

**THERMOSOLVATOCHROMISM,  
ELECTROCHEMICAL, TRANSPORT AND  
KINETIC INVESTIGATIONS IN IONIC LIQUID  
SYSTEMS**

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**FOR THE DEGREE OF  
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## DECLARATION

I hereby declare that the work incorporated in the thesis entitled **“Thermosolvatochromism, Electrochemical, Transport and Kinetic Investigations in Ionic Liquid Systems”** submitted for the degree of Doctor of Philosophy to the University of Pune, has been carried out by me at the Physical Chemistry Division, National Chemical Laboratory, Pune from July, 2006 to February, 2011 under the supervision of Dr. Anil Kumar (Research Guide). The work is original and has not, in full or in part, formed the basis for the award of any degree, diploma, associateship, fellowship, titles in this or any other University or other institution of higher learning. I further declare that the results presented in the thesis and the considerations made therein contribute to the advancement of knowledge in the field of Chemistry, in general and to the field of solvent effects, in particular.

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## **CERTIFICATE**

Certified that the work incorporated in the thesis entitled “**Thermosolvatochromism, Electrochemical, Transport and Kinetic Investigations in Ionic Liquid Systems**” submitted by Mr. Nageshwar D. Khupse for the degree of Doctor of Philosophy to the University of Pune, was carried out by the candidate under my supervision in Physical Chemistry Division, National Chemical Laboratory, Pune. Such material as has been obtained from other sources has been duly acknowledged in the thesis.

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**To**  
**My Loving *Mother***

***Dedicated to the  
loving memory of  
My  
Dear Father***

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*Date:*

*Nageshwar D. Khupse*

# ABSTRACT

## THERMOSOLVATOCHROMISM, ELECTROCHEMICAL, TRANSPORT AND KINETIC INVESTIGATIONS IN IONIC LIQUID SYSTEMS

The work in the present thesis is concerned with the physico-chemical properties of ionic liquids and study of the solvent effects on electrochemical process and the kinetics of organic reactions.

**Chapter 1** describes a critical literature survey of synthesis, properties of ionic liquids and their applications in different fields. Ionic liquids are known to possess many interesting physical properties. Hence, understanding the variations in the physico-chemical properties of ionic liquids including viscosity, polarity and other thermodynamic properties etc. are important part of my research work. These properties vary with structure of ionic liquids and the composition of cation and anions. Ionic liquids have been classified on the basis of different cationic components – for example, imidazolium, pyridinium, pyrrolidinium, phosphonium, ammonium, sulfonium etc. based ionic liquids have been reported in the literature. Out of these classes of ionic liquids, the imidazolium based ionic liquids have been studied in greater detail. There are other classes of ionic liquids which are found to be promising but warrant a detailed investigation. The attempts to quantitatively study the influence of alkyl chain length, cations and anions for these classes of ionic liquids other than the imidazolium based ionic liquids, have been made.

The principal approach employed for studying the physico-chemical properties like viscosity and polarity has also been described in brief in **Chapter 2**. It enumerates the objectives of the planned research based on the literature survey of solvent effects. It also describes the organization of the thesis.

In **Chapter 3**, Attempts to understand the solute-solvent interactions affected in pure ionic liquids and binary mixtures of ionic liquids with molecular solvents are described. The chapter is further divided into two sections:

**Section 3.1** is related to polarity of pure ionic liquids - “solvatochromism” - and effect of temperature on polarity of ionic liquids - “thermosolvatochromism”. Solvatochromism in ionic liquids has been studied in the pyridinium, pyrrolidinium and phosphonium based ionic liquids.

In order to investigate the anionic effect on polarity of these ionic liquids, three major classes of anions - namely bis(trifluoromethylsulphonyl)imide  $[\text{NTf}_2]^-$ , tetrafluoroborate  $[\text{BF}_4]^-$  and [amino acid] $^-$ -based species have been selected. The hydrogen bond donating property ( $\alpha$ ), hydrogen bond accepting property ( $\beta$ ), polarizability ( $\pi^*$ ) and the electronic transition energy parameter ( $E_T^N$ ) are determined for different combinations of cations and anions using three indicator dyes – Reichardt’s dye, *N,N*-diethyl-4-nitroaniline and 4-nitroaniline at 298.15K. The effect of the chain length of the alkyl substituent on the cation influencing the values of the polarity parameters has been explained.

The contrasting behavior of  $E_T^N$  value with temperature for the pyridinium-based against the pyrrolidinium and phosphonium-based ionic liquids has been studied in terms of cationic effect to change the polarity with change in temperature. The polarity of phosphonium ionic liquids is noted to increase with an increase in temperature. This behavior is in contrast to that observed for the pyridinium and pyrrolidinium-based ionic liquids. Similarly, the variation in the magnitude of other parameters like as  $\alpha$ ,  $\beta$ , and  $\pi^*$  with temperature are reported in this section with structural correlation of ionic liquids.

The preferential solvation in the binary mixture of ionic liquids with molecular solvents has been discussed in **Section 3.2**. In order to investigate preferential solvation in ionic liquids systems, the pyridinium based ionic liquids such as  $[\text{BP}][\text{BF}_4]$ ,  $[\text{3MBP}][\text{BF}_4]$ ,  $[\text{4MBP}][\text{BF}_4]$  and molecular solvents like water, methanol, dichloromethane have been selected for the study. Two models proposed by Skwierczynski and Connors have been

used to study solvent-exchange processes in these binary mixtures, which can be defined by two preferential solvation parameters,  $f_{2/1}$  and  $f_{12/1}$ , measuring the tendency of the indicator to be solvated by solvents  $S_2$  and mixture  $S_{12}$  with reference to solvent  $S_1$ . In the case of binary mixture of ionic liquids with water and dichloromethane, parameters  $f_{2/1}$  shows higher values indicating that the dye is more preferentially solvated by ionic liquids than either of the cosolvents. The binary mixture of ionic liquids-methanol shows synergetic effect, in which polarity of mixture is higher than that of pure two components. The  $f_{12/1} > f_{2/1}$  indicates that the dye is more solvated by mixture of two components than either of the pure component.

The transport behavior in ionic liquids changes with the composition, addition of cosolvents and effect of temperature has been discussed in **Chapter 4** which involves two sections.

**Section 4.1** is related to the dramatic change in viscosity of ionic liquids on addition of cosolvents like water, methanol and dichloromethane. The viscosities  $\eta$  is measured for several mixtures of ionic liquids with molecular solvents measured throughout the composition range at 298.15 K. It has been observed that the decrease in viscosity of ionic liquids depends on the cosolvent added. The polarity of solvents plays an important role in deciding the magnitude of the change in viscosity of the binary mixture. The addition of more polar water brings down the viscosity of ionic liquids more as compared to methanol and dichloromethane. Further, the temperature dependant viscosity of pure as well as aqueous ionic liquids is analyzed. The data for aqueous [4-MBP][BF<sub>4</sub>] shows that the decrease in the viscosity of pure ionic liquid is less prominent at higher temperatures owing to faster movement of ions at higher temperatures. The data of these ionic liquids cannot be represented by Arrhenius equation. A modified VFT equation has been employed to analyze the data.

**Section 4.2** is a description of a new method to correlate viscosities of ionic liquids in aqueous and non aqueous solutions. The method involves two parameters characterizing solvation number and ion-solvent interaction coefficient. The strength of

the proposed method lies in the fact that both the parameters are well documented quantities.

The electrochemical oxidation of anthracene in three series of ionic liquids is discussed in **Chapter 5**. These measurements involve study of single electron transfer kinetics to determine the diffusion coefficient and their correlation with structure of ionic liquids. Irreversible oxidation of anthracene in different ionic liquids is found to be related to the structure of ionic liquids. The two sections included in the chapter are:

In **Section 5.1** describes the measurement of the diffusion coefficient of anthracene in pyridinium, pyrrolidinium, and imidazolium based ionic liquids by cyclic voltmetric measurements. The effect of chain length on the electrochemical process parameters has also been noted. The diffusion process varies with structure of ionic liquids and fails to correlate exactly with the Stoke-Einstein relation.

In **Section 5.2** the mechanistic aspect of oxidation of anthracene has been explained. Alkyl chain substitution on cation affects the oxidation of anthracene. It is quasireversible process and follows an electron transfer followed by chemical reaction (EC) mechanism. The change in mechanism of oxidation of anthracene from quasireversible to irreversible on alkyl chain length substitution varying from butyl to hexyl to octyl chain length on cation is interesting. The effect is more pronounced in pyrrolidinium based ionic liquids.

**Chapter 6** deals with kinetics of Diels-Alder reaction of anthracene-9-carbinol with *N*-ethyl maleimide in binary mixture ionic liquids with molecular solvents. The kinetics has been followed in-situ by decrease in concentration of anthracene-9-carbinol using UV-visible spectroscopic method. Pyridinium based ionic liquids such as [BP][BF<sub>4</sub>], [3MBP][BF<sub>4</sub>], [4MBP][BF<sub>4</sub>] and molecular solvents like water, methanol, and chloroform are chosen for this study. The plot of second order rate constants  $k_2$  vs. concentration of ionic liquids shows that the decrease in rate constant  $k_2$  on addition of ionic liquids is observed. It is due to increase in viscosity of medium with increasing concentration of ionic liquids. In the case of binary mixture of ionic liquid and water the change in  $k_2$  is higher in water rich region.

**Chapter 7** summarizes the work in the present thesis in bringing out the structure-property and property-effect correlations for potentially useful classes of ionic liquids. Some interesting observations like the irregular trends in thermosolvatochromism and the peculiar interactions at the electrode-electrolyte interface bring out the unexplored aspects of the subject under investigation. The observations and the models used to explain the same provide useful tools for selection of an optimum solvent composition in the future.

## List of Abbreviations

[BMIM]	1-butyl-3-methyl imidazolium
[EMIM]	1-ethyl-3-methyl imidazolium
[PMIM]	1-propyl-3-methyl imidazolium
[OMIM]	1-octyl-3-methyl imidazolium
[DMIM]	1, 3-dimethyl imidazolium
[BP]	1-butyl pyridinium
[HP]	1-hexyl pyridinium
[OP]	1-octyl pyridinium
[3MBP]	1-butyl-3-methyl pyridinium
[3MHP]	1-hexyl-3-methyl pyridinium
[4MBP]	1-butyl-4-methyl pyridinium
[BMPyrr]	1-butyl-1-methyl pyrrolidinium
[HMPyrr]	1-hexyl-1-methyl pyrrolidinium
[OMPyrr]	1-octyl-1-methyl pyrrolidinium
[TBP]	tetra butyl phosphonium
[Ala]	alanate
[Val]	valinate
[BF <sub>4</sub> ]	tetrafluoroborate
[NTf <sub>2</sub> ]	bis(trifluoromethylsulphonyl)imide
[PF <sub>6</sub> ]	hexafluorophosphate
DCM	dichloromethane
DMSO	dimethyl sulphoxide
IMDA	intramolecular Diels–Alder reaction
TST	transition state theory

## List of Symbols

$E_T(30)$	Electronic transition energy of Reichardt's dye, kcal mol <sup>-1</sup>
$E_T^N$	Normalised $E_T$ scale
$\alpha$	Hydrogen bond donor acidity
$\beta$	Hydrogen bond acceptor basicity
$\varepsilon$	Relative permittivity
$\eta$	Viscosity of a fluid, cP/mPa.s
$\lambda$	Wavelength, nm
$\pi^*$	Solvent polarizability parameter
$E_a$	Energy of activation of a reaction, J mol <sup>-1</sup>
$\Delta^\#G$	Free energy of activation, J mol <sup>-1</sup>
$\Delta^\#H$	Enthalpy of activation, J mol <sup>-1</sup>
$\Delta^\#S$	Entropy of activation, J mol <sup>-1</sup> T <sup>-1</sup>
$k'$	<i>pseudo</i> first rate constant, s <sup>-1</sup>
$k_2$	Second-order rate constant, M <sup>-1</sup> s <sup>-1</sup>
$k_{\text{rel}}$	Relative rate constant
$t$	Time, s
$T$	Temperature, K

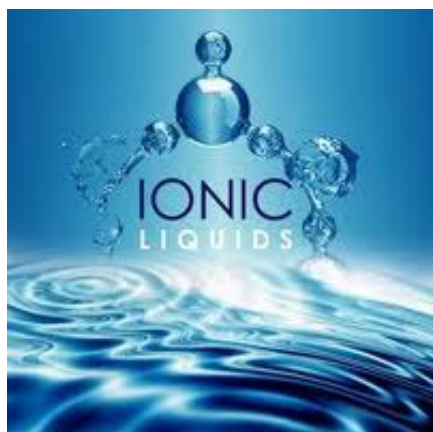


**Chapter 1**  
**Introduction**

## 1. Introduction

# 1. Introduction

*“In science, read, by preference, the newest works; in literature, the oldest.”- Albert Einstein*



Green chemistry is the environmentally benign approach of synthesizing bulk and fine chemicals, achieving enhanced selectivity and yields in the process. It efficiently utilises raw materials, eliminates waste and avoids the use of toxic and/or hazardous reagents and solvents in the manufacture and application of chemical products. Today, most chemical manufacturing processes are carried out in volatile organic solvents (VOC) at the industrial scale.<sup>1</sup> The use of such volatile organic solvents causes environmental pollution, which is hazardous to mankind. The rapid expansion of industrialisation also implies an exponentially increasing threat to the environment. Environmental pollution agencies surveyed many European and American countries related release of different organic compound into the environment. Based on the toxicity release index (TRI) supplied by the industries in the United States for 2007-08, the estimated contribution from the chemical industry is unsurprisingly among the highest in all cases as compared to that from the other industries. A useful measure of the potential environmental acceptability of chemical processes is the E factor,<sup>2</sup> defined as the mass ratio of waste to desired product. The magnitude of E factors decides the waste problem in chemical industries at various parts. It has been observed that pharmaceutical industries and fine chemical industries have a much higher E factor index and contribute more towards the environment pollution than the bulk chemical industries.<sup>3</sup>

The last two decades have witnessed an increasing awareness about the need for environmental conservation. There have been numerous attempts to reduce the toxic output from the chemical industry. The basic principles of Green Chemistry, as

## 1. Introduction

proposed by the United States Environmental Protection Agency and John C. Warner have been instrumental guidelines through the 12 principles of green chemistry in this direction.<sup>4</sup> Among those, there is an urgent need to focus on the principle of using environmentally benign reaction conditions (including solvents) and reduce toxic emissions in the environment. In order to solve the problem of environmental pollution, there is a need of utilising alternative media instead of organic solvents for organic reactions. The most popular alternatives to conventional volatile solvents include water, supercritical fluids, polyethylene glycol, ionic liquids etc.

Of all these media, ionic liquids have immense unexplored potentials and the present thesis basically emphasizes the physico-chemical studies and structural aspects of ionic liquids and their few applications.<sup>5</sup>

### 1.2 Historical Background of Ionic Liquids

Several definitions of ionic liquids are reported in the literature.<sup>5</sup> Each liquid with solely ionic constituents is an ionic liquid, thus including molten inorganic salts like alkali halides with melting points typically above 600 °C. At present, the most widely accepted definition of ionic liquids considers salts with a non-organic cation and a non-organic/inorganic anion, having melting points below the boiling temperature of water. The expressions ionic liquid and room temperature ionic liquid are mutually exchangeable and this convention will be followed throughout the thesis.

Aside from different interactions and bonding forces, they also constitute an electrolyte solution of high concentration giving them superior performance in electrochemical processes. For the earliest high temperature molten salts, the high melting points above room temperature limited both their scientific investigation and their incorporation in technological applications such as energy storage in battery devices. This problem set ground for scientists to come up with low melting salts, e.g. by including organic ionic species.

In 1914, the first ionic liquid, ethylammonium nitrate (EAN)  $[\text{EtNH}_3][\text{NO}_3]$  (mp 12 °C) was synthesized by Paul Walden. Walden defined ionic liquid as “materials composed of cations and anions that melt around 100 °C or below as a arbitrary temperature limit.” This definition identifies the difference from molten salts that

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have also been known for a long time and are inorganic salts with high melting temperatures. Despite this early discovery, a little attention has been paid to the ionic liquids, whereas the chemistry of inorganic molten salts and eutectics has been significantly developed. Although it is widely agreed upon as the starting point of the new materials class of ionic liquids, not much progress was made in the next few decades. The thread was taken up again in 1948 when first applications for aluminium chloride-based ionic liquids were patented.<sup>6</sup> It was shown that compositions of  $\text{AlCl}_3$  and 1-alkyl pyridinium bromide have a small room temperature liquidus window for certain concentrations of  $\text{AlCl}_3$ . In the following decades, considerable research efforts were put into organic chloride-aluminium chloride ionic liquids – chloroaluminate ionic liquids, which can be regarded as the first generation of ionic liquids. By then, many electrochemists were fully aware of versatile potentials of the ionic liquids. Due to their hygroscopic nature, however, they were difficult to prepare, which ultimately prevented their widespread use for day-to-day applications. Therefore, it was not before the synthesis of air and water stable ionic liquids in 1992 that interest in them was virtually exploding. Based on an imidazolium cation, 1-alkyl-3-methylimidazolium  $[\text{RMIM}]^+$  (R=alkyl) and either hexafluorophosphate  $[\text{PF}_6]^-$  or tetrafluoroborate  $[\text{BF}_4]^-$  as anion, these systems can be seen as the second generation of ionic liquids. Although they can generally be prepared and stored outside of an inert atmosphere, long time exposure can drastically change their properties, for both  $[\text{PF}_6]^-$  and  $[\text{BF}_4]^-$  decompose in the presence of water under formation of HF. To avoid such undesired reactions with water, more hydrophobic and chemically stable anions have received considerable attention in recent years, such as trifluoromethanesulfonate  $[\text{CF}_3\text{SO}_3]^-$ , bis((trifluoromethyl)sulfonyl)amide  $[\text{NTf}_2]^-$ , etc. Ionic liquids comprising of these anions can be regarded as the third and most recent generation. The “next generation” ionic liquids are yet to come and are expected to be task-specific, i.e. optimized for dedicated applications.

While early work in the field tended to presume that ionic liquids had very similar properties as a class, it is now widely recognized that they offer a very wide range of properties and that one of the only properties that can be thought of as being ubiquitous among ionic liquids is ionic conductivity. As the field has thus grown in recent years, producing a wide range of properties in an even wider range of salts

## 1. Introduction

structures, the synthetic methods applied to the preparation of these salts have become more sophisticated and capable of targeting more complex compounds. A number of the purification and characterization issues arise and these are, in some cases, unique to the ionic liquids field because of the very nature of the compounds involved.

Nowadays, research in ionic liquids is increasing drastically, with more than thousands of studies reported per year underlining the extreme growing interest in this field. Ionic liquids are frequently termed “green solvents” or “designer solvents”. These are often considered as future solvents for catalysis, chemical reactions, extractions, electrochemical purpose and many other potential applications. However the question arises whether ionic liquids are really green? The thesis is aimed to investigate the question in terms of the crucial physical properties of ionic liquids and their mixtures with a focus on the implications for their potential applications.

### 1.3 Chemical Composition of Ionic Liquids

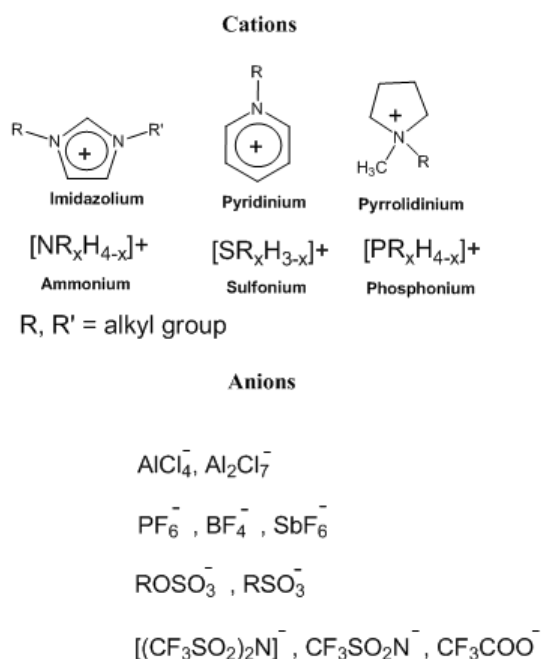
Ionic liquids are composed of organic cations with low symmetry, while the anions may be organic or inorganic. The cationic centre most often involves a positively charged nitrogen or phosphorus atom. Ionic liquids those are investigated so far are based on ammonium, sulphonium, phosphonium, imidazolium, pyridinium, picolinium, pyrrolidinium, thiazolium and pyrazolium cations.

The more recent research has mainly focused on room temperature ionic liquids composed of a symmetric dialkylimidazolium cations with a variety of anions. The modification of the cation and anions changes the properties of the liquid, notably the melting point and liquid range, viscosity and miscibility with other solvents can be altered. On the basis of the cation, ionic liquids may be broadly divided into different groups for example, five-membered heterocyclic cations (e.g. imidazolium cations), six-membered heterocyclic cations (pyridinium cations) and acyclic cations (ammonium, phosphonium and sulphonium based cations). A few ionic liquids also have chiral cations with potential applications in asymmetric synthesis. The different families of ionic liquids are shown below (Scheme 1.1).

Imidazolium-based ionic liquids have been used for many applications as they were explored in detail. Initially chloroaluminate ionic liquids were in existence as

## 1. Introduction

first generation ionic liquids. Aluminum (III) halides are extremely sensitive to even the smallest amounts of water. Hence, when a chloroaluminate ionic liquid is exposed to water a non exothermic reaction occurs with the evolution of HCl. The reaction produces oxide- and proton-containing species, both of which can interact with other solutes. Because of its highly hygroscopic nature further applications could not be explored. Ionic liquids composed of air- and water- stable anions like  $[\text{PF}_6]^-$  and  $[\text{BF}_4]^-$  were invented and real story of research of ionic liquids started. But recently trifluoroacetate  $[\text{CF}_3\text{COO}]^-$  and  $[\text{NTf}_2]^-$  anions based ionic liquids found to be interesting and has been used for many applications in different fields, which are also known to third generation ionic liquids.



**Scheme 1.1:** Structures of typical cations and anions.

A few ionic liquids also have chiral cations with potential applications in asymmetric synthesis. The different families of ionic liquids are shown below (Scheme 1.1).

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Imidazolium-based ionic liquids have been used for many applications as they were explored in detail. Initially chloroaluminate ionic liquids were in existence as a first generation ionic liquids. Aluminum (III) halides are extremely sensitive to even the smallest amounts of water. Hence, when a chloroaluminate ionic liquid is exposed to water a non-exothermic reaction occurs with the evolution of HCl. The reaction produces oxide- and proton-containing species, both of which can interact with other solutes. Because of its highly hygroscopic nature further applications could not be explored. Ionic liquids composed of air- and water- stable anions like  $[\text{PF}_6]^-$  and  $[\text{BF}_4]^-$  were invented and real story of research of ionic liquids started. But recently trifluoroacetate  $[\text{CF}_3\text{COO}]^-$  and  $[\text{NTf}_2]^-$  anions based ionic liquids found to be interesting and has been used for many applications in different fields, which are also known to third generation ionic liquids.

### 1.4 Physicochemical Properties of Ionic Liquids

Some of the properties of ionic liquids that make them an effective and popular alternative to conventional organic solvents are given below:

#### 1.4.1 Broad Liquid Range

The liquidus range of ionic liquids is of the same order as for most high temperature molten salts and in consequence broader than for any molecular liquid but just shifted towards lower melting points as compared to the high temperature counterparts. Ionic liquid contains organic cation and inorganic anions, which increases the spatial distance between the charges, hence diminishing the Coulombic interaction strength. For example, in the dialkylimidazolium  $[\text{RMIM}][\text{anion}]$  ionic liquids, for an increase in chain length from methyl up to butyl group, a melting point reduction was observed whereas for higher alkyl group after butyl the melting point increases<sup>7</sup>. The melting points are affected by the symmetry and mobility, increasing asymmetry lowers the melting point as long as the cost in mobility does not get too high. Although low melting points are crucial for economic industrial processes, it still remains difficult to reliably predict them. Even for known systems, a precise determination of the melting point often proves to be difficult due to glass formation in a supercooled state.

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Melting points of organic salts have an important relationship to the symmetry of the ions, increasing symmetry in the ions increases melting points, by permitting more efficient ion-ion packing in the crystal cell. Conversely, a reduction in the symmetry of the cations causes a distortion from ideal close-packing of the ionic charges in the solid state lattice, a reduction in the lattice energy, and depression of melting points. A change from spherical or high symmetry ions such as  $\text{Na}^+$  or  $[\text{N}(\text{CH}_3)_4]^+$  to lower-symmetry ions such as imidazolium cations distorts the Coulombic charge distribution. In addition, cations such as the imidazolium cations contain alkyl groups that do not participate in charge delocalization. More asymmetric structure of ions in salts, lower is the melting points. Ionic liquids constitute the cation and anions, which are highly asymmetric in nature and melt at low temperature. Changes in ion types, substitution, and composition produce new ionic liquid systems, each with a unique set of properties that can be explored and hopefully applied to these issues.

However, it is clear from the observation that the principle distinction between the materials of interest today as ionic liquids and conventional molten salts is that ionic liquids contain organic cations rather than inorganic ones. But there is possibility that 'molten salts' may have lower melting points than some 'ionic liquids'. The wide liquid ranges exhibited by ionic liquids, combined with their low melting points and potential for tailoring size, shape, and functionality offer opportunities for control over reactivity unobtainable with molecular solvents.

### 1.4.2 Tunable Solvent Properties

Since ionic liquids are known to be designer solvents, they can be "designed" for particular applications in different fields. Hence the properties of ionic liquids changes by varying alkyl group, anion and functional group. The solvation capability of a solvent is mostly defined by its polarity. For molecular liquids, polar solutes tend to dissolve in polar solvents and *vice versa*. Ionic liquids exhibit more complex solvation properties. Being highly polar in general, their solvation behavior with respect to different solutes can be changed drastically by ion replacement. Hence ionic liquids have been found to be highly flexible and tunable solvents.



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### 1.4.3 Insignificant Vapor Pressure and High Thermal Stability

Ionic liquids have insignificant vapor pressures. They are non-flammable, stable at high temperature, have a decomposition temperature about 500 °C or higher and exist as liquid over a wide range of temperature. These properties are governed by the strength of the incorporated heteroatom-carbon and heteroatom-hydrogen bonds.

Most ionic liquids exhibit high thermal stability; the decomposition temperatures reported in the literature are generally greater than 400 °C, with minimal vapour pressure below their decomposition temperatures. It has been suggested that the stability dependence on the anion is  $[\text{PF}_6]^- > [\text{Tf}_2\text{N}]^- \cong [\text{BF}_4]^- > \text{halides}$ .<sup>8</sup> Also an increase in cation size, from  $-\text{C}_4\text{H}_9$  to  $\text{C}_8\text{H}_{17}$ , 1-butyl-3-methyl imidazolium [BMIM] to 1-octyl-3-methyl imidazolium [OMIM], does not appear to have a large effect. The thermal stability of ionic liquids has, however, been revised recently,<sup>9</sup>

### 1.4.4 Wide Electrochemical Window

Ionic liquids are specially designed for electrochemical studies because of their wide electrochemical window – defined as the electrochemical potential range over which an electrolyte is neither be reduced nor oxidized at an electrode. In most cases, this window is a higher multiple of the electrochemical window of water of 1.2V, e.g. 4.1V for [BMIM][BF<sub>4</sub>] and 5.5V for [BMP][NTf<sub>2</sub>] at a glassy carbon electrode. This area has been the subject of an increasing number of publications concentrating mainly on their use for electrochemical processes, organic reactions, catalysis, separation technology, etc.<sup>10, 11</sup>

## 1.5 Structures of Ionic Liquids

The structure of ionic liquids is disparate from the conventional salts or electrolyte. For example, conventional salts like sodium chloride form crystals with simple cubic symmetry. In this arrangement, each ion is surrounded by six ions of the opposite charge; the surrounding ions are located at the vertices of a regular octahedron. Upon dissolution, the structure of the electrolytes in different solvents shows that ions are solvated by the solvent molecule. The solvation of the ions depends on the size, charge of ions and solvent. There is no regular arrangement of ions observed in the

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electrolyte solution. Since ionic liquids consist of ions in the liquid state, they do not conform to either of these possible scenarios. It is thus interesting to study the structure of pure ionic liquids and understand the arrangement of cation and anions around each other.

Ionic liquids are known to possess a highly ordered supramolecular arrangement, both in pure form and in solutions. For example, the formation of amphiphilic association structures within ionic liquids, such as micelles, vesicles, microemulsions and liquid crystalline phases has been reviewed recently.<sup>12</sup> The formation of micelles and liquid crystals in EAN was already investigated in the 1980s by Evans and coworkers. The self-aggregation of common ionic and non-ionic surfactants in imidazolium based ionic liquids was also reported. Anderson *et al.* documented micelle formation of SDS in 1-butyl-3-methylimidazolium chloride [BMIM][Cl] and 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF<sub>6</sub>], respectively. The aggregation behaviour of poly(ethyleneglycol)-ethers in [BMIM][BF<sub>4</sub>], [BMIM][PF<sub>6</sub>] and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide, [BMIM][Tf<sub>2</sub>N] has been investigated. From all these observations it has been observed that compared to water the values for critical micelle concentrations (cmc) in ionic liquids are significantly higher.

Furthermore, the micellar aggregation numbers in ionic liquids are smaller than those for their solutions in water, while the area per molecule is also reduced compared to water.<sup>13</sup> With increasing 1-hexadecyl-3-methylimidazolium chloride [C<sub>16</sub>MIM][Cl] concentration aggregates of different morphologies have been observed that show many similarities to those found in aqueous systems.

In addition to micellar regions, typical liquid crystalline phases, such as normal hexagonal (*H1*), lamellar (*L $\alpha$* ) and reverse bicontinuous cubic (*V2*) phases have been reported. Surprisingly, most studies did not benefit from the excellent thermal stability of ionic liquids compared to water. The high temperature stable self-assembled structure highlights the major advantage of aggregates formed in room temperature ionic liquids.

In the past, investigations of the structure of liquids have, in general, been focussed on the arrangements in molecular solvents such as water, *t*-butanol and simple

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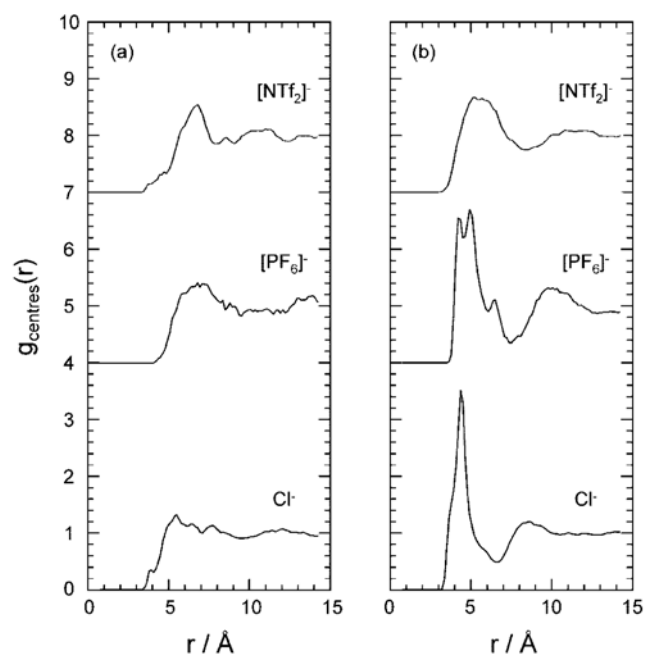
chlorinated solvents. The field of molten salts and the structures thereof is much less studied, and within this field, the study of the structure of room-temperature ionic liquids is in its infancy. Interest in ionic liquids stems from their physical properties discussed before. These properties may be varied with change in the structure of ionic liquids.

A variety of experimental techniques have been used to investigate liquid structure including neutron diffraction, X-ray scattering and extended X-ray absorption fine structure (EXAFS), and NMR spectroscopy. The importance of the elucidation of liquid structures is clear because this gives an indication as to which interactions are important within the phase and therefore dominate the chemical and physical properties of the liquid including solvation, density, viscosity and polarity. With respect to the study of molten salt/ionic liquid structure, Enderby and co-workers were the pioneers and clearly demonstrated that the structure of molten NaCl, for example, was dominated by alternating anion and cation interactions.<sup>14</sup> In this case, the local order extended out to three to four anion–cation pairs and the molten salt is a highly structured liquid. Since this time, experimental determination of ionic media has expanded significantly with the examination of a wide range of single-component and two-component salts. Neutron diffraction has been used to examine the structure of symmetric 1, 3-dimethylimidazolium [DMIM] salts, having higher melting points than asymmetric cations, as examined using neutron diffraction.<sup>15</sup> The probability distribution of chloride around a central imidazolium cation [DMIM][Cl], determined from modelling the neutron data using the empirical potential structural refinement (EPSR) process based on fitting the experimental data with a reverse Monte Carlo procedure.<sup>16</sup>

Strong charge ordering was found to be present in this ionic liquid with the anions and cations alternating in the radial distribution. Similarly, probability distribution functions have also been determined for the corresponding ionic liquids with [PF<sub>6</sub>]<sup>-</sup> and [NTf<sub>2</sub>]<sup>-</sup> anions.<sup>17</sup> An examination of the cation–cation distance shows that in [DMIM][Cl], the cations are separated by 5.5 Å, while for the [PF<sub>6</sub>]<sup>-</sup> and [NTf<sub>2</sub>]<sup>-</sup> anions, the spacings are 6.3 and 7.0 Å, respectively. Thus, the cation to cation contacts become larger as the size of the anion is increased, Cl<sup>-</sup> < [PF<sub>6</sub>]<sup>-</sup> < [NTf<sub>2</sub>]<sup>-</sup>.

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Similarly, the anion–cation distances are expanded with anion size 4.2 Å  $\text{Cl}^-$ , 4.5 Å  $[\text{PF}_6]^-$ , and 5.2 Å  $[\text{NTf}_2]^-$ .



**Figure 1.1:** The partial radial distribution functions for (a) the cation–cation distribution and (b) the cation–anion distribution for the cation 1,3-dimethylimidazolium  $[\text{DMIM}]^+$ , and anions  $[\text{Cl}]^-$ ,  $[\text{PF}_6]^-$  and  $[\text{NTf}_2]^-$  salts from molecular dynamic study.

Although in each case charge ordering was observed, the anion–cation–anion alternating pattern is less pronounced in the case of  $[\text{DMIM}][\text{NTf}_2]$  than for either the  $[\text{DMIM}][\text{Cl}]$  or  $[\text{DMIM}][\text{PF}_6]$  liquids as shown by the almost coincident position of the second shells of the cations and anions in  $[\text{DMIM}][\text{NTf}_2]$ . An examination of the cation–cation contacts shows that in  $[\text{DMIM}]\text{Cl}$  the cations are separated by 5.5 Å, while for the  $[\text{PF}_6]$  and  $[\text{NTf}_2]$  analogues, the spacings are 6.3 and 7.0 Å, respectively, that is the cation to cation contacts become larger as the size of the anion is increased,  $[\text{Cl}]^- < [\text{PF}_6]^- < [\text{NTf}_2]^-$ . Similarly, the anion–cation distances are expanded with anion size: 4.2 Å  $\text{Cl}^-$ , 4.5 Å  $[\text{PF}_6]^-$  and 5.2 Å  $[\text{NTf}_2]^-$ . Although in each case charge ordering was observed, the anion–cation–anion alternating pattern is less pronounced

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in the case of [DMIM][NTf<sub>2</sub>] than for either the [DMIM][Cl] or [DMIM][PF<sub>6</sub>] liquids as shown by the almost coincident position of the second shells of the cations and anions in [DMIM][NTf<sub>2</sub>] at 13 Å. (Figure 1.1)

The main observations are that progressing from [Cl]<sup>-</sup> to [PF<sub>6</sub>]<sup>-</sup> to [NTf<sub>2</sub>]<sup>-</sup>, the anions have weaker interactions with the cationic ring hydrogens affecting the relative positions of the cations and anions shown in Figure 1.1. The point-charge-like behavior decreases as the anionic size increases and the charge becomes more delocalized. This has the effect of reducing the hydrogen bonding accepting ability of the anion, and thus the interaction with the ring hydrogens reduces. A further consequence of this delocalization of the charge is that ionic bonding in the liquid becomes softer and results in increased overlap of the anions and cations in the radial distribution, as observed for [DMIM][NTf<sub>2</sub>]. Moreover, as the anion size increases, the anions and cations must occupy mutually exclusive positions in order to pack most efficiently, and thus it is only in the chloride liquid that an “onion-skin structure” of alternating cationic and anionic layers, may be achieved.

