EFFECT OF CO-SOLVENTS ON BULK AND INTERFACIAL CHARACTERISTICS OF ROOM TEMPERATURE IONIC LIQUIDS

DISSERTATION

Submitted in partial fulfillment of the requirements
provided for the award of Degree of

Master of Philosophy

In

CHEMISTRY

By

ROOHI JAN

Under the supervision of

Dr. G. M. Rather

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF KASHMIR
Srinagar – 190006, J&K, India
April
2012

Dedicated to my noble parents

Dr. Ghulam Mohammad Rather
Ph. D
Associate Professor

University of Kashmir
Srinagar-190006
J&K, India

DEPARTMENT OF CHEMISTRY

CERTIFICATE FROM SUPERVISOR

This is to certify that the work presented in this dissertation entitled "*EFFECT OF CO-SOLVENTS ON BULK AND INTERFACIAL CHARACTERISTICS OF ROOM TEMPERATURE IONIC LIQUIDS*" is original and has been carried out by **Ms. Roohi Jan** under my supervision. This piece of work is suitable for submission for the award of M.Phil Degree in Chemistry. It is further certified that the work has not been submitted in part or full for award of any degree in this or any other University.

(Dr. G. M. Rather)
Supervisor

DECLARATION

I hereby declare that the work incorporated in the present dissertation was carried out by me in the Department of Chemistry, University of Kashmir, Srinagar 190006. The entire work or any part of it has never been submitted before for any prize or degree anywhere.

(Roohi Jan)

ACKNOWLEDGEMENTS

Praise be to Allah for his continued blessings. Praise be to Allah for blessing me with noble parents whose love and meliflous affection made this whole journey wonderful and successful. Words are meaningless to express my unaccountable feelings to them for their belief in me, unequivocal support, kind understanding, patience and preservance and above all in making me what I am today. I wish them all the happiness and adventure that they have ensured that I had the opportunity to experience. **I owe them more than anything else in the world.**

It is a matter of great previlage for me to work under the able and highly academic guidance of Dr. G. M. Rather, Associate Professor, Department of Chemistry, University of Kashmir who irreversibly cooperated with me and always gave me ample freedom. His energetic smile, optimistic attitude, critical jugdements and never ending enthusiasm made the realization of this dissertation possible.

Praise be to Allah for blessing me with an opportunity to meet an exceptional man Dr. Mohsin Ahmad Bhat, Assistant Professor, Department of Chemistry who nurtured my capabilities and above all his trust in my abilities kept me going and ultimately towards the attainment of this goal. His scholarly guidance, experienced words, meticulous practical training, displined and magnanimous nature, unlimited sincerity and affection towards students had always inspired me and I feel extremely fortunate to be his student. His devotion and dedication to work, passion for knowledge, inquisited mind and scientific attitude have made an everlasting impact on me and boosted my confidence. His exceptional guidance and invaluable comments during the period of the research and the writing of the study are very much appreciated. This research has been a remarkable adventure and I am indebted to him for making it a challenging and learning journey. Thank You Sir for being so patient and loving to me during the analysis of data. Thank You Sir for all your love and I am excited to spend everyday of my life thanking You over and over again. **Really Sir You are the Real Mentor of the World of Research**.

I would extend my special thanks Dr. Aijaz Ahmad Dar, Assistant Professor, Department of Chemistry, University of Kashmir for his wise counseling and kind concern.

My special thanks to present Head of Department of Chemistry for allowing me to work in the department. All other faculty members are also acknowledged for all the guidance and assistance they provided me whenever I approached them. I would also like to mention the non teaching staff especially Altaf Ahmad Mir for their assistance in every possible way.

No less had been the incessant help and constant encouragement provided by Muzaffer Hussain Najar and Raashid Baya during the course of the study. I am very much thankful to them for their invaluable advice and moral support.

Nevertheless I am not missing out this opportunity to acknowledge and appreciate Oyais Baya whose infinite care and affection had always strengthened my determination. His kind concern, wise counseling and timely tips are invaluable for me. He gave me great insight and guidance on how to push forward and his never ending support helped to make this journey possible. Thank you Oyais Baya for encouraging me always and replenishing my energy to work during the study.

Special thanks to Mudasir Nazir my research copartner for all the generosity and encouragement he has provided to me during the study.

I feel it my gratitude to appreciate and acknowledge my lab mates and of course good friends of mine- Roohi Masrat, Suraya Jabeen, Masrat Maswal , Sabreena Yousuf, Uzma Khan,and Rais Ahmad Shah for their kind concern, timely assistance, love, moral support and amicable cooperation in scientific and social fronts of life. Their infinite cooperation, hard work, sincerity and dedication to work are source of inspiration to me. Really, I was fortunate enough to have such a wonderful labmates who made this whole journey very exciting and unique. The moments

which I spent with my lab mates are most memorable moments of my life. It is really very much painful to depart from such a company who always in one or other way tried to channelize all my negative feelings of research to a successful journey.

I would also extend my special thanks to people from IIIM Srinagar Dr. Khursheed Ahmad Bhat, Shabir Hussain Lone and Shakeel Baya for their timely assistance and kind support.

A special and Deep acknowledgement to my elder Sister, Rehana Akhter for her unwavering love, priceless prayers, for providing financial assistance and for nourishing me like her daughter. I respectfully offer thanks to my Jiju, Mushtaq Ahmad Bhat for his kind concern and invaluable advice. Thanks to my nieces Mehvish Mushtaq, Huma Mushtaq and Adeeva Mushtaq for their innocent love and care. Their innocent talks and actions always refreshed me whenever I was entrapped by the frustration of research.

I would also like to thank my brother Waheed Ahmad Wani for giving me strength of will to pursue what I believed and strength of character to lead a righteous life. Thanks to my Sister-in-law Bilkees jan for her constant support, infinite love and encouragement. And of course my heartfelt and sweet thanks to my sweet nephew Mohammad Aman Wani for his pious love. His innocent actions and babbling talks drain magically all sort of negative feelings from my mind.

I am very much thankful to Allah for blessing us with this mini angel who innocently makes the life of my family very much exciting and enthusiastic.

I feel my pleasure to acknowledge my two younger sisters, Samiya Jan and Nelofer Akhter for their priceless prayers, invaluable suggestions, concern, support and encouragement. Thanks for being my Special Friends.

I would like to extend my deepest appreciation to all my friends Usma Gul, Rukaya Khaliq, Sakeena Akhter Umul Maurifa, Rasika Jan, Momin Bashir, Shubnum Bashir, Fozia Ashraf, Saima Riyaz and especially Raafia Najam for being there, whenever I was in need of them the most and for their love, support and encouragement.

Very special thanks to Syeed Zeeshan Fathima who accompanied and supported me always. She has also inspired me through her openness and straightforwardness.Thank you Zeeshan for directly or indirectly making this period very successful and immemorable.

Most people are lucky to have friends as constant and close to their heart as Ulfat Araf Jan (school friend) is to mine. She always motivated and elated me and gave me immense love and care from my school days.

I feel short of words for my roommate Kurat D for making my stay comfortable and enjoyable during this period.

I am forever grateful to my granddadi whose foresight and values gently offer counsel and unconditional support at each turn of the road.

This piece of work is a tribute to my beloved parents and to an exceptional man from a student still anxious to learn from him

Overall it was remarkable and incredible experience of my life.

Roohi Jan

List of Publications:

1. **Roohi Jan**, Ghulam Mohammed Rather, Mohsin Ahmad Bhat, *Association of ionic liquids in solution: Conductivity studies of [bmim][Cl] and [bmim][PF$_6$] in binary mixture of Acetonitrile + Methanol*. ***Journal of Solution Chemistry*** **2012** (accepted)

2. **Roohi Jan**, Ghulam Mohammed Rather, Mohsin Ahmad Bhat, *Effect of co-solvents on bulk and interfacial characteristics of N-alkylimidazolium based ionic liquids [bmim][PF$_6$] and [bmim][BF$_4$]*. (Communicated)

CONTENTS

LIST OF FIGURES

LIST OF TABLES

List of Schemes

Chapter 1

General Introduction

Ionic liquids (ILs) are special class of molten salts constituted by large and asymmetric organic cations and inorganic or organic anions, with melting temperatures below 100°C. Due to the large size and the conformational flexibility of constituent ions, ILs present low lattice enthalpies and large entropy changes upon melting which favour the liquid state. ILs with melting point below ambient temperatures are regarded as Room Temperature Ionic Liquids (RTILs). RTILs have attracted increasing attention in recent years [1-5] from both academia and industry due to their interesting properties and potential applications. RTILs as a hybrid of neutral and ionic entities, exhibit many unique physicochemical properties, such as negligible volatility, nonflammability under ambient conditions, large liquidus range, high thermal and chemical stability, wide electrochemical window, wide range of densities and viscosities, high potential for recycling, high ionic conductivity, and miscibility with a wide range of organic and inorganic compounds [1, 3, 6-12] which confer them their reputation as "*green solvents*" and make them a good alternative to traditional organic solvents [7,10,13-18]. In addition, the high polarity of the ILs makes them to form very strong effective adsorption films and redy tribochemical reactions, which contributes to their prominent antiwear capability [19]. On account of above mentioned specialities, RTILs have found wide applications in chemical synthesis, catalysis, lubrication, thermal separation processes and electrochemistry [4, 13, 20-26].

ILs were initially synthesized in the early 20th century and at present there are 200 different types of ILs which have been reportedly prepared. The first report of ionic liquid (formerly called a room-temperature molten salt), ethyl ammonium nitrate goes back to 1914, which was composed of ethylammonium cation and nitrate anion and had a melting temperature of 12°C [27]. However, this ionic liquid did not attract further application based research due to its explosive nature. Latter, organic chloroaluminates were developed by Hurley and Thomas in 1951 [28]. However, interest in these salts advanced only after the development of binary ionic liquids from mixtures of aluminium (III) chloride and *N*-alkylpyridinium [29] or 1, 3-dialkylimidazolium chloride [30]. During 1970s ionic liquids were studied mainly for electrochemical applications and in the mid-1980s, ionic liquids were proposed as solvents for organic synthesis [31, 32]. In the 1990s many air and water stable ionic liquids were introduced and since then they have become increasingly popular in academia and industry [33].

The most fascinating aspect of ionic liquids is that their physical and chemical properties can be tailored for specific applications by adjusting the structure and species of cations/anions; it is in this context that these valuable solvents are being referred to as '*Designer Solvents*'. As an example, the combination of 1-butyl-3-methylimidazolium [bmim] with tetrafluoroborate $[BF_4]^-$ ion results in a hydrophilic IL, whereas the association of the same cation with hexafluorophosphate $[PF_6]^-$ ion produces a strongly hydrophobic compound, and, in general the hydrophobicity of the cation increases with the length of the alkyl chain [2]. In fact, the possible combination number of cations and anions is uncountable with vast and still unexplored possibilities [34, 35]. To facilitate the selection of an optimum ionic liquid for a particular application, it is useful to consider their fundamental transport and thermodynamic properties. An understanding of microstructures and interactions of ionic liquids at molecular level, as pure compounds or in the presence of dissolved species, is useful to design suitable ionic liquids [36, 37]. The chemical constitution of ionic liquids determines the nature of intramolecular and intermolecular interactions and thus the macroscopically observable properties such as thermodynamic and transport properties [38]. A deeper understanding of the effect of the molecular structure and microscopic properties of ionic liquids is paramount in understanding and improving the macroscopic properties of the system [39].

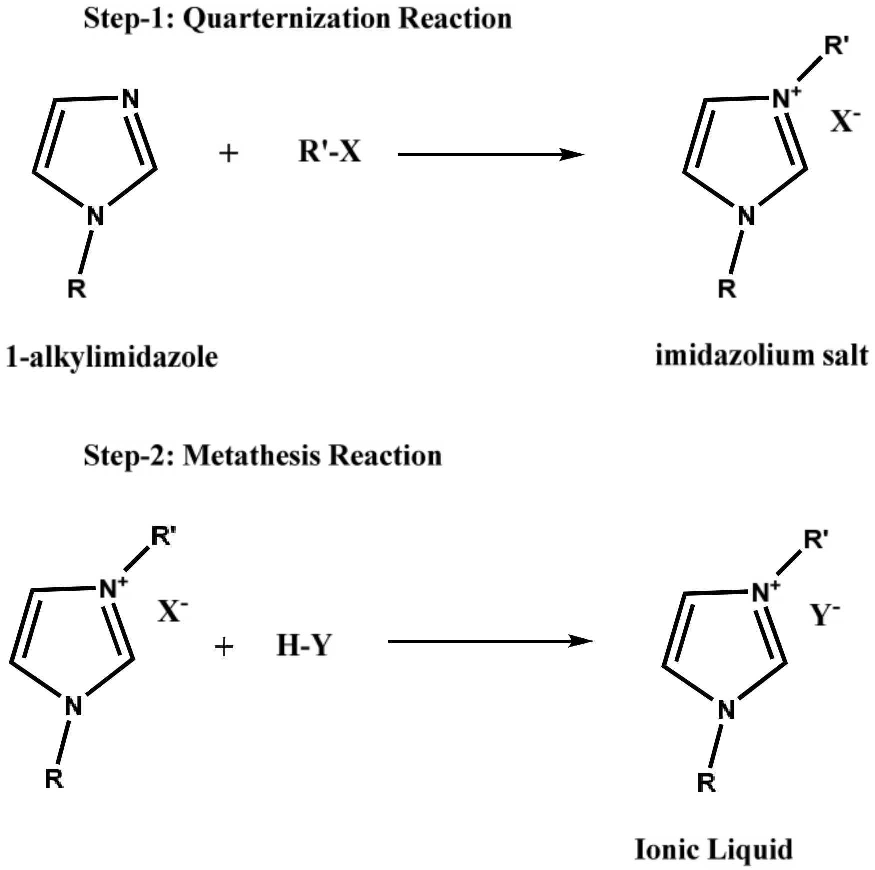
Recently, the synthesis of functionalized task-specific ionic liquids (TSILs) with special functions according to the requirement of a specific reaction has become an attractive field due to their tunable features for various targeted chemical tasks and the advantages as reusable homogenous supports, reagents, and catalysts with green credential. The TSILs often serve the dual role of catalyst and reaction medium. Endowed with catalytically active groups, functional ionic liquids have been developed and successfully applied as catalysts in a number of chemical transformations. Like a basic functionalized ionic liquid, 1-butyl-3-methylimidazolium hydroxide [bmim][OH], catalyzes the three component condensation reaction of acid chlorides, amino acids, and dialkyl acetylenedicarboxylates in water to afford functionalized pyrroles in high yields [40]. Bellina *et al.* [41] synthesized a series of glycerylimidazolium based task specific ionic liquids aiming their applications to palladium catalyzed coupling reactions. Wang and coworkers developed [42] a variety of structurally diverse Bronsted acidic benzimidazolium based ionic liquids and explored their use as environmentally benign catalysts for acetalization of various aldehydes using substituted 1, 2-ethanediols affording protected acetals in high yields. Wang et al. have designed [43], synthesized and used an ethanolamine functionalized TSIL, 4-di (hydroxyethyl)aminobutyl tributylammonium bromide for the Heck coupling reaction where IL performs the role of base, ligand and reaction medium simultaneously, with added advantage of recyclability of the system. SO_3H-functionalized ionic liquids have been employed as an alternative reaction medium to conventional acid catalysts for oligomerization of various olefins, to produce branched olefin derivatives in high conversions and excellent selectivity. The TSILs maintain the unique properties of ionic liquids, therefore can be easily recycled and reused as homogenous small molecular catalysts. Up to now, functionalized ionic liquid (FIL) catalysis has been mainly focused on exploring acid or base mediated reactions. Considering the 'designer' properties of ionic liquids, there seems a tremendous unexplored potential for FIL catalysis [44-47].

1.1. Composition of Room Temperature Ionic Liquids

The fact that an ionic liquid is composed of ions and is still liquid at ambient conditions is reason enough to evoke curiosity among researchers as far as their properties and applications are concerned. A sufficient and systematic understanding of molecular structure-physicochemical properties relationship is a basic requirement for molecular design in chemistry with a view to create new materials having desirable properties. The general strategy of designing RTILs is to destabilize the crystalline phase of an ionic substance with respect to its melt. Choosing large size, diffuse charge and unsymmetrical ions in such combinations leads to weak coulombic interactions and the low symmetry hampers their efficient packing in the crystal. Both these goals are achieved through selection of large size unsymmetrical organic cations and weakly coordinating inorganic/organic anions. In addition to molecular symmetry and charge delocalization, size mismatch of ions, side chain elongation and fluorination of hydrocarbon chain continue to be the popular methods for inventing new RTILs. The most common ionic liquids comprise salts of tetraalkylphosphonium, tetraalkylammonium, N-alkylpyridinium or N, N′-dialkylimidazolium cations. Common cations contain 1-18 carbon alkyl groups, and include the ethyl, butyl and hexyl derivatives of N-alkyl-N′-methylimidazolium and N-alkylpyridinium. Other cations include pyrrolidinium, pyridazinium, pyrimidinium, pyrazinium, pyrazolium, triazolium, thiazolium and oxazolium. A wide range of anions can be matched with the cation component for achieving an ionic liquid with desired physicochemical properties. Commonly used anions include carboxylates, fluorinates, carboxylates, sulfonates, fluorinated sulfonates, imides, borates, phosphates, antimonates, halides, halometallates, etc. [48]. Because of enormous choice of available cations and anions one can design large number of RTILs with desired physical properties by employing a proper combination of cation and anion. Owing to some potential advantages like high air and water stability, low toxicity, appreciable conductivity and structural organization, imidazolium based RTILs are more oftenly used especially for electrochemical applications [49, 50].

