ENTHALPY EFFECTS IN IONIC LIQUIDS
AND
MIXING SCHEMES IN AQUEOUS IONIC SYSTEMS

A THESIS SUBMITTED TO THE
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BY

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DECLARATION

I hereby declare that the work incorporated in the thesis entitled “**Enthalpy Effects in Ionic Liquids and Mixing Schemes in Aqueous Ionic Systems**” submitted for the degree of Doctor of Philosophy to the University of Pune, has been carried out by me at the Physical and Materials Chemistry Division, National Chemical Laboratory, Pune from January, 2009 to April, 2012 under the supervision of Dr. Anil Kumar (Research Supervisor). The work is original and has not, in full or in part, formed the basis for the award of any degree, diploma, associateship, fellowship, titles in this or any other University or other institution of higher learning. I further declare that the results presented in the thesis and the considerations made therein contribute to the advancement of the knowledge in the field of Chemistry, in general and to the field of ionic liquids, in particular.

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CERTIFICATE

Certified that the work incorporated in the thesis entitled “Enthalpy Effects in Ionic Liquids and Mixing Schemes in Aqueous Ionic Systems” submitted by Ms. Gitanjali Rai for the degree of Doctor of Philosophy to the University of Pune, is carried out by the candidate under my supervision in the Division of Physical and Materials Chemistry, National Chemical Laboratory, Pune. Such materials as has been obtained from other sources have been duly acknowledged in the thesis.

Dr. Anil Kumar
(Research Supervisor)

Date:
Place: Physical and Materials Chemistry Division,
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Pune- 411 008

To

All of them, who have been a part of this journey

&

My son "ANHAD", who taught me what patience is all about!!

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Acknowledgements

> ***"Thou hast given so much to me, give one thing more,- a grateful heart; Not thankful when it pleaseth me, As if thy blessings had spare days, But such a heart whose pulse may be thy praise" (anonymous)***

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At the end, we are so often caught up in our destinations that we forget to appreciate the journey, especially the goodness of the people we meet on the way. Appreciation is a wonderful feeling, don't overlook it.

[Gitanjali Rai]

Abstract

ENTHALPY EFFECTS IN IONIC LIQUIDS AND MIXING SCHEMES IN AQUEOUS IONIC SYSTEMS

The present thesis is concerned with the enthalpic quantification of ionic liquid (IL) solutions. ILs have recently emerged as potent alternative for replacing the volatile organic solvents (VOCs) causing serious environmental pollution. ILs are considered suitable alternatives because of their useful properties like negligible vapor pressure, recyclability, large electrochemical windows, catalytic properties, and long liquidus range rendering them to be useful in a variety of applications in chemical transformations, chemical processes, separation processes, energy devices etc.

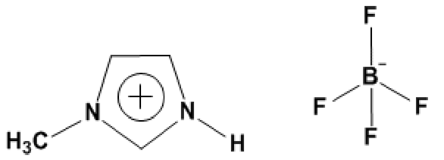
An IL is consisted of a cation mostly organic and an anion either organic or inorganic in nature. Unfortunately, many ILs are viscous in nature and it is established by experiments that chemical processes are hindered by viscous behavior of these ILs. It is possible, however, to reduce the viscosity of ILs by several times by adding a co-solvent. The sharp reduction in viscosity is the consequence of the dramatic changes in the ion-ion and ion-solvent interactions operating in IL-cosolvent systems.

Chapter 1 deals with the introduction of ILs. This chapter is divided into two parts: Part 1 introduces ionic liquids to the readers, while Part 2 provides the critical information on ILs like structures, vapor pressure, melting point, viscosities, polarities etc. This chapter provides a systematic mention of the relevant information available on ILs. The information thus provided in this chapter indicates the virgin area of research to be undertaken.

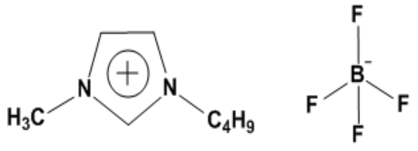
As a consequence of the detailed literature survey, it was clear that a study of these interactions should be precisely made for obtaining a better understanding of these interactions for their future applications of these ionic liquid-cosolvent solutions. The aims and objectives are therefore outlined in **Chapter 2**.

Since the research reported in the thesis is centered around enthalpic assessments, in the form of excess partial molar enthalpy, H^{E}_{IL}, the experimental details are of significance and are given in **Chapter 3**. A discussion on Isothermal Titration Calorimeter (ITC) together methodology is provided herein.

Chapter 4 elaborates on the interactions taking place between protic ionic liquids (PILs, shown below for an example) and molecular solvents of varied polarities. The PILs chosen for the study involve imidazolium, pyrrolidinium and pyridinium as their core cationic rings. Thermal effects in the form of excess partial molar enthalpy, H^{E}_{IL} and other enthalpic values of partial and apparent in nature were experimentally obtained using ITC or calculated using standard thermodynamic relations were discerned using the Pitzer equations to provide information on the ion- ion and ion-solvent interactions.



1-methylimidazolium tetrafluoroborate
(PIL)



[BMIM][BF_4] 1-butyl-3-methylimidazolium
tetrafluoroborate (APIL)

The work presented in **Chapter 5** de
the most commonly used ILs. This case study was taken to study the above-mentioned IL in detail in the presence of various commonly used solvents. A total of 9 solvents, water, methanol, ethanol, 1-propanol, ethylene glycol, formamide, DMSO and DMF were employed to probe the nature of ion- ion and ion- solvent interactions prevailing in the systems of IL and solvents of varied nature. Very importantly, an interesting

reversal in the enthalpic behavior from endothermic to exothermic on increasing the carbon chain length attached to the imidazolium ring in ILs has been presented (Fig. 1). Further this chapter elaborates how these interactions change when a different counter anion *i.e.* $[NTf_2]^-$ is combined with the core cation $[BMIM]^+$.

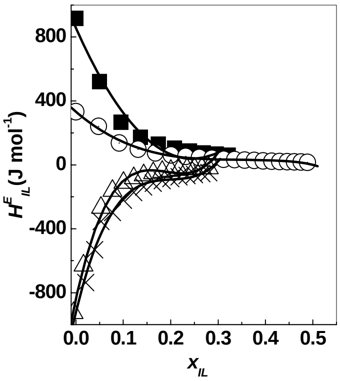


Fig. 1: A reversal in the trend: Variations in H^E_{IL} with respect to x_{IL} for (■) [EMIM][BF_4], (⦿) [BMIM][BF_4], (Δ) [HMIM][BF_4] and (x) [OMIM][BF_4] in water

Further, it is great interest to examine how a hydrophilic IL interacts with the hydrophobic one. **Chapter 6** explains the ionic interactions of ILs in the presence of another IL. The first part of the chapter details the mixing of electrolytes of hydrophilic and hydrophobic ones such as guanidinium chloride, sodium chloride, lithium chloride. The second part of the chapter deals with the mixing of aqueous solutions of a hydrophobic and a hydrophilic IL. The last part elucidates the mixing of pure ILs (both hydrophilic and hydrophobic).

The ionic interaction parameters ($H^E_{IL\text{-}IL}$) deduced out of the basic experimental quantity H^E_{IL} for various IL-solvent systems are described in **Chapter 7**. This chapter discusses quantification of the interactions prevailing at molecular level.

Chapter 8 summarizes the findings of the efforts made in this thesis. In nutshell, this thesis contributes to our understanding on the thermal effects when an ionic liquid (either PIL or APIL) is titrated against a solvent. The H^{E}_{IL} at infinite dilution property can be correlated with the specific properties of the solvents. A change in the enthalpic behavior from endothermic to exothermic on increasing the carbon chain length attached to the imidazolium ring in ILs has been an important addition to the current knowledge on ionic liquids. The ionic interaction theory of Pitzer is a useful tool in analyzing the deduced thermal quantities for both endo- and exothermic thermal effects. Thermal effects on mixing of ionic liquids and also of electrolytes possessing hydrophilic and hydrophobic nature have been quantified.

At the end, as the results given in the thesis show, it has been possible to ascertain that the thermal effects arising out of these interactions can be treated as a probe or signature to understand the unique nature of these IL systems.

CHAPTER 1: INTRODUCTION

"Besides the four resources of science and nature, fire, water, air and earth, a fifth element which can be considered as the most essential part of chemistry itself, which chemists boastfully, no doubt with reason, prefer above all others, and because of which they triumphantly celebrate, and to which they attribute above all others the marvelous effects of their science. And this they call the solvent (menstruum)."

Hermannus Boerhaave (1668- 1738)
De menstruis dictis in chemia, in:
Elementa Chemiae (1733)

“Alkahest”, a chemist’s incessant dream manifests the importance of a solvent. Many of solvents discovered till present may not be the Alkahest in true sense, but one of the most important searches of Alchemists states that much of the chemistry takes place in solutions. Right from the birth of the earth planet, myriad of the processes is being complied in the natural reservoirs of the solutions that are seas. These vast bodies of aqueous salt solutions and physiological fluids showed the first sign of origin of life on earth. Nature and natural products contain mixtures of ionic solutions with non-electrolytes both in essentially aqueous medium. The first solvent used by civilization was certainly the hydrocarbons derived from wood sources. Ancient Syrian and Egyptian civilizations found and synthesized these solvents for medicinal, cosmetic and winery purposes.

Although the solvent usage can trace its roots into antiquity, it was only after industrial revolution during the period of the 18th and 19th centuries throughout United Kingdom, Western Europe, North America, Japan and eventually the world, it actually became an industry. Today all the industries, consumer products, almost everything used by us contains or used in its processing, a solvent. The number of solvents generally available to chemists is between 250 and 300 and this number is ever increasing. Besides this count, there is an infinite number of the solvent mixtures. With these many number of solvents available, the selection of proper solvent and solvent mixture is not only important but also a challenge for both chemists and chemical process engineers.

Industrialization all over the world has led to the production and use of numerous solvents that vaporized into our environment causing great harm to human life and other vegetation.

These solvents are often volatile organic compounds abbreviated as VOCs. These VOCs exhibit:

(a) toxicity,

(b) flammability,

(c) ability to dissolve landfill liners,

(d) ability to carry other toxics,

(e) high volatility,

(f) contribution to smog,

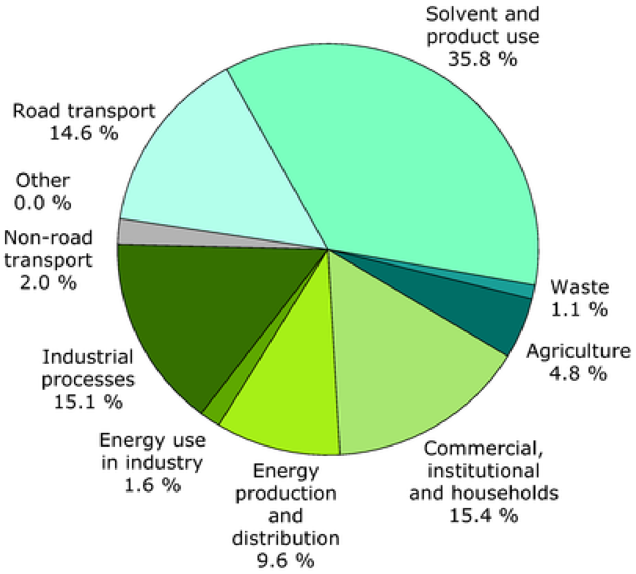
(g) long half life,

(h) toxic degradation products,

(i) resistance to biodegradation and

(j) stratospheric ozone degradation.

Solvent wastes were among the first to be banned by the U.S., Environmental Protection Agency (EPA). These VOCs are the workhorses of petrochemical and pharmaceutical industries, with a worldwide usage of about U.S. $ 5.49 billion annually. Higher E- factor suggests more waste and greater negative environmental impact. There was a paradigm shift of the larger E-factors in the fine chemicals and pharmaceutical industries (see Fig. 1.1, Table 1.1).[1] Fig. 1.2 depicts Indian scenario among 217 countries with regard to the use of VOCs.



Source: http://www.eea.europa.eu/data-and-maps

Fig. 1.1: Sector share of volatile organic compounds emissions by the European Environment Agency (EEA)

In 1984, the world's so called "the worst industrial accident in history" occurred due to the release of almost 30 tons of lethal methyl isocyanate gas in Bhopal, India from a Union Carbide plant. This resulted into the immediate death of thousands of people. Deaths and disabilities continued to plague the populace for years following.

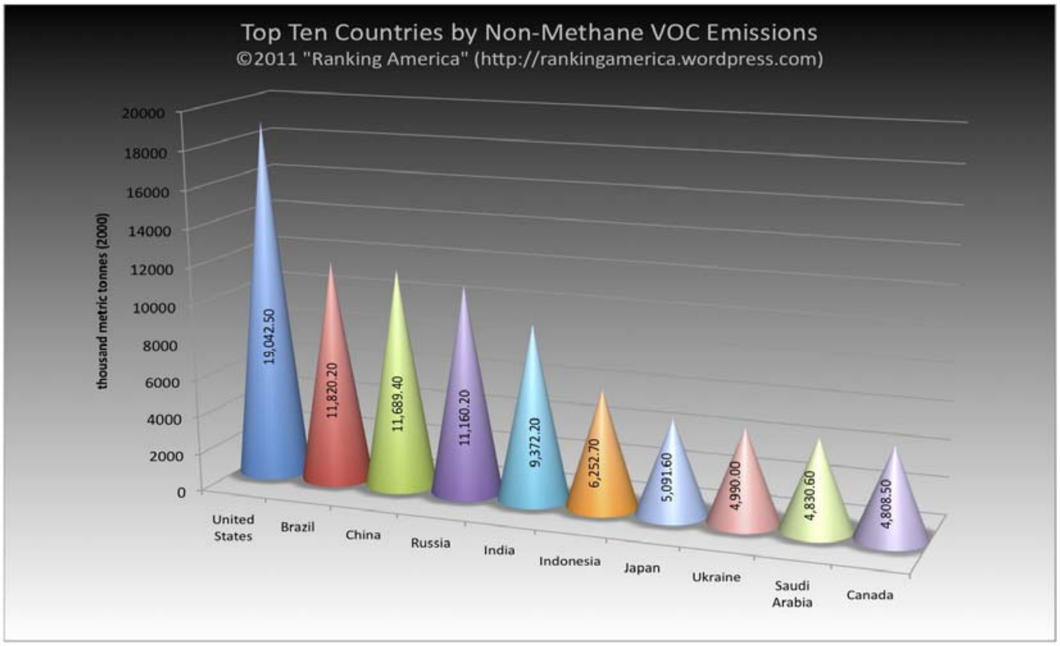
There are countless numbers of such incidents recorded in the past and the present scenario does not look even a fraction different from the yesteryears, the situation has even more worsened.

In view of the above, an urgent requirement was felt among academicians, scientists, technologists to eschew these noxious volatile compounds. To limit the usage of these hazardous chemicals U.S. EPA was founded, which began its operation on 2nd

December, 1970. This agency along with its partners ACS-GCI (American Chemical Society- Green Chemistry Institute) is working extensively to promote and advance an implementation of the 12 principles of green chemistry.[2]

Table 1.1: Production and E factor data for different industries

Industry	Production (tones/year)	E factor
Oil refining	$10^6 – 10^8$	< 0.1
Bulk chemicals	$10^4 – 10^6$	< 1- 5
Fine chemicals	$10^2 – 10^4$	< 5 -50
Pharmaceuticals	$10^1 – 10^3$	< 25 – 100



Data from World Resources Institute
http://earthtrends.wri.org/searchable_db/index.php?step=countriescID[]=0Chart1llcountries=checkbox5:33 AMheme=3ariable_ID=815Chart1ction=select_years

Fig. 1.2: Indian scenario among 217 countries in volatile organic compound emission

These principles focus on the prevention of waste by using renewable feedstock and designing such chemical syntheses that can avoid the possibility of chemical derivatives and promote those products, which can be degraded after their usage. It also provides a framework, in which there is a maximization of atom economy and minimization of chances of accidents.

Despite progress in reducing pollution because of the seamless efforts of EPA and their global partners, the attention of the whole chemical community has shifted to the emergence of more environmentally friendly solvents/methods. The possible alternatives to reduce the usage of the VOCs are given below:

(1) using sonochemical methods to carry out chemical reactions,

(2) water as a solvent medium,

(3) supercritical (H_2O/CO_2) fluids as solvent media,

(4) carry out chemical process using microwave and

(5) ionic liquids as solvent media.

In the quest of an alkahest, ionic liquids seem to be one of the most suitable candidates. Not to despise the importance of other alternatives, ionic liquid is evolving as the most versatile and potential prospect for many applications. Though these ionic liquids hold immense potential and scope for future, the utility of these compounds cannot be explored due to the lack of fundamental data on the characteristics of ionic liquids. The link between ionic liquids and green chemistry is directly related to the solvent properties of ionic liquids.

1.1 General information on ionic liquids:

The history of ionic liquids goes back to 19th centaury holding the progenitors and the progenitures of the present day ionic liquids. A working definition of ionic liquids, is that an ionic liquid is a salt with a melting temperature below the boiling point of water

(<100°C).[3,4,5,6] Most of the salts considered to be an ionic liquid are liquid at or around room temperature and often to substantially lower temperature. Most of the ionic liquids

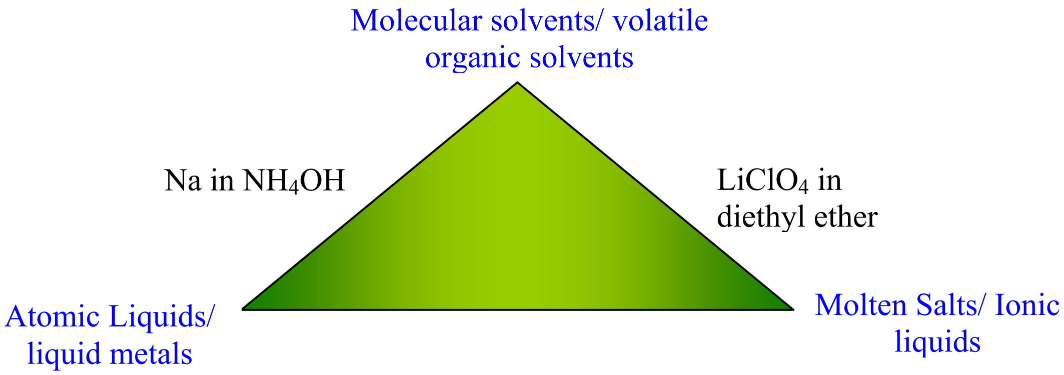


Fig. 1.1.1: Different solvents on the basis of their characteristic chemical bonding

contain organic cation and inorganic anion. Ionic liquids are typically organic salts or eutectic mixtures (a eutectic mixture is a mixture of two or more phases at a composition that has the lowest melting point, and where the phases simultaneously crystallize from molten solution at this temperature) of an organic salt and an inorganic salt (Fig. 1.1.1).

Various synonyms and abbreviations used for molten organic salt with low melting points for the purpose of literature search by electronic means are:

(1) ionic liquids (ILs),

(2) room temperature ionic liquids (RTILs),

(3) ambient temperature ionic liquids,

(4) non aqueous ionic liquids (NAILs),

(5) molten organic salts,

(6) fused organic salts,

(7) low melting salts,

(8) neoteric solvents and

(9) designer solvents.

The first ever documented ionic liquid observed by chemists, was the ‘Red Oil’ (Fig. 1.1.2) formed as a separate phase during Friedel-Crafts reactions in 1877.[7] The long–presumed stable intermediate in the Friedel-Crafts reactions called the sigma complex was later on identified by the Japanese chemists. It consisted of an alkylated aromatic ring cation and a chloroaluminate anion. The ‘Red Oil’ therefore, was an ionic liquid.

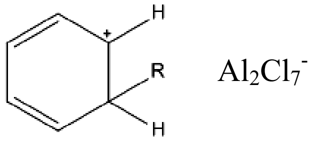


Fig. 1.1.2: Structure of the first ionic liquid, heptachlorodialuminate salt, the “Red Oil”

Later, in 1888, Gabriel reported the discovery of the protic ionic liquid, Ethanol Ammonium Nitrate, with a melting point of 52- 55°C. This was the first organic salt with a melting point of less than 100°C. Much later to these early discoveries, Paul Walden discovered the first room temperature ionic liquid as Ethyl Ammonium Nitrate in 1914.[8] With a subsequent slower progress in the field, the real explosion of the interest started around 1998- 2000. The most significant events in the history of ionic liquids are summarized as under:

1888: discovery of protic ionic liquid, ethanol ammonium nitrate (m.p. 52- 55°C), by Gabriel, 1914: discovery of first room temperature ionic liquid, ethyl ammonium nitrate (m.p. 12.5°C), by Paul Walden,

1934: discovery of cellulose dissolving ionic liquid, 1-ethyl pyridinium chloride (m.p. 118°C), by Graenacher,

1961: Bloom coined the term 'Ionic Liquid' for pure molten salts,

1976: first report on carrying out an organic reaction (Friedel Crafts Alkylation) in room temperature molten salt medium: a melt of aluminium chloride and ethyl pyridinium bromide by Osteryoung and coworkers,

1992: first air and water stable ionic liquid, 1-ethyl-3-methyl imidazolium ionic liquid with weakly coordinating anion like tetrafluoroborate (BF_4^-) and hexafluorophosphate (PF_6^-) reported by J. S. Wilkes and M. Zaworotko,

1996: first hydrophobic ionic liquid with bis(trifluoromethylsulfonyl)imide anion (NTf_2^-) was synthesized,

2003: BASF announced an industrial process (BASIL) that used ionic liquids to scavenge acids from reaction mixtures,

2005: over 2500 papers on the topic ionic liquid published during that year compared to mere 37 in 1999 and 76 in 2000, and

2012: almost 2 lakh hits for the keyword ionic liquid, in google search engine.

Ionic liquids can be classified on the basis of their origin, structures, specificity of their applications:

(a) On the basis of their origin-:

First Generation Ionic Liquids: These are the eutectic mixtures of aluminium chloride and ethyl pyridinium halides, dialkyl imidazolium chloroaluminate and are used as solvents and catalysts for Friedel-Crafts and organic reactions, extremely hygroscopic in nature.

Second Generation Ionic Liquids: Non haloaluminate ionic liquids, dialkyl imidazolium ionic liquids with weakly coordinating anions like BF_4^- and PF_6^-. They undergo hydrolysis resulting in the formation of toxic and corrosive hydrogen fluoride (HF), hydrophobic dialkyl imidazolium ionic liquids with NTf_2^- anion are air and water stable. These second generation ionic liquids are extensively used as solvents in organic reactions.

Third Generation Ionic Liquids: The third generation is the task specific ionic liquids and chiral liquids emerged only in early 2000s.

(b) On the basis of structures-: On the basis of structure the ionic liquids can either be classified as-: (i) Organic and inorganic ionic liquids or (ii) Protic or aprotic ionic liquids.

Most of the ionic liquids studied so far consist of organic cations and organic/ inorganic anions. Such ionic liquids are called organic ionic liquids. e.g. 1-butyl-3-methyl imidazolium tetrafluoroborate, $[BMIM][BF_4]$, ethyl pyridinium tetrafluoroborate, $[EtPY][BF_4]$. Those low melting salts, which contain inorganic cation and inorganic / organic anion, are known as inorganic ionic liquids. e.g.

$[N_2H_5]Br$, hydrazinium bromide (m.p. 86.5). Also, a binary mixture of $LiNO_3$ and NH_4NO_3 is an example of inorganic ionic liquids.

Aprotic ionic liquid has attracted the maximum attention so far. Aprotic ionic liquids are those which contain, (a) a quartenized (through the alkyl groups) cation and its counter anion e.g. $[BMIM][BF_4]$ and $[BMPYRR][BF_4]$.

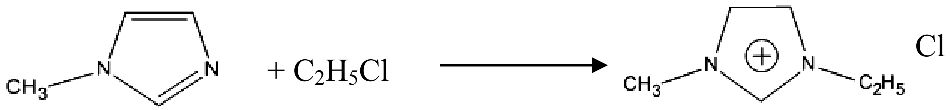
Protic ionic liquids are the salts that contain (a) a protonated cation with its (b) counter anion. It is formed by the proton transfer from an acid *i.e.* a Bronsted acid (HA) to a base *i.e.* Bronsted base (B)-:

$$HA + B \longrightarrow [BH]^+ + A^-$$

The classic example of a protic ionic liquid is ethyl ammonium nitrate, $[C_2H_5NH_3][NO_3]$.

Synthesis of ionic liquids: Till date, almost 500 ionic liquids are produced commercially.[9] Some of the most commonly used methods to synthesize them are as follows:[10,11,12,13,14]

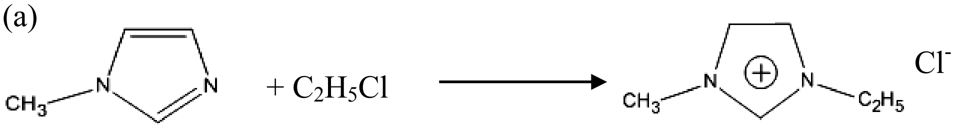
(1) Alkylation:



1-methyl imidazole chloroethane Ionic liquid (m.p. 87°C)

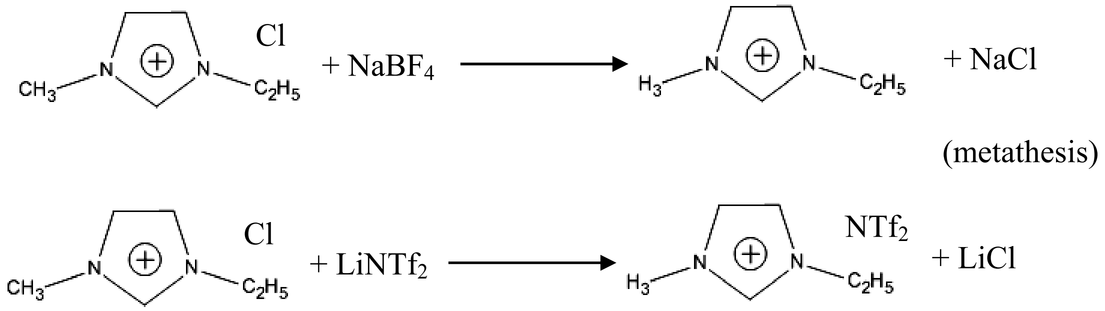
(2) Anion Exchange:

(a)



(alkylation)

(b) Anion exchange step



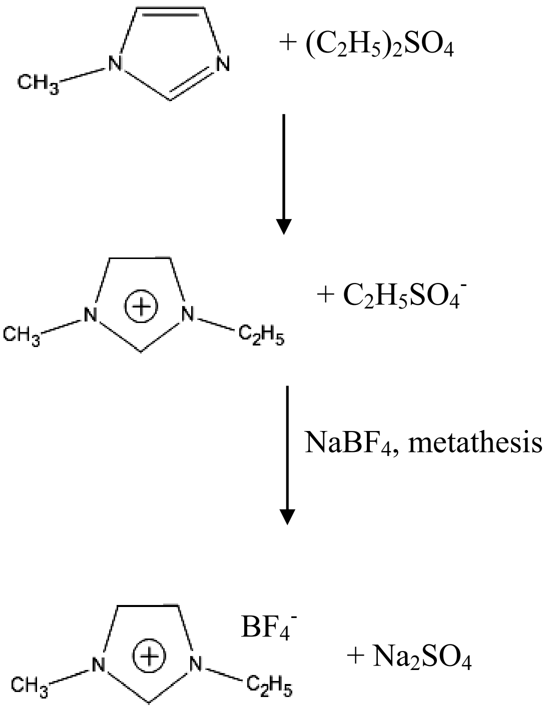
Scheme 1.1.1: Different methods of synthesis of ionic liquids

(3) *Microwave and ultrasound assisted synthesis:* Varma and Namboordiri suggested that the synthesis the of ionic liquid by refluxing 1-methylimidazole with excess of alkyl halide in the presence of solvents like toluene could be performed by the use of microwaves without employing a solvent and within much improved time.[15] Similarly, in 2002 Leveque and coworkers described in that ultrasonic waves could reduce the reaction time with higher yields and improved quality of the products.[16]

(4) *Halide free synthesis:* The second step of ionic liquid synthesis involves metathesis, which contaminates the ionic liquid with unwanted halide salts. These halide salts with higher boiling points are difficult to separate from the product, which are known to have a dramatic effect on the physical properties of an ionic liquid. To avoid this contamination, In the year of 2000, Holbrey and coworkers proposed to synthesize 1,3-dialkylimidazolium alkyl sulfate as the

first step of ionic liquid synthesis. Further, these ionic liquids can be used to prepare other ionic liquids by metathesis. Scheme 1.1.2 presents a sketch of the halide free synthesis of ionic liquids.

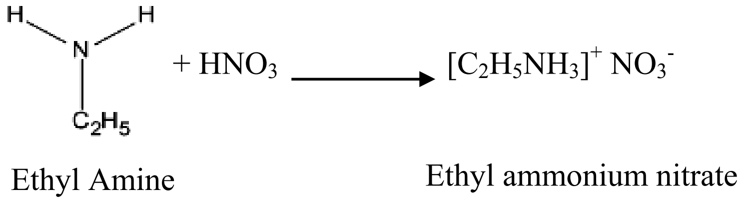
General Synthesis of ionic liquids: The initial step during the synthesis of ionic liquids is the quarternization leading to the formation of the cation. The second step is the anion exchange/metathesis, in which synthesis of ionic liquid with desired anion is facilitated. A flow chart to show the synthesis paths for the preparation of ionic liquids exemplified for an imidazolium salt is given in Fig. 1.1.5[17]



Scheme 1.1.2: Path of the halide-free synthesis

(5) *Synthesis by protonation:*

$$\underset{\text{Bronsted Acid}}{HA} + \underset{\text{Bronsted Base}}{B} \longrightarrow [HB]^+ + A^-$$



$+ HNO_3 \longrightarrow [C_2H_5NH_3]^+ NO_3^-$

Scheme 1.1.3: Ionic liquid synthesis by protonation

Properties of ionic liquids-: The advent of a new class of solvents called ionic liquids and their subsequent popularity in academia and industry owe to the unique characteristic properties of this class. These unique properties favor applications in diverse fields such as synthesis, catalysis, biocatalysis, separation technology, electrochemistry, analytical chemistry and nanotechnology.[14,18,19] Out of many properties, those *sui generis* for ionic liquids are discussed in the text that follows further.

(1) *Insignificant vapor pressures:* This is the most significant property of ionic liquids that places them in the class of "Green Solvents" and also differentiates them from volatile organic compounds. The minimal vapor pressure helps to reduce the solvent loss to the environment and thus checks the possibility of environmental and safety problems.[3]

(2) *Contain poorly coordinating anions:* Most of the ionic liquids studied so far consist of poorly or non- coordinating ions. This property enhances the possibility of ionic liquid effectively participating in the organic reaction field as they constitute the class of non- coordinating yet highly polar solvents. Thus "no" apprehensions about the side products can be experienced while using ionic liquids.[10]

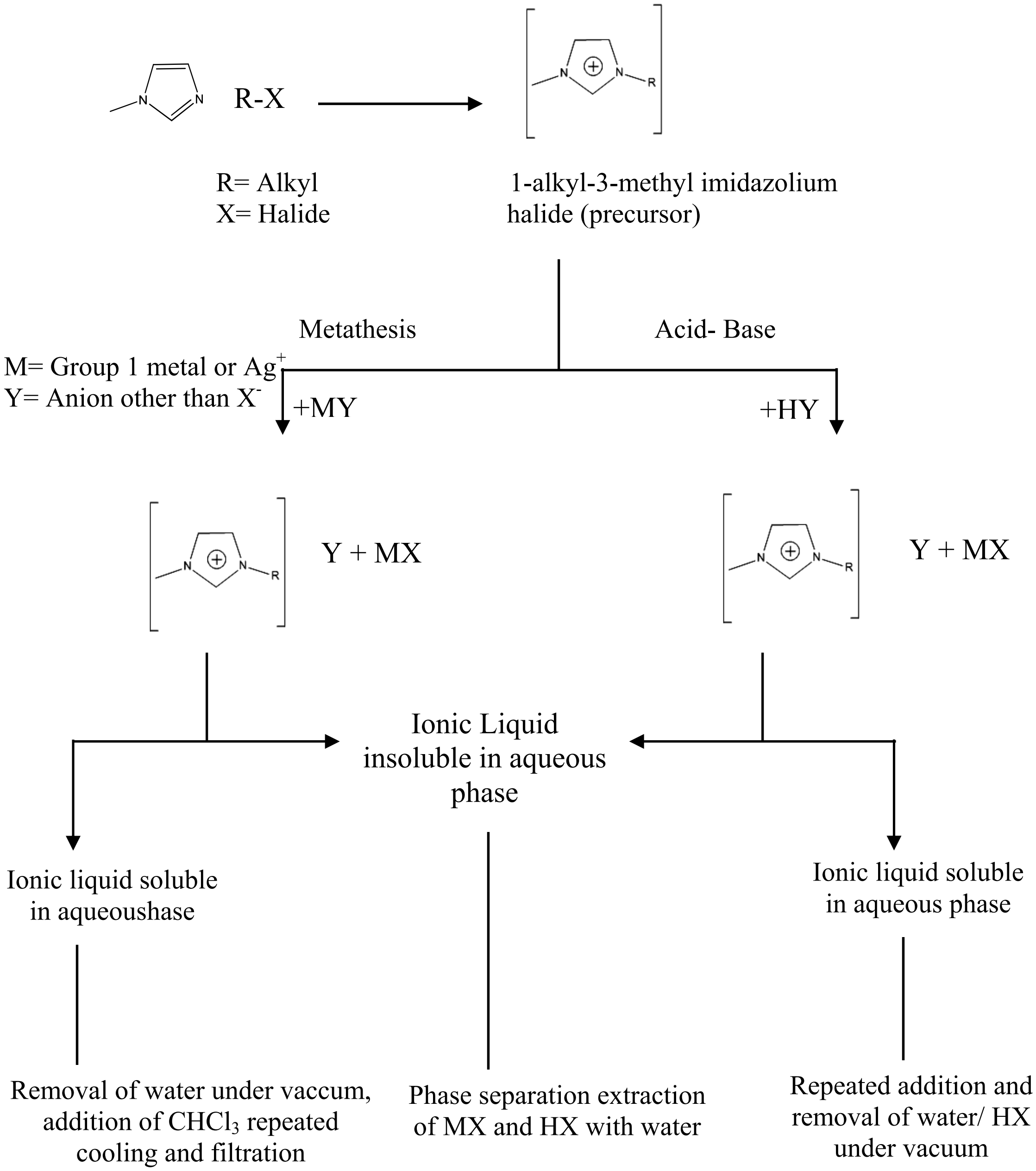


Fig. 1.1.3: General synthetic scheme for the preparation of ionic liquids

(3) *Unbiased dissolution:* “Like Dissolve Like” principle does not hold good for this novel class of solvents. Ionic liquids can dissolve the materials of both organic and inorganic in nature.[20] It thus gives an opportunity to the chemists to explore a super solvent that can dissolve maximum number of substances known. Ionic

liquids make a very unusual combination of reagents into the same phase, where the organic domain of ionic liquids dissolves the organic materials and the inorganic counterpart takes care of the materials that are inorganic in nature.

(4) *Immiscible with organic solvents:* There are ionic liquids reported in literature, which have very limited or no solubility in organic solvents. These ionic liquids may provide a non-aqueous, polar alternative for the biphasic extraction systems. Hydrophobic ionic liquids such as $–NTf_2^-$ based, can also be used as immiscible polar phase with water in the extraction systems.[18,21]

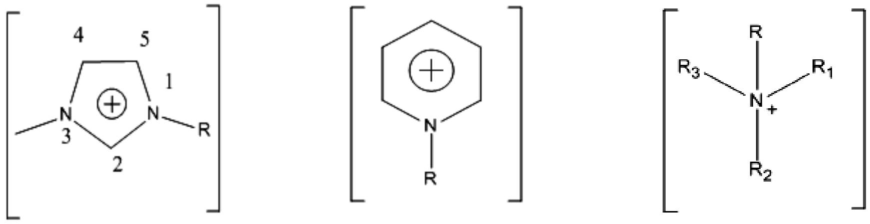
(5) *Thermally Robust:* An attractive feature of ionic liquids is their wide temperature operating range with no apparent vapor pressure. Ionic liquids show significant vapor pressure or thermal decomposition at 300-400°C. This robustness provides an opportunity to carry out chemical transformations in ionic liquids at elevated temperatures. Besides these properties, low flammability, high conductivity, large electrochemical windows, low corrosion tendencies, large density differences compared to other process fluids to speed up the phase separation are other favorable properties.

(6) *Recyclability*: The possibility of recycling ionic liquids is one of the most environmentally- beneficial aspects of using ionic liquids. Also, the catalysts immobilized in ionic liquids can be recovered back. This possibility not only reduces the waste of expensive materials such as catalysts and ionic liquids, which ultimately reduces the costs. In 1998, Anderson and coworkers described an early example of recycling power of ionic liquids.[22] They reported that the

ionic liquid/catalyst system can be reused several times, giving reproducible results.

Fig. 1.1.4: Some of the commonly used ionic liquids: their building blocks, nomenclature and acronyms

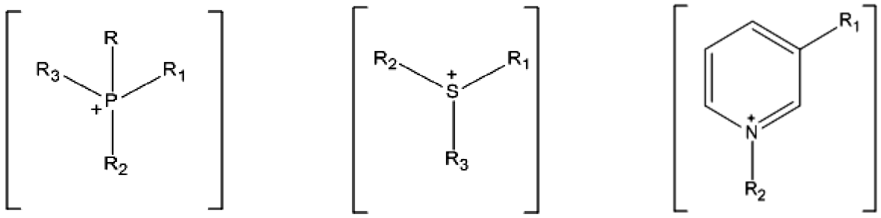
Cations:



1-alkyl-3-methyl imidazolium

N-alkyl pyridinium

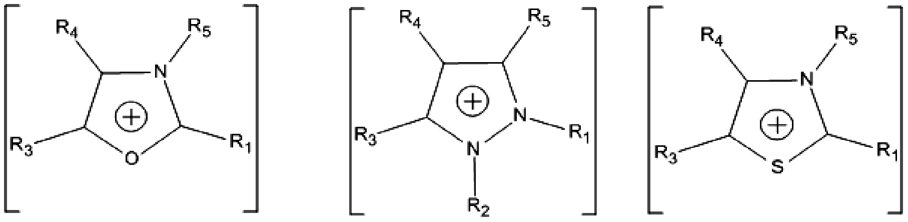
Tetraalkyl ammonium



Tetraalkyl phosphonium

Sulphonium

Picolinium



Oxazolium

Pyrazolium

Thiazolium

Possible Anions:

Water insoluble ⟶ Water soluble

$[PF_6]^-$
$[(CF_3SO_2)_2N]^-$
$[BR_1R_2R_3R_4]^-$

$[BF_4]^-$
$[CF_3SO_3]^-$

$[CH_3CO_2]^-$
$[CF_3CO_2]^-$, $[NO_3]^-$
Br^-, Cl^-, I^-
$[Al_2Cl_7]^-$, $[AlCl_4]^-$

Commonly used alkyl chains:

$-C_2H_5$, $-C_4H_9$, $-C_6H_{13}$, C_8H_{17} etc.

