

***Ionic Liquids: Hydrophobicity, Enthalpic  
Effects Accompanying Ionic Interactions  
and their Transport Properties***

*Thesis Submitted to*

**Academy of Scientific & Innovative Research  
(AcSIR) for the degree of  
Doctor of Philosophy  
*In*  
Chemical Sciences**



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April 2017**

## CANDIDATE'S DECLARATION

I, hereby declare that all the experiments in this thesis entitled "**Tonic Liquids: Hydrophobicity, Enthalpic Effects Accompanying Ionic Interactions and their Transport Properties**" submitted for the award of degree of **Doctor of Philosophy** in Chemical Sciences to Academy of Scientific & Innovative Research (AcSIR) have been carried out by me at Physical & Materials Chemistry Division, CSIR-National Chemical Laboratory, Pune-411008, India under the supervision of Dr. Anil Kumar. The work is original and has not been submitted by me to any other institution or university. Research materials obtained from other sources have been duly cited and acknowledged in this thesis.

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## CERTIFICATE

This is to certify that the work incorporated in this thesis entitled, “**Ionic Liquids: Hydrophobicity, Enthalpic Effects Accompanying Ionic Interactions and their Transport Properties**” submitted by **Preeti Jain**, to Academy of Scientific and Innovative Research (AcSIR) in fulfilment of the requirements for the award of degree of **Doctor of Philosophy in Chemical Sciences**, embodies original research work under my supervision in the Physical & Materials Chemistry Division, CSIR-National Chemical Laboratory, Pune-411008, India. I further certify that this work has not been submitted to any other University or Institution in part or full for the award of any degree or diploma. Research material obtained from other sources has been duly acknowledged in the thesis. Any text, illustration, table etc., used in the thesis from other sources, have been duly cited and acknowledged.

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***Dedicated with Extreme Affection and***

***Gratitude***

***To***

***My Dada, Dadi, Mummy and Papa***

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# Acknowledgments

Research is a journey that combines various sciences together and the combination of whose yields a tool, to add those infinitesimal changes in the available knowledge domain to humankind, which result in betterment of human life or improvement in technology, or both. Towards the end of this long journey of small contribution of my research work in science through my doctoral studies, I hereby take opportunity to wish my sincere gratitude to all the members who have been part of it.

First of all, I would like to express the sincere gratitude to my advisor **Dr. Anil Kumar** for his patience, constant encouragement, and helpful guidance over the entire course. I sincerely thank him for considering each and every small idea that came into my mind and giving it a scientific approach that helped me to learn and develop my research skills and abilities. His advice on both research as well as on my career have been priceless. Without his significant contribution and involvement, it was not possible to carry out the work. I am surprised at his patience, which encouraged me when I was depressed during constant failure of my work. His expertise in the subject and ambitious approach will always be a source of encouragement for throughout my life.

I gratefully acknowledge members of my Doctoral Advisory Committee, Dr. Sudip Roy, Dr. Ravi Kumar, Dr. A. A. Kelkar, Dr. B.L.V Prasad, and Dr. Nithyanandhan for their constructive comments throughout the course work evaluation. Their suggestions were always enlightening on different aspects and helped me in improvements in my research and presenting skills.

Many thanks to, Dr. Jitender Sharma and Dr. Akhil Barjatya, who sowed the interest of research into me and directed me towards this excellent field to pursue my doctoral research. I would also take the opportunity to thank all my professors

## Acknowledgments

---

Prof. P. D. Sharma, Dr. Alka Sharma, Dr. Rajshree Pandya from Maharani College and University of Rajasthan during my bachelors and masters studies.

My acknowledgement will never be complete without the special mention of my lab seniors who have taught me the lab culture and have lived by example to make me understand the hard facts of life. I would like to acknowledge. Dr. Nageshwar Khupse, Dr. Gitanjali Rai, Dr. Anshu Singh, Dr. Arpan Manna, Dr. Shashi Kant Shukla, Dr. Amit S. Nagare for all their support and motivation during the initial days of my stay in the lab. I also owe thanks to my seniors Dr. Diganta Sharma, Dr Shraedha Tiwari, Dr. Suvarna Despande, Dr. Rohini Biraydayani, Dr. Pramod Sonawane, Dr. Dilip Satpute and Shri Sanjay Pawar for sharing few but extremely enriching moments. Special thanks to Dr. Gitanjali Rai for exchanging her experimental knowledge. I also thank my cheerful labmates Geetanjali Di, Shashi Da, Raju Da, Arpan Da, Anshu Di, Amit Da, Sachin Da, Vijay for keeping friendly environment in lab and improving my interest and efficiency of work. They have also been cheerful in research and non-research discussions during these years. A very special thanks to Amit Da and Anshu Di for their help during the difficult time.

My thanks to the staff of Physical Chemistry Division for their innumerable help. A special word of gratefulness to Shri. Akbar, Shri. Praksh Panwar, Shri Punekar and Shri Gulabrao Dudhale, who have gone out of way to help me with several official matters. I am grateful to Dr. Ashwini Nangia, Director NCL, and Dr. P. A. Joy, Chair, Physical & Materials Chemistry Division, CSIR-NCL for giving me an opportunity to work in this institute and making the facilities available for carrying out research.

I will always remember the memories of my dearest roommates Ekta Sanghtani, Rajeshwari Rathore and Zenia Motiwala who made my stay at NCL enjoyable. I also Acknowledge my friends Ekta Shukla, Rupa, Nivedita, Veer, Ragini, Amit, Manoj, Leena, Preeti Gupta, Mausami, Preeti Agarwaal, Sandeep, Sarabjot, Rohini,

Prachi, Arthi, Shailja, Ketan, Milan, Ashish, Anupam who recreated the amiable atmosphere and were always a pleasure to interact with. I am also grateful to my far off friends Vijaya, Deepika, Bhawana, Mohit, Faiz who were always in touch. Thank you all!

I would like to thank the hostel mess cooks Sujeet and Chotu for serving us healthy food over the years.

My greatest gratitude goes to the duos, my very close friends, Dr. Pooja Maheswari and Mrs. Devshree Bakliwal. They have constantly supported me in the highs and lows during my life. Special thanks to Dr. Anil Mhashal, for valuable advices, motivation and supporting me through this entire period professionally and personally. My joy, enjoyments and disappointments were always shared by all of them. Thanks to all of you!

Last but not the least, I am grateful to my parents who mean world to me, for their unconditional love and encouragement. They laid the foundation of my perseverance, values and education. Thanks to my Papa for supporting me in achieving my true passion, Research. I thank my cute nephew “Manan”, my sister-in-law Ankita, brothers Sourabh, Hitesh, Gaurav and my cousins specially Rahul for constantly cheering and supporting me. Their prayers have sustained me throughout this journey. I conclude the section with the statement;

*“Acknowledgement is the only way to keep love alive”*

*Barry Long*



## ***Abstract***

# ***Ionic Liquids: Hydrophobicity, Enthalpic Effects Accompanying Ionic Interactions and their Transport Properties***

Chemists are always confronted with the difficult task of selecting appropriate solvents for the chemical processes due to several ecological and economical concerns. Commonly, volatile organic solvents are used on a larger scale due to the wide solubility window. But, the main concerns of using organic solvents arise due to their high volatility and toxicity. In past few years, greener solvents are receiving high demand in both academia and industry as an alternative to conventional volatile organic solvents. Currently, concepts such as atom economy and efforts towards minimization of auxiliary chemicals are the other main concerns. Ionic liquids considered as a new class of solvents and a better substitute to the volatile solvents. Henceforth, as a promising solution to these problems, throughout our thesis we have focused on the designing and application of the ionic liquids. Ionic liquids have different internal environment and physico-chemical properties as compared to the traditional molecular solvents. A systematic study of the intermolecular interactions in the ionic liquids might lead the better understanding of their structural properties and enhance their applicability. Till date significant amount of information is available

from various studies. However, interpretation of the ion-ion and ion-solvent interactions in the pure and binary mixture of ionic liquids is not fully understood. A small amount of solvent can cause large differences in the physico-chemical properties of ionic liquids.

Therefore, in the present thesis we thoroughly investigate the ionic liquids in several chapters addressing different physico-chemical properties relevant to their use as solvents in extraction and separation processes, chemical processes and energy storage applications. Our study also sheds a light on the efforts that have been made since years in understanding the properties of ionic liquids. The physico-chemical properties of ionic liquids and ionic liquid mixtures such as transport properties diffusion, viscosity, conductivity, hydrophobicity and intermolecular interactions are studied. These are important features in designing ionic liquids for their applications as solvents and its mixtures for different industrial processes. The present thesis focuses on the conductivity, viscosity of the binary mixture of ionic liquids and hydrophobicity of the ionic liquids. In addition to this, we also investigate the cation-cation interactions, ion-ion and ion-solvent interactions in terms of excess partial molar enthalpies.

For the convenience, different features of the present research work have been discussed in eight different chapters. Below is given brief descriptions of these chapters:

**Chapter 1:** This chapter introduces a brief introduction, quest and need of the ionic liquids. A detailed literature survey of their evolution, unique physico-chemical properties and wide array of their applications has been discussed. The efficacy of ionic

liquids is often dependent on their viscosity. It drastically changes when added with molecular solvents. The changes in the physico-chemical properties of the binary mixtures of ionic liquids attributed to the interionic interactions. We investigate the nature and consequences of various molecular solvents on the physico-chemical properties of ionic liquids. Various intra/inter molecular interactions such as hydrogen bonding, hydrophobic packing and polarity has been critically examined. The measurement scale of hydrophobicity, partition coefficient has also been discussed.

**Chapter 2:** This chapter briefly outlines the aims and objectives of the proposed research work. The thesis emphasizes on the physico-chemical properties of ionic liquids with molecular solvents and intermolecular interactions.

**Chapter 3:** This chapter describes a detailed experimental procedures used to carried out the experiments. The basic principles and working of the instruments is also been described thoroughly. Additionally, this chapter also includes the detailed procedure of the synthesis of employed protic and aprotic ionic liquids with their purification methods.

**Chapter 4:** This chapter deals with the investigation of the hydrophobicity of alkyl sulfate anion based ionic liquids in the 1-octanol/water biphasic system. This chapter presents a brief but critical survey of the literature about the partition coefficient of various ionic liquids in 1-octanol/water biphasic system with particular emphasis on the intriguing properties of ionic liquids in connection with their intermolecular interactions. Herein, we accentuate the partition coefficient of ionisable species such as ionic liquids as the apparent partition coefficient ( $\log P$ ). Ionic liquids show a greater

tendency to dissociate in the water rich phase. In this chapter, we illustrate the  $\log P$  values of alkyl sulfate based ionic liquids as a function of their initial concentrations. Furthermore, the effect of the cationic ring as well as anions on the  $\log P$  values of ionic liquids is also analysed and discussed in this chapter.

**Chapter 5:** This chapter elaborates our current understanding of the effect of addition of co-solvents to the ionic liquids. Besides increasing the solubility window, co-solvents can have profound effect on the physico-chemical properties of the ionic liquids. The conductance of the binary mixtures of ionic liquids is thoroughly investigated. The chapter 5 is further divided into three sections focusing on different mixtures:

**Section I:** this section emphasizes on the solute-solvent interactions in the binary mixture of alkyl sulfate based ionic liquids with water and alcohols. The molar conductance,  $\Lambda_m$  and viscosities,  $\eta$  of the  $[\text{HSO}_4]^-$  and  $[\text{EtSO}_4]^-$ -based ionic liquids in their binary mixtures is measured at 298.15 K over a range of concentration. Ionic association and solute-solvent interactions in the binary mixture of ionic liquids is quantified from the  $\Lambda_m$  measurement. The limiting molar conductance ( $\Lambda_m^\circ$ ) values correlate well with the structural aspects of ionic liquids and properties of the solvents. To our surprise,  $[\text{HSO}_4]^-$ -based ionic liquids show higher  $\Lambda_m$  in water with respect to other ionic liquids.. We observe that the anions have considerable effect on the  $\Lambda_m$  and association constant of the  $[\text{HSO}_4]^-$  and  $[\text{EtSO}_4]^-$ -based ionic liquids. Additionally, the effect of the relative permittivity of solvents on  $\Lambda_m$  values is discussed thoroughly in this chapter. The intra/inter molecular interactions are investigated using IR



spectroscopy. The study also report diffusion coefficient,  $D^o$  and transport number,  $t$  and ionic mobility,  $\mu$  of cations and anions which are in consistent with the  $\Lambda_m$  values of ionic liquids in their aqueous solution. The chapter focuses on the interplay between hydrogen bonding and availability of free ions.

**Section II:** The ionic nature of the ionic liquids (ionicity) is expressed in terms of free ions in their solutions. The ionic association of alkyl sulfate based ionic liquids in aqueous solutions is measured using Walden plot in terms of ionicity. Ionicity is a measure of association arises from the inter-ionic interactions and a vital parameter for the characterization of ionic liquids. The anomalous observation of ionicity is observed  $\text{EtSO}_4^-$  and  $\text{HSO}_4^-$ -based ionic liquids due to the high basicity of the anions.

**Section III:** This section emphasizes on the conductance measurements in ternary mixtures as ionic liquids + molecular solvent + water at the 298.15 K. The conductivity data correlates with the various solvent properties such as viscosity and relative permittivity of the binary mixtures of solvents (molecular solvent + water) and articulated in this chapter. An interesting interplay of hydrogen bonding and viscosity of the solvent mixtures is described and discussed thoroughly in this chapter. The observations reported in this section are of importance for further implementation of these ionic liquids in various applications such as complex reaction media.

**Chapter 6:** This chapter comprises the enthalpic quantification of ionic liquid solutions. The impact of the solvents on the physico-chemical properties of ionic liquids can be precisely demonstrated by measuring the excess partial molar enthalpies,

$H_{\text{IL}}^{\text{E}}$  of the ionic liquid-solvent mixtures. The chapter is further divided into two sections:

**Section I:** this section envisages the effect of solvents on ionic liquids in terms of enthalpies of the system. We measure  $H_{\text{IL}}^{\text{E}}$  to understand the effect of the alcohol-rich environment on the imidazolium-based ionic liquids.. Interestingly, all the ionic liquids show negative  $H_{\text{IL}}^{\text{E}}$  values with 1-butanol molecules as compared to the other alcohols suggesting possible favorable interactions between ionic liquids and with 1-butanol. The anomalous behavior of 1-butanol is demonstrated in terms of the comparative values of  $\alpha$  and  $\beta$  ( $\alpha \approx \beta \approx 0.84$ ) values. The enthalpic interaction parameters,  $H_{\text{IL-IL}}^{\text{E}}$  and the apparent molar enthalpy,  $\phi_{\text{L}}$  is calculated from the  $H_{\text{IL}}^{\text{E}}$  values for the studied systems and discussed in this chapter.

Ethylated residuals on both the cations of the ionic liquid and the alcohol molecules do not follow the trend exhibited by other ionic liquids-alcohol systems. We further explore the enthalpic measurements of the binary mixture of ionic liquids and solvents having similar alkyl groups.

**Section II:** This section illustrates the enthalpic behavior of ionic liquid-solvent mixtures by measuring the  $H_{\text{IL}}^{\text{E}}$  values. It focuses on the effect of hydrocarbon groups in the cationic part of ionic liquid and solvents to envisage ion-solvent and ion-ion interactions in terms of packing. This section comprises the  $H_{\text{IL}}^{\text{E}}$  values of ionic liquids (one containing ethyl group, [EMIM][BF<sub>4</sub>] and another one is with butyl group, [BMIM][BF<sub>4</sub>]) in their binary mixture with ethylated solvents. Linear Solvation Energy Relationship (LSER) is used as an investigating tool to delineate the respective

contributions of solvent properties. To the surprise we observe, ion-solvent interactions even at the concentrated region of ionic liquids. This is examined and elaborated in terms of  $H_{\text{IL-IL}}^{\text{E}}$  and  $\phi_{\text{L}}$  values.

**Chapter 7:** In this chapter, we elucidate the interactions between the strong electrolytes with those of ionic liquids in aqueous media. This chapter elaborates the ionic interactions of the aqueous solution of ionic liquids with the aqueous solution of salts (inorganic salts). Further the detailed analysis of the role of cation of ionic liquids on the mixing is reported and discussed. This chapter describes in detail, the understanding of nature of cation-cation interactions between the cationic core of ionic liquids and cation of salts which is one of the important physical aspects of the ionic liquids. It also incorporates information that how the solvation of the protic ionic liquids with the aromatic cationic ring is enthalpically varied as compared to the protic ionic liquids having non-aromatic cationic ring. We explain the mixing of ionic liquids possessing aromatic or non-aromatic cationic ring in terms of the enthalpy of mixture.

The results and conclusions of the work undertaken in this thesis are summarized in **Chapter 8.**

The work presented in the thesis provide a fresh outlook of the intermolecular interactions in the binary/ternary mixture of ionic liquids which gives the better understanding and formulating their usage as environmental-benign media in various applications.



## *List of Abbreviations\**

[EMIM]	1-ethyl-3-methyl imidazolium
[BMIM]	1-butyl-3-methyl imidazolium
[HMIM]	1-hexyl-3-methyl imidazolium
[OMIM]	1-butyl-3-methyl imidazolium
[dEIM]	1,3-diethylimidazolium
[BEIM]	1-butyl-3-ethyl imidazolium
[EOIM]	1-ethyl-3-octyl imidazolium
[BPy]	<i>N</i> -butyl pyridinium
[OPy]	<i>N</i> -octyl pyridinium
[MIM]	1-methyl imidazolium
[Py]	pyridinium
[MPyrr]	1-methylpyrrolidium
Cl <sup>-</sup>	chloride
[BF <sub>4</sub> ] <sup>-</sup>	tetrafluoroborate
[NTf <sub>2</sub> ] <sup>-</sup>	bis(trifluoromethylsulphonyl)imide
[HSO <sub>4</sub> ] <sup>-</sup>	bisulfate
[EtSO <sub>4</sub> ] <sup>-</sup>	ethyl sulfate

(\* common abbreviations only)



## List of Symbols<sup>†</sup>

$\log P$	Apparent partition coefficient
$\varepsilon$	Relative permittivity
$\sigma$	Electrical conductivity, S cm <sup>-1</sup>
$G$	Conductance, S
$K$	Cell constant, cm <sup>-1</sup>
$\Lambda_m$	Molar conductivity, S cm <sup>2</sup> mol <sup>-1</sup>
$\Lambda_m^0$	Limiting molar conductivity, S cm <sup>2</sup> mol <sup>-1</sup>
$t_i$	Transport number
$\mu_i$	Mobility
$\eta$	Viscosity, cP
$D$	Self-diffusion coefficient, m <sup>2</sup> s
$E_T^N$	Normalized $E_T$ Scale
$\alpha$	Hydrogen bond accepting ability
$\beta$	Hydrogen bond donating ability
$E_a$	Activation energy, kJ mol <sup>-1</sup>
$H_{IL}^E$	Excess partial molar enthalpy, J mol <sup>-1</sup>
$H_{IL}^{E,\infty}$	Limiting excess partial molar enthalpy, J mol <sup>-1</sup>
$\phi_L$	Apparent molar enthalpy, J mol <sup>-1</sup>
$H_{IL IL}^E$	Enthalpic interaction parameter,
$R$	Gas constant, 8.314 J K <sup>-1</sup> mol <sup>-1</sup>
$T$	Absolute temperature, K
$F$	Faradays constant
$R_H$	Hydrodynamic radius
$N_A$	Avogadro's number
$t$	Time, s

(<sup>†</sup> common symbols only)

# ***Chapter 1***

## ***Introduction***

*A comprehensive literature survey on the discovery of ionic liquids is examined in this chapter. The importance and quest of the 'green' solvent media like ionic liquids is discussed and their unique physico-chemical properties are addressed. This chapter stress upon the usefulness of the ionic liquids in the various fields due to their task specific applicability.*





### 1.1. Journey towards a Green Solvent

Solvents play crucial role in the day to day life that ranges from the smallest biological cell to the large chemical industries. Solvents can modulate solubility, stability and reaction rates and therefore, by selecting an appropriate solvent one can have thermodynamic and kinetic control over a chemical reaction. In the chemical industries, solvents are used as media for chemical reactions and for extraction, separation and purification of chemicals. Despite being beneficiary in the industries, a subject of concern is their potential toxicity. Hence, there is a need for extensive experimentation to understand the risk and the hazards associated with the use of solvents. So far, volatile organic compounds (VOCs) as solvent have been extensively used at industrial scale in most of the chemical manufacturing processes.<sup>[1]</sup> This has given rise to the environmental pollution and hazardous to life on earth. According to the toxicity release index (TRI) the estimated release of VOCs from chemical industries are surprisingly highest as compared to the other industries. The sustainability of a chemical product or process is a consequence of the complex interactions with environment, technological and economical factors. It is very difficult to predict these factors. Therefore, a framework for the environmental consideration of the solvents has been proposed by Fischer and co-workers.<sup>[2]</sup> It deals with the major characteristics of the environmental performance of solvents in chemical production and also incorporates health and safety issues. This framework involves application of two different environmental analysis methods. Environmental, health and safety (EHS) method is a screening method to classify the potential hazards of chemicals.<sup>[3]</sup> The

second method, life cycle assessment (LCA) gives detailed assessment of emission to the environmental as well as resources use over the full life cycle of a solvent, including the production, use, disposal, re-use and recycling.<sup>[4]</sup> Further, the environmental accessibility of different chemical processes can be estimated by the two variables that are E-factor and atom efficiency.<sup>[5, 6]</sup> The E factor can be defined as the mass ratio of waste to desired products. The atom efficiency is the ratio of the molecular weight of all the desired products to the sum of the molecular weight of all the substances. The higher E-factor for a chemical process is an indicator of higher production of waste materials greater negative environmental effect.

Therefore, in recent time, there is increase in demand for environmentally acceptable procedure developed in chemical industry and is widely accepted by the scientific community. The branch of chemistry that deals with such practice emerged as a “Green Chemistry” or “Sustainable Chemistry”.<sup>[7-9]</sup> One of the important tasks of green chemistry is to design and efficiently utilize of chemical products and processes in the manufacture and potential applications of chemical products by avoiding the toxic and hazardous materials. In addition to this, an appropriate selection of the solvent can improve the sustainability of the chemical processes. These concerns arise in three areas: the source and synthesis of the solvent, its properties in use, accompanied by accidental discharge and disposal. Therefore, the Environmental Potential Agency (EPA) and their chief chemist Paul Anastas developed the principles of green chemistry as a set of guidelines to reduce pollution in the chemical industry and to make chemical processes safer and further sustainable.<sup>[7, 8]</sup> For the better practice of

Green Chemistry by different chemical and industrial processes, one should have to follow its 12 principles.<sup>[7, 8]</sup> Among all, there is an urgent need to practice chemistry in less hazardous media for reducing the environmental pollutions.

The idea of green solvents suggests the goal to minimize the environmental impact, hence, few guidelines towards green solvents have been developed;

1. Substitution of hazardous solvents with ones that show better EHS properties, such as increased biodegradability,
2. use of 'bio-solvent' *i.e.* solvents produced with renewable resources such as ethanol produced by fermentation of sugar containing feeds,
3. substitution of organic solvents either with supercritical fluids that are environmentally harmless and
4. ionic liquids that have low vapor pressure and less emission to air.

### **1.2. Ionic Liquids**

The history of ionic liquids may be assessed as a relatively recent one, or one extending from 19<sup>th</sup> century. An ionic liquid is a salt with a melting temperature below the boiling point of water.<sup>[10, 11]</sup> Most of the ionic liquids identified in the literature are liquid at room temperature. Their unique physico-chemical properties make them an ideal green solvent. Ionic liquids are generally made up of ions and short lived ion-pairs. These substances also denoted as liquid electrolytes, ionic melts, ionic fluids, fused salts, liquid salts, ionic glasses, liquid organic salts, low temperature molten salts,

room temperature molten salts, ambient temperature molten salts and designer solvents.<sup>[12]</sup>

### 1.2.1. History of Ionic Liquids

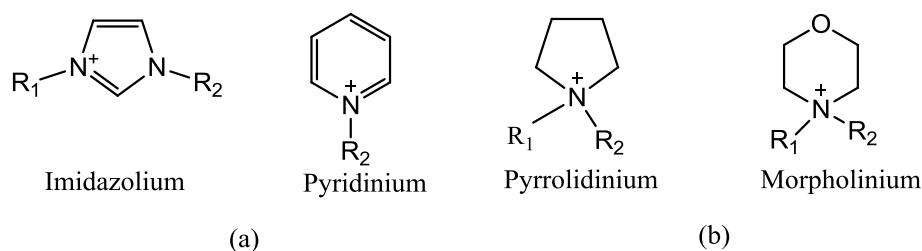
In order to search for the origin of ionic liquids, one has to look back in the 19<sup>th</sup> century, when low-melting organic salts have been discovered for the first time. It was a by-product in the reaction of benzene alkylation, Friedel-Craft reaction, with aluminium chloride ( $\text{AlCl}_3$ ) as a catalyst.<sup>[13]</sup> In 1888, Gabriel and Weiner obtained ethanolanmonium nitrate with the melting point of 52 °C.<sup>[14]</sup> The first synthesized ionic liquid was an ethylammonium nitrate ( $[\text{EtNH}_3][\text{NO}_3]$ ), which was reported by Paul Walden in 1914.<sup>[15]</sup> The 1950s brought interest to organic liquid salts. In 1963, Yoke described a reaction of copper (I) chloride with triethylammonium hydrochloride which yielded a liquid product.<sup>[16]</sup> Ionic liquids received a significant attention after the series of studies accomplished in the 1960s and 70s at the U.S. Air Force Academy by King and co-workers. These studies were aimed to find an electrolyte for the thermal battery.<sup>[17]</sup> In the 1970s and 1980s, alkyl substituted imidazolium and pyridinium cations based ionic liquids with the halide or tetrahalogenoaluminate anions were developed as the potential electrolytes (1<sup>st</sup> generation ionic liquids).<sup>[18, 19]</sup> Ionic liquid precursors are quaternary ammonium halides, known from the 1890s, which were extensively used and tested in the 20<sup>th</sup> century.<sup>[20]</sup> In 1996, Seddon and Rogers defined ionic liquids as chemical compounds with ion structure, which have the melting point below 100 °C.<sup>[10, 11]</sup> A cell was developed containing an ionic liquid formed in the reaction of aluminium chloride with 1-ethylpyridinium bromide as an electrolyte, latter

1-ethylpyridinium chloroaluminate used as a solvent in catalytic reactions.<sup>[21]</sup> Further improvisation was achieved by changing cation to 1,3-dialkylimidazolium.<sup>[19]</sup> Ionic liquids can also trigger chemical reactions. Ionic liquids formed by combining 1-ethyl-3-methylimidazolium chloride with aluminium chloride were used by Wilkes and co-workers as a solvent in the Friedel-Craft reactions, thus demonstrated its catalytic activity at the same time.<sup>[22]</sup> However, both of these ionic liquids are highly unstable in air and water as pyridinium and imidazolium chloroaluminate breaks down immediately when comes in contact with water/air. The sensitivity of ionic liquids to air and moisture was a major impediment in their wide spread applications.<sup>[13]</sup> In the 1990s, Wilkes and Zaworotko demonstrated the preparation of new combinations of cations and anions giving air and moisture stable ionic liquids (2<sup>nd</sup> generation ionic liquids).<sup>[23]</sup> Therefore, replacing a chloroaluminate anion with another anion resulted in obtaining ionic liquids that were absolutely stable with an aqueous solution. Water insensitive ionic liquids dialkylimidazolium cation based ionic liquids, with insensitive inorganic ( $\text{BF}_4^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ) and organic ( $\text{CH}_3\text{COO}^-$ ) anions were synthesized.<sup>[23]</sup>

### **1.2.2. Classification of Ionic Liquids**

A generalized classification of ionic liquids is complicated. They are classified based on the physical differences of a cation and anion, or on their potential applications. It mainly depends on the type of an atom carrying positive charge (cation), such as ammonium, phosphonium, sulfonium etc. The cation classification is further affected by subtle differences in the structure. A positively charged atom may have separate, not interconnected alkyl substituents, known as aliphatic cations (tetraalkylammonium,

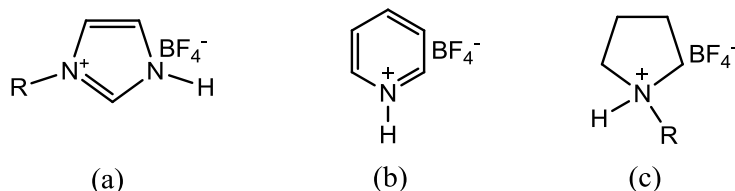
tetraalkylphosphonium etc.).<sup>[24]</sup> A great diversity has been seen in such cation conformations which directly affects their physico-chemical properties.<sup>[25]</sup> Heterocyclic cations are the opposite of the aliphatic cations. In this case, each charged atom is a part of a cyclic or polycyclic group with condensed rings. Heterocyclic cations can be separated into the aromatic heterocyclic cations and non-aromatic heterocyclic cations of ionic liquids as shown in **Figure 1.1**.



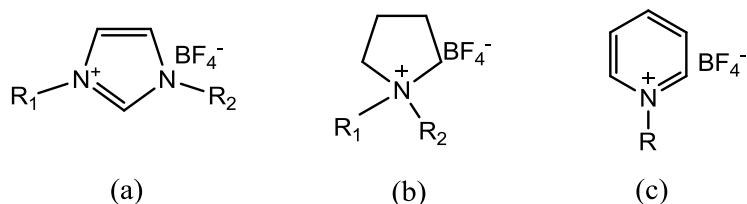
**Figure 1.1.** Names and structures of some aromatic (a) and non-aromatic (b) heterocyclic cations.

Apart from the elements that are positively charged in the cation structure, the consequent classification criterion is further distinguished on the basis of hydrogen atom. If the positively charged atom is chemically bonded with at least one hydrogen atom, the salts are known as protic ionic liquids.<sup>[26]</sup> Therefore, the presence of hydrogen atom at a central cation leads to the formation of a network of strong hydrogen bonds, which is characteristic property of the protic ionic liquids.<sup>[27]</sup> Protic ionic liquids are produced through proton transfer from a brønsted acid to a brønsted base. The first protic ionic liquid, ethanolanmonium nitrate was synthesized by Gabriel in 1888.<sup>[14]</sup> However, if the positively charged atom is attached with the alkyl groups, such ionic liquids called as aprotic ionic liquids.<sup>[28]</sup> Some examples of the

protic and aprotic ionic liquids are presented in **Figure 1.2 and 1.3**, respectively. Ionic liquids can be distinguished in terms of their physico-chemical properties. They can be categorized into three generations based on their designability or chemical composition (also shown in **Scheme 1.1**).<sup>[29]</sup> The ionic liquids have been modified and improvised over the past few decades. The 1<sup>st</sup> generation includes alkyl substituted imidazolium and pyridinium cations based ionic liquids with the halide or tetrahalogenoaluminate anions.<sup>[18, 19]</sup>



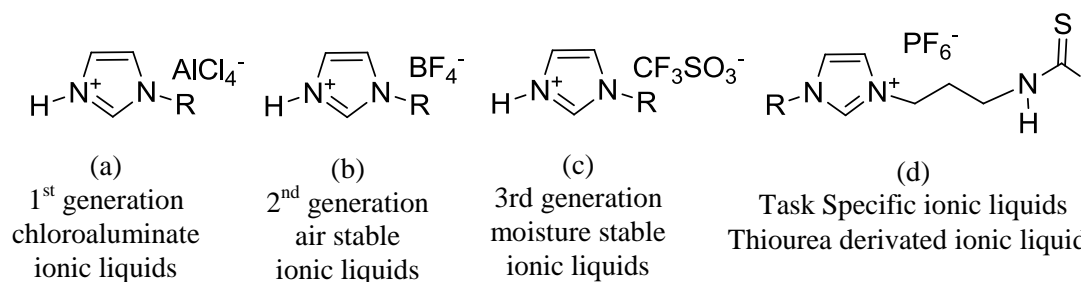
**Figure 1.2.** Names and structures of the protic ionic liquids (a) *N*-alkylimidazolium tetrafluoroborate, (b) pyridinium tetrafluoroborate and (c) *N*-alkylpyrrolidinium tetrafluoroborate.



**Figure 1.3.** Names and structures of the aprotic ionic liquids (a) *N,N*-dialkylimidazolium tetrafluoroborate, (b) *N,N*-dialkylpyrrolidinium tetrafluoroborate, and (c) *N*-pyridinium tetrafluoroborate, (c).

However, the use of 1<sup>st</sup> generation ionic liquids was typically limited due to their unstability in the presence of water and air. Later on, the 2<sup>nd</sup> generation of ionic liquids was synthesized using new combinations of cations and anions giving air stable ionic liquids. 2<sup>nd</sup> generation of ionic liquids mainly contains the dialkylimidazolium as cation

with inorganic anions such as tetrafluoroborate ( $[\text{BF}_4]^-$ ) and hexafluorophosphate ( $[\text{PF}_6]^-$ ).<sup>[23]</sup> The 2<sup>nd</sup> generation ionic liquids were still limited as the anions were unstable towards the moisture. Therefore, water stable trifluoromethanesulfonate, ( $[\text{CF}_3\text{SO}_3]^-$ ) and bis-(trifluoromethylsulfonyl)imide, ( $[\text{NTf}_2]^-$ ) anion based ionic liquids has been received significant consideration and recognized as the 3<sup>rd</sup> generation ionic liquids.<sup>[23]</sup> Currently, researchers have focused on the task specific ionic liquids which designed for their particular application purposes.<sup>[30, 31]</sup>



**Scheme 1.1.** Various generations of ionic liquids

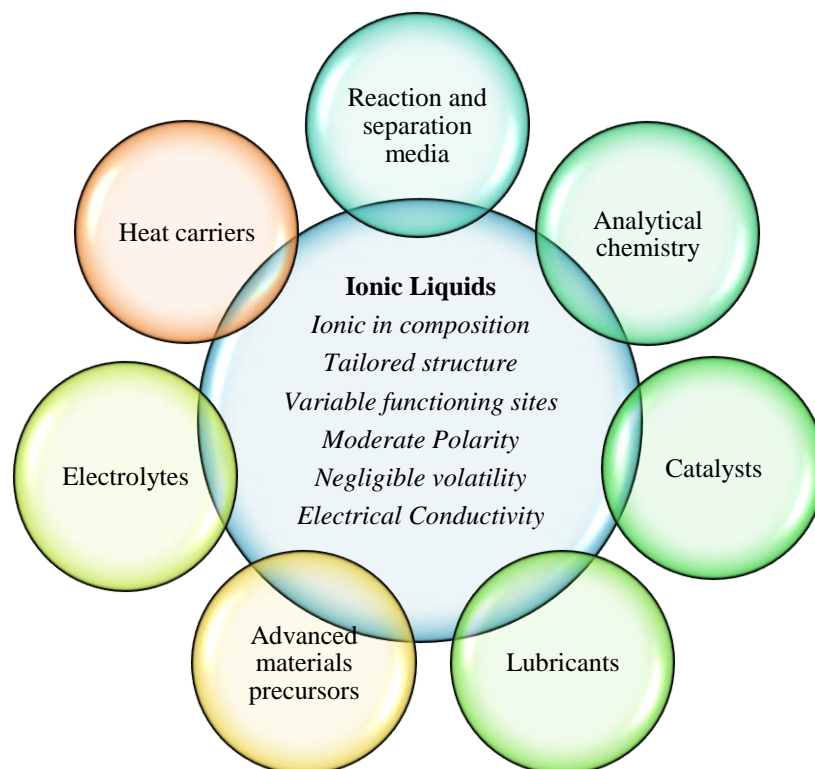
### 1.3. Constituents of Ionic Liquid

Ionic liquids consist mainly of cations and anions. The cations are generally based on imidazolium, ammonium, pyridinium, pyrrolidinium, phosphonium and sulfonium derivatives. The anions used may be of inorganic or organic nature. Some general examples of inorganic anions are halides, tetrachloroaluminate, tetrafluoroborate, hexafluorophosphate and bis(trifluoromethanesulfonyl)imide and common organic anions are the derivatives of sulfate or sulfonate esters, trifluoroacetate, lactate, acetate and dicynamide.



## 1.4. Salient Features of Ionic Liquids

Ionic liquids are defined as salts that are liquid below 100 °C.<sup>[10, 11]</sup> Low melting salts or ionic liquids have been thoroughly investigated in past few decades. Since ionic liquids have negligible vapor pressure, they cannot contribute to the air pollution.<sup>[32]</sup> Ionic liquids mainly used as solvents for chemical reactions, separation and extraction processes.<sup>[33-35]</sup> The great interest comes because ionic liquids possess attractive properties such as high chemical and thermal stability, wide liquidus range, non-flammability, high ionic conductivity, wide electrochemical window, and ability to act as catalyst and finally tenability.<sup>[12, 36]</sup> A schematic representation of properties and applications of ionic liquids is shown in **Figure 1.4**.



**Figure 1.4.** A schematic representation of physico-chemical properties and applications of ionic liquids in various fields.

One can tailor the properties of ionic liquids by changing the chemical composition of ions makes them more attractive. Ionic liquids can be designed by the wise selection of cations, anions and substituents to obtain a compound with prerequisite physico-chemical properties. Therefore, it is possible to synthesize task specific ionic liquids designed to perform a specific application. The number of possible combinations of a cation and anion was estimated to design a structure that provides optimum properties for very specific purposes. This directly translates into several potential applications of ionic liquids in various technological processes.

### **1.5. Physico-Chemical Properties of Ionic Liquids**

Designing a new ionic liquid is moderately easy, but determining its effectiveness as a solvent requires a much more considerable speculation in the determination of physical and chemical properties. It is clear from the observations that a major distinction between the ionic liquids, specifically room temperature ionic liquids and conventional molten salts is that the ionic liquids generally contain the organic cation rather than inorganic cation. The efficacy of the ionic liquids was demonstrated by Osteryoung,<sup>[37]</sup> Wilkes and Hussey<sup>[19, 38]</sup> who established the use of *N*-butylpyridinium and 1-ethyl-3-methylimidazolium containing ionic liquids as liquid electrolytes for electrochemical studies.

The following discussion will concern the some important physico-chemical properties of ionic liquids, such as liquidus range, thermal stability, melting point, viscosity,

solvatochromic parameters, electrochemical properties, ionic conductivities and transport properties.

### 1.5.1. Liquidus Range and Thermal Stability

The wide liquid range demonstrated by ionic liquids, the potential for tailoring size, shape and functionality offer opportunities for control in reactivity unattainable with molecular solvents. The liquidus range of ionic liquids is much greater than that found in common molecular solvents.<sup>[39]</sup> The lower temperature limit, solidification is governed by the structure and interactions between the ions. For example, 1-ethyl-3-methylimidazolium chloride, [EMIM]Cl, 1-ethyl-3-methylimidazolium dicyanamide, [EMIM][N(CN)<sub>2</sub>], melts at 87 °C and -21 °C, respectively.<sup>[39]</sup> Ionic liquids are comprised of ionic components with relatively weak ion-pairing, insignificant low vapor pressure as compared to the molecular solvents.<sup>[40]</sup> The upper limit of the liquid phase of the ionic liquids is usually the thermal decomposition rather than vaporization. Therefore, many researchers have investigated and confirmed that the decomposition temperature ( $T_d$ ) of ionic liquids in most of the cases are high and depend on the strength of interactions between cations and anions.<sup>[41, 42]</sup> The most efficient method for measuring the  $T_d$  is the thermogravimetric analysis (TGA). Ionic liquids have broad liquidus range up to 400 °C as compared to the molecular solvents such as acetone, dichloromethane, ethanol, methanol, ethyl acetate, 2-ethoxyethanol etc.<sup>[39]</sup> Ionic liquids possesses a very large liquid range, for example, 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([BMIM][NTf<sub>2</sub>]) has -89 to 450 °C as compared to water from 0 to 100 °C and for ethanol is -114 to 78 °C.<sup>[39]</sup>

### 1.5.2. Melting Point

The solid-liquid transition temperature of ionic liquids ideally is below ambient as low as 100 °C.<sup>[10, 11]</sup> The widely used method for measuring the transition temperature is Differential scanning calorimeter (DSC). It is known that the characteristic properties of ionic liquids vary with the choice of anion, cation and their symmetry. This property is a result of large size variation between an organic cation of expanded asymmetric structure and small organic/inorganic anion. The diminution in the melting point has been observed due to the decrease in the magnitude of the Coulombic interactions, disturbance of crystal packing and reduction of the crystal lattice energy. Hence, reduction in the melting point can simplistically be achieved by increasing the size of the cation or anion. In general, increasing anion size leads to lower melting points in ionic liquids. However, in case of tetraphenylborate anion based ionic liquids, due to the additional attractive interactions such as  $\pi$ - $\pi$  stacking have higher melting point.<sup>[43]</sup> Reduction in cation symmetry lowers the freezing point and distinctly increases the range of room temperature liquid salts. Increased asymmetric substitution on 1-alkyl-3-methylimidazolium salts expands the asymmetric interruption and deformation of the Coulombic packing of ions leading to the considerable decrease in the melting point. Melting point of few ionic liquids reported as [EMIM][AlCl<sub>4</sub>],<sup>[44]</sup> [BMIM][AlCl<sub>4</sub>],<sup>[44]</sup> [EMIM][NTf<sub>2</sub>]<sup>[45]</sup> and [BMIM][BF<sub>4</sub>]<sup>[46]</sup> are 84, 65, 4 and -81 °C, respectively.

### 1.5.3. Viscosity

The viscosity of the fluid depends on the internal friction of the fluid, and it noticeable itself particularly as the resistance of the fluid to flow. As a class of alternative solvents to VOCs, ionic liquids are more viscous than the most ordinary molecular solvents. Ionic liquids viscosities range from 10 cP (lower value) to 500 cP as higher limit at room temperature.<sup>[47]</sup> For example, the viscosity of [BMIM][BF<sub>4</sub>] and [BMIM][PF<sub>6</sub>] are 219 cP and 450 cP, respectively at 25 °C.<sup>[48]</sup> The viscosity of ionic liquids increases upon increasing the alkyl chain length of cation for imidazolium, pyrrolidinium and phosphonium based ionic liquids such as [MMIM][NTf<sub>2</sub>] < [EMIM][NTf<sub>2</sub>] < [BMIM][NTf<sub>2</sub>] < [OMIM][NTf<sub>2</sub>].<sup>[49]</sup> It also varies with the nature of anions of ionic liquids, i.e. Br<sup>-</sup> based ionic liquid are more viscous than that of [NTf<sub>2</sub>]<sup>-</sup> based ionic liquids. Hydrogen bonding and symmetry of ions also affect the viscosity of ionic liquids.<sup>[44, 50]</sup> Interestingly, in the presence of co-solvents in ionic liquid lead to remarkable reduction in the viscosity of ionic liquids.<sup>[51-55]</sup>

### 1.5.4. Polarity

It is known that the choice of a solvent can have a dramatic effect upon a chemical reaction.<sup>[56]</sup> Primarily, solvent effects in the chemical reactions are based on the solvent polarity. Quantitative ideas of polarity can be elucidated by the obtained observations such as ‘like dissolve like’ and are well established and understood. The macroscopic property polarity is the sum of the all possible intermolecular interactions between a solute and the solvent. The most common measure of polarity used by

chemists in general the relative permittivity ( $\epsilon$ ). It has been measured for a large number of molecular solvents. Although some values for ionic liquids have been derived indirectly, which requires a non-conducting medium is not available for ionic liquids. The efficacy of relative permittivity as an estimation of polarity of ionic liquids should also be considered. Polarity of ionic liquids has also been measured by using microwave dielectric spectroscopy as considered by Weingartner *et al.*<sup>[57]</sup> One of reasons for the estimation of the relative permittivity as a measure of polarity is the large number of solvent phenomena models rely on considering the solvent to be a continuous dielectric medium. Therefore, ionic liquids do not have continuous dielectric media due to the presence of two different species cation and anion which are highly interconnected. The normalized polarity ( $E_T^N$ ) has been calculated from polarity ( $E_T$ ) by using the equation 1.1. The polarity measurement using probing molecules is one of the popular methods used till date.

$$E_T^N = \frac{E_{T(Solvent)} - 30.7}{32.4} \quad (1.1)$$

The response of the probe to the solvent in which it is dissolved is determined by all the possible solvent-probe interactions.<sup>[58, 59]</sup> The first solvatochromic dye to be used with an ionic liquid was Nile red.<sup>[60]</sup> The  $E_T^N$  values for the ionic liquids have been measured and it has been observed that the values are mainly dominated by the nature of cations and anions. It has been seen that the ionic liquids containing same cation with different anions have different  $E_T^N$  values. To separate the non-specific effects of the local electric field from hydrogen bonding effects for a small group of ionic liquids by using the  $\pi^*$  scale of dipolarity/polarizability, and specific interactions by using the

$\alpha$ -scale of hydrogen-bond donor acidity and the  $\beta$ -scale of hydrogen-bond accepting basicity.<sup>[58, 59]</sup> The results are dependent on the experimental details. It reported that the  $\pi^*$  values of the all investigated ionic liquids are high as compared to the molecular solvents.<sup>[61]</sup> The  $\pi^*$  values result from measuring the ability of the solvent to induce a dipole in the probe solute and should be expected to incorporate the effect of Coulombic interactions from the ions as well as dipole and polarizability effects. The  $\alpha$  and  $\beta$  values are mainly determined by the availability of hydrogen-bond donor sites on the cation whereas, the  $\beta$  represents hydrogen bond acceptor site on anions. A considerable amount of research has been conducted on understanding the polarities of ionic liquids. The study suggested that different cation-anion combinations results in different polarities.<sup>[62, 63]</sup> However, the polarities of the studied ionic liquids are within the range of the molecular solvents.

### **1.5.5. Electrochemical Properties of Ionic Liquids**

In the early years, the research was mainly focused on their application as electrochemical solvent.<sup>[17]</sup> Ionic liquids were developed as electrolytes for battery and capacitor.<sup>[64]</sup> They gained remarkable attention because of their wide applicability, especially 3<sup>rd</sup> generation and task specific ionic liquids contributed exponential rise in their research.

Ionic liquids possess an array of properties such as wide electrochemical potential window, reasonably good electrical conductivity and solvent transport properties etc. make them as attractive and beneficial solvents for electrochemical processes. The

quantification of the electrochemical properties is often limited by the viscosity of the ionic liquids, which essentially diminishes upon addition of molecular solvents. However this phenomenon turned out to be the subject of research interest to many other scientists. Later in the similar line, the electrochemical properties of binary and ternary mixtures of ionic liquids have been investigated and thoroughly studied.<sup>[65-68]</sup>

#### **1.5.5.1. Electrochemical Potential Window**

Electrochemical stability is a key parameter for the selection of a solvent for electrochemical processes, which is measured by the range of voltages over which the solvent is electrochemically inert.<sup>[69]</sup> The electrochemical potential window depends on the oxidative and reductive stability of the solvent.<sup>[69]</sup> The most common method used to determine potential window of an ionic liquid is cyclic voltametry. In ionic liquids, the electrochemical potential window mainly depends on the resistance of the cation to reduction and the resistance of the anion to the oxidation.<sup>[70]</sup> Ionic liquids have a wide range of electrochemical potential window varies from 2.1 V to 7.0 V.<sup>[71, 72]</sup> In 1999 Sun, MacFarlane and Forsyth synthesized a novel ionic liquids and reported that the pyrrolidinium cation combined with bis(trifluoromethylsulfonyl)imide anion had a wider electrochemical window around 6.0 V.<sup>[73]</sup> Protic ionic liquids containing chloride, bromide, and iodide anions having narrow electrochemical window which is due to the easy oxidation of these halide anions as compared to the  $[\text{BF}_4]^-$ ,  $[\text{PF}_6]^-$  and  $[\text{NTf}_2]^-$ .<sup>[74]</sup> Most stable anion is tris-(pentafluoroethyl)trifluorophosphate ( $[\text{FAP}]^-$ ) and have a very wide electrochemical



window of 7.0 V was reported for tetrabutylammonium tris(pentafluoroethyl)trifluorophosphate, ([N<sub>4,4,4,4</sub>][FAP]).<sup>[75]</sup>

### 1.5.5.2. Ionic Conductivity

The ionic conductivity ( $\sigma$ ) is a crucial factor in the selection of a solvent for an electrochemical application. The conductivity of an electrolyte is a measure of the available charge carrier and their mobility. Conductivity of ionic liquids obtained by the following expression;

$$\sigma = \frac{l}{AR} \quad (1.2)$$

where,  $l$  is the distance between two electrodes of cell,  $A$  is the area of electrodes,  $R$  is the resistance of the systems. The quantity  $l/A$  is known as the cell constant and determined by measuring the conductivity of standard aqueous KCl solution.

In general, ionic liquids expected to acquire very high conductivities because they are entirely composed of ions but unfortunately, this is not the case. Lower ionic conductivity of ionic liquids have been observed due to the high viscosity, ion pairing, ion aggregation and also large ion size found in many ionic liquids.<sup>[76, 77]</sup> As a class, ionic liquids obtain good ionic conductivities comparable to the best non-aqueous solvent electrolyte systems. The idea to use ionic liquids as novel types of electrolytes for batteries is definitely not new. L. King at the U.S. Air Force Academy tried to replace molten salts based on LiCl-KCl that were used in thermal batteries.<sup>[36]</sup> Hussey and Wilkes replaced the alkyl pyridinium cation, which can be reduced too easy, by

the dialkylimidazolium cation.<sup>[19]</sup> Koch *et al* and Bonhote and Gratzel identified the bis(trifluoromethylsulfonyl)imide anion based ionic liquids with imidazolium and pyridinium cations as the hydrophobic, air and water stable ionic liquids and substituted the 1<sup>st</sup> and 2<sup>nd</sup> generation ionic liquids.<sup>[45, 78, 79]</sup> Conductivity measurements of ionic liquids are essential for understanding the ionic interactions in these systems.<sup>[80, 81]</sup> The temperature dependence of conductivity for an ionic liquid involves a complex interchange of short and long range forces that is strongly affected by the structure and nature of cation and anion.<sup>[82, 83]</sup> The conductivity of ionic liquids increases upon the addition of co-solvents.<sup>[84]</sup> After addition of molecular solvents the viscosity of ionic liquids dramatically decreases and hence greatly enhances the ionic conductivity which enhances the efficacy of ionic liquids for energy requirements in industrial process.<sup>[68]</sup>

### 1.5.5.3. Ionicity

The conductivity and viscosity of ionic liquids are often described in the framework of “Walden rule”,<sup>[85]</sup>

$$\Lambda\eta = \text{constant} \quad (1.3)$$

where,  $\Lambda$  and  $\eta$  are the molar conductance and viscosity of ionic liquids respectively. Ideally, the Walden product ( $\Lambda\eta$ ) remains constant for an ionic liquid, despite of temperature. The relationship between conductivity and viscosity can be explained with Walden plot ( $\log \Lambda$  versus  $\log (1/\eta)$ ).<sup>[86]</sup> Generally, a direct linear relationship has been obtained for the ionic liquids in Walden plot, which clearly demonstrates that

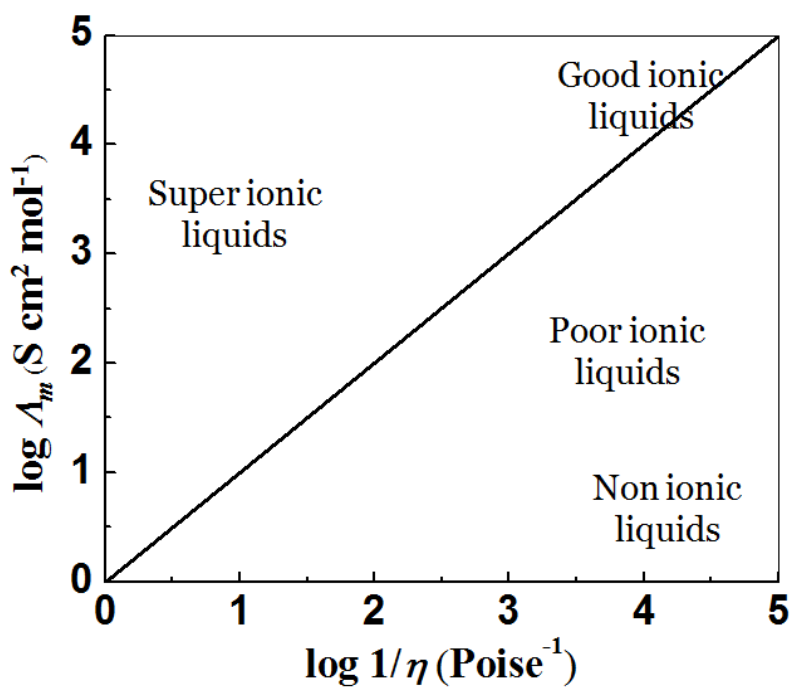
viscosity and conductivity of ionic liquids are strongly coupled. The Walden rule was initially developed for dilute aqueous solutions, but it has extended for non-aqueous electrolyte solutions and molten salts.<sup>[87]</sup>

The conductivity in ionic liquids is mainly derived from the mobility of charged carriers. The ionic nature of the ionic liquids (ionicity) is expressed in terms of amount/number of free ions in their solutions. Ionicity of the ionic liquids and their solutions can be measured by using Walden plot<sup>[68, 88-94]</sup> and the molar conductance ( $\Lambda_{\text{imp}}/\Lambda_{\text{NMR}}$ ) ratios of the systems.<sup>[49, 95-98]</sup> The Walden plot is an appropriate and versatile tool for measuring the ionicity in ionic liquids and it is based on the established concept of the Walden rule.<sup>[68, 88-94]</sup> The straight line with unity slope shows ideal ionicity which corresponds to 0.01 M aqueous KCl solution and this system is known to be fully dissociated. The deviation from the ideal line of KCl relates to the extent of ionicity in ionic liquid solutions. Angell and co-workers have elucidated that the deviation is measured by the vertical distance between ideal line and the plot of the ionic liquids and is denoted by  $\Delta W$ .<sup>[89]</sup> Thus, % ionicity can be calculated from  $\Delta W$  as

$$\% \text{ ionicity} = 10^{(-\Delta W)} \times 100 \quad (1.4)$$

The Walden plots are of special significance as ionic liquids can be classified as super ionic liquids, good ionic liquids, and poor ionic liquids as shown in **Figure 1.5** on the basis of the vertical distance from the ideal line.<sup>[89]</sup> However, greater vertical distance from the ideal line depicts incomplete ionization of those ionic liquids. An increase in

molar conductance of certain ionic liquids may be attributed to the free ions available for the conductance. MacFarlane elucidated the ion-pairing and association behavior of ionic liquids on the basis of a degree of ionicity through Walden plot.<sup>[91, 93]</sup> MacFarlane *et al* have explained the ionicity of phosphonium and pyrrolidinium based ionic liquids with  $[\text{NTf}_2]^-$  anions.<sup>[93, 99]</sup> The Walden plot for a number of phosphonium based aprotic ionic liquids appears to be relatively low degree of ionicity due to the strong ion pairing.<sup>[91]</sup> Apparently, most of the aprotic ionic liquids fall just below to the ideal line and may exhibit higher ionicity.<sup>[93]</sup> The high ionicity of the ionic liquids was achieved by structural modification of the neat ionic liquid.



**Figure 1.5.** Classification of ionic liquids as super ionic liquids, good ionic liquids, poor ionic liquids and non ionic liquids based on the Walden plot.

#### 1.5.5.4. Transport Properties

The behavior of ionic liquids as electrolyte is strongly influenced by the transport property of their constituent ions.<sup>[100]</sup> The transport properties depend on the rate of ion movement and the form in which ion move such as individual ions, ion pairs and ion aggregates. Fundamentally, two quantities used to evaluate the transport properties of electrolytes are ion diffusion coefficient and ion transport number. The diffusion coefficient is a measure of the rate of movement of an ion in a solution, whereas transport number is a measure of the fraction of charge carried by that ion in the presence of an electric field.

The diffusion coefficient of the constituent ions in ionic liquids is commonly measured using either by electrochemical or Nuclear Magnetic Resonance (NMR) methods. Electrochemical method measures the diffusion coefficient of an ion in the influence of a concentration gradient,<sup>[101]</sup> whereas the NMR method measures the diffusion coefficient of an ion without any concentration gradient (self diffusion).<sup>[102]</sup>

Transport number defines the fraction of the total ionic current carried by the individual ions in an electrolyte. Watanabe and co-workers compared the molar conductivities of a variety of imidazolium based ionic liquids measured by the impedance method ( $A_{\text{imp}}$ ) with their molar conductivities calculated from NMR self-diffusion data ( $A_{\text{NMR}}$ ).<sup>[49, 95-98]</sup> They revealed that the magnitude of difference,  $A_{\text{imp}} < A_{\text{NMR}}$  in molar conductance fundamentally depends on the length of alkyl groups on

imidazolium cation and the nature of the anions. They elucidated that the higher magnitude of  $A_{\text{NMR}}$  was due to the movement of neutral ion pairs and ion-pairing which is comes from intermolecular interactions between the cations and anions of ionic liquids.<sup>[103]</sup> It is also reported that the cations are the major contributor to the phenomena as they carries the major portion of the charge. These results were very surprising from ion size perspective *i.e.*, the large size of the cation as compared to the anion. It is proposed that these observations result from the fact that the smaller anions are more structurally constrained in the charge transport process.<sup>[104]</sup>

## 1.6. Classification of Solute-Solvent Interactions

### 1.6.1. Hydrogen Bonds

Hydrogen bonds have significant importance in Chemistry. Hydrogen bonds are the basis of life on earth as they assists water's unique solvent capabilities, holding DNA strands, protein structures, and in ionic conductors. The hydrogen bond is the attractive force between the hydrogen attached to an electronegative atom of one molecule and an electronegative atom of a different molecule.<sup>[105]</sup> Hydrogen bonds are typically weaker than most covalent bonds but significantly stronger than van der Waals interactions. The bond is of order of 5-65 kJ mol<sup>-1</sup> for neutral molecules whereas, for the ionic compounds the range of bond strength rises to 40-190 kJ mol<sup>-1</sup> higher than van der Waals forces (< 8 kJ mol<sup>-1</sup>).<sup>[106]</sup> It is very well studied that the hydrogen bonded networks often help in transferring protons from one place to other therefore can contribute to the conductance. There are studies in the literature emphasizing the

role of hydrogen bonds in ionic liquids assisting conductance.<sup>[107-109]</sup> Hydrogen bonding between cation and anion of ionic liquids has been studied widely by using spectroscopic techniques. As we know Infrared Vibrational Spectroscopy is an established technique to explore the structural and dynamic properties of ionic liquid mixtures, mainly the hydrogen bonding between ions.<sup>[110-114]</sup>

### **1.6.2. Hydrophobic Effect**

The origin of the hydrophobic effect is not fully understood. Some argue that the hydrophobic interaction is mostly an entropic effect initiating from the disruption of highly ordered hydrogen bonds between molecules of liquid water by the nonpolar solute. The term ‘hydrophobic effect’ refers to the poor solubility of nonpolar substances in water as compared to the organic solvents. A simple way to elucidate the hydrophobic effect is the transfer of a small nonpolar molecule from the gas phase or organic solvents to water which has a characteristic thermodynamic signature: positive free energy, negative enthalpy and large negative entropy. Preliminary factors to be accounted for hydrophobic effects are (a) breaking solute-solute interactions, (b) formation of cavity in the medium, (c) solute water interactions and (d) reorientation of water molecules around the nonpolar substance. Hydrophobic effect comprises two distinct processes; hydrophobic hydration and hydrophobic interactions.<sup>[115, 116]</sup> The hydrophobic hydration designates the way in which the nonpolar solutes affect the organization of the water molecules in the immediate vicinity of nonpolar solutes, whereas the hydrophobic interaction reveals the tendency of nonpolar molecules to assemble together in the aqueous media.

