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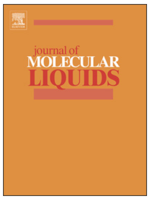

Short Communication

Theoretical evaluation on solubility of synthesized task specific ionic liquids in water

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ABSTRACT

Task specific ionic liquids (TSILs) are synthesized and utilized for extraction of different metal atoms from their complexes. Since physico-chemical properties of ionic liquids (ILs) are modified by water (H_2O) molecules, less hydrophilic ILs are suitable for the liquid–liquid metal extraction process. Recently, we have synthesized amino acid functionalized imidazolium based TSILs for extraction of rare earth metals. The synthesized ILs have a common functionalized cation $[C_{20}H_{28}N_3O_3]^+$ and different anions namely, bromide-$[Br]^-$ and bis(trifluoromethylsulfonyl)imide-$[NTF_2]^-$. In this study, various first principles (Hatree–Fock and density functional theory) and molecular mechanics calculations are done to understand intermolecular interactions between H_2O and the synthesized TSILs. The results of gas phase cluster calculations project the difference in solubility of these two TSILs in H_2O.

1. Introduction

Ionic liquids are a class of organic salts with low melting temperature below 100 °C and they are composed of cations and anions. Most of the cations are imidazolium, pyridinium, phosphonium or ammonium derivatives and the anions are typically halides such as F^-, Cl^- or Br^-, large fluorinated organic compounds and so on. Scientific reports on ionic liquids (ILs) have made their debut more than a century ago. However, intensive research has begun from the end of twentieth century when second generation of ILs has been created. Since then many ILs are being synthesized and characterized by both experimental and theoretical methods worldwide [1–23]. The relatively lower vapor pressure of ILs allows using them without causing damages to the environment. Hence, ILs are considered to be perspective compounds for green chemistry in many applications such as electrochemistry [1,2], for chemical synthesis as solvents [1,3], for catalysis [1,3], for rare elements extraction [1,4,5], for energy storage applications [1], for organic compound and gases separation [6] and so on. The properties of ILs are dependent on the size and nature of both the cations and anions. For example, symmetric ILs are less viscous than asymmetric ones [7]. Other attractive property of some ILs is their high stability up to several hundred degrees that allows them to lead chemical reactions at very high temperatures. In recent years, apart from the conventional ILs, a new kind of designer solvents called task specific ionic liquids (TSILs) are synthesized and utilized for specific applications where conventional ILs fail to accomplish the required tasks. ILs are modified by covalently functionalizing them with different chemical groups to obtain TSILs to achieve the targeted application [8,9].

Since ILs are easily affected by moisture, the goals of many scientific investigations on ILs are mainly focused on construction of hydrophobic ILs with minimal viscosity and with the pre-determined useful properties. Water (H_2O) is recognized as the usual impurity in ILs such that it can significantly influence on the structure and transport properties of ILs [10–13]. Also, the presence of trace of water in ILs changes their physicochemical properties significantly [14] and may also affect reaction rates and selectivity [15]. It is reported that the hydrophobicity depends on the anions and length of the alkyl chains in cations [16]. In particular, ILs with hydrophilic anions such as halides (i.e. F^-, Cl^- and Br^-) are known to be miscible with water [17] and ILs with hydrophobic anion, such as NTF_2^- and PF_6^- are immiscible with water. The H_2O molecules interact strongly with anions of ILs via ion–dipole interactions, which can be accompanied by the formation of hydration shells