Ionic liquids	Acronyms
1-methylimidazolium tetrafluoroborate	[MIM][BF_4]
1-methylpyrrolidinium tetrafluoroborate	[hPYRR][BF_4]
1-methylpyridinium tetrafluoroborate	[hPY][BF_4]
1-ethylpyridinium chloride	[EtPY][Cl]
1-ethylpyridinium bromide	[EtPY][Br]
1-ethyl-3methylimidazolium tetrafluoroborate	[EMIM][BF_4]
1-ethyl-3methylimidazolium hexafluorophosphate	[EMIM][PF_6]
1-butyl-3-methylimidazolium tetrafluoroborate	[BMIM][BF_4]
1-hexyl-3-methylimidazolium tetrafluoroborate	[HMIM][BF_4]
1-octyl-3-methylimidazolium tetrafluoroborate	[OMIM][BF_4]
N-butyl-*N*-methylpyrrolidinium tetrafluoroborate	[BMPYRR][BF_4]
1-butyl-2-methylpyridinium tetrafluoroborate	[BMPY][BF_4]
1-ethyl-3-methylimidazolium bis(trifluoromethylsulphonyl)imide	[EMIM][NTf_2]
1-butyl-3-methylimidazolium bis(trifluoromethylsulphonyl)imide	[BMIM][NTf_2]
1-hexyl-3-methylimidazolium bis(trifluoromethylsulphonyl)imide	[HMIM][NTf_2]
1-octyl-3-methylimidazolium bis(trifluoromethylsulphonyl) imide	[OMIM][NTf_2]
Ethanolammonium nitrate	[$C_2H_4OHNH_3$][NO_3]
Ethylammonium nitrate	[$C_2H_5NH_3$][NO_3]
Dialkylimidazolium chloroaluminate	[R_1R_2MIM][Al_2Cl_7]
1-ethyl-3,5-dimethylimidazolium tetrafluoroborate	[EMM_5IM][BF_4]
1,3-diethylimidazolium tetrafluoroborate	[EEIM][BF_4]
1-butyl-3-ethylimidazolium tetrafluoroborate	[BEIM][BF_4]

1.2 Critical information on ionic liquids:

Knowledge about the physical, chemical and biological properties of ionic liquids is limited compared with the conventional organic solvents. The determination of the properties of ionic liquids and the trends in these properties is critical in designing the ionic liquids for specific applications. For enlarging the scope of applications of ionic liquids in future, it is important to work out the generalization of the properties associated with them. An examination is also needed whether these generalizations are the class specific. Properties of ionic liquids vary widely from acidic to basic to neutral, from water miscible to other solvent miscible and from toxic to non-toxic.

Though this type of variation provides an opportunity to modify the properties of cations and anions independently, it is equally difficult to document them for each of the ionic liquid reported. To answer, why do all the ionic liquids, even within the same class *i.e.* with same parent ring, the same counter-anions and the same type of residual alkyl tail, behave in a different manner; it is important to examine their structural aspects.

Structural aspects of ionic liquids: Besides spectroscopic methods such as small angle neutron spectroscopy, inelastic neutron scattering, NMR, tetrahertz and dielectric, optical Kerr effect, X-ray scattering and interfacial nonlinear optical spectroscopy and theoretical studies like an initio electronic structure calculations, molecular dynamics simulations have provided some of the intricate details of dynamics and interactions in pure ionic liquids.[23,24,25,26] X-ray crystal studies suggest that some ionic liquids tend to crystallize into disordered solids.[27,28] Depending upon their rate of cooling, crystal polymorphism can also be observed in the case of ionic liquids.[29] Thus, for ionic liquids, the gain in energy upon formation of the crystal ($\triangle_{latt}H$ = 411 to 492 kJ mol^{-1}) is not as large as in conventional inorganic salts such as NaCl, ($\triangle_{latt}H$ = 800 kJ mol^{-1}, $\triangle_{latt}S$ = 0.158 kJ mol^{-1}K^{-1}) and also not enough to compensate for the loss in entropy ($\triangle_{latt}S$ = 0.324 to 0.387 kJ mol^{-1}K^{-1}) that accompanies the formation of the ionic liquid crystals at room temperature. These systems have a tendency towards glassy behavior. Depending upon the length of alkyl substituents in the cation, their properties range from those of normal liquids to glassy or even liquid crystals.

Ionic liquids are non-trivial solvents and are composed of asymmetric, flexible and medium sized ions (10-100 atoms).[30] Interactions in ionic liquids are predominantly Coulombic, van der Waals forces, polarization and charge delocalization in nature. Regarding these interactions, Watanabe and collaborators studied the dynamic properties of the imidazolium ionic liquids as a function of the alkyl side chain length. They found that with the increasing length of the side chains, strong electrostatic interactions between the charged groups were diluted and finally replaced by weaker van der Waals forces.[31] Ionic liquids are the so called “Supramolecular Solvents” because of the self-organization of the ionic liquid units. This self-organization is often explained by a network of hydrogen bonds binding the units to form a patterned arrangement. 1,3-dimethyl imidazolium ([dmim]$^{+}$) salts provide generic information about ionic liquids.[32] Information collected using neutron diffraction and further modified by empirical potential structure refinement (EPSR) process based on the fitting of the experimental data with a reverse Monte Carlo procedure show that there is a strong charge ordering present in the above mentioned symmetrical ionic liquids.[33] The cations and anions are alternately arranged in their radial distribution functions. Considering the ([dmim]$^+$) cation with different anions [PF$_6$]$^-$ and [NTf$_2$]$^-$ and Cl$^-$ show difference in their radial distribution functions. The cation-cation contacts show that in [dmim]Cl, the cations are separated by 5.5Å, while for the hexafluorophosphate [PF$_6$]$^-$ and bis{trifluoromethylsulfonyl}imide [NTf$_2$]$^-$[34] based ionic liquids this distance is 6.3 Å and 7.0 Å, respectively. As the size of the anion increases, the trend of the cation-cation contact becomes Cl$^-$ < [PF$_6$]$^-$ < [NTf$_2$]$^-$. Also, the cation-anion distance increases upon increasing the anion size: [NTf$_2$]$^-$ (5.2 Å) > [PF$_6$]$^-$ (4.5 Å) > Cl$^-$ (4.2 Å).

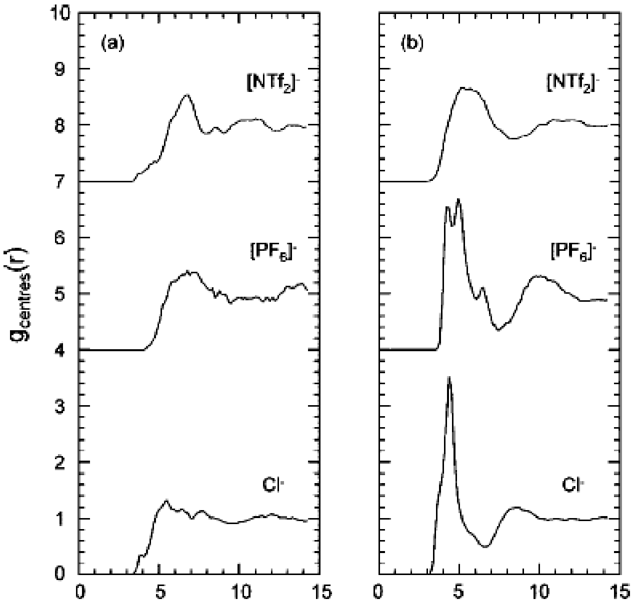


Fig. 1.2.1: Partial radial distribution functions for (a) cation- cation distribution, (b) cation-anion distribution for 1,3-dimethylimidazolium Cl$^-$, PF$_6^-$and NTf$_2^-$ *(Reproduced by permission from American Chemical Society)*

The cation-anion-cation alternating pattern is less pronounced in the case of [dmim][NTf$_2$] than in [dmim][PF$_6$] or [dmim][Cl]. The cation-anion-cation pattern is shown by the position of second shells of cation and anion, which is coincident at ~ 13

Å (Fig. 1.2.1). The spatial probability distribution for [dmim]Cl, [dmim][PF_6] and [dmim][NTf_2] suggest that with the increase in the anion size, the interaction between ring hydrogens and anions deter and the cations and anions begin to occupy different positions (Fig. 1.2.1). With the increment in the size and the delocalization of the charge, the ionic bonding in the liquid becomes softer and results into the increased overlap of the cations and anions in the radial distribution of [dmim][NTf_2]. In the crystal structure, the closest distance between the cations is found to be a van der Waals contact distance between two methyl hydrogens in adjacent cation dimers at 2.5 Å.

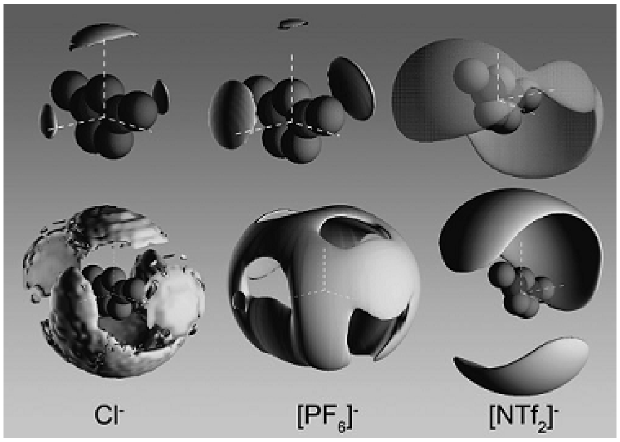


Fig. 1.2.2: Probability distribution of (a) the anions and (b) the imidazolium cations around an imidazolium cation for 1,3-dimethylimidazolium Cl^-, PF_6^- and NTf_2^- *(Reproduced by permission from American Chemical Society)*

In the EPSR model of ionic liquid ([dmim]Cl) structure, the hydrogen-anion contacts dominate the interaction with each cation interacting with six anions. Pure imidazolium ionic liquids are polymeric hydrogen-bonded supramolecules.[35,36,37] They are also regarded as nano-structured materials with polar and non-polar regions which are not found in other homogeneous solvents.[38,39] These nano-structured materials are with atoms arranged in nanosized clusters which subsequently become the constituent grains or building blocks of ionic liquids. To further illustrate the structure of ionic liquid, a case study of 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) is discussed in detail.

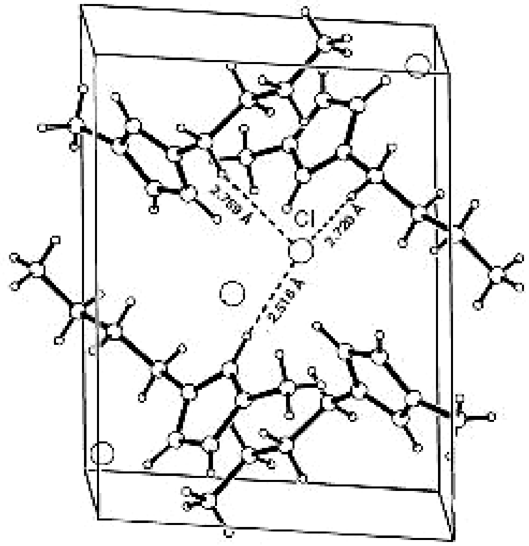


Fig. 1.2.3: An overview of the crystal structure of [BMIM]Cl *(Reproduced by permission from Chemical Society of Japan)*

[BMIM]Cl is a prototypic ionic liquid showing the crystal polymorphism (material existing in more than one crystal structures). It has two polymorphs (crystal (1) and crystal (2)) coexisting in the liquid state.[40]

The $[BMIM]^+$ ion causes different properties of ionic liquid, when combined with different anions. It is therefore important to know the details of $[BMIM]^+$ ion.

[BMIM]Cl is a white crystalline solid with rectangular shaped crystals. The X-ray diffraction experiment suggests the presence of asymmetric unit consists of one $[BMIM]^+$ and one Cl^-, while the unit contains four of each (Fig. 1.2.3). The crystal structure reveals that the imidazolium ring is a planar pentagon. The average bond length for the N_1-C_2 and C_2-N_3 bonds is 1.32 Å. The bond length suggests the conjugated double bond nature of these two bonds.

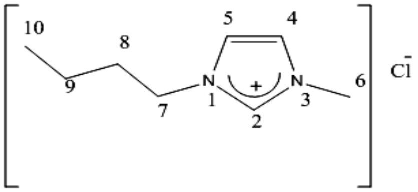


Fig. 1.2.4: Denotation and electronic structure of 1-butyl-3-methyl imidazolium chloride

The C_4-C_5 bond length is 1.34 Å and the average bond length is considerably shorter than that of pure C-N single bond, which is 1.47 Å of length. The π-electrons are highly delocalized in the imidazolium ring. The carbon atom of the methyl group attached to the N_3 is on the plane of the imidazolium ring. The C_7 carbon has a deviation of about 1.8 Å from the plane of the imidazolium ring. Rest of the carbon atoms of the butyl group are considerably out of plane and acquire trans-configuration. The all trans-configuration assist in the interaction of the two cations through hydrophobic interaction between the butyl groups (Fig. 1.2.4).

The anion (Cl^-) is generally far from the methyl group and closer to the hydrophobic region produced by butyl groups. The distance between C_2 proton and the anion is of the order of hydrogen bonding distance. The observed H_2-Cl^- distance is 2.52 Å and the C-H-Cl^- angle is 157.5°. The distance between two Cl^- anions is 4.84 Å, which is too long to have any specific interaction between them. Ionic liquid units are corrugated to form sheets in which the angle between two imidazolium rings belonging to two different sheets is 69.49°. Also the two butyl groups are associated with each other creating a hydrophobic region. The methyl group attached to the imidazolium ring seems to have no dominant role in the crystal structure. The crystal structure of [BMIM][Cl] ionic liquid results from a delicate balance of three type of interactions:

1. the electrostatic interactions among the cations and the anions,
2. the hydrogen bonding interaction among the chloride anions (Cl^-) and the ring as well as alkyl chain hydrogens and
3. the hydrophobic interaction between the two butyl groups of the $[BMIM]^+$ cations.

On the basis of the details of the structure of ionic liquids some of their microscopic properties discussed:[41]

Melting point and Crystal Structure: The melting points of ionic liquids represent the lower limit of the temperature at which it can remain liquid. Melting point together with thermal stability defines the interval of temperatures within which ionic liquids can be used as solvents. The melting point of ionic liquids can be tuned by varying the cation and/ or anion[42] and it can be easily correlated with their structures. For most of the ionic liquids especially imidazolium-cation based, that the melting point decreases with the increase of cationic size and its asymmetry.[43] An increase in the branching on the alkyl chain increases the melting point.

Understanding the anion effect,[44] though difficult, yet it has been found that the anions with more charge delocalization and relative inability e.g. OTf^- and Tf_2N^- to form hydrogen bonding with the cations results in lower melting points. Ionic liquids containing soft unsymmetrical ions show low melting points e.g. $[BMIM]^+$ ionic liquids with substituted tetraphenylborates (Ph_4B^-) as counter anions, the increasing bulk and orientational flexibility of substituents on the aromatic rings of the anion depress the melting point of these salts.[45] Efforts are going on to create computer programs for predicting the melting point of yet unsynthesized ionic liquids.[46] Melting points of some of the commonly used ionic liquids are given in Table 1.2.1.

Table 1.2.1: Melting points of some of commonly used ionic liquids

Ionic Liquids	Melting Points (°C)
$[EMIM][BF_4]$	15
[EMIM]Br	81
$[EMIM][NTf_2]$	-3
[BMIM]Br	66
$[BMIM][BF_4]$	-81
$[BMIM][NTf_2]$	-4
$[HMIM][BF_4]$	-81
$[OMIM][BF_4]$	-79
$[hPYRR][BF_4]$	-32

Density: Density is one of the most unambiguous properties of ionic liquid which is required in nearly all the applications involving ionic liquids. Densities of ionic liquids are the least sensitive property to temperature. Ionic liquids are generally denser than water.[47] The nature of the anion majorly controls[48] the density of ionic liquids. Greater is the molar mass of the anion lower is the density of anion. Densities of non-haloaluminate ionic liquids are also affected by the organic cation. It is found that the density of ionic liquids decreases as the size of cation increases.[49] This behavior can be attributed to the fact that packing may become more compact as the alternating positive and negative species become larger/ more even in size. The order of increasing density for ionic liquids composed of a common cation is: $[CH_3SO_3]^- \sim [BF_4]^- < [CF_3CO_2]^- < [CF_3SO_3]^- < [C_3F_7CO_2]^- < [(CF_3SO_2)_2N]^-$

For the substituted imidazolium cations with a common triflate anion:

$[EMIM]^+ > [EMM_5IM]^+ > [EEIM]^+ > [BMIM]^+ > [BEIM]^+$

Diffusion Coefficient and Conductivity: Transport properties of ionic liquids are among the most important ones, with reference to their application in the reaction kinetics in chemical processes and electrochemical devices.[50] Despite the fact, ionic liquids are purely composed of ions; they are significantly less conductive than concentrated aqueous electrolytes. As compared to non-aqueous solvent/ electrolytes, ionic liquids possess reasonably good conductivities.[51] The conductivity of ionic liquids usually exhibits classical linear Arrhenius behavior above room temperature.[52] As the temperatures of these ionic liquids approach their glass transition temperatures, the conductivity displays a negative deviation from the linearity. The temperature dependence of conductivity is strongly affected by the nature of cations and anions[53],[54] (Fig. 1.2.5).

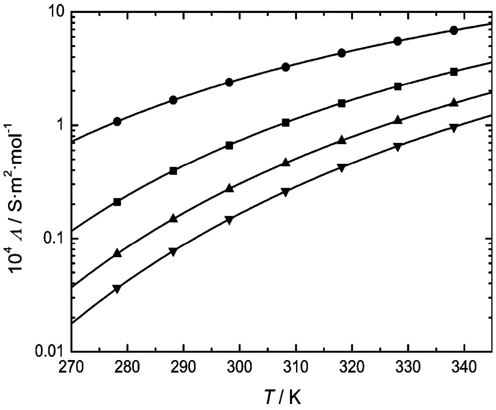


Fig. 1.2.5: Temperature dependence of molar conductivity for (•) [EMIM][BF$_4$], (▪) [BMIM][BF$_4$], (▲) [HMIM][BF$_4$], (▼) [OMIM][BF$_4$][53d] *(Reproduced by permission from American Chemical Society)*

The overall the trend in conductivity with respect to cation type follows the order: Imidazolium ≥ Sulfonium > Ammonium ≥ Pyridinium. There is no clear relationship between anion size and conductivity apart from the higher conductivities observed for [BF$_4$]$^-$ based ionic liquids. Also ionic liquids having larger anions exhibit higher conductivities than those with smaller anions e.g. $k_{[(CF3SO2)2N]^-} > k_{(CH3CO2)^-}$

The diffusion coefficient is a measure of the rate of movement of an ion in a solution and the transport number is a measure of the friction of charge carried by that ion in the presence of an electric field. A typical diffusion coefficient in ionic liquids is of the order of 1×10^{-7} cm^{2}s^{-1}. The diffusion coefficient values commonly found in ionic liquids are lower by almost 2 folds than those measured in conventional organic electrolytes. For [EMIM][BF_4], [EMIM][Tf_2N], [BPY][BF_4] and [BPY][Tf_2N], the order of sum of cationic and anionic diffusion coefficients is as follows:

[EMIM][Tf_2N] > [EMIM][BF_4] > [BPY][Tf_2N] > [BPY][BF_4]

The relationship between the diffusion coefficient, viscosity and molar conductivity can be applied in terms of Stokes-Einstein and Nernst-Einstein equations. The ionic diffusivity (D) obeys the equation:

$$D = k\,T / c\,\pi\,\eta\,r \qquad (1)$$

where k = Boltzmann constant, T = absolute temperature, c = constant and r = effective hydrodynamic/stokes radius and η is the viscosity.

Viscosity: Ionic liquids are generally more viscous than most common molecular solvents.[55] At room temperature, the viscosity of ionic liquids range from 10 cP to 2000 cP. Such high viscosity is one of the strongest barriers to the application of ionic liquids. Generally, viscosity follows a Non-Arrhenius behavior but sometimes it can also be interpreted in terms of Vogel-Tammann-Fulcher (VFT) equation.[56] Viscosity remains constant with increasing shear rate and ionic liquids can be classified in terms of Newtonian fluids.[57] Ionic liquids showing Non-Newtonian behavior are also observed in the literature. The increase in the viscosity upon changing the anion or cation can be attributed to the increase in the van der Waals forces. Hydrogen bonding between counter anions also affects the viscosity. A combination of the decreased anion size, less diffused charge and large increase in hydrogen bonding increases the viscosity of ionic liquids[58] (Fig.1.2.6).

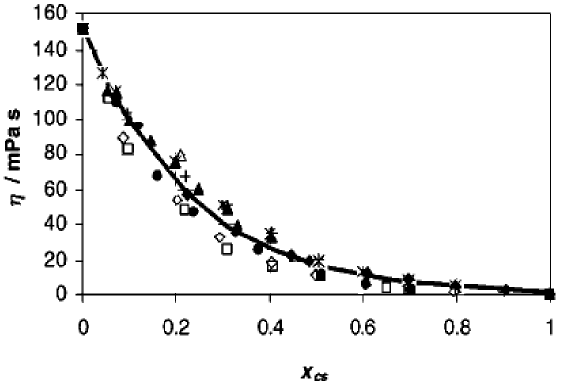


Fig. 1.2.6: Viscosity of cosolvent-[C_4mim][BF_4] mixture vs. mole fraction of cosolvent at 20°C, (×) 1-methylimidazole, (◆) water, (▲) toluene, (∆) 1,4-dimethylbenzene, (◊) 1,2-dimethoxyethane, (•) ethanenitrile, (▫) 2-propenenitrile, (-) trimethylethanenitrile *(Reproduced as a result of open access policy of IUPAC)*

The symmetry of the inorganic anion is considered as the additional parameter to decrease the viscosity in the order $Cl^- > [PF_6]^- > [BF_4]^- > [NTf_2]^-$. Viscosity of many ionic liquids strongly depends upon the temperature e.g.[59] The viscosity of [BMIM][PF_6] increases 27% with a 5 degree change between 298 to 293 K. Small amount of impurities show a dramatic impact on the viscosity of ionic liquids.[60] As little as 2 wt% water reduced the observed viscosity of [BMIM][BF_4] by more than 50%. The general order of increasing viscosity with respect to the anion is $[(CF_3SO_2)_2N]^- \leq [CF_3SO_3]^- < [(C_2H_5SO_2)_2N]^- < [C_3F_7CO_2]^- < [CH_3CO_2]^- \leq [CH_3SO_3]^- < [C_4H_9SO_3]^-$[61] This trend does not correlate with the anion size, which suggests that there might be some other anion property such as their ability to form weak hydrogen bonds with cation that can affect the viscosity.[62] Studies suggest there is an inverse relationship between the conductivity and viscosity of ionic liquids[63] (Fig. 1.2.7).

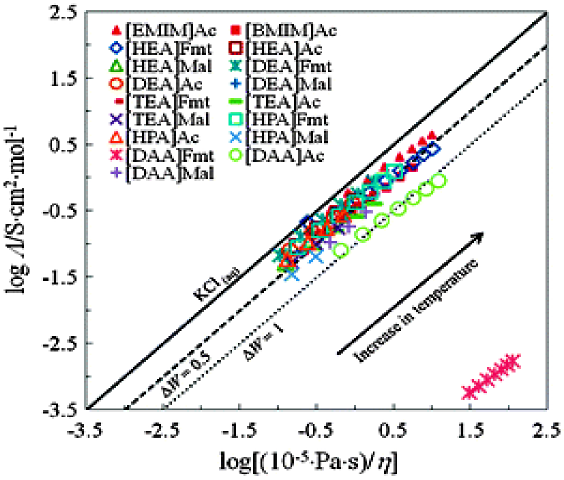


Fig. 1.2.7: The conductivity-viscosity correlation for different ionic liquids at temperatures from 278 to 358 K. *(Reproduced by permission from Royal Society of Chemistry)*

Surface Tension: Surface tension is an important property for the application of ionic liquids in multiphase processes. For the ionic liquid catalyzed reactions, which are carried out under multiphase homogeneous conditions, usually occur at the interface between the ionic liquid and the overlying organic phase.[64,65] These types of reactions are therefore dependent on the access of the catalyst to the surface and on the transfer of the material across the interface. Thus, the rates of these processes are dependent on surface tensions. Generally, liquid/ air surface tension values for ionic liquids are higher than those for conventional solvents [(3.3-5.7)× 10^{-4} N/cm] but less than water. Surface tension values vary with temperature and both the surface excess entropy and energy are affected by the alkyl chain length. In general, for a fixed cation, larger anion has the higher surface tension.

Refractive Index: This parameter is the measure of polarizability/dipolarity of the medium and the excess molar refraction is used to predict the solute distribution. The values found for [BMIM][X] salts are comparable to those of organic solvents.[66] Some examples are given below in Table 1.2.2.

Table 1.2.2: List of some of the important properties of ionic liquids

Ionic liquid	Density(25°C) (g mL^{-1})	Viscosity (cP) (t)	Conductivity (mScm^{-1})	Refractive index (n)
[EMIM][NTf$_2$]	1.519	28 (25°C)	8.8	1.423
[BMIM][NTf$_2$]	1.436	52 (25°C)	-	1.427
[HMIM][NTf$_2$]	1.372	-	-	-
[OMIM][NTf$_2$]	1.320	-	-	-
[BMPYRR][NTf$_2$]	1.410	85 (25°C)	2.2	-
[BMIM][BF$_4$]	1.120	233 (25°C)	1.7	1.429

Polarity: For ionic liquids, it is important to develop empirical solvent polarity scales, which can help to explain differences in solvent-mediated reaction pathway, reaction yields, synthesis product ratios, chromatographic retention and extraction coefficients.[67] Empirical polarity parameter scales were described by observing the effect of the solvent on solvent-dependent processes, such as the rate of chemical reactions, the adsorption of light by solvatochromic and fluorescent dyes and also partition coefficients.[68] Solute-solvent interactions are easy to probe by means of solvatochromic probes.[69] Each probe is sensitive to a particular kind of interaction (hydrogen bonding, dipolarity/ polarizibility)[70]. Solvent polarity arises from the sum of all possible intermolecular interactions and therefore different probes offer different polarity scales. (1**) Neutral Probes:** Nile red and aminophthalimides; Nile red was the first solvatochromic dye used by Carmicheal and Seddon on a series of 1-alkyl-3-methyl imidazolium ionic liquids.[71] They proposed that the polarity of these ionic liquids is comparable to that of short chain alcohols. For the $[BMIM]^+$ ionic liquids, the polarity decreases through the series, $[NO_2]^-$ > $[NO_3]^-$ > $[BF_4]^-$ > $[NTf_2]^-$ > $[PF_6]^-$, which can be correlated with the anion size.

The fluorescent probes *i.e.* 4-aminophthalimide (AP) and *N,N'*-dimethyl-4-aminophthalimide (DAP) show that $[BMIM][PF_6]$ is more polar than acetonitrile and less than methanol. The imidazolium salts are more polar than pyridinium and the polarity of pyridinium ionic liquid is nearly the same as that of acetonitrile. For these two dyes the replacement of anions do not change the polarity of ionic liquids.

(2) **Reichardt's Dye:** This is the most widely used zwitter-ionic dye which suggests the normalized scale of polarity [$E_T(30)$]. This probe detects the hydrogen bond donor ability of the solvent.

(3) **Abboud-Kamlet-Taft parameters:** It is difficult to determine the polarity of ionic liquids using the above mentioned solvatochromic probes solely. In lieu of this complexity, Crowhurst et al.[69(e)] applied the Abboud-Kamlet-Taft method using three solvatochromic dyes *i.e* the Reichardt's dye, *N,N*-diethyl-4-nitroaniline and 4-

nitroaniline dye to determine the solvent parameters, π^*, α, β of several imidazolium and pyrrolidinium ionic liquids.[71] About 20 years ago, the Abboud-Kamlet-Taft (AKT) method was proposed to separate non-specific effects of the local electrical fields from the hydrogen bonding effects.[72] This method evaluates the solvent properties in particular, dipolarity or polarizability (π^*), H-bond basicity (β) and H-bond acidity (α). Table 1.2.3 enlists AKT parameters of some ionic liquids for ready reference.

Table 1.2.3: A list of Abboud-Kamlet-Taft solvent parameters for different ionic liquids[70]

Ionic liquid	E_T^N	π^*	α	β
[BMIM][BF_4]	0.670	1.047	0.627	0.376
[BMIM][PF_6]	0.669	1.032	0.634	0.207
[BMIM][NTf_2]	0.644	0.984	0.617	0.243
[BMPYRR][NTf_2]	0.544	0.954	0.427	0.252
[OMIM][PF_6]	0.633	-	-	-
[OMIM][NTf_2]	0.629	0.961	0.595	0.291

1.3 Phase Behavior of Ionic Liquids:

For the design of separation processes involving ionic liquids, such as gas absorption, liquid-liquid extraction and membrane separation, the phase behavior of ionic liquid mixture is of great importance.[72,73] The phase behavior of binary, ternary and multicomponent ionic liquid systems has been widely studied by many leading groups in the area of ionic liquids. The phase behavior of binary ionic liquid systems can roughly be divided into three classes:[74] (1) ionic liquids with dissolved gases, (2) ionic liquids with water and (3) ionic liquids with organic solvents. The first class involves vapor-liquid equilibrium data and the last two classes involve liquid-liquid equilibrium data. The most investigated binary ionic liquid systems are mixtures with carbon dioxide (CO_2).[75] Lachwa et al have shown how the fluid-phase behavior (liquid-liquid miscibility window) can be fine tuned by adjusting the nature of ionic liquid or the molecular component.[76]

It has been known for a long time now that the presence of low fractions of water in the ionic liquid phase can dramatically alter their physical properties and may also affect the rates and selectivity of reaction involving ionic liquids.[77] Ionic liquid ions (constituent cation and anion) are solvated in the aqueous solutions causing structural changes in the aqueous environment.[78] In solution, the solvation/ interactions of ions or ion pair with solvent determine the unique properties of these systems.[79],[80] Volumetric and acoustic properties of electrolytic and non-electrolytic solutions elucidate the various solute-solvent interactions that exist in these solutions. Acoustic, volumetric and osmotic data are relevant in assessing the intermolecular interactions between ionic liquid and solvents and also for the development of thermodynamic models specific to ionic liquid-containing systems.[81] These data can also be used to obtain the isoentropic compressibility, apparent molar volumes, apparent molar compressibility, activity and activity coefficients of ionic liquids at different concentrations.[82] The data of the limiting partial molar volume and compressibility can specifically differentiate between ionic liquid-water and ionic liquid-ionic liquid interactions.

The thermal data on a given system gives the precise information about the solute-solvent interactions and the reorientation of solvent molecules around a solute molecule. Thermal data for ionic liquids are very scarce in the literature therefore deserve serious attention of researchers around the world. This is essential for understanding the intermolecular interactions between the ionic liquid and solvent.

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CHAPTER 2: AIMS & OBJECTIVES

“A thorough literature search on the ionic liquids (ILs) suggests that albeit a plethora of documents is available with regard to the various aspects of these materials, there are very few reports on their thermal properties in mixtures with different solvents. Hence, it is imperative to design experiments and rationalize the experimental data to gather scrupulous information on their thermal behavior. This present chapter briefly outlines the aims and objectives of the proposed research topic. It also details the methodology adopted to carry out these studies.”

The quest of suitable solvents for replacing the volatile organic solvents has given birth to a neoteric class of solvents known as ionic liquids. They have emerged as potentially safe candidates to reduce the air pollution and are proving to be useful chemicals required in a variety of applications. However, ionic liquids are quite viscous in nature and therefore, can have very restricted applications in chemical processes. The detrimental effect of viscosity of ionic liquids on the kinetics of organic reactions is evident from the recent work. In order to use ionic liquids with greater efficiency, it is possible to reduce the viscosity of ionic liquids by several times by adding a co-solvent. Such solutions are very effective in carrying out organic reactions as seen recently in our laboratory. The sharp reduction in viscosity of ionic liquids is the result of the dramatic changes in the ion-ion and ion-solvent interactions operating in ionic liquid-cosolvent systems.

In view of the above, the following objectives were envisaged for carrying out this work. These objectives were aimed at gathering a better knowledge of binary mixtures of ionic liquids during the future course of the research work:

- to elucidate the interactions taking place between protic ionic liquids (PILs) with different ring structures and molecular solvents of varied polarities. The thermal effects thus, obtained experimentally using Isothermal Titration Calorimeter (ITC), are expected to be useful in probing the ion-ion and ion-solvent interactions existing between PIL entities and different molecular solvents,

- as a case study, the ionic liquid, $[BMIM][BF_4]$, one of the most commonly used materials is investigated in detail. A total of nine solvents: water, methanol, ethanol, propanol, ethylene glycol, formamide, dimethylsulfoxide and *N,N'*-dimethylformamide were employed to probe the nature of ion-ion and ion-solvent interactions prevailing in the systems of IL and solvents of diverse nature,
- to discern the role of a different counter anion *i.e.* $[NTf_2]^-$ combined with the core cation $[BMIM]^+$ in modifying the ion-solvent and ion-ion interactions. It gives an insight into the different interactions operational at molecular level in terms of the change in enthalpies of the IL-solvent systems,
- to study the ionic interactions prevailing in the mixtures of two pure ionic liquids and also in their aqueous solutions. The study would help in comprehending the role of water as the structure modifier for ionic liquids and
- to investigate the mixing behavior of common electrolytes such as guanidinium chloride, sodium chloride, lithium chloride, tetra alkyl ammonium salts. This study would help in quantifying the effect of a structure breaker electrolyte on other structure-maker or structure-breaker electrolytes in terms of thermal changes. Also, it would be further helpful in comparing the common electrolytes with ionic liquids, the so called potential electrolytes and labeling them as structure-maker or structure-breaker.

The enthalpic analysis of the binary mixtures of ionic liquids in very dilute range using ITC has been done for the first time. The experiments are planned 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 modified, as we increase the number of these ions in the solution. ITC is a powerful tool to obtain high precision enthalpy data in very dilute solutions.

CHAPTER 3: EXPERIMENTAL

"It was a great step in science when men became convinced that, in order to understand the nature of things, they must begin by asking, not whether a thing is good or bad, noxious or beneficial, but of what kind it is? And how much is there of it? Quality & Quantity were then first recognized as primary features to be observed in scientific inquiry."

James Clerk Maxwell (15th September 1870)
Address to the Mathematical & Physical
Sections of British Association, Liverpool.

The present thesis deals with two different type of materials, (1) ionic liquids and (2) Inorganic/organic solvents. The ionic liquids employed for the experimets were (a) protic and (b) aprotic in nature.

The representative synthetic methods for both the classes were taken from the reported procedures mentioned with each case.

3.1 Synthesis of protic ionic liquids:

Protic ionic liquids were synthesised by the dropwise addition of an freshly distilled acid in equimolar ratio (to ensure the complete neutralization) to the base with constant stirring. The products were confirmed by ^{1}H NMR. The synthesized protic ionic liquids were dried under vacuo at 80°C for 10-12 h prior to their use[1].

3.2 Synthesis of Aprotic ionic liquids:

Aprotic ionic liquids are synthesised in two steps[2,3,4,5,6,7,8]: (1) formation of cation by alkylation and (2) anion exchange/metathesis. The latter step of the synthetic method is used to either synthesise a hydrophilic or a hydrophobic ionic liquids.

Ionic liquid precursor (1-methyl imidazole etc.) was refluxed with n-alkyl bromide in 1:1.2 ratio at 50-60°C with constant stirring for 12-15 h. The product was an ionic liquid, which was washed 5-6 times with ethylacetate. The ionic liquid was solubilized in ethylacetate phase and the excess unreacted alkali halide was removed by simple decantation. After riguorous washing the ionic liquid was put on high vaccum for 12 h. After the ionic liquid is dried up twice, sodiumtetrafluoroborate/ lithium bis(trifluoromethyl sufonyl)imide (1:1.2 ratio) was added in excess of dichloromethane/water. The hydrophilic ionic liquids form sepearte phase with dichloromethane and the hydrophobic ionic liquids are insoluble in water. There is also an insoluble phase of crystalline sodium halide/lithium halide. Hence by simple filteration method, pure ionic liquids can be removed out by simple filteration method. These freshly prepared ionic liquids were put on high vaccum for 12-14 h. The water content was checked using a Karl-Fischer titrator, which was found to be <30 ppm. The residual halide contents were estimated by Volhard's titration method[2,9] and were in the acceptable range of 30 to 100 ppm depending upon the nature of anion of ionic liquids synthesized halide contents. Besides Volhard's titration method, ion chromatography is considered to be a precise methodology. However, the standard Volhard titration has been validated using a chloride-selective electrode.[2] All the ionic liquids were also checked by ^{1}H NMR which are attaced at the end of this chapter. The ^{1}H NMR are in good agreement with those of the reported values in literature[3-8]. These spectra are given at the end of this chapter.

The solvents employed in the study were of spectroscopic grade. Each solvent was dried using the standard techniques in order to eliminate any water contents. Throughout the measurements, all efforts were made to minimize water content both in the synthesizing ionic liquids and solvents. Water employed in the measurement was of deionized quality with its specific conductance less than 0.055 x 10^{-6} S cm^{-1}. D_2O was used as procured.

The basic deduced experimental quantity was the excess partial molar enthalpy of the ionic liquid, H^{E}_{IL} in its solution with a solvent, which was measured using an Isothermal Titration Calorimeter (ITC), MicroCal, LLC-VP 2000. A typical ITC unit is shown in Fig. 3.1.

Fig. 3.1: A typical isothermal titration calorimeter (VP-ITC, LLC Microcal 2000)

Isothermal titration calorimeter is the gold standard for measuring molecular level interactions. When solute solvent interact with each other, heat is either generated or absorbed. ITC is a thermodynamic technique that directly measures this generated or absorbed heat. Measurement of this heat allows accurate determination of enthalpy of the molecular interactions. ITC is usually used for determining the total thermodynamic profile of the biomolecules. This instument has been used for the first time to probe the molecular level interactions taking place between ionic liquids (solute) and various solvents in very dilute range.

3.3 Working principle of an isothermal titration calorimeter:

An isothermal titration calorimeter is composed of two identical coin shaped cells. These cells are made up of highly efficient thermal conducting and chemically inert material such as hastelloy alloy and are surrounded by an adiabatic jacket. To detect the difference between the reference cell (filled with pure solvent *i.e.* water) and the sample cell (filled with same solvent as that in the reference cell). Prior to the addition of the solute, a constant power (30 μcal) is applied to the reference cell. This directs a feed back circuit, activating a heater located on the sample cell. The difference between the temperature of the reference cell and the sample cell is then measured. This difference is calibrated to power units and referred as the DP signal or the differential power. This signal is used to maintain the temperature equilibrium (Fig. 3.3.1).