### 1.6.2.1. Hydrophobic Hydration

The curiosity in hydrophobic hydration accelerated mainly after Butler who explained the peculiar thermodynamics associated with the transfer of nonpolar molecules from gas phase to water.<sup>[117]</sup> The classical explanation of hydrophobic effects was given by Frank and Evans in 1945.<sup>[118]</sup> Later on, Nemethy and Scherega quantified the model which is known as the “iceberg model”.<sup>[119-121]</sup> After Frank and Evans model, in 1959 Kauzmann emphasized on the importance of hydrophobic effects in protein folding.<sup>[122]</sup>

It is expected that upon transfer of a nonpolar molecule from the gas phase to water, the process will be entropically driven and enthalpically highly unfavorable. The accommodation of a solute molecule in the aqueous solution is considered to be energetically expensive with the cost of broken intra-water hydrogen bonds. Moreover, it has been investigated that interactions between solute molecules with the surrounding water molecules are often comparable to and sometimes even stronger than the same solute molecules in the pure liquid state.<sup>[123-125]</sup> Size and shape of the nonpolar solute also affect the formation of hydrophobic hydration shell. Small spherical particles allow the formation of hydrophobic hydration shell without significant sacrifice of hydrogen bonds. Hydration of a flat surface is characterized by the breaking of large number of hydrogen bonds.

### 1.6.2.2. Hydrophobic Interactions

Conventionally, hydrophobic interactions demonstrate the relations between water and nonpolar solute molecules. Hydrophobic interactions are implied to be driven by the



release of water molecules from the hydrophobic hydration shells of nonpolar solute molecules and their aggregation. Hydrocarbons have very low solubility in water so the dissolution process is unfavorable with the change in Gibbs free energy,  $\Delta G > 0$ . The change in enthalpy of the system,  $\Delta H < 0$  follows that  $\Delta G = \Delta H - T\Delta S$ , entropy of the system must decrease ( $\Delta S$ , change in entropy). Therefore, the mixing of hydrocarbons and water molecules is not spontaneous. If two hydrocarbons mixed in an aqueous solution, aggregation of hydrophobe may take place with restructuring of the water molecules. It is energetically constructive for nonpolar molecules to aggregate with the exclusion of water molecules from their hydration shells. In order to minimize the unfavorable solute (nonpolar)-water interactions, the nonpolar solute will interact preferentially, thus decreasing the number of water molecules in the immediate vicinity of nonpolar solutes. This is very well known as hydrophobic interactions. The water molecules around the nonpolar solutes are more structured than in the bulk liquid.

The hydrophobic effect can be quantified by measuring the partition coefficient of nonpolar molecules between two immiscible phases such as water and octanol.<sup>[126]</sup> The partition coefficient can also be determined in terms of free energy of transfer of a solute from nonpolar phase to aqueous phase which includes the enthalpic and entropic components,  $\Delta G = \Delta H - T\Delta S$ .

### 1.7. Partition Coefficient

The determination of the octanol/water partition coefficient ( $K_{OW}$ ) of a chemical compound serves as a key parameter to evaluate the environmental risk of that chemical and to explore the properties of solvents in the separation and extraction processes.<sup>[33, 127]</sup>  $K_{OW}$  values are important for predicting the potential impact of a chemical on the aqueous environment. Since ionic liquids do not evaporate and most are highly soluble in water, the most probable way of environmental exposure is through aqueous waste or accidental spills.<sup>[32]</sup>  $K_{OW}$  can be correlated to the ecosystem parameters such as bio-concentration, bio-accumulation factors, soil sorption coefficients and toxicity.<sup>[128, 129]</sup> The  $K_{OW}$  values of various ionic liquids would be of considerable to a person selecting an ionic liquid with minimal environmental impact prior to bulk, industrial implementation. Assessment of the environmental acceptability of ionic liquids possessing different combinations of the cation and anion pair, through the measurements of  $K_{OW}$ , is likely to improve their wide applications in industries, where biologically active compounds as well as medicinal compounds are being isolated from bulk reactants or solvents.<sup>[130]</sup>

The 1-octanol/water partition coefficient is an indicator to estimate the environmental acceptability of various chemical compounds because 1-octanol being an amphiphilic solvent have relative permittivity which is almost comparable to the comprehensive lipid phase as well as comprise similar molecular structures, both 1-octanol and lipids contain a polar, hydrophilic oxygen at the end of long hydrophobic alkyl chain.<sup>[131]</sup> The relative permittivity of a compound plays a pivotal role in deciding its dissolution in

any solvent. Therefore, the 1-octanol/water partition coefficient of any biological compound is analogous with its partition in water and living systems.

The distribution of a solute between two immiscible phases after getting equilibrium and at a given concentration depends on the molecular interactions between the solute and the two liquid.<sup>[132]</sup> The  $K_{OW}$  is defined by the following equation;

$$K_{OW} = \frac{c^O}{c^W} \quad (1.5)$$

where,  $c^O$  is the molar concentration of solute in the 1-octanol rich phase, and  $c^W$  is the molar concentration of solute in the water-rich phase. Preferably, concentration of the same solute species is measured in two liquid phases when determining  $K_{OW}$  values. This measurement can be difficult for the species such as acids or salts, where the solute may dissociate more in the aqueous phase than in the 1-octanol phase. For ionisable species such as ionic liquids, the partition coefficient is reported as the apparent partition coefficient ( $\log P$ ). Ionic liquids have a greater tendency to dissociate in the water rich phase. When the solute dissociation is expected, the  $K_{OW}$  usually reported as the ratio of the concentration of both dissociated and associated salt in the octanol-rich phase to the concentration (both dissociated and associated) in water-rich phase.

The partition coefficient of any solute is dependent on the solute-solute or solute-solvent interactions. The solute-solvent and solute-solute interactions can be precisely expressed in terms of their thermodynamic and thermo-physical properties. This may include excess chemical potential,  $\mu_{LL}^E$ , excess partial molar enthalpy,  $H_{LL}^E$ , excess

partial molar entropies,  $S_{IL}^E$  etc.  $H_{IL}^E$  is rarely used in the thermodynamics however, it can provide an absolute and a very precise information about the intermolecular interactions. In the binary mixture of ionic liquids, enthalpic measurements can be very useful to delineate properties of ionic liquids and the underlying interactions at molecular level between ions of ionic liquids and solvent molecules.

### **1.8. Excess Partial Molar Enthalpy, $H_{IL}^E$**

A considerable amount of research has been dedicated to the organic synthesis of ionic liquids and the study of chemical reactions in ionic liquids. However, viscosity of ionic liquids is quite high and therefore limits their applications in chemical reactions.<sup>[133]</sup> The efficiency of the ionic liquids can be improved by decreasing their viscosity. There are reports in the literature which showed that an addition of co-solvent in the ionic liquid significantly reduces their viscosity.<sup>[51-55]</sup> The change in viscosity may be a result of the ion-ion and ion-solvent interactions upon addition of the co-solvent. The impact of the solvent can be precisely demonstrated, for example, in terms of the  $H_{IL}^E$  values of the ionic liquid-solvent mixtures. Systematic investigations of the thermodynamic and thermo-physical properties of ionic liquids are still rare. Even though, these properties are of substantial importance for selecting appropriate ionic liquids and their mixtures to enhance their applicability.

A survey of the literature reveals that the enthalpies of some aprotic ionic liquid solutions have been measured.<sup>[134]</sup> The activity coefficients at infinite dilutions for these ionic liquids were employed to estimate the  $H_{IL}^E$  values.<sup>[135]</sup> The molar solution

enthalpies of some aprotic ionic liquids have also been reported.<sup>[136]</sup> Katayanagi et al has been studied the hydration characteristics of room temperature ionic liquids in terms of the  $\mu_{IL}^E$ ,  $S_{IL}^E$ , and  $H_{IL}^E$  in ionic liquid-water systems at 25 °C by.<sup>[137]</sup> From our group, a systematic investigation of the ion-solvent and ion-ion interactions in the ionic liquid-solvent systems has been done in terms of the  $H_{IL}^E$  values and illustrate the distinct state of the solutions as a function of their concentrations.<sup>[138-142]</sup> Nebig et al<sup>[143]</sup> measured the enthalpies of mixing for 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, [C<sub>1</sub>C<sub>4</sub>Im][NTf<sub>2</sub>] and 1-hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, [C<sub>1</sub>C<sub>6</sub>Im][NTf<sub>2</sub>] with ketones. The  $H_{IL}^E$  of mixing of ionic liquid solutions were observed to be consistent with those calculated by the method based upon the CHELPG (Charges from Electrostatic Potentials using a Grid-based method) atomic charges.<sup>[144-146]</sup> A soft statistical associating fluid theory, SAFT equation of state has also been used to model the pyridinium-based ionic liquids and their mixtures.<sup>[147]</sup> An approach known as Perturbed-chain statistical soft statistical associating fluid theory (PC-SAFT) combined with modified UNIFAC (Dortmund) was used to model properties ionic liquids and their mixtures with solvents.<sup>[148]</sup>

The  $H_{IL}^E$  values can be obtained experimentally by using Isothermal Titration Calorimeter (ITC). ITC is a powerful tool to measure enthalpy data in very dilute solutions with a great precision. In the present thesis we have measured the  $H_{IL}^E$  values for binary mixtures of ionic liquids as;

$$H_{IL}^E = \frac{DH}{n_{IL}} \quad (1.6)$$

where,  $DH$  is the changes in heat, observed after each injection and  $n_{IL}$  indicates the number of moles of ionic liquids added in each titration. By using the  $H_{IL}^E$ , the enthalpic interaction parameters,  $H_{IL}^E$ , calculated graphically by the following equation;

$$H_{IL}^E = (1 - x_{IL}) \frac{\delta H_{IL}^E}{\delta x_{IL}} \quad (1.7)$$

**1.8. References**

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## ***Chapter 2***

### ***Aims and Objectives***

*A brief note on the aims and objectives of the present thesis is comprehended in this chapter. A broad statements of desired outcomes, and the general intentions of the research is described in this chapter.*



## 2.1 Scope of Research

This Chapter briefly describes the aims and objectives of the research work carried in the present thesis. The broad objective here is to seek a deep understanding towards the physico-chemical properties of ionic liquids. This thesis mainly emphasizes on the quantification of physico-chemical properties of ionic liquids to understand the ion-ion and ion-solvent interactions in their mixtures with molecular solvents.

The present thesis is oriented in the investigation of intriguing questions such as: (i) how ionic liquids distribute themselves in the 1-octanol/water biphasic system, (ii) how the transport properties differ of ionic liquids in the binary and ternary mixtures and (iii) how ionic liquids interact with the molecular solvents and the cations of the salts (cation-cation interactions) in their binary mixtures enthalpically?

To address these questions, we synthesized ionic liquids and investigated their properties employing several techniques. In the initial part of the thesis, we measured the concentration dependent apparent partition coefficient of ionic liquids as these are used as a solvent medium for separation and extraction processes in industries. A detailed analysis of the transport properties of ionic liquid mixtures studied using conductance and viscosity measurements due to their wide applications in different energy devices. Furthermore, comprehensive information about the ion-ion and ion-solvent interactions at the molecular level is elucidated energetically in terms of the excess partial molar enthalpy as ionic liquids have applications as solvent in different organic and enzymatic reactions.

## 2.2 Thesis Overview

The objectives of the present thesis are presented below as:

- ✚ The first part of the thesis is intended for understanding the hydrophobic effect of alkyl sulfate anion based ionic liquids which indeed can assist in improving the efficacy of ionic liquids in the separation and extraction techniques. Distribution of ionic liquids between 1-octanol/water biphasic systems presents more insight into the hydrophobic effects of ionic liquids. The alkyl sulfate anions are biodegradable and alkyl sulfate based ionic liquids widely used in the petrochemical industry for extraction processes, and as solvents for organic reactions. Therefore, the understanding of the hydrophobic effect and a quantitative measure of hydrophobic effect; apparent partition coefficient ( $\log P$ ) is useful measure for the researchers in selecting a better ionic liquids. The understanding of the effect of concentration, alkyl chain length, cationic core and anions adds more insight into the existing knowledge of the apparent partition coefficient of ionic liquids.
- ✚ The thesis also focuses on the investigation of physico-chemical properties such as, conductivity, molar association constant, diffusion coefficient, transport number, viscosity, activation energy of diffusional and translational motion. One of the important findings, we report here that the high electron density and the ability of hydrogen bond accepting and donating of alkyl sulfate anions make them more useful as the electrolytes for various electrochemical processes.
- ✚ Transport properties of the ionic liquids have also been investigated in the ternary mixture of ionic liquids; ionic liquids/molecular solvents/water. Our finding can

help researchers to determine the suitable ionic liquid/co-solvent mixture to design the complex reaction mixtures.

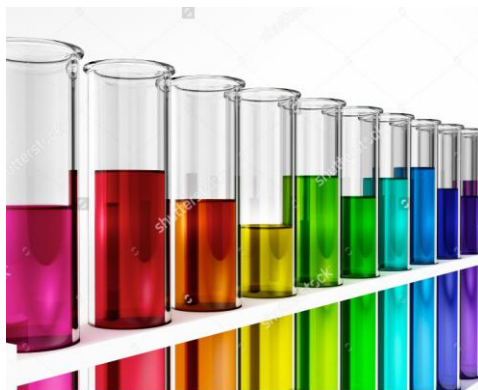
- ✚ This thesis also emphasize on understanding the interactions of the ionic liquid solutions in mono alcohols and ethylated solvents. The thermal effects obtained experimentally using Isothermal titration calorimeter (ITC), are used to delineate the ion-ion and ion-solvent interactions existing between ionic liquids and molecular solvents. This study provides an insight on the interactions at the molecular level between ions of ionic liquids and solvent molecules.
- ✚ In the latter part of thesis, we aim to examine the mixing behavior of common electrolytes such as NaCl, NaBF<sub>4</sub> with the ionic liquids. This investigation sheds a light on the Young's mixing rule and the cation-cation interactions between the large asymmetric organic cations and small symmetric inorganic cations. We investigated the enthalpic behavior of mixing of aqueous solution of ionic liquids with salts and report that the salts have the substantial effects on the ionic liquid solutions containing different cationic cores. It gives the precise information about the interactions at molecular level, prevailing between like charged ions.

Finally we conclude the thesis with the remarks suggesting the importance of the present thesis which can be useful in terms of designing the target specific ionic liquids/co-solvent mixtures with the desired properties. The present thesis will contribute for better understanding of the ionic liquids which can be increase the implementation of green solvents and their efficiency.

## ***Chapter 3***

### ***Materials and Methods***

*This chapter includes the research methodology for carrying out the experimental work. A detailed description of the synthesis of protic and aprotic ionic liquids has been described in this chapter. The experimental tools and techniques used for measuring the physico-chemical properties of ionic liquids are briefly discussed in this chapter.*



### 3.1. Introduction

In this chapter we focus on the synthesis procedure of wide range of ionic liquids and discussion regarding the basic principles of the experimental techniques used. We have synthesized both protic and aprotic ionic liquids as described in the introduction. The ionic liquids were also characterized. The physico-chemical properties of ionic liquids in the present thesis are measured using experimental techniques such as;

- i. Shake flask method was used to quantify the hydrophobic effect of ionic liquids in octanol/water biphasic system.
- ii. Conductometer and viscometer was used for measuring the transport properties of binary mixture of ionic liquids.
- iii. The ion-ion and ion-solvent interactions at the molecular level in the solutions of ionic liquids was studied by using ITC.

### 3.2. Synthesis of Ionic Liquids

#### 3.2.1. Materials and Chemicals

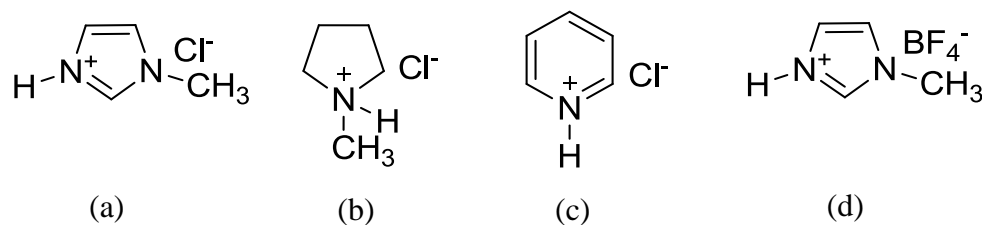
1-Methylimidazole, pyridine, *N*-methylpyrrolidine, 1-ethylimidazole, 1-butylimidazole, 1-octylimidazole, bromoethane, 1-bromobutane, 1-bromohexane and 1-bromooctane (all with purity > 99%), hydrochloric acid (38 wt % in water) and tetrafluoroboric acid (48 wt% in water), NaCl, and NaBF<sub>4</sub> were procured from M/s. Sigma Aldrich Co. These chemicals were distilled prior to their use for experiments. Salts were kept in the oven before the experiment to eliminate the water content. 1-Octanol (with > 99.5%

purity) was purchased from M/s. Fluka Co. and used without further purification. The solvents *N,N*-dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF), acetonitrile, ethanol, methanol, 1-propanol, 1-butanol, 1-hexanol, ethyl acetate, toluene, diethyl sulfate, dibutyl sulfate, sulphuric acid and ethylene glycol of high purity grade were purchased from M/s. Merck Co. and used as procured. Deionised water (resistivity 18.2 M  $\Omega$  cm) was used throughout the experimental measurements.

### 3.2.2. Synthesis of Protic Ionic Liquids

The protic ionic liquids; *N*-methylimidazolium chloride ([MIM]Cl), *N*-methylpyrrolidinium chloride ([MPyrr]Cl), pyridinium chloride ([Py]Cl) and *N*-methylimidazolium tetrafluoroborate ([MIM][BF<sub>4</sub>]) were synthesized and purified according to the reported procedure in the literature.<sup>[1-5]</sup> All the protic ionic liquids were synthesized by mixing the equimolar amounts of brønsted acid and brønsted base. The synthesis was carried out under vigorous stirring, by equimolar and drop-wise addition of brønsted acid (hydrochloric acid and tetrafluoroboric acid) to stirred solution of brønsted base (1-methylimidazole, *N*-methylpyrrolidine and pyridine). As the acid-base reaction is strongly exothermic, the mixture temperature is maintained below 25 °C during the addition of acid under ice cold conditions. Stirring is maintained for 8 h at ambient temperature. Water from the mixture was removed by using a rotavapor at 80 °C under reduced pressure. The synthesized ionic liquids (structures are given in **Figure 3.1**) were further dried under reduced pressure for 12.





**Figure 3.1.** Structures of the synthesized protic ionic liquids, (a) *N*-methylimidazolium chloride ([MIM]Cl), (b) *N*-methylpyrrolidinium chloride ([MPyrr]Cl), (c) pyridinium chloride ([Py]Cl), (d) *N*-methylimidazolium tetrafluoroborate ([MIM][BF<sub>4</sub>]).

### 3.2.3. Synthesis of Aprotic Ionic Liquids

All aprotic ionic liquids employed in the present thesis, were synthesized by the following established procedures.<sup>[1, 6-9]</sup>

#### 3.2.3.1. Synthesis of BF<sub>4</sub><sup>-</sup> and HSO<sub>4</sub><sup>-</sup>-based Ionic Liquids

The synthesis involved two steps;

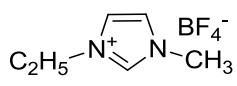
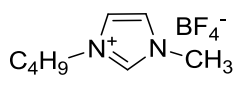
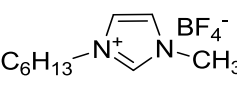
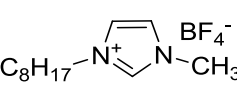
##### a) Quarterisation Reaction:

1-Methylimidazole was added to the excess haloalkane, 1:1.2, (bromoethane, 1-bromobutane, 1-bromohexane and 1-bromooctane) in a round bottom flask fitted with a reflux condenser for 12 h and the temperature was maintained at 343 K. The unreacted starting material was removed by washing with ethylacetate (3-4 times). The excess solvent was removed by using a rotary evaporator under the reduced pressure. Thereafter, the quaternized product was further dried in vacuum for 10 h in order to remove trace of volatile residues.

**b) Metathesis:****(i)  $\text{BF}_4^-$ -based Ionic Liquids**

To a stirred solution of halogenated product of first step, *N,N*-dialkylmethylimidazolium bromide (1 mol) dissolved in 10 ml of dichloromethane (DCM),  $\text{NaBF}_4$  (1.05 mol) was added and the reaction mixture was stirred for 12 h. The crude ionic liquid (**Table 3.1**) in DCM was filtered and dried by rotary evaporator.

**Table 3.1.** Names, structures and acronyms of the  $\text{BF}_4^-$ -based ionic liquids.

Name of Ionic Liquids	Structure	Acronym
1-ethyl-3-methylimidazolium tetrafluoroborate		[EMIM][ $\text{BF}_4$ ]
1-butyl-3-methylimidazolium tetrafluoroborate		[BMIM][ $\text{BF}_4$ ]
1-hexyl-3-methylimidazolium tetrafluoroborate		[HMIM][ $\text{BF}_4$ ]
1-methyl-3-octylimidazolium tetrafluoroborate		[OMIM][ $\text{BF}_4$ ]

**(ii)  $\text{HSO}_4^-$ -based Ionic Liquids**

The halogenated product was dissolved in the acetonitrile and then followed by a drop-wise addition of concentrated sulphuric acid (1.07 mol) to the stirred solution (under ice cold conditions). This addition was carried out in two necked round bottom flask. The reaction mixture was refluxed for 48-72 h and the temperature of reaction mixture was maintained at 343 K.  $\text{HBr}$  formed as a

byproduct was distilled out of the condenser. The excess solvent was removed by a rotary evaporator and ionic liquids (**Table 3.2**) further dried under high vacuum.

**Table 3.2.** Names, structures and acronyms of the  $\text{HSO}_4^-$ -based ionic liquids.

Name of Ionic liquids	Structure	Acronym
1-ethyl-3-methylimidazolium bisulphate		[EMIM][HSO <sub>4</sub> ]
1,3-diethylimidazolium bisulphate		[dEIM][HSO <sub>4</sub> ]
1-butyl-3-ethylimidazolium bisulphate		[BEIM][HSO <sub>4</sub> ]
1-butyl-3-methylimidazolium bisulphate		[BMIM][HSO <sub>4</sub> ]
1-hexyl-3-methylimidazolium bisulphate		[HMIM][HSO <sub>4</sub> ]
1-octyl-3-methylimidazolium bisulphate		[OMIM][HSO <sub>4</sub> ]
1-butyl-3-methylimidazolium butylsulphate		[BMIM][BuSO <sub>4</sub> ]
<i>N</i> -butyl-pyridinium bisulphate		[BPy][HSO <sub>4</sub> ]
<i>N</i> -octyl-pyridinium bisulphate		[OPy][HSO <sub>4</sub> ]

### 3.2.3.2. Synthesis of [EtSO<sub>4</sub>]<sup>-</sup>-based Ionic Liquids

1-methylimidazole (1 mol) was taken in an ice cold bath containing 10 ml of toluene; the drop-wise addition of diethyl sulfate (1 mol) was carried out in pre-cooled 1-methylimidazole solution in toluene in order to maintain the temperature of reaction at 313 K. Following continuous stirring for 4 h, the upper organic layer was decanted carefully. To remove the impurity, the product i.e. the ionic liquid was dried by a rotary vacuum under the reduced pressure and 368 K. Other ethylsulfate-based ionic liquids (**Figure 3.3**) were also prepared by the following similar procedure.

**Table 3.3.** Names, structures and acronyms of the EtSO<sub>4</sub><sup>-</sup>-based ionic liquids.

Name of Ionic liquids	Structure	Acronym
1-ethyl-3-methylimidazolium ethyl sulphate		[EMIM][EtSO <sub>4</sub> ]
1,3-diethylimidazolium ethyl sulphate		[dEIM][EtSO <sub>4</sub> ]
1-butyl-3-ethylimidazolium ethyl sulphate		[BEIM][EtSO <sub>4</sub> ]
1-ethyl-3-octylimidazolium ethyl sulphate		[EOIM][EtSO <sub>4</sub> ]

### 3.2.4. Purification of Ionic Liquids

The volatile impurities were separated by the process of distillation therefore all the starting materials were distilled prior to their use to avoid the halide and other impurities. The impurity possible to be present in major concentration in most of the ionic liquids has been water. Hence, freshly prepared ionic liquids were dried under high vacuum for 12 h at 70 °C to achieve the acceptable low level of water concentration prior to each experiment. The water content of ionic liquids was further checked using Karl-Fischer titration and observed to be 40 ppm. The halide contents were estimated using Volhard titration.<sup>[10]</sup> Further, purity of all the synthesized ionic liquids was ensured with the help of <sup>1</sup>H-NMR spectra (Appendix A).

### 3.3. Methods and Techniques

#### 3.3.1. Method for Measuring the 1-Octanol/Water Partition Coefficient ( $K_{OW}$ )

A shake-flask method, high performance liquid chromatography (HPLC), and slow-stirring method are commonly used to measure the partition coefficient.<sup>[11, 12]</sup> However, each of these methods has certain limitations. The main problem with the HPLC is the comparison of the retention time of a test chemical with the reference chemical.<sup>[13]</sup> Hence measurement of  $K_{OW}$  ( $K_{OW} = c_o/c_w$ ) values by HPLC method is relative and also this method is good in case of chemicals having  $K_{OW}$  values higher than 0.<sup>[13]</sup> On the other hand, the slow-stirring method is limited due to the possibility of formation of micro-droplets of octanol in the

water phase.<sup>[12, 14]</sup> For ionisable species such as ionic liquids, the partition coefficient is reported as apparent partition coefficient ( $\log P$ ).

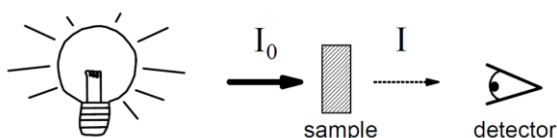
We have used the shake flask method for the measurement of  $\log P$ , which is relatively better than the above-mentioned methods for the current study.<sup>[15]</sup> It essentially avoids emulsification or formation of micro-droplets of octanol in water phase. 1-Octanol and water are not completely immiscible at 298 K. The solubility of water in 1-octanol is quite high approximately up to  $x_w = 0.275$  of water, but the solubility of 1-octanol in water is  $x_o = 7.5 \times 10^{-5}$ .<sup>[16, 17]</sup> We used the mutually saturated 1-octanol and water to determine the  $\log P$  values for the studied ionic liquids. For the estimation of  $\log P$  of ionic liquids, 1:1 (v:v) ratio of water saturated with 1-octanol and 1-octanol saturated with water were taken. The solutions of ionic liquids with known concentration (0.01-0.05 M) were prepared in 1-octanol (presaturated with water) and then equal volume of water (presaturated with 1-octanol) was added to the solution. The sample solution was stirred for 24 h with 170 rpm by orbital shaker at room temperature ( $298 \pm 2$  K). The sample solutions were kept for 24 h to get the equilibrium.

After the equilibration, water and 1-octanol phases were collected separately with a syringe. Molar absorption coefficient ( $\epsilon$ ) was measured by UV-visible spectrophotometer (Varian make, Cary 50) in both phases (water saturated with 1-octanol and 1-octanol saturated with water) in order to calculate the concentration in both the phases by applying the Lambert-Beer Law. UV-visible spectrophotometer was employed to measure absorbance at absorption maxima ( $\lambda_{\max}$ ) of the substances in the

extracted solvents. Water saturated with 1-octanol and 1-octanol saturated with water was used in the sample cell. The concentrations of the dissolved solute were determined from absorbance value obtained from UV-visible spectrophotometer through a pre-calibrated graph. The accuracy of all the measurements was estimated to be  $\pm 3\%$ . The measured data, an average of triplicate measurements are precise to within  $\pm 1\%$ .

### 3.3.2. UV-visible Spectroscopy

Light when falls on the chemical substance can cause several phenomenon such as absorbance, reflection, scattering fluorescence and phosphorescence. A molecule is UV-visibly active when it have a pair of non-bonding electrons or an unsaturated group (double or triple bonds). In UV-visible spectroscopy we measure the change in the intensity of the incident light ( $I_0$ ) after passing through the matter (**Figure 3.2**) by using Lambert Beer law.



**Figure 3.2.** A schematic representation of the absorption phenomenon of light.

The working principal of the UV-vis spectroscopy is based on the Lambert Beer law;

$$A = -\log \frac{I}{I_0} = \epsilon c l \quad (3.1)$$

where,  $I_0$  = intensity of the incident light,

$I$  = intensity of the light after passing through the sample,

$\varepsilon$  = molar absorption coefficient ( $M^{-1} \text{ cm}^{-1}$ )

$c$  = molar concentration,

$l$  = length of the sample cell (cm)

After absorption of light the electrons in the molecule get excited and when they come back to the ground state, it releases characteristic energy. There are several possibilities of electronic transitions as describe below;

$\sigma \rightarrow \sigma^*$  electronic transition from the bonding  $\sigma$  orbital to the anti-bonding  $\sigma^*$  orbital lies in the region  $< 150 \text{ nm}$ ,  $n \rightarrow \sigma^*$  electronic transition from the non-bonding  $n$  orbital to the anti-bonding  $\sigma^*$  orbital held  $< 250 \text{ nm}$ . These transitions are not seen in UV-visible spectroscopy.  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  electronic transitions from the non-bonding  $n$  orbital to the anti-bonding  $\pi^*$  orbital and from the bonding  $\pi$  orbital to the anti-bonding  $\pi^*$  orbital, these transitions takes place in the region  $200\text{-}700 \text{ nm}$ . These transitions fall in the UV-visible region. When a sample having an UV-visible active compound is placed in the spectrophotometer (UV-visible spectrophotometer, Varian make, Cary 50 used in the present thesis), then it absorbs the light and the spectrometer records the wavelength at which absorption of the sample occurs.

### 3.3.3. Conductometer

Conductivity of an electrolyte solution is an assessment of its ability to conduct electricity. In ionic liquid solutions current carried by the charged species *i.e.* cations and anions. Conductivity of solution depends on a number of factors such as;



concentration, mobility of ions, valence of ions and temperature. The high consistency, sensitivity, prompt, and economical cost of conductivity instruments make it a potential primary parameter and used characteristically in many industrial applications to quantify the ionic content in solution. We measured the conductivity of ionic liquids using Systronics Conductometer model 306. The calibration of the instrument has been done by the standard aqueous solution of KCl. The resistance of the solution ( $R$ ) can be calculated using Ohm's law;

$$V = R \times I \quad (3.2)$$

Where,  $V$  = voltage (volts),  $I$  = current (amperes),  $R$  = resistance of the solution (ohms), Conductance ( $G$ ) is defined as the reciprocal of the electrical resistance ( $R$ ) of a solution between two electrodes.

$$G = 1/R \quad (3.3)$$

The conductivity meter essentially measures the conductance, and show the reading converted into conductivity.

Cell constant is the ratio of the distance ( $l$ ) between the electrodes to the area ( $a$ ) of the electrodes.

$$K = l/a \quad (3.4)$$

$K$  = cell constant ( $\text{cm}^{-1}$ ),  $a$  = effective area of the electrodes ( $\text{cm}^2$ ),  $l$  = distance between the electrodes (cm)

---

$$\kappa = G K \quad (3.5)$$

$\kappa$  = conductivity ( $\text{Scm}^{-1}$ ),  $G$  = conductance (S), where  $G = 1/R$ ,  $K$  = cell constant ( $\text{cm}^{-1}$ )

The molar conductance ( $\Lambda_m$ ) has been calculated by using  $\kappa$  by the following equation;

$$\Lambda_m = \frac{\kappa}{M} \times 1000 \quad (3.6)$$

#### 3.3.4. Viscometer

The viscosity of the studied systems in the present thesis is measured using Brookfield cone-plate viscometer. Fundamentally, it is a torque measuring system which consists of a beryllium-copper spring connecting to the rotating cone. It probes the frictional force experienced by the rotating cone inside the stationary plate containing the fluid. This frictional force or resistance experienced by the rotating cone produces torque inside the system which is proportional to the shear stress experienced by the fluid. The viscometer displays the torque and shear stress experienced by the fluid which is converted into the absolute centipoises (mPa.s) unit from the known geometric constants of the viscometer. The viscosity using a Brookfield cone-plate viscometer has been obtained by using the following equation:

$$\eta = (100/\text{RPM})(\text{TK})(\text{torque})(\text{SMC}) \quad (3.7)$$

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

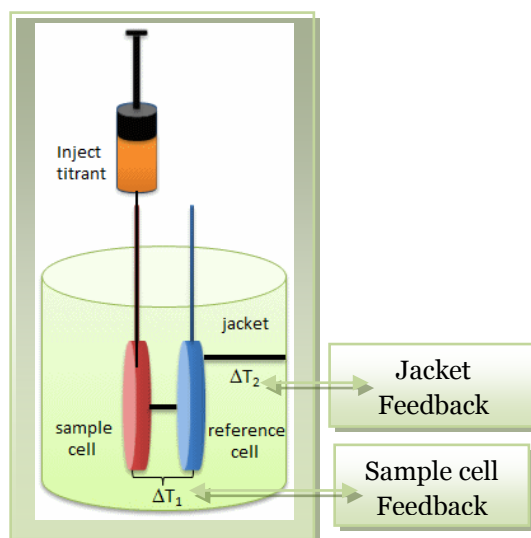
### 3.3.5. Isothermal Titration Calorimeter (ITC)

ITC is the standard and widely used technique to measure the thermal interactions at molecular level. In the present thesis we have measured the excess partial molar enthalpy,  $H_{IL}^E$  of ionic liquid solutions by using the ITC, Microcal, LLC-VP 2000. Fundamentally, ITC measures the thermal change that occurs due to interactions between two substances. Heat is either liberated or absorbed in consequence of the interactions between two substances. ITC monitors these heat changes by measuring the power which required retaining zero temperature difference between the reference and sample cell. By using these measurements of heat we have elucidated an accurate determination of enthalpy of the interionic interactions at molecular level.

#### 3.3.5.1. Working Principle of ITC

In VP-ITC a spinning syringe is used for injecting and subsequent mixing of reactants. A pair of identical coin shaped cells is enclosed in an adiabatic outer shield (Jacket). These cells are made up of highly efficient thermal conducting and chemically inert material such as hastelloy alloy. Access stems travel from the top exterior of the instrument of the cells. Both the coin shaped cell and stems filled with liquid (solution or solvent) during the operation. The capacity of the cell volume is 1.8 ml but the working volume of the cell is 1.4 ml. Temperature difference between the reference cell and sample cell are measured and calibrated to power units. The data is referred to as the DP (differential power) signal between the reference cell and the sample cell. This signal is used to maintain the temperature equilibrium (**Figure 3.3**). The syringe

containing a titrant (solution of ionic liquid) is titrated (injected) into the cell containing the solvent (same solvent in which solution of ionic liquid is prepared).



**Figure 3.3** Working principle of an isothermal titration calorimeter.

The total capacity of titration syringe is 250  $\mu\text{l}$ . An injection which results in the evaluation of heat within the sample cell causes a negative change in the DP power since the heat liberated chemically gives heat that the DP feedback is no longer essential to provide and vice versa occurs for the endothermic processes. Since the DP has units of power, the time integral of the peak yields a measurement of thermal energy,  $\Delta H$ . this heat is released or absorbed in direct proportion to the interactions held between the titrant (solution of ionic liquid) and the solvent (inside the sample cell). When the solvent (in sample cell) becomes saturated with the added titrant solution, the heat signals weakens until only the background heat of dilution is observed. These observations are plotted as the power required to maintain the

isothermal condition throughout the experiment against time. Therefore, the experimental raw data consist of series of heat flow, with each spike analogous to the titrant injection. The pattern of these heat effects as a function of the concentration of the titrant can be analysed to give the thorough information of the interactions between solute and solvent molecules. With the VP-ITC system the whole experiment takes place under the computer control through contribution of the experimental parameters (temperature, number of injections, injection volume) given by users. For the measurement of excess partial molar enthalpies of studied systems in the present thesis, the titrations were carried out between the dilute solutions of ionic liquids as titrant (due to the high viscosity of ionic liquids) with pure solvents in the sample cell. The aliquot of 10  $\mu\text{l}$  were injected in the sample cell after duration of 1200 s the long spacing between the two successive injections ensured the establishment of equilibrium inside the sample cell before the subsequent injection. All the experiments were carried out at room temperature, 298.15 K and rigorous stirring at the rate of 307 rpm. Raw data produced during the experiments was checked for the sharp peaks ensuring that no saturation occurred at each injection.

#### **3.3.5.2. Calibration of the ITC**

Prior to the experiments, the instrument was calibrated using the Y-axis calibration method.<sup>[18, 19]</sup> Along with this DP calibration method, which is a crude calibration assessment method, the equipment was further calibrated using the water-water system and titration of 1-propanol with water at 298.15 K.<sup>[18]</sup> After the completion of 1-propanol-water system, excess partial molar enthalpy,  $H_{\text{IP}}^{\text{E}}$  compared with the reported

$H_{1P}^E$  as  $\delta H_{1P}^E$  (our  $H_{1P}^E$  – reported  $H_{1P}^E$ ). An unsystematic scattering of the  $H_{1P}^E$  values with an average of  $\pm 5\%$  indicates the reliability of our measurements. However, the  $\delta H_{1P}^E$  values can be observed as high as  $\pm 8\%$  for the very dilute solutions. The  $H_{IL}^E$  values obtained from the changes in heat DH observed after each injection as;

$$H_{IL}^E = \frac{DH}{n_{IL}} \quad (3.8)$$

where,  $n_{IL}$  indicates the number of moles of ionic liquids added in each titration. The experimental method has been published from our laboratory.<sup>[20, 21]</sup> The experiments are designed in such a way so as to give the information about the interactions at molecular level, prevailing between ions of ionic liquids and solvent molecules. The quantification of the experimental data also gives insight about how these interactions are tailored, as upon increase the number of these ions in the solution. ITC is a powerful tool to obtain high precision enthalpy data in very dilute solutions.

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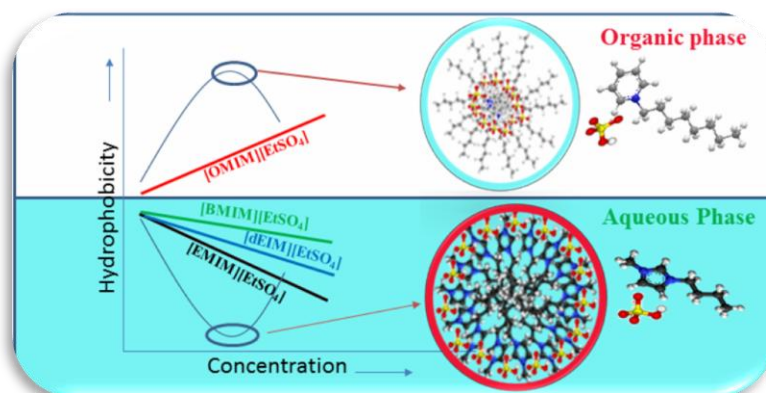




## Chapter 4

### ***Determination of Concentration dependent Apparent Partition Coefficient of Ethyl and Bisulphate anion-based Ionic Liquids***

*This chapter highlights the concentration dependent apparent partition coefficients ( $\log P$ ) which are carefully carried out to elucidate the hydrophobicity of ionic liquids. The effect of anions with the cationic ring and alkyl groups on the  $\log P$  values of ionic liquids is investigated and discussed here. An interesting effect of bisulfate anions on  $\log P$  is observed and discussed thoroughly in this chapter.*



#### 4.1. Introduction

Partition coefficient is a measure of the distribution of a solute molecule between two solvent phases. It depends on their solubility as well as interactions of solute molecules with the two immiscible solvents. 1-Octanol and water are the most commonly used solvents to determine the partition coefficient of substance. This technique is practiced since long time to isolate the natural products such as essence of flowers, medicinal compound from plants etc.

The first systematic study of the distribution between two immiscible liquids was carried out by Berthelot and Jungfleisch.<sup>[1]</sup> They measured the distribution of  $I_2$  and  $Br_2$  in  $CS_2$  and water biphasic system. It was observed from the study that the ratio of the concentrations of solute distributed between two immiscible solvents was a constant, regardless of volume of solutions. However, it partly depends upon the temperature. In 1891, Nernst made a significant contribution to this subject which is known as the Nernst's distribution law.<sup>[2]</sup> He emphasized the fact that partition coefficient would be independent to the concentration of solute if a single molecular species were being considered as partitioned between two phases.

The association and dissociation of solutes in different phases is the most complicated problem in studying partition coefficients. For a true partition coefficient, one must consider the same species in each phase. Afterwards in 1909, Herz proposed an equation which correlated the partition coefficient ( $K_{OW}$ ) to the number of extractions required to removal of solute molecules from the

solution.<sup>[3]</sup> Partition coefficient has also been used as thermodynamic reference parameters for the “hydrophobic bonding” in biochemical and pharmacological systems.<sup>[4]</sup> The hydrophobic effect can be quantified by measuring the partition coefficient of nonpolar molecules between two immiscible phases such as water and 1-octanol a brief discussion has been given in Chapter 1.

The interest in ionic liquids as alternative to VOCs in liquid/liquid separation and extraction process<sup>[5-10]</sup> focuses on the unique combination of properties demonstrated by ionic liquids that distinguish them from molecular level. For using ionic liquids as solvent in separation and extraction processes, the partitioning information of ionic liquid is needed in order to design systems in which extraction can be performed efficiently. In this chapter, we discuss about the partition coefficient of ionic liquids as apparent partition coefficient in 1-octanol/water biphasic system. Unique physico-chemical properties of ionic liquids (discussed in Chapter 1) make them beneficial from the perspective of separation science and technology and also used in many chemical and biochemical reactions.<sup>[11-13]</sup> The overall awareness regarding greenness and sustainability in using ionic liquids as alternative reaction media to the currently used hazardous VOCs has been considered by many researchers especially for industrial applications.<sup>[14]</sup> It is normally considered that hydrophilic ionic liquid shows high miscibility with water, whereas hydrophobic ionic liquid absorbs a small amount of water. The physico-chemical properties like viscosity, conductivity, surface tension of pure ionic liquids vary drastically in the presence of small quantity of water present in ionic liquids.<sup>[15]</sup> This necessitates

rigorous studies of the physicochemical properties akin to the miscibility and fate of ionic liquids in relation to the environment.

The importance and significant features of measuring the partition coefficients have been discussed in Chapter 1 (section 1.7). Evaluation of the environmental acceptability of ionic liquids possessing different combination of cation and anion pair, through the measurements of  $K_{OW}$ , is likely to enhance their wide applications in industries, where biologically active compounds as well as medicinal compounds are being isolated from bulk reactants or solvents.<sup>[16-18]</sup>

For ionisable species such as ionic liquids, the partition coefficient is reported as apparent partition coefficient ( $\log P$ ). Unlike ionic liquids, most of the compounds have the concentration-independent partition coefficient over a wide range of concentration, whereas ionic liquids show a significant dependence on concentration<sup>[19]</sup> due to their distinct behavior towards water and 1-octanol phase. The  $\log P$  value represents the logarithm of the distribution ratio of an ionic liquid in both water and 1-octanol. In both water and 1-octanol, an ionic liquid may acquire three forms: intact ion pair, loose ion pair and the solvent separated ions in highly dilute conditions. At such highly dilute conditions, the precise estimation of each individual form is extremely difficult. We have measured the concentration in each phase by using UV-visible spectroscopy, which detects the imidazolium cationic ring in the all forms discussed above (whether dissociated or associated).

Some reports exist on the determining  $K_{ow}$  values of ionic liquids and on the effect of alkyl chain length of the cationic group of ionic liquids on their partition in both the phases.<sup>[20-23]</sup> Brennecke et al have measured the 1-

octanol/water partition coefficient of dialkylimidazolium ionic liquids by varying the anions ranging between 0.003-11.1 at room temperature.<sup>[23]</sup> The binary liquid-liquid equilibrium (LLE) data of alkylimidazolium chlorides with both water as well as 1-octanol have been measured and the solubility data used to estimate  $K_{ow}$  values.<sup>[24, 25]</sup> Apart from experimental methods, many new different methods have been established to predict  $K_{ow}$  such as a sum of fragment contributions or atom derived group equivalents.<sup>[26, 27]</sup> Most of the ionic liquids, the partition coefficient of which has been reported till date contain different halides as their anions. The use of halide as an anion in an ionic liquid gives rise to great limitation in industrial applications. Recently, ionic liquids have been modified structurally for enhancing their biodegradability. It has been studied that the imidazolium-based ionic liquids are biodegradable and therefore the biodegradability of various classes of ionic liquids should be explored predominantly on the basis of modification of the anion.<sup>[28-30]</sup> The replacement of the halide-based anion by alkyl sulphate anion, enhances their biodegradability to 54%. This is relatively close to the 60%, an acceptable level for a substance to be categorised as readily biodegradable.<sup>[31-33]</sup> Alkyl sulphate anion-based ionic liquids are widely used in the petrochemical field for extraction processes,<sup>[34-36]</sup> alternatives to the routine hydrodesulfurization,<sup>[37]</sup> as azeotrope breaker in extractive distillation,<sup>[38]</sup> and can be synthesized efficiently as well as in a halide free way at reasonable costs.<sup>[39]</sup> Recent studies have shown that 1-ethyl-3-methylimidazolium ethyl sulphate possesses an acceptable level of toxicity.<sup>[40]</sup> Besides their application in extraction processes, the alkyl sulphate-

based ionic liquids are used as solvents for organic reactions resulting in many remarkable and successful outcomes.<sup>[41-43]</sup> As the alkyl sulphate-based ionic liquids possess unique physico-chemical properties like biodegradability and adequate level of toxicity, these should be further explored and analysed in depth for their better applications such as solvents in separation, liquid-liquid extraction and for the removal of nitrogen and sulphur containing compounds from currently used fuels. The lack of partition data of alkyl sulphate anion-based ionic liquids diminishes their use as alternative solvents in the industries.

No reports as such are available in the literature on the concentration dependent study of apparent partition coefficients of alkyl sulphate based ionic liquids. The study of the relationship between the apparent partition coefficient and the initial concentration of alkyl sulphate based ionic liquids in 1-octanol/water binary phase is of high interest and significance. The purpose of using the bisulphate and ethyl sulphate anion-based ionic liquids as discussed above and an additional feature as ethyl sulphate anion ( $[\text{EtSO}_4]^-$ ) possesses higher electron density as evident from the hydrogen bond acceptor ability or basicity denoted by a solvent parameter called  $\beta$ . The  $\beta$  values for  $\text{EtSO}_4^-$  containing ionic liquids ( $\approx 0.788$ ) is close to that of DMSO, a polar aprotic solvent ( $\approx 0.748$ ).<sup>[41, 43]</sup> Due to the high charge density and the basicity, DMSO can solvate the cations. Similarly,  $\text{EtSO}_4^-$  anion possesses high charge density and basicity, therefore it can interact with imidazolium cation to a greater extent and can be present as an intact ion pair.

In this Chapter, we present the variation in the  $\log P$  by altering the substituents present in both cations and anions of ionic liquids. The ionic liquids investigated

in the present study are 1-ethyl-3-methylimidazolium ethyl sulphate ([EMIM][EtSO<sub>4</sub>]), 1,3-diethylmethylimidazolium ethyl sulphate ([dEMIM][EtSO<sub>4</sub>]), 1-butyl-3-ethylimidazolium ethyl sulphate ([EBIM][EtSO<sub>4</sub>]), 1-ethyl-3-octylimidazolium ethyl sulphate ([EOIM][EtSO<sub>4</sub>]), 1-butyl-3-methylimidazolium bisulphate ([BMIM][HSO<sub>4</sub>]), 1-hexyl-3-methylimidazolium bisulphate ([HMIM][HSO<sub>4</sub>]), 1-methyl-3-octylimidazolium bisulphate ([OMIM][HSO<sub>4</sub>]), *N*-butyl-pyridinium bisulphate ([BPy][HSO<sub>4</sub>]), *N*-octyl-pyridinium bisulphate ([OPy][HSO<sub>4</sub>]) and 1-butyl-3-methylimidazolium butyl sulphate ([BMIM][BuSO<sub>4</sub>]). A thorough synthesis process and structure of these ionic liquids have been described in Chapter 3. In this work, first, the  $\log P$  values of these ionic liquids have been measured and illustrated over a wide range of concentrations (0.01 to 0.05 M) as a function of their initial concentration. Subsequently, the effect of the cationic ring as well as anions analysed on the  $\log P$  of ionic liquids by comparing the  $\log P$  data of [BPy][HSO<sub>4</sub>], [OPy][HSO<sub>4</sub>], [BMIM][HSO<sub>4</sub>], [BMIM][BuSO<sub>4</sub>], and [OMIM][HSO<sub>4</sub>]. Eventually, we investigate the effect of number of carbon atoms on the  $\log P$  values.

#### **4.2. Measurement of 1-Octanol/Water $\log P$**

By the definition ‘1-octanol-water partition coefficient’ represents the ratio of the solubility of a given compound between 1-octanol and water at a given temperature. If compound ‘X’ is dissolved in 1-octanol/water biphasic system, equilibrium will be reached after certain period of time for both the phases at



certain temperature. It is known that during the prevalence of equilibrium of distribution of the compound X between 1-octanol-rich phase and water-rich phase, activity will be same in both the phases. Activity can be expressed as ‘*a*’ = *c* × *γ* i.e. multiplication of molar concentration, *c* and the activity coefficient, *γ*. Since activity of the compound ‘X’ is same in both the phases, then  $X_{aw} = X_{ao}$  ( $X_{aw}$  indicates the activity at water;  $X_{ao}$  indicates activity at 1-octanol phase of the compound X). At equilibrium,

$$X_{aw} = X_{ao} \quad (4.1)$$

$$c_w \times \gamma_w = c_o \times \gamma_o \quad (4.2)$$

$$\frac{c_o}{c_w} = \frac{\gamma_o}{\gamma_w} \quad (4.3)$$

At constant temperature and pressure, if the compound ‘X’ is present in the water and 1-octanol phases at extremely dilute condition, the ‘infinite dilute’ condition activity coefficients remain invariable with small variation in the concentrations. It implies that the ratio of concentrations ( $c_o/c_w$ ) at equilibrium remain constant i.e.  $K_{ow} = c_o/c_w$  represents constant unit less value, independent of composition at constant temperature. The log *P* value of ionic liquids has been measured by using following expression;

$$\log P = \log \left( \frac{c_o}{c_w} \right) \quad (4.4)$$

A detailed description of the shake flask method which we have used to measure the log *P* values of ionic liquids given in Chapter 3.

### 4.3. Results and Discussion

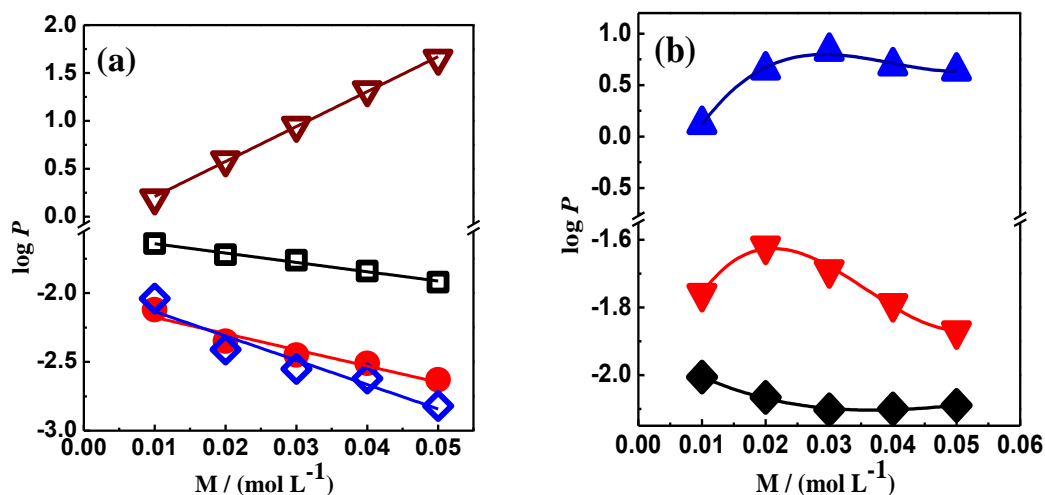
This Chapter mainly demonstrates the effect of concentration on  $\log P$  values of ionic liquids. Therefore, the effect of cationic core and anions has also been observed and discussed as below in several parts.

#### 4.3.1 Effect of Concentration on Log $P$

It is interesting to know that how the  $\log P$  of ionic liquids varies with the concentration of a given ionic liquid. The  $\log P$  values as a function of concentration of the ionic liquid are shown in **Figure 4.1** for [EMIM][EtSO<sub>4</sub>], [dEIM][EtSO<sub>4</sub>], [BEIM][EtSO<sub>4</sub>], [EOIM][EtSO<sub>4</sub>], [BMIM][HSO<sub>4</sub>], [HMIM][HSO<sub>4</sub>] and [OMIM][HSO<sub>4</sub>]. As seen from **Figure 4.1**, the  $\log P$  values of these ionic liquids depend upon their concentrations. Negative  $\log P$  value indicates the hydrophilic nature whereas positive  $\log P$  value shows the hydrophobic nature of a solute. In the present study, we have observed that the hydrophobicity or hydrophilicity of an ionic liquid linearly increases by enhancing the concentration of the ethyl sulphate anion-based ionic liquids. The ionic liquids with lower alkyl group are hydrophilic in nature, and their hydrophilicity increases linearly with concentration as shown in **Figure 4.1(a)**. The  $\log P$  values vary from -2.04 to -2.82, -2.12 to -2.63, and -1.64 to -1.92 for [EMIM][EtSO<sub>4</sub>], [dEIM][EtSO<sub>4</sub>] and [BEIM][EtSO<sub>4</sub>], respectively over a wide range of concentrations from 0.01 to 0.05 M (**Table 4.1**). On the other hand, the hydrophobicity of [EOIM][EtSO<sub>4</sub>] varies from 0.19 to 1.65 as a function of

concentration in the range of 0.01 to 0.05 M as shown in **Figure 4.1 (a)**. The  $\log P$  values obtained for  $[\text{HSO}_4^-]$ -based ionic liquids demonstrated interesting results about the concentration dependent hydrophilicity or hydrophobicity. We have observed flip-flop behaviour in hydrophobicity or hydrophilicity for  $[\text{HSO}_4^-]$ -based ionic liquids with respect to the concentration as seen in **Figure 4.1(b)**. These ionic liquids show unusual behaviour beyond a particular concentration. In the case of  $[\text{BMIM}][\text{HSO}_4]$ , upon increasing the concentration from 0.01 to 0.03 M, the  $\log P$  value decreases from -2.01 to -2.11 and beyond this concentration, the  $\log P$  value a small change has been observed (-2.10 and -2.09 at 0.04 and 0.05 M, respectively). These results reveal that  $[\text{BMIM}][\text{HSO}_4]$  possesses hydrophilic behavior at lower concentrations and shifts towards hydrophobic behavior upon increasing their initial concentrations. The  $\log P$  values of  $[\text{HMIM}][\text{HSO}_4]$  increase from -1.76 to -1.62 with increasing the concentrations from 0.01 to 0.02 M and above that concentration, the  $\log P$  values decreases up to -1.87. It is observed that up to 0.02 M concentration, the hydrophilicity decreases and beyond that concentration, the hydrophilicity of the ionic liquids increases. Similarly, in the case of  $[\text{OMIM}][\text{HSO}_4]$ , the  $\log P$  value increases from 0.12 to 0.83 on an increase in the concentration from 0.01 to 0.03 M (**Table 4.2**). After that it decreases from 0.83 to 0.64 as concentration increases from 0.03 to 0.05 M. On moving towards  $[\text{HMIM}][\text{HSO}_4]$ , the polarity of ionic liquid decreases so the interactions with water become less favorable.  $[\text{HMIM}][\text{HSO}_4]$  shows higher  $\log P$  values as compared to  $[\text{BMIM}][\text{HSO}_4]$  and lower to  $[\text{OMIM}][\text{HSO}_4]$  as shown in **Figure 4.1(b)**. The change from

hydrophobic to hydrophilic nature and *vice-versa* of these ionic liquids may occur due to self-aggregation. It has also been reported that self-aggregation of ionic liquids may occur in aqueous solution.<sup>[44, 45]</sup> The  $\log P$  data obtained in the study revealed the formation of aggregates in the aqueous phase during the distribution of ionic liquids between 1-octanol/water binary system.



**Figure 4.1.** Variation of  $\log P$  with concentration,  $M$  ( $\text{mol L}^{-1}$ ) (a) for [EMIM][EtSO<sub>4</sub>] (◇), [dEIM][EtSO<sub>4</sub>] (●), [BEIM][EtSO<sub>4</sub>] (□), [EOIM][EtSO<sub>4</sub>] (▽) and (b) For [BMIM][HSO<sub>4</sub>] (◆), [HMIM][HSO<sub>4</sub>] (▼), [OMIM][HSO<sub>4</sub>] (▲).

The [HSO<sub>4</sub>]<sup>-</sup>-based ionic liquids show different behaviour as compared to [EtSO<sub>4</sub>]<sup>-</sup>-based ionic liquids, because of the less basicity and the possibility of formation of aggregates. At lower concentrations, ionic liquids exist as intact ion pairs in aqueous phase.

**Table 4.1.** Apparent partition coefficient ( $\log P$ ) values of [EtSO<sub>4</sub>]<sup>-</sup>-based ionic liquids as a function of concentration at 298 K.