1.2. Synthesis of Room Temperature Ionic Liquids

Conventionally a two step procedure is used in the synthesis of RTILs [51, 52]. The first step is usually a quaternization reaction, wherein alkylation of heteroatom in an organic moiety is performed to produce salt of desired organic cation. In the second step the anion (usually a halide) of the salt synthesized in step first is substituted by the anion of choice through anion exchange reaction [Scheme 1].



Scheme 1: General reaction scheme for synthesis of Ionic liquids

A variety of synthetic procedures are available in the literature for the synthesis of RTILs and often the purity of final product happens to be a matter of concern in these procedures. Impurities even in the lowest concentration regime have drastic and undesired effects on the physicochemical characteristics of RTILs, especially those of electrochemical concern. Gordon and co-workers [53] have recommended a three pronged approach, viz.

(i) Purification of starting materials

(ii) Control of conditions for quarternization and metathesis reactions and

(iii) Purification of the synthesized ionic liquids for research grade purity.

The conventional synthesis and purification procedures for RTILs are time consuming and often give low yields. Low yields, waste generation, complicated workup procedures and non-green aspects of synthesis and purification processes for RTILs are current obstacles in the path of their generalized use. Hence many groups have extensively investigated these issues and subsequently non-conventional approaches like use of microwaves [54, 55] and ultrasound [56-58] have been tested for the synthesis and purification of RTILs with better yield and purity, fast conversions and easy workup of synthetic and purification steps in mind. Various approaches for purification of RTILs have been a subject matter of many publications [59-62]. Making the RTIL synthetic procedures greener, with maximum purity and stability of the synthesized product and designing new choices of cation-anion combinations, besides the structural modifications in the cation-anion skeleton to achieve desired properties in a low cost RTIL continue to be an area of immense interest for synthetic chemists. Synthesis of RTILs from biorenewable natural products is currently a new area of research in this regard [63, 64].

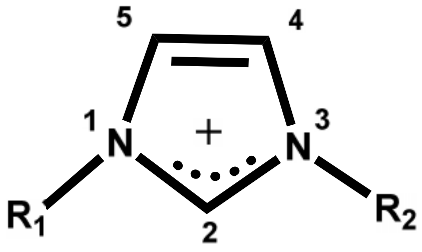
1.3. Physicochemical properties of RTILs

1.3.1. Structure of Imidazolium based Ionic Liquids.

As solvents ionic liquids present a completely different environment from that of polar and non-polar molecular solvents. In addition to the interactions existing in conventional organic solvents (hydrogen bonding, dipole-dipole and van der Waals interactions) ionic liquids being constituted exclusively by ions experience strong inter-ionic interactions that yield long- lived association of ions [38]. The nature and type of interactions and interconstituent forces in the bulk ionic liquids affects their physical and chemical properties and how they interact with other solutes [65]. There are, however, still many questions related to the nature and the precise origin of the possible interaction in RTILs, which are yet to be assumed satisfactorily.

1.3.1.1. Features of Imidazolium Ionic Liquids

Stability and excellent liquescency of Imidazolium ring [Scheme 2] makes the imidazolium ionic liquids most widely used and studied families of ILs [66]. The unique properties of these cations are founded in the electronic structure of their aromatic ring which contains delocalized 3-center-4-electron configuration across the N1-C2- N3 moiety, a double bond between C4 and C5 at the opposite side of the ring, and a weak delocalization in the central region [67]. The hydrogen atoms C2-H, C4-H, and C5-H carry almost the same charge, but carbon C2 is positively charged owing to the electron deficit in the C=N bond, whereas C4 and C5 are practically neutral. The resulting acidity of the hydrogen atoms is the key to understand the properties of these ionic liquids. The hydrogen on the C2 carbon (C2-H) has been shown to bind specifically with a solute molecule [68, 69] or its counter ion [70] as a good hydrogen bond donor.



Scheme 2: Electronic structure of 1,3-dialkylimidazolium cation

1.3.1.2. Nanostructural Organization of Imidazolium based Ionic Liquids

Ionic liquids are composed solely of ions so that long-range coulomb interactions may play a major role giving rise to structure and dynamics that are unique to ionic liquids [71]. Many of the novel features of ionic liquids are likely to originate from these unique structures and dynamics [72]. From macroscopic point of view, an ionic liquid can be considered as a continuum system characterized by its macroscopic constants, such as boiling point, vapour pressure, density, surface tension. However, from microscopic point of view it is a discontinuum which consists of individual, mutually interacting molecules, characterized by molecular properties such as dipole moment, electronic polarizability, hydrogen-bond donor (HBD) and hydrogen bond acceptor (HBA) capability, electron-pair donor (EPD) and electron-pair acceptor (EPA) capability, etc. The types and extent of these interactions determine the macroscopic properties of ionic liquids and their possibilities for different applications.

Many studies have been carried out to examine the structure and interactions of ionic liquids, mostly imidazolium based ionic liquids, by using different approaches. Specifically, the structure of these ionic liquid systems exhibits unique spatial heterogeneity that results from their inherent polar/nonpolar phase separation. The underlying reason for the microphase segregation is due to the interplay between electrostatic interactions (between polar imidazolium ring and anion) and van der Waals interaction between the nonpolar alkyl tails of the cation [73].

Nanosegregation of imidazolium based ionic liquids between polar and non-polar regions was first predicted through molecular dynamics simulation studies [74-77] and later confirmed by neutron [78] and X- ray diffraction [78] techniques. The molecular dynamics simulations done on 1-alkyl-3-methylimidazolium cations with anions (F^-, Cl^-, Br^-, and $[PF_6]^-$) show that regions above and below the imidazolium ring are the preferential ones in case of large anions, however, nearest-neighbour anions are pushed away from the volume occupied by the flexible alkyl chain on increasing alkyl chain length [75]. The charged anion and the cation head groups distribute homogeneously because of the strong electrostatic interactions, while the neutral tail groups tend to aggregate due to the collective short-range interaction of longer alkyl chain [77].

The local structural heterogeneity of imidazolium based ionic liquids has been probed by coherent anti-Stokes Raman scattering (CARS) [71, 72]. Neutron diffraction measurements on 1, 3-dimethyl Imidazolium based ionic liquids show the effects of charge distribution and anion size on their nanostructural segregation. As the ions increase in size, the charge becomes more delocalized and the cation–anion interaction is reduced, resulting in less charge ordering and nanostructural segregation [79]. Divalent anions, such as sulphate (SO_4^{2-}), thiosulphate ($S_2O_3^{2-}$), chromate (CrO_4^{2-}), dichromate ($Cr_2O_7^{2-}$), carbonate (CO_3^{2-}) and oxalate ($C_2O_4^{2-}$) increase the electrostatic interactions due to enhanced intermolecular structuring [80].

The existence of structural organization of 1-alkyl-3-methylimidazolium based ionic liquids with $[Cl]^-$ and $[BF_4]^-$ studied by X-ray diffraction reveal that size of structural heterogeneities depend on alkyl chain length [78, 81]. The effects of cation symmetry on properties of imidazolium based ionic liquids have also been reported [82-84]. Symmetric 1, 3- didecyl Imidazolium hexafluorophosphate and asymmetric 1-decyl-3-methylimidazolium hexafluorophosphate are liquids irrespective of their symmetry [82]. However, the greater structural organization in symmetric cation than 1-decyl-3-methylimidazolium hexafluorophosphate was reported [83]. Both experimental and molecular dynamic simulation results show that symmetric 1, 3-dialkyl-imidazolium bis(trifluoromethylsulfonyl)imide ionic liquids have the same morphology; however, nanoscale ordering is considerably enhanced in symmetric cation based ionic liquids [73, 84]. The effect of conformational heterogeneity of cations and anions in nanostructure organization of ionic liquids has also been reported [85]. For example, the coexisting trans-trans and trans-gauche conformations of n-butyl chain in 1-butyl-3-methylimidazolium cations was found to be crucial in lowering the melting point of this 1-butyl-3-methylimidazolium based ionic liquids [85].

1.3.2. Viscosity

RTILs are viscous liquids with viscosities 1-3 orders of magnitude greater than the conventional solvents [86]. Owing to the impact of viscosity on the rate of mass transport and conductivity, high viscosity of RTILs is presently the main concern for their use in electrochemical setups [49, 87]. It has been found that cation as well as anion of the RTIL have a significant impact on their overall viscosity. Hole theory [88] has been successfully used [89] to analyze the RTIL viscosity and its tuning through structural variations. It has been shown that viscosity of RTILs can be modeled by assuming that they behave like an ideal gas whose motion is restricted by the availability of sites for the ions to move into. Hence for an RTIL

$$\eta = \frac{(m\bar{c}/2.12\sigma)}{(P(r>R))} \qquad (1.1)$$

where η is the coefficient of viscosity, m is the geometric mean of the constituent ion molecular mass, is $\bar{c}$ the average speed of the molecule $(= 8kT/\pi.m)^{1/2}$, σ the collision diameter $(4\pi R^2)$ and $P(r \geq R)$ is the probability of finding a hole of radius r, greater than the R of the RTIL whose value can be evaluated through,

$$Pdr = \frac{16}{15\sqrt{\pi}} a^{7/2} r^6 e^{-ar^2} dr \qquad (1.2)$$

where a is given by

$$a = \frac{4\pi\gamma}{\kappa T} \qquad (1.3)$$

γ being the surface tension. Good correlation between η calculated on the basis of Hole theory and that measured experimentally has been reported. As evident from the above equations, RTIL viscosity can be decreased by decreasing the surface tension, increasing the free volume or by decreasing the ionic radius. This is the reason for low viscosity of RTILs with fluorinated anions. Various groups have extensively studied the impact of cation, anion, their size, symmetry and charge delocalization on the η values of RTILs in detail [90–93]. Viscosity of RTILs has been demonstrated to be temperature sensitive [94, 95]. While temperature dependence of η in most RTILs obeys an Arrhenius type relationship, Guzman-Andrade (GA) law,

$$\eta = A.\exp\left(\frac{E_a}{RT}\right) \tag{1.4}$$

where E_a is the activation energy for viscous flow, for many RTILs Vogel-Tamman-Fulcher (VTF) equation,

$$\eta = \eta_0.\exp\left(\frac{B}{T-T_0}\right) \tag{1.5}$$

with η_0, B and T_0 as constants, better explains the variations of η with temperature. In general, RTILs with asymmetric cations without any functional group in alkyl chains generally follow GA law while those with symmetrical low molar mass cations follow VTF equation [95]. An overall analysis of the viscosity data leads to the general conclusion that for RTILs electrostatic interactions, hydrogen bonding and van der Waals interactions are the determining factors for their overall viscosity [92]. Regarding mass transport in RTILs, diffusion coefficients have been found to vary with η in accordance with Stokes-Einstein relation [96, 97], qualitatively suggesting their conventional solvent like behavior. Worth to mention, there are reports in literature [98, 99] where validity of fractional Stokes-Einstein behavior in RTILs has been demonstrated. In spite of many detailed and comprehensive experimental and molecular dynamical studies, mass transport in RTILs is yet to be completely understood [100].

1.3.3: Conductivity

Composed entirely of ions, RTILs are considered as concentrated electrolyte fluids, with appreciable conductivity values that abrogates the need of supporting electrolyte in their use as solvents in electrochemical setups [49, 87, 94]. Conductivity values from 0.1- 20 mS cm^{-1} have been reported [94] and found to be strongly dependent on the overall composition of the RTIL. Among all the RTILs, those based on imidazolium based cations have higher conductivities of the order of 10 mS.cm^{-1} [101], which is one of the reasons for their extensive use in electrochemistry [49]. Conductivity is found to be an inverse function of the RTIL viscosity as per Stokes-Einstein equation. An interesting observation in this regard has been the mismatch between the experimentally observed conductivity and the value calculated theoretically on the basis of magnitudes of diffusion coefficients [91, 92, 102-104]. This mismatch has been explained in terms of ion aggregates and correlated ionic motions in RTILs [91, 92, 103-105]. Besides viscosity, ion size, charge delocalization, density, ion aggregation and correlated ionic motions influence the RTIL conductivity [90, 91, 102, 106–109]. Furthermore conductivity strongly depends upon temperature, obeying an Arrhenius type equation,

$$ln\sigma = ln\sigma_0 - \frac{E_\Lambda}{RT} \qquad (1.6)$$

where E_Λ is the activation energy for the conduction and σ_0 is a constant.

1.4. Solute-Solvent Interaction in systems containing Imidazolium based Ionic Liquids

Ionic liquids can dissolve a wide range of polar or nonpolar, organic or inorganic compounds. The ability of an ionic liquid to dissolve polar and non-polar compounds is related to its structural segregation [74, 110]. The segregation of polar and nonpolar domains and diverse environment in ionic liquids helps to understand how solutes physically fit into the bulk liquid and how much the overall structure is affected. Different solutes interact preferably with certain domain of the ionic liquids. Each domain located at different site acts as a specific solvent for a given class of solutes and due to contrasting polarities of these domains ionic liquids are called “two-in one” solvents [110] or (pseudo) different solvents [111].

The solutes are generally classified into three groups depending on where and how they interact with ionic liquids [110]:

(a) Associating solutes: interact strongly with polar network.

(b) Dipolar solutes: prefer the non- polar regions of ionic liquids and

(c) Non-polar solutes: can orient themselves at the interface between the polar and non-polar regions of ionic liquids.

1.4.1. Associating Solutes

Associating solutes form strong hydrogen bonds with the charged parts of the ionic liquid domains [112], specifically with atoms of anions [110]. The most common examples are water and methanol.

One of the most studied solute-solvent interactions involving ionic liquids is the interaction between water and imidazolium based ionic liquids. Both the experimental [113-115] and theoretical works [116] show water molecules preferentially interact with polar domain of ionic liquids through hydrogen bonding. Cammarata et al. [115] studied interactions between ionic liquids and water by attenuated total reflectance (ATR) infrared spectroscopy and concluded that water molecules preferentially interact with anions through hydrogen bonding. In addition, they found that ionic liquids containing $[BF_4]^-$ and $[PF_6]^-$ anions form symmetric complexes with water molecule (both protons of water bound to two discrete anions) as X…H-O-H…X (where X represents the anion in the ionic liquid). Similar observations were reported through vibrational spectroscopy measurement and DFT calculation [117, 118].

The interaction between methanol and ionic liquid is dominated by hydrogen bond interaction due to its both hydrogen bond donor and acceptor properties [116]. The only differences are: methanol interacts with both polar and non polar domains of ionic liquids and interaction between methanol and C2-H is weaker than that of water molecule [116]. The infrared spectroscopy and two dimensional correlation and multivariate curve resolution on mixtures of methanol and $[bmim][BF_4]$ and $[bmim][PF_6]$ have established hydrogen bonding interactions between methanol OH group and anionic fluorine [113,116] in RTIL + methanol mixtures. The OH stretching band was observed to show red shift on addition of methanol in ionic liquid and the observed shift was found to be greater for $[BF_4]^-$ than $[PF_6]^-$ indicating stronger interaction of former than later. The results from these reports also indicated the presence of weaker interactions between methanol and cation hydrogen through methanol oxygen and acidic hydrogen of imidazolium cation. The density functional theory (DFT) calculations by Zhu et al. [119] also show anions prefer to occur near hydroxyl atom of methanol due to its positive charge.

1.4.2. Dipolar Solutes

Dipolar solutes interact with the charged head groups of the ions and nonpolar domains. They orient themselves at the interface between the polar and non-polar regions of the ionic liquids [110]. This makes them excellent solvents for many ionic liquids. Acetone, acetonitrile, and small halogenated hydrocarbons are some of the solutes in these categories. Acetone and acetonitrile are soluble at all compositions in [bmim][PF_6] whereas the solubility of hexane and water is 0.11 and 0.29 mole fraction at 330K [120, 121].