### 1.6 Ionic Liquids as Solvents

As a consequence of their characteristic structural arrangement and unique physicochemical properties, ionic liquids present an interesting range of solvent properties which are still being explored. The solute-solvent interactions observed in ionic liquids can range from very weak (almost inert) to the very strong interactions. In order to optimize the performance of ionic liquids for future applications, it is important to understand the origin and manifestation of such solvent properties, in detail. Very recently the group of Strassner<sup>18</sup> and the groups of Davis<sup>19</sup> and West independently formulated and synthesized new ionic liquids having low melting point and viscosity. It has been shown that ionic liquid crystals easily “tunable” with variably substituted alkyl and aryl substituents termed this new group of ionic liquids “TAAILs” (tunable aryl-alkyl ionic liquids). The combination of effects such as inductive, mesomeric, steric effects and  $\pi$ - $\pi$  interactions effectively suppress crystal packing and lead to decrease in melting point of ionic liquids. They have also synthesized a series of methylimidazolium bis(trifluoromethylsulfonyl)imide salts

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bearing a long fatty acid side chain (C<sub>16</sub>-C<sub>20</sub>). The melting points and viscosities of ionic liquids closely resemble that for fatty acids.<sup>20</sup> The present work is focused on the study of two such important solvent properties of ionic liquids – viscosity and polarity.

### 1.6.1 Viscosity of Ionic Liquids

One of the largest barriers to the application of ionic liquids arises from their high viscosity. A high viscosity may produce a reduction in the rate of many organic reactions and a reduction in the diffusion rate of the redox species. Current research for new and more versatile ionic liquids is driven, in part, by the need for materials with low viscosity.

#### 1.6.1.1 Viscosity of pure ionic liquids

The viscosity of ionic liquids is much higher than that of water, similar to those of oils. Generally, viscosity follows non-Arrhenius behaviour but, sometimes, the thermal effect on viscosity can be fitted with the Vogel–Tammann–Fulcher (VTF) equation. Furthermore, viscosity remains constant with increasing shear rate and ionic liquids can be classified as Newtonian fluids, although non-Newtonian behaviours have been observed.<sup>21</sup> Examining various anion–cation combinations, the increase in viscosity observed on changing selectively the anion or cation has been primarily attributed to an increase in the van der Waals forces. For example, for both [RMIM][PF<sub>6</sub>] and [RMIM][NTf<sub>2</sub>], viscosity increases with increase in number of carbon atoms in the linear alkyl group attached to the imidazolium cation. The trends are, however, different in details – a linear dependence has been found for the viscosity of [NTf<sub>2</sub>]<sup>−</sup> salts with increasing alkyl chain length whereas a more complex behaviour characterized the [PF<sub>6</sub>]<sup>−</sup> salts. Branching of the alkyl chain in 1-alkyl-3-methylimidazolium salts always reduces viscosity. Finally, also the low viscosity of ionic liquids bearing polyfluorinated anions has been attributed to a reduction in van der Waals interactions. Hydrogen bonding between counter ions is another factor known to affect viscosity. The large increase in viscosity recently found on varying the anion of several ionic liquids (imidazolium, pyrrolidinium and ammonium salts) from [NTf<sub>2</sub>]<sup>−</sup> to [Ms<sub>2</sub>N]<sup>−</sup> has been attributed to the combination of the decreased

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anion size, less diffuse charge and large increase in hydrogen bonding. Finally, the symmetry of the inorganic anion has sometimes been considered as an additional parameter; viscosity decreases in the order  $[\text{Cl}]^- > [\text{PF}_6]^- > [\text{BF}_4]^- > [\text{NTf}_2]^-$ .

Hussey and coworkers contributed significantly to determine several physico-chemical properties of this chloroaluminate, an early class of ionic liquids.<sup>6</sup> A compilation on the viscosities of a number of air- and moisture-stale ionic liquids is available in the literature.<sup>22</sup> The major problem in handling this class of ionic liquids is with regard to their sensitivity to water and chloride impurities<sup>23</sup> and hence measurements should be made with utmost care. The presence of small amounts of chloride impurities could lead to a dramatic increase in the viscosity of ionic liquids. The variation of viscosity of pure ionic liquids changes with a variation in the structure of ionic liquids. The effect of cation is smaller as compared to anion effect. The  $[\text{NTf}_2]^-$  anion offers low viscosity compared to several other anions, while  $[\text{PF}_6]^-$  anion contributes significantly to the viscosity increase of ionic liquids. The  $[\text{EtSO}_4]^-$  anion shows increase in viscosity compared to the  $[\text{BF}_4]^-$  anion.

**Table 1.1. Viscosities of Ionic Liquids at 298.15 K**

<b>Ionic liquids</b>	<b><math>\eta/\text{cP}</math></b>
$[\text{BMIM}][\text{BF}_4]$	92 <sup>21</sup> , 115 <sup>24</sup> , 219 <sup>25</sup>
$[\text{BMIM}][\text{NTf}_2]$	44 <sup>26</sup> , 52 <sup>27</sup>

The fact that the viscosity of ionic liquids is sensitive to the presence of small amounts of impurities is responsible for the disagreement in the values. The drastic discrepancies in the literature values of ionic liquids  $[\text{BMIM}][\text{BF}_4]$  and  $[\text{BMIM}][\text{NTf}_2]$  are shown in Table 1.1. However, the same fact can be employed to our advantage, since the addition of small amounts of cosolvents can reduce the viscosity to suit our needs, without compromising on the promising capabilities of ionic liquid media. For example, the viscosity of  $[\text{BMIM}][\text{BF}_4]$  increased by 25% in the presence of  $0.5 \text{ mol.kg}^{-1}$  of chloride content. The presence of water had a stronger

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but inverse effect i.e. the viscosity decreased greatly in the presence of small amounts of water for not only hydrophilic but also hydrophobic ionic liquids.

The effect of anions on viscosity of imidazolium based ionic liquids can be broadly depicted as  $[\text{BMIM}][\text{NTf}_2] < [\text{BMIM}][\text{CF}_3\text{CO}_2] < [\text{BMIM}][\text{CF}_3\text{SO}_3] < [\text{BMIM}][\text{BF}_4] < [\text{BMIM}][(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}] < [\text{BMIM}][\text{PF}_6]$ . The alkyl ammonium-based ionic liquids exhibit a higher viscosity than the imidazolium-based ionic liquids with the same anion. The viscosity of ionic liquids increases with the length of the alkyl chain on the imidazolium ring.<sup>28</sup> e.g.  $[\text{EMIM}][\text{NTf}_2] < [\text{MIM}][\text{NTf}_2] < [\text{BMIM}][\text{NTf}_2] < [\text{HMIM}][\text{NTf}_2] < [\text{OMIM}][\text{NTf}_2]$ . One would expect that the overall contribution of the strong electrostatic terms to the interactions diminishes with an increase in the side-chain length. However, the contribution of weaker, non-associating, dispersion forces also enhances the viscosity. This results into higher viscosity, as the size of the non-polar part of the cations becomes larger. The justification put forward by Bonhote *et al.*<sup>7</sup> is that it is the increase in the van der Waal's interactions due to the presence of a long alkyl chain that leads to higher viscosities. Methylation at C(2) position in the imidazolium cation leads to a greater increase in viscosity as compared to that at C(4) position. This was contrary to the expectation that H-bonding suppression was expected to reduce the viscosity. This was explained on the basis of a decrease in the entropy of the system due to the constraints in ionic interactions.<sup>29</sup>

### 1.6.1.2 Viscosity of binary mixtures

As mentioned in the previous section, the viscosity of pure ionic liquids is affected on addition of cosolvent, i.e. a significant decrease in viscosity of ionic liquids is observed on addition of the cosolvent. The decrease in viscosity depends on the cosolvent added and the extent of resulting dissociation of ionic liquids into ions. In 1995, Hussey *et al.*<sup>30</sup> showed that the addition of cosolvents to  $[\text{EMIM}][\text{Cl}]+\text{AlCl}_3$  results in considerable improvements in both the viscosity and conductivity of this molten salt. For example, the addition of 12 % mass acetonitrile to the mole fraction of ionic liquids  $x_2 = 0.49$  ionic liquid caused the viscosity to decrease by about 70% of its value for the pure ionic liquid and the conductivity doubled. Furthermore, the



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magnitude of these changes in viscosity was noted to be the greatest for acetonitrile and the least for benzene. This suggests that the organic cosolvents "solvate" the constituent ions of the molten salt, resulting in a decrease in the aggregation of these ions. However, the addition of benzene beyond 35 % caused the specific conductance to decrease due to a decrease in the concentration of charge-carrying ions. The maxima observed in the plots of specific conductivity with  $w_{f,1}$  ( $=1-w_{f,2}$ ) are simply due to the fact that addition of benzene beyond  $w_{f,1}=0.35$  progressively decreases the concentration of free ions in the solution, resulting in a decrease in specific conductivity. No maxima was obtained during the addition of benzene to basic [EMIM][Cl] + AlCl<sub>3</sub>. In addition, NMR studies indicate that ion-ion interactions are much weaker in acidic melt than in basic melt. Thus, a solvent with a low relative permittivity such as benzene ( $\epsilon = 2.28$  at 293.15 K) may be more effective at disrupting ion-ion interactions in acidic melt than in basic melt, leading to the maximum observed in the plots of conductivity with  $w_{f,1}$ .

The rheological behaviour of binary mixtures of imidazolium-based ionic liquids has been studied extensively. Addition of cosolvents like ethanenitrile, trimethylethanenitrile, 2-propenenitrile, 1-methylimidazole, toluene, 1,4-dimethylbenzene, 1,2-dimethoxyethane et c. also results in a similar decrease in viscosity values. For the ionic liquid [BMIM][PF<sub>6</sub>], the viscosity at 293 K is four times lower in the saturated sample compared to the viscosity of pure one. It has also been reported that the temperature affects the viscosity of both, pure ionic liquids as well as water saturated ones.<sup>31</sup> It is found that effect of water on the viscosity of pure ionic liquid is less prominent at higher temperatures.

The viscosities of dried imidazolium based ionic liquids are in the range of from 40 to 376 cP at 293 K and for water saturated ionic liquids 22 to 85 cP at 298 K. Water may therefore be termed as a viscosity-reducer for ionic liquids. The hydrophobic ionic liquids, which are immiscible in water, are also affected by the presence of small amount of water.<sup>32</sup> Wang and *et. al*<sup>33</sup> have studied the viscosity behavior of pure and binary mixtures of [BMIM][BF<sub>4</sub>] ionic liquids with acetonitrile, dichloromethane, 2-butanone and *N,N*-dimethylformamide at 298.15 K. An

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exponential function based on concentration parameter has been fitted to the data. The viscosity for the binary mixtures of [BMIM][PF<sub>6</sub>] with tetrahydrofuran, methanol, dimethylsulfoxide, acetonitrile has been reported.<sup>34</sup> The negative values of viscosity deviation of the system suggested that viscosities of associates formed between unlike molecules are relatively less than those of pure component. The results were discussed in term of ion-dipole interaction between the cation of the ionic liquids and organic solvents. This leads to the prediction of the viscosity of the mixture as a function of concentration of dissolved solvents and in terms of polarity of the solvents. Mention should be made of the attempts made for determining the critical viscosity near liquid-liquid phase transition in [HMIM][BF<sub>4</sub>] + 1-pentanol.<sup>35</sup> It is observed that the critical viscosity follows the Arrhenius behavior. Data also exist on the viscosity of [EMIM][BF<sub>4</sub>] in H<sub>2</sub>O at various temperatures.<sup>36</sup> It was also reported that viscosity is more sensitive to temperature than density. It is to be noted that the viscosity of [EMIM][BF<sub>4</sub>] is 1 or 2 orders greater in magnitude than that of the organic solvents.

The effect of cosolvent like water on the viscosity of hydrophilic ionic liquids is more pronounced than that for hydrophobic ones. However, even hydrophobic ionic liquids, which are not miscible with water rapidly, absorb water from the atmosphere and which decreases its viscosity. The effect of water on hydrophobic ionic liquids is mostly determined by the anions, i.e. [NTf<sub>2</sub>]<sup>-</sup> based ionic liquids as these are less water-miscible as compared to [PF<sub>6</sub>]<sup>-</sup>. In the case of [BMIM][PF<sub>6</sub>] viscosity decreased by 17% upon addition of 0.19% water, while in the case of [BMIM][NTf<sub>2</sub>] the viscosities decrease by 30% upon addition of 1% water.<sup>37</sup> The decrease in viscosity depends on the ability of anions to form hydrogen bond with water - [NTf<sub>2</sub>]<sup>-</sup> form strong hydrogen bond with water than [PF<sub>6</sub>]<sup>-</sup>. The effect of organic solvents ethyl acetate, acetone, 2-butanone, 3-pentanone, cyclopentanone on the physicochemical properties of the ionic liquid [BMIM][PF<sub>6</sub>], especially on the viscosities, has been studied.<sup>38</sup> The viscosity for binary mixtures of [OMIM][Cl] with methanol, ethanol, and 1-propanol shows negative viscosity deviations at 0.1MPa and different temperatures.<sup>39</sup> The deviations become more negative from methanol to 1-propanol.

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The decrease in viscosity is greater for solvents with higher relative permittivity. This is due to the ion dipole interactions operating between ions and solvents, since polar solvents shows better miscibility with ionic liquids while nonpolar solvents shows poorer miscibility with ionic liquids. This indicates that polar molecules have stronger interaction with ionic liquids. Further studies at molecular level have revealed that addition of solvents to ionic liquids changes the molecular structure of ionic liquids,<sup>40-42</sup> due to hydrogen bonding between the solvent molecules and the anions of ionic liquids.<sup>43-45</sup>

### 1.6.1.3. Modeling the viscosity of ionic liquids

The experimental data for different properties obtained from a laboratory need to be compared to those obtained as a result of plausible models in order to understand the interactions taking place at a molecular level. An algebraic form of the equation with different components is used for the representation of the data of the binary mixture of ionic liquids with molecular solvents. In the literature, several empirical and theoretical equations have been used to account for the concentration dependence of  $\eta$ , but they deviate sharply when applied to highly concentrated solutions. However, the Vand equation and its modifications<sup>46</sup> have been able to account for the concentration dependence of  $\eta$  at an extreme concentration of electrolyte, although the theoretical concept on which the Vand equation and its modifications are based cannot be validated for highly concentrated solutions. The new proposed equation for different composition of salts in solution proposed by Kumar<sup>47</sup> for analyzing the viscosity of an organic melt miscible in a molecular solvent was given by Eq.1.1

$$\eta = \eta_0 \exp (b_0x_2 + b_1x_2^2 + b_2x_2^3) \quad (1.1)$$

where  $\eta_0$  is a viscosity of a pure solvent and  $x_2$  is the mole fraction of salts and  $b_0$ ,  $b_1$ ,  $b_2$  are correlation coefficients. The Redlich-Kister equation is known to be another popular equation used for modulation of different properties of the solution.<sup>48</sup> As a criteria for choosing the appropriate model equation, it is important that the treatment of experimental data should eliminate inconsistencies without distorting the results by

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imposing a arbitrary conditions, it should be flexible enough to cover all important cases and it should be simple in operation. For the present work, the initial discussion is given for binary system and later it has been extended to systems of more than two components. The viscosity of binary mixture of ionic liquids with molecular solvents decreases exponentially with addition of ionic liquids. The exponential nature of the data correlated with different forms of the Eq. 1.2.<sup>23</sup>

$$\eta = \eta_{IL} \exp(-x_s / a) \quad (1.2)$$

In this equation,  $\eta_{IL}$  is the viscosity of the pure ionic liquid,  $x_s$  is the mole fraction of the organic solutes and  $a$  is a constant. The excess viscosity of solution is given by the Eq. 1.3.

$$\ln \eta = \ln \eta_{mix} - (x \eta_{IL} + (1-x) \eta_s) \quad (1.3)$$

where  $\Delta \ln \eta$  is the excess viscosity of while  $\eta_{IL}$ ,  $\eta_s$  and  $\eta_{mix}$  are viscosities of ionic liquids, organic solutes and their mixtures at 298 K, respectively. These properties were mathematically represented by the generalized Redlich–Kister polynomials as

$$Y^E = x(x-1) \sum_{j \geq 1} B_j (1-2x)^j \quad (1.4)$$

where  $Y^E$  is excess property and  $B_j$  are the adjustable parameters obtained from the least squares method.

The viscosities are presented for [EMIM][BF<sub>4</sub>] + H<sub>2</sub>O binary systems over the entire range of the compositions at different temperature fitted to the model proposed by the Redlich-Kister equation. From the results it has been observed that viscosities of aqueous ionic liquid solution are strongly dependant on water content and weakly on temperature.

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### 1.6.1.4 Effect of temperature on viscosity of ionic liquids

Temperature dependence of transport properties like viscosities and the conductivities of ionic liquids display non-Arrhenius temperature dependence typically associated with glass forming ionic liquids. Temperature-dependent activation energies are derived for these transport processes by using the Vogel-Fulcher-Tammann-(VFT) equation. Harris *et. al.*<sup>49</sup> has studied the temperature dependence viscosity and density of ionic liquids. The viscosity of ionic liquids is fitted to the two-coefficient Litovitz equation (1.5) given by

$$\eta = A \exp(B/RT^3) \quad (1.5)$$

Modified Vogel-Fulcher-Tammann (VFT) equation is used to represent the temperature dependence viscosity of ionic liquids Eq. 1.6.

$$\eta = A \exp(B / (T - T_0)) \quad (1.6)$$

where A and B are the fitting parameters, and  $T_0$  is the glass transition temperature.

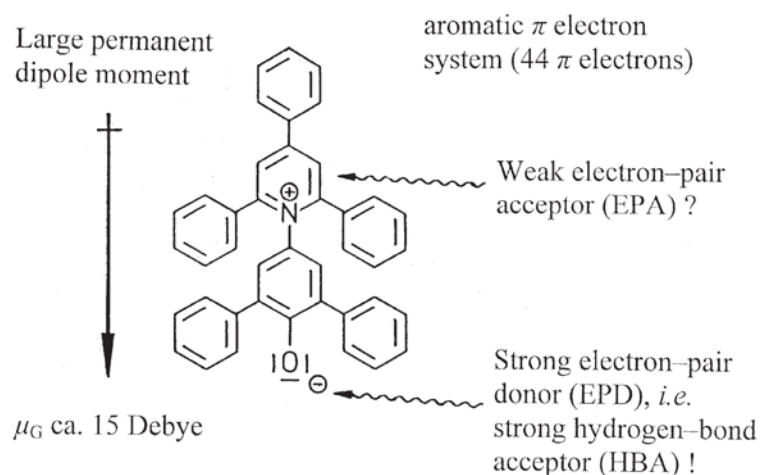
### 1.6.2 Polarity of Ionic Liquids

Chemists usually attempt to understand solvent effects on chemical processes in terms of the solvent polarity. Since the polarity of a solvent is too complicated to be expressed in terms of a single property, chemists have resorted to the use of empirical polarity parameters based on properly selected model processes. Most popular polarity scales are based on spectroscopic properties, chemical equilibria or kinetic measurements.<sup>50</sup> The sum of all the aforementioned interactions possible between a given solvent and the solute molecules is termed as *polarity* of the solvent. The polarity of a solvent represents its overall solvating ability. As a result of the failure of any individual physical parameter to successfully describe polarity in quantitative terms, it is often defined in terms a sum total of numerous empirical parameters. Some examples of such empirical scales include the  $\alpha$ -scale of hydrogen-bond donor acidity, the  $\beta$ -scale of hydrogen-bond acceptor basicity, the  $\pi^*$ -scale for polarizability,

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Dimroth's  $E_T$  scale etc.<sup>51</sup> Polar molecules interact through dipole–dipole interactions and hydrogen bonds. Chemists have often used relative permittivities, dipole moments, and refractive indices as macroscopic physical solvent polarity parameters. The interactions between the solute and solvent can be specific and nonspecific. The interactions like polarizability, dipole moment and charge are responsible for nonspecific interaction forces, whereas hydrogen-bond donor (HBD) and hydrogen-bond acceptor (HBA) abilities are responsible for specific interaction forces. These multiples of solute–solvent interactions, macroscopic physical solvent parameters have often led to failure in correlating solvents effects qualitatively and quantitatively with the structure and other properties. Therefore, solvent polarity should be defined in a more precise manner. The solvent polarity is simply defined as the ‘overall solvation capability (or solvation power) for (i) products, which influences chemical equilibria; (ii) reactants and activated complexes (‘transition states’), which determines reaction rates; and (iii) ions or molecules in their ground and first excited state, which is responsible for light absorptions in the various wavelength regions. The solvent polarity defined in this way cannot be measured by single macroscopic physical solvent parameters like relative permittivity, dipole moment, and refractive index. Solvent polarity, so defined, is much better described empirically by molecular–microscopic solvent-dependent reference processes. The solvents are considered as a discontinuous, more or less structured medium, consisting of individual, mutually interacting solvent molecules. The polarity of several ionic liquids has been studied in terms of  $E_T(30)$  (electronic transition energy in kcal/mol) and the Kamlet-Taft polarity parameters.<sup>51,52</sup> The  $E_T(30)$  value is calculated from maximum absorption of Betaine dye shown in Figure 1.2., which shows large negative solvatochromism, suitable as a UV/visible spectroscopic indicator of solvent polarity, using its long-wavelength intramolecular charge-transfer (CT) absorption as solvent dependent reference process for the empirical determination of solvent polarity parameter  $E_T(30)$ . It is widely thought, though yet to be generally demonstrated, that under this definition, ionic liquids will be highly polar solvents. The longest wavelength absorption band of Reichardt's dye (2,4,6-triphenylpyridinium *N*-4-(2,6-diphenylphenoxide) betaine shows one of the largest solvatochromic shifts known (375 nm between diphenyl ether and water).

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**Figure 1.2:** Molecular structure and ground-state properties of the negatively solvatochromic standard betaine dye used for the determination of  $E_T(30)$  values: 2,6-diphenyl-4-(2,4,6-triphenylpyridinium-1-yl)phenolate.

It can register effects arising from the solvent dipolarity, hydrogen bonding, and Lewis acidity and is considered to be a good general polarity scale. The  $E_T^N$  values for alkylammonium nitrate, thiocyanate, and sulfonate salts have been recorded in the range of 0.95- 1.01 for monoalkylammonium nitrates and thiocyanates, which are close to that of water, whereas quaternary ammonium sulfonates, imidazolium, pyrrolidinium and pyridinium-based ionic liquids lies in the range give lower values of ca. 0.45-0.65, which are more typical of polar organic solvents such as DMSO. Ionic liquids are capable of exhibiting a large variety of solute-solvent interactions as opposed to the interactions found in conventional solvents, which are dominated by a limited number of factors. The net charges on the ions may lead to partial charge ordering and screening of dipole-dipole interactions require a fundamentally different environment of solvation as compared to molecular liquids. A number of studies have focused on the ‘preferential solvation’<sup>53</sup> in ionic liquids in addition to conventional polarity studies.<sup>54</sup> Sarkar *et. al.* have reported interesting “hyperpolarity” behavior in binary mixture of ionic liquid [BMIM][PF<sub>6</sub>] with tetraethylene glycol.<sup>55</sup> Ionic liquids are also capable of acting as polar solvents in organic reactions containing polar molecules and as relatively nonpolar solvents in the presence of less polar molecules.<sup>56</sup>

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Several recent publications have shown that the commonly used ionic liquids are reasonably polar solvents.<sup>57-59</sup> A comprehensive account of the polarity of ionic liquids has been recently presented by Reichardt.<sup>52</sup> The polarity data of ionic liquids have revealed many interesting characteristics in these novel media, which were not observed earlier or were too “weak” to be observed in conventional solvents. For example, ionic liquids show a strong tendency of preferential solvation for a probe molecule in their binary mixtures with water or organic cosolvents. Although preferential solvation was also observed in conventional binary mixtures, the effect was not as drastic as is seen in ionic liquid mixtures. The polarity studies on the binary mixture of tetraethylene glycol with the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate, [BMIM][PF<sub>6</sub>], showed interesting synergetic effects, which was termed as “hyperpolarity”.<sup>60</sup> It is believed that such phenomena arise due to the formation of highly ordered microsegregated phases in the binary mixtures of ionic liquids. Another interesting aspect is the substantial temperature dependence of polarity parameters or “thermosolvatochromism” observed in ionic liquids. The polarity of ionic liquids is known to be sensitive to the changes in temperature. The temperature effect on the solvatochromic shift in ionic liquids was much more pronounced along with the influence of substituting alkyl length on the cation on polarity parameters as reported by Lee *et al.*<sup>58</sup> Thermosolvatochromism of the probe molecule in solvents like cyclohexane, di-isopropyl ether and tetrahydrofuran was earlier reported by Suppan *et al.*<sup>61</sup>

There are reports available on thermo-solvatochromism phenomena for Reichardt's dye in aqueous alcohols and very recently El Seoud *et al.*<sup>62</sup> studied the thermosolvatochromism in aqueous [BMIM][BF<sub>4</sub>] and compared it with those of aqueous alcohols. However, in that particular system employed for the study, the small magnitude of the temperature effect on polarity made it difficult to obtain reliable results. On the basis of temperature dependence of polarity of [BMIM][PF<sub>6</sub>], Baker *et al.*<sup>63</sup> had concluded that the hydrogen bond donor strength of the imidazolium cation was strongly temperature dependent, while the hydrogen bond accepting ability was a weak function of temperature. Weingartner *et al.*<sup>64</sup> explained the polarity of ionic liquids with different cations by measuring a static dielectric



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constant using microwave dielectric spectroscopy. The polarities determined by microwave dielectric spectroscopy were lower than those obtained by using solvatochromic dyes. The effect of cations and anions of ionic liquids on the thermosolvatochromism in ionic liquids has not been studied in detail to date.

### 1.7. Applications of Ionic Liquids

Ionic liquids have been used in many applications as a solvent in organic synthesis, catalysis, separation technology, electrochemistry and now a day it has been used in space research. Two of these applications, pertaining to the use of ionic liquids as reaction media and electrolytes are discussed in detail here.

#### 1.7.1. Organic Reactions in Ionic liquids

Several organic reactions have been carried out in ionic liquids. One of the most commonly studied organic reactions in ionic liquids is the Diels-Alder reaction. The Diels-Alder reaction is a [4+2] cycloaddition reaction of crucial significance in chemistry, both in terms of its synthetic potential and its reaction mechanism. The rate and stereoselectivity of Diels-Alder reaction were assumed to be unaffected by the solvents, due to the isopolar transition state, until the studies by Berson *et. al.*<sup>65</sup>

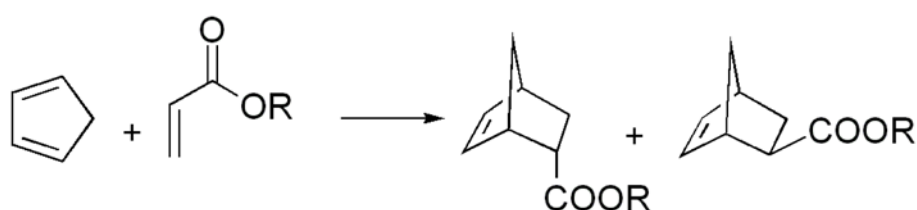
There are many reports related to use ionic liquids used as solvent media many organic reactions, including the Diels-Alder reactions.<sup>66</sup> Because of many advantages of ionic liquids discussed earlier, the ionic liquids are findings as highly effective reaction media in accelerating organic reactions, including Diels-Alder reactions.<sup>67,68</sup> Kumar and Pawar have reported about the selectivity in Diels-Alder reaction in ionic liquids.<sup>69</sup> It has been observed that Diels-Alder reactions show *endo* selective in chloroaluminate ionic liquids, which is opposite to conventional organic solvent showing *exo* selective. This reversal in the stereoselectivity seems to be controlled by the Lewis acid effect of  $\text{AlCl}_3$  as the increasing concentration of  $\text{AlCl}_3$  in the chloroaluminates leads to a decrease in *exo*-product and therefore an enhanced *endo*-product. The reaction is carried out in pyridinium based chloroaluminate ionic liquids 1-butyl pyridinium chloroaluminate [BP][ $\text{AlCl}_3$ ] and is confirmed by carrying out the

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same reaction in imidazolium based chloroaluminates ionic liquids 1-ethyl-3-methyl imidazolium chloroaluminate [EMIM][AlCl<sub>3</sub>]. Higher *endo:exo* ratios was found in [EMIM][AlCl<sub>3</sub>] of 11.5: 1 than [BP][AlCl<sub>3</sub>] of 6: 1 for same concentration of 60% AlCl<sub>3</sub>. The dimerization of cyclopentadiene in chloroaluminate based ionic liquids was studied by the same group, which found that the rate of dimerization of cyclopentadiene was higher in the [EMIM][AlCl<sub>3</sub>] than in the [BP][AlCl<sub>3</sub>]. Rate of acceleration of the dimerization process takes place with increase in concentration AlCl<sub>3</sub> in [BP][AlCl<sub>3</sub>] and [EMIM][AlCl<sub>3</sub>] and this effect is attributed by the Lewis acidity of AlCl<sub>3</sub>.<sup>70</sup> The rates of Baylis-Hillman reactions in chloroaluminate ionic liquids using DABCO as catalyst shown was shown to be higher as compared to the reaction carried out in conventional organic solvents.<sup>71</sup>

The *endo* selectivity of the isomer products of Diels alder reaction is enhanced in EAN as compared to in organic solvents.<sup>68</sup> Dialkylimidazolium salts were also employed as a Lewis acid catalyst for the Diels-Alder reaction.<sup>72</sup>

Recently, Tiwari and Kumar have reported that how ionic liquids lead to constraints on the reaction rates the Diels-Alder reaction of cyclopentadiene and acrylate.<sup>73</sup> It was observed that high viscosity of ionic liquids is a detrimental quantity towards the kinetic study of Diels Alder reaction Scheme 1.2. It has been observed that rate of the reaction in water is 10 times higher as compared to 1-butyl-3-methyl imidazolium iodide [BMIM][I] ionic liquids. (Scheme 1.2)

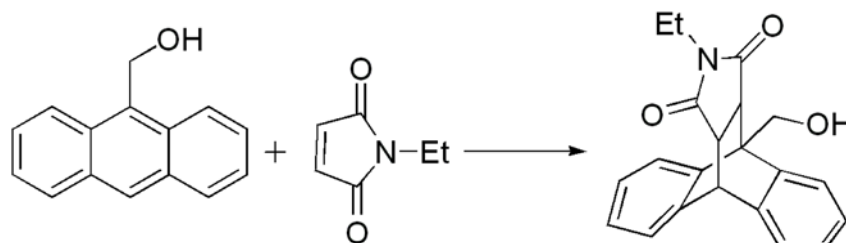


**Scheme 1.2**

The Diels-Alder reaction of Anthracene-9-carbinol and *N*-ethyl maleimide has been investigated in the different aqueous salt solution at different concentration (Scheme

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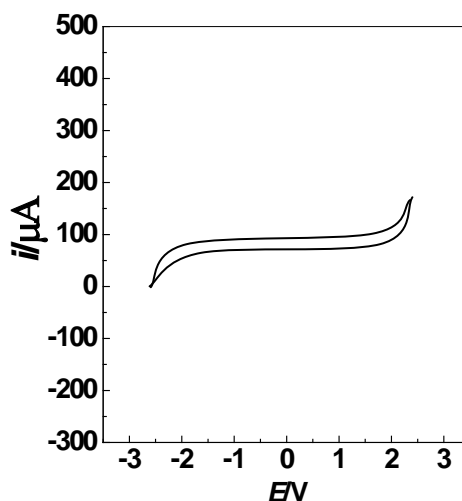
1.3) in order to know the salting-in and salting out behaviour of the salts for which the effect of different salts on rate of this reaction has been studied.<sup>74</sup>



**Scheme 1.3:**

### 1.7.2. Electrochemical Investigations in Ionic Liquids.

In order to realise the numerous applications of ionic liquids in electrochemistry, there is need to design ionic liquids which have desirable electrochemical properties like high electrochemical window. Recently air and water stable ionic liquids consisting of  $[\text{BF}_4]$ ,  $[\text{PF}_6]$  and  $[\text{NTf}_2]^-$  have shown some interesting properties related to their stability and are being used in many electrochemical devices like Li ion battery, actuator, fuel cell, dye sensitized solar cell, etc.<sup>75, 76</sup>



**Figure1.3.** Electrochemical window of  $[\text{BMIM}][\text{BF}_4]$  measured by cyclic voltammetry using W, Pt electrodes.

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However, the fundamental requirement for an ionic liquid to be useful in developing applications in electrochemistry is that it should be able to offer a wide electrochemical window. While aqueous systems possess about 1.23V as electrochemical window, propylene carbonate and acetonitrile can offer electrochemical window as high as 4V (Table 1.2). For the purpose of illustration, Table 1.2 contains values of electrochemical window and reference electrodes for some ionic liquids. From an examination of Table 1.2, it can be seen that many ionic liquids offer electrochemical window in the range of 4 to 5V, while the most common and popular ionic liquid, [BMIM][BF<sub>4</sub>] possesses electrochemical window as high as 6.1V shown in Figure 1.3. One notes that the selection of reference electrode is a very important criteria in enhancing electrochemical stability.

**Table 1.2: Electrochemical Window of Ionic Liquids**

<b>Ionic liquids</b>	<b>Electro-chemical window</b>	<b>Working electrode</b>	<b>Ref. electrode</b>
[BMIM][BF <sub>4</sub> ]	6.1	W	Pt
[BMIM][NTf <sub>2</sub> ]	4.6	Pt	Ag/Ag <sup>+</sup> in DMSO
[PMIM][PF <sub>6</sub> ]	4.3	GC	Li/Li <sup>+</sup>
[EMIM][NTf <sub>2</sub> ]	4.5	Pt	Ag/Ag <sup>+</sup> in DMSO
[PMPyrr][NTf <sub>2</sub> ]	5.3	Pt	Ag wire
[BP][BF <sub>4</sub> ]	3.4	Pt	Ag/AgCl-wire

The property may be important in electrochemical studies because it may exert a strong effect on the rate of mass transport within solution and on the conductivity of the salts. For any electrochemical process, the conductivity is a property of primary importance and the conductivity of the ionic liquids has been reviewed on several occasions.<sup>77, 78</sup> But the high viscosity of ionic liquids is considered as major drawback in electrochemistry, since it lowers the conductivity of ions. Since ionic liquids are composed of cation and anions and supposed to be among the most concentrated electrolytic fluids with many charge carriers, they are expected to have high conductivity. The ionic liquids exhibit conductivities in the broad range of 0.1-20 mS

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$\text{cm}^{-1}$ ,<sup>79, 80</sup> excepts ionic liquids based tricyanomethanide anion and the  $[\text{N}(\text{CN})_2]$  anion has highest conductivities of  $36 \text{ m S cm}^{-1}$  which is lower than the conventional electrolyte.<sup>81</sup> Tetraalkyl ammonium based ionic liquids exhibits lower conductivity  $2 \text{ mS cm}^{-1}$  as compared to pyrrolidinium based ionic liquids which show high conductivity.<sup>82</sup> In addition to the cation effect, the high viscosity of the ionic liquids has a major impact on the conductivities because the conductivity is inversely linked to the viscosity.<sup>83</sup> The correlation between viscosity and conductivity is generally observed. The viscosity is not a factor to correlate the conductivity behavior due to aggregation and correlated ionic motions of the ions. The degree of “ionicity” in ionic liquids found to be in the range of 0.3 -0.8 for all the ionic liquids. The ionic conductivity of  $[\text{NTf}_2]$  based ionic liquids are lower than the corresponding  $[\text{BF}_4]$  based ionic liquids.<sup>84</sup> This contrary to viscosity conductivity relation since  $[\text{NTf}_2]$  based ionic liquids exhibits lower viscosity. It has been also reported that strong ion pair association leads to lowering of the viscosity.<sup>84</sup>

The Ionic liquids generally exhibit a wide potential window of 4.5-7V towards particular electrode, which is a highly desirable property for applying the Ionic liquids as electrochemical solvents.<sup>85</sup> The electrochemical window of an electrolyte depends on the purity of the electrolyte. The diffusion process is an important process in electrochemistry. The diffusion of electroactive species through ionic liquids is slow as compared to common solvents due to high viscosity of ionic liquids. There are different methods available in the electrochemistry like chronoamperometry, cyclic voltammetry, square wave voltammetry, impedance spectroscopy and polarization measurements to determine diffusion coefficients of electroactive species in ionic liquids.<sup>86</sup> The diffusion coefficients of triiodide in a mixture of two imidazolium based ionic liquids are studied recently.<sup>87</sup> Ionic liquids having large electrochemical window (6V) show wide applications in electrochemical process. In early 1940s Hurley and Wier used ionic liquids for electrochemical study.<sup>88</sup> Recently, the studies have been focused on reactivity of electrogenerated organic species.<sup>89</sup> Compton *et. al.*<sup>90</sup> has done comparative studies on electrochemical diffusion in ionic liquids and organic solvents. The diffusion of given species is found to be 1000 times greater in organic solvent as compared to ionic liquids, due to the higher viscosity of ionic

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liquids. According to Stokes-Einstein law shown below, the viscosity and diffusion coefficient in a given liquid are inversely related (Eq. 1.7).

$$D_o = \frac{kT}{6\pi\eta R} \quad (1.7)$$

where  $k$  is the Boltzmann constant,  $T$  is the temperature,  $R$  is the hydrodynamic radius,  $\eta$  is the viscosity. Recently, Compton *et. al.*<sup>91</sup> investigated the  $D_o - \eta^{-1}$  relationship for different ionic liquids and found very interesting information that reduction of oxygen in ionic liquids showed approximate behavior. There are few reports suggesting that this relationship does not hold good universally.

