

# Unique Structure and Solute –Solvent Interaction in Imidazolium Based Ionic Liquids: A Review

G. Gonfa, M.A. Bustam, Z. Man, M. I. Abdul Mutalib

**Abstract**—Ionic liquids have attracted wide attention lately and their potential applications in different areas have been explored. Most of the current researches on ionic liquids are concentrated on investigating what can be done by ionic liquids and why they work the way they do. The latter provide the insight into the molecular factors that determine their properties ranging from quantitative thermodynamic and physical data and qualitative trends that guide in searching the best ionic liquids for particular purpose. Many of the applications rely upon the interaction of ionic liquids with other components. Ionic liquids exhibit nanoscale phase segregation into polar and nonpolar regions. The nanoscale self-organisation is the result of interplay between Coulomb and van der Waals interactions which leads to the formation of high charge density permeated non-polar regions. This characteristic determines how different molecular solutes interact with certain domain of the ionic liquids and distinct local environment. However, the complexities of the nature and size of cation-anion interactions and intermolecular forces in liquids phase give rise to controversies. This Review discusses the current development in understanding molecular structure, cation- anion interaction, intermolecular forces and their effects of solvation. This work is mainly concentrated on imidazolium based ionic liquids.

**Index Terms**— Anion, Cation, Ionic liquid, Solute-solvent Interaction

## I. INTRODUCTION

THE application of simple inorganic salts for chemical process is impractical due to their high melting points and most process takes place in molecular solvents. However, the advent of salts with organic ions (ionic liquids), which are liquid at room temperature, opened a window for the advent of salts with organic ions (ionic liquids), which are liquid at room temperature, opened a window for the application these salts

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in different processes. The term “ionic liquid” refers to organic salts that are liquid at or near room temperature,

taking 100 °C as an arbitrary upper limit [1]. The first report of ionic liquid (formerly called a room-temperature molten salt), ethyl ammonium nitrate goes back to 1914 [2]. Latter, organic chloroaluminates was developed by Hurley and Thomas in 1951 [3]. However, interest in these salts advanced only after the development of binary ionic liquids from mixtures of aluminum (III) chloride and *N*-alkylpyridinium [4] or 1, 3-dialkylimidazolium chloride [5]. During 1970s ionic liquids were studied mainly for electrochemical applications and in the mid-1980s, ionic liquids were proposed as solvent for organic synthesis [6, 7]. In the 1990s many air and water stable ionic liquids were introduced and since then they have become increasingly popular in academia and industry [8]. Review of history of ionic liquids can be found somewhere else [9].

Ionic liquids have attracted attention for their excellent properties, stable at high temperatures [10], non-inflammable [11], negligible vapor pressure [12, 13], wide liquid electrochemical windows [14] and wide liquid ranges [15]. Ionic liquids have appealing properties as a possible replacement for conventional solvents in separation process [16, 17], electrochemistry [18, 19], media for chemical and biological reactions [20, 21], catalyst [22], thermo fluids [23, 24], sensor [25] and tribology [26].

The properties of ionic liquids could be tailored for specific application by adjusting the structure and species of cations and/or anions. In fact, the possible combination number of cations and anions is uncountable with vast and still unexplored possibilities [27, 28]. To facilitate the selection of an optimum ionic liquids for a particular application; it is useful to consider their fundamental transport and thermodynamic properties. An understanding of microstructures and interactions of ionic liquids at molecular level, as pure compounds or in the presence of dissolved species, is useful to design of suitable ionic liquids [29, 30]. The chemical constitution of ionic liquids determines the nature of intramolecular and intermolecular interactions and thus the macroscopically observable properties such as thermodynamic and transport properties [31]. A deeper understanding of the effect of the molecular structure and microscopic properties of ionic liquids is paramount in understanding and improving the macroscopic properties of the system [32]

The aim of this review is to describe the current knowledge and controversies of the structural foundation

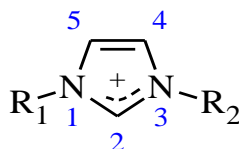
of ionic liquids; specifically imidazolium based ionic liquids, and their properties in the presence of other molecular solutes. We focused on the major development and controversies in micro scale structural organization and solute-solvent in systems involving ionic liquids. The first section covers the intermolecular forces and the resulting structure of imidazolium based ionic liquids. The solvent behaviour of ionic liquids with different solutes will be discussed in the second section.

## II. STRUCTURE OF IMIDAZOLIUM BASED IONIC LIQUIDS

Ionic liquids are typically based on bulky organic cations with the charge balanced by organic cations and inorganic/organic anions. The most important cations are imidazolium, pyridinium, pyrrolidinium, tetraalkylammonium, phosphonium and their functionalized cations. Anions are weakly basic inorganic or organic compounds that have a diffuse or protected negative charge. Much work has focused on ionic liquids based on halides such as  $[\text{BF}_4]^-$  or  $[\text{PF}_6]^-$  ions which has unfavorable properties and are strongly hygroscopic [33]. The most preferred anions are with more complex perfluorated anions such as bis(trifluoromethane sulfonyl)amide or trifluoromethanesulfonate, or halogen-free ions, such as dicyandiamide, tosylate, or n-alkyl sulfates [1].

