Computer Simulation Studies of Intermolecular Structure, Microheterogeneity and Dynamics in Room Temperature Ionic Liquids

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To My Parents

DECLARATION

I hereby declare that the matter embodied in the thesis entitled “**Computer Simulation Studies of Intermolecular Structure, Microheterogeneity and Dynamics in Room Temperature Ionic Liquids**” is the result of investigations carried out by me at the Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, India under the supervision of Prof. S. Balasubramanian and that it has not been submitted elsewhere for the award of any degree or diploma.

In keeping with the general practice in reporting scientific observations, due acknowledgement has been made whenever the work described is based on the findings of other investigators. Any omission that might have occurred by oversight or error of judgement is regretted.

Srinivasa G. Raju

CERTIFICATE

I hereby certify that the matter embodied in this thesis entitled "**Computer Simulation Studies of Intermolecular Structure, Microheterogeneity and Dynamics in Room Temperature Ionic Liquids**" has been carried out by Mr. Srinivasa G. Raju at the Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, India under my supervision and that it has not been submitted elsewhere for the award of any degree or diploma.

Prof. S. Balasubramanian
(Research Supervisor)

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Preface

The thesis presents results of investigations on imidazolium cation based room temperature ionic liquids (RTILs) using classical molecular dynamics simulations.

Chapter 1 presents a general introduction to RTILs describing their physical properties and applications. The current status of experimental and theoretical research in this area is reviewed. The chapter also contains a brief discussion on the classical molecular dynamics simulation method.

In Chapter 2, the behavior of a model room temperature ionic liquid under shear is explored using non-equilibrium molecular dynamics simulations. A coarse-grained model of liquid [C_{10}mim][PF_6], subjected to planar Couette shear flow is studied. The external field reduces intermolecular structure in the liquid. However, orientational ordering of the molecules in the form of a nematic phase is observed under shear. This chapter is reproduced with permission from Institute of Physics (IOP). S. G. Raju and S. Balasubramanian, "Intermolecular correlations in an ionic liquid under shear," *J. Phys.: Condens. Matter*, **21**, 035105, (2009).

In Chapter 3, a dilute aqueous solution of the salt, 1-*n*-butyl,3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) has been studied using atomistic molecular dynamics simulations to investigate the effect of ions on water and vice versa. In the solution, the anion is found to diffuse faster than the cation, in contrast to observations in the pure ionic liquid. Distributions of pair energies have been employed to identify ion association, and around 13% of the ions were found to exist as pairs.

The mean potential energy of water molecules present in the coordination shell of an anion is lesser than that of water molecules coordinated to a cation. The former kind also exhibit two distinct orientational preferences with respect to the anion. The larger diffusion coefficient of the anion is related to the faster dynamics of water molecules in its hydration layer, as evidenced from the relaxation of their residence time correlation function. This chapter is reproduced with permission from S. G. Raju and S. Balasubramanian, "Aqueous solution of [bmim][PF_6]: Ion and Solvent Effects on Structure and Dynamics," *J. Phys. Chem. B*, **113**, 4799 (2009) Copyright 2009 Americal Chemical Society.

In Chapter 4, the morphology of a room temperature ionic liquid, 1,3-didecylimidazolium hexafluorophosphate has been predicted from a coarse grain molecular dynamics simulation. The liquid is seen to spontaneously self-assembly into a lamellar phase. The non-polar alkyl tails attached to the imidazolium ring of the cation, form brushes separating the parallel sheets containing the charged species. A high degree of parallel stacking of the imidazolium rings is observed. The structure factor of the liquid exhibits a sharp feature at 3.3 nm^{-1} and a weaker one at 1.8 nm^{-1}. This chapter is reproduced by permission of Royal Chemical Society. S. G. Raju and S. Balasubramanian, "Emergence of nanoscale order in room temperature ionic liquids: simulation of symmetric 1,3-didecylimidazolium hexafluorophosphate," *J. Mater. Chem.*, **19**, 4343 (2009).

In Chapter 5, molecular dynamics simulations of a series of bis(trifluoromethylsulfonyl)imide anion based room temperature ionic liquids have been carried out in order to identify the effects of the molecular symmetry of the cation on the structure and dynamics of the liquid. Simulations of ionic liquids with imidazolium cation containing varying lengths of alkyl groups were performed. The calculated density and total X-ray scattering function of the liquids agree well with experimental data. Liquids containing symmetric cations ([$C_nC_n$im][NTf_2]) are found to be more structured than those with asymmetric ones ([$C_nC_1$im][NTf_2]), manifested in greater intermolecular ordering and slower dynamics. This chapter is reproduced with permission from S. G. Raju and S. Balasubramanian, “Role of cation symmetry in intermolecular structure and dynamics of room temperature ionic liquids: Simulation studies,” *J. Phys. Chem. B*, **114**, 6455 (2010) Copyright 2010 Americal Chemical Society.

RTILs contain molecular ions which are in general, monovalent. In Chapter 6, we have explored the intermolecular structure, dynamics and intermediate range structure in a model ionic liquid whose cation and anion are mono- and divalent respectively. Charge compensation is met by doubling the mole fraction of the cations in the sample. Through coarse grained molecular dynamics simulations, we observe an enhancement of electrostatic interactions in the liquid which leads to greater ordering and sluggish dynamics, relative to traditional room temperature ionic liquids. The nanoscale heterogeneity inherent to RTILs is also further increased in these divalent systems. This chapter is reproduced with permission from S. G. Raju and S. Balasubramanian, “Molecular dynamics simulation of model room temperature ionic liquids with divalent anions” *Indian J. Chem. A*, **49**, 721 (2010).

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Chapter 1

Introduction

1.1 Room Temperature Ionic Liquids

The common definition of room temperature ionic liquids (RTILs) [1–6], is that they are liquids that are composed entirely of ions and are fluid below 100 °C. Purely inorganic salts such as sodium chloride however melt at high temperatures, say 800 °C or higher. RTILs possess both organic and inorganic moieties. Typically they consist of large bulky and asymmetric organic cations based on methylimidazolium [Rmim], N-butylpyridinium [RNbupy], N-methylN-alkylpyrrolidinium, quaternary ammonium, quaternary phosphonium ions (Fig. 1.1), and many others; and anions (Fig. 1.2) such as hexafluorophosphate $[PF_6]^-$, tetrafluoroborate $[BF_4]^-$, alkylsulfates $[RSO_4]^-$, alkylsulfonates $[RSO_3]^-$, halides, nitrate $[NO_3]^-$, sulfate $[SO_4]^-$, aluminum chloride $[AlCl_4]^-$, triflate $[CF_3SO_3]^-$, bis(trifluoromethylsulfonyl)imide $[(CF_3SO_2)_2N$ or $Tf_2N]^-$, etc. [7–15].

Figure 1.1: (a)1-butyl-3-methylimidazolium (b)N-ethyl-methylpyrrolidinium (c) Tetramethylammonium. Colours : Nitrogen–blue, Carbon–cyan, Hydrogen–gray

Figure 1.2: (a)Tetrafluoroborate$[BF_4]^-$ (b)Hexaflourophosphate$[PF_6]^-$
(c)Bis(trifluoromethanesulfonyl)imide$[NTf_2]^-$
(d)Trifluoromethanesulfonate$[CF_3SO_3]^-$ (e) Dicyanamide $[N(CN)_2]^-$.

The R group of the cation is variable, typical examples are alkyl chains such as methyl, ethyl, butyl, etc., but can also be any of a variety of other functional groups (e.g., fluoroalkyl, alkenyl, methoxy). The variability of the anion and of the R groups in the imidazolium, pyridinium, pyrrolidinium, ammonium or phosphonium cations may be used to adjust the properties of the ionic liquids. Therefore, the possibility arises to optimize the ionic liquid for a specific application by stepwise tuning the relevant solvent properties. For this reason ionic liquids have been referred to as designer solvents.

Ionic liquids have a wide liquidus range, ranging from 75 °C to 300 °C , which allows a better kinetic control on reactions. The liquidus region is defined as the range of temperatures between the normal freezing point and boiling point. The narrow liquidus range of common solvents means that they are all relatively volatile at process conditions. Due to the fact that an ionic liquid is a salt, it has a negligible vapor pressure. Furthermore, they are nonflammable, can have a high thermal stability and a high ionic conductivity. These properties permit their use in many fields. They are used as reaction media to substitute volatile organic compounds (VOCs), as homogeneous catalysts, and as extractive media in liquid-liquid extraction processes [1–15]. However, the use of ionic liquids also has some disadvantages: the physical properties are not always known, their viscosity is usually higher than that of common solvents and their toxicity is unknown. For a successful application of ionic liquids in industrial processes, these aspects must be taken into consideration.

1.1.1 Physical and Chemical Properties

The notable characteristics of ionic liquids are their nonmeasurable vapor pressure (however, several authors have actually shown in a recent paper that there is a small but non negligible vapor pressure [16]), nonflammability (decomposition products of

ILs can, however, be flammable [17]), thermal stability, wide liquid range, and solvating properties for diverse kinds of materials. Another important feature of ionic liquids is their designability: miscibility with water or organic solvents can be tuned through side chain lengths on the cation and by the choice of anion. Furthermore, they can be functionalized to act as acids, bases, or ligands. The change of anion dramatically affects the chemical behavior and stability of the ionic liquid, and the change of cation has a profound effect on the physical properties, such as melting point, viscosity, and density [18–22]. Cations are typically big, bulky and asymmetric, accounting for the low melting points. Increasing the length of an alkyl chain tends to decrease water solubility by increasing the hydrophobicity of the cation. In addition, chemical and physical properties can be changed dramatically by the choice of anion. For example, imidazolium salts with halide, acetate, nitrate and trifluoroacetate anions are totally miscible with water, while $[PF_6]^-$ and $[(CF_3SO_2)_2N]^-$ imidazolium salts are immiscible, and $[BF_4]^-$ and $[CF_3SO_3]^-$ imidazolium salts can be totally miscible or immiscible depending on the substituents on the cation [20]. The anions are chosen to control the chemistry [23] and the cations are chosen to determine the physical properties [21]. In this way, a vast range of ionic liquids can be created. The number of possible anions [24–27] and cations [28–30] is rapidly increasing.

Melting Point

Ionic liquids have been defined to have melting points below 100 °C and most of them are liquid at room temperature. Both cations and anions contribute to the low meting points of ionic liquids. The increase in anion size leads to a decrease in melting point [12]. For example, the melting points of 1-ethyl-3-methylimidazolium type ionic liquids with different anions, such as $[BF_4]^-$, $[Tf_2N]^-$ and $[C_2H_5SO_4]^-$ are 15 °C [31], −3 °C [26] and −20 °C, respectively. Size and symmetry of the cations make an important impact on the melting points of ionic liquids and melting point generally increases with increasing substituents chain length. Large cations and increased asymmetric substitution at the nitrogen sites results in a melting point reduction [32].

Density

Ionic liquids in general are denser than water with values ranging from 1 to 1.6 g/cm^3 and their densities decrease with increase in the length of the alkyl chain in the cation [34]. The order of increasing density for ionic liquids composed of a single cation is: $[CH_3SO_3]^- \approx [BF_4]^- < [CF_3CO_2]^- < [CF_3SO_3]^- < [C_3F_7CO_2]^- < [(CF_3SO_2)_2N]^-$ [37]. The densities of ionic liquids decrease almost linearly with increasing temperatures [35]. The densities of ionic liquids are also affected by the identity of anions. For example, the densities of 1-butyl-3-methylimidazolium type ionic liquids with different anions, such as $[BF_4]^-$, $[PF_6]^-$, and $[Tf_2N]^-$ are 1.20 g/cm^3, 1.37 g/cm^3 and 1.43 g/cm^3, respectively.

Viscosity

Generally, ionic liquids are more viscous than common molecular solvents and their viscosities are ranging from 10 mPa.s to about 500 mPa.s at room temperature. The viscosity of ionic liquids is determined by van der Waals forces and hydrogen bonding. Alkyl chain lengthening in the cation leads to an increase in viscosity [26], due to stronger van der Waals forces between cations leading to increase in the energy required for molecular motion. Also, the ability of anions to form hydrogen bonding has a pronounced effect on viscosity. The fluorinated anions such as $[BF_4]^-$ and $[PF_6]^-$ form viscous ionic liquids due to the formation of complexes with hydrogen bonding donors [33]. Electrostatic forces may also play an important role. In general, all ionic liquids show a significant decrease in viscosity as the temperature increases [20, 21, 35, 36, 38].

Thermal stability

Ionic liquids can be thermally stable up to 500 °C. The thermal stability of ionic liquids is limited by the strength of their heteroatom-carbon and their heteroatom-hydrogen bonds, respectively [12]. The ionic liquids 1-ethyl-3-methylimidazolium tetrafluoroborate, 1-butyl- 3-methylimdazolium tetrafluoroborate and 1,2-dimethyl-3-propylimidazolium bis(trifluorosulfonyl)imide are stable up to temperatures of 445, 423 and 457 °C , respectively [39]. However, the long-term thermal stability of ionic liquids containing dicyanamide or tricyanomethide anions is significantly lower than might be expected from temperature-ramped thermogravimetric analysis (TGA) studies, and these anions, combined with N-based cations, yield polymeric products during thermal decomposition [40].

Electrochemical Window

The electrochemical window is an important property and plays a key role in using ionic liquids in electrodeposition of metals and semiconductors. By definition, the electrochemical window is the electrochemical potential range over which the electrolyte is neither reduced nor oxidized at an electrode. This value determines the electrochemical stability of solvents. As known, the electrodeposition of elements and compounds in water is limited by its low electrochemical window of only about 1.2 V. On the contrary, ionic liquids have significantly larger electrochemical windows, e.g., 4.15 V for [bmim]$[\mathrm{PF}_6]$ at a platinum electrode [41], 4.10 V for [bmim]$[\mathrm{BF}_4]$ [41] and 5.5 V for [bmpyrr]$[\mathrm{Tf}_2\mathrm{N}]$ at a glassy carbon electrode [42]. In general, the wide electrochemical windows of ionic liquids have opened the door to electrodeposit metals and semiconductors at room temperature which were formerly obtained only from high temperature molten salts. For example, Al, Mg, Si, Ge, and rare earth elements can be won from room temperature ionic liquids. The thermal stability of ionic liquids allows to electrodeposit Ta, Nb, V, Se, and presumably many other elements at elevated temperature.

1.1.2 Applications

Solvents for Synthesis and Catalysis

Room-temperature ionic liquids have the potential to provide environmentally friendly solvents for the chemical and pharmaceutical industries because of their nonvolatile nature. Many reactions have been demonstrated in IL solvents, although in some cases without any obvious benefits over other solvents. The nature of the IL components can significantly influence reaction outcomes, either as catalysts, or modifying the reactivity of components. The activity of nucleophiles in ILs can be moderated by the anion of the IL [49,50]. This 'buffering' action is effectively utilized [23], demonstrating how different reaction outcomes are obtained from IL+HNO_3 systems depending on the different anions present in the IL solvent.

Solvents for Catalysis

Molten tetraalkylphosphonium and ammonium salts were investigated as reaction solvents/catalysts for industrial hydroformylation and hydrogenation reactions [43]. Since ILs are stable, nonvolatile solvents and since the product may be separated by decantation or simple distillation [43], these properties are now considered fundamental to the application of ILs as solvents for clean syntheses. Many homogeneous catalysis reactions have subsequently been demonstrated [3,4,11–13,48–55]. In cases where reactions proceed through ionic transition states, ILs can be used to tailor the transition metal complexes central to the catalyst systems. Palladium-catalyzed Heck couplings have been extensively investigated [58–61] and ILs are presumably the best solvents for these reactions [63]. Acid-catalyzed reactions [64] including

Friedel-Crafts alkylations [57] and olefin alkylation, oligomerization, and polymerization have been studied.

Biocatalysis

Attention has recently been focused on the use of enzymes in ionic liquids [51, 65–74]. It was already noted that enzymes can be relatively stable in a mixture of ILs and water. The enzyme displayed excellent stability when suspended in the ionic liquid and the activity was equal to that observed in ethyl acetate-water. The kinetic resolution of 1-phenylethanol with nine different lipases in ten different ionic liquids was investigated [74]. Good activities and, in many cases, improved enantioselectivities were observed compared with the same reaction in methyl tert-butyl ether (MTBE). Based on these initial studies the use of enzymes in ionic liquids would appear to open up a new field of nonaqueous enzymology. Ionic liquids could have added benefits for performing biotransformations with highly polar substrates, e.g., carbohydrates and amino acids, which are sparingly soluble in common organic solvents.

Electrochemical Applications

ILs can be designed with wide electrochemical windows and high electrically conductivity [75]. When combined with wide liquid ranges and thermal stability, ILs can be used in place of traditional solvent-based electrolytes for a wide range of metal-purification, plating, and refining processes, increasing the scope of electrochemical reactions. Many IL-based electrochemical devices have been developed, including batteries [31, 76–79], capacitors [80–82] and solar cells [27, 83, 84]. IL electrolytic systems are also useful for electrosynthesis [85] and electrodeposition of metals [86, 87].

Analytical Applications

ILs are increasingly used in analytical chemistry, such as in chromatography, spectroscopy, and electrochemistry [22, 88–91, 93]. They are, for instance, employed as stationary phases in gas-liquid chromatography, because of their high viscosity, high thermal stability, low vapor pressure and wetting ability toward common supports such as fused-silica capillary tubing.

Separations

The use of ionic liquids in separations is presently mostly in the extraction of metal ions with [bmim][PF_6], [hmim][PF_6] and other $[PF_6]^-$ based ILs and with [Tf_2N] based ILs [94–96]; of alcohols using [Rmim][PF_6] (R = butyl, pentyl, heptyl, or octyl) and [emim][Tf_2N] [97–99]; separation of alcohols and alkanes or alkenes with [omim][Cl], [hmim][BF_4] or [hmim][PF_6] [100, 101]; desulfurization of oils with [emim][$AlCl_4$], [bmim][$AlCl_4$], [bmim][BF_4], [bmim][PF_6], trimethylamine hydrochloride/AlCl3 , [emim][ethyl sulfate] and [bmim][octyl sulfate] [102–105]; and separation of ethers from ethanol with [omim][Cl] and [bmim] [triuoromethanesulfonate] [106, 107].

1.2 Previous work

Several experimental [19,108,110] and theoretical methods [111–113] have been used to study RTILs. Koel [114] has studied several imidazolium based ionic liquids using thermogravimetry, IR and UV-VIS spectroscopic methods and has also determined the solubility of ionic liquids in several organic solvents. Huddleston *et al* [115] have carried out extensive studies on the characterization of hydrophilic and hydrophobic ionic liquids based on imidazolium cation. Tokuda *et al* [169] and Jacquemin *et al* [116] characterized the effect of temperature on the transport properties of the

ILs.