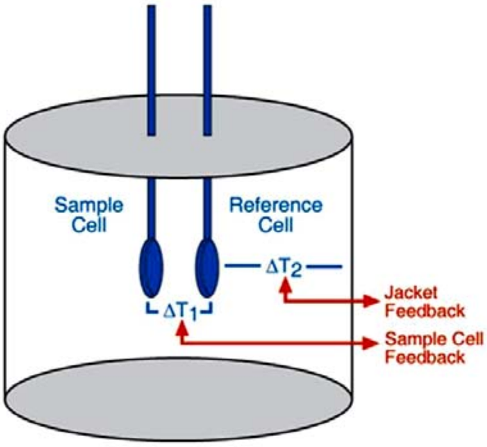


Fig. 3.3.1: Working principle of an isothermal titration calorimeter

The syringe (titration syringe) containing the titrant/ solute (ionic liquid solution) is titrated into the cell (sample) containing the same solvent, which is used for preparing the ionic liquid solution. Total capacity of the titration syringe and the sample cell is 250 μL and 1.8mL, respectively. The working volume of the sample cell is 1.4 mL (Fig. 3.3.2). If the addition of the titrant aliquot results in the evolution of heat inside the sample cell, it causes a negative change in the DP power since the chemically evolved heat provides the heat that the DP feedback is no longer required to provide and vice versa happens for heat absorbing reactions. The DP has units of power, the time integral of the peak yields a measurement of thermal energy, ΔH. This heat is released or absorbed in direct proportion to the interactions between the titrant and the material inside the sample cell.

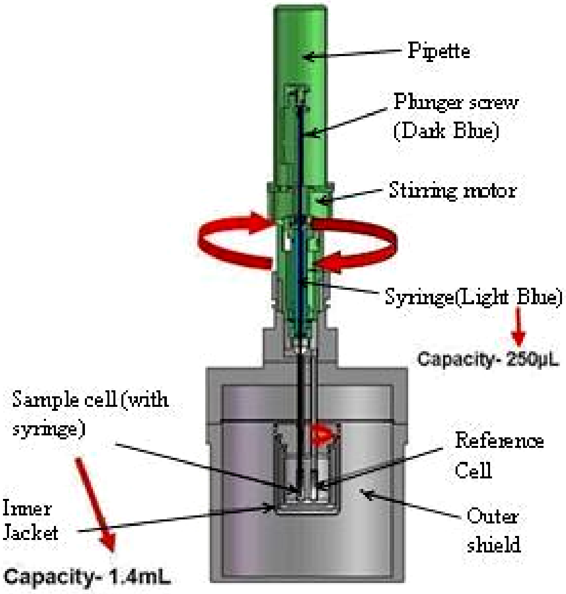


Fig. 3.3.2: Diagrammatic representation of the components of a typical ITC

When the reference substance present in the sample cell becomes saturated with the added titrant, the heat signal diminishes until only the background heat of dilution is observed. These observations are plotted as the power needed to maintain an isothermal condition throughout the experiment between the refrence and the sample cell against time. Thus, the experimental raw data consist of a series of heat flow (power), with each spike corresponding to one titrant injection. These heat flow spikes are integrated with respect to time, giving the total heat exchanged per injection. The pattern of these heat effects as a fuction of the concentration of the titrant can be analysed to give the thermodynamic profile of the interactions between solute and solvent corresponding to the system under study.

For the systems mentioned in the present thesis, the titrations were carried out with pure solvents in the sample cell. In view of high viscosity of ionic liquids, dilute solutions of ionic liquids were taken in the injector syringe. The aliquots of 10 μL were injected in the sample cell after an interval of 10 min. It was ensured that before the next aliquot was added, equilibrium was reached in the solution present in the sample cell. Raw data produced during the experiments were checked for the sharp peaks ensuring that no saturation occurred at each injection. In Fig. 3.3.3 are shown saturated peaks, while the sharp peaks are displayed in Fig. 3.3.4 for the convenience of readers. All the experiments were performed at 298.15 K and at a stirring speed of 300 rpm.

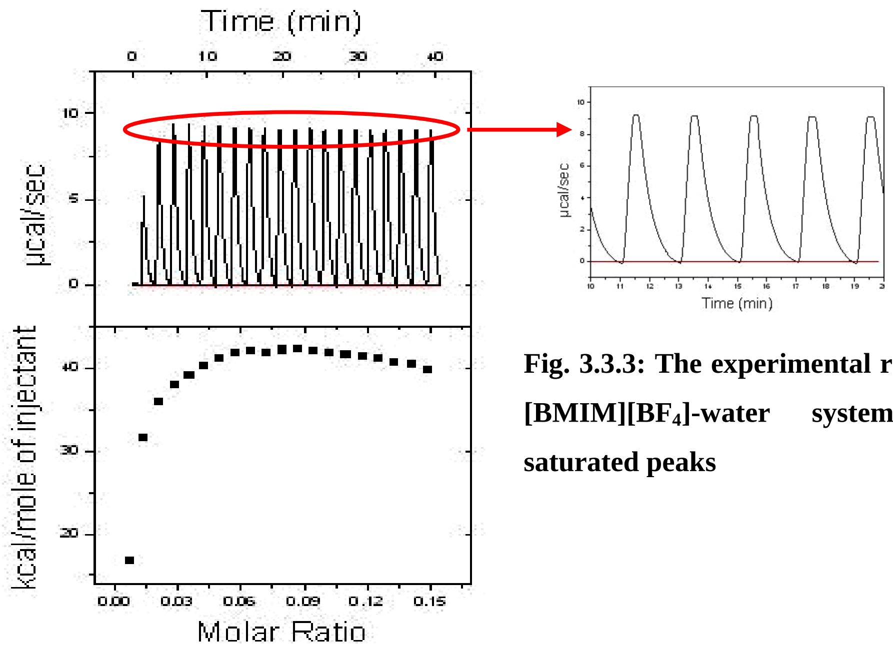


Fig. 3.3.3: The experimental raw data for [BMIM][BF$_4$]-water system showing saturated peaks

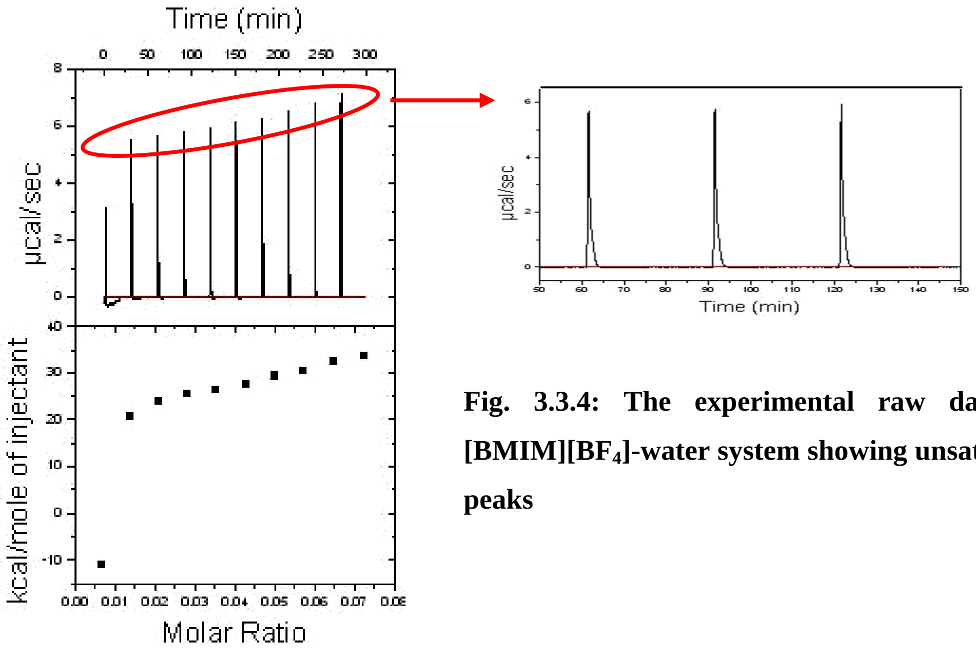


Fig. 3.3.4: The experimental raw data for [BMIM][BF$_4$]-water system showing unsaturated peaks

Before charging the solution and solvent in the injector syringe and sample cell, respectively were degassed for 5 min under vacuum on a thermovac with constant stirring. Temperature of the samples was maintained 1°C below the desired experimental temperature. All the precautions were taken to ensure that no air bubbles were present in any solvent or solutions. A schematic representation of the experimental procedure is given in Fig. 3.3.5.

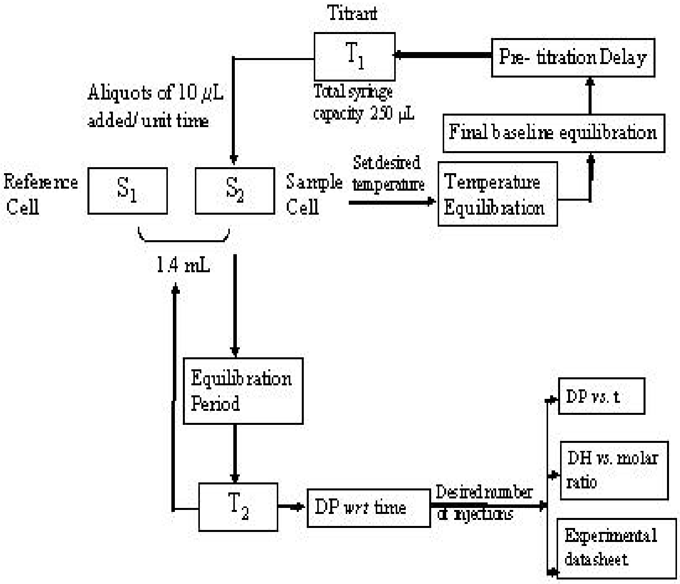


Fig. 3.3.5: Diagrammatic representation of the scheme to design an experiment on ITC

3.4 Calibration of the instrument:

The instrument was calibrated using the experimental $H^E{}_{IL}$ data on aqueous 1-propanol system at 298.15 K[10].Goodness of the calibration of the equipment is demonstrated in Fig. 3.4.1, in which we have plotted the difference, % δH^{E}_{1P} defined by (our H^{E}_{1P} – reported interpolated H^{E}_{1P}) x 100/ our H^{E}_{1P} as a function of molality, m of 1-propanol. A random scattering of the δH^{E}_{1P} values with an average of ±5% can be witnessed lending confidence in our measurements. However, the δH^{E}_{1P} values can go as high as ± 8% in very dilute solutions. Before starting the experiments the instrument was calibrated using water-water titration and the baseline was calibrated using the Y-axis calibration by employing pulse method. The H^{E}_{IL} values were obtained from the changes in heat DH observed after each injection by H^{E}_{IL} (J mol^{-1}) as H^{E}_{IL} = DH / n_{IL}. The quantity, n_{IL} indicates number of moles of ionic liquid. For convenience, ionic liquid is denoted by the subscript IL throughout this manuscript. Note that $x_{IL} + x_{solv.} = 1$, where x indicates mole fraction of a species and the subscript solv. denotes a solvent.

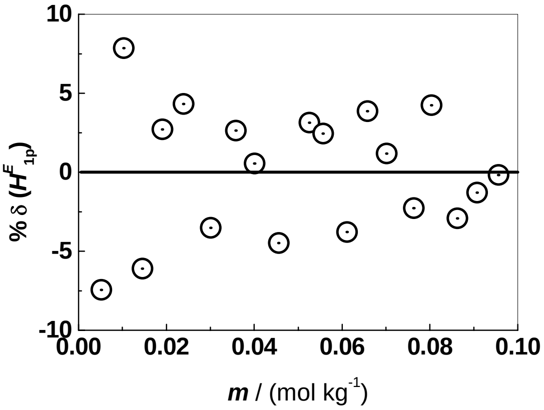
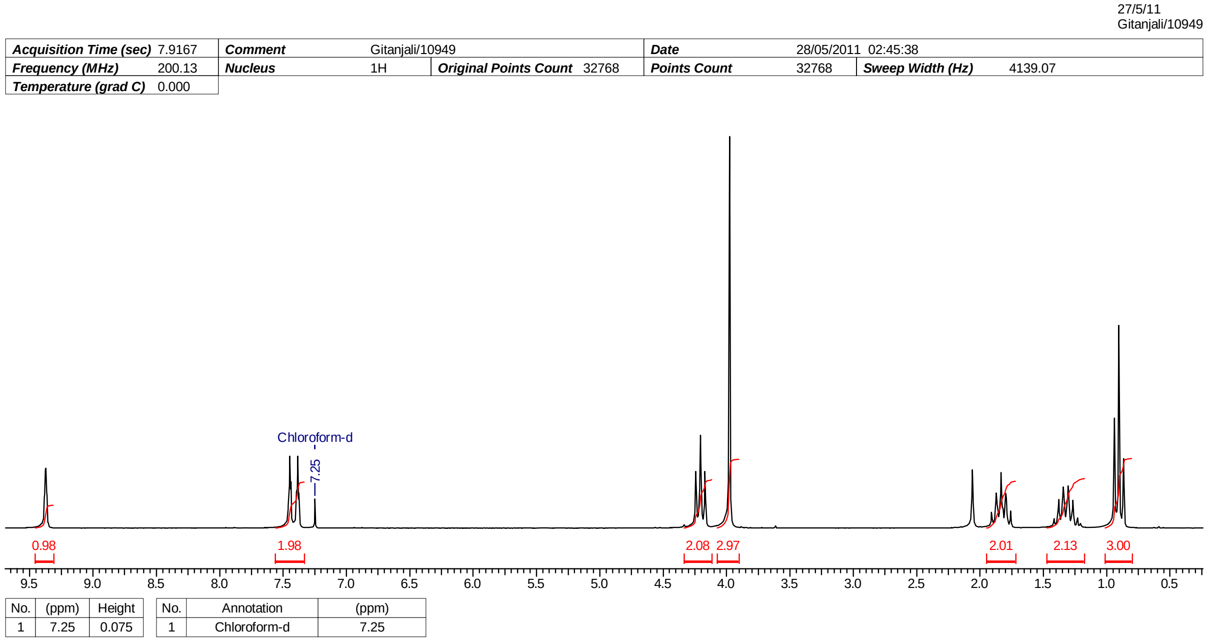


Fig. 3.4.1: Percent deviation, *% δ (H^{E}_{1P})* calculated from between ours and the literature[10]

3.5 **Characterization of the ionic liquids:**

[BMIM][BF_4]



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Gitanjali/10949

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Sweep Width (Hz) 4139.07

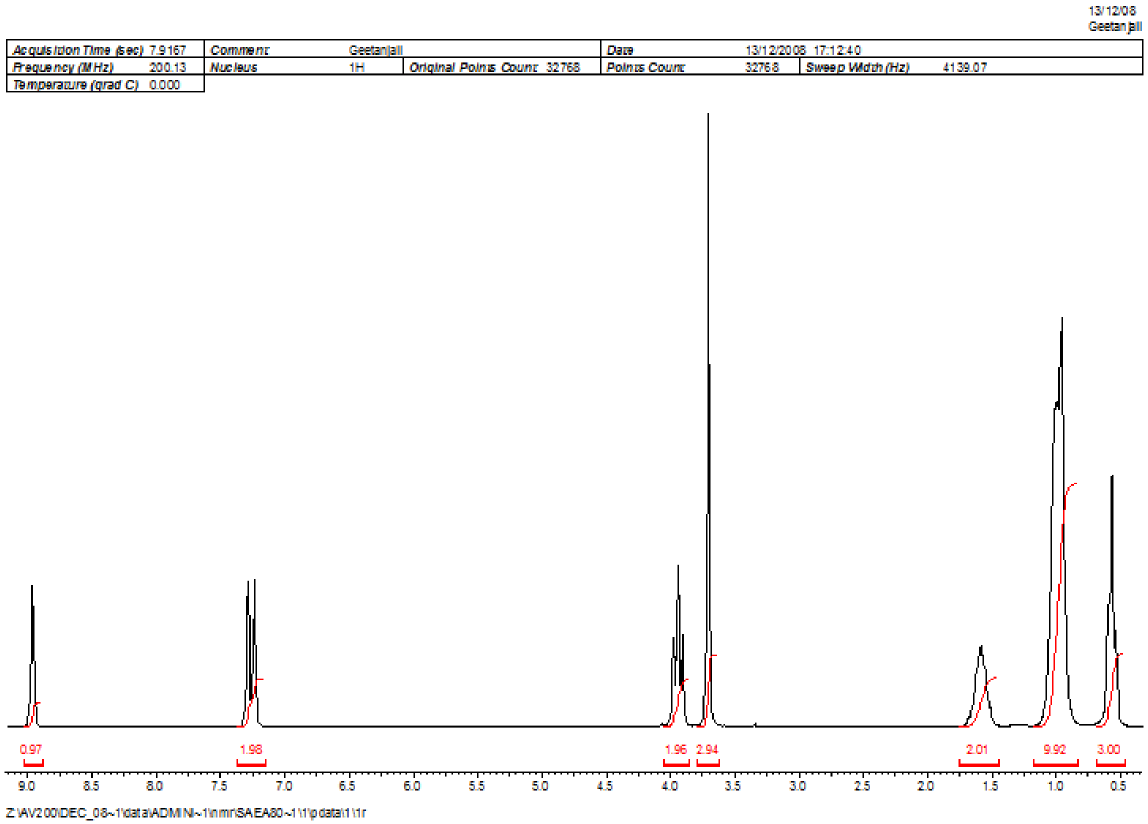
No.	(ppm)	Height
1	7.25	0.075

No.	Annotation	(ppm)
1	Chloroform-d	7.25

Fig. 3.5.1: A ^{1}H NMR for 1-butyl-3-methylimidazolium tetrafluoroborate

Z:\AV200\MAY_11~1\data\ADMINI~1\nmr\FR89E1~1\1\pdata\1\1r

[OMIM][BF_4]



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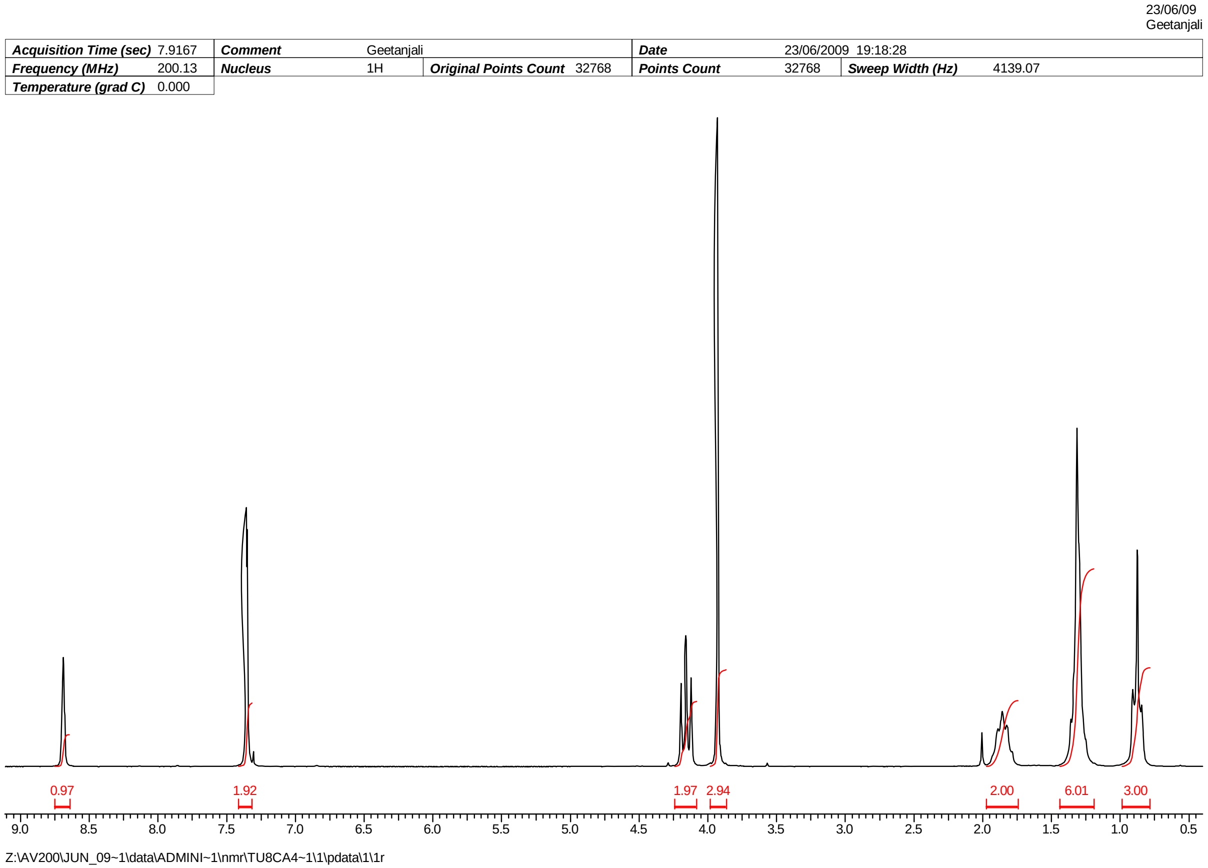
Temperature (grad C)	0.000								

Z:\AV200\DEC_08~1\data\ADMINI~1\nmr\SAEA80~1\1\pdata\1\1r

Fig. 3.5.2: A ^{1}H NMR spectra for 1-octyl-3-methylimidazolium tetrafluoroborate

[HMIM][NTf_2]



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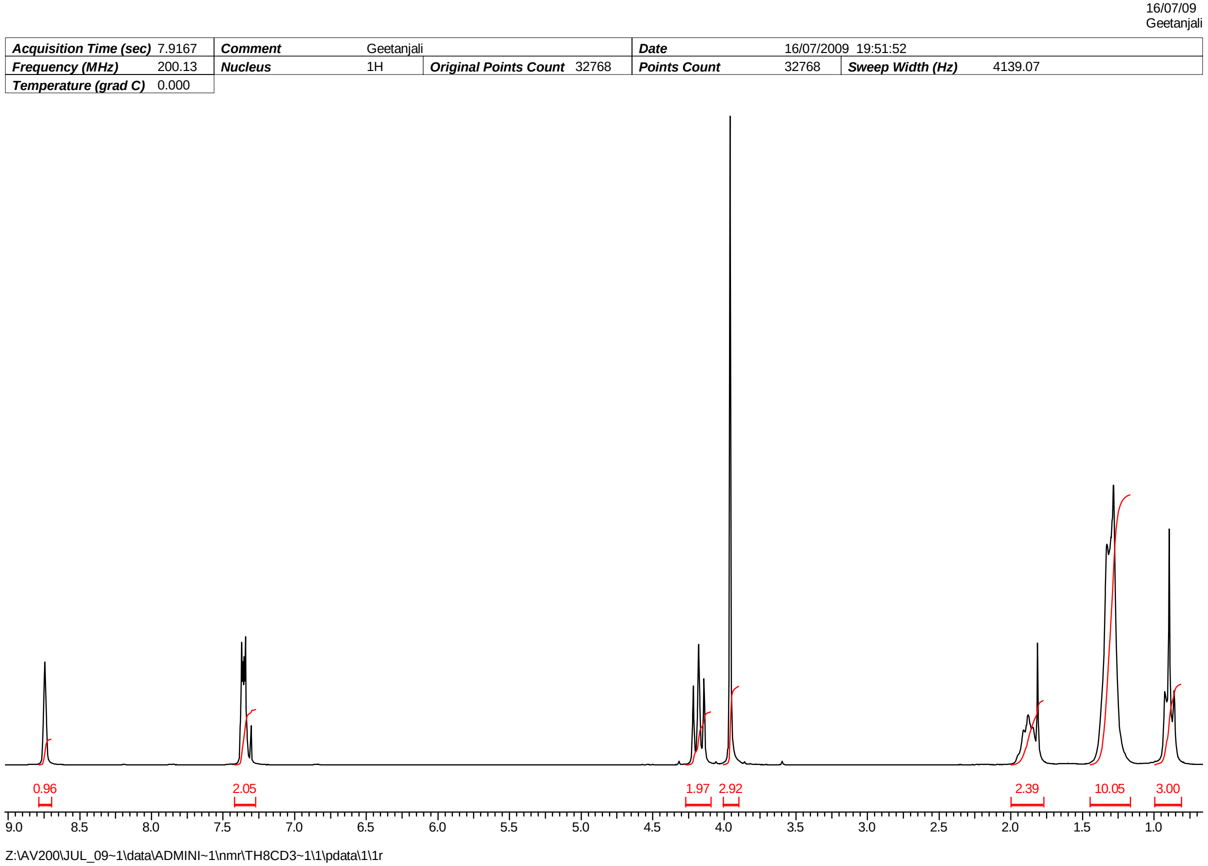
Temperature (grad C)	0.000								

Z:\AV200\JUN_09~1\data\ADMINI~1\nmr\TU8CA4~1\1\pdata\1\1r

Fig. 3.5.3: A ^{1}H NMR spectra for 1-hexyl-3-methylimidazolium bis(trifluoromethylsulphonyl)imide

[OMIM][NTf$_2$]



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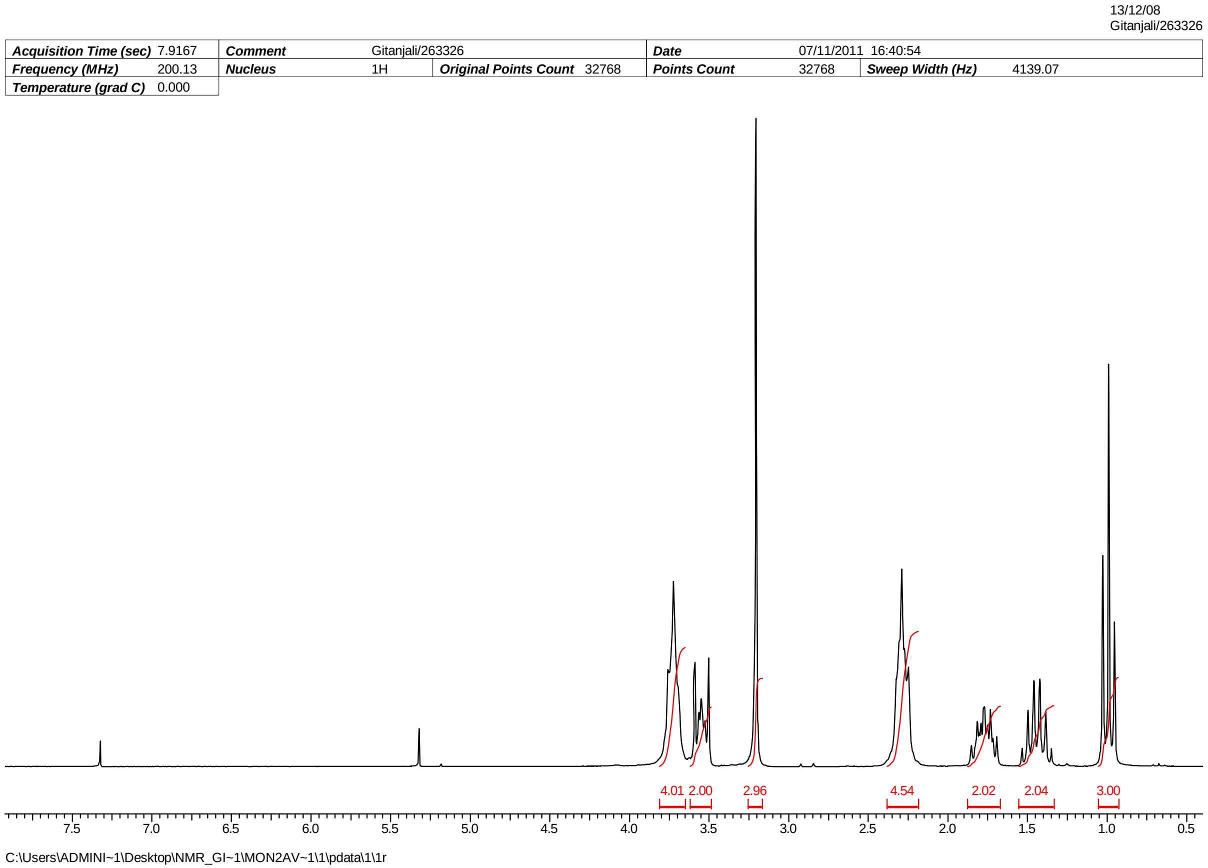
Temperature (grad C)	0.000								

Z:\AV200\JUL_09~1\data\ADMINI~1\nmr\TH8CD3~1\1\pdata\1\1r

Fig. 3.5.4: A ^{1}H NMR spectra for 1-octyl-3-methylimidazolium bis(trifluoromethylsufonyl)imide

[BMPyrr][BF_4]



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Temperature (grad C)	0.000								

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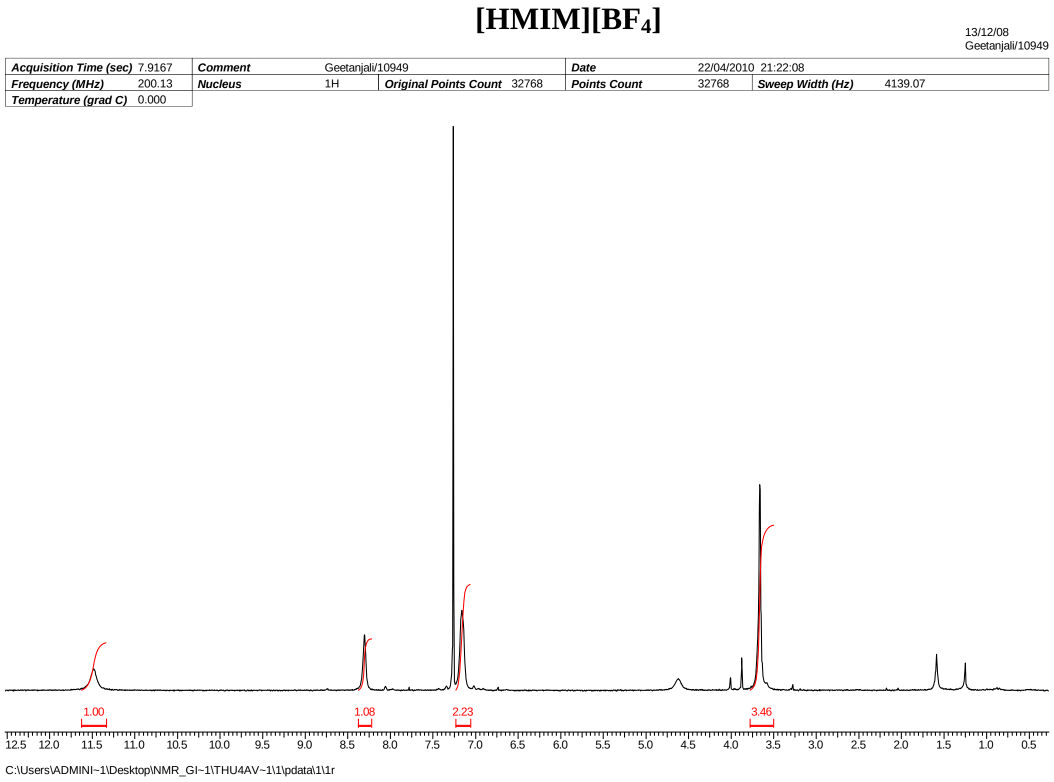
Fig.3.5.5: A ^{1}H NMR spectra for *N,N*-butylmethylpyrrolidinium tetrafluoroborate



[HMIM][BF_4]

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Geetanjali/10949

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Temperature (grad C)	0.000								

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Fig. 3.5.6: A ^{1}H NMR spectra for 1-methylimidazolium tetrafluoroborate

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CHAPTER 4: THE PIL-SOLVENT SYSTEMS

"Designer by choice, tailor made by need, eco-friendly by nature and intrinsically safer solvents; in the race PILs are the dark-horses, which are anticipated to go a long way. They are the most promising and potential candidates for the next generation proton-conducting materials for the fuel cell chemistry. From the proton diffusion perspective, the cheese of the fuel cell stack, the fuel cell membrane, need to be as liquid as possible and for the stability of the cell, solid the better. And PILs assorted with polymers can do that wonder."

The Ionic Liquid Community

Protic ionic liquids (PILs) or the liquid acidic salts are the subset of ionic liquid, prepared through proton transfer from a Brönsted acid to a Brönsted base.[1] The main feature of PILs is their ability to form hydrogen bonds[2], for which they are being investigated as amphiphile self assembly media[3], biological solvents[4] and polymer membrane fuel cell[5]. The binary mixtures of PILs with protic solvents like water provide very high conductivities[6], which can prove to be very useful in fuel cell applications. Recently, PILs and their binary mixtures have been extensively used in organic synthesis as catalysts.[7,8,9,10] There are limited reports on PILs dealing with their different aspects.[1(d,e),11,12] Unfortunately, the reports on thermal behavior of ionic liquids are very scarce. The present chapter shows the thermal behavior of the binary mixtures of PILs with a view to discern the molecular level interactions operating in the protic ionic liquid-solvent systems.

4.1 Relevant thermodynamic properties for the present study:

In solution, the solvation and the interactions of the ions or ion pair with the solvent determine the unique properties of these systems. A complete thermodynamic profile of IL-containing systems can be derived from the calorimetric quantity H^{E}_{IL}. This information is of paramount information for chemical process engineers.

When a given amount of solution (titrant) is added to the pure solvent (sample), it is accompanied by absorption or evolution of heat. This heat corresponds to the dilution of the solution with pure solvent. For a general solution process taking place at constant temperature and pressure,

$$\left[\begin{array}{l}\text{Solution of } n_1 \text{ solvent} \\ \text{and } n_2 \text{ solute}\end{array}\right] + n_1' \text{ solvent (l)} \longrightarrow \left[\begin{array}{l}\text{Solution of } (n_1+ n_1') \text{ solvent} \\ \text{and } n_2 \text{ solute}\end{array}\right]$$

$$\Delta H = H(soln) - (n_1 H_1^0 + n_2 H_2^0) \tag{1}$$

H^0 refers to the molar enthalpies of the pure components; $H\ (soln)$ is the total enthalpy of solution. This thermal effect (ΔH) is termed as the integral heat of solution:

$$H(soln) = (n_1 H_1^0 + n_2 H_2^0) + \Delta H \tag{2}$$

.

$$H(soln) = n_1 \overline{H_1} + n_2 \overline{H_2} \tag{3}$$

where $\Delta\overline{H_1}$ and $\Delta\overline{H_2}$ are the partial or differential molar heats of solvent and solute

$$\overline{H_1} = (\partial H / \partial n_1)_{T, P, n2} \tag{4}$$

$$\overline{H_2} = (\partial H / \partial n_2)_{T, P, n1} \tag{5}$$

another thermodynamic parameter apparent molar enthalpy, ϕ_H, can be defined as:

$$\phi_H = (H(soln) - n_1 \overline{H_1}^0) / n_2 \tag{6}$$

and the relative apparent molar enthalpy (ϕ_L), which is equal and opposite in sign to the heat of dilution (ΔH_{dil}) of one mole of solute with an infinite amount of solvent:

$$\phi_L = \Delta H_{dil} = \phi_H - \phi_H^0 \tag{7}$$

the relative enthalpies can be given as:

$$L = n_1 \overline{L}_1 + n_2 \overline{L}_2 \tag{8}$$

and

$$L = n_2 \phi_L \tag{9}$$

relative apparent molar enthalpy can be used to determine the relative partial molar heat content of solute $\bar{L}_2$ and solvent $\bar{L}_1$,

$$\bar{L}_2 = \phi_L + n_1 (\partial \phi_L / n_2) = (\partial L / n_2)_{T,P,n1} \tag{10}$$

$$\bar{L}_1 = -(n_2^2 / n_1) (\partial \phi_L / n_2) = (\partial L / n_1)_{T,P,n2} \tag{11}$$

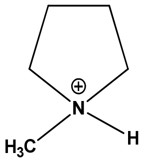
The heat of mixing can be obtained by:

$$\Delta H_{mix} = L - n_2 L_2 \tag{12}$$

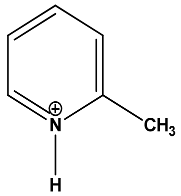
L_2 is the relative partial molar heat content of the pure solute, which is equal to the negative standard molar enthalpies of solution ($\Delta H^0_m = L_2$) and can be obtained by extrapolating molar solution enthalpy to infinite dilution. It can also be obtained by plotting the data of $\bar{L}_2$against n_1/n_2 and extrapolation to zero value of n_1/n_2.

4.2 PIL-solvent systems:

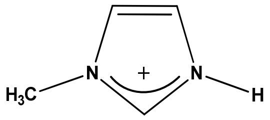
It is very important to understand the ion-solvent and ion-ion interactions in the PILs-solvent systems. The PILs chosen for the study are with parent rings of different nature, from aromatic to non-aromatic.



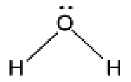
pyrrolidinium



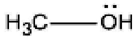
pyridinium



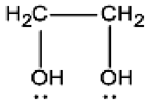
imidazolium



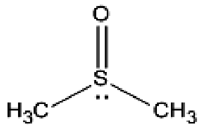
Water



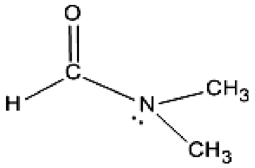
Methanol



Ethylene Glycol



Dimethyl Sulfoxide



N,N'-dimethylformamide

Fig. 4.2.1: A List of protic ionic liquids and the solvents employed in the study

The solvents chosen are based on the difference in their relative permittivity. The PILs and the solvents employed in the present study are listed in Fig. 4.2.1.

The PIL-solvent mixture was prepared in a very dilute range, which was taken it the titration syringe (250μL) and the pure solvent (1.4 mL) is taken in the sample cell. The 10 μL aliquots of the titrant were added to the sample cell after an interval of 10 min. This interval helps the system to attain the thermal equilibrium before the addition of next aliquot. The basic experimental quantity is the excess partial molar enthalpy H^{E}_{IL} (J mol^{-1}), which is derived out of the experimental calorimetric data (DH) by using the following equation:

$$H^{E}_{IL} = \mathrm{DH}/\ \mathrm{n}_{IL} \tag{13}$$

where DH= differential heat, n_{IL}= no. of moles of ionic liquid

The excess enthalpies can provide a starting point for understanding the species interactions and it can be best explained as the difference in the strength of interactions between unlike species compared to like species. H^{E}_{IL} can be compared for all the three PILs to distinguish the ring effect on the interaction between a PIL having different ring structures and solvents of varied properties (Fig. 4.2.2). The effect of changing the nature of the parent ring is clearly visible. The H^{E}_{IL} values for the three PILs and a common anion $[BF_4]^-$, in the presence of water display the following trend:

$$[hPYRR]^+ > [hPY]^+ > [MIM]^+$$

The H^{E}_{IL} values for these PILs are very high in magnitude suggesting the interactions of very high order between the two entities[13]. The PILs studied belong to two different groups, (a) non-aromatic PILs and (b) aromatic PILs.

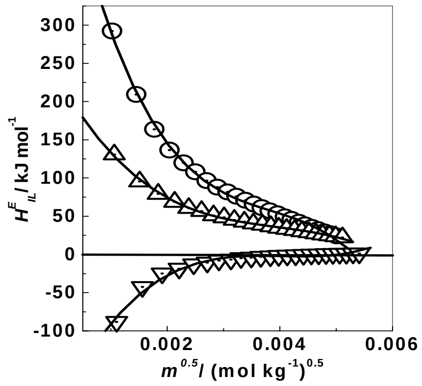


Fig. 4.2.2: A comparative H^{E}_{IL}- $m^{0.5}$ plot for, (⊙) [hPYRR][BF_4]; (△) [hPY][BF_4]; (▽) [MIM][BF_4]

Out of the three PILs employed in this study, pyridinium and imidazolium belong to aromatic class and pyrrolidinium is a non-aromatic PIL. The pyrrolidinium and pyridinium-based PILs show endothermic behavior with water, whereas the imidazolium based ionic liquids show exothermic behavior. This behavior can be explained on the basis of following factors:

(1) a. Among the aromatic class of PILs, the smaller size of the imidazolium-based PIL (Fig. 4.2.3) allows more solute molecules to fit into the cavities, which are spontaneously formed in the solvent phase. Once they fit into these localized cavities, the solvent weakens the Coulombic interaction prevailing between the cation and the anion. In the imidazolium cation $[MIM]^+$, the charge developed on the ring shuttles between the two nitrogens (N1 and N3), which are separated by a carbon atom, thus make the $[MIM]^+$cation a conjugated system (N1-C2-N3). The charge on the parent ring is partially delocalized, hence the interaction between the $[MIM]^+$ cation and the counter anions are stronger as compared to the pyridinium based PIL. During the solvation of these imidazolium based PILs, a huge amount is energy is released due to the rupture of bonds holding the solvent network system as well as the Coulombic bonding between the ions of opposite charge.

