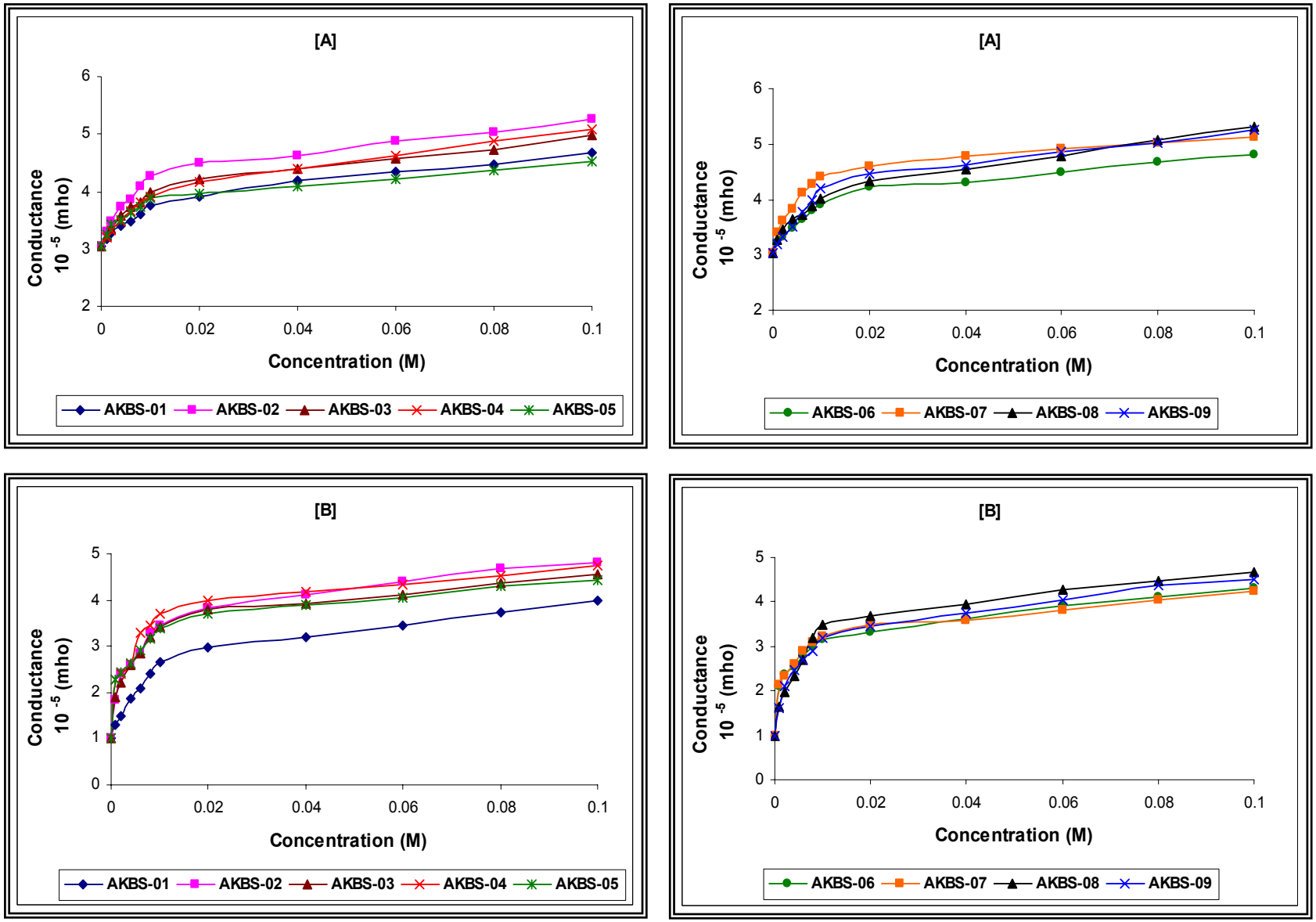

Figure 3.3: The variation of equivalent conductance with √C for Chalcones in [A] DMF and [B] $CHCl_3$ at 308.15 K.

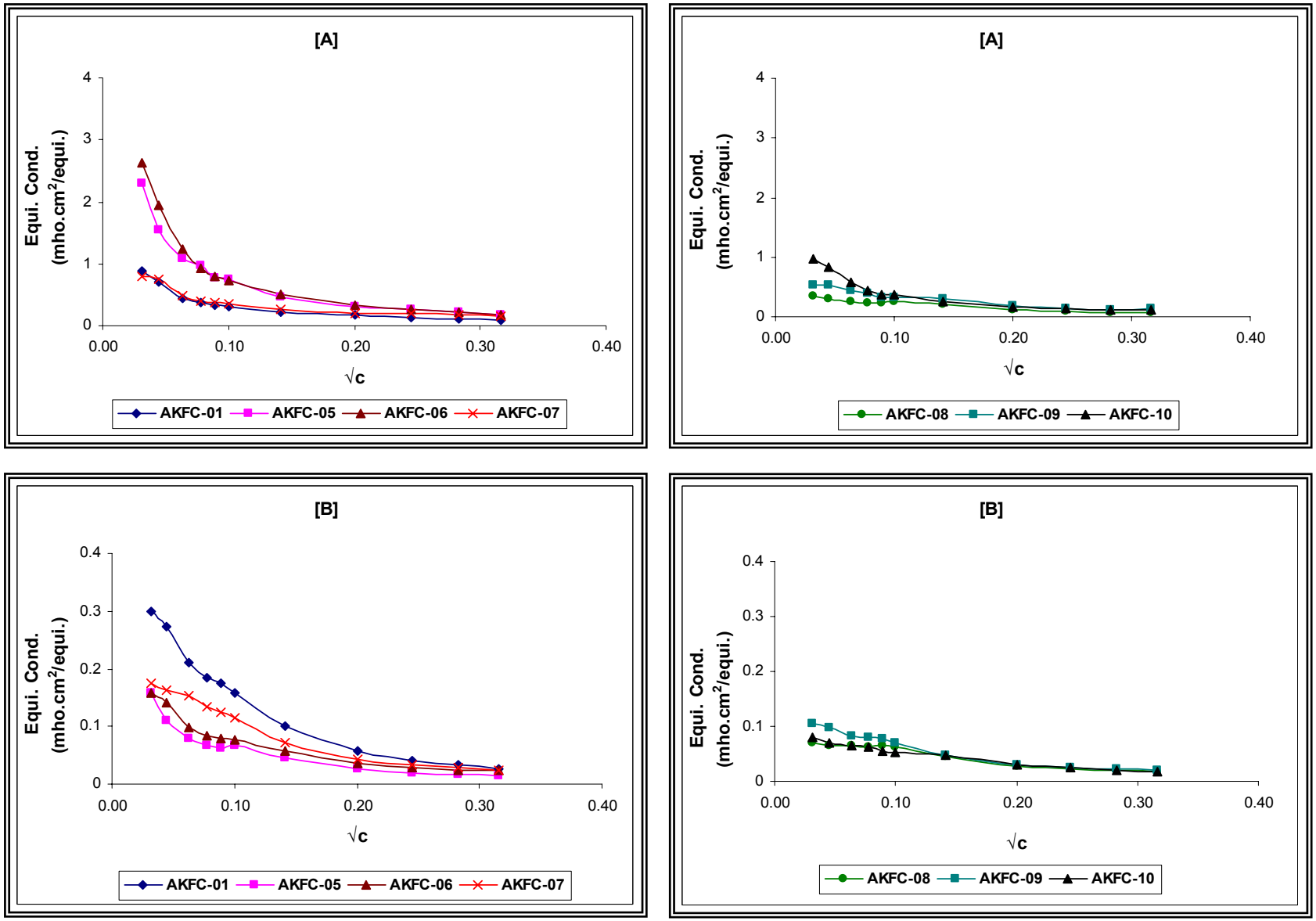

Figure 3.4: The variation of equivalent conductance with √C for Schiff bases in [A] DMF and [B] DMSO at 308.15 K.

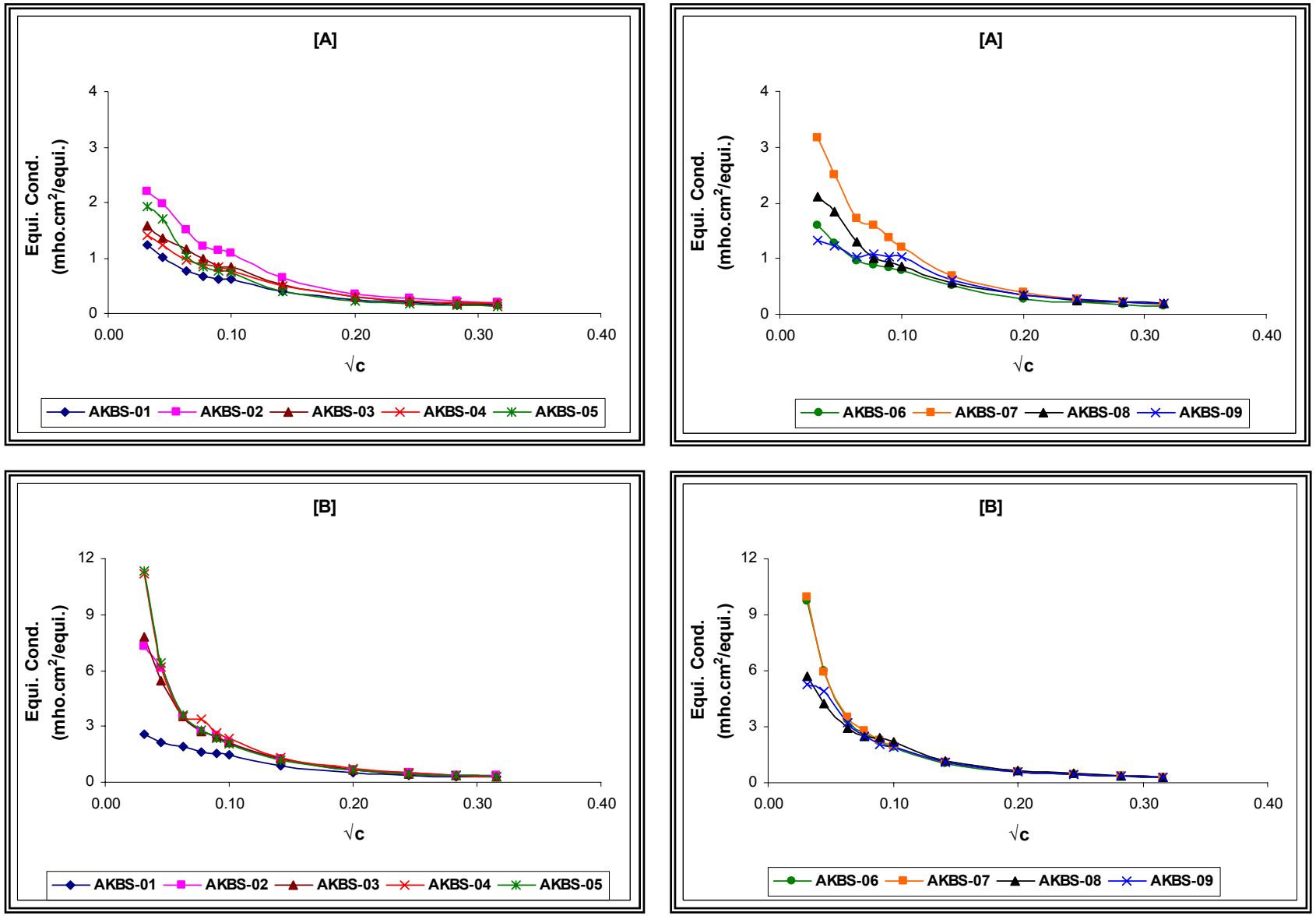

Table 3.5: The limiting equivalent conductance (λ_0) of chalcones in DMF and $CHCl_3$ at 308.15 K.

Compounds Code	λ_0 mho.cm^2/equi.	
	DMF	$CHCl_3$
AKFC-01	1.15	0.36
AKFC-05	-	0.22
AKFC-06	-	0.20
AKFC-07	1.90	0.20
AKFC-08	0.50	0.08
AKFC-09	0.71	0.14
AKFC-10	1.70	0.09

Table 3.6: The limiting equivalent conductance (λ_0) of all the Schiff bases in DMF and DMSO at 308.15 K.

Compounds Code	λ_0 mho.cm^2/equi.	
	DMF	DMSO
AKBS-01	1.55	3.25
AKBS-02	2.74	-
AKBS-03	2.02	-
AKBS-04	1.56	-
AKBS-05	3.09	-
AKBS-06	2.60	-
AKBS-07	-	-
AKBS-08	2.92	6.84
AKBS-09	1.60	7.80

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Section-IV

Heat of Solutions

INTRODUCTION

The addition of some solutes to a solvent will raise the temperature of the solution, while others may lower the temperature and still others will have no noticeable effect. This behavior depends on the nature of solute in a particular solvent.

Thus, dissolution of a solute in a solvent is accompanied by the heat change i.e., enthalpy change (ΔH) of the system. If the heat is absorbed i.e., the solution is cooler then ΔH is positive. If the heat is evolved i.e., the solution is warmer then ΔH is negative. Thus, the heat of solution is defined as the change in enthalpy when one mole of substance is dissolved in specified quantity of solvent at a given temperature.

The molar heat of solution and melting temperature of a substance can be determined from the solubility measurements at different temperatures [(1)]. Literature survey shows that various workers studied thermodynamic properties of several electrolytes in various pure and mixed solvents [(2-10)]. The heat of solution for many inorganic, organic, drugs and polymeric compounds has also been reported [(11-18)]. In our laboratory, heat of solution of some organic compounds has also been determined [(19, 20)].

In the present work, heat of solution for some chalcones and Schiff bases derivatives was determined in N,N-dimethylformamide (DMF) and 1,4 dioxan at different temperatures (298.15K to 318.15K). Further, Gibb's free energy and entropy of different solutions have also been evaluated.

EXPERIMENTAL

The solvents used for the measurements were purified and fractionally distilled prior to use by the method reported in the literature [21].

The saturated solution of each Chalcone/Schiff base was prepared in DMF/1, 4-Dioxan at desired temperature. A portion of this solution was filtered. From the filtrate, a known volume was transferred in a pre-weighed beaker. The weight of beaker along with solution was taken and the solvent was evaporated to dryness at room temperature until constant weight is obtained. All the weights were taken using an electronic balance (Mettler Toledo AB204-S, Switzerland) with an uncertainty of $\pm$ 0.0001 g. This gives the weight of solute present in known volume of saturated solution. Three replicate measurements were carried out at a particular temperature and average value of weight was taken for calculation. The experiment was repeated at other temperatures also. Subtraction of weight of solute from the weight of solution gives the weight of solvent in a known volume of saturated solution.

RESULTS AND DISCUSSION

The solubility (*x*) of synthesized compounds (chalcones and Schiff bases) in DMF and 1, 4 Dioxan are given in Tables 4.1 - 4.4 respectively. It is evident from the Tables that the solubility of both the series increases with temperature in both the solvents. Comparison of solubility in the two solvents shows that overall solubility is greater in DMF than that in 1,4 Dioxan for both chalcones and Schiff bases. This is expected because the dielectric constant and dipole moment of DMF (36.71, 3.86) are greater than that of 1,4 Dioxan (2.209, 0). Thus, these properties of solvent play an important role on the solubility.

The temperature dependence solubility in solvents is described by the modified Apelblat equation [22, 23]

$$\ln x = A + B(T/K) \qquad \text{..... (4.1)}$$

where x is the solubility of compounds; T is the absolute temperature and A and B are the coefficients. The values of these coefficients were evaluated from the ln x verses T and are given in Tables 4.5 and 4.6. Using these values of A and B, calculated solubilities x_c were evaluated and are reported in Tables 4.1 to 4.4, along with experimental solubility.

Further, the relative deviations (*RD*) between the experimental and calculated values of solubilities are calculated by the following eq. and are given in Tables 4.1 to 4.4.

$$\text{Relative Deviation} = \left(\frac{x\text{-}x_{ci}}{x} \right) \qquad \text{..... (4.2)}$$

The relative average deviation (*ARD*) and root mean square deviations (*rmsd*) were also calculated by equations.

$$ARD = \frac{1}{N} \sum_{i}^{N} \frac{x_i\text{-}x_{ci}}{x_i} \qquad \text{..... (4.3)}$$

$$rmsd = \left[\sum_{i=1}^{N} \frac{(x_{ci}\text{-}x_i)^2}{N-1} \right]^{1/2} \qquad \text{..... (4.4)}$$

where N is the number of experimental points. These values are given in Tables 4.5 and 4.6.

Table 4.1: The experimental solubility (x), calculated solubility (x_c) and relative deviation (RD) of Chalcones in DMF at different temperatures.

Temp. K	x. 10^3	x_c. 10^3	100 RD	x. 10^3	x_c. 10^3	100 RD
	AKFC-01			**AKFC-06**		
298.15	11.1508	11.1486	-0.0224	7.0453	7.1254	0.2101
308.15	11.3219	11.2606	-0.0489	7.1360	7.2331	0.2555
318.15	11.7779	11.3737	-0.0246	7.2546	7.3420	0.2263
	AKFC-02			**AKFC-07**		
298.15	2.3739	2.3524	-0.1678	9.8328	9.9009	0.1313
308.15	2.4364	2.4023	-0.2519	9.9806	10.0605	0.1552
318.15	2.4776	2.4533	-0.1821	10.1482	10.2228	0.1415
	AKFC-03			**AKFC-08**		
298.15	6.0358	6.0993	0.1868	6.6487	6.7056	0.1523
308.15	6.1363	6.1853	0.1384	6.7541	6.8411	0.2381
318.15	6.2037	6.2725	0.1992	6.9158	6.9793	0.1656
	AKFC-04			**AKFC-09**		
298.15	2.6382	2.6414	0.0028	9.4028	9.4729	0.1413
308.15	2.6407	2.6441	0.0039	9.5000	9.5681	0.1356
318.15	2.6433	2.6467	0.0040	9.5886	9.6643	0.1511
	AKFC-05			**AKFC-10**		
298.15	4.5019	4.4674	-0.1604	6.9569	6.9408	-0.0645
308.15	4.6830	4.6126	-0.3001	7.1006	7.0668	-0.1143
318.15	4.8030	4.7626	-0.1762	7.2138	7.1952	-0.0704

Table 4.2: The experimental solubility (x), calculated solubility (x_c) and relative deviation (RD) of Chalcones in 1, 4 Dioxan at different temperatures.

Temp. K	x. 10^3	x_c. 10^3	100 RD	x. 10^3	x_c. 10^3	100 RD
	AKFC-01			**AKFC-06**		
298.15	7.3170	7.2316	-0.2566	4.8876	4.9293	0.1419
308.15	7.3674	7.2897	-0.2338	4.9513	4.9938	0.1432
318.15	7.4410	7.3482	-0.2740	5.0138	5.0591	0.1521
	AKFC-02			**AKFC-07**		
298.15	2.2924	2.2916	-0.0234	5.5346	5.6106	0.2444
308.15	2.3888	2.3708	-0.1430	5.6539	5.7125	0.1811
318.15	2.4543	2.4528	-0.0279	5.7331	5.8162	0.2610
	AKFC-03			**AKFC-08**		
298.15	5.9583	5.8827	-0.2668	5.7296	5.7117	-0.0785
308.15	6.0152	5.9419	-0.2577	5.8158	5.8038	-0.0580
318.15	6.0841	6.0016	-0.2855	5.9174	5.8974	-0.0838
	AKFC-04			**AKFC-09**		
298.15	2.4506	2.4938	0.2731	7.0521	7.0437	-0.0419
308.15	2.5024	2.5416	0.2421	7.0964	7.0861	-0.0473
318.15	2.5492	2.5904	0.2507	7.1383	7.1287	-0.0449
	AKFC-05			**AKFC-10**		
298.15	2.7128	2.6868	-0.1810	6.1717	6.1454	-0.1018
308.15	2.7748	2.7465	-0.1918	6.2202	6.2009	-0.0788
318.15	2.8369	2.8076	-0.1947	6.2858	6.2570	-0.1084

Table 4.3: The experimental solubility (x), calculated solubility (x_c) and relative deviation (RD) of Schiff bases in DMF at different temperatures.