The mechanism of many electron transfer reactions in ionic liquids using cyclic voltammetry study is reported. The reaction between *N,N*-dimethyl-*p*-toluidine (DMT) and the radical cation generated through its one-electron oxidation has been studied electrochemically in the ionic liquids 1-butyl 3-methyl pyrrolidinium bis(trifluoromethyl sulfon)imide, [BMPyrr][NTf<sub>2</sub>]. At higher scan rates the homogeneous reactions following the initial electron transfer were effectively out-run and the mechanism established for the same reaction in acetonitrile, involving dimerization of the DMT radicals following an initial and rate-determining proton transfer step.

## 1.8 Conclusions

In the view of above development, it is proposed to delineate interactions in ionic liquids as exhibited by viscosity, thermosolvatochromism and electrochemical studies. It will be interesting to understand how the kinetics of simple organic reactions are influenced by some of these properties of ionic liquids.

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**Chapter 2**  
**Aims and Objectives**

## 2. Aims and Objectives

### 2. Aims and Objectives

Room Temperature Ionic liquids (RTILs) represent a new class of liquid solvents having some characteristics of molten salts have attracted considerable interest during the last few years. Their melting points are distinctly below room temperature and also air and water stable. Because of interesting physical properties of RTILs, increases their applications in many fields like electrochemistry, organic reactions, catalysis, extraction, etc. In order to use these RTILs for variety of applications, there is need of studying their physicochemical properties and their correlation with structure.

The physical-organic studies for reactions in ionic liquids were comparatively lesser in number. An increasing number of successful applications are described in the literature. The utilization of RTILs in industrial chemistry requires a systematic study of their physicochemical properties which are required for chemical process design. Room Temperature Ionic Liquids are one of environment solvent media. Interesting properties of Physical–organic studies of the organic reactions in aqueous media had been extensively carried out to varying degrees of qualitative and quantitative details. Reactions in aqueous media thus studied were greatly influenced by the properties of the reaction medium. The numerous types of interactions possible between the solvent and solute molecules in an aqueous system had proved to be promising opportunities disguised by the challenge of our limited understanding. The following were some salient features that merited further investigation:

- To select a class of ionic liquids and binary solvent systems after a thorough literature survey.
- To investigate the variation in polarity of ionic liquids and their binary mixtures with composition and temperature.
- To study the transport properties of ionic liquids and their binary mixtures in terms of viscosity in a range of temperatures and solvent composition.

## 2. Aims and Objectives

- To study the electrochemical oxidation of anthracene as a model electrochemical process in the selected ionic liquid systems.
- To determine the variation in the rates of a bimolecular organic reaction in the ionic liquid mixture in terms of the rate constants and activation parameters.
- To explore the possible correlation between the results of the electrochemical / kinetic studies and the physicochemical properties of the ionic liquid systems.



## **Chapter 3**

# **Polarity of Ionic Liquids: Thermosolvatochromism and Preferential Solvation**



### **3. Polarity of Ionic Liquids: Thermosolvatochromism and Preferential Solvation**

The effect of structure, temperature and composition on the polarity of ionic liquids has been investigated in the present chapter. In Section 3.1, the thermal effect on solvatochromism of probe molecules in pyridinium, pyrrolidinium and phosphonium-based ionic liquids has been studied in detail as a function of the structure of the cation and anion. Based on the observations, it has been possible to formulate general guidelines about the effect of structural variations on the thermal response of polarity. The variation in polarity parameters with respect to the composition in binary mixtures of ionic liquids, have been investigated in Section 3.2. An in-depth analysis by preferential solvation of such binary systems has been instrumental in elucidating the complex behaviour of ionic liquid – cosolvent systems.

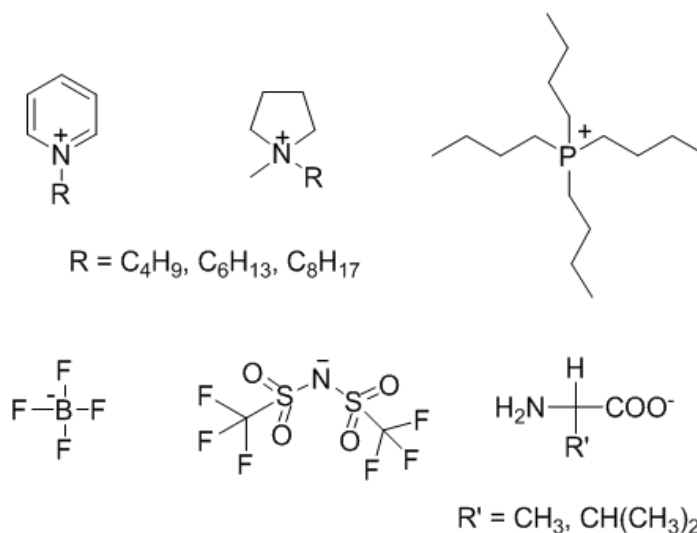
#### **3.1 Thermosolvatochromism in Ionic liquids**

##### **3.1.1 Introduction**

The polarity of ionic liquids can play a crucial role in optimizing the reaction conditions for organic transformations in addition to other vital applications.<sup>1</sup> For example, the high polarity of a Brønsted acidic pyrrolidinium ionic liquid was considered to be an important factor for the oxidative desulphurization of diesel fuel in the presence of H<sub>2</sub>O<sub>2</sub>.<sup>2</sup> The polarity of several ionic liquids has been studied in terms of  $E_T(30)$ <sup>3</sup> (electronic transition energy in kcal mol<sup>-1</sup>) and the Kamlet-Taft polarity parameters.<sup>4</sup> Several recent publications have shown that the commonly used ionic liquids are reasonably polar solvents, having polarity greater than those of solvents like acetone, dimethyl sulfoxide, etc. but less than those of water and short-chain alcohols.<sup>5, 6, 7</sup> A comprehensive account of the polarity of ionic liquids has been recently presented by Reichardt.<sup>3</sup>

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Another interesting aspect is the substantial temperature dependence of polarity parameters or ‘thermosolvatochromism’ observed in ionic liquids. The polarity of ionic liquids is known to be sensitive to the changes in temperature.<sup>6</sup> Thermosolvatochromism of probe molecule in solvents like cyclohexane, di-isopropyl ether and tetrahydrofuran was earlier reported by Suppan *et. al.*<sup>8</sup> Again, the magnitude of change in polarity with temperature was not very prominent. Few attempts have been made to measure thermosolvatochromism in ionic liquids. There are reports available on thermosolvatochromism phenomenon for Reichardt's dye in aqueous alcohols and very recently El Seoud *et. al.*<sup>9</sup> studied the thermosolvatochromism in aqueous [BMIM][BF<sub>4</sub>] and compared it with aqueous alcohols. However, the small magnitude of the temperature effect on polarity made it difficult to obtain reliable results. The temperature effect on the solvatochromic shift in ionic liquids was much more pronounced and the influence of substituting alkyl length on the cation on polarity parameters as reported by Prausnitz.<sup>6</sup>



**Figure 3.1:** Structures of the ionic liquids used for thermosolvatochromic studies

Based on temperature dependence of polarity of [BMIM][PF<sub>6</sub>], Baker *et al.* had concluded that the hydrogen bond donor strength of the imidazolium cation was strongly

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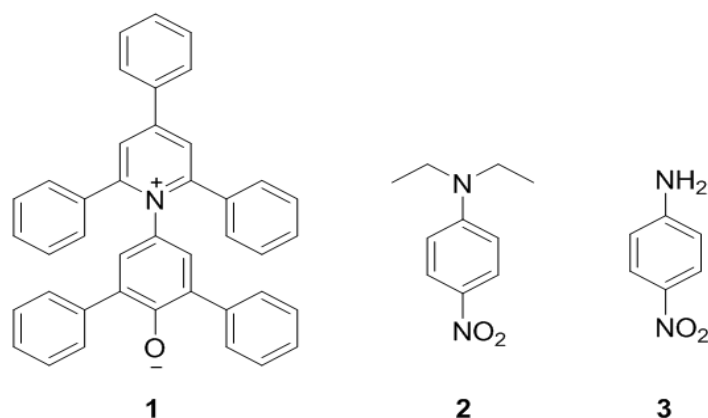
temperature dependent, while the hydrogen bond accepting ability was weak function of temperature.<sup>10</sup> Weingartner explained the polarity of ionic liquids with different cations by measuring static dielectric constant using microwave dielectric spectroscopy.<sup>11</sup> The polarities determined by microwave dielectric spectroscopy were lower than those obtained by using solvatochromic dyes.

These interesting observations merit more systematic studies of the temperature and composition dependence of polarity in ionic liquids and their binary mixtures. For example, the effect of cations and anions of ionic liquids on the thermosolvatochromism in ionic liquids has not been studied till date. In the present chapter, three cationic species of ionic liquids – pyridinium, pyrrolidinium and tetrabutylphosphonium – were selected as the representative cases. (Figure 3.1) In order to investigate anionic effect on polarity of these ionic liquids, anions like bis(trifluoromethylsulfonyl)imide  $[\text{NTf}_2]^-$ , tetrafluoroborate  $[\text{BF}_4]^-$  and [amino acid] $^-$ -based species were chosen. The complete list of ionic liquids and their abbreviations is seen in Table 3.1.

**Table 3.1: Abbreviated Forms of the Ionic Liquids Employed for the Thermosolvatochromic Studies**

Abbreviations	Names of Ionic Liquids
[BP][BF <sub>4</sub> ]	1-butylpyridinium tetrafluoroborate
[OP][BF <sub>4</sub> ]	1-octylpyridinium tetrafluoroborate
[BP][NTf <sub>2</sub> ]	1-butylpyridinium bis (trifluoromethylsulfonyl) imide
[HP][NTf <sub>2</sub> ]	1-hexylpyridinium bis (trifluoromethylsulfonyl) imide
[OP][NTf <sub>2</sub> ]	1-octylpyridinium bis (trifluoromethylsulfonyl) imide
[BMPyrr][NTf <sub>2</sub> ]	1-butyl-1-methylpyrrolidinium bis (trifluoromethylsulfonyl) imide
[HMPyrr][NTf <sub>2</sub> ]	1-hexyl-1-methylpyrrolidinium bis (trifluoromethylsulfonyl) imide
[OMPyrr][NTf <sub>2</sub> ]	1-octyl-1-methylpyrrolidinium bis (trifluoromethylsulfonyl) imide

[TBP] [Ala]	Tetrabutylphosphonium alanate
[TBP][Val]	Tetrabutylphosphonium valinate



**Figure 3.2:** Reichardt's dye (**1**), *N,N*-diethyl-4-nitroaniline (**2**) and 4-nitroaniline (**3**) used as probe molecules for polarity determination

The hydrogen bond donating property ( $\alpha$ ), hydrogen bond accepting property ( $\beta$ ), polarizability ( $\pi^*$ ) and the electronic transition energy parameter ( $E_T^N$ ) were determined for different combinations of cations and anions using three indicator dyes – Reichardt's dye (**1**), *N,N*-diethyl-4-nitroaniline (**2**) and 4-nitroaniline (**3**) (Figure 3.2).

### 3.1.2 Experimental Section

**Materials:** The spectroscopic indicator dyes **1** and **3** were used as obtained from M/s. Sigma Aldrich. The dye **2** was purchased from Frinton Laboratories (99% purity). *N*-methyl pyrrolidine, pyridine and 1-bromobutane were distilled prior to their use. 99% pure 1-bromooctane, 1-bromohexane, 40% aqueous tetrabutylphosphonium hydroxide, alanine, valine and bis(trifluoromethylsulfonamide)lithium  $\text{Li}(\text{NTf}_2)$  salt were used as purchased.

### 3. Thermosolvatochromism and Preferential Solvation

**Synthesis of ionic liquids:** The ionic liquids are synthesized according to the previously reported literature procedure.<sup>12</sup> The synthesis of ionic liquids was carried out in two steps, (1) formation of cation by quaternization reaction and (2) a metathesis, anion exchange reaction. The characterization and their purity were determined by NMR.<sup>12</sup> The water content of the pure and dried ionic liquids as measured by Karl Fischer coulometer analysis did not exceed 50 ppm.

**Polarity measurement:** The stock solution of the required dye was freshly prepared in dichloromethane prior to use. The stock solution was added dropwise to the ionic liquid and the solvent was evaporated under vacuum. The ionic liquid was then transferred to the cuvette under nitrogen atmosphere and sealed with a septum. The  $\lambda_{max}$  was measured at different temperatures using UV-visible spectrophotometer.<sup>6</sup> All the polarity values were within a reproducibility limit of  $\pm 0.4\%$ . The temperature of the cell was controlled using the single cell accessory having an accuracy of  $\pm 0.1$  K.

**Solvatochromic probe analysis:** The polarizability  $\pi^*$  parameter is determined from the spectroscopic shift of *N, N*-diethyl-4-nitroaniline (probe 2, Figure 3.2) using Eq. 3.1

$$\nu(\mathbf{2})_{\max} = 27.52 - 3.182\pi^* \quad (3.1)$$

The hydrogen bond acceptor ability  $\beta$  parameter is determined using the spectroscopic shift of 4-nitroaniline (probe 3) with respect to *N, N*-diethyl-4-nitroaniline and Eq. 3.2

$$\nu(\mathbf{3})_{\max} = 1.035\nu(\mathbf{2})_{\max} - 2.8\beta + 2.64 \quad (3.2)$$

The electronic transition energy  $E_T(30)$  parameter is obtained from the spectroscopic shift of Reichardt's dye 30 (probe 3) and is simply the electron transition energy of the dissolved dye, as defined by Eq 3.3.

$$E_T(30) = hc\nu_{\max}N_A = 2.8591\nu(\mathbf{1})_{\max} \quad (3.3)$$

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The dimensionless normalized  $E_T^N$  scale was introduced, using water ( $E_T^N = 1.00$ ) and tetra methyl silane TMS ( $E_T^N = 0.00$ ) as reference solvents to fix the scale, in accordance with Eq. 3.4.

$$\begin{aligned} E_T^N &= [E_T(\text{solvent}) - E_T(\text{TMS})]/[E_T(\text{water}) - E_T(\text{TMS})] \\ &= [E_T(\text{solvent}) - 30.7]/32.4 \end{aligned} \quad (3.4)$$

The  $\alpha$  parameter can then be calculated using  $E_T(30)$  with respect to  $\pi^*$  by

$$\alpha = 0.0649 E_T(30) - 2.03 - 0.72\pi^* \quad (3.5)$$

#### 3.1.3 Results and Discussions

The polarity parameters  $E_T(30)$ ,  $\alpha$ ,  $\beta$ ,  $\pi^*$  values for pyridinium, pyrrolidinium and phosphonium ionic liquids were initially determined at 298 K for comparison with literature.<sup>6</sup> The phosphonium-based ionic liquids had higher melting points (> 293 K) and hence their polarity parameters could not be determined at 298 K. The lowest temperature of measurement for the phosphonium-based ionic liquids was 303 K due to their melting point. In order to ascertain the accuracy of our measurements, the polarity parameters were first determined for organic solvents reported in the literature for the purpose of comparison (Table 3.2).<sup>13</sup> Further, the values for pyridinium, pyrrolidinium and phosphonium ionic liquids from this work are in good agreement with the values reported in the literature.<sup>6, 3</sup> Among the different classes studied, the phosphonium-based ionic liquids show highest polarity, in general, while the pyridinium ionic liquids show the least.

**Table 3.2: Polarity Parameters of Ionic Liquids and Organic Solvents at 298 K. The Values in Parentheses Indicate Reported Values.**

Solvents / Ionic liquids	Polarity Parameters			
	$E_T^N$	$\alpha$	$\beta$	$\pi^*$
[BP][BF <sub>4</sub> ] <sup>[a]</sup>	0.656 (0.639)	0.532	0.213	1.081



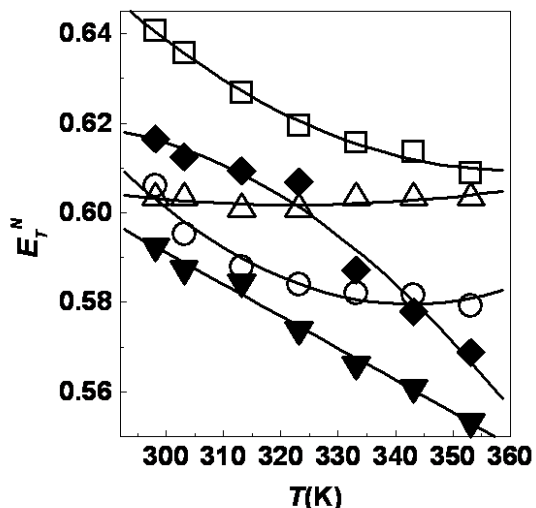
### 3. Thermosolvatochromism and Preferential Solvation

[OP][BF <sub>4</sub> ]	0.606	0.535	0.340	0.974
[BP][NTf <sub>2</sub> ] <sup>[a]</sup>	0.603 (0.648)	0.643	0.123	0.816
[HP][NTf <sub>2</sub> ]	0.593	0.500	0.065	0.984
[OP][NTf <sub>2</sub> ] <sup>[b]</sup>	0.617 (0.588)	0.564	0.115	0.965
[BMPyrr][NTf <sub>2</sub> ]	0.672	0.734	-0.108	0.890
[HMPyrr][NTf <sub>2</sub> ]	0.657	0.759	0.058	0.811
[OMPyrr][NTf <sub>2</sub> ]	0.651	0.801	0.084	0.733
[TBP] [Ala] <sup>[c]</sup>	0.773	0.879	1.035	0.984
[TBP][Val] <sup>[c]</sup>	0.790	0.956	1.459	0.927
Methanol <sup>[d]</sup>	0.769 (0.762)	1.055 (1.05)	0.600 (0.610)	0.733 (0.730)
Tetrahydrofuran <sup>[d]</sup>	0.222 (0.206)	-0.005 (0.0)	0.595 (0.54)	0.607 (0.60)

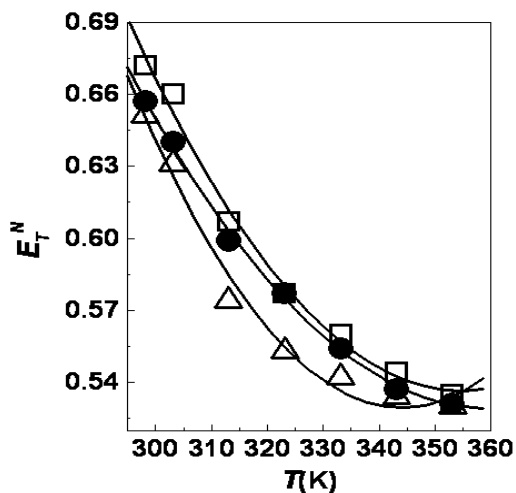
[a] Ref [3] [b] Ref. [6] [c] at 303 K, [d] Ref. [12]; values within reproducibly of  $\pm 0.4\%$

As observed from Table 3.2, an increase in the chain length of the alkyl substituent on the cation influences the values of the polarity parameters, although not always in a predictable manner. For example, on increasing the chain length from butyl to hexyl to octyl in the pyrrolidinium-based ionic liquids, the  $E_T^N$  values decrease from 0.672 to 0.651. For the pyridinium-based ionic liquids, however, the  $E_T^N$  value decreases from 0.603 for the butyl-substituted ionic liquid to 0.593 for the hexyl substitution but again increases to 0.617 when an octyl substituent is present. Thus, in case of pyrrolidinium ionic liquids the polarity follows the trends as [BMPy][NTf<sub>2</sub>] > [HMPy][NTf<sub>2</sub>] > [OMPy][NTf<sub>2</sub>], which is in agreement with the literature. However, in the case of the pyridinium ionic liquids the observed trend is [OP][NTf<sub>2</sub>] > [BP][NTf<sub>2</sub>] > [HP][NTf<sub>2</sub>]. The temperature-dependence of the polarity parameters or thermosolvatochromism for all the ionic liquids was then studied from 298 to 353 K (303 to 353 K for phosphonium ionic liquids). Depending on the cationic and anionic species, the polarity values showed either a direct or an inverse relation with the change in temperature.

3.1.3.1.  $E_T^N$  Electronic transition energy



**Figure 3.3:** Temperature dependent  $E_T^N$  parameters for the pyridinium-based ionic liquids [BP][BF<sub>4</sub>](□), [OP][BF<sub>4</sub>](○), [BP][NTf<sub>2</sub>](△), [HP][NTf<sub>2</sub>](▼) and [OP][NTf<sub>2</sub>](◆)

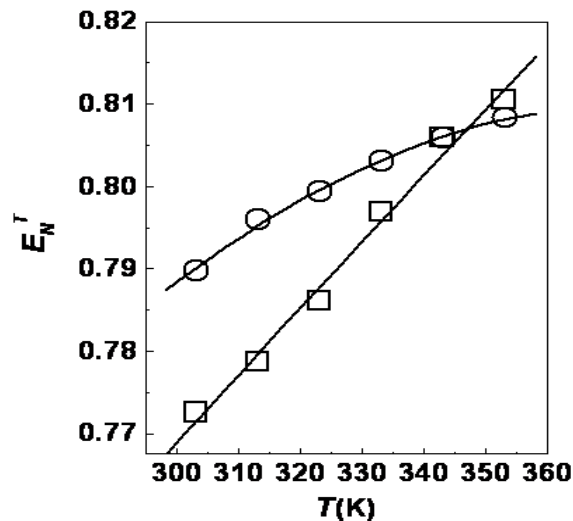


**Figure 3.4:** The  $E_T^N$ - $T$  plots for the pyrrolidinium-based ionic liquids [BMPyrr][NTf<sub>2</sub>](□), [HMPyrr][NTf<sub>2</sub>](●) and [OMPyrr][NTf<sub>2</sub>](△).

The  $E_T^N$  value decreases with temperature for the pyridinium-based (Figure 3.3) and pyrrolidinium-based ionic liquids (Figure 3.4), but increases with temperature for the phosphonium ionic liquids (Figure 3.5). This indicates that the choice of the cation can

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determine the response of the polarity to a change in temperature. In the case of [BP][NTf<sub>2</sub>] the  $E_T^N$  value remains almost constant with increasing temperature



**Figure 3.5:** Temperature dependent  $E_T^N$  parameters for the phosphonium-based ionic liquids [TBP][Ala] (□) and [TBP][Val] (○).

The values for [BP][BF<sub>4</sub>] show a small decrease from 0.656 to 0.624 with temperature (Figure 3.3), thus demonstrating the considerable sensitivity of the temperature – dependent properties of polarity to the anionic species of ionic liquids. The  $E_T^N$  values for [BP][NTf<sub>2</sub>] is insensitive to temperature. The  $E_T^N$  values decrease from 0.593 to 0.553 for [HP][NTf<sub>2</sub>] and from 0.617 to 0.569 for [OP][NTf<sub>2</sub>] in the temperature range of 298 to 353 K. This indicates that the substitution with a longer alkyl chain on the cation leads to a greater effect of temperature on the variation in  $E_T^N$

**Table 3.3:**  $E_T^N$  Electronic Transition Energy for Pyridinium Based Ionic Liquids

Temperature T/K	[BP][BF <sub>4</sub> ]	[OP][BF <sub>4</sub> ]	[BP][NTf <sub>2</sub> ]	[HP][NTf <sub>2</sub> ]	[OP][NTf <sub>2</sub> ]
298.15	0.656	0.606	0.603	0.593	0.617

### 3. Thermosolvatochromism and Preferential Solvation

303.15	0.651	0.595	0.603	0.587	0.612
313.15	0.641	0.588	0.601	0.584	0.609
323.15	0.635	0.584	0.601	0.574	0.607
333.15	0.631	0.582	0.603	0.566	0.587
343.15	0.629	0.582	0.603	0.561	0.578
353.15	0.624	0.579	0.603	0.553	0.569

**Table 3.4:  $E_T^N$  Electronic Transition Energy for Pyrrolidinium Based Ionic Liquids**

Temperature <i>T/K</i>	[BMPyrr][NTf <sub>2</sub> ]	[HMPyrr][NTf <sub>2</sub> ]	[OMPyrr][NTf <sub>2</sub> ]
298.15	0.672	0.657	0.651
303.15	0.660	0.640	0.631
313.15	0.607	0.599	0.574
323.15	0.577	0.577	0.553
333.15	0.560	0.554	0.542
343.15	0.544	0.537	0.534
353.15	0.535	0.531	0.530

In the case of pyrrolidinium ionic liquids, the effect of temperature is larger as compared to the pyridinium ionic liquids. [BMPyrr][NTf<sub>2</sub>] shows a decrease in  $E_T^N$  from 0.672 to 0.535 on increasing the temperature from 298 to 353 K. The effect of increasing the alkyl chain length of the cationic substituents is reflected by the greater variation of  $E_T^N$  with the temperature. The  $E_T^N$  value for [HMPyrr][NTf<sub>2</sub>] changes from 0.657 to 0.531

### 3. Thermosolvatochromism and Preferential Solvation

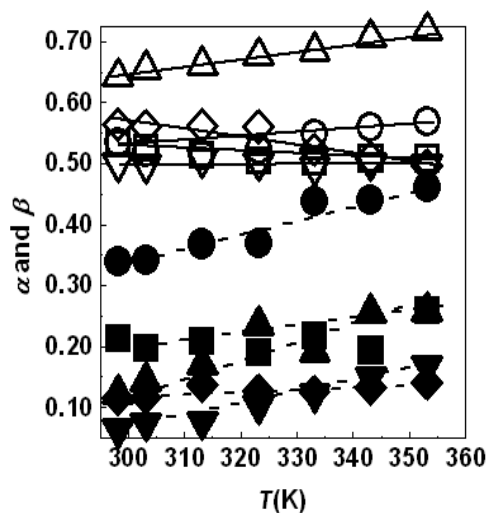
while the  $E_T^N$  value for [OMPyrr][NTf<sub>2</sub>] vary from 0.651 to 0.530 upon an increase in temperature from 298 to 353 K (Figure 3.4).

**Table 3.5:  $E_T^N$  Electronic Transition Energy for the Phosphonium Based Ionic Liquids**

Temperature T/K	[TBP][Ala]	[TBP][Val]
303.15	0.773	0.790
313.15	0.779	0.796
323.15	0.786	0.799
333.15	0.797	0.803
343.15	0.806	0.806
353.15	0.810	0.808

Interestingly, the polarity of phosphonium ionic liquids is noted to increase with an increase in temperature. This behavior is in contrast to that observed for the pyridinium and pyrrolidinium-based ionic liquids. The  $E_T^N$  values for [TBP][Ala] and [TBP][Val] increase from 0.772 to 0.810 and 0.789 to 0.808, respectively in the temperature range of 303 to 353 K (Figure 3.5). This enhancement of  $E_T^N$  values of [TBP][Ala] and [TBP][Val] with increase in temperature seems to be an example of solvent stabilization of the ground and excited states. Such complex behavior was also noted by Reichardt. Normally the temperature increase leads to a decrease in the polarity. The increase in the polarity may be due to electrolytic properties growth via the dissociation of [TBP][Ala] and [TBP][Val] ionic liquids. This situation can be useful for explaining the complicated temperature effect on the rate and equilibrium constants in ionic liquids, and on values of activation and reaction parameters.<sup>13, 14</sup>

#### 3.1.3.2. $\alpha$ Hydrogen bond donor ability (HBD): acidity



**Figure 3.6:** The temperature dependence of  $\alpha$  (solid line with hollow symbol) parameter: [BP][BF<sub>4</sub>] (□), [OP][BF<sub>4</sub>] (○), [BP][NTf<sub>2</sub>] (△), [HP][BF<sub>4</sub>] (▽), [OP][NTf<sub>2</sub>] (◇) and  $\beta$  (dash with solid symbol) parameters: [BP][BF<sub>4</sub>] (■), [OP][BF<sub>4</sub>] (●), [BP][NTf<sub>2</sub>] (▲), [HP][NTf<sub>2</sub>] (▼), [OP][NTf<sub>2</sub>] (◆) for pyridinium-based ionic liquids.

The variations in the  $\alpha$  parameter are more difficult to generalize. For the pyridinium-based ionic liquids, the hydrogen bond donating capacity as expressed by  $\alpha$  of [BP][BF<sub>4</sub>] shows a small decrease with an increase in temperature, while that for [OP][BF<sub>4</sub>] increases slightly from 298 to 353 K. The behavior of the [NTf<sub>2</sub>]-based pyridinium ionic liquid is more interesting. The value of  $\alpha$  for [BP][NTf<sub>2</sub>] increases from 0.643 to 0.718 but remains constant around 0.499 for [HP][NTf<sub>2</sub>]. A decrease in the  $\alpha$  values from 0.564 to 0.496 is seen for [OP][NTf<sub>2</sub>] in the temperature range of 298 to 353 K (Figure 3.6). Thus, increasing the length of the alkyl substituent can change the thermosolvatochromic response of the  $\alpha$  parameter from positive to negative, in the substituted pyridinium bis (trifluoromethylsulfonyl) imide class of ionic liquids.

**Table 3.6: Hydrogen Bond Donor ( $\alpha$ ) for Pyridinium Based Ionic Liquids**

Temperature T/K	[BP][BF <sub>4</sub> ]	[OP][BF <sub>4</sub> ]	[BP][NTf <sub>2</sub> ]	[HP][NTf <sub>2</sub> ]	[OP][NTf <sub>2</sub> ]
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### 3. Thermosolvatochromism and Preferential Solvation

298.15	0.532	0.535	0.643	0.500	0.564
303.15	0.525	0.519	0.655	0.498	0.560
313.15	0.513	0.514	0.663	0.507	0.563
323.15	0.504	0.523	0.677	0.502	0.560
333.15	0.502	0.548	0.685	0.494	0.523
343.15	0.508	0.559	0.707	0.502	0.510
353.15	0.508	0.569	0.718	0.499	0.496

**Table 3.7: Hydrogen Bond Acceptor ( $\beta$ ) for Pyridinium Based Ionic Liquids**

Temperature <i>T/K</i>	[BP][BF <sub>4</sub> ]	[OP][BF <sub>4</sub> ]	[BP][NTf <sub>2</sub> ]	[HP][NTf <sub>2</sub> ]	[OP][NTf <sub>2</sub> ]
298.15	0.213	0.340	0.123	0.065	0.115
303.15	0.197	0.341	0.143	0.075	0.117
313.15	0.208	0.368	0.170	0.077	0.137
323.15	0.190	0.370	0.235	0.104	0.127
333.15	0.218	0.438	0.191	0.122	0.126
343.15	0.194	0.440	0.256	0.149	0.132
353.15	0.259	0.462	0.259	0.169	0.141

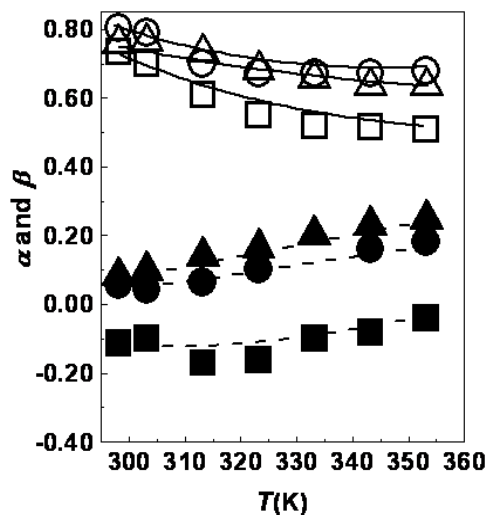
The  $\alpha$  value decreases with an increase in temperature for the pyrrolidinium-based ionic liquids (Figure 3.7). The variation in the sensitivity of the  $\alpha$  values towards changes in temperature follows the order [BMPyrr][NTf<sub>2</sub>] > [HMPyrr][NTf<sub>2</sub>]  $\approx$  [OMPyrr][NTf<sub>2</sub>]. The variations in the  $\alpha$  parameter with temperature for the phosphonium ionic liquids are again opposite in sign to that observed for the previous two classes of ionic liquids studied (Figure 3.8). For example, the  $\alpha$  value for [TBP][Ala] increases from 0.879 at 303 K to 1.060 at 353 K. The hydrogen bond acceptor property  $\beta$  is observed to increase nonlinearly with an increase in the temperature for the pyridinium ionic liquids (Figure 3.6). For the ionic liquids with the tetrafluoroborate anion, increasing the alkyl chain substituent from butyl to octyl increases the thermosolvatochromic response. On the other hand, the sensitivity of the  $\beta$  parameter with temperature in the bis

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(trifluoromethylsulfonyl) imide ionic liquids follows the trend:  $[\text{BP}][\text{NTf}_2] \geq [\text{HP}][\text{NTf}_2] > [\text{OP}][\text{NTf}_2]$ .

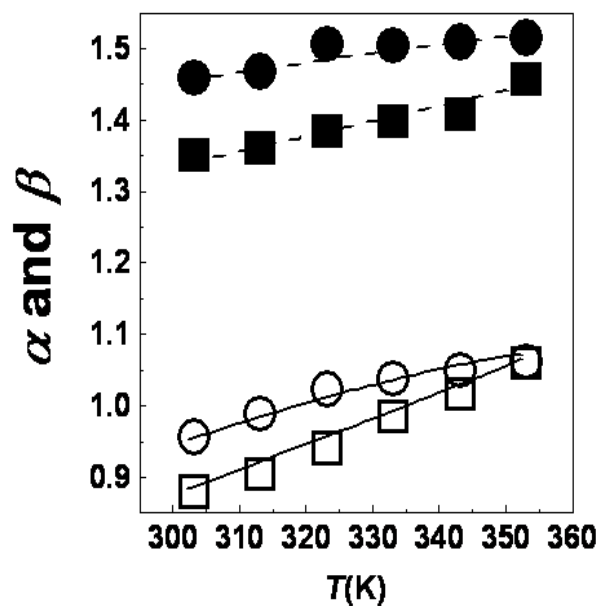
**Table 3.8: Hydrogen Bond Donor ( $\alpha$ ) for Pyrrolidinium Based Ionic Liquids**

Temperature <i>T</i> /K	[BMPyrr][NTf <sub>2</sub> ]	[HMPyrr][NTf <sub>2</sub> ]	[OMPyrr][NTf <sub>2</sub> ]
298.15	0.734	0.759	0.804
303.15	0.700	0.765	0.791
313.15	0.610	0.734	0.700
323.15	0.550	0.683	0.671
333.15	0.520	0.660	0.672
343.15	0.516	0.637	0.671
353.15	0.510	0.637	0.678



**Figure 3.7:** Temperature dependent  $\alpha$  (solid line with hollow symbol) parameter: [BMPyrr][NTf<sub>2</sub>](□), [HMPyrr][NTf<sub>2</sub>](○), [OMPyrr][NTf<sub>2</sub>](△) and  $\beta$  (dashed line with solid symbol) parameters: [BMPyrr][NTf<sub>2</sub>](■), [HMPyrr][NTf<sub>2</sub>](●), [OMPyrr][NTf<sub>2</sub>](▲) for Pyrrolidinium-based ionic liquids.





**Figure 3.8:** Temperature dependent  $\alpha$  (solid line with hollow symbol) parameter: [TBP][Ala] (□), [TBP][Val] (○) and  $\beta$  (dash with solid symbol) parameters: [TBP][Ala](■), [TBP][Val](●), for phosphonium-based ionic liquids

### 3.1.3.3. $\beta$ Hydrogen bond acceptor ability (HBA): basicity

**Table 3.9:** Hydrogen Bond Acceptor ( $\beta$ ) for Pyrrolidinium Based Ionic Liquids

Temperature $T/K$	[BMPyrr][NTf <sub>2</sub> ]	[HMPyrr][NTf <sub>2</sub> ]	[OMPyrr][NTf <sub>2</sub> ]
298.15	-0.108	0.058	0.084
303.15	-0.100	0.045	0.099
313.15	-0.170	0.065	0.141
323.15	-0.160	0.102	0.165
333.15	-0.100	-	0.203
343.15	-0.080	0.162	0.231

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353.15	-0.040	0.181	0.249
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**Table 3.10: Hydrogen Bond Donor ( $\alpha$ ) for Phosphonium Based Ionic Liquids**

Temperature <i>T/K</i>	[TBP][Ala]	[TBP][Val]
303.15	0.879	0.956
313.15	0.903	0.988
323.15	0.940	1.023
333.15	0.984	1.037
343.15	1.016	1.049
353.15	1.060	1.061

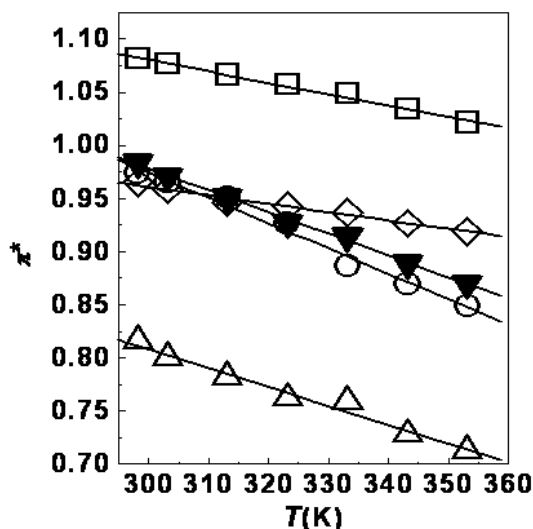
The trend in the thermosolvatochromism for the pyrrolidinium-based ionic liquids (Figure 3.7) is similar to that for the phosphonium-based ionic liquids (Figure 3.8) showing an increase in the  $\beta$  values with an increase in the temperature.