### A. Features of Imidazolium Ionic Liquids

One of the most widely used and studied ionic liquids families is the one based on imidazolium cation. The imidazolium ring is often selected due to the stability and excellent liquescency [34]. The unique properties of these cations are founded in the electronic structure of the aromatic cations. The electronic structure of these salts contain delocalized 3-center-4-electron configuration across the  $\text{N}_1\text{-C}_2\text{-N}_3$  moiety, a double bond between  $\text{C}_4$  and  $\text{C}_5$  at the opposite side of the ring, and a weak delocalization in the central region [35]. The hydrogen atoms  $\text{C}_2\text{-H}$ ,  $\text{C}_4\text{-H}$ , and  $\text{C}_5\text{-H}$  carry almost the same charge, but carbon  $\text{C}_2$  is positively charged owing to the electron deficit in the  $\text{C}=\text{N}$  bond, whereas  $\text{C}_4$  and  $\text{C}_5$  are practically neutral. The resulting acidity of the hydrogen atoms is the key to understand of the properties of these ionic liquids. The hydrogen on the  $\text{C}_2$  carbon ( $\text{C}_2\text{-H}$ ) has been shown to bind specifically with a solute molecule [36, 37] or its counter ion [38] as a good hydrogen bond donor.



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

### B. Nano Structural Organization of imidazolium Based Ionic Liquids

Ionic liquids are composed solely of ions so that long-range coulomb interaction may play a major role in these liquids. The long-range coulomb interactions give rise to structure and

dynamics that are unique to ionic liquids but are not associated with molecular liquids [39]. Many of the novel features of ionic liquids are likely to originate from these unique structures and dynamics [40]. From macroscopic point of view, ionic liquids can be considered as a continuum system characterized by its macroscopic constants, such as boiling point, vapour pressure, density, surface tension. However, from microscopic point of view it is a discontinuum system which consists of individual, mutually interacting molecules, characterized by molecular properties such as dipole moment, electronic polarizability, hydrogen-bond donor (HBD) and hydrogen bond acceptor (HBA) capability, electron-pair donor (EPD) and electron-pair acceptor (EPA) capability, etc. The types and extent of these interactions determine the macroscopic properties of ionic liquids and their possibilities for different applications.

Many studies have been carried out to examine the structure and interactions of ionic liquids, mostly imidazolium based ionic liquids by using different approaches. Specifically, the structure of these ionic liquids systems exhibits unique spatial heterogeneity that results from their inherent polar/nonpolar phase separation. The underlying reason for the microphase segregation is due to the interplay between electrostatic interactions (between polar imidazolium ring and anion) and van der Waals interaction between the nonpolar alkyl tails of the cation [41].

Nano-segregation of imidazolium based ionic liquids between polar and non-polar regions was first predicted by molecular dynamics simulation studies [42-45] and later confirmed by neutron diffraction [46] and x-ray diffraction [46] techniques. The molecular dynamics simulations done on 1-alkyl-3-methylimidazolium cations with anions ( $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $[\text{PF}_6]^-$ ) shows regions above and below the imidazolium ring are the preferential ones in case of large anions, however, nearest-neighbor anions are pushed away from the volume occupied by the flexible alkyl chain on increasing alkyl chain [43]. The charged anions and cations head groups distribute homogeneously because of the strong electrostatic interactions, while the neutral tail groups tend to aggregate due to the collective short-range interaction for longer alkyl chain [45].

Visualization of the charged and nonpolar domains has been achieved by applying different a colouring code. Lopes and Pa'dua [47] coded polar domain (anion, imidazolium ring and the groups of the cation directly linked to it) with red and the alkyl-side chain of the cation (starting from the second methylene group) with green. The red-green colour code is easy way to "see" the segregation and the corresponding domains in ionic liquids and their mixtures. Recently, alternative color schemes were applied by painting red, blue and gray the negative and positive parts of the polar network and the non-polar alkyl chains respectively [48]. Details on both coding scheme can be found in the work reported by Shimizu and collaborators [48].

The local structural heterogeneity of imidazolium based ionic liquids has been probed by coherent anti-Stokes Raman scattering (CARS) [39, 40]. The measurements carried out on

three imidazolium based ionic liquids  $[C_n\text{mim}][\text{PF}_6]$  and  $[C_n\text{mim}][\text{Tf}_2\text{N}]$  shows the presence of local domains which increases alkyl chain length. The neutron diffraction measurements on 1, 3-dimethyl imidazolium based ionic liquids shows the effects of charge distribution and anion size on nanostructural segregation of ionic liquids. As the ions increase in size, the charge becomes more delocalized and the cation-anion interaction reduced resulting in less charge ordering and nanostructural segregation [49]. Divalent anions, such as sulphate ( $\text{SO}_4^{2-}$ ), thiosulphate ( $\text{S}_2\text{O}_3^{2-}$ ), chromate ( $\text{CrO}_4^{2-}$ ), dichromate ( $\text{Cr}_2\text{O}_7^{2-}$ ), Carbonate ( $\text{CO}_3^{2-}$ ) and oxalate ( $\text{C}_2\text{O}_4^{2-}$ ) increase the electrostatic interactions between cations and anions and enhance of intermolecular structuring [50].