Temp. K	x. 10^3	x_c. 10^3	100 RD	x. 10^3	x_c. 10^3	100 RD
	AKBS-01			**AKBS-06**		
298.15	6.6251	6.6149	-0.0487	4.5519	4.5624	0.0249
308.15	6.7161	6.6880	-0.1016	4.6119	4.6360	0.0791
318.15	6.7740	6.7620	-0.0534	4.6992	4.7108	0.0280
	AKBS-02			**AKBS-07**		
298.15	7.3062	7.3392	0.0736	5.3202	5.2532	-0.2600
308.15	7.4207	7.4352	0.0219	5.4064	5.3379	-0.2622
318.15	7.4973	7.5325	0.0777	5.4982	5.4240	-0.2791
	AKBS-03			**AKBS-08**		
298.15	3.6945	3.7170	0.0906	9.5027	9.5346	0.0540
308.15	3.7755	3.7845	0.0249	9.5748	9.6208	0.0851
318.15	3.8290	3.8532	0.0958	9.6734	9.7077	0.0585
	AKBS-04			**AKBS-09**		
298.15	7.8677	7.7792	-0.2514	8.5279	8.4139	-0.3003
308.15	7.8898	7.7948	-0.2680	8.5667	8.4561	-0.2909
318.15	7.9058	7.8104	-0.2687	8.6217	8.4985	-0.3207
	AKBS-05			**AKBS-10**		
298.15	6.1672	6.1261	-0.1491	4.3007	4.3352	0.1288
308.15	6.2623	6.2063	-0.1949	4.3362	4.3744	0.1431
318.15	6.3331	6.2875	-0.1608	4.3767	4.4139	0.1380

Table 4.4: The experimental solubility (x), calculated solubility (x_c) and relative deviation (RD) of Schiff bases in 1, 4 Dioxan at different temperatures.

Temp. K	x. 10^3	x_c. 10^3	100 RD	x. 10^3	x_c. 10^3	100 RD
	AKBS-01			**AKBS-06**		
298.15	6.4294	6.4089	-0.0811	4.2314	4.1950	-0.1761
308.15	6.5512	6.5057	-0.1563	4.3335	4.2969	-0.1738
318.15	6.6275	6.6040	-0.0887	4.4423	4.4012	-0.1893
	AKBS-02			**AKBS-07**		
298.15	6.7018	6.6776	-0.0901	5.1738	5.2195	0.1493
308.15	6.7850	6.7717	-0.0571	5.2530	5.2931	0.1270
318.15	6.8939	6.8672	0.0959	5.3181	5.3677	0.1595
	AKBS-03			**AKBS-08**		
298.15	3.6088	3.6370	0.1206	7.1412	7.1165	-0.0879
308.15	3.6995	3.7142	0.0531	7.2357	7.2024	-0.1112
318.15	3.7622	3.7930	0.1281	7.3170	7.2894	-0.0947
	AKBS-04			**AKBS-09**		
298.15	4.7218	4.7028	-0.0931	7.7973	7.8820	0.2047
308.15	4.8201	4.7786	-0.1799	7.9066	7.9692	0.1450
318.15	7.8774	4.8557	-0.1018	7.9660	8.0573	0.2179
	AKBS-05			**AKBS-10**		
298.15	5.5149	5.5030	-0.0595	3.7788	3.7885	0.0280
308.15	5.5830	5.5806	-0.0262	3.8402	3.8458	0.0079
318.15	5.6725	5.6592	-0.0630	3.8936	3.9039	0.0295

Table 4.5: Coefficient A and B of equation 4.1, relative average deviation (ARD) and root mean square deviation (rmsd) of chalcones in DMF and 1, 4 Dioxan.

Compounds	A	B	10^7 rmsd	100 ARD	A	B	10^7 rmsd	100 ARD
	DMF				1, 4 Dioxan			
AKFC-01	-5.3159	0.0027	0.3551	-0.2453	-5.1687	0.0008	0.1461	-0.2548
AKFC-02	-6.6795	0.0021	0.0147	-0.2006	-7.0933	0.0034	0.0021	-0.0648
AKFC-03	-5.5179	0.0014	0.0745	0.1748	-5.4348	0.0010	0.1191	-0.2700
AKFC-04	-5.9673	0.0001	0.0002	0.0035	-6.5615	0.0019	0.0341	0.2553
AKFC-05	-6.3660	0.0032	0.0517	-0.2122	-6.5764	0.0022	0.0155	-0.1892
AKFC-06	-5.3922	0.0015	0.1570	0.2306	-5.7011	0.0013	0.3744	0.1457
AKFC-07	-5.0930	0.0016	0.1106	0.1427	-5.7207	0.0018	0.1074	0.2288
AKFC-08	-5.6020	0.0020	0.0989	0.1853	-5.6432	0.0016	0.0057	-0.0735
AKFC-09	-4.9583	0.0010	0.1020	0.1427	-5.1354	0.0006	0.0017	-0.0447
AKFC-10	-5.5079	0.0018	0.0116	-0.0831	-5.3613	0.0009	0.0126	-0.0963

Table 4.6: Coefficient A and B of equation 4.1, relative average deviation (ARD) and root mean square deviation (rmsd) of Schiff bases in DMF and 1, 4 Dioxan.

Compounds	A	B	10^7 rmsd	100 ARD	A	B	10^7 rmsd	100 ARD
	DMF				1, 4 Dioxan			
AKBS-01	-5.3473	0.0011	0.0068	-0.0679	-5.4982	0.0015	0.0202	-0.0010
AKBS-02	-5.3030	0.0013	0.0169	0.0577	-5.4273	0.0014	0.0097	-0.0008
AKBS-03	-6.1325	0.0018	0.0078	0.0704	-6.2437	0.0021	0.0131	0.0010
AKBS-04	-4.9168	0.0002	0.1728	-0.2627	-5.8376	0.0016	0.0169	-0.0012
AKBS-05	-5.4837	0.0013	0.0459	-0.1683	-5.6208	0.0014	0.0021	-0.0004
AKBS-06	-5.8679	0.0016	0.0055	0.0440	-6.1904	0.0024	0.0289	-0.0017
AKBS-07	-5.7269	0.0016	0.0978	-0.2671	-5.6737	0.0014	0.0411	0.0014
AKBS-08	-4.9220	0.0009	0.0288	0.0659	-5.3040	0.0012	0.0164	-0.0009
AKBS-09	-4.9278	0.0005	0.2691	-0.3040	-5.1720	0.0011	0.1296	0.0018
AKBS-10	-5.7103	0.0009	0.0269	0.1367	-6.0240	0.0015	0.0015	0.0002

According to van't Hoff analysis [24], the standard enthalpy change of solution is obtained from the slope the *ln x* versus *1/T* plot. However, in recent thermodynamic treatment, some modifications have been introduced in the van't Hoff equation to diminish the propagation of errors and consequently to separate the chemical effects from those due to statistical treatment used when enthalpy-entropy compensation plots are developed [25]. For this reason, the mean harmonic temperature (T_{hm}) is used in the van't Hoff analysis, which is calculated by the following equation.

$$T_{hm} = \frac{n}{\sum_{i}^{n}\left(1/T\right)} \qquad \text{..... (4.5)}$$

where n is the number of temperatures studied. In the present case, the T_{hm} value obtained is 307.93 K.

So, the modified van't Hoff equation is [26, 27].

$$\frac{\partial \ln x}{\partial\left(1/T - 1/T_{hm}\right)_P} = -\frac{\Delta H_S}{R} \qquad \text{..... (4.6)}$$

where ΔH_s is the heat of solution and R is the gas constant.

Figures 4.1 and 4.2 show the van't Hoff plots for AKFC-01 (Chalcone) and AKBS-01 (Schiff base) respectively, in DMF and 1, 4 Dioxan solutions. From these liner plots, ΔH_s values were calculated from the slope of straight line. From the intercept of these plots ΔG values were evaluated by the equation [26].

$$\Delta G = -RT \times \text{Intercept} \qquad \text{..... (4.7)}$$

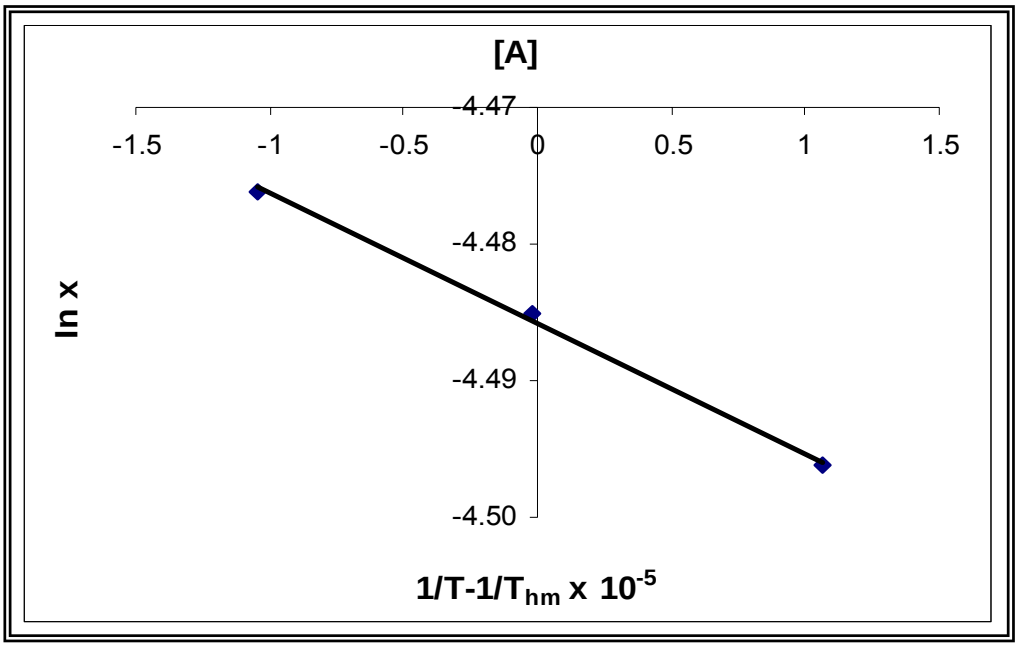
Using these evaluated ΔH and ΔG values, the entropies of solutions ΔS were obtained from equation 4.8.

$$\Delta S = \frac{\Delta H_S - \Delta G}{T_{hm}} \qquad \text{..... (4.8)}$$

All these thermodynamic parameters are given in Tables 4.7 and 4.8.

It is evident from tablets that for all the compounds ΔH_s and ΔG values are positive whereas ΔS values are negative. When stronger bonds are broken and weaker bonds are formed, energy is consumed and so, ΔH_s become positive [28]. This indicates endothermic dissolution of compounds where the enthalpy term contributes to an unfavorable positive value of ΔG.

Figure 4.1: Van't Hoff plots for AKFC-01 (Chalcone) in [A] DMF and [B] 1,4 Dioxan.



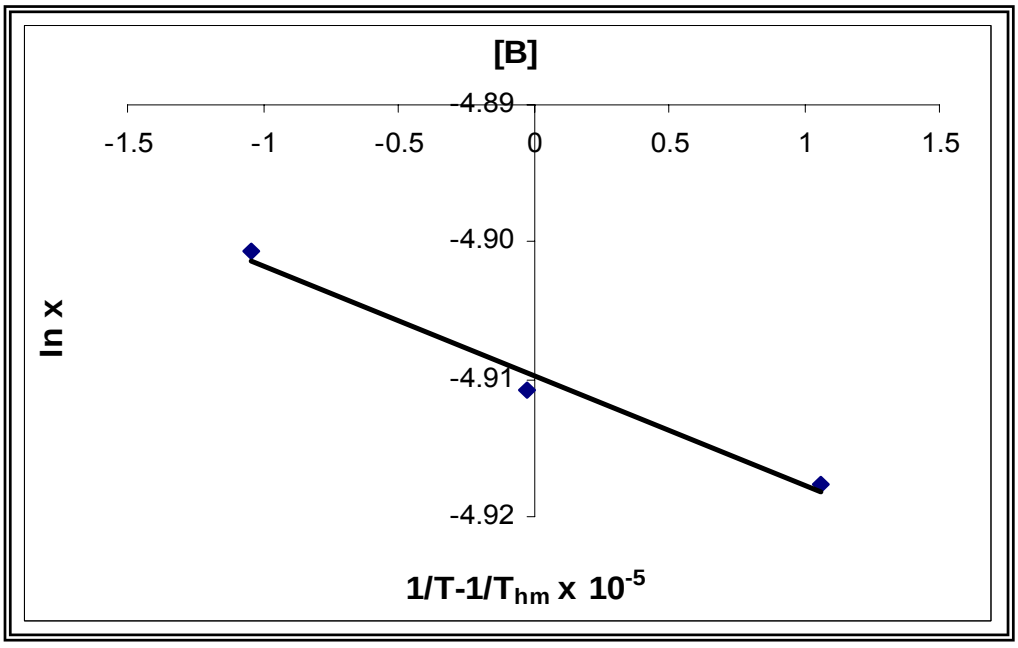
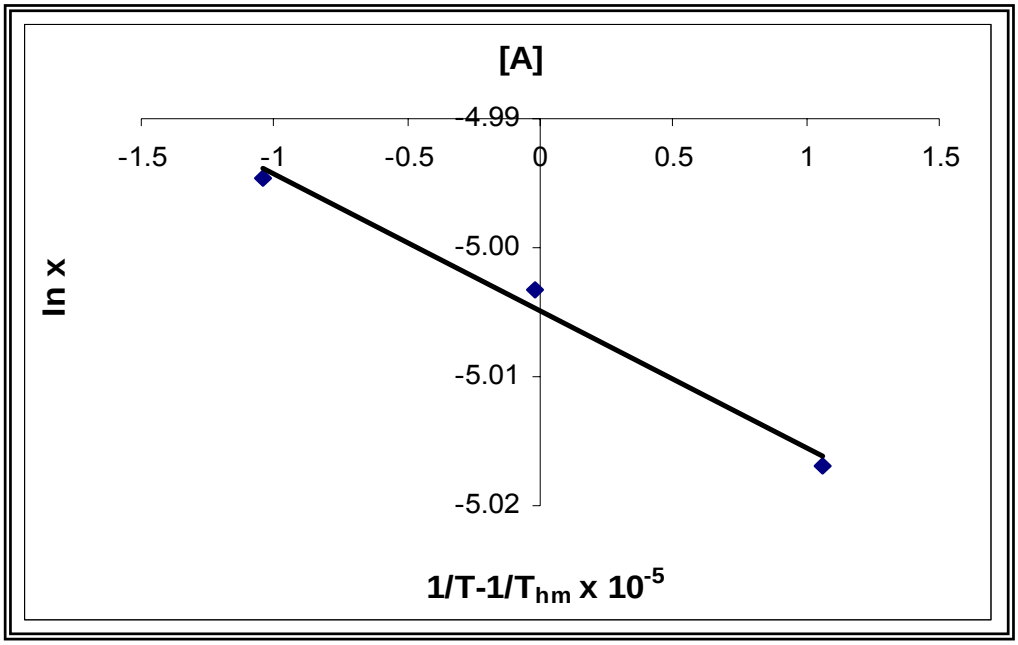


Figure 4.2: Van't Hoff plots for AKBS-01 (Schiff base) in [A] DMF and [B] 1,4 Dioxan.



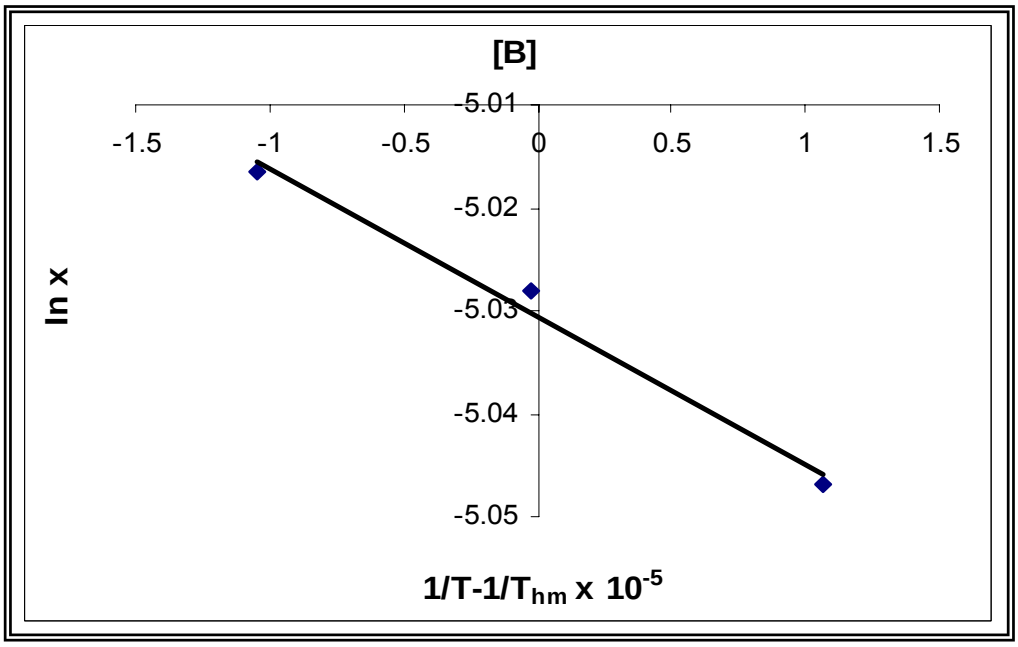


Table 4.7: Thermodynamic parameters of chalcones in DMF and 1, 4 Dioxan at 307.93 K (T_{hm}).

Compounds	ΔH_s (cal/mol)	ΔG (kcal/mol)	ΔS (cal/mol.k)	ΔH_s (cal/mol)	ΔG (kcal/mol)	ΔS (cal/mol.k)
	DMF			1, 4 Dioxan		
AKFC-01	189.53	2.7447	-8.2977	158.08	3.0040	-9.2422
AKFC-02	403.99	3.6836	-10.6504	644.44	3.6966	-9.9120
AKFC-03	258.92	3.1176	-9.2837	196.67	3.1283	-9.5204
AKFC-04	18.15	3.6324	-11.7373	371.78	3.6658	-10.6974
AKFC-05	421.38	3.6022	-10.3296	421.38	3.6022	-10.3296
AKFC-06	275.29	3.0234	-8.9245	240.22	3.2478	-9.7672
AKFC-07	297.27	2.8185	-8.1877	332.64	3.1681	-9.2082
AKFC-08	370.33	3.0562	-8.7224	303.53	3.1488	-9.2401
AKFC-09	184.46	2.8493	-8.6540	114.44	3.0276	-9.4606
AKFC-10	342.10	3.0281	-8.7229	172.29	3.1077	-9.5326

Table 4.8: Thermodynamic parameters of Schiff bases in DMF and 1, 4 Dioxan at 307.93 K (T_{hm}).

Compounds	ΔH_s (cal/mol)	ΔG (kcal/mol)	ΔS (cal/mol.k)	ΔH_s (cal/mol)	ΔG (kcal/mol)	ΔS (cal/mol.k)
	DMF			1, 4 Dioxan		
AKBS-01	209.86	3.0623	-9.2632	286.72	3.0779	-9.0644
AKBS-02	243.74	3.0013	-8.9550	265.90	3.0543	-9.0552
AKBS-03	337.53	3.4153	-9.9949	393.00	3.4277	-9.8552
AKBS-04	45.51	2.9628	-9.4740	306.45	3.2660	-9.6112
AKBS-05	250.58	3.1049	-9.2694	264.96	3.1736	-9.4457
AKBS-06	299.42	3.2901	-9.7121	458.04	3.3292	-9.3239
AKBS-07	309.91	3.1938	-9.3655	259.44	3.2122	-9.5890
AKBS-08	167.42	2.8437	-8.6912	229.26	3.0161	-9.0502
AKBS-09	102.84	2.9120	-9.1227	202.29	2.9627	-8.9645
AKBS-10	164.89	3.3287	-10.2746	282.13	3.4038	-10.1375

Thus, positive values of ΔG indicates that the dissolution process is not spontaneous [28]. The negative entropy indicates less randomness in solutions [28].

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Section-V

Partition Coefficient

INTRODUCTION

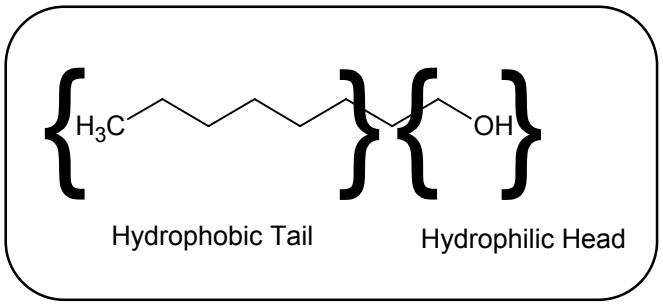
The extent of the solubility of a solute in a given solvent depends upon solvent-solute interactions. In a mixture of the two immiscible solvents, if a solute, which is soluble in both solvents, is added, the ratio of the concentration of the solute in the two solvents always remains constant. This is known as partition or distribution coefficient.

The knowledge of partition coefficient is utilized in many branches of chemistry, biology and their associated technologies [(1)]. In the fields of chemistry, organic and medicinal chemistry are main branches in which partition (P) or distribution coefficient (D) parameter is of great importance. Recently, it is used in QSAR.