It is difficult to characterize the gaseous phase of ionic liquids due to the negligible vapour pressure. However, electrospray ionization mass spectrometry (ESI-MS) has been used to isolate and study the stability of ion clusters [117–119]. Such studies have identified an array of charged and uncharged ion clusters of different sizes. Armstrong *et al* [120] have succeeded in evaporating ionic liquids in high vacuum and analyzing the vapor by mass spectrometric methods. Their results imply that this vapor only comprises neutral ion pairs and that the larger charged and uncharged aggregates found by electrospray mass spectrometry are not present.

Quantum chemical calculations [38, 121, 122] and ab-initio molecular dynamics simulations [125–134, 157] have been used to determine the molecular and electronic structure of an ion pair. The strong electrostatic interactions result in binding energies up to 400 kJmol^{-1}, which are an order of magnitude larger than those of pairs of uncharged molecules. There is a strong hydrogen bonding interaction between the acidic hydrogen atom (hydrogen attached to the carbon on the imidazolium ring between the two nitrogen atoms) and the anion.

Compton *et al* [135] have first noticed nanostructures in RTILs similar to those observed in concentrated solutions of surfactants and were more broadly discusssed by Dupont [136]. They have argued that ILs may not be liquids in the conventional sence, but may rather be considered as mesophases. The existance of mesoscopic organization of ILs has indicated that the morphology of ILs is far more complex than originally expected on the basis of the properties of simple inorganic salts. The most direct evidence for mesoscopic structures comes from the formation of liquid-crystalline phases of salts with long alkyl chains, for example, imidazolium salts with alkyl chains $\mathrm{C}_n \geq \mathrm{C}_{12}$ [137]. Crystal structures of salts with shorter alkyl chains also indicate the presence of structural domains [138].

Recent work has shown that intermediate range structures also exist in ILs with shorter alkyl chains, such as imidazolium salts with alkyl chains $C_n \geq C_4$. Wang and Voth [139–141] used a multiscale coarse-graining model to investigate the unique aggregation of cations in ionic liquids through computer simulation. The tail groups of the cations with a sufficient side-chain length are found to aggregate forming spatially heterogeneous domains. This is due to the competition between the electrostatic interactions between the charged head groups and the anions and the collective short-range interactions between the neutral tail groups. Using coarse grain molecular dynamics simulations, Bhargava *et al* [142] show the existence of a bicontinuous morphology in the liquid, whose character is influenced by the length of the alkyl group. The molecular origin of this behavior lies in the formation of disordered or winding sheets of anions between which the interdigitated alkyl groups are sandwiched. Lopes and Padua [143] indicate the presence of hydrophilic domains that are formed by the head groups of the cations and anions and of nonpolar domains that are formed by the alkyl groups. With increasing size of the alkyl chains these domains grow and begin to link together [143, 144].

X-ray scattering experiments on 1-alkyl-3-methylimidazolium salts ($4 \leq C_n \leq 10$) by Triolo *et al* [145–147] have given direct experimental evidence for such mesoscopic structures. The scattering patterns show a diffraction peak arising from structural inhomogeneities on the nanometer scale. The size of the inhomogeneities is proportional to the length of the alkyl chains. In molecular liquids, the formation of mesophases is often driven by the shape anisotropy of the molecules and the strong orientation dependence of electrostatic and van der Waals interactions. Dupont [136] proposed that mesoscopic structures in ILs may be driven by a three-dimensional hydrogen-bonded network. To interpret the observed structural dependency of the diffraction peak on alkyl tail length, the following idea is proposed by Triolo [146]. Interdigitation of cation tails or the formation of micelles could account for the alkyl tail length dependence on the q value at which the prepeak shows in Triolos SAXS experiments. This type of interpretation involving the notion of complex longrange multication correlations to form micelles, strands, and other more complex morphologies even in the case of imidazolium systems of modest tail lengths such as $[C_5mim]^+$ has become quite popular [148] . However, recent work by Hardacre [149] and Margulis [150] has suggested that the prepeak is a simple consequence of cationic anisotropy, which imposes certain patterns of coordination along the direction of the longer alkyl tail and not due to complex long-range morphologies.

Apart from molecular dynamics, experimental methods such as dielectric spectroscopy in the microwave and far-infrared [151, 152] regime, optical Kerr effect (OKE) spectroscopy [34, 153, 154, 156], nuclear magnetic relaxation (NMR) [157–159], and quasi-elastic neutron scattering (QENS) [160, 161] can be used to study molecular motions in neat ionic liquids. It is difficult to make hard and fast generalizations in the dynamical properties of ILs due to the enormous diversity in the constituents of ILs. However, some common features are slow translational dynamics at room temperature, large seperation of time scales for different motions and dynamical heterogeneity.

In some of the earliest MD studies, Margulis and Berne [162], Del Popolo and Voth [163] and Morrow and Maginn [164] all reported dynamical behavior that was characterized by slow dynamics, reminiscent of a supercooled liquid. Del Popolo and Voth [163] computed the dynamics of $[C_2mim][NO_3]$ and saw evidence of dynamic heterogeneity which they quantied using a non-Gaussian parameter $\alpha(t)$. The extent to which this parameter is non-zero is indicative of dynamic heterogeneity characteristic of sub-diffusive motion. These authors found that, even at 400 K, the ionic liquid $[C_2mim][NO_3\ ]$ exhibited non-Gaussian behavior after more than 500 ps of simulation time. This result called into question some of the earliest studies where self-diffusivities were estimated from MD simulations of much shorter duration than this. Hu and Margulis [165] found that translational mobility is totally decoupled from rotational mobility for the [PF_6] anion, but the two are coupled tightly for the [C_4mim] cation.

By studying [C_4mim][PF_6] using classical MD, Maginn et.al. [164] found that the small anion rotates rapidly, with a rotational time constant at 298 K of about 30 ps and the large cation, however, exhibits a rotational time constant about its longest axis of several nanoseconds, indicating a large separation of timescales. Other work [166] has shown similar behavior for other systems, but larger anions do show slower rotational dynamics. Interestingly, for most imidazolium systems, the translational motion of the larger cation is actually slightly faster than that of the smaller anion. This has been consistently observed in a number of simulation [164, 167] and experimental [168–170] studies.

In an attempt to explain this behavior, Urahata and Ribeiro [167], using MD simulations, indicate that this phenomenon was due to preferential displacement of the cation ring along the direction of the carbon at the 2 position (between the two nitrogen atoms) of the imidazolium ring. This is the same direction that exhibits the lowest frequency contribution to the vibrational density of states obtained by Fourier-transforming velocity time correlation functions. This suggests that other large cations may not display such behavior, a finding consistent with subsequent studies using pyridinium cations.

1.3 Molecular Dynamics

Molecular Dynamics [171–174] is a technique for computing the equilibrium and transport properties of a classical many-body system. In this context, the word *classical* means that the nuclear motion of the constituent particles obey the laws of classical mechanics. Only when we consider the translational or rotational motion of light atoms or molecules or vibrational motion with a frequency ν such that $h\nu > k_B T$ should we worry about quantum effects. Molecular dynamics simulation consists of the numerical, step-by-step solution of the classical equations of motion, which for a simple atomic system may be written as

$$m_i \ddot{\mathbf{r}}_i = \mathbf{f}_i \tag{1.1}$$

$$\mathbf{f}_i = -\frac{\partial U}{\partial \mathbf{r}_i} \tag{1.2}$$

For this purpose, we need to be able to calculate the forces $\mathbf{f}_i$ acting on atoms, and these are usually derived from a potential energy $U(\mathbf{r}^N)$, where $\mathbf{r}^N = (\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)$ represents the complete set of 3N atomic coordinates.

The part of the potential energy $U_{non-bonded}$ representing non bonding interactions between atoms is traditionally split into 1-body, 2-body, 3-body ... terms:

$$U_{non-bonded}(\mathbf{r}^N) = \sum_i u(\mathbf{r}_i) + \sum_i \sum_{j>i} v(\mathbf{r}_i, \mathbf{r}_j) + ... \tag{1.3}$$

The $u(\mathbf{r})$ term represents an externally applied potential field or the effects of the container walls; it is usually dropped for fully periodic simulations of bulk systems. Also, it is usual to concentrate on the pair potential $v(\mathbf{r}_i, \mathbf{r}_j) = v(r_{ij})$ and neglect three-body (and higher order) interactions. The most commonly used pair potential is the Lennard-Jones potential.

$$v^{LJ} = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right] \tag{1.4}$$

It has two parameters: σ, the diameter, and ε, the well depth. The electrostatic interactions are handled using the Coulomb potential.

$$v^{Coulomb}(r) = \frac{Q_1 Q_2}{4\pi\varepsilon_0 r} \tag{1.5}$$

For molecular systems, we simply build the molecules out of site-site potentials of the form of Eq.(1.4) or similar. Typically, a single-molecule quantum-chemical calculation may be used to estimate the electron density throughout the molecule, which may then be modelled by a distribution of partial charges via Eq.(1.5). For molecules we must also consider the intramolecular bonding interactions. The simplest molecular model will include terms of the following kind:

$$\begin{aligned} U_{intramolecular} &= \frac{1}{2}\sum_{bonds} k^{r}_{ij}(r_{ij}-r_{eq})^2 + \frac{1}{2}\sum_{angles} k^{\theta}_{ijk}(\theta_{ijk}-\theta_{eq})^2 \\ &+\frac{1}{2}\sum_{torsion}\sum_{m} k^{\phi,m}_{ijkl}(1+cos(m\phi_{ijkl}-\gamma_m)) \end{aligned} \tag{1.6}$$

A simulation package force-field will specify the precise form of Eq.(1.6), and the various strength parameters k and other constants therein. Having specified the potential energy function $U(r^N)$, the next step is to calculate the atomic forces using Eq.(1.2).

Consider a system composed of atoms with coordinates $\mathbf{r}^N = (\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)$ and potential energy $U(\mathbf{r}^N)$, we introduce the atomic momenta $\mathbf{p}^N = (\mathbf{p}_1, \mathbf{p}_2, ..., \mathbf{p}_N)$, in terms of which the kinetic energy may be written $K(p^N) = \sum_{i=1}^{N} |p_i|^2/2m_i$. Then the energy, or hamiltonian, may be written as a sum of kinetic and potential terms $H = K + U$. The classical equations of motion can be written as

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i} \tag{1.7}$$

$$\dot{\mathbf{p}}_i = \mathbf{f}_i \tag{1.8}$$

This is a system of coupled ordinary differential equations. A standard method for solution of such equations is the finite difference approach. The general idea is as follows. Given the molecular positions, velocities, and other dynamic information at time t, we attempt to obtain the position, velocities etc. at a later time $t + \delta t$, to a sufficient degree of accuracy. The equations are solved on a step-by-step basis; the choice of the time interval δt will depend somewhat on the method of solution, but δt will be significantly smaller than the typical time taken for a molecule to travel its own length. Care has to be taken to ensure that advancement of the coordinates fulfils two functions: (1) accurate calculation of dynamical properties, especially over times as long as typical correlation times τ_a of properties a of interest; (2) accurately staying on the constant-energy hypersurface, for much longer times $\tau_{run} >> \tau_a$, in order to sample the correct ensemble.

Several algorithms have been developed to solve the equations of motion over time, e.g., position Verlet [175, 176] algorithm, Leap-Frog algorithm [177] , velocity Verlet [178] algorithm, Gear predictor-corrector algorithm etc. Verlet algorithms are the simplest and efficiently adequate for most of the MD simulation. The velocity Verlet algorithm can be written as

$$\boldsymbol{p}_i(t + \frac{1}{2}\delta t) = \boldsymbol{p}_i(t) + \frac{1}{2}\delta t \boldsymbol{f}_i(t) \tag{1.9}$$

$$\boldsymbol{r}_i(t + \delta t) = \boldsymbol{r}_i(t) + \delta t \boldsymbol{p}_i(t + \frac{1}{2}\delta t)/m_i \tag{1.10}$$

$$\boldsymbol{p}_i(t + \delta t) = \boldsymbol{p}_i(t + \frac{1}{2}\delta t) + \frac{1}{2}\delta t \boldsymbol{f}_i(t + \delta t) \tag{1.11}$$

Important features of the velocity Verlet algorithm are: (a) it is exactly time reversible; (b) it is symplectic (which implies that volume in phase space is conserved); (c) it is low order in time, hence permitting long timesteps; (d) it requires just one (expensive) force evaluation per step; (e) it is easy to program.

1.3.1 Long-range Forces

Those interactions that decay no faster than r^{-n} where n is the dimensionality of the system, can be a problem as their range is often greater than half the box length.

The charge-charge interaction, which decays as r^{-1}, is particularly problematic in molecular simulations. It is important to properly model these long-range forces, which are particularly acute when simulating charged species such as molten salts. One way to tackle the errors introduced by an inadequate treatment of long-range forces would be to use a much larger simulation cell, but this is usually impractical. Ewald summation method is very popular among the methods that have been developed to handle long-range forces.

In this method, a particle interacts with all the other particles in the simulation box and with all of their images in an infinite array of periodic cells. The position of each image box can be related to the central box by specifying a vector, each of whose components is an integral multiple of the length of the box, $(\pm iL, \pm jL, \pm kL)$; i,j,k = 0,1,2,3, etc. In general, for a box which is positioned at a cubic lattice point $\mathbf{n}$ $(= (n_xL, n_yL, n_zh)$ with n_x, n_y, n_z being integers): The charge-charge contribution to the potential energy due to all pairs of charges in the central simulation box can be written as :

$$V = \frac{1}{2} \sum_{|\mathbf{n}|=0}^{\prime} \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{q_i q_j}{4\pi\epsilon_o |\mathbf{r}_{ij} + \mathbf{n}|} \tag{1.12}$$

The prime on the first summation indicates that the series does not include the interaction $i = j$ for $\mathbf{n} = 0$. The summation in the above equation is conditionally convergent and converges extremely slowly. This summation can be converted to two series, each of which converges much more reapidly like the following function.

$$\frac{1}{r} = \frac{f(r)}{r} + \frac{1 - f(r)}{r} \tag{1.13}$$

In the ewald method each charge is considered to be surrounded by a neutralizing charge distribution of equal magnitude but of opposite sign. A gaussian charge distribution of the following form is commonly used.

$$\rho_i(\mathbf{r}) = \frac{q_i\alpha^3}{\pi^{3/2}} exp(-\alpha^2 r^2) \tag{1.14}$$

The sum over point charges is now converted to a sum of the interactions between the charges plus the neutralising distributions. The real space summation is given by:

$$V = \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\sum_{|\mathbf{n}|=0}^{\prime} \frac{q_i q_j}{4\pi\epsilon_o}\frac{erfc(\alpha|\mathbf{r}_{ij}+\mathbf{n}|)}{|\mathbf{r}_{ij}+\mathbf{n}|} \tag{1.15}$$

erfc is the complementary error function, which is:

$$erfc(x) = \frac{2}{\sqrt{\pi}}\int_x^{\infty} exp(-t^2)dt \tag{1.16}$$

In the Ewald method, erfc(r) is used for the function f(r) in equation (1.13). The new summation involving the error function converges very rapidly and beyond some cutoff distance, its value can be considered negligible. The rate of convergence depends upon the width of the cancelling Gaussian distributions; the wider the Gaussian (α), the faster the series converges. A second charge distribution is now added to the system which exactly counteracts the first neutralising distribution. The contribution from this second charge distribution is:

$$V = \frac{1}{2}\sum_{k\neq 0}\sum_{i=1}^{N}\sum_{j=1}^{N}\frac{1}{\pi L^3}\frac{q_i q_j}{4\pi\epsilon_o}\frac{4\pi^2}{k^2} exp\left(-\frac{k^2}{4\alpha^2}\right) cos(\mathbf{k}.\mathbf{r}_{ij}) \tag{1.17}$$

The real space summation converges more rapidly for large α, whereas the resiprocal-space summation converges more rapidly for small α. Thus there is a clear need to balance the real-space and resiprocal space summations. The following term needs to be added to account for the interaction of each gaussian with itself in the real space.

$$V = -\frac{\alpha}{\sqrt{\pi}} \sum_{k=1}^{N} \frac{q_k^2}{4\pi\epsilon_o} \tag{1.18}$$

A correction term is added to the summation to account for the medium surrounding the sphere of simulation boxes. For a medium with a relative permittivity of 1 (vacuum) the correction term is:

$$V_{correction} = \frac{2\pi}{3L^3} \left| \sum_{i=1}^{N} \frac{q_i}{4\pi\epsilon_o} \mathbf{r}_i \right|^2 \tag{1.19}$$

The sum of equations (1.15,1.17,1.18,1.19) is the Ewald sum. The Ewald summation is computationally very expesive to implement and it scales as N^2 where N is the number of particles in the simulation cell. When fast Fourier transform is used to compute the reciprocal space simulation, it scales as $N\ lnN$. The FFT method requires that the data are not continuous but are discrete values. In order to employ the fast Fourier transform in the Ewald summation the point charges with their continuous coordinates must be replaced by a grid-based charge distribution. Variants on this general theme use the fast Fourier transform algorithm, but they differ in other aspects of their implementation. These include the particle-mesh Ewald method [179] and the particle-particle-particle-mesh approach [180].

1.3.2 Periodic boundary condition and Minimum imaging

Since simulation methods enable 'macroscopic' properties to be calculated using relatively small numbers of particles, correct treatement of boundaries and boundary effects needs to be ensured. In a three-dimensional N-particle system with free boundaries, the fraction of all molecules that is present at the surface is proportional to $N^{-1/3}$. For instance in a simple cubic crystal of 1000 atoms, some 49% of all atoms are at the surface, and for 10^6 atoms this fraction has decreased to only 6%. Periodic boundary conditions enable a simulation to be performed using a relatively small number of particles, in such a way that the particles experience forces as if they were in bulk fluid. Particles in a cubic box (for example) are replicated in all directions to give a periodic array. In three dimensions each box would have 26 nearest neighbours. The coordinates of the particles in the image boxes can be computed simply by adding or subtracting integral multiples of the box sides. Should a particle leave the box during the simulation then it is replaced by an image particle that enters from the opposite side. The number of particles within the central box thus remains constant.