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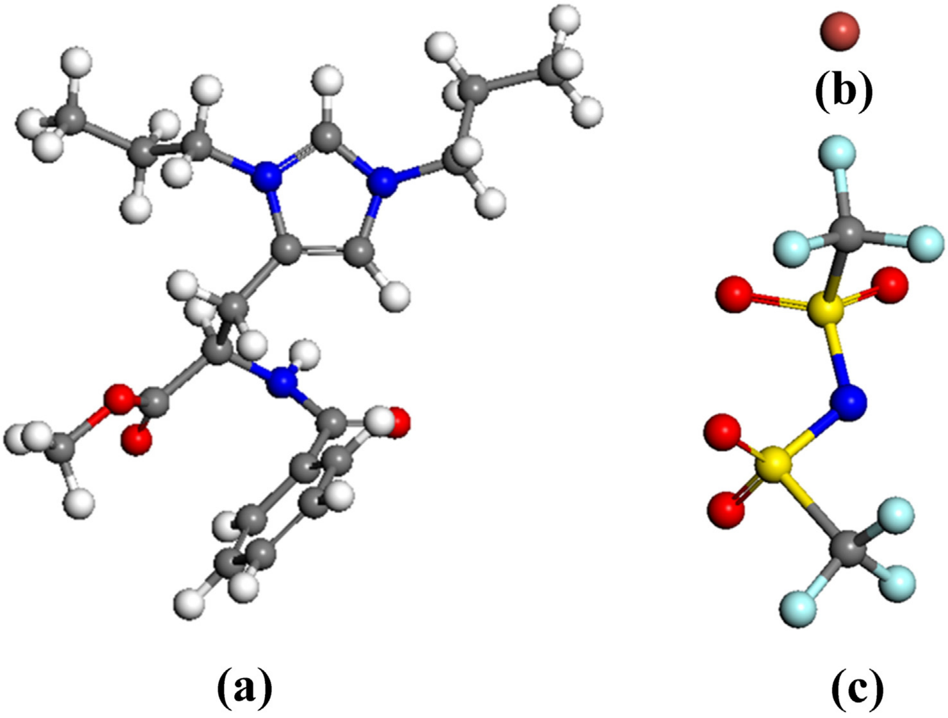

Fig. 1. Structures of (a) L-histidine derived imidazolium cation, (b) $[Br]^-$ anion and (c) $[NTF_2]^-$ anion (spheres with white, gray, blue, red, brown, yellow and light blue represent hydrogen, carbon, nitrogen, oxygen, bromine, sulfur and fluorine atoms respectively). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

around hydrophilic ions resulting in a change in the physical properties [18] such as diffusion of ions, viscosity, surface tension and so on.

Several computational techniques have been used, including classical molecular mechanics and molecular dynamics (MD), ab-initio molecular dynamics (AIMD), Monte Carlo (MC) simulations and quantum chemical calculations to study the influence of water on ILs [18–21]. The quantum chemical calculations, unlike the other computational techniques are the best choice for investigating specific interactions between the component ions of ILs and water. Analysis of the hydrated states of the ions would give better understanding of the physicochemical properties of the IL/water mixtures.

In 2005, L-histidine (amino acid) derived imidazolium based TSILs have been synthesized and utilized as ligands for palladium and rhodium salts [24]. Our experimentalists have focused on such kind of complexation ability of TSILs for liquid–liquid extraction of rare earth metals. Hence, with respect to Ref. [24] two different L-histidine derived imidazolium based TSILs are synthesized with two different anions namely, $[Br]^-$ and bis(trifluoromethylsulfonyl) imide $[NTF_2]^-$ (Fig. 1) respectively. The TSILs namely $[C_{20}H_{28}N_3O_3]^+[Br]^-$ and $[C_{20}H_{28}N_3O_3]^+[NTF_2]^-$ are denoted as IBr and ITF_2 respectively in the rest of the manuscript. Experimentally, it has been observed that IBr is more soluble than ITF_2. Since metallurgists recommend liquid–liquid (biphasic) phase metal extraction method, a more hydrophobic IL is preferred [8,22]. In this study, the influence of water on structure and electronic properties of these TSILs are examined by ab-initio quantum chemical [25] and molecular mechanics calculations [26,27] with a viewpoint to understand the difference in solubility of water in these two TSILs.