M/ mol L <sup>-1</sup>	$\log P$			
	[EMIM][EtSO <sub>4</sub> ]	[dEIM][EtSO <sub>4</sub> ]	[EBIM][EtSO <sub>4</sub> ]	[EOIM][EtSO <sub>4</sub> ]
0.01	-2.04 ± 0.13	-2.12 ± 0.08	-1.64 ± 0.02	0.19 ± 0.02
0.02	-2.41 ± 0.02	-2.35 ± 0.05	-1.72 ± 0.02	0.59 ± 0.05
0.03	-2.55 ± 0.05	-2.45 ± 0.03	-1.76 ± 0.00	0.95 ± 0.07
0.04	-2.62 ± 0.06	-2.51 ± 0.02	-1.84 ± 0.00	1.32 ± 0.03
0.05	-2.82 ± 0.03	-2.63 ± 0.03	-1.92 ± 0.00	1.65 ± 0.01

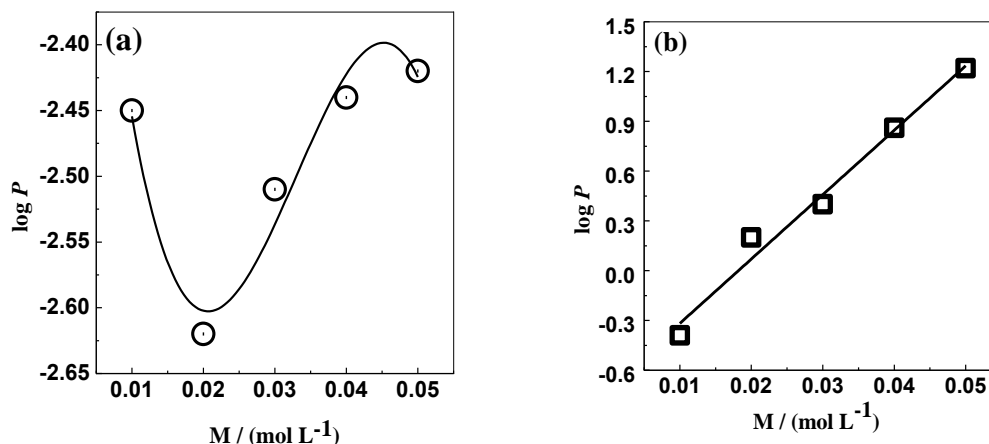
At lower concentrations of ionic liquids, strong van der Waals interactions take place between the hydrophobic alkyl chain of ionic liquids and the hydrophobic part of the 1-octanol thereby decreasing the hydrophilicity. However, upon moving towards the higher concentration the possibility of aggregate formation increases. The aggregate formation takes place due to the van der Waals interactions between the hydrophobic parts of ionic liquids. The flip-flopping in the hydrophilicity/hydrophobicity depends on the orientation of aggregates. Orientation of the imidazolium-based ionic liquid in an aggregate form favours the hydrogen bonding between [HSO<sub>4</sub>]<sup>-</sup> and the aqueous phase. In the case of imidazolium-based ionic liquids, the hydrophobic tail of ionic liquids resides away from the water molecules, whereas hydrophilic head of ionic liquid and counter ions towards the aqueous phase due to lesser possibility of  $\pi$ - $\pi$  stacking.

**Table 4.2.** Apparent partition coefficient ( $\log P$ ) values of  $[\text{HSO}_4^-]$ -based ionic liquids as a function of concentration at 298 K.

M /	$\log P$					
mol L <sup>-1</sup>	[BMIM] [HSO <sub>4</sub> ]	[HMIM] [HSO <sub>4</sub> ]	[OMIM] [HSO <sub>4</sub> ]	[BPy] [HSO <sub>4</sub> ]	[OPy] [HSO <sub>4</sub> ]	[BMIM] [BuSO <sub>4</sub> ]
0.01	-2.01 ± 0.02	-1.76 ± 0.02	0.12 ± 0.02	-2.45 ± 0.02	-0.39 ± 0.02	-0.59 ± 0.04
0.02	-2.07 ± 0.03	-1.62 ± 0.02	0.66 ± 0.02	-2.63 ± 0.01	0.20 ± 0.01	-0.69 ± 0.05
0.03	-2.11 ± 0.02	-1.69 ± 0.02	0.83 ± 0.04	-2.51 ± 0.01	0.40 ± 0.07	-0.76 ± 0.03
0.04	-2.10 ± 0.00	-1.79 ± 0.01	0.69 ± 0.01	-2.44 ± 0.00	0.86 ± 0.03	-0.70 ± 0.03
0.05	-2.09 ± 0.00	-1.87 ± 0.02	0.64 ± 0.02	-2.42 ± 0.00	1.22 ± 0.09	-0.67 ± 0.02

The orientation of an ionic liquid above the critical aggregate concentration ( $c_{ac}$ ) favors its interactions in aqueous phase over the organic phase, leading to an increase in the hydrophilicity of the ionic liquid beyond the  $c_{ac}$ . These observations are consistent with the earlier reports that the partition coefficient of ionic species is concentration dependent.<sup>[19]</sup> A similar trend has also been observed in the case of  $[\text{OPy}][\text{HSO}_4^-]$  and  $[\text{BPy}][\text{HSO}_4^-]$  as shown in **Figure 4.2**. The value of  $\log P$  decreases from -2.45 to -2.63, as the concentration increases from 0.01 M to 0.02 M. However, beyond this concentration,  $\log P$  value increases to -2.42 at 0.05 M (**Table 4.2**) in  $[\text{BPy}][\text{HSO}_4^-]$  as shown in **Figure 4.2(a)**. It is shown in **Figure 4.2(b)** that upon increasing the concentration from 0.01 M to 0.05 M, the  $\log P$  value increases from -0.39 to 1.22, respectively. In the case of the pyridinium-based ionic liquids, the structure of aggregates is different from those observed for the imidazolium-based ionic liquids. The

pyridinium-based ionic liquids show favourable arrangement for  $\pi$ - $\pi$  stacking between rings. At lower concentrations of [BPy][HSO<sub>4</sub>], the ionic liquid remains as intact ion pair and thus shows favourable interactions with aqueous phase through hydrogen bonding between [HSO<sub>4</sub>]<sup>-</sup> and water.

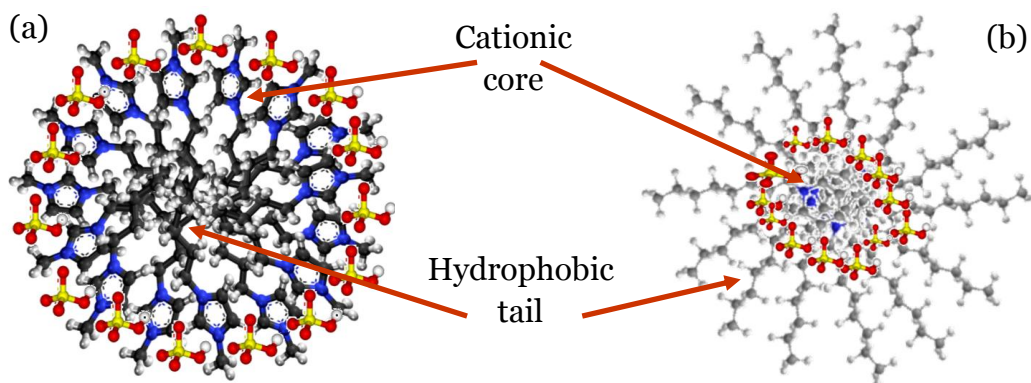


**Figure 4.2.** Variation of  $\log P$  with concentration,  $M$  (mol L<sup>-1</sup>) for (a) [BPy][HSO<sub>4</sub>] and (b) [OPy][HSO<sub>4</sub>].

With an increase in the concentration of the ionic liquid, the possibility of aggregate formation also increases. The  $\pi$ - $\pi$  stacking between rings orients the hydrophilic head residue away from the water molecules and hydrophobic part towards it (**Figure 4.3**). Similarly, the orientation of aggregates of the pyridinium-based ionic liquids favours the interaction with 1-octanol phase, as van der Waals interactions are enhanced between the hydrophobic part of aggregates and the hydrophobic tail of 1-octanol. The observed  $\log P$  value reveals that the hydrophilicity of [BPy][HSO<sub>4</sub>] increases in lower concentration,

but beyond cac (0.02 M), the hydrophilicity of the ionic liquid decreases as the orientation of aggregate favours the interactions with organic phase. The hydrophobicity of [OPy][HSO<sub>4</sub>] increases linearly with the concentration.

At 0.01 M,  $\log P$  (-0.39) of [OPy][HSO<sub>4</sub>] shows hydrophilic behavior but on increasing the concentration, the hydrophobicity of ionic liquid increases linearly. In the case of [OPy][HSO<sub>4</sub>], at a lower concentration of 0.01 M, it shows high interactions with water but as we increase the concentration of the ionic liquid, the longer alkyl group resides towards the aqueous phase due to the  $\pi$ - $\pi$  stacking between the pyridinium ring leading to a decrease in the interaction with water. As the concentration of [OPy][HSO<sub>4</sub>] increases, it results in favorable interaction with 1-octanol owing to the orientation of aggregates.

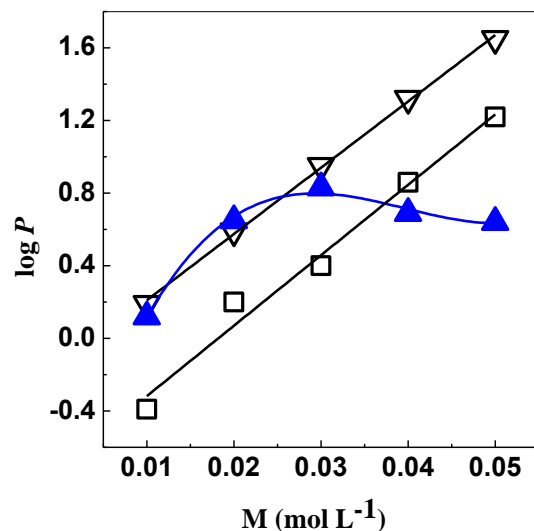


**Figure 4.3.** A probable structure of aggregates for the imidazolium (a) and pyridinium (b) based ionic liquids.



### 4.3.2 Effect of Cationic Ring and Anions on $\log P$ :

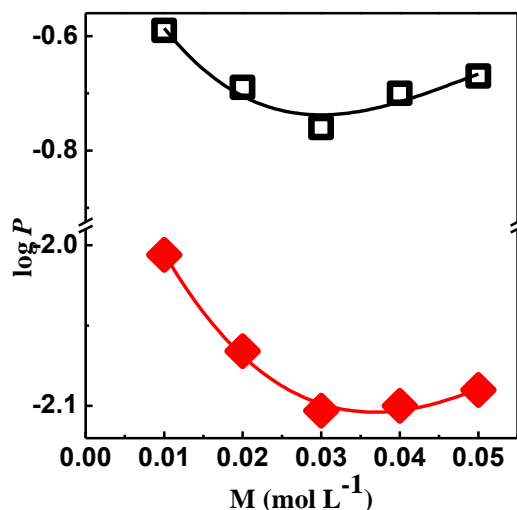
As demonstrated in the first section, the hydrophobicity of [OPy][HSO<sub>4</sub>] increases linearly with an increase in concentration, whereas flip-flopping observed in the case of [OMIM][HSO<sub>4</sub>]. In order to compare the effect of the cationic ring on  $\log P$  values, we have chosen imidazolium and pyridinium cationic ring. Imidazolium ring is smaller in size and less aromatic in nature as compared to pyridinium. Imidazolium ring shows strong interactions with water as compared to pyridine. Imidazolium ring shows strong interactions with water as compared to pyridine. **Figure 4.4** shows that the  $\log P$  value of [OPy][HSO<sub>4</sub>] is higher than that of [OMIM][HSO<sub>4</sub>] indicating that pyridine is less hydrophilic as compared to that of imidazole. Also the effect of cationic has been seen and discussed in the above section as the probable structure of aggregates.



**Figure 4.4.** A comparative study of  $\log P$  with concentration,  $M$  ( $\text{mol L}^{-1}$ ) for [OPy][HSO<sub>4</sub>] (□), [OMIM][HSO<sub>4</sub>] (▲) and [EOIM][EtSO<sub>4</sub>] (▽).

In the present study, the effect of anions on the  $\log P$  was also noted. This effect of anions on  $\log P$  values has been observed in sulphate-based Ionic liquids by changing the alkyl group on anion such as  $[\text{HSO}_4]^-$ ,  $[\text{EtSO}_4]^-$ , and butylsulphate ( $[\text{BuSO}_4]^-$ ). All the alkyl sulphate anion containing ionic liquids show higher interactions with water. The basicity of anions increases on increasing the carbon number in anions. Upon increasing the basicity; electrostatic interactions between cations and anions increase. It was also noted that  $[\text{EtSO}_4]^-$  anion has similar behavior as that of DMSO in terms of  $\beta$  values. Similar to DMSO,  $[\text{EtSO}_4]^-$  anion interacts with imidazolium cations to a greater extent as compared to  $[\text{HSO}_4]^-$  anion. Simultaneously, hydrophobicity of anion also increases upon increasing the number of carbon atoms and hence  $[\text{HSO}_4]^-$  anions are more hydrophilic in nature as compared to  $[\text{EtSO}_4]^-$  and  $[\text{BuSO}_4]^-$ . As we move from  $[\text{HSO}_4]^-$  to  $[\text{EtSO}_4]^-$  it is noted that the ionic liquids possessing  $[\text{HSO}_4]^-$  anion shows higher interactions with water as compared to  $[\text{EtSO}_4]^-$  due to the absence of  $-\text{C}_2\text{H}_5$  group and the possibility of aggregate formation. Hydrophobicity is induced by the  $-\text{C}_2\text{H}_5$  group in  $[\text{EtSO}_4]^-$ , whereas it is not observed in the case of  $[\text{HSO}_4]^-$ . The electro negativity of oxygen atoms attached to the alkyl chain (hydrogen or ethyl) is increased upon increasing the alkyl group length leading to an enhanced electrostatic interaction. It is reported that upon increasing the number of carbon atoms in cations as well as, anions, a favorable interactions with 1-octanol or high solubility in 1-octanol is seen. **Figure 4.1** depicts that  $[\text{HSO}_4]^-$ -based ionic liquids behave differently as a function of concentration as compared to  $[\text{EtSO}_4]^-$ -based ionic liquids. Therefore, the  $[\text{HSO}_4]^-$  containing ionic liquids show greater ionic liquid-water interactions due to less hydrophobicity and large negative charge on the anion oxygen

atom. Increasing the alkyl chain length on the sulphate anion increases the negative charge of the oxygen atom and holds a strong electrostatic interaction between cations and anions. This lowers the ionic liquid/water interaction and hence the solubility or interaction with 1- octanol increases. The  $\log P$  values are mentioned in **Table 4.2** for the ionic liquids having different anions cationic rings. [BMIM][HSO<sub>4</sub>] and [BMIM][BuSO<sub>4</sub>] have similar cationic ring but different alkyl groups in anion. Since both the anions possess higher capability of hydrogen bonding with water, negative  $\log P$  values are obtained. However, in the case of [BuSO<sub>4</sub>]<sup>-</sup> anion, the presence of butyl group imparts some degree of hydrophobicity in comparison to that of [HSO<sub>4</sub>]<sup>-</sup> anion. This enhanced hydrophobicity of the [BuSO<sub>4</sub>]<sup>-</sup> ion is also reflected in the  $\log P$  values of [BMIM][BuSO<sub>4</sub>] i.e.  $\log P$  values reside on the higher side as compared to [BMIM][HSO<sub>4</sub>], as shown in **Figure 4.5**.



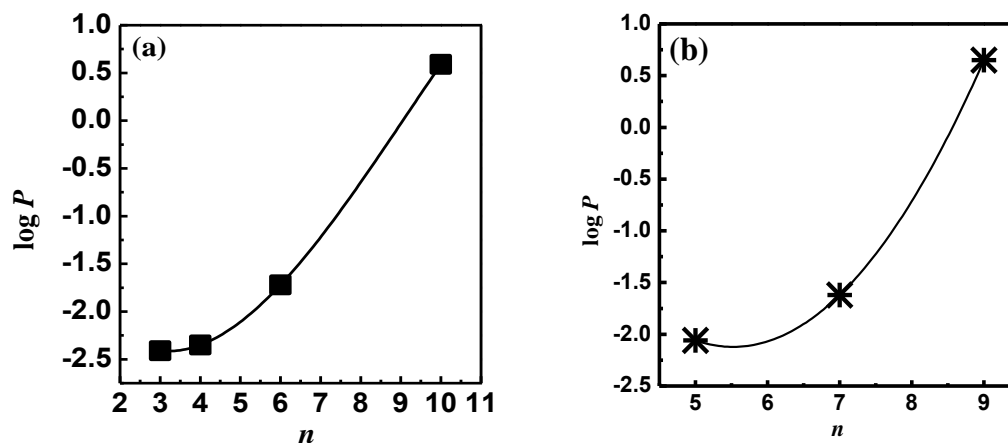
**Figure 4.5.** A comparative study of  $\log P$  with concentration,  $M$  (mol L<sup>-1</sup>) for [BMIM][BuSO<sub>4</sub>] (□) and [BMIM][HSO<sub>4</sub>] (◆).

### 4.3.3 Effect of Number of Carbon Atoms Attached to the Cationic Ring of Ionic Liquids on $\log P$ :

As illustrated above, the  $\log P$  values increase with increases in size of the alkyl chain attached to the cationic ring.  $[\text{EtSO}_4]^-$  is hydrophilic in nature. A change from  $[\text{EMIM}]^+$  to  $[\text{dEIM}]^+$  leads to a decrease in the hydrophilicity of ionic liquids by a marginal amount as identified by  $\log P$  values ( $\log P$  for  $[\text{EMIM}][\text{EtSO}_4] = -2.41$ ;  $\log P$  for  $[\text{dEIM}][\text{EtSO}_4] = -2.35$ ) at a particular concentration of 0.02 M. However, a value of  $\log P = -1.72$  for  $[\text{BEIM}][\text{EtSO}_4]$  indicates that the hydrophilicity again decreases (**Table 4.1**) and shows the marginal behavior lying between hydrophobicity and hydrophilicity of these ionic liquids. From **Figure 4.6 (a)** it is clear that on increasing the alkyl chain length on the cationic ring of the  $[\text{EtSO}_4]^-$ -based ionic liquids ( $[\text{EMIM}][\text{EtSO}_4]$ ,  $[\text{dEIM}][\text{EtSO}_4]$ ,  $[\text{BEIM}][\text{EtSO}_4]$  and  $[\text{EOIM}][\text{EtSO}_4]$ ) the  $\log P$  value changes from negative to positive. These changes occur because the non-polarity of the above ionic liquids increase with the introduction of additional alkyl groups, thus, the solubility in 1-octanol of ionic liquid increases.  $[\text{EOIM}][\text{EtSO}_4]$  possess positive  $\log P$  value (0.59), whereas for  $[\text{EMIM}][\text{EtSO}_4]$ ,  $[\text{dEIM}][\text{EtSO}_4]$ , and  $[\text{BEIM}][\text{EtSO}_4]$  have negative  $\log P$  values.  $[\text{EOIM}][\text{EtSO}_4]$  is hydrophobic in nature. The effect of alkyl chain length on the  $\log P$  values for the  $[\text{HSO}_4]^-$ -based ionic liquids were obtained as shown in **Figure 4.6 (b)**. The  $\log P$  values of  $[\text{BMIM}][\text{HSO}_4]$ ,  $[\text{HMIM}][\text{HSO}_4]$ , and  $[\text{OMIM}][\text{HSO}_4]$  are -2.01, -1.76, and 0.12, respectively at 0.01 M (**Table 4.2**). The  $\log P$  values indicate that

hydrophilicity of ionic liquid decreases on moving from butyl to hexyl group. In the case of [OMIM][HSO<sub>4</sub>], due to the larger hydrophobic alkyl group, its solubility increases in 1-octanol thus showing the positive  $\log P$  values. The [HSO<sub>4</sub>]<sup>-</sup>-based ionic liquids show similar trend as noted in the case of [EtSO<sub>4</sub>]<sup>-</sup>-based ionic liquids. The  $\log P$  values are anion dependent. Upon increasing alkyl chain length on cationic ring, there is a possibility of strong van der Waals interactions between alkyl group of ionic liquid and hydrophobic part of 1-octanol. This behavior of hydrophobicity can also be explained by their polarity values. As the size of alkyl group in ionic liquid increases; its polarity decreases.<sup>[46]</sup> This inhibits its ability to interact with water.<sup>[47, 48]</sup> The lengthening of the aliphatic chain at positions 1 and 3 (in imidazolium ring) on the cation also affects the interaction of ionic liquids with solvents. Many interactions like van der Waals interactions (between hydrophobic part of ionic liquids and solvents), hydrogen bonding, Coulombic interactions etc. are responsible for solubility. On increasing the carbon atoms on cations show the strong van der Waals interactions with the hydrophobic part of 1-octanol. Acidic C2 proton on imidazolium cationic ring shows hydrogen bonding with water but upon increasing the alkyl chain length on the ring, the acidity of C2 proton decreases thereby increasing hydrophobicity of cationic rings. Ionic liquids having smaller alkyl groups at 1 and 3 positions shows favorable interactions with water.<sup>[49]</sup> This supports our experimental results that upon increasing the alkyl chain length on imidazolium cations solubility of ionic liquids in water decreases. The increasing order of hydrophobicity by varying the alkyl chain is as; [EMIM][EtSO<sub>4</sub>] <

$[\text{dEIM}][\text{EtSO}_4] < [\text{BEIM}][\text{EtSO}_4] < [\text{EOIM}][\text{EtSO}_4]$ . Similarly, for the  $[\text{HSO}_4]^-$ -based ionic liquids hydrophobicity increases in the order as;  $[\text{BMIM}][\text{HSO}_4] < [\text{HMIM}][\text{HSO}_4] < [\text{OMIM}][\text{HSO}_4]$ .



**Figure 4.6.** Variation of  $\log P$  with the number of carbon atoms ( $n$ ) in alkyl groups attached to the cationic ring of ionic liquids (a)  $[\text{EtSO}_4]^-$  and (b)  $[\text{HSO}_4]^-$ -based ionic liquids.

For the purpose of convenience,  $\log P$  values for the investigated ionic liquids have been summarized in the form of adjustable parameters of a polynomial equation (**Table 4.3**). At the end, we state that  $\log P$  scale may not act as a robust tool to predict hydrophobicity in ionic liquids, as the structural aspects of both cations and anions lead to complex properties. In an excellent review published by van Rantwijk and Sheldon,<sup>13</sup> the miscibility aspects of ionic liquids have been discussed. The constituent anions of the ionic liquid seem to reflect on the miscibility of the ionic liquids in water. For example, 1-butyl-3-methylimidazolium tetrafluoroborate ( $[\text{BMIM}][\text{BF}_4]$ ) and 1-butyl-3-methylimidazolium methyl sulphate ( $[\text{BMIM}][\text{MeSO}_4]$ ) are water-miscible,

while 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF<sub>6</sub>]) and 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide ([BMIM][Tf<sub>2</sub>N]) are not, though these ionic liquids possess nearly similar polarity on the Reichardt scale.<sup>[50]</sup> In addition, the coordination strengths of the [BF<sub>4</sub>] and [PF<sub>6</sub>] anions are also comparable.<sup>[51]</sup> Examining the  $\log P$  values of the ionic liquids suggest that  $\log P$  predicts the partitioning of ionic liquids between water and 1-octanol.

**Table 4.3.** Values of the adjustable parameters to describe concentration dependence of  $\log P$  by  $\log P = q_0 + q_1c + q_2c^2 + \dots$ ;  $c$  = molar concentration (mol L<sup>-1</sup>) with correlation coefficient ( $r^2$ ).

Ionic Liquids	Parameters			
	$q_0$	$q_1$	$q_2$	$r^2$
[EMIM][EtSO <sub>4</sub> ]	-1.957 ± 0.096	-17.70 ± 2.89	-	0.9015
[dEIM][EtSO <sub>4</sub> ]	-2.058 ± 0.055	-11.80 ± 1.68	-	0.9238
[BEIM][EtSO <sub>4</sub> ]	-1.572 ± 0.013	-6.800 ± 0.400	-	0.9863
[EOIM][EtSO <sub>4</sub> ]	-0.155 ± 0.022	36.50 ± 0.67	-	0.9987
[BMIM][HSO <sub>4</sub> ]	-1.922 ± 0.012	-9.734 ± 0.905	128 ± 14.80	0.9810
[HMIM][HSO <sub>4</sub> ]	-1.864 ± 0.113	16.24 ± 8.60	-336 ± 140	0.6971
[OMIM][HSO <sub>4</sub> ]	-0.478 ± 0.222	74.23 ± 16.92	-1057 ± 277	0.8545
[BPy][HSO <sub>4</sub> ] <sup>a</sup>	-1.928 ± 0.182	-77.07 ± 23.83	2717 ± 884	0.7910
[OPy][HSO <sub>4</sub> ]	-0.706 ± 0.097	38.80 ± 2.93	-	0.9775
[BMIM][BuSO <sub>4</sub> ] <sup>a</sup>	-0.353 ± 0.079	-30.02 ± 9.03	720 ± 288	0.8679

<sup>a</sup> contains  $q_3$  for [BPy][HSO<sub>4</sub>] = -27500 ± 9764, and for [BMIM][BuSO<sub>4</sub>] = -4907 ± 2730

#### 4.4. Conclusions

To summarize the present chapter;

- i. Apparent partition coefficient of ionic liquids is concentration dependent and predominantly influenced by the nature of anions.
- ii. The  $[\text{HSO}_4]^-$ -based ionic liquids show flipping in  $\log P$  values as a function of concentration due to the formation of aggregates, whereas  $[\text{EtSO}_4]^-$ -based ionic liquids possess linear relation of  $\log P$  with concentration.
- iii. This different behavior of  $[\text{HSO}_4]^-$  and  $[\text{EtSO}_4]^-$ -based ionic liquids can be correlated with the variations in hydrogen bond accepting basicity ( $\beta$ ) of these anions as well as the possibility of aggregate formation.
- iv. A change in the cationic core from imidazolium to pyridinium significantly modifies the  $\log P$  values due to:  $\pi$ - $\pi$  interactions, number of electronegative atoms present in cationic ring and the hydrophobicity of cationic ring.
- v. The alkyl chain length in cationic and anionic part of ionic liquids also affects the  $\log P$  values, hydrophobicity of anions increases as;  $[\text{HSO}_4]^- < [\text{EtSO}_4]^- < [\text{BuSO}_4]^-$ .



At last, the apparent partition coefficients can illustrate the scale of hydrophobicity or hydrophilicity of ionic liquids.

The partition coefficient of any solute is dependent on the intra-solute or solute-solvent interactions which finally decide their distribution in two immiscible solvents. Therefore, in next chapter we further emphasized on these interactions by measuring their conductance and transport properties in their binary mixtures.

**4.5. References**

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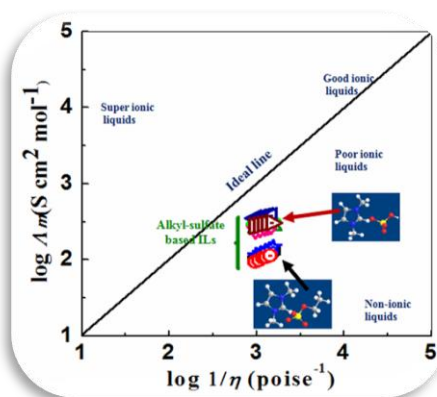
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## Chapter 5

### **Transport Properties of Ethyl and Bisulfate Anion based Ionic Liquids**

The effect of molecular solvents on the conductance of ionic liquids is investigated in the present chapter. This chapter is divided into three sections. A comparison of the molar conductance of bisulfate and ethyl sulfate based ionic liquids in various alcohols and water is presented in Section 5.1 with subsequent estimation of their association constant and transport properties. The role of anions in determining the ionicity is thoroughly described in the Section 5.2. Finally, an extension of the study to the conductance of ionic liquids in their ternary mixtures is discussed in Section 5.3.



## ***5.1. Probing the Solute-Solvent Interactions in the Binary Mixtures of Ionic Liquids by Conductance, Viscosity and IR Spectroscopy***

### **5.1.1. Introduction**

Structure, functions and applications of ionic liquids have been investigated in recent years.<sup>[1-4]</sup> It is reported that the viscosity, polarity and solvation properties of ionic liquids differ drastically in the presence of a co-solvent.<sup>[5, 6]</sup> Ionic liquids form strong ion pairs in both the gas as well as in their solution phases.<sup>[7-13]</sup> Avent *et. al.* explained an association of 1-butyl-3-methylimidazolium chloride, [BMIM]Cl in water, dichloromethane, and acetonitrile through multilayer NMR and conductivity measurements.<sup>[14]</sup> Ionic association of 1-butyl-3-methylimidazolium tetrafluoroborate, [BMIM][BF<sub>4</sub>], 1-butyl-3-methylimidazolium hexafluorophosphate, [BMIM][PF<sub>6</sub>], and *n*-alkyl-3-methylimidazolium bromide, [C<sub>n</sub>MIM]Br in different molecular solvents have also been reported.<sup>[15]</sup> Ion-pair formation in the ionic liquid solutions has been observed on diluting the ionic liquids.<sup>[4, 15-23]</sup> Association of ionic liquids has also been demonstrated by experimental and simulation studies in neat ionic liquids as well as in their solutions.<sup>[11, 23-26]</sup> Hefer has pointed out that the major problem in determining the association constant is to find an appropriate method to quantify the association constant of ionic liquids in dilute range. The limitations of the certain spectroscopic techniques in determining the association constants have been reviewed previously.<sup>[27]</sup> We have employed conductivity measurement which is probably the best possible method for quantification of association constant. This technique is widely used with the commercially available instruments that can measure conductivities with significant

accuracies.<sup>[27, 28]</sup> The conductance of binary mixtures of ionic liquids emphasize on the nature of solute-solute and solute-solvent interactions and the structural changes of the solvent molecules. The electrical conductance of binary mixtures of ionic liquids with molecular solvents has been studied in past years.<sup>[4, 29-33]</sup> It has been reported over a wide temperature and concentration range which can quantify the association constant directly.<sup>[3, 7, 30, 31, 34-36]</sup> The properties of ionic liquids and co-solvent mixtures can be define by the intermolecular interactions. It is essentially measured in terms of the electrical conductance in the solution.<sup>[27, 28]</sup> Several other spectroscopic techniques have also been used to investigate the mixing behavior and interactions between ionic liquids and co-solvents.<sup>[37, 38]</sup> Infrared Vibrational Spectroscopy is an established technique to explore the structural and dynamic properties of ionic liquid mixtures, mainly the hydrogen bonding between ions.<sup>[23, 39-42]</sup> IR spectroscopy has been used to investigate the intermolecular interactions in the binary mixture of water and 1-ethyl-3-methylimidazolium ethyl sulfate ([EMIM][EtSO<sub>4</sub>]). The study shows that the hydrogen bond involved the anion group (-SO<sub>3</sub>) was enhanced and the cation group (aromatic -C-H) weakened in the presence of water.<sup>[37]</sup> The mixing behavior and interactions in the binary systems [EMIM][EtSO<sub>4</sub>]-water, [EMIM][EtSO<sub>4</sub>]-methanol and [EMIM][EtSO<sub>4</sub>]-ethanol have also been investigated at molecular level by Raman spectroscopy.<sup>[38]</sup>

Several ionic liquids are toxic in nature.<sup>[43, 44]</sup> In recent years, ionic liquids have been modified structurally to enhance their biodegradability.<sup>[45, 46]</sup> In the similar line the alkyl sulfate based anionic ionic liquids emerged to be one of the most promising class



of ionic liquids as the anions are biodegradable and non-toxic in nature.<sup>[45, 46]</sup> These ionic liquids have been used as a substitute to the hydrodesulfurization process<sup>[47]</sup> and as suitable reaction media.<sup>[48, 49]</sup> The properties such as high charge density and basicity of alkyl sulfate based imidazolium ionic liquids render them highly beneficial in electrochemical processes. The alkyl sulfate based imidazolium ionic liquids are chosen for the current study because they have a halogen free anion, suitable for large scale applications due to the reasonable cost.<sup>[50, 51]</sup> A variety of physico-chemical properties of the alkyl sulfate based ionic liquids have also been investigated. The electrical conductance of 1-alkyl-3-methyl imidazolium alkyl sulfate based ionic liquid has also been measured with ethanol and water. Rilo *et. al.* measured the density and thermodynamic properties of the binary mixture of the alkyl sulfate based ionic liquids with water and ethanol.<sup>[51]</sup> It has been observed that the density decreases as the alkyl chain of the anion and temperature increases.<sup>[51]</sup>

In this Chapter, we measure conductance to delineate the effect of cations and anions on the molar conductance and association of alkyl sulfate based imidazolium ionic liquids in their solutions. In Chapter 4, we explained the distribution of these ionic liquids between water and 1-octanol biphasic system in terms of the apparent partition coefficient,  $\log P$ .<sup>[52]</sup>

In this work, we elucidate the conductance of binary mixtures of ionic liquids in different molecular solvents including water, methanol, 1-butanol, 1-hexanol, and 1-octanol. This Chapter includes the molar conductance of binary mixtures of a series of bisulfate,  $[\text{HSO}_4]^-$  and ethyl sulfate,  $[\text{EtSO}_4]^-$ -based imidazolium ionic liquids by changing the alkyl chain length of the imidazolium ring. The cations used are 1-ethyl-

3-methylimidazolium [EMIM]<sup>+</sup>, 1, 3-diethylimidazolium [dEIM]<sup>+</sup>, 1-butyl-3-ethylimidazolium [BEIM]<sup>+</sup>, 1-butyl-3-methylimidazolium [BMIM]<sup>+</sup>, 1-hexyl-3-methylimidazolium [HMIM]<sup>+</sup> and 1-octyl-3-methylimidazolium [OMIM]<sup>+</sup>. The synthesis procedures with their structures are given in Chapter 3. The study emphasizes on the infrared spectrum of pure ionic liquids and their solutions in polar protic solvents to understand the intermolecular interactions, H-bonding between cation and anion. The temperature dependent viscosity ( $\eta$ ) and molar conductance ( $\Lambda_m$ ) measurements of aqueous solution of ionic liquids have also been carried out. Activation parameters of fluidity ( $1/\eta$ ) and conductivity as well as of the limiting molar conductivities ( $\Lambda_m^\circ$ ), mobility ( $\mu$ ) and transport number ( $t$ ) of cations and anions, diffusion coefficient (D) and hydrodynamic radius ( $R_H$ ) of ionic liquids in their aqueous solutions are also calculated and reported.

### 5.1.2. Experimental Section

The specific conductance,  $\kappa$  of the ionic liquids was measured by using a Systronics 306 Conductometer at 1 kHz. The conductivity meter was calibrated by using a 0.1 M potassium chloride (KCl) solution followed by the reported procedure described in Chapter 3. The uncertainties were estimated to be  $\pm 3\%$  for conductivity measurements. The temperature of the jacket was maintained at  $298.15 \pm 0.01$  K using a Julabo thermostat. Viscosity was measured with a Brookfield-ultra rheometer with cone plate arrangement as described in the Chapter 3 and the accuracy of the instrument was recorded as  $\pm 1\%$ . The fundamental details of the calibration and experimental

procedures are given in Chapter 3. IR spectra obtained at a resolution of  $4\text{ cm}^{-1}$  with Nicolet Fourier transform infrared (FTIR)/Nexus 870 spectrometer at room temperature. A small droplet of aprotic ionic liquids and their binary mixtures with polar protic solvents were placed on the KBr pallets. The synthesis procedure of the all studied alkyl sulfate based ionic liquids has also been described in Chapter 3.

### 5.1.3. Results and Discussion

The experimental conductance data of the  $[\text{HSO}_4]^-$  and  $[\text{EtSO}_4]^-$ -based imidazolium ionic liquids have been measured in different molecular solvents at 298.15 K in the concentration range from 0.0006 to  $0.1\text{ mol L}^{-1}$  for the ionic liquids. There are several expressions available in the literature to analyse the conductance data of the ionic solutions. Due to the non-availability of physical parameters of some ionic liquids, the low concentration chemical model (LcCM)<sup>[53]</sup> and Fuoss and Hsia equations<sup>[54, 55]</sup> could not be used. We therefore, employed the equation proposed by Mahiuddin and Ismail<sup>[56]</sup> for analyzing the molar conductance of the ionic liquid solutions. The equation is:

$$\Lambda = \Lambda_m^\circ \exp (A_\Lambda M + B_\Lambda M^2) \quad (5.1.1)$$

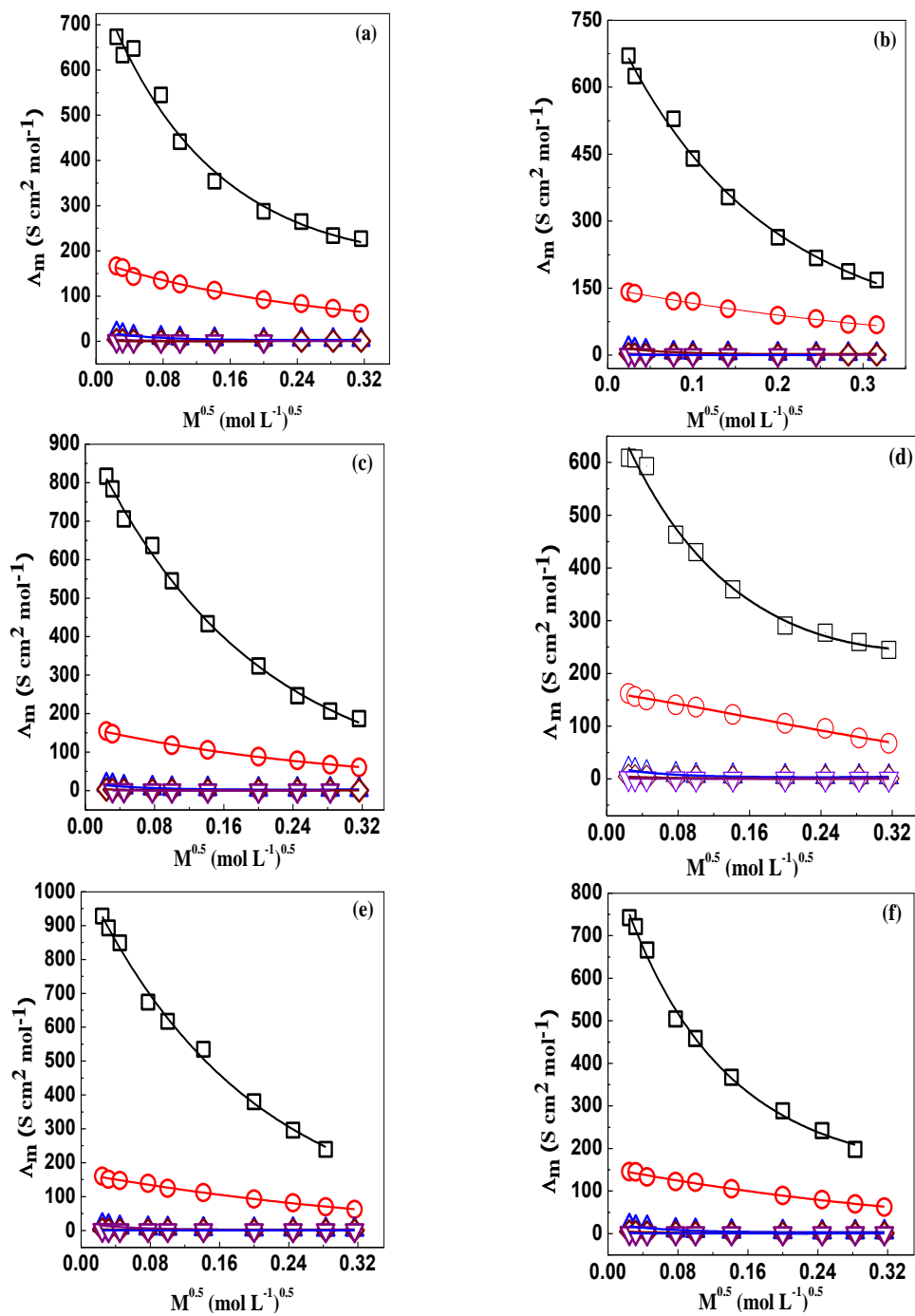
where,  $\Lambda_m^\circ$  is the limiting molar conductance of an ionic liquid in a solvent,  $A_\Lambda$  and  $B_\Lambda$  are the adjustable parameters and  $M$  is the molar concentration ( $\text{mol L}^{-1}$ ) of solution. The  $\Lambda_m$  and concentration data were fitted with an average standard deviation of 5%. **Table 5.1.1** enlists the values of  $\Lambda_m^\circ$  with standard errors for the ionic liquids in various solvents.

### 5.1.3.1. Effect of Relative Permittivity ( $\epsilon$ ) of Solvents and Anions of Ionic Liquids on their Molar Conductance of Binary Mixtures

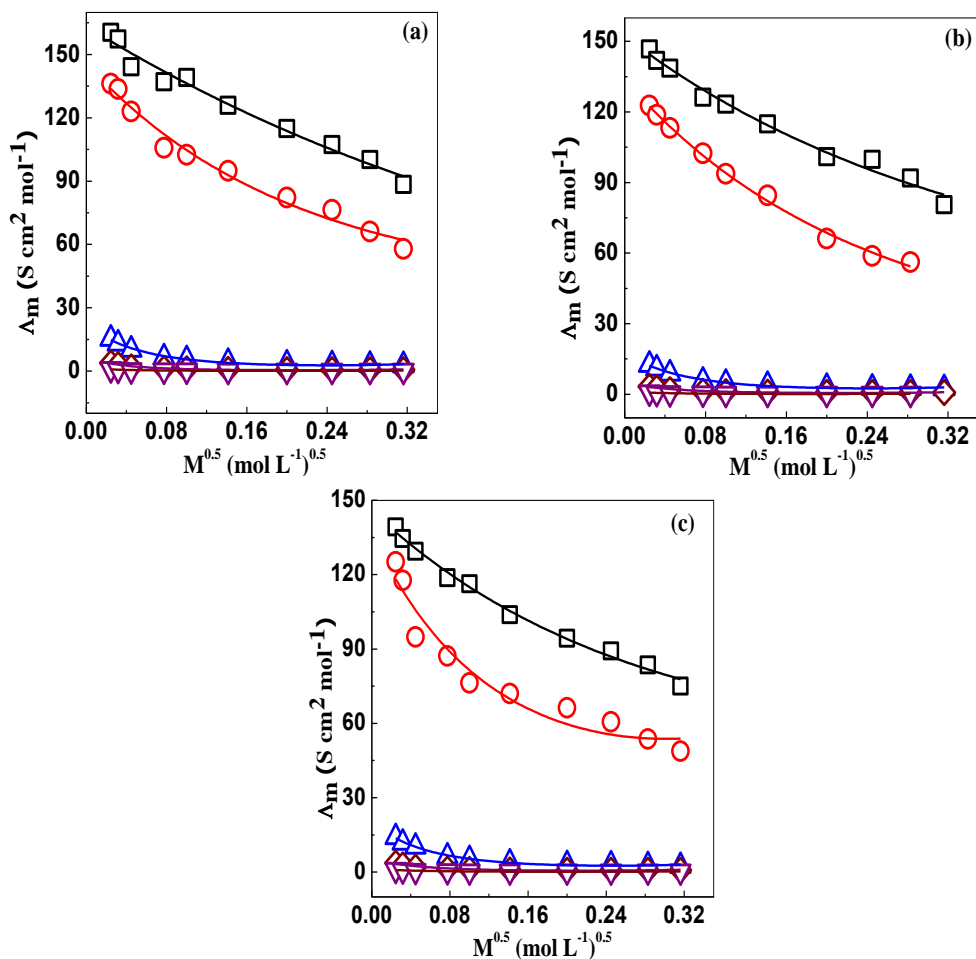
The experiments were carried out in order to understand the nature and extent of various intermolecular interactions existing between ions and solvent molecules in their solutions. **Figures 5.1.1** and **5.1.2** show the values of  $\Lambda_m$  as a function of the square root of their molar concentration,  $M^{0.5}$  of the  $[\text{HSO}_4]^-$  and  $[\text{EtSO}_4]^-$ -based ionic liquids, respectively in different molecular solvents *i.e.*, water, methanol, 1-butanol, 1-hexanol, and 1-octanol. From **Figures 5.1.1** and **5.1.2**, a gradual decrease in  $\Lambda_m$  is observed with the increase in their molar concentrations.

**Table 5.1.1.** The limiting molar conductivities,  $\Lambda_m^\circ$  of the aprotic ionic liquids in different molecular solvents at 298.15 K.

Ionic liquids/ Solvents	$\Lambda_m^\circ / (\text{S cm}^2 \text{ mol}^{-1})$				
	Methanol	1-Butanol	1-Hexanol	1-Octanol	Water
[EMIM][HSO <sub>4</sub> ]	175 ± 3.1	24.56 ± 1.89	5.571 ± 0.462	1.014 ± 0.053	799 ± 32
[dEIM][HSO <sub>4</sub> ]	151 ± 2.5	22.87 ± 1.71	5.170 ± 0.411	0.9412 ± 0.105	747 ± 13
[BMIM][HSO <sub>4</sub> ]	175 ± 4.6	20.93 ± 1.98	5.773 ± 0.453	1.123 ± 0.145	730 ± 19
[BEIM][HSO <sub>4</sub> ]	164 ± 1.4	20.88 ± 1.47	5.168 ± 0.354	1.198 ± 0.129	921 ± 11
[HMIM][HSO <sub>4</sub> ]	172 ± 2.0	23.28 ± 2.21	5.564 ± 0.452	1.207 ± 0.102	1050 ± 18
[OMIM][HSO <sub>4</sub> ]	156 ± 1.9	25.84 ± 1.29	7.013 ± 0.667	1.474 ± 0.171	900 ± 20
[EMIM][EtSO <sub>4</sub> ]	139 ± 3.3	21.96 ± 1.19	6.367 ± 0.695	1.408 ± 0.168	163 ± 2.8
[dEIM][EtSO <sub>4</sub> ]	135 ± 3.2	17.62 ± 0.79	4.821 ± 0.431	1.179 ± 0.134	150 ± 2.4
[BEIM][EtSO <sub>4</sub> ]	127 ± 9.3	17.81 ± 1.68	4.246 ± 0.542	1.333 ± 0.148	142 ± 1.8



**Figure 5.1.1.** The plots of  $\Lambda_m$  as a function of  $M^{0.5}$  for (a) [EMIM][HSO<sub>4</sub>], (b) [dEIM][HSO<sub>4</sub>], (c) [BEIM][HSO<sub>4</sub>], (d) [BMIM][HSO<sub>4</sub>], (e) [HMIM][HSO<sub>4</sub>], (f) [OMIM][HSO<sub>4</sub>] in water (□), methanol (○), 1-butanol (△), 1-hexanol (◇), 1-octanol (▽).

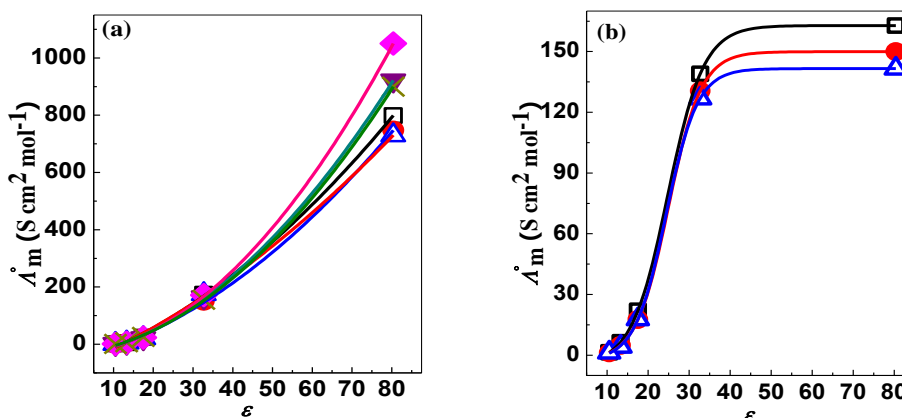


**Figure 5.1.2.** The plots of  $\Lambda_m$  as a function of  $M^{0.5}$  for (a) [EMIM][EtSO<sub>4</sub>], (b) [dEIM][EtSO<sub>4</sub>], (c) [BEIM][EtSO<sub>4</sub>] in water ( $\square$ ), methanol ( $\circ$ ), 1-butanol ( $\triangle$ ), 1-hexanol ( $\diamond$ ), 1-octanol ( $\nabla$ ).

It is noted that the  $[\text{HSO}_4]^-$ -based ionic liquids are found to have higher  $\Lambda_m$  values in water as compared to in other molecular solvents. The  $\Lambda_m$  of binary mixtures of ionic liquids mainly depends on the solvent's  $\epsilon$  due to its role in the dissociation of ionic liquid into its ions. A significant difference is noted in  $\Lambda_m$  of these ionic liquids in water and methanol than in other low relative permittivity solvents. The effect of  $\epsilon$

values of the solvents on the  $\Lambda_m^\circ$  values is shown in **Figure 5.1.3 (a)** and **(b)** for the  $[\text{HSO}_4]^-$  and  $[\text{EtSO}_4]^-$ -based ionic liquids, respectively.

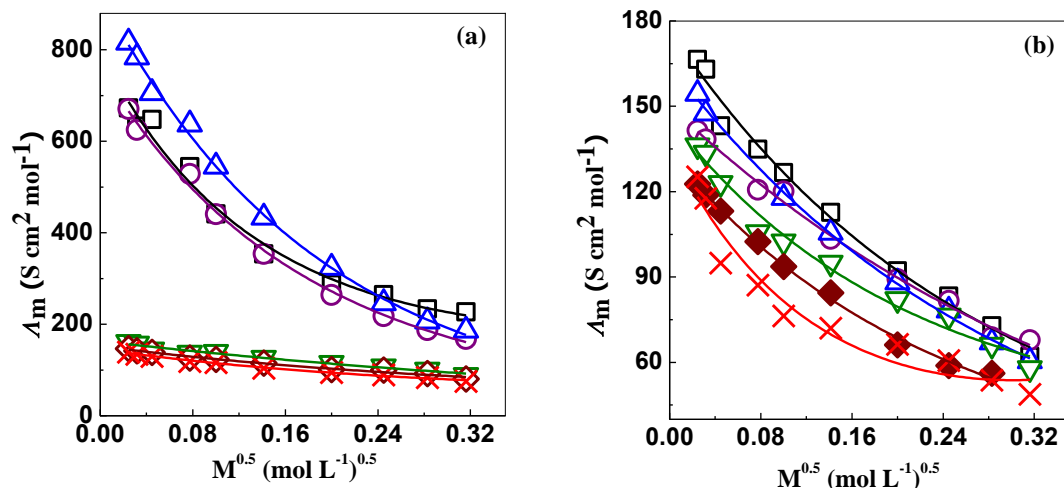
Apart from these, the effect of different solvents on the  $\Lambda_m$  values of the ionic liquids can be clearly seen from **Figures 5.1.1** and **5.1.2**. The increase in the  $\Lambda_m$  values with  $\epsilon$  can be a result of difference in interactions between the ions and solvents. It is known that solvents of high  $\epsilon$  exhibit better miscibility with ionic liquids where the non-polar solvent fails. This is an indication of the strong molecular interactions between solvents and ionic liquids. It is reported that cations and anions form individual solvated ions in the high  $\epsilon$  solvents after getting dissociated.<sup>[19]</sup> Therefore, the solvents of high  $\epsilon$  are more efficient in the balancing of electrostatic interactions between ions of ionic liquids hence the ionization of the ionic liquids and their molar conductance increase.



**Figure 5.1.3.** The plots of  $\Lambda_m^\circ$  with relative permittivity ( $\epsilon$ ) of solvents (a) for  $[\text{EMIM}][\text{HSO}_4]$  ( $\square$ ),  $[\text{dEIM}][\text{HSO}_4]$  ( $\bullet$ ),  $[\text{BEIM}][\text{HSO}_4]$  ( $\blacktriangledown$ ),  $[\text{BMIM}][\text{HSO}_4]$  ( $\triangle$ ),  $[\text{HMIM}][\text{HSO}_4]$  ( $\blacklozenge$ ),  $[\text{OMIM}][\text{HSO}_4]$  ( $\times$ ) and (b) for  $[\text{EMIM}][\text{EtSO}_4]$  ( $\square$ ),  $[\text{dEIM}][\text{EtSO}_4]$  ( $\bullet$ ),  $[\text{BEIM}][\text{EtSO}_4]$  ( $\triangle$ ).

To delineate the effect of anions on  $A_m$ , we compare the  $A_m$  values of [EMIM][HSO<sub>4</sub>], [dEIM][HSO<sub>4</sub>], [BEIM][HSO<sub>4</sub>], [EMIM][EtSO<sub>4</sub>], [dEIM][EtSO<sub>4</sub>], and [BEIM][EtSO<sub>4</sub>] in polar protic solvents such as water and methanol (**Figure 5.1.4**). The  $A_m^\circ$  values of the [HSO<sub>4</sub>]<sup>-</sup>-based imidazolium ionic liquids (**Table 5.1.1**) are approximately 4-5 times higher in water than in methanol. It is probably due to the available proton in the aqueous solution of the [HSO<sub>4</sub>]<sup>-</sup>-based imidazolium ionic liquids. The shuttling of such protons within solvent molecules from one molecule to the next contributes to the elevated  $A_m$ . This is best known as “Grotthuss mechanism”.<sup>[57]</sup> It involves the exchange of covalent and hydrogen bond between water oxygen and hydrogen, resulting into a net displacement of positive charge. The charge of proton is transported in aqueous solutions of the [HSO<sub>4</sub>]<sup>-</sup>-based imidazolium ionic liquids suggesting higher  $A_m^\circ$  values. It is also observed in their methanolic solutions but to the lesser extent as compared to in water (**Figure 5.1.4**). It is also observed that  $A_m^\circ$  of the [HSO<sub>4</sub>]<sup>-</sup>-based ionic liquids is around 4-5 times higher as compared to the [EtSO<sub>4</sub>]<sup>-</sup> based ionic liquids in their aqueous solutions. It reveals that the availability of the protons for charge transfer is higher in the [HSO<sub>4</sub>]<sup>-</sup> than [EtSO<sub>4</sub>]<sup>-</sup>-based imidazolium ionic liquids. It also favors the “Grotthuss mechanism” in the [HSO<sub>4</sub>]<sup>-</sup>-based imidazolium ionic liquids. It appears from the **Figures 5.1.1** and **5.1.2** that no significant correlation exists between the alkyl chain length of cationic ring and molar conductance of the ionic liquid solutions. The  $A_m$  and  $A_m^\circ$  values of the [HSO<sub>4</sub>]<sup>-</sup>-based ionic liquids initially decrease, as we increase the number of carbon atoms of alkyl group (up to butyl) attached to the cationic ring. Then, the  $A_m$  and  $A_m^\circ$  values increase for the higher alkyl group containing ionic liquids (maximum  $A_m$  and  $A_m^\circ$  values obtained for [HMIM][HSO<sub>4</sub>]).



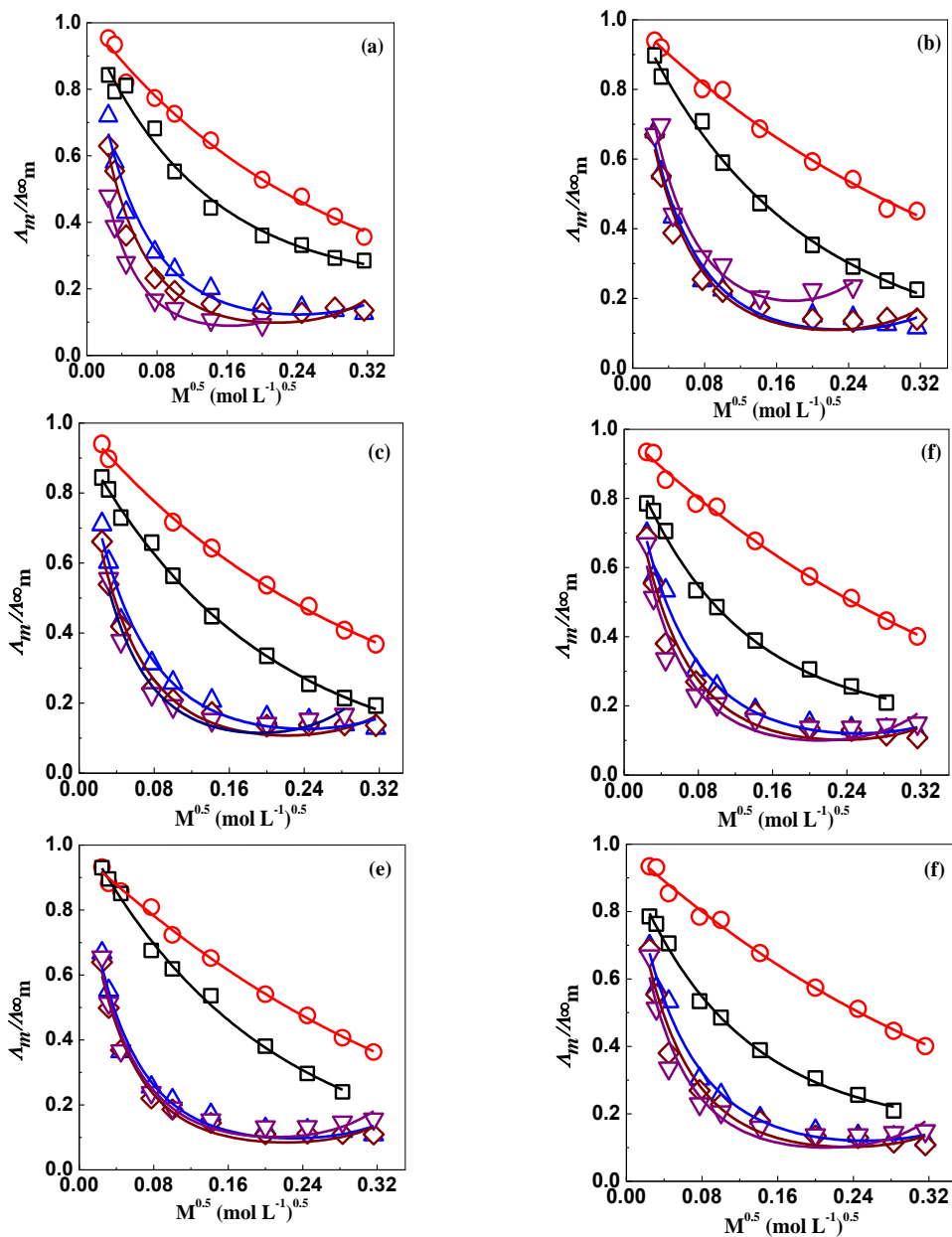


**Figure 5.1.4.** The plots of  $\Lambda_m$  as a function of concentration in water (a), and methanol (b) for [EMIM][HSO<sub>4</sub>] ( $\square$ ), [dEIM][HSO<sub>4</sub>] ( $\circ$ ), [BEIM][HSO<sub>4</sub>] ( $\Delta$ ), [EMIM][EtSO<sub>4</sub>] ( $\nabla$ ), [dEIM][EtSO<sub>4</sub>] ( $\blacklozenge$ ), [BEIM][EtSO<sub>4</sub>] ( $\times$ ).