The most time-consuming part of a molecular dynamics simulation is the calculation of the non-bonded energies. The numbers of bond-stretching, angle-bending and torsional terms in a force field model are all proportional to the number of atoms but the number of non-bonded terms that need to be evaluated increases as the square of the number of atoms (for a pairwise model) and is thus of order N^2. In principle, the non-bonded interactions are calculated between every pair of atoms in the system. However, for many interaction models this is not justified. The Lennard-Jones potential falls off very rapidly with distance: at 2.5σ the potential has just 1% of its value at σ. This reflects the r^{-6} distance dependence of the dispersion interaction. The most popular way to deal with the non-bonded interactions is to use a non-bonded cutoff and to apply the minimum image convention. In the minimum image convention, each atom 'sees' at most just one image of every other atom in the system (which is repeated infinitely via the periodic boundary method). The energy is calculated with the closest atom or image. When a cutoff is employed, the interactions between all pairs of atoms that are further apart than the cutoff value are set to zero, taking into account the closest image. When periodic boundary conditions are being used, the cutoff should not be so large that a particle sees its own image, or indeed the same molecule twice. This has the effect of limiting the cutoff to no more than half the length of the cell.

1.3.3 Methods of Analysis

MD simulations provides us with a trajectory (positions and velocities of all the atoms as a function of time) in phase space for the system with given initial configuration. This trajectory can be used to study the structural and dynamical properties of the system. Radial distribution functions (pair distribution functions) are a useful way to describe the structure of a system, particularly of a liquid. g(r), gives the probability of finding a particle at a distance r from another particle compared to the ideal gas distribution. g(r) is thus dimensionless. g(r) is calculated as follows. Configurations are read and the minimum image separation r_{ij} of all the pairs of atoms are calculated. These separations are sorted into a histogram where each bin has a widht δr and extends from r to $r + \delta r$. After all the configurations have been processed, the histogram is normalized to calculate g(r). Suppose there are τ steps on the tape, and a particular bin b of the histogram, corresponding to the interval $(r, r + \delta r)$, contains $n_{his}(b)$ pairs. Then the average number of atoms whose distance from a given atom in the fluid lies in this interval, is

$$n(b) = n_{his}(b)/(N \times \tau) \tag{1.20}$$

The average number of atoms in the same interval in an ideal gas at the same density ρ is

$$n^{id}(b) = \frac{4\pi\rho}{3}[(r + \delta r)^3 - r^3] \tag{1.21}$$

By definition, the radial distribution function is

$$g(r + \frac{1}{2}\delta r) = n(b)/n^{id}(b) \tag{1.22}$$

Time correlation functions provide microscopic insight into the dynamics of the system. Experimentally measurable transport coefficients such as diffusion constant, viscosity, thermal conductivity, that are accessible from non-equilibrium MD, can also be calculated from equilibrium simulations [181, 182]. This can be achieved using linear response theory that relates these transport coefficients to the time integral of the TCF of some dynamical variable.

The time correlation function of functions A and B is defined as

$$C_{AB}(t) = \langle A_0 B_t \rangle \tag{1.23}$$

where C_{AB} is the correlation coefficient. For identical phase functions, C_{AA}(t) is called an autocorrelation function and its time integral (from t=0 to t=∞) is a correlation time t$_A$. These functions are of great interest in computer simulation because they give a clear picture of the dynamics in a fluid, their time integrals t$_A$ may often be related directly to macroscopic transport coefficients and their Fourier transforms $\widehat{C}_{AA}(\omega)$ may often be related to experimental spectra.

Transport coefficients are defined in terms of the response of a system to a perturbation. For example, the diffusion coefficient relates the particle flux to a concentration gradient, while the shear viscosity is a measure of the shear stress induced by an applied velocity gradient. Such perturbations can be introduced into the Hamiltonian and the distribution function may be calculated. The transport coefficient is obtained by the integration of the autotime correlation function and is given by

$$\gamma = \int_0^\infty dt \langle \dot{A}(t) \dot{A}(0) \rangle \tag{1.24}$$

where γ is the transport coefficient and A is a variable appearing in the perturbation term in the Hamiltonian. Associated with the relations of this kind, one can also write an ‘Einstein relation’,

$$2t\gamma = \langle (A(t) - A(0))^2 \rangle \tag{1.25}$$

that is true at large t (compared with the correlation time of A).

The transport coefficients in computer simulations can be calculated from equilibrium correlation functions or by conducting suitable non-equilibrium simulations from first principles.

The diffusion coefficient D, which is an important property characterizing a liquid [183, 184] is given (in three dimensions) by

$$D = \frac{1}{3}\int_0^\infty dt \langle \vec{v}_i(t) \cdot \vec{v}_i(0) \rangle \tag{1.26}$$

where $\vec{v}_i(t)$ is the centare-of-mass velocity of a single molecule. The corresponding Einstein relation that is valid at long times, is

$$2tD = \frac{1}{3}\langle |\vec{r}_i(t) - \vec{r}_i(0)|^2 \rangle \tag{1.27}$$

where $\vec{r}_i(t)$ is the molecule position. In the simulations, these averages would be computed for each of the particle and the results would be added together and divided by N to improve the statistical accuracy.

The vibrational density of states (VDOS) can also be obtained by Fourier transforming the normalized velocity autocorrelation function. The power spectrum C(ω) is defined as

$$C(\omega) = \int_{-\infty}^{\infty} C(t) e^{-i\omega t} dt. \tag{1.28}$$

where C(t) is given by

$$C(t) = \frac{\langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle}{\langle \mathbf{v}(0) \cdot \mathbf{v}(0) \rangle} \tag{1.29}$$

1.4 Software and Hardware used

All the classical molecular dynamics simulations studies mentioned in this thesis have been carried out by using LAMMPS [32] program. All the analysis of the MD trajectory have been carried with home developed codes, using Fortran 90. Xmgr, Xmgrace, and Gnuplot software have been used for plotting data.VMD [186], has been used for visualization of the coordinates. The computations were carried out on our groups dedicated clusters as well as on the centers (JNCASR) clusters. The group's clusters used are: a 32 processor Xeon cluster (Shabala), a 184 Harpertown processor cluster (Kamadhenu) and the Centers 512 Woodcrest core cluster (Sampige).

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Chapter 2

Intermolecular correlations in an ionic liquid under shear

2.1 Introduction

Room temperature ionic liquids based on the imidazolium cation are fascinating compounds that exhibit interesting phase behavior [1–6]. The microscopic origin of the variety in phases is the competition between Coulombic and dispersive interactions [7]. The former contributes to the ordering between cation's head group and the anion, while the latter manifests itself in alkyl tail-tail interactions. The interplay of these forces lead for example, to structural order in the nanoscale regime in an otherwise homogeneous liquid. This nanoscale ordering has been demonstrated through computer simulations [8–12] and also by small angle X-ray scattering experiments [13, 14].

The effect of shear on atomic and molecular liquids have been investigated by molecular dynamics simulations earlier [15, 16]. Apart from orientational ordering in a direction parallel to the shear, such studies have also shown hexagonal in-plane ordering, particularly in simple, atomic fluids. Whether room temperature ionic liquids too exhibit such a behavior is yet unknown. There have been reports of formation of liquid crystalline phases in ILs, under the application of shear [17]. Here, we report molecular dynamics simulations of an IL with a medium length alkyl tail subjected to planar Couette shear flow. Anticipating our results, we find evidence for nematic ordering of the molecular ions, and significant changes in the intermolecular structure.

2.2 Details of Simulation

A coarse grained (CG) model was used to simulate liquid [C_{10}mim][PF_6]. We provide here a brief description of the model which is illustrated in Figure 2.1. Details can be found in Ref. [11]. The cation in [C_{10}mim][PF_6] contains 43 atoms. The coarse grained representation of the cation, in turn, contains 6 beads. The imidazolium ring along with the methyl and methylene groups bonded to the nitrogen atom constitute three beads, while the alkyl tail is represented by three beads, CM, CM, and CT. The former three beads are charged, while the latter three are neutral. Neighbouring beads in the cation are connected by a harmonic spring, and a pair of beads separated by two bonds interact via a harmonic angle bending term as well. The parameters for these interactions are calculated by fitting the probability distribution of pair distances and angles obtained from an atomistic MD simulation. The anion (PF_6), being spherical, is easily represented by one bead. The potential of interaction between the CG beads contain Coulombic (charge-charge) as well as a soft dispersive term (the 9-6 interaction). The CG model has been validated against experimental results and atomistic simulations earlier [11].

The simulated system consisted of 3375 ion pairs with a total of 23,625 beads (super-atoms). Our earlier work on equilibrium simulations of ionic liquids using the CG model vividly brought out the nanoscale ordering in them [11]. The ordering is

Figure 2.1: Schematic of [C_{10}mim][PF_6], illustrating the mapping between atoms and coarse grain beads.

due to microphase segregation of polar and non-polar moieties. The starting configurations for the current simulation non-equilibrium simulations were obtained from our earlier study. Prior to the MD runs under shear, the system was equilibrated under constant NVT conditions for 400 ps. The equilibrated liquid was subjected to a shear stress in the planar Couette geometry. The linear velocity flow was in the x direction and the velocity gradient was in the y direction. The SLLOD [18] equations of motion as implemented in the LAMMPS code [32] were integrated with a time step of 4fs. The simulations were carried out at 300K. Temperature control was achieved using Nosé-Hoover thermostats [20] with a time constant of 200fs. Three dimensional periodic boundary conditions consistent with the flow geometry were applied. The system was studied under four different shear rates, 0.00001, 0.00005, 0.0001, 0.001 (all in units of fs^{-1}). Here, we report results at equilibrium and at the highest two shear rates. A trajectory of duration 400ps was generated in each of these runs. The coordinates of all the beads were stored every 400fs and were analyzed later. Typically, the initial 50ps of the trajectory was discarded to schemaallow the system to reach a steady state.

Coulombic interactions were treated using the particle-particle particle-mesh Ewald method with an accuracy of 10^{-6}. Pair correlation functions, g(r) between distinct pairs of beads were obtained, from which the isotropic structure factor, S(k) was calculated using the following relations.

The isotropically averaged partial structure factor between a pair of atom types α and β is given by,

$$S_{\alpha\beta}(k) = \delta_{\alpha\beta} + 4\pi\sqrt{\rho_\alpha \rho_\beta}\int_0^\infty r^2[g_{\alpha\beta}(r) - 1]\frac{sin(kr)}{(kr)}dr \tag{2.1}$$

where $\rho_\alpha = \frac{N_\alpha}{V}$. N_α is the number of beads of type α and V is the volume of the system. The upper limit in the integral was replaced with half the box length. The isotropic, total x-ray structure factor is defined as,

$$S(k) = \sum_\alpha \sum_\beta c_\alpha c_\beta \frac{f_\alpha(k) f_\beta(k)}{\langle f(k)\rangle^2} S_{\alpha\beta}(k) \tag{2.2}$$

where c_α is the concentration of bead type α in the system. f_α is the form factor (or scattering length) of bead α and $\langle f(k)\rangle = \sum_\alpha c_\alpha f_\alpha(k)$.

In view of the the presence of the symmetry breaking external field (shear), the structure factor was also calculated at each of the reciprocal space vector, **k**. The total scattering factor, $F_T(\mathbf{k})$ is defined as [21],

$$F_T(\mathbf{k}) = \sum_{j=1}^{N} a_j(\mathbf{k}) e^{i\mathbf{k}.\mathbf{r}_j} \tag{2.3}$$

and the scattering intensity is,

$$I_T(\mathbf{k}) = F_T(\mathbf{k})F_T^*(\mathbf{k}) \tag{2.4}$$

where a_j is the atomic form factor of the j-th species, and N is the total number of atoms.

The intramolecular contribution to the scattering function and the corresponding intensity are

$$F_s^m(\mathbf{k}) = \sum_{j=1}^{N^m} a_j(\mathbf{k})e^{i\mathbf{k}.\mathbf{r}_j} \tag{2.5}$$

$$I_s(\mathbf{k}) = F_s^m(\mathbf{k})F_s^{m^*}(\mathbf{k}) \tag{2.6}$$

where N^m is the total number of molecules. The intermolecular contribution to the scattered intensity which provides an idea of molecular ordering is given by,

$$I_i(\mathbf{k}) = I_T(\mathbf{k}) - I_s(\mathbf{k}) \tag{2.7}$$

This scattering intensity (I$_i$($\mathbf{k}$)) was analyzed using contour plots in the three different Cartesian planes.

2.3 Results and Discussion

Figure 2.2 compares the isotropically averaged, neutron weighted structure factor at three shear rates: zero, 0.0001, and 0.001 per fs. The low wave vector peak at 0.3Å^{-1} signifies intermediate range order of a length scale around 21Å. This corresponds to roughly twice the length of the cation. Thus, the liquid at equilibrium consists of polar regions rich in cationic heads and anions, while the alkyl tail of the cation constitutes the non-polar part. The low angle peak prominently present at

Figure 2.2: Isotropically averaged, neutron weighted structure factor of liquid [C_{10}mim][PF_6] subjected to shear flow at different rates. Legends are rates in units of fs^{-1}.

equilibrium, decreases in intensity with increasing shear rate. Thus, shear reduces the nanoscale ordering that is intrinsically present in the ionic liquid at equilibrium. Apart from a reduced intensity, the low angle peak also shifts marginally to higher wave vectors implying the decrease in the length scale of the nanoscale ordering.

Our earlier work showed that the 0.3Å^{-1} peak in the total structure factor had substantial contributions from partial structure factors of tail-tail, head-head and anion-anion pairs. It is thus important that we examine these pair correlation functions. In Figure 2.3, we show the head-anion, head-head and tail-tail g(r)s, at equilibrium and under shear. The head group of the cation is denoted here by the I1 bead (see Figure 2.1 for definitions of the beads) and the tail by the CT bead. The first peak in these three functions moves to smaller distances and its intensity is reduced at high shear rates. The picture that emerges is that the liquid gets less structured under shear. Also, the distinctions between different sites (for instance,

Figure 2.3: Partial pair correlation functions. (a) Cation's head group - Anion, (b) Cation's head group - head group, (c) Cation's tail bead - tail bead.

charged versus uncharged) are reduced in the presence of the external field.

In contrast to this generic behaviour, two pair correlation functions exhibit an increase in the intensity of the first peak with increasing shear rate. These are for tail-anion and head-tail pairs and are shown in Figure 2.4. The first peak in the g(r) for both these pairs shifts to lower distances and increases in height with increasing shear rate. Combined with the earlier observation in Figure 2.2 of a decrease in nanoscopic order, this data implies that anions no longer have to preferentially coordinate the cation heads; they can also be present near the tails of the cation.

The externally imposed shear field can be expected to induce orientational ordering in the system. In Figure 4.4 we show the probability distribution of the angle that the head to tail vector of the cation makes with the three Cartesian axes. Even at a shear rate of 0.0001 per fs, the preference for cation ordering along the X-axis is discernible. At the highest shear rate, this preference dominates. One finds clear evidence for the long axis of the cation to be parallel to the shear direction. Note that there is equal preference for the cation head to be along the positive and the negative X-axis.

Are the cations layered along the x-axis? Evidence for the absence of layering at 300K comes from calculations of the q-dependent scattered intensity, $\mathrm{I}_i(\mathbf{k})$, defined in Eq. 2.7. In Figures 2.6 and 2.7, we show contour plots of $\mathrm{I}_i(\mathbf{k})$ at equilibrium and at a shear rate of 0.001 fs^{-1} along the three Cartesian planes, xy, xz and yz. For instance, what is shown in Figure 2.6 for the xy plane is the sum of $\mathrm{I}_i(\mathbf{k})$ over all possible z values. Notice the nearly circular contour curves in all the three planes, at equilibrium. Under shear, one finds two crescents appearing along the meridian in the xy and xz planes, with a circular plot in the yz plane. This signifies nematic ordering in the system [22] and the director is the x-axis. If the system showed layering, one would have observed a four-spot pattern implying smectic ordering. The absence of the four-spot pattern and the presence of crescents confirms the nematic nature of the system under shear. The nematic ordering is observed to

Figure 2.4: Partial pair correlation functions. (a) Cation's tail - Anion, (b) Cation's head group - tail bead.

Figure 2.5: Probability distributions of the angle, θ made by the cation's head group - tail vector with respect to the Cartesian axes. Numerical values in the legend are shear rates in units of fs^{-1}.

relax back to a equilibrium configuration, once the shear stress is relieved.

2.4 Conclusions

We have studied the effect of planar Couette shear flow on the intermolecular ordering and structure of a room temperature ionic liquid, $[\mathrm{C_{10}mim}][\mathrm{PF_6}]$. Our simulations reveal interesting changes in the system upon shear. With increasing shear rate, we find a decrease in the magnitude of structural correlations at the nanoscale with a concomitant decrease in the length scale of such correlations as well. The loss in nanoscale order is likely due to decreased structuring at the near neighbor level of cations and anions. These have been documented using partial pair correlation functions. Interestingly, two partial pair correlation functions, that of tail-anion and of head-tail show an increase in the height of the first peak with increasing shear rate. These can be explained as due to a dilution of specific interactions (charged

Figure 2.6: Contour plots of the contribution to the scattering intensity from intermolecular correlations (see Eq. 2.7) in the ionic liquid at equilibrium, along the three distinct reciprocal lattice planes.

Figure 2.7: Contour plots of the contribution to the scattering intensity from intermolecular correlations (see Eq. 2.7) in the ionic liquid at a shear rate of 0.001 fs^{-1}, along the three distinct reciprocal lattice planes.

versus uncharged) at high shear rates. Shear imposes a orientational preference for the cations so as to align their long axes with the shear direction – here the x-axis. Apart from demonstrating this preference through orientational distribution functions, contour plots of structure factor clearly show the emergence of a nematic order in the system, away from equilibrium. Wang [23] studied the effect of external electric field on the spatial heterogeneity of ionic liquids. He noticed that as the external electric field strength increases, the ionic liquid structure is first disordered from spatially heterogeneous to spatially homogeneous, and is then reordered to nematic-like. The ionic self-diffusion and the system volume increase in the spatially homogeneous region and decrease in the nematic-like region. Our results on shear induced nematic order is analogous to their observation of electric field induced nematic ordering.

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Chapter 3

Aqueous Solution of [bmim][PF_6] : Ion and Solvent Effects on Structure and Dynamics

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3.1 Introduction

The physical chemistry of aqueous ionic solutions is vast and rich. A large number of experimental [1–3], theoretical [4–6] and simulation [7–12] studies of dilute aqueous ionic solutions containing common inorganic ions have been carried out, to study various aspects of these solutions. Simple but effective models for ion-water interaction and its influence on the structure of hydration water has demonstrated the relationship between the charge density of the ion, ion-dipole interaction and hydrogen bonding [13]. In particular, small ions break water-water hydrogen bonds, while larger ones do not destabilize the hydrogen bond network of liquid water to that extent. It would thus be interesting to compare the behavior of aqueous solutions of neoteric salts such as room temperature ionic liquids (RTIL), with traditional ionic solutions.