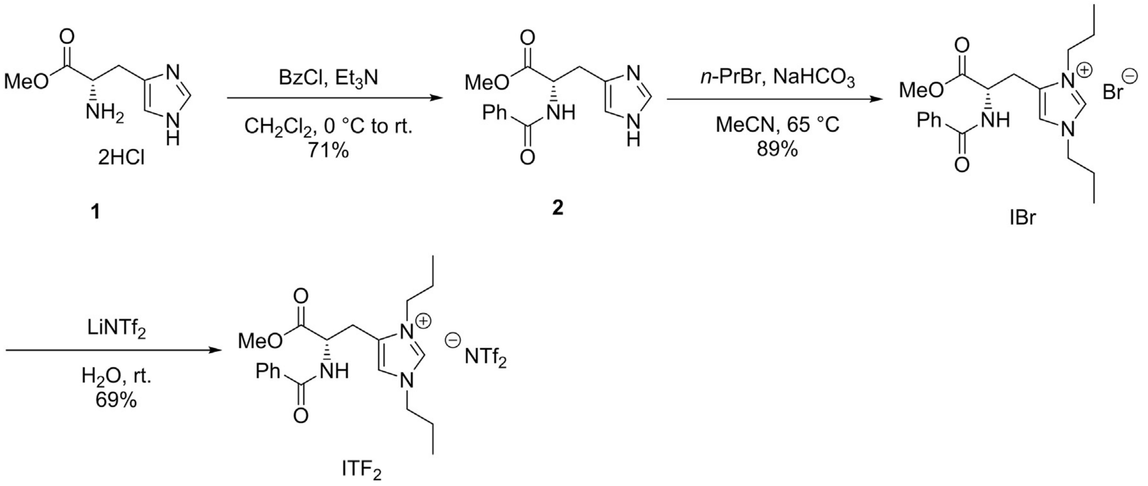

Fig. 2. Synthesis route of IBr and ITF_2.

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Table 1
The energies of interaction between water molecules as well as between ILs and water molecule within different approaches, kJ/mol.

Method/basis set	IBr–H_2O	ITF_2–H_2O	$H_2O + H_2O$
HF/6-31++G	−45.95	−25.67	−20.11
HF/TZVP	−45.78	−24.93	−20.11
B3LYP/TZVP	−59.22	−23.17	−25.07
B97D/TZVP	−76.19	−57.24	−24.41
WB97xD/TZVP	−77.41	−52.23	−26.28
Experiment			−22.60 ± 2.90

2. Experimental and computational details

2.1. Synthesis of IBr and ITF_2

Commercially available reagents of synthetic grade are purchased and used without purification. Super dehydrated solvents are purchased from WAKO. The synthesis of TSILs has been carried out as shown in Fig. 2. All the chemical reactions have been carried out under argon atmosphere. ^{1}H NMR spectra have been recorded on an AVANCE III 400 spectrometer and are obtained at 400 MHz with reference to tetramethylsilane singlet at 0.00 ppm. The recorded NMR data of all the synthesized compounds are given in the supplementary data.

2.1.1. Synthesis of N-benzoyl-L-histidine methyl ester (2)

Benzoyl chloride (0.50 mL, 4.34 mmol, 1.05 eq.) is added dropwise to a solution of L-histidine methyl ester dihydrochloride (**1**, 1.00 g, 4.13 mmol, 1.0 eq.) and triethylamine (2.9 mL, 20.7 mmol, 5.0 eq.) in CH_2Cl_2 (80 mL) at 0 °C. After the addition of benzoyl chloride, the mixture is warmed to room temperature and stirred for 1 day. The reaction is quenched with the addition of saturated $NaHCO_3$ aqueous solution. The organic layer is separated and washed with water and brine, followed by drying over anhydrous $MgSO_4$. The solid is removed by filtration, and the filtrate is evaporated. The crude residue is purified by flash column chromatography ($CHCl_3$/MeOH = 100/1–10/1). Compound (**2**) is obtained in 71% yield (0.81 g).