The aim of Quantitative Structure-Activity Relationship (QSAR) techniques is to develop correlations between any property or form of activity normally biological activity and the properties, usually physicochemical properties of a set of molecules. There are many physicochemical parameters in QSAR like hydrophobic, electronic, theoretical and steric parameters. Out of these parameters hydrophobic parameter is one of the most important parameter in QSAR study. The ability of drug to permeate across biological membranes has traditionally been evaluated using its distribution in octanol (representing lipid membrane) and water systems. Hydrophobicity governs the partition behavior between aqueous and nonaqueous phases in natural, technical, and pharmacological processes.

Normally one of the solvents chosen is water while the second is hydrophobic such as octanol. Occasionally, other organic solvents like chloroform, ether, and hexane have also been used as lipid solvents instead of octanol to evaluate drug partitioning behavior. n-octanol is an important molecule both for biological and environmental reasons [(2)].

Figure:- 5.1



- **Biological importance of n-octanol:-**

  n-Octanol is an amphiphilic liquid at room temperature, in which one end is hydrophilic and the other is hydrophobic (Fig-5.1). Due to this property, it is pharmaceutically useful. n-Octanol is a model of phospholipid membranes [3, 4]. Hydrophobic drugs with high partition coefficients are preferentially distributed to hydrophobic compartments such as lipid bilayers of cells while hydrophilic drugs preferentially are found in hydrophilic compartments such as blood serum.

- **Environmental Significance of n-Octanol.**

  In addition to its pharmaceutical uses, the octanol-water partition coefficient is also used to determine bioavailability and environmental fate—that is where pollutants end up in ecosystems. Hydrophobic materials are more likely to settle into organic dirt and sediment than in water. Hydrophilic compounds, on the other hand, will be found more in the aqueous layer of the partition and therefore are more likely to be absorbed in blood and aqueous body systems. They are also more likely to be found in water than in sediment [5]. n-Octanol is also an important model for organic atmospheric aerosols, which come from many sources, including the oxidized organic emissions of plants, fuel vapors, and exhaust from incomplete combustion. Organic aerosols can be very complex, containing hundreds of different compounds made mostly of carbon and hydrogen, but these aerosols can be approximated for study by model molecules. n-Octanol itself does not make up a large portion of atmospheric aerosols, but it shares similar

properties with many of the molecules found in organic aerosols. For example, n-octanol has a localized partial charge and is not very soluble in water [6].

The distribution between water and an immiscible nonpolar solvent is acknowledged as a useful descriptor for the hydrophobicity of a substance. n-Octanol and water are widely accepted as the best two-phase system to model the partitioning between biomass and water. Relationships between the partition coefficient of this system and bioconcentration, [7-10] soil sorption, [11, 13] and toxicity [14, 15] for fish have also been found.

The partition coefficient (log P) value in the range of 1 to 3 has good passive absorption across lipid membranes, and log P greater or less than 3 have often poor transport characteristics.

The traditional method for the determination of K_{ow} values described in the guidelines for testing chemicals by the Organization for Economic Cooperation and Development (OECD) is the shake-flask technique (SF) [16-18]. In this method, water and octanol containing the analyte are shaken until equilibrium is reached. Emulsions may form easily so that accurate determinations of the concentrations in the water phase and hence of $\log K_{ow}$ for highly lipophilic substances are difficult [19]. To overcome this difficulty, the stir-flask method (SS) was developed in which the two phases are not shaken but stirred in a vessel [20]. Another approach for the measurement of partition constants is the generator column method in which water is pumped through a column that is filled with a solid support coated with water saturated octanol containing a known concentration of the analyte [21-23]. Partition between the two phases takes place, and the $\log K_{ow}$ value of highly hydrophobic substances can be determined by analyzing the concentration in the water phase. Unfortunately, the technique is elaborate and relatively hardware intensive. Indirect log K_{ow} determinations from chromatographic retention data have been explored extensively [24-27]. Gasslander *et al.* [28] have measured polymer-water partition coefficient by using organic modifiers in the aqueous phase.

In the present study, partition coefficients of chalcones have been studied in n-Octanol-water system by UV spectroscopy at different pH.

The partition coefficient is highly influenced by pH. So, in the present study, a wide range of pH (0.84 to 8.0) is selected. For 0.84 pH, 0.1 N HCl was taken whereas for 6.0, 7.4 and 8.0, phosphate buffer was used. These values of pH are selected due to their existence in human body. As HCl exists in gastric juice in stomach, 0.1 N HCl is taken. Blood has 7.4 pH, so the study is done at pH 7.4. Further, the middle and upper range of body pH is 6.0 and 8.0 respectively, so study was done at these pH also.

EXPERIMENTAL

n-Octanol is of analytical grade. The purity of solvent was checked by GC and found to be 99.9%. Distilled water was used throughout for all experiments.

Preparation of standard solution:-

10 mg sample was dissolved in n-Octanol to give 100 ml solution of 100 ppm. This solution was known as standard solution. λ_{max} values were measured using UV spectrophotometer (Shimadzu, UV-1700, Pharmaspec) from this solution. Suitable dilutions were made from this standard solution (8 μg to 20 μg) and absorbance (OD) was measured and the calibration curve of OD versus concentration of compounds was drawn.

Determination of Partition coefficient:-

A known amount of the compound under investigation was dissolved in n-Octanol at a concentration not higher than 20 μg. Equal volumes of this solution and water is mixed in oven dried stoppered flask and the mixture was stirred for 24 hrs. at room temperature. After 24 hrs. the solution was transferred into 250 ml of separating funnel and allow it to stand in order to separate the aqueous and organic layers. The organic layer will be upper one while lower will be aqueous. The organic layer was then analyzed by UV spectrophotometer. Using calibration curve, the concentration of compounds in organic layer was then evaluated.

THEORY

Partition coefficient (P) is defined as the ratio of the compounds in organic phase to that present in the aqueous phase. i.e. [29],

$$P = \frac{C_{org}}{C_{aq}} \qquad \ldots(5.1)$$

where C_{org} and C_{aq} are concentration of solute in organic and aqueous phases respectively.

In the present case, concentrations were determined by UV measurement so, equation (5.1) written as [30]:

$$P = \frac{B_E}{B_E - A_E} \qquad \ldots(5.2)$$

where, B_E=Absorbance before extraction and A_E=Absorbance after extraction From equation (5.2) log P were calculated for each set of experiment.

RESULTS AND DISCUSSION

The values of log P for the studied compounds at different pH are given in Table 5.1 and Figure 5.1. The log P values depends upon the hydrophilic and hydrophobic character of compounds. These values are higher for compounds having hydrophobic nature whereas lower log P is for compounds of hydrophilic type.

Table 5.1 shows that when the log P value is higher then the compounds to be hydrophobic and when the log P value is lower then the compounds to be hydrophilic.

It is observed that AKFC-08 is highly hydrophobic in nature among all the compounds whereas AKFC-01 is highly hydrophilic. Thus, AKFC-08 will not be absorbed in blood, and is less likely to spread in the body. However, it is more likely to accumulate in fatty tissues [31, 32]. Overall the decreasing order of hydrophobicity of compounds is:

AKFC-08 > AKFC-07 > AKFC-10 > AKFC-06 > AKFC-03 > AKFC-05 > AKFC-02 > AKFC-01.

In 0.1N HCl-octanol system also, AKFC-08 is again highly hydrophobic whereas AKFC-06 is highly hydrophilic in nature. Thus, in gastric juice also, AKFC-08 will not be absorbed whereas AKFC-06 can be easily absorbed. In this case the decreasing order of hydrophobicity of compounds is:

AKFC-08 > AKFC-05 > AKFC-07 > AKFC-10 > AKFC-02 > AKFC-03 > AKFC-01 > AKFC-06.

In 7.4 pH range, among all these compounds AKFC-02 has minimum log P values whereas maximum is observed for AKFC-06 which can be considered more hydrophobic in nature. The decreasing order of hydrophobicity of compounds is:

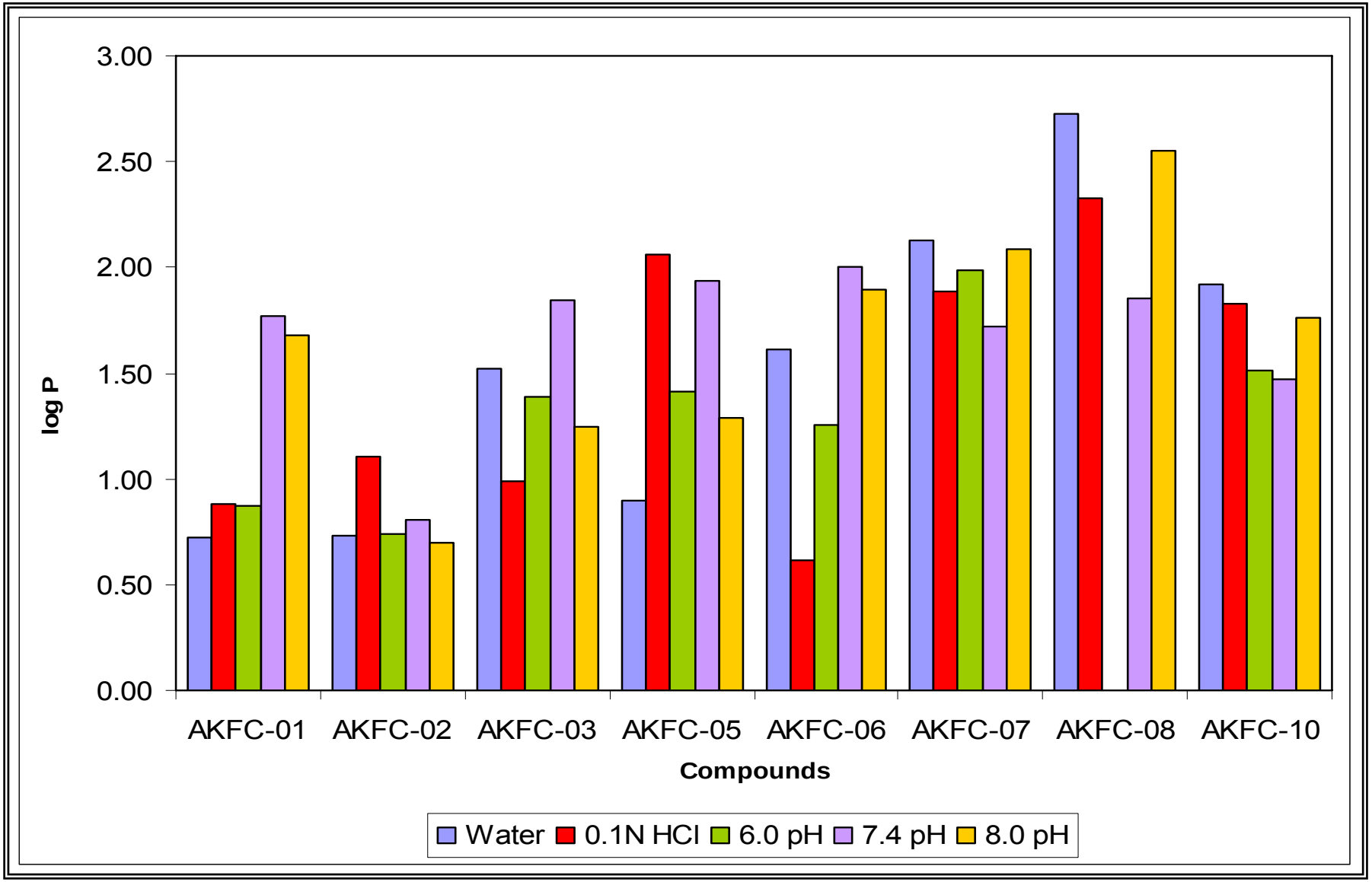
AKFC-06 > AKFC-05 > AKFC-08 > AKFC-03 > AKFC-01 > AKFC-07 > AKFC-10 > AKFC-02.

At 6.0 pH no distribution of AKFC-08 was observed, which in indicate that AKFC-08 is highly hydrophilic in nature. However AKFC-07 showed maximum hydrophobicity. Thus, the results again prove that AKFC-08 can be easily absorbed by the blood, and is likely to spread about the body. Overall the decreasing order of hydrophobicity of compounds is:

Table 5.1. log P values of chalcones

Compounds Code	Max absorption Wavelength/nm	log P				
		Water	0.1N HCl	6.0 pH	7.4 pH	8.0 pH
AKFC-01	378	0.720	0.882	0.875	1.766	1.681
AKFC-02	398	0.728	1.107	0.741	0.802	0.697
AKFC-03	389	1.523	0.988	1.386	1.847	1.245
AKFC-05	382	0.893	2.062	1.409	1.937	1.284
AKFC-06	383	1.610	0.614	1.255	1.999	1.894
AKFC-07	379	2.124	1.887	1.989	1.718	2.086
AKFC-08	394	2.724	2.326	0.000	1.849	2.548
AKFC-10	273	1.918	1.831	1.511	1.474	1.758

Figure 5.1. log P for the studied compounds at different pH.



AKFC-08 > AKFC-02 > AKFC-01 > AKFC-06 > AKFC-03 > AKFC-05 > AKFC-10 > AKFC-07.

However, the nature of AKFC-08 is reversed at pH 8.0. the log P is highest for AKFC-08 and minimum for AKFC-02. Thus, at alkaline pH 8.0 will not be absorbed by the blood but can be accumulated in fatty tissues as observed by Rowe *et al.* [31] and Fresta *et al.* [32]. The decreasing order of hydrophobicity of compounds is:

AKFC-08 > AKFC-07 > AKFC-06 > AKFC-10 > AKFC-01 > AKFC-05 > AKFC-03 > AKFC-02.

Thus, it is concluded that out of 8 studied compounds, AKFC-08 exhibits maximum hydrophobic nature.

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Section-VI

Thermal Properties

INTRODUCTION

Today, an impressive array of powerful, elegant and automated tools is available with physical and material chemists for obtaining quantitative and qualitative information about the composition, structure and characteristics of materials. Among the several instruments and technique, thermal analysis has grown rapidly in recent years. This increasing importance is due to the advancement of thermal analysis technology, relative cheapness of the equipment and time required to achieve the desired results.

Thermal analysis has been used to determine the physical and chemical properties of polymers, geological materials and coals [1-3]. Both quantitative and qualitative analysis can be carried out and one can identify and characterize the samples by qualitative investigations of their thermal behaviors. Current areas of applications include environmental measurements, composition analysis, product reliability, stability, chemical reaction and dynamic properties. Further, various reversible and non-reversible reactions [4, 5], the decomposition of molecules absorbed on a surface, phase transitions etc. can also be studied. This analysis also provides the measurement of overall kinetic parameters of thermally simulated reactions which permit a deeper insight in to the mechanism of high energetic compounds.

Thermal analysis includes a group of techniques in which specific physical properties of a material are measured as a function of time or temperature. The well facilated instrument can measure transition temperature, weight losses, energies of transition, dimensional changes, modulus changes and viscoelectric properties.

Some of commonly used thermal techniques are Differential Scanning Calorimetry (DSC), Differential Thermal Analysis (DTA), Thermo Gravimetric Analysis (TGA), Evolved Gas Detection (EGD), Evolved Gas Analysis (EGA) etc.

In TGA technique, the mass change in a sample is recorded continuously as a function of temperature or time when it is subjected to a programmed temperature change in specific atmosphere. A derivative of

thermo gravimetric curve is useful in resolving the partially over lapping steps in the multi-steps reactions involving the formation of weakly stable intermediates. The shape of any TGA curve depends on the nature of apparatus and the way in which it is used. By TGA, thermal stability, kinetic parameters, compositional analysis etc. can be measured.

Differential Scanning Calorimetry (DSC) has become the most widely used thermal analysis technique. The difference in temperature between the samples and a thermally inert reference material is measured as a function of temperature. Reaction kinetics, purity analysis and polymer cures are the typical applications of DSC. Further, DSC provides useful information about crystallinity, stability of crystallites, glass transition temperature, kinetics parameters etc.

Literature survey shows that thermal analysis has been reported for a number of materials in various fields. Such as pharmaceutical industry [6-13], forensic science applications [14, 15], chemistry [16-18], textile [19, 20], food industry [21, 22], nuclear fuel [23], ceramics [24-26], and polymer industry [27-30] etc. Wendlandt and Collins [31] used DTA and TG technique for the characterization and identification of commercial non prescription analgesics. A number of investigators have studied the physical and chemical properties of various inorganic and organic materials [32-43] by using thermal methods. Kinetic studies of thermal decomposition of various metal complexes have also been reported by several workers [43-53]. Khraisha and Shabib reported thermal analysis of Shale oil [54]. Ruiz et al. have been studied the effect of temperature on cement paste [55]. Wendlandt [56] have applied TGA to study the thermal stability of EDTA as free acid. Further, various workers used this technique as a tool in the characterization of natural rubber and styrene butadiene blends [57, 58].

In this chapter, thermal properties of some chalcones derivatives have been studied by using TGA and DSC techniques.

In these methods, it is assumed that thermal and diffusion barriers are negligible because small quantity of material is used. Further, Arrhenius equation is valid in all these methods.

The kinetic treatments are generally based on the relationship of the type:

$$\frac{dC}{dt} = K\, f(C) \qquad \text{..... (6.1)}$$

where C is the degree of conversion, t is time and K is rate constant. f(C) is a temperature independent function of C.

The constant K is assumed to have to have Arrhenius form:

$$K = A\, e^{-E/RT} \qquad \text{..... (6.2)}$$

C can also be defined as:

$$C = 1-(W/W_0) \qquad \text{..... (6.3)}$$

Where W_0 and W are the initial weight t=0 and weight at any time t of the material.

Equation (6.3) can be written as:

$$(W/W_0) = (1-C) \qquad \text{..... (6.4)}$$

W/W_0 is known as residual weight fraction.

Thus, the rate of conversion is,

$$dC/dt = -\left(1/W_0\right)\left(dW/dt\right) \qquad \text{..... (6.5)}$$

For homogeneous kinetics, the conversion is assumed to be of the form:

$$f(C) = (1-C)^n \qquad \text{..... (6.6)}$$

where n is the order of the reaction.

Substituting the values from equation (5.2) and (5.6) in equation (5.1) gives:

$$\left(dC/dt\right) = A\, e^{-E/RT}(1-C)^n$$

or

$$\left(dC/dt\right) = \left(A/\beta\right) e^{-E/RT}(1-C)^n \qquad \text{..... (6.7)}$$

where A is the frequency factor, β is the rate of heating and E is the energy of activation.

Various methods for single and multiple heating rates have been reported.

The methods of single heating rate are as follows:

1. Freeman-Carroll [59] and Anderson-Freeman Method [60]:

At a single heating rate, Freeman and Carroll gave the following relation to analysis TGA data:

$$\frac{\ln\left(dC/dt\right)}{\ln\left(1-C\right)} = n - \frac{E}{R}\left[\frac{1/T}{\Delta\ln(1-C)}\right] \quad \text{..... (6.8)}$$

A plot of left hand side against (1/T)/(Δln(1-C)) gives a straight line with aslope equal –E/R and the intercept is equal to n.

Anderson and freeman then derived the following equation by using equation (6.8):

$$\Delta \ln\left[dC/dt\right] = n(\Delta \ln(1-C)) - E/R\,\Delta(1/T) \quad \text{..... (6.9)}$$

The plot of (Δln[dC/dt]) against (Δln(1-C)) for equal intervals of Δ(1/T) gives a straight line with slope equal to n and intercept –E/RΔ(1/T).

2. Sharp-Wentworth Method [61]:

To analyse the TGA data for first order kinetics (n=1), Sharp and Wentworth gave the reletion:

$$\log\left[\frac{dC/dt}{(1-C)}\right] = \log\left(\frac{A}{\beta}\right) - \left(\frac{E}{2.303R}\right).\left(\frac{1}{T}\right) \quad \text{..... (6.10)}$$

The plot of log [(dC/dt)/(1-C)] against 1/T would be a straight line with slope equal to –(E/2.303R) and intercept equal to log (A/β).

3. Chatterjee Method [62]:

Based on the weight units, the following relation was developed by Chatterjee:

$$n = \frac{\left[\log\left(dW/dt\right)_1 - \log\left(dW/dt\right)_2\right]}{(\log W_1 - \log W_2)} \quad \text{..... (6.11)}$$

where w_1 and w_2 are the sample weights.

4. Horowitz and Metzger Method [63]:

In this method, the value of energy of activation E can be determined from a single TG curve by the relation:

$$\ln\left[\ln(1-C)^{-1}\right] = \left(E/RT_s^2\right)\theta \quad \text{..... (6.12)}$$

Where $\theta=(T-T_s)T_s$ is the temperature at which the rate of decomposition is maximum. The frequency factor A and entropy change ΔS can be determined by the following equations:

$$\ln E - \ln\left(RT_s^2\right) = \ln A - \ln\beta - E/RT_s \qquad \text{..... (6.13)}$$

$$A = \left(\frac{k_b T}{h}\right) e^{\Delta S/R} \qquad \text{..... (6.14)}$$

where k_b is Boltzmann constant and h is Planck's constant.