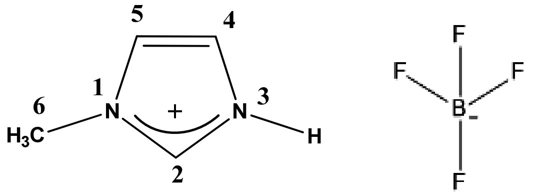


Fig. 4.2.3: An imidazolium-based protic ionic liquid

b. Once the PIL is dissociated into cation $[MIM]^+$ and counter anion $[BF_4]^-$, then the dispersion forces begin to operate in the system. There is a dominant role of ion-solvent interactions in further stabilizing the ionic species within the solvent. The proton (H^+) attached to the N3 and the C2 protons are acidic in nature as compared to other protons (H4, H5 and H6). The interactions between these two protons and oxygen of the solvent are the most favorable to form the hydrogen bond. The H-bonding helps in the restructuring of the solvent up to some extent but is not sufficient to compensate for the loss of energy due to the expensive breaking of the bonds. Thus, the cumulative effect of the destruction of the solvent network for the cavity formation and the breaking up of the ionic bonds between the ionic species, makes the solvation of the imidazolium-based PIL into water more exothermic.

(2) a. For another aromatic PIL *i.e.* pyridinium-based PIL (Fig. 4.2.4), this solvation and restructuring process takes a different course as compared to the imidazolium-based PIL. The pyridinium cation $[hPY]^+$ has a long aromatic system, in which the charge is completely delocalized over the entire ring. This results into the weaker electrostatic forces between the $[hPY]^+$ and $[BF_4]^-$. Thus, the addition of water does not significantly affect the structure of pyridinium-based PIL because of the weak electrostatic interactions between the ions and hence the breaking of bonds existing in the solvent network and those between the oppositely charged entities result in the evolution of heat.

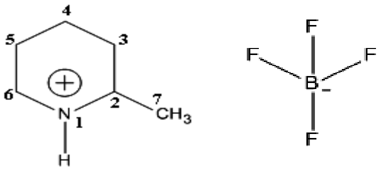


Fig. 4.2.4: A pyridinium-based protic ionic liquid

b. All the aromatic protons present in the [hPY]$^+$ are capable of making hydrogen bonds with the solvent. Thus the number of hydrogen bonds formed in the case of [hPY]$^+$ are much more than existing in the case of [MIM]$^+$ cation. Another fact is that the strength of H-bonding between the [hPY]$^+$ and counter anion [BF$_4$]$^-$ is equivalent to that between [hPY]$^+$ and water thus energetically it will not make any significant difference whether the PIL is intact as ion pair or dissociated and the cation is complexed with water molecule after the dissociation.

Hence, the heat evolved during the insertion of solute ([hPY][BF$_4$]) into solvent *i.e.* water will not only be stabilized, but the latter process of stabilization of the charges governs the whole solvation process of pyridinium based PIL. So, the whole process of solvation in water becomes endothermic in nature.

(2) a. The pyrrolidinium-based PIL (Fig. 4.2.5) show the highest value of interaction with water, which is evident from Fig. 4.2.2. The reason for this extreme behavior may lie in the non-aromatic behavior of this PIL. Because of its non-aromatic nature the charge on the parent ring remains localized on the nitrogen group of pyrrolidinium cation [hPYRR]$^+$. Because of the nature of this positive charge the Coulombic interaction between the cation [hPYRR]$^+$ and the anion [BF$_4$]$^-$ is too strong. The size of the [hPYRR]$^+$ cation is also bigger as compared to the other two cations *i.e.* [MIM]$^+$ and [hPY]$^+$. Due to these two factors the dissolution of pyrrolidinium-based PIL becomes extremely exothermic.

b. The [hPYRR]$^+$ cation, once formed has the maximum chances of forming hydrogen bonding with the oxygen atom of water molecule. Being non-aromatic in

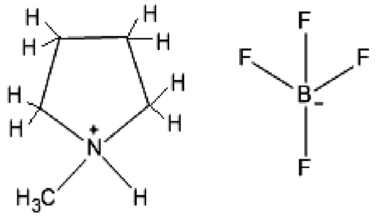


Fig. 4.2.5: A pyrrolidinium-based protic ionic liquid

in nature it contains the maximum number of protons, which contribute to the total enthalpy of the system by compensating to the heat evolved during the first step. Also, because of the formation of a number of hydrogen bonds the system becomes more compact which utilizes the energy of the system to make the overall process highly endothermic. Thus in terms of the hydrogen bonding capacity the interaction between solute and solvent is maximum in the case of pyrrolidinium-based PIL followed by pyridinium and imidazolium.

Apart from water, other solvents were also employed to probe the behavior of each of the three ionic liquids. This solvent dependency of $H^E{}_{IL}$ is shown in Fig. 4.2.6.

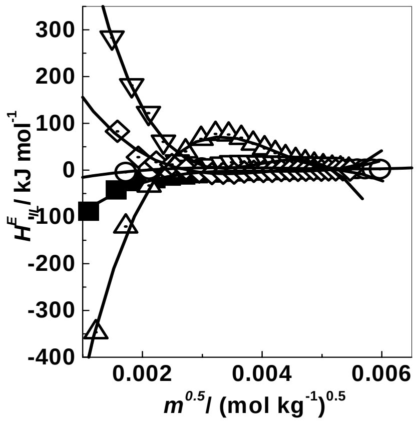


Fig. 4.2.6: Solvent dependency of $H^E{}_{IL}$ for imidazolium based protic ionic liquid (▽) DMSO, (◈) DMF, (⊙) ethylene glycol, (■) water, (△) methanol

On the basis of the H^{E}_{IL} values for imidazolium based PIL, the solvents can be divided into two groups and the observation can be explained on the basis of the solvent properties. The first group of solvents is the protic polar solvents including water, methanol and ethylene glycol and the other group is referred as the aprotic polar group which includes DMF and DMSO. The order shown by these solvents is:

$$\underbrace{\text{Methanol} < \text{Water} < \text{Ethylene Glycol}}_{\text{Protic polar}} < \underbrace{\text{DMF} < \text{DMSO}}_{\text{Aprotic polar}}$$

These results can be explained on the basis of the structural features of the solvents. The solubility parameter (δ^{d}, $J^{1/2}\ cm^{3/2}$) and the Trouton's constant ($\Delta S^{V} / R = \Delta H^{V}(tb) / R$, dimensionless), suggest that the stiffness or the orderness of the solvents follow the trend, water (47.9, 13.1), ethylene glycol (32.4, 13), methanol (29.3, 12.6), DMSO (26.6, 11.2) and DMF (24.1, 10.8).[14] For the protic polar ionic liquids, methanol is the most loosely packed solvent system, thus it becomes easier for the solute to make a cavity for itself at a lesser expense of energy. The insertion of a solute molecule inside the solvent system would result in the major rupture of the solvent system. This breaking up of the bonds results into the highly exothermic process, which is shown by the enthalpy profile in Fig. 4.2.6. Once the cavity is formed and the solute is dissolved, then short-range donor-acceptor type interactions between solute and solvent start the interplay. The methanol molecules are chain-like-arranged[15] and their hydrogen bond accepting ability is quite high so they can form hydrogen bonds with solute molecules and as the concentration of the solute is increased, the number of hydrogen bonds also increase. This increased bonding results into endothermic process, thus the dissolution of solute into methanol initially is an exothermic process and with the increase in the concentration of the solute becomes endothermic.

Going from methanol to water increases the hydrogen bonding capability, thus more number of hydrogen bonds are formed as compared to methanol. The process becomes endothermic, which in ethylene glycol is even more energy consuming hence more endothermic. On the basis of the fact that protic polar solvents are too rigid systems and for the cavity formation a large amount of bonds have to be broken up, this leads to the exothermic behavior of PILs in the dilute concentration range and as the concentration is increased due to the bond formation the whole process shifts towards the endothermic behavior.

In the case of aprotic polar solvents, as the solvents become less structured the solute dissolution becomes easier. Both DMF and DMSO are capable of making H-bonds with PIL. The interaction between PIL cation and the solvent will be more intense in the case of DMF and DMSO because there are methyl groups to intensify the charge on the electronegative oxygens. The strong bonding between aprotic polar solvents and the PILs and lesser loss of energy to break the solvent network therefore makes the H^{E}_{IL} values positive suggesting the endothermic behavior.

Similarly, for pyridinium-based ionic liquids, the dissolution process depends on the solvent properties but the process also depends on how the PILs behave in the presence of these solvents of varied nature (Fig. 4.2.7). No specific trend was observed for the interaction of PIL and solvents in terms of solvent properties. The reason may be

Water < DMF < methanol < ethylene glycol < DMSO that $[hPY]^+$ cation acquires an aromatic behavior and the charge is more delocalized over the entire ring. Because of this delocalization the solvents are not able to interact to their maximum capacity. Thus the trend is arising due to a competition between a variety of interactions between the solute and the solvent *i.e.* the ion-dipole, dipole-dipole, Coulombic and hydrophobic interactions. All the solvents show endothermic enthalpic profile, because the interactions taking place between the solute and solvent are much energy consuming than the process of cavity formation inside the solvents. For pyrrolidinium based PIL , the H^E_{IL} trend in various solvents can be shown in Fig. 4.2.8. The H^E_{IL} values for various solvents with pyrrolidinium based ionic liquid follows the order: Ethylene glycol < methanol < water < DMSO < DMF. This trend can be explained on the basis of the donor acceptor and other solvent properties. As observed earlier the two subgroups of solvents, (i) protic polar PILs, which include water,

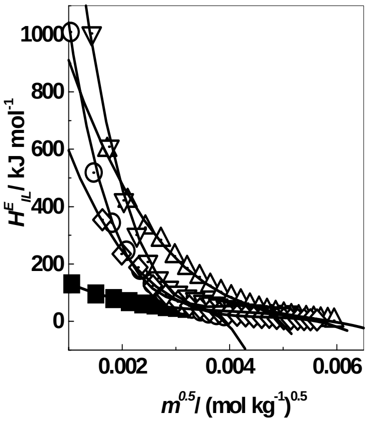


Fig. 4.2.7: Solvent dependency of H^E_{IL} for pyridinium-based protic ionic liquid (▽) DMSO, (◇) DMF, (⊙) ethylene glycol, (■) water, (△) methanol

methanol and ethylene glycol and (ii) aprotic polar solvents *i.e.* DMF and DMSO show distinct behavior around PILs. The values of H^E_{IL} values increase in the order of decreasing ability of the solvents to donate protons to the solute (α) to make a hydrogen bond between the solute and the solvent. For the protic polar solvents, water (1.456) shows the highest value of H^E_{IL} followed by methanol (3.26) and ethylene glycol (6.46). The reason for this kind of behavior can arise from the fact that $[hPYRR]^+$ cation is non-aromatic in nature and has maximum numbers of hydrogen (more than pyridinium and imidazolium) capable of forming hydrogen bonds with the other entities present in the solution. Thus the solvents offering more hydrogen bonds have lesser chances to interact with the PIL cation.

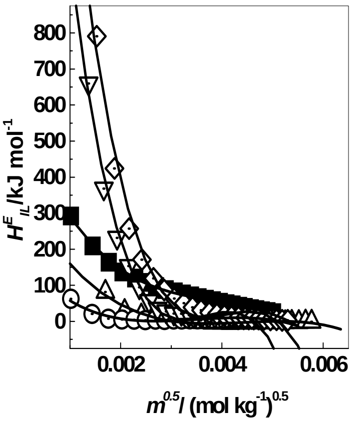


Fig. 4.2.8: Solvent dependency of H^E_{IL} for pyrrolidinium-based protic ionic liquid (▽) DMSO, (◇) DMF, (⊙) ethylene glycol, (■) water, (△) methanol

For aprotic polar solvents, the same trend is repeated as in the case of protic polar solvents. DMF have lesser value of α *i.e.* 7.90 interacts more than DMSO having higher α value of 7.99. Thus those solvents, which have lower tendency to donate their protons to the solute forms stronger bonds in case of pyrrolidinium-based PIL. But, the aprotic polar solvents do not follow the protic polar solvents. Despite having higher hydrogen bond donating tendency (α), both DMSO and DMF show higher values of $H^{E}{}_{IL}$ than even water. The reason for this observation can be that both these solvents do not have acidic hydrogens that can be donated to $[\mathrm{hPYRR}]^{+}$ cation in order to form hydrogen bonds, instead they are more capable in accepting the protons. Thus they show the highest values in the order as $[\mathrm{hPYRR}]^{+}$ cations provide them with the protons to form the hydrogen bonds between $[\mathrm{hPYRR}]^{+}$-DMF and $[\mathrm{hPYRR}]^{+}$-DMSO. The $H^{E}{}_{IL}$ data were fitted to the equation of the form:

$$H^{E}{}_{IL} = H^{E,\infty}{}_{IL} + \mathrm{h}_0\, \mathrm{m}_{\mathrm{IL}}{}^{0.5} + \mathrm{h}_1\, \mathrm{m}_{\mathrm{IL}} + \mathrm{h}_2\, \mathrm{m}_{\mathrm{IL}}{}^{1.5} \qquad (14)$$

where, h_0, h_1 and h_2 are the adjustable parameters and $H^{E,\infty}{}_{IL}$ is the limiting excess partial molar enthalpy. Sufficient weights were assigned in the lower concentration range while extrapolating these values. The $H^{E,\infty}{}_{IL}$ values for these ILs are given in Table 4.2.1.

The $H^{E,\infty}{}_{IL}$ values in our case indicate standard molar enthalpy of solution, as the dissolution of an ionic liquid in water has already taken place. The $H^{E,\infty}{}_{IL}$ are also correlated with the number of hydrogens (Fig. 4.2.9) present in the PIL cation to find a possibility of dependency between the intrinsic property of the system *i.e.* $H^{E,\infty}{}_{IL}$ and the microscopic property *i.e.* the hydrogen bond donor ability of the PIL cations.

Table 4.2.1: The limiting partial molar excess enthalpies, $H^{E,\infty}_{IL}$ / J mol^{-1} of the tetrafluoroborate-based PILs in different solvents

	Imidazolium	Pyridinium	Pyrrolidinium
Water	-215 ± 11	239 ± 5	561 ± 123
Methanol	-1202 ± 37	1561 ± 59	365 ± 31
Ethylene glycol	433 ± 4	2885 ± 138	175 ± 13
DMF	387 ± 27	1182 ± 32	3100 ± 169
DMSO	1285 ± 61	3700 ± 129	2670 ± 102

The correlation (Fig. 4.2.9) suggests that as the system moves towards the non-aromaticity, the infinite dilution property experiences a sharp fall for all the solvents except water and DMF.

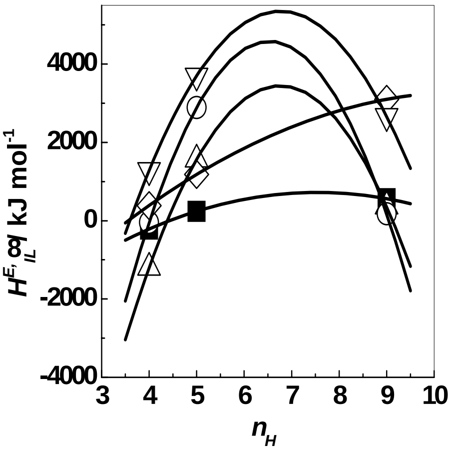


Fig. 4.2.9: Dependence of $H^{E,\infty}_{IL}$ on n_H (number of hydrogen atoms on the parent rings) of the ionic liquid cation, (■) water, (◇) DMF, (⊙) ethylene glycol, (△), methanol, (∇) DMSO

The reason of this sharp fall may be due to the fact that in the case of non-aromatic systems like pyrrolidinium based PIL, the oppositely charged ions are bonded with each other by additional hydrogen bonds in addition to the Coulombic force of attraction, which may make the dissolution of these PILs a little more difficult than the aromatic ones. The graph also suggests the water-like-behavior of DMF, which is an interesting behavior and can be further explored.

The $H^{E,\infty}{}_{IL}$ values for the ionic liquids in solvents can be correlated with the solvent properties. Several properties of solvents are examined to correlate them with the limiting partial molar excess enthalpies of the PILs in different solvents. The rigorous examination suggests that the behavior of PILs with different nature is justified by the combination of different properties of solvents.[16] For the imidazolium-based PIL, a combination of three properties hydrogen bond donor ability (α), Hildebrand solubility parameter (δ) and the normalized Dimroth-Reichardt polarity parameter, E_T^N is the most effective for the purpose of correlation.[17] The E_T^N value is defined as the excitation energy of the solvatochromic indicator, 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)-1-phenolate dye in a solvent. The energy is calculated from its longest wavelength intramolecular charge-transfer absorption band. The E_T^N parameter depicts both the hydrogen bond acidity and the dipolarity characteristics of the solvent. The correlation used for the imidazolium and pyridinium-based PILs is given as:

$$H^{E,\infty}{}_{IL} = \mathrm{a}_1 + \mathrm{a}_2\, \alpha + \mathrm{a}_3\, \delta + \mathrm{a}_4\, E_T^N \qquad (15)$$

The values of α, δ and E_T^N of the ionic liquids were taken from the literature. The values of coefficients, a_1, a_2 and a_3 are given in Table 4.2.2. The impact of many solvent properties on the $H^{E,\infty}{}_{IL}$ values of the PILs were analyzed thoroughly. It was however observed in this investigation that best correlation can be achieved by a combination of the α, β, δ, π^* and E_T^N values.

For Pyrrolidinium-based PIL:

$$H^{E,\infty}_{IL} = a_1 + a_2\,\alpha + a_3\,\delta + a_4\,E_T^N \qquad (16)$$

The importance of these solvent properties is demonstrated by comparing the $H^{E,\infty}_{IL}$ values obtained from the experiments ($H^{E,\infty}_{IL,EXP}$) with those from the correlation ($H^{E,\infty}_{IL,CAL}$) for the studied PILs in various solvents (Fig. 4.2.10). The agreement between the two quantities is quite good for all the ionic liquids suggesting us to widen the scope of such a correlation in future, when more data become available. The correlation is successful in wide range covering a variety of PILs with different rings and solvents of varied properties. The values suggest that the interactions between the PILs and the solvents depends upon the hydrogen bond acceptor-donor ability, polarizability, dipolarity and the solubility parameters of solvents under the study.

Table 4.2.2: The Analysis of $H^{E,\infty}_{IL}$ - Solvent Properties by Equations (15) and (16)

Parameters	[MIM][BF$_4$]	[hPY][BF$_4$]	[hPYRR][BF$_4$]
a_1x10^{-8}	-0.44 ± 0.096	-1.06 ± 0.62	-0.098 ± 0.036
a_2x10^{-5}	-2.81 ± 0.80	-9.72 ± 5.13	-0.18 ± 0.045
a_3x10^{-7}	-1.39 ± 0.27	-3.05 ± 1.72	1.098 ± 0.34
a_4x 10^{-6}	1.16 ± 0.26	2.98 ± 1.68	5.47 ± 1.34
Corr. Coeff. r^2	0.991	0.836	0.975

Another relevant thermodynamic quantity, which specifically illustrates the ion-solvent and ion-ion interactions, is the relative apparent molar enthalpy, (ϕ_L). *ϕ_L, is the heat that can be attributed to one mole of solute in solution if it is assumed that the solvent contributes the same enthalpy it has in the pure state.*

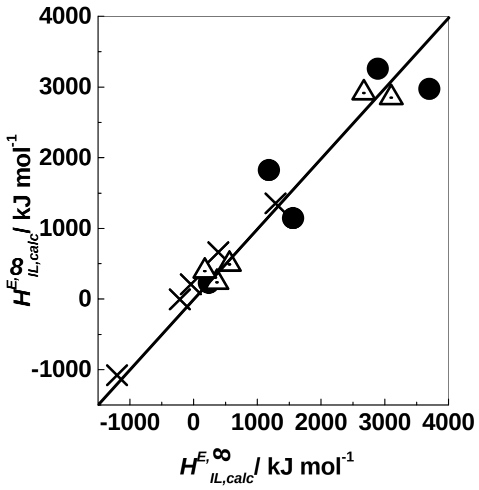


Fig. 4.2.10: A comparison between $H^{E,\infty}_{IL,EXP}$ and $H^{E,\infty}_{IL,CAL}$ for (x) [MIM][BF$_4$], (●) [hPY][BF$_4$], (■) [hPYRR][BF$_4$] in different solvents

For the above mentioned systems (Fig 4.2.1), the ϕ_L values are shown in Figs. 4.2.11, 4.2.12 and 4.2.13. The order of ϕ_L for the imidazolium-based PIL in different solvents is: methanol > water ≈ ethylene glycol > DMF > DMSO and for the pyridinium-based PIL is: water > DMF > methanol > DMSO > ethylene glycol.

For pyrrolidinium-based PIL: water ≈ ethylene glycol > methanol > DMF > DMSO These ϕ_L values of PILs in various solvents are further evaluated using a semi-empirical equation known as Pitzer's ion-interaction model. The Pitzer equations are very effective in understanding the behavior of ions in very dilute range of their concentration. Pitzer equations are the linear combination of parameters, a virial expansion of the excess thermodynamic properties, which characterize the interactions amongst the ion and the solvent.

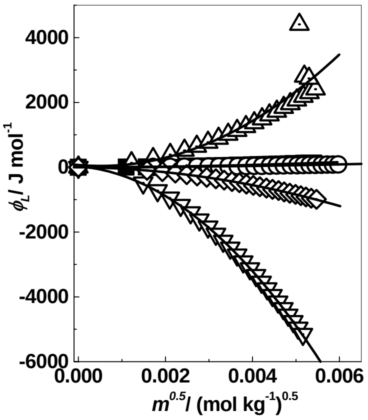


Fig. 4.2.11: The molality dependence of ϕ_L for the imidazolium-based PILs in various solvents; (▽) DMSO, (◇) DMF, (⊙) ethylene glycol, (■) water, (△) methanol

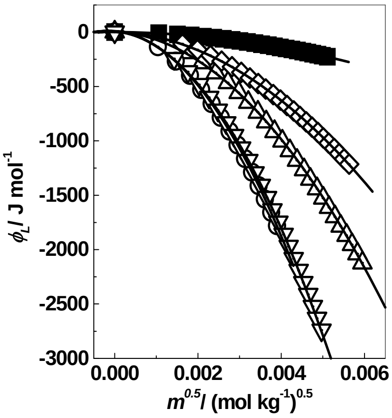


Fig. 4.2.12: The molality dependence of ϕ_L for the pyridinium-based PILs in various solvents; (▽) DMSO, (◇) DMF, (⊙) ethylene glycol, (■) water, (△) methanol

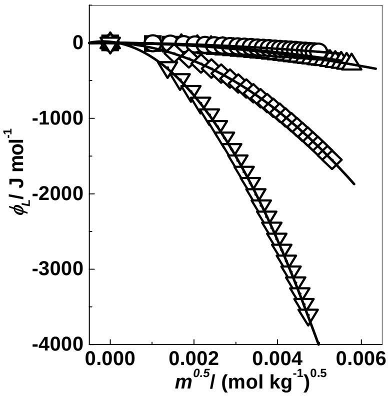


Fig. 4.2.13: The molality dependence of ϕ_L for the pyrrolidinium based PILs in various solvents; (▽) DMSO, (◇) DMF, (⊙) ethylene glycol, (■) water, (△) methanol

The first virial equation was given by McMillan and Mayer[18] to evaluate the intermolecular forces operating between the different components of the solutions.

$$PV = RT + AP + BP^2 + CP^3 \ldots\ldots\ldots\ldots \quad (17)$$

Where P = pressure, V = volume, T = temperature, A, B, C…… are the virial coefficients. The first term on the right side is for an ideal gas and the remaining terms quantify the departure from the ideality with changing pressure. The second and the third virial coefficients arise from the intermolecular forces between two and three molecules subsequently. The Debye-Hückel theory[19] was a modification to the McMillan-Mayer theory, which suggests that for the solutions of uncharged molecules the electrostatic interactions of the electrolytes should be taken into account. The basic assumption of the Debye-Hückel theory is that each ion is surrounded by a spherical cloud made up of ions of the opposite charge. This theory was very successful for 1:1 electrolytes at sufficiently low concentrations. This theory is restricted to deal very dilute solutions. Also, the Debye-Hückel theory takes no account of the specific properties of ions such as size or shape.

$$\ln\gamma = a\, m^{1/2} - 2\beta m \quad (18)$$

$$1 - \phi = (\alpha / 3)\, m^{1/2} + \beta m \quad (19)$$

where, γ = activity coefficient , ϕ = osmotic coefficient, the activity coefficient not only depends on the ionic strength but also on the concentration of the specific ion which in turn depends on the parameter β. Another set of semi-empirical equations, the SIT theory was first proposed by Brönsted[20] and was further developed by Guggenheim.[21] Scatchard[22] extended the theory to allow the interaction coefficients to vary with the ionic strengths. The basic idea of the SIT theory was that the activity coefficients can be expressed as:

$$\log \gamma_j = - Z_i^2\, 0.51\, I^{1/2} / 1 + 1.5\, I^{1/2} + \sum \varepsilon_{jk}\, m_k \qquad (20)$$

where, z = electrical charge on the ion, I = ionic strength, ε = interaction coefficients and m = concentration. The summation extends over the other ions present in solution, which includes the ions produced by the background electrolyte. The first term in this expression comes from Debye-Hückel theory. The second term shows how the contributions from "interaction" are dependent on concentration. Thus, the interaction coefficients are used as corrections to Debye-Hückel theory when concentrations are higher than the region of validity of that theory. The activity coefficient of a neutral species can be correlated to the ionic strength by the equation:

$$\log \gamma = k_m I \qquad (21)$$

where, k_m is the Setchenow coefficient and I = ionic strength

The SIT approach is based on the pair-wise interactions between oppositely charged ions but the Pitzer approach[23,24] allows for the higher order (between three ions) interactions. These equations are important for the understanding of the behaviour of ions in natural waters such as rivers, lakes and sea-water.

These Pitzer equations are successfully tested for analyzing equilibrium thermodynamic data of numerous electrolytes in aqueous solutions at 298.15 K with the concentration ranges up to their saturation point. These equations account for long range and short range interaction forces. The long range interaction forces are denoted by a modified Debye-Hückel term, where as the short range interactions by a set of virial coefficients. The working equation of the Pitzer model for correlating ϕ_L with concentrations are developed using standard equations[25]. The Pitzer equations for correlating various equilibrium thermodynamic properties of aqueous single and mixed electrolyte solutions are detailed elsewhere.[23,24]

$$\phi_L = \underset{\text{Long range}}{\overbrace{(A_L / 1.2) \ln (1 + 1.2\, m^{0.5})}^{\textbf{\textit{Debye-Hückel term}}}} \; \underset{\text{Short range}}{\overbrace{- 2\, RT^2\, m\, (\beta^{(0)L} - 2\, \beta^{(1)L}\, [1 - (1 + 2\, m^{0.5})\, \exp(-2\, m^{0.5})] / (2\, m^{0.5})^2 - C^L\, m)}^{\textbf{\textit{Set of virial coefficients}}}} \tag{22}$$

A_L = Debye-Hückel limiting slope, values of A_L for different solvents are listed in Table 4.2.3, $\beta^{(0)L}$ and $\beta^{(1)L}$ = virial coefficients to quantify the binary interactions between the opposite and the like charges; C^L = virial coefficient for ternary interactions, the values of $\beta^{(0)L}$, $\beta^{(1)L}$ and C^L are listed in Table 4.2.4.

Table 4.2.3: The A_L values for different solvents at 298.15 K

Solvents	A_L/ J kg^{-1}mol$^{-3/2}$
Water	2879
Methanol	4717
Ethylene Glycol	7450
DMF	4186
DMSO	5418

From Table 4.2.4, it is noted that the virial coefficients follow the same order as observed in the case of H^E_{IL} data. The values of virial coefficients also suggest that the increase in the hydrogen bond donor-acceptor ability of both solute (PIL) and solvent, positively affects the nature of interactions between them. One more interesting aspect observed is that, in spite being in the very dilute range, the PIL-solvent data requires a higher order virial coefficient for an accurate fitting. It suggests that in case of PILs there are higher order interactions prevailing even in the dilute range. This can be correlated to the low ionicity of these PILs as reported by many authors in the literature recently.[26] Our observation and the poor ionicity of PILs are coherent for all the PILs having different ring structures and with all the solvents.

Table 4.2.4: The Pitzer coefficients for various ionic liquid-solvent systems

	Pitzer coefficients		
IL/Solvent	$\beta^{(0)}$	$\beta^{(1)}$	C^{Φ}
[MIM][BF$_4$]			
Water	-1.08±0.02	-1.22±0.02	3.15±0.14
Methanol	-4.13±0.05	-4.42±0.05	-18.44±0.39
Ethylene Glycol	-1.30±0.02	-1.46±0.02	5.60±0.17
DMF	0.33±0.06	0.25±0.06	13.58±0.44
DMSO	7.54±0.21	7.78±0.22	46.60±1.73
[hPYRR][BF$_4$]			
Water	-0.39±0.01	-0.43±0.01	7.22±0.11
Methanol	-0.66±0.03	-0.79±0.03	7.38±0.21
Ethylene Glycol	-1.21±0.04	-1.36±0.04	9.86±0.32
DMF	0.28±0.06	0.20±0.06	28.78±0.47
DMSO	3.55±0.13	3.63±0.14	65.08±1.11
[hPY][BF$_4$]			
Water	-0.23±0.02	-0.27±0.02	6.26±0.14
Methanol	0.39±0.06	0.31±0.07	31.20±0.49
Ethylene Glycol	1.46±0.14	1.42±0.15	54.89±1.22
DMF	-0.05±0.05	-0.14±0.05	21.37±2.31
DMSO	2.69±0.09	2.75±0.10	44.07±0.

To show the validity of the Pitzer equation for all the systems studied having both exothermic and endothermic behavior, the ϕ_L data obtained for all the PILs in methanol were tested against the ϕ_L data obtained from the correlation by the use of the Pitzer equations. The comparison of the two ϕ_L data shows the excellent accuracy of these equations in calculating these values. The comparison is done for all the PILs studied in methanol which brings out the utility of Pitzer equations in dealing with both endo and exothermic behavior and also with different nature of the cationic parent rings of PILs and solvents.

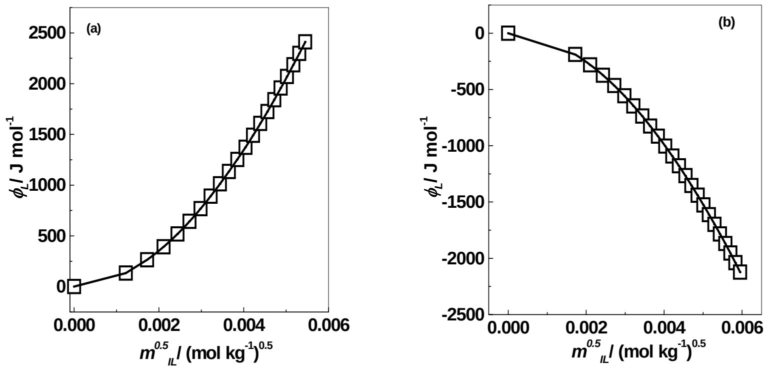


Fig. 4.2.14: The molality dependence of ϕ_L for the (a) [MIM][BF$_4$] and (b) [hPY][BF$_4$]-ethanol system, solid symbols are experimental values, solid line represents values generated by the Pitzer equations

From the foregoing, it is clear that the Pitzer equations serve as a powerful tool to analyze the enthalpy data of solutions of ionic liquids, though a model accounting for the heterogeneous environment around cation of a PIL will be highly desirable. This heterogeneous nature of PILs due to very strong interactions operating between cations and anions in the presence of a solvent has been reported.$^{24(d,e),27}$

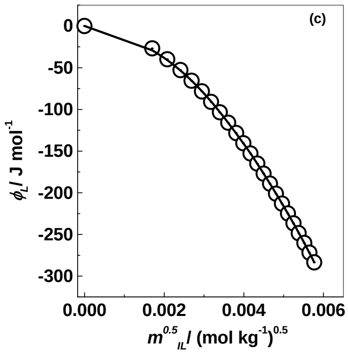


Fig 4.2.14(c): The molality dependence of ϕ_L for the [hPYRR][BF$_4$]-methanol system, solid symbols are experimental values, solid line represents values generated by the Pitzer equations

The virial coefficients derived out of Pitzer equations suggests the possibility of correlating the enthalpy data and the ion-solvent interaction. The data clearly suggest that there is a need of higher order virial coefficient such as C^L to account for the higher order interactions such as cation-anion, cation-cation and anion-anion interactions. These higher order interactions are due to the smaller size and the higher charge density on the cations, which leads to the stronger interactions between various entities of PILs.

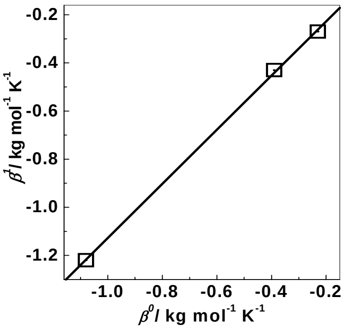


Fig. 4.2.15: The correlation of Pitzer virial coefficients $\beta^{(0)L}$ and $\beta^{(1)L}$

The Fig. 4.2.15 demonstrates linear correlation between the $\beta^{(0L}$ and $\beta^{(1)L}$ values for the studied PILs. An attempt was also made to correlate the Pitzer virial coefficients,

$\beta^{(0)L}$ and $\beta^{(1)L}$ and C_L with the % carbon content and the number of hydrogen atoms involved in the parent cationic ring (Figs. 4.2.16, 4.2.17). It is observed that as the carbon content increases in going from the imidazolium parent ring to the pyridinium, the magnitude of virial coefficients also increases linearly suggesting that there are increased ion-ion interactions.

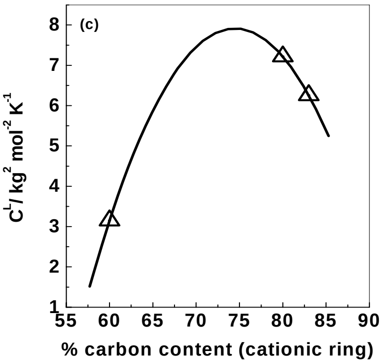


Fig. 4.2.16: Dependence of Pitzer virial coefficients (a)$\beta^{(0)L}$, (b)$\beta^{(1)L}$ and (c) C^L on the % carbon content of the cationic rings of the imidazolium, pyridinium and pyrrolidinium-based PILs

But in the case of the higher order coefficient C_L, this increase is not as sharp as in case of the first two coefficients. It may be due to some leveling of effect of different interactions in the case of pyrrolidinium and pyridinium based PIL.

As the number of hydrogen bond donating sites on the PIL cations are enhanced, it results in the increased interactions between the cation and the solvent (Fig. 4.2.17).These interactions are very strong in the case of DMSO as can be seen from both $\beta^{(0)L}$ and $\beta^{(1)L}$ values.

DMSO imparts the strongest interaction to all the PIL cations, the reason for this observation may be that DMSO is a very good solvator of cations and has the maximum hydrogen bond accepting tendency. There is also a very interesting observation about methanol that it imparts very strong interactions to PILs but the trend is opposite to that of noted in DMSO. The reason may be that though the hydrogen bond acceptor ability for methanol ($\beta = 0.77$) is equivalent to that of DMSO ($\beta = 0.77$) hence they may offer a similar kind of interactions to the PIL moieties after their dissolution but the initial process *i.e.* the introduction of solute in the solvent system is little different in both the cases *i.e.* methanol and DMSO.

The methanol system being loosely bound system can be disturbed at the lesser expense of energy and further the intense hydrogen bonding between the PIL cations & methanol molecules make the whole process exothermic while in DMSO, the solute requires a lot of energy for the solvation/ cavity formation inside DMSO and thus the process becomes more endothermic. It is evident from both the experimental H^{E}_{IL} values as well as the virial coefficients obtained from the Pitzer correlation (Fig 4.2.17).

Thus, the observations from this study suggest that there are strong interactions possible between the PIL cations and the solvent molecules. Apart from these cation-solvent interactions, for some solvents there may also be a possibility of interaction between the anion of the PIL and the solvent. These interactions can also be quantified by using the semi-empirical equations like the Pitzer equations. The total enthalpic effect evolved due to these interactions can be segregated in ion-solvent and ion-ion interaction terms by employing the Pitzer equations.

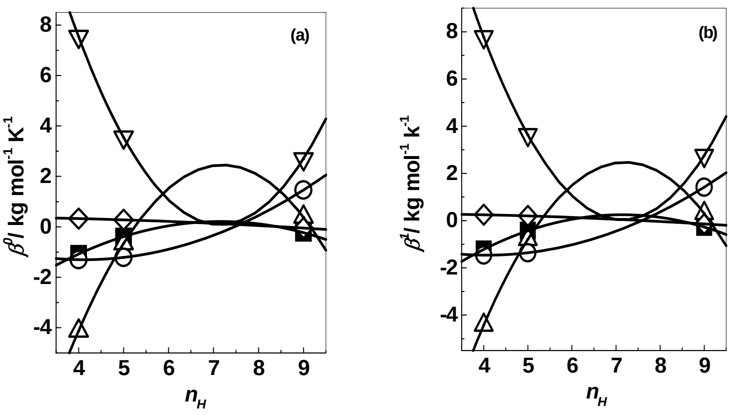


Fig. 4.2.17: Dependence of (a)$\beta^{(0)L}$, (b)$\beta^{(1)L}$ on n_H (number of hydrogen atoms on the parent rings) of the imidazolium, pyridinium and pyrrolidinium PIL cation, (■) water, (◈) DMF, (⊙) ethylene glycol, (△), methanol, (∇) DMSO

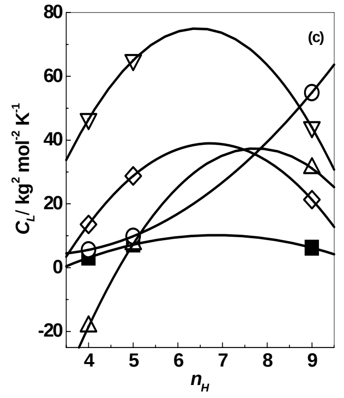


Fig. 4.2.17(c): Dependence of C_L on n_H (number of hydrogen atoms on the parent rings) of the (a) imidazolium, (b) pyridinium and pyrrolidinium PIL cation, (■) water, (◈) DMF, (⊙) ethylene glycol, (△), methanol, (∇) DMSO

The experimental data corresponding to the above mentioned observations and the other thermodynamic quantities calculated for different PILs in water are given in Tables 4.2.5, 4.2.6 and 4.2.7 at the end of this chapter.