The NMR experiment and *ab initio* calculations on acetone and [C_4mim][PF_6], [C_6mim][PF_6], [C_8mim][PF_6] and [C_6mim][BF_4]) indicated hydrogen bonds between the ring protons, alkyl chain of the ionic liquids and the carbonyl oxygen of the acetone molecules [122]. The results show that the strength of the hydrogen bond is influenced by the type of anion and the length of alkyl chain on the imidazolium ring.

Acetonitrile interacts with the polar and non-polar domain of ionic liquids at different proportions [112]. The simulation work by Lopes and coworkers [116] on [bmim][BF_4] and [bmim][PF_6] + methanol/acetonitrile mixtures show that both acetonitrile and methanol interact strongly with both anions. The differences between methanol and acetonitrile are: the anion-methanol interaction is stronger than that of anion-acetonitrile and C2-H-acetonitrile interaction is conversely stronger for acetonitrile than that of methanol [116]. The molecular dynamics of acetonitrile and [bmim][BF_4] mixture shows interaction between nitrogen of CH_3CN and imidazolium ring hydrogens [123].

Zang et al. (124) investigated the properties of the mixtures of deuterated dimethyl sulfoxide (DMSO-*d*6) and 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]) by IR and quantum chemical calculations. They found that hydrogen bonds are preferentially formed between imidazolium C2-H and oxygen of DMSO than anion-DMSO alkyl chain hydrogens. In addition, the interaction between oxygen of DMSO and C4-H/ C5-H was observed to have insignificant importance in ionic liquid-DMSO interaction [125]. The intermolecular interactions of DMSO ionic liquids have also been analyzed using the measured excess properties [126, 127].

1.4.3. Non polar solutes

The nonpolar molecules such as alkanes tend to reside in the nonpolar domains of ILs and are excluded from the ionic network because of the cohesive energy of the charged groups [112]. The simulation work by Padua et al [112] shows a strong peak radial distribution function appears between the methyl groups of n-hexane and end carbon alkyl side chain of cation, and very weak correlation observed between the alkane and both cation head group and anion in hexane + [bmim][PF_6] mixtures.

The difference in relative position, orientation, and specific interaction between solutes and different domains of ionic liquids shows the complex microscopic structures of ionic liquid fluid phase. The position of solutes in ionic liquids depends on the size and morphology of ionic liquid microstructures and affinity of solute for each domain.

Ionic liquids have attracted wide attention lately and their potential applications in different areas are continuously being explored. Most of the current researches on ionic liquids are concentrated on investigating what can be achieved through ionic liquids and why they work the way they do. The latter provide insight into the molecular factors that determine their properties ranging from quantitative thermodynamic and physical data and qualitative trends that guide in searching the best ionic liquids for particular purpose. Many of the applications rely upon the interaction of ionic liquids with other components. Ionic liquids exhibit nanoscale phase segregation into polar and nonpolar regions. The nanoscale self-organisation is the result of interplay between Coulomb and van der Waals interactions which leads to the formation of high charge density permeated non-polar regions. Like in any other associated liquid, the structural organization of constituents makes RTILs to behave as very viscous fluids. Presently the high viscosity of ionic liquids is a constraint in obtaining optimum application in many electrochemical devices, in addition to its detrimental role in chemical kinetics. There exist three possibilities for handling the high viscosity of ionic liquids:

(1) To synthesize ionic liquids with low viscosity but these may not be suitable for a given application as one needs to replace either the cation or anion by another species imparting the low viscosity. This may lead to a decrease in the effectiveness of the ionic liquids itself.

(2) To use viscous ionic liquids in conjunction with molecular solvents to provide a clear liquid phase that will offer low viscosity but still be useful for a variety of applications.

(3) To increase the temperature. However, increase of temperature may be unsuitable when chemicals/ devices are poorly heat resistant.

So the use of co-solvents seems as a better option to overcome viscosity related challenges of RTILs. There are many reports available on the physical properties of pure and binary mixtures of imidazolium ionic liquids with co-solvents. The physicochemical properties in these reports have been studied and correlated with the structures of ionic liquids in terms of variations in the cations and anions [128, 129].

Seddon et al. [130] have reported the effect of chloride, water and organic solvents on the physical properties of various ionic liquids. Yang et al. [131] observed the effect of water and cosolvents on the viscosity of the ionic liquids, 1-butyl 3-methyl imidazolium hexafluorophosphate [bmim][PF_6], 1-butyl 3-methyl imidazolium tetrafluoroborate [bmim][BF_4] and 1-butyl 3-methyl imidazolium trifluoroacetate [bmim][CF_3CO_2]. It has been found that a change in the nature and concentration of co-solvents affects the viscosity and conductivity of RTIL very significantly. The solvents of higher dielectric constant seem to have a larger effect on the viscosity and the conductivity of the solution indicating that organic solvents enhance ionic association of the ionic liquids, an effect that is due to the dielectric properties of the solvents.

Motivated by the literature reported concerns and missing links associated with the fundamental and applied aspects of ion association characteristics and the co-solvent impact on the physicochemical aspects of RTILs, we attempted to explore the impact of cosolvent on structural, transport and interfacial properties of N-alkylimidazolium ionic liquids. The resulting studies are presented as two chapters;

In chapter 2 of this dissertation we present results from our detailed conductometric investigations regarding the ion association characteristics of [bmim][Cl] and [bmim][PF_6] in molecular solvents viz. methanol and acetonitrile. Chapter 3rd presents results from our studies aimed at to explore the impact of organic co-solvents viz. acetonitrile and methanol on the bulk and interfacial characteristics of [bmim][BF_4] and [bmim][PF_6].

References

1. Wilkes, J. S. *Green Chem*. **2002,** *4*, 73.

2. Huddleston, J. G.; Visser, A. E.; Reichert, W. M.; Willauer, H. D. *Green Chem*. **2001**, *3*, 156.

3. Hagiwara, R.; Ito, I. *J. Fluorine Chem*. **2000**, *105*, 221.

4. Wasserscheid, P.; Welton, T. *Ionic Liquids in Synthesis*; Wiley-VCH Verlag GmbH Co. KGaA: Weinheim, Germany, 2003.

5. Heintz, A. *J. Chem. Thermodyn.* **2005**, *37,* 525.

6. Earle, M. J.; Esperanca, J. M. S. S.; Gilea, M. A.; Canongia-Lopes, J. N.; Rebelo, L. P. N.; Magee, J. W.; Seddon, K. R.; Widegren, J. A. *Nature*(*London, U.K.)* **2006**, *439*, 831.

7. Rogers, R. D.; Seddon, K. R. *Science* **2003**, *302*, 792.

8. Fannin, A. A.; King, L.A.; Levisky, J. A.; Wilkes, J. S. *J. Phys. Chem*. **1984**, *88*, 2609.

9. Wakai, C.; Oleinikova, A.; Ott, M.; Weingartner, H. *J. Phys*. *Chem.* B **2005**, *109*, 17028.

10. Earle, M. J.; Seddon, K. R. *Pure Appl. Chem*. **2000**, *72*, 1391.

11. Hussey, C. L. *Pure Appl. Chem.* **1988,** *60*, 1763.

12. Bonhote, P.; Dias, A.; Papageorgiou, N.; Kalyanasundaram, K.; Gratzel, M. *Inorg. Chem*. **1996,** *35*, 1168.

13. Welton, T. *Chem. Rev*. **1999,** *99*, 2071.

14. Rogers, R. D.; Seddon, K. R. *Ionic Liquids, Industrial Applications to Green Chemistry*; ACS Symposium Series, 818; American Chemical Society: Washington DC, 2002.

15. Rogers, R. D.; Seddon, K. R. *Ionic Liquids as Green Solvents: Progress and Prospects*; ACS Symposium Series, 856; American Chemical Society: Washington DC, 2003.

16. Wasserscheid, P.; Keim, W. *Angew. Chem*., *Int. Ed*. **2000**, *39*, 3772.

17. Holbrey, J. D.; Seddon, K. R. *Clean Prod. Proc* **1999**, *1*, 223.

18. Bates, E. D.; Mayton, R. D.; Ntai, I.; Davis, J. H. *J. Am. Chem. Soc.* **2002**, *124*, 926.

19. Zhou, F.; Liang, Y.; Liu, W. *Chem.Soc.Rev*.**2009**, *38*, 2590.

20. Liu, W.; Fadeev, A. G.; Qi, B.; Smela, E.; Mattes, B. R.; Ding, J.; Spinks, G. M.; Mazurkiewicz, J.; Zhou, D.; *Wallace Science* **2002,** *297*, 983.

21. Liu, W.; Ye, C.; Gong, Q.; Wang, H.; Wang, P. *Tribol. Lett.* **2002,** *13*, 81.

22. Xu, W.; Angell, C. A. *Science* **2003**, *302*, 422.

23. Seki, S.; Kobayashi, Y.; Miyashiro, H.; Ohno, Y.; Usami, A.; Mita, Y.; Watanabe, M.; Terada, N. *Chem. Commun*. **2006**, *2006*, 544.

24. Anderson, J. L.; Armstrong, D. W.; Wei, G. *Anal. Chem*. **2006**, *78*, 2892.

25. Fabregat-Santiago, F.; Bisquert, J.; Palomares, E.; Otero, L.; Kuang, D.; Zakeeruddin, S. M.; Gratzel, M. *J. Phys. Chem. C* **2007**, *111*, 6550.

26. Han, X.; Armstrong, D. W. *Acc. Chem. Res*. **2007**, *40,* 1079.

27. Walden, P. *Bull. Acad. Imper. Sci (St. Petersburg*) **1914**, *8*, 405.

28. Hurley F. H.; WIer Jr, T. P. *J. Electrochem. Soc.* **1951,** *98*, 207.

29. Chum, H. L.; Koch, V.; Miller, L.; Osteryoung, R. *J. Am. Chem. Soc*. **1975**, *97,* 3264.

30. Wilkes, J. S.; Levisky, J. A.; Wilson R. A.; Hussey C. L. *Inorg. Chem.* **1982**, *21*, 1263.

31. Boon, J. A.; Levisky, J. A.; Pflug, J. L.; Wilkes, J. S. *J. Org. Chem.* **1986,** *51,* 480.

32. Fry S. E.; Pienta, N. J. *J. Am. Chem. Soc.* **1985,** *107*, 6399.

33. Cravotto, G.; Gaudino, E.C.;Boffa, L.; Lévêque, J. M. ; Estager, J.; Bonrath, W. *Molecules,* **2008**, *13*, 149.

34. Huang, J. F.; Chen, P.Y.; Sun, I. W.; Wang, S. P. *Inorg. Chim. Acta,* **2001,** *320*, 7.

35. Letcher, T. Ed., *Development and Applications in Solubilty*. Cambridge: RSC Publishing, 2007.

36. Dong, K.; Zhang, S.; Wang, D.; Yao, X. *J. Phys. Chem. A* **2006**, *110*, 9775.

37. Zhu, S. S.; Staats, H.; Brandhorst, K.; Grunenberg, J.; Gruppi, F.; Dalcanale, E.; Luetzen, A.; Rissanen, K.; Schalley, C. A. *Angew. Chem., Int. Ed.* **2008**, *47*, 788.

38. Zhao, W.; Leroy, F.; Heggen, B.; Zahn, S.; Kirchner, B.; Balasubramanian, S.; ller- Plathe, M. F. *J. Am. Chem. Soc.* **2009***, 131*, 15825.

39. Gao, Y.; Zhang, L.; Wang, Y.; Li, H. *J. Phys. Chem. B* **2010,** *114*, 2828.

40. Yavari, I.; Kowsari, E. *Synlett.* **2008**, 897.

41. Bellina, F.; Bertoli, A.; Melai, B.; Scalesse, F.; Signori, F.; Chiappe, C. *Green Chem.* **2009**, *11*, 622.

42. Wang. Y.; Jiang, D.; Dai, L. *Catal.Commun.***2008**, *9*, 2475.

43. Wang, L.; Li, H.; Li, P. *Tetrahedron,* **2009**, *65*, 364.

44. Shen, J.; Wang, H.; Liu, H.; Sun, Y.; Liu, Z. *J. Mol. Catal. A: Chem*. **2008**, *280,* 24.

45. Wang, W.; Shao, L.; Cheng, W.; Yang, J.; He, M. *Catal. Commun*. **2008**, *9*9, 337.

46. Xing, H.; Wang, T.; Zhou, Z. ; Dai, Y. *Ind. Eng. Chem. Res.* **2005**, *44,* 4147.

47. Luo, S.; Mi, X.; Zhang, L.; Liu, S.; Xua, H.; Cheng, J.P. *Tetrahedron* **2007**, 63, 1923.

48. Tempel, T. J. Us patent 7282084 (2007).

49. Hapiot, P.; Lagrost, C. *Chem. Rev.* **2008**, *108,* 2238.

50. (a) Anderson, J. L.; Ding, J.; Welton, T.; Armstrong, D.W. *J. Am. Chem. Soc*. **2002**, *124,* 14247. (b) Lagrost, C.; Preda, L.; Volanschi, E.; Hapiot, P. *J. Electroanal. Chem.* **2005**, *585*, 1. (c) O'Toole, S.; Pentlavalli, S.; Doherty, A. P. *J. Phys. Chem. B* **2007**, *111*, 9281.

51. Dupont, J.; Consorti, C. S.; Saurez, P. A. Z.; de Souza, R. F. *Org. Synth*. **2002**, *79*, 236.

52. Dupont, J.; Consorti, C. S.; Saurez, P. A. Z.; de Souza, R. F. *Org. Synth*. **2004**, *10*, 184.

53. Gordon, C. M.; McLean, A. J.; Dunkin, I. R. in Ionic Liquids as Green Solvents: Progress and Prospects; Rogers, R. D.; Seddon, K. R. Eds.; ACS Symposium Series 856; American Chemical Society: Washington, DC, 2003.

54. Varma, R. S.; Namboodri, V. V. *Chem. Commun.* **2001**, 643.

55. Deetlefs, M.; Sedon, K. R. *Green Chem*. **2003**, *5,* 181.

56. Leveque, J. M.; Luche, J-L.; Petrier, C.; Roux, R.; Bonrath, W. *Green Chem*. **2002**, *4*, 357.

57. Leveque, J. M.; Desset, S.; Suptil, J.; Fachinger, C.; Draye, M.; Werner, B.; Cravotto, G. *Ultrason. Sonochem*. **2006**, *13*, 189.

58. Varma, R. S.; Namboodri, V. V. *Org. Lett*. **2002**, *4*, 3161.

59. Earle, M. J.; Gordon, C. M.; Plechkova, N. V.; Seddon, K. R.; Welton, T. *Anal*. *Chem*. **2007**, *79*, 758.

60. Nockemann, P.; Binnemans, K.; Driesen, K. *Chem. Phys. Lett*. **2005**, *415,* 131.

61. Burrell, A. K.; Del Sesto, R. E.; Baker, S. N.; McCleskey, T. M.; Baker, G. A. *Green Chem.* **2007**, *9*, 449.

62. Page, P. M.; McCarty, T. A.; Baker, G. A.; Baker, S. N.; Bright, F. V. *Langmuir* **2007**, *23*, 843.

63. Handy, S. T.; Okello, M.; Dickenson, G. *Org. Lett*. **2003**, *5*, 2513.

64. (a) Abbott, A. P.; Capper, G.; Davies, D. L.; Munro, H. L.; Rasheed, R. K.; Tambyrajah, V. *Chem. Commun*. **2001**, 2010. (b) Abbott, A. P.; Capper, G.; Davies, D.L.; Rasheed, R. K.; Tambyrajah, V. *Green Chem.* **2002***, 4,* 24. (c) Abbott, A. P.; Capper, G.; Davies, D. L.; Rasheed, R. K.; Tambyrajah, V. *Chem. Commun*. **2003**, 70. (d) Wasserscheid, P.; Boesmann, A.; Bolm, C. *Chem. Commun*. **2002**, 200.

65. Fernandes, A. M.; Rocha, M. A. A.; Freire, M. G.; Marrucho, I. M. Coutinho, J. A. P; Santos, L. M. *J. Phys. Chem. B* **2011***, 115*, 4033.