EXPERIMENTAL

The Differential Scanning Calorimetry (DSC) and Thermo Gravimetric Analysis (TGA) measurements were made on the instrument “PerkinElmer Thermal” and “Universal V2.6D TA” respectively at the heating rate of 10°C/min in nitrogen atmosphere for all the chalcones derivatives.

RESULT AND DISCUSSION

The TGA and DSC thermograms of chalcones (AKFC-01 and AKFC-02) are given in Figures 6.1 and 6.2. Various thermal properties such as initial decomposition temperature, the decomposition temperature range and the maximum degradation along with the percentage weight loss of chalcones are reported in Table 6.1.

For all the compounds, degradation is multi step process. Each step is of different order. Further, the variation in the trend of thermal decomposition might be interpreted by taking into account some intermolecular interactions (structural as well as electronic) and also because of several experimental factors. However, AKFC-04 is found to be most stable whereas AKFC-10 is less stable. This suggests that the presence of amino group (as in AKFC-04) causes greater stability than that of chromen group (as in AKFC-10).

Further, from the thermograms, various kinetic parameters, such as order of the degradation (n), energy of activation (E), frequency factor (A) and entropy change (ΔS) have also been calculated for each step and are reported in Tables 6.2 and 6.3.

It is evident from Tables 6.2 and 6.3 that order of reaction is quite different in different steps for different chalcones. For first step, order of reaction varies from 1.00 to 6.50, for second step it varies from 3.50 to 9.10.

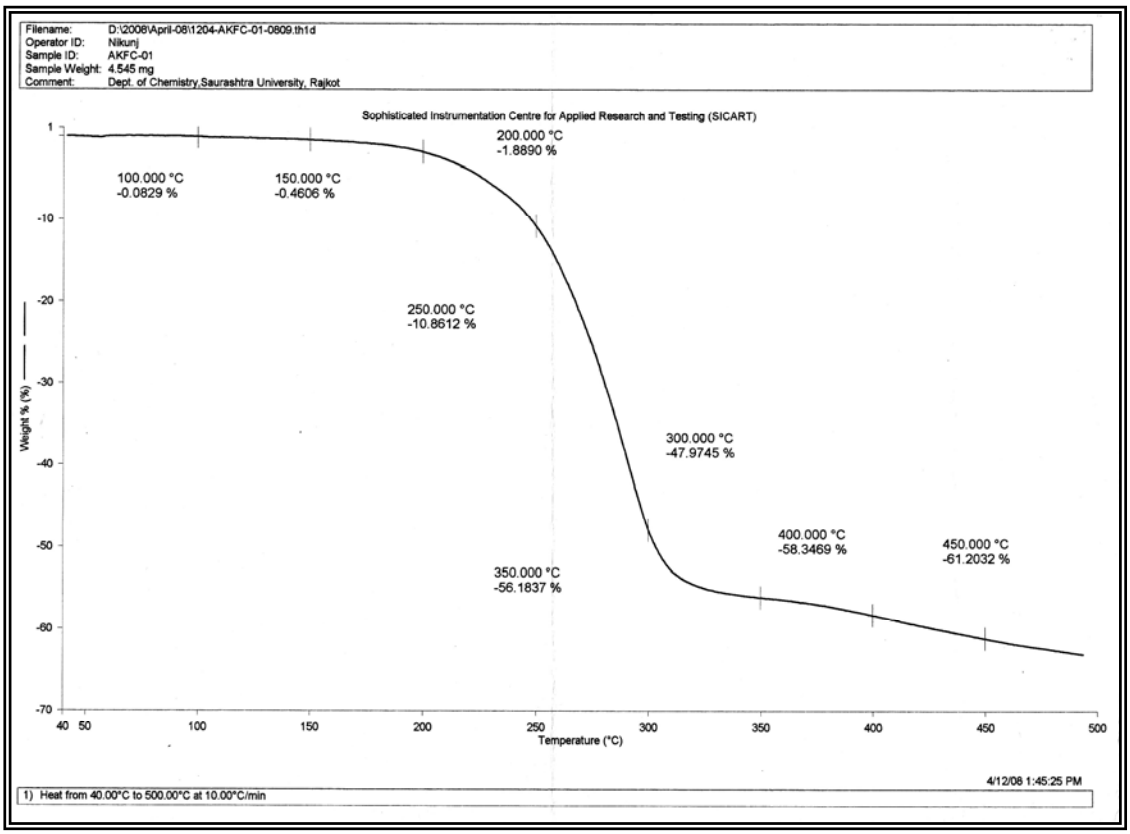
In first step, energy of activation (E) is maximum for AKFC-03 and minimum for AKFC-05. The frequency factor (A) also varies in the same order i.e., maximum for AKFC-03 and minimum for AKFC-05. In second step, energy of activation is found to be maximum for AKFC-10 and minimum for AKFC-09. The frequency factor A follows the same order. AKFC-01 and AKFC-02 degraded in one step only. Comparison of E and A values in Tables 6.2 and 6.3 shows that the values of E and A are minimum for second steps of all the chalcones.

Further, change in entropy (ΔS) for all these reactions were also calculated by equation (6.14) and are reported in Tables 6.2 and 6.3. For the first step, change in entropy (ΔS) values is found to be negative for AKFC-05 and AKFC-10 whereas for other chalcones, ΔS values are positive. For second step, ΔS values are negative for all the studied chalcones.

The positive values of ΔS indicates that the transition state is less ordered than the original compound whereas negative value of ΔS corresponds to an increase in the order of transition state than the reactants (64).

Thus, the degradation in the studied chalcones is multi step process with different order of reaction. Further, thermal stability depends upon the type of substituent present. It is observed that in the above studied chalcones, the presence of amino group (as in AKFC-04) increases the stability whereas chromen group (as in AKFC-10) decreases the stability.

Figure 6.1: The TGA and DSC graphs of AKFC-01



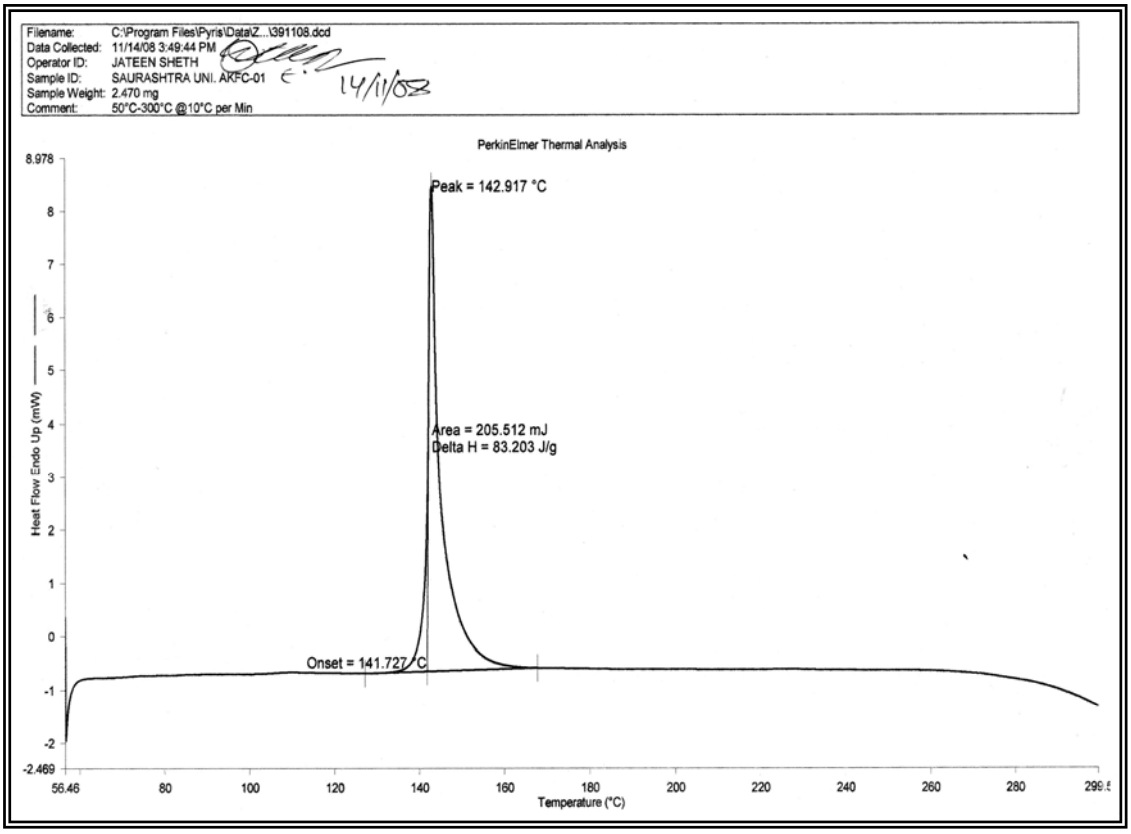
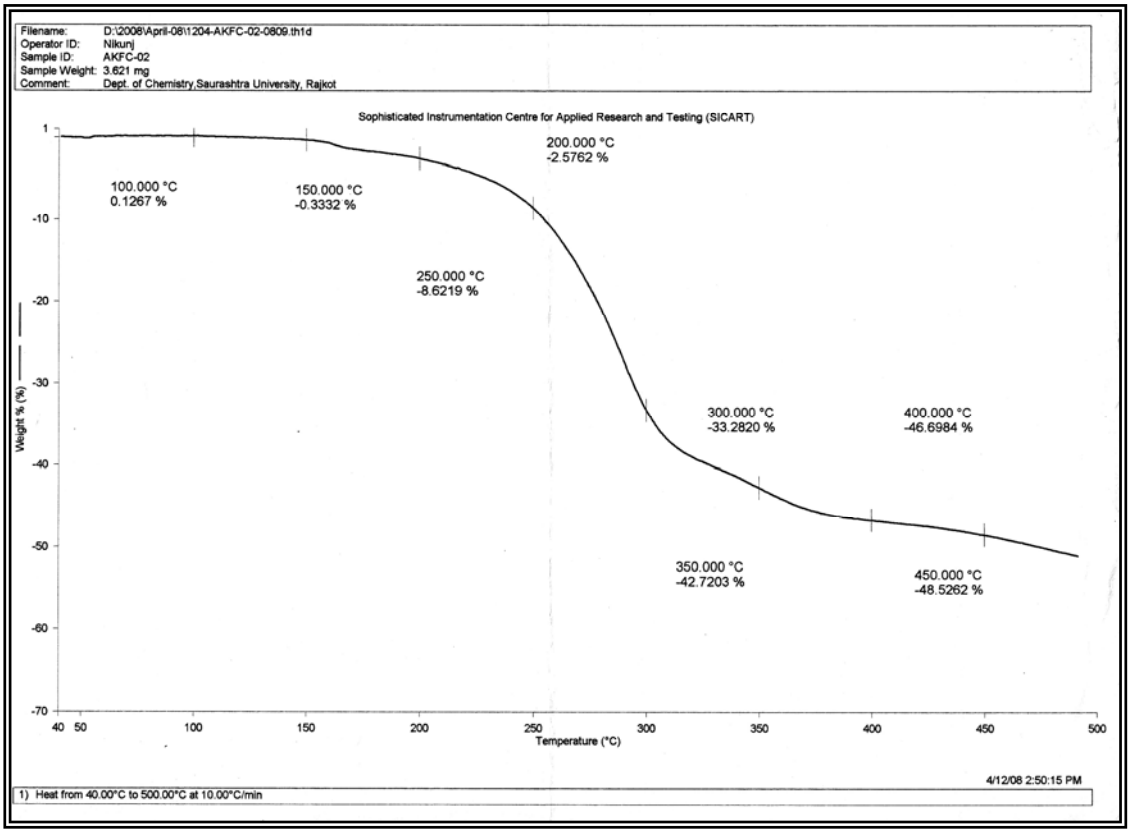


Figure 6.2: The TGA and DSC graphs of AKFC-02



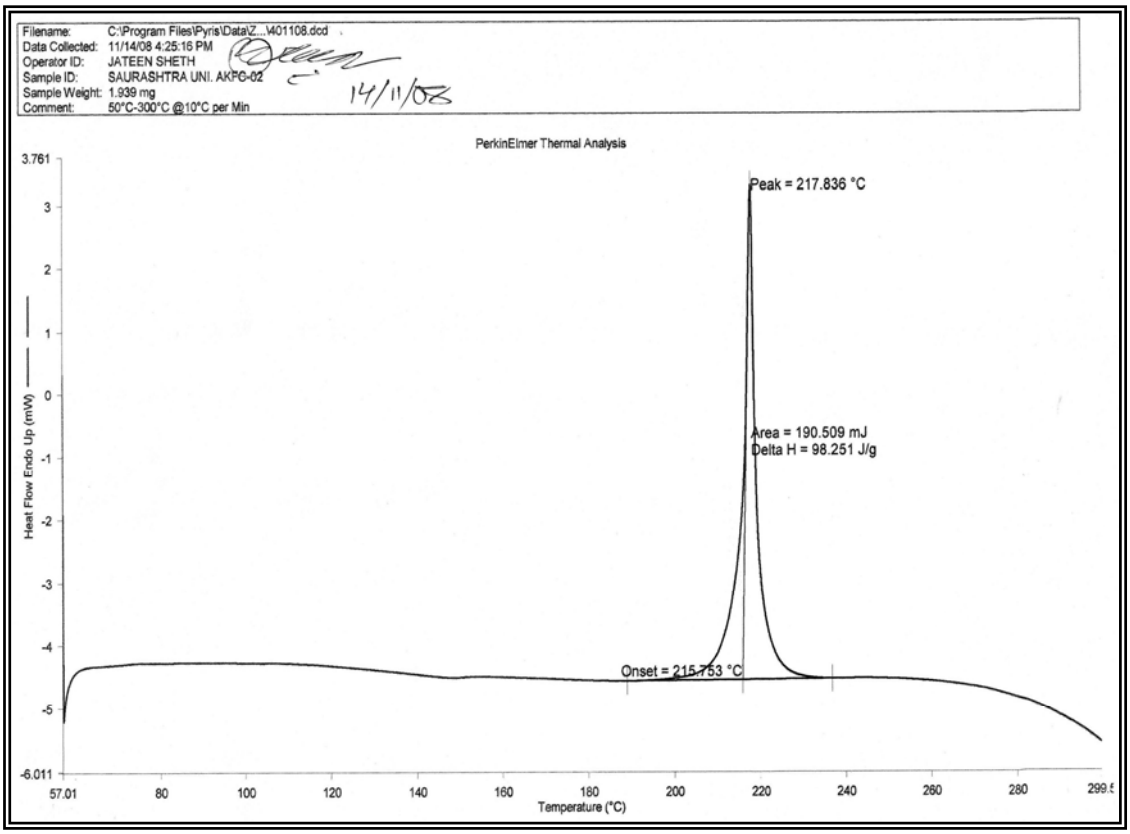


Table 6.1: TGA and DSC data for synthesized chalcones derivatives.

Compound Code	Amount (mg.)	Initial Decomp. Temp. (°C)	Decomp. Range (°C)	% Wt. loss	Residual wt. loss (mg.)	Max. Degradation Temp. (°C)	Transition	DSC Temp. (°C)
AKFC-01	4.545	179	179-325	55.71	2.5320	325	Endo	142.91
AKFC-02	3.621	210	210-450	53.00	1.9191	450	Endo	217.83
AKFC-03	10.399	231	231-645	13.50	1.4038	645	Endo	189.41
AKFC-04	9.393	272	272-745	3.00	0.2818	745	Endo	166.44
AKFC-05	4.053	169	169-671	24.80	1.0051	671	Endo	177.06
AKFC-06	4.413	186	186-706	34.82	1.5357	706	Endo	158.42
AKFC-07	4.307	176	176-689	20.00	0.8614	689	Endo	145.53
AKFC-08	4.845	179	179-782	32.40	1.5697	782	Endo	157.08
AKFC-09	4.235	189	189-292	15.42	0.6530	292	Endo	180.96
AKFC-10	4.194	110	110-735	47.22	1.9804	735	Endo	176.71

Table 6.2: The kinetic parameters for all the chalcones derivatives for 1st step.

Compound code	n	E (kJ)	A (sec^{-1})	$\Delta S°$ (kJ^{-1})
AKFC-01	3.20	64.66	1.36×10^{5}	1.35×10^{-3}
AKFC-02	6.00	381.05	5.01×10^{37}	625.22
AKFC-03	6.50	623.55	2.30×10^{56}	981.70
AKFC-04	6.00	166.28	6.52×10^{13}	166.82
AKFC-05	3.30	35.38	178.43	-53.60
AKFC-06	3.72	136.58	2.54×10^{12}	140.00
AKFC-07	1.50	475.08	9.06×10^{45}	783.10
AKFC-08	1.00	554.26	2.60×10^{55}	964.41
AKFC-09	3.00	155.88	8.71×10^{14}	189.00
AKFC-10	4.80	593.85	970.54	-42.12

Table 6.3: The kinetic parameters for all the chalcones derivatives for 2nd step.

Compound code	n	E (kJ)	A (sec^{-1})	$\Delta S°$ (kJ^{-1})
AKFC-01	-	-	-	-
AKFC-02	-	-	-	-
AKFC-03	9.10	33.25	6.42	-84.00
AKFC-04	5.40	33.25	7.81	-82.10
AKFC-05	5.20	13.93	0.16	-113.90
AKFC-06	5.30	14.84	1.98	-99.00
AKFC-07	3.50	24.94	1.52	-95.00
AKFC-08	7.00	27.71	2.32	-92.00
AKFC-09	4.30	6.23	0.02	-134.00
AKFC-10	6.50	78.98	577.55	-48.97

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Section-VII

Dissociation Constants

INTRODUCTION

The constants, which are used to measure the strength of acid or bases are known as dissociation constants. These constants are also known as acidity constant, ionization constant or formation constant. The dissociation or ionization constant is determined by determining one of the species, at equilibrium. The activity or concentration of the others can be calculated from the amount of the acid or base initially introduced and the stoichiometry of the acid base equilibrium. For the measurement of dissociation constants, various methods have been developed, such as potentiometry including pH metry[1] spectrophotometry, conductometry, solubility measurements [2], cryoscopy [3], measurements of the rates of acid catalyzed hydrolysis of esters [4], measurement of the relative distribution of an acid between two immiscible solvents [5] and magnetic measurements.

A literature survey shows that various workers studied the dissociation constants of a number of substances [6-12]. Marshall *et al.* [13] have measured thermodynamic parameters for the ionization reactions of acetic and chloroacetic acids in aqueous ethanol. The ionization constants of various other acids in pure and mixed solvents have also been studied [14-20].

Feng *et al.* [21] have determined formation constant of some compounds by spectrophotometry. Allen et al. have studied the acid dissociation constants of ionizable drugs by using multiwavelength spectrophotometer [22] Spectrophotometric determination of the dissociation constants of methyl yellow in mixed protic solvents have also been reported [23]. Urquiza and Beltran [24] have determined the dissociation constants of sulfonated azo dyes by capillary zone electrophoresis and spectrophotometry methods. Lachenwitzer [25] have reported dissociation constant for bisulphate by using subtractively normalized interfacial Fourier transform infrared spectroscopy. Evagelou *et al.* [26] have also reported the dissociation constants of the cephalosporins, cefepime and cefpirome by using UV spectrometry and pH potentiometry. The spectrophotometric determination of dissociation constants of crown ethers has also been reported[27]

Spectrometry is an ideal method when a substance is not soluble enough for potentiometry or when its pK_a value is particularly low or high [28-31].

(less than 2 or more than 11). The method depends on the direct determination of the molecular species, that is the neutral molecules to the corresponding ionized species in a series of nonabsorbing buffer solutions where pH values are either known or measured.

There are many applications of dissociation constants. The nature of the functional groups can be determined by simple comparison of acidity or dissociation constant of the unknown compound with those of known compounds. The dissociation or formation constant also provide useful informations about tautomeric equilibria [32, 33], solvent-solute interactions [34] etc.

EXPERIMENTAL

The synthesized chalcones were recrystallized from DMF. DMF used in the present study was of LR grade and was distilled by the reported method [35].

100 ppm solution of sample was prepared in DMF. This solution known as standard solution was used to determine λ_{max} using UV spectrophotometer (SHIMADZU PHARMA SPEC-1700 UV VISIBLE) equipped with 1 cm path length cell, controlled by computer. The instrument was calibrated by usual procedure.

The following set of mixtures were prepared for determination of pK_a values

(1) 2 ml HNO_3 (0.01 M) + 4 ml $NaNO_3$ (0.01 M) + 19 ml DMF

(2) 2 ml HNO_3 (0.01 M) + 4 ml $NaNO_3$ (0.01 M) + 2 ml ligand solution (15 ppm) + 17 ml DMF

Thus, total volume of each set of solution was 25 ml and DMF:water ratio was 90:10(v/v).

To each set of solution, pH and OD were measured after each addition of 0.1 ml NaOH till there was no change in OD.