Table 4.2.5: The experimental H^E_{IL} and other derived thermodynamic quantities for [MIM][BF$_4$] with water as a solvent

m x10^6/ mol kg^{-1}	H^E_{IL}/ J mol^{-1}	ϕ_L/ J mol^{-1}	$\bar{L}_1$ x 10^5 / J mol^{-1}	$\bar{L}_2$ / J mol^{-1}	L x10^6 / J mol^{-1}	ΔH_{mix} / J mol^{-1}
0	0	0	0	0	0	0
1.221	-88142	5.92	-6	2631.71	7.22	-0.016
2.442	-42541	11.74	-20	3666.24	28.66	-0.031
3.663	-24826	17.50	-30	4438.36	64.09	-0.046
4.883	-18501	23.21	-40	5074.78	113.36	-0.062
6.104	-12958	28.89	-60	5624.58	176.33	-0.077
7.325	-10560	34.52	-80	6112.90	252.88	-0.093
8.546	-7918	40.13	-100	6554.69	342.90	-0.108
9.768	-6696	45.70	-122	6959.67	446.31	-0.124
10.988	-4837	51.24	-144	7334.60	563.00	-0.139
12.209	-4216	56.76	-168	7684.41	692.90	-0.154
13.430	-3195	62.25	-192	8012.79	835.92	-0.170
14.650	-2517	67.71	-218	8322.64	992.00	-0.185
15.871	-1969	73.15	-244	8616.24	1161.05	-0.200
17.092	-1385	78.58	-271	8895.46	1343.01	-0.216
18.313	-1030	83.98	-299	9161.81	1537.82	-0.231
19.534	-601	89.35	-328	9416.59	1745.41	-0.246
20.755	-246	94.71	-357	9660.86	1965.72	-0.261
21.976	-26	100.05	-387	9895.56	2198.69	-0.277
23.196	471	105.37	-418	10121.48	2444.28	-0.292
24.417	629	110.68	-450	10339.31	2702.41	-0.307
25.638	934	115.96	-482	10549.67	2973.03	-0.322
26.859	939	121.23	-514	10753.08	3256.11	-0.338
28.080	1311	126.48	-547	10950.02	3551.57	-0.353
29.300	1330	131.72	-581	11140.92	3859.39	-0.368

Table 4.2.6: The experimental H^E_{IL} and other derived thermodynamic quantities for [hPY][BF_4] with water as a solvent

$m \times 10^6$ / mol kg^{-1}	H^E_{IL} / J mol^{-1}	ϕ_L / J mol^{-1}	$\bar{L}_1 \times 10^5$/ J mol^{-1}	$\bar{L}_2$ / J mol^{-1}	$L \times 10^5$ / J mol^{-1}	ΔH_{mix} / J mol^{-1}
1.134	130620	-10.64	10	-4907	-1.21	0.026
2.268	95412	-21.10	28	-6831	-4.79	0.053
3.401	79182	-31.45	50	-8266	-10.70	0.079
4.535	68651	-41.72	77	-9447	-18.92	0.105
5.669	60589	-51.90	106	-10466	-29.42	0.132
6.803	56820	-62.02	138	-11370	-42.19	0.158
7.936	51083	-72.07	173	-12188	-57.20	0.184
9.070	48434	-82.07	210	-12937	-74.44	0.210
10.204	45141	-92.01	249	-13630	-93.88	0.236
11.338	42851	-101.90	289	-14276	-115.53	0.263
12.471	40369	-111.75	332	-14882	-139.36	0.289
13.605	38826	-121.54	375	-15454	-165.36	0.315
14.739	36773	-131.30	421	-15995	-193.52	0.341
15.873	34917	-141.01	468	-16510	-223.83	0.367
17.007	33251	-150.69	516	-17001	-256.27	0.393
18.140	31702	-160.33	565	-17470	-290.84	0.419
19.274	30243	-169.93	616	-17919	-327.52	0.445
20.408	28901	-179.49	667	-18351	-366.30	0.471
21.542	27385	-189.02	720	-18766	-407.18	0.497
22.675	26078	-198.51	774	-19166	-450.14	0.523
23.809	24879	-207.98	829	-19552	-495.17	0.549
24.943	23672	-217.41	885	-19926	-542.28	0.575
26.077	22232	-226.81	942	-20287	-591.44	0.600

Table 4.2.7: The experimental H^E_{IL} and other derived thermodynamic quantities for [hPYRR][BF$_4$] with water as a solvent

m x10^6 / mol kg^{-1}	H^E_{IL} / J mol^{-1}	ϕ_L / J mol^{-1}	$\bar{L}_1$x 10^5/ J mol^{-1}	$\bar{L}_2$ / J mol^{-1}	L x10^5/ J mol^{-1}	ΔH_{mix} / J mol^{-1}
0	0	0	0	0	0	0
1.152	292201	-8.26	8	-4019	-0.86	0.022
2.303	209143	-16.46	21	-5655	-3.44	0.045
3.455	163766	-24.64	39	-6899	-7.72	0.067
4.607	136564	-32.79	60	-7941	-13.70	0.089
5.758	119775	-40.92	83	-8852	-21.37	0.112
6.910	108013	-49.03	109	-9672	-30.73	0.134
8.061	96554	-57.12	136	-10421	-41.77	0.156
9.213	87981	-65.20	166	-11116	-54.48	0.178
10.365	81764	-73.26	198	-11765	-68.87	0.201
11.516	76008	-81.31	231	-12376	-84.92	0.223
12.668	70775	-89.34	266	-129556	-102.60	0.245
13.820	65799	-97.36	303	-135066	-122.03	0.267
14.971	61266	-105.36	340	-14033	-143.06	0.289
16.123	57198	-113.36	380	-14538	-165.76	0.312
17.275	53110	-121.34	420	-15023	-190.11	0.334
18.426	49181	-129.31	462	-15491	-216.10	0.356
19.578	45681	-137.27	505	-15943	-243.74	0.378
20.730	41949	-145.22	549	-16380	-273.03	0.400
21.881	38690	-153.16	595	-16804	-303.95	0.422
23.033	35236	-161.09	641	-17216	-336.51	0.444
24.184	32393	-169.01	689	-17616	-370.71	0.466
25.336	29376	-176.92	737	-18006	-406.54	0.488
26.488	27033	-184.82	787	-18386	-444.00	0.510
27.639	24105	-192.71	838	-18756	-483.09	0.532

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CHAPTER 5: APROTIC IONIC LIQUIDS: TUG OF WAR BETWEEN SOLVATION AND HYDROPHOBICITY

"Ionic Liquids are ***runny solids*** *than* ***Liquids****"*

(Tom Welton, APCIL2, 2010, Dalian)

Aprotic Ionic Liquids are not just solvents anymore as they have found their applications in electrochemical devices, catalyzing and increasing the selectivities of various reactions including biological processes, lunar observatories, biodegradation, medicinal chemistry as a pharmacophore, food processessing, waste management, storing solar thermal energy and the list is ever increasing. The field of Ionic liquids is the most rapidly growing field of chemistry in the modern times. It is obvious that in times to come the ionic liquid will remain a toy for scientists, because the search for ionic liquid will be like the search for a holy grail.

Aprotic Ionic Liquids: Tug of war between solvation and hydrophobicity

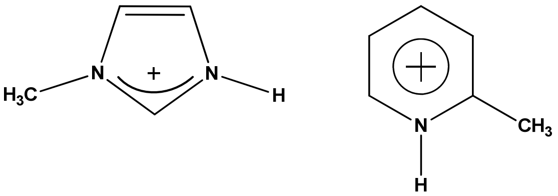
Ionic Liquids are out of the "Ivory Tower" and have started taking a plunge into the real time applications, may it be on a lab scale or industrial scale. Now, the recent attention of the whole pool of academia and industry has been directed towards correlating the structure and the properties of ionic liquids (ILs). Working out this relationship can help in employing them in variety of applications without much hit and trial. The present chapter is an addition to this effort, where we have tried to gain two fold knowledge about these ILs, (1) how does an IL having a substituted ring (aprotic ILs) differ from an unsubstituted IL like protic ILs among (2) Among the substituted ILs, which factor makes their behavior distinctly different from each other?

5.1: A comprehensive study of –tetrafluoroborate-based ionic liquids: *effect of alkyl and ring substitution*

A large number of investigations have focused on the aprotic imidazolium, pyridinium, pyrrolidinium and ammonium-based ILs (APILs) with a series of different anions[1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18]. These studies suggest that apart from the Coulombic interactions prevailing being the structural analogues of high temperature molten salts, traces of non-covalent interactions between their ions is the determinant force on the properties of ILs[19, 20]. These non-covalent interactions include the van der Waals (dipole, induced dipole), hydrogen bonds, possible π-π, p-π stacking and account for the complex behavior of these materials[1,5, 9, 19]. Here we have tried to correlate the IL-solvent interactions (representing their structures) with their enthalpy profiles. The ionic liquids for the present study (Fig. 5.1.1) were chosen to acquire two-fold information:

(a) how do the enthalpic patterns can be correlated to the substitution on the parent rings? and

(b) does the change in the basic structure of the parent rings also have the influence on their enthalpic profiles?

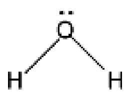


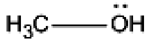
Imidazolium Pyridinium Pyrrolidinium

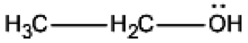
Fig. 5.1.1: APIL cations with different parent ring structures

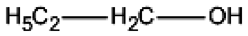
where, R = -C_2H_5, -C_4H_9, -C_6H_{13}, -C_8H_{17} (for imidazolium-based ILs) and for pyridinium and pyrrolidinium-based ILs, R = -C_4H_9

Choice of the solvents for all the above mentioned ILs was based on their relative permittivities. A vast variation in their relative permittivities was a basic and simple probe to discern the interactions prevailing among the ionic species of ionic liquids.

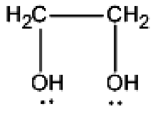




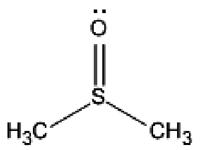




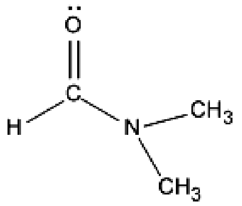
Water Methanol Ethanol 1-Propanol



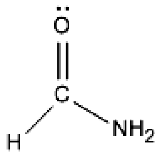
Ethylene Glycol



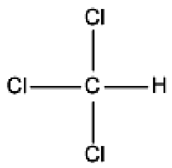
Dimethyl Sulphoxide



N,N'-Dimethyl Formamide



Formamide



Chloroform

The reason behind the choice of the solvent was that if there are only Coulombic interactions present in ILs, the enthalpies of the IL-solvent systems which are the indirect measure of all the interactions involved, should therefore follow the order of the enthalpies recorded for their analogues *i.e.* higher temperature molten salts.

All the ILs chosen for this study were clearly soluble in the solvents chosen giving clear solutions. The IL-solvent systems were taken in a very dilute range of their concentration in order to comprehend the interactions imparted by the solute (IL) to various solvents. The basic experimental quantity is the excess partial molar enthalpy (H^E_{IL}), which is calculated from the change in the enthalpy of the pure solvent by adding subsequent moles of solute. The methods of calculating this quantity and other derived thermodynamic quantities are described previously.

For the imidazolium-based IL, the plot of H^E_{IL} as a function of mole fraction of ionic liquids (x_{IL}) discerns the effect of alkyl substitution on the imidazolium ring (Fig 5.1.2). The enthalpic behavior shown by these ILs is quite interesting. It was noted that for smaller alkylated ILs ($[EMIM]^+$ and $[BMIM]^+$), the pattern is endothermic. For $[BMIM]^+$ this behavior is moderate as compared to $[EMIM]^+$, where as increasing the chain length from $[BMIM]^+$ to $[HMIM]^+$ shifts the enthalpy behavior from endothermic to exothermic. This exothermic behavior becomes even more pronounced in the case the alkyl chain length increases to $[OMIM]^+$.

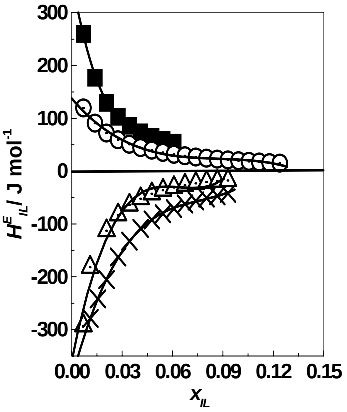


Fig. 5.1.2: Variations in H^E_{IL} with respect to x_{IL} for (■) $[EMIM][BF_4]$, (⊙) $[BMIM][BF_4]$, (△)$[HMIM][BF_4]$, (X) $[OMIM][BF_4]$

The magnitude of H^E_{IL} for all the four ILs in water follows the order: $[EMIM]^+ > [BMIM]^+ > [HMIM]^+ > [OMIM]^+$. Since $[BF_4]^-$ is a common anion in all the ILs, this effect primarily originates from the interaction between the IL cation and the solvent molecules. The trend can be explained on the basis of two simultaneous processes occurring during the whole process of salvation of an IL in any solvent; (1) the hydration/ solvation effect: when an IL is dissolved in a given solvent it readily dissociates into its ionic counterparts. This process disrupts the pre-existing solvent network because the solute (IL) tends to create a cavity for itself. This event costs a lot of breaking of the bonds, which increase the energy of the system (endothermic). This increase in energy can be compensated by the reformation of the broken bonds between the solvent molecules. (2) the hydrophobic/ solvophobic effect: the solvent molecules at the surface of the cavity created by these IL solutes try to rearrange themselves in order to regenerate the broken bonds. For ILs with smaller alkyl tails the water dipoles have more chance to interact with the positive charge present on the cation as it is less hidden by the alkyl tails present on the cations. But these ion-dipole interactions between the smaller IL cations and water molecules are not sufficient to completely compensate for the enthalpy changes taken place due to the bond breaking during the first step of solvation.

Thus the overall process of solvation for lower alkylated ILs in water turns out to be endothermic. Now, for higher alkylated ILs the process of hydration is endothermic as for the lower alkylated ones but another process *i.e.* the hydrophobic interactions overshadows the endothermic contribution of the first step. When the water molecules start reforming themselves on the surface of the cavities, in which the IL cations are residing, the alkyl tails of the higher alkylated ILs, which happen to lie on the interface, pose a hydrophobic repulsion towards the solvent particles and this helps in the closer approach of the water molecules. The result is the higher degree of local ordering of the water molecules around these hydrophobic solutes and there is a stronger makeshift of the bonds. This regeneration of the broken bonds and increased structuredness of the water molecules around the hydrophobic moieties of the bigger IL cations masks the effect of increase in the enthalpy due to the solvation and cause the observed heating of the solution[21].

This suggests that the enthalpic behavior for the imidazolium-based ionic liquids is presided by the hydration, which is a predominant phenomenon for lower alkylated and hydrophobicity and is a governing factor for higher alkylated ILs. The Enthalpic effects are more pronounced in the water-rich region with $x_{IL} \leq 0.2$. At higher concentration with $x_{IL} \geq 0.2$, the cations and anions of ILs tend to come closer to each other to form clusters. The larger endo and exothermic variations in the very dilute region become smaller in this range. In this range, ionic species of ionic liquids tend to come together and form clathrates either directly or as mediated by water. The clathrate formation via the cation aggregation is also substantiated by the simulation studies[22, 23,24]. In the water-poor region the ions reorganize themselves and hence a larger part of ILs remains as the ion-pairs. At this concentration the environment around these clusters seems to be similar as that in the pure state of these ILs. The IL-water system at this higher concentration can be considered as the aqueous solution of non-electrolytes. Now, the water molecules are adhered on the surface of these clusters without any hydrogen bond formation and thus the change in the enthalpy of the system becomes almost invariant with the increase in the concentration of ILs. Thus, in the dilute range the electrostatic as well as the hydrogen bonds are the predominant forces while, as the IL concentration increases these two forces are replaced and dominated by the other weaker van der Waals forces.

Changing the water as solvent media for these imidazolium-based ILs to other non-aqueous solvents[25] that are protic polar, aprotic polar and also the non polar in nature, it is noteworthy to see how the solvation pattern of these ILs vary (Fig. 5.1.3). The values of H^{E}_{IL} for [BMIM][BF$_4$] in different non-aqueous solvents follow the order:

1-propanol > ethanol > methanol > ethylene glycol > formamide > DMF

1-propanol, ethanol, methanol, ethylene glycol and formamide belong to the protic polar group of solvents where as DMF is an aprotic polar solvent. For [BMIM]$^+$-based IL, among the non-aqueous solvents, the alcohols show more pronounced enthalpic effects as compared to other solvents. This trend of H^{E}_{IL} values follows the structuredness[26] of the solvents. For protic polar solvents, the values of H^{E}_{IL} decrease with increasing structuredness of the solvents, 1-propanol ($\delta = 24.4$) > ethanol ($\delta = 26.0$) > methanol ($\delta = 29.3$) > ethylene glycol ($\delta = 32.4$) > formamide ($\delta = 39.6$). The more stiff network of the solvents make the interaction between IL entities and solvents difficult and as the concentration of IL is increased the IL cations tend to come closer and form clathrate – like structure which decreases the IL-solvent interaction even more sharply. For the aprotic polar solvent DMF (δ = 24.1) the solvent network is loosely arranged as compared to other solvents, hence the approach for IL cations towards the solvent molecules becomes more facile and the solvent molecules form strong hydrogen bonding with the IL cation. For this reason the solvation of ILs in DMF becomes exothermic in nature.

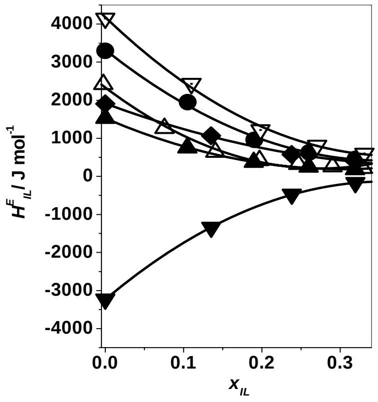


Fig. 5.1.3: The H^E_{IL} versus x_{IL} plots for [BMIM][BF$_4$] in (△) methanol, (●) ethanol, (▽) propanol, (◆) ethylene glycol, (▲) Formamide, (▼) DMF

Now, we shall examine the enthalpic behavior of ILs other than imidazolium-based. The solvents chosen for these ILs are the same as employed in studying the imidazolium ones. Fig. 5.1.4 compares the behavior of three ILs with different parent rings *i.e.* imidazolium, pyridinium and pyrrolidinium-based ILs with water as a common solvent.

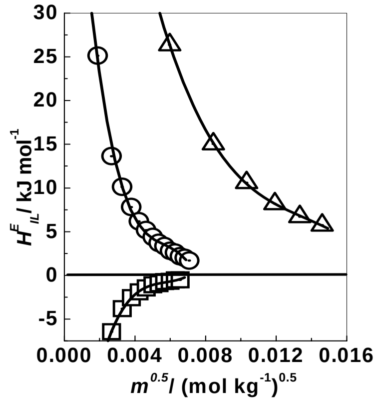


Fig. 5.1.4: Comparison of H^E_{IL} for (△) imidazolium, (⊙) pyrrolidinium, (⊡) pyridinium-based ILs in water

The order of H^E_{IL} followed by these three different ILs is: imidazolium > pyrrolidinium > pyridinium. It is clear from the figure that the imidazolium-based IL shows the most endothermic behavior followed by pyrrolidinium and pyridinium-based ILs converting to exothermic in nature. The reason behind this behavior may be that when an IL is dissolved in an aqueous system it causes breaking of bonds existing between the solvent molecules thus the dissolution process for the ILs become endothermic as it requires energy and the process increases the energy of the system. But if an IL is dissolved in the solvent system, then those ILs, which can increase the number of bonds or the extent of interactions cause the later process to be exothermic. For example in pyridinium, there are sites that can be hydrogen bonded to the water molecules and also the cations can involve into π-π stacking kind of interactions. Thus the extent of bonded molecules that are involved in different interactions increases in the IL solution. Because of this increased bonding, the over all process of dissolution of pyridinium based ILs becomes exothermic in nature.

For pyrrolidinium-based ionic liquids, the hydrogens which are present on the parent ring $[BMPYRR]^+$ though are more in number but less acidic than those present on the $[BMPY]^+$ cation. Thus the extent of effective hydrogen bonding is lesser as compared to $[BMPY]^+$ cation. For this reason, energy gained by the system during the dissolution of IL cannot be compensated at this stage of bond formation and results in the endothermic solvation behavior. Now, comparing the enthalpic behavior of pyrrolidinium-based IL with that of imidazolium-based IL, $[BMIM]^+$ cation has lesser number of hydrogens present on the parent ring. In addition to it the C2 proton, which is the main hydrogen bonding site in $[BMIM]^+$ is sandwiched in between the two aromatic nitrogen (N1 and N3), which are substituted by methyl and butyl groups. This crowding around the most capable hydrogen bonding site screens strong interactions between the $[BMIM]^+$ cation and the water molecules and thus the solvation behavior for imidazolium-based IL turns out to be most endothermic as compared to the pyrrolidinium and the pyridinium-based IL. How the solvation behavior of these two ILs does alter with changing the solvent system can be understood from Fig. 5.1.5. This figure suggests how the H^E_{IL} values are modified by different non-aqueous solvents. The enthalpy effects upon dilution are quite large in methanol, ethanol and 1-propanol. We also observe a shift from endothermic to exothermic enthalpy behavior, while going from $[EMIM][BF_4]$ to $[OMIM][BF_4]$ in non-aqueous solvents.

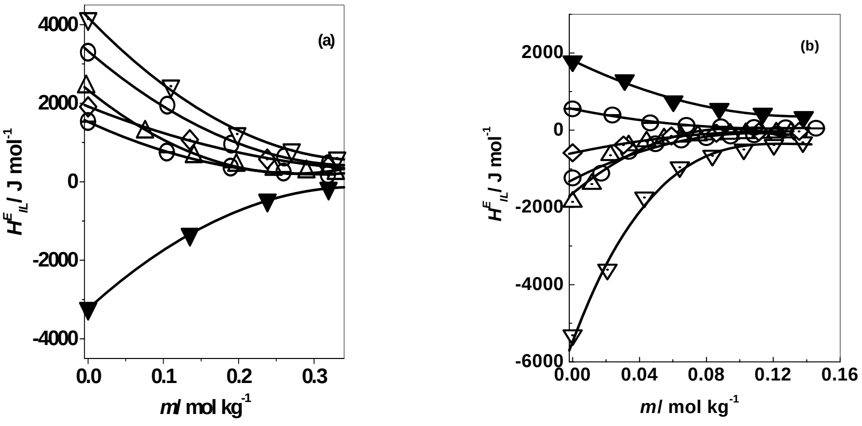


Fig. 5.1.5: The $H^{E,}_{IL}$ *versus m plots* for (a) [BMIM][BF_4] and (b) [OMIM][BF_4] in (Δ) methanol, (O) ethanol, (▽) 1-propanol, (◇) ethylene glycol, (⊖) formamide, (▼) DMF

This changeover from endo- to exothermic behavior of ionic liquids is significant in alcohols. In the case of [BMIM][BF_4], the H^E_{IL} values vary in order of methanol < ethanol < 1-propanol, while they are reversed in the alcoholic solutions of [OMIM][BF_4]. Though we are currently investigating the effect of increasing carbon-chain length of alcohol up to C_{18} on the above order, it seems at this stage that the increased hydrophobicity on account of increasing carbon chain length of alcohols gives rise to higher degree of reorganization of the alcohol molecules around cation of the ionic liquid leading to the exothermic behavior of the system. The order of H^E_{IL} for [BMIM][BF_4] in various non-aqueous solvents is:

1-propanol > ethanol > methanol > ethylene glycol > formamide > DMF

Similarly, the order of H^E_{IL} for [OMIM][BF$_4$] in various non-aqueous solvents is completely reversed in the following manner:

DMF > formamide > ethylene glycol > methanol > ethanol > 1-propanol

The H^E_{IL} values for [BMIM][BF$_4$] in protic solvents like alcohols decrease with an increase in the relative permittivity of the solvents. However no such trend is observed in aprotic solvent like DMF (Fig. 5.1.5a). This trend is however reversed in the solutions of [OMIM][BF$_4$], where a decrease in the H^E_{IL} values with decreasing relative permittivity of the protic solvents is witnessed. No definite order was again seen in DMF-[OMIM][BF$_4$] system (Fig. 5.1.5b) as was noted in the case of its solution with [BMIM][BF$_4$]. Execpt not following the trend of varying H^E_{IL} values with respect to changing relative permittivity shown by most of the solvents employed, DMF also shows unusually high enthalpy values with all the ionic liquids. This observation suggests that some other factors in addition to the polarity of solvents are also involved in governing the reorganization of aprotic solvent molecules around ionic liquid species.

The H^E_{IL} data were also recorded for all the ILs in chloroform but omitted from the Fig. 5.15 a & b, for the sake of clarity. It causes the maximum interaction with all the solvents and the H^E_{IL} values were exceptionally higher as compared to other polar solvents. [HMIM][BF$_4$] and [OMIM][BF$_4$] are less polar than [BMIM][BF$_4$] due to the presence of alkyl chains in their structures. Since $CHCl_3$ is a non-polar solvent with its relative permittivity as low as 4, when mixed with [BMIM][BF$_4$] results into weak interactions leading to low H^E_{IL} values. As the size of the chain length increases (higher analogues of the ionic liquids), it renders more non-polarity to the ionic liquid systems[27] and thereby increasing the interactions between $CHCl_3$ and [HMIM][BF_4] and [OMIM][BF_4] as evidenced by higher H^E_{IL} values.

For pyridinium-based IL the order followed by all the solvents is (Fig. 5.1.6):

Formamide > ethylene glycol > methanol > DMF > ethanol > 1-propanol.

This order of the H^E_{IL} values for various pyridinium ILs-solvent systems (see: Fig. 5.1.6 a) vary in the order of their increasing β values. The maximum positive values of the H^E_{IL} values indicating the weaker interactions of solvents with IL are demonstrated by

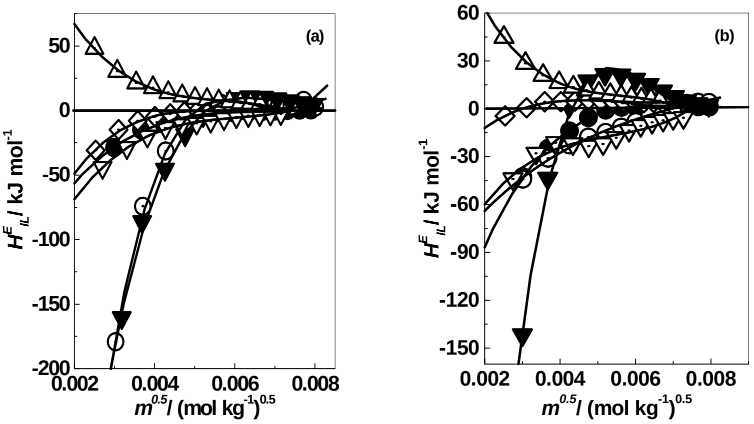


Fig. 5.1.6: The H^E_{IL} versus x_{IL} plots for (a) [BMPY][BF_4] and (b) [BMPYRR][BF_4] in (●) methanol, (⊙) ethanol, (▼) propanol, (◇) ethylene glycol, (△) Formamide, (▽) DMF

formamide (β = 0.48) followed by negative H^E_{IL} values of IL in ethylene glycol (β = 0.52), methanol (β = 0.66), DMF (β = 0.69), ethanol (β = 0.75) and 1-propanol (β = 0.84) suggesting[28] that as the hydrogen bond accepting tendency of these solvents increase the interactions between the ILs and the solvents increase and the system move towards more exothrmic behavior. The explanation holds good for both the ILs consisting of $[BMPY]^+$ and $[BMPYRR]^+$ cations. Fig. 5.1.6 b also suggests that in the pyrrolidinium-based IL, the interactions between IL cation and solvent molecules are more or less of the same order for many solvents as the curves are merging into each other in contrast to the pyridinium-based IL, where the H^E_{IL} curves are distinct from each other.

The H^E_{IL} data for various IL-solvent systems were fitted to obtain the limiting excess partial molar enthalpy ($H^{E,\infty}_{IL}$) using the following equation:

$$H^E_{IL} = H^{E,\infty}_{IL} + \mathrm{h}_0\, m_{IL}^{0.5} + \mathrm{h}_1\, m_{IL} + \mathrm{h}_2\, m_{IL}^{1.5} \qquad (1)$$

Due to the extreme dilute conditions, it was needed to assign sufficient weights for the fitting of the $H^{E,\infty}_{IL}$ data. These $H^{E,\infty}_{IL}$ values thus obtained from the above fitting are reported in Tables 5.1.1 and 5.1.2. Tables 5.1.1 and 5.1.2 report the $H^{E,\infty}_{IL}$ values for the imidazolium-based ILs with different substituted alkyl chains in different solvents and Table 5.1.2 presents these values for, ILs with different parent rings i.e pyridinium and pyrrolidinium are presented: Both the tables also include the standard errors in the calculations of the $H^{E,\infty}_{IL}$ values

Table 5.1.1: The limiting partial molar excess enthalpies, $H^{E,\infty}_{IL}$ / kJ mol^{-1} of imidazolium-based ILs in different solvents

	$[EMIM][BF_4]$	$[BMIM][BF_4]$	$[HMIM][BF_4]$	$[OMIM][BF_4]$
Water	916 ± 43	332 ± 14	-922 ± 69	-1050 ± 23
Methanol	3056 ± 140	1854 ± 76	648 ± 25	-1858 ± 142
Ethanol	-	3294 ± 117	310 ± 6	-1236 ±82
1-propanol	-	4147 ± 140	-2845 ± 123	-5310 ± 398
Ethylene glycol	847 ± 21	1906 ± 48	139 ± 6	-584 ±43
Formamide	1738 ± 67	1529 ± 63	1285 ± 59	550 ± 36
DMF	-2204 ± 87	-3231 ± 135	-2319 ± 104	1785 ± 84
$CHCl_3$	-	-329 ± 122	4403 ± 412	14498 ± 738
D_2O	-	197 ± 10	-	-

Table 5.1.2: The limiting partial molar excess enthalpies, $H^{E,\infty}_{IL}$ / kJ mol^{-1} of the pyridinium and pyrrolidinium-based ILs in different solvents

	$[BMPY][BF_4]$	$[BMPYRR][BF_4]$
Water	-33 ± 1.8	68 ± 3.6
Methanol	-158 ± 9.8	-235 ± 11.0
Ethanol	-1310 ± 73.0	-122 ± 21.8
Propanol	-846 ± 5.4	-1280 ± 55.0
Ethylene glycol	-185 ± 10.7	-68 ± 6.6
formamide	209 ± 11.8	193 ± 10.0
DMF	-196 ± 11.5	-159 ± 47.9

The $H^{E,\infty}_{IL}$ values for these experiments also suggest the standard molar enthalpy because the ionic liquids are already diluted into their corresponding pure solvents before employing them into the experiments. We have also attempted to correlate the effect of hydrogen atoms present on the IL cation (both parent ring and alkyl tails) on the $H^{E,\infty}_{IL}$ values.

The correlation between the $H^{E,\infty}_{IL}$ values and the potential hydrogen bonding sites gives a plausible explanation to the assumption that the structural features of the IL entities are one of the guiding factors for the probable interactions between the IL and solvent molecules.

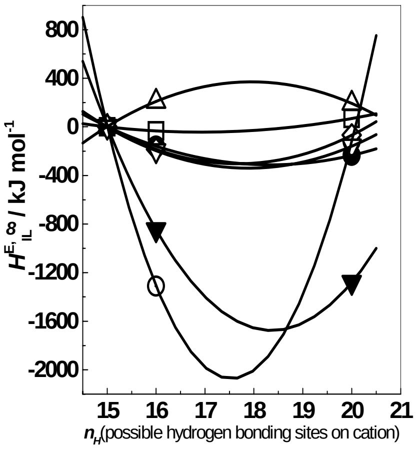


Fig. 5.1.7: Dependence of $H^{E,\infty}_{IL}$ on n_H (number of hydrogen bonding sites on IL cationic rings) of the different ionic liquid cations, (⊡) water, (▽) DMF, (◇) ethylene glycol, (●), methanol, (⊙) ethanol, (▼) 1-propanol, (△) formamide

The $H^{E,\infty}_{IL}$-n_H correlation (Fig. 5.1.7) suggests that as the number of potential hydrogen bonding sites increase, the interactions between the IL cation and the solvent molecules also increase and thus the exothermic behavior. The interactions are not only affected by the number of sites but also by the strength of the hydrogen bonding established between the IL cation and the solvent molecules. Thus, the [BMPYRR]$^+$ cation having more number of hydrogens with but weaker acidic behavior tends to show more endothermic behavior than the $[BMPY]^+$ cation. Where as $[BMIM]^+$ cation show marginally endothermic behavior with all the solvents showing that there is a counter balance of the heat absorbed during the dissolution process and the heat evolved during the bond formation between the $[BMIM]^+$ cations and the solvent molecules. This important link prompted us to try for a more rigorous correlation between other microscopic properties of solvents and the $H^{E,\infty}{}_{IL}$ of APIL solutions[29]. This correlation could give a more sound explanation for the distinct behavior of APILs. For the purpose different solvents were examined for their properties that can give the best correlation with the $H^{E,\infty}{}_{IL}$ values. It was found out that for the imidazolium-based ILs two properties of the solvents namely polarity index, π^* and the normalized Dimroth-Reichardt polarity parameter, E_T^N were noted to be effective for the purpose of correlation. For the description of these parameters and some other solvent parameters, the readers are directed to Chapter 4 dealing with protic ILs. The correlation used in the present work is given as:

$$H^{E,\infty}{}_{IL} = a_1 + a_2\,\pi^* + a_3\,E_T^N \qquad (2)$$

Eq 2 was applied to all the $\Delta_{sol}H^{\infty}$ values for four ionic liquids in several solvents studied herein with the values of π^* and E_T^N taken from the literature. The values of coefficients, a_1, a_2 and a_3 are given in Table 5.1.3.

Table 3: The Analysis of the $H^{E,\infty}_{IL}$ - Solvent Property Data for imidazolium-based ILs by Eq (2)

	[EMIM][BF$_4$]	[BMIM][BF$_4$]	[HMIM][BF$_4$]	[OMIM][BF$_4$]
a_1	1265±344	2626±614	1996±800	7668±653
a_2	-7519±484	-9497±590	31±19	10145±608
a_3	8465±1264	8775±1395	2921±399	-21938±2430
Corr. Coeff. r^2	0.798	0.775	0.695	0.735

Though it has been possible for us to analyze the impact of many solvent properties on the $H^{E,\infty}_{IL}$ values of the ionic liquids, we observed, in this investigation, the best correlation based upon π^* and E_T^N values. In Fig. 5.1.8, we demonstrate the importance of π^* and E_T^N values by comparing the $H^{E,\infty}_{IL}$ values obtained from our experiments ($H^{E,\infty}_{IL,EXP}$) with those from correlation ($H^{E,\infty}_{IL,CAL}$) for the studied ionic liquids in various solvents. The agreement between the two quantities is quite good for all the

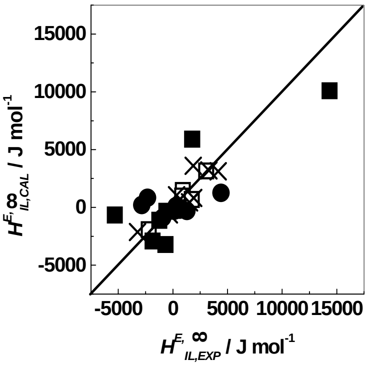


Fig. 5.1.8: A comparison between $H^{E,\infty}_{IL,EXP}$ and $H^{E,\infty}_{IL,CAL}$ for (□) [EMIM][BF$_4$], (x) [BMIM][BF$_4$], (•) [HMIM][BF$_4$] (■) [OMIM][BF$_4$] in different solvents

ionic liquids suggesting us to widen the scope of such a correlation in future when more data become available. The correlation is successful in wide range of both endo- and exothermic thermal effects as shown in Fig. 5.1.8. An examination of the a_1 values shows that the energy required to overcome solute-solute interactions is significant. The standard errors given against a_1 parameters for all the four ionic liquids indicate this point. The negative sign of the a_2 coefficient for π^* in [EMIM][BF_4] and [BMIM][BF_4] ionic liquids suggests an exothermic contribution to the solution enthalpies. The importance of all these coefficients being noted here, the coefficient for the E_T^N property for [OMIM][BF_4] has very large negative value insisting upon the significant role of both the hydrogen bond acidity and the dipolarity characteristics of the solvent on the solution enthalpies of [OMIM][BF_4].

This model was also tested for two other ILs *i.e.* [BMPY][BF_4] and [BMPYRR][BF_4] with different solvents. It was noted that for these two systems more number of solvent parameters were required to correlate their $H^{E,\infty}_{IL}$ values. A set of different properties namely α (hydrogen bond donor ability), β (hydrogen bond aceeptor ability), π^* (polarizability/ dipolarity), δ (Hildebrand solubility parameter) and E_T^N (normalized polarity parameter) were required in different permutation and combination for different ILs. For pyridinium-based IL, the equation used for the correlation is:

$$H^{E,\infty}_{IL} = a_1 + a_2\,\alpha + a_3\,\pi^* + a_4\,\delta + a_5\,E_T^N \qquad (3)$$

and for the pyrrolidinium-based IL

$$H^{E,\infty}_{IL} = a_1 + a_2\,\alpha + a_3\,\beta + a_4\,\delta + a_5\,E_T^N \qquad (4)$$

The values of these solvent properties are taken from the literature. The values of the fitting coefficients are given in Table 5.1.4.

Table 5.1.4: The Analysis of the $H^{E,\infty}_{IL}$ - Solvent Property Data for pyridinium and pyrrolidinium-based ILs by Eqs (3) and (4)

Parameters	[BMPY][BF$_4$]	[BMPYRR][BF$_4$]
$a_1 x10^{-6}$	-3.96 ± 0.81	11.5 ± 3.5
$a_2 x10^{-7}$	2.03 ± 0.63	-2.27 ± 0.84
$a_3 x10^{-5}$	-1.38 ± 0.6	1.62 ± 0.71
$a_4 x10^{-6}$	-7.04 ± 2.17	6.69 ± 2.52
$a_5 x10^{-6}$	-1.52 ± 1.38	-9.1 ± 2.35
Corr. Coeff. r^2	0.938	0.934

The $H^{E,\infty}_{IL}$ values thus obtained from both the methods ($H^{E,\infty}_{IL,cal}$ and $H^{E,\infty}_{IL, EXP}$) are plotted against each other (Figs 5.1.8 and 5.1.9) to show the validity of this model and also the significance of these solvent properties in correlating the $H^{E,\infty}_{IL}$ data . This model was found to be successful in correlating the limiting excess partial molar enthalpy with different solvent properties.

An important observation was noticed in case of the PILs for which lesser number of solvent parameters were required for the correlation purpose. But as we move towards the APILs, not only the number of solvent parameters increase for the better correlation but also the goodness of the correlation decrease. It suggests that for APILs, the number of possible interactions are increased as well as they are different in nature as compared to the PILs.