66. Nobuoka, K.; Kitaoka, S.; Iio, M.; Harran, T.; Ishikawa, Y. *Phys. Chem. Chem. Phys.* **2007**, *9*, 5891.

67. Hunt, P. A.; Kirchner, B.; Welton, T. *Chem. Eur. J.,* **2006**, *12,* 6762.

68. Aggarwal, A.; Lancaster, N. L.; Sethi, A. R.; Welton, T. *Green Chem.* **2002**, *4*, 517.

69. Znamenskiy,V.; Kobrak, M. N. *J. Phys. Chem. B* **2004**, *108,* 1072.

70. Dieter, K. M.; Dymek, C. J.; Heimer, N. E.; Rovang, J. W.; W&es, J. S. *J. Am. Chem. Soc.* **1988***, 110*, 2726.

71. Iwata, K.; Okajima, H.; Saha, S.; Hamaguchi, H. O. *Acc. Chem. Res.* **2007**, *40*, 1174.

72. Shigeto, S.; Hamaguchi, H. O. *Chem. Phys. Let.* **2006**, *427*, 329.

73. Raju, S. G.; Balasubramanian, S. *J. Phys. Chem. B* **2010**, *114,* 6455.

74. Lopes, J. A. C.; Pa´dua, A. A. H. *J. Phys. Chem. B* **2006**, 110, 3330.

75. Urahata ,S. M.; Ribeiro, M. C. C. *J. Chem. Phys.* **2004**, 120, 1855.

76. Wang, Y.; Voth, G. A. *J. Phys. Chem. B* **2006***, 110*, 18601.

77. Wang, Y. T.; Voth, G. A. *J. Am. Chem. Soc.* **2005**, *127,* 12192.

78. Triolo, A.; Russina, O.; Bleif, H. J.; Cola, E. D. *J. Phys. Chem. B* **2007**, *111,* 4641.

79. Deetlefs, M.; Hardacre, C.; Nieuwenhuyzen, M.; Padua, A. A. H. ; Sheppard, O.; Soper, A. K. *J. Phys. Chem. B* **2006**, 110, 12055.

80. Raju, S. G.; Balasubramanian, S. *Indian j. chem.* **2010**, *49*, 721.

81. Triolo, A.; Russina, O.; Fazio, B.; Appetecchi, G. B.; Carewska, M.; Passerini, S. *J. Chem. Phys.* **2009**, 130, 164521.

82. Dzyuba, S. V. and Bartsch, R. A. *Chem. Commun.* **2001***,* 1466.

83. Katayanagi, H.; Nishikawa, K.; Shimozaki, H.; Miki, K.; Westh, P. Koga, Y. *J. Phys. Chem. B* **2004***, 108,* 19451.

84. Xiao, D.; Hines, L. G. ; Jr. S. L.; Bartsch, R. A.; Quitevis, E. L. *J. Phys. Chem. B* **2009**, *113,* 6426.

85. Hamaguchi, H. O.; Saha, S.; Ozawa, R.; Hayashi, S. **2005**, 68.

86. Zhang, S.; Sun, N.; He, X.; Lu, X.; Zhang, X. *J. Phys. Chem. Ref. Data* **2006**, *35,*1475.

87. Zhang, J.; Bond, A. M. *Analyst* **2005**, *130*, 1132.

88. Bockris, J. O'M.; Reddy, A. K. N. Modern Electrochemistry 1970, Plenum Press, New York, Vol. 1. Ch.6.

89. Abbott, A. P. *ChemPhysChem* **2004**, *5*, 1242.

90. Jiqin, Z.; Jian, C.; Chengyue, L.; Weiyang, F. *J. Chem. Eng. Data* **2007**, *52*, 812.

91. Tokuda, H.; Hayamizu, K.; Ishii, K.; Susan, M. A. B. H.; Watanabe, M. *J. Phys. Chem. B* **2004**, *108,* 16593.

92. Tokuda, H.; Hayamizu, K.; Ishii, K.; Susan, M. A. B. H.; Watanabe, M. *J. Phys. Chem. B* **2005**, *109,* 6103.

93. Papaiconomou, N.; Salminen, J.; Lee, J. M.; Prausnitz, J. M. *J. Chem. Eng. Data* **2007***, 52,* 833.

94. Ohno, H., Ed.; in Electrochemical Aspects of Ionic Liquids John Wiley and Sons: Hoboken, NJ, **2005.**

95. Okoturo, O. O.; VanderNoot, T. J. *J. Electroanal. Chem*. **2004**, *568,* 167.

96. Rogers, E. I.; Silvester, D. S.; Poole, D. L.; Aldous, L.; Hardacre, C.; Compton, R.G. *J. Phys. Chem. C* **2008**, *112*, 2729.

97. Evans, R. G.; Klymenko, O. V.; Hardacre, C.; Seddon, K. R.; Compton, R.G. *J. Electroanal. Chem*. **2003**, *556*, 179.

98. Roland, C. M.; Bair, S.; Casalini, R.; *J. Chem. Phys*. **2006**, *125*, 124508.

99. Harris, K. R. *J. Chem. Phys.* **2009***, 131*, 054503.

100. Castner, E. W.; Wishart, J. F. *J. Chem. Phys.* **2010**, *132*, 120901.

101. Every, H. A.; Bishop, A. G.; Forsyth, M.; MacFarlane, D. *Electrochim*. *Acta* **2000**, *45*, 1279.

102. Every, H. A.; Bishop, A. G.; MacFarlane, D.; Oradd, G.; Forsyth, M. *Phys. Chem. Chem. Phys*. **2004**, *6,* 1758.

103. Noda, A.; Hayamizu, K.; Watanabe, M. *J. Phys. Chem. B* **2001**, *105,* 4603.

104. Tokuda, H.; Ishii, K.; Susan, M. A. B. H.; Tsuzuki, S.; Hayamizu, K.; Watanabe, M. *J. Phys. Chem. B* **2006**, *110*, 2833.

105. MacFarlane, D. R.; Forsyth, Maria.; Izgorodina, E. I.; Abbott, A. P.; Annata, G.; Frasera, K. *Phys. Chem. Chem. Phys*. **2009**, *11*, 4962.

106. Bonhote, P.; Dias, A. P.; Papageorgiou, N.; Kalyanasundaram, K.; Gratzel, M. *Inorg. Chem.* **1996***, 35*, 1168.

107. Fitchett, B. D.; Knepp, T. N.; Conboy, J. C. *J. Electrochem. Soc*. **2004**, *151*, 219.

108. McEwen, A. B.; Ngo, H. L.; LeCompte, K.; Goldman, J. L. *J. Electrochem. Soc*. **1999**, 146, 1687.

109. Dzyuba, S. V.; Bartsch, R. A. *ChemPhysChem* **2002**, *6*, 161.

110. Shimizu, K.; Gomes, M. F. C.; Pádua, A. A. H.; Rebelo, L. P. N.; Lopes, J. N. C. *J. Mol. Struct: THEOCHEM* **2010**, 946, 70.

111. Pison L.; Lopes, J. N. C.; Rebelo, L. P. N.; Padua, A. A. H. and M. F. C. Gomes J. Phys. Chem. B **2008**, 112, 12394.

112. Pádua, A. A. H.; Gomes, M. F. C.; Lopes, J. N. A. C. *Acc. Chem. Res.* **2007**, 40, 1087.

113. Lépez-Pastor, M.; Ayora-Cańada, M. A. J.; Valcárcel, M.; Lendl, B. *J. Phys. Chem. B* **2006**, *110,* 10896.

114. Chang, H. C.; Jiang, J. C.; Tsai, W. C.; Chen, G.C.; Lin, S. H. *J. Phys. Chem. B* **2006**, 110, 3302.

115. Cammarata, L.; Kazarian, S. G.; Salterb, P. A.; Welton, T. *Phys. Chem. Chem. Phys.* **2001**, *3*, 5192.

116. Lopes, J. N. C.; Gomes, M. F. C. Pa´dua, A. A. H. *J. Phys. Chem. B* **2006**, *110*, 3330.

117. Danten, Y.; Cabac, M. I. Besnard, M. *J. Phys. Chem. A* **2009**, *113*, 2873.

118. Fazio, B.; Triolo, A.; Di Marco, G. *J. Raman Spectrosc.* **2008***, 39,* 233.

119. Zhu, X.; Sun, H.; Zhang, D.; Liu, C. *J. Mol. Modell.* **2010**, 1-8.

120. Domanska, U.; Marciniak, A. *J. Chem. Eng. Data,* **2003**, *48*, 451.

121. Zafarani-Moattar, M. T.; Shekaari, H. *J. Chem. Eng. Data,* **2005**, *50*, 1694.

122. Zhai, C.; Wang, J.; Zhao, Y.; Tang, J.; Wang, H. *Z. Phys. Chem.* **2006**, *220*, 775.

123. Wu, X.; Liu, Z.; Huang, S.; Wang, W. *Phys. Chem. Chem. Phys.* **2005**, *7*, 2771.

124. Zhang, L.; Wang, Y.; Xu, Z.; Li, H. *J. Phys. Chem. B* **2009**, *113*, 5978.

125. Jiang, J. C.; Lin, K. H.; Li, S. C.; Shih, P. M.; Hung, K. C.; Lin, S. H.; Chang, H. C. *J. Chem. Phys.* **2011**, *134,* 044506.

126. Govinda, V.; Attri, P.; Venkatesu, P.; Venkateswarlu, P. *Fluid Phase Equilib*. **2011**.

127. Sadeghi, R.; Shekaari, H.; Hosseini, R. *Int. J. Thermophys.* **2009**, *30,* 1491.

128. Tokuda, H.; Hayamizu, K.; Ishii, K.; Susan, M. A. B. H.; Watanabe, M. *J. Phys. Chem. B* **2004**, *108*, 16593.

129. Tokuda, H.; Hayamizu, K.; Ishii, K.; Susan, M. A. B. H.; Watanabe, M. *J. Phys. Chem. B* **2005**, *109*, 6103.

130. Seddon, K. R.; Stark, A.; Torres, M. J. *Pure Appl. Chem*. **2008**, *72,* 2275.

131. Li, W.; Zhang, Z.; Han, B.; Hu, S.; Xie, Y.; Yang, G. *J. Phys. Chem. B* **2007**, *111,* 6452.

Chapter 2

Association of Ionic Liquids in solution: Conductivity studies of [bmim][Cl] and [bmim][PF_6] in binary mixture of acetonitrile + methanol

Prelude

Concentration dependence of molar conductance for 1-butyl-3-methylimidazolium chloride ([bmim][Cl]) and 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) in binary mixtures of acetonitrile + methanol was investigated to explore the ion association behavior of imidazolium based ionic liquids. The limiting molar conductance (Λ_m^0), association constants (K_a^0) and the maximal distance between the oppositely charged ions in ion pair formation (R_{ij}) in the mixed solvent mixtures were evaluated following the framework of Barthel' s low-concentration chemical model (lcCM). It is reported that the investigated ILs display opposing trends in ion association behavior with change in binary solvent composition. The results are discussed in the light of ionic liquid and solvent specific ion-solvent and ion-ion interactions in the mixed solvent systems.

2.1. Introduction

Ionic liquids (ILs) in recent years have been attracting considerable attention from the scientific and industrial community in general and electrochemists in particular [1-4]. On account of their unique and tunable inherent physicochemical characteristics, ILs are now increasingly being used as reaction media, novel solvents for separation and analysis and as electrolytes in electrically, photochemically or chemically driven electrochemical setups [1-3, 5]. A comprehensive understanding of ion-ion and ion-solvent interactions in ILs and IL + co-solvent mixtures is must to achieve the desired characteristics of ILs in such systems. Among the large variety of ILs known till date, those based on imidazolium cations are probably the most intensively investigated and used, perhaps on account of their high air, moisture, thermal, electrochemical and chemical stability [3, 6]. The imidazolium based ILs are very complex innovative systems which are capable of interacting simultaneously with other molecules via dispersive, ionic, π-π, dipolar and hydrogen bonding interactions. These interactions when understood completely can be intelligently made use of in changing the course of chemical or electrochemical reactions through a proper use of ILs as solvents or electrolytes [7–10, 4, 11]. In view of the recent developments related to theory of conductance of electrolyte solutions [12, 13], conductometry is increasingly being used as a reliable, affordable and convenient bench level technique that provides valuable information about the ion-ion and ion-solvent interactions in electrolyte solutions. In view of the fact that mixed solvents enable the variation of properties such as dielectric constant and viscosity over a wide range, conductometric investigations of ILs in mixed solvent systems seems very interesting. Such studies are expected to shed new light on the mechanism and extent of ion-ion and ion-solvent interactions and solvation of ILs in solutions, wherein nonelectrostatic forces contribute significantly to the equilibrium and dynamic characteristics of constituent ions.

In view of the above mentioned facts we carried detailed conductometric investigations of 1-butyl-3-methylimidazolium chloride ([bmim][Cl]) and 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) in binary mixtures of acetonitrile + methanol mixed solvent systems. The studies were aimed at exploring the solvent and ion specific transport and ionic association characteristics of imidazolium based IL electrolyte solutions. Such studies are of considerable interest for the optimal and desired use of IL + mixed organic solvent systems in high energy batteries [14] and other electrochemical systems and for understanding the ion pair effect and organic reaction mechanisms [7, 8, 15].

2.2. Experimental

Acetonitrile (GR grade, 99.9%) and Methanol (GR grade, 99.9%) were purchased from Merck, India and purified following reported standard methods [16]. Electrochemical purity grade ILs used were synthesized following a two step procedure [17] as reported earlier [7, 8]. Briefly, in the first step 1-methylimidazole was refluxed with n-butyl chloride for 90 hrs under argon atmosphere for the synthesis of 1-butyl-3-methylimidazolium chloride as a white crystalline solid. In the next step the halide anion was exchanged with $[PF_6]^-$ on treatment with HPF_6. The ILs were vacuum dried and stored in desiccators under inert atmosphere and were characterized through ^{1}H-NMR, mass spectrometry and ^{13}C-NMR spectroscopy. The water content of dried ILs was less than 50 ppm, as analyzed by Karl Fischer titration. Binary solvent mixtures were prepared by mixing the required volumes of acetonitrile and methanol. The value of relative dielectric constant (ε_r) and coefficient of viscosity (η) of the solvent mixtures were obtained by interpolation of the literature reported [18] values of these parameters for acetonitrile + methanol mixtures at 298.15 K. The physical properties of the used composition mixtures are listed in Table 2.1.

Stock solutions of ILs were prepared by adding their required mass into the mixed solvent system to be investigated. Conductivity was recorded by a digital microprocessor based conductivity meter (CYBERSCAN CON 500) from Eutech instruments having sensitivity of 0.1 μS cm^{-1}; details are reported elsewhere [19]. During data processing the conductivity of solvent system was subtracted from the recorded values to obtain IL only conductivity in the solution. Numerical calculations and data fitting was performed through codes written in Origin 8.0 (Microcal Software Inc.)

Table 2.1: Dielectric constant (ε_r) and viscosity (η) of Methanol (MeOH) + Acetonitrile (MeCN) mixtures at 298.15 K, the values were calculated by interpolation of the literature reported [18] values for these parameters for acetonitrile + methanol mixed solvent systems

solvent mixture (W_{MeOH} %)	ε_r	η/m Ps s
0	35.96	0.3413
10	35.62	0.3421
20	35.37	0.3486
30	35.17	0.3613
40	34.99	0.3791
50	34.78	0.4012
60	34.52	0.427
70	34.19	0.4559
80	33.78	0.4874
90	33.29	0.521
100	32.63	0.5438

2.3. Results and Discussions

The concentration dependent molar conductance values (Λ_m) for [bmim][Cl] and [bmim][PF_6] in acetonitrile + methanol mixtures with changing weight fractions of methanol (w_{MeOH}) are presented as Figure 2.1. The conductance results were analyzed by following the framework of Barthel's low-concentration chemical Model (lcCM) [13]. According to this framework, the molar conductance Λ_m of a partially associated strong electrolyte in solution is given by

$$\Lambda_m = \square\, (\Lambda_m^0 - S(\square\, C)^{1/2} + E \square\, C ln(\square\, c) + J_1 \square\, C - J_2(\square\, C)^{3/2} \quad (2.1)$$

$$K_a^0 = \frac{1-\square}{\square^2 C(y_\pm)^2} \qquad (2.2)$$

$$y_\pm = \exp\left(\frac{-k_D q}{1+ k_D R}\right) \qquad (2.3)$$

$$k_D = (16\pi N_A q \,\square\, C)^{1/2} \qquad (2.4)$$

$$q = \frac{e^2}{8\pi\varepsilon_o\varepsilon_r k_B T} \qquad (2.5)$$

where Λ_m^0 is the molar conductivity at infinite dilution, (1-α) is the fraction of charged ions bound as ion pairs and K_a^0 is the standard state association constant.

The activity coefficient of the free cation (y_+) and free anion (y_-) are related as

$$(y_\pm)^2 = y_+ y_- \qquad (2.6)$$

k_D is the Debye parameter, e is the proton charge, ε_o the permitivity of the vacuum and ε_r the dielectric constant of solvent system. T is the Kelvin temperature and N_A and k_B are the Avogadro's and Boltzman constants respectively.