### 5.1.3.2. Reduced Molar Conductance ( $\Lambda_m / \Lambda_m^\circ$ ) and Association Constant ( $K_A$ ):

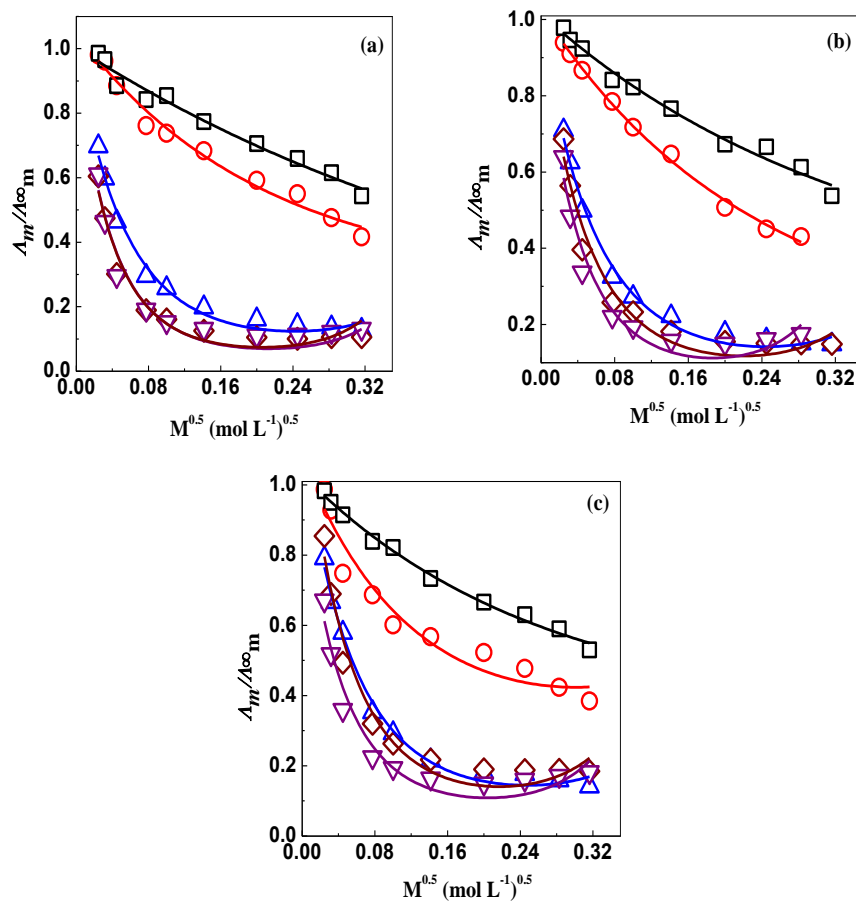
The  $\Lambda_m$  values mainly depend on  $\epsilon$  of the solvent as seen above. These values decrease rapidly as we move from methanol to 1-octanol suggesting the effective role of the  $\epsilon$  of the solvent. This essentially depends on the number of available ions in their solutions. The pronounced tendency of ion association in imidazolium ionic liquids is clearly seen from **Figures 5.1.5** and **5.1.6** for the [HSO<sub>4</sub>]<sup>-</sup> and [EtSO<sub>4</sub>]<sup>-</sup>-based ionic liquids, respectively, which compares the reduced molar conductance,  $(\Lambda_m / \Lambda_m^\circ)$  of the studied ionic liquids in the investigated solvents at room temperature. The  $(\Lambda_m / \Lambda_m^\circ)$  values are extremely low in 1-butanol, 1-hexanol, and 1-octanol as compared to the methanol and water indicating the minimum availability of free ions in the former systems. We

ascribe this to the water molecules that separate the ion-pair structures by solvating them thereby increasing ionization of the solution.



**Figure 5.1.5.** The plots of reduced molar conductance ( $\Lambda_m/\Lambda_m^\infty$ ) as a function of concentration in water ( $\square$ ), methanol ( $\circ$ ), 1-butanol ( $\triangle$ ), 1-hexanol ( $\diamond$ ), 1-octanol ( $\nabla$ ), for [EMIM][HSO<sub>4</sub>] (a), [dEIM][HSO<sub>4</sub>] (b), [BEIM][HSO<sub>4</sub>] (c), [BMIM][HSO<sub>4</sub>] (d), [HMIM][HSO<sub>4</sub>] (e), [OMIM][HSO<sub>4</sub>] (f).

It has also been reported that at low concentration water interacts strongly with the anion hence the possibility of hydrogen bonding increases between water and the anion of ionic liquids.<sup>[37, 38]</sup>



**Figure 5.1.6.** The plots of reduced molar conductance ( $\Lambda_m/\Lambda_m^\circ$ ) as a function of concentration in water ( $\square$ ), methanol ( $\circ$ ), 1-butanol ( $\triangle$ ), 1-hexanol ( $\diamond$ ), 1-octanol ( $\nabla$ ), for [EMIM][EtSO<sub>4</sub>] (a), [dEIM][EtSO<sub>4</sub>] (b), [BEIM][EtSO<sub>4</sub>] (c).

In this study, we observed that the concentration of free ions of [HSO<sub>4</sub>]<sup>-</sup>-based imidazolium ionic liquids is higher in methanol as compared to the water. On the contrary, the [HSO<sub>4</sub>]<sup>-</sup>-based imidazolium ionic liquids show higher  $\Lambda_m$  in water as

compared to methanol. The observation of high values of  $\Lambda_m$  inspite of lower concentration of free ions in water indicates the possible existence of “Grotthuss Mechanism” in these ionic liquids. However, we note that further dissociation of the  $[\text{HSO}_4]^-$  is difficult due to the very less dissociation constant (0.00103) at room temperature.<sup>[58, 59]</sup> The  $(\Lambda_m/\Lambda_m^\circ)$  values of the  $[\text{EtSO}_4]^-$ -based imidazolium ionic liquids exhibit a similar trend as obtained for molar conductance of these ionic liquids in the molecular solvents. The higher deviation observed in the  $\Lambda_m$  values of ionic liquids upon the addition of solvent of low relative permittivity has also been reported.<sup>[17]</sup> It indicates that all the organic solvents used in this work incline towards to promote ionic association, which is in agreement with some reported data.<sup>[15, 17]</sup> The ionic liquids are solvated to a different extent by the molecular solvents, and ionic association is affected significantly by ionic solvation and the relative permittivity of the solvent.

In order to explain the intermolecular interactions and trend of  $\Lambda_m$  values of the investigated imidazolium ionic liquids, we have calculated the association constant ( $K_A$ ) of the ionic liquids in different molecular solvents.  $K_A$  defines the cation-anion interactions in the binary mixtures of ionic liquids and the obtained values are given in **Table 5.1.2**. The  $K_A$  is calculated by using the following equation,<sup>[60]</sup>

$$K_A = \frac{1-\alpha}{c\alpha^2 \gamma_{\pm}^2} \quad (5.1.2)$$

where,  $\alpha$  is the degree of ionization ( $\Lambda/\Lambda_m^\circ$ ),  $c$  is the molar concentration, and  $\gamma_{\pm}$  is the mean activity coefficient of the free ions for 1:1 electrolytes,  $\gamma_{\pm}$  is calculated by the

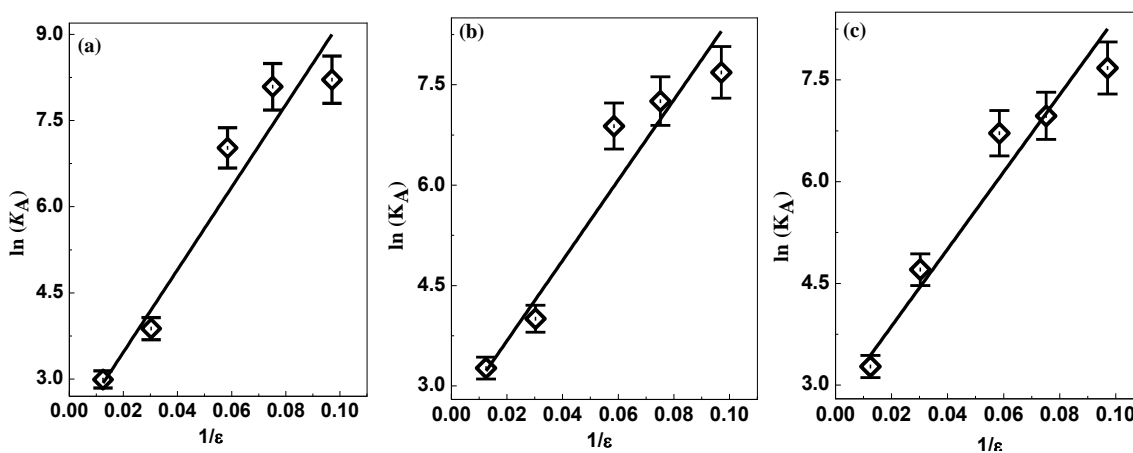
Debye-Huckel limiting law followed by the reported procedure.<sup>[60]</sup> It is seen from **Table 5.1.2** that the  $K_A$  values of  $[\text{HSO}_4]^-$ -based ionic liquids are higher in water as compared to the methanol. High values of  $K_A$  for the imidazolium ionic liquids with  $[\text{BF}_4]^-$ ,  $\text{Br}^-$ , and  $[\text{PF}_6]^-$  in their aqueous solutions have also been noted in the past.<sup>[15]</sup> This suggests strong electrostatic interactions between cation and  $[\text{HSO}_4]^-$  of the ionic liquids. One can understand the hydrogen bond formation capability of  $[\text{HSO}_4]^-$  anion as compared to the rest of anions which is in agreement with the reported data.<sup>[14, 26, 42]</sup>

**Table 5.1.2.** The association constant ( $K_A/\text{M}^{-1}$ ) of ionic liquids in different molecular solvents at concentration  $0.01\text{ mol L}^{-1}$  and  $298.15\text{ K}$ .

Ionic liquids/ Solvents	$K_A (\text{M}^{-1})$				
	Methanol	1-Butanol	1-Hexanol	1-Octanol	Water
[EMIM][ $\text{HSO}_4$ ]	52.06	1116	2158	4354	146
[dEIM][ $\text{HSO}_4$ ]	33.21	1136	1366	1120	117
[BMIM][ $\text{HSO}_4$ ]	37.03	850	1366	1084	119
[BEIM][ $\text{HSO}_4$ ]	55.13	1113	1813	2204	138
[HMIM][ $\text{HSO}_4$ ]	52.94	1675	2359	2231	99.72
[OMIM][ $\text{HSO}_4$ ]	37.30	1134	1488	1887	219
[EMIM][ $\text{EtSO}_4$ ]	48.27	1123	3261	3686	19.92
[dEIM][ $\text{EtSO}_4$ ]	54.82	976	1415	2175	26.25
[BEIM][ $\text{EtSO}_4$ ]	110	824	1064	2157	26.47

The  $K_A$  values for the  $[\text{HSO}_4]^-$  and  $[\text{EtSO}_4]^-$ -based ionic liquids increase with a decrease in the relative permittivity of the solvent. The  $K_A$  values signify that  $[\text{HSO}_4]^-$

and  $[\text{EtSO}_4]^-$ -based ionic liquids show high electrostatic interactions between cation and anion as compared to other ionic liquids because of the high basicity, charge density and the tendency of hydrogen bonding. The experimental data obtained in this study of the  $[\text{EtSO}_4]^-$ -based imidazolium ionic liquids demonstrate a linear correlation between  $\ln K_A$  and the reciprocal of the  $\epsilon$  of the solvent (**Figure 5.1.7**) agreeing with the association theory of the electrolytes.<sup>[28]</sup>

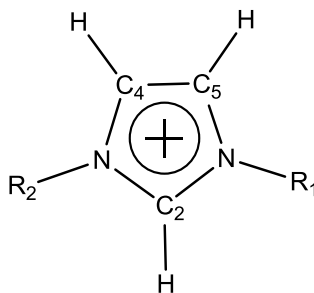


**Figure 5.1.7.** The plots of the  $\ln K_A$  versus the reciprocal of the relative permittivity ( $1/\epsilon$ ) of the solvents at 298.15 K for (a) [EMIM][EtSO<sub>4</sub>], (b) [dEIM][EtSO<sub>4</sub>], (c) [BEIM][EtSO<sub>4</sub>].

This suggests that electrostatic interactions between the cation and anion are basically responsible for their association as in typical electrolytes. However, a large deviation has been observed in the case of  $[\text{HSO}_4]^-$ -based ionic liquids. An effort was made to understand the H-bonding between cation and anion of the ionic liquids by using the IR experiments.

### 5.1.3.3. Vibration Frequencies and Cation-Anion Interactions in the $[\text{HSO}_4]^-$ and $[\text{EtSO}_4]^-$ -based Ionic Liquids:

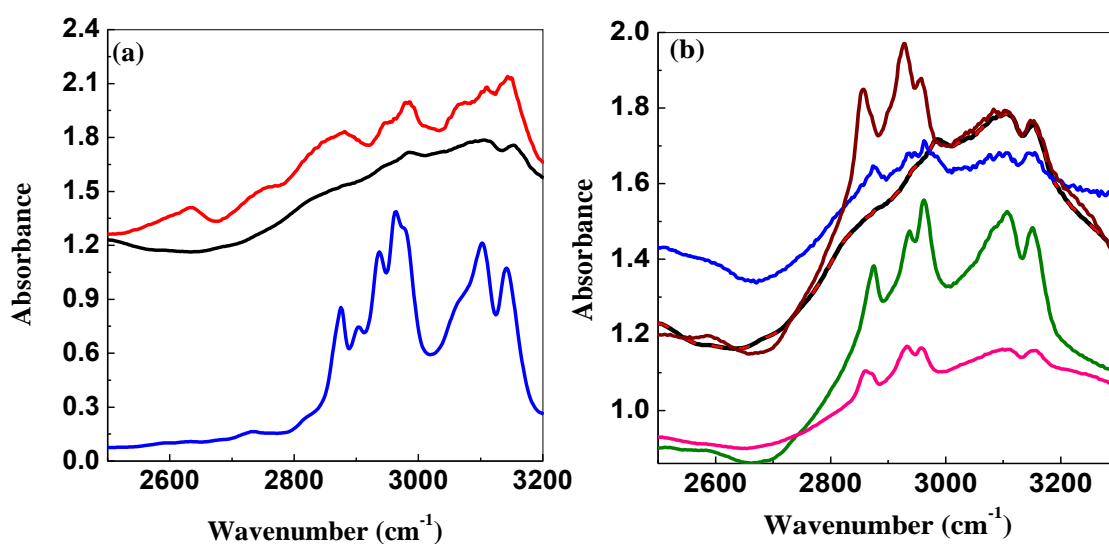
In order to support the calculated  $K_A$  values in the above systems, the infrared (IR) spectra of the employed ionic liquids and their solutions in the polar protic solvents were investigated. The IR spectra of the pure ionic liquids in the region 2800 to 3200  $\text{cm}^{-1}$  as shown in **Figure 5.1.8** with the corresponding C-H stretching frequencies reported in **Table 5.1.3**. The IR spectra of  $[\text{BMIM}][\text{HSO}_4]$  is in good agreement with the previously reported values.<sup>[39]</sup> The IR spectral region from 3000 to 3200  $\text{cm}^{-1}$  is mainly ascribed to the coupled aromatic C-H stretching vibrations of the three hydrogen atoms of the imidazolium ring. The intensity and width of  $\text{C}_2\text{-H}$  bands are larger than those of  $\text{C}_{4,5}\text{-H}$  indicating that anion interacts mainly with the  $\text{C}_2\text{-H}$  proton (See **Scheme 5.1.1**).  $\text{C}_{4,5}\text{-H}$  stretching frequencies of the  $[\text{EtSO}_4]^-$ -based imidazolium ionic liquids are much lower than the  $[\text{HSO}_4]^-$ -based imidazolium ionic liquids suggesting stronger hydrogen bonding between  $\text{C}_{4,5}\text{-H}$  of imidazolium cationic ring and  $[\text{EtSO}_4]^-$ .



**Scheme 5.1.1.** Nomenclature of protons of the imidazolium ring.

**Table 5.1.3.** Frequencies of C-H stretching of the imidazolium ring C<sub>2</sub>-H and C<sub>4,5</sub>-H bonds of the employed aprotic ionic liquids.

Ionic liquids	$\nu$ (C <sub>2</sub> -H)	$\nu$ (C <sub>4,5</sub> -H)
[EMIM][HSO <sub>4</sub> ]	3106	3153
[dEIM][HSO <sub>4</sub> ]	3106	3150
[BMIM][HSO <sub>4</sub> ]	3107	3151
[HMIM][HSO <sub>4</sub> ]	3101	3152
[OMIM][HSO <sub>4</sub> ]	3105	3154
[EMIM][EtSO <sub>4</sub> ]	3108	3149
[dEIM][EtSO <sub>4</sub> ]	3110	3143
[BEIM][EtSO <sub>4</sub> ]	3102	3141



**Figure 5.1.8.** The Absorption IR spectra in the range 2800 to 3200 cm<sup>-1</sup> for pure ionic liquids, (a) [EMIM][EtSO<sub>4</sub>] (Green), [dEIM][EtSO<sub>4</sub>] (Red), [BEIM][EtSO<sub>4</sub>] (Pink) and (b) [EMIM][HSO<sub>4</sub>] (Blue), [dEIM][HSO<sub>4</sub>] (Red), [BMIM][HSO<sub>4</sub>] (Pink), [HMIM][HSO<sub>4</sub>] (Sky Blue), [OMIM][HSO<sub>4</sub>] (Green).



[EtSO<sub>4</sub>]<sup>-</sup> has higher electron density as evident from the hydrogen bond acceptor ability or basicity denoted by a solvent parameter called hydrogen bond acceptor basicity ( $\beta$ ). The  $\beta$  values for the [EtSO<sub>4</sub>]<sup>-</sup> containing ionic liquids (0.788) are similar to that of DMSO solvent (0.748).<sup>[48, 49]</sup> As a result of high charge density and basicity, DMSO can solvate the cations. Similarly, [EtSO<sub>4</sub>]<sup>-</sup> possesses high charge density and basicity, therefore, it interacts with imidazolium cation to a greater extent also observed in IR spectra. It is interesting to note that the frequency of C<sub>2</sub>-H for [HMIM][HSO<sub>4</sub>]<sup>-</sup> is significantly lower than those for the other [HSO<sub>4</sub>]<sup>-</sup>-based aprotic ionic liquids. It reveals the strong hydrogen bonding between C<sub>2</sub>-H proton and [HSO<sub>4</sub>]<sup>-</sup> ion of [HMIM][HSO<sub>4</sub>]<sup>-</sup> and  $K_A$  values also indicate the strong hydrogen bonding between these.

#### **5.1.3.4. Vibration Frequencies in Binary Mixtures of the [HSO<sub>4</sub>]<sup>-</sup> and [EtSO<sub>4</sub>]<sup>-</sup> based Imidazolium Ionic Liquids:**

The absorption IR spectra of [EMIM][HSO<sub>4</sub>]<sup>-</sup> and [EMIM][EtSO<sub>4</sub>]<sup>-</sup> have been illustrated in their binary mixtures with methanol and water (20 % (v/v)). The C<sub>2</sub>-H and C<sub>4,5</sub>-H absorption peaks of the investigated aprotic ionic liquids almost remain constant in their binary mixtures with methanol (**Table 5.1.4**).

However, in water the C<sub>2</sub>-H absorption peak shifts from 3106 to 3111 cm<sup>-1</sup> for [EMIM][HSO<sub>4</sub>]<sup>-</sup> and from 3108 to 3111 cm<sup>-1</sup> for [EMIM][EtSO<sub>4</sub>]<sup>-</sup>. It seems that upon addition of the water molecules to imidazolium ionic liquids, the formation of strong hydrogen bond with water as O-H-----OSO<sub>3</sub>H<sup>-</sup> can take place. This essentially weakens the H-bonding of cation and anion of ionic liquids hence blue shift was observed. It is

also evident that due to this H-bonding between anion and water molecules the availability of proton increases and therefore the molar conductance. The C<sub>2</sub>-H absorption peak of [EMIM][EtSO<sub>4</sub>] also shifts because of the interaction of the water molecule with anion, but the degree of weakening of H-bonding of cation and anion is smaller than the [EMIM][HSO<sub>4</sub>].

**Table 5.1.4.** Frequencies of C-H stretching of the imidazolium ring C<sub>2</sub>-H and C<sub>4,5</sub>-H bonds of the employed aprotic ionic liquids in their binary mixtures with methanol and water.

Binary mixture of aprotic ionic liquids (20% (v/v))	$\nu$ (C <sub>2</sub> -H)	$\nu$ (C <sub>4,5</sub> -H)
[EMIM][HSO <sub>4</sub> ] in Methanol	3106	3154
[EMIM][HSO <sub>4</sub> ] in Water	3111	3154
[EMIM][EtSO <sub>4</sub> ] in Methanol	3108	3153
[EMIM][EtSO <sub>4</sub> ] in Water	3111	3155

#### 5.1.3.5. Transport properties:

The limiting molar conductance,  $A_m^\circ$  is the conductance of ionic liquids in the absence of solute-solute interactions. For 1:1 electrolytes, the  $A_m^\circ$  value is sum of the limiting molar conductance of cation ( $\lambda_+^\circ$ ) and anion ( $\lambda_-^\circ$ ). We have determined the  $\lambda_+^\circ$  and  $\lambda_-^\circ$  values of cations and anions to describe the behavior and contribution of individual ions in their aqueous solutions by using the expression;

$$A_m^\circ = \lambda_+^\circ + \lambda_-^\circ \quad (5.1.3)$$

The  $\lambda_-^\circ$  values of [HSO<sub>4</sub>]<sup>-</sup> was calculated through NaHSO<sub>4</sub> in water. The  $\lambda_+^\circ$  of Na<sup>+</sup> is 50.1 S cm<sup>2</sup> mol<sup>-1</sup> at 298.15 K. By using the  $\lambda_-^\circ$  values, 604.49 S cm<sup>2</sup> mol<sup>-1</sup> of [HSO<sub>4</sub>]<sup>-</sup> the  $\lambda_+^\circ$  of all [HSO<sub>4</sub>]<sup>-</sup>-based imidazolium ionic liquids were calculated by using

equation 5.1.3 and the values given in **Table 5.1.5**. Ionic liquids with smaller alkyl group exhibit strong electrostatic interactions and hydrogen bonding between cations and anions, whereas with higher alkyl group, the interaction between cations and anions decreases. It is observed in the present study that  $\lambda^{\circ}_{+}$  decreases upon increasing the alkyl group on cationic ring upto butyl group and shows that association increases. Ionic liquids having larger alkyl group exhibit large values of  $\lambda^{\circ}_{+}$  may describe the less electrostatic interactions between cations and anions. The ionic mobility of an ion in aqueous solution at any concentration shows the directly proportional relationship with conductance. The ionic mobility of cations ( $\mu^{+}$ ) and anions ( $\mu^{-}$ ) are calculated by using equation 5.1.4.

$$\mu^{\pm} = \frac{\lambda^{\circ}_{\pm}}{F} \quad (5.1.4)$$

where,  $F$  is the Faraday constant. The values of ionic mobility of cations and anions are given in **Table 5.1.5**. It is observed that ionic mobility of  $[\text{HSO}_4]^{-}$  anion is very high *i.e.*  $0.00623 \text{ V}^{-1} \text{ cm}^2 \text{ s}^{-1}$  as compared to cations and  $[\text{BMIM}]^{+}$  cation possess the smallest value  $0.0013 \text{ V}^{-1} \text{ cm}^2 \text{ s}^{-1}$ .

The fraction of total current carried by the individual ionic species in the aqueous solution is defined by its transport number. The transport numbers for cations ( $t^{+}$ ) and anions ( $t^{-}$ ) of ionic liquids were calculated using the following equation and are given in **Table 5.1.5**.

$$t^{\pm} = \frac{\lambda^{\circ}_{\pm}}{\lambda^{\circ}} \quad (5.1.5)$$

where,  $t^+$  and  $t^-$  are cationic and anionic transport numbers, respectively. From **Table 5.1.5**, it is observed that the  $t^-$  values for all ionic liquids are higher as compared to  $t^+$  values in water. The anionic transport number  $t^-$  for  $[\text{HSO}_4]^-$  is higher than 0.5. This indicates that the current is predominantly carried through the anions ( $> 50\%$ ). The values of  $t^-$ ,  $\mu^-$ , and  $\lambda_-^\circ$  for  $[\text{HSO}_4]^-$  anion are high which is possibly due to the smaller size. This small anion ( $[\text{HSO}_4]^-$ ) diffuses faster thus show higher  $\lambda_-^\circ$  and transport number. The present study reveals that upon increasing the alkyl chain length of the alkyl groups attached to the imidazolium ring, transport properties ( $\Lambda_m$ ,  $\Lambda_m^\circ$ ,  $\lambda_{\pm}^\circ$ ,  $t^{\pm}$ ,  $\mu^{\pm}$  etc.) decreases from ethyl to butyl group. Ionic liquids containing higher alkyl groups ( $[\text{HMIM}][\text{HSO}_4]$  and  $[\text{OMIM}][\text{HSO}_4]$ ) have higher values of the transport properties.

**Table 5.1.5.** The limiting molar conductivities  $\lambda_{\pm}^\circ$  and transport numbers  $t^+$  and  $t^-$ , ionic mobility  $\mu^+$ ,  $\mu^-$  of cations and anions of the ionic liquids in water at 298.15

S. No.	Ionic liquids	$\lambda_+^\circ (\text{S cm}^2 \text{ mol}^{-1})$	$t^+$	$t^-$	$\mu^+ (\text{V}^{-1} \text{ cm}^2 \text{ s}^{-1})$
1	$[\text{EMIM}][\text{HSO}_4]$	194	0.2431	0.7569	0.0020
2	$[\text{dEIM}][\text{HSO}_4]$	143	0.1908	0.8092	0.0015
3	$[\text{BMIM}][\text{HSO}_4]$	125	0.1716	0.8284	0.0013
4	$[\text{BEIM}][\text{HSO}_4]$	363	0.3751	0.6249	0.0038
5	$[\text{HMIM}][\text{HSO}_4]$	393	0.3941	0.6059	0.0041
6	$[\text{OMIM}][\text{HSO}_4]$	340	0.3601	0.6399	0.0035

We have obtained the highest values of transport properties for the  $[\text{HMIM}][\text{HSO}_4]$ . The strongest hydrogen bonding has also been observed from the IR study. Therefore, the availability of  $\text{H}^+$  (dissociating from  $[\text{HSO}_4]^-$ ) increases in  $[\text{HMIM}][\text{HSO}_4]$  as

compared to the other ionic liquids. Further, the dissociation of  $\text{HSO}_4^-$  in the alcohols is unlikely.

### 5.1.3.6. Diffusion Coefficient and Hydrodynamic Radius:

The  $\lambda_+^\circ$  and  $\lambda_-^\circ$  values of an ionic liquid have been used to calculate the diffusion coefficients,  $D_{IL}^o$  at infinite dilution and hydrodynamic radii,  $R_H^+$  using Stokes equation. Diffusion of the  $[\text{HSO}_4^-]$ -based aprotic ionic liquids in water is considered as the diffusion of electrolyte, rather as a single molecule. The diffusion coefficient of an ionic liquid,  $D_{IL}^o$  is related to the  $\lambda_+^\circ$  and  $\lambda_-^\circ$  values of cations and anions by the Nernst-Haskell equation.<sup>[61]</sup>

$$D_{IL}^o = \frac{RT(|z_+| + |z_-|)\lambda_+^\circ \lambda_-^\circ}{F^2|z_+||z_-|(\lambda_+^\circ + \lambda_-^\circ)} \quad (5.1.6)$$

where,  $R$  the universal gas constant,  $T$  the absolute temperature,  $F$  the Faraday constant,  $z^+$  and  $z^-$  are the charge on cations and anions, respectively. The  $D_{IL}^o$  values of the ionic liquids thus obtained are given in **Table 5.1.6**. Also listed in **Table 5.1.6** are the values of diffusion coefficients of cations,  $D^{0+}$  and of  $\text{HSO}_4^-$   $D^{0-}$  as calculated by:

$$D_+^o = \frac{RT\lambda_+^\circ}{F^2} \quad (5.1.7)$$

with a similar equation 5.1.7 for anion. The observation that the diffusion coefficient of  $[\text{HSO}_4^-]$  is higher as compared to other cations suggests that  $[\text{HSO}_4^-]$  diffuses faster than other cations. This supports the ionic mobility values of  $[\text{HSO}_4^-]$  and other cations. These results are also consistent with their transport numbers. The diffusion coefficients obtained are in the range of  $7.8$  to  $11.6 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ . The hydrodynamic radii of ions,  $R_H$  calculated by  $R_H = kT/6\pi\eta D$  are also listed in **Table 5.1.6**, where  $k$

stands for Boltzmann constant. The hydrodynamic radius of the anion is very small as compared to those of cations (**Table 5.1.6**). In order to ascertain this, we repeated the measurement of conductivities ( $\Lambda_m$ ) of the HSO<sub>4</sub><sup>-</sup> based ionic liquids reported herein and noted that these are much higher than those of the imidazolium-based protic ionic liquids with different anions in water.<sup>[4]</sup> Such higher values of  $\Lambda_m$  and therefore of the  $\Lambda_m^\circ$  and of diffusion coefficients of the ionic liquids in the current work may be responsible for low hydrodynamic radii noted in our work.

**Table 5.1.6.** Diffusion coefficient of ionic liquids  $D_{\text{IL}}^\circ$ , cation  $D^{\text{O}^+}$  and anion  $D^{\text{O}^-}$  of ionic liquids in aqueous solution and the hydrodynamic radius of the anion ( $R_{\text{H}}^-$ ) and cation ( $R_{\text{H}}^+$ ) at 298.15 K.

S. No.	Ionic liquids	$D_{\text{IL}}^\circ (10^{-5} \text{ cm}^2 \text{ s}^{-1})$	$D^{\text{O}^+} (10^{-5} \text{ cm}^2 \text{ s}^{-1})$	$R_{\text{H}}^+ (\text{pm})$
1	[EMIM][HSO <sub>4</sub> ]	7.827	5.171	47.27
2	[dEIM][HSO <sub>4</sub> ]	6.143	3.796	64.39
3	[BMIM][HSO <sub>4</sub> ]	5.524	3.334	73.31
4	[BEIM][HSO <sub>4</sub> ]	12.08	9.665	25.29
5	[HMIM][HSO <sub>4</sub> ]	12.69	10.47	23.34
6	[OMIM][HSO <sub>4</sub> ]	11.59	9.059	26.98

$D^{\text{O}^-}$ :  $16.09 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ,  $R_{\text{H}}^-$ : 15.18 pm

### 5.1.3.7. Temperature Dependency on Fluidity and Molar Conductance:

**Figures 5.1.9** and **5.1.10** show the variation in molar conductance and fluidity ( $1/\eta$ ) of aqueous solution of ionic liquids as a function of temperature. The fluidity and molar conductance of the aqueous solution of ionic liquids at a fixed concentration *i.e.* 0.04 mol L<sup>-1</sup> can be described in terms of temperature dependent Arrhenius equation shown below;

$$\log A_m = \log A_m^\circ - \frac{E_A}{2.303RT} \quad (5.1.8)$$

$$\log 1/\eta = \log 1/\eta^\circ - \frac{E_{1/\eta}}{2.303RT} \quad (5.1.9)$$

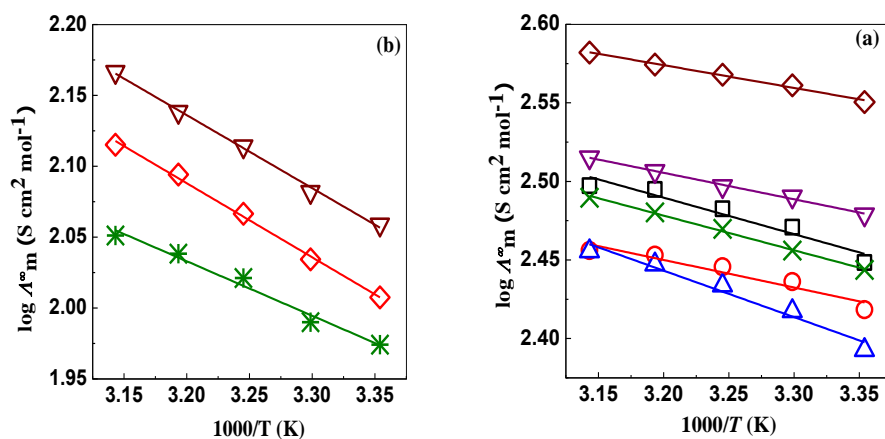
The concerned adjustable parameters for these ionic liquids are tabulated in **Table 5.1.7** and **5.1.8** with the standard errors and correlation coefficients,  $r^2$ . Activation barrier for molar conductance and fluidity of the ionic liquids can be determined from the slope of the above equations. It is observed that the temperature have a very subtle effect on the charge transfer for the  $[\text{HSO}_4]^-$ -based imidazolium ionic liquids as compared to the  $[\text{EtSO}_4]^-$ -based imidazolium ionic liquids (**Figure 5.1.9**).

**Table 5.1.7.** The adjustable parameters of Arrhenius equation to describe the effect of temperature on  $A_m$  by using equation  $\log A_m = \log A_m^\circ - q_1/T$  ( $q_1=E_A/2.303R$ ) with correlation coefficients ( $r^2$ ).

Ionic liquids	$\log A_m^\circ$ ( $\text{S cm}^2 \text{ mol}^{-1}$ )	$q_1$ ( $\text{S cm}^2 \text{ mol}^{-1} \text{ K}^{-1}$ )	$r^2$
[EMIM][ $\text{HSO}_4$ ]	$3.15 \pm 0.04$	$-0.23 \pm 0.01$	0.914
[dEIM][ $\text{HSO}_4$ ]	$2.92 \pm 0.01$	$-0.18 \pm 0.002$	0.906
[BMIM][ $\text{HSO}_4$ ]	$3.39 \pm 0.10$	$-0.30 \pm 0.03$	0.994
[BEIM][ $\text{HSO}_4$ ]	$3.04 \pm 0.02$	$-0.17 \pm 0.01$	0.960
[HMIM][ $\text{HSO}_4$ ]	$3.04 \pm 0.02$	$-0.14 \pm 0.01$	0.991
[OMIM][ $\text{HSO}_4$ ]	$3.18 \pm 0.02$	$-0.22 \pm 0.01$	0.995
[EMIM][ $\text{EtSO}_4$ ]	$3.79 \pm 0.05$	$-0.52 \pm 0.02$	0.996
[dEIM][ $\text{EtSO}_4$ ]	$3.76 \pm 0.05$	$-0.52 \pm 0.02$	0.996
[BEIM][ $\text{EtSO}_4$ ]	$3.26 \pm 0.10$	$-0.38 \pm 0.03$	0.976

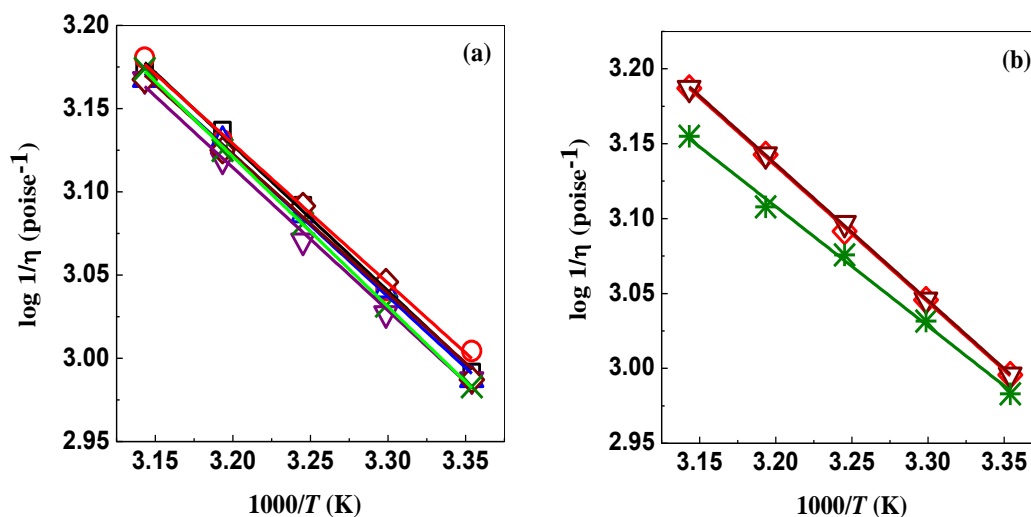
**Table 5.1.8.** The adjustable parameters of Arrhenius equation to describe the effect of temperature on  $1/\eta$  by using equation  $\log 1/\eta = \log 1/\eta^\circ - q_1/T$ ; ( $q_1 = E_{1/\eta}/2.303R$ ) with correlation coefficients ( $r^2$ ).

Ionic liquids	$\log 1/\eta^\circ$ (Poise <sup>-1</sup> )	$q_1$ (Poise <sup>-1</sup> K <sup>-1</sup> )	$r^2$
[EMIM][HSO <sub>4</sub> ]	$5.93 \pm 0.07$	$-0.87 \pm 0.02$	0.998
[dEIM][HSO <sub>4</sub> ]	$5.81 \pm 0.09$	$-0.84 \pm 0.03$	0.995
[BMIM][HSO <sub>4</sub> ]	$5.86 \pm 0.08$	$-0.86 \pm 0.02$	0.995
[BEIM][HSO <sub>4</sub> ]	$5.86 \pm 0.10$	$-0.86 \pm 0.03$	0.997
[HMIM][HSO <sub>4</sub> ]	$5.80 \pm 0.13$	$-0.84 \pm 0.04$	0.991
[OMIM][HSO <sub>4</sub> ]	$6.01 \pm 0.03$	$-0.90 \pm 0.01$	0.999
[EMIM][EtSO <sub>4</sub> ]	$6.05 \pm 0.02$	$-0.91 \pm 0.01$	0.999
[dEIM][EtSO <sub>4</sub> ]	$6.05 \pm 0.03$	$-0.91 \pm 0.01$	0.999
[BEIM][EtSO <sub>4</sub> ]	$5.66 \pm 0.08$	$-0.80 \pm 0.02$	0.996



**Figure 5.1.9.** The Arrhenius plots of  $\log A_m$  versus  $1000/T$  for aqueous solution of ionic liquids, (a) for [EMIM][HSO<sub>4</sub>] ( $\square$ ), [dEIM][HSO<sub>4</sub>] ( $\circ$ ), [BEIM][HSO<sub>4</sub>] ( $\nabla$ ), [BMIM][HSO<sub>4</sub>] ( $\triangle$ ), [HMIM][HSO<sub>4</sub>] ( $\diamond$ ), [OMIM][HSO<sub>4</sub>] ( $\times$ ), (b) for [EMIM][EtSO<sub>4</sub>] ( $\nabla$ ), [dEIM][EtSO<sub>4</sub>] ( $\diamond$ ), [BEIM][EtSO<sub>4</sub>] (\*).





**Figure 5.1.10.** The Arrhenius plots  $\log 1/\eta$  versus  $1000/T$  for aqueous solution of ionic liquids, (a) for [EMIM][HSO<sub>4</sub>] ( $\square$ ), [dEIM][HSO<sub>4</sub>] ( $\circ$ ), [BEIM][HSO<sub>4</sub>] ( $\nabla$ ), [BMIM][HSO<sub>4</sub>] ( $\triangle$ ), [HMIM][HSO<sub>4</sub>] ( $\diamond$ ), [OMIM][HSO<sub>4</sub>] ( $\times$ ), (b) for [EMIM][EtSO<sub>4</sub>] ( $\nabla$ ), [dEIM][EtSO<sub>4</sub>] ( $\diamond$ ), [BEIM][EtSO<sub>4</sub>] (\*).

**Table 5.1.9.** The values of the activation energy,  $E_a$  for the conductance and fluidity.

Name of Ionic Liquid	$E_A$ (kJ mol <sup>-1</sup> )	$E_{1/\eta}$ (kJ mol <sup>-1</sup> )
[EMIM][HSO <sub>4</sub> ]	4.40	16.66
[dEIM][HSO <sub>4</sub> ]	3.45	16.08
[BMIM][HSO <sub>4</sub> ]	5.74	16.47
[BEIM][HSO <sub>4</sub> ]	3.26	16.47
[HMIM][HSO <sub>4</sub> ]	2.68	16.08
[OMIM][HSO <sub>4</sub> ]	4.21	17.23
[EMIM][EtSO <sub>4</sub> ]	9.96	17.42
[dEIM][EtSO <sub>4</sub> ]	9.96	17.42
[BEIM][EtSO <sub>4</sub> ]	7.28	15.32

However, the  $E_a$  value of fluidity of the aqueous solution of ionic liquids is almost equal for both  $[\text{HSO}_4]^-$  and  $[\text{EtSO}_4]^-$ -based imidazolium ionic liquids and higher as compared to the activation energy of charge transfer as given in **Table 5.1.9**. The observed data of temperature dependent conductance and fluidity reveal that the effect of temperature on viscosity is higher as compared to on the conductance.

#### **5.1.4. Conclusions**

To summarize, the molar conductance of the bisulfate and ethylsulfate based imidazolium ionic liquids have been investigated in different molecular solvents as a function of their concentrations. It was observed that a) the bisulfate and ethylsulfate based imidazolium ionic liquids possess higher association constant, molar conductance and availability of free ions as compared to those of other imidazolium ionic liquids, b) the infrared spectroscopic data confirm strong hydrogen bonding between cation and anion of bisulfate and ethylsulfate based imidazolium ionic liquids and in their solutions, and c) in spite of their higher association constant and lower diffusivity, bisulfate based imidazolium ionic liquids yield high molar conductance which can be attributed mainly due to the “Grotthuss mechanism” in the aqueous solutions.

We further elaborated the association of the ionic liquids in terms of ionicity in the next section.

## ***5.2. Ionicity of the Bisulfate and Ethyl Sulfate based Ionic Liquids in Their Aqueous Solutions***

### **5.2.1. Introduction**

Ionic liquids are essentially organic salts, which can be modulated for task specific applications by the appropriate selection of cation and anion. However, their use is often restricted due to the limited knowledge of their physico-chemical properties in their solutions. The properties of ionic liquids alter drastically in their solutions due to the complexities in intra/inter molecular interactions. The basicity of the anions in ionic liquid is one of the important factors that determine the behavior of the ionic liquids. It mainly disturbs or modifies the inter-ionic Coulombic interactions. Therefore, it's challenging to predict the properties of task specific ionic liquids.

Ionicity is a measure of association/dissociation arises from the inter-ionic interactions and hence it considered as a vital parameter for the characterization of ionic liquids. The ionic nature of the ionic liquids (ionicity) is expressed in terms of free ions in their solutions. There are reports available in the literature describing the quantification of the ionicity of ionic liquids.<sup>[4, 7, 62-72]</sup> Ionicity of the ionic liquids and their solutions can be measured by using Walden plot<sup>[4, 62-68]</sup> and the molar conductance ( $\Lambda_{\text{imp}}/\Lambda_{\text{NMR}}$ ) ratios of the systems.<sup>[7, 69-72]</sup> The Walden plot ( $\log$  molar conductance ( $\Lambda_m$ ) versus  $\log$  fluidity ( $\eta^{-1}$ )) is a suitable method for determining the ionicity of the ionic liquid solutions.<sup>[4, 62-68]</sup> An ideal line in the Walden plot is drawn by using the data of dilute aqueous KCl solution that passes through the origin. The Walden plots are of special

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significance as ionic liquids can be classified as super ionic liquids, good ionic liquids, and poor ionic liquids on the basis of the vertical distance from the ideal line.<sup>[63]</sup> However, greater vertical distance from the ideal line assumed to be the incomplete ionization of those ionic liquids. An increase in molar conductance of certain ionic liquids may be attributed to the less possibility of formation of ion-pairs and aggregates. MacFarlane explained the ion-pairing and association behavior of ionic liquids on the basis of a degree of ionicity through Walden plot.<sup>[65, 67]</sup> The Walden plot for a number of phosphonium based aprotic ionic liquids appear to be relatively low degree of ionicity due to the strong ion pairing.<sup>[65]</sup> Apparently, most of the aprotic ionic liquids fall just below to the ideal line and may exhibit higher molar conductance.<sup>[67]</sup>

The molar conductance ( $\Lambda_{\text{imp}}/\Lambda_{\text{NMR}}$ ) ratio has also been used to determine the ionicity of the ionic liquids by Watanabe *et al.*<sup>[7, 69-72]</sup> where  $\Lambda_{\text{imp}}$  is the molar conductance obtained from ionic conductance measurements and  $\Lambda_{\text{NMR}}$  is from ionic diffusivity by pulse-gradient spin echo nuclear magnetic resonance (PGSE-NMR) measurements. Watanabe *et al.* also reported a comparison of the polarity scale with the molar conductance ( $\Lambda_{\text{imp}}/\Lambda_{\text{NMR}}$ ) ratios of ionic liquids.<sup>[71]</sup> Ionicity for aprotic ionic liquids reported by Watanabe *et al.*<sup>[72]</sup> ranges from 52% to 76%. The magnitude of the deviation below the ideal line, depending on the anionic structure is consistent with the order of the Lewis basicity which alters the Coulombic interactions between the ions and in turn influence the ionicity.<sup>[71]</sup>

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The ionicity of the protic ionic liquids depends on different driving forces for the proton transfer. The extent of proton transfer in protic ionic liquids however, is not fully understood. Several reports in the literature explain the degree of proton transfer in protic ionic liquids on the basis of  $\Delta pK_a$ .<sup>[62, 73-75]</sup> Watanabe et al. reported that 1, 8-Diazabicyclo [5, 4, 0] undec-7-ene (DBU) based protic ionic liquids with  $\Delta pK_a \geq 15$  are good ionic liquids (a classification based on Walden plot) and protic ionic liquids with lower  $\Delta pK_a$  values, indicating incomplete proton transfer and the formation of ion pairs.<sup>[73]</sup> Some protic ionic liquids with lower  $\Delta pK_a$  fall significantly below to the ideal line. It has been observed that DBU with  $[CH_3CO_2]$  and  $[CF_3CO_2]$  anion based protic ionic liquids having ionicity around 30 and 50%, respectively.<sup>[73]</sup>

Some of the reports in the literature have elaborated the efficiency of ethylsulfate anion based ionic liquids as high ionicity ionic liquids in the presence of inorganic salts and their applications in the separation of alkanols and alkanes.<sup>[76-78]</sup> However, to the best of our knowledge, ionicity of the alkyl sulfate anion based aprotic ionic liquids in their aqueous solutions not explored till date.

Therefore, in this section, we demonstrate the ionicity of ethylsulfate ( $[EtSO_4^-]$ ) and bisulfate ( $[HSO_4^-]$ ) anion-based aprotic ionic liquids in their aqueous solutions. The cations used in the present study are 1-ethyl-3-methylimidazolium  $[EMIM]^+$ , 1, 3-diethylimidazolium  $[dEIM]^+$ , 1-butyl-3-ethylimidazolium  $[BEIM]^+$ , 1-butyl-3-methylimidazolium  $[BMIM]^+$ , 1-hexyl-3-methylimidazolium  $[HMIM]^+$  and 1-octyl-3-methylimidazolium  $[OMIM]^+$  with their structures are given in Chapter 3. It has been

observed that multivalent anions are expected to possess excellent thermal and transport properties including proton conduction also.<sup>[79]</sup>

## 5.2.2. Results and Discussion

### 5.2.2.1. Ionicity of Bisulfate and Ethylsulfate based Ionic Liquids:

The molar conductance ( $A_m$ ) of the ionic liquids and viscosity data are given in **Table 5.2.1**. The Walden plots for  $[\text{HSO}_4]^-$  and  $[\text{EtSO}_4]^-$ -based aprotic ionic liquids in water is shown in **Figure 5.2.1(a)** and **(b)** respectively. The relation between  $A_m$  and  $\eta$  can be demonstrated by equation 5.2.1 and 5.2.2.<sup>[80, 81]</sup>

$$A \eta^\alpha = \text{constant} \quad (5.2.1)$$

$$\log A_m = \log C + \alpha \log \eta^{-1} \quad (5.2.2)$$

The slope of the line is  $\alpha$  in the Walden plot and value of  $\alpha$  reflects the dissociation of ions. In the present investigation, all  $\alpha$  values of the aqueous solutions are smaller than unity. The fitted  $\alpha$  values and the intercept are given in the **Table 5.2.2**.

These aprotic ionic liquids show a deviation from the ideal line. The deviation from the ideal line of KCl relates to the extent of ionicity in ionic liquid solutions.<sup>[81]</sup> Angell and co-workers have elucidated that the deviation is measured by the vertical distance between ideal line and the plot of the ionic liquids and is denoted by  $\Delta W$ .<sup>[63]</sup> Thus, % ionicity can be calculated from  $\Delta W$  as;

$$\% \text{ ionicity} = 10^{(-\Delta W)} \times 100 \quad (5.2.3)$$

The vertical distance,  $\Delta W$  in Walden plot for  $[\text{HSO}_4]^-$  (**Figure 5.2.1 (a)**) and  $[\text{EtSO}_4]^-$  (**Figure 5.2.1 (b)**)-based aprotic ionic liquids varies from 0.43 to 0.60 and 0.93 to

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1.01, respectively, which is significantly high as compared to many other aprotic ionic liquids. The  $\Delta W$  value for some aprotic ionic liquids in their aqueous solutions has been reported as from 0.08 to 0.11, which is comparatively low as reported for  $[\text{HSO}_4]^-$  and  $[\text{EtSO}_4]^-$ -based aprotic ionic liquids as investigated here.<sup>[68]</sup> Higher  $\Delta W$  values, as given in **Table 5.2.1** for  $[\text{HSO}_4]^-$  and  $[\text{EtSO}_4]^-$ -based aprotic ionic liquids elucidate the ionic association of ionic liquids. A linear relationship exhibits between the molar conductance of ionic liquids and the fluidity, as a function of temperature as shown in **Figure 5.2.1**.

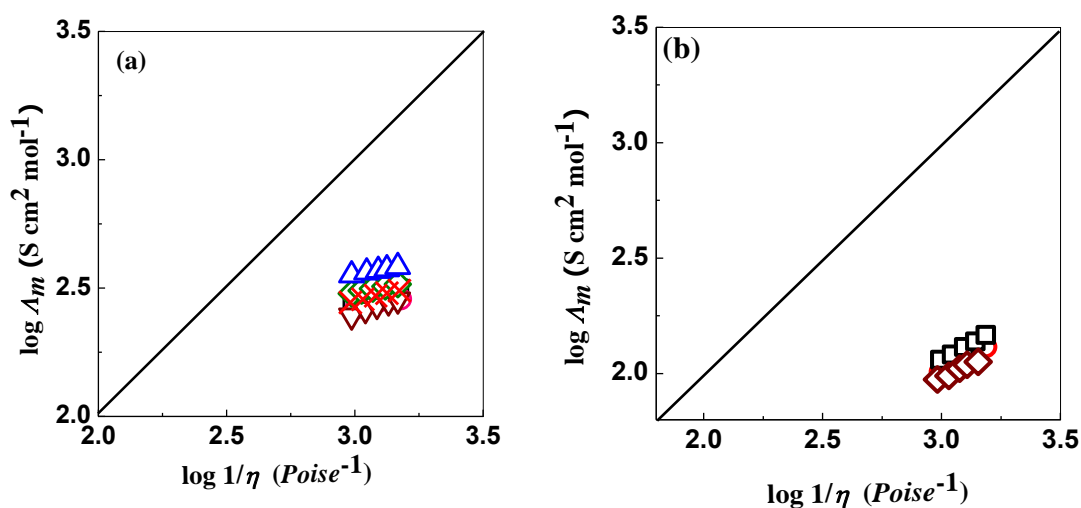
The ionicity of these  $[\text{EtSO}_4]^-$ -based aprotic ionic liquids is very low and comparable as in the case of aqueous solution of protic ionic liquids.<sup>[4, 68]</sup>  $[\text{EtSO}_4]^-$ -based aprotic ionic liquids possess approximately 10% ionicity, illustrating that the possibility to remain as ion pair is greater in  $[\text{EtSO}_4]^-$ -based aprotic ionic liquids as compared to  $[\text{HSO}_4]^-$ -based aprotic ionic liquids. It is reported that few aprotic ionic liquids also fall well below the reference line exhibiting the incomplete ionization of ionic liquids.<sup>[67]</sup>  $[\text{EtSO}_4]^-$  anion has higher electron density as evident from the hydrogen bond acceptor ability or basicity denoted by a solvent parameter called hydrogen bond acceptor basicity ( $\beta$ ). The  $\beta$  values for  $[\text{EtSO}_4]^-$  containing ionic liquids (0.788) are similar to that of DMSO solvent (0.748).<sup>[48, 49]</sup> As a result of high charge density and basicity, DMSO can solvate the cations. Similarly,  $[\text{EtSO}_4]^-$  anion possesses high charge density and basicity, therefore, it interacts with imidazolium cation to greater extent. This indicates that the  $[\text{EtSO}_4]^-$ -based aprotic ionic liquids exist in the form of intact ion pairs and cannot be easily dissociated into the ions. The electrostatic interactions are

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stronger in the sulfate based ionic liquids. The formation and life span of these ion pairs are dependent on the electrostatic and dispersive forces interacting between the ions.<sup>[82]</sup> The formation of the cation-anion aggregates in the liquids is dominated by the anionic basicity confirmed from interaction energy calculations also.<sup>[71]</sup> This is in good agreement with the results obtained for ionicity of the  $[\text{EtSO}_4]^-$ -based aprotic ionic liquids.  $[\text{HSO}_4]^-$  is a conjugate base of sulphuric acid and is highly basic in nature as compared to  $\text{ClO}_4^-$ ,  $\text{I}^-$ ,  $\text{Br}^-$ ,  $\text{Cl}^-$  anions; but having lesser basicity as compared to  $[\text{EtSO}_4]^-$ . It is noticeable that the possibility of forming intact ion pair formation is higher in  $[\text{EtSO}_4]^-$ -based aprotic ionic liquids as compared to  $[\text{HSO}_4]^-$ -based aprotic ionic liquids.

The ionicity of ionic liquids basically depends on the nature of anions such as Lewis basicity and charge density. Aprotic ionic liquids having less basic anions acquiring higher ionicity values such as ionic liquids consist of anions like  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{BF}_4^-$ ,  $\text{NTf}_2^-$  etc.  $[\text{HSO}_4]^-$ -based aprotic ionic liquids having higher ionicity as compared to  $[\text{EtSO}_4]^-$ -based aprotic ionic liquids as shown in **Figure 5.2.1**, because  $[\text{HSO}_4]^-$  is lesser basic than  $[\text{EtSO}_4]^-$ . Ionicity of the aqueous solution of  $[\text{HSO}_4]^-$  and  $[\text{EtSO}_4]^-$ -based aprotic ionic liquids is comparable to those reported for some protic ionic liquids in their aqueous solution<sup>[4, 68]</sup> and the phosphonium based ionic liquids with sweetener anions.<sup>[65]</sup> One may classify the aqueous solution of these ionic liquids as the intermediate state between the true ionic and true molecular liquids as reported by MacFarlane et al.<sup>[65]</sup>





**Figure 5.2.1** The Walden plot of 0.04 M aqueous solution of (a) for [EMIM][HSO<sub>4</sub>] (□), [dEIM][HSO<sub>4</sub>] (○), [BEIM][HSO<sub>4</sub>] (◇), [BMIM][HSO<sub>4</sub>] (▽), [HMIM][HSO<sub>4</sub>] (△), [OMIM][HSO<sub>4</sub>] (X), and (b) for [EMIM][EtSO<sub>4</sub>] (□), [dEIM][EtSO<sub>4</sub>] (○), [BEIM][EtSO<sub>4</sub>] (◇) from 298.15 to 318.15 K.

**Table 5.2.1.** Data used to obtain the Walden plot of 0.04 M aqueous solution of aprotic ionic liquids at 298.15 K.

Ionic liquids	$\Delta_m$ (S cm <sup>2</sup> mol <sup>-1</sup> )	$\eta$ (cP)	$\Delta W$	Ionicity (%)
[EMIM][HSO <sub>4</sub> ]	285.75	1.02	0.54	29
[dEIM][HSO <sub>4</sub> ]	266.00	0.99	0.58	26
[BMIM][HSO <sub>4</sub> ]	247.00	1.03	0.60	25
[BEIM][HSO <sub>4</sub> ]	301.25	1.03	0.51	31
[HMIM][HSO <sub>4</sub> ]	355.25	1.03	0.43	37
[OMIM][HSO <sub>4</sub> ]	277.75	1.04	0.53	30
[EMIM][EtSO <sub>4</sub> ]	114.50	1.01	0.93	11
[dEIM][EtSO <sub>4</sub> ]	101.73	1.01	0.94	11
[BEIM][EtSO <sub>4</sub> ]	94.23	1.04	1.01	10

**Table 5.2.2.** Linear fitting parameters with standard errors and correlation coefficients ( $r^2$ ) for Fractional Walden plot according to equation 5.2.1.

Ionic liquids	$\log C$ (S cm <sup>2</sup> mol <sup>-1</sup> )	$\alpha$	$r^2$
[EMIM][HSO <sub>4</sub> ]	1.749 ± 0.040	0.2360 ± 0.0130	0.988
[dEIM][HSO <sub>4</sub> ]	1.895 ± 0.023	0.1767 ± 0.0075	0.993
[BMIM][HSO <sub>4</sub> ]	1.356 ± 0.079	0.3481 ± 0.0258	0.978
[BEIM][HSO <sub>4</sub> ]	1.897 ± 0.033	0.1954 ± 0.0106	0.988
[HMIM][HSO <sub>4</sub> ]	2.033 ± 0.011	0.1732 ± 0.0036	0.998
[OMIM][HSO <sub>4</sub> ]	1.714 ± 0.030	0.2447 ± 0.0098	0.994
[EMIM][EtSO <sub>4</sub> ]	0.3603 ± 0.0510	0.5662 ± 0.0165	0.997
[dEIM][EtSO <sub>4</sub> ]	0.2879 ± 0.0633	0.5742 ± 0.0204	0.995
[BEIM][EtSO <sub>4</sub> ]	0.5408 ± 0.1336	0.4800 ± 0.0435	0.968

We have also examined the temperature dependence of Walden product. The temperature dependent Walden product has been studied and correlated with Stokes hydrodynamic radius ( $r_s$ ) of ionic liquids as;<sup>[3]</sup>

$$\eta\lambda o = \frac{8.204Z_i}{r_s} \quad (5.2.4)$$

where,  $Z_i$  is the charge number of the ion and  $r_s$  is the hydrodynamic radius. The temperature dependent Walden products of the [HSO<sub>4</sub>]<sup>-</sup> and [EtSO<sub>4</sub>]<sup>-</sup>-based aprotic ionic liquids are tabulated in **Table 5.2.3** and **5.2.4**, respectively.

**Table 5.2.3.** The Walden products as a function of temperature for the  $[\text{HSO}_4]^-$ -based aprotic ionic liquids in their aqueous solutions.

$T$ (K)/ Ionic Liquids	$A_m \eta$ ( $\text{cm}^{-1} \text{mol}^{-1} \text{s}^2 \text{A}^2$ )					
	[EMIM] [HSO <sub>4</sub> ]	[dEIM] [HSO <sub>4</sub> ]	[BMIM] [HSO <sub>4</sub> ]	[BEIM] [HSO <sub>4</sub> ]	[HMIM] [HSO <sub>4</sub> ]	[OMIM] [HSO <sub>4</sub> ]
298.15	0.29	0.26	0.25	0.31	0.37	0.29
303.15	0.26	0.25	0.24	0.29	0.33	0.27
308.15	0.24	0.22	0.23	0.27	0.30	0.24
313.15	0.23	0.21	0.21	0.24	0.28	0.23
318.15	0.21	0.19	0.19	0.22	0.26	0.21

**Table 5.2.4.** The Walden products as a function of temperature for the  $[\text{EtSO}_4]^-$ -based aprotic ionic liquids in their aqueous solutions.

$T$ (K)/ Ionic Liquids	$A_m \eta$ ( $\text{cm}^{-1} \text{mol}^{-1} \text{s}^2 \text{A}^2$ )		
	[EMIM][EtSO <sub>4</sub> ]	[dEIM][EtSO <sub>4</sub> ]	[BEIM][EtSO <sub>4</sub> ]
298.15	0.12	0.10	0.10
303.15	0.11	0.10	0.09
308.15	0.10	0.09	0.09
313.15	0.10	0.09	0.09
318.15	0.10	0.08	0.08

The Walden product of these aprotic ionic liquids was noted to be temperature independent within experimental errors. It is evident from the present study that the effective size of  $[\text{BMIM}]^+$  ion is comparatively larger than the other cations of  $[\text{HSO}_4]^-$ -based aprotic ionic liquids. However, we obtained an inverse correlation between

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the effective radius of  $[\text{BMIM}]^+$  ion and its  $\Lambda_m^\circ$ . The larger size of the ion essentially decreases its mobility or diffusivity thus the conductance. The effective size of the cations of  $[\text{EtSO}_4]^-$ -based aprotic ionic liquids is larger as compared to the cations of the  $[\text{HSO}_4]^-$ -based aprotic ionic liquids.