**Table 3.11: Hydrogen Bond Acceptor ( $\beta$ ) for Phosphonium Based Ionic liquids.**

Temperature <i>T/K</i>	[TBP][Ala]	[TBP][Val]
303.15	1.035	1.459
313.15	1.360	1.468
323.15	1.384	1.506
333.15	1.398	1.505
343.15	1.409	1.509
353.15	1.457	1.515

### 3.1.3.4. $\pi^*$ Polarizability

The polarizability parameter  $\pi^*$  is based on  $\pi$ - $\pi^*$  spectral electronic transition of *N,N*-diethyl-4-nitroaniline, which indicates the magnitude of the interaction of the chromophore with its cybotactic environment. At 303 K, the  $\pi^*$  value for all three classes of ionic liquids are similar. These values are much larger in magnitude than those for short chain alcohols, but lower than those for DMSO and water. This is in agreement with the previously reported results.<sup>17,21</sup> The  $\pi^*$  values decrease almost linearly with an increase in temperature from 298 to 353 K as seen in the effect of alkyl chain length of the cation is negligible for pyridinium-based ionic liquids (Figure 3.9). This is consistent with the earlier report.<sup>16, 17</sup>



**Figure 3.9:** The temperature dependence of  $\pi^*$  parameters for the pyridinium-based ionic liquids [BP][BF<sub>4</sub>](□), [OP][BF<sub>4</sub>](○), [BP][NTf<sub>2</sub>](△), [HP][NTf<sub>2</sub>](▼) and [OP][NTf<sub>2</sub>](◇).

In contrast, the pyrrolidinium ionic liquids show nonlinear temperature dependence. The decrease in the  $\pi^*$  values is from 0.890 to 0.800 for [BMPyrr][NTf<sub>2</sub>], 0.811 to 0.611 for [HMPyrr][NTf<sub>2</sub>] and 0.733 to 0.553 for [OMPyrr][NTf<sub>2</sub>] in the temperature range of 298 to 353 K. Thus, the thermosolvatochromism in the

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pyrrolidinium-based ionic liquids is more sensitive to the variation in chain length (Figure 3.10).

**Table 3.12: Polarizability ( $\pi^*$ ) for Pyridinium Based Ionic Liquids**

Temperature <i>T/K</i>	[BP][BF <sub>4</sub> ]	[OP][BF <sub>4</sub> ]	[BP][NTf <sub>2</sub> ]	[HP][NTf <sub>2</sub> ]	[OP][NTf <sub>2</sub> ]
298.15	1.081	0.974	0.816	0.984	0.965
303.15	1.076	0.965	0.800	0.971	0.958
313.15	1.066	0.951	0.782	0.951	0.946
323.15	1.057	0.927	0.762	0.927	0.943
333.15	1.048	0.887	0.759	0.914	0.937
343.15	1.034	0.870	0.728	0.889	0.927
353.15	1.021	0.849	0.713	0.870	0.919

**Table 3.13: Polarizability ( $\pi^*$ ) for Pyrrolidinium Based Ionic Liquids**

Temperature <i>T/K</i>	[BMPyrr][NTf <sub>2</sub> ]	[HMPyrr][NTf <sub>2</sub> ]	[OMPyrr][NTf <sub>2</sub> ]
298.15	0.890	0.811	0.733
303.15	0.890	0.753	0.693
313.15	0.890	0.715	0.652
323.15	0.870	0.683	0.632
333.15	0.860	0.650	0.597
343.15	0.820	0.632	0.576
353.15	0.800	0.611	0.553

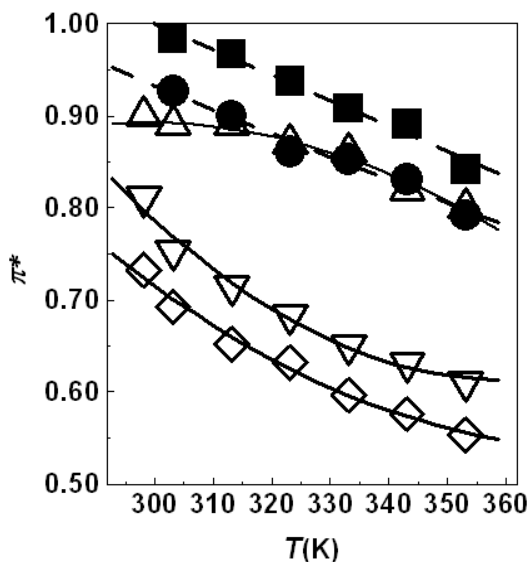
The  $\pi^*$  values for [TBP][Ala] decreases from 0.984 at 303 K to 0.842 at 353 K, while for [TBP][Val], they fall from 0.927 at 303 K to 0.791 at 353 K in a linear fashion (Figure 3.10). These observations indicate that the temperature dependence of the polarity

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parameters in ionic liquids is a complex function of the cationic and anionic structures. The substituent on the cation, for example, cannot only affect the magnitude of temperature dependence but change an “inversely proportional correlation” to the “direct proportional are”.

**Table 3.14: Polarizability ( $\pi^*$ ) for Phosphonium Based Ionic liquids**

Temperature <i>T</i> /K	[TBP][Ala]	[TBP][Val]
303.15	0.984	0.927
313.15	0.967	0.900
323.15	0.938	0.861
333.15	0.908	0.853
343.15	0.891	0.831
353.15	0.842	0.791



**Figure 3.10:** The  $\pi^*$  -  $T$  plots for the pyrrolidinium-based ionic liquids [BMPyrr][NTf<sub>2</sub>]( $\Delta$ ), [HMPyrr][NTf<sub>2</sub>]( $\nabla$ ) and [OMPyrr][NTf<sub>2</sub>]( $\square$ ) and phosphonium-based ionic liquids [TBP][Ala]( $\blacksquare$ ), [TBP][Val]( $\bullet$ ).

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It is worthwhile to note that while a given probe like Reichardt's dye shows positive thermosolvatochromism (thermochromic red shift) in the pyridinium or pyrrolidinium-based ionic liquids, it shows negative thermosolvatochromism (thermochromic blue shift) in the phosphonium ionic liquids. This opposite temperature effect on the same probe molecule in different solvents has not been reported previously for molecular solvents. Ionic liquids are unique with respect to solvation interactions. The observation can be explained only by considering the characteristic of ground state and excited state of the probe molecule and resultant solvation patterns. The variation in polarity with temperature property provides enormous possibilities of optimizing the solvent composition in order to meet the polarity requirements of the process at any given temperature.

#### 3.1.4. Molecular Origin of Thermosolvatochromism in Ionic Liquids

It is important to understand the solute-solvent interactions in ionic liquids that cause such drastic variations with temperature. The betaine dye systems are known to show a negative solvatochromism due to differential solvation of more polar ground state (dipole moment of ground state  $\mu_G = 15\text{D}$ ) as compared to the less polar excited state (dipole moment of excited state  $\mu_E = 6\text{D}$ ).<sup>15</sup> This explains the blue shift of absorption maxima for betaine dye with increasing solvent polarity. In polar solvents, the ground state is stabilized due to stronger solute-solvent interaction as compared to excited state. When the temperature is increased, the ground state solvent interactions are weakened, thus reducing the energy gap between the ground state and the excited state of betaine molecule. As a result, an increase in temperature should cause a red shift in absorption maximum of betaine dye in polar solvents. This is precisely the case observed in the case of the pyridinium- and pyrrolidinium-based ionic liquids. The opposite effect of temperature in the case of the phosphonium-based ionic liquids must then be explained along similar lines. The blue shifts in the solvatochromism indicate that the phosphonium ionic liquids solvate the excited state of betaine dye more efficiently as compared to the ground state. The greater stabilization of the excited state is also reflected in lower  $E_T^N$  value at 303 K in phosphonium-based ionic liquids as compared to the pyrrolidinium

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ionic liquids when the temperature increases. The weakening of stabilizing excited state-solvent interactions should lead to an increase in energy gap between the ground state and excited state of betaine molecule. This causes the observed blue shift in the thermosolvatochromism.

The results present an interesting contrast to Suppan's generalization that "absorption bands which give solvatochromic blue shifts are expected, on this basis to show thermo-chromic red shift".<sup>8</sup> The present line of reasoning implies that while pyridinium and pyrrolidinium-based ionic liquids are perceived as "polar" solvent by betaine molecule, the phosphonium-based ionic liquids acts as "non-polar" solvents for the same probe molecule. It would be interesting to validate this implication further by analyzing the reasons for the apparent contrast. Since the betaine dye is neither a hydrogen bond donor nor a Lewis acid, it is reasonable to assume that there is no direct interaction of the molecule with the anions of the ionic liquids. The betaine dye is capable of exhibiting strong dipole-dipole, dipole-induced dipole, H-bond acceptor and dispersion interactions (due to large polarizability). The cation-betaine molecule interaction should then be the primary interaction while the influence of anion is accounted for only in an indirect manner.

Among the cations, pyridinium has a polarizable  $\pi$  electron cloud but it is weak hydrogen bond donor due to charge dispersion. In contrast, the pyrrolidinium cation is incapable of dispersion interactions but can act as a strong hydrogen bond donor ( $\alpha = 0.734$  for [BMPyr][NTf<sub>2</sub>],  $\alpha = 0.532$  for [BP][NTf<sub>2</sub>]). The phosphonium shows higher  $\alpha$  values as compared to pyridinium and pyrrolidinium ionic liquids ( $\alpha = 0.879$  [TBP][Ala],  $\alpha = 0.956$  for [TBP][Val]). As alkyl chain length substitution increases from the butyl to hexyl to octyl the interactions between the probe and ionic liquids become weak. An increase of solvent polarity for probe **2** leads to bathochromic shift of  $\nu_{max}$ . This is consistent with series of  $\pi-\pi^*$  transitions, which go from relatively charge diffuse ground state to excited state, wherein electronic charges are more concentrated and charge centers are more separated. Hence, more polar solvents stabilize the electronic ground state with

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the effect of shifting  $\nu_{max}$  to lower energy. As the temperature increases the solute solvent interactions are weakened. In case of dye **2** this entails that the relative stabilization of excited state decreases as the temperature increases. The results in increasing in excited energy is reflected by decreasing  $\pi^*$  value with temperature for all the ionic liquids studied.

It is difficult to discuss the variation in  $\alpha$  and  $\beta$  parameters along similar lines, since these parameters are determined by the combination of responses of two or more solute probes. A thorough computational investigation into the interesting variations in thermochromic behavior of the dye molecules with the structure of the ionic liquids would be desirable in the future.

#### 3.1.5 Conclusions

The results indicate that the polarity of ionic liquids is sensitive to the changes in the temperature. The temperature dependence or thermosolvatochromism observed does not follow a uniform trend and is determined by the identity of the cation as well as the anion. Further studies are needed to understand the origin of these effects. The observations also mean that the polarity of ionic liquids can be altered by controlling the temperature optimize the yields and selectivities.

## 3.2 Preferential Solvation

### 3.2.1 Introduction

The effect of solute-solvent and solvent-solvent interactions on the preferential solvation of solvatochromic indicators in binary mixtures of ionic liquids with molecular solvents has been investigated. The binary mixtures of the pyridinium based ionic liquids: 1-butyl pyridinium tetrafluoroborate [BP][BF<sub>4</sub>], 1-butyl-3-methyl pyridinium tetrafluoroborate [3-MBP][BF<sub>4</sub>] and 1-butyl-4-methyl pyridinium tetrafluoroborate [4-MBP][BF<sub>4</sub>] with molecular solvents like water, methanol and dichloromethane have been selected for this investigation. The effect of addition of ionic liquids to molecular solvents on the polarity parameters  $E_T^N$ , Kamlet-Taft parameters, hydrogen bond donor ability (HBD) ( $\alpha$ ),



### 3. Thermosolvatochromism and Preferential Solvation

hydrogen bond acceptor ability (HBA) ( $\beta$ ) and polarizability ( $\pi^*$ ) was obtained.<sup>4</sup> The polarity parameters of the mixture display nonideality on addition of ionic liquids to water and dichloromethane. On the other hand, strong synergetic effects were seen in the ionic liquid-methanol binary mixtures. The preferential solvation models have been employed to analyze the collected data in order to achieve information on solute-solvent interactions in these binary mixtures.

The polarity of many ionic liquids has been studied in terms of  $E_T(30)$  (electronic transition energy in kcal/mol) and the Kamlet-Taft polarity parameters,<sup>4</sup>  $\alpha$  the hydrogen bond donor ability HBD: acidity,  $\beta$  the hydrogen bond acceptor ability HBA: basicity and  $\pi^*$  polarizability were determined using three indicator dyes – Reichardt's dye (**1**), *N,N*-diethyl-4-nitroaniline (**2**) and 4-nitroaniline (**3**) (Figure 3.1).

Solute-solvent and solvent-solvent interactions using solvatochromic probes or dyes can vary with the amount and nature of cosolvents, even at trace impurities. The interaction of a dye in a binary solvent system depends on the composition of solvation sphere since solute-solvent interaction is much more complex in mixed solvent systems than in pure solvents. The solute can interact to a greater extent with one of the solvents present in the mixture, and in turn, the solvent-solvent interactions can also strongly affect solute-solvent interactions. In a pure solvent, the composition of the sphere of solvation of the indicator is the same as in the bulk solvent. However, in a mixed solvent, the solvatochromic indicator interacts to a different extent with the solvents of the mixture and hence the composition of the solvation sphere is different from the composition of the bulk solvent. This phenomenon is known as *selective* or *preferential solvation*. There are many reports available on the solute-solvent and solvent-solvent interaction in binary mixtures of conventional organic solvent binary mixtures. The data have been fitted to models, which gives information about the preferential solvation of dye by either of solvent and mixed solvents. Preferential solvation model was used by Roses *et. al.*<sup>16</sup>, for example, to explain the polarity of binary mixtures of formamides with hydroxylic solvents having similar  $E_T(30)$  values.

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On the other hand, the significant lowering of viscosity of ionic liquids upon addition of cosolvents is a result of changes in ionic interactions of ionic liquids and cosolvents. This situation from point of view of polarity in the ionic liquids + cosolvents has been investigated to a lesser extent. The solute-solvent interactions and behavior of a solvation probe or dye in binary mixture of ionic liquids with molecular solvents has recently been investigated.<sup>17</sup> It has been shown that the dye Reichardt's is more preferentially solvated by ionic liquids and mixed solvents with respect to cosolvent added. The hyperpolarity within the [BMIM][PF<sub>6</sub>] and tetraethylene glycol mixture has also been studied. The polarity as well as Kamlet-Taft parameters for mixtures have higher values as compared to pure solvents.<sup>18</sup> This behaviour is also known as the synergetic effect, wherein the measured property shows deviations in magnitude greater than the values in the pure components themselves. Such a behavior is easily observable in the form of a pronounced maxima or minima when plotted as a function of the mole fraction of either of the solvents. In view of the scarcity of experimental data on the polarity of the ionic liquids solutions, it is difficult to interpret the phenomenon.

The cosolvents were chosen with a wide range of polarity values, in order to understand the effect of cosolvent polarity on the solvation in the binary mixtures of ionic liquids. We have measured the polarity parameters for three ionic liquids – as 1-butyl pyridinium tetrafluoroborate [BP][BF<sub>4</sub>], 3-methyl-1-butylpyridinium tetrafluoroborate [3-MBP][BF<sub>4</sub>] and 4-methyl-1-butylpyridinium tetrafluoroborate [4-MBP][BF<sub>4</sub>]. The cosolvents used were water, methanol and dichloromethane.

#### 3.2.2 Experimental Section

**Materials:** The spectroscopic indicator dyes **1** and **3** were used as obtained. The dye **2** was purchased from Frinton Laboratories (99% purity). Pyridine, 3-picoline, 4-picoline and 1-bromobutane were distilled prior to their use. Sodium tetrafluoroborate NaBF<sub>4</sub> was used as purchased without further purification. Deionised water having conductivity 18.2 Ω was used in the investigation. Spectroscopic grade methanol and dichloromethane were used for all the polarity measurements.

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**Synthesis of ionic liquids:** The ionic liquids studied in this work are synthesized and characterized according to the previously reported literature procedure.<sup>12</sup> All the ionic liquid samples were thoroughly dried under vacuum for several hours prior to their use. Also the water content of the ionic liquids was measured before making solution by Karl-Fischer coulometer and did not exceed 50 ppm for any sample.

**Polarity Measurements:** The measurements of the polarity have been carried out according to procedure described in earlier section of this chapter. Different concentrations of ionic liquids, [BP][BF<sub>4</sub>], [3-MBP][BF<sub>4</sub>] and [4-MBP][BF<sub>4</sub>] in water, methanol, dichloromethane are prepared. The freshly prepared solution of dye in dichloromethane was added drop wise to a precisely measured volume of pure ionic liquids and the dichloromethane was removed under high vacuum. The solvents water, methanol, dichloromethane were added in appropriate amounts, to ionic liquids in order to prepare the required solutions. The solution of dye added to cuvette for measurement of wavelength at maximum absorption.<sup>6</sup> The temperature of the cuvette was stabilized at 298 K using a peltier setup with an accuracy of  $\pm 0.01$ K. The calculation of polarity parameters were done as given below. All the polarity parameters are reproducible to  $\pm 0.4\%$ . Throughout this manuscript,  $x_2$  refers to the mole fraction of the ionic liquids remembering  $x_1 + x_2 = 1$ , where  $x_1$  is the mole fraction of the solvent.

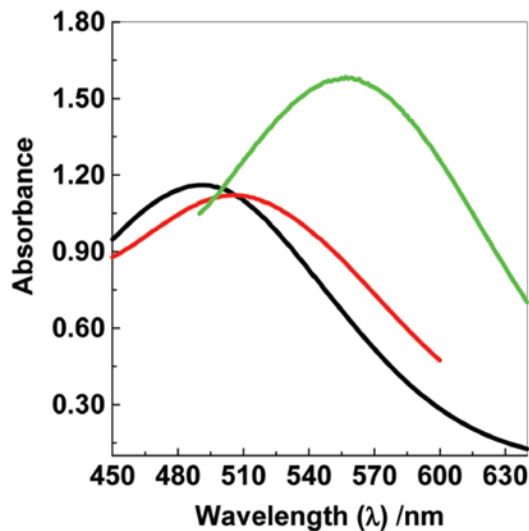
**Solvatochromic Polarity Analysis:** the calculation of the polarity parameters is calculated from the reported procedure.

#### 3.2.3 Results and Discussion

The microscopic properties of the solvents are always reflected through bulk or macroscopic properties like dielectric permittivity, dipole moment, refractive index and polarity. The microscopic properties are a measure of the structure and dynamics of the solvation sphere of dye through macroscopic parameters,  $E_T^N$  and Kamlet-Taft parameters of dipolarity/polarizability ( $\pi^*$ ), hydrogen-bond acceptor basicity ( $\beta$ ) and hydrogen-bond donor acidity ( $\alpha$ ). The microscopic parameters were determined from solvatochromic measurements, which measure the properties in the solvation sphere of

### 3. Thermosolvatochromism and Preferential Solvation

the solvatochromic indicator. The pure solvents do not give rise to preferential solvation, since the composition of the solvation sphere and bulk solvent are identical.



**Figure 3.11:** Typical UV-visible spectra for Reichardt's dye 30 in pure [BP][BF<sub>4</sub>] (green line), for  $x_2$ ) 0.024 (black line), for  $x_2$ ) 0.284 of [BP][BF<sub>4</sub>] (red line) in water

In binary mixtures, preferential solvation is a fairly common phenomenon, which leads to many interesting consequences. In case of ionic liquids, such preferential interactions may be manipulated to give the desired outcome of any chemical process. The polarity parameters for pure ionic liquids and solvents at 298 K are shown in Table 3.15. As expected, the polarity of ionic liquids is lower than water and methanol but higher than that of solvents like dichloromethane. The polarity values of the pure liquids confirm to the values reported in the literature.<sup>5, 6, 7</sup>

**Table 3.15: Polarity Parameters of Ionic Liquids and Solvents**

S. No.	Solvents/Ionic Liquids	$E_T^N$	$\alpha$	$\beta$	$\pi^*$
1	[BP][BF <sub>4</sub> ]	0.637 <sup>a</sup>	0.520	0.450	1.082
2	[3-MBP][BF <sub>4</sub> ]	0.651	0.560	0.423	1.071

3	[4-MP][BF <sub>4</sub> ]	0.636	0.530	0.533	1.066
4	Water	1.000	1.120	0.178	1.325
5	Methanol	0.762	1.030	0.578	0.771
6	Dichloromethane	0.309	0.040	0.059	0.733

<sup>a</sup> Ref. 11, 13

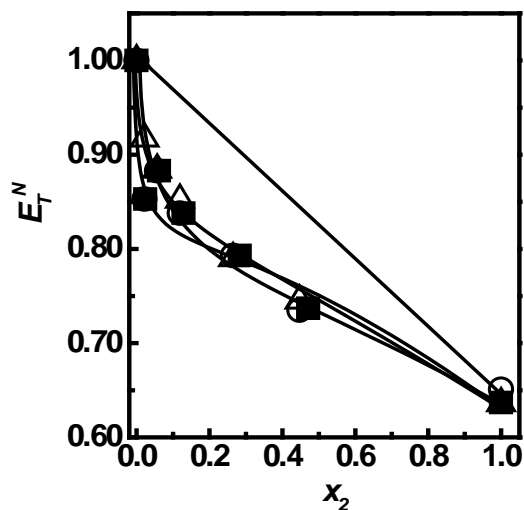
After ascertaining the purity of our samples and observing the good agreement between the literature values and experimentally measured values, we focused our attention on binary mixtures of ionic liquids. We were interested in understanding if the hyperpolarity trends observed in the literature were restricted to the particular combination of ionic liquid + molecular solvents or were a more general phenomenon in nature

### 3.2.3.1 $E_T^N$ Electronic transition energy

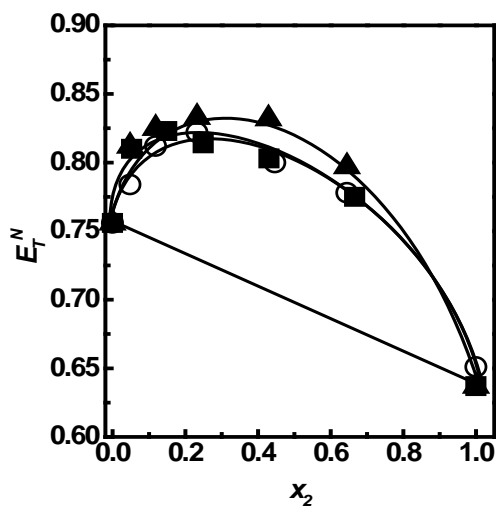
Figure 3.12, 3.13, 3.14 shows the plots of  $E_T^N$  with  $x_2$  of binary mixtures of the pyridinium based ionic liquids in water, methanol and dichloromethane, respectively. The polarity observed above shows a strongly nonideal behavior in all binary studied. There are some interesting variations related to the cosolvent used. For the binary mixtures of the pyridinium ionic liquids in water, it is observed that the polarity of mixtures decreases with increase in concentration of all the ionic liquids. All the three ionic liquids show this peculiar nonideal behavior on the addition of ionic liquids to water, indicating a similar strong solvent specific interaction between the water and ionic liquids. In the case of binary mixture of ionic liquids in methanol, the variations in the polarity parameters are different in nature, as shown in Figure 3.13. For the binary mixtures in methanol,  $E_T^N$  shows a positive deviation, in fact suggesting a strong synergistic effect – in which the polarity of the mixture is higher than that of either of the pure solvents. This is apparently opposite to the trend observed in the aqueous mixtures. The fact that methanol differs from water by the presence of only a methyl group makes such a difference more relevant.

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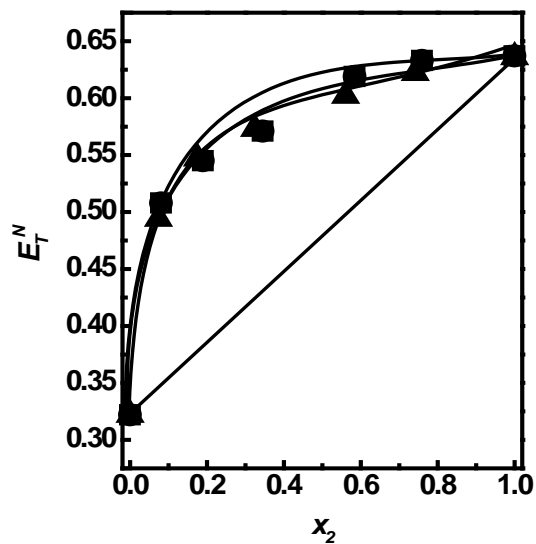
In dichloromethane, the nonideality observed is greater than that seen in aqueous binary mixtures, but no synergistic attenuation of polarity is observed.



**Figure 3.12:** The plots of  $E_T^N$ - $x_2$  for binary mixtures of [BP][BF<sub>4</sub>](■), [3-MBP][BF<sub>4</sub>](○) and [4-MBP][BF<sub>4</sub>](▲) in water.

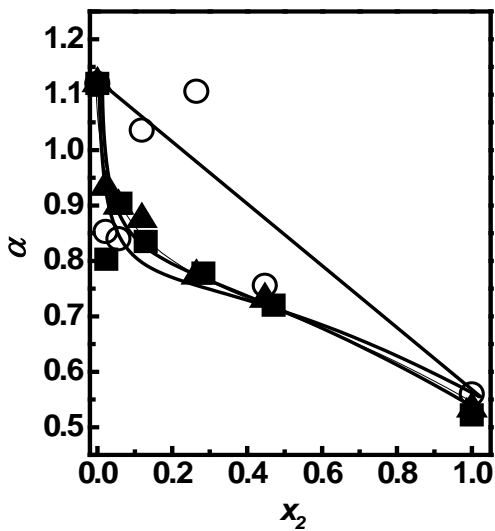


**Figure 3.13:** The plots of  $E_T^N$ - $x_2$  for binary mixtures of [BP][BF<sub>4</sub>](■), [3-MBP][BF<sub>4</sub>](○) and [4-MBP][BF<sub>4</sub>](▲) in methanol.



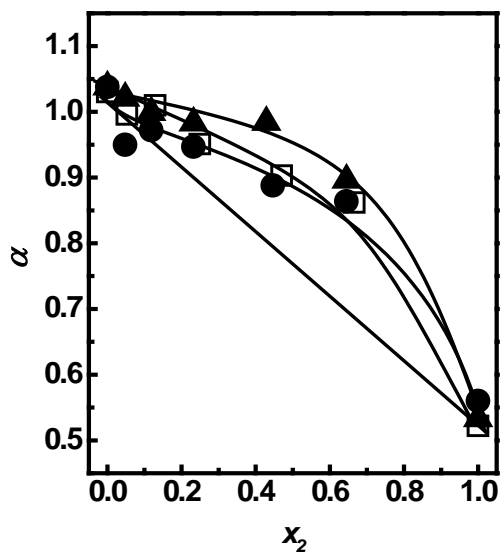
**Figure 3.14:** The plots of  $E_T^N$ - $x_2$  for binary mixtures of [BP][BF<sub>4</sub>](■), [3-MBP][BF<sub>4</sub>](○) and [4-MBP][BF<sub>4</sub>](▲) in dichloromethane

### 3.2.3.2 $\alpha$ Hydrogen bond donor ability (HBD): acidity



**Figure 3.15:** The plots of  $\alpha$  against  $x_2$  for the binary mixtures of [BP][BF<sub>4</sub>](■), [3-MBP][BF<sub>4</sub>](○) and [4-MBP][BF<sub>4</sub>](▲) in water.

### 3. Thermosolvatochromism and Preferential Solvation



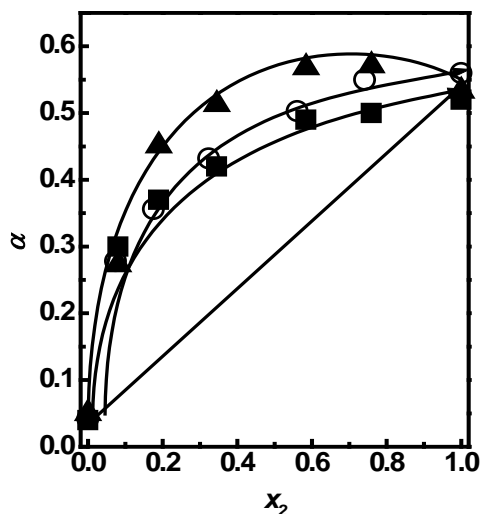
**Figure 3.16:** The plots of  $\alpha$  against  $x_2$  for the binary mixtures of [BP][BF<sub>4</sub>](□), [3-MBP][BF<sub>4</sub>](●) and [4-MBP][BF<sub>4</sub>](▲) in methanol.

The HBD parameter  $\alpha$  shows analogous behavior as  $E_T^N$  with respect to the composition of the binary mixtures (Figures 3.15, 3.16 and 3.17). This is expected since both parameters reflect the hydrogen bond donor ability of the solvents. The  $E_T^N$  parameter is a scale with multiple contributions, but the hydrogen bond donor ability is one of the more dominant one of all, along with the polarizability interactions. In other words, the ability of the solvents to stabilize the ground state and excited state of the Reichardt's dye determines the observed values to a very large extent. Accordingly, in the present work, the  $\alpha$  parameter was determined indirectly – from the measurements of  $E_T^N$  and polarizability of the binary mixtures. Hence, it is expected that the variations with composition is reflected in both the systems. But nonetheless, some subtle differences can provide useful insights into the nature of probe-dependent solute-solvent interactions. For example, the  $\alpha$  parameter does not show the synergistic effect in the ionic liquid + methanol binary mixtures as seen for the Reichardt's dye. On the contrary, a marginal synergistic effect is seen for the binary mixtures with dichloromethane (especially for the [4-MBP][BF<sub>4</sub>] + dichloromethane system) although it was not observed for the  $E_T^N$  measurements for these systems. The presence and position of alkyl substituent's do not



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affect the variations to a very great extent in binary mixtures with water or methanol, but considerable difference is seen when dichloromethane is employed as a cosolvent (Figures 3.15, 3.16 and 3.17)



**Figure 3.17:** The plots of  $\alpha$  against  $x_2$  for the binary mixtures of [BP][BF<sub>4</sub>](■), [3-MBP][BF<sub>4</sub>](○) and [4-MBP][BF<sub>4</sub>](▲) in dichloromethane.

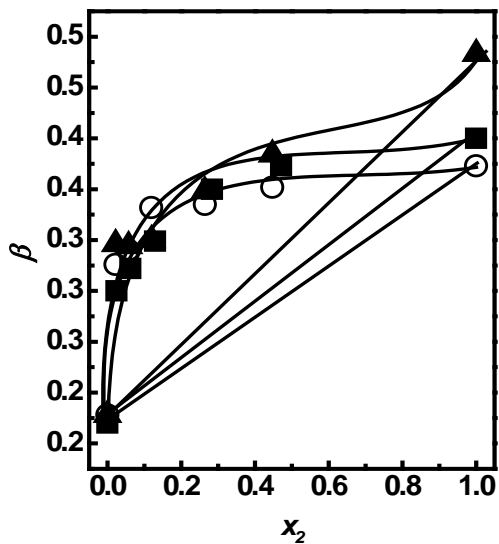
The difference between the synergy of the  $E_T^N$  and  $\alpha$  parameters in the ionic liquid + methanol binary systems needs to be analyzed in a greater detail. It has been proposed earlier that synergistic effects are not entirely characteristic of the mixtures studied but are also determined by the systems employed to study the mixtures.<sup>19</sup>

#### 3.2.3.3 $\beta$ Hydrogen bond acceptor ability HBA: basicity

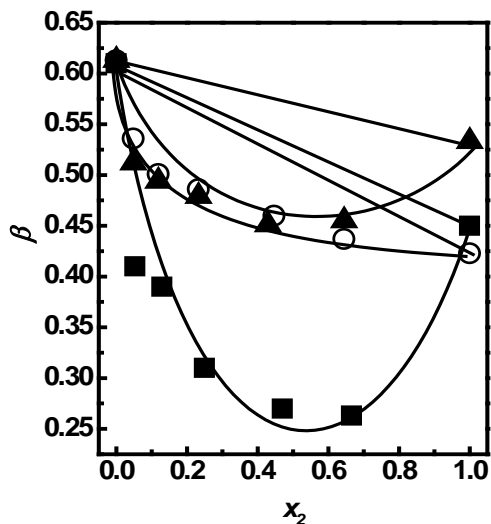
The choice of the systems – the polarity probe, for example – can be decisive in determining the nature of the molecular interactions and the extent of synergy observed. This approach also explains the stark difference of the hydrogen bond acceptor capacity as measured by the  $\beta$  parameter in comparison to the parameters discussed earlier. (Figure 3.18, 3.19, 3.20). The  $\beta$  parameter increases with the increasing concentration of an ionic liquid in aqueous systems, since an ionic liquid possesses higher  $\beta$  value than that of water. While the binary mixtures in water and dichloromethane show strong degree of

### 3. Thermosolvatochromism and Preferential Solvation

nonideality, it is the ionic liquid + methanol systems that are remarkable for their highly synergistic hydrogen bond acceptor property.

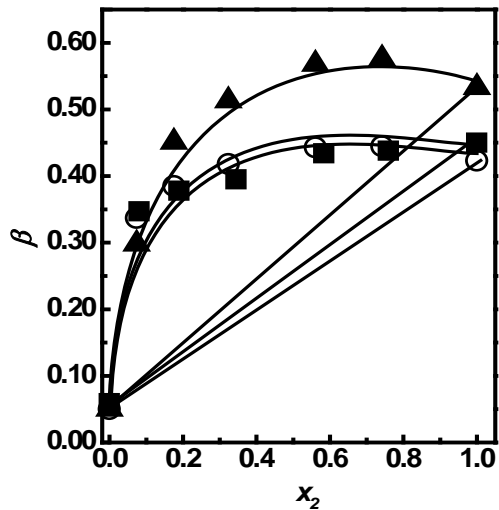


**Figure 3.18:** The plots of  $\beta$  against  $x_2$  for binary mixtures of [BP][BF<sub>4</sub>](■), [3-MBP][BF<sub>4</sub>](○) and [4-MBP][BF<sub>4</sub>](▲) in water.



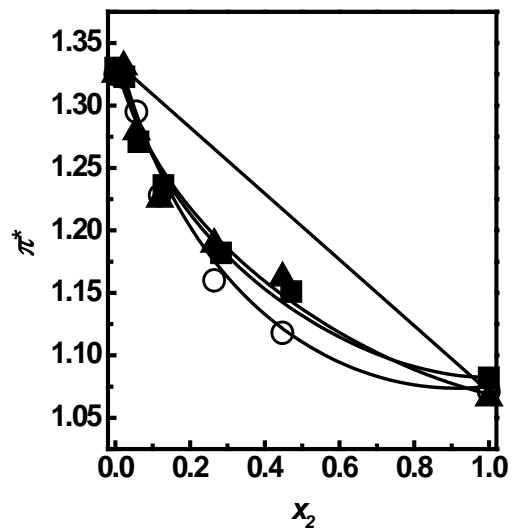
**Figure 3.19:** The plots of  $\beta$  against  $x_2$  for binary mixtures of [BP][BF<sub>4</sub>](■), [3-MBP][BF<sub>4</sub>](○) and [4-MBP][BF<sub>4</sub>](▲) in methanol

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**Figure 3.20:** The plots of  $\beta$  against  $x_2$  for binary mixtures of [BP][BF<sub>4</sub>](■), [3-MBP][BF<sub>4</sub>](○) and [4-MBP][BF<sub>4</sub>](▲) in dichloromethane.