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The existence of structural organization at of 1-alkyl-3-methylimidazolium based ionic liquids with  $[\text{Cl}]^-$  and  $[\text{BF}_6]^-$  were also studied by x-ray diffraction. It was observed that the size of structural heterogeneities depend on alkyl chain length [46, 51]. The x-ray scattering result of 1-alkyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide ( $[C_n\text{mim}][\text{NTf}_2]$ ) shows aggregation occurs for  $n \geq 3$  and sizes depend on the length of the alkyl chain [52]. However, the charge ordering found in  $[C_n\text{mim}][\text{NTf}_2]$  is significantly smaller compared with analogous chloride and hexafluorophosphate salts [52], which is consistent with neutron diffraction measurements.

The most common imidazolium-based ionic liquids contain asymmetric alkyl chain, usually methyl group at the 3-position and a longer alkyl group at the 1-position. The effects of cation symmetry on properties of imidazolium based ionic liquids were also reported. Symmetric (1, 3-didecyl imidazolium hexafluorophosphate) and asymmetric (1-decyl-3-methylimidazolium hexafluorophosphate) are liquids irrespective of their symmetry [53]. However, the possible formation of structural organization in symmetric cation than 1-decyl-3-methylimidazolium hexafluorophosphate was reported [54]. Both experimental and molecular dynamic simulation results show symmetric 1,3-dialkyl-imidazolium bis(trifluoromethylsulfonyl)imide ionic liquids have the same morphology, however, nanoscale ordering is considerably enhanced in symmetric cation based ionic liquids [41, 55].

The effect of conformational heterogeneity of cations and anions nanostructural organization of ionic liquids was also reported. For example, the coexisting trans-trans and trans-gauche conformations of n-butyl chain in 1-butyl-3-methylimidazolium cations seems to be crucial in lowering the melting points of this 1-butyl-3-methylimidazolium based ionic liquids [56]. An example for conformational equilibria of anions is bis imide  $[\text{Tf}_2\text{N}]$  which forms trans- and cis conformers.

### C. Ionic Liquids in Gas Phase

The general belief that ionic liquids are not volatile, hence cannot be distilled, can probably be traced back to a report on first-generation ionic liquids until recently unfounded. Rebelo et al. [12] performed preliminary distillation tests on 1-decyl-3-methylimidazolium and 1-dodecyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide at a reduced pressure (1 Pa and 450 K). This is followed by indirect determinations of the vapour pressure and enthalpy of vaporization of 1-butyl-3-methylimidazolium bis (trifluoromethylsulfonyl)imide [57]. Earle et al. (2006) demonstrated that 1-alkyl-3-methylimidazolium bis [(trifluoromethyl) sulfonyl] imides can be vaporized in vacuum. The majority of 1-alkyl-3-methylimidazolium bis [(trifluoromethyl) sulfonyl] imide ionic liquids distilled without decomposition. After this experiment the nature of gas phased ionic liquid species was investigated using Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS) [58, 59], Electron ionization (EI) mass spectra [60-62]. The results indicate that aprotic ionic liquids ( $\text{A}^+\text{X}^-$ ) pass into the vapor phase with their constituent anions and cations, keeping their integrity as tight neutral ion pairs (AX) with no free ions or higher aggregates (either charged or neutral). However, the gas phase above protic ionic liquids ( $[\text{BH}]^+\text{X}^-$ ) consists of isolated neutral molecules, B and HX. Protic ionic liquids, dissociate on heating to produce the molecular base, B, and the molecular acid, HX. Protic ionic liquids are volatile by their nature because the acidic proton can be abstracted by the basic anion at ambient temperature [63].

### D. Inter Ionic (cation-anion) interaction

The environment constituted by ionic liquids is completely different from that of polar and non-polar molecular solvents. In addition to the interactions existing in conventional organic solvents (hydrogen bonding, dipole-dipole and van der Waals interactions) ionic liquids have strong electrostatic interactions. Ionic liquids are constituted exclusively by ions and hence experience strong inter-ionic interactions that yield long-lived association of ions [31]. The nature and type of cation anion interactions and intermolecular forces in bulk ionic liquids affects their physical and chemical their properties and how they interact with other solutes [64]. There are, however, questions remaining about the nature and the precise origin of this possible association.

#### Ion Pairs in Gas phase

It has been proposed by some authors that cations and anions are hold together through hydrogen bonding and others consider its relevance minor compared with the role of electrostatic interaction. The ab initio calculation made on the gas-phase ion pairs of 1-butyl-3-methylimidazolium chloride ionic liquid found multiple stable conformers with the chloride anion positioned (in-plane) around the imidazolium ring or above the  $\text{C}_2\text{-H}$  [35, 65]. Conformers with the Cl ion in front  $\text{C}_2\text{-H}$  bond and on top of  $\text{C}_2$  of imidazolium ring are more stable than  $\text{C}_4\text{-H}$  and  $\text{C}_5\text{-H}$  [65]. In multiple atomic anion such as 1-ethyl-3-methylimidazolium hexafluorophosphate  $[\text{emim}][\text{PF}_6]$  the anions are not only

bonded to C<sub>2</sub>-H of imidazolium ring but also with C-H fragment of the alkyl chain [29, 66]. In stable ion pair of structure of [C<sub>2</sub>mim][PF<sub>6</sub>] the [PF<sub>6</sub>]<sup>-</sup> anion placed over imidazolium ring with three fluorine atoms forming a triangle with a short contact to C<sub>2</sub>-H and hydrogen atoms of alkyl group [66-68]. Chang et al. [67] also observed hydrogen bond-like interactions between [PF<sub>6</sub>]<sup>-</sup> and the H atoms on the alkyl side chains in pure 1-butyl-3-methylimidazolium hexafluorophosphate using infrared spectroscopy.