An unusual behavior of the  $[\text{HSO}_4]^-$ -based aprotic ionic liquids is seen. Usually, the protic ionic liquids retain higher deviations from the ideal line and hold lower molar conductance value. On the contrary,  $[\text{HSO}_4]^-$ -based aprotic ionic liquids show high molar conductance as compared to other aprotic ionic liquids.

In spite of having higher  $\Delta W$  values and lower ionicity of the  $[\text{HSO}_4]^-$ -based aprotic ionic liquids, the molar conductance is considerably high and is in the range from 600 to  $1000 \text{ S cm}^2 \text{ mol}^{-1}$ .  $[\text{HSO}_4]^-$ -based aprotic ionic liquids show 4-5 times higher molar conductance values in water as compared to the  $[\text{EtSO}_4]^-$ -based aprotic ionic liquids as discussed in the earlier section. Interestingly, the anomalous behavior is probably due to the possible Grotthuss mechanism<sup>[57]</sup> in the  $[\text{HSO}_4]^-$ -based aprotic ionic liquids. The possibility of formation of hydrogen bonds with water is greater in  $[\text{HSO}_4]^-$  anion than  $[\text{EtSO}_4]^-$  due to the high charge density, presence of hydrogen atom and smaller size of  $[\text{HSO}_4]^-$  anion. Unlike in  $[\text{EtSO}_4]^-$ ,  $[\text{HSO}_4]^-$  anion has both possibility of hydrogen bond accepting and donating through oxygen and hydrogen atoms, respectively with the water molecule and exhibit the higher molar conductance by the Grotthuss mechanism.

### 5.2.3. Conclusions

To summarize, we have demonstrated that,

- i. the substitution of the  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{PF}_6^-$ ,  $\text{BF}_4^-$ ,  $\text{NTf}_2^-$  anions by  $[\text{EtSO}_4]^-$ ,  $[\text{HSO}_4]^-$  anion in the imidazolium-based aprotic ionic liquids significantly reduces the ionicity resemble to those offered by some of the aqueous solution of protic ionic liquids and phosphonium based ionic liquids with sweetner anions, and
- ii. in spite of having lesser ionicity, the molar conductance of bisulfate based aprotic ionic liquids is exceptionally high which can be attributed to the Grotthuss mechanism.



### ***5.3. The Molar Conductance of [EMIM][HSO<sub>4</sub>] and [EMIM][EtSO<sub>4</sub>] in Their Ternary Mixtures with Molecular Solvents and Water***

#### **5.3.1. Introduction**

Out of interest, the ternary mixtures of ionic liquids with molecular solvents and water has been studied in past and has aided in the better understanding of ionic liquids in different environments. The ternary mixtures of ionic liquids are of importance as they can assist in very complex reaction systems. Methanol, 1-propanol, 1-butanol, dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF), acetonitrile (AN), and their mixtures with water, independently have well known fundamental importance in various chemical processes.<sup>[83-86]</sup> Han *et. al.* studied the conductivity and viscosity of [BMIM][PF<sub>6</sub>] + water + ethanol and [BMIM][PF<sub>6</sub>] + water + acetone ternary mixtures.<sup>[87]</sup> Gao *et. al.* determined the conductivity and viscosity of 1-allyl-3-methylimidazolium chloride + water + ethanol as a function of temperature from 293.15 to 333.15 K.<sup>[88]</sup> The viscosity of ionic liquids depends on hydrogen bonding and the van der Waals interactions.<sup>[89]</sup> Other parameter, conductivity depends on the molecular weight, density, size of the ions and viscosity.<sup>[89]</sup> An addition of some molecular solvents often decreases the viscosity of ionic liquids and enhances the conductivity due to mobile ions.<sup>[87, 90]</sup> Till today, most of the studies dealing ionic liquids are limited to the binary ionic liquid-solvent mixtures.

In the present study we prepared the ternary mixtures of ionic liquids with molecular solvents (methanol, 1-propanol, 1-butanol, acetonitrile, DMSO and DMF) and water.

We further determined the conductivities of these mixtures and reported the behavior of the ionic liquids in different solvents.

### 5.3.2. Results and Discussion

The experimental conductance data of the [EMIM][HSO<sub>4</sub>] and [EMIM][EtSO<sub>4</sub>] have been measured in different ternary mixtures (*i.e.* ionic liquid + solvent (methanol, 1-propanol, 1-butanol, acetonitrile, DMSO and DMF) + co-solvent (water)) at 298.15 K over a concentration range of ionic liquids. Relative molar conductance,  $A_{m,r}$  of solutions were determined by taking the ratio of  $A_m$  of ternary mixture to that of the  $A_m$  of binary ionic liquid-solvent mixture. The  $A_{m,r}$  with molarity,  $M$  (mol L<sup>-1</sup>) were fitted by least squares to the Jones-Dole type equation<sup>[91]</sup>

$$A_{m,r} = 1 + BM + CM^2 + DM^3 \quad (5.3.1)$$

Where  $B$ ,  $C$  and  $D$  are the empirical coefficients. Generally, the Jones-Dole equation is used for the interpretation of viscosity data in the ternary mixture.<sup>[91]</sup> Viscosity and conductivity are reciprocal to each other and hence we made an attempt to fit the conductance data of ternary mixture with their molarity using Jones-Dole type equation. In general, the  $B$ -coefficient measures the solute-solvent interactions whereas  $C$ -coefficient reflects solute-solute interactions as well as solute-solvent interactions. In the present study the interpretation of  $C$ -and  $D$ -coefficients is difficult due to the presence co-solvent. The values of  $B$ ,  $C$  and  $D$  coefficients are enlisted in **Table 5.3.1**. We note that the conductance data obtained for ionic liquids in acetonitrile-water mixture was discrete and therefore was not fitted to the equation.



### 5.3.2.1. Molar Conductance of [EMIM][HSO<sub>4</sub>] and [EMIM][EtSO<sub>4</sub>] in the Binary Solvent Mixtures

The conductance of an electrolyte solution depends upon relative permittivity among other parameters of a solvent in which the solution is prepared. The variation in the  $A_{m,r}$  values of ternary mixtures with the molarity,  $M$  of ionic liquids (in mixture solvent + co-solvent) is shown in **Figures 5.3.1**. The  $A_{m,r}$  values of [EMIM][HSO<sub>4</sub>] and [EMIM][EtSO<sub>4</sub>] show different variations with their molarity in the different binary solvent mixtures. The  $A_{m,r}$  values of [EMIM][HSO<sub>4</sub>] and [EMIM][EtSO<sub>4</sub>] mainly depend on the macroscopic properties of the solvent mixtures such as viscosity ( $\eta$ ), relative permittivity ( $\epsilon$ ) etc. of the binary solvent mixtures. We found that the  $A_{m,r}$  of the ionic liquid mixtures initially decreases upon addition of water into the ionic-liquid-solvent binary mixture. Later on, it was observed to be increased after the certain molarity of ionic liquids. The transition point (in terms of molarity) at which the  $A_{m,r}$  values are lowest varies with the solvent used. The transition point has not been observed in for [EMIM][HSO<sub>4</sub>] and [EMIM][EtSO<sub>4</sub>] in the 1-butanol + water and 1-propanol + water mixture. On the other hand, the transition in the  $A_{m,r}$  of ternary mixture of [EMIM][HSO<sub>4</sub>] and [EMIM][EtSO<sub>4</sub>] is clearly distinguished in methanol, DMSO, DMF and AN mixtures. These mixtures (molecular solvent + water) show variations in their physico-chemical properties as a mole fraction of water molecules ( $x_{H_2O}$ ). In general, the interactions in the mixture of two liquids A and B can be described by the three type of interactions; A-A, B-B, A-B. In the ionic liquid mixtures these are mainly hydrogen bonded interactions with solvent molecules.<sup>[92, 93]</sup>The

hydrogen bonding and intermolecular interactions in the mixtures of solvent can be understood by from viscosity and dielectric constant. The viscosity measurements for the studied solvent-water mixtures are already reported. The  $\Lambda_{m,r}$  in individual solvent mixtures is discussed as follow;

**(a) Methanol-water:** The  $\Lambda_{m,r}$  values of [EMIM][HSO<sub>4</sub>] and [EMIM][EtSO<sub>4</sub>] are shown in **Figure 5.3.1 (a)**. The non-linearity of  $\Lambda_{m,r}$  of [EMIM][HSO<sub>4</sub>] and [EMIM][EtSO<sub>4</sub>] has been observed in the methanol-water mixtures. The  $\Lambda_{m,r}$  values for [EMIM][HSO<sub>4</sub>] and [EMIM][EtSO<sub>4</sub>] initially decrease upon addition of water to the ionic liquid solution and increase after it reaches to the transition point at  $x_{\text{H}_2\text{O}} = 0.35$ . Methanol exhibits amphiphilic nature, with a single hydrophilic (-OH) group and single hydrophobic (-CH<sub>3</sub>) group. Methanol can display both one/two dimensional hydrogen bonded network.<sup>[94]</sup> It is observed that the behavior of methanol-water solution is more complex than the simple molecules. The viscosities of these mixtures measured previously shows a minima when the mixing ratio is altered.<sup>[83]</sup> In the binary solvent mixture of methanol-water, as one move along the fraction number of water, stronger intermolecular interactions initially increases the viscosity increases followed by a drop after  $x_{\text{H}_2\text{O}} = 0.75$ . Therefore, the higher viscosities as a result of addition of water, decreases the conductance in the solution. The minima of  $\Lambda_{m,r}$  and the maxima of viscosity is observed at the different mole fraction of water. This might be observed due to the different possibility of interactions between methanol-water and ionic liquid-methanol-water system. The higher viscosities essentially slows down the mobility of

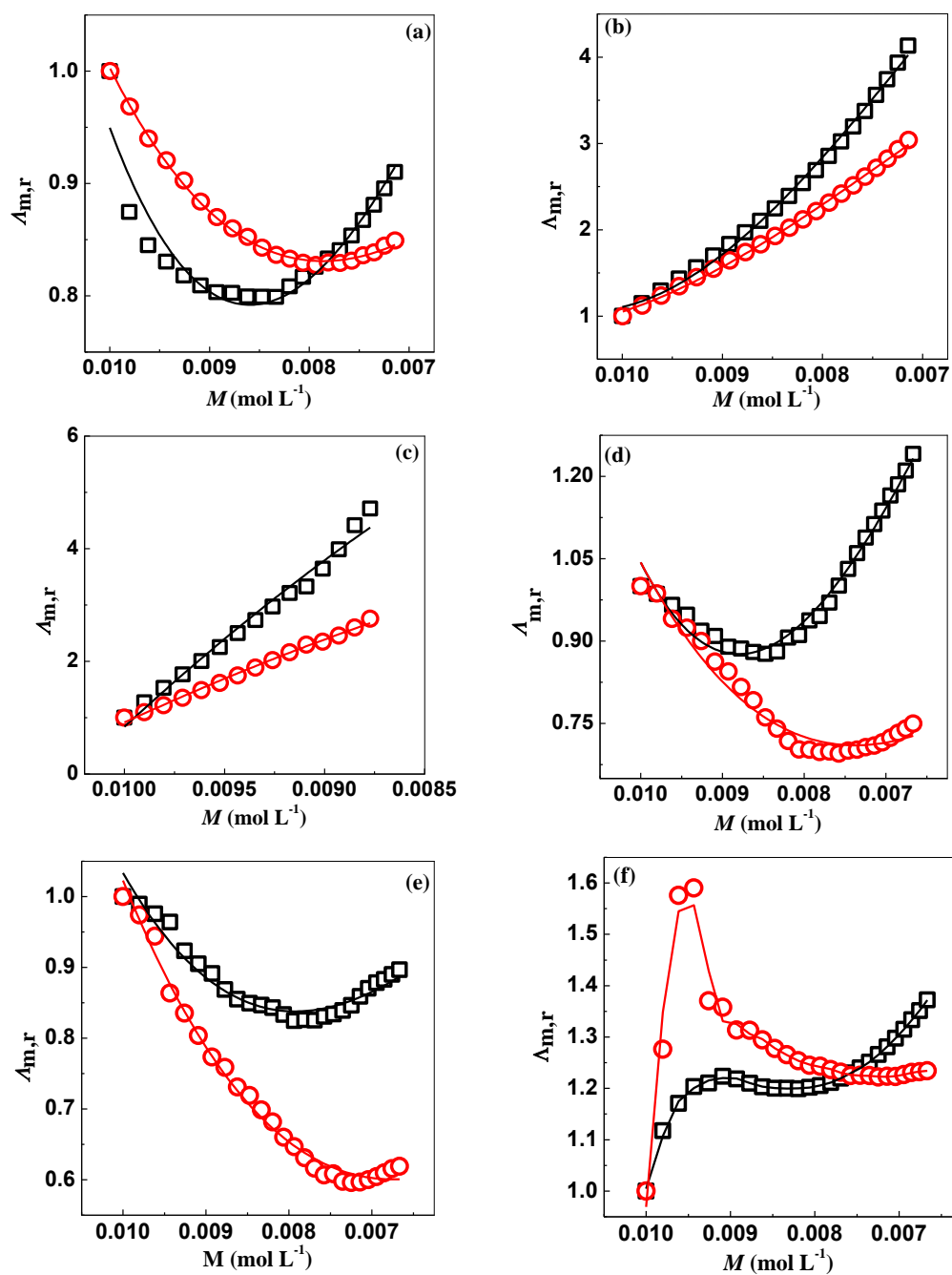
the ions and after the transition point, further dilution may increase the mobility of ions.

**(b) 1-Propanol-water:** We observed that the  $A_{m,r}$  of [EMIM][HSO<sub>4</sub>] and [EMIM][EtSO<sub>4</sub>] in the 1-propanol + water mixture increases linearly upon the dilution as shown in **Figure 5.3.1 (b)**. In this case, increasing amount of water reduces the inter-ionic interactions and makes them available for conductance. Earlier study reported a non-linearity viscosity for 1-propanol-water mixture which suggests the intermolecular interactions between them.<sup>[95]</sup> The  $A_{m,r}$  values of ionic liquids in 1-propanol-water increases upon the dilution but in the studied composition range, the viscosity of 1-propanol-water also increases. Therefore, it is expected that the  $A_{m,r}$  values depend on the viscosity of solvent mixtures. As a result, in the mixture (1-propanol-water) the mobility of ions increases hence,  $A_{m,r}$  increases upon the addition of water molecules.

**(c) 1-Butanol-water:** We have also investigated the  $A_{m,r}$  values of [EMIM][HSO<sub>4</sub>] and [EMIM][EtSO<sub>4</sub>] in 1-butanol-H<sub>2</sub>O mixtures. The hydroxyl group of alcohols and water molecules has a similar tendency to form the hydrogen bonding network. The alcohols cannot be stabilized through the interactions with water with an increase in the alkyl chain length of alcohols.<sup>[96]</sup> Therefore, the self-association/aggregation of alcohol has been observed due to hydrophobic interactions, at higher alcohol concentrations.<sup>[96]</sup> 1-Butanol-water system is only miscible at lower concentrations.<sup>[96]</sup> Therefore, we have taken the composition range of 1-butanol-water in the complete dissolution range of ionic liquids. The similar trend for the  $A_{m,r}$  values of [EMIM][HSO<sub>4</sub>] and

[EMIM][EtSO<sub>4</sub>] in the 1-butanol-water is observed as for 1-propanol-water mixtures. The viscosity increases upon increasing the mole fraction of water but the interactions between water and 1-butanol are less favorable as compared to the small alcohols-water.<sup>[97]</sup> Therefore, the mixture (1-butanol/1-propanol-water) increase the mobility of ions and  $A_{m,r}$  increases upon the addition of water molecules as shown in the **Figure 5.3.1 (c)**. The  $A_{m,r}$  values also indicates the lesser extent of interactions between 1-butanol-water.

**(d) DMSO-water:** The non-linearity of the  $A_{m,r}$  values as shown in **Figure 5.3.1 (d)** indicates the strong interactions between DMSO-water mixture. The reported values of viscosities, densities and heat of mixing of DMSO-water mixture also indicate a strong association of the liquids which may be attributed to the hydrogen bonding.<sup>[98]</sup> A greater degree of association in DMSO-water mixtures than in water alone has been observed.<sup>[99]</sup> The polar sulfoxide group of DMSO are more likely to have stronger hydrogen bond than the hydrogen bonds between water and also impart the networked waters in the first solvation shell.<sup>[100]</sup> Therefore, the association in DMSO-water mixtures responsible for the non-linear plot of  $A_{m,r}$  of [EMIM][HSO<sub>4</sub>] and [EMIM][EtSO<sub>4</sub>] in the DMSO-water mixtures. In methanol-water the minima of  $A_{m,r}$  and maxima of viscosity observed at different mole fraction of water. The minima of  $A_{m,r}$  values of [EMIM][HSO<sub>4</sub>] has observed at  $x_{H_2O} = 0.41$  and for [EMIM][EtSO<sub>4</sub>] at  $x_{H_2O} = 0.55$ , whereas the maxima of viscosity at  $x_{H_2O} = 0.65$ .



**Figure 5.3.1.** The plots of (a)  $\Lambda_{m,r}$  versus molarity ( $\text{mol L}^{-1}$ ) for [EMIM][HSO<sub>4</sub>] ( $\square$ ) and [EMIM][EtSO<sub>4</sub>] ( $\circ$ ) in the ternary mixture of ionic liquid for (a) methanol-water, (b) 1-Propanol-water, (c) 1-butanol-water, (d) DMSO-water, (e) DMF-water, (f) AN-water.

The higher  $\Lambda_{m,r}$  and the minima at the low mole fraction of water for [EMIM][HSO<sub>4</sub>] than [EMIM][EtSO<sub>4</sub>] indicates less favorable interactions of [EMIM][HSO<sub>4</sub>] with DMSO-water mixture this makes more ions available for conductance. The  $\Lambda_{m,r}$  values of [EMIM][HSO<sub>4</sub>] and [EMIM][EtSO<sub>4</sub>] depends on the viscosity of DMO-water system. The variation in the mole fraction of viscosity maxima and  $\Lambda_{m,r}$  minima of ionic liquids is observed due to the interactions retained between ionic liquids and DMO-water.

**(e) DMF-water:** The viscosity and  $\varepsilon$  data indicates that the DMF molecules tend to break the intra-water hydrogen bonds and exhibit strong DMF-water interactions. The excess enthalpies data of mixing are negative over the entire concentration range of DMF-water mixture suggesting strong interaction between DMF and water.<sup>[101]</sup> Viscosity measurements indicate the formation of the DMF-water complex.<sup>[102]</sup> The viscosity data suggest the formation of DMF-water complex which may be preventing the mobility of ions of ionic liquids (**Figure 5.3.1 (e)**). The  $\Lambda_{m,r}$  values of [EMIM][HSO<sub>4</sub>] and [EMIM][EtSO<sub>4</sub>] in the DMF-water mixture are in good agreement with the previously reported viscosity data.<sup>[102]</sup> The minima of  $\Lambda_{m,r}$  of [EMIM][HSO<sub>4</sub>] obtained at  $x_{H_2O} = 0.55$  and of [EMIM][EtSO<sub>4</sub>] at  $x_{H_2O} = 0.60$  and reveals that the  $\Lambda_{m,r}$  values of [EMIM][HSO<sub>4</sub>] and [EMIM][EtSO<sub>4</sub>] in the solvent mixtures depend on their viscosity.

**(f) AN-water:** The distinct behavior of the  $\Lambda_{m,r}$  of [EMIM][HSO<sub>4</sub>] and [EMIM][EtSO<sub>4</sub>] has been observed in the AN-water mixtures as shown in **Figure 5.3.1 (f)**. We have observed that the  $\Lambda_{m,r}$  values (**Figure 5.3.1 (f)**) of [EMIM][HSO<sub>4</sub>] show two transition

points. Upon the addition of water molecules,  $\Lambda_{m,r}$  increases upto  $x_{H_2O} = 0.22$  and then slightly decreases upto  $x_{H_2O} = 0.45$  and after that again increases. Whereas, the  $\Lambda_{m,r}$  values of [EMIM][EtSO<sub>4</sub>] increase upto the  $x_{H_2O} = 0.15$  then it decreases. It is reported that when the AN content in its aqueous mixture is sufficiently high the structure is micro heterogeneous, it contains clusters of molecules of one type, either AN or water.<sup>[103]</sup> Therefore, the  $\Lambda_{m,r}$  values of [EMIM][HSO<sub>4</sub>] and [EMIM][EtSO<sub>4</sub>] initially increase due to dilution because at low concentration the interactions between water and AN are less favorable as reported. Marcus and Migron also reported that AN is solvated by water at low mole fractions of AN, and micro heterogeneity observed in above  $x_{AN} = 0.22$ .<sup>[104]</sup> Therefore, the mobility of ions of ionic liquids decreases causing a decrease in  $\Lambda_{m,r}$  of [EMIM][HSO<sub>4</sub>] and [EMIM][EtSO<sub>4</sub>].

We observed a significant effect of solvent mixture on the  $\Lambda_m$  of ionic liquids. Among all the binary solvent mixtures, the  $\Lambda_m$  of [EMIM][HSO<sub>4</sub>] is high than the [EMIM][EtSO<sub>4</sub>], exception is methanol-H<sub>2</sub>O mixture where the  $\Lambda_m$  of [EMIM][EtSO<sub>4</sub>] is high than the [EMIM][HSO<sub>4</sub>]. In general, addition of the solvent to the ionic liquids decreased the viscosity of ionic liquids solution. This essentially makes ions free for the conductivity hence the conductance increases. The variation in the viscosity of a solvent upon addition of another solvent (in the present study water) shows a significant profile for the solvent mixtures as reported earlier. Interestingly, the solvent mixtures used in the present study exhibit different interactions with the water molecules and it explained based on viscosity and conductance data.

**Table 5.3.1.** The adjustable parameters of equation 5.3.1 for the studied ternary mixture of ionic liquids (IL) with correlation coefficient ( $r^2$ ).

[EMIM][HSO <sub>4</sub> ]				
Ternary System	<i>B</i>	<i>C</i>	<i>D</i>	$r^2$
Methanol-water-IL	205 ± 19	-4509 ± 420	24559 ± 2278	0.853
1-Propanol- water-IL	994 ± 40	-18978 ± 875	90404 ± 4741	0.998
1-Butanol-water-IL	594 ± 17	5954 ± 179	-	0.987
DMSO-water-IL	279 ± 8	-6061 ± 170	32267 ± 937	0.989
DMF-water-IL	113 ± 7	-2619 ± 147	14885 ± 809	0.963
[EMIM][EtSO <sub>4</sub> ]				
Ternary System	<i>B</i>	<i>C</i>	<i>D</i>	$r^2$
Methanol-water-IL	99.82 ± 1.30	-2315 ± 28	13168 ± 153	0.999
1-Propanol-water-IL	469 ± 20	-8456 ± 440	37660 ± 2386	0.999
1-Butanol-water-IL	296 ± 4	-2965 ± 40	-	0.997
DMSO-water-IL	122 ± 11	-2950 ± 237	17324 ± 1305	0.972
DMF-water-IL	93.05 ± 7.07	-2399 ± 156	14707 ± 860	0.993

### 5.3.3. Conclusions

To summarize, we obtain a direct correlation between the conductivity and the viscosity of solvent mixtures. Low conductivity is observed when the alkyl chain of the anion increased. This brings about the size of the ions increase hence mobility decreases. Dilution of ionic liquid mixture essentially brings about the availability of ions for conductance. We observe that upon addition of a co-solvent (dilution with water) the  $\Lambda_m$  of [EMIM][HSO<sub>4</sub>] and [EMIM][EtSO<sub>4</sub>] initially decreases upto certain



mole fraction (vary with solvent-water mixture) then increases. Exceptionally, the  $\Lambda_m$  of [EMIM][HSO<sub>4</sub>] and [EMIM][EtSO<sub>4</sub>] increases in the studied mole fraction range of water for 1-propanol and 1-butanol (solubility limit). The minima in the  $\Lambda_m$ -molarity plot have been observed in the solvent-water mixtures due to the strong interactions and association of solvent and water molecules which has been explained by their viscosity data. It has been concluded from the present study that the conductivity of ionic liquids in the binary solvent mixture mainly depends on their viscosity.

### 5.5. References

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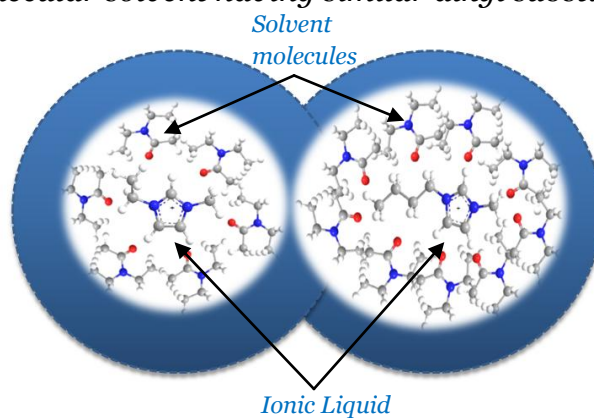
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## Chapter 6

### ***Isothermal Titration Calorimetric Study of the Ionic Liquid Solutions: An Investigation of Ion-Solvent Interactions***

*This chapter elaborates an extensive and quantitative study of the ion-solvent interactions of ionic liquids with molecular solvents in terms of the excess partial molar enthalpy ( $H^{E_{IL}}$ ) using Isothermal Titration Calorimeter. It is divided into two separate sections. Section 6.1 deals with the enthalpic measurements of ionic liquids with alcohols in extremely dilute conditions. Here, an unusual trend is seen for ionic liquid-1-butanol mixture which is elaborated. The Section 5.2 of the thesis investigates the enthalpic behavior of ionic liquids with molecular solvent having similar alkyl substituents.*





## **6.1. Isothermal Titration Calorimetric Study of the Ionic Liquid Solutions in Alcohols under Extreme Dilutions**

### **6.1.1. Introduction**

This chapter is intended to understand the effect of the alcohol-rich environment on the imidazolium-based ionic liquids at 298.15 K using an isothermal titration calorimeter (ITC). The physico-chemical properties of ionic liquid systems can be modulated by varying their structures by changing the cationic core, anions and composition. A substantial amount of the research is dedicated to the study of the structure-property relations for different class of ionic liquids.<sup>[1-5]</sup> Highly viscous nature of many ionic liquids is adverse to the progress of the organic reactions.<sup>[6]</sup> It has been observed that the addition of molecular solvents in ionic liquids reduces their viscosities without affecting their properties.<sup>[7-10]</sup> The impact of these solvents can be precisely demonstrated, for example, in terms of the excess partial molar enthalpies of the ionic liquid-solvent mixtures. The experimentally measured excess partial molar enthalpies can be a useful parameter to quantify the ion-solvent and ion-ion interactions in the ionic liquid-solvent systems and illustrate the distinct state of the solutions as a function of their concentrations.<sup>[7, 11-17]</sup>

Nebig et al<sup>[18]</sup> measured the enthalpies of mixing of 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, [BMIM][NTf<sub>2</sub>] and 1-hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, [HMIM][NTf<sub>2</sub>] with ketones. The negative enthalpy of mixing, ( $\Delta_{\text{mix}}H$ ) indicate an exothermic mixing process of the ionic liquid

and ketone binary mixtures. The effect of ionic liquid structure on the mixing properties with nitromethane has also been investigated.<sup>[19, 20]</sup> The  $\Delta_{\text{mix}}H$  for several imidazolium and pyridinium-based ionic liquids with nitromethane were determined experimentally at 303.15 K and 0.1 MPa over the whole composition range.<sup>[19, 20]</sup> Pyrrolidinium cation based ionic liquids show positive values of the mixing and excess partial molar enthalpies, ( $H_{IL}^E$ ) as compared to the imidazolium-based ionic liquids.<sup>[21]</sup> A soft statistical associating fluid theory (SAFT), equation of state was used to model the pyridinium-based ionic liquids and their mixtures.<sup>[22]</sup> Another approach, perturbed-chain soft statistical associating fluid theory (PC-SAFT) combined with modified UNIFAC (Dortmund) was used to model properties of ionic liquids and their mixtures with solvents.<sup>[23]</sup> Enthalpies of mixing depends on the structure of different apolar compounds has also been examined.<sup>[18, 24-26]</sup> Negative  $\Delta_{\text{mix}}H$  (enthalpically favorable) have been reported for benzene and toluene whereas for *n*-hexane, methylcyclohexane, and 1, 3- cyclohexadiene, the enthalpy of mixing is positive (enthalpically unfavorable).<sup>[18, 27]</sup> The additional  $-\text{CH}_3$  group on the  $\text{C}_2$  carbon of the imidazolium ring as in  $[\text{C}_1\text{C}_1\text{C}_4][\text{NTf}_2]$  as compared to the  $[\text{C}_1\text{C}_4\text{Im}][\text{NTf}_2]$  leads to a unfavorable mixing with 1,3-cyclohexadiene.<sup>[27]</sup> Enthalpies of some aprotic ionic liquid solutions have also been calculated.<sup>[28, 29]</sup> The activity coefficients at infinite dilutions for these ionic liquids were employed to estimate the  $H_{IL}^E$  values.<sup>[30]</sup> The  $H_{IL}^E$  values of ionic liquid solutions has been observed and to be reliable with those calculated by the method based upon the CHELPG (Charges from Electrostatic Potentials using a Grid-based method) atomic charges.<sup>[17, 31, 32]</sup> The  $H_{IL}^E$  values of mixing of two piperidinium-

based ionic liquids in ethanol and 1-propanol was analyzed using isothermal titration with their accurate representation by the PC-SAFT equation of state.<sup>[33]</sup> The positive  $H^E_{IL}$  values of the ionic liquid for alcoholic systems signifies the interactions between the ionic liquid and alcohol molecules are less favorable when compared to the interactions prevailing between the pure components. These interactions are enhanced with increasing the length of the alkyl chain both on the ionic liquid cations and the alcohol molecules reported earlier.<sup>[33]</sup> A detailed literature survey has revealed the ion-solvent and ion-ion interactions existing in ionic liquids-alcohol solutions.<sup>[15, 29, 33-38]</sup> The  $H^E_{IL}$  data obtained for these binary mixtures were positive in the entire mole fraction range signifying the existence of weaker ionic liquid-alcohol interactions. The binary mixtures of 1-ethyl-3-methylimidazolium dimethyl phosphate ([EMIM][DMP]) with methanol and ethanol have revealed a very strong exothermic behavior shown as negative  $H^E_{IL}$  values over the whole composition.<sup>[39]</sup> Several  $H^E_{IL}$  data collected from different sources have been used for developing and testing a semi-quantitative COSMO-RS model for the alcoholic mixtures of various ionic liquids.<sup>[40]</sup> Both experimental data and the COSMO-RS model suggested an increase in the endothermic  $H^E_{IL}$  values by increasing the alkyl chain length on the alcohol molecules *i.e.* shifting from methanol to 1-butanol. It was noted that in the alcohol-rich region, the  $H^E_{IL}$  data exhibited overlapping with no definitive trends. On the other hand, these endothermic titration curves followed the order of decreasing dielectric constants of alcohols in the ionic liquid-rich solutions.<sup>[39]</sup> The ternary solutions of these ionic liquids in water and alcohol showed highly negative  $H^E_{IL}$  values suggesting the favorable interactions operating between ionic liquid and alcohol.<sup>[41]</sup> All the above experimental and

theoretical efforts for various ionic liquids-alcohol binary mixtures have been made in the full concentration range of ionic liquids/alcohols.

In view of the above work, we focus our investigations on the alcohol-rich region (extreme dilute range of the ionic liquid solutions) in order to extract the information of ion-solvent and ion-ion interactions.<sup>[29, 33-38]</sup> This study emphasizes on;

- i. the  $H_{IL}^E$  values of ionic liquids in extremely dilute alcoholic solutions,
- ii. the solvation behavior of these ionic liquids in alcoholic environment, and
- iii. the effect of change in the length (number of carbon atoms,  $n$ ) of the alkyl chain of both ionic liquid's cation and alcohol molecules on the solvation.

In the current investigation, several binary mixtures of the imidazolium-based ionic liquids (structures have been given in Chapter 3) in various mono alcohols with varying the alkyl chain length of both ionic liquid's cation and alcohol molecules, investigated for seeking quantitative information on the enthalpic interactions in extremely dilute ionic liquid solutions.

### 6.1.2. Experimental Section

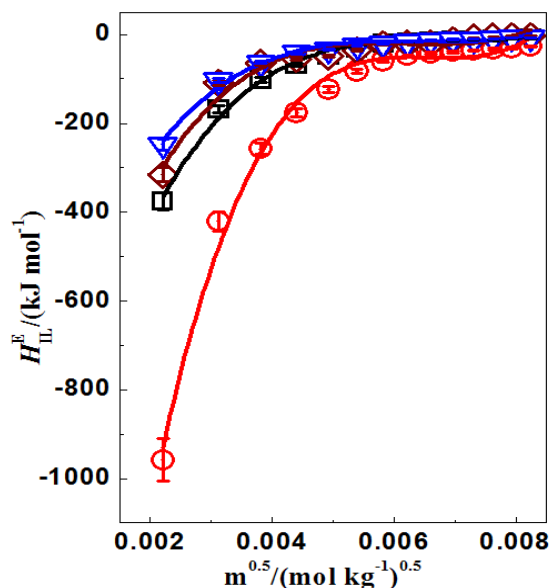
The isothermal titration calorimeter (ITC; model: MicroCal LLC, VP-ITC2000) controlled by the VP-Viewer 2000 software was employed to measure the excess partial molar enthalpy of mixing of the binary mixtures of ionic liquid and alcohol molecules at 298.15 K. The fundamental details of the calibration and experimental procedures are given in Chapter 3.

### 6.1.3. Results and Discussion

#### 6.1.3.1. $H_{IL}^E$ of [RMIM][BF<sub>4</sub>]-Alcohol: Effect of Variation in the Alkyl Chain on Alcohols as well as Cation of Ionic Liquids

In this section, we illustrate the  $H_{IL}^E$  values for 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF<sub>4</sub>]) in ethanol, 1-butanol, 1-hexanol and 1-octanol. It is of interest to understand how the  $H_{IL}^E$  values of the ionic liquids are influenced in the presence of different alcoholic environment. **Figure 6.1.1** presents the variations in the [EMIM][BF<sub>4</sub>]  $H_{IL}^E$  values as a consequence of increasing alkyl chain length on the alcohol molecules when mixed in ethanol, 1-butanol, 1-hexanol and 1-octanol. The enthalpic curves obtained from the titration experiments suggests that the  $H_{IL}^E$  values follow the trend of 1-butanol < 1-hexanol < 1-octanol for a [EMIM][BF<sub>4</sub>] in all the studied alcohols having intermediate to long alkyl residues (C<sub>4</sub>-C<sub>8</sub>). In case of [EMIM][BF<sub>4</sub>], 1-butanol offers the highest exothermic  $H_{IL}^E$  values as compared to those obtained for other alcohols. The linear alcohols are small amphiphilic molecules with strong ability to play role as both hydrogen bond donor and hydrogen bond acceptor. The hydrogen bond donating and accepting abilities of a solvent are expressed as  $\alpha$  and  $\beta$ , respectively.<sup>[42]</sup> The alcohols consist of a polar -OH group linked to an apolar alkyl tail. On the other hand, ionic liquids behave as amphiphiles with charged cationic core and long alkyl hydrophobic tail. The hydrogen bond donating ( $\alpha = 0.84$ ) and hydrogen bond accepting ( $\beta = 0.84$ ) tendency of 1-butanol are comparable with each other.<sup>[42]</sup> 1-Butanol can, therefore, offer collective hydrogen bonding, greater

in extent as compared to the hydrogen bonding offered by other alcohols. For all the  $\text{BF}_4^-$ -based ionic liquids studied here, 1-butanol offers the maximum interactions and hence exhibits maximum exothermic behavior.



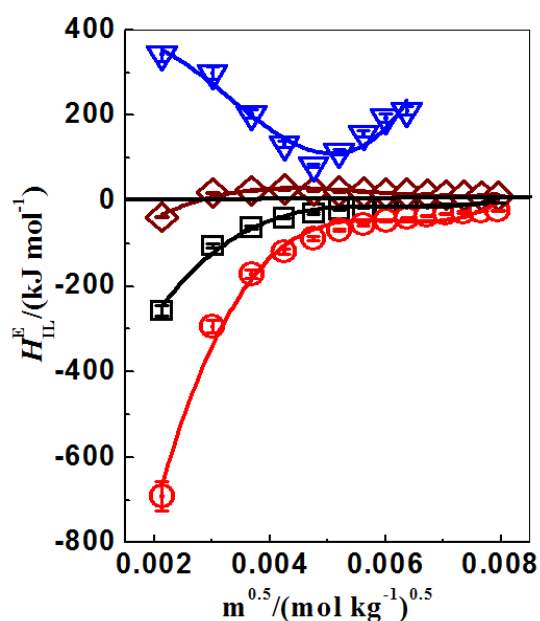
**Figure 6.1.1.** The comparison of the  $H_{IL}^E$  plots for  $[\text{EMIM}][\text{BF}_4]$  in ethanol ( $\square$ ), 1-butanol ( $\odot$ ), 1-hexanol ( $\diamond$ ) and 1-octanol ( $\nabla$ ).

Our results illustrated the maximum interactions between all the ionic liquids in 1-butanol as compared to the other alcohols. Our investigations are supported by the SFG spectroscopy and MD simulation. The study indicates the highly inhomogeneous environment for the butyl chains of both 1-butyl-3-methylimidazolium cation ( $[\text{BMIM}]^+$ ) and 1-butanol molecules.<sup>[43-45]</sup> It was revealed that 1-butanol molecules can be segregated into (i) those forming hydrogen bonds to the hexafluorophosphate ( $\text{PF}_6^-$ ) anions and (ii) others facing oppositely from the  $[\text{BMIM}]^+$  to form a quasi-bilayers type structure like lipid bilayers in the 1-butanol- $[\text{BMIM}][\text{PF}_6]$  mixture.<sup>[43]</sup>



This dual ability of 1-butanol molecules enhances the possibility of interactions between the ionic liquid and 1-butanol molecules.

In the case of the 1-methyl-3-octylimidazolium tetrafluoroborate ([OMIM][BF<sub>4</sub>)]-alcoholic systems (**Figure 6.1.2**), out of all the alcohols, 1-butanol offers maximum interactions to the ionic liquid molecules in terms of  $H_{IL}^E$ . For the [OMIM][BF<sub>4</sub>]-alcohol systems, the  $H_{IL}^E$  values change from exothermic to endothermic with the increase in the length of the alcohol molecules from 1-butanol to 1-octanol. This observed flip in the thermal behavior for higher alcohol *i.e.* 1-octanol may be caused due to the increased repulsion of the hydrophobic alkyl groups between the octyl tails of [OMIM][BF<sub>4</sub>] ionic liquid and 1-octanol molecules. This augmentation in hydrophobicity causes the instability of the [OMIM][BF<sub>4</sub>]-1-octanol system exhibited through positive excess enthalpy.



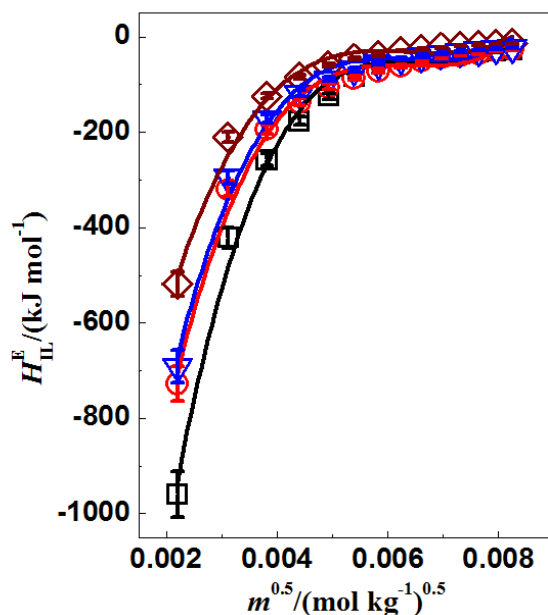
**Figure 6.1.2.** The comparative plot of the  $H_{IL}^E$  curves for [OMIM][BF<sub>4</sub>] in ethanol ( $\square$ ), 1-butanol ( $\odot$ ), 1-hexanol ( $\diamond$ ) and 1-octanol ( $\nabla$ ).

A comparison between the alcoholic mixtures of [EMIM][BF<sub>4</sub>] and [OMIM][BF<sub>4</sub>] suggests that the addition of longer alkylated ionic liquid *i.e.* [OMIM][BF<sub>4</sub>] to an alcohol forms a relatively unstable system than shorter alkylated ionic liquids in alcohols. The  $H^E_{IL}$  values were found to be maximum for 1-hexyl-3-methylimidazolium tetrafluoroborate ([HMIM][BF<sub>4</sub>])-alcoholic systems. The  $H^E_{IL}$  data possess the range from -1000 kJ mol<sup>-1</sup> to -5 kJ mol<sup>-1</sup> for [EMIM][BF<sub>4</sub>], from -750 kJ mol<sup>-1</sup> to -10 kJ mol<sup>-1</sup> for [BMIM][BF<sub>4</sub>], from -500 kJ mol<sup>-1</sup> to 2000 kJ mol<sup>-1</sup> for [HMIM][BF<sub>4</sub>] and from -1100 kJ mol<sup>-1</sup> to 300 kJ mol<sup>-1</sup> for [OMIM][BF<sub>4</sub>] systems. Both **Figures 6.1.1 and 6.1.2** highlight an unusual behavior of ethanol towards the studied ionic liquids. The  $H^E_{IL}$  values measured for all the ionic liquid-ethanol systems do not conform to the trend observed for other ionic liquid-alcoholic systems *i.e.* higher exothermicity for smaller alcohols. It is noted that all the ionic liquid-ethanol systems at discrete positions in the enthalpic trend of 1-butanol < 1-hexanol < 1-octanol, upon changing the ionic liquid counter-part of the ethanolic systems.

In addition to the alkyl chain attached to the alcohol molecules, the variation in the size of alkyl chains on the imidazolium cations imposes a change in their enthalpic behavior as shown in **Figure 6.1.3**. However, these enthalpic responses of different ionic liquids in a common alcoholic environment around them cannot be presented in terms of a general trend. As a representative plot, **Figure 6.1.3** shows the overlapping  $H^E_{IL}$  curves for different ionic liquids in 1-butanol. Present study reveals that in an extremely dilute solution the ionic liquid molecules recognize the change in the alcoholic environment around them, as evident from **Figures 6.1.1 and 6.1.2**, but the *vice versa* does not

appear to be valid. The alcohols studied in this present work fail to detect the imposed change in the alkyl residues on the imidazolium cations in terms of  $H_{IL}^E$  values. The lower alkylated ionic liquids such as [EMIM][BF<sub>4</sub>] and [BMIM][BF<sub>4</sub>] (**Figure 6.1.3**) becomes unstable upon increasing the length of alkyl chain on cation, *i.e.* increasing endothermicity, whereas the higher alkylated ionic liquids such as [HMIM][BF<sub>4</sub>] and [OMIM][BF<sub>4</sub>] show the opposite trend.

An interesting thing to note from **Figure 6.1.3** is that a combination of the C<sub>6</sub>-based ionic liquid *i.e.* [HMIM][BF<sub>4</sub>] in ethanol and an opposite combination of C<sub>2</sub>-based ionic liquid *i.e.* [EMIM][BF<sub>4</sub>] in C<sub>6</sub>-based alcohol (1-hexanol) forms their binary mixtures produce unusual enthalpic values ( $H_{IL}^E$ ), which do not follow the trend stated above.



**Figure 6.1.3.** The plots of the  $H_{IL}^E$  values for [EMIM][BF<sub>4</sub>] (□), [BMIM][BF<sub>4</sub>] (⊙), [HMIM][BF<sub>4</sub>] (⊠) and [OMIM][BF<sub>4</sub>] (▼) in 1-butanol.

The reason for this peculiar behavior of the mixing of the C<sub>6</sub>-C<sub>2</sub> combination of alkyl residues on the cation of the ionic liquids and alcohols is still unknown. However, it can be assumed that the spatial arrangements of both the groups around each other may be responsible for this anomalous behavior.

### 6.1.3.2. Excess Partial Molar Enthalpies at Infinite Dilution ( $H_{IL}^{E,\infty}$ )

We now calculate the values of excess partial molar enthalpy of mixing at infinite dilution,  $H_{IL}^{E,\infty}$ . The experimentally measured  $H_{IL}^E$  were fitted against  $m^{0.5}$  by using following equation;

$$H_{IL}^E = H_{IL}^{E,\infty} + a_0 m^{0.5} + a_1 m + a_2 m^{1.5} + \dots \quad (6.1.1)$$

where,  $a_0$ ,  $a_1$  and  $a_2$  are the adjustable parameters and the  $H_{IL}^{E,\infty}$  values denote the limiting excess partial molar enthalpy. These values were obtained by using a least squares method to minimize the difference between the observed and the fitted quantities. The  $H_{IL}^{E,\infty}$  values obtained for these experiments indicate the standard molar enthalpy of the solution as the dissolution of ionic liquids. The obtained values of  $H_{IL}^{E,\infty}$  are presented in **Table 6.1.1**. The fitted  $H_{IL}^{E,\infty}$  obtained from the above fitting procedure discern the impact of induced variations in the structure of both ionic liquids and alcohols on the enthalpic stability of the system. The  $H_{IL}^{E,\infty}$  values suggest that increasing the size of the residual alkyl chains on both alcohol molecules and ionic liquid cations the binary system shifts towards the instability. This nicely fits with the previously reported observations for ionic liquid-water system.<sup>[11-14]</sup>

**Table 6.1.1.** The values of limiting excess partial molar enthalpies,  $H_{IL}^{E,\infty}$  / kJ mol<sup>-1</sup> obtained from equation 6.1.1 for the ionic liquid-alcohol systems.

Ionic Liquids/ Solvent	$H_{IL}^{E,\infty}$ (kJ mol <sup>-1</sup> )			
	[EMIM][BF <sub>4</sub> ]	[BMIM][BF <sub>4</sub> ]	[HMIM][BF <sub>4</sub> ]	[OMIM][BF <sub>4</sub> ]
ethanol	-1197 ± 65	-1055 ± 59	-1052 ± 90	-870 ± 53
1-butanol	-3073 ± 174	-2379 ± 145	-1930 ± 112	-2073 ± 138
1-hexanol	-1082 ± 112	-1649 ± 110	1433 ± 49	-269 ± 31
1-octanol	-822 ± 53	-561 ± 52	7953 ± 309	912 ± 130

We observe  $H_{IL}^E$  values for ethanol in order [EMIM][BF<sub>4</sub>] (-1197 kJ mol<sup>-1</sup>) > [BMIM][BF<sub>4</sub>] (-1055 kJ mol<sup>-1</sup>) ≈ [HMIM][BF<sub>4</sub>] (-1052 kJ mol<sup>-1</sup>) > [OMIM][BF<sub>4</sub>] (-870 kJ mol<sup>-1</sup>) and for 1-butanol [EMIM][BF<sub>4</sub>] (-3073 kJ mol<sup>-1</sup>) > [BMIM][BF<sub>4</sub>] (-2379 kJ mol<sup>-1</sup>) > [HMIM][BF<sub>4</sub>] (-1930 kJ mol<sup>-1</sup>) ≈ [OMIM][BF<sub>4</sub>] (-2073 kJ mol<sup>-1</sup>). On the other hand, we did not observe any trend in the systems comprising of larger alcohols.

Here, we attempt to analyze the observed enthalpic trends on the basis of the increasing hydrophobicity of alcohol and ionic liquid molecules. However, it was observed that the sole hydrophobicity does not explain the enthalpic trends for these systems.

### 6.1.3.3. Effective Amphiphilicity and the Enthalpic Behavior in the Ionic Liquid-Alcohol Mixtures

Ionic liquids and alcohols are amphiphilic molecules consisting of a polar head group and apolar alkyl tail. It is a combination of the normalized polarity parameter,  $E_T^N$ , the solubility parameter,  $\delta$  of alcohols, the ratio of the effective hydrogen bond donor

acidity,  $\alpha'$  and effective hydrogen bond acceptor basicity,  $\beta'$  parameters which effectively explains the enthalpic behavior of these alcoholic mixtures. The values of  $\alpha'$  and  $\beta'$  indicate the responses of ionic liquids and alcohol molecules towards hydrogen bond donor acidity,  $\alpha$  and hydrogen bond acceptor basicity,  $\beta$ . The reported  $\alpha$  and  $\beta$  values for ionic liquids and alcohols are enlisted in **Table 6.1.2**.<sup>[45-48]</sup> An additional parameter, effective amphiphilicity,  $\chi$ , is also calculated for ionic liquid-alcohol mixture. It is calculated as;

$$\chi = \frac{(E_T^N)_{\text{ROH}} + \left(\frac{\alpha'}{\beta'}\right)_{\text{IL-ROH mix}}}{\delta_{\text{ROH}}} \quad (6.1.2)$$

$$\text{where, } \left(\frac{\alpha'}{\beta'}\right)_{\text{IL-ROH mix}} = \frac{(\alpha_{\text{IL}}\beta_{\text{ROH}})}{(\alpha_{\text{ROH}}\beta_{\text{IL}})} \quad (6.1.3)$$

The  $\chi$  depends upon the structure and size of both ionic liquid and alcohol molecules. We observe that in the case of ethanol the  $\chi$  parameter exhibits maximum variation upon varying the alkyl chain on the ionic liquid cation from C<sub>2</sub>, [EMIM]<sup>+</sup>, ( $\chi = 0.1160/\text{J}^{-1/2} \text{ cm}^{3/2}$ ) to C<sub>4</sub>, [BMIM]<sup>+</sup>, ( $\chi = 0.0569/\text{J}^{-1/2} \text{ cm}^{3/2}$ ). However, the variation of alkyl chain length from C<sub>4</sub> ( $\chi = 0.0569/\text{J}^{-1/2} \text{ cm}^{3/2}$ ) to C<sub>6</sub>, [HMIM]<sup>+</sup>, ( $\chi = 0.0498/\text{J}^{-1/2} \text{ cm}^{3/2}$ ) to C<sub>8</sub>, [OMIM]<sup>+</sup>, ( $\chi = 0.0491/\text{J}^{-1/2} \text{ cm}^{3/2}$ ) shows a stationary effect in the values of the parameter. The parameters corresponding to C<sub>4</sub>, C<sub>6</sub> and C<sub>8</sub> substituted ionic liquid cations were observed to be slightly decreasing with the increase in the alkyl chain length on the ionic liquid cations. A similar trend was noticed when the alcoholic environment was changed to 1-butanol. This suggests that a combination of above mentioned properties resulting into the above parameter effectively explains the

enthalpic behavior of ionic liquids in the extremely dilute alcoholic solutions. The enthalpic behavior of ionic liquids in smaller alcohols *i.e.* ethanol and 1-butanol, changes from exothermic to endothermic with decreasing values of  $\chi$  for these ionic liquid-alcohol solutions. It can be inferred that increasing the size of the alkyl groups on ionic liquid cations, enhances the cost for the solvation energy which overcome the stabilizing inter-molecular interactions between ionic liquids and alcohol molecules.

**Table 6.1.2.** Values of hydrogen bond donor acidity ( $\alpha$ ) and hydrogen bond acceptor basicity ( $\beta$ ) of the studied ionic liquids and solvents.<sup>[45-48]</sup>

Ionic liquids and solvents	$\alpha$	$\beta$
[EMIM][BF <sub>4</sub> ]	0.70	0.26
[BMIM][BF <sub>4</sub> ]	0.63	0.38
[HMIM][BF <sub>4</sub> ]	0.44	0.60
[OMIM][BF <sub>4</sub> ]	0.62	0.40
Ethanol	0.83	0.75
1-Butanol	0.84	0.84
1-Hexanol	0.80	0.84
1-Octanol	0.77	0.81

However, as we move toward higher alcohols, the ionic liquid cations especially substituted with longer alkyl groups loose the recognition of the solvent environment. It can be referred to the critically minimal difference between the effective  $\chi$  values calculated for these ionic liquids in higher alcohols; ( $C_4 = 0.0712$ ,  $C_6 = 0.0609$ ,  $C_8 = 0.0601$  in 1-hexanol and  $C_4 = 0.0736$ ,  $C_6 = 0.0629$ ,  $C_8 = 0.0619$  in 1-octanol), which is

not sufficient for the ionic liquid cations to distinguish the change in the alcoholic environment around them. Hence, fails to produce any enthalpic trend after increasing the size of alkyl residues on the ionic liquid cations in higher alcohols *viz.* 1-hexanol and 1-octanol.

The enthalpic behavior of ionic liquids in alcoholic environment was found to be governing by the properties, which represent the structuring of both ionic liquids and alcohols in addition to their bond formation capabilities.

#### 6.1.3.4. The Enthalpic Interaction Parameter ( $H_{IL-IL}^E$ )

In this section, we elucidate the detailed behavior of ionic liquids in the alcohol-rich regions. The experimentally measured  $H_{IL}^E$  are differentiated with respect to the composition of the ionic liquid in their binary mixtures with alcohols to evaluate the interactions between the two ionic liquid molecules in terms of an enthalpic parameter known as the enthalpic interaction parameter ( $H_{IL-IL}^E$ ).<sup>[7, 49-51]</sup>

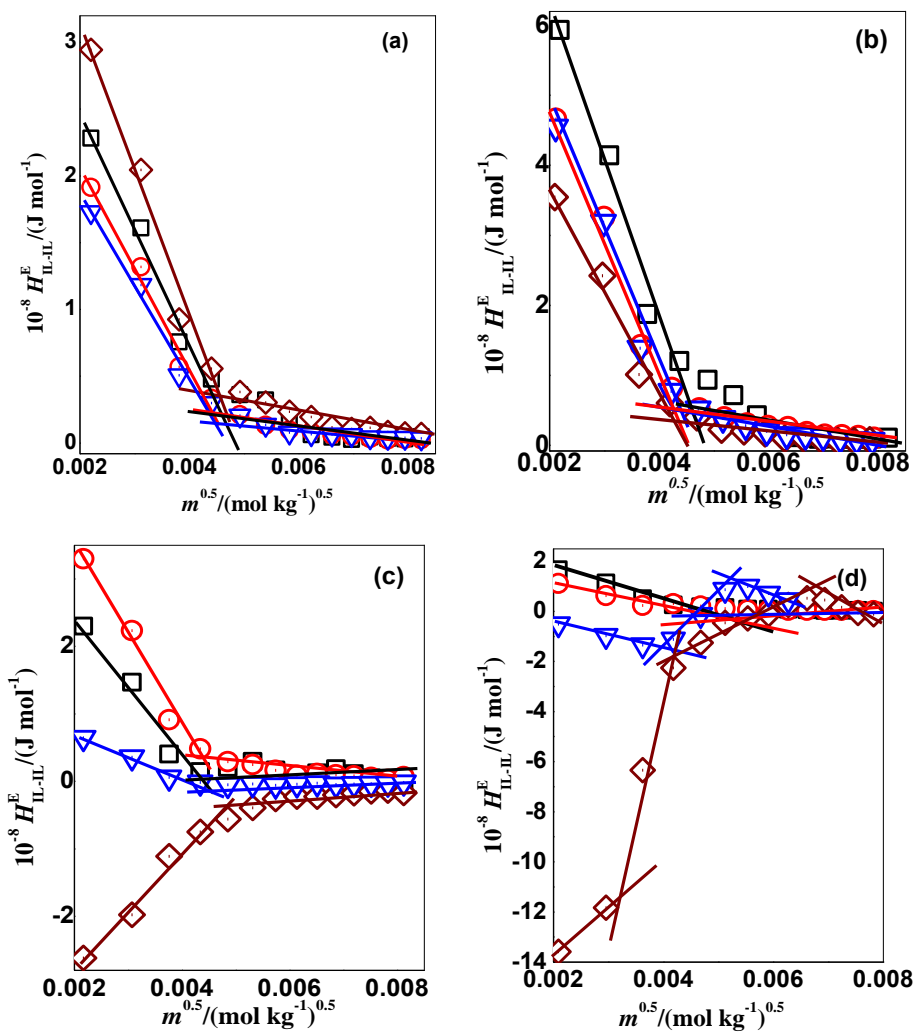
$$H_{IL-IL}^E = (1 - x_{IL}) \left( \frac{\partial H_{IL}^E}{\partial n_{IL}} \right) \quad (6.1.4)$$

where,  $x_{IL}$  represents the mole fraction of the ionic liquids in ionic liquid-alcohol mixtures. In the ionic liquid-alcohol mixtures,  $H_{IL}^E$  represents the actual contribution of one mole of ionic liquids in terms of enthalpy, whereas the quantity  $H_{IL-IL}^E$  represents the enthalpic contribution of initially added ionic liquid molecules once the entire system is perturbed by introducing another mole of ionic liquids. The  $H_{IL-IL}^E$  parameters quantifying the favorable or unfavorable interactions existing between the



subsequently added ionic liquid molecules in terms of the system enthalpies. The quantification of intermolecular interactions between two ionic liquid molecules in terms of the interaction parameter is a model free graphical method, which was introduced by Koga and co-workers for both aqueous and non-aqueous solutions of electrolytes.<sup>[7, 49-51]</sup> This graphical differentiation method has been used in the past for the binary mixtures of ionic liquids in a variety of solvents with a reasonable precision to demonstrate the concentration dependent interactions between ionic liquid molecules in terms of the enthalpies of these systems. **Figure 6.1.4** represents the concentration dependencies of the  $H_{IL-IL}^E$  parameters for the systems under investigation. It is suggested that in the case of ionic liquid-alcohol systems especially with lower alcohols, in extremely dilute range, the ion-ion interactions between the ionic liquid ionic components decrease with increasing the ionic liquid concentration. The absolute values of the  $H_{IL-IL}^E$  parameters decrease with increasing ionic liquid concentration in the binary mixture. This suggests that concentration range the solvent is capable of completely dissolving the added ionic liquids in the present study. The increased amount of ionic liquid is not enough to overcome the solvent (solvation energy) barrier and allow the ionic liquid components in the vicinity of each other. It is likely that the amphiphilic nature of both the solute and the solvent results into the enhanced solubility and hence the decreasing ion-ion interactions. However, upon increasing the size of the alcohol molecules may result the ionic liquid components to escape through the solvent voids. This would facilitate the approach of ionic liquid components and hence the  $H_{IL-IL}^E$  parameter increases with increasing ionic liquid concentration.

Interestingly, in **Figure 6.1.4** the  $H_{IL-IL}^E$  parameter shows a very steep fall up to  $m^{0.5} \approx 0.005 \text{ mol kg}^{-1}$  for all the ionic liquid-alcohol systems. However, as we further increase the ionic liquid concentration beyond  $m^{0.5} = 0.005 \text{ mol kg}^{-1}$  it results into stationary  $H_{IL-IL}^E$  parameter curves.