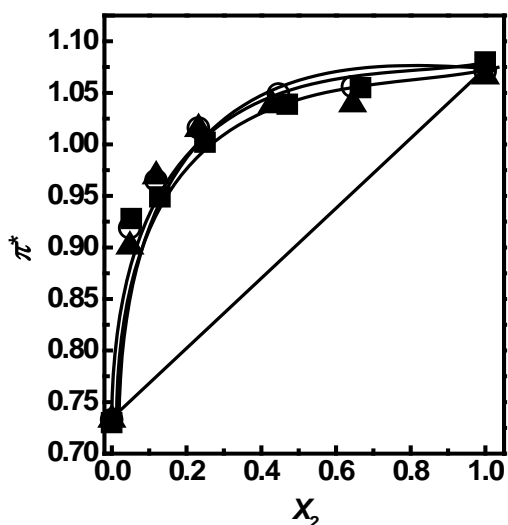
#### 3.2.3.4 $\pi^*$ Polarizability



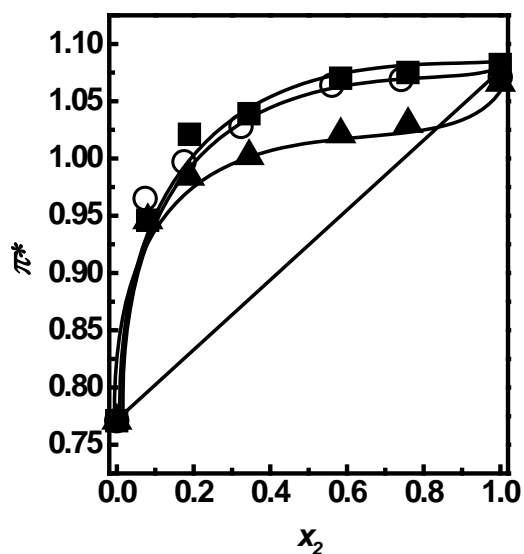
**Figure 3.21:** The plots of  $\pi^* - x_2$  for the binary mixtures of [BP][BF<sub>4</sub>](■), [3-MBP][BF<sub>4</sub>](○) and [4-MBP][BF<sub>4</sub>](▲) in water.

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The polarizability parameter  $\pi^*$ , show a decrease with an increase in the concentration of ionic liquids (see Figure 3.21, 3.22, 3.23). However, no strongly synergistic trends in this variation are witnessed for the binary mixtures in all the three cosolvents. This makes the synergy observed for the  $E_T^N$  parameter for the ionic liquid mixtures in methanol more interesting – since both the dominant contributing parameters do not reflect the synergy, its origin must be some interesting molecular interactions. At this stage, it would be difficult to speculate about the nature of such interactions. But the emergence of such variation in synergy among the same binary mixtures emphasizes the need for more extensive studies in the near future. The parameters  $E_T^N$ ,  $\alpha$ ,  $\beta$  and  $\pi^*$  exhibit non-ideal behavior. However, for the binary mixtures of ionic liquids in methanol, the  $E_T^N$ ,  $\alpha$  and  $\pi^*$  parameters show positive deviations while  $\beta$  shows negative deviation. This is opposite to the trend observed in aqueous mixtures. The fact that methanol differs from water in the presence of only a methyl group makes this difference more relevant due to decrease in extent of strong hydrogen bonding in methanol. For ionic liquid-methanol mixtures, the  $E_T^N$  parameter shows an interesting synergetic effect, in which the polarity of mixtures is higher than that of either of the pure solvents



**Figure 3.22:** The plots of  $\pi^*$  -  $x_2$  for the binary mixtures of [BP][BF<sub>4</sub>](■), [3-MBP][BF<sub>4</sub>](○) and [4-MBP][BF<sub>4</sub>](▲) in methanol.



**Figure 3.23:** The plots of  $\pi^* - x_2$  for the binary mixtures of [BP][BF<sub>4</sub>](■), [3-MBP][BF<sub>4</sub>](○) and [4-MBP][BF<sub>4</sub>](▲) in dichloromethane.

The synergetic effect is observed when HBD, acidity  $\alpha$  of the solvent (ionic liquids in this case) is complemented by a strong HBA basicity  $\beta$  of the solvent, methanol having similar polarity in terms of  $E_T^N$  values. Such complementary interactions lead to the formation of hydrogen bonding complexes with interesting deviations from the ideal behavior. There is a formation of hydrogen bond complex between two solvents, which is more polar than pure methanol and ionic liquids.

The binary mixtures of ionic liquids with dichloromethane show a more pronounced non-ideal behavior as compared to binary mixtures ionic liquids with water and methanol. The polarity difference between ionic liquids and dichloromethane is large, so that for an ionic solute, the preferential solvation of the dye or probe is greater by ionic liquids rather than dichloromethane. The non-ideality is thus observed for ionic liquid mixtures with highly polar solvents like water and methanol as well as nonpolar solvents like dichloromethane. A detailed analysis of these synergetic effects and non-ideal behavior would lead to a greater understanding of the solute-solvent interactions. Below we attempt to correlate the obtained data with the help of two models and compare

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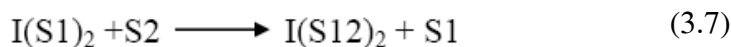
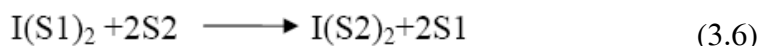
the results in order to understand which one of them explains the observations more satisfactorily.

#### 3.2.4 Preferential Solvation Model

It has been proposed that preferential solvation is measure of deviation of  $E_T(30)$  values from the linearity with addition of cosolvents in the binary mixtures.<sup>19</sup> The preferential solvation equations were derived on the basis of the same solvent exchange theory and used it for the description of the  $E_T(30)$  values of binary mixtures of ionic liquids with molecular solvents.<sup>20</sup> The synergism observed by the HBA and HBD solvents by forming hydrogen bond complex which is more polar than either of two pure solvents. Hence these models allow us to understand the both synergetic as well and nonsynergetic effect in binary mixtures of solvents from the correlation parameters. The transition energy of a solvatochromic indicator is an average of the transition energies of solvent in solvation microsphere of the indicator and changes with mole fraction of solvents added.

##### 3.2.4.1 Model 1

The preferential solvation model is based on the two-step solvent exchange model first proposed by Skwierczynski and Connor<sup>21</sup>



where S1 and S2 indicate the two pure solvents and S12 represents a solvent formed by the interaction of solvents 1 and 2.  $I(S1)_2$ ,  $I(S2)_2$ , and  $I(S12)_2$  indicate that the Reichardt's dye (I) solvated by solvents S1, S2 and S12, respectively. The two solvent-exchange processes can be defined by two preferential solvation parameters,  $f_{2/1}$  and  $f_{12/1}$ , which measure the tendency of the indicator to be solvated by solvents S2 and S12 with reference to solvent S1 solvation.

$$f_{2/1} = \frac{x_2^s/x_1^s}{(x_2^0/x_1^0)^2} \quad (3.8)$$

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$$f_{12/1} = \frac{x_{12}^s/x_1^s}{(x_2^0/x_1^0)^2} \quad (3.9)$$

In eqs 3.8 and 3.9,  $x_1^s$ ,  $x_2^s$  and  $x_{12}^s$  are the mole fractions of solvents S1, S2, S12 respectively in the sphere of solvation of indicator and  $x_1^0$  and  $x_2^0$  are the mole fractions of the two solvents in the bulk mixed solvent, respectively.

The  $E_T^N$  polarity of the mixed solvent is calculated as an average of the  $E_T^N$  values of solvents S1, S2 and S12 in the sphere of solvation of the indicator.

$$E_T^N = x_1^s E_{T1}^N + x_2^s E_{T2}^N + x_{12}^s E_{T12}^N \quad (3.10)$$

From Eqs 3.8–3.10, a general equation that relates the  $E_T^N$  polarity of a binary mixture to the  $E_T^N$  polarities of the two pure solvents, the preferential solvation parameters and the solvent composition can be derived according to

$$E_T^N = \frac{E_{T1}^N(1 - x_2^0)^2 + E_{T2}^N f_{2/1} (x_2^0)^2 + E_{T12/1}^N f_{12/1} (1 - x_2^0) x_2^0}{(1 - x_2^0)^2 + f_{2/1} (x_2^0)^2 + f_{12/1} (1 - x_2^0) x_1^0} \quad (3.11)$$

$$E_{T12}^N = \frac{E_{T1}^N + E_{T2}^N}{2} \quad (3.12)$$

Eqn. 3.11 is an operative expression to correlate the polarities in the solution of ionic liquids. But this model could not explain for synergetic mixtures. In the case of synergetic mixtures, we explained the preferential solvation using model 2 as shown below.

#### 3.2.4.2 Model 2

Model 1 is more generalized model and defined by solvent exchange process. But it could not explain synergetic behavior observed in methanol-ionic liquids binary mixture. In order to explain the synergetic effect, Model 2 has been introduced and described the hydrogen bond complex formation in methanol and ionic liquids. We also attempted to fit

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this model 2 for water-ionic liquids and dichloromethane-ionic liquids binary mixtures but the estimated parameters were showing high errors.

$$E_T^N = E_{T1}^N + \frac{a(x_2^0)^2 + c(1 - x_2^0)x_2^0}{(1 - x_2^0)^2 + f_{2/1}(x_2^0)^2 + f_{12/1}(1 - x_2^0)x_1^0} \quad (3.13)$$

where  $a$  and  $c$  are the fitting parameters.

#### 3.2.5 Results of Correlations

The experimental data were subjected to the above models using eqs 3.11 and 3.13 using only one parameter,  $E_T^N$ . Model 1 is used for water and dichloromethane and model 2 is for methanol.

The regression parameters are shown in Table 3.16 and 3.17.

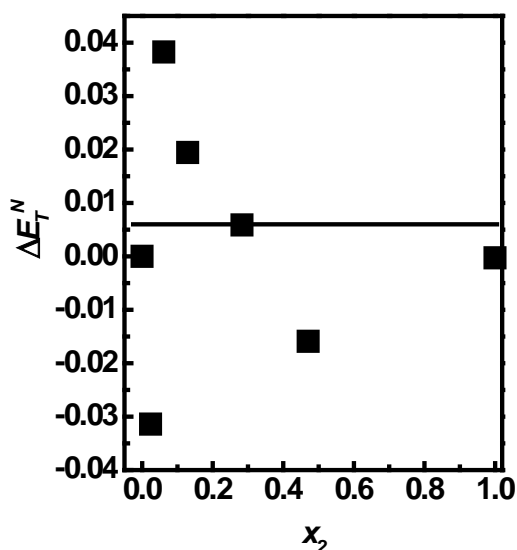
##### 3.2.5.1 Ionic liquids-water binary mixtures

From the model 1, two parameters  $f_{2/1}$  and  $f_{12/1}$  were determined. The parameter  $f_{2/1}$  is the tendency of solvent 2 (ionic liquid) to solvate the dye with reference to solvent 1 while  $f_{12/1}$  measured the tendency of the indicator to be solvated by mixture with reference to solvent 1. The  $f_{2/1}$  and  $f_{12/1}$ , for ionic liquids [BP][BF<sub>4</sub>]-water system are 45.66 and 67.05 respectively. In Figure 3.24 are shown the  $\Delta E_T^N$  values as a function of  $x_2$  for [BP][BF<sub>4</sub>] in water.  $\Delta E_T^N$  is defined as the difference between  $E_{T_{exp}}^N$  and  $E_{T_{corr}}^N$ .  $E_{T_{exp}}^N$  is the value of  $E_T^N$  obtained from our experimental work while  $E_{T_{corr}}^N$  the value of  $E_T^N$  from the use of the model. The values of  $f_{2/1} \gg 1$  designate that the dye is more solvated by [BP][BF<sub>4</sub>], even if water is more polar than [BP][BF<sub>4</sub>]. The solvation sphere is enriched with ionic liquid rather than water. This may partially arise due to the hydrophobicity of the probe molecule. Also the  $f_{12/1} > f_{2/1}$ , show that mixture forms complex which has greater affinity towards the dye as compared to the pure [BP][BF<sub>4</sub>]. Similarly, for the system [3-



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MBP][BF<sub>4</sub>]-H<sub>2</sub>O the parameters  $f_{12/1}$  and  $f_{2/1}$  are 80.79 and 86.08, respectively and for [4-MBP][BF<sub>4</sub>]-H<sub>2</sub>O, system  $f_{12/1}$ ,  $f_{2/1}$  are 23.56 and 26.73. It is obvious that the composition of the solvation sphere is greatly affected more by methyl substitution on the pyridinium cation. Additionally, the values of  $f_{12/1}$  and  $f_{2/1}$  for [3-MBP][BF<sub>4</sub>]-H<sub>2</sub>O are higher than two other systems. It may be due to the asymmetric nature of cation of [3-MBP][BF<sub>4</sub>] leads to stronger solute-solvent interactions as compared to the symmetric cations – [BP]<sup>+</sup> and [4-MBP]<sup>+</sup>. The dye is more preferentially solvated by the mixture and by [3-MBP][BF<sub>4</sub>] at same rate. For the [4-MBP][BF<sub>4</sub>]-H<sub>2</sub>O system, parameters  $f_{12/1}$ ,  $f_{2/1}$  are 23.56 and 26.73, respectively indicate that the dye is preferentially solvated by [4-MBP][BF<sub>4</sub>] as compared to water. The difference in the values of  $f_{12/1}$  and  $f_{2/1}$  for all the system shows that methyl group substitution plays an important role in preferential solvation study.



**Figure 3.24:** The plot of  $\Delta E_T^N$  vs  $x_2$  for the [BP][BF<sub>4</sub>]-water system

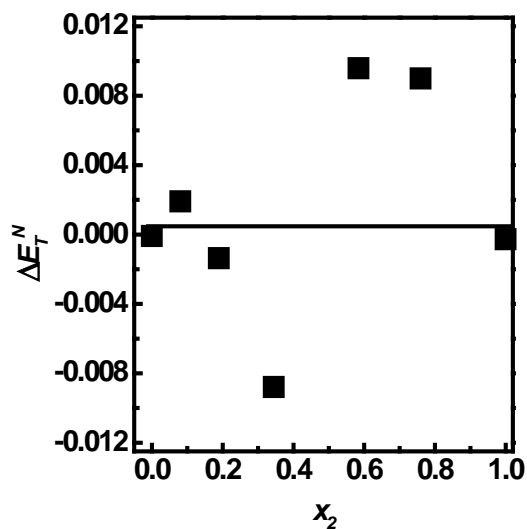
**Table 3.16: Fitting Parameters Obtained From the Model 1**

S. No.	Solvents	Ionic Liquids	$E_{T1}^N$	$E_{T2}^N$	$E_{T12}^N$	$f_{2/1}$	$f_{12/1}$	$\sigma$

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1	Water	[BP][BF <sub>4</sub> ]	1	0.637	0.819	45.66	67.05	0.001
2		[3-MBP][BF <sub>4</sub> ]	1	0.651	0.826	80.79	86.08	0.001
3		[4-MBP][BF <sub>4</sub> ]	1	0.636	0.818	23.56	26.73	0.001
4	DCM	[BP][BF <sub>4</sub> ]	0.322	0.637	0.480	556.0	161.5	0.001
5		[3-MBP][BF <sub>4</sub> ]	0.322	0.651	0.487	118.3	39.52	0.001
6		[4-MBP][BF <sub>4</sub> ]	0.322	0.636	0.480	366.4	105.3	0.004

#### 3.2.5.2 Ionic liquids-dichloromethane binary mixtures



**Figure 3.25:** The plot of  $\Delta E_T^N$  vs  $x_2$  for the [BP][BF<sub>4</sub>]-dichloromethane system

The preferential solvation of ionic liquids-dichloromethane is investigated through model 1 and estimated parameters are shown in Table 3.16. In the case of binary mixture of [BP][BF<sub>4</sub>]-dichloromethane, the parameters  $f_{12/1}$  and  $f_{2/1} \gg 1$  indicate that the indicator dye is strongly preferentially solvated by ionic liquids and mixture only. The values  $f_{12/1}$  and  $f_{2/1}$  are 156 and 161.54, respectively demonstrated that solvation is more pronounced

### 3. Thermosolvatochromism and Preferential Solvation

by ionic liquids compared to mixture with reference to dichloromethane. The observed trend for preferential solvation for all the system is as [BP][BF<sub>4</sub>] - dichloromethane > [4-MBP][BF<sub>4</sub>] - dichloromethane > [3-MBP][BF<sub>4</sub>] - dichloromethane. The results of the application of model 1 are shown for the system in Figure 3.25 in which the  $\Delta E_T^N$  values are plotted as a function of  $x_2$ .

#### 3.2.5.3 Ionic liquid-methanol binary mixtures

Model 2 is used for studying preferential solvation in the ionic liquids-methanol binary mixtures from three parameters,  $f_{12/1}$ ,  $f_{2/1}$  and  $E_{T12}^N$  were determined. The  $E_T^N$  values of both [BP][BF<sub>4</sub>], methanol are close to each other and hence synergism is observed.

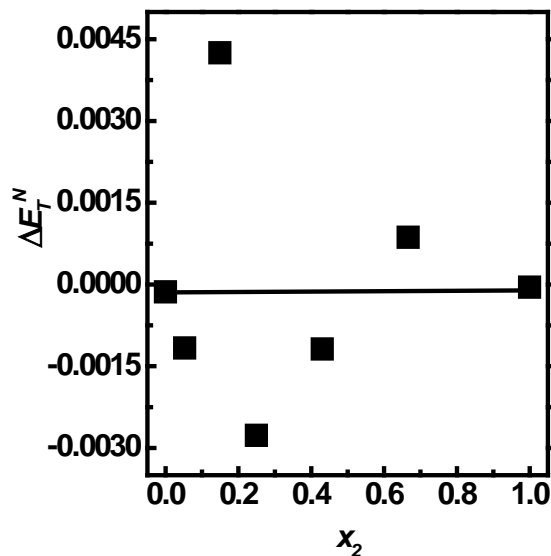
**Table 3.17: Fitting Parameters Obtained From the Model 2**

S. No.	Solvent	Ionic Liquids	$E_{T1}^N$	$E_{T2}^N$	$E_{T12}^N$	$f_{2/1}$	$f_{12/1}$	$\sigma$
1	Methanol	[BP][BF <sub>4</sub> ]	0.756	0.637	0.833	11.15	51.89	0.001
		[3-MBP][BF <sub>4</sub> ]	0.756	0.636	0.859	3.50	9.45	0.003
		[4-MBP][BF <sub>4</sub> ]	0.756	0.651	0.859	4.321	22.06	0.002

The synergism effect observed in [BP][BF<sub>4</sub>]-methanol, [3-MBP][BF<sub>4</sub>]-methanol, [4-MBP][BF<sub>4</sub>]-methanol are shown in Figure 3.26. It can be observed that  $E_{T12}^N$  obtained from the model 2 is higher than the pure solvents, which is observed from the plots. The parameters  $f_{12/1}$ ,  $f_{2/1}$  and  $E_{T12}^N$  obtained from the model 2 are shown in Table 3.17. The values of  $f_{12/1}$  and  $f_{2/1}$  for the [BP][BF<sub>4</sub>]-methanol system are 11.15 and 51.89 shows that the preferential solvation by the mixture and of [BP][BF<sub>4</sub>] and methanol more than pure [BP][BF<sub>4</sub>] with reference to methanol due to synergism. The same is observed for the methanolic solution of [3-MBP][BF<sub>4</sub>] and [4-MBP][BF<sub>4</sub>]. The dye is preferentially solvated by the hydrogen bond complex is as [BP][BF<sub>4</sub>]-methanol > [4-MBP][BF<sub>4</sub>] - methanol > [3-MBP][BF<sub>4</sub>] - methanol.

### 3. Thermosolvatochromism and Preferential Solvation

An examination of Figures 3.24, 3.25, 3.26 shows that  $E_T^N$  parameter for all three types of mixtures of ionic liquids can be successfully represented by the use of model 1 and 2. The  $\Delta E_T^N$  values are within the experimental errors.



**Figure 3.26:** The plot of  $\Delta E_T^N$  vs  $x_2$  for the [BP][BF<sub>4</sub>]-methanol system.

### 3.2.6 Conclusions

In summary, we have demonstrated that the electronic transition energies of a binary mixture of ionic liquids are not the linear function of the compositions of the mixtures. Both positive and negative deviations from the ideal mixing are witnessed. This behavior is also shown by other polarity parameters. The behavior explained using preferential solvation models. Solute-solvent and solvent-solvent interaction are delineated with help of estimated parameters. The parameters obtained explain the strong synergism observed for some of the mixtures, which form the strong hydrogen bond complexes between methanol and ionic liquids.

### 3.3 References

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## **Chapter 4**

# **Viscosity Behavior in Ionic Liquid Systems**

## 4. Viscosity Behavior in Ionic Liquids Systems

*"We can't solve problems by using the same kind of thinking we used when we created them."*

### 4.1. Viscosity of Binary Mixtures of Ionic Liquids

#### 4.1.1. Introduction

Viscosity of ionic liquids is a crucial property in optimizing the conditions required for many chemical processes.<sup>1, 2</sup> High viscosity of ionic liquids is a constraint in obtaining the optimum application in many electrochemical devices in addition to its detrimental role in chemical kinetics.<sup>3</sup> There exists two possibilities of handling high viscosity of ionic liquids 1) to synthesize ionic liquids with low viscosity but may not be suitable for a given applications as one needs to replace either cation or anion by another species imparting low viscosity. This may lead to decrease in effectiveness of ionic liquids itself and 2) to use viscous ionic liquids in conjunction with molecular solvents to provide a clear liquids phase that will offer low viscosity but still useful for a variety of applications. There are numbers of reports are available on physical properties of pure and binary mixtures of ionic liquids based on imidazolium based with cosolvents described in the chapter Introduction. The physicochemical properties are studied and correlated with the structures of ionic liquids in terms of variation in the cations and anions.<sup>4, 5</sup> In spite of the importance of ionic liquids in chemical processes, very little is known about the behavior of ionic liquids in organic molecular solvents. It was shown that as change in solvent affected the viscosity and conductivity significantly. The solvents of higher dielectric constant seem to have a larger effect on the viscosity and the conductivity of the solutions, which indicate that organic solvents enhance the ionic association of the ionic liquids and effect due to dielectric properties of the solvents.

In this connection, we present viscosities of some ionic liquids and their mixtures with molecular solvents. Ionic liquids undertaken for the study include *N*-butyl pyridinium tetrafluoroborate [BP][BF<sub>4</sub>], *N*-butyl 3-methyl pyridinium tetrafluoroborate [3-MBP][BF<sub>4</sub>], *N*-butyl 4-methyl pyridinium tetrafluoroborate [4-MBP][BF<sub>4</sub>], tetra-butyl



#### 4. Viscosity behavior

phosphonium alaninate [TBP][Ala] and tetra-butyl phosphonium valinate [TBP][Val]. Water, dichloromethane and methanol were selected as molecular solvents in the study.

##### 4.1.2 Experimental Section

Ionic liquids used in the present investigation were synthesized and purified according to the reported procedures.<sup>6-9</sup> The ionic liquids were synthesized in two steps. First step included the synthesis of organic cation and the second the addition of anion. The ionic liquids were characterized by <sup>1</sup>H NMR spectroscopy. The ionic liquids were dried under vacuum in order to remove excess water contents. The water content in each ionic liquid as measured by a Karl-Fischer coulometer did not exceed 50 ppm.

The solvents employed in the study were of AR grade and were purified by the standards techniques. De-ionized water with specific conductance of  $0.55 \times 10^{-6} \text{ S} \cdot \text{cm}^{-2}$  was used for preparing mixtures of ionic liquids. The mixtures of ionic liquids with solvents were prepared on the basis of the volume fraction  $V_f$ , defined as the ratio of volume of the ionic liquid to volume of the solvent.

Thus, the volume fraction of the ionic liquid,

$$V_{f,IL} = 1 - V_{f,S} \quad (4.1)$$

where  $V_{f,S}$  is the volume fraction of the solvent. The  $V_f$  scale was preferred due to its easy use in organic reactions.

The viscosities were measured using a Brookfield ultra rheometer. The viscosities were obtained using the equation:

$$\eta = (100 / RPM) * TK * \text{torque} * SMC \quad (4.2)$$

where  $RPM$ ,  $TK$  (0.09373) and  $SMC$  (0.327) are the speed, viscometer torque constant and spindle multiplier constant, respectively.

The instrument was calibrated against the standard viscosity samples supplied with the instruments, water and aqueous  $\text{CaCl}_2$  solutions.<sup>10</sup> Temperature of the solution was maintained to within  $\pm 0.01^\circ\text{C}$  using a Julabo constant temperature thermostat bath.

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The viscosities were measured with an accuracy of 1 %. Each measurement reported in this report is an average of triplicate reading with a precision of 0.3 %.

#### 4.1.3 Results and Discussions

##### 4.1.3.1 Viscosity of binary mixture of ionic liquids with molecular solvents

**Table 4.1 Changes in the Viscosity,  $\eta$  of Pure Ionic Liquids upon Addition of the Molecular Solvents at 298.15 K**

Composition $V_{f,IL}$	$\eta / cP$		
	Water	Methanol	Dichloromethane
	<b>[BP][BF<sub>4</sub>]</b>		
0	0.93	0.66	0.40
0.20	1.33	0.93	1.25
0.40	2.03	1.57	-
0.60	3.35	4.15	9.33
0.80	7.29	14.97	32.70
0.85	10.80	24.93	63.56
0.90	13.90	40.38	73.94
0.93	25.50	55.83	84.46
0.96	41.95	82.16	113.33
0.98	75.35	115.77	124.00
1.00	145.23	145.23	145.23
	<b>[3-MBP][BF<sub>4</sub>]</b>		
0	0.93	0.66	0.40
0.20	1.42	0.88	1.31
0.40	2.41	1.53	3.62
0.60	4.02	3.38	10.53
0.80	7.97	13.92	32.25
0.85	11.37	22.40	44.36
0.90	18.16	36.18	65.70
0.93	27.32	51.80	90.33
0.96	45.52	59.40	120.10
0.98	78.13	113.03	140.30
1.00	166.70	166.70	166.70
	<b>[4-MBP][BF<sub>4</sub>]</b>		
0	0.93	0.66	0.40

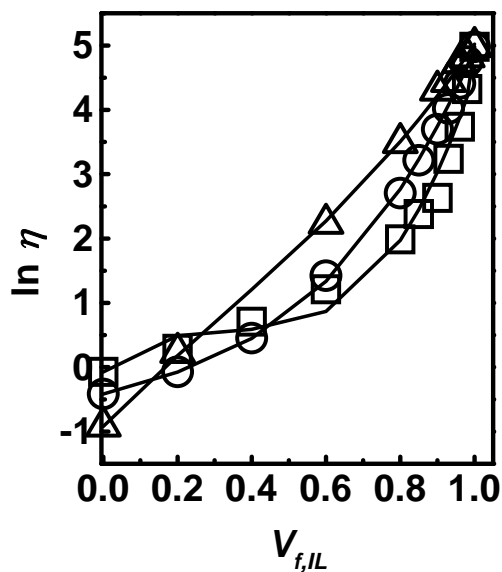
#### 4. Viscosity behavior

0.20	1.40	0.90	0.85
0.40	1.92	1.48	3.42
0.60	2.84	3.47	9.48
0.80	5.32	14.00	33.50
0.85	11.70	18.90	45.13
0.90	17.40	37.50	74.40
0.93	35.43	64.63	84.30
0.96	46.00	97.53	121.30
0.98	78.06	115.33	157.33
1.00	200.65	200.65	200.65
<b>[TBP][Val]</b>			
0	0.93	0.66	0.40
0.20	2.10	1.45	0.93
0.40	5.53	3.88	2.20
0.60	14.25	9.99	13.38
0.80	45.35	38.37	55.55
0.85	-	47.46	63.00
0.90	103.8	122.73	160.50
0.96	185.0	240.8	316.30
0.98	250.07	297.9	344.50
1.00	419.50	419.15	419.15
<b>[TBP][Ala]</b>			
0	0.93	0.66	0.40
0.20	2.23	1.12	0.82
0.40	6.02	2.79	3.17
0.60	13.63	9.20	10.35
0.80	33.18	37.58	33.20
0.85	52.90	40.80	49.00
0.90	88.43	97.03	102.20
0.96	150.45	159.96	204.80
0.98	210.85	260.25	244.80
1.00	338.50	338.50	338.50

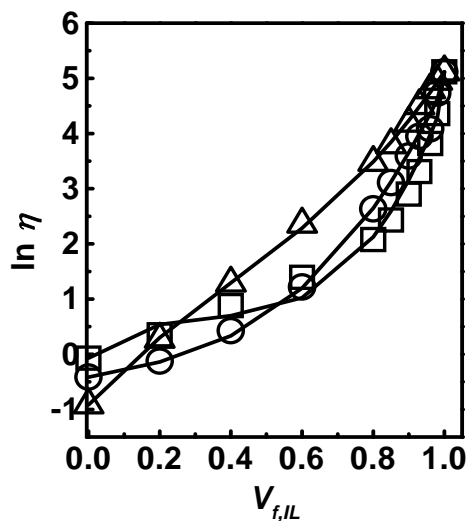
The viscosities  $\eta$  of several mixtures of ionic liquids with molecular solvents measured throughout the composition range at 298.15 K and are listed in Table 4.1. In order to demonstrate the effect of mixture compositions on the viscosities, these data are depicted in the form of the  $\ln \eta - V_{f,IL}$  plots in Figs. 4.1 to 4.5. As seen in Figure 4.1, the viscosity of [BP][BF<sub>4</sub>] falls very sharply upon addition of water. For example, the

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viscosity of [BP][BF<sub>4</sub>] decreases by about 48 % upon addition of water ( $V_{f,IL} = 0.98$ ). Similarly, a decrease of 54, 61, 35, and 42 % in viscosity of [3-MBP][BF<sub>4</sub>], [4-MBP][BF<sub>4</sub>], [TBP][Ala], [TBP][Val], respectively, is noticed, where a little water is added to pure ionic liquids at 298.15 K (Figures. 4.2 to 4.5).



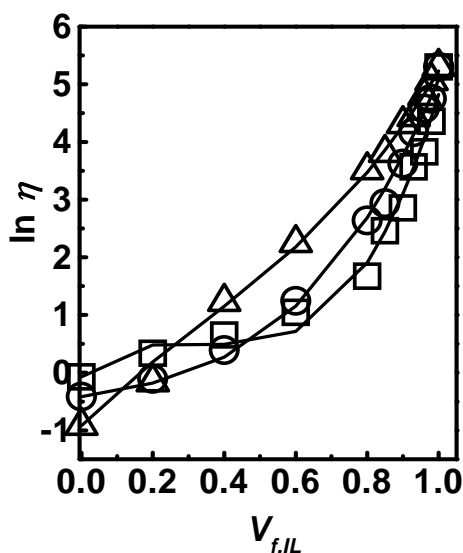
**Figure 4.1:** The  $\ln \eta - V_{f,IL}$  plots for the mixtures of [BP][BF<sub>4</sub>] with water ( $\square$ ), methanol ( $\circ$ ), dichloromethane ( $\triangle$ ) at 298.15 K.



**Figure.4.2:** The  $\ln \eta - V_{f,IL}$  plots for the mixtures of [3-MBP][BF<sub>4</sub>] with water ( $\square$ ), methanol ( $\circ$ ), dichloromethane ( $\triangle$ ) at 298.15 K

#### 4. Viscosity behavior

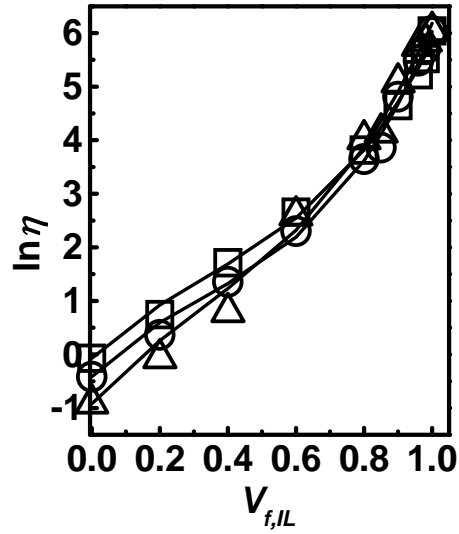
On the other hand, an addition of methanol results into drop in viscosity by 30, 42, and 51 % for [BP][BF<sub>4</sub>], [3-MBP][BF<sub>4</sub>] and [4-MBP][BF<sub>4</sub>] systems, respectively. This decrease in viscosity for [TBP][Ala] and [TBP][Val] on addition of methanol is noted 31 and 42 %, respectively.



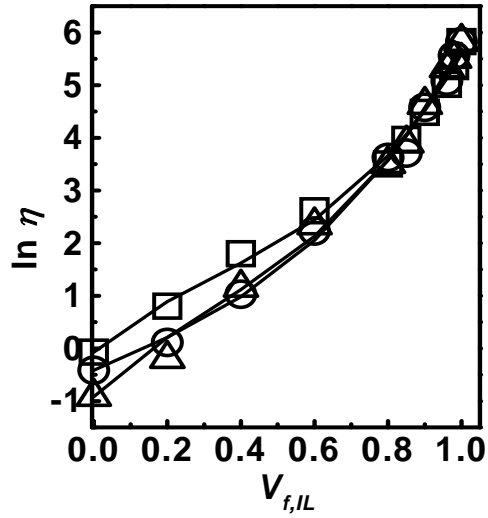
**Figure 4.3:** The  $\ln \eta - V_{f,IL}$  plots for the mixtures of [4-MBP][BF<sub>4</sub>] with water ( $\square$ ), methanol ( $\circ$ ), dichloromethane ( $\triangle$ ) at 298.15 K

The viscosities were also measured in the presence of dichloromethane. However, the viscosities of ionic liquids did not sharply decrease upon addition of dichloromethane. This decrease in the viscosity value was about 15 % from the viscosity data except for [TBP][Val], where the viscosity of pure ionic liquids declined by about 22 %. The mixtures of [BMIM][BF<sub>4</sub>] in water at 298.15 K exhibited the above observed behavior when plotted against molar concentration or mole fraction of ionic liquids.<sup>11</sup> On the contrary such behavior was not witnessed when one ionic liquids was mixed with another ionic liquids.<sup>12</sup>

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**Figure 4.4:** The  $\ln \eta - V_{f,IL}$  plots for the mixtures of [TBP][Val] with water ( $\square$ ), methanol ( $\circ$ ), dichloromethane ( $\triangle$ ) at 298.15 K.



**Figure 4.5:** The  $\ln \eta - V_{f,IL}$  plots for the mixtures of [TBP][Ala] with water ( $\square$ ), methanol ( $\circ$ ), dichloromethane ( $\triangle$ ) at 298.15 K

The viscosities of these mixtures can be fitted to the equation of the form:

$$\ln \eta = \sum_{i=1} q_i V_{f,S}^{(i-1)} \quad (4.3)$$

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where,  $q_i$  s are the adjustable parameters.

The mixture viscosity data were regressed using Eq. 4.3 to give the values of these parameters, which are listed in Table 4.2 together with root mean squares of fits,  $\sigma$ .

**Table 4.2 The Adjustable Parameters,  $q_1, q_2, q_3$  and  $q_4$  of Eq. (4.3) for Correlating  $\ln \eta$  With  $V_{f,IL}$  at  $T = 298.15$  K Together with Root Mean Squares Deviation,  $\sigma$**

Solvents	$q_1$	$q_2$	$q_3$	$q_4$	$\sigma$
<b>[BP][BF<sub>4</sub>]</b>					
Water	4.9783	-22.405 ± 1.792	37.629 ± 5.463	-20.434 ± 3.993	0.349
Methanol	4.9783	-13.645 ± 0.284	13.222 ± 0.867	-4.991 ± 0.625	0.055
Dichloromethane	4.9783	-7.402 ± 0.314	1.549 ± 0.375	0	0.126
<b>[3-MBP][BF<sub>4</sub>]</b>					
Water	5.1162	-22.646 ± 1.829	38.584 ± 5.767	-21.303 ± 4.158	0.369
Methanol	5.1162	-16.330 ± 0.873	19.109 ± 2.662	-8.382 ± 1.919	0.170
Dichloromethane	5.1162	-7.775 ± 0.351	1.895 ± 0.419	0	0.140
<b>[4-MBP][BF<sub>4</sub>]</b>					
Water	5.3016	-25.563 ± 1.813	43.800 ± 5.526	23.764 ± 3.984	0.353
Methanol	5.3016	-17.672 ± 0.690	21.609 ± 2.103	-9.707 ± 1.516	0.135
Dichloromethane	5.3016	-8.967 ± 0.431	2.802 ± 0.515	0	0.172

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		<b>[TBP][Ala]</b>				
Water	5.8245	-14.699 ± 0.978	19.591 ± 2.962	-10.875 ± 2.122	0.183	
Methanol	5.8245	-13.872 ± 0.964	13.021 ± 2.920	-5.451 ± 2.092	0.180	
Dichloromethane	5.8245	-10.887 ± 0.601	4.249 ± 0.718	0	0.238	
		<b>[TBP][Val]</b>				
Water	6.0382	-14.147 ± 1.191	16.579 ± 3.517	-8.612 ± 2.465	0.194	
Methanol	6.0382	-14.981 ± 0.757	16.605 ± 2.292	-8.130 ± 1.642	0.141	
Dichloromethane	6.0382	-10.814 ± 0.451	3.876 ± 0.538	0	0.178	

In order to examine the temperature dependence of the viscosities of binary mixture of one of the ionic liquids, [4-MBP][BF<sub>4</sub>] was chosen for the convenience in water as a function of temperature at constant compositions. These data (Table 4.3) are plotted in Figure 4.6 at two different temperatures to demonstrate the effect of temperature.