A systronic pH meter (Model No. EQ 664) was used for the pH determination. pH meter was calibrated by known buffer solutions. The glass electrode and a saturated calomel electrode were used as indicator and reference electrodes respectively.

THEORY

The protonation of a weak B can be represented as:

$$BH^+ \rightleftharpoons B + H^+ \quad \text{..... (7.1)}$$

So, the equilibrium constant (K) can be given as:

$$K = \frac{a_{H^+}.a_B}{a_{BH^+}} \quad \text{..... (7.2)}$$

where a represents the activity of each species. The activity a is related to concentration c by the equation:

$$a = c.\gamma \quad \text{..... (7.3)}$$

where γ is the activity coefficient.

Substituting the values of a in eq. (7.2) gives,

$$K = a_{H^+}.\frac{\gamma_B}{\gamma_{BH^+}}\frac{[B]}{[BH^+]} \quad \text{..... (7.4)}$$

where square brackets indicate the concentration of the species.

Combining the activity coefficient with K yields the mixed conditional constant K_a (one that incorporates both activity and concentration) [36] gives:

$$K_a = a_{H^+}.\frac{[B]}{[BH^+]} \quad \text{..... (7.5)}$$

Taking logarithm of above equation (7.5) gives:

$$pK_a = pH + \log\frac{[BH^+]}{[B]} \quad \text{..... (7.6)}$$

Rearrangement of above equation gives:

$$\log\frac{[B]}{[BH^+]} = pH - pK_a \quad \text{..... (7.7)}$$

A plot of $\log\frac{[B]}{[BH^+]}$ versus pH will therefore yield a straight line and pH=pK_a when $\log\frac{[B]}{[BH^+]}$=0, providing that the temperature and ionic strength are held constant [36].

The concentrations of the individual species BH^+ and B can be determined spectrophotometrically by measuring the absorbance (OD) at

particular wavelength. However, if a series of solutions is prepared at various pH and the total concentration of compound $c_t = [BH^+]+[B]$ is constant, it can be shown that the ratio of the conjugate forms is given by [36]

$$\frac{C_a}{C_b} = \frac{A - A_b^0}{A_a^0 - A} = I \qquad (A_a{}^0 > A_b{}^0) \qquad \text{..... (7.8 a)}$$

or

$$\frac{C_a}{C_b} = \frac{A_b^0 - A}{A - A_a^0} = I \qquad (A_b{}^0 > A_a{}^0) \qquad \text{..... (7.8 b)}$$

where C_a and C_b represent $[BH^+]$ and [B] respectively. A, $A_a{}^0$ and $A_b{}^0$ represent the measured absorbance, absorbance when $[BH^+]=c_t$ and absorbance when $[B] = c_t$ respectively. A plot of absorbance, obtained on the series of solutions at a single wavelength, can then is plotted according to equation (7.7) to determine pK_a.

However, for some weak bases, it is reported that if slope m of the plot (Fig.2) is not unity, pK_a value should be calculated by the following equation:

$$pK_a = m.H^{1/2} \qquad \text{..... (7.9)}$$

where $H^{1/2}$ represents the pH at half protonation at log I=0.

RESULTS AND DISCUSSIONS

Table 7.1 shows the experimental data of pH and OD for the studied compounds. The plot of OD versus pH is shown in Figure 7.1 for AKFC-01. Using equation 7.8 (a or b), log I value were calculated and plotted against pH. The plot is a straight line and pK_a value is evaluated at log I=0. This value of pK_a is taken as half protonation ($H^{1/2}$) by Ogretir *et al.* [37, 38]

Further, at each pH, from the absorbance data, pK_a value was evaluated from equation (7.7) and average of this is reported in Table 7.2 along with the value calculated from the graph.

In the studied compounds, the slope (m) of the plot (Figure 7.2) was also calculated. It is reported [37, 38] that if m values are between 0.85 and 1.05 then the bases are of Hammett type. In that case, m can be taken as unity. Thus, in the present study, m values are found to be between 0.85 and 0.89, so the studied compounds can be considered as of Hammett type and so $H^{1/2}$ is equal to pK_a, which is same as reported in Table 7.2.

Table 7.3 shows the compounds in their increasing order of acidity or basicity. It is observed that the NH_2 groups at para position of the phenyl ring makes AKFC-04 the least acidic or most basic one, whereas AKFC-05 is found to be most acidic due to the halogen (Cl).

Table 7.1. Experimental data of pH and Absorbance (OD) of Chalcones.

AKFC-01 (λ_{max} = 378)		AKFC-02 (λ_{max} = 398)		AKFC-03 (λ_{max} = 389)		AKFC-04 (λ_{max} = 391)		AKFC-05 (λ_{max} = 382)	
pH	**OD**	**pH**	**OD**	**pH**	**OD**	**pH**	**OD**	**pH**	**OD**
2.35	1.4822	2.86	1.4798	3.34	1.4936	2.78	1.5048	2.75	1.5148
2.67	1.4798	3.82	1.4758	3.88	1.4900	3.68	1.4998	3.59	1.5088
2.93	1.4765	4.22	1.4685	4.35	1.4856	4.18	1.4952	4.28	1.5012
3.38	1.4728	5.58	1.4622	5.46	1.4823	5.62	1.4902	5.67	1.4952
3.82	1.4655	6.12	1.4558	6.55	1.4659	6.20	1.4886	6.20	1.4886
4.22	1.4588	7.35	1.4225	7.42	1.4123	7.38	1.4613	7.32	1.4772
4.53	1.4546	7.99	1.3854	8.02	1.3622	7.92	1.4220	7.98	1.4523
4.96	1.4488	8.62	1.2954	8.66	1.3212	8.62	1.3545	8.56	1.3998
5.58	1.4325	9.62	1.2258	9.74	1.2202	9.53	1.2858	9.62	1.2226
6.26	1.4222	10.38	1.1656	10.26	1.1725	10.26	1.2012	10.32	1.1835
7.08	1.4012	11.15	1.1522	11.48	1.1400	11.25	1.1548	11.36	1.1548
7.95	1.3523	11.81	1.1458	11.88	1.1386	11.56	1.1498	11.65	1.1442
8.62	1.2823	12.35	1.1329	12.36	1.1369	12.32	1.1356	12.32	1.1352
9.46	1.1962	12.88	1.1320	12.62	1.1360	12.72	1.1319	12.75	1.1392
9.98	1.1698	13.25	1.1318	12.88	1.1359	13.20	1.1318	13.32	1.1318
10.36	1.1426								
11.02	1.1022								
11.86	1.092								
12.35	1.089								
12.88	1.089								

Continue….

Continue….

AKFC-06 (λ_{max} = 383)		AKFC-07 (λ_{max} = 379)		AKFC-08 (λ_{max} = 394)		AKFC-09 (λ_{max} = 350)		AKFC-10 (λ_{max} = 273)	
pH	**OD**	**pH**	**OD**	**pH**	**OD**	**pH**	**OD**	**pH**	**OD**
2.90	1.5098	3.23	1.4982	2.81	1.5048	2.52	1.4823	2.47	1.4789
3.62	1.5088	3.88	1.4953	3.62	1.4998	3.23	1.4800	3.52	1.4702
4.32	1.5012	4.22	1.4926	4.18	1.4925	4.33	1.4756	4.00	1.4685
5.67	1.4978	5.53	1.4889	5.58	1.4888	5.57	1.4721	5.68	1.4622
6.29	1.4886	6.42	1.4826	6.20	1.4825	6.45	1.4621	6.22	1.4559
7.42	1.4782	7.32	1.4651	7.42	1.4556	7.67	1.4023	7.42	1.4212
7.80	1.4530	7.91	1.4426	7.89	1.4154	7.99	1.3667	8.12	1.3654
8.36	1.3988	8.29	1.3856	8.62	1.3245	8.35	1.3112	8.62	1.2945
9.68	1.2256	9.56	1.2524	9.56	1.2358	9.34	1.2202	9.43	1.2121
10.36	1.1812	10.45	1.1825	10.28	1.1656	10.16	1.1625	10.21	1.1556
11.25	1.1578	11.36	1.1567	11.25	1.1548	11.48	1.1422	11.26	1.1402
11.50	1.1458	11.99	1.1462	11.65	1.1498	11.90	1.1386	11.92	1.1356
12.38	1.1352	12.26	1.1362	12.32	1.1356	12.32	1.1359	12.35	1.1354
12.65	1.1322	12.62	1.1356	12.75	1.1399	12.79	1.1355	12.88	1.1352
13.02	1.1308	12.98	1.1354	13.20	1.1318	12.98	1.1354	13.21	1.1348

Table 7.2. pK_a value from graph and Average pK_a of chalcones

Compound Code	pK_a value from graph ($H^{1/2}$)	Average pK_a value	Correlation coefficient
AKFC-01	8.96	9.22	0.9725
AKFC-02	8.94	9.21	0.9799
AKFC-03	8.99	8.63	0.9878
AKFC-04	9.15	8.93	0.9963
AKFC-05	8.44	9.31	0.9801
AKFC-06	8.57	9.23	0.9904
AKFC-07	8.99	9.14	0.9588
AKFC-08	8.62	8.87	0.9847
AKFC-09	9.09	8.58	0.9934
AKFC-10	9.02	8.50	0.9965

Table 7.3 Arrange chalcones in order of increasing acidity or decreasing basicity strength by half protonation values as follows:

Compound Code	**$H^{1/2}$**	**Groups**	**Acidity or basicity**
AKFC-04	9.15	4-NH_2	**Decreasing basicity or increasing acidity** ↓ / ↑ **increasing basicity or Decreasing acidity**
AKFC-09	9.09	2- furayl	
AKFC-10	9.02	3-coumarin	
AKFC-03	8.99	3-NO_2	
AKFC-07	8.99	-phenyl	
AKFC-01	8.96	-OCH_3	
AKFC-02	8.94	4-NO_2	
AKFC-08	8.62	4-OH	
AKFC-06	8.57	4-Br	
AKFC-05	8.44	4-Cl	

Figure 7.1: The variation of OD with pH for AKFC-01.

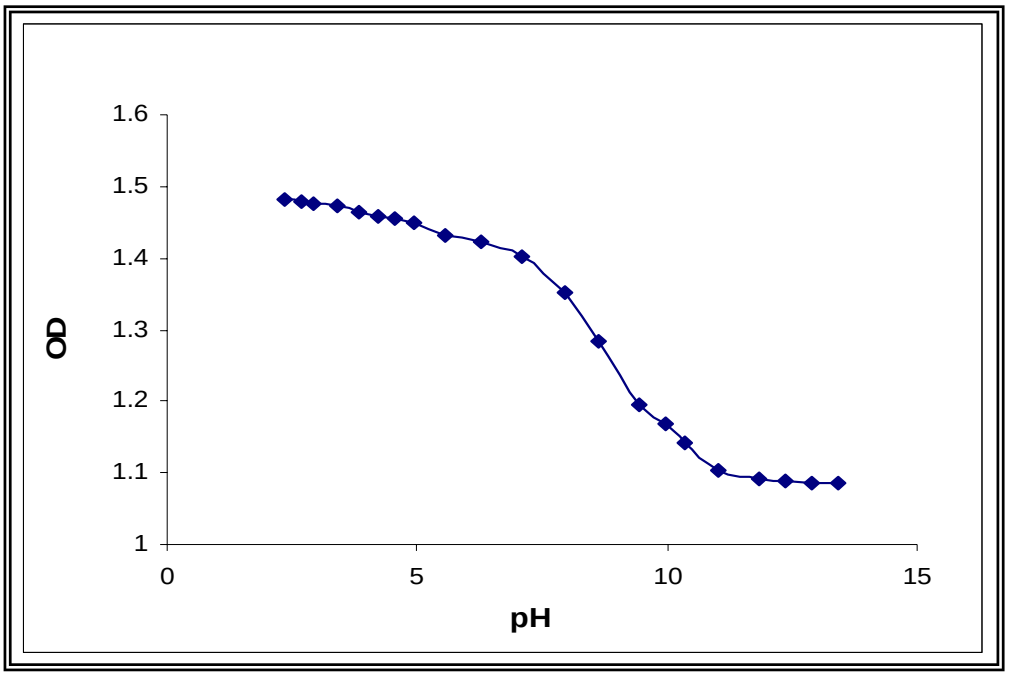
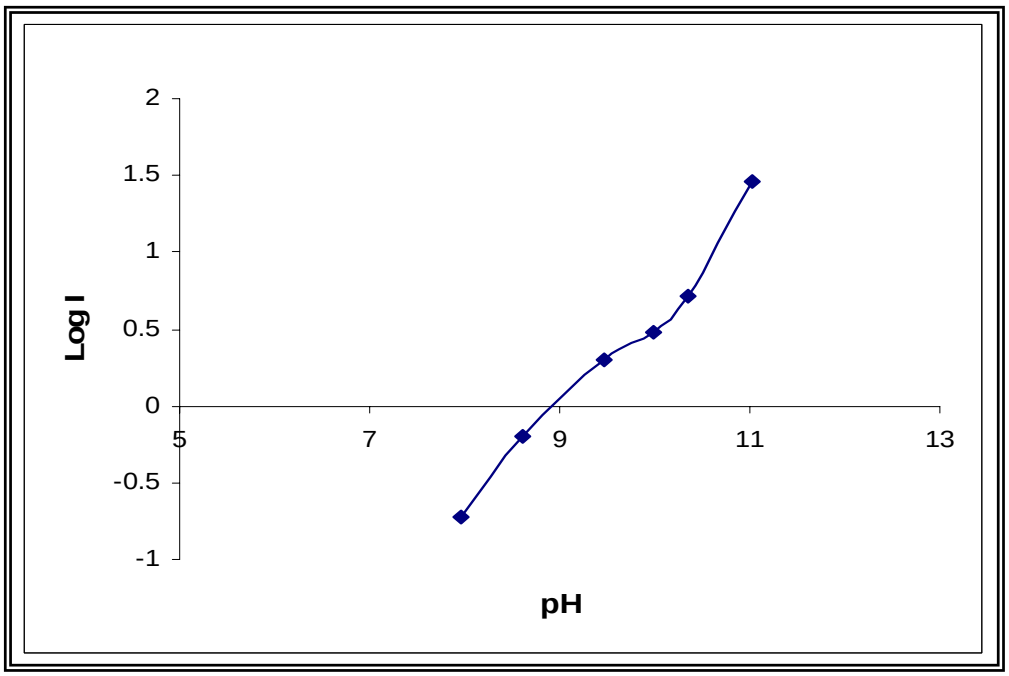


Figure 7.2 : The plot of log I versus pH for AKFC-01.



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Chapter-4

Biological Activities

INTRODUCTION

Biological activity spectrum of a compound represents the pharmacological effects, physiological and biochemical mechanisms of action, specific toxicity which can be revealed in compound's interaction with biological systems. Further, it describes the intrinsic properties of the compound, which depends on its structure.

A literature survey shows that benzothiazole derivatives possess various biological activities [1-5]. Further, the Schiff bases have been reported to demonstrate a wide range of pharmacological activities [6-10], which include antibacterial [11-13], antitumor [14, 15], anti-inflammatory [16, 17], antifungal [18, 19], anti HIV [20] etc.

With a variety of biological activity, thiazolidinone are useful in pharmaceuticals. They are associated with biological activities like antibacterial [21-23], anticancer [24-27], antiviral [28], and anti HIV [29, 30].

Much research has been carried out with the aim to finding therapeutic values of furan moiety. A large number of substituted furan derivatives are prepared and tested for variety of biological activities like pesticidal [31], insecticidal [32], antifungal [33, 34], antitumor [35-37], anti-inflammatory [38, 39] and antidepressant [40] etc. Further, the chalcones have been reported to a wide range of pharmacological activities like cardiovascular [41], antiulcer [42-44], fungicidal [45-47], anticancer [48-50] and anti HIV [51-52] etc.

Thus, in this chapter, antibacterial activity and antifungal activity of the synthesized Schiff bases, Thiazolidinone and Chalcones has been studied in DMSO and DMF respectively.

EXPERIMENTAL

All the synthesized compounds were recrystallized prior to use. The solvent DMSO and DMF were also purified before use by standard method [53].

The antibacterial and antifungal activities of all the synthesized compounds, were studied in DMSO and DMF respectively.

The choice of different solvents for Schiff bases, Thiazolidinone, and Chalcones is due to their solubility problem.

Further, two different methods were adopted for the study: Agar disc diffusion and Agar well diffusion method.

For Schiff bases and thiazolidinone, Agar well diffusion method was used while chalcones Agar disc diffusion method was used.

Schiff bases and Thiazolidinones:

Preparation of the test compound

The synthesized Schiff bases and Thiazolidinone were dissolved in DMF and DMSO at concentration of 2 mg/100μl.

Test microorganisms

The synthesized Schiff bases and Thiazolidinone were tested for its antibacterial activity against two Gram positive *Bacillus cereus* (ATCC 11778) and *Micrococcus flavus* (ATCC 10240), two Gram negative bacteria viz. *Escherichia coil* (ATCC 25922) and *Proteus mirabilis* (NCIM 2241) and two fungus *Cryptococcus luteolus* (ATCC 32044) and *Candida tropicalis* (ATCC 4563). Microorganisms were obtained from National Chemical Laboratory (NCL), Pune, India. Microorganisms were maintained at 4°C on nutrient agar slants.

Agar well diffusion method [54, 55]

The antibacterial evaluation was done by agar well diffusion method using Mueller Hinton Agar No. 2 as the nutrient medium. The bacterial strains were activated by inoculating a loop full of test strain in 25 ml of N-broth and the same was incubated for 24h in an incubator at 37°C. 0.2 ml of the activated strain was incubated in Mueller Hinton Agar. Mueller Hinton Agar

kept at 45°C was then poured in the Petri dishes and allowed to solidify. After solidification of the media, 0.85 cm well was made in the plates using a sterile cork borer. Each well was filled with 0.1 ml of the test solution. The plates were incubated for 24h at 37°C. The mean value obtained for the three wells was used to calculate the zone of growth inhibition of each sample. The controls were maintained for each bacterial strain, where pure solvent (DMSO and DMF) were inoculated into the well. The inhibition zone formed by these compounds against the particular test bacterial strain determined the anti microbial activities of the synthetic compounds.

Chalcones:

Preparation of test compounds:

The synthesized chalcones were dissolved in DMSO and DMF at a concentration 2 mg/100 μl.

Test microorganisms:

The synthesized chalcones were tested for its antibacterial activity against two Gram positive *Bacillus cereus* (ATCC 11778) and *Micrococcus flavus* (ATCC 10240), two Gram negative bacteria viz. *Klebsiella pneumoniae* (NCIM 2719) and *Proteus mirabilis* (NCIM 2241) and two fungus *Cryptococcus luteolus* (ATCC 32044) and *Candida tropicalis* (ATCC 4563). Microorganisms were obtained from National Chemical Laboratory (NCL), Pune, India. Microorganisms were maintained at 4°C on nutrient agar slants.

Agar disc diffusion method [56]

The antibacterial assay was evaluated by the method of agar disc diffusion method. The media used for the antibacterial assay were Mueller Hinton Agar No. 2 and SDA media. The test strain (200μ) was inoculated into the media (inoculums size 10^8 cell/ml) when the temperature reached 40-42°C and poured into Petri dishes (Hi-media). 20μl of the test compound was impregnated in to sterile discs (7 mm, Hi media), allowed to dry and was introduced on the upper layer of the seeded agar plates. The plates were incubated overnight 37°C. the experiment was performed under strict aseptic conditions. Microbial growth was determined by measuring the diameter of zone of inhibition. For each bacterial strain controls were maintained where pure solvent was used instead of the solution. The result was obtained by

measuring the zone diameter. The experiment was done three times and the mean values are presented.

RESULTS AND DISCUSSION

SCHIFF BASES:

[A] Against Gram positive bacteria:

Figure 4.1 shows the zone of inhibition against the two Gram positive bacteria in DMF and DMSO.

It is observed in DMF that against *B. cereus*, AKBS-09 exhibited maximum activity, AKBS-01, AKBS-03, AKBS-04, AKBS-05, AKBS-06, AKBS-07, AKBS-08 and AKBS-10 exhibited moderate activity. While AKBS-02 exhibited minimum activity. AKBS-09 contains naphthalene substitution whereas AKBS-02 contains o-hydroxy substitution. Thus, for *B. cereus*, naphthalene substitution is most effective. Against *M. flavus*, AKBS-07 exhibited maximum activity followed by AKBS-01, AKBS-02, AKBS-03, AKBS-05, AKBS-08 and AKBS-10. While AKBS-09 exhibited minimum activity. AKBS-04 and AKBS-06 could not affect this bacterium. Thus, for this bacterium, phenyl acrylic substitution is most effective.