According to the lcCM model two oppositely charged ions are counted as ion pairs if the inter-ionic distance, r, is within the limits of $a < r < R$, where a is the distance of closest approach and taken as the sum of their crystallographic radii ($a = a_+ + a_-$) and R the upper limit of distance of approach for ion pair formation taken as

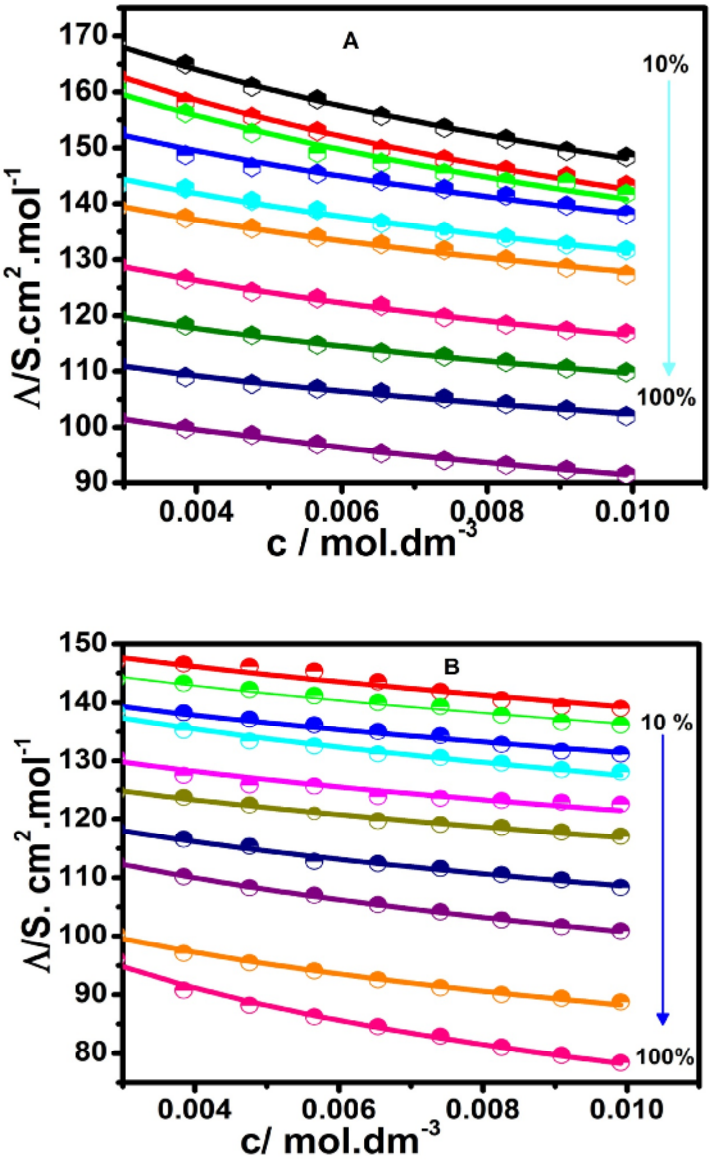


Fig.2.1. Molar conductivities (Λ) of (A) [bmim][Cl] and (B)[bmim][PF$_6$] in methanol + acetonitrile mixtures in the composition range 10 to 100 % methanol (by volume) in step of 10%. Lines show the results of the lcCM calculations.

$R = a + n.s$ .Expressions for the coefficients S, E, $J_1$and J_2 as given by Barthel et al. [13] are listed in Table 2.2. The limiting slope S and the parameter E are fully defined by the known values of ε_r and η (Table 2.1) of the solvent system. The coefficients $J_1$and J_2 are both functions of distance parameter *R*, representing the distance up to which oppositely charged ions can move as freely moving particles in solution. In the present study data analysis was carried out by a non-linear least square fitting procedure with the coefficients S, E and J_1 preset to their calculated values and with Λ_m^0, K_a^0 and J_2 as the adjustable parameters. For these calculations a_+ = 0.330 nm [20], a_{Cl^-}= 0.181 nm [13] and $a_{PF_6^-}$ = 0.256 nm [21] were used. In the calculations for *R*, *n* was taken as 1 and in view of the literature reports [22] s = 0.47 nm for methanol and s = 0.58 nm for acetonitrile, s for the mixed solvent systems employed in present study was calculated through the equation;

$$s = X_{MeOH}.0.47 + (1 - X_{MeOH}).0.58 \tag{2.7}$$

X_{MeOH} is the mole fraction of methanol in the mixed solvent system.

Figure 2.1 compares the experimental Λ_m values for [bmim][Cl] (Figure 2.1(A)) and for [bmim][PF_6] (Figure 2.1(B)) solutions in the mixed solvent systems of changing composition with the results of the lcCM calculations (equations 2.1-2.5). The estimated values for Λ_m^0 together with the K_a^0 and the distance parameter R_{ij} calculated from the last term of equation 2.1 are presented in Table 2.3. The value of R_{ij} can be used as a compatibility control of the fit as it should be similar to the input radius $R = a + n.s.$ chosen for calculation of J_2 and $y_\pm$. As evident from the Table 2.3, R and R_{ij} are in good agreement for both the ILs. The values of Λ_m^0 estimated for the investigated ILs in the present work seem a bit higher than those reported in methanol and acetonitrile in earlier reports [23-25].

Table 2.2: Coefficients of the conductance equation

$$S = S_1\Lambda_m^0 + S_2$$

$$S_1 = 0.82043.\,10^6\;.\,z^3(\varepsilon\,T)^{-3/2}$$

$$S_2 = 82.484.\,10^{-5}.\,z^2.\,(\varepsilon T)^{-1/2}\,.\,\eta^{-1}$$

$$E = E_1\Lambda_m^0 - 2E_2$$

$$E_1 = 2.94227.\,10^{12}.\,z^6.\,(\varepsilon T)^{-3}$$

$$E_2 = 0.433204.\,10^3.\,z^5.\,(\varepsilon T)^{-2}\,.\,\eta^{-1}$$

$$J_1 = \sigma_1\Lambda_m^0 + \sigma_2$$

$$J_2 = \sigma_3\Lambda_m^0 + \sigma_4$$

$$\sigma_1 = 2.\,E_1.\left(\frac{2b^2+2b-1}{b^3} + 0.9074 + ln\left(0.50290.\,10^{12}.\,z.\,(\varepsilon T)^{-1/2}R\right)\right)$$

$$\sigma_2 = E_2.\left(\frac{35}{3b} + \frac{2}{b^2} - 2.0689 - 4.\,ln\left(0.50290.\,10^{12}.\,z.\,(\varepsilon T)^{-1/2}R\right)\right)$$

$$\sigma_3 = E_1.\left(0.50290.\,10^{12}.\,z.\,(\varepsilon T)^{-1/2}R\right)\left(0.6094 + \frac{4.4748}{b} + \frac{3.8284}{b^2}\right)$$

$$\sigma_4 = E_2\left(0.50290\,.\,10^{12}.\,z.\,(\varepsilon T)^{-1/2}R\right)\;\left(-\,1.3693 + \frac{34}{3b} - \frac{2}{b^2}\right)$$

with $b = 16.709.\,10^{-6}.\,z^2.\,(\varepsilon T)^{-1}R^{-1}$ and $z = z_+ = |z_-|$

However the data presented in earlier reports related to conductance of ILs in molecular solvents [23-26] indicate a significant variation in the values of Λ_m^0, reported for same ILs in same solvents. Such discrepancy in the reported values of Λ_m^0 is being attributed to (a) estimation of Λ_m^0 through use of different conductivity equations and (b) the use of concentration data in different ranges for the estimation of said values. As clearly seen from the entries in Table 2.3, the values of Λ_m^0 for [bmim][PF_6] and [bmim][Cl] fall with the increase in methanol fraction in the mixed solvent system. This is in line with the decrease in the dielectric constant of solvent and increase in its viscosity with decrease of acetonitrile fraction in the solvent system. Nevertheless it was observed that the Walden product ($\Lambda_m^0 .\eta$) does not remain constant as expected in case where ion-solvent interactions do not vary with changing composition of solvent [12]. This implies that the changing mole fractions of acetonitrile and methanol lead to change in ion-solvent interactions in present case. Similar observations have been made for RTILs in earlier studies [27]. Interestingly for all solvent compositions (except at $w_{MeCN} =0$) investigated, Λ_m^0 values for [bmim][Cl] were found to be higher than the corresponding values for [bmim][PF_6]. It is also seen that the relative difference the observed variations in Λ_m^0 can be attributed to differences in solvation and mobility characteristics of Cl^- and $[PF_6]^-$ in the mixed solvent systems. As has been reported in literature [28], while methanol interacts strongly with anions in such systems, acetonitrile on the contrary interacts preferentially with the imidazolium cation suggesting that the observed variations in Λ_m^0 are anion driven. In the light of our observations, it can be safely argued that while in acetonitrile the mobility of Cl^- is more than that for $[PF_6]^-$, in methanol the reverse is true. This trend suggests that greater the size of anion, smaller is its mobility in

Table 2.3. Association constant (K_a^0), Limiting molar conductivities (Λ_m^0), input radii (R) and parameters (R $_{ij}$) for [bmim][Cl] and [bmim][PF$_6$] in Acetonitrile + Methanol mixed solvent systems at 298.15 K.

solvent mixture (W_{MeOH} %)	K_a^0 (dm^3.mol^{-1})	Λ_m^0 (S. cm^2.mol^{-1})	R (nm)	R $_{ij}$ (nm)
		[bmim][Cl]		
0	88.5	196.52	1.089	1.093
10	58.3	189.27	1.077	1.092
20	48.9	184.46	1.064	1.061
30	45.3	179.89	1.052	1.052
40	35.4	167.41	1.04	1.037
50	29.8	158.35	1.029	1.033
60	27.8	152.41	1.019	1.022
70	33.9	142.39	1.009	1.012
80	28.4	131.16	0.999	1.005
90	25.8	120.96	0.99	1.974
100	20.7	114.56	0.981	1.966
		[bmim][PF$_6$]		
0	27	158.52	1.166	1.184
10	15.1	156.8	1.152	1.153
20	14.8	153.24	1.139	1.137
30	15.7	148.26	1.127	1.125
50	19	139.14	1.108	1.103
60	19	133.89	1.094	1.094
70	26.1	128.39	1.084	1.088
80	37.9	124.9	1.074	1.083
90	45.5	112.33	1.065	1.071
100	100.8	116.46	1.056	0.996

acetonitrile, while in methanol the reverse is true, which we attribute to differing ion solvating abilities of the two solvents. In view of its smaller size Cl^- has a higher charge density than that of $[PF_6]^-$, thus the former interacts with methanol more than later which is more solvated by acetonitrile on account of its higher polarizability.

More interesting findings of the present investigations are the relative magnitudes of the K_a^0 and its variations in the mixed solvent systems for the two ILs with common cation. As seen from Table 2.3, while at lower fractions of methanol in the mixed solvent system the K_a^0 of [bmim][Cl] was higher than that observed for [bmim][PF_6], in methanol rich solvent systems the reverse was observed. Besides while for [bmim][Cl], K_a^0 value decreases with increase of methanol fraction in the mixed solvent system, for [bmim][PF_6] an increasing trend was observed. While the trend observed for variation of K_a^0 of [bmim][Cl] with the change in content of methanol fraction in the solvent system is quite expected in light of the resulting variations in ε_r, the trend observed in case of [bmim][PF_6] is quite unexpected. We observed a similar trend for the IL [bmim][BF_4]. From molecular dynamic studies [28] it has been established that hydrogen bonding solvents like methanol strongly solvate halide ions through hydrogen bonds, while non hydrogen bonding solvents like acetonitrile interact more strongly with easily polarizable solutes through ion-dipole interactions. In light of these reports, on account of its smaller size and higher charge density, Cl^- is expected to show a weaker ion-solvent but stronger ion-ion interactions with its imidazolium counterpart and hence larger K_a^0 in solvents like acetonitrile. However in solvents like methanol where Cl^- is expected to be strongly solvated due to its ability to get engaged in strong hydrogen bonding, opposite trend is expected. For [bmim][PF_6], where anion is more polarizable, the ion-solvent interactions are expected to be stronger and hence K_a^0 values lower than for [bmim][Cl] homologue in solvents like acetonitrile. However, in methanol the ion-ion interactions for [bmim][PF_6] are expected to be stronger and hence expected to show larger K_a^0 than its chloride counterpart. In light of these facts we propose that for IL with smaller anions, like [bmim][Cl], the stronger ion-ion plus weak ion-solvent interactions are replaced by weaker ion-ion and stronger ion-solvent interactions with increase of methanol fraction in the acetonitrile + methanol solvent system which is responsible for the resulting decrease in K_a^0. On the contrary in ILs with larger anions like [bmim][PF_6], the weaker ion-ion plus stronger ion-solvent interactions are replaced by stronger ion-ion and weaker ion-solvent interactions with increase of methanol fraction in the acetonitrile + methanol mixed solvent system resulting in the observed variations in K_a^0 with changing fraction of methanol. This is in agreement with the report by Mohammed et al. [29] wherein it has been proved that while the interaction energy for [bmim][PF_6] + acetonitrile system is negative, for [bmim][PF_6] + methanol the same is positive. Present studies are an excellent example of tuning the physic-ochemical characteristics of closely related IL electrolytes through alterations in solvophobicity achieved through similar variations in the composition of the mixed solvent systems.

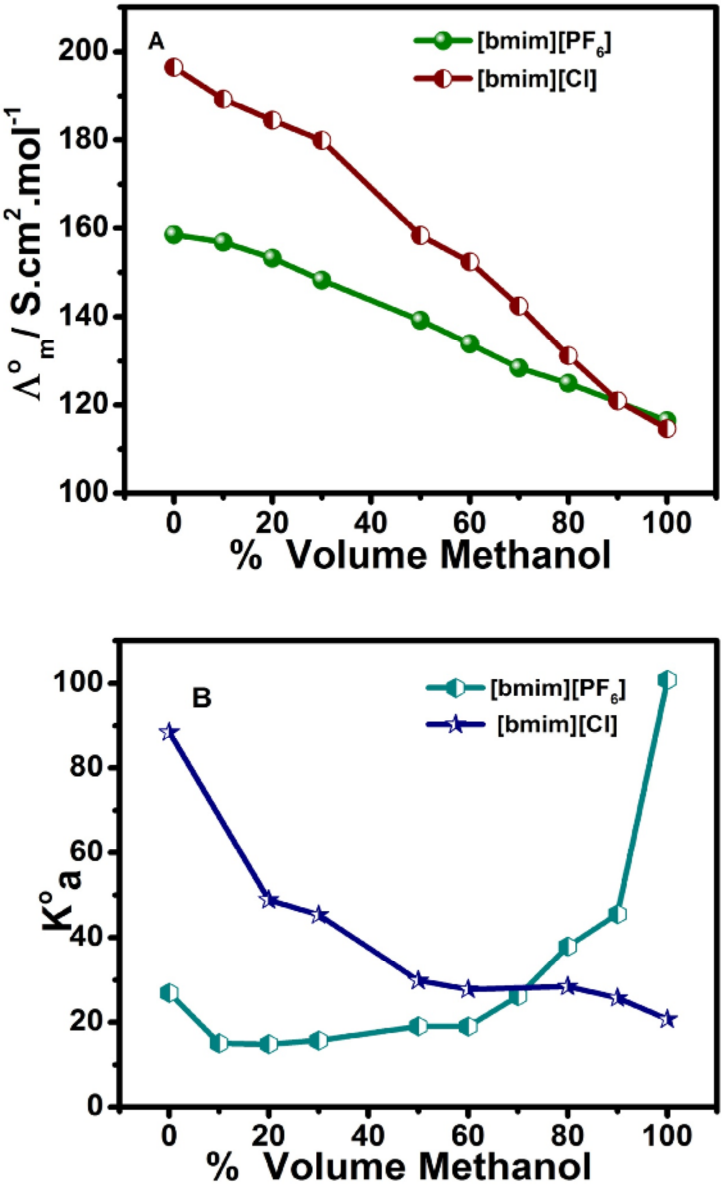


Fig. 2 .2. (A) Limiting ion conductance (Λ_m^0) and (B) ion association constant (K_a^0) of [bmim][Cl] and [bmim][PF$_6$] in methanol + acetonitrile mixtures in the composition range 0 to 100 % methanol (by volume) in step of 10%.

2.4. Conclusion

Conductometric investigations of imidazolium based ILs viz 1-butyl-3-methylimidazolium chloride ([bmim][Cl]) and 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) in binary mixtures of acetonitrile + methanol were performed. The data analyzed with Barthel's low-concentration chemical model establish that the conducting behavior and ion association is highly specific to the nature of IL and composition of mixed solvent system. Thus while in methanol ion-association and Λ_m^0 is more for [bmim][PF_6] than [bmim][Cl], in acetonitrile the opposite was observed. Also, with increase in methanol fraction in acetonitrile + methanol mixed solvent systems, while Λ_m^0 was observed to decrease for both the ILs investigated, opposing trends were observed in the variation of K_a^0. For [bmim][PF_6] there was an increase in K_a^0 while for [bmim][Cl] a decrease in the said value was observed.