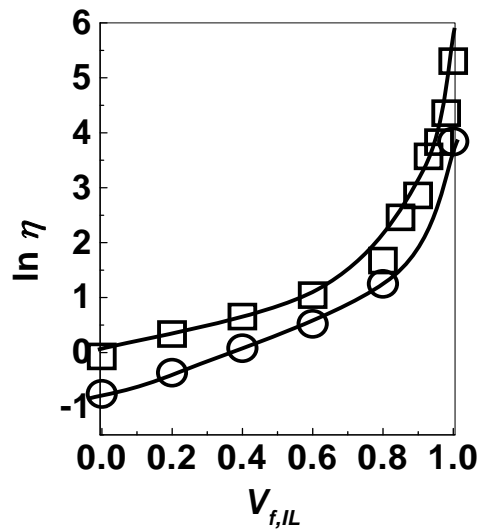
**Table 4.3: Viscosities,  $\eta$  of the Binary Mixtures of [4-MBP][BF<sub>4</sub>] in Water as a Function of Temperature**

Composition $V_{f,IL}$	$T/K$					
	298.15	303.15	308.15	313.15	318.15	323.15
	$\eta / \text{mPa. S}$					
0	0.93	0.84	0.76	0.66	0.53	0.47



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0.20	1.40	1.18	1.04	0.94	0.81	0.69
0.40	1.92	1.69	1.50	1.34	1.21	1.08
0.60	2.84	2.47	2.17	2.05	1.89	1.68
0.80	5.32	4.73	4.16	3.83	3.59	3.49
1.00	200.65	138.10	100.87	77.15	59.76	46.53



**Figure 4.6:** The plots of  $\ln \eta$  vs  $V_{f,IL}$  for aqueous [4-MBP][BF<sub>4</sub>] ionic liquid at 298.15 K (□) and 323.15 K (○)

The viscosity data were also fitted to the equation of the following form:

$$\ln \eta = \sum_{i=1} (\sum_{j=1} a_{ij} T^{(j-1)}) V_{f,s}^{(i-1)} \quad (4.4)$$

where  $a_{ij}$ s, the adjustable parameters are used to describe temperature dependence of viscosities.

**Table 4.4** The Adjustable Parameters  $a_{ij}$  of Eq. (4.4) to Describe the Composition  $V_{f,s}$  and Temperature Dependence for the Viscosities of the [4-MBP][BF<sub>4</sub>]-Water Mixtures

#### 4. Viscosity behavior

<i>J</i>	<i>i = 1</i>	<i>2</i>	<i>3</i>	<i>4</i>
1	81.26	-1018.60	2562.95	-1675.31
2	-0.437	6.096	-15.602	10.285
3	0.0006	-0.0093	0.0238	-0.0159

Pure ionic liquids are characterized by the presence of aggregates, caused by short range interaction forces. Molecular organization of ionic liquids as revealed by diffraction data<sup>13</sup> can be considered in term of enhanced local structure in contrast to that noted in homogeneous liquids. The presence of aggregates in pure ionic liquids has been supported by computer simulations<sup>14</sup> suggesting the aggregation of alkyl tails through van der waal attraction. On the other hand, the ionic head groups and the anions are distributed more homogeneously forming a continuous network of ionic channels. Upon addition of solvents like water in pure ionic liquids, these aggregates begin to dissociate into free cations and anions. Cations and anions are more free in the water-rich mixtures than in the water-poor regions. This is probably the reason of sharp decline in the viscosity of pure ionic liquids when water or any solvent is added. Water because of its high relative permittivity weakens electrostatic force operating between ions. However, methanol or dichloromethane when added to pure ionic liquid cannot fully dissociate cations and anions due their lower relative permittivity. This is due to the difference in the ion-dipole interactions between the ions and solvents. The polar or dipolar solvents of high dielectric constant show better miscibility with ionic liquids while nonpolar solvents shows poorer miscibility,<sup>15</sup> indicating that polar solvents have stronger molecular interaction with ionic liquids. Thus, solvents of high dielectric constant are more effective in reducing the electrostatic attraction between the ions of ionic liquids and hence reduce the viscosity more effectively than the solvents of lower dielectric constant. Recently, it has been found that the addition of water may change the molecular structure of ionic liquids,<sup>16, 17</sup> probably due to hydrogen bonding between the water molecules and the anions of the ionic liquids.<sup>18, 19</sup> So it is expected that water has the largest effect on the

#### 4. Viscosity behavior

viscosity of the ionic liquids in the ionic liquids rich region due to the high relative permittivity of water and the ability to form hydrogen bonds.

Currently we are determining the aggregation in pure ionic liquids using small angle neutron scattering to understand the origin of forces operating in ionic liquids and their mixtures with solvents.

##### 4.1.3.2 Temperature dependence viscosity of ionic liquids

The data for aqueous [4-MBP][BF<sub>4</sub>] shows that the decrease in the viscosity of pure ionic liquid is less prominent at higher temperatures owing to faster movement of ions at higher temperatures. The increased temperature also leads to the loosening of aggregates in pure ionic liquids. This is in agreement with the observations made by one of the authors, who measured the viscosities of tetra butyl ammonium picrate and anisole at different above the melting point of tetra butyl ammonium picrate.<sup>20</sup> The system was characterized to possess liquid phase throughout the composition. This observation was noted by Pitzer on the basis experimental viscosity data of the system at 298.15 K.<sup>21</sup>

The effect was also made to determine temperature dependence of viscosities pyridinium based ionic liquids shown in Figure 4.7.

**Table 4.5: Viscosities,  $\eta$  of the Pyridinium Based Ionic Liquids as Function of Temperature**

Temperature <i>T/K</i>	<i><math>\eta</math> /cP</i>		
	[BP][BF <sub>4</sub> ]	[3-MBP][BF <sub>4</sub> ]	[4-MBP][BF <sub>4</sub> ]
298.15	145.23	166.7	200.65
303.15	90.60	95.53	138.10
308.15	66.10	70.20	100.86
313.15	49.95	52.26	77.15
318.15	38.23	40.96	59.76
323.15	30.27	33.00	46.53
328.15	24.90	-	-

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333.15	21.17	-	-
338.15	17.90	-	-
343.15	15.60	-	-

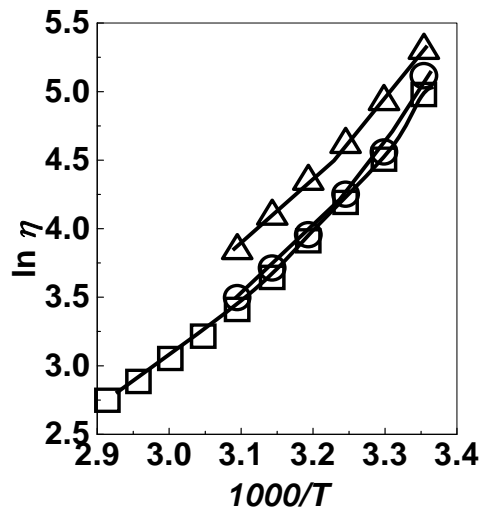
The plots indicate that the viscosity data of these ionic liquids (Table 4.5) cannot be represented by Arrhenius equation. Attempts were also made to initially fit these data to the original VFT equation.<sup>22-25</sup> The use of the equation, however, did not result into accurate fitting of the  $\ln \eta - 1/T$  data.

The modified VFT equation is of the form.

$$\ln \eta = \ln A + 0.5 \ln T + k / (T - T_0) \quad (4.5)$$

where,  $T_0$  is glass transition temperature,  $k$  and  $A$  are the adjustable parameters.

The values of  $A$ ,  $k$  and  $T_0$  as determined from the least squares analysis of the viscosity data tabulated in Table 4.6.



**Figure 4.7:** The  $\ln \eta - 1000/T$  plots for ionic liquids [BP][BF<sub>4</sub>] (□), [3-MBP][BF<sub>4</sub>] (○), [4-MBP][BF<sub>4</sub>] (△)

#### 4. Viscosity behavior

**Table 4.6: Correlation Parameters of VFT Equation as Expressed by Eq. (4.5) with  $\sigma$  of Fits**

Ionic liquids	$\ln A$	$K / T$	$T_o / K$	$\sigma(\ln \eta_o)$
[BP][BF <sub>4</sub> ]	$-2.9010 \pm 0.1647$	$270.84 \pm 23.69$	$244.10 \pm 3.00$	0.017
[3-MBP][BF <sub>4</sub> ]	$-1.4103 \pm 0.3976$	$114.55 \pm 32.42$	$266.87 \pm 5.39$	0.034
[4-MBP][BF <sub>4</sub> ]	$-3.9149 \pm 0.7083$	$521.64 \pm 131.58$	$216.15 \pm 11.50$	0.012

From the examination of Table 4.6 it is confirmed that the temperature dependence of viscosity of these ionic liquids can be fitted the modified VFT equation. However, no direct relationship between the VFT parameters and the structures of ionic liquids can be established at this stage of the work. Experimental viscosity data of many ionic liquids at different temperatures are required before a definite statement can be made on this aspect.

#### 4.1.4 Conclusions

In summary, we have demonstrated a sharp decline in viscosities of ionic liquids upon the addition of solvent like water, which is an environment-benign solvent. It is possible to dilute the high viscosities-ionic liquids with water to reduce viscosities of solvent systems to allow a chemical reaction to realize at a faster rate, as reactions, for example, bi-molecular ones have been noted to retard in ionic liquids possessing high viscosities. The miscibility of an ionic liquid in solvent like water however remains a pre-requisite for such a condition.

## **4.2. Correlation of Viscosities of Ionic Liquids in Aqueous and Non Aqueous Solutions**

### **4.2.1 Introduction**

A new method is developed to correlate viscosities of ionic liquids of aqueous and non aqueous solutions. The method involves two parameters characterizing solution number and ion-solvent interaction coefficient. The strength of the proposed method lies in the fact that both the parameters are well documented quantities.

Viscosities of the dilute ionic solution have been correlated with their concentration using simple Jones-Dole equation.<sup>26</sup> Jones-Dole equation is two parameter equation based upon regression of viscosity –concentration data. Later modification of the Jones-Dole equation has been presented to account for the concentration effect.<sup>27</sup> Viscosity of solvent plays important role in influencing kinetics of organic reactions. For example, we have recently demonstrated that the rates of bimolecular Diels-Alder reactions increased in various organic solvents possessing the range of viscosities as high as 1.2 cP.<sup>28</sup> Further, a drop in rates was observed in solvents having viscosities higher than or equal to 1.2 cP. These enhanced rates were discussed in terms of vibration activation theory, while the inhibiting effect by the diffusional barrier in the encounter controlled region.

However, the use of volatile organic solvents during the organic or other chemical processes has come under scanner due to the environment pollution posed by them. In search of developing alternative solvent media for the organic reactions, ionic liquids have attracted attention of organic chemist and chemical process engineers. Ionic liquids possess negligible vapor pressure are easy to synthesize and can be recycled several times to give comparable yields. Several reports are available on structure, properties of ionic liquids and their applications to a variety of phenomena.

Viscosity of ionic liquids can be very high and there ore can be detrimental to the progress of chemical reactions. Very recently, we showed that the rate constant of simple Diels- Alder reactions decreased with an increased in viscosities of ionic liquids chosen for the study.<sup>3</sup> These experiments were designed to conduct the above reactions in ionic liquids of graded viscosities. In last we have demonstrated that the viscosity of ionic

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liquids can be dramatically reduces by adding a very small amount of solvents. The extent of fall in viscosities of ionic liquids on adding molecular solvents was noted to depend on the polarity of the solvents. It was seen that higher is the relative permittivity of the solvent, higher is the fall in the viscosities.

#### 4.2.3. Results and Discussions

In order to develop a suitable method to correlate viscosity with composition of an ionic liquid, we assume that the ionic liquid, MX forms a solvation complex with solvent molecules, S as



where  $q$  indicates number of molecules of the solvents involved in forming solvation complex.

Now that since ionic liquid is soluble in the solvent, it is dissociated into its ions in the solution. Note that molar ratio of MX and S is related to the concentration of MX. In the situation, where MX is too low and solvent S is in the excess, the value of  $q$  will be a governing factor for the molar ratio. In this region  $[\text{S}]/[\text{MX}] \geq q$  assuming that entirely saturated factor coordination sphere is predominant. This means that this is a solution of MX. $q$ S. In the region in which the solvent is in deficit quantity, we assume the process of desolvation of above complex MX. $q$ S. to take place. This process contains the complex species such as MX. $q$ S, MX. $(q-1)$ S, MX. $(q-2)$ S and so on.

We prefer mole fraction as a concentration scale. Let us now denote the number of moles of ionic liquids, solvent and of solvation complex by  $N_{\text{IL}}$ ,  $N_{\text{S}}$  and  $N_{\text{c}}$  to yield following definitions of mole fractions of corresponding quantities as

$$x_{\text{IL}} = N_{\text{IL}} / (N_{\text{IL}} + N_{\text{S}}) \quad (4.7)$$

$$x_{\text{c}} = N_{\text{c}} / [N_{\text{c}} + (N_{\text{S}} - qN_{\text{c}})] \quad (4.8)$$

and  $x_{\text{s}} = 1 - x_{\text{IL}} - x_{\text{c}} \quad (4.9)$

Assuming that  $N_{\text{IL}} = N_{\text{c}}$ , it is possible to obtain  $N_{\text{S}}$  from Eq. 4.7 as

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$$N_s = N_c(1 - x_c/x_{IL}) \quad (4.10)$$

Substitution of  $N_s$  from Eq. 4.10 in to Eq. 4.8 gives rise to

$$x_c = x_{IL}/(1 - x_{IL} \cdot q) \quad (4.11)$$

Eq. 4.11 connects the mole fraction of ionic liquids with that of solvent complex.

Following the proportionality between viscosities and concentration and assuming that one of the species of the complex is predominant.<sup>29</sup>

$$(\eta_{rel} - 1) \propto x_c = Bx_c/(1 - x_c q) \quad (4.12)$$

where  $\eta_{rel} = \eta/\eta_o$ ,  $\eta$  and  $\eta_o$  are the viscosities of the solution and solvents, respectively and  $B$  is constant.

The above equation can be conveniently expressed as

$$1/(\eta_{rel} - 1) = -q/B + 1/Bx_c \quad (4.13)$$

is an operational equation to analyse the viscosity of ionic liquids solutions. This is a linear expression with respect to  $1/x_c$ . One should note that the  $B$  value is extracted on mole fraction basis which can be converted to  $\text{dm}^3 \text{mol}^{-1}$  using Jones-Dole equation. However, these units are interconvertible using density of the solution.

Out of these two coefficient in Eq. 4.13 the coefficient hydration or solvation number of ionic species a monograph published by Marcus offers details discussion on physical significance of ' $q$ ' values in solution chemistry. In absence, hydration or solvation number of ion is a number of water or solvent molecule associate with ion in specified manner and leads to different values for specific ion depending on the methodology used. The  $B$  value is a well established quantity in the literature was first extracted from the use of Jones-Dole equation for analyzing viscosity data of dilute electrolyte solution. The  $B$  values indicate the ion solvent interactions and have been widely used for valuable information regarding the structure making and structure breaking capabilities of ionic species. A detailed discussion on this aspect is given by Feakins and Lawrance.<sup>30</sup>

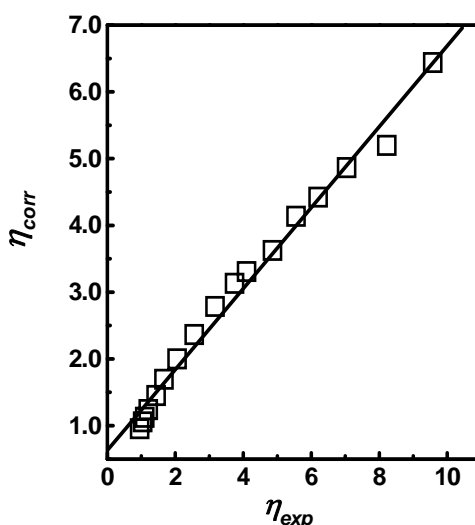
First Eq. 4.13 was applied to analyse the viscosity data of aqueous  $\text{CaCl}_2$  at 298.15 K for the purpose of testing of viscosity of aqueous electrolyte. The analysis resulted into values of  $q = 6$  with  $B = 19.30$ . The correlation coefficient  $r$  and root mean square  $\sigma$  for



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the equation are 0.999 and 0.198, respectively for a total number of 17 points.<sup>31</sup> The correlated viscosity,  $\eta_{corr}$  of aqueous  $\text{CaCl}_2$  are plotted against  $\eta_{exp}$  in Figure 4.8.

where we observed excellent ability of Eq. 4.13 to correlate viscosity of concentrated aqueous  $\text{CaCl}_2$ . Both the values  $q$  and  $B$  are in good agreement with the literature. With a confidence in our method, Now the Eq. 4.13 is used to analyze viscosity data of binary mixtures of the imidazolium and pyridinium-based ionic liquids with different molecular solvents.



**Figure 4.8:** The plots of  $\eta_{corr}$  versus  $\eta_{exp}$  for  $\text{CaCl}_2$ -water system.

First the viscosity data of the imidazolium –based ionic liquids were analysed in a variety of solvents. The temperature dependant viscosity data are also used for determining the  $q$  and  $B$  parameters in order to study the temperature effect. A simple ionic liquid, called 1-butyl-3-methyl imidazolium tetrafluoroborate abbreviated as [BMIM][ $\text{BF}_4$ ] in 13 different solvents with varying properties was analyzed for their viscosities. The results of these calculations are given in Table 4.7, where the values of  $q$  and  $B$  are listed together with  $r$ ,  $\sigma$  and  $N$  values. The values of  $r$ ,  $\sigma$  and  $N$  indicate correlation coefficient, rmsd and number of data points, respectively. The result of the regression of the experimental viscosity  $\eta$  data on the imidazolium ionic liquids are listed in Table 4.7.

## 4. Viscosity behavior

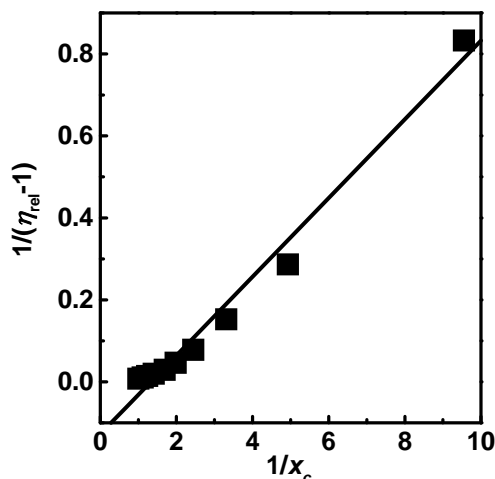
**Table 4.7: The Tabulated Data for the Parameters  $q$  and  $B$  for Ionic liquids**

Solvents/ Parameters	$q$	$B$	$N$	$r$	$\sigma$
<b>[BMIM][BF<sub>4</sub>]</b>					
Water	1.326	10.42	10	0.991	0.037
Dichloromethane	1.310	21.52	10	0.975	0.019
Chloroform	12.22	39.82	10	0.987	0.008
Methanol	0.668	23.78	10	0.973	0.039
1-Propanol	0.744	6.93	10	0.996	0.148
2-Propanol	1.143	6.59	10	0.999	0.031
Acetone	1.473	12.10	14	0.997	0.031
Methyl formate	1.664	12.94	14	0.991	0.575
Ethyl formate	1.671	9.72	14	0.990	0.079
Methyl acetate	1.617	9.51	14	0.995	0.058
Acetonitrile	1.40	14.13	14	0.999	0.019
Dichloromethane	1.549	14.22	12	0.996	0.036
2-Butanone	1.561	9.74	14	0.997	0.045
<i>N, N</i> dimethyl formamide	1.830	8.59	14	0.999	0.032
<b>[OMIM][BF<sub>4</sub>]</b>					
Methanol	1.781	12.24	13	0.993	0.054
Ethanol	1.560	10.53	13	0.997	0.039
1-propanol	1.470	8.73	13	0.999	0.033
2-propanol	1.419	9.21	13	0.999	0.237
<b>[BP][BF<sub>4</sub>]</b>					
Water	1.042	21.37	10	0.999	0.009
Methanol	1.798	11.40	10	0.995	0.084
Dichloromethane	1.161	22.06	10	0.996	0.014
<b>[3-MBP][BF<sub>4</sub>]</b>					
Water	1.071	23.74	10	0.999	0.028

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Methanol	1.992	10.07	10	0.999	0.126
Dichloromethane	1.255	25.78	10	0.994	0.017
<b>[4-MBP][BF<sub>4</sub>]</b>					
Water	0.194	21.89	10	0.994	0.078
Methanol	1.851	10.66	10	0.995	0.095
Dichloromethane	1.473	13.05	10	0.973	0.067

An examination of the results of  $r$  and  $\sigma$  presented in the Table 4.7 shows that Eq. 4.13 can correlate the viscosities of [BMIM][BF<sub>4</sub>] in different solvents with high accuracy as the average  $r$  and  $rmsd$  values are 0.995 and 0.041, respectively without the system involving methyl formate for which  $rmsd$  was quite high as 0.575. A total of 156 points were taken under consideration.

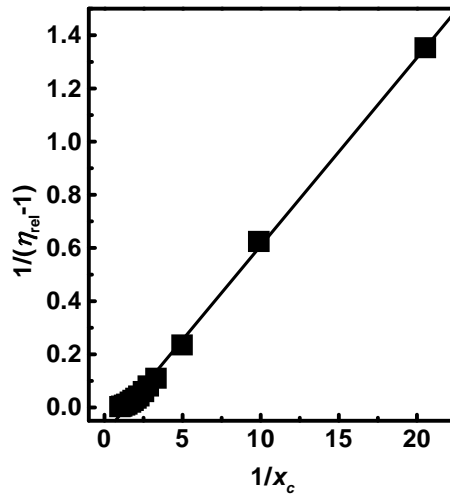


**Figure 4.9:** The plots of  $1/(\eta_{rel}-1)$  versus  $1/x_c$  for the [BMIM][BF<sub>4</sub>]-water system at 298.15K.

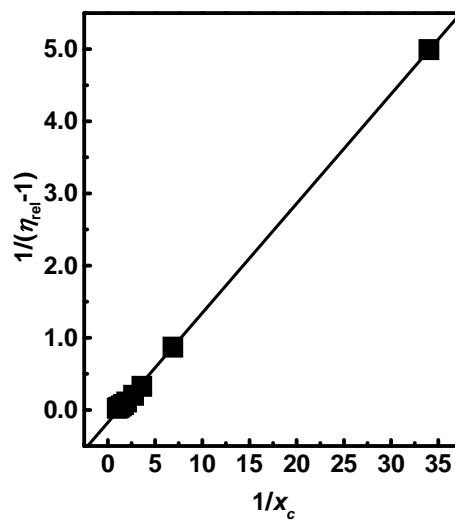
The results of our work are plotted in Figure 4.9, in which  $1/(\eta_{rel}-1)$  is plotted against  $1/x_c$  showing reasonably straight line. The results on some ionic liquids in water, acetonitrile and 2-propanol, respectively are shown in Figures 4.9 to 4.11, in which  $1/(\eta_{rel}-1)$  is plotted against  $1/x_c$  showing fair linear relationship.

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Further, the viscosity data for four different systems comprising [OMIM][BF<sub>4</sub>] in methanol, ethanol, 1-propanol and 2-propanol were investigated. While the correlation of  $\eta$  values for these systems was accounted for methanol, ethanol and 1-propanol systems, higher rsmd of 0.237 as compared to an average rsmd of 0.037 was noted.



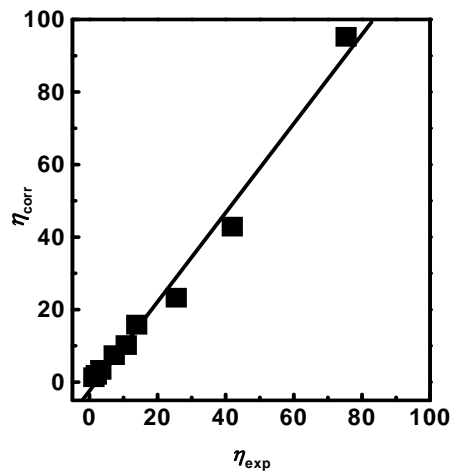
**Figure 4.10:** The plots of  $1/(\eta_{rel}-1)$  against  $1/x_c$  for the [BMIM][BF<sub>4</sub>]-acetonitrile system at 298.15K



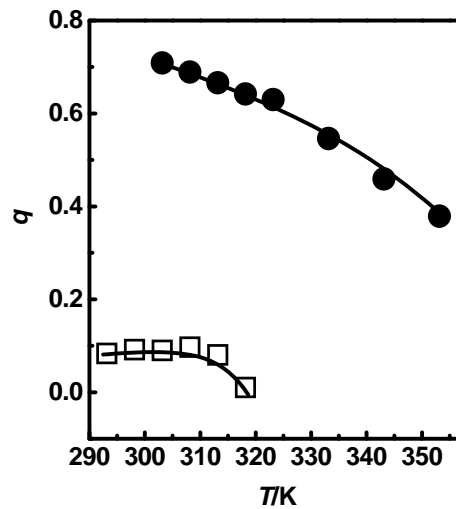
**Figure 4.11:** The plots of  $1/(\eta_{rel}-1)-1/x_c$  for the [BMIM][BF<sub>4</sub>]-2-propanol system

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We now examine the viscosity data for three pyridinium-based ionic liquids in three different solvents possessing different polarities. The results are summarized in Table 4.7. The evidence of the fitting ability of Eq. 4.13 is demonstrated in Figure 4.12 in which the  $\eta_{\text{exp}}$  values plotted against  $\eta_{\text{corr}}$  for [BP][BF<sub>4</sub>] in water. An examination of the plots drawn in Figure 4.12 demonstrates that one can correlate the viscosity of these ionic liquids solutions with high accuracy as shown in terms of an average  $\sigma$  of 0.009 with all 13 experimental data points under taken during correlations.



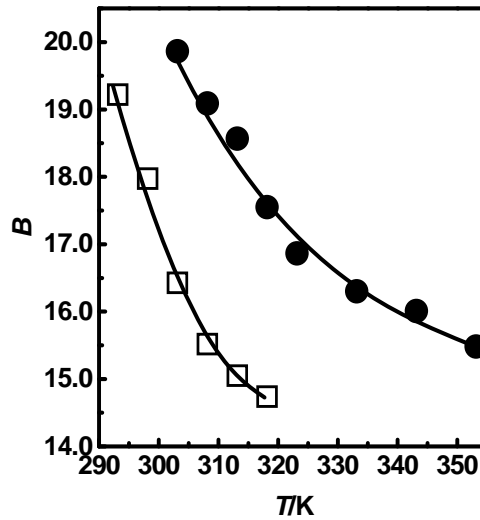
**Figure 4.12:** The plots of  $\eta_{\text{corr}}$  versus  $\eta_{\text{exp}}$  for [BP][BF<sub>4</sub>]-water system at 298.15K



**Figure 4.12:** The plots of  $q$  versus  $T$  for [EMIM][BF<sub>4</sub>]-water (□) and [BMIM][BF<sub>4</sub>]-water systems(●).

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Further, the values of  $q$  in all the system is in the range of 1 to 2. The ionic liquids possess cations which are often attached with alkyl groups. The presence of these alkyl groups gives rise to hydrophobic hydration.<sup>32</sup> In such a case, the water molecules do not come in the vicinity cationic charge thereby leading to a very less hydration or solvation number as indicated by the  $q$  values reported in Table 4.7.



**Figure 4.13:** The plots of  $B - T$  for aqueous  $[\text{EMIM}][\text{BF}_4]$  ( $\square$ ) and  $[\text{BMIM}][\text{BF}_4]$  systems ( $\bullet$ ).

Temperature dependent of viscosity data can also be analyzed in the light of this approach. Both the parameters show appreciable temperature dependence, which can be expressed in terms of:

$$q_T = q_0 + q_1(T - 298.15) + q_2(T - 298.15)^2 \quad (4.14)$$

where  $q_T$  is the value of  $q$  at temperature  $T$ . The  $q_0$ ,  $q_1$  and  $q_2$  are the adjustable parameters. Similarly, the temperature dependence of  $B$  expressed in terms of  $b_0$ ,  $b_1$  and  $b_2$  can be seen as  $b_0 = 0.723 \pm 0.009$ ,  $b_1 = -0.0026 \pm 0.0007$  and  $b_2 = -0.0007 \pm 0.0001$  for aqueous  $[\text{BMIM}][\text{BF}_4]$  solution. A typical temperature dependence of  $q$  and  $B$  is shown in Figure 4.12 and 4.13, respectively. A set of  $q_0$ ,  $q_1$  and  $q_2$  values, for example. For

#### 4. Viscosity behavior

[BMIM][BF<sub>4</sub>] in water are  $20.81 \pm 0.25$ ,  $-0.192 \pm 0.020$  and  $0.0017 \pm 0.0003$ , respectively.

In summary, an attempt has been made to correlate viscosities of the solution of ionic liquids with the help of two adjustable parameters. Both the parameters possess physical significance and are well established quantities. One can correlate the viscosities of the ionic liquids using this model with good accuracy.

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## **Chapter 5**

# **Electrochemical Oxidation of Anthracene in Ionic Liquids: Existence of Organized Interfacial Layers**

## 5. Electrochemical Oxidation of Anthracene in Ionic Liquids: Existence of Organized Interfacial Layers

### 5.1 Introduction

The main aim driving the discovery of ionic liquids was to design efficient materials used in different fields<sup>1</sup> especially in electrochemistry. The high electrochemical window of ionic liquids has indeed lead to increasing attention in recent years especially in area of electrochemical applications of these novel media. Since ionic liquids can act as both solvent and electrolyte, they are also being used in an increasing number of electrochemical applications, including supercapacitors,<sup>2, 3</sup> batteries,<sup>4, 5</sup> dye-sensitized solar cells,<sup>6, 7</sup> and electrodeposition.<sup>8, 9</sup> First-generation haloaluminate ionic liquids initially received much attention for electrochemical applications. However, because of substantial air- and moisture sensitivity, wider applications of haloaluminate ionic liquids have been limited. Second-generation ionic liquids containing anions such as tetrafluoroborate,  $[\text{BF}_4]^-$ ,  $[\text{PF}_6]^-$ , and  $[\text{NTf}_2]^-$ , were subsequently developed, which showed better air and water stability. Of these ionic liquids, those containing the  $[\text{NTf}_2]^-$  anion showed the best stability as they do not form HF when in contact with water.<sup>10</sup>

Electrochemical investigations of the mass and charge-transfer kinetics of a variety of redox species have been studied using water- and air-stable ionic liquids.<sup>11, 12</sup> Efficient removal of water can also be extremely important as the electrochemical potential window of many ionic liquids narrows as the water content increases.<sup>13</sup> Adventitious water can also have a dramatic effect on viscosity. The most commonly used method for water removal from ionic liquids is heating under reduced pressure.

The reports available on the cyclic voltammetry and kinetics of  $\text{TMPD}/\text{TMPD}^+$  (*N,N,N,N*-tetra methyl-*p*-phenylenediamine) and  $\text{Ag}/\text{Ag}^+$  was studied in the different type of ionic liquids calculated diffusion coefficient and compared heterogeneous rate constants of TMPD and Ag in ionic liquids.<sup>14</sup> The diffusion coefficients of a redox couple vary considerably between the neutral and radical ion forms of the molecule in ionic liquids. In room temperature ionic liquids, organic molecules display some important variations of their diffusion coefficients when

reduce to their corresponding radical anions.<sup>15</sup> These results are explained on the basis of ion-pairing associations between the electrogenerated radical anion and the ionic liquid cation. Compton explained the behavior of heterogeneous electron transfer rate constants for anodic oxidation of anthracene and substituted anthracene in different ionic liquids. It has been observed that the rate constants for electrogenerated radical cations and dimerization of anthracene are independent of viscosity of ionic liquids. The formation of 9,10-anthraquinone and bianthrone was observed even expose to water. The effect of the addition of water is to favour the former product.<sup>16</sup> The different group has studied the electrochemical study of different analyte and investigated the diffusion coefficient and rate constants. Literature details show that there is no report available regarding the structure of ionic liquids.

In this chapter, the diffusion of electroactive species like anthracene in different classes of ionic liquids having structural variation has been studied. Diffusion of the electroactive species occurs due to concentration gradient along the electrode-electrolyte interface. Ionic liquids demonstrate very interesting trends in the reduction of oxygen. Our interest is to investigate the influence of structure of ionic liquids on diffusion process. There are few reports of this relationship which has been shown that the Stokes-Einstein relation does not hold, but there have also been reports to the contrary.<sup>17, 18</sup> The apparent contrast might be related to subtle variations in the physicochemical properties and resulting interactions, brought about by the variations in the structure of the cation and/or anion.

## 5.2 Experimental Section

### Chemical reagents

*N*-methyl pyrrolidine, 1-methyl imidazole, pyridine and 1-bromobutane were distilled prior to use. 1-bromohexane, 1-bromooctane and anthracene purchased from Sigma Aldrich. Bis(trifluoromethanesulfonyl)imide lithium, Li(NTf<sub>2</sub>) salt were used as obtained from Fluka.

### Synthesis of ionic liquids

Synthesis of ionic liquids carried out according to reported procedure.<sup>10, 19, 20</sup> The characterization and purity of ionic liquids was carried out using <sup>1</sup>H NMR method.

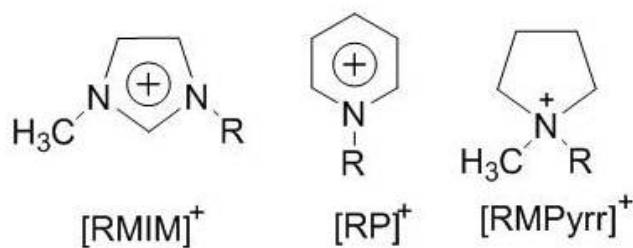
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The water content of ionic liquids was measured by Karl Fischer Titration method and did not exceed 50 ppm. The viscosity measurement carried out using Brookfield ultra rheometer (LV DII Model).

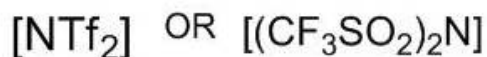
### Instrumental technique

All cyclic voltammetry experiments were carried out using a computer-controlled Autolab potentiostat (Mehtron Switzerland). A three-electrode arrangement, consisting of a 5 mm-diameter platinum working electrode, platinum wire as a counter electrode (having a surface area 1000 times greater than that of the working electrode) and platinum wire as a quasi-reference, was used throughout. The electrodes were housed in a T-cell. The electrode radius of working electrode was calibrated by analyzing the steady-state voltammetry of a 2 mM solution of ferrocene in acetonitrile containing 0.1 M TBAP supporting electrolyte. A value of  $2.3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  for the diffusion coefficient of ferrocene at 293 K was adopted.<sup>21</sup>

The oxidation of anthracene was studied in three series of ionic liquids, imidazolium, pyridinium, pyrrolidinium-based ionic liquids with Bis(trifluoromethylsulphonyl)imide,  $[\text{NTf}_2]^-$  as anion shown in Scheme 5.1.



R=alkyl group



**Scheme 5.1:** Structure of ionic liquids studied.

The ionic liquids are generalized as  $[\text{RMIM}][\text{NTf}_2]$ ,  $[\text{RP}][\text{NTf}_2]$ ,  $[\text{RMPyrr}][\text{NTf}_2]$  and list of all ionic liquids studied with their abbreviated form are tabulated in Table 5.1.