2.1.2. Synthesis of IBr

n-Propyl bromide (6.4 mL, 70.5 mmol, 25.0 eq.) is added dropwise to a solution of compound (**2**) (0.77 g, 2.82 mmol, 1.0 eq.) and $NaHCO_3$ (0.95 g, 11.3 mmol, 4.0 eq.) in CH_3CN (30 mL). After the addition of *n*-propyl bromide, the mixture is heated to 65 °C and stirred overnight. The solid is removed by filtration, and the solvent is removed in vacuo. The crude residue is dissolved in water, and then the solution is washed with $CHCl_3$. The aqueous phase is evaporated, and the residue is dried in vacuo. The product IBr is obtained in 89% yield (1.1 g).

2.1.3. Synthesis of ITF_2

A portion of $LiNTf_2$ (2.26 g, 7.87 mmol, 2.15 eq.) is added to the solution of IBr (1.60 g, 3.65 mmol) in H_2O (18 mL). After the mixture is stirred for 2 h at room temperature, the product is extracted with CH_2Cl_2. The organic layer is washed with water and dried over anhydrous $MgSO_4$. The solid was removed by filtration, and the solvent is removed in vacuo. The product ITF_2 is obtained as color-less oil in 69% yield (1.6 g).

2.2. Computational methods

Both the first-principles calculations and molecular mechanics have been performed in order to find the most stable configurations of different fragments as well as the interaction energies between water molecules and the two TSILs. The first principle calculations are performed using the Gaussian 09 program [22] to obtain electronic structure of the TSILs and charge redistribution in the presence of water (H_2O)