Experiments [14] on aqueous ionic liquid (IL) solutions have shown that water is mainly hydrogen bonded to the anion and that the strength of H-bonding between water molecule and different anions increase in the following order : $[PF_6]^- < [SbF_6]^- < [BF_4]^- < [(CF_3SO_2)_2N]^- < [ClO_4]^- < [CF_3SO_3]^- < [NO_3]^- < [CF_3CO_2]^-$. Studies on water-IL mixtures of [bmim][BF$_4$], [bmim][I] and [Na][Cl] show that at infinite dilution, the IL dissociates but the hydration of RTIL ions is much weaker than that for [Na][Cl] [15]. In particular, thermodynamic quantities such as the excess molar free energy and excess partial molar free energy are negative for [bmim][I] and [Na][Cl], while they are positive for [bmim][BF$_4$] [15]. Some authors suggest the existence of a weak interaction between the acidic proton (present in the imidazolium ring of the cation) and the oxygen of water as well [16, 17]. Studies on imidazolium based ILs show that the length of alkyl chain affects their miscibility in water, as expected [18]. Kanakubo *et al* reported a remarkable enhancement of transport properties of ions in solutions containing small concentrations of water. Though water was not found to affect ion dissociation, it increased the self diffusion of anion considerably [19]. Li and coworkers have used two-dimensional vibrational spectroscopy to study different concentrations of [bmim][BF$_4$] in water [20]. With increase in water concentration, the cohesion between ions reduced. Upon further dilution, the three dimensional network of the IL was destroyed to give rise to ionic clusters and later, into ion pairs surrounded by water. Within the range of $0.02 \leq X_{D_2O} \leq 0.90$, the IL was found to be largely associated. In a related recent work, Freire et al have examined the role of inorganic salts on the miscibility of water in RTILs (and vice versa) [21]. Pandey and coworkers have studied steady state fluorescence of probes dissolved in aqueous dilute solutions of [bmim][PF$_6$] [22]. They conclude that the properties of liquid water are drastically altered by the dissolution of small concentrations of [bmim][PF$_6$] salt.

Molecular dynamics (MD) simulations of [bmim][PF_6] and [bmim][Cl] solutions with water show that at low concentrations, water exists as small clusters and at high concentrations, as a continuous network [23]. Excess thermodynamic functions, reorientational correlation times, and water diffusion coefficients were found to be significantly different between the two IL solutions mainly due to the greater hydrophibicity of PF_6 compared to Cl. Voth *et al* [24] have simulated solutions of 1-*n*-octyl-3-methylimidazolium nitrate [C_8mim][NO_3] in water at different concentrations. Apart from the screening of the polar network by the intruding water, they have noticed that the structural organization of the water network and the micelle formed by the long chain cations exhibit a turnover. Bhargava and Klein have observed cation aggregation in aqueous IL solutions containing a cation with a long alkyl tail [25]. By dividing the ternary system [bmim]/[PF_6]/water into six binary networks, Steinhauser *et al* have noticed a reduction in strength of cation-anion network, due to the concurring anion-water network [26]. The dipolar field exerted by water is responsible for the blurring of cation-anion orientational structure. Kirchner and coworkers have examined dilute aqueous IL solutions using ab initio MD method [27]. In a simulation of [emim][Cl], they observe significant changes in the structure of the hydration shell around an ion pair, compared to bulk water. Within the time scales of their simulation, they did not observe the dissociation of the ion pair. Freire *at al* [28] have conducted a systematic experimental study of the mutual solubilities between hydrophobic pyridinium-based ionic liquids and water in the temperature range 288.15-318.15 K

While significant attention has been devoted to the study of aqueous solutions in the RTIL-rich part of the binary phase diagram, dilute aqueous RTIL solutions have not been studied using simulations [29, 30]. The present work is aimed at providing a detailed microscopic behavior of a dilute RTIL solution. Specifically, we study a dilute solution of [bmim][PF_6] in water. Crystalline [bmim][PF_6] melts at 6 °C, and

Figure 3.1: Schematic of [bmim] cation.

the liquid at room temperature is quite viscous ($\eta \simeq 270$ cP), compared to water. In the next section, we provide details of the simulation, following which the structure, dynamics and energetics of the ions and the hydration layer water are presented. Conclusions drawn from these results are summarized later.

3.2 Simulation Details

A schematic of the molecular structure and connectivity of $[\text{bmim}]^+$ and $[\text{PF}_6]^-$ ions is provided in Figure 3.1.

The force field parameters used for [bmim]$[\text{PF}_6]$ are from the all atom model developed by Bhargava and Balasubramanian [31]. For water, the flexible SPC/Fw model [32] was used. Lorentz-Berthelot combination rules were employed for cross interactions.

To start with, a water box containing approximately 8000 water molecules was generated using VMD [33]. Ten ion pairs (as dissociated ions) of [bmim]$[\text{PF}_6]$ were inserted into this box and water molecules in hard contact were eliminated. The solution contained 10 ion pairs in 7736 water molecules and a total of 23,528 atoms, corresponding to 2 wt% of [bmim][PF_6] in water. This value represents the experimentally observed solubility limit of [bmim][PF_6] salt in water. The configuration was relaxed using standard energy minimization methods. The system was then slowly brought to 300K after performing constant NVT simulations at 10K, 50K, 150K. A trajectory of length 200 ps was generated later under constant NPT conditions in order to obtain the average box length (and thus density). This value of the box length (61.59Å) was used in carrying out further MD simulations under constant NVT conditions using a Nosé-Hoover thermostat. The density of the simulated system at 300K is 0.997 g/cc and is within 1% of the experimentally reported density of 1.005 g/cc [22]. Three dimensional periodic boundary conditions were employed.

Five independent configurations were generated by heating a particular configuration to different temperatures (330K, 340K, 350K, 360K,and 370K), equilibrating at that temperature, and then cooling them back to 300K. To calculate the activation energies of diffusion, five configurations were similarly generated at 290K and 320K. Trajectories of 8 ns were generated from each of the configurations at these temperatures with an integration time step of 0.5 fs. The coordinates were written out every ps for further analyses. Coulombic interactions were handled using the PPPM Ewald method. All the simulations were carried out using the LAMMPS [35] package.

3.3 Results and Discussion

In the following, we denote the oxygen and hydrogen atoms of water by O_w and H_w respectively. We first investigate the ions in solution, and later their hydration layer.

3.3.1 The Ions: Energetics, Structure, Dynamics

We present the distribution of potential energies of the ions in pure IL and in the aqeuous solution in Figure 3.2. Relative to the pure IL, the cation is destabilized and the anion is stabilized in solution. The former is likely due to the hydrophobicity of the butyl group. The width of this “monomer” energy distribution arises from various structural arrangements that an ion is part of – the more varied its neighborhood, the larger the width. A careful examination of the width (and the peak height) of the distributions suggests that the anion perceives a larger variety of coordination compared to the anion in pure IL and to the cation in solution, implying a more heterogeneous local environment. This aspect will be studied further in the next subsection.

The (de)stabilization of the ions in solution can be understood when one examines the contributions to their potential energy (alternatively, we use the term monomer energy). The major contribution to the potential energy of a cation comes from its interaction with water molecules. In Figure 3.3, we present the distribution of pair energies (PED) of anions (or cations) interacting with water molecules. Such distributions were introduced in pioneering works on liquid water [36,37]. The PED of water molecules interacting with anions shows a peak at -25.1 kJ/mol, which is absent in the PED of water molecules with cations. This demonstration of a specific interaction between anions and water molecules explains the stabilization of anions in solution. Also note that the PED of anions extends into the positive values more than that for the cation. This feature is explained in the next section. The large peak at zero is a simple consequence of the existence of numerous “neighbors” at large distances.

The distribution of pair energies of cations with anions in the pure IL and in the solution is shown in Figure 3.4. The tall peak at zero arises from innumerable pairs present at large distances from an ion. It is interesting to note the feature at

Figure 3.2: Distribution of monomer potential energies in pure [bmim][PF_6]in the [bmim][PF_6]-water solution. (a) Cation (b) Anion.

Figure 3.3: Distribution of pair energies (PED) of anion or cation interacting with water molecules in the solution.

energies less than -125.52 kJ/mol. *This broad peak in the PED is a clear evidence for the presence of cation-anion dimers in solution and is one of the central results of this work.*

We have used the PED data to identify cation-anion dimers. If the potential energy between a cation and an anion is less than -125.52 kJ/mol and if the distance between them is less than 7.3Å, we consider them to form a dimer complex. Note that 7.3Å is the minimum in the RDF of cation around anion in the solution (see later). On average, we observed about 13% of the ions to be dimerized (i.e., as associated ion pairs) configuration, with the rest present as individual, water solvated ions. Despite the use of close to 8,000 water molecules, the number of ions in our simulation is relatively small. This is due to the fact that the concentration studied here is low (2 wt%) which is the solubility limit of this IL in water. The percentage of free ions (or of pairs) could be influenced by the limitation in system size. One can use the average concentrations of these species to calculate equilibrium constants of the reversible reaction between a dimer and free ions formed out

Figure 3.4: Distribution of pair energy (PED) of cations interacting with anions in solution and in pure IL.

of it. This equilibrium constant can in turn be used to calculate the difference in the chemical potential, ΔA between configurations of the solution in which an ion pair is associated and one in which it is not. We obtain ΔA to be 16 kJ/mol, in favor of the latter over the former. Clusters of ions larger than a dimer were also observed in solution; however these were water mediated and hence are ignored in this discussion. Chen and Pappu [12] have investigated aspects of ion clustering in MD simulations of aqueous alkali halide solutions.

Let us examine the PED of the pure IL further (Figure 3.4). In comparison to that of the solution, the PED of the pure IL exhibits two distinct humps, one between -125.5 kJ/mol to -182.4 kJ/mol and the other ranging between -182.4kJ/mol to -205.0 kJ/mol. In order to identify the origin of these two features, we have calculated the spatial distribution functions (or, spatial density maps) of anions around cation whose pair energies fall in either of these two energy ranges. These are shown in Figure 3.5 for the pure IL. When the pair energies are more negative, anions are

Figure 3.5: Spatial distribution functions of anions around cation at an isosurface value of 0.0337 $\mathring{A}^{-3}$ in pure IL (a) With pair energy in the range -125.5 kJ/mol to -182.4 kJ/mol (b) With pair energy in the range -182.4 kJ/mol to -205.0 kJ/mol.

Figure 3.6: Radial distribution function and potential of mean force (inset) between cation and anion.

seen to be present near $H_A(C_R)$, while less negative pair energies are contributed by anions which are present near the $H_A(C_w)$, i.e., towards the methyl group. So, the cation-anion interaction is stronger through $H_A(C_R)$ than through $H_A(C_w)$. Other workers have also made such an observation, using quantum chemical methods [38, 39] albeit on isolated ion pairs. Our work demonstrates this aspect in bulk liquid.

Similarly, we have analyzed the spatial distribution functions in the solution (data not shown), although the cation-anion PED in solution does not show two distinct peaks unlike in pure IL. When the pair energy is more negative (-182.4 kJ/mol to -205.0 kJ/mol), we found the anions to be predominantly present above and below the cation ring, while in the energy range of -125.5 kJ/mol to -182.4 kJ/mol anions did not show any site preference around the cation. Spatial distribution functions of anion around the cation in solution could not be obtained at the same isosurface value as in pure IL, due to poor statistics (small number of ions in solution).

We present the cation-anion pair correlation function in Figure 3.6. The center of the imidazolium ring is taken to be the position of the cation, while the phosphorous coordinate is the position of anion. The first peak is present at 5.1Å with a coordination number (up to the first minimum of g(r)) of 0.18. The absence of any further peaks in the g(r) shows the lack (or negligible presence) of clusters larger than a cation-anion dimer, in the solution. The extent of stabilisation of this solvated dimer can be gauged by examining the potential of mean force (PMF = -k_BTln(g(r))), obtained from the pair correlation function. The PMF is shown as inset to Figure 3.6. The solvent stabilised ion pair has an energy of about -5.02 kJ/mol, relative to independent ions separated by water. A subtle point about the cation-anion g(r) needs to be mentioned. The pair correlation function may appear to have a value slightly larger than unity at distances beyond the first peak position. However, on closer examination, it shows weak oscillations which are rather spread out. These correspond to ion "pairs" which are separated by a large number of water molecules.

The mean squared displacements, averaged over five independent trajectories, of cation, anion and water in the [bmim][PF_6]-water solution and for cation and anion in pure [bmim][PF_6] are shown in Figure 3.7. The diffusion coefficients of various species are calculated from their mean squared displacements using the Einstein relation

$$D = \frac{1}{6} \lim_{t \to \infty} \frac{d}{dt} \langle |\vec{r}_i(t) - \vec{r}_i(0)|^2 \rangle \tag{3.1}$$

While the cation diffuses faster than the anion in pure [bmim][PF_6] [31, 40], the converse is true in the dilute solution studied here. Unfortunately, there is no experimental data for diffusion coefficients at this mole fraction, and hence we are unable to make a comparison. However, self diffusion coefficients obtained from NMR at a larger concentration of salt (0.25 mole fraction) shows that dilution of the [bmim][PF_6] salt with water increases the diffusion rate of the anion more than that of the cation [19]. An earlier MD simulation study of the interface between water and [bmim][PF_6] reports a higher diffusion coefficient for [PF_6] than [bmim]

Figure 3.7: Mean square displacement. (a) Anion, cation and water in [bmim][PF_6]-water solution, (b) Anion and cation in pure [bmim][PF_6].

Table 3.1: Calculated diffusion co-efficients of anion and cation in the 2 wt % [bmim][PF_6] aqueous solution at different temperatures. Error bars are standard error on the mean.

Temperature (K)	D_{an} ($\times 10^{-5}$ cm^2s^{-1})	D_{cat} ($\times 10^{-5}$ cm^2s^{-1})
290	1.49±0.08	0.64±0.02
300	1.59±0.03	0.90±0.05
320	2.12±0.05	1.25±0.08
E_D(kJ/mol)	9.4 (Anion)	16.8 (Cation)

in the bulk water phase [41]. Our observations are consistent with these results.

To understand this feature, the activation energies of diffusion have been calculated from the temperature dependence of D. Values of D of various species in the solution at different temperatures are provided in Table 3.1. The table also shows the activation energies, E_D obtained from an Arrhenius fit of the diffusion data. The barrier height for the anion is smaller than that for the cation, leading to its larger diffusion coefficient.

3.3.2 Hydration Layer

Structure

The radial distribution functions (RDF) of O_w around the cation (the center of imidazole ring) and around the phosphorus atom of PF_6 are shown in Figure 3.8. The first peak with respect to the anion is taller and is also present at a shorter distance compared to that with the cation. The coordination number (measured at the first minimum of the respective g(r)) for water surrounding an anion and cation are 28 and 27 respectively. These values are quite large when compared to those for traditional inorganic ions – approximately four or six waters surrounding a lithium or potassium ion respectively. Also to note is the rather large width of the first peak in the anion-O_w g(r). The first coordination shell of water around the anion is quite thick. We shall examine this hydration layer in much detail, later.

Figure 3.8: Pair correlation functions of cation-water and anion-water in [bmim][PF_6]-water solution.

Figure 3.9: Pair correlation functions of oxygen of water around $H_A(C_R)$ and hydrogen atoms of water around fluorine of PF_6.

The observation through the ion-water g(r), that water interacts better with the anion than with the cation, is consistent with earlier NMR data [19]. The predominant means of interaction between water and the ions is hydrogen bonding. In Figure 3.9, we show the RDF of O_w around the acidic hydrogen of cation $H_A(C_R)$ and H_w around the fluorine atoms of PF_6. Once again, the F-H_w g(r) exhibits a peak at around 2.15Å which is absent in the corresponding g(r) with the cation site. The hydrogen bond between $[PF_6]$ and water is weaker than that between two water molecules, consistent with recent far infrared spectroscopic measurements [42].

The spatial distribution of water molecules around the ions shown in Figures 3.10 is interesting. The distribution of water around the cation is very similar to that of the anion around cation in pure IL [31]. However, the region adjacent to the butyl tail is devoid of water, as expected. The dominant isosurface is also seen to be shifted slightly away from the side of the imidazolium ring that contains the butyl tail. A likely reason for this behavior is that the butyl group being conformationally flexible, repels the water molecules, tending to move them towards the other side of the ring. In Figure 3.10, the cation is shown with a representative conformation of the butyl ring.

The oxygen atoms of water molecules coordinating the anion are found to lie near the octahedral holes formed by three P-F bond vectors. The isosurface shown in Figure 3.10 is at a density which is roughly three times the density of bulk water. The P-O_w RDF (Figure 3.8) shows a broad first peak and a very weak minimum at 6.2Å. Obviously, a large fraction of water molecules present within 6.2Å of the phosphorus atom are not directly coordinating the anion; only a few do.

Let us examine the orientation of the water molecules with respect to the ions. In Figure 3.11, we present the C_R–H_A–O_w and F–H_w–O_w angle distributions. To obtain the former , water molecules whose oxygen atoms lie within 3.75Å (first minima in RDF of O_w around H_A) of H_A were considered. Similarly, the hydrogen

Figure 3.10: Spatial distribution functions at an isosurface value of 0.0937 $\AA^{-3}$ (a) Of water around cation (b) Of water around anion (c) Of water around anion in a different orientation.

Figure 3.11: C_R–H_A–O_w and F–H_w–O_w angle distributions.

atoms of water molecules present within 2.45Å (the position of the first minimum in the F-H_w RDF) of the fluorine atom of PF_6 were used to calculate the F–H_w–O_w angle distribution.

The distribution of C_R–H_A–O_w angles shows a peak at 137 °. It is similar to the C_R–H_A–F angle distribution in pure [bmim][PF_6] [31] which shows a peak at around 139 °. From the figure, we find that anions have a much greater probability of forming linear hydrogen bonds compared to cations. Since one knows that a typical hydrogen bond is weaker if the h-bond angle is farther from linearity, this data indicates the ability of anions to interact stronger with water than cations do, in agreement with our earlier observation that anions are more stable (energetically) than cations in the [bmim][PF_6]-water solution.

The orientational dependence of a water molecule in the hydration shell of an ion is determined primarily by the competition between the ion-dipole and dipole-dipole interactions. Here, the dipole refers to that of the water molecule. Dill and

Figure 3.12: Distribution of angle between the water-ion distance vector and the dipole vector of water molecules in the hydration shell of (a) cation, (b) anion. Distances in the legend denote radii of spherical shells in which waters used in this analysis are present.

coworkers [13] have studied this aspect elegantly through MD simulations of aqueous solutions containing many conventional inorganic ions. We study the orientational preferences for water molecules in the hydration shell of ions further. Shown in Figure 3.12 is the probability distribution of the angle between the water-ion distance vector and the dipole vector of the water molecule. Part (a) of the figure exhibits the data for waters present around the cation in specified spherical shells, while Part (b) is the corresponding data around the anion. The closest water molecules around the cation prefer to make larger than 90° angles with the cation, while similarly positioned water molecules around the anion prefer acute angles. This is expected on Coulombic grounds – the lone pair of the oxygen will be oriented towards a cation, while the hydrogen atom of the water molecule will be oriented towards an anion.