References

1. Welton, T. *Chem. Rev*. **1999**, *99*, 2071.
2. Ohno, H.; (Ed) Electrochemical Aspects of Ionic Liquids; John Wiley and Sons: Hobokin. NJ (**2005**).
3. Hapiot, P.; Lagrost, C. *Chem. Rev*. **2008**, *108*, 2238.
4. Lagrost, C.; Hapiot, P.; Vaultier, M. *Green Chem*. **2005**, *7*, 468.
5. Hans, X. X.; Armstrong, D. W. *Acc. Chem. Res.* **2007**, *40,* 1079.
6. Weingartner, H. *Angew. Chem., Int. Ed.* **2008**, *47*, 654.
7. Bhat, M. A.; Chaudhari, V. R.; Ingole, P. P.; Haram, S. K. *J. Phys. Chem. B* **2009**, *113*, 2848.
8. Bhat, M. A.; Ingole, P. P. Electrochemica Acta http.// dx.doi.org/10.1016/ j. electacta, 2012.03.115.**(2012)**.
9. Behar, D.; Gonazalez, C.; Neta, P. *J. Phys. Chem. A* **2001**, *105*, 7607.
10. Grodkowski, J.; Neta, P.; Wishart, J. F. *J. Phys. Chem*. A **2003**, *107*, 9794.
11. Matsuoka, H.; Nakamoto, H.; Susan, M. A. B. H.; Watanabe, M. *Electrochim. Acta*. **2005**, *50*, 4015.
12. Robinson, R. A.; Stokes, R. H.; Electrolyte Solutions, 2nd Revised Edition, Dover Publications, INC, New York, **2002**.
13. Barthel, J. M. G.; Krienke, H.; Kunz, W. Physical chemistry of electrolyte solutions- Modern aspects, Stinkopff, Springer: Darmstatdt, New York, **1998**.
14. Aurbach, D.; Non-aqueous Electrochemistry, Marcel Dekker, Inc.; New York, **1999**.
15. Korm, J. A.; Petty, J. T.; Streitweser, A. *J. Am. Chem. Soc*. **1993**, *115*, 8024.
16. Perrin, D. D.; Armarego, W. L. F.; Purification of Laboratory Chemical, Pregamon Press, Great Britian, 3rd Edition, **1998**.
17. (a) Dupont, J.; Consorti, C. S.; Saurez, P. A. Z.; deSouza, R. F. *Org. Syn*. **2002**, *79,* 236. (b) Dupont, J.; Consorti, C. S.; Saureez, P. A. Z.; deSouza, R. F. *Org. Syn*. **2004**, *10,* 184.
18. (a) Nikam, P. S.; Shirsat, L. N.; Hasan, M. *J. Chem. Eng. Data* **1998***, 43,*

732.(b) Cunninggham, G. P.; Vidulich, G. A.; Kay, R. I. *J. Chem. Eng. Data* **1967**, 12, 336.

19. Bhat, M. A.; Dar, A. A.; Rasheed, P.I.; Rather, G. M. *J. Chem. Thermodyn.* **2007**, *39,* 1500.

20. Tokuda, H.; Hayamizu, K.; Ishii, K.; Susan, M. A. B. H. *J. Phys. Chem. B* **2004**, *108,* 16593.

21. Katsuta, S.; Imai, K.; Kuda, Y.; Takeda, Y.; Seki, H.; Nakakoshi, M. *J. Chem. Eng. Data* **2008**, *53,* 1528.

22. Barthel, J.; Neudar, R.; Shro der, in Electrolyte Data Collection, Part 1c: Conductivities, Transference Numbers, Limiting Ionic Conductivities of Solutions of Aprotic, Protophobic Solvents. I: Nitriles, ed. R. Eckermann and G. Kreysa. Dechema, Frankfurt, vol. XII **(1996).**

23. Bester-Rogac, M.; Hunger,J.; Stoppa, A.; Buchner, R. *J. Chem. Eng. Data* **2010**, 55, 1799.

24. Wang, H.; Wang, J.; Zhang, S.; Pei, Y.; Zhuo, K. *ChemPhysChem* **2009**, *10,* 17588.

25. Bester-Rogac, M.; Stoppa, A.; Hunger, J.; Hefter, G.; Buchner, R. *Phys. Chem. Chem. Phys.* **2009***, 10*, 2516.

26. Ali, M.; Sarkar, A.; Tariq, M.; Ali, A.; Pandey, S. *Green Chem.* **2007**, *9,* 1252.

27. Shekaari, H.; Mansoori, Y.; Kazempour, A. *Electrochim. Acta* **2012**, *62,* 104.

28. Hanke, C. G.; Atamas, N. A.; Lynden-Bell, R. M. *Green Chem*. **2002**, *4*, 107.

29. Zafarani-Moattar, M.T.; Shekaari, H. *J. Chem. Thermodyn.* **2006**, *38*, 1377.

Chapter 3

Effect of co-solvents on Bulk and Interfacial Characteristics of N- alkylimidazolium based ionic liquids [bmim][BF$_4$] and [bmim][PF$_6$]

Prelude

A systematic study of the electrical conductivity and surface tension of solutions of imidazolium based Room Temperature Ionic Liquids (RTILs) viz. 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) and 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]) in co-solvents methanol and acetonitrile in the mole fraction range 0.05-0.7 at 298.15K is presented. The influence of co-solvents on bulk and interfacial characteristics of these ionic liquids is discussed in terms of structure-composition-property relations. An interesting outcome of the present work is that both RTILs retain their inherent structural characteristics upto a high dilution limit, and this limit is higher in acetonitrile than in methanol. The present findings establish that in comparison to methanol, acetonitrile is a better co-solvent that can be used for enhancing the transport parameters of RTILs for electrochemical and other applications.

3.1. Introduction

Recent physicochemical studies have established Room Temperature Ionic Liquids (RTILs) as a new class of compounds that can be used as novel green solvents, catalysts, additives, and lubricants[1-2]. Presently researchers from diverse fields are showing an increasing interest in studies aimed at the use of RTILs for different application fields, such as catalysis, organic synthesis, lubrication, thermal separation processes and electrochemistry [1-9]. Poor transport properties, high viscosity and low conductivity of RTILs are some of the major obstacles that limit the generalized use of RTILs in various applications. Working at high temperatures [10-12] and/or addition of a co-solvent that reduces the viscosity are the two options currently advocated by solution chemists to overcome the viscosity limitations of RTILs [13-15]. Interestingly RTIL + co-solvent mixtures in some cases have been reported to possess altered and in some cases improved physicochemical properties [16, 17]. The low viscosity of such mixtures ensures easy mass transport, thereby minimizing the energy requirements for the use of RTILs in many engineering processes. However, addition of a co-solvent always leads to loss in structural organization in RTILs which is the main factor responsible for many of their desirable characteristics. The above mentioned facts imply that the generalized use of RTILs as an alternative to conventional solvents in industry and academia demand detailed and comprehensive investigations about the physicochemical properties of the RTIL + co-solvent binary mixtures. In view of such demands and presaged potential applications, recently there has been a significant upsurge in the studies related to RTIL + co-solvent and RTIL mixtures and much useful data about physicochemical properties of such binary mixtures have been published [18-24].

The work presented in the current chapter was carried with an aim to study the impact of methanol and acetonitrile as co-solvents on the bulk and interfacial characteristics of [bmim][BF_4] and [bmim][PF_6] at 298.15K. The solvents methanol and acetonitrile were chosen not only because of their industrial/environmental relevance but also because of the different nature of the molecular interactions they can engage the chosen RTILs constituents into. Thus, while methanol interacts mainly through hydrogen bonding and is regarded as highly associating liquid, acetonitrile is a dipolar non-associating molecule.

3.2. Experimental

Chemicals

The RTILs [bmim][BF_4] and [bmim][PF_6] were synthesized, purified and dried according to the already reported procedure [25-27]. The synthesized RTILs were vacuum dried and stored in dessicators under inert atmosphere and were characterized through ^{1}H-NMR, mass spectrometry and ^{13}C-NMR spectroscopy. The water content of dried RTILs was less than 50 ppm, as analysed by Karl Fischer Titration. Acetonitrile (GR grade, 99.9%) and methanol (GR grade, 99.9%) were purchased from Merck India and purified following reported standard methods [28].

Measurements

The electrical conductivity of the solutions of varying RTIL mole fraction in the composition range (0.05-0.7) were measured by CYBERSCAN CON 500 conductivity meter from Eutech instruments having sensitivity of 0.1µS cm^{-1}.

Surface tension measurements of the solutions were made using K9 Tensiometer (Kruss, Germany) by the ring detachment technique. Temperature was maintained at 25°C (within ± 0.1° C) by circulating water from a HAAKE GH bath through the thermostatable vessel holder. The accuracy of the measurements was within ± 0.1dyne cm^{-1}.

3.3. Results and Discussion

3.3.1. Co-solvent Effects of Acetonitrile and Methanol on the Bulk Characteristics of [bmim][BF$_4$] and [bmim][PF$_6$]

Conductance studies have been proved to be one of the reliable means of extracting information about bulk characteristics of fluid phase conducting media. While Figure 3.1 depicts the relative influence of co-solvent mole fraction of (A) Acetonitrile (B) Methanol on the conductivity of two ionic liquids [bmim][BF$_4$] and [bmim][PF$_6$], Figure 3.2, on the other hand, compares the effect of the two co-solvents on the same ionic liquid (A) [bmim][BF$_4$] and (B) [bmim][PF$_6$]. Similar patterns of behaviour for conductivity verses composition have been reported earlier for RTIL + organic co-solvents [29-32] and have generated immense interest among researchers and many explanations and advantages associated with it have been proposed [32, 33]. A correlation of the observed variations of κ with mole fraction of RTILs in light of earlier reports [32, 33] indicate that a variety of factors, viz. formation of RTIL-cosolvent/ RTIL- supramolecular associates and entrapping of the cosolvent within the RTIL-supramolecular aggregates, whose fraction varies with mole fraction of the RTIL, can be responsible for the observed trends. While the electrical conductivity increases with the increase of RTIL concentration at low concentrations, the incremental electrical conductivity does not follow linear behaviour as anticipated for conventional electrolyte + solvent mixtures; instead it reaches a maxima and then falls again. Similar trends have been reported for the variation of κ with addition of co-solvents [32, 33].

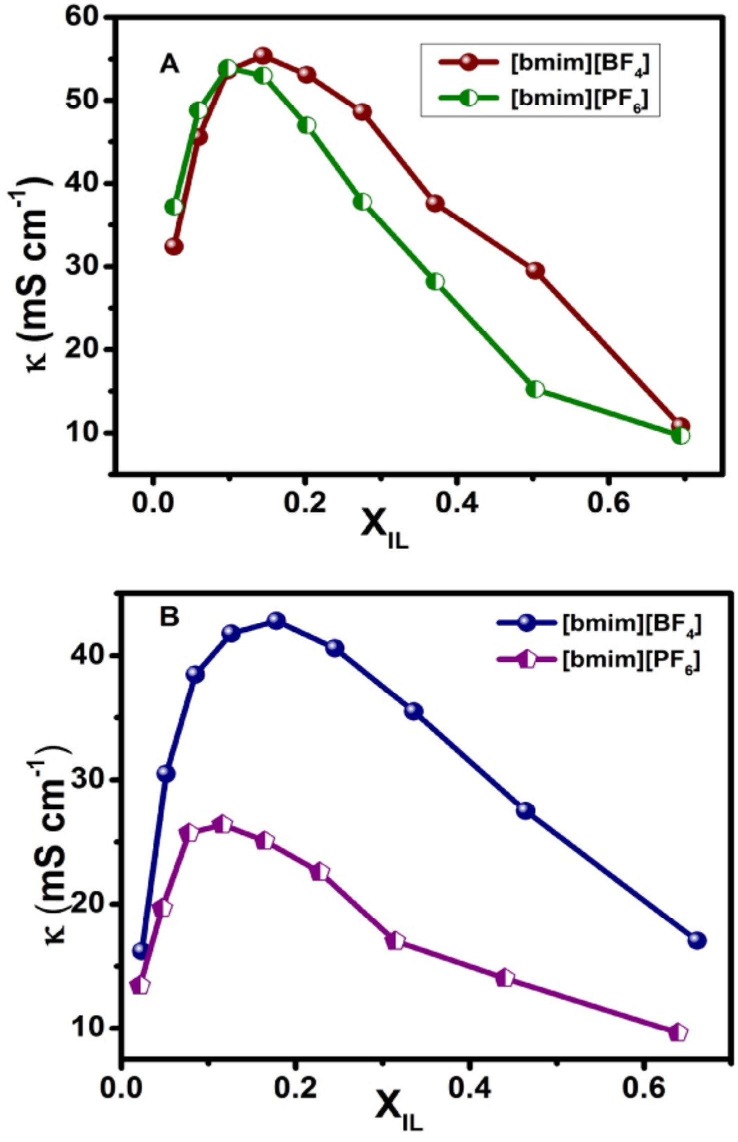


Fig.3.1. Specific conductance (κ) of [bmim][BF$_4$] and [bmim][PF$_6$] as a function of composition in (A) Acetonitrile and (B) Methanol respectively.

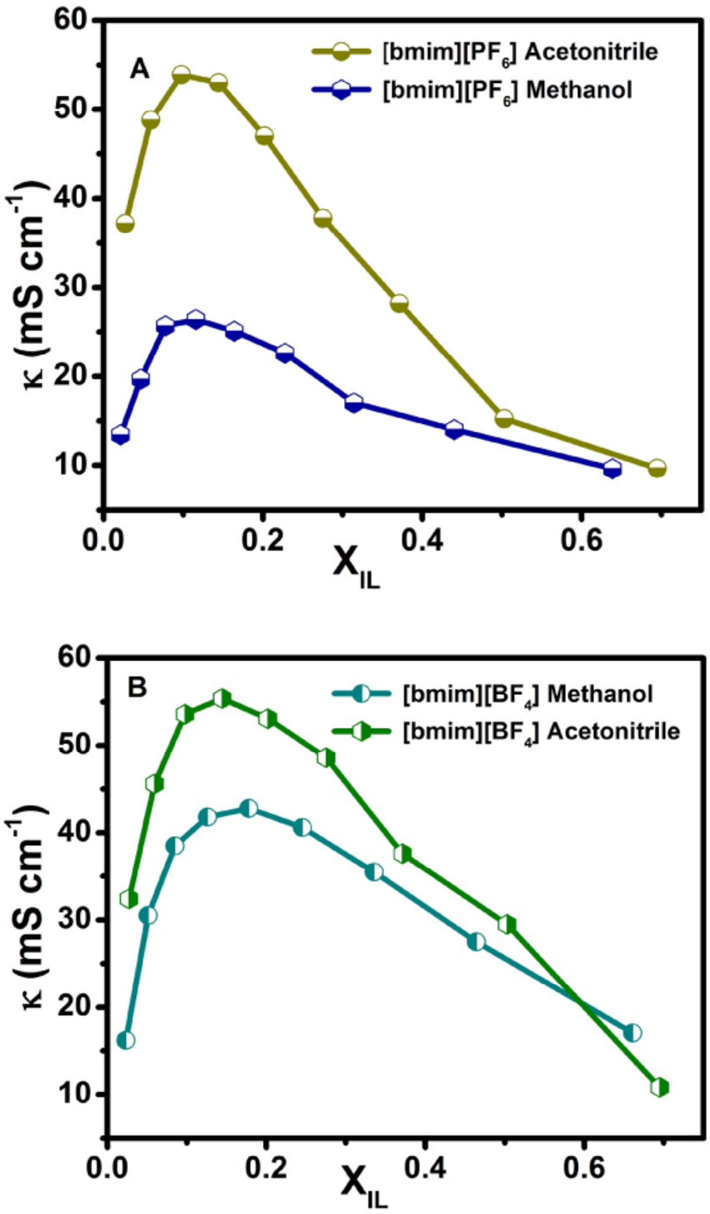


Fig.3.2. Specific conductance (κ) as a function of composition in Acetonitrile and Methanol (A) [bmim][PF$_6$] (B) [bmim][BF$_4$].

The observed variations of the conductivity with composition can be attributed to net effect of two competing factors:

(1) Increase in the number of charge carriers on account of dissociation of added RTIL (dominates the low concentration regime)

(2) Aggregation of ions that leads to increase in size and hence decrease in mobility and charge besides an increase in viscosity of the solution (dominates the RTIL rich regime).

The electrical conductivity has a relationship with ion mobility and number of charge carriers [19, 34] which is expressed as

$$\kappa = \Sigma n_i q_i \mu_i \qquad (3.1)$$

where n_i is the number of charge carriers of charge q_i and the ionic mobility μ_i of species *i*. In the low RTIL regime, the increase in conductivity due to increase in the number of charge carriers on account of increasing RTIL fraction overweighs the decrease in conductivity on account of their reduced mobility. However in the RTIL rich fraction the aggregate formation on account of strong ion-ion interactions becomes the dominant factor and hence leads to the overall decrease in the ionic mobility and hence conductivity [35-37].