The role of hydrogen bonds between imidazolium ions and larger anions is the subject of discussion. Tsuzuki et al. (2005) reported that the electrostatic interaction is the major source of attraction, hydrogen bonding with the C<sub>2</sub>-H of imidazolium is not essential for the attraction in the ion pair. It was reported that hydrogen bond only contributes to the stabilization energy cation-anion pairs in [C<sub>2</sub>mim][PF<sub>6</sub>] and [C<sub>2</sub>mim][BF<sub>4</sub>] ionic liquids [66, 69]. They concluded that hydrogen bond exists in these ionic liquids but it is far from dominating its structure and dynamics and the ionic liquid is held together by Coulomb force. The C<sub>2</sub>-H...X interaction in 1, 3-dimethylimidazolium tetrafluoroborate ([dmim][BF<sub>4</sub>]) is considerably different from that of conventional hydrogen bonds and its magnitude of the interaction depends mainly on the distance between the imidazolium ring and anion and nearly inversely proportional to the distance between cation and anion [69]. This shows which shows that the charge - charge interaction is the dominant interaction in the attraction and the effect of hydrogen bond is negligible. On the other hand some authors found hydrogen bond between cations and anions; however, its effect is minor compared to electrostatic interaction. Zao et al. [31] reported that hydrogen bonds between cations (ring hydrogens) and anion (fluorine) in 1-n-butyl-3-methylimidazolium hexafluorophosphate ([C<sub>4</sub>mim][PF<sub>6</sub>]) is weaker than expected. The same result was observed for 1-ethyl-3-methylimidazolium tetrafluoroborate using IR and Raman spectra analyses and theoretical calculations [70].

Some authors reported the essentiality of hydrogen bond in cations and anions ion-pairs. The Raman and infrared spectra result and density functional theory calculation by Talaty et al. [68] on a series of 1-alkyl-3-methylimidazolium hexafluorophosphate ([C<sub>2-4</sub>MIM][PF<sub>6</sub>]) indicate hydrogen bonding interactions between the fluorine atoms of the [PF<sub>6</sub>]<sup>-</sup> anion and the C<sub>2</sub> hydrogen on the imidazolium ring. They also reported additional interaction between [PF<sub>6</sub>]<sup>-</sup> and the H atoms on the adjacent alkyl side chains. The importance of hydrogen bond in cation-anion interaction was also reported by Hunt and co-workers Gould (2006) by ab initio theoretical in 1-butyl-3-methylimidazolium chloride ionic liquid..

#### *Ion pair in the liquid phase*

Ion-pairs have been found in dilute solutions of ionic liquids using experiments [71, 72] and molecular dynamics simulations [73, 74]. However, the presence of ion-pair in ionic liquid bulk liquid phase is controversial [31]. Some authors reported that cations and anions form ion-pair in bulk liquid phase due to their strong electrostatic charges [59, 74]. This is consistent with the deviation of conductivity from

Nernst-Einstein approximation [31, 75-77] due to the reduction of effective number of ions available for reduction through ion pair formation [31]. However, there is no evidence of long-lived ion pair in liquid phase [78-80]. In addition, it was also reported that the deviation might result from the short correlation in motion of the neighboring cations and anions [81]. The theoretical tools to describe ion-pairing that have been developed in the context of dilute solutions [73, 82] may not be adaptable because neighborhoods of ions in neat ionic liquids present significant fluctuations of the local charge density which is not present in dilute solutions [31]. Further studies on cation anion interaction at molecular level are needed to settle this debate.

### III. SOLUTE-SOLVENT INTERACTION IN SYSTEMS CONTAINING IMIDAZOLIUM BASED IONIC LIQUIDS

Ionic liquids can dissolve a wide range of polar or nonpolar, organic or inorganic compounds. The ability of ionic liquid to dissolve polar and non-polar compounds is related to its structural segregation [42, 48]. The segregation of polar and nonpolar domains and diverse environment in ionic liquids helps to understand how solutes physically fit in to the bulk liquid and how much the overall structure is affected. Different solutes interact preferably with certain domain of the ionic liquids. Each domain located at different site and acts as a specific solvent for a given class of solutes and ionic liquids are called "two-in one" solvents [48] or (pseudo) different solvents [83].

In general solutes can be classed into three groups depending on where and how they interact with ionic liquids [48]: a) associating solutes (those interact strongly with polar network), b) those prefer the non-polar regions of ionic liquids, and c) those that can orient themselves at the interface between the polar and non-polar regions of ionic liquids.

#### *A. Associating Solutes*

Associating solutes form strong hydrogen bonds with the charged parts of the ionic liquid domains [84], specifically with atoms of anions [48]. The most common examples are water and methanol.