In case of DMSO, for *B. cereus* AKBS-02 exhibited maximum activity. While AKBS-03 exhibited minimum activity. AKBS-02 contains o-hydroxy substitution, while AKBS-03 contains p-chloro substitution. Thus, the presence of hydroxy substitution in ortho position increases the inhibition against *B. cereus*. For *M. flavus*, AKBS-03 exhibited maximum activity. While AKBS-08 exhibited minimum activity. AKBS-05, AKBS-06, AKBS-09 and AKBS-10 did not exhibit inhibition against this bacterium. Thus, in this case, p-chloro substitution is more effective.

Comparison of zone of inhibition in DMF and DMSO shows that inhibition is more in DMSO. Thus, for these compounds and for these two Gram positive bacteria, DMSO is good solvent. However, *M. flavus* is most resistant in DMSO than in DMF.

[B] Against Gram negative bacteria:

Figure 4.2 shows the zone of inhibition against the two Gram negative bacteria in DMF and DMSO.

It is observed in DMF against *E. coli*, AKBS-05 exhibited maximum activity whereas AKBS-02 and AKBS-04 exhibited equally minimum activity. AKBS-01, AKBS-03 and AKBS-09 showed no inhibition against this bacterium. AKBS-05 contains m-nitro substitution whereas AKBS-02 and AKBS-04 contain o-hydroxy and m-chloro substitution. Thus, m-nitro substitution is most effective. Against *P. mirabilis*, AKBS-10 containing anthracene substitution exhibited maximum activity while AKBS-08 (having p-fluoro substitution) exhibited minimum activity. AKBS-05 and AKBS-06 also showed some inhibition of same magnitude. Other compounds could not inhibit this bacterium. Thus, it is again proofed that the presence of halogen substitution decreases the activity of compound.

In case of DMSO, against *E. coli*, AKBS-02 exhibited maximum activity. AKBS-01, AKBS-04, AKBS-08 and AKBS-09 exhibited moderate activity. While AKBS-03 exhibited minimum activity. AKBS-05, AKBS-06, AKBS-07 and AKBS-10 had no effect. Thus, again o-hydroxy substitution is most effective. AKBS-03 contains p-chloro substitution, which decrease the activity of compound. Against *P. mirabilis*, all compounds showed inhibition and AKBS-01 and AKBS-02 exhibited equally maximum activity. AKBS-03 exhibited minimum activity. Again the halogen substitution decreases and hydroxy substitution increases the activity of compound.

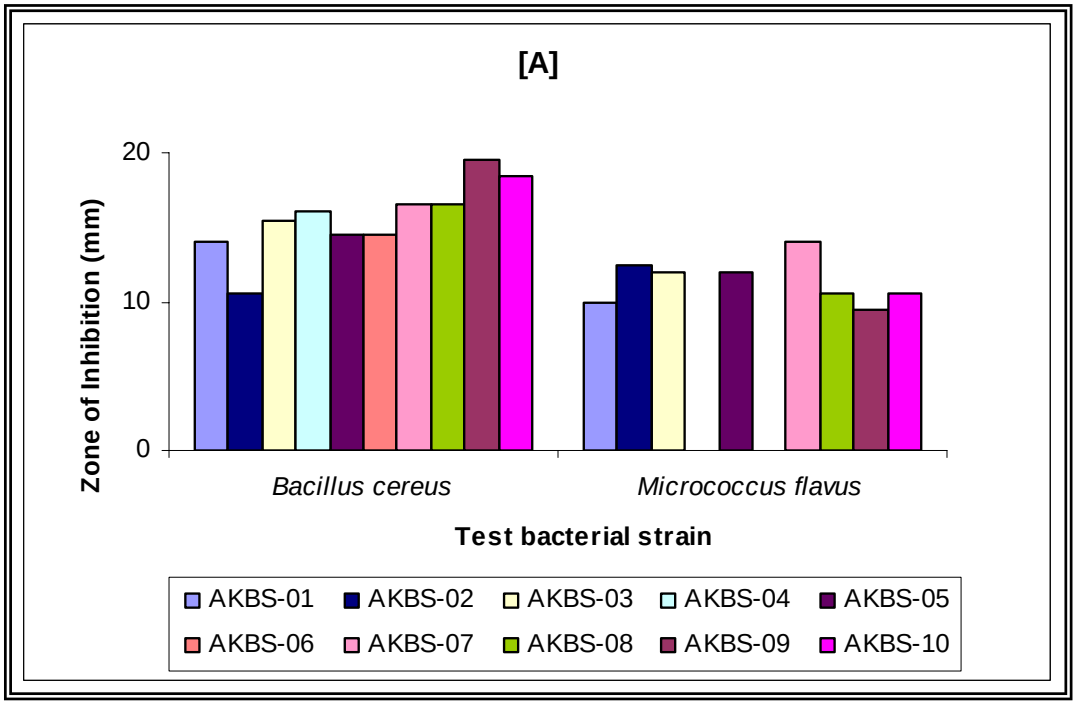
[C] Against Fungus:

Figure 4.3 shows the zone of inhibition against two fungus in DMF and DMSO.

It is observed in DMF that for *C. luteolus*, only four compounds AKBS-07 to AKBS-10 exhibited inhibition. AKBS-08 and AKBS-09 exhibited equally maximum activity, while AKBS-07 exhibited minimum activity. Other compound AKBS-01 to AKBS-06 did not exhibit inhibition. Against *C. tropicalis*, only AKBS-03 is found to be ineffective. AKBS-09 exhibited maximum activity. AKBS-05 exhibited minimum activity. Overall, inhibition is very less for this strain as compared to *C. luteolus.* In both the strains AKBS-09 exhibit maximum inhibition which suggests that naphthalene substitution give maximum inhibition.

In case of DMSO, against *C. luteolus* exhibited same results like DMF, AKBS-08 and AKBS-09 exhibited maximum activity, which contains fluoro and naphthalene substitution respectively. While AKBS-10 exhibited minimum activity, which contains Anthracene substitution. Against *C. tropicalis*, all compounds exhibited inhibition. AKBS-01 containing p-hydroxy substitution exhibited maximum activity, while AKBS-05 containing m-nitro substitution exhibited minimum activity. Thus, again hydroxy substitution is proved to be more active.

Figure 4.1: Antimicrobial activity of Schiff bases against Gram-positive bacteria in DMF [A] and DMSO [B].



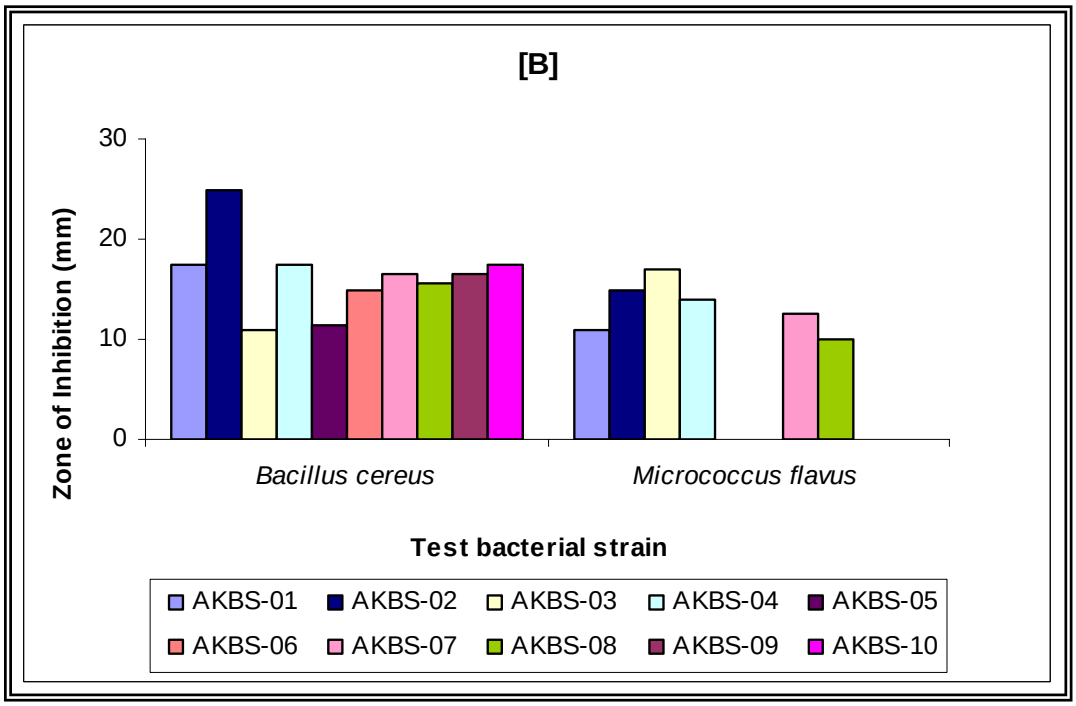
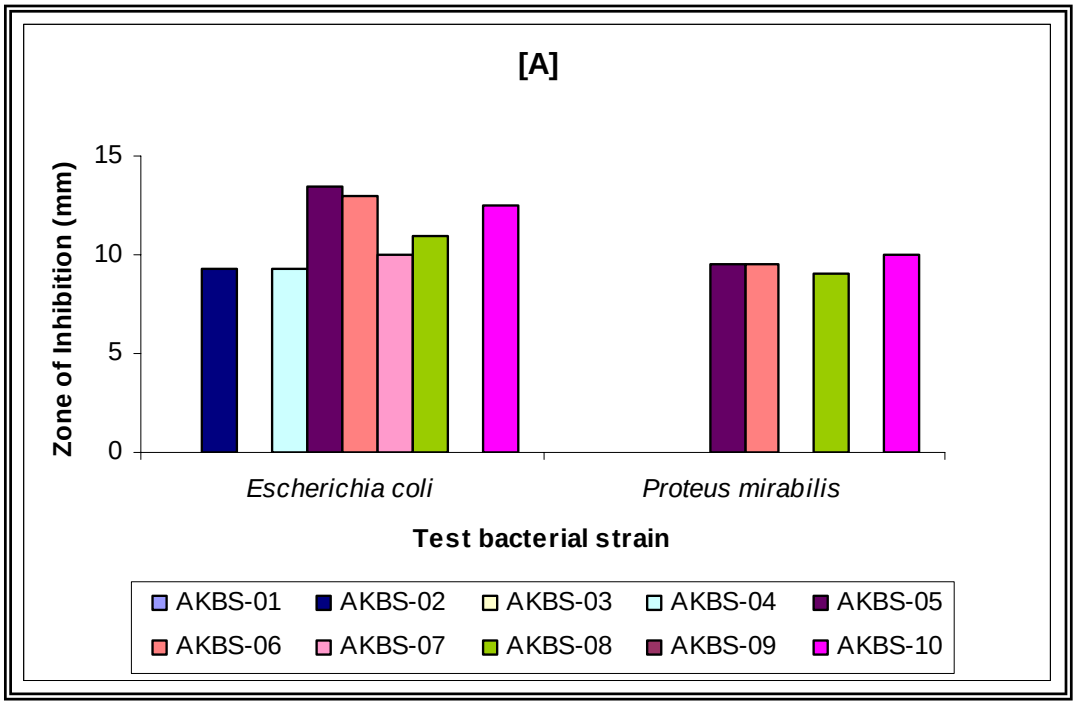


Figure 4.2: Antimicrobial activity of Schiff bases against Gram-negative bacteria in DMF [A] and DMSO [B].



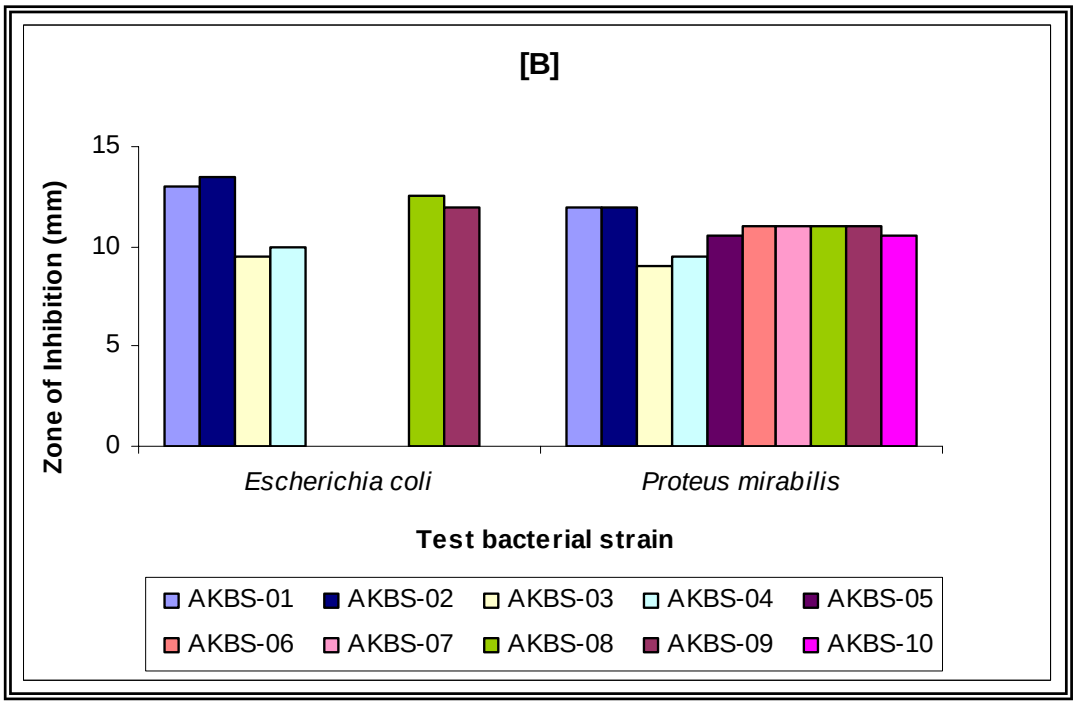
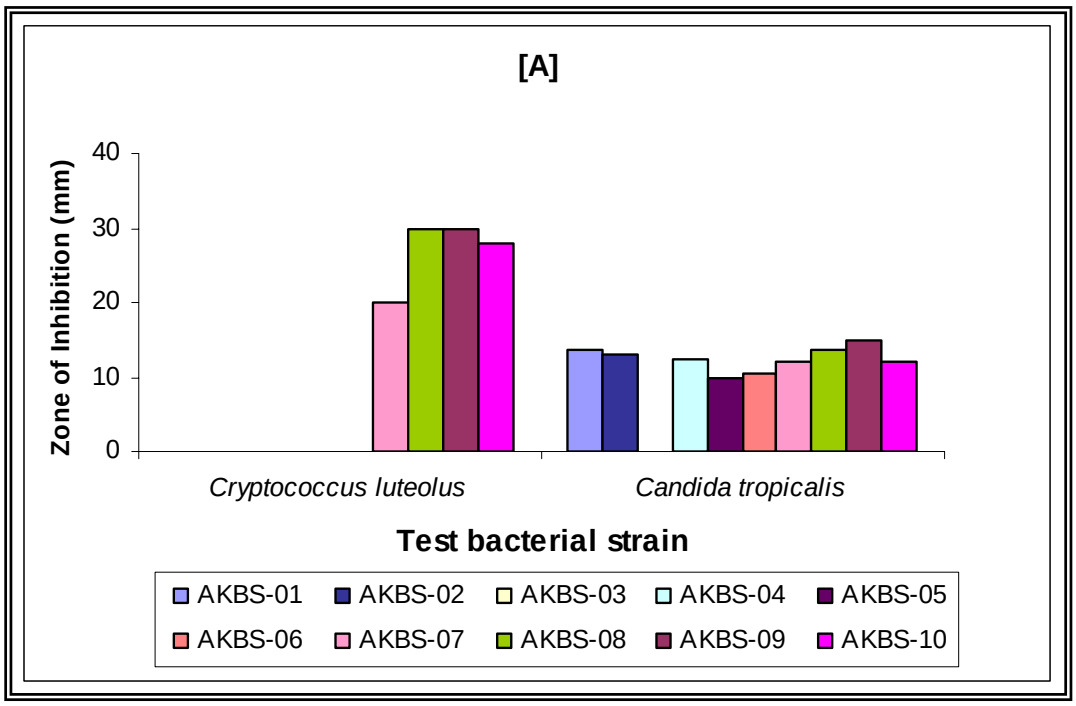
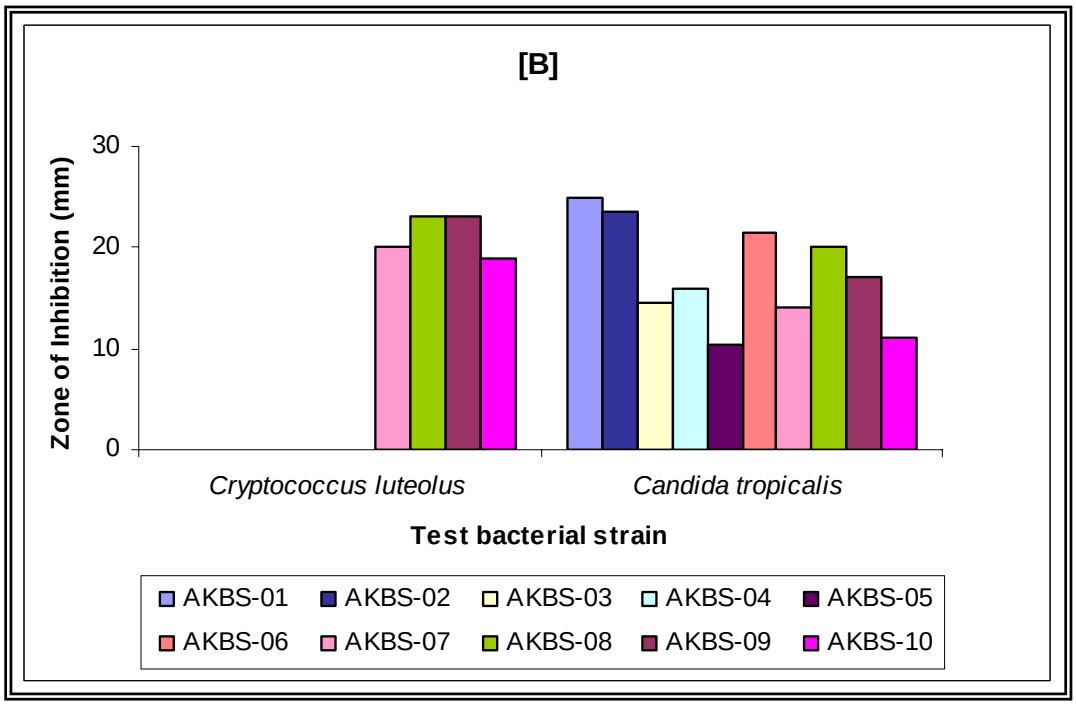


Figure 4.3: Antimicrobial activity of Schiff bases against fungus in DMF [A] and DMSO [B].





THIAZOLIDINONE:

[A] Against Gram positive bacteria:

Figure 4.4 shows the zone of inhibition against the two Gram positive bacteria in DMF and DMSO.

It is observed in DMF that against *B. cereus*, ABT-01(a) showed no activity. ABT-01(e) and ABT-01(g) exhibited maximum activity. Minimum activity is observed by ABT-01(b). Thus, m-nitro (as in ABT-01 (e)) and phenyl acrylic (as in ABT-01 (g)) are more effective. Against *M. flavus*, ABT-01(g) and ABT-01(j) exhibited equally maximum activity. ABT-01(e) and (h) exhibited moderate activity. While ABT-01(d) exhibited minimum activity. Other compounds had no activity against this bacterium. So, phenyl acrylic and anthracene substitution are more effective in this case.

In case of DMSO, for *B. cereus*, ABT-01(f) and ABT-01(h) had no effect. ABT-01(j) exhibited maximum activity followed by ABT-01(g). ABT-01(b) exhibited minimum activity. Against *M. flavus*, ABT-01(j) exhibited maximum activity, while ABT-01(e) exhibited minimum activity. Other compound did not exhibit activity. Thus, in DMSO, for both Gram positive bacteria, anthracene substitution is most effective.

Comparison of zone of inhibition in DMF and DMSO shows that inhibition is more in DMSO. Thus, for these compounds and for these two Gram positive bacteria, DMSO is good solvent. However, *M. flavus* is most resistant in DMSO than in DMF.

[B] Against Gram negative bacteria:

Figure 4.5 shows the zone of inhibition against the two Gram negative bacteria in DMF and DMSO.

It is observed that in DMF against *E. coli*, ABT-01(h) and ABT-01(j) exhibited equally maximum activity. ABT-01(c), ABT-01(d) and ABT-01(f) exhibited no activity and ABT-01(b) exhibited minimum activity. Thus, p-fluoro (as in ABT-01(h)) and anthracene (as in ABT-01(j)) are good for inhibiting this bacterium. Against *P. mirabilis* ABT-01(c) exhibited maximum activity. ABT-01(a) and ABT-01(b) exhibited moderate activity. While ABT-01(f) exhibited minimum activity. Other

compound had no effect. In this case, p-chloro substitution is good for inhibition.