The observed dependence of conductivity as a function of RTIL mole fraction in the organic co-solvents was analysed using Casteel-Amis equation [38, 39].

$$\kappa = \kappa_{max}(\frac{x}{x_{max}})^a exp[b(x - x_{max})^2 - \frac{a}{x_{max}}(x - x_{max}) \qquad (3.2)$$

where κ_{max} is the maximum conductivity and $x_{\mathrm{max}}$the corresponding mole fraction of RTIL and *a* and *b* are fitting parameters that depend upon the shape of the conductivity species. The fits to the equation are represented as lines in the Figure 3.3 and 3.4 and their corresponding fit parameters are presented in Table 3.1. All these observations indicate that acetonitrile better boosts the conductivity in the investigated RTILs with less impact on the structural organisation of the constituent ions in comparison to methanol. This is in agreement with the recently reported predictions by Chaban et al for imidazolium based RTIL + co-solvent mixtures [40].

Comparing the RTIL mole fraction corresponding to the maxima x_{max} gives a clear indication that the investigated RTILs maintain their structural aggregation characteristics down to lower concentration with acetonitrile as co-solvent than with methanol. This is of considerable importance for investigations wherein addition of co-solvents to the RTILs to enhance their transport characteristics without influencing the structural organization within the RTILs is desired.

A comparative analysis of the molar conductivity values indicate that specific conductance (κ) of RTILs in acetonitrile is more than that observed in methanol at all the compositions. This can be attributed to higher viscosity of methanol than acetonitrile which impedes the motion of ions. Additionally due to the lower dielectric constant of methanol, ion association in RTILs is expected to be more in methanol than that in acetonitrile.

According to the simulation studies by Padua et al. [41] the imidazolium based ionic liquids possess a characteristic nanostructural organization wherein nonpolar domains permeate the polar channels formed by imidazolium cations and anions. The incremental addition of co-solvents to the RTILs can lead to initial aggregation of these solutes in their preferred domains, that causes a disruption of the structural network. Further addition of solvent is expected to make the ions to aggregate into small clusters that in turn dissociate like conventional electrolytes at low concentration of RTIL. Both methanol (protic solvent) and acetonitrile (aprotic solvent) belong to the

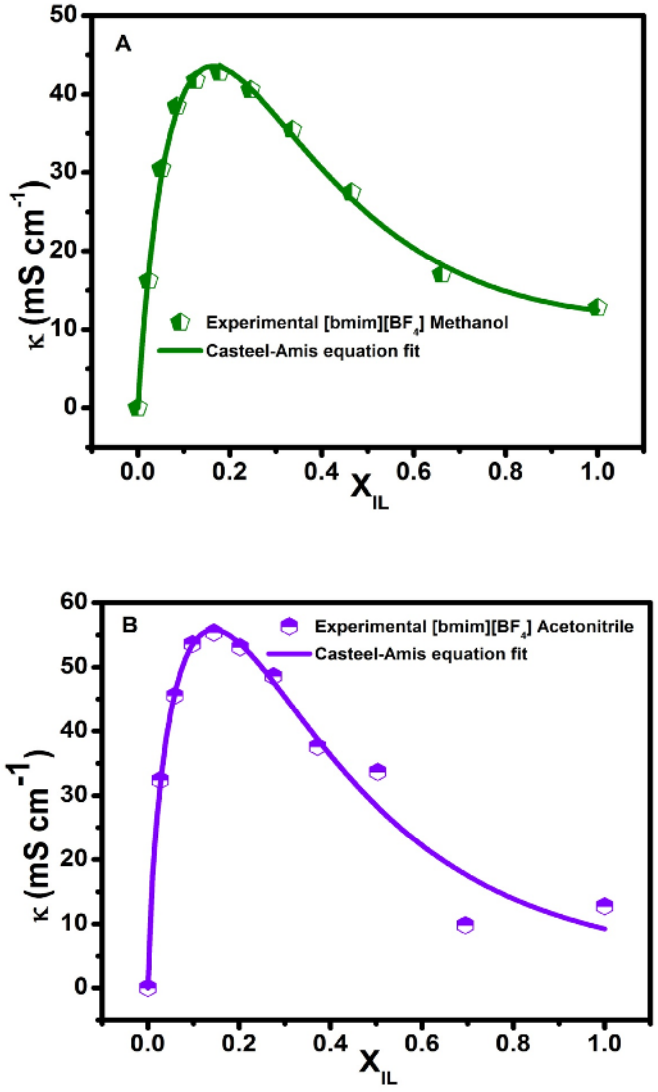


Fig.3.3. Conductivities (κ) of [bmim][BF$_4$] in (A) Methanol and (B) Acetonitrile at 298.15K. Experimental values represented by symbols and lines show Casteel Amis fit.

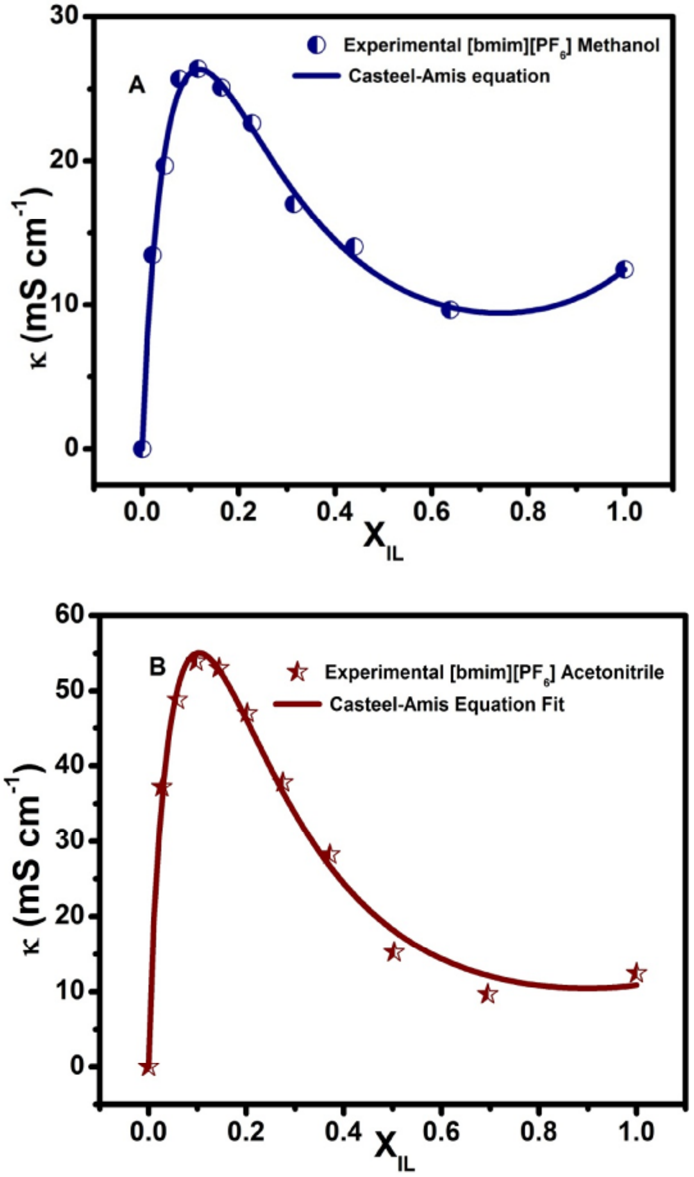


Fig.3.4. Conductivities (κ), [bmim][PF$_6$] in (A) Methanol and (B) Acetonitrile at 298.15 K. Experimental values represented by symbols and lines show Casteel Amis fit.

Table 3.1: Fitted Values of the Empirical Parameters, κ_{max}, x_{max}, a, b and the standard error (s) of [bmim][BF$_4$] and [bmim][PF$_6$] in Methanol and Acetonitrile according to the Empirical Casteel - Amis Equation at 298.15K.

RTIL		κ_{max} (mS cm$^{-1)}$	x_{max}	*a*	*B*
		Methanol			
[bmim][BF$_4$]		43.60	0.164	0.898	2.44
	s	0.543	0.00349	0.0478	0.3115
[bmim][PF$_6$]		26.37	0.118	0.840	4.79
	s	0.384	0.00273	0.0469	0.3123
		Acetonitrile			
[bmim][BF$_4$]		55.79	0.144	0.680	1.26
	s	2.252	0.01128	0.1496	1.2328
[bmim][PF$_6$]		55.08	0.103	0.779	4.20
	s	1.208	0.00386	0.0768	0.6253

co-solvent category that has significant affinity for both polar and non polar domains present in imidazolium based RTILs.It is on account of these factors that both these co-solvents are fairly soluble in [bmim][BF_4] and [bmim][PF_6] in all compositions. Simulation studies [42] have established that both acetonitrile and methanol interact strongly with the anions [BF_4]$^-$, the interaction being less directional in case of acetonitrile in comparison to methanol. It has been observed that while in methanol the -OH group interacts with the anion and the Me-group faces the imidazolium cation, in acetonitrile, the Me-group points preferentially towards the anion. Thus, it can be argued that compared to methanol, the interaction of imidazolium cation with the acetonitrile is stronger. Also in view of the higher Lewis basicity of [BF_4]$^-$ it is expected to interact more strongly with methanol in comparison to [PF_6]$^-$. In the light of these facts it can be safely argued that the dilution limit up to which RTIL can maintain the structural ordering of its constituents will be higher when acetonitrile is used as co-solvent in comparison to dilution with methanol. On similar grounds it can be assumed that the said limit will be higher in case of [bmim][BF_4] than in [bmim][PF_6]. This is also clearly evident from the data presented in Table 3.1. In view of the data reported therein it seems that compared to methanol, acetonitrile is a better co-solvent, that can be made use for enhancing the transport properties of imidazolium RTILs without affecting the structural ordering of the constituents.

3.3.2. Co-solvent effects of Methanol and Acetonitrile on the Interfacial Characteristics of [bmim][BF_4] and [bmim][PF_6]

Structural aspects of IL/solid, liquid and gas interface are of prime importance in many areas related to applications of such interfaces [43-45]. Hence a comprehensive molecular level understanding of such interfaces is a must in order to utilize their novel features for interface based applications [46-48].

Surface composition and molecular orientation prevailing at the interface are two different but related aspects that fix the various physicochemical properties of interfaces. Thus a comprehensive understanding of fundamental and applied aspects of interfaces demands complete information about the composition and structural organization prevailing in the interface. While surface composition implies the identification of the molecules in the surface region and whether there is enhancement or depletion of constituents or parts of the constituents with respect to bulk, the structural organization implies complete information about the orientation (ordering and geometry of the constituents or parts of constituents) prevailing at the surface.

Surface properties of IL + co-solvent mixtures are of particular interest for two reasons; first, they are often considered as key to obtain valuable information about the transfer of mass and energy of dissolved molecules across the IL based interfaces and also provides information about the aggregation behaviour and drop formation in IL based partially miscible liquid mixtures. Such information is valuable in understanding the behaviour of ILs as components in mixed solvent systems, which is very useful for their use in processes like liquid-liquid extraction. Secondly, these properties provide valuable information about composition of mixture at the interface region which usually differs from that in the bulk phase. The principle of independent surface action formulated by Langmuir [49] has often been used to describe the microscopic structure of a liquid surface. According to this principle, each part of a molecule possesses a local surface energy; hence surface tension is an indicator of the molecular orientation at the interface. Direct Recoil Spectrometry (DRS) studies [50, 51] of RTIL surface have shown that both the anion and cation are present at the surface of ILs and hence both do contribute to the overall surface free energy. Since the bulk stoichiometry in RTILs should be preserved up to the surface, the electroneutrality requirement demands that the surface cannot be preferentially enriched by any of the IL constituent ions.

Figure 3.5 depict the variation in surface tension of RTILs viz. [bmim][BF_4] and [bmim][PF_6] with change in mole fraction of the RTIL in acetonitrile and methanol. As obvious from the plots, surface tension of [bmim][PF_6] as well as [bmim][BF_4] increases with increase in mole fraction of RTIL in both methanol and acetonitrile, but the variation is clearly not linear. These observed deviations from linear behaviour are an indication of non-ideal mixing and Domanska et al. [52] have also reported similar observations for addition of alcohols to imidazolium based RTILs. To visualize the nonideal mixing more clearly we calculated the deviations for observed γ values from those expected for ideal values using the equation

$$\Delta\gamma = \gamma - (X_{IL}\gamma_{IL} + X_{ACN}\gamma_{ACN}) \qquad (3.3)$$

and the variation of Δγ as a function of RTIL mole fraction is depicted in Figure 3.6. The Figure clearly shows that the mixing of RTIL with acetonitrile and methanol is nonideal. While the deviation from ideal behaviour is more pronounced for [bmim][PF_6] than [bmim][BF_4] in acetonitrile, opposite is the case in methanol. This can be attributed to the composition dependent structural organization and ion-solvent interactions for RTIL-co-solvent mixtures. Since γ is the measure of cohesive forces among constituents at the interface, the nonlinearity in γ vs. RTIL mole fraction clearly indicate that there might be some sort of transition in nature of forces responsible for nonideal variation of γ and Δγ. We propose that introduction of RTIL into the organic solvent leads to formation of strong associates in the lower mole fraction range, which are ultimately replaced by supramolecular aggregates of RTILs entrapping the small fraction of organic solvent.

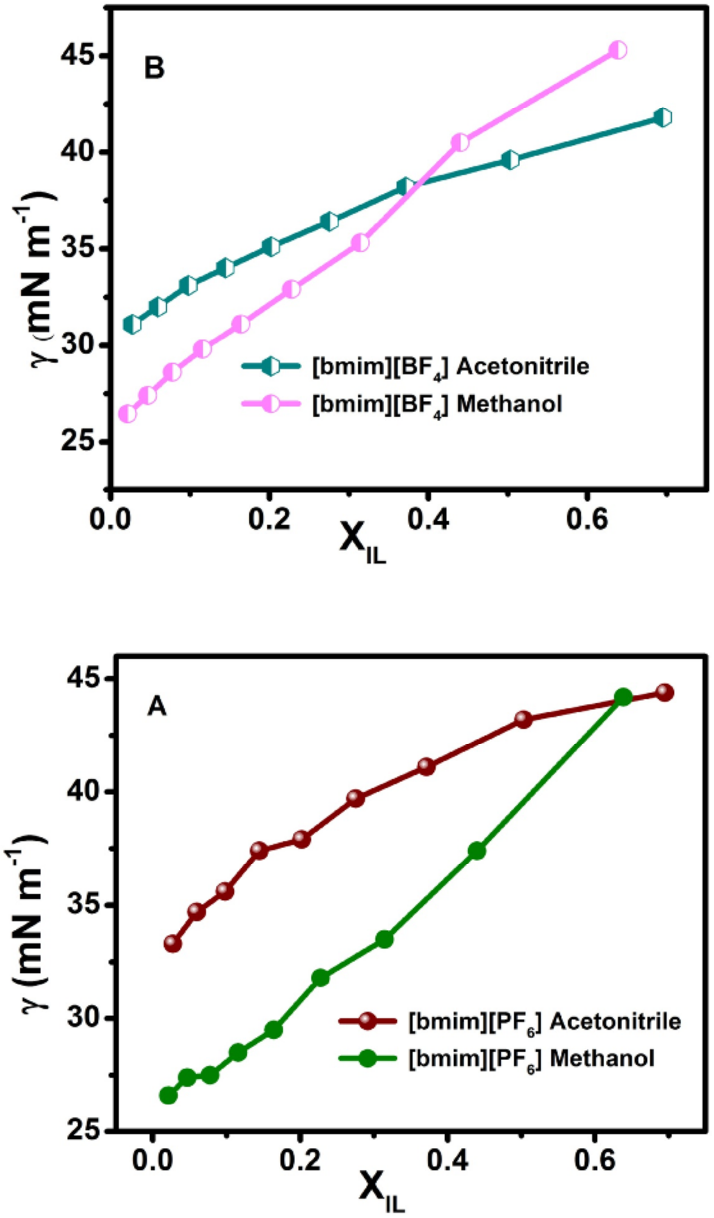


Fig.3.5. Surface Tension (γ) as a function of composition in Methanol and Acetonitrile (A) [bmim][PF$_6$] (B) [bmim][BF$_4$]

In the low RTIL concentration region cation- anion interaction is weakened due to stronger solvation by co-solvents leading to low surface tensions, but when concentration of RTIL is increased in the mixture, cation-anion interaction predominates, due to which surface tension increases.