##### *Water*

One of the most studied solute-solvent interactions involving ionic liquids is the interaction between water and imidazolium based ionic liquids. Both the experimental [47, 67, 85] and theoretical works [86] shows water molecules preferentially interact with polar domain of ionic liquids through hydrogen bonding. Cammarata et al. (2001) studied interactions between ionic liquids and water by attenuated total reflectance (ATR) infrared spectroscopy and concluded that water molecules preferentially interact with anions through hydrogen bonding. In addition, they found that ionic liquids containing [BF<sub>4</sub>]<sup>-</sup> and [PF<sub>6</sub>]<sup>-</sup> anions forms symmetric complex with water molecule (both protons of water bound to two discrete anions) as X...H-O-H...X (where X represents the anion in the ionic liquid). Similar observations were reported through vibrational spectroscopy measurement and DFT calculation [87, 88].

Molecular dynamics simulation by Hanke and coworkers[89] also demonstrated that the water molecule form strong hydrogen bonded to two chloride anion forming dimer. However, Wang et al.[44] proposed a different dimer formation scheme in water and ionic liquids with  $[\text{BF}_4]$  anion. They reported that water molecules form dimer with  $[\text{BF}_4]$  anion via  $\text{H-O-H}\cdots\text{BF}_4\cdots\text{H-O-H}$  models than  $\text{BF}_4\cdots\text{H-O-H}\cdots\text{BF}_4$  model. Their simulation work on water and  $[\text{emim}][\text{BF}_4]$  complex shows the dimer  $\text{BF}_4\cdots\text{H-O-H}\cdots\text{BF}_4$  is not stable structure. The authors did not find stable complex for hydrophobic anion  $[\text{PF}_6]$  with water molecules.

Most of the early investigations suggested that the miscibility of ionic liquid with water is mostly determined by the associated anion [85, 90]. The possibilities that water that may interact via H-bonding between the oxygen atom of water and acidic proton in the imidazolium ring was investigated latter. It was reported that water molecules do not directly interact with acidic imidazolium ring ( $\text{C}_2\text{-H}$ ) [87, 88]. However, acidic imidazolium ring ( $\text{C}_2\text{-H}$ ) affects the amount of water absorbed and the strength of hydrogen bond formed between anion and water molecules [85, 91]. They reported that as the hydrogen bond donor ability of the cation decreases (on replacing hydrogen of  $\text{C}_2$  with methyl) the strength of the hydrogen bond between water and the anion increases due to less competition between the imidazolium ring and water for the hydrogen bond acceptor sites of the anions. The introduction of methyl substituent in the position  $\text{C}_2$  of the imidazolium ring decreases the cation anion interaction [64] hence favour water- anion interaction.

However, some authors reported that water can also interact with cation through acidic hydrogen ( $\text{C}_2\text{-H}$ ) by forming hydrogen bond with oxygen in water molecules [92, 93]. The nuclear magnetic resonance (NMR) spectroscopy study[92, 93] on  $[\text{bmim}][\text{BF}_4]$  shows the evidence of cation - water interaction through acidic hydrogen ( $\text{C}_2\text{-H}$ ) and water oxygen in addition to the anion-water interaction through fluorine and hydrogen of water molecules. In addition, Chang and coworkers[94] proposed additional water-ionic liquid interaction site through hydrogen bonding between imidazolium alkyl side chain hydrogen and oxygen of water. The infrared spectroscopy measurement shows both methyl C-H and imidazolium C-H groups are favorable sites for  $\text{C-H}\cdots\text{O}$  hydrogen bonding in a dilute 1, 3-dimethylimidazolium methyl sulfate water mixture [67]. The simulation work by Lopes et al.[42] on  $[\text{bmim}][\text{PF}_6]$  water mixture identified hydrogen bond between imidazolium hydrogen and anion fluorine with water molecule, the former to less extent. Wang and coworkers[95] also proposed mechanisms of water- ionic interaction for ionic liquids based on the imidazolium cation with the anions  $[\text{Cl}^-]$ ,  $[\text{Br}^-]$ ,  $[\text{BF}_4^-]$ , and  $[\text{PF}_6^-]$  through quantum chemical calculations. They investigated the interaction between water oxygen and the  $\text{C}_2\text{-H}$ ,  $\text{C}_4\text{-H}$ , and  $\text{C}_5\text{-H}$  of the imidazolium ring. The interaction energies at B3LYP/6-31++G\*\*//B3LYP/6-31G\* level for  $\text{C}_2\text{-H}$ ,  $\text{C}_4\text{-H}$  and  $\text{C}_5\text{-H}$  are -38.03, -30.72, and -34.09 kJ/mol respectively which is in the range of traditional hydrogen bond [95]. The quantum chemical calculations also shows

additional water - ionic liquid interaction which involves the approach of the two or three water oxygen atoms toward the protons in the imidazolium ring forming stable structure.