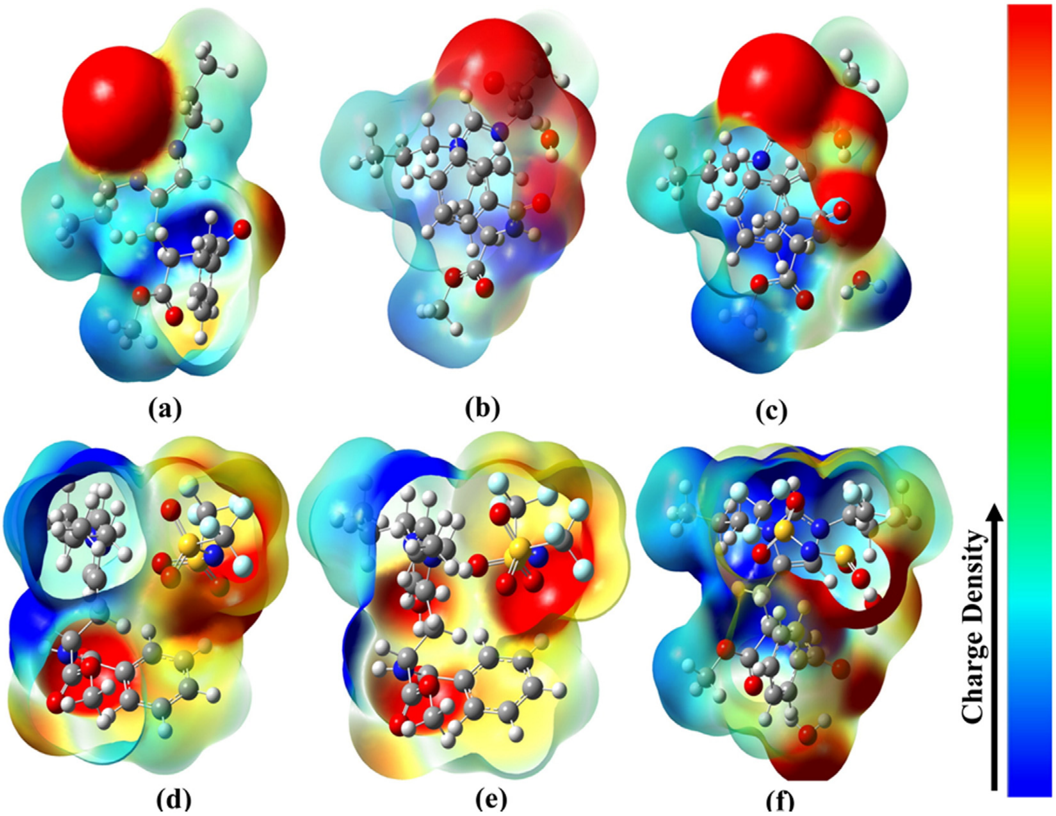

Fig. 3. Charge distribution in (a) IBr, (b) IBr–H_2O, (c) IBr–$2H_2O$, (d) ITF_2, (e) ITF_2–H_2O, and (f) ITF_2–$2H_2O$ (spheres with white, gray, blue, red, brown, yellow and light blue represent hydrogen, carbon, nitrogen, oxygen, bromine, sulfur and fluorine atoms respectively). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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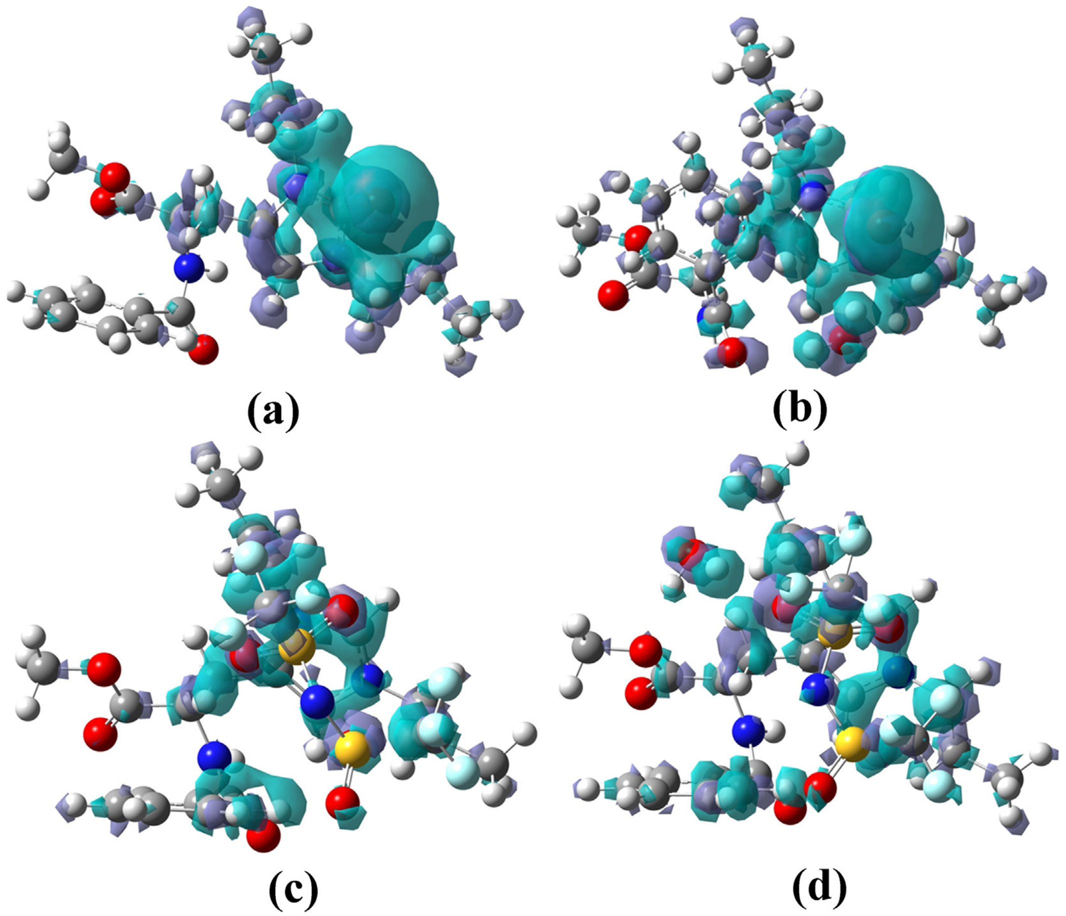

Fig. 4. Difference in electron density between cation and anion of ILs in the presence of water molecules. (a) IBr, (b) IBr–H_2O, (c) ITF_2 and (d) ITF_2–H_2O (spheres with white, gray, blue, red, brown, yellow and light blue represent hydrogen, carbon, nitrogen, oxygen, bromine, sulfur and fluorine atoms respectively).