In DMSO, for *E. coli*, only three compounds showed inhibition. ABT-01(d) exhibited maximum activity whereas ABT-01(f) exhibited minimum activity. Thus, m-chloro substitution is effective. Against *P. mirabilis*, all compounds showed inhibition and ABT-01(j) containing anthracene substitution exhibited maximum activity.

[C] Against Fungus:

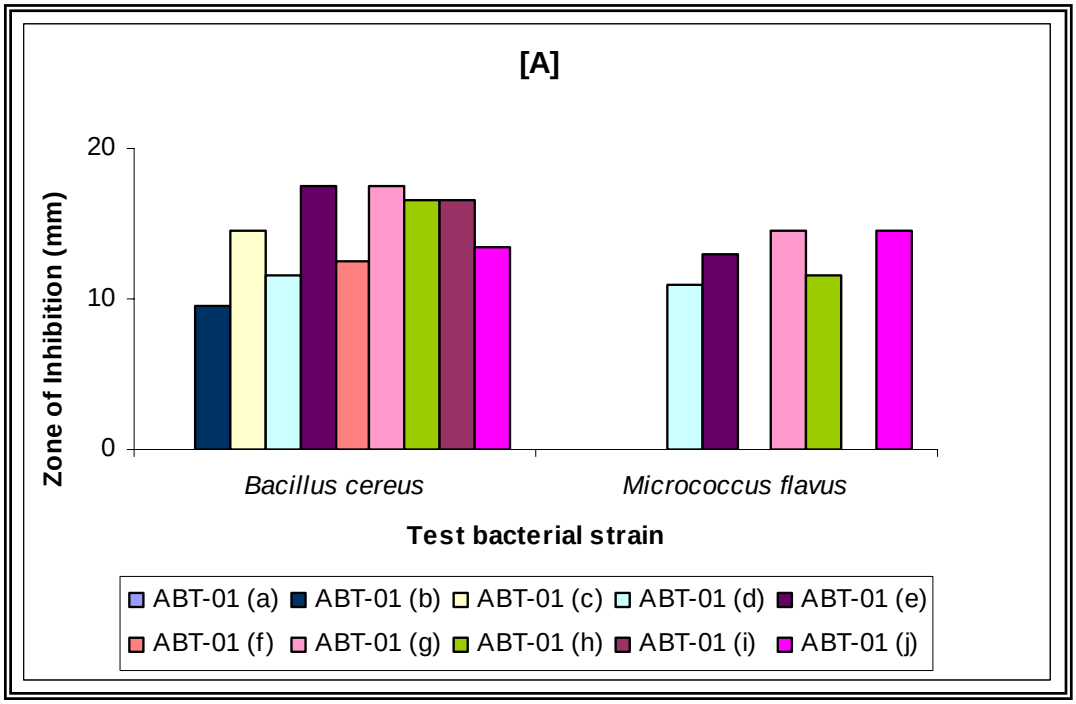
Figure 4.6 shows the zone of inhibition against the two fungus in DMF and DMSO.

It is observed in DMF that against *C. luteolus*, all compounds are found to be effective but ABT-01(d) exhibited maximum activity. Minimum activity is observed by ABT-01(b). Against *C. tropicalis* also, ABT-01(d) exhibited maximum activity. Other compounds showed almost same activity. Thus, in DMF, for these two bacteria strains m-chloro substitution is found to be most effective.

In case of DMSO again for *C. luteolus,* all compounds showed inhibition and ABT-01(d) exhibited maximum activity. Against *C. tropicalis* also, ABT-01(d) exhibited maximum activity. ABT-01(f), ABT-01(i), and ABT-01(i) exhibited no inhibition.

Thus, ABT-01(d) which contains m-chloro substitution is most effective for both the fungal strains in both the solvents.

Figure 4.4: Antimicrobial activity of 5-methyl 4-thiazolidinone against Gram-positive bacteria in DMF [A] and DMSO [B].



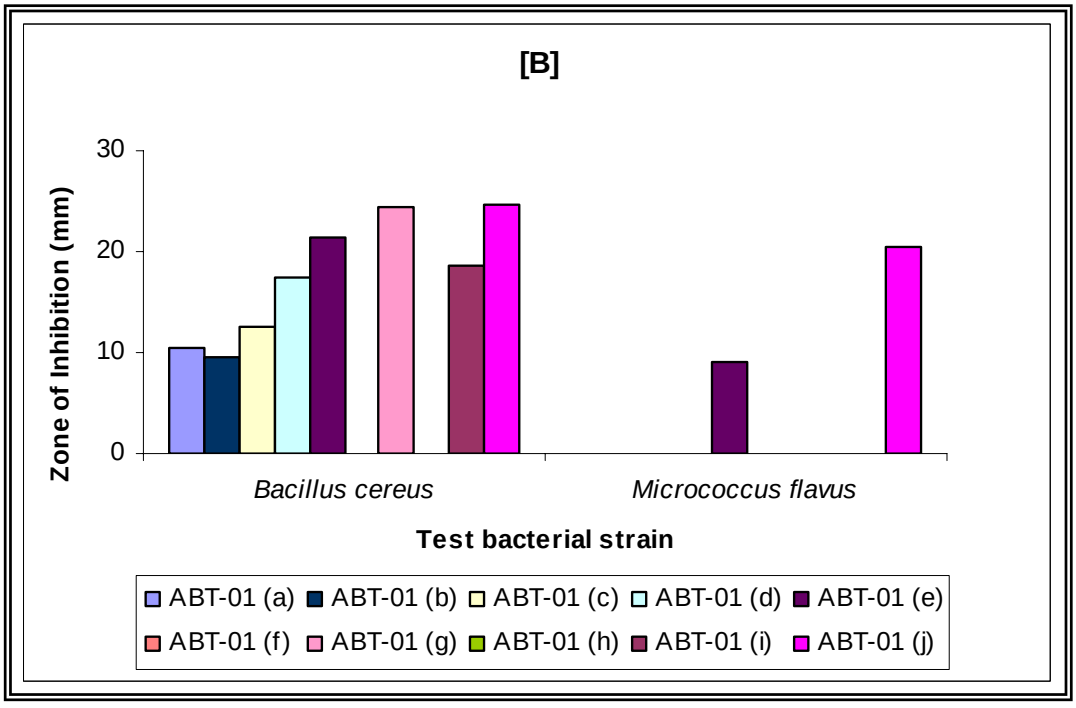
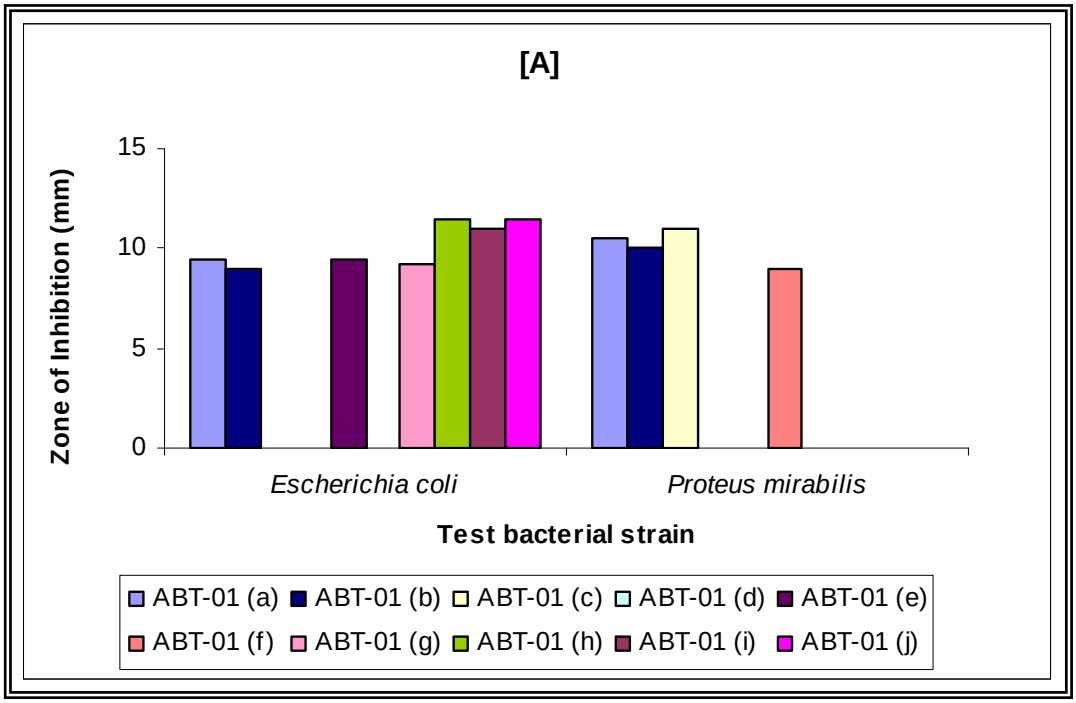


Figure 4.5: Antimicrobial activity of 5-methyl 4-thiazolidinone against Gram-negative bacteria in DMF [A] and DMSO [B].



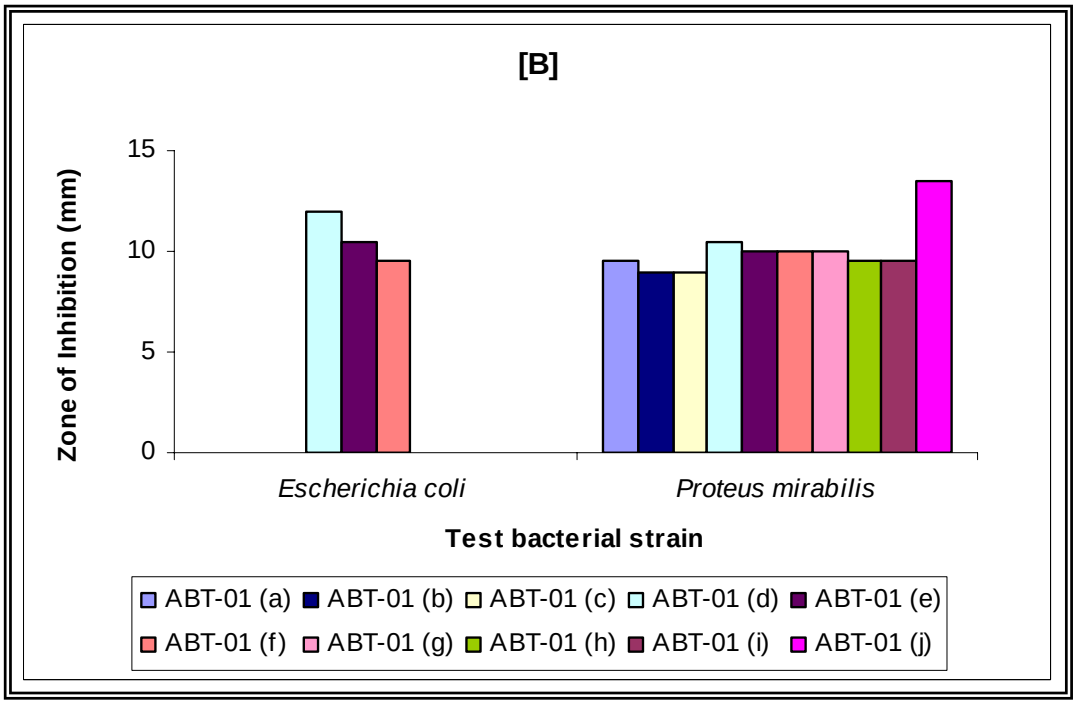
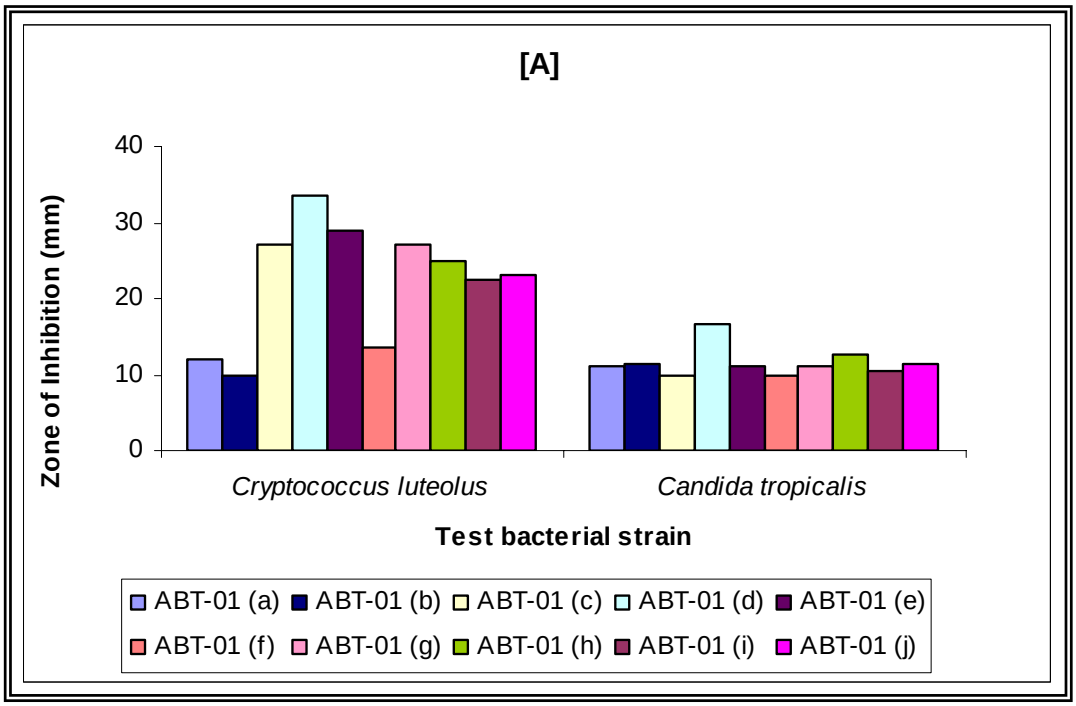
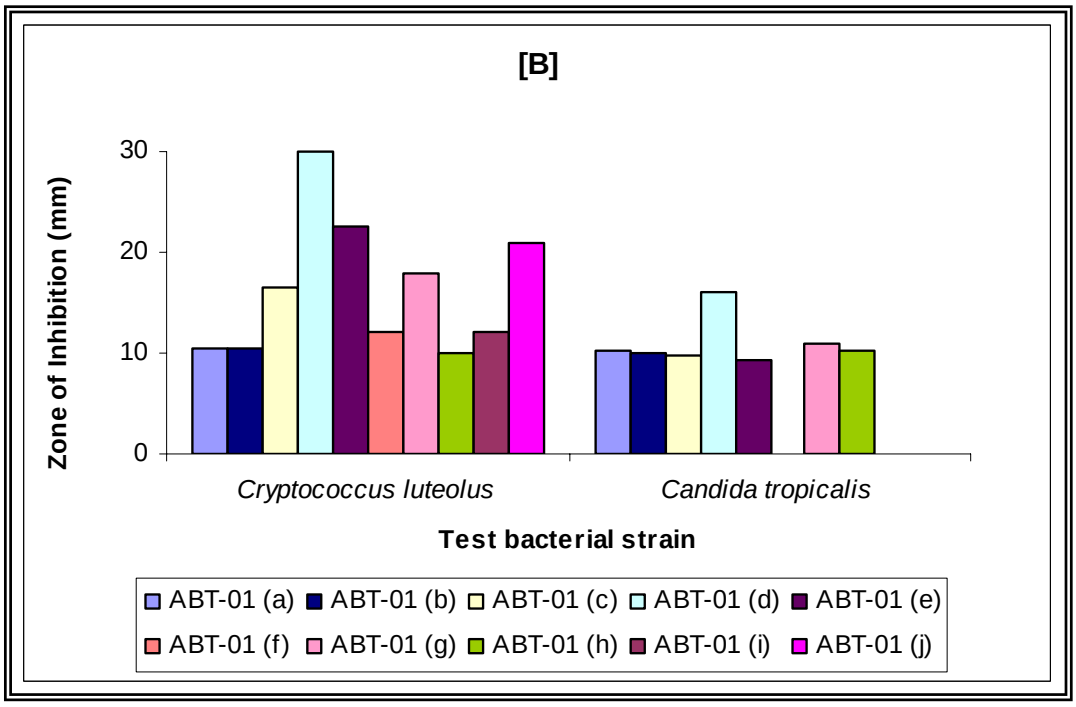


Figure 4.6: Antimicrobial activity of 5-methyl 4-thiazolidinone against fungus in DMF [A] and DMSO [B].





CHALCONES:

[A] Against Gram positive bacteria:

Figure 4.7 shows the zone of inhibition against the two Gram positive bacteria in DMF and DMSO. It is observed that in DMF, no compound could inhibit *B. cereus* whereas against *M. flavus*, only AKFC-01 shows activity. Other compounds did not exhibit inhibition against this bacterium.

In DMSO, AKFC-01, AKFC-04 and AKFC-05 exhibited equally maximum inhibition and AKFC-10 shows minimum inhibition against *B. cereus*. AKFC-07 and AKFC-8 showed no inhibition at all. In AKFC-01, AKFC-04 and AKFC-05 substitution are p-methoxy, p-amino and p-chloro substitution which is found to be more effective against these bacteria in DMSO. Against *M. flavus*, all compounds did not exhibit inhibition. Thus, In DMF *B. cereus* is resistant whereas in DMSO, *M. flavus* is resistant bacteria. So, type of bacterial strain, solvent and structure affect the inhibition.

[B] Against Gram negative bacteria:

Figure 4.8 shows the zone of inhibition against the two Gram negative bacteria in DMF and DMSO.

In case of DMF, it is observed that against *K. pneumoniae*, AKFC-01 and AKFC-04 exhibited equally maximum activity followed by AKFC-05, AKFC-09 and AKFC-10, which exhibited equally minimum activity. AKFC-07 and AKFC-08 did not exhibit inhibition against this bacterium. Thus, p-methoxy (as in AKFC-01) and p-amino (as in AKFC-04) are effective more than other substitutions. Against *P. mirabilis*, only AKFC-04 and AKFC-09 showed activity and it is maximum for AKFC-09. Other compounds did not exhibit inhibition against this bacterium. In this case, furan substitution is more effective than p-amino substitution.

In case of DMSO, it is observed that against *K. pneumoniae*, only AKFC-07 and AKFC-10 showed inhibition, AKFC-10 exhibited maximum activity which contains coumarin substitution while AKFC-07 exhibited minimum activity which contains phenyl ring. Other compounds did not exhibit inhibition against this bacterium. Against *P.*

mirabilis AKFC-10 exhibited maximum activity while AKFC-08 exhibited minimum activity which contains p-hydroxy substitution. Again other compounds did not exhibit inhibition. Thus, coumarin substitution is most effective against the studied Gram negative bacteria in DMSO.

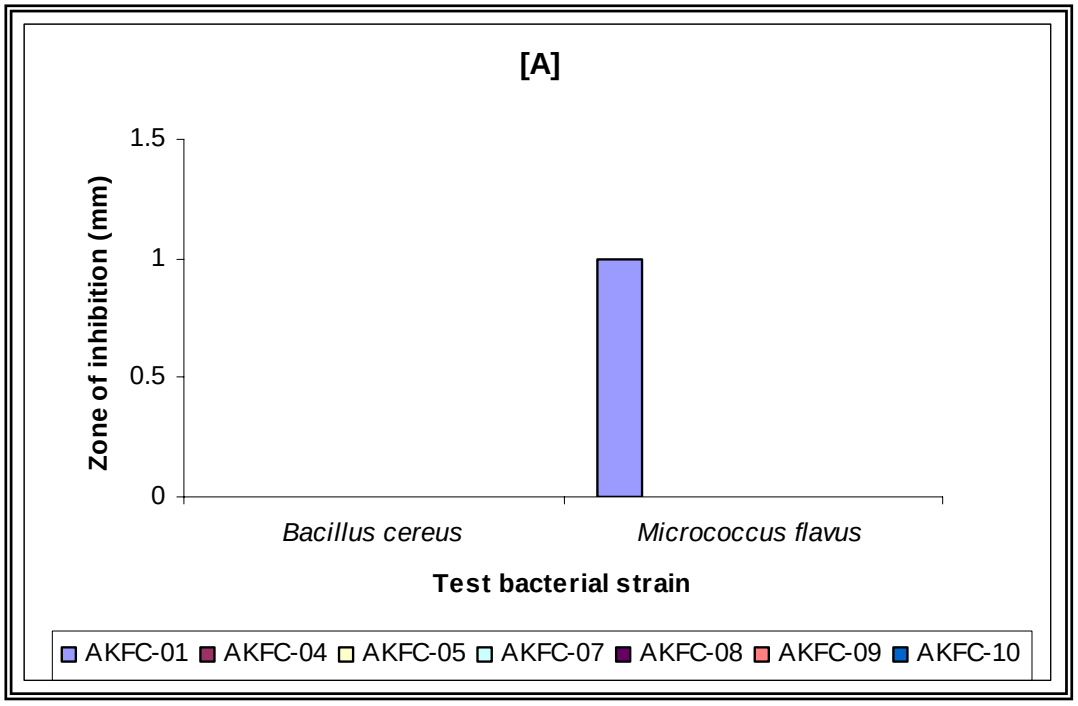
[C] Against Fungus:

Figure 4.9 shows the zone of inhibition against the two fungus in DMF and DMSO.