**Table 5.1: Abbreviated Forms of the Ionic Liquids.**

<b>Abbreviations</b>	<b>Name of Ionic Liquids</b>
[BP][NTf <sub>2</sub> ]	1-butylpyridinium bis(trifluoromethylsulfonyl)imide
[HP][NTf <sub>2</sub> ]	1-hexylpyridinium bis(trifluoromethylsulfonyl)imide
[OP][NTf <sub>2</sub> ]	1-octylpyridinium bis(trifluoromethylsulfonyl)imide
[BMIM][NTf <sub>2</sub> ]	1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
[HMIM][NTf <sub>2</sub> ]	1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
[OMIM][NTf <sub>2</sub> ]	1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
[BMPyrr][NTf <sub>2</sub> ]	1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide
[HMPyrr][NTf <sub>2</sub> ]	1-hexyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide
[OMPyrr][NTf <sub>2</sub> ]	1-octyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide

## 5.3 Results and Discussion

### 5.3.1 Diffusion of Anthracene in Ionic Liquids

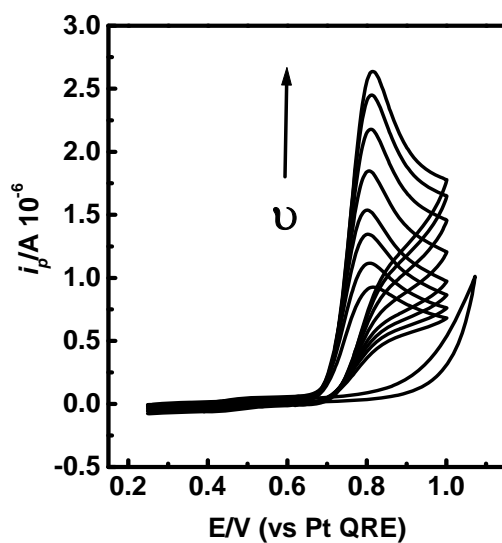
Ionic liquids are ionic in nature and hence are pure electrolytes. The reactivity of ionic species is different as compared to parent molecule. The electron-transfer reactions involving aromatic hydrocarbons have been widely studied in molecular electrochemistry because the resulting cation or anion radicals participate in a large variety of reaction types or mechanisms such as electrophilic, nucleophilic, or free-radical substitutions, additions, or eliminations. The electrochemical oxidation of aromatic molecule, anthracene and its derivatives has been one of the most widely studied.<sup>22</sup> Since the life-time for anthracene cation radicals is in the range of millisecond, hence they are known to be weaker acids as compared to alkylbenzene cation radicals. Then, a nucleophilic attack by residual water nucleophilic species that

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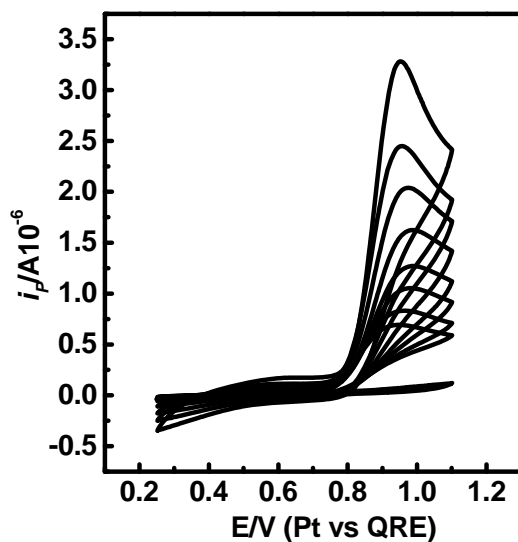
are present in ionic liquids that leads to oxidation of anthracene to produce the corresponding quinone occurs preferably to a deprotonation reaction leading to a side chain oxidation.<sup>23</sup> To investigate the structure and properties of ionic liquids and its effect on diffusion of species in ionic liquids, the electrochemical diffusion of anthracene in the series of ionic liquids is compared in detail. This has led to interesting observations about how the structure of ionic liquids affects the diffusion process and also the mechanism of electron transfer.

The cyclic voltammogram for oxidation of anthracene in different ionic liquids was studied at scan rates of 10, 20, 50, 100, 250, 500, 700, 1000  $\text{mVs}^{-1}$ . A typical cyclic voltammogram for oxidation of anthracene in [BMIM][NTf<sub>2</sub>], [BP][NTf<sub>2</sub>] and [BMPyrr][NTf<sub>2</sub>] are shown in Figures 5.1, 5.2 and 5.3, respectively. The nature of cyclic voltammogram is similar for all the ionic liquids selected for the study. With the conventional cyclic voltammetry at the scan rate below 1V/s, reversible cyclic voltammogram were hardly observed both in the oxidation and the reduction of anthracene because the voltammograms were distorted owing to the subsequent reactions, so that it was very difficult to determine the formal redox potentials. By contrast, reversible or quasireversible cyclic voltammograms were observed for anthracene by eliminating the subsequent reactions at the fast scan rate from 1000V/s to 30000V/s. The current increases with increasing scan rate.

The electrochemical oxidation of anthracene is reversible at high scan rate but irreversible at low scan rate.<sup>24</sup> To limit the interference of the residual ohmic drop with experimental measurements due to the working electrode resistance, special care was taken to compensate the residual ohmic drop, especially for the highest scan rates. Although ionic liquids are pure electrolytes, it was observed that they show a high magnitude of ohmic drop, indicating that the ionic liquids as electrolyte media are more resistant despite their ionic characters. The resistance values with imidazolium-based ionic liquids were low enough to be fully compensated. The behavior is similar to that observed for the well-known one-electron transfer in conventional media. The voltammogram of oxidation of anthracene shows that the electrochemical species generated is stable, forming a cation radical. The irreversible oxidation was observed at scan rates varying between 1-1000  $\text{mV s}^{-1}$ .



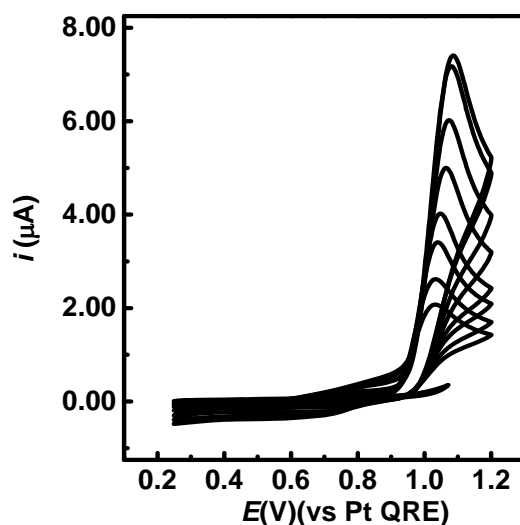
**Figure 5.1:** Cyclic voltammogram for oxidation of anthracene in [BMIM][NTf<sub>2</sub>] at different scan rates



**Figure 5.2:** Cyclic voltammogram for oxidation of anthracene in pyridinium-based ionic liquids [BP][NTf<sub>2</sub>]

The electrochemical oxidation of anthracene has shown that at higher scan rate (greater than  $100 \text{ V s}^{-1}$ ) the oxidation process shows reversible behavior. The peak current  $i_p$  varies linearly with square root of scan rate  $v^{1/2}$  for all ionic liquids showing (Figure 5.4) that a diffusion-controlled electrochemical process occurs at the electrode.





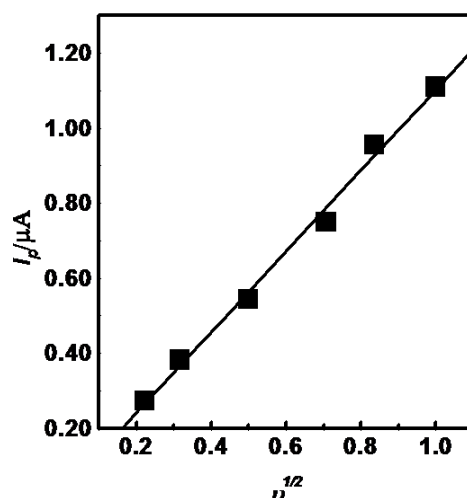
**Figure 5.3:** Cyclic voltammogram for oxidation of anthracene Pyrrolidinium-based ionic liquid [BMPyrr][NTf<sub>2</sub>]

Assuming that system is reversible, we have studied diffusion of anthracene in the ionic liquids and two organic solvents, DMSO and acetonitrile. From slope of the plots of  $i_p$  vs  $\nu^{1/2}$  used for calculation of diffusion coefficient. Using Butler Volmer Eq. 5.1 the diffusion coefficient is calculated in all studied ionic liquids along with two organic solvents shown in Table 5.2.

$$i_p = (2.66 \times 10^5) \alpha^{1/2} A C_0 D^{1/2} \nu^{1/2} \quad (5.1)$$

where  $i_p$  = peak current,  $\alpha$  = charge transfer coefficient,  $A$  = area of electrode,  $C_0$  = concentration of anthracene,  $D$  = diffusion coefficient,  $\nu$  = scan rate.

The diffusion coefficient of anthracene in ionic liquids is found to be 1000 times slower than the conventional organic solvents, dimethyl sulfoxide and acetonitrile. The higher diffusion of anthracene is observed in acetonitrile and dimethyl sulfoxide having  $2.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  and  $1.58 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ , respectively is due to their very low viscosity as compared to ionic liquids which is evident according Stokes-Einstein relation given by Eq. 5.2. In the case of ionic liquids, diffusion process shows different behaviour for different ionic liquids. It is to be noted that since the [NTf<sub>2</sub>] anion is common among all the ionic liquids used, the variations can be attributed to the cation structure.



**Figure 5.4:** The Plots of peak current  $i_p$  vs  $v^{1/2}$  for [HMIM][NTf<sub>2</sub>] for oxidation of anthracene.

The observed diffusion coefficients for pyrrolidinium-based ionic liquids decrease from [BMPyrr][NTf<sub>2</sub>] to [HMPyrr][NTf<sub>2</sub>] to [OMPyrr][NTf<sub>2</sub>] as  $4.68 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$  to  $1.59 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$  to  $0.91 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$  with their corresponding viscosity increases as 79.93 cP to 107.93 cP to 135.77 cP, which is in good agreement with Stoke-Einstein relation shown in Eq. 5.2.

$$D_o = \frac{kT}{6\pi\eta R} \quad (5.2)$$

where  $D_o$  = diffusion coefficient,  $k$  = Boltzmann constants,  $\eta$  = viscosity of medium and  $R$  = hydrodynamic radius. Interestingly, a difference is observed in the case of imidazolium and pyridinium-based ionic liquids, in which opposite trend is observed. The diffusion coefficient for imidazolium-based ionic liquids show an interesting trend as, [OMIM][NTf<sub>2</sub>] ( $2.08 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ ) > [BMIM][NTf<sub>2</sub>] ( $1.95 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ ) > [HMIM][NTf<sub>2</sub>] ( $1.70 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ ) and viscosity varies as [BMIM][NTf<sub>2</sub>] < [HMIM][NTf<sub>2</sub>] < [OMIM][NTf<sub>2</sub>]. This indicates that the diffusion coefficient and viscosity inverse correlation (as represented by the Stoke-Einstein relation) does not hold true. Also for the pyridinium-based ionic liquids, the viscosity increases as [BP][NTf<sub>2</sub>] < [HP][NTf<sub>2</sub>] < [OP][NTf<sub>2</sub>] but the diffusion coefficient of anthracene in these ionic liquids increases as [BP][NTf<sub>2</sub>] < [OP][NTf<sub>2</sub>] < [HP][NTf<sub>2</sub>]. In this series of

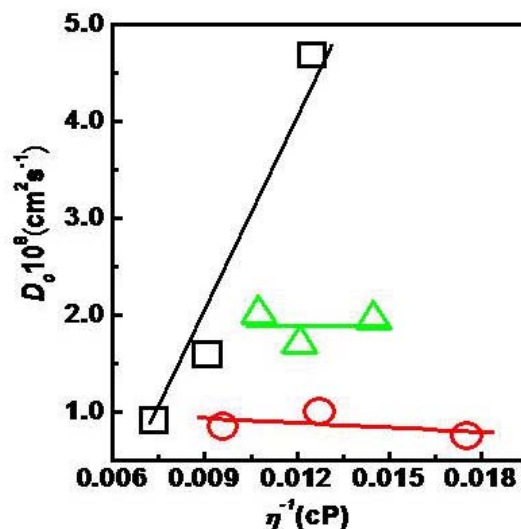
ionic liquids, the change of the current function  $i_p/v^{1/2}$  indicate diffusion coefficients are rather sensitive to structure.

**Table 5.2: Diffusion Coefficient of Anthracene in Ionic Liquids and Solvents at 298.15 K**

Solvents/ Ionic Liquids	$D_0/ \text{cm}^2\text{s}^{-1}$	$\eta/ \text{cP}$
[BMPyrr][NTf <sub>2</sub> ]	$4.68 \times 10^{-8}$	79.93
[HMPyrr][NTf <sub>2</sub> ]	$1.59 \times 10^{-8}$	107.93
[OMPyrr][NTf <sub>2</sub> ]	$0.91 \times 10^{-8}$	135.77
[BP][NTf <sub>2</sub> ]	$0.75 \times 10^{-8}$	57.00
[HP][NTf <sub>2</sub> ]	$1.00 \times 10^{-8}$	78.47
[OP][NTf <sub>2</sub> ]	$0.86 \times 10^{-8}$	107.13
[BMIM][NTf <sub>2</sub> ]	$1.95 \times 10^{-8}$	69
[HMIM][NTf <sub>2</sub> ]	$1.70 \times 10^{-8}$	82.7
[OMIM][NTf <sub>2</sub> ]	$2.08 \times 10^{-8}$	93.0
Acetonitrile	$2.50 \times 10^{-5}$	0.34
Formamide	$1.58 \times 10^{-5}$	3.30

The comparison plots of diffusion coefficient  $D_0$  vs viscosity  $\eta^{-1}$  for all the ionic liquids are shown in Figure 5.5. From the plot, it is seen that the pyrrolidinium-based ionic liquids show linear relation between  $D_0$  and  $\eta^{-1}$ , that is diffusion coefficient decreases with increase in viscosity of ionic liquids. The pyridinium and imidazolium-based ionic liquids shows constant behavior that is the diffusion coefficient does not change consistently with a change in viscosity of these ionic liquids. The observed behaviour probably arises due factors other than viscosity, which can influence the transport phenomenon. In pyrrolidinium-based ionic liquids, the cation consists of a five-membered cyclic ring, having quaternized nitrogen as hetero atom. The relation between  $D_0$  vs  $\eta^{-1}$  shown in Figure 5.5 follows the Stokes – Einstein relation, indicating that the viscosity of pyrrolidinium ionic liquids is dominant over other interactions as the decisive parameter affecting the diffusion of anthracene. But in the case of imidazolium-based ionic liquids, a  $\pi$  electron cloud is

present above and below the cationic ring. The relation  $D_0$  vs  $\eta^{-1}$  for imidazolium-based ionic liquids does not follow according to Stoke-Einstein relation.



**Figure 5.5:** The plots of diffusion coefficient  $D_0$  vs  $\eta^{-1}$  pyrrolidinium (□), pyridinium (○) and imidazolium (△) based ionic liquids.

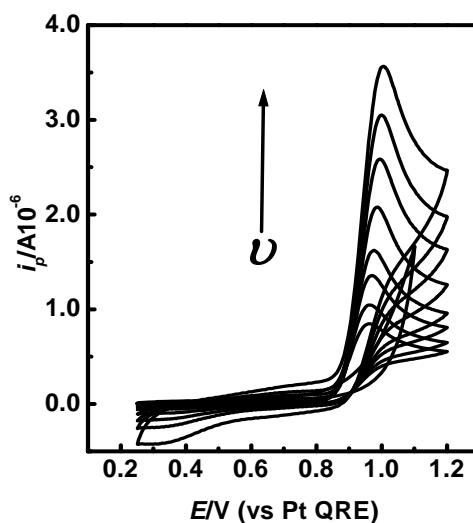
This demonstrates that the viscosity is not the sole factor responsible for diffusion of anthracene in imidazolium-based ionic liquids. It has been observed that the anthracene molecule, having an extended  $\pi$  electron system, is capable of interacting with the imidazolium cations through  $\pi$ - $\pi$  stacking interaction. There are reports available for the evidences of  $\pi$ - $\pi$  stacking interaction present in the anthracene and benzene-related compounds.<sup>25, 26</sup> For confirmation of this conclusion we have studied diffusion of anthracene in pyridinium-based ionic liquids which also have a  $\pi$ -electron delocalised over the cation. The ionic liquids are [BP][NTf<sub>2</sub>], [HP][NTf<sub>2</sub>], [OP][NTf<sub>2</sub>] and their viscosity increases as (57 cP) [BP][NTf<sub>2</sub>] < (78.47cP) [HP][NTf<sub>2</sub>] < (107.31 cP) [OP][NTf<sub>2</sub>]. It has been observed that the pyridinium-based ionic liquids show behaviour similar to the imidazolium-based ionic liquids. This confirms the hypothesis that the aromatic cation-anthracene  $\pi$ -stacking interactions lead to a complex diffusion process. Such interactions can have implications for the mechanistic aspects of the electrochemical process being studied.

### 5.3.2 Mechanistic Aspect of Oxidation of Anthracene in Ionic Liquids

#### 5.3.2.1 Reversible and irreversible oxidation of anthracene

As a general rule, the electrode kinetics determined through heterogeneous standard rate constants can be studied at higher scan rates of  $3000\text{-}5000\text{Vs}^{-1}$  using ultramicroelectrode. It has been reported that the rate constants  $k_s$  in ionic liquids are about  $0.7$  and  $0.1\text{ cm s}^{-1}$ .<sup>24</sup> These values are about 10 times lower than those observed in more conventional media. The plots of the peak current for the heterogeneous electron-transfer step versus the anodic peak potential  $E_p$  of the cyclic voltammogram shows that the electrochemical process is reversible or irreversible. Under these conditions, the charge-transfer process is intrinsically slow, and the kinetic control of the electrochemical reaction is not significantly affected by the follow-up reaction.

The assumption of reversibility in the previous section for determining diffusion coefficients needs a closer inspection, due to the observed inconsistency with respect to the Stokes-Einstein equation.

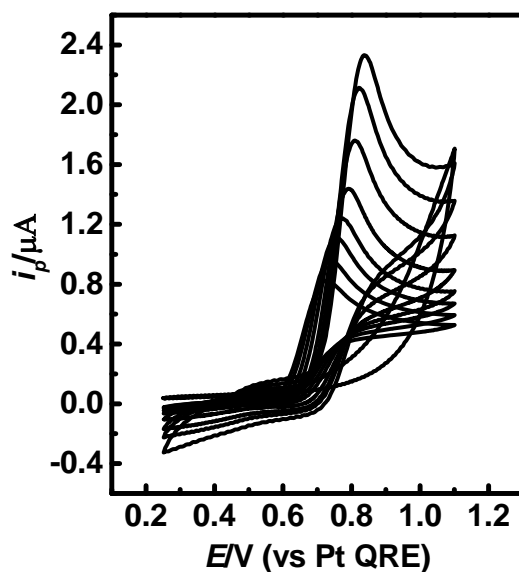


**Figure 5.6:** Plot of  $i_p$  vs  $E$  for oxidation of anthracene [OMIM][NTf<sub>2</sub>] ionic liquids.

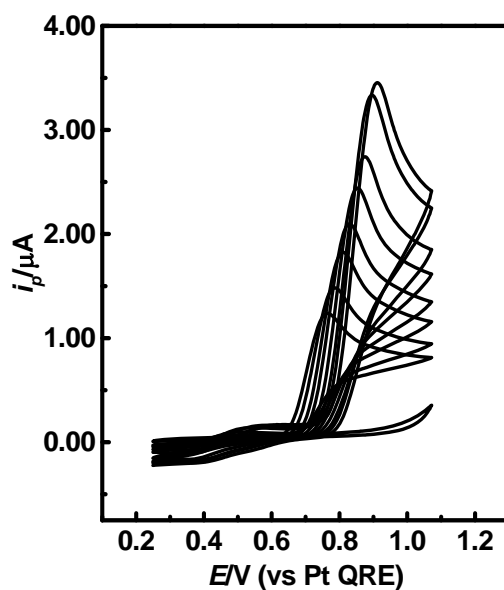
The mechanistic aspects of oxidation of the anthracene in ionic liquids found to be interesting. The peak potential shifts to higher value with increase in scan rate. From the cyclic voltammogram of oxidation of anthracene in imidazolium-based ionic liquids shown in Figures 5.1 and 5.6, it is observed that the shift in peak potential with scan rates increases with increasing alkyl chain length. Hence, the alkyl chain length on the cation plays an important role to decide the mechanism of oxidation of

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anthracene. Similar observations are observed in the case of pyridinium and pyrrolidinium-based ionic liquids. Thus, greater extent of irreversibility in the oxidation of anthracene is found in higher alkyl chain substituted ionic liquids. The pyrrolidinium-based ionic liquids [OMIM][NTf<sub>2</sub>] shows more sensitivity for the shift in the peak position to higher potential as compared to imidazolium and pyridinium-based ionic liquids.



**Figure 5.7:** Plot of  $i_p$  vs  $E$  for oxidation of anthracene in [OP][NTf<sub>2</sub>] ionic liquids



**Figure 5.8:** Plot of  $i_p$  vs  $E$  for oxidation of anthracene [OMPyrr][NTf<sub>2</sub>] ionic liquids.

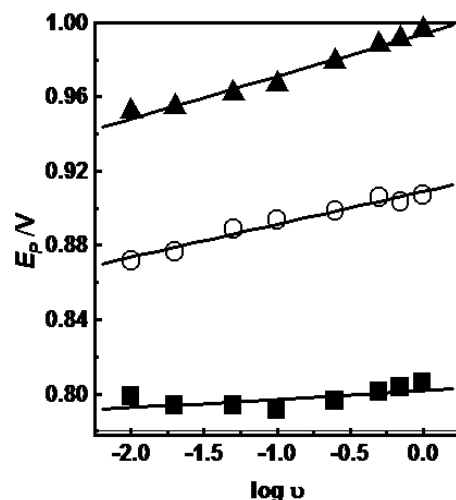
The first indication that the heterogeneous electron transfer from the oxidation of anthracene is totally irreversible was readily apparent in the current independence of the sweep rates. In order to examine irreversibility in oxidation of anthracene, we have extended to our study to higher alkyl substituted pyridinium and pyrrolidinium-based ionic liquids. Following Figures 5.7 and 5.8 show the cyclic voltammogram for oxidation of anthracene in [OP][NTf<sub>2</sub>] and [OMPyrr][NTf<sub>2</sub>] ionic liquids, respectively.

### 5.3.2.2 Quantitative criteria for reversibility and irreversibility

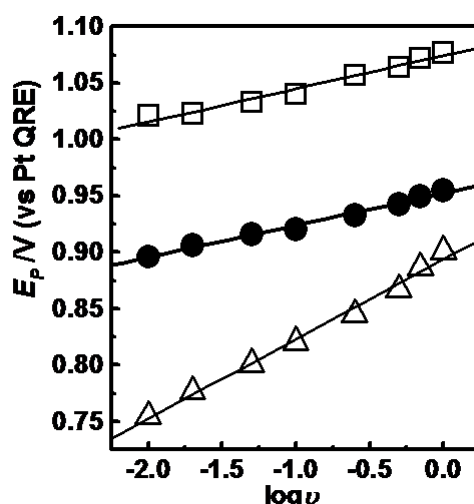
In order to establish that the charge-transfer reaction in the anodic oxidation of anthracene is the electrochemical process is either irreversible or irreversible, we have applied eq. 5.3 and Fick's laws of diffusion to develop the following criteria.<sup>27, 28</sup> One of the principal tests for electrochemical reversibility rests on the magnitude of the slope in the plot of  $E_p$  vs.  $\log \nu$ .<sup>29, 30</sup> The Slopes between the limits of 0 and 30 mV per decade are indicative of reversible electron transfer and provide information about the order of the follow-up chemical reactions. In contrast, values greater than 30 mV per decade are predicted for totally irreversible waves on the basis of Eq. 5.3. The peak potential  $E_p$  was found to vary linearly as a function of  $\log \nu$ . Slopes close to 20mV/ $\log \nu$  were found when the solvent was an ionic liquid, indicating that the reaction step consecutive to the formation of the anthracene cation radical involves a second-order pathway.

$$E_p = (2.303 RT/2\alpha\xi) \log \nu + \text{constant} \quad (5.3)$$

The representative plots for oxidation of anthracene of the dependence of the peak potential on the sweep rate are illustrated in bellow Figures. The plots of the peak potential verses scan rate for oxidation of anthracene in imidazolium-based ionic liquids are illustrated in Figure 5.9. The observed slopes for imidazolium-based ionic liquids [BMIM][NTf<sub>2</sub>], [HMIM][NTf<sub>2</sub>] and [BMIM][NTf<sub>2</sub>] are 2mV, 18mV and 22 mV, respectively and significantly lower than expected for a irreversible process. These results provide strong evidence for a reversible electron-transfer process in imidazolium-based ionic liquids. Also it has been observed that the alkyl chain substitution play an important role in mechanism of oxidation of anthracene process.



**Figure 5.9:** Plots of  $E_p - \log \nu$  for [BMIM][NTf<sub>2</sub>] (■), [HMIM][NTf<sub>2</sub>] [BMIM][NTf<sub>2</sub>] (○), [OMIM][NTf<sub>2</sub>] (▲) imidazolium-based ionic liquids.



**Figure 5.10:** Plots of  $E_p - \log \nu$  for [BMPyrr][NTf<sub>2</sub>] (□), [HMPyrr][NTf<sub>2</sub>] (●), [OMPyrr][NTf<sub>2</sub>] (△) pyrrolidinium based ionic liquids

The slope increases from butyl to hexyl to octyl. This indicates that the mechanism of oxidation of anthracene shifts from reversible to irreversible with alkyl group substitution. The lifetime for anthracene cation increases with alkyl chain due to stabilization of cation by ionic liquid cations. The plot of  $E_p$  vs scan rate,  $\log \nu$  for the pyrrolidinium-based ionic liquids are shown in Figure 5.10. The slope for [BMPyrr][NTf<sub>2</sub>], [HMPyrr][NTf<sub>2</sub>] and [OMPyrr][NTf<sub>2</sub>] are 29.4, 28.4 and 70.6 mV, respectively.



In pyrrolidinium-based ionic liquids, the irreversibility of oxidation of anthracene increases with increase in alkyl chain length from butyl to hexyl to octyl. The [OMPyrr][NTf<sub>2</sub>] ionic liquid shows highest slope of 70.4 mV, which proves that the irreversibility is higher in the case of [OMPyrr][NTf<sub>2</sub>]. This points out that the irreversible oxidation of anthracene in higher alkyl chain ionic liquids show electron transfer followed by chemical reaction (EC) mechanism.

### 5.4 Conclusions

The present work shows interesting variations in the reversibility of electrochemical processes and diffusion of electroactive species in ionic liquids. These trends have been correlated to the changes in the cationic structure – namely the presence of a delocalized electron cloud over the cation and the length of the alkyl substituent on the cation of the ionic liquids. In order to generalize the results, the experiments have to repeat for a wide database of ionic liquids. The systematic selection and detailed observation in the present work, however, provide sufficient indications of the strong intermolecular interactions between the analyte and ionic liquid electrolyte. Such interactions, if understood, can be manipulated to improve the efficiency of the future electrochemical devices employing ionic liquids.

### 5.5 References

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## 5. Electrochemical Oxidation of Anthracene in Ionic Liquids

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## **Chapter 6**

# **Bimolecular Diels-Alder Reaction in Binary Mixtures of Ionic Liquids**

## 6. Bimolecular Diels-Alder Reaction in Binary Mixtures of Ionic Liquids

### 6.1 Introduction

Many organic reactions are studied in organic solvents in order to understand the solvent effect on kinetic and mechanistic aspect of the reaction. The use of excessive organic solvent to carry out the organic process causes environmental pollution. The research on the use of alternatives to these conventional organic solvents is under extensive focus. Despite the widespread interest in the potential applications of the novel solvents, very little is known about their effect on the reaction mechanism, rate and stereoselectivity. Diels-Alder reactions, normally exhibit small solvent effects and consequently studies on this topic have traditionally been scarce. The rate constants for Diels –Alder reactions in water are larger than those in organic solvents which contradict with common notion that Diels-Alder reactions are rather insensitive to solvent effects.<sup>1</sup> In addition to obvious economical and environmental advantages, water is known to have surprising beneficial effects on organic reactions, which has popularized water as a reaction medium due to several solvent properties.<sup>1-6</sup> Studies on solvent effects are generally carried out by means of relationships between reactivity properties that are reaction rate or several types of selectivity and empirical parameters representing different kinds of solute–solvent interactions.<sup>7-9</sup> Ionic liquids have recently been considered as an alternative to replace volatile organic solvents in current chemical processing, due to their special interesting physico-chemical properties.<sup>10-13</sup> There are few reports available on kinetics of Diels –Alder reaction in ionic liquids in order to study the solvent effect.<sup>14, 15</sup> The advantages of using ionic liquids have been discussed in several reports.<sup>10-13, 16</sup> Based on the studies made so far, the conclusion has been drawn that ionic liquids are highly effective in accelerating organic reactions, including Diels–Alder reactions.<sup>17-21</sup> Previous reports have demonstrated that kinetics of the Diels Alder reaction of cyclopentadiene with methyl acrylate in different ionic liquids is impeded by the viscosity and found that high viscosity of ionic liquids is one of the major constraints for their use.<sup>22</sup> As discussed in

## 6. Kinetics of Diels-Alder Reaction

Chapter 4, the addition of cosolvents to ionic liquids causes a dramatic decrease in the viscosity of the solution. The extent of decrease in viscosity of the ionic liquids depends on the cosolvent added. The polarity parameters of the ionic liquid – cosolvent binary mixtures also show interesting deviations from ideality. The non-ideality of these binary systems is bound to influence the rates and selectivities of organic processes in a remarkable manner. The Diels–Alder reaction in binary mixtures of [BMIM][BF<sub>4</sub>] with water and methanol is studied at 298.15K and second order rate constants were interpreted by various solute–solvent interaction parameters.<sup>23</sup>

In the present chapter, the Diels Alder reaction between anthracene-9-carbinol (**1**) and *N*-ethylmaleimide (**2**) has been studied in different binary mixtures of ionic liquids with molecular solvents. (Scheme 6.1) The relative effect of viscosity of the medium in relation to the other solute-solvent interactions in governing the organic reaction has been discussed.

### 6.2 Experimental Section

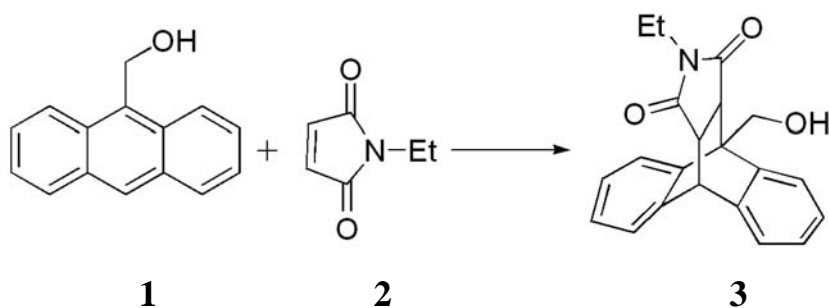
#### Materials

Pyridine was obtained from the Spectrochem and was distilled prior to use. 3-picolene, 4-picolene, *N*-ethyl maleimide were purchased from Aldrich. Anthracene-9-carbinol and sodium tetrafluoroborate (NaBF<sub>4</sub>) were used as obtained. All the organic solvents used for preparing binary mixtures with ionic liquids were spectroscopic grade. De-ionized water with specific conductance of  $0.55 \times 10^{-6} \text{ S cm}^{-2}$  was used for preparing mixtures of ionic liquids. Ionic liquids used in the present investigation were synthesized and purified according to the reported procedures. The ionic liquids were synthesized in two steps. First step included the synthesis of organic cation and the second the addition of anion. The ionic liquids were characterized by <sup>1</sup>H NMR spectroscopy. The ionic liquids were dried under vacuum in order to remove excess water contents. The water content in each ionic liquid, as measured by a Karl-Fischer coulometer, did not exceed 50 ppm. The viscosity measurement was carried out according to reported procedure mentioned in the Chapter 4.

## 6. Kinetics of Diels-Alder Reaction

### Kinetic Measurements

0.022g of anthracene-9-carbinol was dissolved in 5 mL of methanol prior to use to give a 0.021M stock solution. 14 $\mu$ L of the stock solution was added to 1 mL of the ionic liquid-solvent binary mixture resulting in 0.3mM solution of the diene and equilibrated at desired temperature for 10-15 min. 0.070g of *N*-ethyl maleimide was dissolved in 5 mL of the methanol to yield a 0.112 M stock solution of the dienophile. 25 $\mu$ L, 50 $\mu$ L, 75 $\mu$ L, 100 $\mu$ L of 0.112M stock solution of *N*-ethyl maleimide was then added to the cuvette containing 1mL of dienophile in binary mixture of ionic liquids in solvents to give final concentration 2.8 mM, 5.6 mM, 8.4 mM, 11.2 mM respectively. The progress of the reaction was monitored by following the time-dependent decay of the absorbance peak of **1** at  $\lambda = 380$  nm. Since the concentration of the dienophile is higher than the diene, the time dependence of the decay is calculated to give the pseudo-first order rate constants,  $k'$ . The four pseudo first-order rate constants were used to determine the second order rate constants  $k_2$ . The reported rate constants are an average of at least three kinetic runs on different samples and were reproducible within  $\pm 5\%$ .



**Scheme 6.1:**

### 6.3 Results and Discussions

The Diels Alder reaction of **1** and **2** was carried out in binary mixtures of pyridinium-based ionic liquids, namely 1-butyl pyridinium tetrafluoroborate [BP][BF<sub>4</sub>], 1-butyl-3-methyl pyridinium tetrafluoroborate [3-MBP][BF<sub>4</sub>], 1-butyl-4-methyl pyridinium tetrafluoroborate [4-MBP][BF<sub>4</sub>] in molecular solvents - water, methanol and chloroform.

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The nature of the cosolvent was an important determinant of the solute-solvent interactions, viscosity and the resulting kinetic parameters; hence the results are discussed independently for water, methanol and chloroform as follows. The activation parameters for the reaction **1** + **2** have been determined from temperature-dependent kinetics in the [BP][BF<sub>4</sub>] + H<sub>2</sub>O, which was selected as a model system, based on which the nature of the solute-solvent interactions has been discussed.

### 6.3.1 Ionic Liquids-Chloroform Binary Mixtures

Figure 6.1 shows second order rate constants  $k_2$  for Diels Alder reaction of **1** with **2** in binary mixtures of pyridinium based ionic liquids in chloroform as a function of the volume fraction of the second component in the binary mixture i.e. ionic liquid,  $V_{f,2}$ . The rate constants are also tabulated in Table 6.1. The rate constant  $k_2$  decreases nonideally with increase in concentration of ionic liquids in the binary mixture. Kinetic measurements were limited to two pyridinium based ionic liquids, [3-MBP][BF<sub>4</sub>] and [4-MBP][BF<sub>4</sub>], since [BP][BF<sub>4</sub>] is insoluble in chloroform due polarity difference and forms a biphasic system. In order to assess the role of viscosity, the rate constants were also plotted as a function of viscosity (Figure 6.2). The monotonic decrease confirms the fact that in the ionic liquid – chloroform system, the rate of the reaction is primarily dominated by the viscosity of the reaction medium, rather than any other solute-solvent interactions.

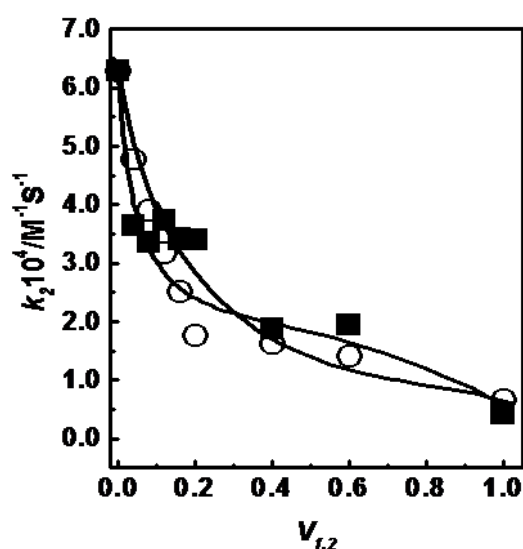
**Table 6.1: Rate Constants for Diels Alder Reactions in Binary Mixtures of Ionic Liquids with Chloroform.**

S. No.	$V_{f,2}$	[3-MBP][BF <sub>4</sub> ]		$V_{f,2}$	[4-MBP][BF <sub>4</sub> ]	
		$10^4 k_2$	$\eta/\text{cP}$		$10^4 k_2$	$\eta/\text{cP}$
1	0	6.279	0.560	0	6.279	0.56
2	0.04	4.770	0.850	0.04	3.629	0.64
3	0.08	3.892	1.140	0.08	3.343	0.70
4	0.12	3.170	1.360	0.12	3.721	0.87



## 6. Kinetics of Diels-Alder Reaction

5	0.16	2.510	1.500	0.16	3.404	0.98
6	0.20	1.753	1.960	0.20	3.386	2.24
7	0.40	1.618	8.950	0.40	1.870	6.95
8	0.60	1.405	18.540	0.60	1.929	17.60
9	0.80	0.397	65.800	0.80	1.203	39.50
10	1.00	0.554	166.700	1.00	0.422	200.65

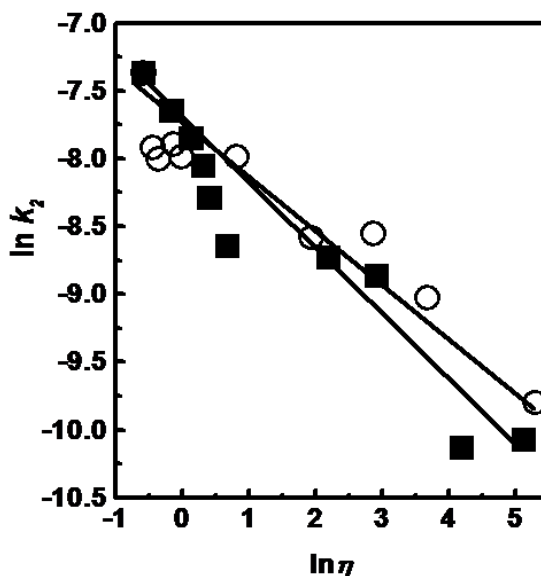


**Figure 6.1:** The plots of rate constants  $k_2$  vs  $V_{f,2}$  in binary mixture of [4-MBP][BF<sub>4</sub>](■), [3-MBP][BF<sub>4</sub>](○) in chloroform.