An interesting feature of these data is that the distribution around the cation shows only a weak dependence on the distance of the water molecule from the cation. However, the angle distributions around an anion change significantly with distance. The larger the distance, the higher the mean angle. At short distances, the distribution shows a peak at around 50^o which is consistent with the hydrophobic nature of the $[PF_6]$ ion. This result is also consistent with the angle distributions around halide ions studied by Dill and coworkers [13], given the ionic radius of $[PF_6]$. The distance dependence of this angle is vividly brought out by a calculation of the 2nd order Legendre function, $P_2(\cos\theta)$ shown in Figure 3.13 for the cation and the anion. θ is once again the angle between the water-ion distance vector and the dipole vector of the water molecule. One finds that this function is largely negative in sign for water molecules present around a cation, throughout the first coordination shell (i.e., up to a distance of 6.25Å). However, water molecules present closer to the anion have a positive P_2 value, and those which are farther away (but within the first coordination shell, based on P-O_w g(r)) exhibit a negative P_2 value. This

Figure 3.13: $P_2(\cos(\theta))$ of the angle made by the dipole moment vector of hydration layer water with the water-ion distance vector. The data is shown for water molecules present in the first coordination shell of either a cation or an anion as a function of its distance from the ion.

complex orientational behavior of water molecules is not anomalous. The closest waters form hydrogen bonds with the fluorine atoms of the [PF_6] anion, hence the immediate layer of water molecules need to reorient themselves so as to form water-water h-bonds with this closest layer. In the case of the cation, as we have already noted in the discussion of pair correlation functions, specific hydrogen bonding sites are few and weak. Hence water molecules around a cation are largely influenced by its static charge; hence the monotonic dependence of the P_2 of such molecules with distance away from the cation. We shall observe more facets of this structural richness in the discussion on the energetics of these hydration shell water molecules.

Using a geometric definition of hydrogen bonds [43] ($r_{OO} \leq 3.5$Å, $r_{OH} \leq 2.5$Å, and $O\hat{O}H \leq 30^o$), we find that the number of hydrogen bonds per water molecule in pure water is 1.80, whereas in the [bmim][PF_6]-water system this value has reduced marginally to 1.60.

Energetics

Figure 3.14(a) shows the monomer potential distribution of pure water and of water in the aqueous IL solution. The latter is narrower with a larger peak height. No shift in the distribution can be discerned.

Although the peak position (and the mean value) of the monomer energy distribution of water molecules in the solution is the same as that in pure water, we find small, but significant shifts in these distributions for hydration shell water. The percentage of water molecules present in the hydration shell of ions is less; hence, the small but non-negligible shift in the monomer energy distribution of hydration shell water does not alter the mean value of the energy in solution, relative to that of pure water.

Let us now examine this shift. In Figure 3.14(b), we show the monomer potential energy distribution of water coordinated to an anion or to a cation. We show only the region near the peaks to highlight the difference in their peak positions. The minimum in the RDF of water around the cation (6.25Å) and around the anion (6.15Å) are used to identify the water molecules present in the hydration shells of the ions. We find that waters present in the coordination shell of an anion are less stable than those which coordinate a cation. The mean energy of an anion bound water is 3.3 kJ/mole higher than that for a cation bound water.

The underlying cause for the destabilization of the anion bound water relative to that around a cation can be identified by examining the contributions to the potential energy of this water species from other water molecules (E_w^{wa}), from anions (E_a^{wa}), and from cations (E_c^{wa}) present in the solution. Here, wa in the superscript denotes a water (w) present in the hydration shell of an anion (a). The subscript denotes the species with which this interaction energy is calculated – c representing the cation, a the anion and w for other water molecules. Similarly, E_w^{wc} would denote the interaction energy of a cation bound water (wc) with other water molecules. The

Figure 3.14: (a) Distribution of potential energies of pure water and of water in the [bmim][PF_6]-water solution. (b) The same distribution for water molecules in the hydration layer of a cation (circles) or an anion (triangles) in the IL-water solution. Only the region near the peak positions is shown.

terms E_a^{wc} and E_c^{wa} are negligible and are not discussed further.

Figure 3.15(a) exhibits the probability distributions of the energies E_a^{wa} and E_c^{wc}. The former distribution is broader than the latter. This shows that water molecules in the hydration shell of the [PF$_6$] anion exhibit a much more diverse behavior than those around the [bmim] cation, consistent with our observations on the orientational distributions of water molecules shown in Figure 3.13. Many water molecules present in the coordination shell of the anion interact strongly with it, much more so than waters present in the hydration shell of the cation. However, this is offset by another set of water molecules (present within the first coordination shell of the [PF$_6$] anion) which interact not so favorably with it. Thus, the mean values (first moment) of the distribution with respect to the anion is higher (i.e., more positive) than that for the cation – by about 0.38 kJ/mole. We had noted earlier that the mean energy of anion bound water is higher by about 3.3 kJ/mole than a cation bound water.

The major contribution to the destabilization of anion bound water molecules, arises however, from their interaction with other water molecules. Figure 3.15(b) shows the distribution of E_w^{wa} and E_w^{wc}. The mean value of E_w^{wa} is larger than E_w^{wc} by 2.7 kJ/mol. This is mainly due to the unique orientation of many water molecules around the anion, i.e., those which are not hydrogen bonded to the fluorine atoms, but are present within the first coordination shell with respect to the phosphorus atom, as explained in section 3.2.1.

To summarize, the mean potential energy of water in the hydration shell of an anion is less stable than that around a cation. The difference arises largely from the interaction with other water molecules. Interaction with proximal ions (cation or anion, as the case may be) makes a small, but non-negligible contribution.

Figure 3.15: (a) Distribution of potential energy of water bound to the cation with cations and the same for water bound to anion with anions. (b) Distribution of potential energy of water bound to the cation with other water molecules, and the same for water bound to anion with other water molecules.

Dynamics

One can obtain an understanding of water dynamics in the hydration layer by studying its residence time correlation function (RTCF), C_R(t). If a water molecule is resident in the hydration shell of an ion (based on whether its distance from the ion is within the first minimum of the corresponding g(r)), one defines a function, R_{ij}(t) to have a value of unity, and zero otherwise. In calculating the RTCF of pure water, the minimum in RDF of oxygen around oxygen (3.50Å) is used to define the hydration shell of water.

$R_{ij}(t) = 1$ if a water molecule j is in the first coordination shell of an ion i at time t.

=0 otherwise

The normalized TCF of this function is C_R(t), which is both ensemble and time averaged. C_R(t) will be non-zero, even if a water molecule leaves the hydration shell, diffuses out into the bulk and returns back to the coordination shell of the same ion.

The residence time correlation function is defined as

$$C_R(t) = \frac{\langle R_i(\tau) R_i(t+\tau)\rangle}{\langle R_i(\tau) R_i(\tau)\rangle}$$

Figure 3.16 shows the residence time correlation function plots. C_R(t) of water molecules coordinated to an anion decays faster than for those around a cation. The water molecules around an anion translate out of the coordination shell more rapidly than those coordinated to a cation. This observation is in line with the results on the diffusion coefficients of the ions. Expectedly, the function around a water molecule is the fastest due possibly to two reasons; (i) the dynamics of hydration water around a water molecule could actually be marginally faster than of that around an ion. (ii) the smaller cut-off of 3.5Å for the hydration layer in pure water could lead to the faster decay of its C_R(t).

The interpretation of the RTCF data assumes that the ion is immobile for the duration of the relaxation of the TCF. However, this is not valid, as the ions are seen to be fairly mobile from the values of their diffusion coefficients discussed earlier.

Figure 3.16: The residence time correlation function of water coordinated to anion, cation and pure water.

Despite this ion mobility, we wish to stress that the faster decay of the RTCF of anion bound water (over the cation bound one) occurs at all timescales. Even for short times (say 10 ps), when the ion is expected not to have translated much, the RTCF of anion bound water relaxes faster than that for the cation bound water.

3.3.3 Conclusions

We have carried out empirical potential MD simulations of 2 wt% [bmim][PF_6] in water. The results reported here are consistent with earlier pioneering works [14, 16, 23, 26] on aqueous solutions of ionic liquid. We have studied this system extensively in order to delineate the microscopic structure, energetics and dynamics of various species and to offer insights into the hydrophobic character of the ions and its influence on the hydration layer.

The key results from this work are:

(i) The faster diffusion of the anion over the cation in solution, in contrast to their behavior in pure IL. This result can be rationalized from the lower energy of activation of the anion in solution.

(ii) The lowering of activation energy is coupled with a decrease in the mean potential energy of the anion in aqueous solution, compared to the pure IL. The opposite is seen for the cation.

(iii) The distribution of pair energies along with a distance threshold aids in the identification of ion pairs in solution. At 2 wt% of IL, we estimate around 87% of the ions to be dissociated in water. The exact value need to be ascertained through simulations containing many more ions than what is studied here. Our results on ion pairing is consistent with recent dielectric spectroscopy experiments of Steinhauser and coworkers [44]. They reported formation of ion pairs in aqueous [bmim][BF_4] solutions. Given the higher hydrophobicity of [bmim][PF_6] over their salt, pair formation to the extent of 13% observed in our simulations is reasonable.

(iv) A pair of solvated free ions is stable with respect to the solvated ion pair by about 16.0 kJ/mole, at the concentration studied here. This value will change as a function of IL concentration in water.

(v) Water molecules interact stronger with the anion than with the cation, in agreement with early predictions from NMR [19].

(vi) The structure of the hydration layer around the ions is rich; around the anion, water molecules with two distinct orientational preferences are observed. Closer to the anion, their orientation is dictated by ion-dipole and hydrogen bonding interactions, while a little distance away but still within the first coordination shell of the anion, their orientation is chiefly determined by water-water (dipole-dipole) interactions. Cation, being devoid of sites capable of forming hydrogen bonds with water shows no such complexity in its hydration layer.

(vii)Water molecules present in the hydration layer of an anion are less stable than those around a cation. The loss in potential energy is attributed chiefly to a decrease in the water-water interaction energy.

(viii)The energetically destabilized water around an anion is shown to exhibit faster dynamics than that around a cation, as demonstrated through the relaxation of the residence time correlation function. It is surmised that the faster diffusion of anion (over cation) in solution is related to the speedy dynamics of its hydration shell water.

The results reported here (pair correlation functions, orientational distributions etc.) are qualitatively reproduced with other potential models as well. Specifically, we have employed the CLP model [45] and that of Soares et al [46] for [bmim][PF_6] and have verified the invariance of the observed results.

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Chapter 4

Emergence of nanoscale order in room temperature ionic liquids: Simulation of symmetric 1,3-didecylimidazolium hexafluorophosphate

4.1 Introduction

Intermediate range ordering in homogeneous bulk liquids is an active area of long standing interest. While liquids composed of small molecules exhibit translational or orientational order up to distances corresponding to two or three molecular neighbours, those consisting of longer molecules could often show arrangements spanning a greater range. The latter can also lead to the formation of new phases, such as, for instance, liquid crystalline [1]. Room temperature ionic liquids (RTIL) are molecular salts having both inorganic and organic components, and hence are capable of dissolving a wide variety of solutes. They have low volatility. Composed purely of ions, the chief interaction between the constituents is electrostatic. However, alkyl groups attached to the cation in many of the ILs interact with each other via van der Waals (vdW) interaction. The interplay between the strong Coulombic forces and the weaker, but abundant vdW interactions can give rise to novel morphology in these complex liquids [2]. Micro phase segregation or microheterogeneity are some of the terms commonly used to describe structural features emerging at nanoscopic length scales, in an otherwise homogeneous bulk liquid [3–7]. A wide variety of sophisticated experimental [8–10] and computational tools [11, 12] have been employed to study these aspects of ionic liquids recently. The time scales of ordering in ILs is undetermined; however, one can estimate them to be in the range of hundreds to thousands of nanoseconds, based on similar processes occurring in the formation of micellar aggregates in surfactant solutions. It is virtually impossible to be able to study this process of selfassembly in ionic liquids using atomistic computer simulations, given the rather long duration required. Yet, such processes and phenomena are being intensively studied using molecular dynamics (MD) simulations which employ accurate molecular models which are not atomistic, but are rather coarse grained [4, 13]. We have recently developed a coarse grain model for 1,3-dialkylimidazolium hexafluorophosphate and were able to successfully predict the formation of microheterogeneous domains in the bulk liquid [14]. Regions rich in polar moieties such as the anion and the imidazolium ring of the cation (where the positive charge is concentrated) were found to be separated from those which were rich in the alkyl tail group of the cation. The morphology was reminiscent of a bicontinuous microemulsion. The length scale of the ordering observed in our simulations matched well with predictions from small angle X-ray scattering experiments [9, 10]. Common to the ionic liquids studied by us as well as by other workers is the methyl group at the C_1 position of the cation. Note that the number of carbon atoms of the alkyl group at the C_3 position determines the range of nanoscale order in these liquids. Given the crucial role played by tail-tail interactions in the microphase segregation exhibited by these compounds, it would be interesting to see if this phenomenon is accentuated in compounds where the cations have two symmetric alkyl tails in the C_1 and the C_3 positions. In this chapter, we report novel results on the morphology, and the emergence of nanoscopic ordering in the ionic liquid, 1,3-didecylimidazolium hexafluorophosphate. The synthesis of ILs containing such symmetric dialkylimidazolium cations was first reported by Dzyuba and Bartsch [15]. Alkyl groups attached to the cation's nitrogen atom, ranging from methyl to decyl were investigated. It was found that compounds with tail lengths longer than butyl were liquids at room temperature, while those with shorter tails were solids. Melting and glass transition temperatures were also reported. The ionic liquid with the didecyl cation was seen to exhibit two 'melting points', one at $-27\,^{\circ}\mathrm{C}$ and another at $16\,^{\circ}\mathrm{C}$. However, vital physical property data such as density or surface tension of these liquids is as yet unknown [16]. Needless to say, scattering or other structural data are not available for these liquids. Hence, the results from our simulations presented here are predictions

4.2 Details of simulations

As stated in the Introduction, MD simulations of 1,3-didecylimidazolium hexafluorophosphate were carried out using a coarse grain model. The interaction parameters were developed by us recently for the case of 1-methyl-3-decylimidazolium hexafluorophosphate, and the same were applied to the symmetric cation as well. A schematic depicting the correspondence between the atomistic and coarse grain representations of the ions is shown in Figure 4.1. The symmetric cation is modelled with nine beads and the anion by one bead (denoted as PF). The cation contains

Figure 4.1: Schematic showing the atomistic and coarse grain representations of the anion (top) and the cation (bottom two panels) of 1,3- didecylimidazolium hexafluorophosphate

a positively charged 'head' made of three atoms: I1, I1 and I3. This is equivalent to the imidazolium ring in the atomistic representation. The cation also contains two tails mimicking the alkyl (C_{10}) groups, which are of the same kind as developed by Klein and coworkers [17]. The simulated system contained 13824 ion pairs (or 138240 beads). Initially, a smaller system was studied, which was repeatedly replicated to obtain the current simulation system. At each step, the liquid was well equilibrated.

The form of the interaction potential is the same as given in Ref. [14]. Intramolecular terms include harmonic bond stretches and angle bends. Coulombic and 9-6 Lennard-Jones interactions mediate non-bonded neighbours. As expected, all these interactions are much softer relative to those in an atomistic simulation. This aspect allows us to use a time step of 4 fs to integrate the equations of motion. Non-bonded interactions were treated with a spherical cut-off of 1.5 nm, and the long range part of the electrostatic interactions was treated using the particleparticle particle mesh Ewald method. The simulations were performed using the LAMMPS code, [18] and configurations were visualized using VMD [19]. Initial runs were carried out under constant NVT conditions, and the pressure of the system was monitored. After about 380 ns, when we visually recognized the emergence of ordered domains, a trajectory of length 30 ns was generated under NPT conditions in order to relax the volume of the system. Then on, NVT conditions were employed. A trajectory of 60 ns was later generated for analyses during which the coordinates of the beads were stored every 20 ps. The temperature of the system was maintained at 300 K using a Nose-Hoover thermostat. The final box length of the system was 22.059 nm, corresponding to a density of 1058 kgm^{-3}. This value is consistent with the trend in the value of density displayed by the series of 1-methyl-3-alkylimidazolium hexafluorophosphates, wherein the density decreases with increasing alkyl tail length, and liquid 1-methyl, 3-decylimidazolium hexafluorophosphate has a density of 1186 kgm^{-3} at 300 K [14]. A large system size is required in order to unequivocally determine the existence (or otherwise) of nanoscale ordering in bulk ionic liquids. Long trajectories too are mandatory due to the rather slow processes of rotation and diffusion of these long molecules. However, coarse grain molecular dynamics (CGMD) simulations are known to overestimate the diffusion coefficients of constituents by about two orders of magnitude relative to experimental values (or of atomistic MD simulations) [20]. Hence, a trajectory length of 400 ns in our CGMD simulations would actually correspond to 40 microseconds of an atomistic simulation. These give us a rough estimate of the time scales of molecular organization studied in this paper. All distinct pair correlation functions were calculated with a bin width in real space of 0.01 nm, from which partial structure factors were calculated using the relation,

$$S_{\alpha\beta}(q) = \delta_{\alpha\beta} + 4\pi\sqrt{\rho_\alpha \rho_\beta}\int_0^\infty r^2[g_{\alpha\beta}(r) - 1]\frac{sin(qr)}{(qr)}dr \tag{4.1}$$

where $\rho_\alpha = \frac{N_\alpha}{V}$. N$_\alpha$ is the number of beads of type α and V is the volume of the system. The upper limit in the integral is replaced by half of the simulation

Figure 4.2: Snapshots of configurations in the simulation cell at two different points in the MD trajectory. Top: After 50ns, Middle: After 450 ns, Bottom: A section of the system at 450 ns. Green and blue spheres denote beads belonging to the imidazolium ring and the alkyl tail of the cation respectively, while red denotes anions

box length. The total neutron (or X-ray) scattering function is obtained from these partial functions using appropriate weights (scattering length or form factor), as given by,

$$S(q) = \sum_{\alpha}\sum_{\beta} c_\alpha c_\beta \frac{f_\alpha(q) f_\beta(q)}{\langle f(q)\rangle^2} S_{\alpha\beta}(q) \tag{4.2}$$

where c_α is the concentration of bead type α in the system. f_α is the form factor (or neutron scattering length) of bead α and $\langle f(q)\rangle = \sum_\alpha c_\alpha f_\alpha(q)$.