molecules on them. Also, the Gaussian methods are applied for evaluating the cluster geometries and TSIL–H_2O interactions. In the Gaussian cluster calculations, several computational approaches (including Hatree–Fock (HF) and density functional theory (DFT) methods) are applied initially to find the best method for calculation of energy and partial charges in the considered systems. As the most convenient DFT method for calculations, B97D within TZVP basis set is chosen in order to include dispersive interactions. Counterpoise correction is used within calculations for pure ILs and also for ILs with H_2O molecules complexes. Initially, the optimization of pure ILs and ILs with one and two H_2O molecules is done. After equilibration of structures, energies and the Mulliken charges on atoms of all the systems have been compared. Molecular mechanics simulations are performed using MMFF94 potential field to find the distribution

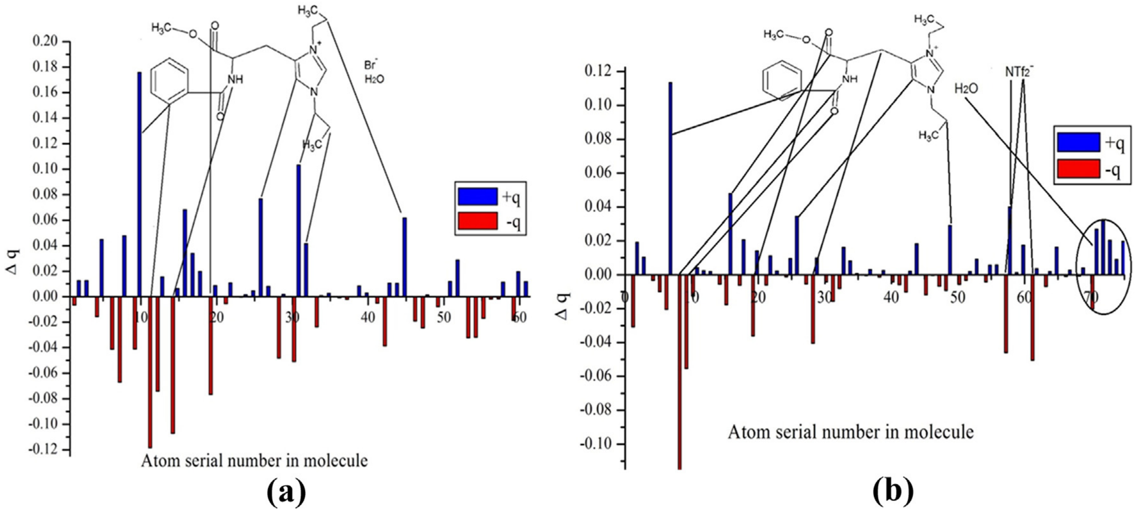

Fig. 5. Change of charge distribution in (a) IBr and (b) ITF_2 in the presence of water molecules.

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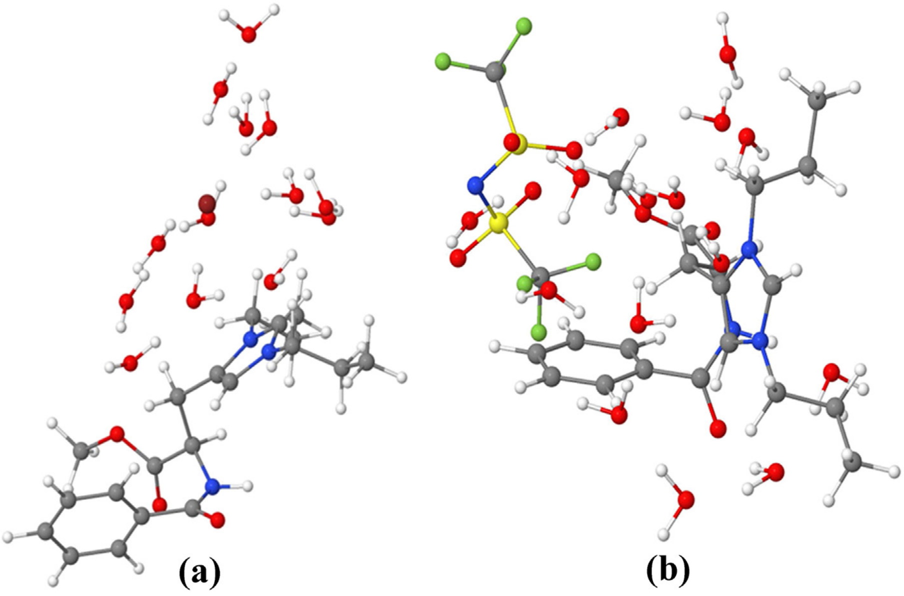