As clearly seen from the Figure 3.5 addition of both methanol and acetonitrile to the investigated RTILs decreases their surface tension. The surface excess of co-solvent in the RTIL and that of RTIL in the co-solvent from the γ vs. concentration data of co-solvent rich and RTIL rich mixtures respectively was estimated by using Gibbs adsorption equation [53]

$$\Gamma = -\frac{1}{RT}\left(\frac{d\gamma}{d\ln c}\right)_T \qquad (3.4)$$

where Γ, c, γ, R, and T are the surface excess, bulk solute concentration, surface tension of the mixture, ideal gas constant and the temperature respectively. The estimated values of surface excess are given in Table 3.2. As clear from the entries in Table 3.2 while the surface excess of RTIL in the investigated co-solvents is negative; the surface excess of co-solvents in RTILs in the RTIL rich regimes is positive. A comparison of the magnitudes of the surface excess indicates that while acetonitrile shows stronger interaction with [bmim][PF_6] than [bmim][BF_4]; in case of methanol the reverse is true. Through molecular dynamic simulation Lopes and co-workers [41, 42] have established that both acetonitrile and methanol interact strongly with the anions $[BF_4]^-$ and $[PF_6]^-$. On account of its smaller size $[BF_4]^-$ interacts more strongly than $[PF_6]^-$. The difference between methanol and acetonitrile interaction with imidazolium based RTILs lies in their interaction with C2-H of imidazolium ion.

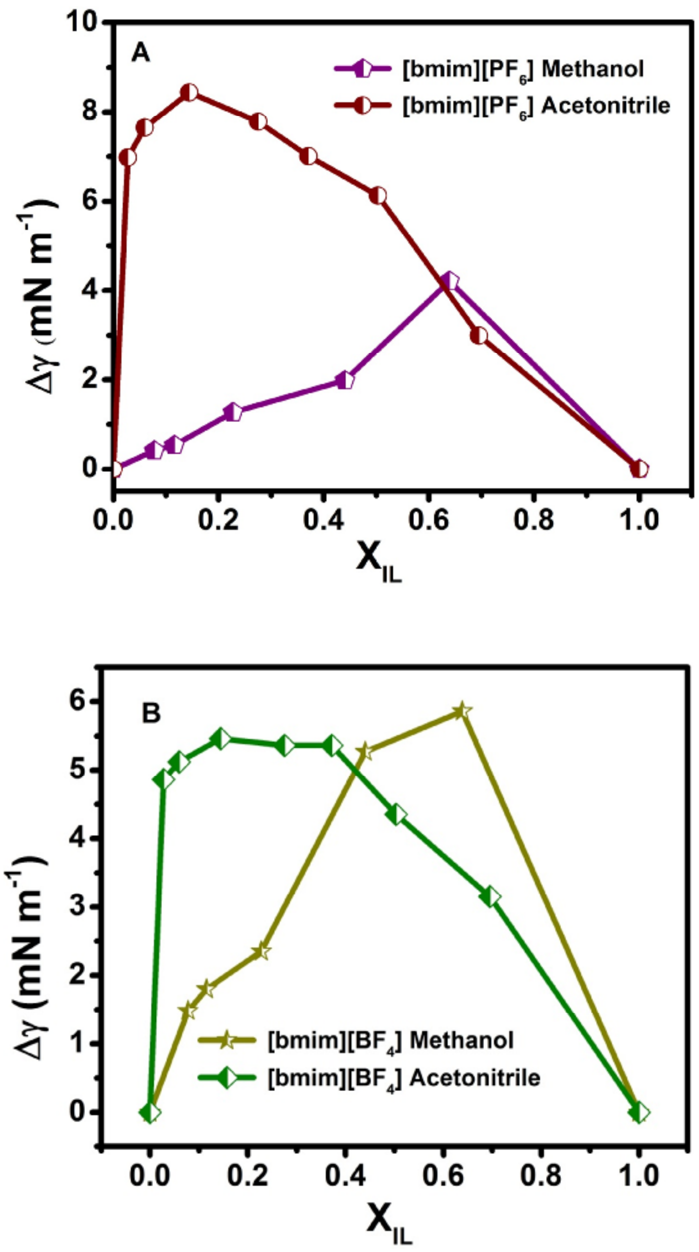


Fig.3.6. Change in surface tension (Δγ) calculated using equation 3.3 as a function of composition in Methanol and Acetonitrile. (A) [bmim][PF$_6$] and (B) [bmim][BF$_4$]

Table 3.2: Surface excess (Γ) of RTILs, [bmim][PF$_6$] and [bmim][BF$_4$] in Methanol and Acetonitrile in lower and higher concentration regions calculated using equation 3.4.

RTIL	Γ(mol m^{-2})	Γ(mol m^{-2})
	Methanol in RTIL	Acetonitrile in RTIL
[bmim][PF$_6$]	3.91E-06	1.17E-06
[bmim][BF$_4$]	3.59E-06	1.33E-06
	RTIL in Methanol	RTIL in Acetonitrile
[bmim][PF$_6$]	-3.63E-07	-8.47E-07
[bmim][BF$_4$]	-7.66E-07	-7.26E-07

This interaction energy is comparatively stronger for acetonitrile than for methanol and same is expected to be more for $[PF_6]^-$ than $[BF_4]^-$ on account of larger polarizability of the former. In light of these facts it can be safely argued that among methanol and acetonitrile as solutes while [bmim]$[BF_4]$ will show stronger interaction energies with methanol, in case of [bmim]$[PF_6]$ acetonitrile will more strongly interact with the RTIL domains than methanol. This, very well justifies the relative variations observed for γ values of [bmim]$[BF_4]$ and [bmim]$[PF_6]$ on addition of methanol and acetonitrile.

An overall view of the observed trends in γ, $\Delta\gamma$ and $\boldsymbol{\kappa}$ make us to propose that addition of RTIL to the co-solvent in low dilution limits leads to formation of free conducting ions and their aggregates besides ion-co-solvent complexes which lead to increase in γ, $\Delta\gamma$, and $\boldsymbol{\kappa}$. Further addition of RTIL favours the formation of ion pairs and aggregates that, besides decreasing the fraction of conducting species, increases the viscosity and γ as well. Higher cohesive energy among RTIL constituents in the aggregates than that of RTIL-co-solvent complexes in turn leads to increase in viscosity, γ and $\Delta\gamma$ and hence decrease in $\boldsymbol{\kappa}$ with further addition of RTIL. Thus, we propose that the maxima in $\Delta\gamma$ and $\boldsymbol{\kappa}$ vs. mole fraction plots actually represent the RTIL-co-solvent composition beyond which the mixture behaves more RTIL like. The observed variation of γ, $\Delta\gamma$ and $\boldsymbol{\kappa}$ with change in molar ratio clearly depict two types of nonidealities in the investigated composition range, attributable to two different tendencies of a RTIL. In low concentration range it behaves as a strongly associated electrolyte which interacts strongly with co-solvent molecules while in high concentration region it behaves as a structured solvent that entraps the co-solvent in interstitial sites.

3.4. Conclusion

Since the high viscosity of ionic liquids is a crucial property in optimizing the conditions required for many chemical processes, it is also a constraint that limits the use of RTILs in many electrochemical devices. The applicability of RTILs can be enhanced either by increasing the temperature or by addition of co-solvent. However, increase of temperature may be unsuitable when chemical/devices are poorly heat resistant. So the use of co-solvents seems a better option to overcome viscosity related challenges of RTILs. The presence of co-solvent molecules reduces the electrostatic attraction between the ions, and decreases the overall cohesive energy, resulting in a decrease in the viscosity. An interesting finding of the present work is that with co-solvent addition RTILs preserve their characteristic structural aspects up to the certain definite limit of dilution; in acetonitrile, x_{IL}= 0.14395 for [bmim][BF_4] and x_{IL} = 0.10319 for [bmim][PF_6]; in methanol, x_{IL}= 0.16383 for [bmim][BF_4] and x_{IL}= 0.11807 for [bmim][PF_6]. In acetonitrile both RTILs retain their chemical characteristics up to a higher dilution limit and there is also better increase of ionic conductivity than methanol. So acetonitrile seems to be a better co-solvent for boosting the conductivity of imidazolium ionic liquids and enhancing their transport for electrochemical and other applications wherein high viscosity limits the use of RTILs.

References

1. Wasserscheid, P.; Welton, T. *Ionic Liquids in Synthesis*; Wiley-VCH Verlag GmbH Co. KGaA: Weinheim, Germany, 2003.

2. Welton, T. *Chem. Rev*. **1999**, *99*, 2071.

3. Liu, W.; Fadeev, A. G.; Qi, B.; Smela, E.; Mattes, B. R.; Ding, J.; Spinks, G. M.; Mazurkiewicz, J.; Zhou, D. *Wallace Science* **2002**, *297*, 983.

4. Liu, W.; Ye, C.; Gong, Q.; Wang, H.; Wang, P. *Tribol. Lett.* **2002**, *13*, 81.

5. Xu, W.; Angell, C. A. *Science* **2003**, *302*, 422.

6. Seki, S.; Kobayashi, Y.; Miyashiro, H.; Ohno, Y.; Usami, A.; Mita, Y.; Watanabe, M.; Terada, N. *Chem. Commun*. **2006**, *2006*, 544.

7. Anderson, J. L.; Armstrong, D. W.; Wei, G. *Anal. Chem*. **2006**, *78*, 2892.

8. Fabregat-Santiago, F.; Bisquert, J.; Palomares, E.; Otero, L.; Kuang, D.; Zakeeruddin, S. M.; Gratzel, M. *J. Phys. Chem. C* **2007**, *111*, 6550.

9. Han, X.; Armstrong, D. W. *Acc. Chem. Res*. **2007**, *40,* 1079.

10. Harris, K. R.; Woolf, L. A. *J. Chem. Eng. Data* **2005**, *50*, 1777.

11. Harris, K. R.; Kanakubo, M.; Woolf, L. A. *J. Chem. Eng. Data* **2007**, *52*, 2425.

12. Jacquemin, J.; Ge, R.; Nancarrow, P.; Rooney, D. W.; Gomes, M. F. C.; Padua, A. A. H.; Hardacare, C. *J. Chem. Eng. Data* **2008**, *53*, 716.

13. Hayamizu, K.; Aihara, Y.; Nakagawa, H.; Nukada, T.; Price, W. S. *J. Phys. Chem. B* **2004**, *108*, 19527.

14. Nicotera, I.; Oliviera, C.; Henderson, W. A.; Appetecchi, G. B.; Passerini, S. J. *J. Phys. Chem. B* **2005**, *109,* 22814.

15. Li, W.; Zhang, Z.; Han, B.; Hu, S.; Xie, Y.; Yang, G. *J. Phys. Chem. B* **2007**, *111*, 6452.

16. (a) Sarkar, A.; Trivedi, S.; Pandey, S. *J. Phys. Chem. B* **2008**, *112,* 9042. (b) Sarkar, A.; Trivedi, S.; Pandey, S. *J. Phys. Chem. B* **2009***, 113*, 7606.

17. Trivedi, S.; Malek, N. I.; Behera, K.; Pandey, S. *J. Phys. Chem. B* **2010**, *114,* 8118.

18. Zhang, S. J.; Li, X.; Chen, H. P.; Wang, J. F.; Zhang, J. M.; Zhang, M. L. *J. Chem. Eng. Data* **2004**, *49,* 760.

19. Xu, H. T.; Zhao, D. C.; Xu, P.; Liu, F. Q.; Gao, G. *J. Chem. Eng. Data* **2005**, *50*, 133.

20. Zhou, Q.; Wang, L. S.; Chen, H. P. *J. Chem. Eng. Data* **2006***, 51*, 905.

21. Herzig, T.; Schreiner, C.; Bruglachner, H.; Jordan, S.; Schmidt, M.; Gores, H. J. *J. Chem. Eng. Data* **2008***, 53*, 434.

22. Domanska, U.; Pobudkowska, A.; Wi_sniewska, A. *J. Solution Chem*. **2006**, *35*, 1337.

23. Ge, M. L.; Ren, X. G.; Song, Y. J.; Wang, L. S. *J. Chem. Eng. Data* **2009**, *54,* 1400.

24. Domanska, U.; Laskowska, M. *J. Chem. Eng. Data* **2009**, *54*, 2113.

25. (a) Dupont, J. ; Consorti, C.S. ; Saurez; P.A.Z.; deSouza, R.F. *Org. Syn*. **2002**, *79* 236 (b) Dupont, J. ; Consorti, C.S. ; Saurez, P.A.Z. ; deSouza, R.F. *Org. Syn*. **2004***, 10*, 184.

26. Bhat, M. A.; Chaudhari, V. R. Ingole, P. P. Harram, S. K. *J. Phys. Chem. B* **2009**, *113*, 2848.

27. Bhat, M.A.;Ingole,P.P.*ElectrochemicaActa*://dx.doi.org/10.1016/j.electacta.2012.03.115.(2012)

28. Perrin, D. D.; Armarego, W. L. F.; Purification of Laboratory Chemical, Pregamon Press, Great Britian,3rd edition, 1998.

29. Ren, R.; Zuo, Y. ; Zhou, Q.; Zhang, H.; Zhang, S. *J. Chem. Eng. Data* **2011**, *56,* 27.

30. W. Liu, T. Zhao, Y. Zhang, H. Wang, M. Yu, *J. Solution Chem***.** **2006**, *35,* 1337.

31. Stoppa, A.; Hunger, J.; Buchner, R. *J. Chem. Eng. Data* **2009**, *54,* 472.

32. Hunger, J.; Stoppa, A.; Buchner, R.; Hefter, G. *J. Phys. Chem. B* **2008**, *112,* 12913.

33. Tokuda, H.; Baek, S. J.; Watanabe*, Electrochemistry* **2005**, **73**, 620.

34. Every, H.; Bishop, A. G.; Forsyth, M.; MacFarlane, D. R. *Electrochim. Acta* **2000***, 45*, 1279.

35. Wang, J. J.; Wang, H. Y.; Zhang, S. L.; Zhang, H. C.; Zhao, Y. *J. Phys. Chem. B* **2007**, *111*, 6181.

36. Shi, L. J.; Li, N.; Yan, H.; Gao, Y. A.; Zheng, L. Q. *Langmuir* **2011**, *27 (5),* 1618.

37. Dorbritz, S.; Ruth, W.; Kragl, U. *Adv. Synth. Catal*. **2005**, *347*, 1273.

38. Casteel, J. F.; Amis, E. S. *J. Chem. Eng. Data* **1972**, *17*, 55.

39. Stoppa, A.; Hunger, J.; Buchner, R. *J. Chem. Eng. Data* **2009***, 54,* 472, 12913.

40. Chaban, V. V.; Voroshylova, I. V.; Kalugin, O.N.; Prezhdo, O. V. *J. Phys. Chem. B* **2012,** *116*(*26*), 7719.

41. Canongia Lopes, J. N. A.; Padua, A. A. H. *J. Phys. Chem. B*. **2006**, *110*,3330.

42. Canongia Lopes, J. N.; Costa Gomes, M.F.; Padua, A. A .H. *J. Phys .Chem. B* **2006***, 110*, 16818.

43. Aliaga, C.; Santos, C. S.; Baldelli, S. *Phys. Chem. Chem. Phys.* **2007**, *9*, 3683.

44. Mezger, M.; Schroder, H.; Reichert, H.; Schramm, S.; Okasinski, J. S.; Schoder, S.; Honkimaki, V.; Deutsch, M.; Ocko, B. M.; Ralston, J.;Rohwerder, M.; Stratmann, M.; Dosch, H. *Science* **2008**, *322*, 424.

45. Lovelock, K. R. J.; Kolbeck, C.; Cremer, T.; Paape, N.; Schulz, P. S.; Wasserscheid, P.; Maier, F.; Steinruck, H. P. *J. Phys. Chem. B* **2009**, *113*, 2854.

46. Carvalho, P. J.; Freire, M. G.; Marrucho, I. M.; Queimada, A. J.; Coutinho, J. A. P. *J. Chem. Eng. Data* **2008**, *53*, 1346.

47. Endres, F.; El Abedin, S. Z. *Phys. Chem. Chem. Phys.* **2006**, *8*, 2101.

48. Baldelli, S. *Acc. Chem. Res.* **2008**, *41*, 421.

49. Langmuir, I. In *Phenomena, Atoms and Molecules*; Philosophical Library, New York 1950, p 72.

50. Gannon, T. J.; Law, G.; Watson, P. R.; Carmichael, A. J.; Seddon, K. R. *Langmuir* **1999,** *15*, 8429.

51. Law, G.; Watson, P. R.; Carmichael, A. J.; Seddon, K. R. *Phys. Chem. Chem. Phys.* **2001**, *3*, 2879.

52. Domanska, U.; Krolikowska, M. *J. Coll. Int. Sci.* **2010**, 348, 661

53. Adamson, A.W. Physical Chemistry of Surfaces, sixth ed., John Wiley & Sons, New York, 1997.

54. Shimizu, K.; Gomes, M.F.C.; Padua, A. A. H.; Rebelo, L. P. N. *J. Mol. Struc. THEOCHEM* **2010***, 946***,** 70.