4.3 Results

Figure 4.2 shows snapshots of the configuration at two time points in the MD trajectory. The system is largely disordered at 50 ns. However, one finds evenly spaced stripe patterns in many regions of the simulation box in the snapshot taken at 450 ns. These stripes (actually, sheets) are locations of the imidazolium ring of the cation and of the anion. In the liquid, one observes domains within which the polar moieties are arranged in nearly parallel planes. The structure of the cation lends itself to an organization of the two tails in a direction normal to these 'polar planes'. Stripes in neighbouring domains are not aligned, thus resulting in grain boundaries. Some regions in the system do not exhibit the stripe arrangement.

A closer examination of these ordered regions is shown in Figure 4.3. The cations are neatly arranged with their long axes parallel to each other. The imidazolium rings (represented as triangles) lie in one plane, and very importantly, the ring planes are parallel to each other. This is a key observation from our simulation. Earlier works, including *ab initio* molecular dynamics simulations have explored the aspect of π stacking in these imidazolium based room temperature ionic liquids [21–23]. In the current system, this effect is accentuated within the ordered domains. It needs to be seen if π stacking (rather, its consequences) can be reproduced using coarse

Figure 4.3: A section of an organized domain taken from simulations. Top: Side view, Middle: Idealized caricature of molecular arrangement in the domain. Bottom: Top view of the anions located in one of the planes. Colour scheme is same as in Figure 4.2 .

Figure 4.4: Probability distribution of the angle between vectors normal to the imidazolium rings of near neighbour cations in 1,3-didecylimidazolium hexafluorophosphate (red) compared with that in 1-methyl,3- decylimidazolium hexafluorophosphate (black).

grain models which represent the imidazolium ring with one bead [4]. The anions are interspersed between the rings of the cations. The alkyl tails on either side of the ring are largely disordered, implying their fluxionality. A section of the top view shows the anions present in a square lattice. Many defects are also observed. The symmetry of the lattice could be influenced by the tail-tail separation (typical values in n-alkane crystals being around 0.45 nm), the cation-anion interaction strength, the ionic radius of the anion, and externally controlled by thermodynamic variables. In Figure 4.4, we quantify the extent of ring stacking. It shows the probability distribution of the angle between vectors which are normal to near-neighbour (within 0.7 nm) imidazolium rings.

Figure 4.5: (a) Total structure factor weighted with neutron scattering lengths (b) Partial structure factors between select pairs of beads

For the sake of comparison, we also provide the same quantity for the RTIL containing only one long alkyl tail, i.e., 1-methyl-3- decylimidazolium hexafluorophosphate, modelled using CGMD. The contrast is remarkable; the substitution of the methyl by a decyl group leads to a major increase in the parallelism between adjacent ring planes. It thus appears that the additional vdW interaction accrued from the decyl tail plays a crucial role in this process of self-assembly.

The intermediate range ordering visualized above can be probed using X-ray or neutron scattering experiments. The neutron weighted total structure factor, S(q) obtained from our simulations is shown in Figure 4.5a. The strong feature at 3.3 nm^{-1} points to ordering at a length scale of 1.9 nm, which corresponds to the most probable end-to-end length of the cation in the liquid. We assign the minor feature at 6.3 nm^{-1} to correlations between CM beads present within one sheet in the ordered domains. The peak at 10 nm^{-1} arises from first shell neighbours of the cation head or the anion. A rather weak shoulder is also observed at around 1.8 nm^{-1} which corresponds to a real space correlation of 3.5 nm. This is likely to arise from the periodic domains. In Figure 4.5b, we show three main partial structure factors: I1-I1, CT-CT and PF-PF. All three functions exhibit a peak at 3.3 nm^{-1} indicating its origin as due to collective organization. The tail-tail partial correlation function exhibits a distinct shoulder at 1.8 nm^{-1}, which contributes to the total structure factor. This feature is relatively weak in Figure 4.5a as it is limited by the domain size (the peak width in the structure factor being inversely proportional to domain size). We cannot discount the possibility that this feature may strengthen if one uses a larger simulation cell. However, this is beyond the scope of our current capability. The mean squared displacement (MSD) of the ions (the I1 and the CT beads of the cation) are shown in Figure 4.6. The data for the anion nearly mirrors that of the I1 bead and hence is not displayed. We notice that although the magnitudes of the displacement are small, the slopes of the curves are positive. This provides us a clue

Figure 4.6: Mean squared displacement of beads belonging to the imidazolium ring (green) and the terminal bead of the alkyl tail (blue) of the cation.

that the simulated system is a sluggish liquid at this temperature. A log-log plot of the data reveals that the dynamics of the ions in the system is sub-diffusive (MSD proportional to t^{β}, with β around 0.2 to 0.3) in these time scales. The tail beads exhibit larger values of MSD than the cation head, consistent with our observations on Fig 4.3.

4.4 Conclusions

We have been able to understand the intermediate range structure and morphology of symmetric 1,3-didecylimidazolium hexafluorophosphate in its liquid state. Large scale, long duration computer simulations have thrown light on the self assembly and organization of these ions. The system consists of domains within which the ions form a layered (lamellar) structure, reminiscent of lipid bilayers and membranes. However, these structures are formed in the neat ionic liquid in the absence of water, and are chiefly a product of electrostatic and van der Waals forces existing between polar and non-polar components of the ionic liquid. The phase behaviour of aqueous surfactant solutions is influenced by the relative sizes of the head and the tail groups. It would be interesting to examine the correspondence between such solutions and the kind of nanoscale order in ionic liquids containing short or long cations. The complex morphology of the ionic liquid observed in our simulations is likely related to the two 'melting points' observed for this substance in experiment [15]. It is possible that the high temperature transition (at 16 °C) seen in the experiment is one from the liquid to the lamellar phase, while the one at lower temperature (at −27 °C) is a transition from the lamellar to the crystalline phase. The crystalline phase will be characterized by an ordering of the alkyl groups. We have observed a large increase in the stacking of the imidazolium rings of the cations in the didecyl system when compared to those with only one long tail. Gordon and coworkers [24] have recently shown the importance of including electron correlation for the stacking of triazolium rings in an ab initio calculation of two pairs of ions. Thus, it should be cautioned that the stacking of cation rings seen in our CGMD simulations is likely to be due to geometric and packing considerations since electronic effects are lacking. The neutron weighted structure factor has also been calculated from these simulations and we predict a strong peak at 3.3 nm^{-1} and the distinct possibility of an additional feature at 1.8 nm^{-1}, corresponding to a real space correlation distance of 3.5 nm. These could be verified using small angle X-ray (SAXS) or small angle neutron (SANS) scattering experiments. Very recent scattering and Kerr effect spectroscopy results on short-chain symmetric cation-based ionic liquids indicate that these compounds are more solid-like than their asymmetric counterparts [25].

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Chapter 5

Role of cation symmetry in intermolecular structure and dynamics of room temperature ionic liquids: Simulation studies

5.1 Introduction

Room temperature ionic liquids (RTIL) [1–6] composed of an organic cation (typically, imidazolium) and an inorganic anion exhibit nanoscale phase segregation into regions which are either predominantly polar or otherwise. The alkyl groups of the cation constitute the latter. Small angle X-ray scattering experiments [28, 29], fluorescence spectroscopy [26, 27] and molecular dynamics simulations [20–25] have provided direct evidence of this microheterogeneity in the otherwise macroscopically homogeneous liquids. The most commonly studied imidazolium based RTILs contain a methyl group at the 1-position and a longer alkyl group at the 3-position, both covalently bonded to nitrogen atoms. Until a decade ago, it was believed that this asymmetry in the length of the alkyl groups prevented crystallization of these compounds, making them liquids under ambient conditions. To test this idea, Dzyuba and Bartsch [17] in 2001 synthesized salts whose cation had symmetric alkyl substitutions at the 1- and the 3-positions and showed that these too were liquids at room temperature. Using large scale coarse grained molecular dynamics (MD) simulations, we have recently showed that one of these compounds, 1,3-didecylimidazolium hexafluorophosphate $[(C_{10})_2im][PF_6]$ could exhibit a lamellar phase near room temperature [18]. Also, the salt behaved more solid-like than the corresponding asymmetric cation based IL, $[C_{10}C_1im][PF_6]$. Independently, Xiao et al [19, 20] had investigated the structure and dynamics of a series of ILs containing symmetric imidazolium cations based on the bis(trifluoromethylsulfonyl)imide, $[NTf_2]^-$ anion through small and wide angle X-ray scattering and Kerr effect spectroscopy. They too observed slower dynamics in these compounds relative to their asymmetric counterparts. They found that the intermolecular part of the OKE spectrum of 1-propyl-3-methylimidazolium bis[(trifluoromethane)sulfonyl]imide ($[C_3C_1im][NTf_2]$) is higher in frequency and broader than that of 1,3-diethylimidazolium bis[(trifluoromethane)sulfonyl]imide ($[(C_2)_2im][NTf_2]$). This difference is attributed to the intermolecular potential being stiffer in $[C_3C_1im][NTf_2]$ than in $[(C_2)_2im][NTf_2]$. The high-frequency tail of the OKE spectrum of ($[(C_2)_2im][NTf_2]$) in the 0-200 cm^{-1} range was anomalously higher in intensity and more structured than that of ($[C_3C_1im][NTf_2]$).

Ionic liquids containing the $[NTf_2]^-$ anion and the asymmetric imidazolium or the pyrrolidinium cation have been studied earlier using MD simulations [21–25]. Bis(trifluoromethylsulfonyl)imide anion is also being referred to as $TFSI^-$, $TFSA^-$, and $[Tf_2N]^-$.

Nanoscale phase segregation in ILs gives rise to a pronounced feature in the scattering function at low wave vectors corresponding to the inverse of the correlation

Figure 5.1: Molecular structure of $[(C_3)_2\mathrm{im}]^+$ and $[\mathrm{NTf}_2]^-$ ions.

length in real space [20–25,28,29]. In symmetric cation $[C_nC_n\mathrm{im}]^+$ based ILs, Xiao et al [19] observed peaks in this quantity at wave vectors in the range of 5 nm^{-1}. These were generally narrower than those found in the corresponding asymmetric cation $[C_nC_1\mathrm{im}]^+$ based ILs. Further, intermolecular dynamics in the former category indicated a hardening of the potential energy surface relative to asymmetric cation based ILs. These observations led the authors to suggest that symmetric cation based ILs were more tightly packed than their asymmetric counterparts. In the current manuscript, we report atomistic MD simulations of ILs studied in these experiments in an effort to identify the specific real space structures which contribute to the experimental small angle X-ray scattering observations. In addition, we also study their dynamics. The following section details the simulation methods adopted which is succeeded by presentation and discussion of the results.

5.2 Simulation Details

The fully flexible, all-atom model developed by Ludwig and coworkers [26] was used to carry out classical MD simulations of 1,3-alkylmethylimidazolium bis(trifluoromethylsulfonyl)imides $[C_nC_1im][NTf_2]$ (the "asymmetric" IL) and 1,3-dialkylimidazolium bis(trifluoromethylsulfonyl)imides $[(C_n)_2im][NTf_2]$ (the "symmetric" IL) with n = 3-5. The molecular structure of ions in the symmetric system, $[(C_3)_2im][NTf_2]$ is shown in Figure 6.1. This potential model has been shown to reproduce well the intermolecular structure and importantly, the spectral features in the far-infra red region which probes the local coordination shell around an ion [27]. MD simulations were carried out using the LAMMPS [32] code. A time step of 0.5 fs was used to integrate the equations of motion. The non-bonded potential was truncated at 12Å and tail corrections to energy and pressure were applied. Coulombic interactions were treated using the particle-particle particle mesh Ewald method with an accuracy of 10^{-4}.

We describe here the methodology adopted to obtain an initial configuration and the process of equilibration. A single ion pair was replicated to obtain a simulation box containing 63 ion pairs. Relaxation of the geometry through energy minimization was carried out followed by MD simulations under constant NVT conditions during which the temperature of the system was increased at intervals of 100K up to a final value of 600K. At each temperature, the duration of the simulation was 200 ps. The system was further equilibrated at 600K for a period of 1 ns with electrostatic interactions turned off to enable a faster mixing of the components. The charges were subsequently restored and the temperature of the system was decreased from 600K to 300K with an interval of 100K, and it was equilibrated for 200 ps at each temperature. At 300K, constant NPT simulations under 1 bar pressure were carried out until the volume converged. The average volume was used to further equilibrate the system at constant NVT conditions.

Table 5.1: Density of ionic liquids predicted from simulation and experiments.

System	Simulation	Experiment [36]	Percentage deviation
[C_3mim][NTf_2]	1.46	1.473	0.88
[C_4mim][NTf_2]	1.42	1.434 [37]	0.98
[C_5mim][NTf_2]	1.39	1.400	0.70
[$(C_3)_2$im][NTf_2]	1.38	1.398	1.28
[$(C_4)_2$im][NTf_2]	1.33	1.341	0.80
[$(C_5)_2$im][NTf_2]	1.28	1.293	1.00

Such fully equilibrated final configurations of each of the compound were replicated in all directions to obtain systems containing 1,701 ion pairs. After generating a short trajectory (62 ps), the size of the system was reduced by selecting arbitrarily placed 1,000 ion pairs. This 1000 ion pair system was equilibrated under NVT and NPT conditions in a manner identical to that described above for the smaller, 63 ion pair system. The converged box lengths of the simulations ranged from a value of 77.32Å for [C_3mim][NTf_2] to a value of 85.88Å for the [$(C_5)_2$mim][NTf_2]. All results reported here are for 1,000 ion pair systems. The predicted densities of these liquids are compared against experimental values in Table 5.1 and the match is good.

Partial pair correlation functions were calculated between all pairs of atoms with a bin width of 0.1 Å. These were used to calculate the partial structure factors using the following equation

$$S_{\alpha\beta}(q) = \delta_{\alpha\beta} + 4\pi\sqrt{\rho_\alpha\rho_\beta}\int_0^\infty r^2[g_{\alpha\beta}(r) - 1]\frac{sin(qr)}{(qr)}dr \qquad (5.1)$$

Here, $\rho_\alpha = \frac{N_\alpha}{V}$. N_α is the number of atoms of type α and V is the volume of the system. Half of the box length is used as the upper limit of the integral. The total

X-ray structure factor is defined as

$$S(q) = \sum_{\alpha} \sum_{\beta} c_{\alpha} c_{\beta} \frac{f_{\alpha}(q) f_{\beta}(q)}{\langle f(q) \rangle^2} S_{\alpha\beta}(q) \tag{5.2}$$

where c_α is the concentration of atom type α in the system. f_α is the form factor of atom α and $\langle f(q) \rangle = \sum_\alpha c_\alpha f_\alpha(q)$. Here c_α is the concentration of atom type α, f_α is the form factor of atom α and $\langle f(q) \rangle = \sum_\alpha c_\alpha f_\alpha(q)$. The X-ray form factors of the atoms were obtained from the NIST [29] website. The values of form factors for each atom are needed at integral multiples of the smallest q, which depends on the length of the simulation box. The values of form factors obtained from NIST were linearly interpolated to obtain form factors at the desired q values.

For each system, in addition to the long trajectory to study the intermolecular structure of the liquids, an additional trajectory of 100 ps was generated with velocities written out every 5 fs. These were used to calculate the velocity auto-correlation functions of the centers of mass of the ions. The velocity auto-correlation of the cation ring center was also calculated. Vibrational density of states were obtained by calculating the Fourier transform of these functions.

5.3 Results and Discussion

5.3.1 Radial Distribution Function

Radial distribution functions (RDF) between the tails of the cations (i.e., the terminal carbon atom of the longer alkyl tail) are shown in Figure 5.2(a). With increase in the length of the alkyl group, the intensity of the first peak in both the asymmetric and symmetric systems increases. In Figure 5.2(b), we compare the RDF between tails of the C_5-C_5 and the C_5-C_1 systems. We note that the first peak for the symmetric system is narrower than that for the asymmetric one, indicating

Figure 5.2: Pair correlation function between tails of cations. (a) Symmetric C_3, C_4 and C_5 systems. Inset shows the data for asymmetric cation based ionic liquids. (b) Comparison between C_5-C_5 and C_5-C_1 ionic liquids.

Figure 5.3: Comparison of RDF between the cation ring centers in symmetric and asymmetric C_5 systems.

a more structured arrangement in the former. However, the intensity of the first peak decreases marginally on symmetrizing the cation. Figure 5.3 shows the RDF between geometric centers of the imidazolium rings in the C_5-C_1 and C_5-C_5 systems. Although there is negligible change in intensity, the peak position increases when the cation is symmetrized.

Conformational fluctuations of the additional longer alkyl group present in the symmetric cation requires more volume than the methyl group present in the asymmetric IL. This could lead to the slight increase in the cation-cation separation observed here. In Figure 5.4 we show the RDF between nitrogen atoms of the anions (anion-anion). Upon symmetrization, there is a decrease in intensity and a marginal increase in the position of the first peak for all the three chain lengths (the data for C_5 is shown), consistent with the results discussed for the cation-cation g(r).

Figure 5.4: Comparison of RDF between the nitrogen atoms of anions in symmetric and asymmetric C_5 ionic liquids.

Figure 5.5: Comparison of RDF between center of the cation ring and nitrogen of the anion in asymmetric and symmetric C_5 ionic liquids.

Figure 5.6: Comparison of the radial distribution function between acidic hydrogen and oxygen, fluorine and nitrogen atoms of the anion in $[C_5C_5im][NTf_2]$ ionic liquid.

Figure 5.7: Comparison of RDF between the center of the cation ring and nitrogen of the anion in asymmetric and symmetric C_4 systems.