**Figure 6.1.4.** A comparison of the concentration dependent plots of the  $H_{IL-IL}^E$  parameters for [EMIM][BF<sub>4</sub>] (□), [BMIM][BF<sub>4</sub>] (⊙), [HMIM][BF<sub>4</sub>] (◇), and [OMIM][BF<sub>4</sub>] (▽) in (a) ethanol, (b) 1-butanol, (c) 1-hexanol and (d) 1-octanol.

All the ionic liquid-alcohol systems show one transition point (values listed in **Table 6.1.3**) beyond which the  $H_{IL-IL}^E$  values gradually attains stationary phase except for the binary mixtures of [HMIM][BF<sub>4</sub>] and [OMIM][BF<sub>4</sub>] in 1-octanol. For these two systems, the  $H_{IL-IL}^E$  parameters exhibit two transition points, the values of which are listed in **Table 6.1.3**.

**Table 6.1.3.** The values of enthalpic interaction parameters,  $10^{-8}H_{IL-IL}^E$ /(J mol<sup>-1</sup>) and their corresponding concentrations,  $m$ /(mol kg<sup>-1</sup>) for all the studied ionic liquid-alcohol systems.

Ionic Liquids	[EMIM][BF <sub>4</sub> ]		[BMIM][BF <sub>4</sub> ]		[HMIM][BF <sub>4</sub> ]		[OMIM][BF <sub>4</sub> ]	
	$10^5 m$	$10^{-8} H_{IL-IL}^E$	$10^5 m$	$10^{-8} H_{IL-IL}^E$	$10^5 m$	$10^{-8} H_{IL-IL}^E$	$10^5 m$	$10^{-8} H_{IL-IL}^E$
ethanol	2.11	0.171	1.94	0.210	2.12	0.356	2.03	0.158
1-butanol	2.21	0.438	1.85	0.564	1.94	0.488	1.85	0.362
1-hexanol	1.94	0.020	1.94	0.365	2.40	-0.348	2.03	-0.184
1-octanol	2.70	-0.327	2.60	-0.184	1.02	-11.33	1.60	-1.372

\* The [HMIM][BF<sub>4</sub>]-1-octanol system shows two more transition points at 0.0042 and 0.0068 mol kg<sup>-1</sup>; [OMIM][BF<sub>4</sub>]-1-octanol also exhibits another transition point at 0.0053 mol kg<sup>-1</sup>.

In order to analyse the ion-ion and ion-solvent interactions in these solutions, we calculated the relative apparent molar enthalpy,  $\phi_L$  using the standard procedure.<sup>[14]</sup> The  $\phi_L$  values with molality can be interpolated using an expression of the type:

$$\phi_L = A_L m_{IL}^{0.5} + q m_{IL} \quad (6.1.5)$$

$A_L$  is a limiting slope, the values of which for different solvents are given in **Table 6.1.4** as calculated by the method given by Ananthaswamy and Atkinson.<sup>[52]</sup> The values of the  $q$  parameters together with the standard errors are given in **Table 6.1.5**.

**Table 6.1.4.** Pitzer-Debye-Huckel limiting slope,  $A_L$  at 298.15 K for solvents used in the present study calculated by the method given by Ananthaswamy and Atkinson.<sup>[52]</sup>

Solvents	$A_L$ (J kg <sup>0.5</sup> mol <sup>-1.5</sup> )
Ethanol	33183
1-Butanol	53748
1-Hexanol	83217
1-Octanol	121397

**Table 6.1.5.** Adjustable parameters for fitting relative apparent molar enthalpy,  $\phi_L$  of different ionic liquid-alcohol systems using equation 6.1.5.

Ionic liquid/Solvent	$10^{-9}q$	Ionic liquid/Solvent	$10^{-9}q$
[EMIM][BF <sub>4</sub> ]		[HMIM][BF <sub>4</sub> ]	
ethanol	-1.67 ± 0.01	ethanol	-2.42 ± 0.01
1-butanol	-4.47 ± 0.02	1-butanol	-3.12 ± 0.02
1-hexanol	-46.7 ± 0.5	1-hexanol	-1.88 ± 0.03
1-octanol	-1.46 ± 0.03	1-octanol	0.125 ± 0.006
[BMIM][BF <sub>4</sub> ]		[OMIM][BF <sub>4</sub> ]	
ethanol	-1.66 ± 0.02	ethanol	-1.52 ± 0.01
1-butanol	-4.09 ± 0.05	1-butanol	-3.96 ± 0.04
1-hexanol	-3.03 ± 0.01	1-hexanol	-3.39 ± 0.01
1-octanol	-77.9 ± 0.002	1-octanol	-0.150 ± 0.043

#### 6.1.4. Conclusions

We report here that all the ionic liquids show favorable interaction with 1-butanol molecules as compared to the other alcohols. In terms of interactions, 1-butanol have the comparative values of  $\alpha$  and  $\beta$  ( $\alpha \approx \beta \approx 0.84$ ). Hence, are more prone to form collective hydrogen bonding with both cation and anion of an ionic liquid. This is higher as compared to the other alcohol molecules and ionic liquid combination. Ethylated residuals on both the cations of the ionic liquid and the alcohol molecules do not follow the trend exhibited by other ionic liquids-alcohol systems. The present study also show that the thermal behavior expressed in terms of the  $H_{IL}^E$  values of ionic liquids in various linear alcohols is governed by the increasing hydrophobicity of the alkyl group attached to the cation of an ionic liquid and the alcohol molecules.

Based on the observations, we turned our attention to the effect of hydrocarbon groups in the cationic part of ionic liquid and solvents to envisage ion-solvent and ion-ion interactions in terms of packing. This can explain the unusual behavior of the ionic liquids with ethyl groups on cation and solvent.



## ***6.2. Do Similar Alkyl Groups in both Ionic Liquid and Solvent Influence the Stability of Binary Mixtures Enthalpically?***

### **6.2.1. Introduction**

Thermodynamic quantities of mixing of ionic liquids and solvents can provide valuable information about interionic interactions and microscopic structure of the mixture. Energetic properties are relevant in both basic and application perspective of the binary mixtures of ionic liquids. At the fundamental level, enthalpy of mixing can be directly connected to the nature of intermolecular or interionic interactions. In general, ionic liquids contain one of the ions as asymmetric, bulky, delocalized electrostatic charge, low charge density and containing nonpolar hydrocarbon chain. These characteristics contribute to increase the complexity of molecular interactions, present in the ionic liquid binary mixtures. The structure of ionic liquids (with different hydrophobic tails) also influences calorimetric properties of the mixtures with molecular solvents.

In this work, we emphasize on the effect of hydrocarbon groups in the cationic part of ionic liquid and solvents to envisage ion-solvent and ion-ion interactions in terms of packing. We measured the excess partial molar enthalpy of ionic liquids in their binary mixture with ethylated solvents.

### **6.2.2. Results and Discussion**

The present study elaborate the  $H_{IL}^E$  of [EMIM][BF<sub>4</sub>] and [BMIM][BF<sub>4</sub>] in 2-ethoxyethanol, ethylene glycol, diethyl amine, ethyl acetate and *N, N*-diethyl acetamide. The interionic interactions between the ionic liquids and ethylated solvents

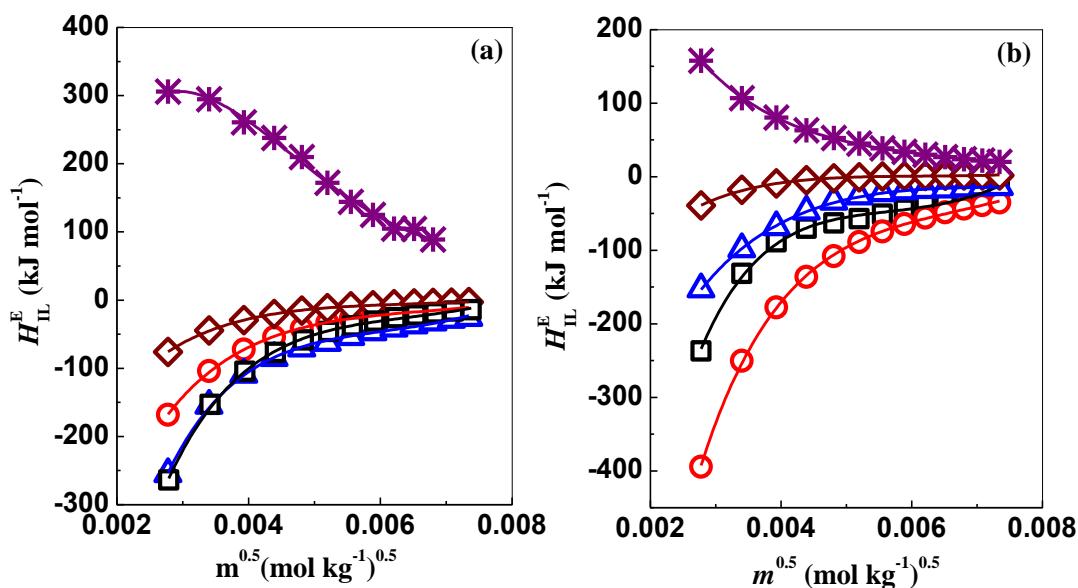
elucidated in terms of various thermodynamic properties such as excess partial molar enthalpy,  $H_{IL}^E$  limiting excess partial molar enthalpy,  $H_{IL}^{E,\infty}$  enthalpic interactions,  $H_{IL}^E$  and the relative apparent molar enthalpy,  $\phi_L$ . A detailed description of these properties is shown below.

### 6.2.2.1. $H_{IL}^E$ of the Binary Mixtures of Ionic Liquid-Ethylated Solvents

In the first section of this Chapter, we illustrated the effect of a change in the length of the alkyl chains on the cationic core of an ionic liquid and the alcohols. In this section, the effect of different ethylated solvents has been discussed in terms of the  $H_{IL}^E$  values of the ionic liquids in their binary mixtures. All the solvent molecules used were consist of electronegative atoms such as oxygen and nitrogen and apolar ethyl groups. Ionic liquids behave as amphiphiles with a charged cationic core and long alkyl residues (ethyl (-C<sub>2</sub>H<sub>5</sub>), and butyl (-C<sub>4</sub>H<sub>9</sub>) in the present study). **Figure 6.2.1** shows the variation in the  $H_{IL}^E$  values of mixing of [EMIM][BF<sub>4</sub>] and [BMIM][BF<sub>4</sub>] in 2-ethoxyethanol, ethylene glycol, *N, N*-diethyl amine, ethyl acetate and *N, N*-diethyl acetamide. A detailed analysis of the enthalpic curves obtained from the titration experiments suggest that  $H_{IL}^E$  values for [EMIM][BF<sub>4</sub>] in all the ethylated solvents follow the trend (endothermic to exothermic) of ethyl acetate < ethylene glycol < *N, N*-diethyl acetamide < 2-ethoxyethanol  $\approx$  *N, N*-diethyl amine. For [EMIM][BF<sub>4</sub>], in ethyl acetate offers the highest endothermic  $H_{IL}^E$  values whereas, other ethylated solvents show exothermic behavior. The solvents used here, are small amphiphilic molecules with both hydrogen bond donor/acceptor capability except ethyl acetate and *N, N*-diethyl acetamide. We ascribe the endothermic behavior in ethyl acetate to the lack of



solvation or ion-solvent interactions through hydrogen bonds. The key characteristics of solvents are to determine how it will interact with potential solutes, for molecular solvents generally describes as the polarity of the pure liquid. In addition to this, some other solvent properties also used to determine the solute-solvent interactions.



**Figure 6.2.1.** A comparison of the  $H_{IL}^E - m^{0.5}$  plots for [EMIM][BF<sub>4</sub>] (a) and [BMIM][BF<sub>4</sub>] (b) in ethyl acetate (\*), ethylene glycol (◇), *N,N*-diethyl acetamide (○), 2-ethoxyethanol (□) and *N,N*-diethyl amine (△).

The complimentary scales, the hydrogen bond donor ability ( $\alpha$ ) and hydrogen bond accepting ability ( $\beta$ ) are used here to delineate the solute-solvent interactions. The  $\alpha$  and  $\beta$  values of the employed solvents are given in the **Table 6.2.2**. The  $\alpha$  value of ethyl acetate is 0 and the value of  $\beta$  is also significantly lower (0.45) as compared to the other ethylated solvents. The  $\alpha$  values of ionic liquids are basically determined by

the nature of cation. It has been reported that imidazolium ring protons are acidic and show the hydrogen bonding to solvent molecules have high  $\beta$  values. The [EMIM][BF<sub>4</sub>] has a slightly higher  $\alpha$  (0.70) value than [BMIM][BF<sub>4</sub>] ( $\alpha = 0.63$ ). This probably results into the endothermic nature of [EMIM][BF<sub>4</sub>]-ethyl acetate mixture. Although *N, N*-diethyl acetamide also have  $\alpha = 0$ , but has the higher value of  $\beta$  (0.78) making it strong hydrogen bond acceptor. It suggests that  $\beta$  is more important for the interactions of ionic liquids with solvents. The higher  $\beta$  value of solvent compensates the effect of lower  $\alpha$  values by interacting through the hydrogen bonding with cations and shows the exothermic behavior. The higher values of both  $\alpha$  and  $\beta$  of 2-ethoxyethanol ( $\alpha = 0.71$ ,  $\beta = 0.73$ ) show the possibility to interact with both the cation and anion of ionic liquids. 2-Ethoxyethanol can act as good hydrogen bond donor-acceptor, therefore interacts favorably with cation and anion of the ionic liquids as compared to the other ethylated solvents. This dual ability of 2-ethoxyethanol enhances the interactions between solvent molecules and ionic liquids, hence maximum exothermicity has been observed in terms of  $H_{IL}^E$  values. [EMIM][BF<sub>4</sub>]-*N, N*-diethyl amine also shows higher possibility of interactions and hence exhibits exothermic behavior. A similar observation are noted for BF<sub>4</sub><sup>-</sup>-based ionic liquids (Chapter 6 (I)) exhibit maximum exothermic behavior in 1-butanol, which has the same  $\alpha$  and  $\beta$  values.<sup>[15]</sup> We note a significant difference in  $\alpha$  and  $\beta$  values between diethyl amine ( $\alpha = 0.30$ ,  $\beta = 0.70$ ). Therefore, exothermic behavior in *N, N*-diethyl amine observed due to the high  $\beta$  value. The exothermicity of [EMIM][BF<sub>4</sub>] decrease from 2-ethoxyethanol  $\approx$  *N, N*-diethyl amine to *N, N*-diethyl acetamide and followed by ethylene glycol. Later

on, the exothermicity changes toward endothermicity in the case of ethyl acetate. The  $\beta$  value decreases from 0.78 to 0.52 to 0.45 for *N, N*-diethyl acetamide, ethylene glycol and ethyl acetate, respectively. This possibly contribute to the changes from exothermic to the endothermic enthalpic behavior of [EMIM][BF<sub>4</sub>]. From these observations, we expect that  $H^E_{IL}$  values depend primarily on the  $\beta$  values of the solvent (exception is *N, N*-diethyl acetamide). As the  $\beta$  values of the solvent increase, the interactions between ionic liquids and ethylated solvents increases, hence exothermicity enhances. For [BMIM][BF<sub>4</sub>]-ethylated solvent systems (**Figure 6.2.1(b)**). In contrast, [BMIM][BF<sub>4</sub>] shows the maximum interactions in *N, N*-diethyl acetamide. However, the  $H^E_{IL}$  values of the [EMIM][BF<sub>4</sub>] and [BMIM][BF<sub>4</sub>] systems follow the similar trend in rest of the solvents. This follows the  $\beta$  values of the solvents. The exceptional case of the comparable values of  $\alpha$  and  $\beta$  of 2-ethoxyethanol has not been seen in [BMIM][BF<sub>4</sub>] as obtained in the [EMIM][BF<sub>4</sub>]. It is expected that in an extremely dilute solution the [EMIM][BF<sub>4</sub>] molecules recognize the change in the solvent (ethylated) environment around them based on the  $\beta$  values of the solvents, as evidenced from **Figures 6.2.1(a)**, whereas the [BMIM][BF<sub>4</sub>] holds the characteristic behavior in the concentrated region also. This probably occurs due to the spatial arrangements of the solvent molecules around ionic liquids. In the case of [EMIM][BF<sub>4</sub>] there is a uniformity of the nonpolar ethyl groups in both the solvents and ionic liquids which is absent in [BMIM][BF<sub>4</sub>].  $H^E_{IL}$  values of the ionic liquid-ethylated solvent mixtures follow the trend of  $\beta$  values of the solvents. Increasing order of  $\beta$  values of the solvents; ethyl acetate < ethylene glycol < *N, N*-diethyl amine < 2-

ethoxyethanol < *N, N*-diethyl acetamide. The order of  $H_{IL}^E$  values of the [BMIM][BF<sub>4</sub>]-ethylated solvent mixtures (endothermic to exothermic); ethyl acetate < ethylene glycol < *N, N*-diethyl amine < 2-ethoxyethanol < *N, N*-diethyl acetamide.

### 6.2.2.2. Excess Partial Molar Enthalpies at Infinite Dilution ( $H_{IL}^{E,\infty}$ )

The excess partial molar enthalpies at infinite dilution have been acquired from the experimentally measured  $H_{IL}^E$  values by using equation 6.1.1. These values were obtained by using the least squares fitting method to minimize the errors. The  $H_{IL}^{E,\infty}$  values obtained for these experiments specify the standard molar enthalpy of the solution as the dissolution of ionic liquids had already been taken place while making the binary mixtures of ionic liquids. The  $H_{IL}^{E,\infty}$  values are given in **Table 6.2.1**. The  $H_{IL}^{E,\infty}$  obtained from the above fitting procedure differentiate the effect of induced variations in the structure of both ionic liquids and ethylated solvents on the enthalpic stability of the system. Increasing the size of the residual alkyl chains on ionic liquid cations from ethyl to butyl the binary system shifts towards the instability for ethyl acetate, ethylene glycol and diethyl amine as seen from  $H_{IL}^{E,\infty}$  values. Although, in 2-ethoxyethanol and *N, N*-diethyl acetamide, binary systems get more stabilized enthalpically while moving from [EMIM][BF<sub>4</sub>] to [BMIM][BF<sub>4</sub>]. The values of  $H_{IL}^{E,\infty}$  for these ionic liquid-ethylated solvent systems suggest that the enthalpic trends observed for the systems containing linear structures depend on the  $\beta$  values of the solvent. The trend (from endothermic to exothermic) in  $H_{IL}^{E,\infty}$  for [EMIM][BF<sub>4</sub>]; ethyl acetate < ethylene glycol < *N, N*-diethyl acetamide < 2-ethoxyethanol  $\approx$  *N, N*-diethyl

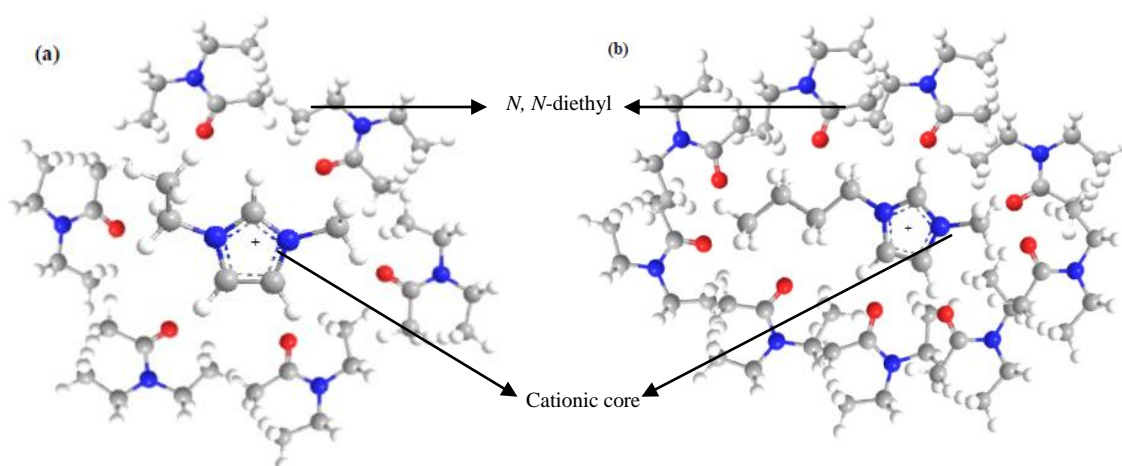
amine and for [BMIM][BF<sub>4</sub>]; ethyl acetate < ethylene glycol < *N, N*-diethyl amine < 2-ethoxyethanol ≈ *N, N*-diethyl acetamide.

**Table 6.2.1.** The  $H_{IL}^{E,\infty}$  values of [EMIM][BF<sub>4</sub>], [BMIM][BF<sub>4</sub>] in different molecular solvents.

Solvents	$H_{IL}^{E,\infty}$ (kJ mol <sup>-1</sup> )	
	[EMIM][BF <sub>4</sub> ]	[BMIM][BF <sub>4</sub> ]
2-Ethoxyethanol	-4925 ± 280	-6084 ± 476
<i>N, N</i> -diethyl amine	-4970 ± 267	-2098 ± 130
Ethylene glycol	-1414 ± 564	-1054 ± 584
Ethyl acetate	825.4 ± 25	2009 ± 767
<i>N, N</i> -diethyl acetamide	-2685 ± 111	-6082 ± 230

The possible reason for a difference in the  $H_{IL}^{E,\infty}$  values for *N, N*-diethyl acetamide is the structure of the solvent molecule. The solvents employed in the present are mostly with a linear structural geometry except *N, N*-diethyl acetamide. *N, N*-diethyl acetamide which have the T-shaped structure. Due to the T-shaped structure of *N, N*-diethyl acetamide and a smaller alkyl group of [EMIM][BF<sub>4</sub>], less number of solvent molecules are present in the solvation shell of the [EMIM][BF<sub>4</sub>]. Therefore, a number of solvent molecules are larger in the solvation shell of [BMIM][BF<sub>4</sub>] (larger alkyl group). [BMIM][BF<sub>4</sub>] interacts favorably with the solvent, in addition due to the elongated alkyl chain it offers larger surface area to the solvent to interact (**Figure 6.2.2**). In contrast, the smaller alkyl chain on [EMIM][BF<sub>4</sub>] do not efficiently interacts with the solvent molecules. We assume that this specific structural orientation of

solvent might enhance the interactions with the butyl group attached to the cationic core of ionic liquids. The longer alkyl tail of [BMIM][BF<sub>4</sub>] may be getting more stabilized in branched *N, N*-diethyl acetamide due to increased possibility of additional hydrogen bonding. Thus, it reflects exothermic behavior. The number of hydrogen bonds forming between cation of ionic liquids and solvents are less (a pictorial diagram (**Figure 6.2.2**) shows the structure of solvated cations [EMIM]<sup>+</sup> and [BMIM]<sup>+</sup> in case of [EMIM][BF<sub>4</sub>] as compared to the [BMIM][BF<sub>4</sub>]. Hence [BMIM][BF<sub>4</sub>] possess highest exothermic  $H_{IL}^{E,\infty}$  values in *N, N*-diethyl acetamide.



**Figure 6.2.2.** A representation of solvation shell around the cations of ionic liquid by *N,N*-diethyl acetamide for (a) [EMIM]<sup>+</sup>, and (b) [BMIM]<sup>+</sup>.

### 6.2.2.3. Linear Solvation Energy Relations (LSERs)

The  $H_{IL}^{E,\infty}$  values tabulated in **Table 6.2.2** suggest that [EMIM][BF<sub>4</sub>] and [BMIM][BF<sub>4</sub>] requires less energy to dissolve them into ethylated solvents except for ethyl acetate.

The  $H_{IL}^{E,\infty}$  values reveal the ion-solvent interactions in the ionic liquid-ethylated solvent

solutions and correlated with the solvent properties of the molecular solvents using linear solvation energy relations (LSERs). The LSER is used to correlate and predict the wide variety of solvent effects as well as to provide an analysis in terms of theoretical concepts of molecular structural effects. A multi-parameter linear model (LSER);

$$H_{IL}^{E,\infty} = f(\alpha, \beta, \delta, \pi^*, E_T^N) \quad (6.2.1)$$

where,  $H_{IL}^{E,\infty}$  is the solvent dependent property of the solute. This model functions with the several parameters  $\alpha$ ,  $\beta$ , Hildebrand solubility parameter ( $\delta$ ), normalized Dimorth-Reichardt polarity parameter ( $E_T^N$ ) and polarizability ( $\pi^*$ ) to name a few. The selection of the solvent properties is made upon the characteristics of both the solute and the solvent. In this multi-parameter approach, the properties are opted to offer the best fit of the quantity of the interest. A rigorous examination suggests that the difference in the behavior of the different alkyl groups attached to the cationic ring in their solutions depends on the solvent properties. The significant solvent properties for these solvents taken from the literature <sup>[46, 48]</sup> are tabulated in **Table 6.2.2**. For the [EMIM][BF<sub>4</sub>]-ethylated solvent systems, a permutation of  $\alpha$ ,  $\beta$ , and  $\pi^*$  is effective to representing the  $H_{IL}^{E,\infty}$  values as shown by;

$H_{IL}^{E,\infty} = 4975 \pm 20 + 4172 \pm 15 \pi^* - 3097 \pm 10 \alpha - 14315 \pm 26 \beta$  (correlation coefficient,  $r^2 = 0.999$ ). While, for [BMIM][BF<sub>4</sub>]-ethylated solvent systems, a permutation of  $E_T^N$ ,  $\alpha$ , and  $\beta$ , is effective to represent the  $H_{IL}^{E,\infty}$  values as shown by;

$H_{IL}^{E,\infty} = 14568 \pm 1793 - 7569 \pm 2582 E_T^N + 2524 \pm 1716 \alpha - 23561 \pm 2480 \beta$  (correlation coefficient,  $r^2 = 0.959$ )

**Table 6.2.2.** Values of the solvatochromic parameters of the considered solvents.<sup>[48]</sup>

solvent	$\alpha$	$B$	$\pi^*$	$E_T^N$
2-Ethoxyethanol	0.71	0.73	0.66	0.627
<i>N, N</i> -diethyl amine	0.30	0.70	0.24	0.145
Ethylene glycol	0.90	0.52	0.92	0.790
Ethyl acetate	0	0.45	0.55	0.228
<i>N, N</i> -diethyl acetamide	0	0.78	0.84	0.330

We perform the linear multiple regression analysis on the data. The coefficient provides an understanding the strength of the correlation as discussed in the literature.<sup>[53]</sup> This suggests that the solvent properties can offer insights into our understanding of the ionic liquid-solvent interactions.

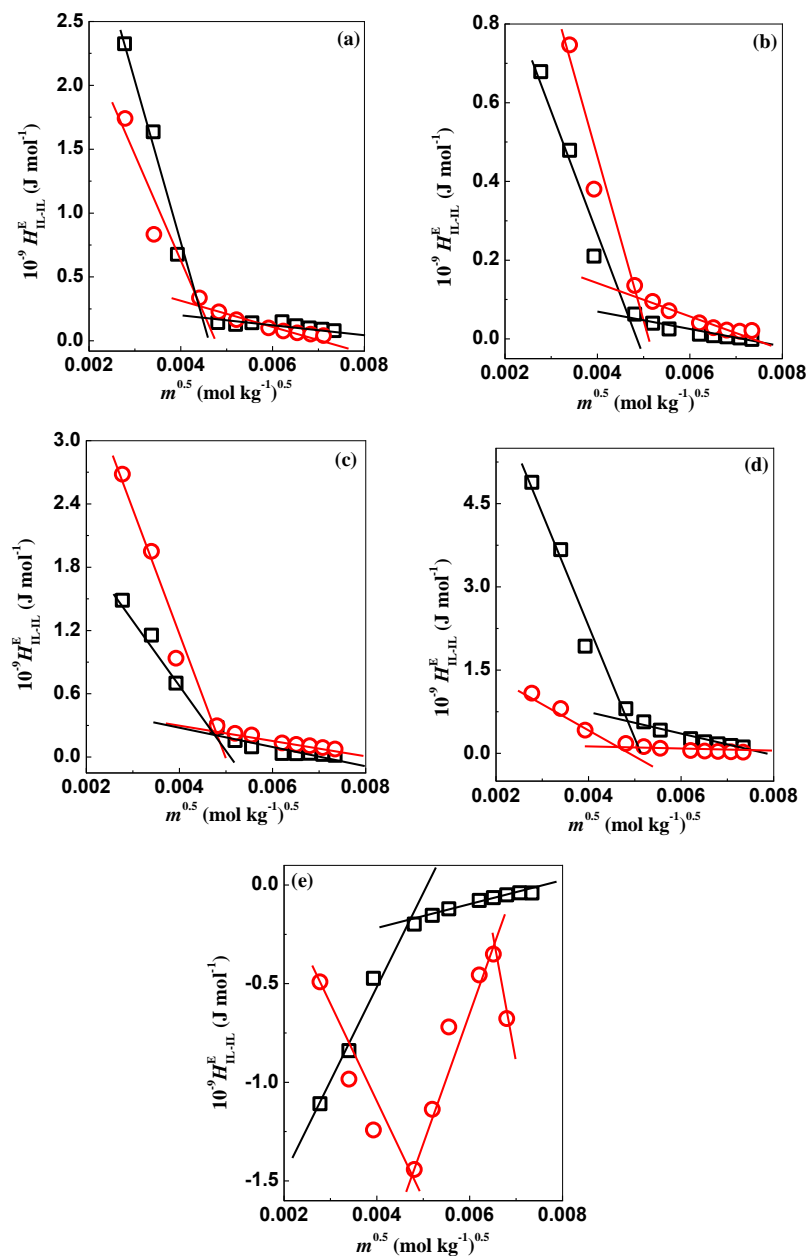
#### 6.2.2.4. The Enthalpic Interaction Parameter ( $H_{IL-IL}^E$ )

We further elaborated the behavior of ionic liquids in the ethylated solvent-rich regions. The experimentally measured  $H_{IL}^E$  values are differentiated with respect to the composition of the ionic liquid in their binary mixtures to evaluate the interactions between the two ionic liquid molecules in terms of the enthalpic interaction parameter ( $H_{IL-IL}^E$ ).<sup>[7, 49-51]</sup> A detailed description of the method has been given in the first section of this Chapter. **Figure 6.2.3** shows the concentration dependent  $H_{IL-IL}^E$  parameters for the studied systems. All ionic liquid-ethylated solvent systems show the similar



behavior except in the ethyl acetate. Upon gradual increase in the concentration, ion-ion interactions decrease till it reaches to the transition point later on a moderate phase is observed. This suggests the complete dissolution the ionic liquids in the studied solvents seen from the decrease in  $H_{IL-IL}^E$ . On decreasing the concentration of ionic liquids, ion-ion interactions diminish slowly. It may be due to the presence of electronegative atoms in the solvent molecules which increases the ion-solvent interactions consequences into the enhanced solubility and diminishes the ion-ion interactions even in the concentrated region. It has been observed from **Figure 6.2.3** that the  $H_{IL-IL}^E$  parameter decreases sharply up to  $m^{0.5} \approx 0.0048 \text{ mol kg}^{-1}$ . As the concentration increases beyond  $0.0048 \text{ mol kg}^{-1}$ , we also observe a decrease in the  $H_{IL-IL}^E$  values. However, the extent is small as compared to the till transition point. The ion-ion interactions increases in the [BMIM][BF<sub>4</sub>]-ethyl acetate system as shown in **Figure 6.2.3(e)** while a contrast behavior has been observed for the [EMIM][BF<sub>4</sub>]-ethyl acetate system. The  $H_{IL-IL}^E$  parameter increases sharply up to  $m^{0.5} \approx 0.0044 \text{ mol kg}^{-1}$  for [BMIM][BF<sub>4</sub>]-ethyl acetate system, however, the  $H_{IL-IL}^E$  parameter decreases sharply up to  $m^{0.5} \approx 0.0045 \text{ mol kg}^{-1}$  for [EMIM][BF<sub>4</sub>]-ethyl acetate system. This anomalous behavior of [BMIM][BF<sub>4</sub>] in ethyl acetate may be observed due to the butyl group attached to the cation core which provides shielding of the ionic liquid towards the solvent molecules. In the case of [EMIM][BF<sub>4</sub>], due to the small and similar alkyl group, the possibility of interaction enhances and the ion-ion interactions reduces. The possible reason for this anomalous behavior of both ionic liquids in ethyl acetate solvent has been discussed in the first section. A notable transition point is seen after

which  $H_{IL-IL}^E$  values gradually decreases for the binary mixture of [EMIM][BF<sub>4</sub>] and ethyl acetate.



**Figure 6.2.3.** A comparison of the concentration dependent plots of the enthalpic interaction parameters ( $H_{IL-IL}^E$ ) for [EMIM][BF<sub>4</sub>] (○), [BMIM][BF<sub>4</sub>] (□) in different ethylated solvents (a) 2-ethoxyethanol, (b) ethylene glycol, (c) *N, N*-diethyl amine, (d) *N, N*-diethyl acetamide, and (e) ethyl acetate.

Upon increasing the concentration of [EMIM][BF<sub>4</sub>] the ion-ion interactions increases. The binary mixture of [EMIM][BF<sub>4</sub>] and ethyl acetate exhibit one another transition point, the values of which are given in **Table 6.2.3**. Systematic analysis of the values of the  $H^E_{IL-IL}$  parameters reveals that the behavior of ionic liquids in the all ethylated solvents is different from ethyl acetate.

**Table 6.2.3.** The values of enthalpic interaction parameters,  $10^{-8} H^E_{IL-IL}$  (J mol<sup>-1</sup>) and their corresponding concentrations,  $m^{0.5}/(\text{mol kg}^{-1})^{0.5}$  for all the studied ionic liquid-ethylated solvent systems.

Ionic Liquid	[EMIM][BF <sub>4</sub> ]		[BMIM][BF <sub>4</sub> ]	
	$m^{0.5}/(\text{mol kg}^{-1})^{0.5}$	$10^{-9} H^E_{IL-IL}/(\text{J mol}^{-1})$	$m^{0.5}/(\text{mol kg}^{-1})^{0.5}$	$10^{-9} H^E_{IL-IL}/(\text{J mol}^{-1})$
Ethyl acetate	0.0048	-1.465	0.0047	-0.1767
Ethylene glycol	0.0049	0.1073	0.0047	0.0503
Diethyl amine	0.0048	0.2560	0.0048	0.2123
<i>N, N</i> -diethyl acetamide	0.0047	0.1234	0.0048	0.5900
2-Ethoxyethanol	0.0044	0.2884	0.0045	0.1794

\* The [EMIM][BF<sub>4</sub>]-ethyl acetate system shows one more transition point at  $(0.0065 \text{ mol kg}^{-1})^{0.5}$ .

### 6.2.2.5. Analysis of Relative Apparent Molar Enthalpy ( $\phi_L$ ):

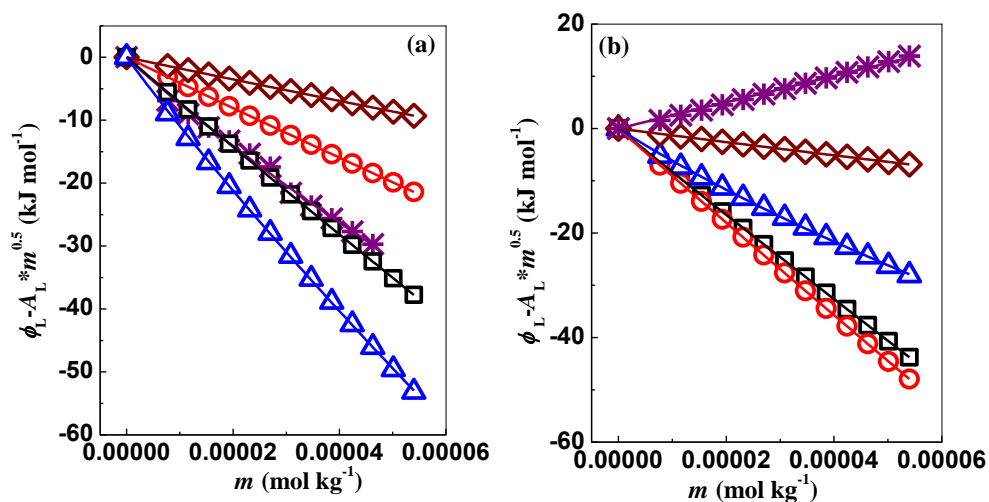
To further evaluate the ion-ion and ion-solvent interactions, we calculated the relative apparent molar enthalpy,  $\phi_L$  using the standard procedure.<sup>[14]</sup> The  $\phi_L$  values of the studied ionic liquid-ethylated solvent systems were analyzed using the following equation;

$$\phi_L = A_L m_{\text{IL}}^{0.5} + q_1 m_{\text{IL}} + q_2 m_{\text{IL}}^{1.5} \quad (6.2.2)$$

where,  $A_L$  is a Debye-Huckel limiting slope,  $q_1$  and  $q_2$  are the virial expansion coefficients. The values of  $A_L$  for employed solvents are tabulated in **Table 6.2.4** as calculated by the method given by Ananthaswamy and Atkinson.<sup>[52]</sup> The values of the virial expansion coefficients with the standard errors are given in **Table 6.2.5**. These  $q_1$  and  $q_2$ , virial expansion coefficients represent the short range doublet and triplet interactions, respectively. The  $\phi_L$  data for all the studied systems plotted against  $m$  in **Figure 6.2.4**. The first term on the right-hand side of the equation 6.2.3 indicates the long range interaction depicted by Debye-Huckel term. The second term on the right-hand side of the equation provides the short range interactions to quantify the binary interactions between opposite and like charges.

**Table 6.2.4.** Pitzer-Debye-Huckel limiting slope,  $A_L$  at 298.15 K for solvents used in the present study calculated by the method given by Ananthaswamy and Atkinson.<sup>[52]</sup>

Solvents	$A_L$ (J kg <sup>0.5</sup> mol <sup>-1.5</sup> )
Ethyl acetate	273271
Ethylene glycol	17437
Diethyl amine	590929
<i>N, N</i> -diethyl acetamide	20093
2-Ethoxyethanol	25064



**Figure 6.2.4.** The plots of the relative apparent molar enthalpies ( $\phi_L$ ) versus molality ( $m$ ) for [EMIM][BF<sub>4</sub>] (a) and [BMIM][BF<sub>4</sub>] (b) in ethyl acetate (\*), ethylene glycol ( $\diamond$ ), *N,N*-diethyl acetamide ( $\circ$ ), 2-ethoxyethanol ( $\square$ ) and diethyl amine ( $\triangle$ ).

**Table 6.2.5.** Adjustable parameters for fitting relative apparent molar enthalpy,  $\phi_L$  of ionic liquid-ethylated solvent systems using equation 6.2.3.

Solvents/Ionic Liquids	[EMIM][BF <sub>4</sub> ]		[BMIM][BF <sub>4</sub> ]	
	$10^{-7}q_1$	$10^{-7}q_2$	$10^{-7}q_1$	$10^{-7}q_2$
2-Ethoxyethanol	$-69.83 \pm 0.04$	$396.1 \pm 6.5$	$-84.82 \pm 0.04$	$507.1 \pm 6.5$
<i>N,N</i> -diethyl amine	$-112.8 \pm 1.1$	$2538 \pm 163$	$-69.31 \pm 1.12$	$2403 \pm 2$
Ethylene glycol	$-17.32 \pm 0.03$	$118.7 \pm 3.8$	$-13.51 \pm 0.03$	$108.8 \pm 4.1$
Ethyl acetate	$-63.68 \pm 0.87$	-	$25.15 \pm 0.21$	-
<i>N,N</i> -diethyl acetamide	$-39.68 \pm 0.03$	$240.1 \pm 4.9$	$-92.36 \pm 0.02$	$480.4 \pm 3.7$

### 6.2.3. Conclusions

To summarize; the variation in excess partial molar enthalpy values depend on the difference in inter-ionic interactions as well as packing between the ionic liquids and ethylated solvents. It occurs as a result of the different alkyl groups attached to the cationic core of ionic liquids and the solvent properties. The excess partial molar enthalpy observed here mainly depends on the hydrogen bond accepting basicity ( $\beta$ ). The linear solvation energy relations evident that the permutation of  $\alpha$ ,  $\beta$ , and  $\pi^*$  is effective to represent the excess partial molar enthalpy values of [EMIM][BF<sub>4</sub>]-ethylated solvent systems, whereas for [BMIM][BF<sub>4</sub>]-ethylated solvent systems, a permutation of  $E_T^N$ ,  $\alpha$ , and  $\beta$  significant. The structural orientation of the ethylated solvent molecules around the ionic liquids stabilizes ionic liquid-ethylated solvent systems. To our surprise, ion-solvent interactions also exist in the concentrated region of ionic liquids. We hypothesize that this might happen due to the presence of electronegative atoms (oxygen and nitrogen) in the ethylated solvents. A detailed analysis of the ion-ion and ion-solvent interactions is examined in terms of enthalpic parameters and the relative apparent molar enthalpies. The thermal behavior of these system changes as the molecular structures and the different solvatochromic parameters of the ethylated solvents.

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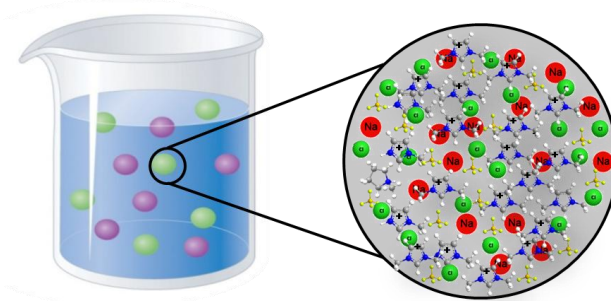
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## Chapter 7

# ***Ion-Ion and Ion-Solvent Interactions in the Mixtures of Salt and Ionic Liquid by Isothermal Titration Calorimeter***

*The ion-ion interactions are quantified and discussed in the present chapter by measuring the enthalpy of mixing of inorganic salts with ionic liquids. These interactions are analysed and compared with the previously reported experimental and theoretical models about the mixing of two salts and ion-ion interactions. An interesting observation of the cation-cation interactions is explained based on the enthalpic measurements*





## 7.1. Introduction

The present study deals with the inter-ionic interactions between the ionic liquid and salt based on the thermodynamic properties such as; excess partial molar enthalpy, relative apparent molar enthalpy and the enthalpic interaction parameters. We conducted a systematic investigation of the enthalpic behavior of aqueous solution of salt and ionic liquids and their mixtures. The present study also emphasizes on how the mixture of aqueous solution of ionic liquids and salts deviate from the ideality in terms of their thermodynamic properties. The deviation from ideality of excess partial molar enthalpy of mixing has been calculated and discussed here.

The interactions in aqueous electrolytic solutions have been studied in the past using calorimeter, volume and activity coefficient measurements. The ionic interactions between like charged ions have been estimated and analysed in the light of Friedman theory. The osmotic and activity coefficients for aqueous mixtures of electrolytes with a common ion were first reported by Owen and Cooke.<sup>[1]</sup> Furthermore, Robinson and coworkers studied the mixtures of alkali halides and alkaline earth metals.<sup>[2-6]</sup> Activity coefficients, densities and excess volumes of aqueous solution of strong electrolytes have been examined systematically by Kumar et al.<sup>[7-12]</sup> A more detailed approach to determine the free energies of mixed electrolyte solutions was proposed by Friedman<sup>[13, 14]</sup> which is further explored by Wood et al.<sup>[15]</sup> These studies only dealt with the inorganic electrolytes. However, the organic electrolytes are still poorly understood. The mixing free energy of these binary mixtures is a useful parameter in terms of understanding the interactions between the like charges. The measures such as

excess free energy changes of mixing of solutions of alkali halides and tetraalkylammonium halides (organic electrolyte) with common anions have been determined by the isopiestic method.<sup>[16]</sup> Studies on volume changes on mixing appear to suggest the importance of cation-cation pair interactions and cation-anion-cation triplet interactions.<sup>[16-19]</sup> Wood and coworkers have shown the concentration dependence of the heat of mixing ( $\Delta H$ ) to discover the importance of pair and triplet interactions.<sup>[20-23]</sup>

Ionic liquids are asymmetric in nature. The shape and size of the both ions may differ widely. These characteristic properties of ionic liquids bring about the variations in interionic interactions and microscopic structures of the binary mixtures of ionic liquids. It would therefore, be of interest to examine how ions of strong electrolytes interact with those of ionic liquids.

With this background, we have undertaken an experimental study based upon Isothermal Titration Calorimetry (ITC), which is reported as an accurate methodology to measure the enthalpic changes accompanying the chemical and biological processes. In this Chapter, we emphasize our study on understanding the nature of cation-cation interactions enthalpically in terms of excess partial molar enthalpy ( $H_{IL}^E$ ), which is one of the important physical aspects of the ionic liquids. In the present study, we have selected strong electrolytes like NaCl, NaBF<sub>4</sub> and protic ionic liquids; *N*-methylimidazolium chloride, [MIM]Cl, *N*-methylpyrrolidinium chloride, [MPyrr]Cl, pyridinium chloride, [Py]Cl, 1-methylimidazolium tetrafluoroborate, [MIM][BF<sub>4</sub>], aprotic ionic liquids such as 1-ethyl-3-methylimidazolium tetrafluoroborate,

[EMIM][BF<sub>4</sub>], 1-butyl-3-methylimidazolium tetrafluoroborate, [BMIM][BF<sub>4</sub>] and 1-hexyl-3-methylimidazolium tetrafluoroborate, [HMIM][BF<sub>4</sub>]. In the present study we systematically deciphered the effect of common anion mixing of organic and inorganic electrolytes and cation-cation interactions of these mixtures.

## 7.2. Experimental Section

The isothermal titration calorimeter (ITC; model: MicroCal LLC, VP-ITC2000) controlled by the VP-Viewer 2000 software was employed to measure the  $H_{IL}^E$  values of mixing of the binary mixtures of aqueous solutions of ionic liquid and salt at 298.15 K. The fundamental details of the calibration and experimental procedures are given in Chapter 3. The synthesis procedures of all the protic and aprotic ionic liquids and their purities with their structures are given in Chapter 3.

## 7.3. Results and Discussion

The results obtained from the experiment are analyzed and discussed in the following sections.

### 7.3.1. $H_{IL}^E$ of Aqueous Solutions of Ionic Liquid and Salt

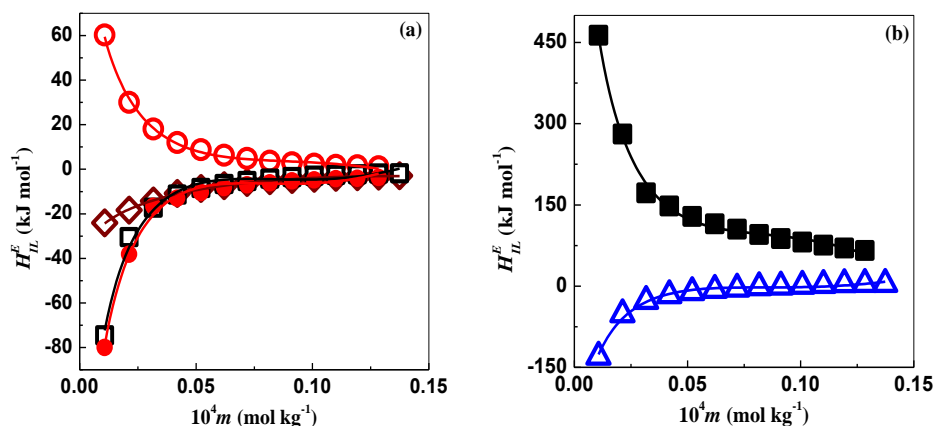
In this chapter, we discuss the behavior of ionic liquid-water systems versus the aqueous solution of strong electrolytes such as NaCl and NaBF<sub>4</sub> in terms of  $H_{IL}^E$  values. It is reported that the protic ionic liquids exhibit unique properties of induced network structure of hydrogen bonding.<sup>[24]</sup> They mimic the hydrogen bonded network of water due to the extended hydrogen bonding between protic ionic liquids.<sup>[24]</sup> The

mixing of protic ionic liquids and water can be proceeding by cavity formation or hydration of ions. The former one, needs energy from the system that is endothermic (positive  $H_{IL}^E$ ) in nature while the hydration process is exothermic (negative  $H_{IL}^E$ ). The reported data suggest that solvent molecules interact with ionic liquids via hydrogen bonds.<sup>[25]</sup> The measured  $H_{IL}^E$  values of the experiments are plotted as the function of molality in **Figure 7.1**. The solvation of ionic liquids changes from endothermic to exothermic as the nature of cation ring changes from the pyridinium to imidazolium to *N*-methylpyrrolodinium and finally a small strong electrolyte sodium ion.  $\text{Cl}^-$  is a common anion in all the protic ionic liquids and strong electrolyte.  $[\text{Py}]\text{Cl}$  exhibit endothermic behavior whereas,  $[\text{MIM}]\text{Cl}$ ,  $[\text{MPyrr}]\text{Cl}$ , and  $\text{NaCl}$  shows exothermic behavior. The switch in enthalpic behavior has been observed from the endothermic to exothermic due to the different mode of interactions of water molecules with the cationic rings. Generally, dissolution of ionic liquid or electrolyte takes place because of the hydration or hydrophobic hydration. The hydration accounts for the variation in enthalpic behavior of the ionic liquids and salts. This suggests that invoking aromaticity in the cationic rings reduces the stability of the protic ionic liquid-water systems. Pyridinium,  $[\text{Py}]^+$ , and 1-methylimidazolium,  $[\text{MIM}]^+$ , cationic rings are aromatic in nature whereas *N*-methylpyrrolidinium,  $[\text{MPyrr}]^+$ , cation ring is non aromatic and bigger in size as compared to the sodium ion. Solvation of ionic liquids or salt disturbs the hydrogen bond network in the water. Water attempts to regain the stable state by with the cost of energy from the system to form hydrogen bonded network. Thus, the process becomes endothermic in nature. The smaller size and the aromaticity of the  $[\text{Py}]^+$  and  $[\text{MIM}]^+$  cationic rings induce cation-cation interactions (*n*-



$\pi$  stacking).  $[\text{Py}]^+$  is more aromatic as compared to  $[\text{MIM}]^+$  hence making the dissolution of  $[\text{Py}]\text{Cl}$  energetically less favorable therefore, it shows the endothermic behavior. The endothermic behavior of  $[\text{Py}]\text{Cl}$  with water can also be explained on the basis of polarity. The polarity of an imidazole ring is 3.61 D while pyridine is 2.2 D. This validates the exothermic behavior of imidazolium based protic ionic liquids and endothermic behavior of  $[\text{Py}]\text{Cl}$ . The  $H_{IL}^E$  values for the  $[\text{MPyrr}]\text{Cl}$ -water are comparable with those of  $\text{NaCl}$ -water solution. The possibility of cation-cation interactions is negligible in  $[\text{MPyrr}]^+$  cationic ring because of non aromatic nature. Also, dissociation of  $[\text{MPyrr}]\text{Cl}$  is thermally more favorable as compared to the other two protic ionic liquids. The  $H_{IL}^E$  values suggest that the non aromatic cationic ring probably exhibits the hydration similar to that for sodium ions and therefore, stabilizes the system. It is quite intuitive that the ionic liquids cannot dissociate completely as  $\text{NaCl}$  does which reduces the possibility of solvation. In  $\text{NaCl}$  solution,  $\text{Na}^+$  ions are completely hydrated due to their smaller size and high charge density. Hence, the  $\text{NaCl}$ -water system shows the negative  $H_{IL}^E$  values. The hydration also depends upon the several other factors such as charge density, size, shape of ions etc. The smaller ions bound more tightly to water molecules than larger ions due to small size and high charge density. Water orientations result from a balance between the electrostatic ordering and water-water hydrogen bonding ordering mechanism. Small cations ( $\text{Na}^+$ ) orient first-shell waters through an electrostatic mechanism.<sup>[26]</sup> Due to smaller in ion size, the water in second shell also experience the influence of ion charge hence get tightly arranged. While increasing the cation size redistributes the charge density and weakens the electrostatic forces of the ion on the water, facilitate intra-water network

around the moiety as reported for hydrophobic hydration. A similar trend has been noted in case of anion.<sup>[26]</sup> The present study show that the dissolution of NaBF<sub>4</sub> is enthalpically unfavorable in the binary aqueous solution, whereas the [MIM][BF<sub>4</sub>] stabilizes the [MIM][BF<sub>4</sub>]-water system as shown in **Figure 7.1(b)**. [MIM][BF<sub>4</sub>] exhibits the exothermic behavior in the aqueous solution. The  $H_{IL}^E$  values suggest that the behavior of protic ionic liquids is comparable to the strong electrolytes. It is clear from **Figure 7.1** and  $H_{IL}^E$  values that the rearrangement of water molecules around the [MIM][BF<sub>4</sub>] is much stronger as compared to NaCl.



**Figure 7.1.** The plots of the excess partial molar enthalpies ( $H_{IL}^E$ ) versus molality ( $m$ ) for aqueous solutions of (a) [MIM]Cl ( $\diamond$ ), [Py]Cl ( $\circ$ ), and [MPyrr]Cl ( $\square$ ) and NaCl ( $\bullet$ ), (b) NaBF<sub>4</sub> ( $\blacksquare$ ) and [MIM][BF<sub>4</sub>] ( $\triangle$ ).

To delineate the ion-water interactions in extremely dilute conditions, the  $H_{IL}^E$  data of the ionic liquids were fitted by the following equation

$$H_{IL}^E = H_{IL}^{E,\infty} + a_0 m^{0.5} + a_1 m + a_2 m^{1.5} \quad (7.1)$$

where,  $a_0$ ,  $a_1$  and  $a_2$  are the adjustable parameters and the  $H_{IL}^{E,\infty}$  values denote the limiting excess partial molar enthalpy. The  $H_{IL}^{E,\infty}$  values obtained for these experiments indicate the standard molar enthalpy of the solution as the well as the dissolved ionic liquids. The  $H_{IL}^{E,\infty}$  values of the studied systems are given in **Table 7.1**. The values of  $H_{IL}^{E,\infty}$  obtained from the above fitting procedure discern the impact of induced variations in the structure of both ionic liquids and electrolytes on the enthalpic stability of the system. Earlier reports also revealed that the interactions established in protic ionic liquid-water systems are considerably stronger as compared to those in the imidazolium based aprotic ionic liquids.<sup>[24]</sup>

**Table 7.1.** Limiting excess partial molar enthalpies,  $H_{IL}^{E,\infty}$  obtained from equation 7.1 for the studied systems.

Ionic liquid systems	$H_{IL}^{E,\infty}$ (kJ mol <sup>-1</sup> )	Ionic liquid systems	$H_{IL}^{E,\infty}$ (kJ mol <sup>-1</sup> )
NaCl - H <sub>2</sub> O	-257 ± 13	[MIM]BF <sub>4</sub> - H <sub>2</sub> O	-468 ± 28
NaBF <sub>4</sub> - H <sub>2</sub> O	1180 ± 48	[EMIM]BF <sub>4</sub> - H <sub>2</sub> O	27 ± 2
[MIM]Cl - H <sub>2</sub> O	-34 ± 1	[BMIM]BF <sub>4</sub> - H <sub>2</sub> O	-145 ± 7
[Py]Cl - H <sub>2</sub> O	370 ± 24	[HMIM]BF <sub>4</sub> - H <sub>2</sub> O	-297 ± 16
[MPyrr]Cl - H <sub>2</sub> O	-265 ± 16		

Previous work from our group on aprotic ionic liquid-water system showed the effect of cationic ring and the alkyl chain length on the hydration pattern. It has been reported that reorganization of hydrogen bond network by water in terms of hydrophobic hydration by the alkyl chain length of the cationic rings.<sup>[27, 28]</sup> The system changes

endothermic to exothermic with the increase in the alkyl chain length of cationic ring from [EMIM]<sup>+</sup> to [BMIM]<sup>+</sup> and [HMIM]<sup>+</sup>.<sup>[27]</sup> The hydration around a hydrophobic part of the ionic liquids is more ordered than bulk water to compensate the enthalpic loss associated with the loss of water-water interactions before. A significant tetrahedral geometry of water in the first hydration shell “iceberg” around the non polar solute has been observed by Frank and Evan.<sup>[29, 30]</sup>

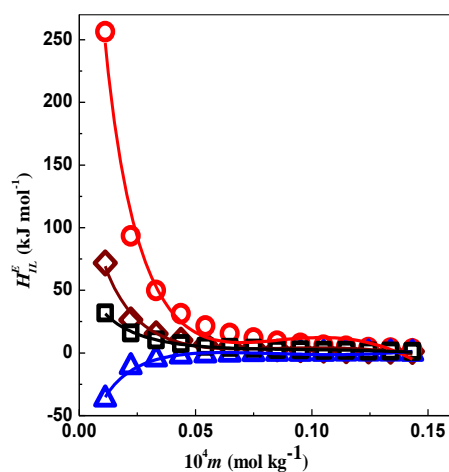
### 7.3.2. Mixing Effect of Aqueous Solutions of Salt and Ionic Liquid

We have measured the  $H_{IL}^E$  values of the mixing of strong electrolytes (aqueous solution) and ionic liquids (aqueous solution) having common anions. Young’s mixing rule postulates that in the mixing of two binary solutions of the same ionic strength to produce a ternary solution, an thermodynamic quantity of the ternary solution may be expressed precisely as the sum of the corresponding thermodynamic quantities of the pure binary solutions.<sup>[31, 32]</sup>

The effect of electrolytes on the structuring of water is an important and interesting subject. The relative influences of cation and anions on the water arrangement have been compared and explained in terms of Hofmeister series.<sup>[33]</sup> Now, we ascribe this effect to the water dynamics and hydration near the ions in the mixture of organic and inorganic electrolytes. Chaotropes form hydrogen bonds to the existing network of water, whereas kosmotropes work as the hydration center without influencing the water characteristic of bulk water away from the hydration shells.<sup>[33]</sup> In the present study the protic ionic liquid-strong electrolyte mixtures having common anion shows

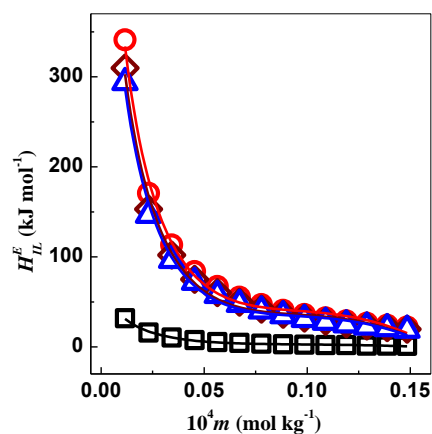
enthalpically different behavior as compared to their individual aqueous solutions. A comparison of the **Figures 7.1, 7.2 and 7.3** shows that the ionic liquid-salt mixtures acquire large  $H_{IL}^E$  values than the ionic liquid-water or salt-water systems. The  $H_{IL}^E$  values of mixing are strongly governed by the solvent structural properties of ions. Based on these facts and  $H_{IL}^E$  values in previous section confirm that NaCl and NaBF<sub>4</sub> as structure maker (kosmotrope) and a structure breaker (chaotrope) in terms of  $H_{IL}^E$  values, respectively. The aqueous solution of [Py]Cl is enthalpically unfavorable which we have discussed in the previous section but the  $H_{IL}^E$  values suggest that the [Py]Cl-NaCl system is much more enthalpically unfavorable. From **Table 7.1**, it is clear that the aqueous solutions of [MIM]Cl, [MIM][BF<sub>4</sub>] and [MPyrr]Cl is enthalpically favorable. Interestingly, their mixtures with strong electrolytes destabilize the water structure which can be reflected from  $H_{IL}^E$  values. All the systems show positive  $H_{IL}^E$  values except [MPyrr]Cl-NaCl. The enthalpic measurement of these protic ionic liquids and aprotic ionic liquids demonstrate that the [MIM]Cl, [MIM][BF<sub>4</sub>], [MPyrr]Cl and NaCl are slightly structure makers and the [Py]Cl and NaBF<sub>4</sub> are structure breaker. This might occur due to the competition between charge effect and the hydrophobic effect. The [MIM][BF<sub>4</sub>] tends to be hydrophobic structure makers as upon increasing the size of alkyl groups attached to the cationic ring. [EMIM][BF<sub>4</sub>] is in the transition region between a structure maker and a structure breaker. As we move towards aprotic ionic liquids with large cationic ring, the hydrophobic hydration probably be dominating over the hydration by charge effect. In common anion mixing of AX and BX, there are three like-charged pair interactions to be considered: solvation of A<sup>+</sup> ion and then the overlapping of hydration shells with each other, Solvation of B<sup>+</sup> ion and

then the overlapping of hydration shells by each other, and the formation of  $A^+B^+$  ion pairs. From the  $H_{IL}^E$  values it is expected that at any given concentration the  $[Py]^+$  cation have more hydration sphere overlap with neighbors as compared to the  $[MIM]^+$  and  $[MPyrr]^+$ .  $[MIM]Cl$  and  $[MIM][BF_4]$  shows the exothermic behavior in their aqueous solution. Therefore, mixing of these solutions with the aqueous solution of salts having common anion shows the endothermic  $H_{IL}^E$  values. This suggests that the  $[MIM]^+-Na^+$  interactions are more prominent as compared to the  $[MIM]^+-[MIM]^+$ . These stronger cation-cation interactions destabilize the water structure and hence show the endothermic behavior. On the other hand, the cation-cation interactions are weaker in case of  $[MPyrr]^+$  cation hence, the mixing of  $[MPyrr]Cl-NaCl$  behaves as a slightly structure maker as shown in **Figure 7.2**. The order of  $H_{IL}^E$  for the protic ionic liquids:  $[Py]Cl-NaCl > [MIM]Cl-NaCl > [MIM][BF_4]-NaBF_4 > [MPyrr]Cl-NaCl > [HMIM][BF_4]-NaBF_4$ .