In terms of solute-solvent interactions, the uniformity in the trend indicates the absence of any highly specific interactions between the reactants and the components of the binary mixture. The intermediate polarity of chloroform is apparently compatible with that of the ionic liquids used, which are known to have similar polarity ranges. (See Chapter 3) It is noteworthy that the sensitivity of the rate constants is greater for the compositions within the lower viscosity range. This could be accounted for by the fact,

## 6. Kinetics of Diels-Alder Reaction

that the extent of reactivity damping by high friction can be saturated beyond a certain limit.



**Figure 6.2:** The plots of  $\ln k_2 - \ln \eta$  in binary mixtures of [3-MBP][BF<sub>4</sub>](■), [4-MBP][BF<sub>4</sub>](○) in chloroform

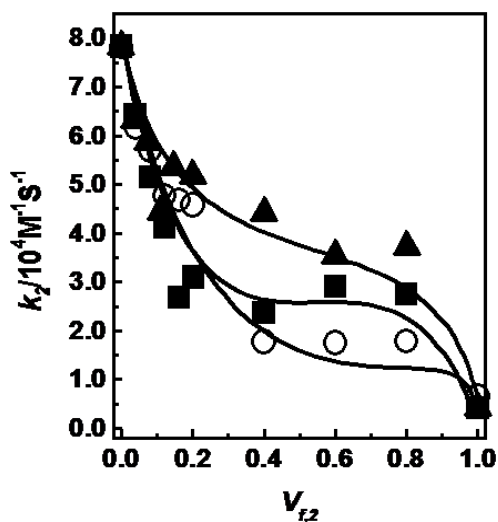
### 6.3.2 Ionic Liquids-Methanol Binary Mixtures

Rate constants for Diels Alder reaction 1 and 2 in binary mixture of all three ionic liquids ([BP][BF<sub>4</sub>], [3MBP][BF<sub>4</sub>] and [4MBP][BF<sub>4</sub>]) with methanol were studied at 25 °C. The rate constants in ionic liquid-methanol binary mixtures tabulated in Table 6.2 show different behaviors as compared to chloroform-ionic liquids mixture (Figure 6.3). The rate constants for Diels Alder reaction in binary mixtures of ionic liquids in methanol decrease with the addition of ionic liquids to methanol. However, the decrease is in a nonideal manner, with the  $k_2$  depicting a sigmoidal trend with an increase in concentration of ionic liquids.

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**Table 6.2: Rate constants for Diels Alder Reactions in Binary Mixtures of Ionic Liquids with Methanol**

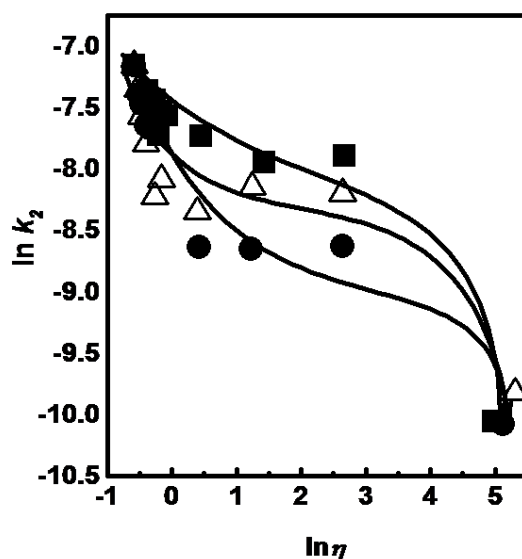
S. No.	$V_{f,2}$	[BP][BF <sub>4</sub> ]		$V_{f,2}$		[3-MBP][BF <sub>4</sub> ]		$V_{f,2}$		[4-MBP][BF <sub>4</sub> ]	
		$10^4 k_2$	$\eta/\text{cP}$	$10^4 k_2$	$\eta/\text{cP}$	$10^4 k_2$	$\eta/\text{cP}$	$10^4 k_2$	$\eta/\text{cP}$		
1	0	7.825	0.56	0	7.825	0.56	0	7.825	0.56		
2	0.04	6.334	0.68	0.04	6.167	0.60	0.04	6.425	0.59		
3	0.07	5.880	0.77	0.08	5.690	0.63	0.08	5.151	0.62		
4	0.11	4.439	0.81	0.12	4.775	0.67	0.12	4.112	0.67		
5	0.15	5.370	0.85	0.16	4.678	0.71	0.16	2.681	0.77		
6	0.20	5.180	0.93	0.20	4.578	0.78	0.20	3.094	0.85		
7	0.40	4.410	1.57	0.40	1.775	1.53	0.40	2.370	1.48		
8	0.60	3.550	4.15	0.60	1.750	3.38	0.60	2.907	3.47		
9	0.80	3.733	14.497	0.80	1.786	13.92	0.80	2.750	14.00		
10	1.00	0.431	145.23	1.00	0.554	166.70	1.00	0.422	200.65		



**Figure 6.3:** The plots of rate constants  $k_2$  vs volume fraction of ionic liquid,  $V_{f,2}$  in binary mixtures of [BP][BF<sub>4</sub>](■), [3-MBP][BF<sub>4</sub>](○), [4-MBP][BF<sub>4</sub>](▲) in methanol.

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The nonideality becomes more apparent when one observes the rate – viscosity correlation plot for the ionic liquid – methanol binary mixtures. (Figure 6.4) The remarkable variation can be attributed to the fact that in addition to the viscosity of the medium, additional solute-solvent specific interactions can play a decisive role in determining the reactivity.



**Figure 6.4:** The plots of  $\ln k_2$  -  $\ln \eta$  in binary mixtures of [BP][BF<sub>4</sub>](■), [3-MBP][BF<sub>4</sub>](●), [4-MBP][BF<sub>4</sub>](△) in methanol.

The polarity of methanol differs significantly from that of the pyridinium ionic liquids. Methanol is also capable of hydrogen bonding with a wide variety of substrates. The spatial inhomogeneity resulting from such binary mixtures was manifested as preferential solvation of the spectroscopic polarity probes in Chapter 3. In the present system, a similar preferential interaction between the reactant /the transition state with either of the components of the binary solvent mixture is certainly plausible. The resulting solute-solvent specificity can overcome the effect of frictional forces in terms of decreasing viscosity. For the Diels – Alder reaction between **1** and **2**, it is seen that the rate constants remain at a nearly constant value – a “plateau” – in the intermediate composition range, where the increasing concentration of ionic liquids causes a 10-fold

## 6. Kinetics of Diels-Alder Reaction

increase in viscosity. The reactant / transition state do not experience the rising ionic liquid proportion coupled with a concomitant decrease in methanol concentration. The observations are indicative of the preferential solvation of the reactant / transition state by the methanol molecules rather than the ionic liquid. The relatively higher proportion of methanol in the solvation shell of the reactants “shields” the reaction from the increasing friction, while probably stabilizing the transition state through hydrogen bonding effects.<sup>24</sup>

### 6.3.3 Ionic Liquids-Water Binary Mixtures

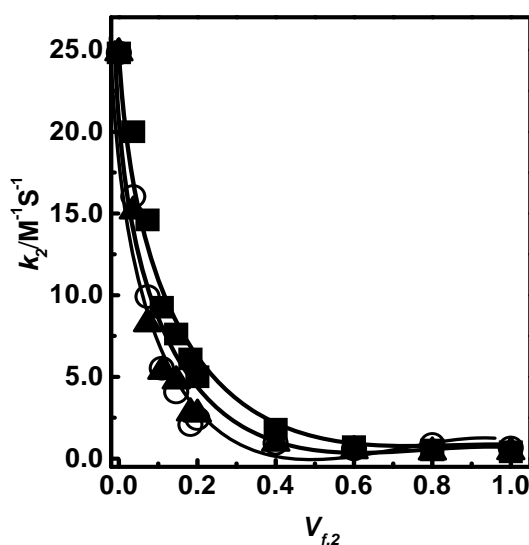
From the plots of rate constants  $k_2$  versus different concentrations of ionic liquids in water is shown in Figure 6.5, it is observed that the rate constants decrease with increase in concentration of ionic liquids in water.

**Table 6.3: Rate Constants for Diels Alder Reaction in Binary Mixtures of Ionic Liquids with Water**

S. No.	$V_{f,2}$	[BP][BF <sub>4</sub> ]		$V_{f,2}$	[3-MBP][BF <sub>4</sub> ]		$V_{f,2}$	[4-MBP][BF <sub>4</sub> ]	
		$10^3 k_2$	$\eta/ \text{cP}$		$10^3 k_2$	$\eta/ \text{cP}$		$10^3 k_2$	$\eta/ \text{cP}$
1	0	24.82	0.89	0	24.82	0.89	0	24.82	0.89
2	0.037	20.00	1.02	0.04	16.04	1.01	0.04	15.14	1.03
3	0.073	14.60	1.09	0.08	9.91	1.03	0.08	8.25	1.08
4	0.11	9.26	1.16	0.12	5.52	1.07	0.12	5.33	1.18
5	0.15	7.62	1.22	0.16	4.07	1.11	0.16	4.75	1.29
6	0.18	--	1.30	0.18	2.44	1.17	0.18	2.79	1.45
7	0.20	5.01	1.33	0.20	2.07	1.42	0.20	2.71	1.40
8	0.40	1.79	2.03	0.40	0.94	2.41	0.40	0.94	1.92
9	0.60	0.73	3.35	0.60	0.59	4.02	0.60	0.49	2.84
10	0.80	0.53	7.29	0.80	0.86	7.97	0.80	0.40	5.32
11	1.00	0.43	145.0	1.00	0.55	166.7	1.00	0.42	200.65

## 6. Kinetics of Diels-Alder Reaction

The viscosity is also increases with increase in concentration of ionic liquid in water. Table 6.3 lists the rate constants corresponding to the composition of the reaction medium. The identity of the ionic liquid does not make an appreciable difference in the observed rate constants, implying that the methyl substituent is distant from the reaction centre in the solvated form of the transition state. A similarity between the rate profiles for the three ionic liquid mixtures is much greater in the presence of water as a cosolvent rather than methanol as the other component.

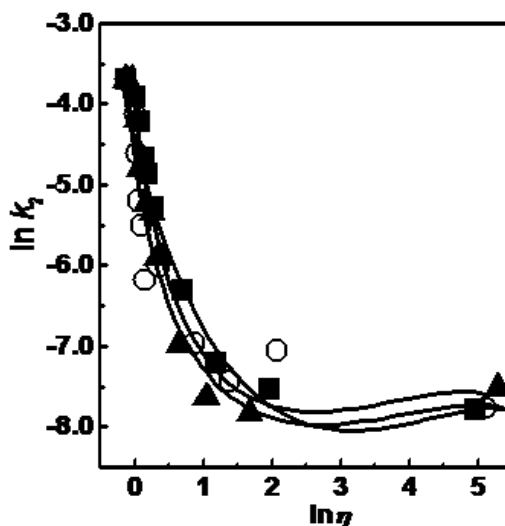


**Figure 6.5:** The plots of rate constants  $k_2$  vs  $V_{f,2}$  in binary mixture of [BP][BF<sub>4</sub>](■), [3-MBP][BF<sub>4</sub>](○), [4-MBP][BF<sub>4</sub>](▲) in water.

In highly aqueous region the rate constants decreases from the  $24.82 \times 10^{-3}$  for pure water to  $5.01 \times 10^{-3}$  for  $V_{f,2} = 0.2$  of [BP][BF<sub>4</sub>] ionic liquids and viscosity increases from 0.89 cP to 1.33 cP. Similarly the rate constants decreases for binary mixture of [3-MBP][BF<sub>4</sub>] and [4-MBP][BF<sub>4</sub>] in water as  $24.82 \times 10^{-3} \text{ M}^{-1}\text{S}^{-1}$  for pure water to  $2.07 \times 10^{-3} \text{ M}^{-1}\text{S}^{-1}$  for  $V_{f,2} = 0.2$  of ionic liquids in water and  $24.82 \times 10^{-3} \text{ M}^{-1}\text{S}^{-1}$  for pure water to  $2.71 \times 10^{-3} \text{ M}^{-1} \text{S}^{-1}$  for  $V_{f,2} = 0.2$  of ionic liquids in water, respectively. The corresponding viscosity increases for [3-MBP][BF<sub>4</sub>]-water mixture from 0.89 cP to 1.42 cP and for [4-MBP][BF<sub>4</sub>]-water mixture from 0.89 cP to 1.40 cP. But beyond this composition the

## 6. Kinetics of Diels-Alder Reaction

viscosity changes is very high but rate constants does not show much change as compared to earlier region.



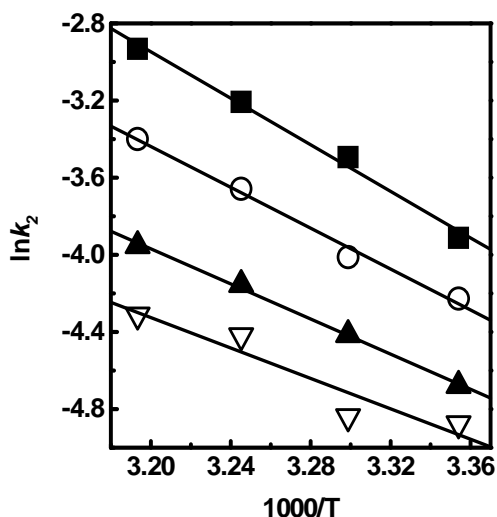
**Figure 6.6:** The plots of  $\ln k_2 - \ln \eta$  in binary mixtures of [BP][BF<sub>4</sub>](■), [3-MBP][BF<sub>4</sub>](○), [4-MBP][BF<sub>4</sub>](▲) in water

The results suggest the presence of additional factors, other than viscosity, in determining the reactivity between **1** and **2**. The difference in the polarity of water and ionic liquid as well as the hydrogen bonding capacity of the water molecule could be the decisive factors, as discussed previously for the binary mixtures of methanol. The high degree of similarity of rate profiles for the different ionic liquids, in addition, indicates an even greater extent of preferential solvation in aqueous systems as compared to methanol binary systems. Earlier reports suggest that the kinetics of organic reaction is drastically accelerated in water due to the hydrophobic effect of water. It is difficult to quantify the extent of the hydrophobic effect for the system under study. The dominant role of hydrophobic effect is, nevertheless, a reasonable explanation for the dramatic increase in reactivity in the highly aqueous region. This hydrophobicity of water decreases with addition of ionic liquids and solvate the reactants more independently, which slow down

## 6. Kinetics of Diels-Alder Reaction

the diffusion process reaction rate. In addition to this one of important property of ionic liquids is surface tension. It has been reported that surface tension of ionic liquids is governed by the anions. Ionic liquids possess the higher surface tension than the water and it decreases with the addition of water. Further discussion of this aspect needs an in-depth analysis with the aid of activation parameters to understand the kinetic determinants of the system.

### 6.4. Temperature Dependence of Kinetics of Diels Alder Reaction



**Figure 6.7:** The plots of  $\ln k_2 - 1000/T$  for  $v_{f,2}$  (volume fraction of [BP][BF<sub>4</sub>] in water): 0.04 (■), 0.07 (○), 0.11 (▲) and 0.15 (▽) for binary mixture of [BP][BF<sub>4</sub>] in water.

The temperature dependant rate constants  $k_2$  are shown in Figure 6.7. The plots shows that the variation in  $k_2$  for Diels – Alder reaction in different compositions of highly aqueous rich region of binary mixture of [BP][BF<sub>4</sub>]-water . The activation parameters of the reaction of **1** with **2** were determined from the temperature dependence of rate constants in [BP][BF<sub>4</sub>]-water binary mixtures shown in Table 6.4 (Figure 6.8). The activation parameters were determined for seven different compositions of [BP][BF<sub>4</sub>] in water. It is seen that the enthalpy of activation,  $\Delta^{\#}H$  decreases from 47.63 kcal mol<sup>-1</sup> to 30.22 kcal mol<sup>-1</sup> for the concentration of [BP][BF<sub>4</sub>] in water from  $V_{f,2} = 0.04$  to  $V_{f,2}$



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=0.15. This remarkable behaviour may indicate the presence of other factors responsible for the kinetics of the reaction. These values were not in agreement with the qualitative prediction that the reactants will have to overcome a “higher barrier” in a more viscous medium, leading to a decrease in the rate of the reaction. It has been also observed that the entropy of activation might play an important role in organic reaction which, leads to phenomenon known as *entropy-enthalpy compensation*. At composition in the highly aqueous region, water becomes even more structured by the formation of hydrophobic hydration shells as seen by numerous spectroscopic studies. As a result, hydrophobic interactions will become entropically slightly more favourable.

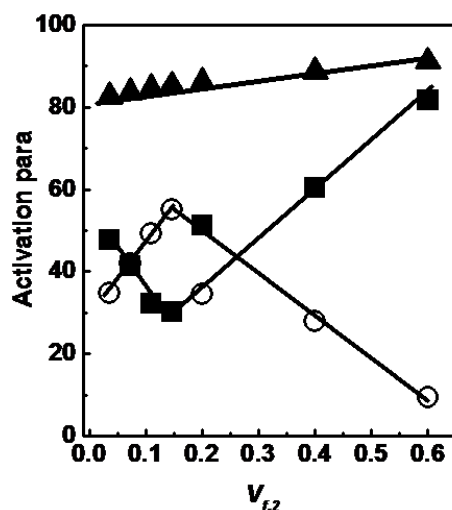
**Table 6.4: Activation Parameters for Diels - Alder Reaction in Binary Mixtures of Ionic Liquids [BP][BF<sub>4</sub>] in Water at 298.15 K**

S. No.	$V_{f,2}$	$\Delta^{\#}H$ kJmol <sup>-1</sup>	$\Delta^{\#}S$ kJmol <sup>-1</sup> T <sup>-1</sup>	$T\Delta^{\#}S$ kJmol <sup>-1</sup>	$\Delta^{\#}G$ kJmol <sup>-1</sup>
1	0.04	47.63	-0.12	-35.00	82.63
2	0.07	41.48	-0.14	-42.09	83.56
3	0.11	35.29	-0.17	-49.30	84.59
4	0.15	30.22	-0.19	-55.03	85.25
5	0.20	51.41	-0.12	-34.72	86.13
6	0.40	60.76	-0.09	-27.95	88.71
7	0.60	81.71	-0.03	-9.40	91.11

The term hydrophobic hydration refers to the interactions of apolar solutes and water, i.e. how an apolar solute affects the water structure in its immediate environment. Introduction of an apolar solute into aqueous solution is characterized by an unfavourable change in standard Gibbs energy at room temperature.<sup>25-27</sup> However, the standard enthalpy of the solution process is usually small and favourable whereas the entropy change is large and negative.<sup>25-28</sup> The dependence of  $\Delta^{\#}H$  and  $T\Delta^{\#}S$  at 298.15 K for the

## 6. Kinetics of Diels-Alder Reaction

reaction of **1** with **2** on the mole fraction of [BP][BF<sub>4</sub>] in dilute aqueous solutions is dramatic. The changes of  $\Delta^{\#}H$  and  $T\Delta^{\#}S$  across the mole fraction range of  $0 < x_2 < 0.15$  are spectacular. The enthalpy of activation decreases upon addition of [BP][BF<sub>4</sub>]. Simultaneously, the entropy of activation exhibits an equally dramatic decrease. The effects almost fully compensate each other.<sup>29-31</sup> Hence in the water-rich media the free energy of activation for the Diels-Alder process is only moderately affected by the addition of ionic liquids to water. The reaction is slowed down by addition of structure-promoting cosolvents. At a critical concentration of water molecules, water gradually losing its typically aqueous character. The diene and the dienophile will become more and more preferentially solvated by the ionic liquids and the driving force for the dramatic rate effect in water will be lost.

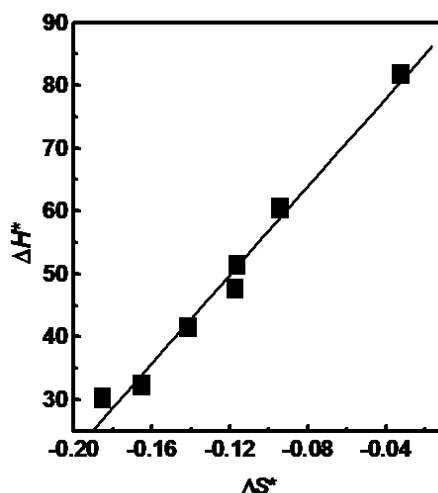


**Figure 6.8:** The plots of activation parameters  $\Delta^{\#}H$  (■),  $-T\Delta^{\#}S$  (○),  $\Delta^{\#}G$  (▲) for the binary mixture of [BP][BF<sub>4</sub>]-water

Finally, beyond these concentrations of ionic liquids, where the concentration fluctuations are at their maximum, the binary mixtures start to behave like a common solvent, leading to smooth changes in rate and activation parameters upon variation of the ionic liquids composition. The unfavourable Gibbs free energy for solution in water is the

## 6. Kinetics of Diels-Alder Reaction

result of strongly negative entropy of solution which prevails over the favourable enthalpic contribution.



**Figure 6.9:** Illustration of enthalpy-entropy compensation plots of  $\Delta^\ddagger H - \Delta^\ddagger S$  for Diels-Alder reaction.

The domination of entropy effects is often found for chemical processes in water and in water-rich solutions.<sup>32, 33</sup> It is found that the association process is entropy driven. The plot of enthalpy – entropy compensation for Diels Alder reaction is shown in Figure 6.9.

### 6.5 Conclusions

The kinetics of Diels – Alder reaction showed interesting variations in binary mixtures of ionic liquids with molecular cosolvents. The reactivity in chloroform –ionic liquids binary mixtures is closely related to the viscosity of the reaction medium, indicating the dominance of the frictional forces. For the methanol and water binary mixtures, a more complex correlation is observed wherein the role of viscosity cannot be completely discounted. However, additional solute-solvent interactions dominate the kinetic profile depending on the property of the cosolvent used. A high degree of preferential solvation is certainly responsible for the deviations from ideality observed. In aqueous systems, the presence of hydrophobic forces is observed distinctly. The activation parameters for the

## 6. Kinetics of Diels-Alder Reaction

aqueous binary mixtures showed enthalpy – entropy compensation effects. Most importantly, despite the strong intermolecular forces, the effect of viscosity is a consistent feature for all the ionic liquid systems studied. The results point towards interesting possibilities of manipulating the reactivity of organic reactions by judicious and well-informed choice of ionic liquid binary systems.

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**Chapter 7**  
**Conclusions**

## 7. Conclusions

The present thesis includes the measurement of physico-chemical properties like polarity and viscosity of pure and binary mixtures of ionic liquids with molecular solvents and their impact on electrochemical and organic reactions. In this thesis, different series of ionic liquids were synthesized in order to investigate the effect of structure of ionic liquids on physico-chemical properties. The relevance of the results for the environmentally benign solvent systems is duly emphasized from the theoretical and practical perspectives. The important observations and conclusions of the thesis have been summarized in the present chapter. The physical properties like polarity and viscosity of pure and binary mixtures of ionic liquids with molecular solvents show interesting structure-property correlation. The solute-solvent interaction in ionic liquids has been investigated through polarity measurements. “Thermosolvatochromism” i.e. the temperature dependant solvatochromism in ionic liquids has been investigated. Preferential solvation in binary mixtures of ionic liquids in molecular solvents has been studied for demonstrating solute-solvent interaction in binary mixtures and to study the structure of the solvation shell.

High viscosity of ionic liquids is a detrimental factor for use of ionic liquids in chemical process. In order to decrease the viscosity of ionic liquids, the addition of cosolvent like water, methanol and dichloromethane to pyridinium and phosphonium based ionic liquids is commonly practised. The decrease in viscosity of ionic liquids depends on the nature of the cosolvent added. The solvent having high dielectric constant separate cation and anion more effectively and decreases the viscosity. Water was found to have a greater effect in bringing down the viscosity of ionic liquids. Using the viscosity of binary mixtures of ionic liquids in different molecular solvents, we proposed a model to determine the solvation number of ionic liquids.

Ionic liquids are known to possess interesting physico-chemical properties which depend on the structure of ionic liquids. The chemical processes carried out in ionic liquids are affected by the properties of ionic liquids and hence, by the structure of ionic liquids. The electrochemical diffusion of anthracene in pyridinium, imidazolium and pyrrolidinium based ionic liquids has been carried out. According to Stoke-Einstein relation, the diffusion process



## 7. Conclusions

is inversely related to the viscosity of the medium. Imidazolium and pyridinium based ionic liquids, having pi electron system, affect the diffusion of anthracene in an unexpected manner with an increase in viscosity of these ionic liquids by increasing alkyl chain length. The pyrrolidinium based ionic liquids which does not have  $\pi$  electron, follow the Stoke-Einstein relation. In the second part of this investigation it has been observed that the mechanism of oxidation changes with ionic liquids. The length of the alkyl chain was found to be more effective in deciding oxidation process of anthracene. The increase in alkyl chain length from butyl to octyl changes the oxidation of anthracene from reversible to irreversible.

In the last part of this thesis, the kinetic investigation of Diels Alder reaction of anthracene-9-carbinol with *N*-ethyl maleimide in binary mixture of ionic liquids in water, methanol and chloroform was carried out. The study of solvent effects of aqueous ionic liquid solutions on organic reactions was undertaken. The solvent systems—aqueous ionic liquids systems — were chosen on the basis of their environmentally benign nature. The method of investigation pursued was mostly kinetic studies, which facilitated the estimation of crucial activation parameters.

## Appendix A

### NMR Spectra of Ionic Liquids

The  $^1\text{H}$  NMR of the pure and dried ionic liquids recorded before using them as reaction media are as follows:

1) **1-butyl-3-methylimidazolium tetrafluoroborate [BMIM][BF<sub>4</sub>]**

$^1\text{H}$  NMR (200 MHz, DMSO- $d_6$ ): 0.78 (t, 3H), 1.26 (m, 2H), 1.60 (m, 2H), 3.78 (s, 3H), 4.15 (t, 2H), 7.46 (s, 2H), 8.97 (s, 1H).

2) **1-butyl-3-methylimidazolium Bis((trifluoromethyl)sulfonyl)imide [BMIM][NTf<sub>2</sub>]**

$^1\text{H}$  NMR (200MHz CDCl<sub>3</sub>): 0.95 (t, 3H), 1.39 (m, 2H), 2.00 (m, 2H), 4.07 (s, 3H), 4.37 (t, 2H), 7.71 (t, 1H), 7.76 (t, 1H), 9.02 (s, 1H).

3) **1-hexyl-3-methylimidazolium Bis((trifluoromethyl)sulfonyl)imide [HMIM][NTf<sub>2</sub>]**

$^1\text{H}$  NMR (400 MHz, CDCl<sub>3</sub>): 0.84 (t, 3H), 1.27(m, 8H), 1.86 (m, 2H), 3.95 (s, 3H), 4.13 (t, 2H), 7.23 (s, 1H), 7.31 (s, 1H), 9.17 (s, 1H).

4) **1-octyl-3-methylimidazolium Bis((trifluoromethyl)sulfonyl)imide [OMIM][NTf<sub>2</sub>]**

$^1\text{H}$  NMR (400 MHz, CDCl<sub>3</sub>): 0.87 (t, 3H), 1.28 (m, 10H), 1.83 (m, 2H), 3.97 (s, 3H), 4.17 (t, 2H), 7.26 (s, 1H), 7.33 (s, 1H), 9.15 (s, 1H).

5) **1-butylpyridinium tetrafluoroborate [BP][BF<sub>4</sub>]:**

$^1\text{H}$  NMR (200 MHz, DMSO- $d_6$ ): 0.85 (t, 3H), 1.08 (m, 2H), 1.84 (m, 2H), 4.30 (t, 2H), 7.48 (t, 2H), 7.62 (t, 1H), 8.30 (d, 2H).

6) **1-octylpyridinium tetrafluoroborate [OP][BF<sub>4</sub>]:**

$^1\text{H}$  NMR (200 MHz, DMSO- $d_6$ ): 0.98 (t, 3H), 1.24 (m, 10H), 1.82 (m, 2H), 4.75 (t, 2H), 7.94 (t, 2H), 8.32 (t, 1H), 8.64 (d, 2H).

7) **1-butyl-3-methylpyridinium tetrafluoroborate [3MBP][BF<sub>4</sub>]:**

$^1\text{H}$  NMR (200 MHz, DMSO- $d_6$ ) 0.74 (t, 3H), 0.95 (m, 2H), 1.48 (m, 2H), 4.30 (t, 2H), 7.51(dd, 1H), 7.98 (d, 1H), 8.31 (d, 1H), 8.38 (s, 1H).

8) **1-octyl-3-methylpyridinium tetrafluoroborate [3-MOP][BF<sub>4</sub>]:**

- $^1\text{H}$  NMR (200 MHz, DMSO- $d_6$ ): 0.98 (t, 3H), 1.24 (m, 10H), 1.95 (m, 2H), 2.51 (s, 3H), 4.53 (t, 2H), 7.84 (dd, 1H), 8.25 (d, 1H), 8.65 (d, 1H), 8.73 (s, 1H).
- 9) **1-butyl-4-methylpyridinium tetrafluoroborate [4-MBP][BF<sub>4</sub>]:**  
 $^1\text{H}$  NMR (200 MHz, DMSO- $d_6$ ): 0.82 (t, 3H), 1.16 (m, 2H), 1.56 (m, 2H), 2.33 (s, 3H), 4.20(t, 2H), 7.55 (d, 2H), 8.47 (d, 2H).
- 10) **1-butylpyridinium bis(trifluoromethylsulphonyl)imide [BP][NTf<sub>2</sub>]:**  
 $^1\text{H}$  NMR (200 MHz, DMSO- $d_6$ ): 0.85 (t, 3H), 1.30 (m, 2H), 1.88 (m, 2H), 4.48 (t, 119 2H), 7.95 (t, 2H), 8.42 (t, 1H), 8.71 (dd, 2H).
- 11) **1-hexylpyridinium bis(trifluoromethylsulphonyl)imide [HP][NTf<sub>2</sub>]:**  
 $^1\text{H}$  NMR (200 MHz, DMSO- $d_6$ ): 0.83 (t, 3H), 1.26 (m, 6H), 1.91 (m, 2H), 4.50 (t, 2H), 7.99 (t, 2H), 8.42 (t, 1H), 8.74 (d, 2H).
- 12) **1-octylpyridinium bis(trifluoromethylsulphonyl)imide [OP][NTf<sub>2</sub>]:**  
 $^1\text{H}$  NMR (200 MHz, DMSO- $d_6$ ): 0.81 (t, 3H), 1.24 (m, 10H), 1.95 (m, 2H), 4.54 (t, 2H), 8.01 (t, 2H), 8.45 (t, 1H), 8.75 (d, 2H).
- 13) **1-buty-1-methyl pyrrolidinium bis(trifluoromethylsulphonyl)imide [BMPyrr][NTf<sub>2</sub>]**  
 $^1\text{H}$ NMR (200MHz, CDCl<sub>3</sub>): 0.90(t, 3H), 1.31(m, 2H), 1.72(m, 2H), 2.10(m, 4H), 3.02(s, 3H), 3.37(m, 2H), 3.52(m, 4H).
- 14) **1-hexyl-1-methyl pyrrolidinium bis(trifluoromethylsulphonyl)imide [HMPyrr][NTf<sub>2</sub>]**  
 $^1\text{H}$ NMR (200MHz, CDCl<sub>3</sub>): 0.93(t, 3H), 1.29(m, 6H), 1.65(m, 2H), 2.06(s, 4H), 2.95(s, 3H), 3.23(m, 2H) 3.33(m, 4H).
- 15) **1-octyl-1-methyl pyrrolidinium bis(trifluoromethylsulphonyl)imide [OMPpyrr][NTf<sub>2</sub>]**  
 $^1\text{H}$ NMR (200MHz, CDCl<sub>3</sub>): 0.95(t, 3H), 1.28(m, 6H), 1.41(m, 4H), 1.63(m, 2H), 2.10(s, 4H), 2.98(s, 3H), 3.27(m, 2H) 3.37(m, 4H).
- 16) **Tetra butyl phosphonium alanate [TBP][Ala]**  
 $^1\text{H}$  NMR (200MHz, DMSO- $d_6$ ): 0.92 (t, 12H) 0.98 (t, 3H) 1.37(m, 16H) 2.214 (m, 8H), 2.77 (q, 1H)
- 17) **Tetra butyl phosphonium valinate [TBP][Val]**  
 $^1\text{H}$  NMR (200MHz, DMSO- $d_6$ ): 0.64 (d, 3H), 0.76(d, 3H), 0.91(t, 12H), 1.35 (m, 16H), 1.85(m, 1H), 2.17(m, 8H), 2.53 (t, 1H).

## Appendix B

### List of Publications

1. **Nageshwar D. Khupse** and Anil Kumar  
“Delineating Solute-Solvent Interactions in Binary Mixtures of Ionic Liquids in Molecular Solvents and Preferential Solvation Approach”  
*Journal of Physical Chemistry B* **2011**, *115*, 711.
2. **Nageshwar D. Khupse** and Anil Kumar,  
“Contrasting Thermosolvatochromic Trends in Pyridinium-, Pyrrolidinium- and Phosphonium-Based Ionic Liquids”  
*Journal of Physical Chemistry B* **2010**, *114*, 376.
3. **Nageshwar D. Khupse** and Anil Kumar  
“Dramatic change in viscosities of pure ionic liquids upon addition of molecular solvents”  
*Journal of Solution Chemistry* **2009**, *38*, 589.
4. Shraeddha Tiwari, **Nageshwar D. Khupse** and Anil Kumar  
“Intramolecular Diels-Alder Reaction in Ionic Liquids: Effect of Ion-Specific Solvent Friction”  
*Journal of Organic Chemistry* **2008**, *73*, 9075.
5. **Nageshwar D. Khupse** and Anil Kumar  
“Solvent-Induced Viscosity Changes in Ionic Liquids”  
(*Proceeding to National Academy of Science* **2010**, *88*, 1).
6. **Nageshwar D. Khupse** and Anil Kumar  
“Ionic Liquids: new material with wide applications”  
*Indian Journal of Chemistry* **2010**, *49A*, 635.
7. **Nageshwar D. Khupse**, Shabana R Kurolikar and Anil Kumar  
“Temperature dependant viscosity of mixtures of ionic liquids at different compositions”  
*Indian Journal of Chemistry* **2010**, *49A*, 727.
8. **Nageshwar D. Khupse** and Anil Kumar  
“Ionic Liquids as Novel Solvent Media for Electrochemical Devices: Merits and Demerits”  
(*ICEP – 2008 Proceedings, Electroactive Polymers: Materials & Devices, Volume-III*).
9. **Nageshwar D. Khupse** and Anil Kumar

A New Method to Correlate Viscosities of Ionic Liquids in Aqueous and Non-Aqueous Solutions. (Communicated).

10. **Nageshwar D. Khupse** and Anil Kumar

Bimolecular Diels-Alder reaction in binary mixtures of ionic liquids: Complex effects of friction and polarity. (Manuscript under preparation).

## Appendix C

### Posters and Oral Presentations

1. Poster presented at "**10<sup>th</sup> CRSI National Symposium on Chemistry**", during 1<sup>st</sup> – 3<sup>rd</sup> February, 2008, Indian Institute of Science, Bangalore.
2. Oral presentation at "**Third International Conference on Electroactive Polymer: Materials and Devices**" during 12<sup>th</sup> -17<sup>th</sup> October, 2008, Jaipur.
3. Poster presented at "**11<sup>th</sup> CRSI National Symposium on Chemistry**", during 6<sup>th</sup> – 8<sup>th</sup> February, 2009, National Chemical Laboratory, Pune.
4. Poster Presented at National Chemical Laboratory, Pune on the occasion of **Science Day Celebrations** on 27<sup>th</sup> February, 2009.
5. Participated in Workshops **Japanese "Science of Ionic Liquids Project" Symposium** (Prof Yukio Ouchi, Chair) during 29<sup>th</sup> -30<sup>th</sup> May 2009
6. Participated in "**Workshop on the Physical & Electrochemical Properties & Applications of Ionic Liquids**" (Dr Mike Horne & Dr Patrick Howlett, Co-chairs): 1pm - 5pm-31<sup>st</sup> May 2009
7. Poster Presented at "**3<sup>rd</sup> Congress on Ionic Liquids (COIL-3)**" during 31<sup>st</sup> May -4<sup>th</sup> June 2009 held at Cairns Convention Centre, Cairns, Australia.
8. Oral presentation at "**Discussion Meeting on Chemical Reaction in Unusual Media**" during 8<sup>th</sup> and 9<sup>th</sup> October, 2009, at National Chemical Laboratory Pune.
9. Poster presented at "**12<sup>th</sup> CRSI National Symposium on Chemistry**", 4<sup>th</sup> – 7<sup>th</sup> February, 2010, at Indian Institute of Technology, Hyderabad.
10. Poster Presented at National Chemical Laboratory, Pune on the occasion of **Science Day celebrations** on 27<sup>th</sup> February 2010. (Received Best Poster Award)
11. Poster presented at "**13<sup>th</sup> CRSI National Symposium on Chemistry**", during 4<sup>st</sup> – 6<sup>rd</sup> February, 2011, Bhubaneswar.

## **Erratum**