Figure 5.5 compares the RDF between the center of the cation ring and the nitrogen of the NTf_2^- anion in asymmetric and symmetric cation based ILs, for the case of C_5 group. Conclusions drawn from these RDFs apply to the C_4 (Figure 5.7) and C_3 systems as well. An increase in the length of the alkyl group increases the cation-anion near neighbor correlation in both symmetric and asymmetric ILs. Seen in conjunction with the results shown in Figure 5.3, we note that the symmetrization of the cation leads to (i) increased cation-anion interaction and (ii) marginal increase in the anion-anion and cation-cation separations. The cation-anion pair correlation function for the asymmetric cation based IL compares well with earlier MD simulation results of Smith and coworkers [21]. A specific region for the presence of the anion around the cation is along the carbon - acidic hydrogen bond of the imidazolium ring [30]. The acidic hydrogen can interact with oxygen, nitrogen and fluorine atoms of the anion [31, 32]. Figure 5.6 compares the RDF between the acidic hydrogen and these sites of the anion. Fluorine approaches the acidic hydrogen at shorter distances compared to oxygen or nitrogen. However, the RDF between acidic hydrogen and oxygen shows the highest intensity indicating that this interaction is the strongest followed by the one between acidic hydrogen and nitrogen. Figure 5.9 compares the RDF between this acidic hydrogen and the oxygen atom of the anion in the asymmetric and symmetric C_5 systems. Figure 5.8 shows similar data for C_4 systems. The dominant peak at around 2.2Å (Figure 5.9) denotes a hydrogen bond of medium strength. Its intensity increases with the length of the alkyl group. Also, the peak intensities are higher upon symmetrization of the cation. These two observations imply that tail-tail interactions can influence cation-anion hydrogen bonding – more hydrogen bonds are formed as the number of methylene (or methyl) groups increase in the cation.

Table 5.2 compares the coordination numbers for various pairs of sites between the C_5-C_1 and the C_5-C_5 ionic liquids. The cation-anion coordination number is

Figure 5.8: Comparison of RDF between the acidic hydrogen of the cation and oxygen of the anion in asymmetric and symmetric C_4 systems.

Figure 5.9: Comparison of RDF between the acidic hydrogen of the cation and the oxygen atom of the anion in asymmetric and symmetric C_5 systems.

Table 5.2: Coordination numbers in the first neighbor shell. Distances at which these were calculated are provided in parantheses. These distances correspond to the minimum of the first peak in the corresponding pair correlation function.

Pair	C_5-C_1	C_5-C_5
Cation-Anion	5.74 (8.95Å)	4.59 (8.75Å)
Acidic hydrogen (cation) - Oxygen (anion)	0.48 (3.55Å)	0.41 (3.45Å)
Tail-Tail	2.87 (7.05Å)	4.30 (6.95Å)
Anion-Anion (N-N)	15.58 (12.75Å)	14.34 (13.25Å)
Cation-Cation	14.30 (12.35Å)	12.51 (12.75Å)

reduced by 1.1 in the C_5-C_5 system relative to the C_5-C_1 system. This trend of a reduction in the coordination number is also observed for the anion-anion and the cation-cation neighbors. The tail-tail coordination number shows an apparent increase from a value of 2.87 to a value of 4.30. However, the number density of tail atoms is twice in the C_5-C_5 IL than in the C_5-C_1 IL. The apparent increase in the tail-tail coordination number is thus much less than what is expected on number density grounds. In summary, almost all near neighbor coordination numbers are reduced in the symmetric IL systems compared to the asymmetric counterparts. This observation is consistent with the marginal narrowing down of the respective RDFs or changes in the peak intensity.

It should also be noted that the ion number density of the C_n-C_n IL is smaller than the C_n-C_1 system; the difference increases with increasing value of n. For instance, the number density of the C_5-C_5 ionic liquid is 0.0016 ion pairs per Å^3, while the corresponding value for the C_5-C_1 system is 0.0019 pairs per Å^3, an increase of around 22%. The decrease in coordination numbers in the symmetric IL agrees with the decrease in its number density.

A reduction in coordination number by itself does not confirm/deny our conclusion that the symmetric C_n-C_n IL is more structured than the corresponding asymmetric IL, C_n-C_1. However, the distribution of neighbor distances (obtained through the RDFs) confirm this view point clearly.

Table 5.3: Heterogeneity order parameter (HOP) of various systems

	Cation	Anion	Tail
C_5-C_5	14.79	14.78	15.09
C_4-C_4	14.78	14.77	14.96
C_3-C_3	14.77	14.77	14.87
C_5-C_1	14.80	14.80	15.16
C_4-C_1	14.79	14.78	15.06
C_3-C_1	14.77	14.77	14.96

Wang and Voth [23] introduced a heterogeneity order parameter (HOP) to demonstrate the aggregation of alkyl tail groups. Table 5.3 which contains the HOP values for different systems showed higher values for the tail than for the ring atoms of the cation or the anion. While the values for the tail increase with the length of the alkyl group, that for the cation ring and the anion were nearly independent of it, within this regime of tail lengths (3 to 5). These results are consistent with those of Wang and Voth [23]. The HOP for the tail of the symmetric IL is slightly lesser than that for the asymmetric IL. The value of HOP is primarily determined by the coordination number, as farther neighbors contribute trivially to this quantity (due to HOP's Gaussian dependence on pair distances). The larger coordination number in the asymmetric system leads to a larger value of HOP.

The *intermolecular* RDF between the geometric center of the imidazolium ring and the tail carbon (i.e., the terminal carbon atom in the alkyl group) provides clues on the effect of symmetrization of the cation on nanoscale ordering in the IL. In the results shown in Figure 5.10, three peaks are found – at 4.6Å, 6.4Å and 10Å. On symmetrizing the cation, there is a decrease in the intensity of the first two peaks and an increase in that of the third peak. Also, the third peak shifts marginally to a lower distance. The distribution of *intramolecular* head-tail distances in the C_5-C_5 IL (Figure 5.11) exhibits two peaks, at 6.0Å and 7.4Å.

The latter is likely to arise from fully extended alkyl groups (*all-trans*), while the

Figure 5.10: Intermolecular RDF between the center of the imidazolium ring and the terminal carbon of the alkyl group in the cation of asymmetric and symmetric C_5 systems.

Figure 5.11: Probability distribution of the intramolecular distance between the geometric center of imidazolium ring of a given cation and its tail

former feature could arise from those alkyls with one or more *gauche* defects. Given this information, we believe that these two peaks (4.6Å and 6.4Å) are likely to arise from neighboring cations which are displaced axially away from one another. This is the manner by which such close "contacts" between the imidazolium ring and the terminal carbon of the alkyl group can arise. Note also that the intensities of these two features are decreased in the symmetric cation based IL. As observed earlier, the symmetric ones display a greater degree of intermolecular order. It is thus natural to expect that the proximity between the ring and the tail should diminish in strength in these systems, as evidently seen in Figure 5.10.

To identify the origin of the dominant peak at 10Å in the intermolecular head-tail g(r) (Figure 5.10), we calculated the probability distribution of intermolecular distance between the imidazolium ring of a given cation and the tail of any cation which is present along the intramolecular head-tail vector of the given cation. In practice, a deviation of 25^o between the latter vector and the intermolecular head-head vector was permitted to allow for possible thermal and configurational disorder that is a generic feature of the liquid state.

We calculated the distance between the imidazolium ring (head) of the central cation and the terminal carbon (tail) of that cation which is along the central cation's intramolecular head-tail vector. The probability distribution of this distance is plotted in Figure 5.12. We note that the position of the peak in this plot (ranging between 8Å and 10Å for C_3, C_4 and C_5 symmetric systems) coincides with that of the third peak in the intermolecular RDF between imidazolium ring and tail. We surmise that the peak at 10Å in the intermolecular head-tail RDF is due to correlations between the ring of a cation and the tail of those cations which are present along the intramolecular head-tail vector of the first cation. Given that the intramolecular head-tail distance is around 7.4Å in a cation with a fully extended C_5 alkyl group, and given that the intermolecular head-tail distance for axially aligned

Figure 5.12: Probability distribution of the intermolecular distance between the geometric center of imidazolium ring of a given cation and the tail of other cations which are located along the intramolecular head-tail vector of the given central cation. Main body: Symmetric C_5, C_4, C_3 systems.

cations is around 10Å, it is unlikely that the alkyl groups of such cations are interdigitated. Interdigitation could likely play a role in the structural ordering of ILs with cations possessing larger alkyl groups than the ones studied here.

5.3.2 Total Structure Factor

Figure 5.13 shows the total X-ray structure factor of the asymmetric and symmetric systems. The following observations can be made. Changing the alkyl length does not affect the intensity or position of the peak present at 13.6nm^{-1}. In the asymmetric (symmetric) systems, the intensity of the peak at 8.6nm^{-1} (8nm^{-1}) decreases with increase in chain length. As the chain length of the cation is increased, the intensity of the peak at 5nm^{-1} increases in both the asymmetric and symmetric systems. Figure 5.14 compares the X-ray total structure factor of the asymmetric and symmetric C_5 systems. There is a marginal shift to lower wave vectors of the

Figure 5.13: Total X-ray structure factor of (a) asymmetric and (b) symmetric cation based ionic liquids.

Figure 5.14: Comparison of the total X-ray structure factor between asymmetric and symmetric C_5 cation based ionic liquids.

8.6nm^{-1} feature for the symmetric C_5-C_5 IL. The intensity of the structure factor is higher for q values below 7nm^{-1} for the symmetric system in comparison to the asymmetric one. This would signify the existence of correlations of larger length scales in the former. Visualization of snapshots of symmetric systems could aid in observing this increased correlation and the same are presented in Figure 6.6. With increase in chain length, there is an increase in the inhomogeneity of the IL. The effect will be accentuated in ILs whose cations possess even larger alkyl tails.

The total structure factors of the symmetric ILs calculated from our simulations are compared against experiments in Figure 5.16, and the match is good. At low wave vectors (less than 3nm^{-1}), the agreement is not perfect, as in this regime the simulation data is limited by the system size. However, structural details up to a distance of around 15Å is well reproduced by our simulations. With a box length of around 80Å, the wave vector resolution is limited in our simulations to around

Figure 5.15: Snapshots of symmetric C_3, C_4 and C_5 systems. Atoms of imidazolium ring and anion are in red (polar regions) and atoms of the alkyl chain are in green (non-polar regions). (a) $[(C_3)_2\mathrm{im}][\mathrm{NTf}_2]$ (80.4Å) (b) $[(C_4)_2\mathrm{im}][\mathrm{NTf}_2]$ (83.2Å) (c) $[(C_5)_2\mathrm{im}][\mathrm{NTf}_2]$ (85.8Å). Values of box length are shown in paranthesis.

Figure 5.16: Comparison of the total X-ray structure factor obtained from experiment [19] and the present simulation, for [C_5C_5im][NTf_2]. Inset shows the comparison for [C_4C_4im][NTf_2]. The experimental data (Figure 2 of Ref. [19]) has been scaled by a constant factor. The simulation data has been smoothened using a cubic spline.

0.8nm^{-1}; A finer resolution would necessitate a much larger box length which is beyond the scope of the present work.

We proceed further to examine the origin of the features present in the total structure factor. This task could be accomplished by studying the contributions from partial structure factors (PSF) to the total. From Figure 5.17 which shows a few PSFs, it is clear that the tail-tail PSF makes the maximum contribution to the peak at 5nm^{-1} followed by the atoms of the anion. For the peak at 7.8nm^{-1}, the correlation between atoms of the anion make the maximum contribution followed by the nitrogen atoms of cation. PSF between tail-tail makes the lowest contribution to this peak.

With increasing length of the alkyl chain, there is a decrease in intensity of the peak around 8.0nm^{-1} in both the symmetric and asymmetric systems, as is evident from Figure 5.13. This was also noticed in experiments [19]. There are two main

Figure 5.17: Partial structure factors (see Eq. 2) for [C_5C_5im][NTf_2].

Figure 5.18: Comparison of the partial structure factor between the geometric center of the imidazolium ring and the terminal carbon of the alkyl group (tail) in asymmetric C_5, C_4 and C_3 systems. Inset shows the same in symmetric cation based ionic liquids.

Figure 5.19: Comparison of the partial structure factor between terminal carbon atoms (tail-tail) in the alkyl chains of symmetric C_5, C_4 and C_3 systems.

reasons for this behavior. Figure 5.18 shows the PSF between the geometric center of the imidazolium ring and the tail (terminal carbon of the alkyl group) for both symmetric and asymmetric C_5, C_4, C_3 systems. There is a decrease in peak intensity of this PSF as the chain length is increased, thus diminishing the amplitude of the total structure factor at wave vector values around 8.0nm^{-1}. In addition, the PSF between tails of the cations in symmetric IL's, in Figure 5.19, shows a shift in the peak from 8.0nm^{-1} to 4.6nm^{-1} as we go from C_3 to C_5. Hence, a change in the correlation distance between tails also contributes to the decrease in intensity of the 8.0nm^{-1} peak in the total structure factor.

The C_5-C_1 and C_3-C_3 systems have the same number of methylene groups and nearly the the same density. But they differ in the symmetry of the cation. A comparison of their total structure factor and the tail-tail PSF shows that the C_5-C_1 system possesses greater spatial heterogeneity and domain size than the C_3-C_3 system.

5.3.3 Dynamics

Figure 5.20 compares the vibrational density of states of the ring center in the low frequency range. As the chain length increases, the peak present at around 40cm^{-1} narrows. There is a slight red shift of this feature as well with increase in chain length. The shift is more prominent in the symmetric systems than in the asymmetric ones. This far infrared feature arises from cage rattling motions and is a spectroscopic measure of the local structure around an ion. The width of the low frequency peak is related to the diversity (both in terms of structure as well as in terms of hardness of the potential well that the ion is present in) in the coordination shell of a given ion. For instance, if every one of the ions is present in an identical environment, all of them will exhibit the same cage frequency, leading to a narrow peak in the vibrational density of states. Wider bands would thus imply varied environments. Figure 5.21 compares the density of states in the low frequency range of the ring center of the cations in the asymmetric and symmetric C_5 systems. The peak present at 30 cm^{-1} in the symmetric C_5 system is narrower than that in the asymmetric C_5 one. A slight red shift in this "mode" is also seen in the symmetric C_5 IL. However, the feature at 160 cm^{-1} exhibits a blue shift in the symmetric cation based IL. A direct correspondence to the OKE results requires the calculation of the polarization time correlation function [33,34] which is beyond the scope of the current study. Yet, the narrowing of the low frequency band in the symmetric IL is a clear indication of it being more structured than the asymmetric one. This observation tallies with the direct results obtained in terms of RDFs, discussed earlier.

We have calculated and compared the mean squared displacement (MSD) of the ions in asymmetric and symmetric systems. Figure 5.22 compares the MSD of the center of mass of cation in symmetric ionic liquids of different chain lengths. We notice that the displacement values of cations at any given time decreases in the

Figure 5.20: Vibrational density of states of the geometric center of the cation ring in a) C_n-C_n (symmetric) and b) C_n-C_1 (asymmetric) cation based ionic liquids.

Figure 5.21: Comparison of the vibrational density of states of the center of the cation ring between symmetric and symmetric C_5 systems.

following order $C_3 > C_4 > C_5$, as expected. The MSD of anions too showed the same trend. Systems with longer alkyl chain exhibit slower dynamics compared to the ones with shorter shorter alkyl chains. This trend is also observed for ions in asymmetric systems. Figure 5.23(a) compares the MSD of cations in asymmetric and symmetric C_5 systems. We notice that the cations in the asymmetric IL have larger MSD values than those in symmetric systems. Similar trend is observed for anions. Symmetrizing the cation leads to slower translational motion of the ions.

The main objective of this article is to study the change in nanoscale order on symmetrizing the cation. Although we have employed a reasonably large system size (1,000 ion pairs) the analysis trajectory is not too long and is around 2-3 ns only. However, ionic liquids in general are known to exhibit slow dynamics. One way to know if the ions in the system have reached diffusive regime is to calculate the linearity parameter β(t) [35], defined as

Figure 5.22: Comparison of the mean squared displacement of cations in symmetric C_5, C_4 and C_3 ionic liquids.

$$\beta(t) = \frac{d\ log\langle \Delta r^2(t)\rangle}{d\ log(t)} \tag{5.3}$$

where $\langle \Delta r^2(t)\rangle$ is the time and ensemble averaged MSD of the ion. A system is said to be in the diffusive regime when β(t)=1. At 2 ns, β(t) values for the anion and the cation in the C_5-C_5 IL were found to be around 0.5 and 0.8 respectively. Thus, in these time scales, the ions are sub-diffusive.

Figure 5.23(b) compares the MSD of cations and anions in the C_3-C_1 ionic liquid. The anion shows larger displacement values than the cation initially and a crossover occurs at around 1.5 ns after which the MSD values of the cation are larger. The inset to Figure 5.23(b) shows the corresponding β(t). We notice that while the cation motion is diffusive in the timescales of 2ns, that for the anion is sub-diffusive. The masses of the anion and the cation in this IL are 280.15 and 125.19 a.m.u. respectively. The MSD values (and the slopes of the MSD curves) beyond the crossover point are consistent with these masses – the cation diffuses faster than the

Figure 5.23: Mean squared displacement(MSD) of ions. (a) For cations in asymmetric and symmetric C_5 cation based liquids. (b) MSD of anion and cation in the C_3-C_1 system; Inset shows β(t) (defined in Eq. 5.3 for the same).

anion. However, at times lesser than 1.5 ns, the anion exhibits larger MSD values. At the crossover time (1.5ns), the value is 60Å^2 which corresponds to a translational distance of around 8Å. The anion is considerably more flexible (more conformational freedom) than the cation. The imidazolium ring of the cation is planar and thus the flexibility of the cation is purely determined by that of the alkyl tail. The absence of such constraints on the anion leads to its greater fluxionality and thus its initial larger MSD values can be rationalized.

To study the rotational motion of the molecules we have calculated the orientational correlation function (OCF), C$_R$(t) as

$$C_R(t) = \frac{\langle \hat{u}(0) \cdot \hat{u}(t) \rangle}{\langle \hat{u}(0) \cdot \hat{u}(0) \rangle} \tag{5.4}$$

Here $\hat{u}$(t) is a body-fixed vector describing the orientation of the cation or anion at time t. C$_R$(t) have been calculated for the following vectors. The vector connecting the two nitrogens of the cation (vector-1), the vector present in the plane of the imidazolium ring and perpendicular to vector-1 (vector-2), the vector normal to the cation ring (vector-3). In general, the TCF of vector-1 shows the slowest decay and those of vector-2 and vector-3 exhibit much faster decay. For the TCF of vector-2 and vector-3 to decorrelate, the cation has to rotate along the molecular axis. However, for vector-1's to decay, the cation will have to rotate along an axis perpendicular to the molecular axis, which is rather difficult. Figure 5.24(a) compares the C$_R$(t) of vector-1 between asymmetric and symmetric systems. The tcf of the asymmetric IL decays more rapidly compared to that of the symmetric one. Similarly, Figure 5.24(b) compares the C$_R$(t) of vector-3 between asymmetric and symmetric systems. Again, there is a faster decay in the case of the asymmetric system compared to the symmetric system.

Integrals of the OCF have been calculated to quantify the slowing down of the rotational motion of the ions. Table 5.4 compares these values for the asymmetric

Figure 5.24: Comparison of the molecular rotational time correlation function, $C_R(t)$ between asymmetric and symmetric C_5 systems. (a) Vector joining the N atoms of the imidazolium ring. (b) Vector normal to the imidazolium ring. Inset compares $C_R(t)$ between asymmetric and symmetric C_3 systems.