**Figure 7.2.** The plots of the excess partial molar enthalpies ( $H_{IL}^E$ ) versus molality ( $m$ ) for the mixtures of aqueous solutions  $[MIM][BF_4]-NaBF_4$  ( $\square$ ),  $[MIM]Cl-NaCl$  ( $\diamond$ ),  $[Py]Cl-NaCl$  ( $\circ$ ), and  $[MPyrr]Cl-NaCl$  ( $\triangle$ ).

Similarly, the  $H_{IL}^E$  values of mixing for aprotic ionic liquid-salt systems are measured. The  $H_{IL}^E$  values indicate that the mixture of aprotic ionic liquid- $\text{NaBF}_4$  is enthalpically favorable as compared to the pure  $\text{NaBF}_4$  but not as the pure ionic liquids. It is evident from  $H_{IL}^E$  values that the effect of  $\text{NaBF}_4$  is more prominent (structure breaker) than hydrophobic hydration of ionic liquids. The  $H_{IL}^E$  values can also indicate lack of cation-cation interactions in these systems. However, the  $H_{IL}^E$  values of these systems are less positive as compared to the pure  $\text{NaBF}_4$  therefore, destabilizes the water structure and behaves as a structure breaker as shown in **Figure 7.3**. The order of  $H_{IL}^E$  for all the  $[\text{BF}_4]^-$ -based ionic liquids:  $[\text{MIM}][\text{BF}_4]-\text{NaBF}_4 > [\text{EMIM}][\text{BF}_4]-\text{NaBF}_4 > [\text{BMIM}][\text{BF}_4]-\text{NaBF}_4$ . **Figures 7.2** and **7.3** demonstrate the strong cation-cation interactions in the aromatic cationic ring. The binary mixtures of salt and ionic liquids with aromatic cationic ring such as imidazolium, pyridinium show structure breaker effect, whereas the non-aromatic cationic ring ( $[\text{MPyrr}]^+$ ) shows exothermic (structure maker) behavior.



**Figure 7.3.** The plots of the excess partial molar enthalpies ( $H_{IL}^E$ ) versus molality ( $m$ ) for the mixtures of aqueous solutions of  $[\text{MIM}][\text{BF}_4]-\text{NaBF}_4$  ( $\square$ ),  $[\text{EMIM}][\text{BF}_4]-\text{NaBF}_4$  ( $\circ$ ),  $[\text{BMIM}][\text{BF}_4]-\text{NaBF}_4$  ( $\diamond$ ), and  $[\text{HMIM}][\text{BF}_4]-\text{NaBF}_4$  ( $\triangle$ ).

**Table 7.2.** Limiting excess partial molar enthalpies,  $H_{IL}^{E,\infty}$  obtained from equation 7.1 for the mixtures of aqueous solution of ionic liquid-salt systems.

Ionic liquid systems	$H_{IL}^{E,\infty}$ (kJ mol <sup>-1</sup> )
[MIM]Cl - NaCl	263 ± 18
[Py]Cl - NaCl	960 ± 63
[MPyrr]Cl - NaCl	-149 ± 11
[MIM]BF <sub>4</sub> - NaBF <sub>4</sub>	99 ± 4
[EMIM]BF <sub>4</sub> - NaBF <sub>4</sub>	1066 ± 52
[BMIM]BF <sub>4</sub> - NaBF <sub>4</sub>	972 ± 49
[HMIM]BF <sub>4</sub> - NaBF <sub>4</sub>	921 ± 45

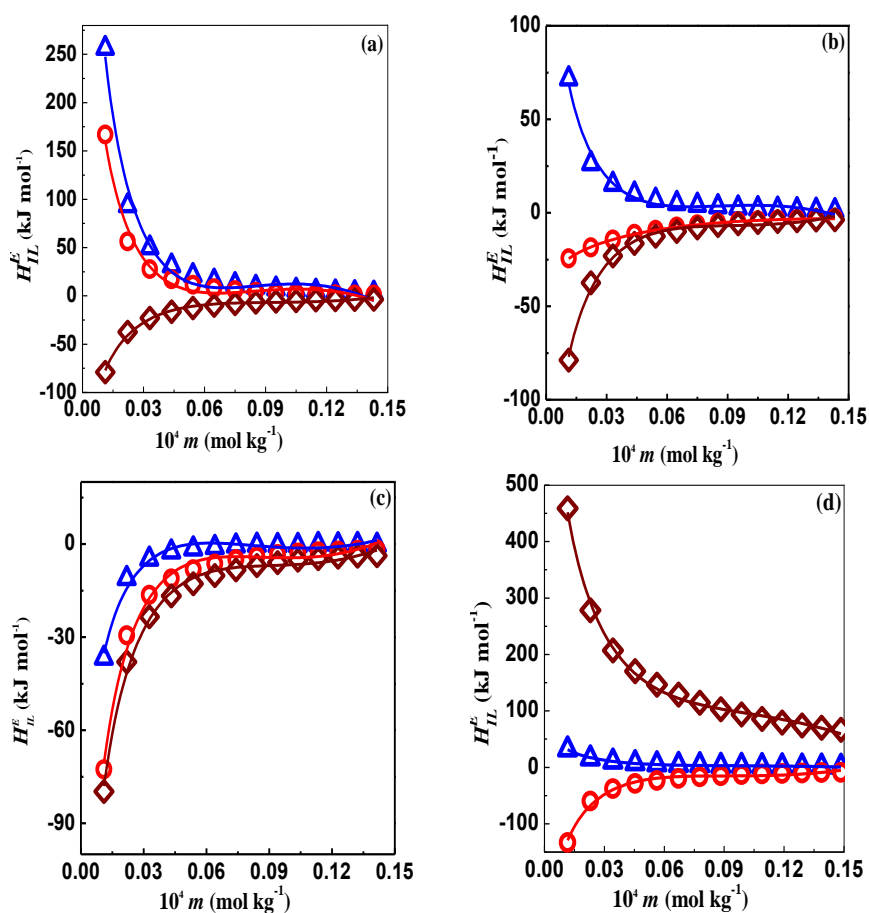
The present study suggest that the mixing of ionic liquids possessing aromatic cationic ring with the salt exhibit endothermic behavior (chaotrope) due to the strong cation-cation interaction, whereas the mixing of ionic liquid having non aromatic cationic ring with salt exhibit exothermic behavior (kosmotrope).

### 7.3.3. Mixing Effects of Salt and Ionic Liquids and Cation-Cation Interactions:

Now, we emphasize on the effect of cation-cation interactions on the  $H_{IL}^E$  values upon mixing aqueous solution of salts and ionic liquids. Here, two type of cation-cation interactions are possible; (a) cation-cation interactions between the cation of ionic liquids (IL<sup>+</sup>-IL<sup>+</sup>), (b) the interactions between Na<sup>+</sup>-IL<sup>+</sup>. **Figure 7.4 (a)** shows the  $H_{IL}^E$  values of aqueous solution of [Py]Cl, NaCl, and [Py]Cl-NaCl systems. The [Py]Cl and [Py]Cl-NaCl system exhibits the similar pattern in the  $H_{IL}^E$ - $m$  plot, whereas NaCl shows the opposite trend. The  $H_{IL}^E$ - $m$  plots clearly indicate the dominant [Py]<sup>+</sup>-[Py]<sup>+</sup>



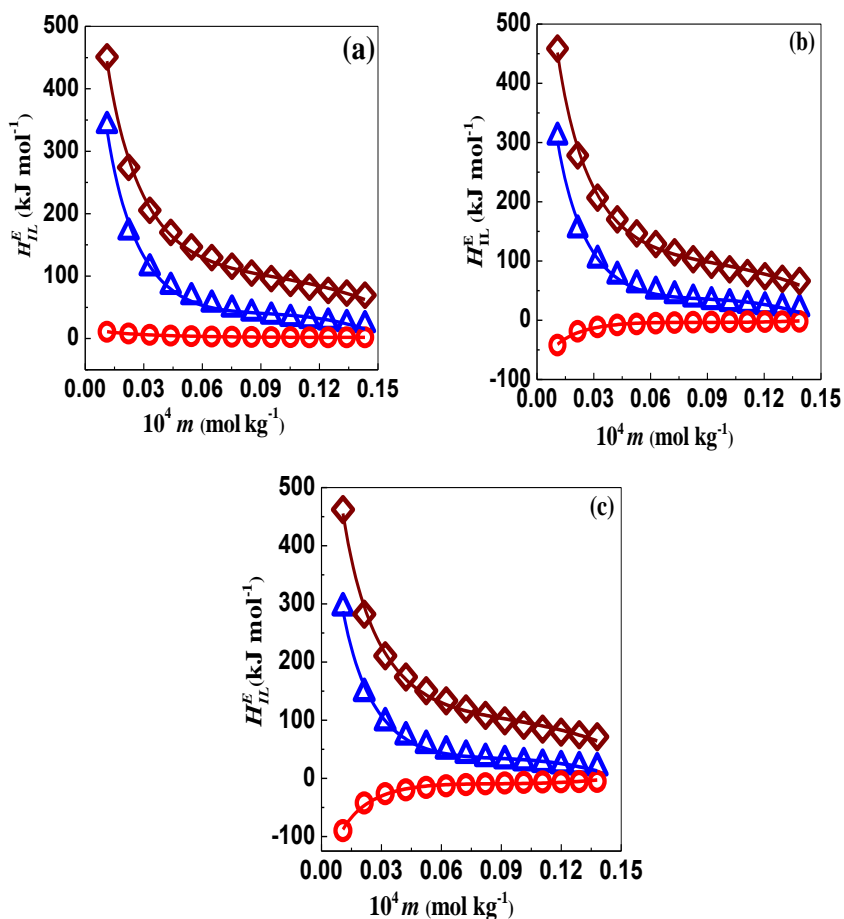
interactions over the hydration of ionic liquid and salt cations. On the other hand, the  $\pi$ - $\pi$  interactions between pyridinium rings is also possible in the [Py]Cl-NaCl system which might make mixing thermally unfavorable. An anomalous behavior is obtained for [MIM]Cl-NaCl system (**Figure 7.4 (b)**). [MIM]Cl-water and NaCl-water systems are thermally favorable and exothermic, whereas [MIM]Cl-NaCl show the positive  $H_{IL}^E$  values (endothermic) which might be due to weakening of hydrogen bonded network of water molecules.



**Figure 7.4.** The plots of the excess partial molar enthalpies ( $H_{IL}^E$ ) versus molality ( $m$ ) for ionic liquid in water ( $\circ$ ), NaCl in water ( $\diamond$ ), mixture of aqueous solutions of ionic liquid and NaCl ( $\triangle$ ), (a) [Py]Cl, (b) [MIM]Cl, (c) [MPyr]Cl, (d) [MIM][BF<sub>4</sub>].

The  $H_{IL}^E$  values for [MIM]Cl-NaCl system suggests dominating cation-cation ( $[MIM]^+-Na^+$ ) interactions over their hydration and releases the free water molecules in the mixture of ionic liquid-salt system. Stronger inter-cation ( $[MIM]^+-Na^+$ ) interactions weakens the hydration of ions results in unfavorable enthalpic behavior. Even though both [Py]Cl-NaCl and [MIM]Cl-NaCl system shows the positive  $H_{IL}^E$  values, the former system show  $[Py]^+-[Py]^+$  interactions and other exhibit  $[MIM]^+-Na^+$  interactions. As mentioned above, the [MPyrr]Cl-water system shows the enthalpic pattern similar to the strong electrolyte (NaCl). Interestingly, the [MPyrr]Cl-NaCl systems possess the exothermic  $H_{IL}^E$  values. As seen in the mixture of this protic ionic liquid with water the hydration of  $[MPyrr]^+$  is similar to that of  $Na^+$ . Focusing on the enthalpy of the system, there is no possibility of cation-cation ( $[MPyrr]^+-[MPyrr]^+$  or  $[MPyrr]^+-Na^+$ ) interactions. The [MPyrr]Cl- NaCl system act as a structure maker whereas the other protic ionic liquids-NaCl system behave like structure breaker. The possibility of cation-cation interactions are also seen in [MIM][BF<sub>4</sub>]. **Figure 7.4 (d)** shows the enthalpic pattern of aqueous solution of [MIM][BF<sub>4</sub>], NaBF<sub>4</sub> and [MIM][BF<sub>4</sub>]-NaBF<sub>4</sub> systems. [MIM][BF<sub>4</sub>] exhibits the structure maker property (exothermic) whereas NaBF<sub>4</sub> imparts strong structure breaking effect. Interestingly, the mixture of [MIM][BF<sub>4</sub>]-NaBF<sub>4</sub> systems lies in between structure making and the structure breaking ability. In the [MIM][BF<sub>4</sub>]-NaBF<sub>4</sub> mixture, the effect of individual has been disappeared and the system is showing the marginal  $H_{IL}^E$  values. From  $H_{IL}^E$  data, it is observed that the effect of [MIM][BF<sub>4</sub>] is dominating over the NaBF<sub>4</sub> and very small positive  $H_{IL}^E$  values obtained for [MIM][BF<sub>4</sub>]-NaBF<sub>4</sub> system. This is probable outcome of the cation-cation ( $[MIM]^+-Na^+$ ) interactions in the [MIM][BF<sub>4</sub>]-

water system. We obtained a similar trend for all the studied aprotic ionic liquids (Figure 7.5 (a), (b) and (c)).



**Figure 7.5.** The plots of the excess partial molar enthalpies ( $H_{IL}^E$ ) versus molality ( $m$ ) for ionic liquids in water ( $\circ$ ), NaCl in water ( $\diamond$ ), mixture of aqueous solutions of ionic liquid and NaCl ( $\triangle$ ), (a) [EMIM][BF<sub>4</sub>], (b) [BMIM][BF<sub>4</sub>], (c) [HMIM][BF<sub>4</sub>].

The aprotic ionic liquid-water systems are enthalpically favorable and the NaBF<sub>4</sub> are enthalpically unfavorable while there mixtures with NaBF<sub>4</sub> showed enthalpically unfavorable process. Therefore, the  $H_{IL}^E$  values indicate that the aprotic ionic liquid-

NaBF<sub>4</sub> is enthalpically favorable as compared to the NaBF<sub>4</sub>. It indicates the NaBF<sub>4</sub> plays a vital role in stabilizing the mixture system. Also, the  $H_{IL}^E$  values of mixture are less positive than the pure NaBF<sub>4</sub>, reveals the negligible possibility of cation-cation interactions.

To emphasize on the cation-cation interactions and about their quantitative information, we further investigate that how these mixtures deviate from their ideality calculated from mathematical expressions.

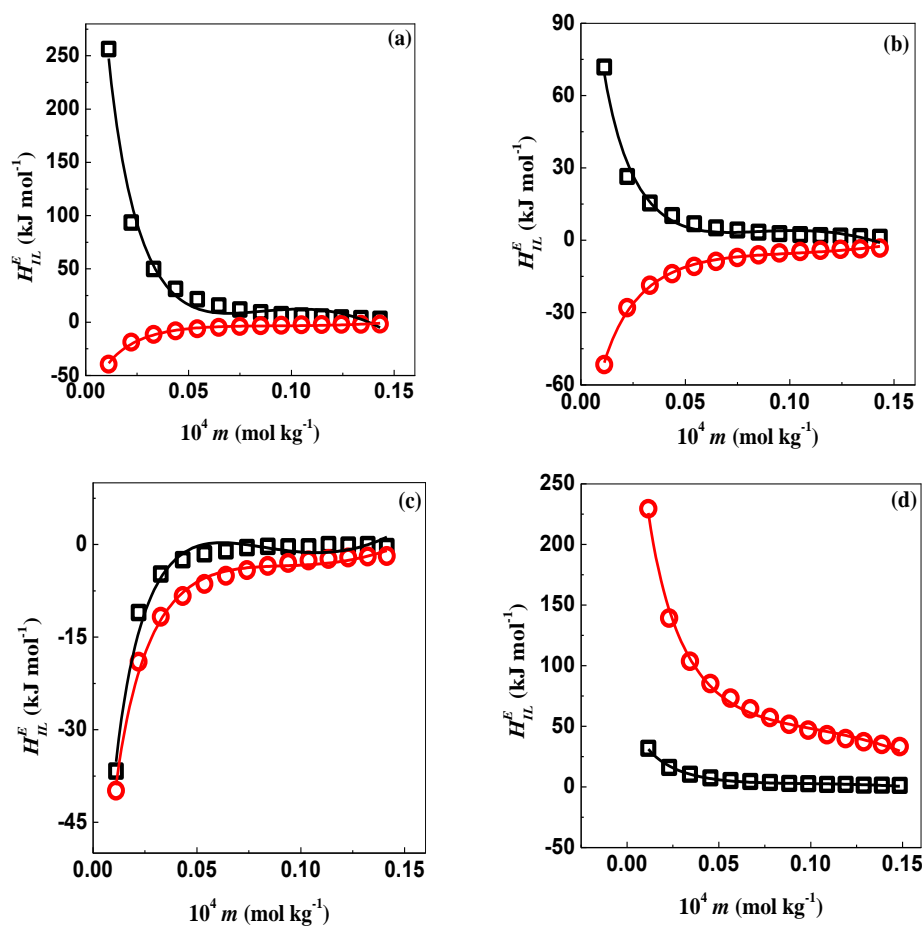
#### 7.3.4. Deviation from Ideality:

Young's mixing rule postulates that, the mixing of two binary solutions of the same ionic strength to produce a ternary solution, thermodynamic quantity of the ternary solution may be expressed precisely as the sum of the corresponding thermodynamic quantities of the pure binary solutions.<sup>[31, 32]</sup> We calculated  $H_{IL}^E$  for ideal mixing of the studied systems by using equation 7.2 to understand how they deviate from the ideality.

$$H_{IL,ideal}^E = \frac{m_{IL}H_{IL}^E + m_{salt}H_{salt}^E}{m_{IL} + m_{salt}} \quad (7.2)$$

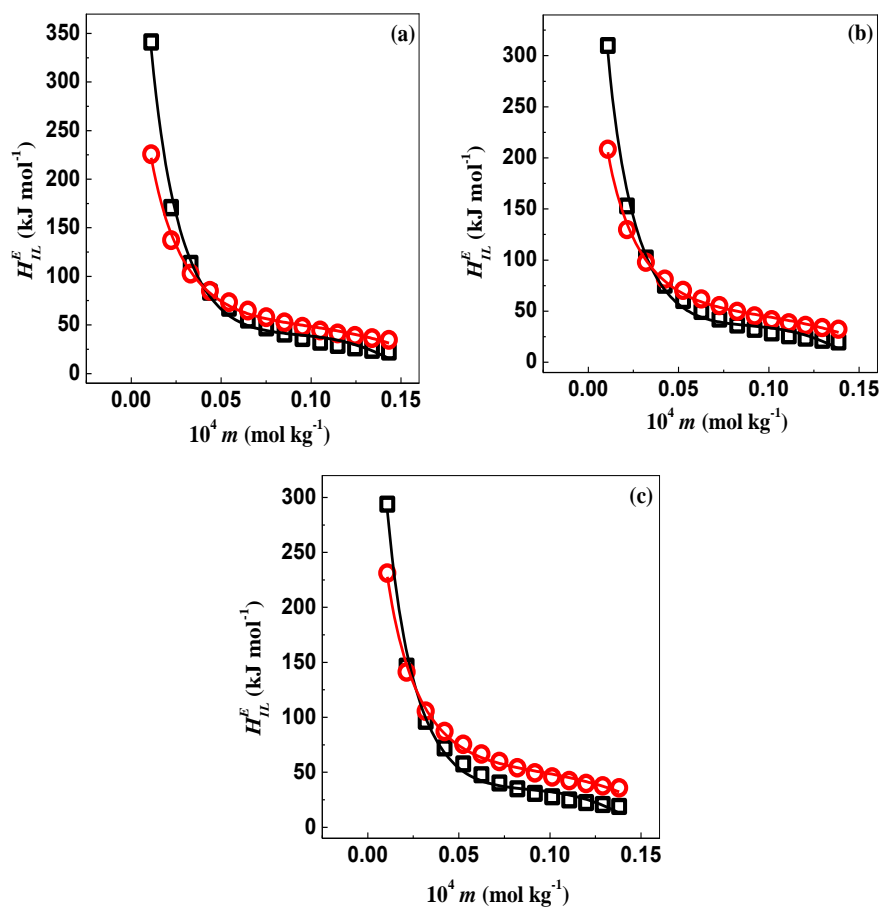
where,  $m_{IL}$  is the molality of the ionic liquids,  $m_{salt}$  and  $H_{salt}^E$  are the molality and excess partial molar enthalpies of the salt. The  $H_{IL,ideal}^E$  and  $H_{IL,exp}^E$  values has been plotted against the molality and fitted by equation 7.1. **Figure 7.6 (a)** and **(b)** evident an opposite curvature on  $H_{IL}^E$  values for experimental and calculated ( $H_{IL,ideal}^E$ ) values. The positive  $H_{IL}^E$  values obtained from experiments. It is expected that when two solvation shells of the cation merge together, releases an excess water from their

solvation which probably costs energy. Therefore, this can be a possible reason for exhibiting the higher  $H_{IL}^E$  values, which can be due to the  $\pi$ - $\pi$  interactions discussed in the earlier section. We also note the similar behavior for [MIM]Cl-NaCl, which is expected from cation-cation interactions of salt and ionic liquid cations. For [MPyrr]Cl, the experimental and ideal  $H_{IL}^E$  values coincide nicely with each other suggesting negligible cation-cation interactions.



**Figure 7.6.** The plots of  $H_{IL}^E$  ideal ( $\circ$ ) and experimental ( $\square$ ), versus  $m^{0.5}$  for the protic ionic liquid-salt systems (a) [Py]Cl-NaCl, (b) [MIM]Cl-NaCl, (c) [MPyrr]Cl-NaCl and (d) [MIM][BF<sub>4</sub>]-NaBF<sub>4</sub>.

A same behavior but with the lower  $H_{IL}^E$  values for the experimental values than calculated is observed for [MIM][BF<sub>4</sub>]. This indicate the less possibility of cation-cation ( $IL^+-IL^+$ ,  $IL^+-Na^+$ ) interactions as compared to the [Py]Cl-NaCl([Py]<sup>+</sup>-[Py]<sup>+</sup>) and [MIM]Cl-NaCl ([MIM]<sup>+</sup>-Na<sup>+</sup>) systems. This suggests that all the protic ionic liquid-salt system deviates from the ideality with different extent (**Figure 7.6**). It supports the existence of the cation-cation interactions between the cation of protic ionic liquids ( $IL^+-IL^+$ ) and Na<sup>+</sup> ( $IL^+-Na^+$ ).



**Figure 7.7.** The plots of  $H_{IL}^E$  ideal ( $\circ$ ) and experimental ( $\square$ ), versus  $m^{0.5}$  for the aprotic ionic liquid-salt systems (a) [EMIM][BF<sub>4</sub>]-NaBF<sub>4</sub>, (b) [BMIM][BF<sub>4</sub>]-NaBF<sub>4</sub> and (c) [HMIM][BF<sub>4</sub>]-NaBF<sub>4</sub>.

Interestingly, it has also been observed from these data that the possibility of cation-cation interaction is greater in [Py]Cl ([Py]<sup>+</sup>-[Py]<sup>+</sup>) followed by [MIM]Cl ([MIM]<sup>+</sup>-Na<sup>+</sup>) then [MIM][BF<sub>4</sub>] ([MIM]<sup>+</sup>-Na<sup>+</sup>) and negligible in the [MPyrr]Cl. Similarly, for the aprotic ionic liquid-NaBF<sub>4</sub> systems, experimental and calculated  $H_{IL}^E$  values (**Figure 7.7**) are overlapping with each other. It indicates that in the mixture of aprotic ionic liquid-NaBF<sub>4</sub> possibility of cation-cation (IL<sup>+</sup>-IL<sup>+</sup> and IL<sup>+</sup>-Na<sup>+</sup>) interactions are negligible.

To further elaborate, we calculated the relative apparent molar enthalpy and the ion-ion interaction parameters of these systems.

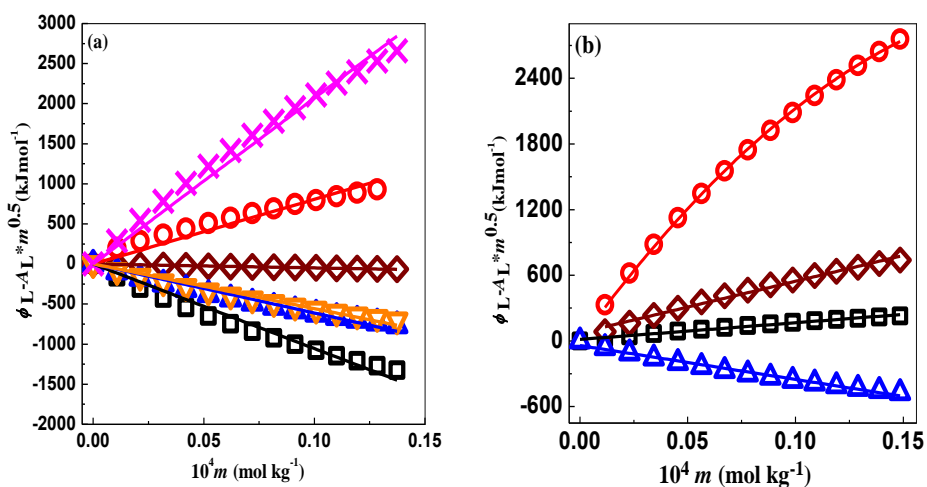
### 7.3.5. Relative Apparent Molar Enthalpy:

To delineate the ion-ion and ion solvent interactions we have calculated the relative apparent molar enthalpy,  $\phi_L$  using the standard procedure reported elsewhere.<sup>[34]</sup> The results are also of interest for the comparison of the  $\phi_L$  values for the aqueous solution of pure ionic liquids, salts and their mixtures. The  $\phi_L$  values with molality can be interpolated using an expression:

$$\phi_L = A_L m_{IL}^{0.5} + q m_{IL} \quad (7.3)$$

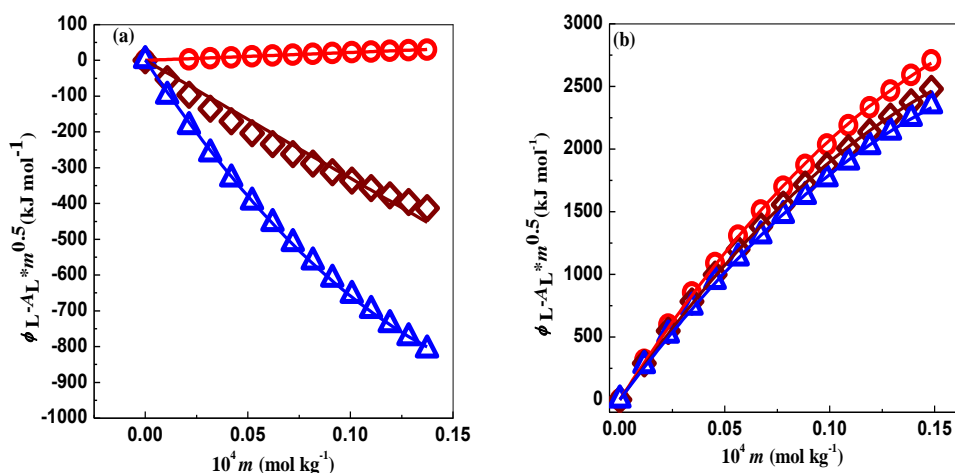
$A_L$  is a limiting slope, the values of which for water is 5641 J kg<sup>1</sup> mol<sup>-1.5</sup> as calculated by the method given by Ananthaswamy and Atkinson.<sup>[35]</sup> The values of the  $q$  parameters together with the standard errors are given in **Table 7.3**. The  $\phi_L$  data for all the studied systems can be correlated with  $m$  to within  $\pm 2\%$ .

In this section, we decipher the effect of the counter anions and mixing of inorganic and organic electrolytes on the enthalpic behavior of ionic liquids in their aqueous solutions. The long range interaction forces are represented by a modified Debye-Huckel term with the short ones by  $q$  parameters. The mixtures, [MIM][BF<sub>4</sub>], [MIM]Cl, [MPyrr]Cl, NaCl shown the negative  $\phi_L$  values whereas, [Py]Cl and NaBF<sub>4</sub> exhibit positive  $\phi_L$  values obtained through the concentration range studied herein as shown in **Figure 7.8** (a). The mixtures of protic ionic liquid-salt have positive  $\phi_L$  values except [MPyrr]Cl-NaCl (negative  $\phi_L$  values) as shown in **Figure 7.8** (b). Interestingly, for the [BF<sub>4</sub>]<sup>-</sup>-based aprotic ionic liquids the  $\phi_L$  values are changes from endothermic to exothermic (negative  $\phi_L$  values) upon increasing the alkyl chain length from [EMIM][BF<sub>4</sub>] to [HMIM][BF<sub>4</sub>]. Hence, the mixture of aprotic ionic liquids-NaBF<sub>4</sub> shows positive  $\phi_L$  values throughout the concentration as shown in **Figure 7.9**.



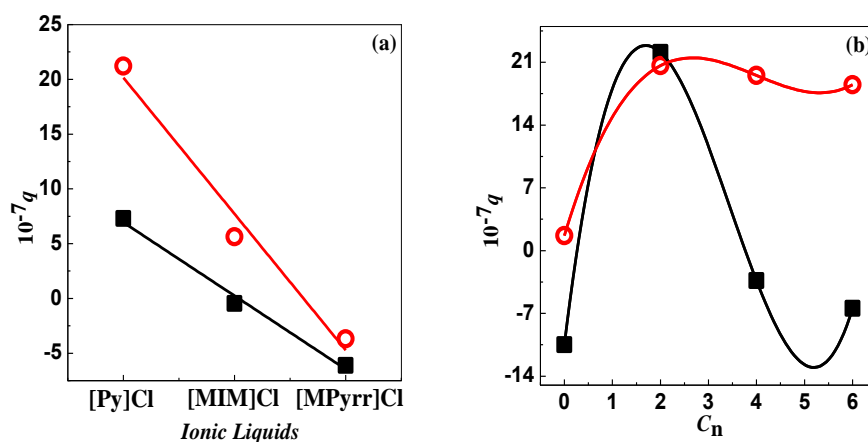
**Figure 7.8.** The plots of the mean apparent molar enthalpies ( $\phi_L$ ) versus molality ( $m$ ) for the mixtures of aqueous solutions of (a) [MIM][BF<sub>4</sub>] (□), [MIM]Cl (◇), [Py]Cl (○), [MPyrr]Cl (△), NaCl (▽) and NaBF<sub>4</sub> (×) and (b) [MIM][BF<sub>4</sub>]-NaBF<sub>4</sub> (□), [MIM]Cl-NaCl (◇), [Py]Cl-NaCl (○), and [MPyrr]Cl-NaCl (△).





**Figure 7.9.** The plots of the mean apparent molar enthalpies ( $\phi_L$ ) versus molality ( $m$ ) for the mixtures of aqueous solutions of (a) [MIM][BF<sub>4</sub>] (□), [EMIM][BF<sub>4</sub>] (○), [BMIM][BF<sub>4</sub>] (◇), and [HMIM][BF<sub>4</sub>] (▽) and (b) [MIM][BF<sub>4</sub>]-NaBF<sub>4</sub> (□), [EMIM][BF<sub>4</sub>]-NaBF<sub>4</sub> (○), [BMIM][BF<sub>4</sub>]-NaBF<sub>4</sub> (◇), and [HMIM][BF<sub>4</sub>]-NaBF<sub>4</sub> (△).

The interactions between protic and aprotic ionic liquids are different in their aqueous solution and their mixtures with salt as shown by  $q$  parameters. A protic ionic liquid with aromatic cationic ring possesses positive value of  $q$ , whereas protic ionic liquid with non-aromatic cationic ring has the negative value of  $q$ . In the present work, the  $q$  values are changed from negative to positive for [BF<sub>4</sub>]<sup>-</sup>-based ionic liquids. [MIM][BF<sub>4</sub>] has negative value of  $q$  while moving towards aprotic ionic liquid such as [EMIM][BF<sub>4</sub>], a positive value of  $q$  has been obtained. The positive  $q$  gradually decreases when we move from [EMIM][BF<sub>4</sub>] to [HMIM][BF<sub>4</sub>]. The values and sign of  $q$  parameters (**Table 7.3**) depend upon the nature of cationic ring and the number of carbon atoms attached to the cation ring. **Figure 7.10** shows the correlation between  $q$  parameters for aqueous solution of pure and mixture of ionic liquids with salts.



**Figure 7.10.** The plots of the  $q$  parameters for aqueous solution of pure ionic liquids (■) and mixtures of ionic liquid-salt (○) with respect to the (a) nature of cationic ring; [Py]Cl (aromatic), [MIM]Cl (aromatic) and [MPyrr]Cl (non-aromatic) and (b) number of carbon atoms ( $C_n$ ) in the substituent alkyl group attached to the imidazolium ring of aprotic ionic liquids.

**Table 7.3.** The Adjustable parameters for fitting relative apparent molar enthalpy data ( $\phi_L$ ) of different aqueous solution of ionic liquid-salt systems using equation 7.3.

system	$10^{-7}q$	system	$10^{-7}q$
NaCl	$-5.42 \pm 0.12$	[MIM][BF <sub>4</sub> ]	$-10.50 \pm 0.24$
[MIM]Cl	$-0.45 \pm 0.01$	[MIM][BF <sub>4</sub> ]- NaBF <sub>4</sub>	$1.66 \pm 0.03$
[MIM]Cl- NaCl	$5.63 \pm 0.13$	[EMIM][BF <sub>4</sub> ]	$22.10 \pm 0.003$
[Py]Cl	$7.29 \pm 0.15$	[EMIM][BF <sub>4</sub> ]- NaBF <sub>4</sub>	$20.62 \pm 0.44$
[Py]Cl- NaCl	$21.20 \pm 0.49$	[BMIM][BF <sub>4</sub> ]	$-3.34 \pm 0.78$
[MPyrr]Cl	$-6.11 \pm 0.14$	[BMIM][BF <sub>4</sub> ]- NaBF <sub>4</sub>	$19.53 \pm 0.42$
[MPyrr]Cl- NaCl	$-3.68 \pm 0.09$	[HMIM][BF <sub>4</sub> ]	$-6.45 \pm 0.15$
NaBF <sub>4</sub>	$19.31 \pm 0.42$	[HMIM][BF <sub>4</sub> ]- NaBF <sub>4</sub>	$18.50 \pm 0.40$

### 7.3.6. The Enthalpic Interaction Parameters ( $H_{IL-IL}^E$ ):

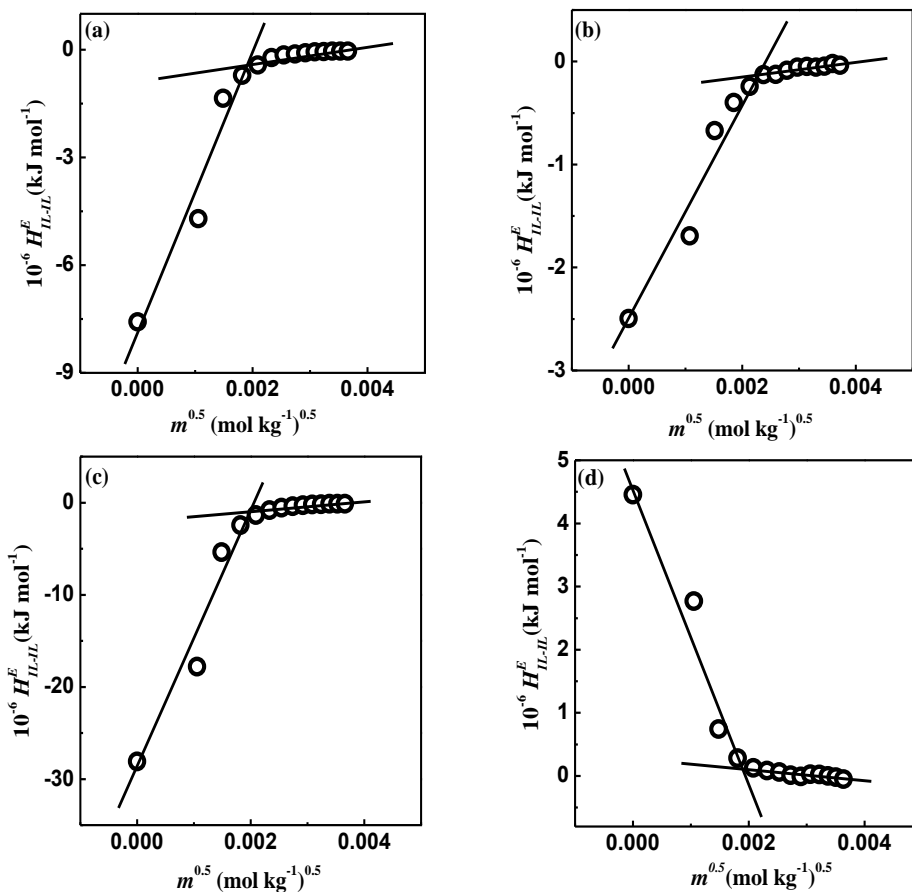
The unique characteristic of water retained in the water-rich region is examined. In the solute-rich composition range, solute molecule tends to cluster together. In their ternary solution, solute-solute interaction imparts the structuring of water. The quantification of intermolecular interactions between two ionic liquid molecules in terms of the interaction parameter is a model free graphical method, which was introduced by Koga and co-workers for both aqueous and non-aqueous solutions of electrolytes.<sup>[36-39]</sup> The quantitative information on the mixing schemes, solvent reorganizations, effect of solutes on the solvent and solute-solute interactions have been find out qualitatively by using the following expression:

$$H_{IL-IL}^E = (1 - x_{IL}) \left( \frac{\partial H_{IL}^E}{\partial x_{IL}} \right) \quad (7.4)$$

Where,  $H_{IL-IL}^E$  is known as the enthalpic interaction parameter, the value of which can be accurately estimated using a graphical method to avoid any fitting program.<sup>[36-39]</sup>

The  $H_{IL-IL}^E$  parameters are demonstrated in the **Figure 7.11** and **7.12** for the mixing of ionic liquids (aqueous solution) and salts (aqueous solution). We noted a sharp change in the  $H_{IL-IL}^E$  values plotted versus the square root of molality,  $m^{0.5}$ . The values of  $m^{0.5}$  at which transition takes place in the systems studied here and the corresponding  $H_{IL-IL}^E$  values are listed in **Table 7.4**. We have noted that the transition takes place at the same composition for all the  $\text{Cl}^-$  anion based protic ionic liquids but the interactions differ. The interactions are much stronger in the [Py]Cl as compared to the [MIM]Cl and followed by [MPyrr]Cl. It evident that the aromatic cation rings shows strong cation-

cation interactions, whereas non aromatic cationic rings do not. While moving towards the  $[\text{BF}_4]^-$ -based ionic liquids, going from protic to aprotic ionic liquids the interactions become stronger (the values are tabulated in **Table 7.4**).

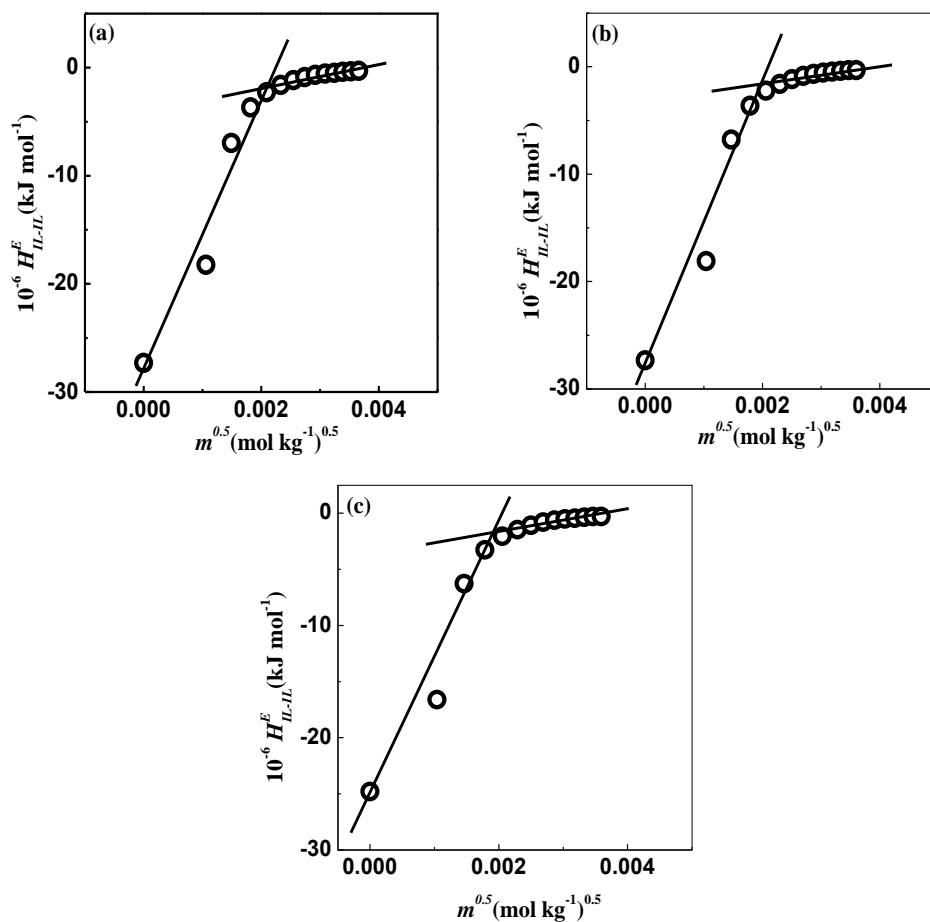


**Figure 7.11.** The plots of  $H_{IL-IL}^E$  parameters versus  $m^{0.5}$  for the protic ionic liquid-salt systems (a)  $[\text{MIM}]\text{Cl}-\text{NaCl}$ , (b)  $[\text{MIM}][\text{BF}_4]-\text{NaBF}_4$ , (c)  $[\text{Py}]\text{Cl}-\text{NaCl}$  and (d)  $[\text{MPyr}]\text{Cl}-\text{NaCl}$ .

**Table 7.4.** The values of the enthalpic interaction parameters ( $H^E_{IL-IL}$ ) and the corresponding molality for the studied systems at intersections.

Ionic liquid systems	$10^{-6}H^E_{IL-IL}$ (kJ mol <sup>-1</sup> )	$m^{0.5}$ (mol kg <sup>-1</sup> ) <sup>0.5</sup>
[MIM]Cl-NaCl	-0.41	0.0019
[Py]Cl-NaCl	-1.48	0.0019
[MPyrr]Cl-NaCl	0.12	0.0019
[MIM][BF <sub>4</sub> ]-NaBF <sub>4</sub>	-0.12	0.0023
[EMIM][BF <sub>4</sub> ]-NaBF <sub>4</sub>	-1.20	0.0021
[BMIM][BF <sub>4</sub> ]-NaBF <sub>4</sub>	-1.35	0.0020
[HMIM][BF <sub>4</sub> ]-NaBF <sub>4</sub>	-2.11	0.0020

It is also expected that alkyl chain length attached to the imidazolium ring is account for an increase in the  $H^E_{IL-IL}$  values. In the present case, the substitution from [MIM][BF<sub>4</sub>]protic to -C<sub>2</sub>H<sub>5</sub>to -C<sub>4</sub>H<sub>9</sub> to -C<sub>6</sub>H<sub>13</sub> alkyl group containing aprotic ionic liquids the  $H^E_{IL-IL}$  values become more negative hence the interactions turn out to be more favorable. The cluster formation starts much early (lower molarity) in the aprotic ionic liquids. Also the interactions are stronger in case of higher alkyl chain containing cations as recommended by the  $H^E_{IL-IL}$  parameter. The trend of the  $H^E_{IL-IL}$  values for the Cl<sup>-</sup> anion based protic ionic liquids; [Py]Cl > [MIM]Cl > [MPyrr]Cl and for [BF<sub>4</sub>]<sup>-</sup> anion based protic and aprotic ionic liquids; [HMIM][BF<sub>4</sub>] > [BMIM][BF<sub>4</sub>] > [EMIM][BF<sub>4</sub>] > [MIM][BF<sub>4</sub>].



**Figure 7.12.** The plots of  $H_{IL-IL}^E$  parameters versus  $m^{0.5}$  for the protic ionic liquid-salt systems (a) [EMIM][BF<sub>4</sub>]-NaBF<sub>4</sub>, (b) [BMIM][BF<sub>4</sub>]-NaBF<sub>4</sub> and (c) [MIM][BF<sub>4</sub>]-NaBF<sub>4</sub>.

#### 7.4. Conclusions

The  $H_{IL}^E$  values of an ionic liquid in a salt solution have been measured and other quantities like  $H_{IL}^{E,\infty}$ ,  $\phi_L$ , and  $H_{IL-IL}^E$  and their deviation from ideality have been estimated at room temperature for the aqueous solution of ionic liquids, salts and their mixtures. The  $H_{IL}^E$  values reveal that the solvation of salts, protic and aprotic ionic liquids largely depend on the nature of cationic ring. The solvation of the protic ionic

liquids with the aromatic cationic ring is enthalpically unfavorable and reflected as positive  $H_{IL}^E$  values. We also observe a hydrophobic hydration in the aqueous solution of aprotic ionic liquids. On the other hand, the mixing of ionic liquids and salts shows different enthalpic behavior as compared to their aqueous solutions. In the present study we have demonstrated that the mixing of ionic liquids possessing aromatic cationic ring with the salt exhibit endothermic behavior (chaotrope) due to the strong cation-cation interactions, whereas the mixing of ionic liquid having non aromatic cationic ring with salt exhibit exothermic behavior (kosmotrope) resulting from the solvation.

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## **Chapter 8**

### **Conclusions**

*The overall conclusions of the experimental study in the present thesis are summarized in this chapter. The general applicability of the current observations and the future directives are briefly discussed. The present thesis brings about the realization that the characteristically complex nature of ionic liquids and their designability can be further harnessed to explore their applicability.*



In summary, we studied the effect of solvents on ionic liquids and their physico-chemical properties. The ionic liquids were chosen on the basis of their interesting properties, applications and environmental feasibility. In the present thesis we focused our investigation on the apparent partition coefficient, conductance, ionicity, viscosity, ion-ion and ion-solvent interaction study of binary mixture of ionic liquids with molecular solvents. The salient features of these investigations are:

- + The work presented here accentuates that apparent partition coefficient ( $\log P$ ) of ionic liquids is concentration dependent and predominantly influenced by the nature of anions. The important outcome reached from the results depicts that  $[\text{HSO}_4]^-$ -based ionic liquids behave differently as a function of concentration as compared to the  $[\text{EtSO}_4]^-$ -based ionic liquids. A flipping in  $\log P$  values as a function of concentration has been observed for the  $[\text{HSO}_4]^-$ -based ionic liquids due to the formation of aggregates, whereas the  $[\text{EtSO}_4]^-$ -based ionic liquids possess linear relation of  $\log P$  with concentration. The anomalous behavior of  $[\text{HSO}_4]^-$  and  $[\text{EtSO}_4]^-$ -based ionic liquids can be correlated with the hydrogen bond accepting basicity ( $\beta$ ) of these anions as well as the possibility of aggregate formation. Changing the cationic core from imidazolium to pyridinium significantly modifies the  $\log P$  values due to  $\pi$ - $\pi$  interactions. The alkyl chain length in cationic and anionic part of ionic liquids also affects the  $\log P$  values as hydrophobicity of anions increases in order of;  $[\text{HSO}_4]^- < [\text{EtSO}_4]^- < [\text{BuSO}_4]^-$ . At last, the  $\log P$

can illustrate the scale of hydrophobicity or hydrophilicity of ionic liquids. The partition coefficient of any solute is dependent on the intra-solute or solute-solvent interactions. Therefore, the solute solvent interactions further explored by the conductance measurements in the next chapter.

✚ We have further investigated these intermolecular interactions in the mixtures of ionic liquid and co-solvent by conductance and IR spectroscopy. We report a higher  $\Lambda_m$  of the  $[\text{HSO}_4]^-$ -based ionic liquids in polar protic solvents (water and methanol) as compared to the  $[\text{EtSO}_4]^-$ -based ionic liquids, even though the  $[\text{HSO}_4]^-$ -based ionic liquids possess higher association constant in water than in methanol. As the length of alkyl chain of alcohols (co-solvent) increased, the  $\Lambda_m$  diminishes and become less pronounced. The observed increase in  $\Lambda_m$  for  $[\text{HSO}_4]^-$ -based ionic liquids in water is mainly attributed to the Grotthuss mechanism. The infrared spectroscopic data confirms a strong hydrogen bonding between cation and anion of  $[\text{HSO}_4]^-$  and  $[\text{EtSO}_4]^-$ -based ionic liquids. The hydrogen bonds also exist between ions and solvent molecules. Comparatively, anions of ionic liquids are exhibit favorable interactions with molecular solvents particularly with the water and alcohols via hydrogen bonding. We report a correlation between  $\Lambda_m$  and properties such as diffusion coefficient,  $D^o$  and transport number,  $t$  and ionic mobility,  $\mu$  of cations and anions of ionic liquids in their aqueous solutions. The present thesis reveals that the ionic liquids with highly basic anions show significantly

high conductance in their binary mixtures with molecular solvents. This provides a better understanding towards the better implementation of ionic liquids in the electrochemical processes.

- ✚ We also report that the substitution of the  $\text{Br}^-$  and  $\text{BF}_4^-$ , anions by  $[\text{HSO}_4]^-$  and  $[\text{EtSO}_4]^-$  in the imidazolium-based aprotic ionic liquids significantly reduces the ionicity in their aqueous solutions resemble to those offered by some of the aqueous solution of protic ionic liquids. Despite of having lesser ionicity, the  $\Lambda_m$  values of  $[\text{HSO}_4]^-$ -based aprotic ionic liquids are exceptionally high possible due to the Grotthuss mechanism.
- ✚ The future studies of reactions in ionic liquids with co-solvents and physico-chemical properties of ternary mixtures of ionic liquids may greatly benefit from the efforts to delineate the conductance measurement of  $[\text{EMIM}][\text{HSO}_4]$  and  $[\text{EMIM}][\text{EtSO}_4]$  in their ternary mixtures prepared herein. The dependence of conductance has been seen mainly on the viscosity of the binary mixtures of solvents (molecular solvent + water).

The study of conductance measurements, ionic association and ionicity of alkyl sulfate based ionic liquids in the binary mixtures with molecular solvents reveals the significance of anions. The anomalous observation for  $[\text{HSO}_4]^-$ -based ionic liquids is due to the high basicity and the possibility of the strong hydrogen bonding of the anions. The conductance measurement in binary and ternary mixtures can be helpful for physical chemists who desire to investigate the high conductive medium for

electrochemical processes. An organic chemist can also explore these mixtures as reaction media for carrying out their reactions.

- + Furthermore, we quantify the enthalpy of the ion-ion and ion-solvent interactions. We obtain negative enthalpy values with 1-butanol molecules as compared to the other alcohols. This indicates the presence of favorable interactions between ionic liquid and alcohol molecules. In terms of interactions, 1-butanol has the comparative values of  $\alpha$  and  $\beta$  ( $\alpha \approx \beta \approx 0.84$ ) hence, are more prone to form collective hydrogen bonding with both cation and anion of an ionic liquid. Interestingly, ethylated residuals on both the cations of the ionic liquid and the alcohol molecules do not follow the trend exhibited by other ionic liquid-alcohol systems. This thesis also emphasizes that the thermal behavior expressed in terms of the  $H_{IL}^E$  values of ionic liquids in various linear alcohols is governed by the increasing hydrophobicity of the alkyl group attached to the cation of an ionic liquid and the alcohol molecules.
- + We report that the variation in  $H_{IL}^E$  values depend on the difference in inter-ionic interactions as well as packing between the ionic liquids and ethylated solvents. The hydrogen bond accepting basicity ( $\beta$ ) plays an important role in determining the  $H_{IL}^E$  values. The linear solvation energy relations of  $H_{IL}^E$  values with solvatochromic parameters of solvents evident that the permutation of  $\alpha$ ,  $\beta$ , and  $n^*$  is effective to represent the excess partial molar enthalpy values of [EMIM][BF<sub>4</sub>]-ethylated solvent systems, whereas for [BMIM][BF<sub>4</sub>]-

ethylated solvent systems, a permutation of  $E_T^N$ ,  $\alpha$ , and  $\beta$  is significant. The structural orientation of the ethylated solvent molecules around the ionic liquids stabilizes ionic liquid-ethylated solvent systems. The thermal behavior of these system changes as the molecular structures and the different solvatochromic parameters of the ethylated solvents..

✚ The nature of cation-cation interactions between the cationic rings of protic and aprotic ionic liquids or cation of ionic liquid and cation of salt describes in detail which is one of the important physical aspects of the ionic liquids. The ionic interactions of the aqueous solution of ionic liquids with the aqueous solution of salts (inorganic salts) has been thoroughly investigated in term if  $H_{IL}^E$  values. It confirms that the solvation of salts, protic and aprotic ionic liquids largely depend on the nature of cationic ring. The solvation of the protic ionic liquids with the aromatic cationic ring is enthalpically unfavorable and reflected as positive  $H_{IL}^E$  values. Hydrophobic hydration in the aqueous solution of aprotic ionic liquids has been explained in terms of  $H_{IL}^E$  values. On the other hand, the mixing of ionic liquids and salts show different enthalpic behavior as compared to their pure aqueous solutions. The present thesis demonstrate that the mixing of ionic liquids possessing aromatic cationic ring with the salt exhibit endothermic behavior (chaotrope) due to the strong cation-cation interaction, whereas the mixing of ionic liquid having non aromatic cationic ring with salt exhibit exothermic behavior (kosmotrope) which results from the solvation.

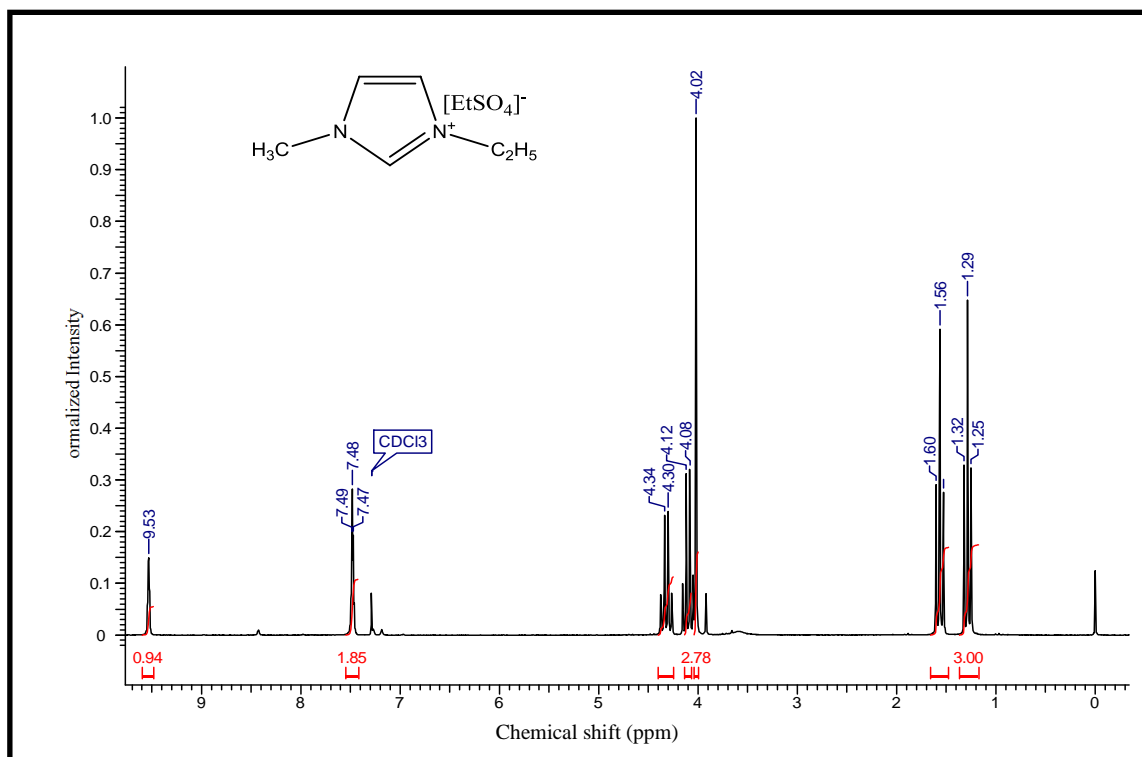
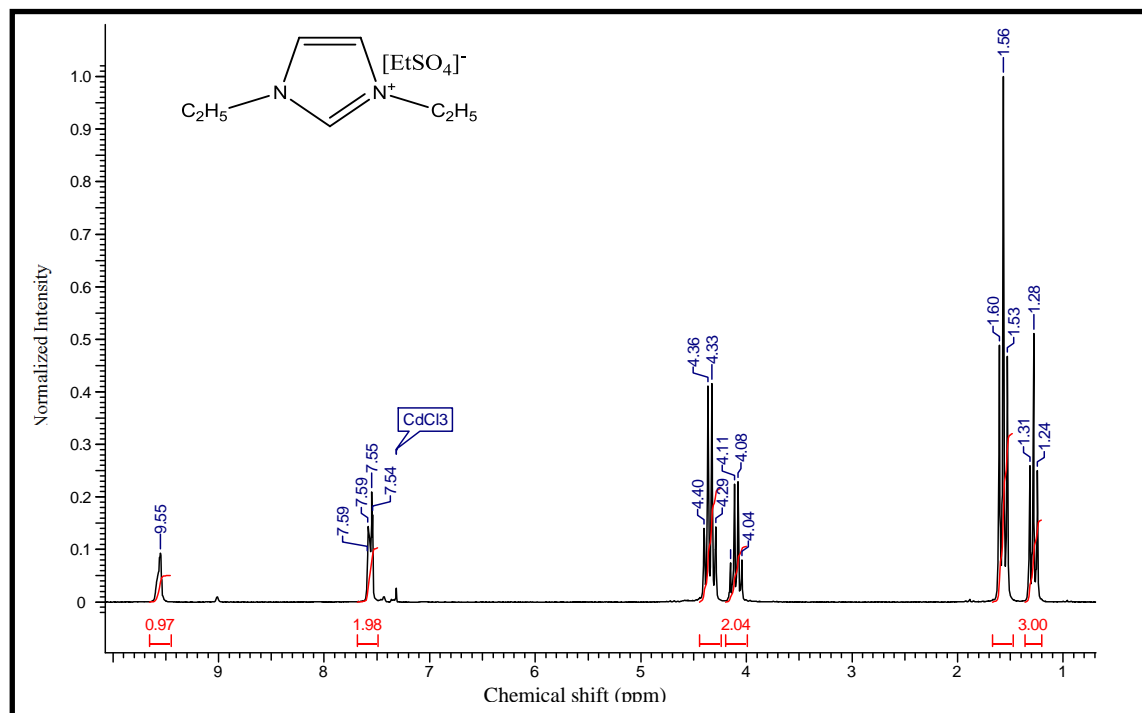
The work presented in the thesis demonstrates that the ionic liquids with more basic anions show interesting physico-chemical properties in their binary mixture with molecular solvents. The systematic study of the physico-chemical properties of ionic liquids in the presence of co-solvent can assist in better understanding of the interionic interactions and effect of solvents on the physico-chemical properties of the environment-benign media. Also a comprehensive database of the physico-chemical properties of all the ionic liquids synthesized till date is very important. The efforts to lower the cost of the ionic liquids would endow with a motivation for large-scale applications in industries. The investigations of the solvent effect on physico-chemical properties in the present study may be encouraging in future studies for enhancing the practical applications of ionic liquids.