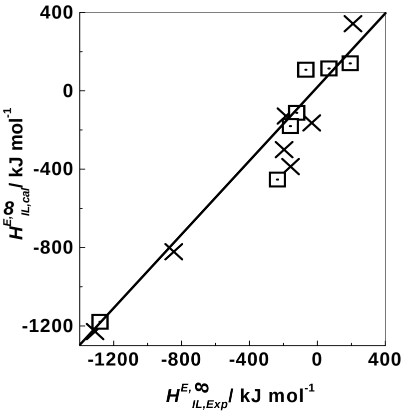


Fig. 5.1.9: A comparison between $H^{E,\infty}_{IL,Exp}$ and $H^{E,\infty}_{IL,Cal}$ for (□) [BMPY][BF_4], (x) [BMPYRR][BF_4] in different solvents

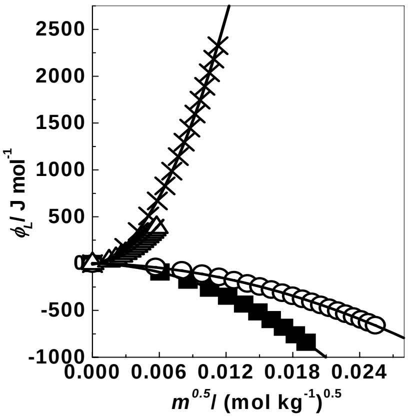


Fig. 5.1.10: The molality dependence of ϕ_L for the imidazolium-based APILs in water; (■) [EMIM][BF_4], (⊙) [BMIM][BF_4], (▲) [HMIM][BF_4], (×) [OMIM][BF_4]

The knowledge gained about APILs, that there exist more complex interactions between different entities present in the solutions, directed us to obtain a rather more relevant thermodynamic quantity, the relative apparent molar enthalpy (ϕ_L), which can give a better insight to these interactions. For the imidazolium, pyridinium and pyrrolidinium-based ILs, these quantities were calculated from the H^E_{IL} values[30] and are presented in Fig. 5.1.10. Fig 5.1.10 presents a comparative picture of all the ϕ_L data corresponding to different imidazolium-based APILs.

The ϕ_L values correspond to the equal but opposite values of the H^E_{IL}. Fig. 5.1.10 suggests that the ϕ_L values are in the same order, which H^E_{IL} values of different imidazolium ILs follow *i.e.* the IL with smallest substitution on the parent ring show the most endothermic behavior but as the length of the alkyl substitution increases the enthalpic behavior of ionic liquids changes to exothermic. Upon changing the cationic parent ring from imidazolium to pyridinium and pyrrolidinium, ϕ_L values show the following pattern:

$$[BMPY][BF_4] > [BMIM][BF_4] > [BMPYRR][BF_4]$$

It is observed from Fig. 5.1.11 that as we move from the aromaticity to non-aromaticity the pattern of the solvation also changes from the exothermic to endothermic behavior. The highest value of $[BMPY][BF_4]$ in the ϕ_L trends, discerns the similar phenomenon learnt from the H^E_{IL} trends, that as the interaction between the solute and the solvent become stronger, the dissolution process becomes more exothermic. It also suggests that the total solvation process of the pyridinium-based IL is more susceptible to the hydrophobicity phenomenon. It is more affected by the processes of solvent reorganization and the bond formation between IL cations and the solvent molecules.

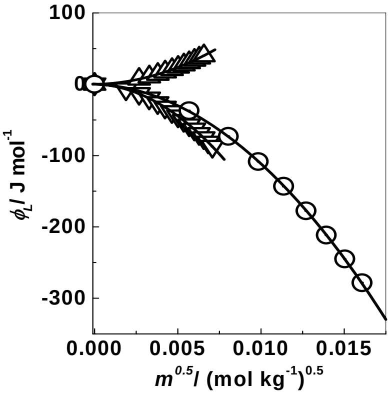


Fig. 5.1.11 A comparative plot of ϕ_L versus $m^{0.5}$ for (△) [BMPY][BF$_4$], (⊙) [BMIM][BF$_4$], (▽) [BMPYRR][BF$_4$]

Moving to a non-aromatic system [BMPYRR][BF$_4$] shows that the first step of the total solvation process *i.e.* the cavity formation /dissolution are of greater consequence than the second step of reorganization. It is also perceived from the figure that the [BMIM][BF$_4$] is lying in between the two extremes of exothermicity and endothermicity. It suggests the mediocre behavior of imidazolium based ILs where the two processes are counter-balanced; hence they are feebly endothermic in nature. These ϕ_L values can be further dissected to obtain much detailed information about different interactions ensuing at the molecular level. For this purpose a semi-empirical Pitzer equation[31,32] has already been tested successfully for predicting the behavior of PILs in solution with different molecular solvents. A detailed introduction to the equation is given in Chapter 4, yet the working equation is given below for the reference:

$$\phi_L = (A_L / 1.2) \ln (1 + 1.2\, m^{0.5}) - 2\, RT^2\, m\, (\beta^{(0)L} - 2\, \beta^{(1)L} [1 - (1 + 2\, m^{0.5}) \exp(-2\, m^{0.5})] / (2\, m^{0.5})^2 - C^L\, m) \qquad (5)$$

A_L = Debye-Hückel limiting slope, A_L values for different solvents are listed in Table 51.5; $\beta^{(0)L}$ and $\beta^{(1)L}$ = virial coefficients to quantify the binary interactions between the opposite and the like charges; C^L = virial coefficient for ternary interactions

Table 5.1.5: The Pitzer-Debye-Hückel limiting slope (A_L) at 298.15 K for different solvents

Solvent	A_L / J kg^{-1} mol$^{-3/2}$	Solvent	A_L / J kg^{-1} mol$^{-3/2}$
Water	2879	Ethylene Glycol	2948
D_2O	2707	Formamide	1394
Methanol	4717	DMF	4186
Ethanol	5622	Chloroform	2800
1-propanol	7002	-	-

With a view to demonstrate the scope of the Pitzer equations to both exothermic and endothermic behavior noted in this investigation, we first show in Fig. 5.1.12 the $\triangle\phi_L$ values (ϕ_L obtained in current study - ϕ_L obtained by the Pitzer equations) against the concentrations of ionic liquids for aqueous ionic liquid systems. An examination of this figure shows a random distribution of the $\triangle\phi_L$ values demonstrating the usefulness of the Pitzer equations in dealing with the enthalpy data of the solutions of ionic liquids. Further, we also tested the Pitzer equations to test the ϕ_L data of [OMIM][BF_4] in methanol.

The ϕ_L values have been noted to be negative throughout the concentration range studied herein (Fig. 5.1.13). As seen from Fig. 5.1.13, the Pitzer equations can analyse the ϕ_L data with excellent accuracy. These examples clearly bring out the utility of the Pitzer equations in dealing with the both endo and exothermic thermal behavior of the solutions of ionic liquids.

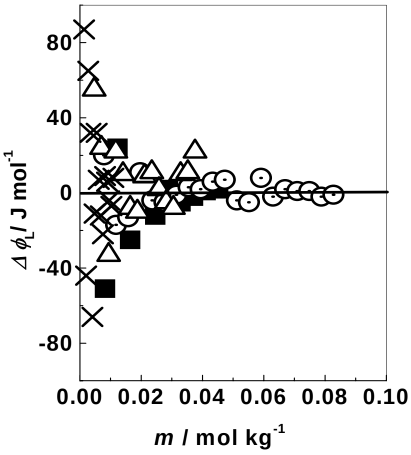


Fig. 5.1.12: The $\Delta\phi_L$ values as a function of molality (■) [EMIM][BF$_4$], (⊙) [BMIM][BF$_4$], (Δ) [HMIM][BF$_4$] and (x) [OMIM][BF$_4$] in water

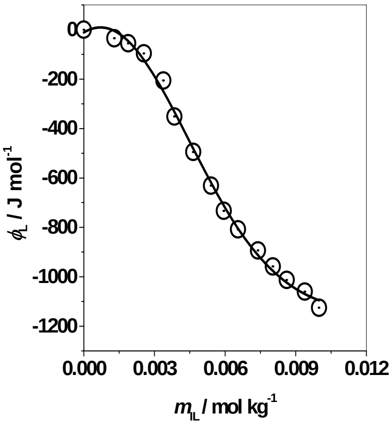


Fig. 5.1.13: The molality dependence of ϕ_L for the [OMIM][BF$_4$]-methanol system, solid symbols are our values, solid line represents values generated by the Pitzer equations

A correlation between the ϕ_L obtained experimentally and calculated by using Pitzer equations can also be shown for the pyridinium and pyrrolidinium based ILs (Fig.

5.1.14). These correlations show the scope of Pitzer equations in handling the data of varied nature. The Pitzer equations in this study are employed for dealing with exothermic and endothermic behavior of ionic liquids and also show a successful correlation for ILs with varying parent rings. Thus these Pitzer equations prove to be powerful tool for analyzing the APILs experimental data to get the further information about the interactions taking place at the molecular level.

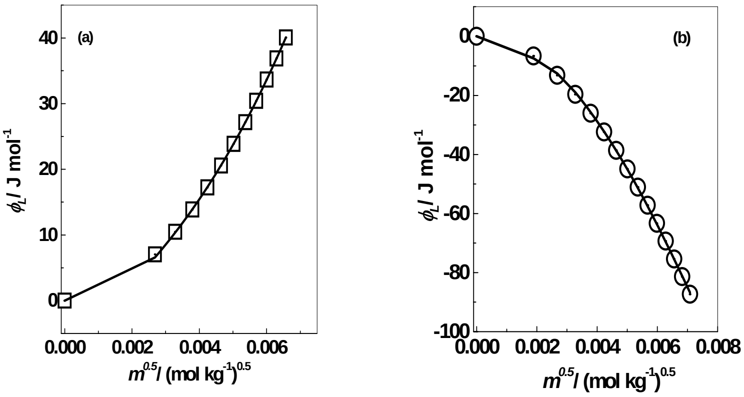


Fig. 5.1.14: The molality dependence of ϕ_L for the (a)[BMPY] [BF$_4$], and (b) [BMPYRR][BF$_4$]-water system, solid symbols are our values, solid line represents values generated by the Pitzer equations

The values of $\beta^{(0)L}$, $\beta^{(1)L}$ and C^L are listed in Table 5.1.6 and provide the intricate information about the interactions operating between the different entities present in the IL solutions. The average root mean squares deviation of the fits was within 5% for all the systems studied herein. An examination of the results given in Table 5.1.6 suggests that the magnitude and sign of the $\beta^{(0)L}$ and $\beta^{(1)L}$ parameters depend upon the number of carbon atoms in the substituent alkyl group attached to the imidazolium ring of ionic liquids. The values of $\beta^{(0)L}$ increase with increasing the number of carbon atoms in the alkyl group substituted on the parent ring. This indicates the increased ion-solvent interactions. There are some discrepancies in the $\beta^{(0)L}$ values of some solvents as they do not follow the same trend throughout it can be a result of different interactions complexed together so that the picture becomes unclear. As a general trend the $\beta^{(1)L}$ also increase with increasing the alkyl chain lengths. The second parameter shows a reversal of the sign while moving to the $[OMIM]^+$ cation. This may be due to the increased packing of the alkyl chains in $[OMIM]^+$ cation which tends to increase the unfavorable interactions between the two cations. There are some unusual behavior also shown by some of the solvents like ethanol, these can be further described by designing more elaborate experiments to probe the specific interactions taking place between IL and these solvents. Probably due to these complexed interactions they do not fit into a generalized frame of solvent behavior.

To probe further into these interactions, we moved from the imidazolium-based ILs to the pyridinium and pyrrolidinium-based ILs. The values of the virial coefficients from the Pitzer fits for the pyridinium and pyrrolidinium-based ILs are presented in Table 5.1.6. The ring effect can be clearly seen from the table as the values of $\beta^{(0)L}$ values show the negative sign along with the $\beta^{(1)L}$, which were negative for imidazolium-based ILs as well. Both the $\beta^{(0)L}$ and $\beta^{(1)L}$ values suggests

Table 5.1.6: Pitzer Coefficients for correlating ϕ_L with concentration of pyridinium and pyrrolidinium-based ILs in different solvents

Solvents ↓	[BMPY][BF$_4$]		[BMPYRR][BF$_4$]	
Pitzer Coefficients →	$-\beta^{(0)}$	$-\beta^{(1)}$	$-\beta^{(0)}$	$-\beta^{(1)}$
Water	0.156	0.185	-0.064	-0.048
Methanol	0.498	0.598	1.113	1.258
ethanol	11.410	12.24	0.660	0.813
1-propanol	3.493	3.879	3.67	4.062
Ethylene glycol	0.746	0.852	0.506	0.599
Formamide	-0.481	-0.502	-0.407	-0.421
N,N'-Dimethyl Formamide	0.642	0.744	0.331	-0.415

that there are stronger interactions prevailing between pyridinium and pyrrolidinium-based ILs and solvent entities as compared to the imidazolium-based ILs. Both ethanol and propanol show abnormally high interactions, which is consistent in all the three APILs.

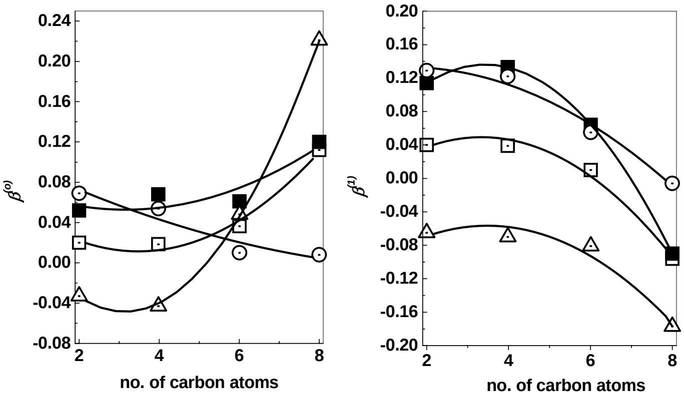


Fig. 5.1.15: Variation of the $\beta^{(0)L}$ and $\beta^{(1)L}$ parameters with the no. of carbon atoms in the substituent alkyl group attached to the imidazolium ring ; (⊡) water, (■) methanol, (⊙) ethylene glycol, (Δ) DMF

As these virial coefficients suggest the possibility and extent of interactions prevailing between the ionic species of ILs and the molecular solvents, we thought of correlating these parameters to the probable interaction sites present on the IL cations. With this idea we herein present the correlation between the virial coefficients, number of carbon atoms in the alkyl chain, carbon content and the number of hydrogen atoms present on the IL cations. Fig. 5.1.15 shows variations in the values of these parameters for different ionic liquids in water, methanol, ethylene glycol and dimethylformamide. The $\beta^{(0)L}$ parameter in water remains positive throughout going from [EMIM][BF_4] to [HMIM][BF_4], while a change in sign takes place in the case of aqueous [OMIM][BF_4]. In general, one can see noticeable change in the values of both these parameters in the case of the solutions of [OMIM][BF_4] due to hydrophobic interactions as discussed earlier. Interestingly both the Pitzer parameters *i.e* $\beta^{(0)L}$ and $\beta^{(1)L}$ show a very conspicuous deviation in the case of DMF, which supports our assumption of some other factors in addition to polarity taking part in the reorganization of aprotic solvent molecules around ionic liquid species. Fig. 5.1.15 also suggests that the interactions between ion-solvent and ion-ion increase upon increasing the alkyl chain length. Thus, the increment of the carbon content in the alkyl chains increases the extent of interactions of both favorable and unfavorable nature.

An attempt was also made to correlate the $\beta^{(0)L}$ and $\beta^{(1)L}$ values for the [BMPY][BF_4] and [BMPYRR][BF_4] in comparison with [BMIM][BF_4] and the number of hydrogen atoms/carbon atoms present on the parent ring.

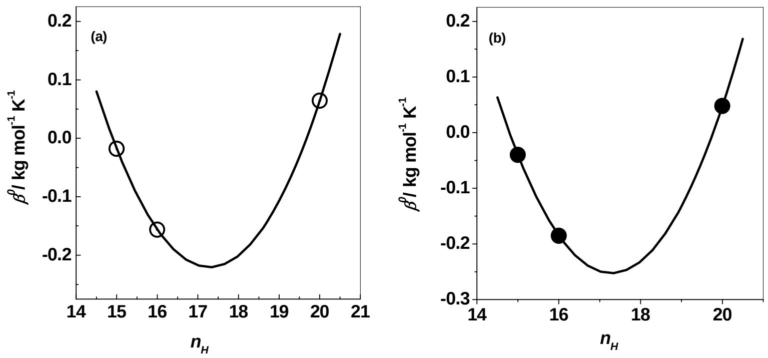


Fig. 5.1.16 A correlation of $\beta^{(0)L}$ and $\beta^{(1)L}$ values with the total number of hydrogen bonding sites (n_H) on the IL cations

Fig. 5.1.16 suggests that with increase in the hydrogen bonding sites the interactions turn out to be more endothermic in nature. ILs with medium number of hydrogen atoms show the maximum exothermic behavior and the one having lowest number of hydrogen bonding sites show the borderline behavior. This observation is consistent with the previously obtained results from the H^E_{IL} values, which reports the exothermic behavior of [BMPY][BF$_4$], feeble endothermic behavior for [BMIM][BF$_4$] and endothermic behavior for [BMPYRR][BF$_4$] ionic liquids.

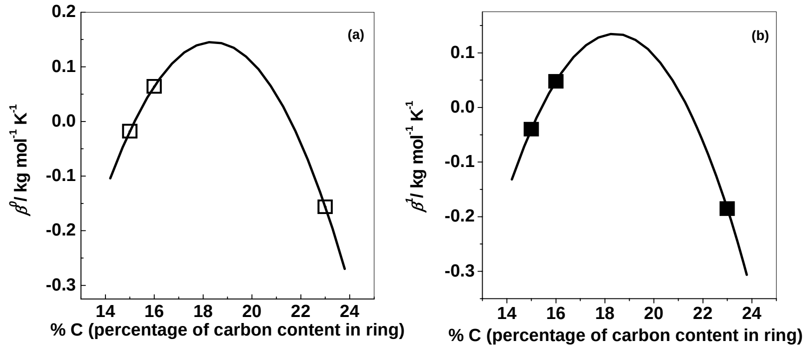


Fig. 5.1.17 The $\beta^{(0)L}$ and $\beta^{(1)L}$ values with respect to the total % of carbon content in the cationic parent ring of different ILs

Fig. 5.1.17 shows that as the carbon content of the cation ring increases it imparts more exothermic behavior to the system. This suggests that as the size of the cation increases there exists a greater possibility of the interactions between the IL cation and the solvent molecules.

From the foregoing, it is clear that the Pitzer equations serve as a powerful tool to analyze the enthalpy data of solutions of ionic liquids, though a model accounting for the heterogeneous environment around cation of an ionic liquid will be desirable. This heterogeneous nature of ionic liquid due to weak interaction forces operating between cations and anions in the presence of a solvent has been reported.[54] We did not attempt to use or develop such a model in the current situation, as the large variations in $H^E{}_{IL}$ are noted in highly solvent-rich region that can be fitted with a square root of the concentration term built in Debye-Hückel type of equation. Moreover, the $H^E{}_{IL}$ - m curves become nearly invariant in the water-poor range.

In summary, we have presented accurate enthalpy data of the solutions of APILs in this section of the present chapter. The effect of alkyl chain length on the data has been estimated and the results have been interpreted in terms of the solvent reorganization around the species of ionic liquids discussed. The Pitzer equations are noted to be very useful in correlating apparent relative molar enthalpies (ϕ_L) of the solutions of ionic liquids with exo- and endothermic enthalpy behavior in different solvents. This knowledge based upon the enthalpy data for ionic liquids with varying length of substituent alkyl chain and the different nature of parent rings has enabled us to extend our understanding the role of solvents in altering the thermal properties of ionic liquids with hydrophilic and hydrophobic characteristics.

The related experimental data for the present study and other derived thermodynamic quantities are presented in Tables 5.1.7, 5.1.8 and 5.1.9.

Table 5.1.7: The experimental H^{E}_{IL} and other derived thermodynamic quantities for [EMIM][BF$_4$] ionic liquid with water as a solvent

m x10^4/ mol kg^{-1}	H^{E}_{IL}/ J mol^{-1}	ϕ_L/ J mol^{-1}	$\overline{L}_1$ x 10^4/ J mol^{-1}	$\overline{L}_2$/ J mol^{-1}	L x10^3/ $J\ mol^{-1}$	ΔH_{mix}/ J mol^{-1}
0	0	0	0	0	0	0
0.369	57560	-89.90	1.75	-354.29	-3.31	0.050
0.737	29382	-177.51	2.95	-399.84	-13.09	0.093
1.106	19078	-263.64	3.29	-428.71	-29.16	0.130
1.475	14252	-348.59	3.02	-462.33	-51.4	0.161
1.843	11416	-432.53	2.48	-507.38	-79.73	0.186
2.212	9494	-515.57	2.03	-566.48	-114.04	0.205
2.581	8246	-597.80	1.99	-640.74	-154.27	0.218
2.949	7344	-679.28	2.72	-730.58	-200.34	0.225
3.318	6658	-760.07	4.54	-836.09	-252.19	0.226

Table 5.1.8: The experimental H^{E}_{IL} and other derived thermodynamic quantities for [BMPY][BF$_4$] ionic liquid with water as a solvent

m x10^5/ mol kg^{-1}	H^{E}_{IL}/ J mol^{-1}	ϕ_L/ J mol^{-1}	$\overline{L}_1$ x 10^4/ J mol^{-1}	$\overline{L}_2$/ J mol^{-1}	L x10^5/ $J\ mol^{-1}$	ΔH_{mix}/ J mol^{-1}
0	0	0	0	0	0	0
0.720	-6447	7.04	-1.64	1271.23	5.07	-0.028
1.080	-3811	10.47	-2.96	1533.16	11.30	-0.042
1.440	-2565	13.87	-4.49	1747.37	19.98	-0.057
1.800	-1898	17.23	-6.20	1931.14	31.03	-0.071
2.161	-1440	20.57	-8.06	2093.36	44.43	-0.085
2.521	-1096	23.87	-10.1	2239.18	60.17	-0.099
2.881	-958	27.15	-12.2	2372.12	78.22	-0.113
3.241	-722	30.41	-14.4	2494.54	98.57	-0.127
3.601	-681	33.65	-16.7	2608.15	121.00	-0.141
3.961	-532	36.90	-19.1	2714.27	146.00	-0.155
4.321	-513	40.07	-21.6	2813.91	173.00	-0.169

Table 5.1.9: The experimental H^{E}_{IL} and other derived thermodynamic quantities for [BMPYRR][BF$_4$] with water as a solvent

m x10^6/ mol kg^{-1}	H^{E}_{IL}/ J mol^{-1}	ϕ_L/ J mol^{-1}	$\overline{L_1}$ x 10^4/ J mol^{-1}	$\overline{L_2}$/ J mol^{-1}	L x10^4/ $J\ mol^{-1}$	ΔH_{mix}/ J mol^{-1}
0	0	0	0	0	0	0
3.584	25123	-6.68	1.11	-1727.03	-0.24	0.025
7.167	13631	-13.22	3.07	-2396.04	-0.95	0.051
0.108	10118	-19.67	5.56	-2891.36	-2.12	0.076
0.143	7818	-26.06	8.44	-3296.94	-3.74	0.101
0.179	6175	-32.38	11.7	-3645.26	-5.80	0.126
0.215	5179	-38.66	15.1	-3952.96	-8.31	0.151
0.251	4396	-44.88	18.9	-4229.95	-11.30	0.176
0.287	3717	-51.06	22.9	-4482.66	-14.60	0.201
0.323	3342	-57.19	27.0	-4715.56	-18.40	0.226
0.358	2803	-63.29	31.4	-4931.90	-22.70	0.251
0.394	2589	-69.35	35.9	-5134.14	-27.30	0.276
0.430	2180	-75.38	40.6	-5324.18	-32.40	0.300
0.466	1997	-81.37	45.5	-5503.54	-37.90	0.325
0.502	1692	-87.33	50.4	-5673.44	-43.80	0.350

5.2: A Comparison between –BF_4^- and –NTf_2^- based ionic liquids: *Does anion play an effective role?*

The current interest in the area of ionic liquids is also to investigate ILs with anions having typically diffuse negative charges[33], which generally display low melting points and fairly low viscosity[34]. These ILs are also very promising candidates for the lithium batteries[35], one of the most efficient and ubiquitous electric-storage devices[36, 37, 38]. In some of the reports, the importance of the anion in determining the physical properties of ILs has also been noted. In specific, ILs containing inorganic perfluorinated sulfonylimide anions are of great interest because of their hydrolytically stable nature[39, 34]. We have already reported in the previous section of this chapter, the behavior of –tetrafluoroborate $[BF_4]^-$ based ILs in the presence of various solvents, where $[BF_4]^-$ is a small-sized anion with the charge centered on the central atom of the anion.

In the first place, the logic behind planning this work was, that if an anion just opposite in morphology, with a bigger size and its charge is diffused all over the anion is substituted in place of the $[BF_4]^-$ anion, (1) how would it modify the interactions prevailing between the cations and the solvent molecules (2) what could be the extent of this change? The ILs chosen for this study are the imidazolium-based with varying chain length and with a common $[NTf_2]^-$ anion. Following the solubility criterion, we have chosen methanol, ethanol, propanol, ethylene glycol, formamide and *N,N'*-dimethylformamide as the solvent systems.

When a small amount of solute (IL) is added to a pure solvent system it is dissolved inside the solvent by dissociating itself into its ionic counterparts. This causes a change in the total enthalpy of the pure solvent system, which is measured to obtain the H^E_{IL} values being extremely sensitive to the amount of solute added and the nature of both solute and the solvent. Fig. 5.2.1 unambiguously shows this change in H^E_{IL} values when the imidazolium cation is substituted with $[NTf_2]^-$ anion in place of $[BF_4]^-$ anion.

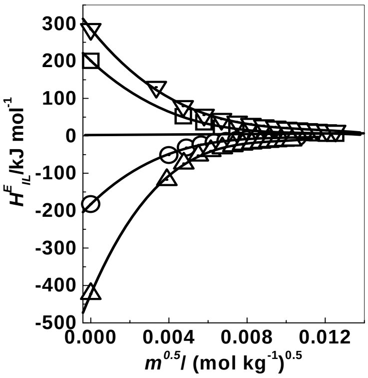


Fig. 5.2.1: A plot comparing H^E_{IL} values for both $[BF_4]^-$ and $[NTf_2]^-$-based ILs; (∇) [BMIM][BF$_4$], (⊡) [BMIM][NTf$_2$], (⊙) [OMIM][BF$_4$], (Δ) [OMIM][NTf$_2$] in methanol

For all the four ILs studied, the H^E_{IL} values for IL-methanol systems follow the order:

$$[BMIM][BF_4] > [BMIM][NTf_2] > [OMIM][BF_4] > [OMIM][NTf_2]$$

There are two sets of information obtained from the Fig. 5.2.1. Each one would be analyzed and explained one by one:

(1) [BMIM][BF$_4$] and [BMIM][NTf$_2$] make a separate group and show the strong endothermic pattern while both [OMIM][BF$_4$] and [OMIM][NTf$_2$] can be included in a different group showing exothermic behavior. Both these groups are distinctly different in their behavior from each other.

(2) The second interesting observation that can be discerned out of Fig. 5.2.1 is that as soon as we increase the length of the substituted alkyl chain on the imidazolium ring from –butyl to –octyl, the enthalpic pattern shifts from endothermic to exothermic behavior. This shift can be clearly seen in the case of both $[BF_4]^-$ and $[NTf_2]^-$ substituted ILs.

These two observations suggest that (i) it is the cation that decides the enthalpic pattern of an IL in a solvent. For the –butyl substituted IL, the endothermic behavior is seen for the different anions *i.e.* $[BF_4]^-$ and $[NTf_2]^-$. But when the anion is substituted from $[NTf_2]^-$ to $[BF_4]^-$, for –butyl substituted ILs the enthalpy pattern becomes less endothermic for $[NTf_2]^-$ based IL than $[BF_4]^-$ one.

For -octyl substituted ILs, more exothermic behavior is observed for the $[NTf_2]^-$ based IL than having $[BF_4]^-$ anion. In both the cases, the $[NTf_2]^-$ anion causes more stabilization in the IL-solvent system. When an IL is dissolved in pure solvent it costs some energy for the cavity formation/breaking of the bonds. Once the IL is dissolved the solvent molecules start reorganizing themselves in this new environment having the IL as solute. This involves the reformation of the new bonds between the IL and the solvent molecules and also between the solvent-solvent molecules. The first step is energy consuming and the second step is energy releasing. Thus if an IL solvation process has a dominating first step, then the whole process turns out to be endothermic where as if it is dominated by the second step then it becomes exothermic.

When we substitute the $[NTf_2]^-$ anion in place of $[BF_4]^-$, the former being larger in size shares weaker Coulombic interaction with the cation and thus requires lesser energy to get dissolved in a solvent as compared to the IL containing $[BF_4]^-$ as counteranion. Later on, when the makeshift of the solvent molecules starts then $[NTf_2]^-$ may provide more sites for the hydrogen bonding and other interaction sites to the solvent. Thus, along with the cation, the anion indulges in more number of interactions, which makes the solvation process more exothermic in nature. This fact can be perceived from Fig. 5.2.1, where both the $[NTf_2]^-$ based ILs tend to show the more bond formation and thus more exothermic tendency than their $[BF_4]^-$ counterparts.

It would be very exciting to see which is the point of the shift from endothermic to exothermic behavior for the ILs having $[NTf_2]^-$ anion, as we increase the length of the alkyl substitution on the parent ring. Will it be same as in the case of ILs having $[BF_4]^-$ anions?

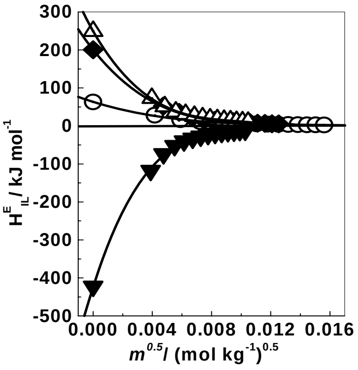


Fig. 5.2.2: A comparative plot of H^E_{IL} versus $m^{0.5}$ for (⊙) [EMIM][BF_4], (◆) [BMIM][BF_4], (△) [HMIM][BF_4], (▼) [OMIM][BF_4] in methanol

In Fig. 5.2.2, a comparison of the H^{E}_{IL} values for different ILs in a common solvent methanol shows that as we increase the size of the cationic moiety in terms of the substituted alkyl chains on the parent rings it causes the increase in the H^{E}_{IL} values.

ILs with lower alkyl chains show lesser endothermic behavior but the behavior is pronounced and more stronger as the length of the alkyl substitution is increased, which is opposite to that shown by the $[BF_4]^-$ based ILs. This endothermic behavior is maximum for the –hexyl substituted ILs and gets reversed upon the further increase in the alkyl chain length. As the chain length increases from –hexyl to –octyl the ILs show the usual change over tendency of endo-exothermic shift, also shown by the $[BF_4]^-$ based ILs. For the lower alkylated ILs, the anion seems to be more effective and controlling the solvation behavior and for the higher alkylated ILs, the solvation behavior is governed by the cations.

An attempt was also made to comprehend the solvation behavior of these $[NTf_2]^-$ based ILs with different solvents other than methanol.

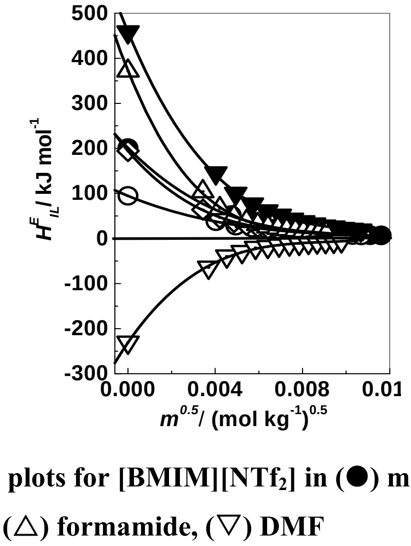


Fig. 5.2.3: The H^{E}_{IL} versus $m^{0.5}$ plots for [BMIM][NTf$_2$] in (●) methanol, (⊙) ethanol, (▼) propanol, (◇) ethylene glycol, (△) formamide, (▽) DMF

The solvents chosen cover the whole relative permittivity range. A comparison of the different solvation behavior for these ILs in different solvents is shown in Fig. 5.2.3.

For [BMIM][NTf$_2$] ionic liquid, the order all the solvents follows: propanol > formamide > methanol > ethylene glycol > ethanol > DMF and

For [OMIM][NTf$_2$] ionic liquid, the H^E_{IL} values for different solvents follow the order: propanol > formamide > ethanol > ethylene glycol > DMF > methanol

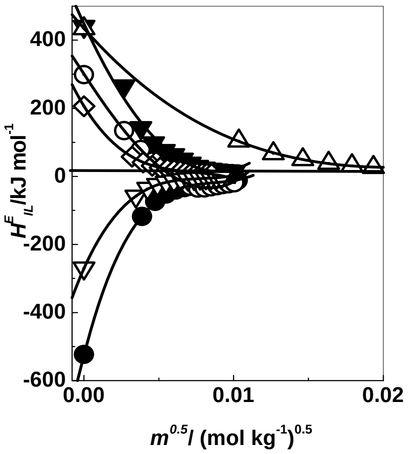


Fig. 5.2.4: The H^E_{IL} versus $m^{0.5}$ plots for [OMIM][NTf$_2$] in (●) methanol, (⊙) ethanol, (▼) propanol, (◇) ethylene glycol, (△) Formamide, (▽) DMF

From both the Figs. 5.2.3 and 5.2.4, the H^E_{IL} values in different solvents suggest that the solvents in both the ILs *i.e.* [BMIM][NTf$_2$] and [OMIM][NTf$_2$], show a zig-zag dependency on various properties of the solvents. Out of many properties of the solvents, no property of the solvent could be singled out which would have a direct influence on the trend of the H^E_{IL} values. It indicates that there are too many parameters, which guide the behavior of these [NTf$_2$]$^-$ based ILs, although as compared to their

$[BF_4]^-$ based counter-parts, they show enhanced interactions with the solvents which is reflected in their higher H^E_{IL} values. One more interesting detail observed was that for both the ILs [BMIM][NTf_2] and [OMIM][NTf_2], despite having different alkyl chains, the magnitude and the trend shown by them in different solvents is more or less similar. Exceptions are methanol and ethanol, which display different positions in the series with ILs having varied alkyl chains.

The H^E_{IL} data were fitted to a polynomial equation (eq. 1) to get the limiting excess partial molar enthalpy ($H^{E,\infty}_{IL}$). These data were extrapolated using sufficient weights in the lower concentration range of the data. The values thus generated are listed in Table 5.2.1.

Table 5.2.1: The limiting partial molar excess enthalpies, $H^{E,\infty}_{IL}$ / kJ mol^{-1} of the $[NTf_2]^-$ based ILs in different solvents

	[EMIM][NTf_2]	[BMIM][NTf_2]	[HMIM][NTf_2]	[OMIM][NTf_2]
Methanol	77 ± 3	252 ± 23	280 ± 10	-523 ± 26
Ethanol	14 ± 4	107 ± 6.4	424 ± 18	299 ± 22
Propanol	265 ± 13	530 ± 23	294 ± 29	440 ± 38
Ethylene glycol	11 ± 1.2	214 ± 7.7	69 ± 2.7	206 ± 9
Formamide	194 ± 11	448 ± 21.6	466 ± 21	434 ± 22
N,N'-Dimethyl Formamide	109 ± 4	-219 ± 19	-190 ± 92	-2701 ± 12

We also tried to correlate these $H^{E,\infty}_{IL}$ values with the number of carbon atoms (n_C) in the alkyl chains on the cations of the ILs (Fig. 5.2.5). There was no proper correlation found between the above mentioned quantities. The inference from the above observation can be drawn that for the $[NTf_2]^-$ based ILs the enthalpy change caused due to the dissolution of one mole of IL in pure solvent doesn't depend on the size of the substitution on the parent ring which is not in accordance with the earlier result established for the $[BF_4]^-$ based ILs.

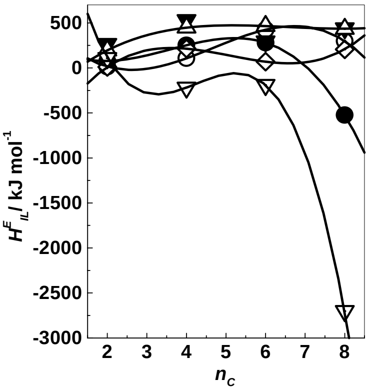


Fig. 5.2.5: Dependence of $H^{E,\infty}_{IL}$ on n_C (number of carbon atoms in the alkyl tail on the parent rings) of the ionic liquid cation, (●) methanol, (⊙) ethanol, (▼) propanol, (◇) ethylene glycol, (△) Formamide, (▽) DMF

To get more precise information about the interactions prevailing in the $[NTf_2]^-$ based IL solutions, we calculated relative apparent molar enthalpy (ϕ_L)[31,32] for the purpose of the fitting by Pitzer equations (eq. 5). The Pitzer fittings provide the virial coefficients, which signifiy the type and strength of the interactions taking place between ILs and the molecular solvents.. Fig 5.2.6 compares the ϕ_L values obtained for ILs with both $[BF_4]^-$ and $[NTf_2]^-$ anions in methanol. It is already known that the relative apparent molar enthalpy (ϕ_L) is equal and opposite in sign to the heat of dilution (ΔH_{dil}) of one mole of solute with an infinite amount of solvent (chapter 4).

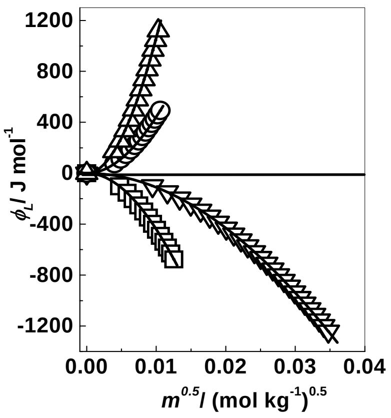


Fig. 5.2.6: A comparison of ϕ_L values for [BF$_4$]$^-$ and [NTf$_2$]$^-$-based ILs; (∇) [BMIM][BF$_4$], (⊡) [BMIM][NTf$_2$], (⊙) [OMIM][BF$_4$], (Δ) [OMIM][NTf$_2$] in methanol

The ϕ_L values in Fig. 5.2.6 show the similar but opposite trend to that shown by the $H^E{}_{IL}$ values for the same ILs in methanol. The Pitzer fitting of these ϕ_L values yielded virial coefficients that are listed in Table 5.2.3 and Table 5.2.4.