Table 5.4: Integrals of orientational time correlation functions

	C_3-C_3 (ns)	C_3-C_1 (ns)
vector 1	0.74	0.42
vector 2	0.15	0.08
vector 3	0.13	0.07

and symmetric C_3 systems. Unlike C_3 systems where the OCF of both the asymmetric and symmetric systems have decayed completely, those for the C_4 and C_5 systems have not. Thus, we compare the integral values for the C_3 systems alone. For all the three vectors, the integrals are larger for the symmetric than for the asymmetric system, signifying a slower decay of OCF in the former. This observation is consistent with the slower translational dynamics of the C_3-C_3 IL than the C_3-C_1 IL. The difference in the integral values between symmetric and asymmetric C_3 systems for the reorientation of vector-1, vector-2 and vector-3 are 0.326, 0.07 and 0.06 ns respectively. Upon symmetrization of the cation, the slowing down of vector-1 is larger than that for vector-2 and vector-3. In summary, molecular ions present in the symmetric cation based ionic liquids exhibit slower dynamics than ones in asymmetric cation based ILs. These observations are consistent with both the structural and vibrational density of states data discussed earlier.

5.3.4 Conclusions

Microphase segregation of polar and non-polar domains is a topic of current research in room temperature ionic liquids. The molecular structure of the imidazolium cation employed in many studies is asymmetric, in the sense that the alkyl group chain lengths attached to the two different nitrogen atoms of the imidazolium ring are of different lengths. One of them is usually a simple methyl group, while the other alkyl group is longer. An underlying reason for microphase segregation is the interplay between electrostatic interactions (the entities being the imidazolium ring of the cation and the anion, both of which are polar) and van der Waals (vdW) interaction between the alkyl tails of the cation. In this chapter, we have systematically examined the effect of increasing the vdW interaction in two ways: (i) by increasing the length of one of the alkyl group in asymmetric cation based ILs, and (ii) by constructing symmetric cations in which the two alkyl groups of the cation are equivalent. The effect of these changes are studied keeping the strength of the electrostatic interactions intact. The ionic liquids investigated here contain the specific anion, $[NTf_2]^-$. The structure and dynamics of these ILs have been studied recently using small angle X-ray scattering and optical Kerr effect spectroscopy experiments [19].

The atomistic interaction model [26] employed by us is able to predict the density of these compounds in good agreement with experiments. The simulation results also agree remarkably well with the total X-ray structure factor over a wide range of wave vectors. The main results of our study can be summarized as follows:
(i) With increase in the length of the alkyl group, tail-tail spatial correlations are enhanced, in both symmetric (C_nC_n) and asymmetric (C_nC_1) cation based ionic liquids.
(ii) Pair correlation functions between many different sites display a common behavior leading to the following conclusion – the symmetric cation based IL is more structured than the one with the asymmetric cation.
(iii) In the symmetric cation based IL, the first coordination shell around any ion is present at a slightly larger distance than in the asymmetric system, due in part to the increased volume of the molecular cation in the former. The symmetrization of the cation also leads to increased cation-anion interaction.
(iv) The nanoscale ordering which is intrinsic to room temperature ionic liquids is considerably enhanced in symmetric cation based ILs. Not only that, the correlation length too is larger in the former systems, due once again to the larger end-to-end

length of the symmetric cation.

(v) As in asymmetric cation based ionic liquids, the real space tail-tail correlation (arising out of the "aggregation" of the alkyl groups) is the major contributor to the low wave vector peak in the total structure factor, which is a signature of nanoscale ordering.

(vi) Analyses of the vibrational density of states at low frequencies corresponding to intermolecular "modes" show that this band is narrower and red shifted in the symmetric cation based ILs relative to the asymmetric systems. These observations imply a more uniform environment for the ions in the former liquid in agreement with the structural data discussed earlier.

(vii) Rotational time correlation functions of various molecular vectors once again demonstrate relatively slower relaxation dynamics in symmetric cation based ILs than in asymmetric systems. Translational dynamics in C_n-C_n ionic liquids too is slower than in the corresponding C_n-C_1liquids.

The simulations presented here agree to a very large extent with recent experiments [19] on the same ionic liquids. The agreement in many cases is nearly quantitative and is thus gratifying. The existence of a lamellar phase in 1,3-didecylimidazolium hexafluorophosphate (an ionic liquid with a symmetric cation) at room temperature was reported by us recently [18]. This observation is consistent with the general trend of the liquid with symmetric cations being more structured, as noted in the current study.

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Chapter 6

Molecular dynamics simulation of model room temperature ionic liquids with divalent anions

6.1 Introduction

Room temperature ionic liquids (RTIL) [1–7] are a class of substances containing only ions and which are liquid at or below 100° C. They are generally composed of an organic cation and an organic or inorganic anion. The presence of a bulky and asymmetric cation makes their crystalline forms to have lower cohesive energies, compared to purely inorganic salts (such as NaCl, $BaCl_2$ etc..). The liquid state is thus favoured at ambient conditions on free energy terms. Since the constituents of ionic liquids interact via strong and long ranged Coulombic forces, they exert practically no vapor pressure. They can be used as solvents for a wide range of polar and non-polar solutes. A combination of different cations and anions in RTIL can in principle, lead to a large number of compounds with varied physical and chemical properties. Many reactions have been shown to be influenced when an ionic liquid is used as a solvent [8–10]. Apart from neat ionic liquids, several studies have been conducted on aquous solutions of ionic liquids [11–16] and aggregation of block copolymers in ionic liquids [17–19].

Molecular dynamics simulations [20–25], fluorescence spectroscopy [26,27] and X-ray scattering experiments [28, 29] have shown that RTILs, especially the ones with imidazolium based cations exhibit nanoscale phase separation. In these systems, the anion and imidazolium ring of the cation constitute the polar moieties while the alkyl chain on the cation is non-polar. The non-polar entities aggregate and so do the polar ones. This leads to microphase segregation in the otherwise isotropic and homogeneous liquid. The spatial heterogeneity is understood to be due to the competition of the collective short-range interactions between the tail groups and the long-range Coulomb interactions between the head groups (of cations) and the anions [23]. As the length of the alkyl chain on the cation is increased, spatial heterogeneity increases due to enhancement in the van der Waals (vdW) interactions between the alkyl chains.

RTILs typically contain monovalent ions and the mole fraction of cations (or anions) is half; the effect of divalent anions such as sulfate ($SO_4{}^{2-}$), thiosulfate ($S_2O_3{}^{2-}$), sulfite ($SO_3{}^{2-}$), chromate ($CrO_4{}^{2-}$), dichromate ($Cr_2O_7{}^{2-}$), carbonate ($CO_3{}^{2-}$) and oxalate ($C_2O_4{}^{2-}$) on the structural and dynamical properties of ionic liquids is, to our knowledge, unexplored. Doubling the charge on the anion need to be necessarily compensated by doubling the mole fraction of the imidazolium cations in the ionic liquid, for reasons of charge neutrality. This would increase electrostatic interactions. The consequence of these changes to the properties of the ionic liquid is the object of the current study. We explore this problem using coarse grained molecular dynamics simulations, an apt tool to study the evolution of microheterogeneity in complex systems.

Figure 6.1: Schematic of $[C_{10}mim][PF_6]$ illustrating the mapping of atoms to coarse grain beads.

6.2 Simulation Details

We have earlier developed a coarse grained model for 1-methyl,3-alkylimidazolium hexafluorophosphate $[C_n mim][PF_6]$. The model has been employed successfully to study the microheterogeneity in RTILs as a function of the alkyl group length [25], the effect of shear on the structure [30], and recently to study the spontaneous formation of a lamellar phase in ionic liquids of the type, $[C_n C_n im][PF_6]$ [31]. A schematic depicting the correspondence between the atomistic and coarse grain representations of the ions is shown in Figure 6.1. The cation has six beads and the anion has one bead. The cation contains a positively charged "head" made of three atoms: I1, I1 and I3. This is equivalent to the imidazolium ring in the atomistic representation. CM and CT are the beads for the alkyl chain on the cation and PF is the bead representing the divalent anion. Information regarding the form of the interaction potential is explained in an earlier work [25]. Intramolecular terms include harmonic bond stretches and angle bends. Coulombic and 9-6 Lennard-Jones interactions mediate non-bonded neighbours. Since we wanted to simulate a RTIL with divalent anion, we have doubled the charge on the anion and considered twice the number of cations (monovalent) as of anions. The charge on a monovalent anion in our model is set to -0.8e [25] and thus the divalent anion studied here carries a charge of -1.6e. The overall charge on the cation is +0.8e. The 9-6 (softer when compared to Lennard-Jones) interactions were the same as that for the PF_6^- anion. The interaction model is not specific to any specific divalent anion; our aim in this work is to capture the generic features of intermolecular (and intermediate range) structure that is brought about by the introduction of divalent anions in RTILs.

Classical molecular dynamics (MD) simulations were performed using the LAMMPS [32] code. A time step of 4 fs was used to integrate the equations of motion. Non-bonded interactions were treated with a spherical cutoff of 1.5 nm, and the long range part of the electrostatic interactions was treated using the particle-particle particle mesh Ewald method. The system consists of a total of 2600 beads with 400 $[C_{10}mim]^+$ cations and 200 anions. A simulation box with randomly arranged coordinates of these ions was taken as the initial configuration and the system was equilibrated under constant NPT conditions for 1.2 μs. Later, the system was simulated under constant NVT conditions for 320 ns. Coordinates stored every 200 ps were later used for analysis. The temperature of the system was maintained at 300K using a Nose-Hoover thermostat. The final box length of the divalent system was 55.1 Å.

Pair correlation functions between the beads of the ions have been calculated using binwidth of 0.01Å. The partial structure factors were calculated from these pair correlation functions using the following relation,

$$S_{\alpha\beta}(q) = \delta_{\alpha\beta} + 4\pi\sqrt{\rho_\alpha \rho_\beta} \int_0^\infty r^2 [g_{\alpha\beta}(r) - 1] \frac{sin(qr)}{(qr)} dr \tag{6.1}$$

where, $\rho_\alpha = \frac{N_\alpha}{V}$. N_α is the number of beads of type α and V is the volume of the system. The upper limit in the integral is replaced by half of the simulation box length. The total neutron scattering function is obtained from these partial functions using appropriate scattering lengths as given by,

$$S(q) = \sum_{\alpha} \sum_{\beta} c_{\alpha} c_{\beta} \frac{f_{\alpha}(q) f_{\beta}(q)}{\langle f(q) \rangle^2} S_{\alpha\beta}(q) \tag{6.2}$$

where c_{α} is the concentration of bead type α in the system. f_{α} is the scattering length of bead α and $\langle f(q) \rangle = \sum_{\alpha} c_{\alpha} f_{\alpha}(q)$.

To understand the effect of increase in charge density on anion, we have also analysed a system with the same cation but with a monovalent anion (PF_6^-). This system have equal number of cations and anions (3375 ions of each kind). We compare the results of this system with the one containing the divalent anion. In the rest of the chapter, we refer to the system containing monovalent anion as system A and the one containing divalent anions as system B.

6.3 Results and Discussion

6.3.1 Radial Distribution Function

Let us take a look at the radial distribution functions (RDFs) between the polar sites of the ions. Figure 6.2 compares the RDFs between system A and system B for a) head-anion (I1-PF), b) anion-anion (PF-PF), and c) head-head (I1-I1). A large increase in the intensity of the first peak in all the RDFs is seen for system B. Also, its position shifts to lower distances in the case of head-anion and head-head correlation functions, while it shifts to the right for the anion-anion RDF. The latter is due to the increased value of charge on the anion. An important observation is the large increase in the peak height of head-head RDF and the closer approach of imidazolium rings of neighbouring cations in system B relative to that in system A. It implies ordering of the cations and possible stacking of the adjacent ring planes.

Figure 6.2: Comparison of RDF between systems A (monovalent anion) and B (divalent anion) for a) I1-PF b) PF-PF c) I1-I1 bead pairs.

The increase in the peak height of the head-anion RDF is due to the enhanced Coulombic interaction between these two groups in view of the anion in system B containing twice the charge as that in system A.

These three RDFs provide us valuable information about the local structure in the polar regions of the IL. They strongly indicate that the increase in charge density of the anion has led to an increase in the strength between the sites constituting the polar regions. There is a similar increase in the intensity of the first two peaks in the RDF between the alkyl tails of the cation in system B compared to that in system A (Figure 6.3(a)). Thus, the non-polar region of the IL (constituted by the alkyl tails) is also more structured in system B than in system A. We now look at the RDFs between head-tail (I1-CT) and anion-tail (PF-CT) in Figure 6.3. There is a large decrease in intensity of the first two peaks for system B, indicating that the correlation between a polar and a non-polar site is drastically reduced in divalent anion based ionic liquid compared to the monovalent one. In summary, the increase in the charge density of the anion leads to a more ordered local structure.

6.3.2 Structure Factor

While structural order at near neighbour distances can be probed in real space readily using radial distribution functions, such ordering at the intermediate to long range distances are often discernible easier in reciprocal space. Calculation of the structure factor, S(q) is thus crucial in order to study the microheterogeneity in any system, and in particular in ionic liquids. A study of the total structure factor (TSF) and the contributing partial structure factors (PSFs) will shed some light on the effect of increase in charge density of anion on the intermediate range spatial correlations. Figure 6.4 compares the TSF between systems A and B. System A exhibits peaks at 0.28Å^{-1}, 0.97Å^{-1} and 1.44Å^{-1} corresponding to real space correlation lengths of 22.4Å, 6.5Å and 4.4Å. System B shows a peak 0.28Å^{-1} whose

Figure 6.3: Comparison of RDFs between systems A and B for a) I1-CT b) PF-CT bead pairs.

Figure 6.4: Comparison of the total neutron weighted structure factor between systems A and B.

intensity is much larger than that in system A. The peak at 0.28Å^{-1} (correlation length of 2.24 nm in real space) is the signature of nanoscale ordering in C_{10}mim cation based ionic liquids. The increase in intensity of this peak in system B indicates a considerable enhancement of spatial heterogeneity in the IL with divalent anion. Molecular dynamics simulations [25] have shown that though all the PSFs contribute to the peak at 0.28Å^{-1}, some PSFs (such as anion-anion) make greater contribution to this peak. Figure 6.5 compares the PSFs between system A and system B. Compared to system A, all the PSFs of system B have peak at 0.28Å^{-1} with larger intensity.

Figure 6.6 shows a snapshot of system B. A similar figure for system A has been published elsewhere [25]. Sites forming the polar head (imidazolium ring) of the cation and the anion are shown in red and the non-polar sites of the tail are shown in yellow. These regions are distributed heterogeneously in the ionic liquid.

Figure 6.5: Comparison of partial structure factors between systems A and B for a) I1-I1 b) PF-PF c) CT-CT bead pairs.

Figure 6.6: Snapshot showing the spatial heterogeneity present in system B (divalent anion). Beads forming the cation head and anion are in red color and the beads of alkyl chain are in yellow. Side length of the simulation box is 55.1Å.

Figure 6.4 also indicates that the intensity of the peak at 0.97$Å^{-1}$ (6.5Å in real space) in system B is lower than that in system A. This feature is related to ring-ring (also called head-head) correlations, as can be identified from the PSF shown in Figure 6.5a). The RDF between I1-I1 (head-head) shown in Figure 6.2c) indicates that the first peak is present at 6.5Å in system A, whereas at the same distance in system B, the RDF shows a minimum. Thus, the reciprocal space correlations at this length scale are diminished in system B, relative to system A. This is also corroborated by the anion-anion (PF-PF) RDF shown in Figure 6.2b). Since anions in system B have larger charge density than system A, they are farther away from each other and the RDF starts having non-zero values only beyond 6Å.

The peak in the wave vector range of 1.4$Å^{-1}$ to 2.2$Å^{-1}$ corresponds to a real space distance of 2.8Å to 4.5Å. Greater intensity of this peak in system B compared to system A indicates a stronger local structure. This was highlighted by radial distribution functions also.

6.3.3 Dynamics

Coarse grained (CG) models in general do not represent the true dynamics of a system. This is so because one employs softer potentials for interaction between beads than what is used for that between atomic sites in an atomistic MD simulation. Also, the absence of the stiff harmonic potentials employed in CG models for bond stretches, angle bends etc.. make the potential energy surface smoother than the rugged landscape characteristic of molecular liquids modelled with atomistic force fields. It is documented by many that CG models often overestimate the diffusion coefficients by two orders of magnitude compared to atomistic ones [33]. Our CG model too shares this trait. Despite the obvious disconnect between the model and experiment (or the real world sample) for dynamical phenomena, we explore the dynamics of systems A and B. We hope that although their dynamics in individual terms may not be representative of the ionic liquids, the differences between the two systems could be realistic.

We now look at the dynamics of system B and compare it against that of system A. Figure 6.7 shows the mean squared displacement (MSD) of beads I1, CT and PF for systems A and B. The slope of the MSD data gives us an idea about the diffusion coefficient of the beads. In both cases, CT has the highest slope of MSD compared to I1 and PF, similar to what is seen in atomistic MD simulations of ILs. While in system A the anions move the fastest (albeit by a small amount), it is the alkyl tail of the cation that shows a large MSD value in system B. System B is characterized by strong electrostatic interactions and thus the polar entities (beads I1 and PF) diffuse slower than the alkyl tail group. Moreover, the overall MSD values themselves in system B are nearly an order of magnitude smaller than that in system A. The observations of dynamics thus agree with the structural data

Figure 6.7: Mean squared displacement of head, tail and anion beads in a) system A and b) system B.

discussed earlier.

6.4 Conclusions

We have carried out coarse grained molecular dynamics simulations of a model ionic liquid – one in which the divalent anions carry twice the charge as that in a traditional ionic liquid. The increase in the anion charge density is compensated by doubling the mole fraction of the cation. A consequence of this change in the potential is an increase in electrostatic interaction between the ions. We have explored the structural and dynamical manifestations of this variation in the interaction potential through coarse grained MD simulations. Our model could be considered to capture the essential features of a room temperature ionic liquid in which the usual monovalent anion is replaced by a divalent one.

Our study suggests considerable enhancement of intermolecular structuring, and a more ordered liquid, at all length scales. It will not be surprising, if in reality, such substances are actually crystalline at room temperature – a possibility which is beyond the scope of the current study to explore. The structural microheterogeneity inherent to RTILs with long alkyl tails is vastly amplified in the IL with divalent anions. The substance is also observed to be highly sluggish compared to an IL with a monovalent anion.

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