It is observed in DMF that for *C. luteolus*, AKFC-07 exhibited maximum activity followed by AKFC-01, AKFC-04, AKFC-05 and AKFC-09, while AKFC-10 exhibited minimum activity. AKFC-08 showed no inhibition. Against *C. tropicalis*, AKFC-01 exhibited maximum activity followed by AKFC-08 and AKFC-10, while AKFC-09 exhibited minimum activity. Other compounds had no effect. Thus, for *C. luteolus*, phenyl ring without substitution and for *C. tropicalis*, p-methoxy substitution is effective

In DMSO, against *C. luteolus*, AKFC-10 exhibited maximum activity, while AKFC-07 and AKFC-08 exhibited equally minimum activity. Other compounds had no effect. So, in this case, coumarin substitution is effective. Against *C. tropicalis*, only AKFC-08 having p-hydroxy substitution exhibited inhibition. Other compounds did not exhibit inhibition against this fungus.

Figure 4.7: Antimicrobial activity of Chalcones against Gram-positive bacteria in DMF [A] and DMSO [B].



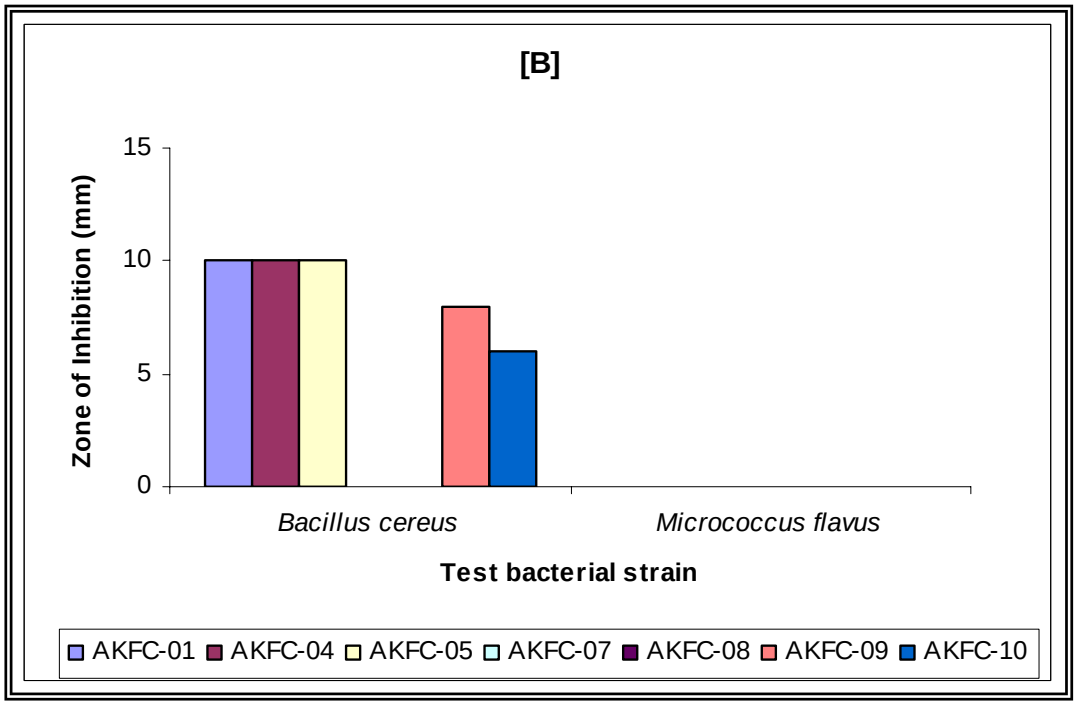
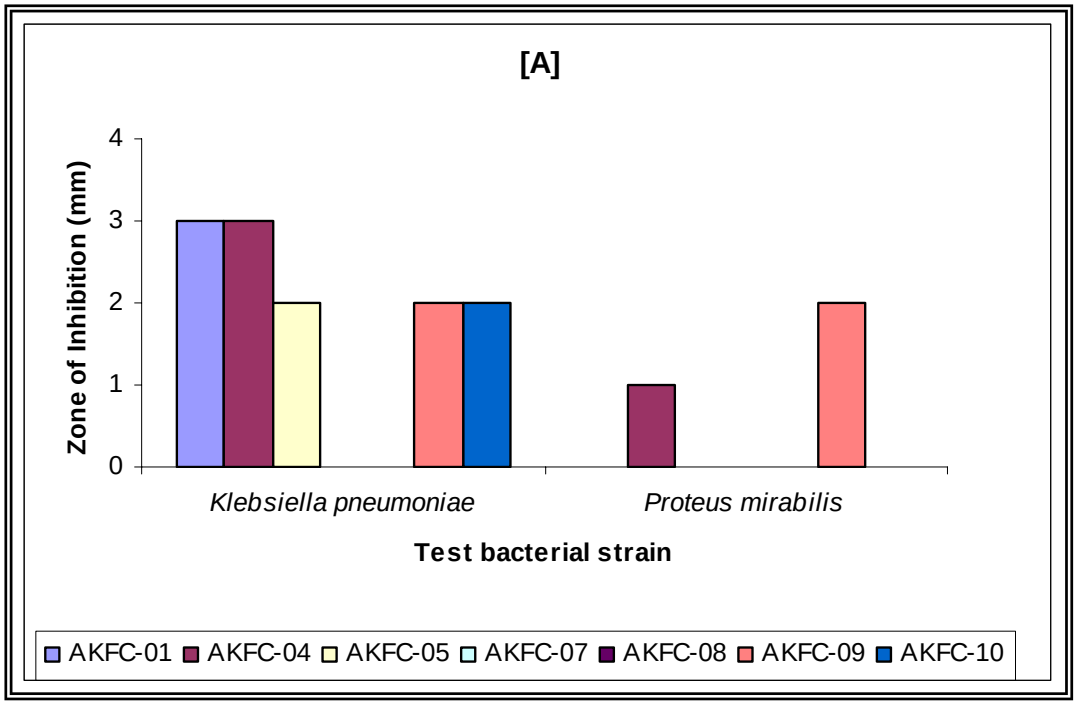


Figure 4.8: Antimicrobial activity of Chalcones against Gram-negative bacteria in DMF [A] and DMSO [B].



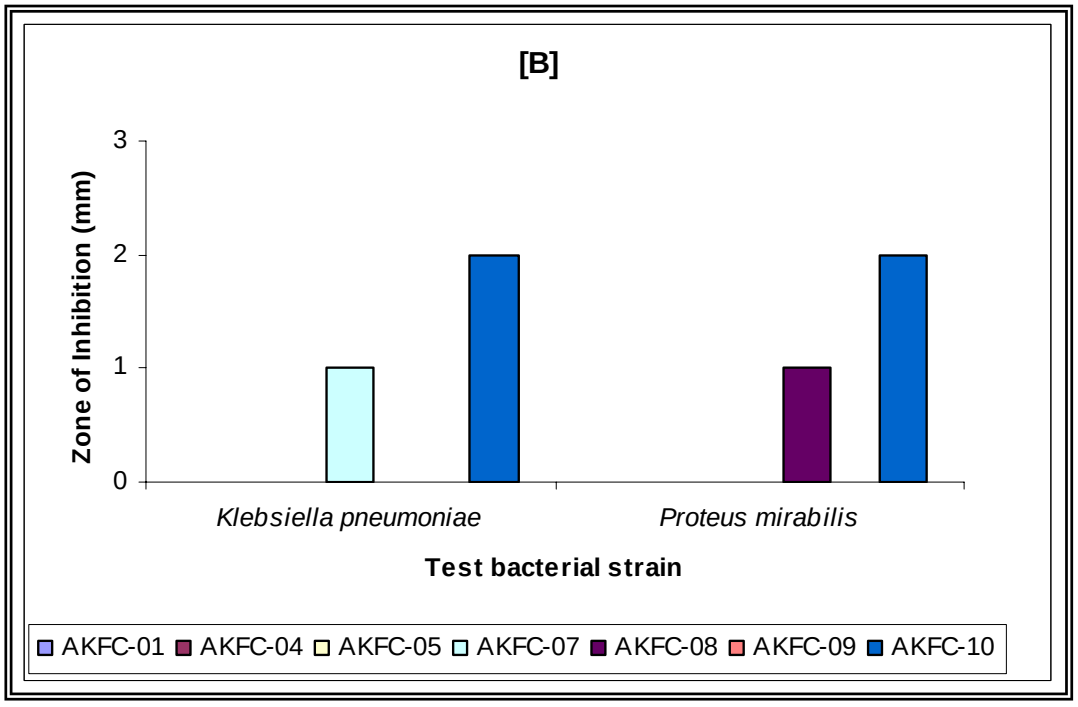
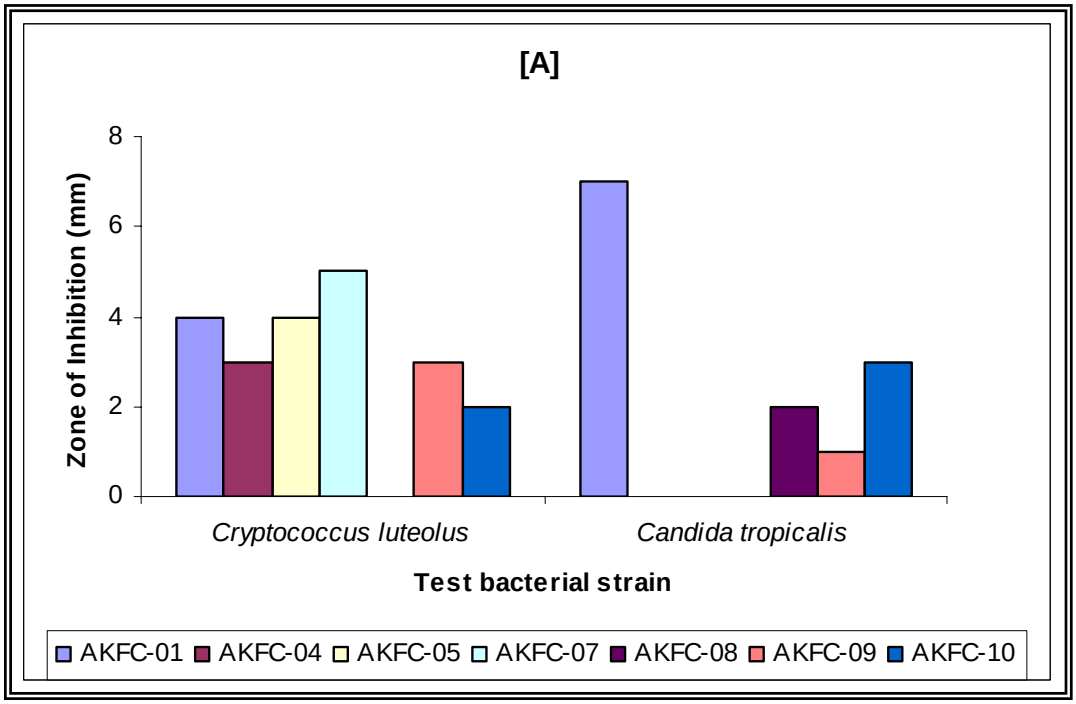
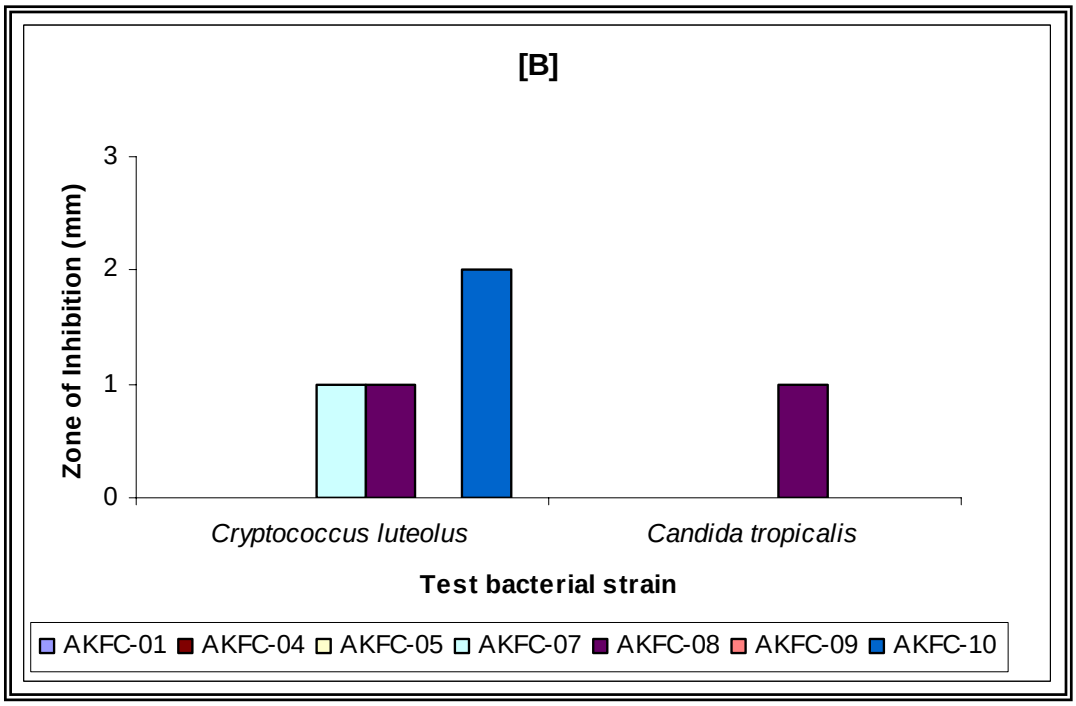


Figure 4.9: Antimicrobial activity of Chalcones against fungus in DMF [A] and DMSO [B].





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A COMPREHENSIVE SUMMARY OF THE WORK

The present work is divided into following chapters:

Chapter-1

This chapter describes the importance of heterocyclic compounds with aim and objective of the present work.

Chapter-2

This chapter divided into following part:

Part-1 deals with the synthesis of Schiff bases, 5-methyl 4-Thiazolidinone and 4-Thiazolidinone bearing benzothiazole moiety whereas in **Part-2** synthesis of chalcones having furan moiety is described along with their physical constant data. In both the parts I and II, the characterizations of synthesized compounds are done by IR, NMR and mass spectral data. The spectra and the characteristic peak position of IR and NMR spectra of some compounds are reported. Further, mass spectra and possible fragmentation schemes are given in this chapter. **Part-3** deals with the comparison of synthesis of Schiff bases by conventional, microwave and ultrasound irradiation methods. It is observed that both microwave and ultrasound method, reaction time is reduced to few minutes (in microwave) and to few hours (in ultrasound technique).

Chapter-3

The physicochemical properties of synthesized Schiff bases and chalcones were also studied. The different properties are given in different sections.

Section-1:

This section deals with the acoustical properties of Schiff bases and chalcones over a wide range of concentrations at 308.15K. For Schiff bases, measurements were done in DMF and DMSO whereas for chalcones DMF and $CHCl_3$ were taken. The choice of different solvents is due to solubility problem. Various acoustical parameters were also evaluated to understand

the different types of interactions occurring in the solutions. It is observed that for the studied compounds, in the studied solvents, solute-solvent interactions dominate.

Section-2:

In this section, the densities of Schiff bases in DMF and DMSO and of chalcones in DMF and $CHCl_3$ were measured respectively at 308.15K. The experimental density values are found to be different than those calculated theoretically for all the studied systems. This may be due to different interactions in different solvents. Further, the molar refraction and refractive index of compounds were evaluated which are also found to be different in each solvent.

Section-3:

This section deals with the conductance of studied compounds: Schiff bases (in DMF and DMSO) and Chalcones (DMF and $CHCl_3$) at 308.15K. It is observed that for both Schiff bases and Chalcones, conductivities are higher in DMF than the other solvent. Further, these compounds exhibit weak electrolytic nature in the studied solvents.

Section-4:

This section describes the heat of solution of all the studied compounds in DMF and 1, 4-Dioxan at different temperatures (298.15-318.15K). It is observed that the solubility of all the compounds increases linearly with temperature in both solvents. Comparison of solubility of these compounds in DMF and 1, 4-Dioxan shows that overall solubility is greater in DMF than in 1, 4 Dioxan. The Gibb's free energy (ΔG) and entropy (ΔS) of different solutions have also been evaluated. ΔH_s and ΔG values are found to be positive whereas ΔS values are negative. Positive ΔH_s indicates endothermic dissolution of compounds whereas positive ΔG suggests that the dissolution process is not spontaneous. Further, the negative values of entropy indicate less random ness in solutions.

Section-5:

The thermal properties of synthesized chalcones are described in this section. DSC and TGA thermo gram were scanned at the heating rate of 10°C per minute. It is observed that thermal stability depends on the presence of substituents in the compound. AKFC-10 having coumarin is found to be unstable whereas AKFC-04 having amino side chain is most stable. This suggests that the presence of amino group causes greater stability than that of coumarin group.

Further, the melting points determined by DSC and by open capillary methods are found to be in good agreement.

From thermograms, various kinetic parameters such as order of reaction, energy of activation, frequency factor and entropy change were also calculated for each step. The order of reaction is quite different in different steps for different compounds. Further, the entropy is found to be both positive and negative in different steps. The positive values of entropy change indicate that the transition state is less ordered than the original compound whereas negative value of entropy change corresponds to an increase in the order of transition state than the reactants.

Section-6:

This section describes partition coefficient of chalcones, which has been studied in n-Octanol-water system by UV spectroscopy at different pH. It is concluded that out of 8 studied compounds, AKFC-08 exhibits maximum hydrophobic nature.

Section-7:

The dissociation constants of chalcones in DMF: water system (90:10) are studied in this chapter. It is observed that acidity is minimum in AKFC-04 having amino group as expected whereas for AKFC-05 having halogen group, acidity is maximum.

Chapter-4:

The antimicrobial activities of all the synthesized compounds in DMF and DMSO are explained in this chapter. Different Gram positive and Gram negative bacterial strains are used for antibacterial study. The antifungal activities have also been studied against two strains. Different bacterial strains and fungal strains behave differently in different solvents. The presence of different substituents at different positions in phenyl ring affects inhibition.

List of Published/Accepted/Communicated Papers

1) S. Baluja, A. Kulshrestha and M. Soni; “Determination of stability constants of some Schiff bases derived from vanillin and 4-amino antipyrine.” Journal of the Institution of Chemists, 80(4), 2008 **(Published)**
2) S. Baluja, N. Vekaria, R. Gajera and A. Kulshrestha; “Synthesis and Acoustical Studies of some Chalcones of Furaldehyde in different solvents at 308.15 K” International J. Applied Chem. 5(1), 2009 **(In Press)**
3) A. Kulshrestha, S. Dwivedi and S. Baluja; “Microwave promoted synthesis of some novel Schiff bases” International J. Synthesis and Characterization. **(Accepted)**
4) A. Kulshrestha, R. Gajera and S. Baluja; “Solubility of biologically active chalcones in 1, 4 dioxane and N, N dimethylformamide from (298.15-318.15) K” J. Chem. Eng. Data, (Manuscript Id-je-2009-003709) **(Communicated)**

List of Papers Presented in Different Conferences/Symposia

1) "Acoustical studies of binary mixtures of acetophenone at 308.15K",Shipra Baluja, Asif Solanki , Nikunj Kachhadia, Nilesh Godvani and Anchal Kulshrestha, 2nd National Conference on Thermodynamics of Chemistry and Biological Systems, Veer Narmad South Gujarat University, Surat, 30th Oct.- 1st Nov. 2006. **(National)**.
2) "Green Chemical Approach for the Synthesis of Schiff Bases under microwave irradiation", A Kulshrestha, S Dwivedi and S. Baluja, International Conference On The Interface of Chemistry-Biology In Biomedical Research, jointly organized by I.S.C.B. and Chemistry Group, Birla Institute of Technology & Science during February 22nd-24th – 2008 **(International)**.
3) "Acoustical studies of some synthetic compounds in different solvents at 308.15 K." S. Baluja, A. Kulshrestha, N. Vekaria and R. Gajera, 20th International Conference on Chemical Thermodynamics. During Aug. 3-8 2008, Warsaw, Poland **(International)**.
4) "Ultrasonic studies of antiprotozoal drug in protic and aprotic solvents at 308.15 K", Mehul Bhatt, Anchal Kulshrestha and Shipra Baluja, 3rd National conference on thermodynamics of chemical and biological systems, Nagpur University, Nagpur, 16-17 Oct- 2008. **(National)**