Table 5.2.3: Values of virial coefficients $\beta^{(0)L}$, $\beta^{(1)L}$ and C^L for [EMIM][NTf$_2$] and [BMIM][NTf$_2$]

Solvents↓	[EMIM][NTf$_2$]			[BMIM][NTf$_2$]	
Pitzer coefficients→	$\beta^{(0)L}$	$\beta^{(1)L}$	C^L	$\beta^{(0)L}$	$\beta^{(1)L}$
Methanol	-0.005	-0.059	-	0.363	0.340
Ethanol	-0.539	-0.673	1.552	-0.124	-0.228
1-propanol	0.216	0.136	-	0.681	0.609
Ethylene glycol	-0.374	-0.454	1.256	0.231	0.194
Formamide	0.315	0.336	-	0.865	0.917
DMF	0.030	-0.017	-	-0.782	-0.895

Table 5.2.4: Values of virial coefficients $\beta^{(0)L}$, $\beta^{(1)L}$ and C^L for [HMIM][NTf$_2$] and [OMIM][NTf$_2$]

Solvents↓	[HMIM][NTf$_2$]		[OMIM][NTf$_2$]	
Pitzer coefficients→	$\beta^{(0)L}$	$\beta^{(1)L}$	$\beta^{(0)L}$	$\beta^{(1)L}$
Methanol	0.460	0.436	-1.356	-1.525
Ethanol	0.483	0.410	0.349	0.268
1-propanol	0.067	-0.056	0.458	0.365
Ethylene glycol	-0.055	-0.110	0.195	0.153
Formamide	0.912	0.966	1.127	1.227
DMF	-0.376	-0.460	-0.777	-0.889

* units of $\beta^{(0)L}$, $\beta^{(1)L}$ = mol kg^{-1} K^{-1} and C^L = kg^2 mol^{-2} K^{-1}

A closer analysis of Tables 5.2.3 and 5.2.4 suggests that the virial coefficients do not have a regular pattern in their values apart from that the values increase as the number of carbon atoms in alkyl chains increase. For [NTf$_2$]$^-$ based ILs, the second virial coefficient *i.e.* $\beta^{(1)L}$ seems to be governing the interactions between ILs and solvents, as their values are higher in magnitude than the first virial coefficient $\beta^{(0)L}$. It suggests that in the [NTf$_2$]$^-$ based ILs the possibility of ion-ion interactions is more than ion-solvent interaction. This observation can be justified by the argument that [NTf$_2$]$^-$ anion is fairly large in size and thus would remain closer to the cation, hence the approach of the solvent molecules towards cation/anion would become difficult. This would result into a lower degree of ion-solvent interactions and the more closer approach of cation and anion, anion and anion would cause higher ion-ion interactions, which is also reflected from the higher $\beta^{(1)L}$ values.

Thus from the above study, it is clear that the anion does change the solvation pattern of the ILs in different solvents. While moving from $[BF_4]^-$ to $[NTf_2]^-$ anion the H^E_{IL} values in methanol show 10-fold increment for $[BMIM]^+$ cations and for $[OMIM]^+$ cations this increment is 4 fold (Fig. 5.2.2). Also, the $[NTf_2]^-$ anion substitution makes the ILs less sensitive towards the solvent recognition and the ILs substituted with $[NTf_2]^-$ anion does not follow any specific trend of solvent properties.

All the related experimental data and some other derived thermodynamic quantities are given in Tables 5.2.5 and 5.2.6

Table 5.2.5: The experimental H^E_{IL} and other derived thermodynamic quantities for [BMIM][NTf$_2$] with methanol as a solvent

m x10^4/ mol kg^{-1}	H^E_{IL}/ J mol^{-1}	ϕ_L/ J mol^{-1}	$\overline{L}_1$ x10^3/ J mol^{-1}	$\overline{L}_2$/ J mol^{-1}	L x10^3/ $J\ mol^{-1}$	ΔH_{mix}/ J mol^{-1}
0	0	0	0	0	0	0
0.225	52011	-103.41	7.53	-10570	-2.32	0.747
0.337	35860	-153.70	13.57	-12732	-5.18	1.118
0.450	21328	-203.35	20.56	-14496	-9.31	1.489
0.561	15129	-252.45	28.33	-16005	-14.17	1.859
0.674	14710	-301.07	36.76	-17334	-20.28	2.227
0.786	13265	-349.24	45.77	-18527	-27.44	2.594
0.898	11408	-397.01	55.29	-19612	-35.65	2.961
1.010	9041	-444.40	65.27	-20609	-44.9	3.326
1.123	8572	-491.44	75.68	-21533	-55.17	3.690
1.235	7170	-538.15	86.47	-22395	-66.45	4.054
1.347	6828	-584.53	97.62	-23202	-78.74	4.416
1.460	5730	-630.62	109.09	-23962	-92.03	4.777
1.572	5519	-676.41	120.87	-24681	-106.31	5.138

Table 5.2.5: The experimental H^E_{IL} and other derived thermodynamic quantities for [BMIM][NTf$_2$] with methanol as a solvent

m x10^3/ mol kg^{-1}	H^E_{IL}/ J mol^{-1}	ϕ_L/ J mol^{-1}	$\bar{L}_1$ x 10^3/ J mol^{-1}	$\bar{L}_2$/ J mol^{-1}	L x10^3/ J mol^{-1}	ΔH_{mix}/ J mol^{-1}
0	0	0	0	0	0	0
1.69	-117542	170.58	-10.21	21266	2.58	-1.017
2.53	-73643	253.64	-18.42	25630	5.75	-1.524
3.38	-52242	335.70	-27.93	29194	10.14	-2.030
4.23	-40096	416.90	-38.5	32247	15.74	-2.534
5.07	-32888	497.34	-49.99	34938	22.53	-3.037
5.92	-27413	577.10	-62.28	37352	30.5	-3.539
6.77	-23080	656.20	-75.29	39556	39.64	-4.040
7.62	-19937	734.72	-88.94	41581	49.93	-4.539
8.47	-17746	812.68	-103.2	43458	61.36	-5.038
9.32	-15704	890.11	-117.9	45210	73.93	-5.535
10.17	-14159	967.05	-133.2	46853	87.62	-6.031
11.03	-12746	1043.51	-148.9	48401	102.43	-6.526
11.18	-11829	1119.52	-165.1	49847	118.35	-7.020

5.3: DMSO: *What makes it an exclusive solvent*?

A thorough literature survey reveals that a significant amount of research is focused on the use of ILs for improving organic transformations.[40, 41, 42, 43, 44, 45] During the rigorous exercise of collecting the thermal data on a variety of ionic liquids with a range of molecular solvents, we observed both positive and negative enthalpy changes resulting from the interactions operating between the IL cations and anions with the solvent molecules. These changes were quite understandable and we could correlate them with the different microscopic properties of molecular solvents. This study on one hand gave results which were explainable to a greater extent, on the other hand it acquiesced a result which could not be explained on the basis of the usual trend of the molecular properties of the solvents. It was quite surprising to spot Dimethyl Sulphoxide (DMSO) showing very feeble endothermic behavior with imidazolium-based ILs (especially with lower alkyl chains) as compared to other molecular solvents, an interesting one though!

DMSO occupies a unique position among the polar solvents, due to its important role in several biochemical processes. DMSO has an extensive usage in several industries especially pharmaceutical industry. DMSO is also a potential solvent for diverse applications in fields such as general and analytical chemistry, physical chemistry, biology and medicine to name a few. It is considered to be a good nucleophilic reagent and has been seen to enhance the rate of several reactions by stabilizing the reaction intermediates. Alike DMSO, ionic liquids as already discussed, are the potential solvents for a variety of applications in the present and recent future. Thus it is very important to identify the interactions taking place between the components of these two potential solvents.

In spite of rapid progress of the research dealing with ILs, there exist very limited reports on their interactions with polar protic, polar aprotic and non-polar solvents. APILs can be termed as mildly polar solvents with their relative permittivity, ε ranging from 9 to 15,[46] while PILs as polar with ε in the range of 33 to 60.[47] It is already reported in the literature that the ILs have polarities similar to those of short-chain alcohols and other polar, aprotic solvents like DMSO and DMF.

In view of the comparable polarities of ILs and DMSO,[48, 49, 50, 51] it is expected that strong solute-solvent interactions will prevail. This work is an effort to probe the nature of interactions operating between DMSO and ILs possessing varied alkyl chain lengths in order to invoke non-polarity. We compared the interactions prevailing in between the DMSO molecules and two different classes of ILs i.e APILs and PILs to discern which factor does govern the weak interactions in some of the systems containing DMSO as a solvent. The ionic liquids employed in the present study are illustrated in Fig. 5.1.1 and the solvents used are water, methanol, DMF and DMSO. The other solvents are chosen for the sake of comparison with other molecular solvents. The criterion behind choosing the molecular solvent was to have molecular solvents which are having either the comparable or greater dielectric constant than DMSO.

First we present a comparison of the H^E_{IL} values of [BMIM][BF$_4$] with four different solvents *i.e.* methanol (ε = 32.8), DMF (ε = 38), DMSO (ε = 46.68) and water (ε = 78.2)[26]. DMF was chosen for the sake of comparison. As clear from the plots, the H^E_{IL} *versus* $m^{0.5}$ curves do not follow the order of the ε values of these solvents. Methanol and DMF exhibit the highest endothermic and exothermic behavior, respectively. The H^E_{IL} values can be arranged in the following order:

methanol > water > DMSO > DMF

Further, one can see notable differences between the plots shown in Fig. 5.3.1. Interestingly, the H^E_{IL} values for the interactions of [BMIM][BF$_4$] with DMSO are marginally endothermic, when compared to with other three solvents. From Fig. 5.3.1 it

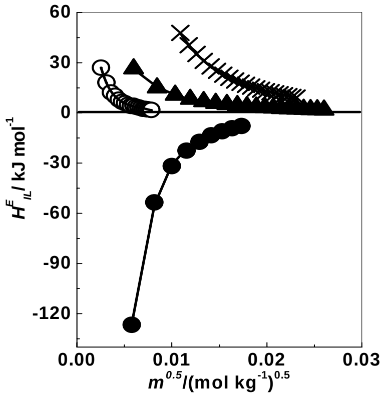


Fig. 5.3.1: A comparison of the H^E_{IL} values for [BMIM][BF$_4$] in (▲) water, (⊙) DMSO, (●) DMF, (X) methanol

is also observed that in the dilute range or the solvent-rich region the enthalpy curves show a very sharp fall which is typical of an electrolyte behavior but as the IL concentration increases the enthalpy curve shows a flattening tendency for all the solvents suggesting the onset of clathrate formation. Focusing the IL-DMSO curve it was noticed this flattening of the curve is much early in case of DMSO which suggests an early onset of clathrates as compared to other solvents. DMSO induces clathrate formation at an early concentration of IL, as it does not allow a complete dissociation of an IL into its ions. This is in contrast to situation noted in the IL-water system,[52] in which the clathrate formation begins at higher concentrations of IL. In very dilute aqueous IL solution, it is difficult for the ions to approach each other to form clathrates. In pure IL state, it is easier for ionic species to approach each other resulting into the cluster formation.

Intrigued by this observation, we titrated isomolar solutions of other ILs such as [MIM][BF_4], [HMIM][BF_4], [OMIM][BF_4] and, [BMIM][NTf_2] against DMSO. The reason to select these ILs is discussed before. The experimental H^E_{IL} data thus obtained are shown in Figure 5.3.2 together with those obtained in NaCl–DMSO system for the sake of comparison. As seen from the data, the nature of interactions of NaCl with DMSO is different from those of ILs in the same solvent. As discussed earlier, the mechanism of hydration or solvation of Na^+ and other alkali metal cations is different from that of the alkyl substituted imidazolium-based cations.[52] The interactions of the

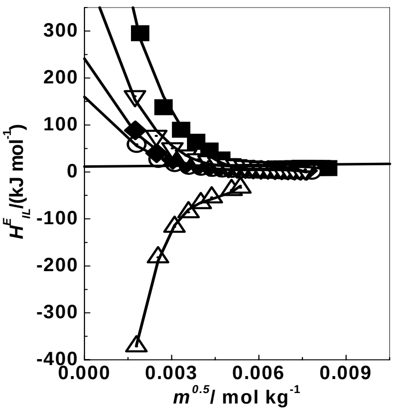


Figure 5.3.2: A comparative plot of the H^E_{IL} values of (■) [MIM][BF$_4$], (▽) [OMIM][BF$_4$], (◆) [HMIM][BF$_4$], (⊙) [BMIM][BF$_4$], (△) NaCl in DMSO

alkyl chain on the imidazolium ring with DMSO are significant. A similar situation exists for these ILs in water, where hydrophobic hydration plays an important role in deciding enthalpic behavior.[52]

The interactions of a PIL *i.e.* [MIM][BF$_4$] with DMSO exhibit the highest H^E_{IL} values. Interestingly, the H^E_{IL} values for the interactions of the APILs with DMSO vary in the order of: [OMIM][BF$_4$] > [HMIM][BF$_4$] > [BMIM][BF$_4$]. This is in contrast to the experimental observations recorded in the case of the APILs in other solvents like water, methanol etc, where one typically notes [BMIM][BF$_4$] > [HMIM][BF$_4$] > [OMIM][BF$_4$].[52] In short, [BMIM][BF$_4$] in water results into high endothermic behavior followed by [HMIM][BF$_4$]. A reversal in the trend, however is observed in the case of [OMIM][BF$_4$], which shows exothermic behavior in the solvents other than DMSO.

The H^{E}_{IL} values for all the ILs in DMSO as shown in Figure 5.3.2 are endothermic with [OMIM][BF_4] exhibiting the strongest endothermic behavior of all. The reason for this anomalous behavior of ILs can be correlated with the specific properties of the solvent, which will be discussed subsequently. Various studies such as cryoscopic and refractive index studies reveal that there exist strong associative forces between DMSO molecules.[53, 54, 55, 56, 57, 58, 59, 60]. IR studies reveal that pure DMSO remains in the form of aggregates.[61, 62.] Thus, the above mentioned behavior of ILs may arise from the associated nature of DMSO.

The above trend can be understood in terms of two issues: (1) why do the PILs show highest H^{E}_{IL} values? and (2) why do APILs show a trend reversal in their enthalpic behavior?

The solution equilibrium properties of ILs in a solvent can be interpreted in terms of cavity formation by an IL in a solvent, dissociation of an IL into ions, and the solvation of ions as a result of interactions between ions and solvent. The cations of PILs are smaller than those of APILs. The smaller cation of a PIL is capable to create a cavity in DMSO at a lesser cost than that of an APIL. This results into strong interactions between PIL and DMSO. In fact, one of the recent reports suggests that the PILs show hyper-polarity closer to that of water. Because of the very high polarity,[47, 63] the PILs should remain in the ionic form in DMSO, giving rise to the enhanced interactions between PIL cation and DMSO molecules as compared to the interactions noted in APILs.

For APILs like [BMIM][BF_4], [HMIM][BF_4] and [OMIM][BF_4], the solvophobic interactions between the alkyl chains present on the imidazolium ring and the $–CH_3$ groups on DMSO molecules, become significant. The polarities of these alkylated ionic liquids are very close to that of DMSO. Thus, DMSO as a solvent will not assist the dissociation of ionic liquids into their ionic counterparts and more number of ionic liquid molecules will exist as ion-pairs. Thus, there would be an increase in a phenomenon more akin to hydrophobic interaction between the alkyl chains of ionic liquid and DMSO. For this reason [OMIM][BF_4] with longest alkyl chain will exhibit the highest enthalpic profile followed by [HMIM][BF_4] and [BMIM][BF_4].

We then thought whether the replacement of anion can bring about any other drastic change in this specific solvation behavior of ILs in DMSO? In place of $[BF_4]^-$ we substituted $[NTf_2]^-$, which is larger in size than $[BF_4]^-$, to check the anion effect (Fig. 5.3.3).

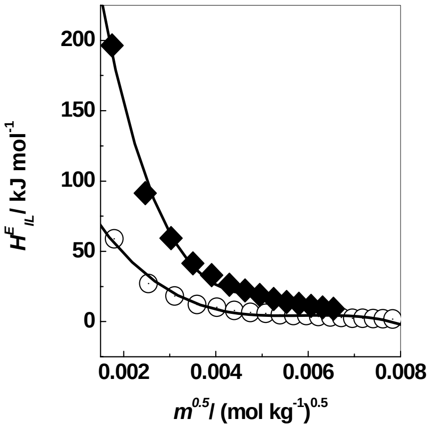


Fig. 5.3.3: A comparison of enthalpic behavior of (◆) [BMIM][NTf_2] and (⊙) [BMIM][BF_4] in DMSO

DMSO is a poor solvator of anion, thus it does not show strong interactions with the anionic species of ILs. This is particularly true if the anions are smaller and with high charge density like $[BF_4]^-$. This effect can be seen in terms of weak interaction enthalpy of the systems.[64] DMSO is considered to be a soft solvent and therefore it can exhibit a mutual polarizability interaction with the large polarizable anions like $[NTf_2]^-$. Also it will be of great interest to examine the interactions between a polarizable solvent and a highly polarizable anion *i.e* $[NTf_2]^-$. The $[NTf_2]^-$ based ionic liquid shows three times more pronounced effects as compared to $[BF_4]$ based ILs. The bulkier $[NTf_2]^-$ species, which is more polarizable anion having more delocalized charge than $[BF_4]^-$ species shows greater affinity towards DMSO.

The experimentally obtained $H^E{}_{IL}$ data were fitted to a polynomial equation to give the limiting excess partial molar enthalpy, $H^{E,\infty}{}_{IL}$. This quantity also indicates the standard molar enthalpy of solution in the present work as the titrations of the diluted solutions of ILs are carried out against DMSO. The equation is of the following form:

$$H^E{}_{IL} = H^{E,\infty}{}_{IL} + a_1\, m^{0.5} + a_2\, m \;....... \qquad (1)$$

where, a_1 and a_2 are the adjustable parameters. The values of $H^{E,\infty}{}_{IL}$, a_1 and a_2 are given in Table 5.3.1.

Table 5.3.1. The limiting excess partial molar enthalpies, $H^{E,\infty}_{IL}$ of the ionic liquids in solvents, including DMSO.

Systems	$H^{E,\infty}_{IL}$/ kJ mol^{-1}	a_1 x 10^5	a_2 x 10^6
[MIM][BF$_4$]- DMSO	796 ± 36	194 ± 1	118 ± 2
[BMIM][BF$_4$- DMSO	60 ± 9	-37 ± 0.5	21 ± 1
[HMIM]BF$_4$- DMSO	241 ± 14	57 ± 1	34 ± 0.5
[OMIM]BF$_4$- DMSO	434 ± 23	-102 ± 1	61 ± 1
[BMIM]NTf$_2$- DMSO*	615 ± 35	-58 ± 0.8	-104 ± 20
NaCl- DMSO!	-1391 ± 74	333 ± 4	-154 ± 11
[BMIM]BF$_4$- Water	90 ± 3	-7.61 ± 0.6	2.3 ± 0.1
[BMIM]BF$_4$- DMF	-529 ± 33	80 ± 1	-30 ± 0.5

The systems with symbol * contains additional terms $q_3 = -333 \times 10^{-8}$; The systems with symbol ! contains $q_3 = -65 \pm 9 \times 10^{-6}$

In order to correlate the thermal data pertaining to the interactions of ILs with DMSO, the H^{E}_{IL} data of these systems were converted to apparent relative molar enthalpies (ϕ_L) by using standard methods.[31] The values of ϕ_L of different ILs in DMSO are shown in Figure 5.3.4.

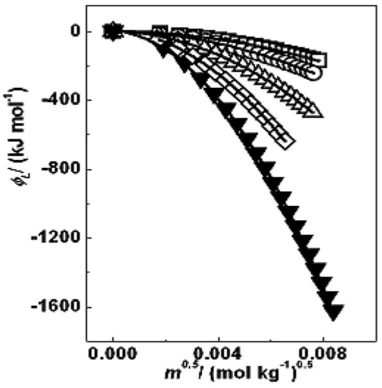


Fig. 5.3.4: A comparative plot of ϕ_L values of (▼) [MIM][BF$_4$], (⊡) [BMIM][BF$_4$], (◈) [BMIM][NTf$_2$], (⊙) [HMIM][BF$_4$], (△) [OMIM][BF$_4$] in DMSO

Further these ϕ_L values were analyzed using Pitzer equations.[31, 32] The Pitzer equations were originally developed for analyzing equilibrium thermodynamic data of aqueous strong electrolyte solutions. These equations account for both long- and short-range interaction forces. The long-range interaction forces are denoted by a modified Debye-Hückel term, whereas the short-range interactions by a set of virial coefficients *i.e.* $\beta^{(0)L}$, $\beta^{(1)L}$ and C^L known as the Pitzer coefficients. The useful form of Pitzer equation for analyzing ϕ_L is given below:

$$\phi_L = (A_L/1.2)\ \ln (1 + 1.2\ m^{0.5}) - 2\ RT^2\ m\ (\beta^{(0)L} - 2\ \beta^{(1)L}\ [1-(1 + 2\ m^{0.5})\ \exp(-2\ m^{0.5})]/(2\ m^{0.5})^2 - C^L\ m) \qquad (2)$$

In eq. (2), A_L denotes the Pitzer-Debye-Hückel limiting slope, the values of which for different solvents are listed in Table 5.3.2. The Pitzer coefficient, $\beta^{(1)L}$ is required to analyze the data in a very dilute concentrations, while C^L in concentrated solutions. Since all the experiments in this study were carried out in the very dilute range the C^L parameter was therefore set to zero during the analysis of data.

Table 5.3.2: The Pitzer-Debye-Hückel limiting slope (A_L) at 298.15 K for solvents used in the present study

Solvent	A_L/ J kg^{-1} mol$^{-3/2}$
DMSO	5418
Water	2879
DMF	4186
Methanol	4717

Table 5.3.3: The Pitzer coefficients for ionic liquids-DMSO systems

Systems	$\beta^{(0)}$/ kg mol^{-1} K^{-1}	$\beta^{(1)}$/kg mol^{-1} K^{-1}
[MIM][BF$_4$]- DMSO	1.95±0.03	2.03±0.04
[BMIM][BF$_4$]- DMSO	0.03±0.01	-0.02±0.01
[HMIM][BF$_4$]- DMSO	0.15±0.01	0.10±0.01
[OMIM][BF$_4$]- DMSO	0.50±0.02	0.47±0.02
[BMIM][NTf$_2$]- DMSO	0.99±0.03	0.99±0.03
NaCl-DMSO	-14.60±0.197	16±0.22
[BMIM][BF$_4$]- Water	0.018±0.003	-0.009±0.004
[BMIM][BF$_4$]- DMF	-0.90±0.01	-1.02±0.01

The values of $\beta^{(0)L}$ and $\beta^{(1)L}$ together with the standard errors in the Pitzer coefficients are reported in Table 5.3.3. The ϕ_L data for all the studied systems in DMSO can be accurately correlated with an average root mean squares deviation of 5% obtained from 125 points. An example of the success of the Pitzer equation in correlating ϕ_L data for [HMIM][BF$_4$]-DMSO system is demonstrated in Figure 5.3.5, in which the experimental

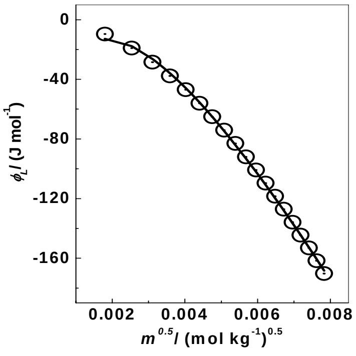


Fig. 5.3.5: The ϕ_L *versus* $m^{0.5}$ for the [BMIM][BF$_4$]-DMSO system, (⊙) Experimental ϕ_L, — Correlated ϕ_L by the Pitzer equation

data (shown in the form symbol) are plotted against $m^{0.5}$ in contrast to the correlated values (shown by a solid line) confirming excellent fit of the ϕ_L data by the use of Pitzer equation.

We have also tried to correlate the virial coefficients obtained from the Pitzer fittings and the number of sites of interactions present on the IL cation. Initially an attempt to correlate the estimated $\beta^{(0)L}$ and $\beta^{(1)L}$ with the number of carbon atom, *nc* in the substituted alkyl group attached to the imidazolium ring of ILs was made. In Fig. 5.3.6 (a) and (b) are shown the dependence of the $\beta^{(0)L}$ and $\beta^{(1)L}$ coefficients on *n*c for different ILs in DMSO. Both these parameters in DMSO show a sharp decrease from PIL to APILs, though this requires confirmation after carrying out the investigation on more systems. We note a significant difference in the plots in DMSO obtained currently and those obtained in our previous study on [BMIM][BF_4] in a series of solvents.[23] Once again, the strong interactions between [MIM][BF_4] in DMSO are reflected in the values of the Pitzer coefficients. Mild variations in the values of these parameters in the case of APILs with higher carbon chain length are due to the solvophobic interactions taking place between alkyl groups and DMSO.

In short, the interactions of ILs with DMSO molecules are different from those noted for other solvents like water, aliphatic alcohols, DMF etc. The behaviour does not follow the order in which the relative permittivity of solvents vary. The weak enthalpic interactions in the IL-DMSO systems indicate weak interactions. The interaction parameters have been deduced from thermal data using Pitzer equation to throw light

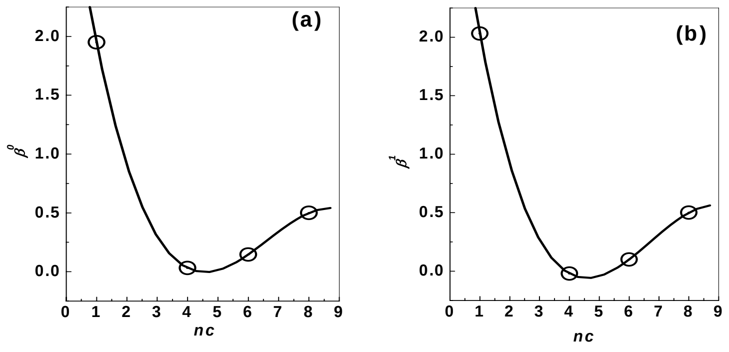


Figure 5.3.6: The $\beta^{(0)L}$ and $\beta^{(1)L}$ variance (a) and (b) with number of carbon atoms n_c in the substituent alkyl chain on the various ILs

on the nature of these interactions. The interactions between ILs and solvent/s can be accurately determined by thermal studies that can prove to be helpful in deciphering the nature of these interactions. In order to achieve this, an availability of enthalpy data on a variety of ILs and solvents in future is desirable.

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CHAPTER 6: IONIC LIQUIDS: KOSMOTROPES OR CHAOTROPES

"The research area of Ionic liquids is nudging from its solvent 'AVATAR' and the researchers are riveting them to more critical fields; according to their fervor the ionic liquids represent a far-fetched academic tool for studying and understanding proteins and enzymatic mechanisms. In future, some of the very specialized ionic liquids can be employed into the whole-cell biotransformations, providing promising and novel approaches. These biological processes in ionic liquids make a complicated system involving ionic liquid, water, protein. Before discussing the ionic liquid-protein interactions, the interactions between each component should be conferred at first. On the basis of these interactions, different ions comprising ionic liquids can be termed as kosmotropes (order-maker) and chaotropes (disorder-maker)."

In the previous chapters we have experimentally established that ionic liquids (ILs) upon dissolving them into a pure solvent system do alter the pre-solvation solvent network. This alteration depends on many factors including the structure of ILs, solvents and the possibility of interactions between the two. The extent to which an IL can disturb the solvent network varies from one IL to other IL. But so far there has not been any model to quantify this tendency of an ionic liquid to modify the solvent structure. As a matter of fact in present scenario there is no clear demarcation between an IL, which can enhance the pre-existing solvent network and an IL which destroys it. In other words, we are still lacking in achieving a heuristic model for these ILs to classify them as kosmotropes and chaotropes.

The terms “Kosmotropes” and “Chaotropes”, which are equivalent terms to the structure maker and structure breaker, were introduced in biophysical context by Collins and Washbough[1]. The appellations “Structure Making” and Structure Breaking”, ascribed to Gurney[2] was based on the effects of ions on the water structure in an electrolytic solution. A general picture of water molecules[3, 4, 5] in a dilute solution of an electrolyte is that the first hydration shell of water molecules exists around most of the ions, including the large univalent ions. A well-defined second hydration shell is common around the highly charged ions. If this arrangement of water molecules in the hydration shell around the ions of an electrolyte increases the extent of hydrogen bonding as compared to that existing in pure water, it suggests that the ion in action is a structure maker and if it decreases the extent of hydrogen bonding the ion is termed as structure breaker. As a rule of thumb, these structure maker and structure breaker ions are arranged in an order on the basis of their ability to denature or stabilize a protein molecule, known as the ‘‘Hofmeister Series’’[6, 7]. Such a generalized series/ notions for ILs are still far from reality.

The present chapter is an effort in the direction of understanding (1) how ILs modify the structure of water and (2) to compare their behavior with the behavior of the common electrolytes in their aqueous solutions. Efforts have been made to discern that how a structure maker would behave in the presence of a structure beaker. The observations made during this study are summarized herein.

6.1 Mixing of strong electrolytes: *Does a competition prevail between the two?*

The structure making and structure breaking notions for the ions of common electrolytes are already established in literature[8, 9, 10], but the drop-wise addition of the aqueous solution of an electrolyte to the pure solvent can serve a more precise and sensitive means to determine the effect of solute on the short range order of the water molecules and to know about the further modification in the water-solute structure caused by the introduction of another electrolyte, which is opposite in nature to the first one added as a solute. Aqueous solutions of different electrolytes, which are varying in nature i.e. the aqueous solutions of Guanidinium chloride (GnCl), NaCl and LiCl were initially titrated against the pure water. These solutions were then titrated against each other to check the behavior of an electrolyte in its aqueous solution in the presence of another electrolyte. The observations made are presented in Fig.6.1.1. From Fig. 6.1.1, the pre-conceptual notions of structure maker and structure breaker for the ions constituting the common electrolytes are reconfirmed.

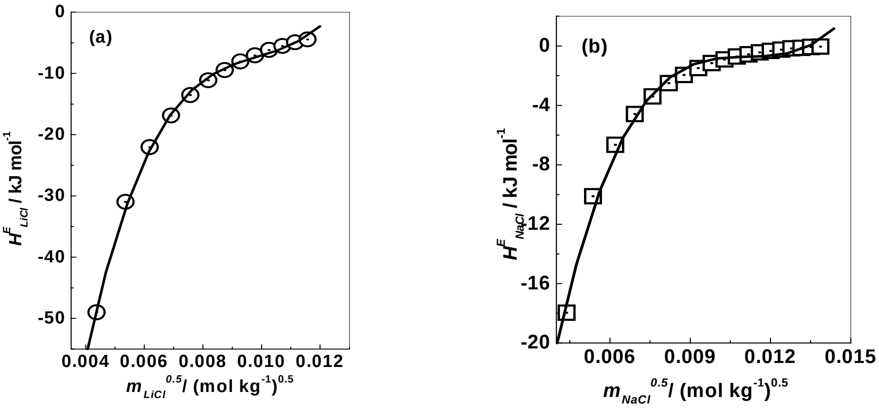

Fig. 6.1.1: molality dependence of $H^E_{LiCl/NaCl}$ for aqueous solution of (a) LiCl, (b) NaCl

It is well known from the literature that the Li^+ and Na^+ ions are the structure makers, whereas Gn^+ as the structure breaker[3] in its aqueous solution. The counter-anion Cl^- in the electrolytic solution is a structure breaker. It is also known that the cations have a pre-dominant role to play in the making or breaking process, though the overall effect is the sum of both the cation and the anion. Another important information is that the Li^+ ion has a stronger structure making ability than the Na^+ ion, due to its smaller size and high charge density[4].

(1) Comparing Fig. 6.1.1 (a) and (b), both LiCl and NaCl show the negetive values of H^E_{salt}. It suggests that the overall process of solvation is exothermic in the case of these two electrolytes. The exothermic behavior arises when the initial process

of dissolution, which requires energy (endothermic) is dominated by the second process, which sees the makeshift of the bonds and thus is a energy releasing process. It indicates the increase in the extent of the bonding, which is a characteristic for the structure maker ions. A closer analysis of the two figures suggests that the H^{E}_{salt} values are less negative for the aqueous solution of NaCl than LiCl, which proves the fact that Na^{+} ion is a weak structure maker as compared to Li^{+} ion.

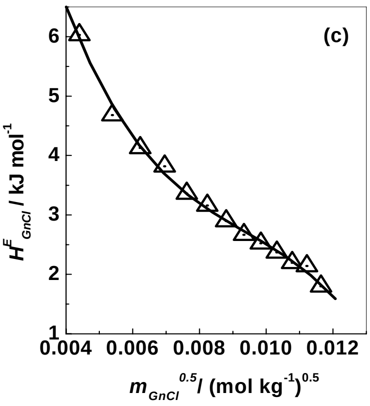

Fig. 6.1.1: Molality dependence of H^{E}_{GnCl} for aqueous solution of GnCl

(2) From Fig. 6.1.1 (c), it shows that the GnCl has an opposite behavior to both LiCl and NaCl solutions. The values of H^{E}_{salt} in the entire range of the composition are positive (endothermic), which suggests that the first step of dissolution of the ion is predominant over the second step which experiences the rearrangement of water molecules and the regain of the broken bonds. Because the extent of

bonding is reduced during the overall salvation process of GnCl, which is implied by the positive H^E_{salt} values, it concludes that Gn^+ is a structure breaker ion. In fact the H^E_{salt} values are milder for aqueous GnCl solution as compared to those produced by aqueous LiCl or NaCl solutions.

With this information, it was thought of setting up the experiments to check for the mixing of the isomolar solutions of these electrolytes. These experiments were grouped into (a) the mixing of electrolytes having same nature (mixing of two structure making electrolytes) and (b) those with different nature (mixing of one structure maker with structure breaker). These experiments were planned to check that if the two electrolytes are mixed together, do they retain their original behavior or their behavior shifts to a modified one in the mixture. The results obtained are presented in Fig. 6.1.2 and are subsequently analyzed with appropriate explanation.

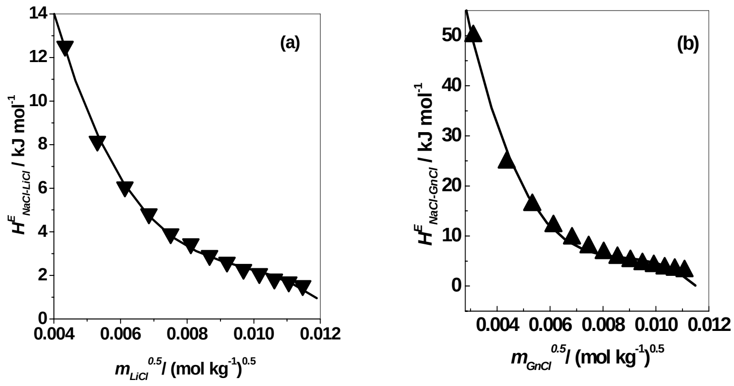

Fig. 6.1.2: The H^E_{salt} versus molality for the mixtures of (a) NaCl-LiCl, (b) NaCl-GnCl

It is already noted that the aqueous solution of LiCl shows the strong exothermic behavior which is followed by the NaCl solution (Fig. 6.1.1 a, b) and the aqueous solution of GnCl shows the endothermic behavior (Fig. 6.1.1 c). When the aqueous solution of LiCl is added to the equimolar aqueous solution of NaCl, the interactions get so modified that the overall solvation process in the case of mixture becomes endothermic in nature. Similarly when the aqueous solutions of two electrolytes of different nature i.e. NaCl and GnCl are mixed together, the overall solvation process again turns out to be endothermic in nature. The mixture of aqueous solutions of LiCl and NaCl (both structure making salts) show feeble endothermic behavior whereas the mixing up of two electrolytes, one with the structure making ability (NaCl) and the other one with structure breaking ability (GnCl), results into a highly endothermic behavior. It suggests that the mixing up of the two electrolytes does not recognize the structure making/breaking ability of the salts. The mixing of the two electrolytes always destabilize the system and the interactions taking place in between different components of the solution are unfavorable which doesn’t allow the makeshift process of the water molecule to take control in order to compensate for the increase in the energy of the system during the dissolution step. In other words, the process of cavity formation for the second solute becomes extremely expensive because of the presence of the first solute particles and that cannot be compensated by the bonding between the ions of different electrolytes and the solvent molecules.

The H^{E}_{salt} data for various salt-solvent systems were fitted to obtain the limiting excess partial molar enthalpy ($H^{E,\infty}_{salt}$) using the following equation:

$$H^{E}_{salt} = H^{E,\infty}_{salt} + \mathrm{h}_0\, m_{salt}^{0.5} + \mathrm{h}_1\, m_{salt} + \mathrm{h}_2\, m_{salt}^{1.5} \qquad (1)$$

These $H^{E,\infty}_{salt}$ values thus obtained from the above fitting are reported in Table 6.1.1.

Table 6.1.1: The limiting excess partial molar excess enthalpies, $H^{E,\infty}_{salt}$ / J mol^{-1} of aqueous solutions of different salts in their mixtures

Salt system/ mixtures	$H^{E,\infty}_{salt}$ / J mol^{-1}
LiCl-H_2O	-214248 ± 9390
NaCl-H_2O	-73748 ± 3782
GnCl-H_2O	16561 ± 1330
LiCl in NaCl-LiCl	51951 ± 2445
GnCl in NaCl-GnCl	157184 ± 7752

This preliminary information fascinated us to look into the probable interactions operating between the different components of the solution. For this information we calculated the relative apparent molar enthalpy (ϕ_L) from the H^{E}_{salt} values following the reported procedures discussed in earlier chapters.

Fig. 6.1.3 represents a comparison of ϕ_L values for the mixtures of electrolytes and that of aqueous solution of electrolytes. The comparison suggests that there is a destabilization of the system for both the mixtures i.e. NaCl + LiCl and NaCl + GnCl in terms of their endothermic behavior. Both the mixtures show the maximum endothermic values (maximum negative values of ϕ_L). The destabilization is more when GnCl is

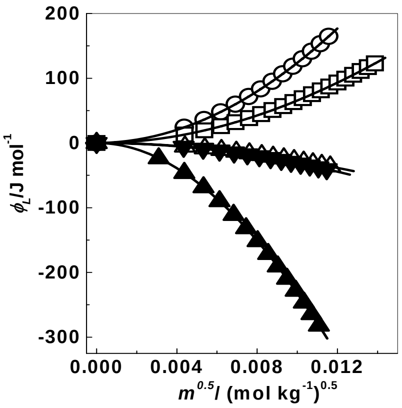

Fig. 6.1.3: A comparative plot of ϕ_L versus molality for (⊙) LiCl-H_2O, (⊡) NaCl-H_2O, (△) GnCl-H_2O, (▼) NaCl-LiCl, (▲) NaCl-GnCl

added to the aqueous NaCl solution than when LiCl is added to it. It implies that if a solute bigger in size and with smaller charge density is added to an aqueous salt solution, it slows down the reorientation of disturbed water molecules and decreases the extent of bonding as compared to the aqueous solutions of the same components (NaCl and GnCl). Hence, it shows the highest endothermic values as compared to the other mixture NaCl + GnCl and the salt solutions of the single components.