The Two-dimensional vibrational spectroscopy on 1-ethyl-3-methylimidazolium tetrafluoroborate to investigate its dilution process in water shows blue shift for  $\text{C}_2\text{-H}$ ,  $\text{C}_{4,5}\text{-H}$ , alkyl C-H and B-F and increases with water content in the mixture [96]. In addition, the shift for  $\text{C}_2\text{-H}$  is much higher than the others implying different interaction strength with different sites. The blue shift of both C-H and the B-F stretching cation and anion implies the influence of water both on cation and anion.

The attenuated total reflectance infrared spectroscopy,  $^1\text{H}$  NMR spectroscopy, and quantum chemical calculations on water and 1-ethyl-3-methylimidazolium ethylsulphate mixture shows C-H groups in the imidazolium ring and  $-\text{SO}_3$  in the ethyl sulfate anion are characteristic groups interacting with water molecules [97]. The result indicates that  $-\text{SO}_3$  group in the ethyl sulfate anion undergoes enhanced hydrogen bonding interaction whereas the C-H groups in the 1-ethyl-3-methylimidazolium cation undergo weakened hydrogen bonding interaction with the increasing concentration of water. They observed that hydrogen bonding interaction between  $\text{H}_2\text{O}$  and  $-\text{SO}_3$  is prior to the interaction between  $\text{H}_2\text{O}$  and the C-H group on the imidazolium ring up to limiting concentration ( $x = 0.6$ ) and interacts with hydrogen atoms on the imidazolium ring at higher concentrations. Singh and Kumer[98] also reported the effect of concentration of water on the interaction site on  $[\text{omim}][\text{Cl}]$ ,  $[\text{bmim}][\text{CH}_3\text{SO}_4]$ ,  $[\text{bmim}][\text{C}_8\text{H}_{17}\text{OSO}_3]$  and  $[\text{bmim}][\text{BF}_4]$  using FTIR spectroscopy. The result shows that at low concentration water molecules are selective for certain part of ionic liquid (preferentially anions) and as the concentration increases the system passes from a regime of selective interaction to a less defined, non -selective solvation. In addition they reported that the strength of water ionic liquid interaction at  $\text{C}_2\text{-H}$ ,  $\text{C}_4\text{-H}$  and  $\text{C}_5\text{-H}$  are found to be almost the same at dilute water concentration [98].

#### *Methanol*

The interaction between methanol and ionic liquid is dominated by hydrogen bond interaction due to its both hydrogen bond donor and acceptor properties as observed for water [86]. The only differences are methanol interacts with both polar and non-polar domains of ionic liquids and the interaction between methanol and  $\text{C}_2\text{-H}$  is weaker than that of water molecule [86]. The Infrared Spectroscopy and Two-Dimensional Correlation and Multivariate Curve Resolution on mixture methanol and  $[\text{emim}][\text{BF}_4]$ ,  $[\text{bmim}][\text{BF}_4]$  and  $[\text{bmim}][\text{PF}_6]$  shows hydrogen bond interaction between methanol OH group and anion's fluorine [47, 86]. The result also indicates the weaker interaction between methanol and cation hydrogen through methanol oxygen acidic hydrogen of imidazolium cation. The OH stretching band is red shifted on adding methanol in the ionic liquids and the shift is much greater for  $[\text{BF}_4]$  indicating stronger interaction for  $[\text{BF}_4]$  anion than  $[\text{PF}_6]$ . The density functional theory (DFT) calculations by Zhu et al.[99] also shows anions prefer to

occur near hydroxyl hydrogen atom of methanol due to its positive charge. It was observed that O-H normal mode  $\nu$  at  $3838.65\text{ cm}^{-1}$  in free methanol molecule red shifted to  $3305.6$ ,  $3401.62$ ,  $3586.97$  and  $3720.11\text{ cm}^{-1}$  in the presence of [emim] Cl<sup>-</sup>, [emim] Br<sup>-</sup>, [emim][BF<sub>4</sub>]<sup>-</sup> and [emim] PF<sub>6</sub><sup>-</sup> respectively in decreasing order of methanol ionic liquid interaction strength [99]. Although, interaction was also identified between methanol alkyl (C-H) and [emim] [BF<sub>4</sub>]<sup>-</sup> / [emim] [PF<sub>6</sub>]<sup>-</sup> anion, the C-H...F bond is much longer than O-H...F and play less important role for stabilization of methanol anion complexes [99].

Ethanol also shows the same properties in ionic liquids; the only difference ethanol has larger alkyl chain so the interaction with non-polar part of ionic liquid may increase. Wu et al (2009) studied the intermolecular interaction in ethanol and 1-allyl-3-methyl imidazolium chloride ([Amim] Cl) and [bmim][BF<sub>4</sub>] ionic liquids using Near-infrared spectroscopy. On addition of ethanol on mixture of [Amim] Cl and water it prefer to compete with water by interacting with imidazolium C<sub>2</sub>-H rather than C<sub>4,5</sub>-H groups through C<sub>2</sub>-H...O hydrogen bond formation, in addition to the strong hydrogen-bond interactions between the Cl<sup>-</sup> and the hydroxyl of the ethanol. On the contrary, while ethanol molecules do not interact specifically with any imidazolium C<sub>2</sub>-H or C<sub>4,5</sub>-H groups of [Bmim] [BF<sub>4</sub>] [100]. Substituting imidazolium C<sub>2</sub> hydrogen with methyl reduces the mutual solubility of alcohol and imidazolium based ionic liquids since it eliminates the possibility of interaction between the C<sub>2</sub> - H alcohol through hydrogen bonding [23]. Preferential interaction for C<sub>2</sub>-H proton and anions were also reported for ethylene glycol in 1-butyl-3-methylimidazolium tetrafluoroborate, 1-octyl-3-methylimidazolium tetrafluoroborate and 1-butyl-3-methylimidazolium octylsulfate ionic liquids [101].

