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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.

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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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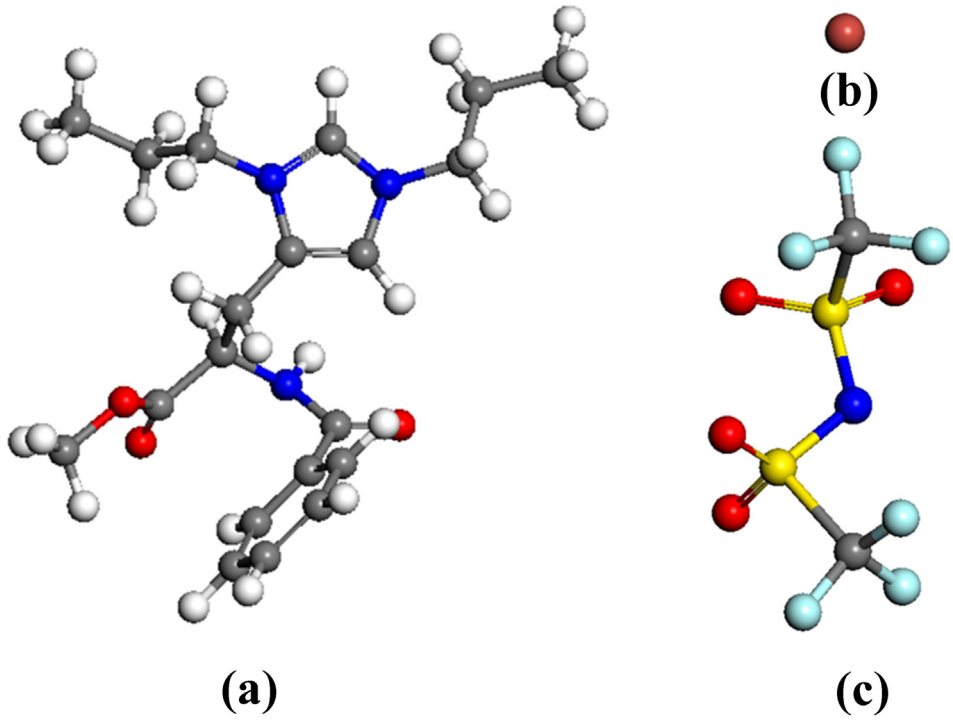

Fig. 1. Structures of (a) L-histidine derived imidazolium cation, (b) $[Br]^-$ anion and (c) $[NTF_2]^-$ anion (spheres with white, gray, blue, red, brown, yellow and light blue represent hydrogen, carbon, nitrogen, oxygen, bromine, sulfur and fluorine atoms respectively). (For interpretation of the 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.

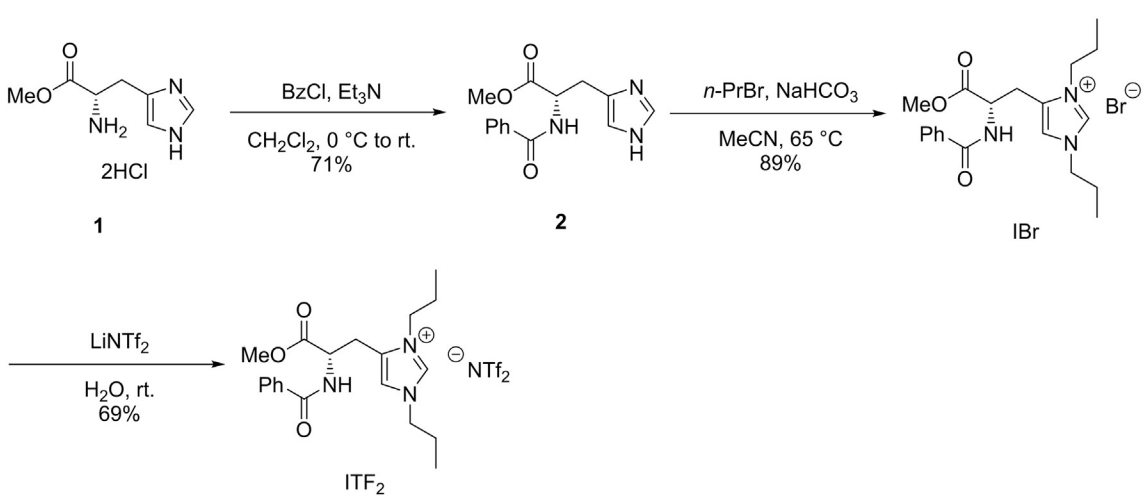

Fig. 2. Synthesis route of IBr and ITF_2.

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