6.2 Mixing of two ionic liquids: *Do they mimic the common electrolytes behavior?*

ILs are the structural analogues of molten salts i.e NaCl. Both of them are composed entirely of oppositely charged ions and when dissolved in a solvent like water these ions get dissociated. For common electrolytes like NaCl and LiCl this dissociation is 100%

but for ILs it is still controversial. Some reports from the literature suggest that a part of ILs always remain intact as ion-pairs[11] even in their dilute aqueous solutions. Not to emphasize the presence of ion-pairs, we would concentrate on the free ions of ILs in their aqueous solutions. If it is assumed that when an IL is dissolved in pure solvent it gets dissociated into its counter ions, these counter ions alter the structure of solvent which we can study in terms of their $H^{E}_{BMIMBF4/BMIMNTf2}$ values. If this contemplation is relevant, is it possible to identify the existing ILs as structure maker or structure breaker, the same way we classify the common electrolytes discussed in the previous section (6.1). We titrated two ionic liquids of different nature against water as a solvent. The first IL chosen was [BMIM][BF_4], which is considered to be hydrophilic in nature and

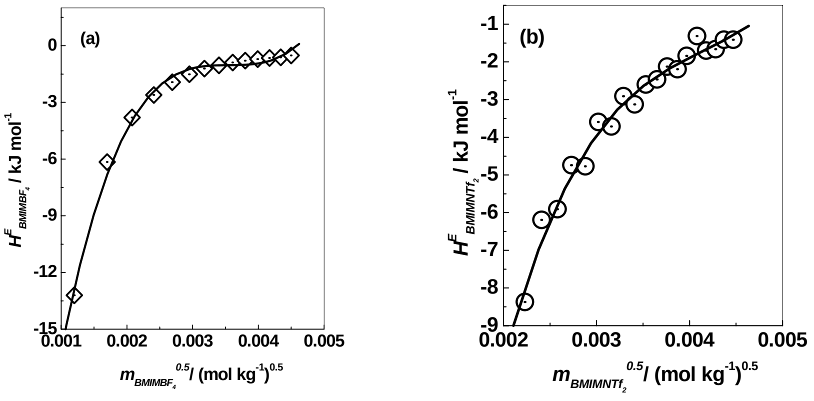

Fig. 6.2.1: The concentration dependent plot of $H^{E}_{BMIMBF4/BMIMNTf2}$ for (a) [BMIM][BF_4], (b) [BMIM][NTf_2]

another IL was the hydrophobic one, [BMIM][NTf$_2$].the results obtained are presented in Fig. 6.2.1. From Fig. 6.2.1 demonstrates that the aqueous solutions of both [BMIM][BF$_4$] and [BMIM][NTf$_2$] when titrated against pure water, show exothermic behavior. In this case, both the ILs irrespective of their hydrophilic or hydrophobic nature stabilize the solvent network in their solutions. It also implies that the extent of bonding in the aqueous IL solution is greater than in the pure water system, which may also be a result of the hydrophobic hydration prevailing in the aqueous IL solutions. Thus in water both the [BMIM][BF$_4$] and [BMIM][NTf$_2$] ILs act as structure makers, though the structure making tendency is more in the case of [BMIM][BF$_4$] solution indicated by the higher negative values of $H^E_{BMIMBF4}$ values. When these two aqueous solutions of ILs are mixed together does this structure making ability of both these ILs

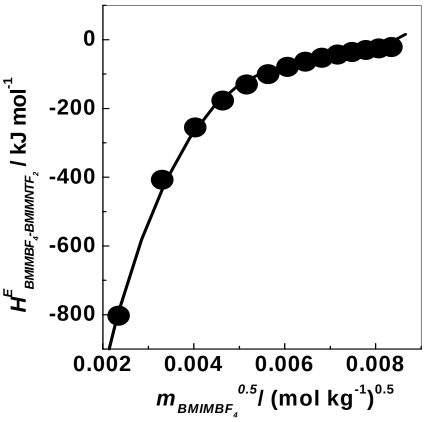

Fig. 6.2.2: The $H^E_{BMIMBF4\text{-}BMIMNTf2}$ versus $m_{BMIMBF4}^{0.5}$ plot for the aq. [BMIM][BF$_4$]-[BMIM][NTf$_2$] mixture

get altered in their mixture? To look into the above matter, we titrated the aqueous solution of [BMIM][BF_4] into the isomolar aqueous solution of [BMIM[NTf_2] and the resultant H^E_{IL} values are shown in Fig. 6.2.2. This drawing suggests that when the two ILs of different nature are mixed together, the resultant mixture is more stabilized system as compared to their aqueous ionic solutions. This enhancement in the stabilization of the mixture indicates the cumulative effect of the stabilization caused by the cations and the anions furnished by the ILs. This is quite an interesting observation regarding ILs.

Now, the next step was to compare these results with those obtained by titrating a pure IL against another pure IL. In this case, [BMIM][NTf_2] was titrated against the pure [BMIM][BF_4]. The results obtained are shown in Fig. 6.2.3. It suggests a complete

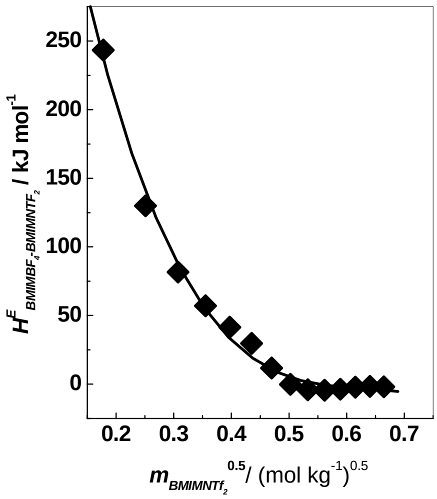

Fig. 6.2.3: A concentration dependent plot of $H^E_{BMIMBF4\text{-}BMIMNTf2}$ for the mixture of pure [BMIM][BF_4] and [BMIM][NTf_2]

opposite behavior of these ILs shown upon mixing in their pure forms than when their aqueous solutions are mixed up. An IL when added as a solute to another IL, which acts as a solvent in the solution, it causes the destabilization of the pre-solvation network of the IL acting as the solvent, which results into the endothermic H^{E}_{IL} values. It also suggests that the extent of bonding is lesser as compared to that of existing in the pure state. The reason can be the comparable polarities of the two ILs, because of which the IL acting as the solvent is not able to dissociate another IL into the counter-ions. Thus, there is a very less possibility of interaction between the ion and the solvent and which reflects from the very high endothermic values of the system. The H^{E}_{IL} data for various IL systems were fitted to obtain the limiting excess partial molar enthalpy ($H^{E,\infty}_{IL}$) using the equation (1). Due to the extreme dilute conditions it was needed to assign sufficient weights for the fitting of the data. These $H^{E,\infty}_{IL}$ values thus obtained from the above fitting are reported in Table 6.2.1.

Table 6.2.1: The limiting excess partial molar excess enthalpies, $H^{E,\infty}_{IL}$ / J mol^{-1} of different IL systems in their mixtures

IL systems/ mixtures	$H^{E,\infty}_{IL}$/ J mol^{-1}
[BMIM][BF_4]-H_2O	-41683 ± 2060
[BMIM][NTf_2]-H_2O	-47125 ± 9882
[BMIM][BF_4] in [BMIM][BF_4]-[BMIM][NTf_2]	-2517840 ± 94902
[BMIM][NTf_2] in [BMIM][BF_4]-[BMIM][NTf_2]	636 ± 42

Further, as a similar treatment that was given to the electrolytes, we calculated the ϕ_L values for these IL systems. The ϕ_L values thus obtained for the IL systems are presented in Fig. 6.2.4.

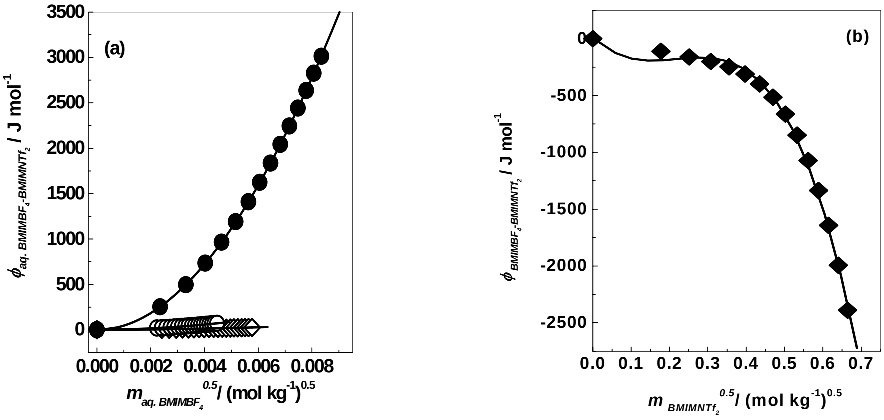

Fig. 6.2.4: A comparative plot of ϕ_L versus molality for (a) aq. [BMIM][BF$_4$]-[BMIM][NTf$_2$] mixture (●), aq. [BMIM][BF$_4$] (◇), aq. [BMIM][NTf$_2$] (⊙) and (b) binary mixture of pure [BMIM][BF$_4$]-[BMIM][NTf$_2$] mixture

Fig. 6.2.4 also comprehends the same information that we noticed by comparing the H^E trends, that the behavior of aqueous solution of ILs and their mixture behave similarly, but the mixture of the same pure ILs behave in a different manner from the above mentioned systems.

From the above, it can be seen that the interactions are weaker for the mixture of pure ILs as compared to the other systems which are water mediated. It suggests that in the absence of a solvent which is more polar in this case than ILs, the ILs do not interact with each other very strongly though they solubilize in each other to give a clear solution. The reason may be that when an IL is added as a solute into another IL which is acting as solvent, for the dissolution the IL has to make a cavity for itself. Due to the high viscosity and comparable polarity of the solvent which is another solvent, the process of dissolution becomes very expensive and it increases the energy of the system after the solute gets dissolved because of the bigger size of the cations and the anions, the ion-solvent and ion-ion interactions become difficult and thus the increased energy of the system does not get stabilized and hence it shows maximum endothermic pattern.

In the present chapter we have tried to establish a generalized notion for ILs, which can be similar to the already established structure maker/ breaker concept or even different from it, specifically for ILs. The preliminary results obtained from the present study show that ILs behave differently from the common electrolytes, though they are their structural analogues. The reason behind their distinct behavior may be a characteristic to their complex structural nature. The ILs though are composed of ions but their structural composition is not similar throughout and there is heterogeneity within the system. This heterogeneity at the molecular level may cause the inconsistency in their solvating patterns. But there are some very interesting observations obtained from this study that can be pursued further to get a generalized picture about the solvation pattern of this neoteric class of compounds.

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CHAPTER 7: THE IONIC LIQUID INTERACTION PARAMETERS

"Mixtures of ionic liquids and molecular solvents may find very wide applications in the industry. It is therefore mandatory to collect thermodynamic data for ionic liquid solutions. In the present chapter a differential approach is followed to quantify the effect of ionic liquid counter-ions on the structure of different solvents. Here, the consequences of the presence of ionic liquids on the pre-solvation structure of molecular solvents are discussed in terms of the an interaction parameter & further how these interactions get modified from solvent to solvent and from ionic liquid to ionic liquid."

Ionic liquids can be used as solvent media or the rate-promoters either in pure form or its solution with other solvent. It has been seen in past that viscosities of common ionic liquids are quite high and therefore several processes may face hindrance during their operational procedures. The pure form of an ionic liquid solely consists of only charged species. These charged species are bound together with the help of van der Waals forces. The individual entity bound in this manner is often called as clathrate and is the result of combining many species in order to maintain electrical neutratility. The charged clathrates in ionic liquids or any ionic systems is a possibility as in aqueous electrolytes and well largely depend upon the definition or redefinition of clathrates or highly accurate experimentations in days to come.

However, on the other hand, if a solvent with moderate relative permittivity is added in small quantities in the solute, these clathrates will begin to separate giving rise to dissociable ionic species in the system. The full dissociation of an ionic liquid into its ions may not be possible, however. It is also possible that some negative ions may get sufficiently close to the central positive ion in the course of quasi-random solution so that their thermal energy would not be sufficient for them to continue with their independent movements in the solution.[1] According to Bjerrum, a pair of oppositely charged ions may get trapped in each other’s Coulombic field leading to the formation of an ion-pair in an ionic solution.[2] The same logic is applicable to ionic liquids as well. The size, symmetry and charge of cation and anion will be decisive factors in the ion-pair formation. The solvent property, *i.e.* relative permittivity will be the governing factor in the dissociation of cation and anion of an ionic liquid. Further, if a solvent possessing low relative permittivity is used, this will enhance the Coulombic interaction forces leading to poor dissociation of the involved ionic species. Thermal energy of the system plays important role in this connection. This may happen that the ion-pair "dipoles" may attract ions to form triplets. In another situation, an ionic liquid may be present in large quantity of a solvent like water. This situation will result into full dissociation with some fraction of the ions still attached or loosely bound with each other.

Since $H^{\mathrm{E}}{}_{\mathrm{IL}}$ values in extremely dilute solutions are very sensitive to the concentrations, these values can be employed as markers for recognizing the concentrations at which clathrates of ionic liquids begin to form. Normally, experimental quantification of such concentrations is a very cumbersome task and often requires the modeling of the system. The use of semi-empirical equations to compute these concentrations will largely depend upon the evaluated adjustable parameters, the physical significance of which remains a question. In view of extremely dilute solutions, the possibly large errors in the adjustable parameters may skew the relevant concentrations. Below, a methodology is described to identify such concentrations and their corresponding enthalpy values. A reference in this connection should be made to the significant contribution made by Prof. Y. Koga of Canada, whose papers will be discussed at appropriate places as and when required.[3,4,5]

Enthalpy of a system is given by:

$$\mathrm{H} = \mathrm{G} - \mathrm{T}\ (\partial \mathrm{G} / \partial \mathrm{T}) \tag{1}$$

and also

$$H^{\mathrm{E}} = G^{\mathrm{E}} - \mathrm{T}(\partial G^{\mathrm{E}} / \partial \mathrm{T}) \tag{2}$$

However, one can obtain deeper information by the following quantities:

$$H_{\mathrm{i}} = (\partial \mathrm{H} / \partial \mathrm{n}_{\mathrm{i}}) \tag{3}$$

and

$$H_{\mathrm{i}}^{\mathrm{E}} = (\partial H^{\mathrm{E}} / \partial \mathrm{n}_{\mathrm{i}}) \tag{4}$$

The $H_{\mathrm{i}}^{\mathrm{E}}$ as discussed in earlier chapter is the excess partial molar enthalpy of solute i in its solution and is a powerful quantity to indicate the enthalpic interactions in a system. Besides this, the quantity shows the contribution of the solute towards the total enthalpy of the system under investigation.

The ITC experiments as mentioned in the previous chapters pertain to the addition of very small amounts of the solute into a solvent. These additions are incremental to allow users to employ graphical methods to evaluate a parameter that can serve key marker to the ion-solvent and ion-ion interactions in an ionic liquid solution. This parameter, in the present case, indicated by $H^{\mathrm{E}}_{\mathrm{IL\text{-}IL}}$ is called as enthalpic interaction parameters. This is given by:

$$H^{\mathrm{E}}_{\mathrm{IL\text{-}IL}} = \mathrm{N}\ (\partial H^{\mathrm{E}}_{\mathrm{IL}} / \partial n_{\mathrm{IL}})$$

$$= (1 - x_{IL})\ (\partial H^E_{IL} / \partial x_{IL}) \qquad (5)$$

The $H^E_{IL\text{-}IL}$ is a third derivative of G, as discussed elsewhere. It should be noted that since the x_{IL} values are very small in magnitude, the $(\partial H^E_{IL} / \partial x_{IL})$ term is likely be associated with errors.

It has been proposed that the values of $H^E_{IL\text{-}IL}$ can be obtained using a graphical method or any fitting program.[6]

In the following, the application of the above methodology is shown for understanding the ion-ion and ion-solvent interactions in the ionic liquid solutions. For the purpose of illustration, a commonly used ionic liquid [BMIM][BF$_4$]-H$_2$O system was undertaken. The necessary conditions required for an accurate determination of the $H^E_{IL\text{-}IL}$ values of the system were followed as recommended. The dilution ratios are

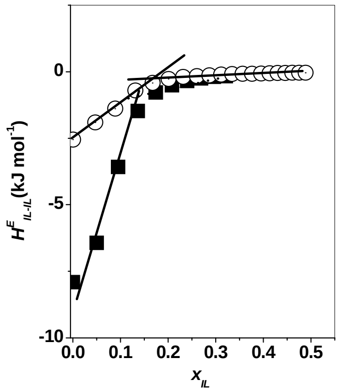

Fig. 7.1: The $H^E_{IL\text{-}IL}$ parameters versus x_{IL} plots for the aqueous (■) [EMIM][BF$_4$] and (⊙)[BMIM][BF$_4$] systems

important to validate the proposed methodology. The $H^{E}_{IL\text{-}IL}$ parameters were obtained from the reported procedure elsewhere.[7] Fig 7.1 shows a plot of $H^{E}_{IL\text{-}IL}$ as a x_{IL}. According to the procedure of Koga, two distinct lines can be drawn giving rise to a clear and sharp intersection between two groups of the data points. First group belongs to the rise and second to the decline of $H^{E}_{IL\text{-}IL}$ parameters. An examination of the plot shows a sharp increase in the $H^{E}_{IL\text{-}IL}$ values in the dilute concentrations of the ionic liquids. In the water-rich zone ions are dissociated, though not completely. The interactions between the cation and anion of an ionic liquid are of long-range and hence can be analyzed in terms of Debye-Hűckel theory. One notes that ions of ionic liquid are unsymmetric in shape and therefore can undergo an entirely different process of hydration as discussed in earlier chapters. The interactions between like charged ions of ionic liquid-solvent system are nearly absent in the water-rich region. The second group is different from the trend noted for first group. The sharp change in the $H^{E}_{IL\text{-}IL}$ data in Fig. 7.1 slowly begins to taper. The $H^{E}_{IL\text{-}IL}$ values in the second zone do not vary sharply. On the other hand, in the case of current ionic liquid, the values decrease very little or are invariant with composition. In this zone, the onset of clathrates begins. This means that the like charged ions like cation-cation or $[BMIM]^{+}$-$[BMIM]^{+}$ interactions gain significance. The interactions between these two cations are weak in nature and are generally of van der Waals type. The intersection point between two zones indicates the concentration at which one can envisage a transition from dissociated species to clathrates. In the case of [BMIM][BF$_4$]-H$_2$O system, the intersection point is observed at x_{IL} = 0.16 with the enthalpy interaction parameter equal to -0.34 kJmol^{-1}.

Having described a case of [BMIM][BF$_4$], a comparison between other imidazolium ionic liquids with regard to the H^E_{IL-IL} parameter should be in order. In Fig. 7.1 is also given the H^E_{IL-IL}-x_{IL} plot for [EMIM][BF$_4$]-water system. In this case, the onset of clathrate formation takes place at higher x_{IL} =0.18 with H^E_{IL-IL} as -0.15 kJ mol^{-1}. It appears that the alkyl chain length attached to the imidazolium ring is responsible for a decrease in the H^E_{IL-IL} parameter. In the present case, the substitution of ethyl by butyl group changes the value of the H^E_{IL-IL} parameters by about 2-times.

In previous chapters it was shown that [EMIM][BF$_4$] and [BMIM][BF$_4$] displayed endothermic behaviors while [HMIM][BF$_4$] and [OMIM][BF$_4$] exothermic. The values and magnitude of the H^E_{IL-IL} will also change with the alkyl chain attached to the parent ring of the cation and so the importance of these interactions (Fig. 7.2).

From Figs. 7.1 and 7.2, it seems that the cation-cation interactions are not very prominent and largely the result of Coulombic interactions, but the onset of clathrate formation starts much early in [BMIM][BF$_4$] whereas in [EMIM][BF$_4$] it required higher concentration of cations to start forming clathrates. Similarly Fig 7.2 compares the interactions between the cations of higher alkyl chain length. The onset of cation interaction starts much early in the case of [OMIM][BF$_4$] as compared to [HMIM][BF$_4$]. Also the interactions are stronger in case of higher alkyl chain carrying cation as suggested by the enthalpic interaction parameter ($H^{E}_{IL\text{-}IL}$). Keeping that understanding in mind, the results given in Table 7.1 can be interpreted. These results for aprotic imidazolium-based ionic liquids are also tabulated for a variety of solvents.

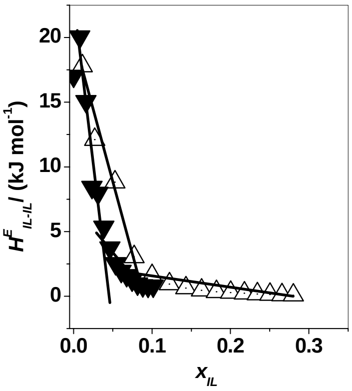

Fig. 7.2: The $H^{E}_{IL\text{-}IL}$ parameters versus x_{IL} plots for the aqueous (Δ) [HMIM][BF$_4$] and (▼) [OMIM][BF$_4$] systems

It is reported in the literature that the values of x_{IL} at which these transitions take place are higher than those reported for aqueous [BMIM][BF$_4$] and [BMIM]I.[4] As mentioned earlier, the reported data were obtained using a pure ionic liquid as compared to the current work, in which the diluted ionic liquid solution was employed in order to handle the viscosity problem. In pure state, it is easier for ionic species to approach each other, which can be seen in terms of cluster formation. In the case of dilute solution of an ionic liquid, it is difficult for the ions to approach each other to form clusters. Thus, the onset of cluster formation in our case is at higher x_{IL} values than those reported.

Table 7.1: The values of intersections for the $H^E_{IL\text{-}IL}$ interaction parameters and the corresponding mole fraction, x_{IL} for the imidazolium-based ionic liquids with BF_4^- in different solvents[1]

ILs	[EMIM][BF$_4$]		[BMIM][BF$_4$]		[HMIM][BF$_4$]		[OMIM][BF$_4$]	
Solvent	x_{IL}	$H^E_{IL\text{-}IL}$ / kJ mol^{-1}	x_{IL}	$H^E_{IL\text{-}IL}$ / kJ mol^{-1}	x_{IL}	$H^E_{IL\text{-}IL}$ / kJ mol^{-1}	x_{IL}	$H^E_{IL\text{-}IL}$ / kJ mol^{-1}
Water	0.16	-0.34	0.18	-0.15	0.11	0.32	0.04	2.1
MeOH	0.20	-0.66	0.26	-0.26	0.15	-0.30	0.05	3.0
EtOH	-	-	0.35	-0.39	0.28	-0.20	0.07	1.0
1-propanol	-	-	0.34	-0.79	0.24	0.55	0.08	4.0
Ethylene glycol	0.03	-4.0	0.40	-0.40	0.49	-41	0.11	0.19
Formamide	0.30	-0.57	0.28	-0.49	0.26	-0.39	0.09	-0.29
DMF	0.33	0.14	0.33	0.78	0.31	0.15	0.12	-0.85
$CHCl_3$	-	-	0.85	-1.1	0.014	-12	0.26	-28
D_2O	-	-	0.34	-0.09	-	-	-	-

[1] The errors associated with the determination of the $H^E_{IL\text{-}IL}$ interaction parameters in some cases may be large depending upon the variations of the $H^E_{IL\text{-}IL}$ values with x_{IL}

The $H^E_{IL\text{-}IL}$ interaction parameters have also been estimated and discussed for different ionic liquids in many solvents. First, in Table 7.2 are listed the values of intersections for the $H^E_{IL\text{-}IL}$ interaction parameters for the imidazolium-based ionic liquids with NTf_2^-.

Table 7.2: The values of intersections for the $H^{E}_{IL\text{-}IL}$ interaction parameters and the corresponding mole fraction, x_{IL} for the imidazolium-based ionic liquids with NTf_2^-

ILs	[EMIM][NTf$_2$]		[BMIM][NTf$_2$]		[HMIM][NTf$_2$]		[OMIM][NTf$_2$]	
Solvent	x_{IL}	$H^{E}_{IL\text{-}IL}$ / 10^{-3} kJ mol^{-1}	x_{IL}	$H^{E}_{IL\text{-}IL}$ / 10^{-3} kJ mol^{-1}	x_{IL}	$H^{E}_{IL\text{-}IL}$ / 10^{-3} kJ mol^{-1}	x_{IL}	$H^{E}_{IL\text{-}IL}$ / 10^{-3} kJ mol^{-1}
MeOH	0.0081	-2.0	0.0084	-4.0	0.0063	-9.0	0.0061	-23.0
EtOH	-	-	0.0057	-6.0	0.0064	-0.5	0.0063	-25.0
1-propanol	0.0092	-5.9	0.0065	-16.0	-	-	0.0065	-22.0
Ethylene glycol	0.0073	-7.5	0.0056	-7.0	-	-	0.0052	-7.5
Formamide	0.0087	-4.5	0.0055	-10.0	0.0055	-14.0	0.0165	-4.0
DMF	0.0083	-20.0	0.0064	7.0	-	-	0.0058	6.2
$CHCl_3$	0.0211	-15.0	0.0048	-0.2	0.0047	-37.5	0.0056	-25.0

A cursory examination of the results reproduced in Table 7.2 indicates that the NTf_2^- possessing imidazolium-based ionic liquids tend to form clathrates early as compared to their counterpart with BF_4^- species. Further, the $H^{E}_{IL\text{-}IL}$ parameters are noted to be quite strong in terms of their negative values suggesting that strong ion-solvent interactions are favored with early clathrate formation. The magnitude of $H^{E}_{IL\text{-}IL}$ is dependent upon whether the system displays endo-or exothermic thermal behavior. However, no definite trend appears between the types of ionic liquids as seen above.

The $H^{E}_{IL\text{-}IL}$ - x_{IL} plot for [BMIM][NTf$_2$] in DMF is shown in Fig. 7.3. It seems that this plot exhibits a contrast with the plot shown in Fig. 7.1, in which a plot is shown for

[BMIM][BF$_4$]-water system. Both the solvents are highly polar in nature and since the anion is uncommon in both the ionic liquids, it is expected that this effect stems out of anion and its interactions with solvent. Note that [BMIM][NTf$_2$] is insoluble in water

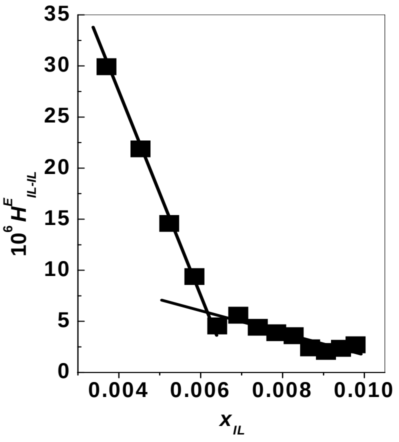

Fig. 7.3: The H^E_{IL-IL} parameters versus x_{IL} plots for the aqueous (Δ) [BMIM][NTf$_2$] in DMF

enforcing one to use DMF in place of water. The interaction of the cation with two different anions may be, for the first approximation, considered nearly equal, though it is not correct to assume. The positive values of the H^E_{IL-IL} values decrease sharply with x_{IL} in the case of [BMIM][NTf$_2$] and proceed toward zero. On the contrary, the negative H^E_{IL-IL} values for [BMIM][BF$_4$] increase and proceed toward zero. The effect of anions in very dilute range can be explained on the basis of Debye-Hückel theory. An opposite case of 1-propanol with [BMIM][NTf$_2$] is shown in Fig. 7.4.

In Table 7.3 are listed the values of intersections for the $H^E_{IL\text{-}IL}$ parameters and the corresponding mole fractions, x_{IL} for the pyridinium and pyrrolidinium-based ionic liquids with BF_4^- species.

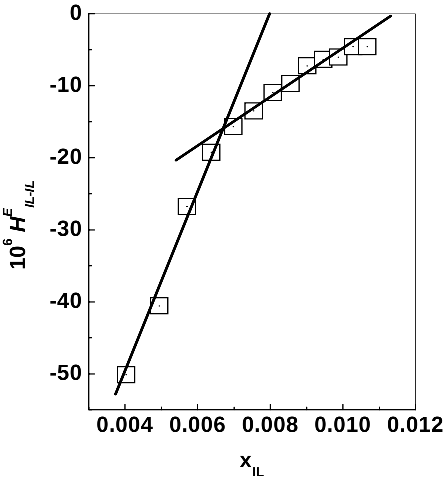

Fig. 7.4: The $H^E_{IL\text{-}IL}$ parameters versus x_{IL} plots for 1-propanol with [BMIM][NTf$_2$]

PILs are known to strongly interact with solvents due to special characteristics of their structures. The measurements reported in the present thesis do indicate toward this statement. The $H^E_{IL\text{-}IL}$ parameters for methanolic solution of [BMPY][BF$_4$] suggest strong interactions between the said PIL with methanol.

Table 7.3: The $H^{E}_{IL\text{-}IL}$ interaction parameters at intersection with the corresponding x_{IL} for the protic pyridinium and pyrrolidinium ionic liquids with BF_4^- species.

ILs	[BMPY][BF_4]		[BMPYRR][BF_4]	
Solvent	x_{IL}	$H^{E}_{IL\text{-}IL}$ / 10^{-6} kJ mol^{-1}	x_{IL}	$H^{E}_{IL\text{-}IL}$ / 10^{-6} kJ mol^{-1}
MeOH	0.0025	-0.22	0.0058	0.12
EtOH	0.0056	-0.32	0.0063	1.3
1-propanol	0.0057	-0.44	0.0053	-1.9
Ethylene glycol	0.0042	0.25	0.0044	-0.14
Formamide	0.0041	-0.27	0.004	-0.75
DMF	0.0049	0.25	0.0043	-0.25
$CHCl_3$	0.0043	-1.0	0.0046	2.0

However, the onset of clathrates can be seen at $x_{IL} = 0.025$. But since the values of the $H^{E}_{IL\text{-}IL}$ parameters increase with an increase in the concentration of the ionic liquid, it may not be very clear marker of the ions coming together.

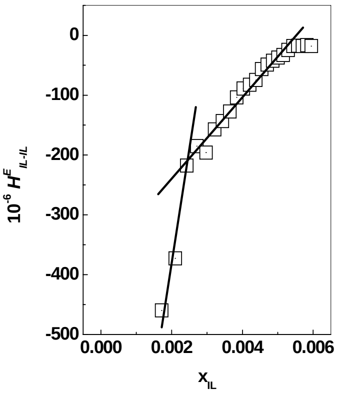

Fig. 7.5: The H^{E}_{IL-IL} parameters versus x_{IL} plots for methanol with [BMPY][BF_4]

As reported in Chapter 5, DMSO manifests exclusive enthalpic behavior in a variety of ionic liquids. Such experimental observations and the reasons thereof have been described previously. It was therefore thought worthwhile to examine the H^{E}_{IL-IL} interaction parameters for different ILs in DMSO with respect to exclusive trend of the enthalpies. For the sake of illustration, in Figure 7.6 are shown the H^{E}_{IL-IL} *versus* $m^{0.5}$ for

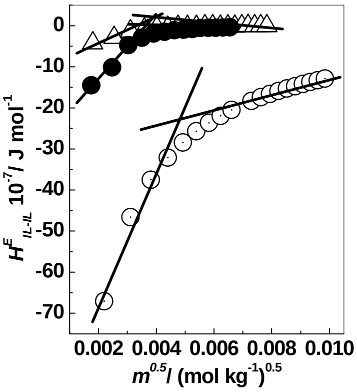

Fig. 7.6: A comparative plot of Koga's interaction parameter H^{E}_{IL-IL} as a function of $m^{0.5}$ for (●) [BMIM][BF_4], (△) [BMIM][NTf_2] and (O) [OMIM][BF_4] in DMSO

[BMIM][BF$_4$], [BMIM][NTf$_2$] and [OMIM][BF$_4$] in DMSO are 10,000, -9850 and -23,000 kJ mol^{-1}, respectively. DMSO induces clathrate formation at an early concentration of IL, as it does not allow a complete dissociation of an IL into its ions. This is in contrast to situation noted in the IL-water system,[23] in which the clathrate formation begins at higher concentrations of IL. In very dilute aqueous IL solution, it is difficult for the ions to approach each other to form clathrates. In pure IL state, it is easier for ionic species to approach each other resulting into the cluster formation. A very sharp transition in the values of the $H^E_{IL\text{-}IL}$ parameters with respect to $m^{0.5}$ in the case of [OMIM][BF$_4$] confirms strong interactions between the alkyl chain attached to the imidazolium ring and DMSO. Relatively weaker interactions are seen for the [BMIM][BF$_4$] system.

In nutshell, a methodology originally developed by Koga has further been explored herein in order to understand the clathrate formation in these systems. This methodology, in fact, is good to examine the solvent reorganization around solute molecule or ion. The present work has revealed that the methodology is not sufficiently accurate to provide interpretation of the data. The reason lies in the fact that the quantity is differentiated leading to errors. Further, since very dilute solutions of ionic liquids are used in the experimental set up, the presence of the small concentration term enhances the error in the determination of the $H^E_{IL\text{-}IL}$ parameters. A more accurate technique in this connection is required for calculating the interaction parameters. Nevertheless, till then, this technique offers good approximation of the ion interactions prevailing in the systems.

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CHAPTER 8: CONCLUSIONS

"The present chapter summarizes the important observations and conclusions drawn out of this study. The present work is a positive contribution towards understanding the environment-benign solvents, ionic liquids. The experiments jointly with the theoretical perspective indicate towards the strong interactions prevailing between the ionic liquids and the solvents. Also the requisite of a more elaborate study to discern the solvent structure altering capabilities of ionic liquids is briefed.

The isothermal titration calorimeter (ITC), thus proves to be a very useful method for probing the nature and strength of the interactions between different ionic species and the solvent component comprised by a binary solution, though biologists have already been using it for the accurate detection of macromolecules-ligand binding for a long time."

The current investigation was undertaken to delineate the ionic interactions in the ionic liquid solutions with the help of excess partial molar enthalpies, H^{E}_{IL} measured by Isothermal Titration Calorimetry (ITC) and other thermal properties calculated therefrom. The necessity of examining ionic liquid systems has arisen out of a possibility to use these materials either as substitutes for volatile organic compounds or as their direct usage in energy-related problems.

The H^{E}_{IL} values provide an understanding the species interactions and it can be best explained as the difference in the strength of interactions between unlike species compared to like species. A systematic effort has been presented to measure the H^{E}_{IL} values of Protic Ionic Liquids (PILs) to distinguish the ring effect on the interaction between a PIL possessing different ring structures and solvents of varied properties. The H^{E}_{IL} values for the three PILs and a common anion $[BF_4]^-$, in the presence of water display the trend as shown $[hPYRR]^+ > [hPY]^+ > [MIM]^+$. The PILs studied belong to non-aromatic and aromatic types. These observations have been discussed in terms of cavitation and solvation processes. The limiting excess partial molar enthalpy denoted by $H^{E,\infty}_{IL}$ for all the PILs studied can be correlated to specific solvent properties of these materials. The apparent molar enthalpies of the ionic liquids in solvents have been analysed with the use of the Pitzer equations to offer accurate representation.

Next, a thorough investigation has been presented with regard to Aprotic Ionic Liquids (APILs). Efforts have been made to address the issues like: 1) how does an IL having a substituted ring (aprotic ILs) differ from a PIL system and 2) among the substituted ILs, which factor is responsible for their behavior clearly different from each other? In an observation exposed herein, an interesting reversal in the enthalpic behavior from endothermic to exothermic on increasing the carbon chain length attached to the imidazolium ring in the imidazolium-based ionic liquids. The reversal trend has been explained on the basis of two simultaneous processes i.e the hydration/ salvation and the hydrophobic/ solvophobic effect. The values of H^{E}_{IL} for [BMIM][BF_4] in different non-aqueous solvents follow the order to be as: 1-propanol > ethanol > methanol > ethylene glycol > formamide > DMF. The derived apparent molar enthalpies for these ionic liquids can also be represented by the Pitzer equations.

An attempt was also made to differentiate between the roles of BF_4^- and NTf_2^- in terms of their effect on the H^{E}_{IL} values. [BMIM][BF_4] and [BMIM][NTf_2] show the strong endothermic pattern, while both [OMIM][BF_4] and [OMIM][NTf_2] exothermic behavior. On increasing the length of the substituted alkyl chain on the imidazolium ring from –butyl to –octyl, the enthalpic pattern shifts from endothermic to exothermic behavior. This shift can be clearly seen in the case of both $[BF_4]^-$ and $[NTf_2]^-$ substituted ILs.

Interactions between ionic liquids and DMSO have been probed in view of its exclusive properties. The H^{E}_{IL} in DMSO have been discussed in terms of solute-solvent interactions. Further, quantitative information on the solvent reorganization and clathrate formation has been obtained and interpreted.

The mixing behavior of common electrolytes and ionic liquids both in their aqueous solutions and pure states were studied. On one hand, the mixing of hydrophilic and hydrophobic electrolytes showed the completely endothermic behavior, while on the other hand, ionic liquids in their aqueous solutions showed an exothermic mixing behavior. The mixing of pure ILs however changed it to endothermic behavior. It implies that the mixing of ILs in their aqueous solutions stabilize the system where as mixing of the pure ones destabilizes it.

At last, a method has been used to calculate enthalpy interaction parameters, called as $H^{E}_{\mathrm{IL-IL}}$ by differentiating the excess partial molar enthalpies of a system. The method requires the use of a graphical method rather than any fitting of the equations. If a plot is drawn between the $H^{E}_{\mathrm{IL-IL}}$ and x_{IL} values, it is possible to observe two distinct lines passing through a majority of experimental data. While the first line indicates the dissociation or the presence of long-range interactions, the second line suggests the formation of clathrates. However, it was realized that a more accurate methodology should be developed in order to locate the point of intersection of these two lines.

Publications

- Gitanjali Rai and Anil Kumar
  Probing Thermal Interactions of Ionic Liquids with Dimethyl Sulphoxide
  ChemPhysChem. Accepted 2012

- Gitanjali Rai and Anil Kumar
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  Phys. Chem. Chem. Phys. **2011**, *13*, 14715

- Gitanjali Rai and Anil Kumar
  A Reversal from Endothermic to Exothermic Behavior of Imidazolium-based Ionic Liquids in Molecular solvents
  Chemical Physics Letters, **2010,** *496*, 143

- Geetanjali Singh and Anil Kumar
  Ionic liquids: Physico-chemical, Solvent Properties and Their Applications in Chemical Processes
  Indian Journal of Chemistry, **2008**, *47A*, 495

- Gitanjali Rai and Anil Kumar
  Do the Interactions Change with Changing the Polarity of Ionic liquids- An Enthalpic Approach towards Probing PILs with Molecular Solvents
  (manuscript under preparation)

- Gitanjali Rai and Anil Kumar
  Role of Anion in Modifying the Interactions between Ionic Liquids and Solvents
  (manuscript under preparation)

- Gitanjali Rai and Anil Kumar
  Towards Understanding the Mixing Phenomenon of Two Ionic Liquids: Mixing of Hydrophilic to Hydrophobic species
  (manuscript under preparation)

- Gitanjali Rai and Anil Kumar
  Revisiting the Pitzer Specific Ion Interaction Theory for the Mixing of Two Electrolytes (manuscript under preparation)

ORAL / POSTER PRESENTATIONS

Talks Delivered:

- Second International Seminar on Engineering Thermodynamics of Fluids, Tarragona (Spain), 22nd- 23rd July 2010

- Physical Chemistry Division and CMC Symposium, held on March 15th 2010, National Chemical Laboratory, Pune (India)

- International Conference on Innovations in Chemistry for Sustainable Development (ICSD-2011), 01-03 December, 2011 Punjab University, Chandigarh, Punjab (India)

Posters Presented:

- Presented Poster during 10th National Symposium in Chemistry, Indian Institute Of Science, Bangalore February 1-3 2008
- Presented Poster during CRSI Zonal Meeting, National Chemical Laboratory, Pune, May 13-14 2011
- Presented Poster during 12th CRSI International Symposium in Chemistry and 4th CRSI- RSC Symposium in Chemistry , Indian Institute Of Technology, Hyderabad February 2-5 2010
- Presented Poster during Annual Divisional Symposium at National Chemical Laboratory, Pune, December 13th 2011

RECOGNITIONS RECIEVED

- “Keerti-Sangoram Award” for the best research scholar in Chemical & Materials Division, National Chemical Laboratory for 2012-2013.
- “Best Poster Award” on National Science Day, held on February 25, 2009.
- “Best Poster Award” in Joint Physical Chemistry Division and CMC Symposium, NCL held on March 15, 2010.