Fig. 6. Molecular structures of (a) $[C_{20}H_{28}N_3O_3]^+[Br]^- + 10H_2O$ and (b) $[C_{20}H_{28}N_3O_3]^+[NTF_2]^- + 10H_2O$ (spheres with white, gray, blue, red, brown, yellow and green represent hydrogen, carbon, nitrogen, oxygen, bromine, sulfur and fluorine atoms respectively). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

of ten H_2O molecules around TSILs using the Avogadro program [23, 24]. After that, the final structures of the two hydrated TSILs are compared.

3. Results and discussions

All the methods have shown (Table 1) that the interaction energy of water with IBr is higher than that of ITF_2–H_2O interaction. The higher energy refers to stronger hydrogen bonding for $[Br]^-$ anion (Fig. S1). The B97D/TZVP method is found to have a good agreement with experimental data for the description of the hydrogen bonding system.

Redistribution of charge clouds on cation and anion molecules has been observed in the vicinity of water molecules (Fig. 3). The presence of water leads to significant charge redistribution (Fig. 4) on the cation in both IBr and ITF_2. Also, we have registered the large changes of Mulliken charges on IL atoms that lie close to the water molecules (Figs. 5, S1 and S2). In addition to the anion and the imidazole ring, we can observe that the charge on the functional group of the cation is largely perturbed in the case of IBr than ITF_2 as indicated in atomic structure plots (Figs. S1 and S2). The maximum changes are observed on the aromatic rings (in cation). The accumulation of negative charge on oxygen (O) atom of H_3COO fragment has resulted in hydrogen bond formation with water molecules. Relatively, a larger charge on O is found in the case of the $[Br]^-$ anion (−0.075) as compared with that (−0.035) for the $[NTF_2]^-$ anion. This indicates the stronger hydrogen bonding interaction for $[C_{20}H_{28}N_3O_3]^+$ $[Br]^-$ (Table 1) and hence the larger charge perturbation.

Partial charge analysis is done in unhydrated and hydrated IL systems (Table S1). In IBr–H_2O, the partial charge of −0.0001e indicates that the water molecule has interacted readily with the system such that we can observe such a negligible negative charge on it. In this case, both anion and cation have equally taken part in the interaction. On adsorption of $2H_2O$, the values of partial charges on each water molecule has become slightly positive (0.01 e/H_2O) indicating the charge transfer from H_2O to IBr that has resulted in a more negative charge on the $[Br]^-$ anion as indicated in Table S1. Due to the presence of large anion along with electron withdrawing atoms like F, O and N, the ITF_2 has withdrawn electrons from water molecules. We can observe that the charge on the very heart of the cation namely, the imidazole ring decreases on adsorption of H_2O and then increases on adsorption of $2H_2O$. The same trend is observed in anion too.

In IBr–H_2O, the change in charge distribution is 27% and that in IBr–$2H_2O$ is 30% when compared with the unhydrated IBr. In ITF_2–H_2O, the change in charge distribution is 12% and that in ITF_2–$2H_2O$ is 17% with respect to the unhydrated ITF_2. Hence, one can conclude that the presence of water molecules changes the environment of IBr more when compared to ITF_2.