### B. Dipolar Solutes

Dipolar solutes interact with the charged head groups of the ions and nonpolar domains. They orient themselves at the interface between the polar and non-polar regions of the ionic liquids [48]. This makes them excellent solvent for many ionic liquids. Acetone, acetonitrile, and small halogenated hydrocarbons are some of the solutes in these categories. Acetone and acetonitrile are soluble at all compositions in [bmim] [PF<sub>6</sub>] whereas the solubility of hexane and water is 0.11 and 0.29 mole fraction at 330 K [102, 103].

#### Acetone

The NMR experiment and *ab initio* calculations on acetone and [C<sub>4</sub>mim][PF<sub>6</sub>], [C<sub>6</sub>mim][PF<sub>6</sub>], [C<sub>8</sub>mim][PF<sub>6</sub>] and [C<sub>6</sub>mim][BF<sub>4</sub>] indicated hydrogen bonds between the ring protons, alkyl chain of the ionic liquids and the carbonyl oxygen of the acetone molecules [104]. The result also shows the strength of the hydrogen bond is influenced by the types of anions and the length of alkyl chain on the imidazolium ring of cations.

#### N, N-dimethylformamide (DMF)

DMF is apolar solvent which is characterised by lack of hydrogen bond, with high dipole moment and dielectric constant and good donor acceptor properties. Attri et al.

(2010) measured the excess properties of ionic liquids and N, N-dimethylformamide (DMF) with the intention to draw molecular level information (solute-solvent interaction) from the microscopic properties. From the negative excess molar volume they proposed strong hydrogen bond formation between DMF oxygen and imidazolium alkyl chain and DMF alkyl chain with anions [105]. The same group studied the effect of temperature on the molecular interaction between ionic liquids and DMF [106]. The result shows at low ionic liquids concentration the salute - solvent interaction increases with temperature. The Raman spectra analyses on binary mixtures of DMF and 1-alkyl-3-methylimidazolium bromide ([C<sub>n</sub>mim] Br) with different alkyl chain (n = 2, 4, 6, 8, 10) shows different alkyl chain leads to different extents of the uncoupling of adjacent DMF molecules. The C = O group of DMF has high dielectric dipole moment and form considerable interaction with adjacent molecules in the solution. The Raman band assigned to this group  $\nu(\text{C} = \text{O})$  mode in N, N-dimethylformamide shifted to different extent for different alkyl chain ionic liquids.

#### Dimethyl sulfoxide

Zang et al. (2009) investigated the properties of the mixtures of deuterated dimethyl sulfoxide (DMSO-*d*6) and 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF<sub>4</sub>]) by IR and quantum chemical calculations. They found that hydrogen bonds formed between imidazolium C<sub>2</sub>-H and oxygen of DMSO than anion-DMSO alkyl chain hydrogens. In addition, the interaction between oxygen of DMSO and C<sub>4</sub>-H/ C<sub>5</sub>-H has insignificant importance in ionic liquid-DMSO interaction. [107]. The intermolecular interactions of DMSO ionic liquids were also analyzed using the measured the excess properties [108, 109].

#### Acetonitrile

Acetonitrile interacts with the polar and non-polar domain of ionic liquids at different proportions [84]. The simulation work by Lopes and coworkers [86] shows both acetonitrile and methanol interacts strongly both anions. The difference between methanol and acetonitrile are the anion - methanol interaction is stronger than that of anion - acetonitrile and C<sub>2</sub>-H-acetonitrile interaction is conversely stronger for acetonitrile than that of methanol [86]. The molecular dynamics of acetonitrile and [bmim][BF<sub>4</sub>] mixture shows interaction between nitrogen of CH<sub>3</sub>CN and imidazolium ring hydrogens [110].

### C. Non polar solutes

The nonpolar molecules such as alkanes tend to reside in the nonpolar domains because they are excluded from the ionic network because of the cohesive energy of the charged groups [84]. The simulation work by Pádua et al. [84] shows a strong peak radial distribution function appears between the methyl groups of n-hexane and end carbon alkyl side chain of cation, and very weak correlation observed between the alkane and both cation head group and anions.

Many aromatics are remarkably soluble in, but rarely completely miscible with ionic liquids [111]. It was reported



that benzene and other aromatics are quite miscible with  $[C_n\text{mim}][\text{NTf}_2]$  for alkyl chain lengths,  $n$ , lower than 10 and become completely soluble at room temperature for  $n > 10$  [111]. Shiflett and co-workers studied the phase behaviour and solute-solvent interaction of halogenated [59, 72, 112] and alkyl substituted benzene [113] in  $[\text{emim}][\text{Tf}_2\text{N}]$ . The result shows that the polarity and the molecular size of substituted benzene played an important role in determining the solubility in the ionic liquids; smaller size and higher polarity molecules lead to higher solubility.