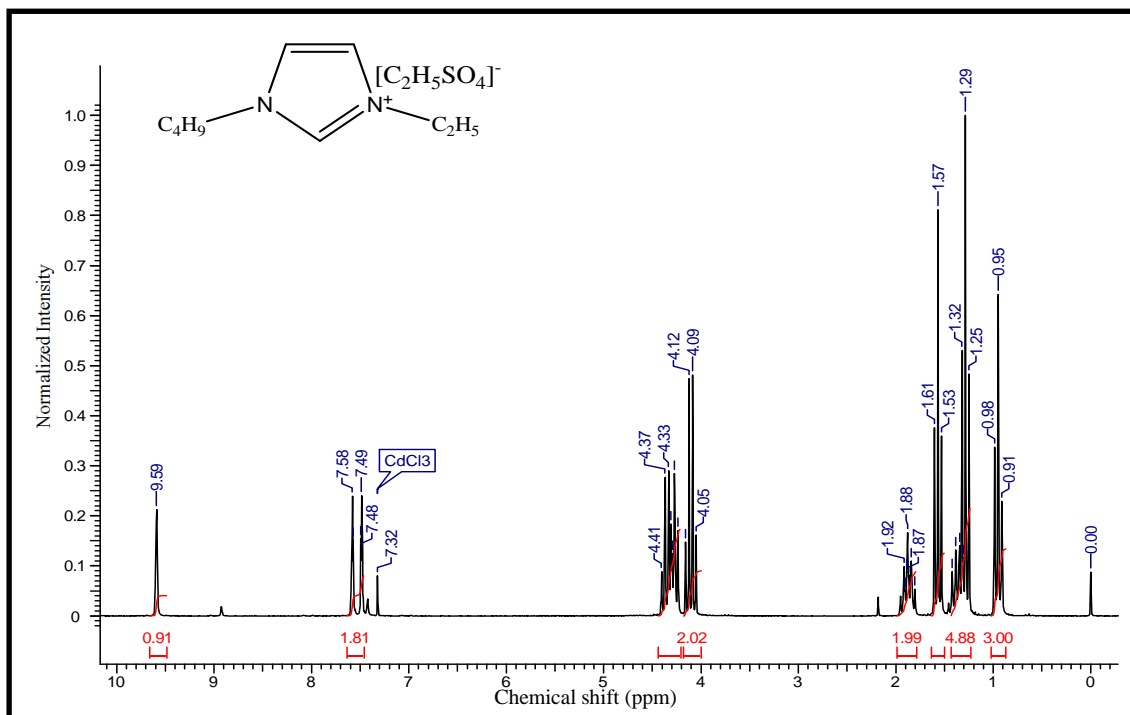
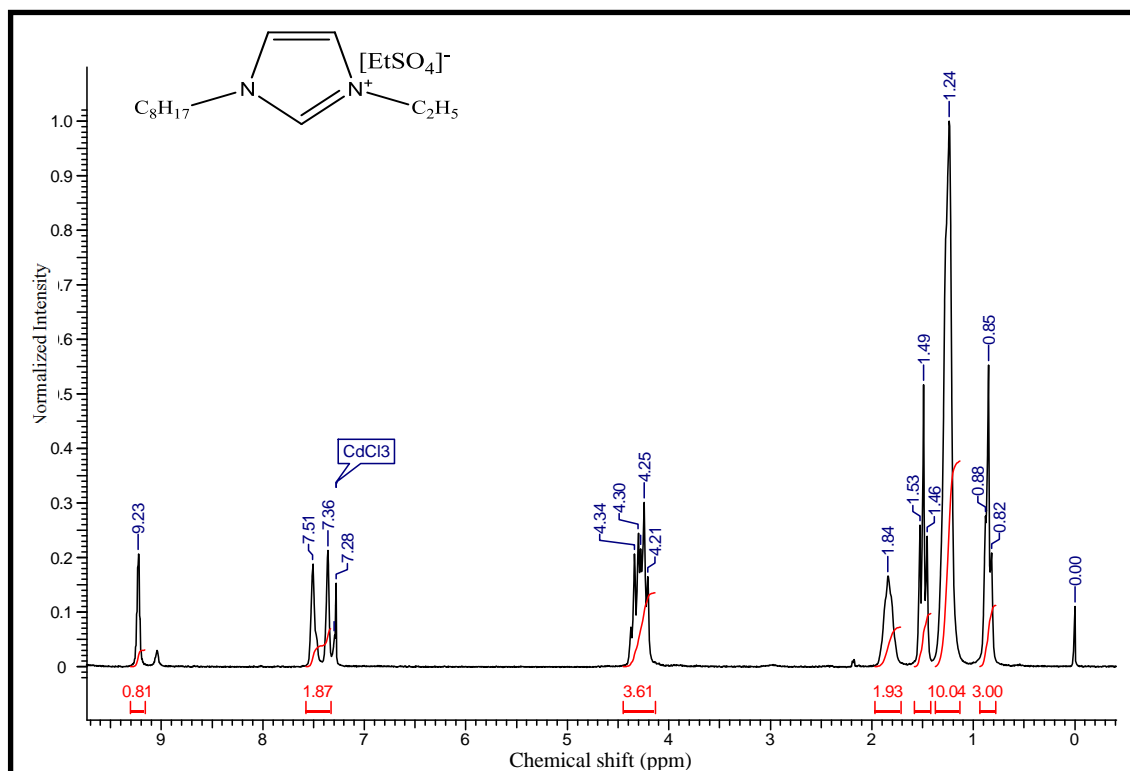


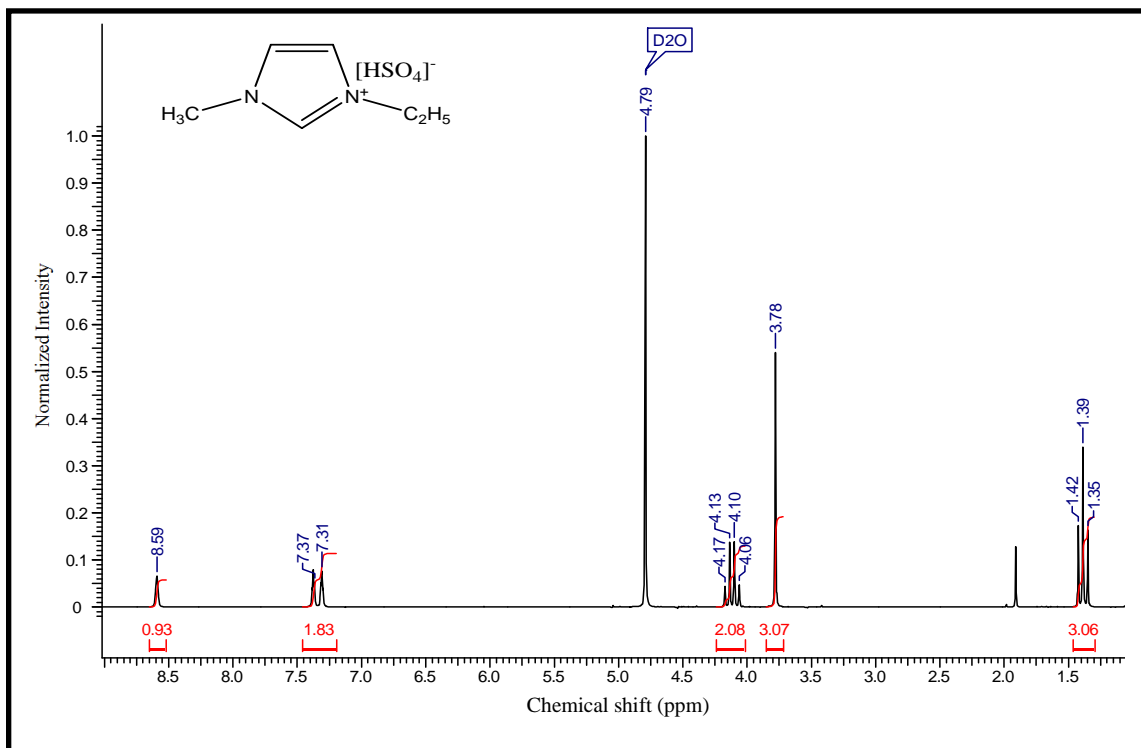
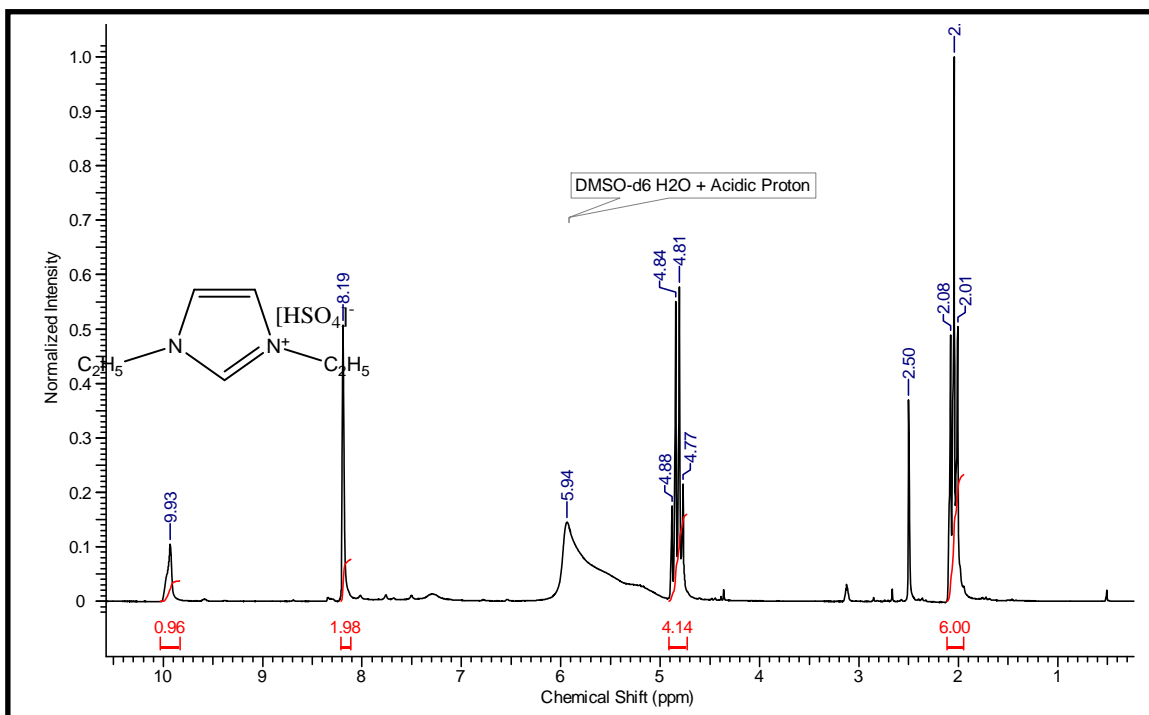
## ***Appendix A***

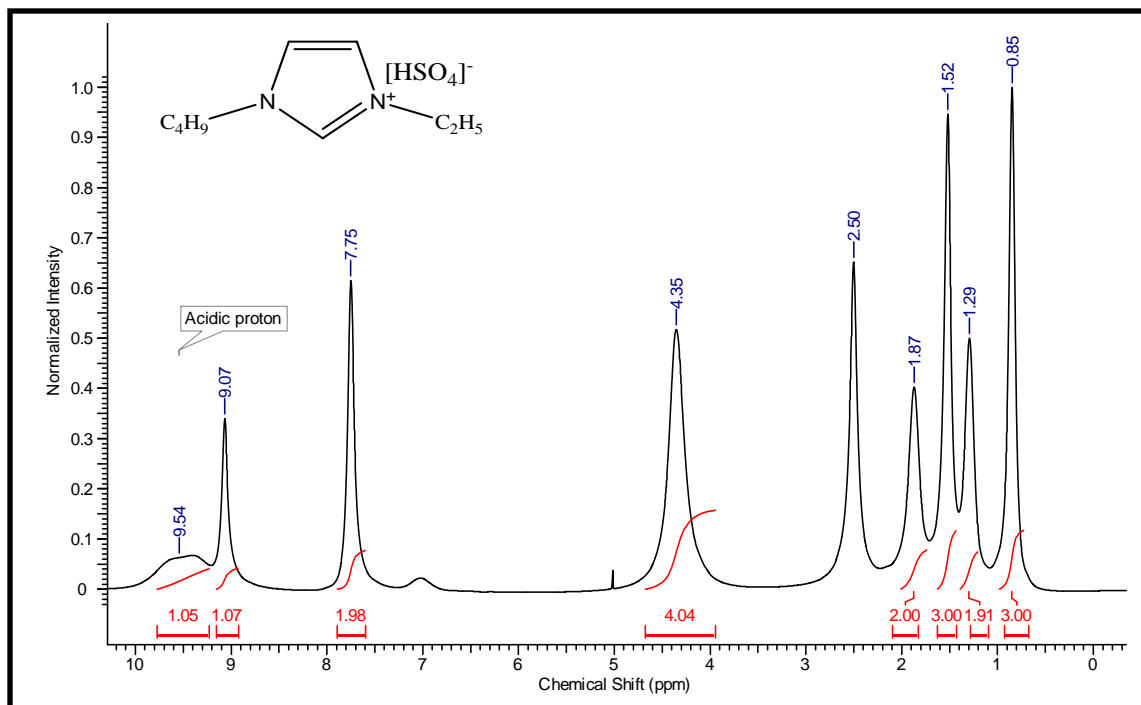
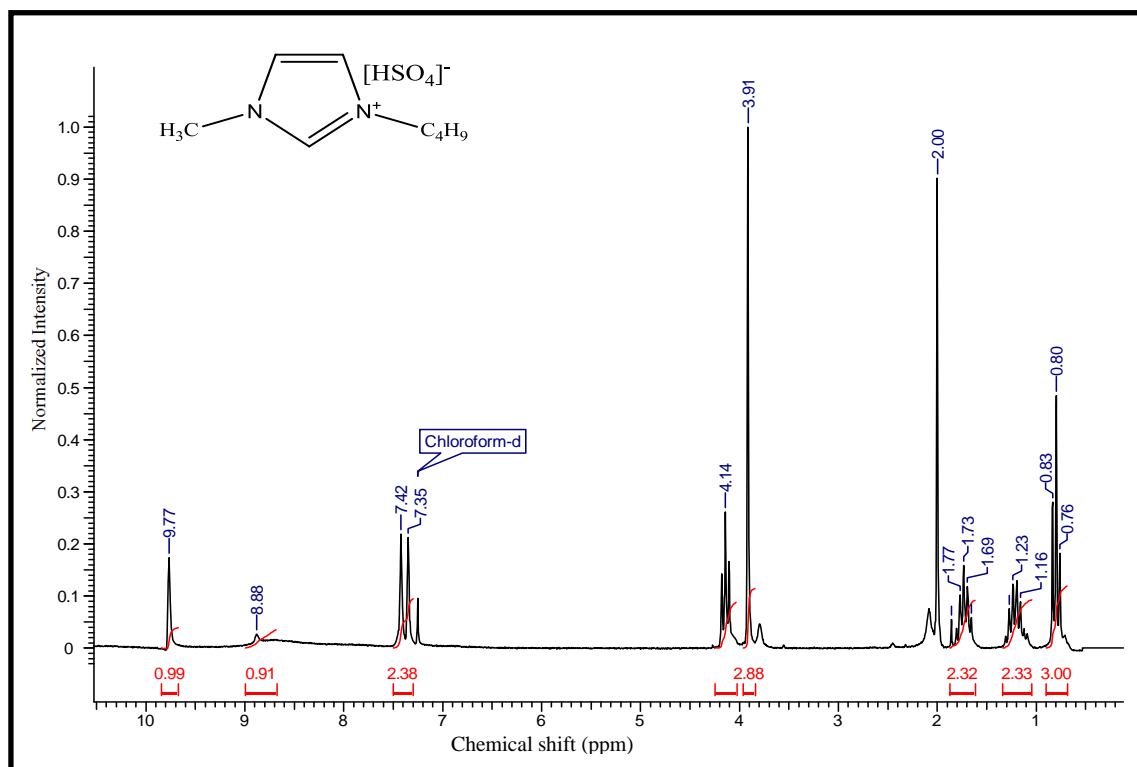
### ***NMR Spectra of Ionic Liquids***

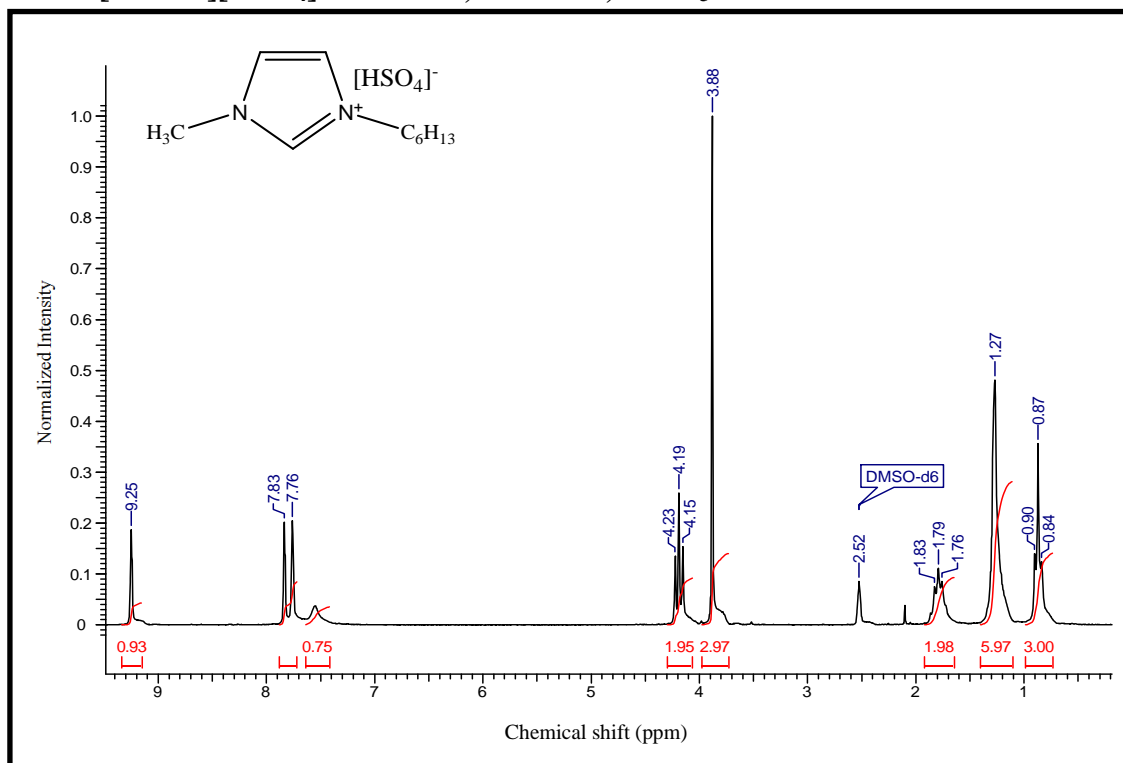
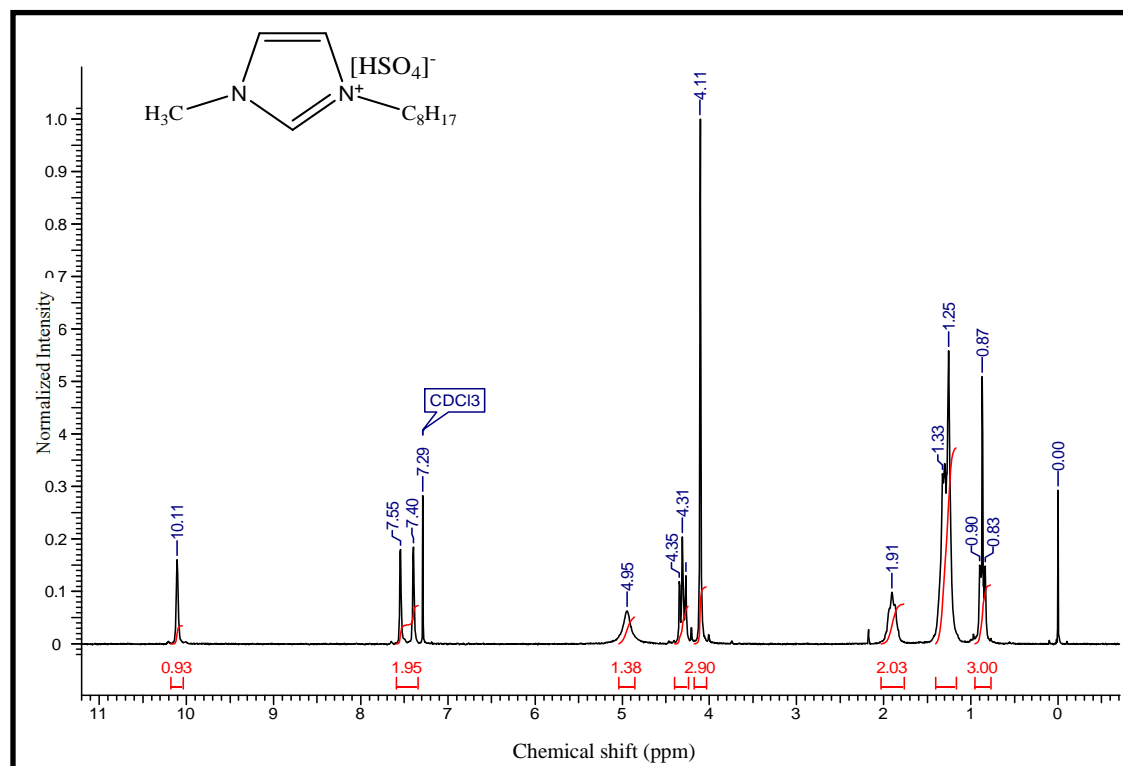


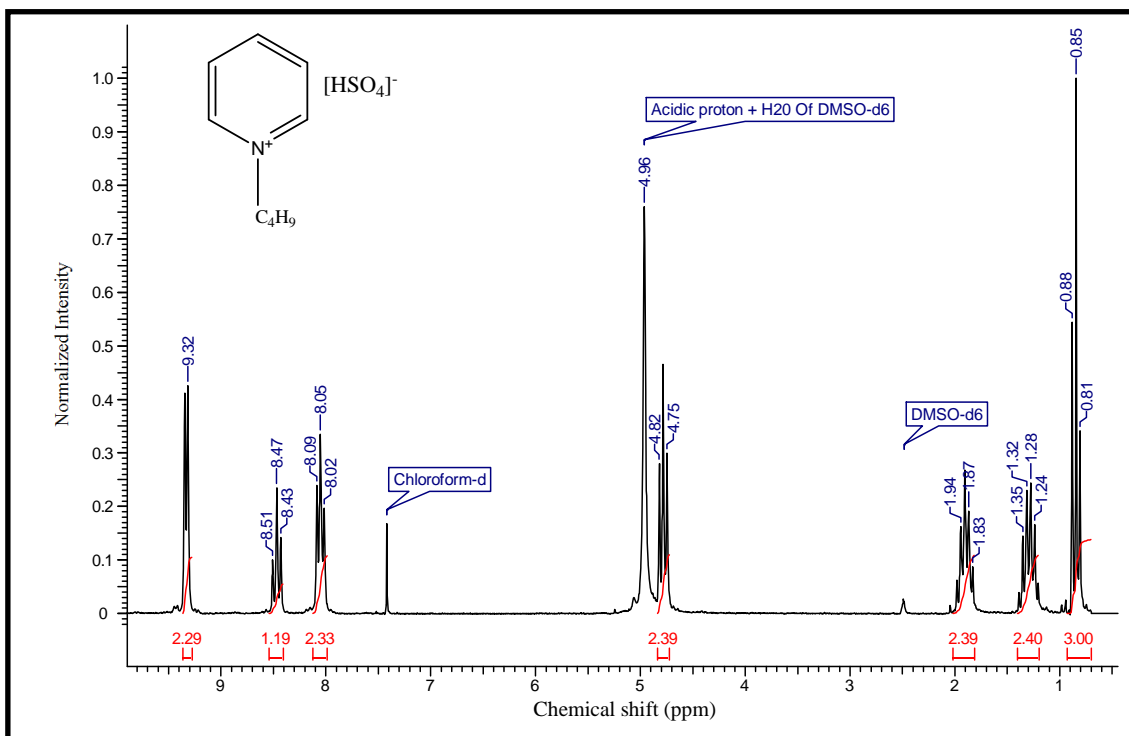
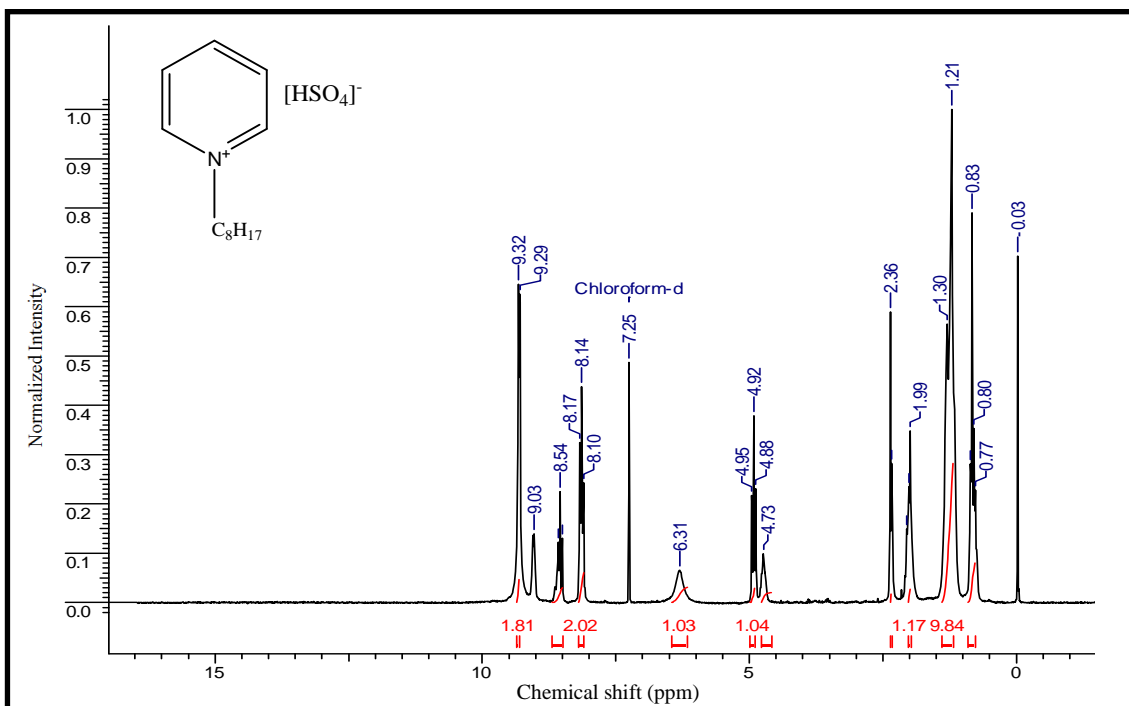
1. [EMIM][EtSO<sub>4</sub>] - <sup>1</sup>H NMR, 200 MHz, CDCl<sub>3</sub>2. [dEIM][EtSO<sub>4</sub>] - <sup>1</sup>H NMR, 200 MHz, CDCl<sub>3</sub>

3. [EBIM][EtSO<sub>4</sub>] - <sup>1</sup>H NMR, 200 MHz, CDCl<sub>3</sub>4. [EOIM][EtSO<sub>4</sub>] - <sup>1</sup>H NMR, 200 MHz, CDCl<sub>3</sub>

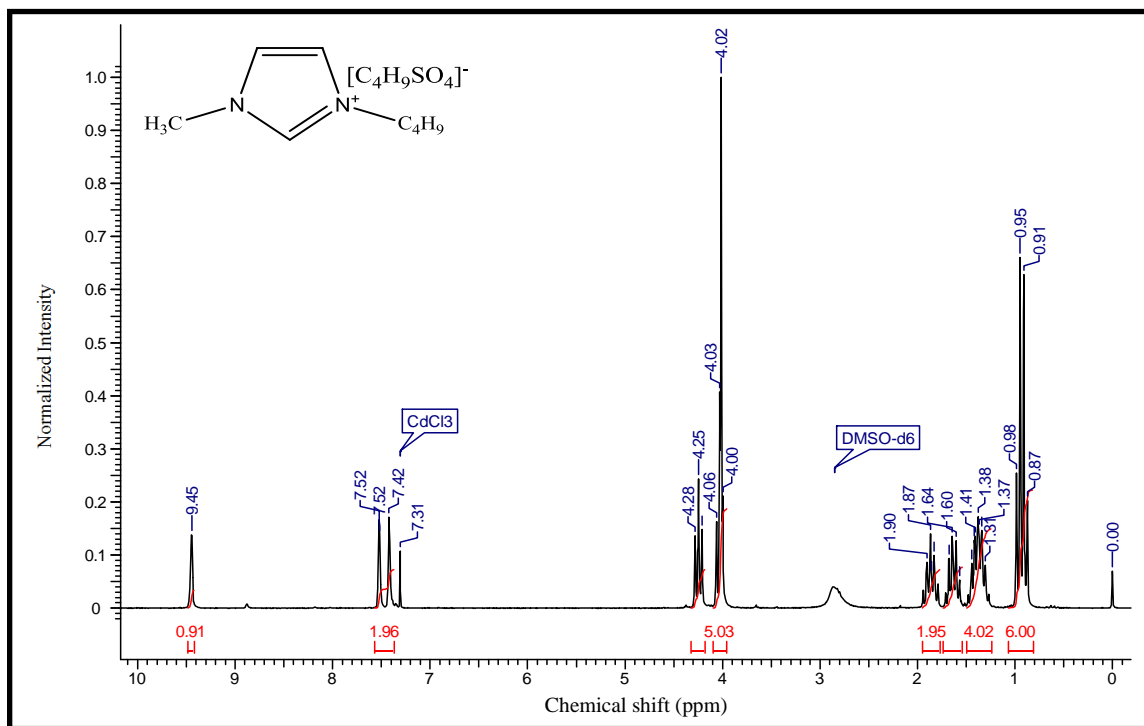
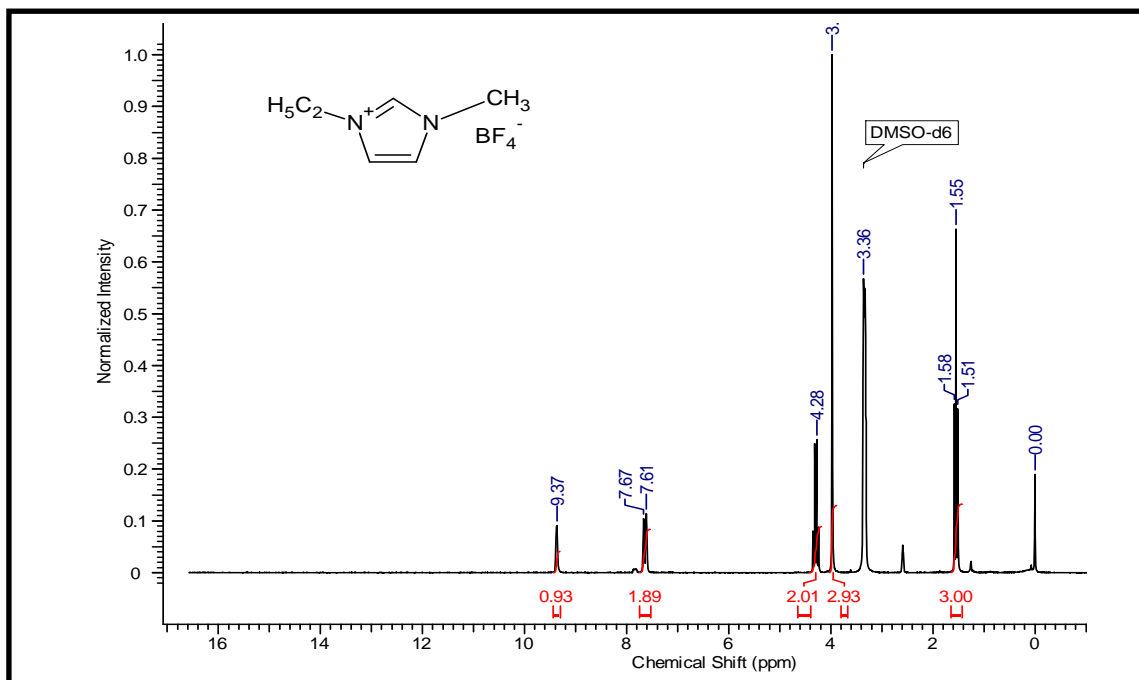
5. [EMIM][HSO<sub>4</sub>] - <sup>1</sup>H NMR, 200 MHz, D<sub>2</sub>O6. [dEMIM][HSO<sub>4</sub>] - <sup>1</sup>H NMR, 200 MHz, DMSO-d<sub>6</sub>

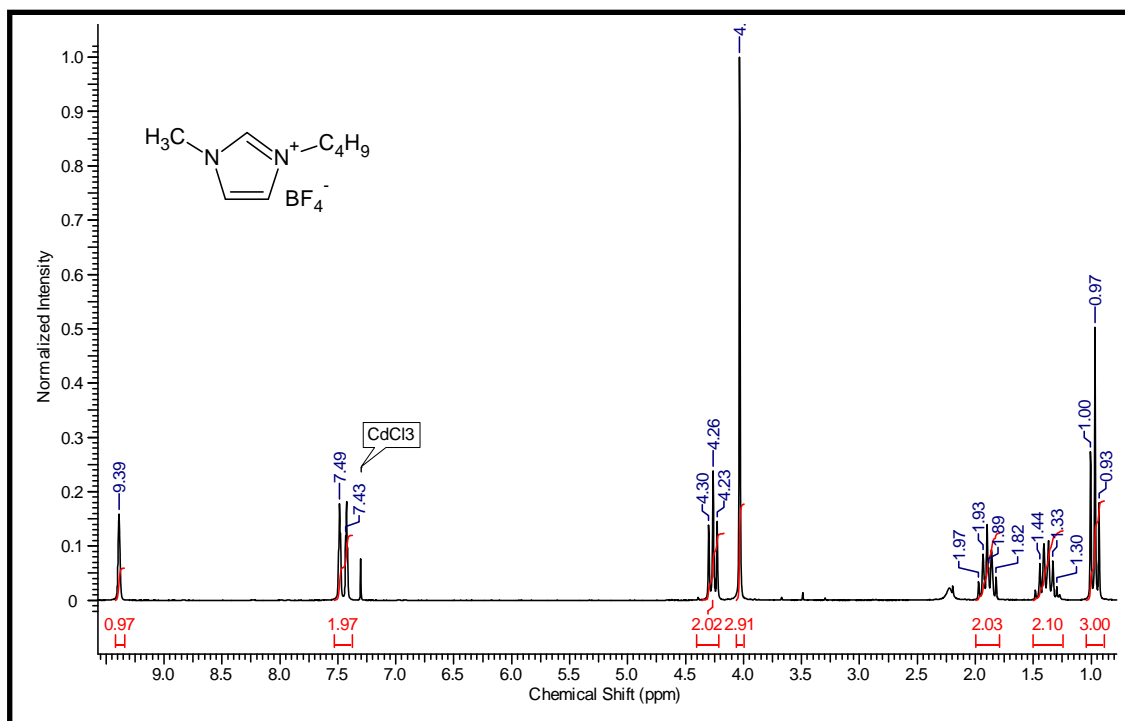
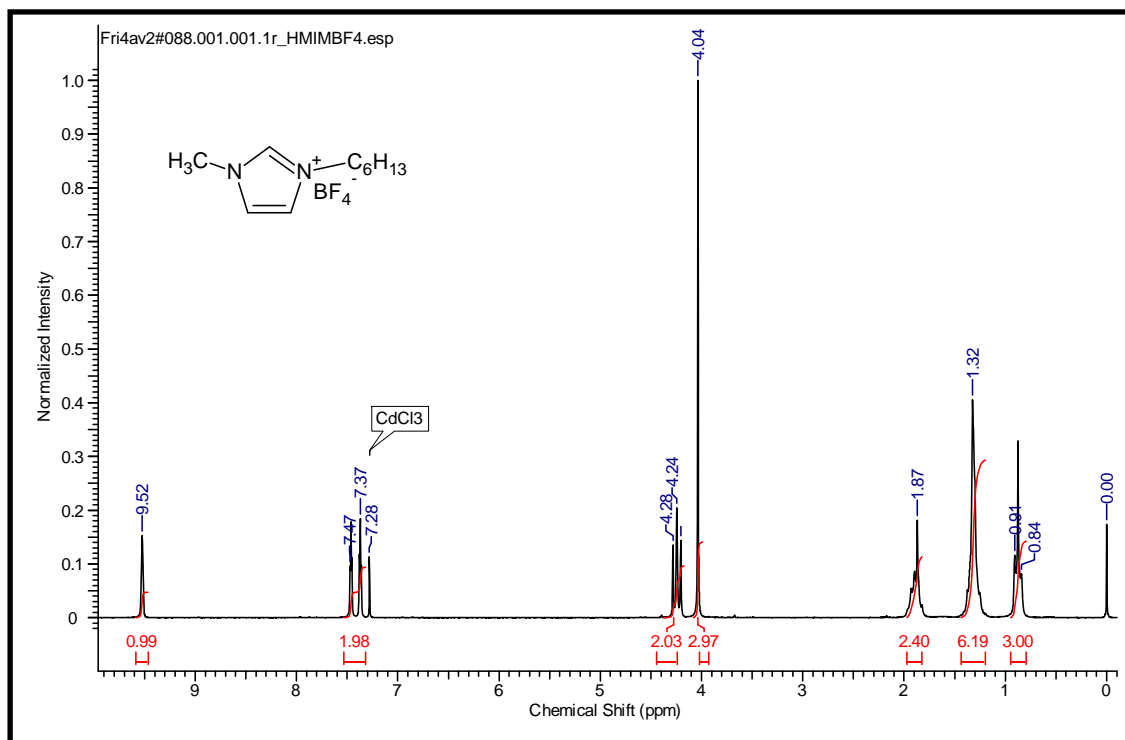
7. [BEIM][HSO<sub>4</sub>]<sup>-</sup> - <sup>1</sup>H NMR, 200 MHz, DMSO-d<sub>6</sub>8. [BMIM][HSO<sub>4</sub>]<sup>-</sup> - <sup>1</sup>H NMR, 200 MHz, CDCl<sub>3</sub> + DMSO-d<sub>6</sub>

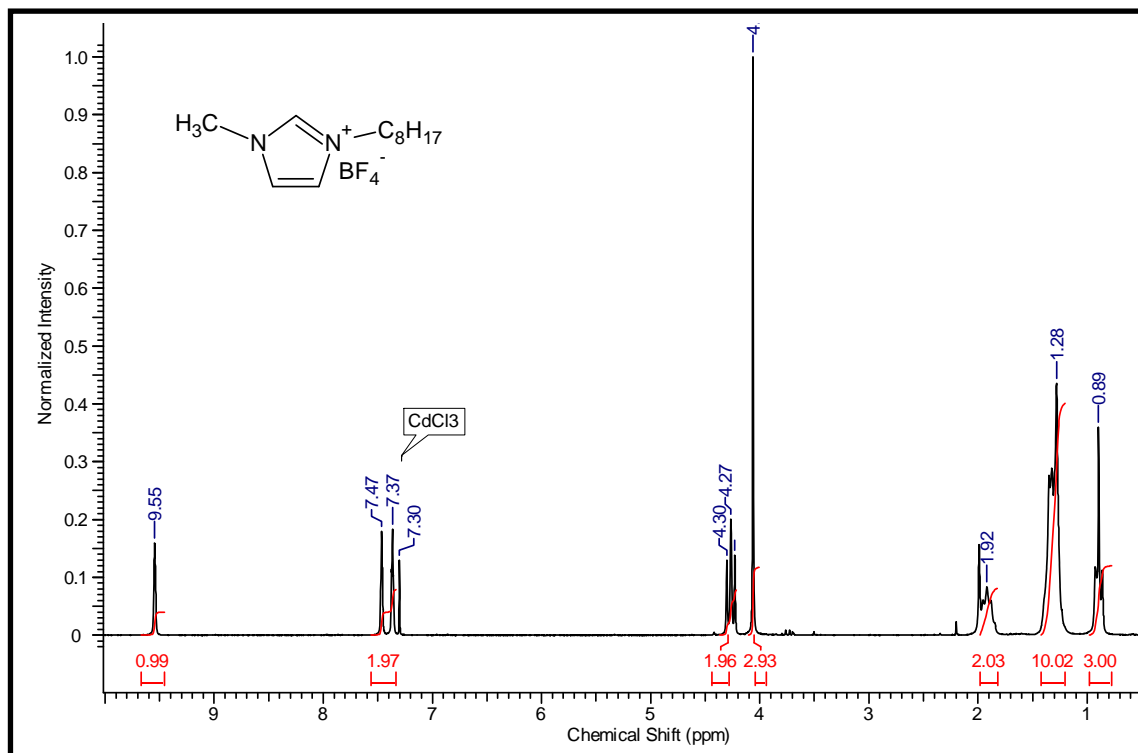
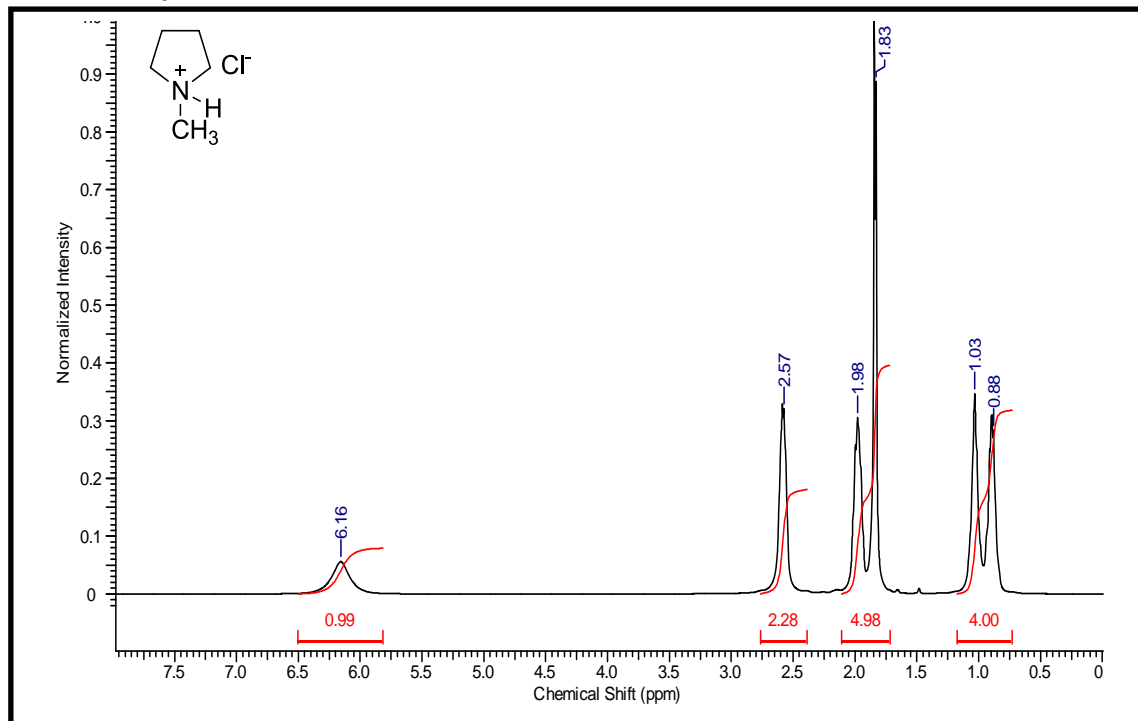
9. [HMIM][HSO<sub>4</sub>] - <sup>1</sup>H NMR, 200 MHz, CDCl<sub>3</sub> + DMSO-d<sub>6</sub>10. [OMIM][HSO<sub>4</sub>] - <sup>1</sup>H NMR, 200 MHz, CDCl<sub>3</sub>

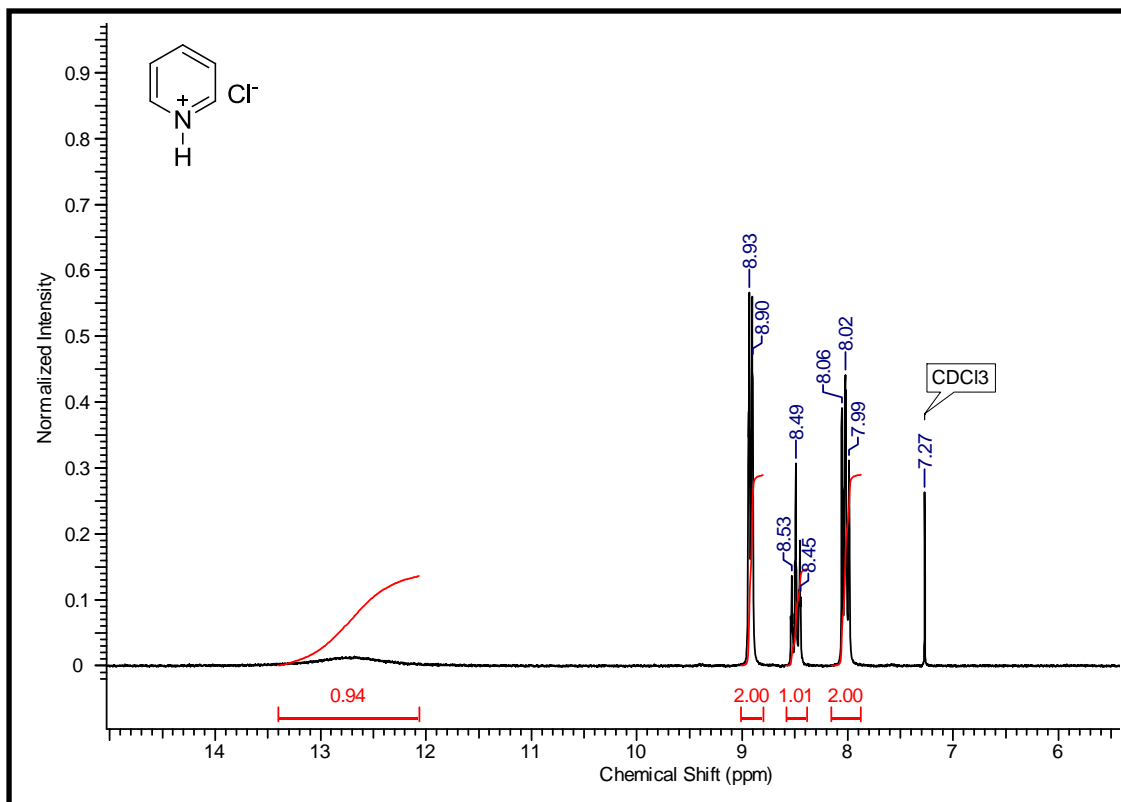
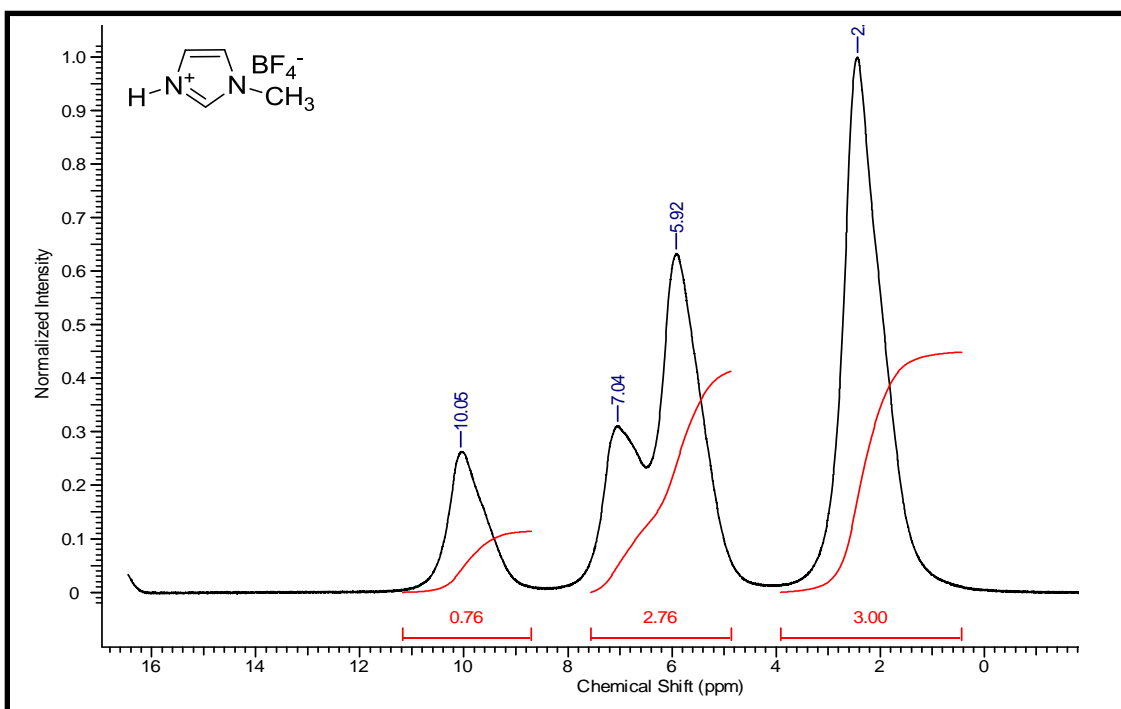
11. [BPy][HSO<sub>4</sub>] - <sup>1</sup>H NMR, 200 MHz, CDCl<sub>3</sub> +DMSO-d<sub>6</sub>12. [OPy][HSO<sub>4</sub>] - <sup>1</sup>H NMR, 200 MHz, CDCl<sub>3</sub>

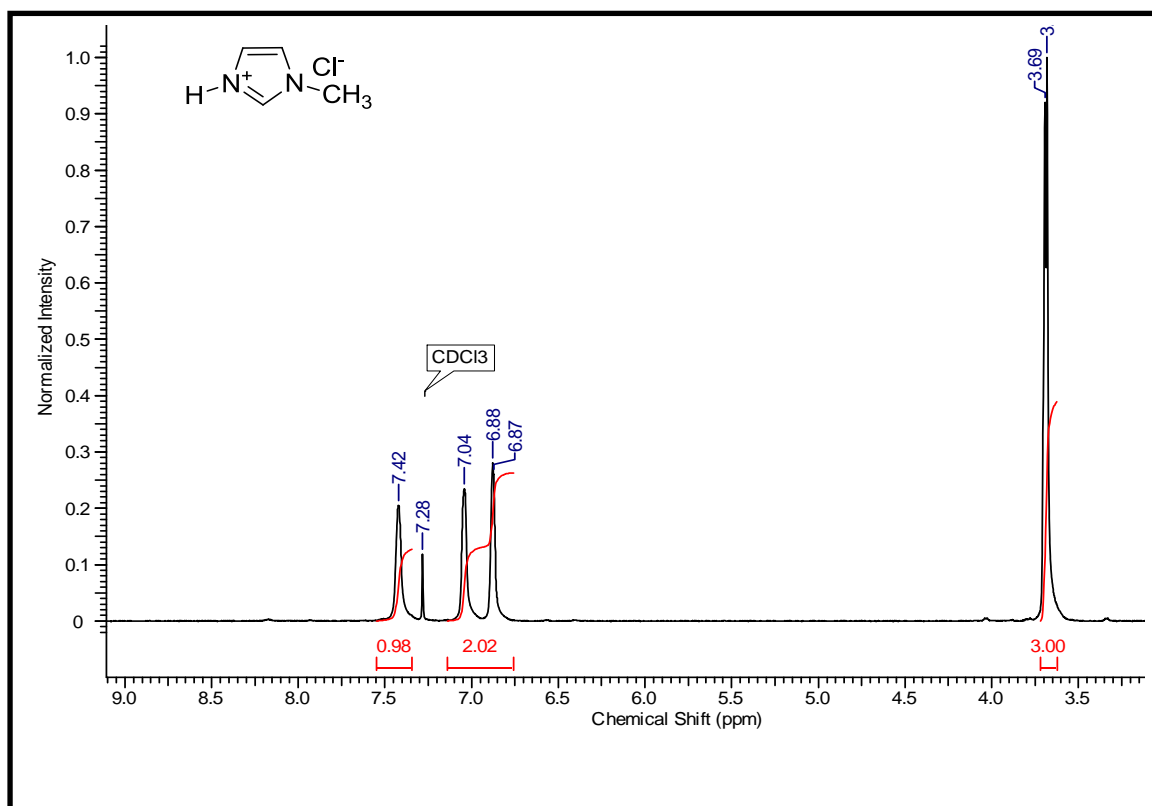


13. [BMIM][BuSO<sub>4</sub>] - <sup>1</sup>H NMR, 200 MHz, CDCl<sub>3</sub> +DMSO-d<sub>6</sub>14. [EMIM][BF<sub>4</sub>] - <sup>1</sup>H NMR, 200 MHz, DMSO-d<sub>6</sub>

15. [BMIM][BF<sub>4</sub>] - <sup>1</sup>H NMR, 200 MHz, CDCl<sub>3</sub>16. [HMIM][BF<sub>4</sub>] - <sup>1</sup>H NMR, 200 MHz, CDCl<sub>3</sub>

17. [OMIM][BF<sub>4</sub>] - <sup>1</sup>H NMR, 200 MHz, CDCl<sub>3</sub>18. [MPyrr]Cl - <sup>1</sup>H NMR, 200 MHz

19. [Py]Cl -  $^1\text{H}$  NMR, 200 MHz,  $\text{CDCl}_3$ 20. [MIM][ $\text{BF}_4$ ] -  $^1\text{H}$  NMR, 400 MHz

21. [MIM]Cl -  $^1\text{H}$  NMR, 200 MHz,  $\text{CDCl}_3$ 



## Appendix B

### List of Publications

✚ **Jain, P.;** Kumar A.

“Concentration-Dependent Apparent Partition Coefficients of Ionic Liquids Possessing Ethyl- and Bi-Sulphate Anions”

*Phys. Chem. Chem. Phys.*, **2016**, *18*, 1105-1113.

✚ Rai, G.; **Jain P.;** Kumar A.

”Isothermal Titration Calorimetric Study of the Ionic Liquid Solutions in Alcohols at Extreme Dilutions: An Investigation of Ion-Solvent Interactions”

*J. Solution Chem.*, **2016**, *45*, 1313-1331.

✚ **Jain, P.;** Kumar A.

“Comparable Ionicity of the Solutions of Aprotic and Protic Ionic Liquids by Anion Substitution”

*J. Solution Chem.* (Accepted).

✚ **Jain, P.;** Kumar A.

“Probing the Solute-Solvent Interactions in the Binary Mixtures of Ionic Liquids by Conductance, Viscosity and IR Spectroscopy”

*(J. Mol. Liq., Manuscript under revision).*

✚ **Jain, P.;** Kumar A.

“Molar Conductance of Ethyl and Bi-Sulphate-Based Ionic Liquids in their Ternary Mixtures with Molecular Solvents”

(Manuscript under preparation)

✚ **Jain, P.;** Kumar A.

“Measurement of Excess Partial Molar Enthalpy and Ion-Ion Interactions of Ideal Mixing of Ionic Liquid-Salt Mixtures”

(Manuscript under preparation)

✚ **Jain, P.;** Kumar A.

“An Enthalpic Investigation of Ion-Ion and Ion-Solvent Interactions and Packing of Ionic Liquids with Ethylated Solvents”

(Manuscript under preparation)



## *Appendix C*

### *Poster and Oral Presentations*

- Presented poster at “**6<sup>th</sup>-International IUPAC Conference on Green Chemistry**”, organized by International Union of Pure and Applied Chemistry (IUPAC) at Venice, Italy from 4<sup>th</sup>-8<sup>th</sup> September, 2016.
- Won **Best Poster Award** for Poster presented at “National Science Day” organized by CSIR-National Chemical Laboratory, Pune on 25<sup>th</sup> & 26<sup>th</sup> February, 2016.
- Poster presented at “National Conference on ILCEE” organized by CSIR-National Chemical Laboratory, Pune from 16<sup>th</sup>-17<sup>th</sup> December, 2015.
- Poster presented at “17<sup>th</sup> CRSI National Symposium in Chemistry (NSC-17)” held at CSIR- National Chemical Laboratory, Pune from 6<sup>th</sup> & 8<sup>th</sup> February, 2015.
- Poster presented at “National Science Day” celebrated at CSIR- National Chemical Laboratory, Pune on 25<sup>th</sup> & 26<sup>th</sup> February, 2015.
- Poster presented at “16<sup>th</sup> CRSI National Symposium in Chemistry (NSC-16)” organized by IIT Mumbai from 7<sup>th</sup> - 9<sup>th</sup> February, 2014.



## ***Erratum***