In IBr, we can observe that the intermolecular distance between cation and $[Br]^-$ is increasing (Table S2). This can be understood in such a way that though the imidazole ring is more positive, the overall negative charge clouds on the cation (Table S2) and anion produces a repulsive effect such that $[Br]^-$ goes away from the cation and its attracted to the positively charged water molecule. This point can be verified with reference to the charge density plots of respective systems (Fig. 2). The inverse effect of IBr is observed in ITF_2, when we have measured the distance between the O62 atom of anion and C32 in the imidazole ring of the cation (Fig. S2, Table S3). However, the interatomic distance is found to be increased with respect to the O61 atom. Therefore, some of the atoms in the large anion, $[NTF_2]^-$ that are not close to water molecules have been attracted towards the cation. In such a way, the distribution of water molecules increases the electrostatic interaction between cation and anion than between water molecules and the anion, $[NTF_2]^-$ (hence, the parallel reduction of partial charge on both cation and anion upon hydration). This is essentially due to the large size and high charge of $[NTF_2]^-$ when compared to $[Br]^-$. Overall, one can understand that H_2O molecules strongly interact with IBr when compared to ITF_2. In both IBr and ITF_2 the hydrogen (H) bonds between the donors (D) and acceptors (A) are in the range of 2.0–2.3 Å (Figs. S1 and S2) and D···H – A bond angles are more than 125°. This is in line with the hydrogen bonding criterion set in the work of Chang et al. [23] on ILs and H_2O mixture.

We have performed molecular mechanics with more H_2O molecules in IBr and ITF_2. It has been found that the H_2O molecules have the tendency to surround the $[Br]^-$ anion to form a hydrogen bonding network (solvation shell). In this case, the $[Br]^-$ anion occurs to be isolated from the positively charged imidazole center that leads to full hydration of IL (Fig. 6(a)). The $[NTF_2]^-$ anion is not fully surrounded by water molecules. In this case, the water molecules have a tendency to form hydrogen bonds with the oxygen atoms of the sulfonyl groups (Fig. 6(b)). The

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negatively charged central nitrogen atom of anion still interacts with the positively charged imidazole ring. Since the hydration process is more complicated in ITF_2, it is slightly soluble. The less solubility of ITF_2 reflects its hydrophobic nature. At this juncture, we emphasize that the charge on the functional group in IBr is largely redistributed than in ITF_2. Thus, one can understand that irrespective of the extra functional group attached to the imidazolium cation, the nature of the anions plays a significant role in the solubility of imidazolium TSILs. Overall, one can understand that small inorganic anions (like $[Br]^-$) have a strong tendency to form hydrogen bonded network with water molecules around them thereby increasing the solubility of ILs. On the other hand, organic anions (like $[NTF_2]^-$) also form hydrogen bonded network with water molecules, but due to initial charge distribution between several atoms, not concentrated on one atom, this network is redistributed and anion–cation interaction is still high. These results are in line with charge density, partial charge and intermolecular bond length analyses.

4. Conclusions

In summary, as a support to the experimental results, the first principles calculations have been performed in order to find the most stable configurations as well as interaction energies between H_2O molecules and the synthesized TSILs followed by molecular mechanics. This integrated theoretical study has projected the solubility mechanism of $[C_{20}H_{28}N_3O_3]^+[NTF_2]^-$ and $[C_{20}H_{28}N_3O_3]^+$ $[Br]^-$ in water. The charge redistribution on cation and anion molecules has been observed in the presence of water. It is found that the water molecules surround the $[Br]^-$ anion through hydrogen bonding network that leads to the full hydration of IL. The $[NTF_2]^-$ anion is not fully surrounded by water molecules where the water molecules have a tendency to form hydrogen bonds with oxygen atoms of the sulfonyl groups. In other words, we can say that the charge density on $[NTF_2]^-$ is more delocalized than $[Br]^-$ and hence the former is more hydrophobic. The analysis of both the systems strongly shows that the hydration of the synthesized imidazolium based TSILs is determined by the chemical coordination nature of the anions with the water molecules.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.molliq.2014.10.028.

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