Shiflett and Yokozeki [59] found the general trend between the magnitude of the dipole moment of the solutes and the solubility in ionic liquids. It was found that solutes with high dipole moment such as 1, 2-difluorobenzene and 1, 2, 3, 4-tetrafluorobenzene are completely soluble in  $[\text{emim}][\text{Tf}_2\text{N}]$ , whereas lower fluorinated benzene such as 1,2,4-trifluorobenzene is partially soluble. The solubility of dimethylbenzene follows the order of *o*-xylene < *m*-xylene < *p*-xylene while nonalkyl-substituted benzenes containing functional groups (-NH<sub>2</sub>, -NO<sub>2</sub>, -OH, and -CHO) are completely soluble in  $[\text{emim}][\text{Tf}_2\text{N}]$  [113].

In some cases the solute molecular size plays an important role in determining the degree of solubility. The aromatic content of the ionic liquids phase is higher for benzene, 0.66 [114] for  $[\text{bmim}][\text{PF}_6]$  and decreases following the order benzene > toluene > xylenes [115]. This is consistent with the solubility of benzene, toluene and  $\alpha$ -methyl styrene in  $[C_n\text{mim}][\text{NTf}_2]$  ( $n = 2, 4, 6, 8, 10$ ) which decreases as benzene > toluene >  $\alpha$ -methylstyrene [111]. Holbrey et al. (2003) observed a similar trend in their study of clathrate formation in mixtures of ionic liquids with aromatics. Higher aromatic contents (0.77 for benzene and 0.66 for hexafluorobenzene) in ionic liquid phases were reported for  $[\text{emim}][\text{Tf}_2\text{N}]$  [72]. Shiflett et al. (2009) found the solubility of monohalogenated benzene in  $[\text{emim}][\text{Tf}_2\text{N}]$  mainly depends on molecular size, thus, the solubility of monohalogenated benzene decreases following the order chlorobenzene > bromobenzene > iodobenzene. For alkyl substituted benzene the solubility in  $[\text{emim}][\text{Tf}_2\text{N}]$  decreases with increasing alkyl chain in the order of benzene < methylbenzene < ethylbenzene < propylbenzene [113].

The molecular dynamic calculations [116] indicates spontaneous formation localized cavities due to small angular rearrangements of the anion where molecules can fit above and below the imidazolium ring. As the solute molecular size increases, less solute can fill limited cavities created by angular rearrangements of the  $[\text{Tf}_2\text{N}]$  anion resulting in less solubility. The smaller size allows more solutes in cavities above and below imidazolium ring [112] forming well organized phases viz. clathrate-type structures in the liquid phase, a phenomenon originally recognized by Surette et al. (1996). Localized cage-structures are formed between on separating the separate cation-anion packing interactions by to interactions between aromatic molecules and ionic liquid ions. The liquid aromatic-ionic liquid clathrates have low viscosity (relative to the initial neat ionic liquids), air- and water-stable, immiscible with excess

aromatic solvents, and non-stoichiometric, but reproducible, compositions [115].

#### IV. CONCLUSIONS AND FUTUR WORK

Both experimental and theoretical techniques provide an increasing insight into the nanoscale phase segregation of imidazolium based ionic liquids. The nanostructural organization can be regarded as the logical step in understanding the microscopic structure of ionic liquids: because these liquids organize its high-charge density portions into local structures that obey electro neutrality and maximize Coulomb interactions. The low-charge density parts of the ions that do not participate in Coulomb interactions will tend to be segregated elsewhere through van der Waals interaction. The interplay between the Coulomb and van der Waals interactions leads to the formation of medium-range structures composed of a high-charge density and cohesive network permeated by low-charge density regions. The interaction between anions and cations produces ionic organized networks with the charge ordering degree determined mainly by the nature of cation and anion and the presence of sufficiently long alkyl groups on imidazolium cations. Many experimental and theoretical works provide understanding on cation- anion interaction through the interplay of hydrogen bond and Coulombic forces. However, the relative importance of hydrogen bond and Coulombic force in cation-anion interaction is still under discussion.

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

Finally, it should be noted that the present experimental and theoretical works on microstructural and solvation studies concentrated on mainly ionic liquids containing  $[\text{BF}_4]$ ,  $[\text{PF}_6]$  and  $[\text{Nf}_2\text{T}]$  ions. Due to the highly variable behavior of ionic liquids with different anions and cation alkyl chain containing functional groups, it may questioned that whether the present knowledge on microstructural organization and solvation reflects a generic future of all imidazolium based ionic liquids. Further studies on ionic liquids varieties cations and anions may help to elucidate the various mechanism of solute-solvent interaction between ionic liquids and solutes.

#### V. SCOPE AND LIMITATIONS OF THEIR RESEARCH WORK

This review was intended to analyse the structure of common imidazolium based ionic liquids and their solute-solvent interactions with common solutes. The nature of ionic liquids varies with the type of the cations, anions the presence and type of functional groups incorporated on cations; such as nitrile, allyl, and hydroxyl on the cations. Therefore, the observations and conclusion made from this paper may not be

applied to other types of ionic liquids based on pyridinium, phosphonium, and ammonium cations.

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