A NEW STRATEGY TOWARD SYNTHESIS OF ROOM-TEMPERATURE IONIC LIQUIDS BASED ON COMPLEXATION REACTIONS OF CATIONS

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ABSTRACT

A new strategy for synthesizing room-temperature ionic liquids based on complexation reactions of cations has been described. Several new classes of ionic liquids can be synthesized via this methodology. These ionic liquids have a unique structural feature, which may highlight the applications in the areas such as separation and catalysis.

INTRODUCTION

Room-temperature ionic liquids (RTILs) have been defined as salts that melt below room temperature (1-2). The most commonly studied classes of RTILs usually include a heterocyclic cation, such as a dialkyl imidazolium (3) or an N-alkylpyridinium ion. These organic cations, which are relatively large and asymmetric compared with simple inorganic cations, account for the low melting points of the salts (1-2). A variety of anions can be utilized to form RTILs, including BF₄⁻, PF₆⁻, AlCl₄⁻, Al₂Cl₇⁻ or other complex anions. Such ionic systems consisting of salts that are liquid at ambient temperatures can act as solvents for a broad spectrum of chemical species (5-13). These ionic liquids are attracting increased attention worldwide because they promise significant environmental benefits (1). Unlike the conventional solvents currently in use, they are nonvolatile and therefore do not emit noxious vapors, which can contribute to air pollution and health problems for process workers. The very unusual intrinsic properties of these melts are that they consist only of ions and that they can be made hydrophobic (14-15)! The applications of ionic liquids as replacement solvents for various catalytic reactions have been extensively explored (9). Several reviews and monographs have recently appeared (2, 5-6, 9-11), providing general overviews of the subject. The use of the ionic liquids for the membrane-based separation of CO₂ (16-17), sensing volatile organic vapors (18), and synthesizing novel materials has also been investigated (19-20). The applications of ionic liquids to carry out separations of mixtures of organic molecules and inorganic ions have been recently reported (21-26). Here, we report a methodology for synthesizing unique RTIL cations through the complexation reactions of metal ions.

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RESULTS AND DISCUSSION

The conventional formation of ionic liquids can be regarded as the complexation reactions of simple anionic species by neutral compounds. The most classic example is the formation of the ionic liquids made of 1-ethyl-3-methylimidazolium chloride (EMI⁺Cl⁻) and aluminum chloride (AlCl₃). When two solids are mixed stoichiometrically, the complexation of Cl⁻ by AlCl₃ gives rise to a RTIL composed of EMI⁺AlCl₄⁻ [eq. 1]. The reaction is thermodynamically favored, resulting in the release of heat. Similarly, the formation of EMI⁺BF₄⁻ can be hypothetically conceived through a reaction of EMI⁺F⁻ and BF₃. Our strategy for synthesizing ionic liquids is through the complexation reactions of metal cations by neutral ligands. The systems we chose to demonstrate the basic principle of our strategy consist of neutral asymmetric crown ethers and metal organic salts.

\[
\text{AlCl}_3 + \text{EMI}⁺\text{Cl}⁻ \rightleftharpoons \text{EMI}⁺\text{AlCl}_4⁻ \quad \text{eq. (1)}
\]

Crown ethers are well known for their strong complexation of metal ions to form cationic complexes (27). This very property forms the basis of many applications of crown ethers in solvent extractions and sensing (27). The application reported here is also based on this fundamental complexation reaction, which is the cationic equivalent of the complexation reaction of Cl⁻ and AlCl₃. The crown ether we used is cyclohexo-15-crown-5 (Parish, Inc.), which is very asymmetric and known to complex strongly with Li⁺. N-lithiotrifluoromethanesulfonimide [Li⁺ TFSN⁻] was used to provide cations to be complexed by the crown ether and conjugate anions. When cyclohexo-15-crown-5 and Li⁺ TFSN⁻ were mixed, a release of heat was observed, resulting in a clear and viscous liquid. This observation is reminiscent of the EMI⁺Cl⁻-AlCl₃ reaction. The basic reaction is given by eq. 2. The conductivity of this new ionic liquid was determined to be 107.8 μS/cm at 24EC.

\[
\text{Li}⁺ \text{TFSN}⁻ \rightleftharpoons \text{Li}⁺ \text{TFSN}⁻ \quad \text{eq. (2)}
\]

This new ionic liquid is also with negligible vapor pressure at ambient conditions. No reduction of mass has been observed under vacuum rotary evaporation at 100EC. The miscibilities of this ionic liquid with a number of organic solvents (e.g., acetonitrile, acetone) are very good. However, it is immiscible with aqueous solutions. Accordingly, it can be utilized as a potential new solvent for solvent extraction of ionic species (22-26). Our preliminary experiments indicated that this IL can undergo facile ion-exchange with metal ions (e.g. Cs⁺, Sr²⁺) in aqueous phase.

Figure 1 compares the Fourier transform infrared (FTIR) spectra of cyclohexo-15-crown-5 and the new RTILs in the characteristic region of C-H stretching vibrations. The shifts...
in C-H stretching vibrational frequencies are consistent with the complexation of the crown ether molecule by Li+. After contacting with water, no change was observed in the C-H region of the vibrational spectrum. This observation indicates that the new RTIL is water stable. The comparison of the Raman spectrum of cyclohexo-15-crown-5 with that of the new RTIL in the C-H stretching region is shown in Figure 2. Clearly, the Raman pattern in this region is considerably changed, supporting the complexation of the crown-ether molecules by lithium ions.

The thermal stability was investigated by thermal gravimetric analysis (TGA). Figure 3 shows the TGA curves for four ILs with different ratios of N-lithiotrifluoromethanesulphonimide and cyclohexo-15-crown-5 (from 1:1 to 2.2: 1). It is clear from Figure 3 that all four ILs are stable up to 250°C. The residue weigh above 400°C can be qualitatively correlated to the concentration of lithium ions.

Another neutral ligand system that can be used to synthesize new ionic liquids based on the complexation of small cations with neutral organic ligands is alkyl amines. It is well documented that many metal ions (e.g. Ag⁺, Cu²⁺, Zn²⁺, Ru²⁺/³⁺, Pd²⁺) can form stable charged coordination compounds with amine ligands. The stereochemistry of this class of coordination compounds is very diverse as shown in Figure 4. Our preliminary results showed that both Ag⁺ and Cu²⁺ can readily form RTILs with this new synthesis strategy.
Figure 2. Raman spectra of (a) pure cyclohexo-15-crown-5 and (b) RTIL prepared with the mole ratio of cyclohexo-15-crown-5 to LiTf$_2$N = 1:1 in C-H stretching region.

CONCLUSIONS

A new methodology for the formation of hydrophobic ionic liquids has been reported. The cations of the new RTILs consist of cationic coordination complexes, which are different from covalent organic cations used in the formation of the conventional RTILs. The hydrophobicity of the new RTILs is introduced by organic ligands and conjugate anions. The chemical properties of these new RTILs are expected to be drastically different from those of the conventional ionic liquids. The novel synthesis strategy highlights new opportunities in RTIL research.

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Figure 3. TGA curves for the new ionic liquids with increasing concentration of lithium salt.

R'-NH₂ → M⁺–NH₂–R''
Linear Coordination Cationic Complexes

Tetrahedral or Square Coordination Cationic Complexes

R⁺–NH₂ → M⁺–NH₂–R''

Octahedral Coordination Cationic Complexes

NH₂–R'''

Figure 4. Structural features of the cations in new ionic liquids made by the complexation reactions of neutral amine ligands with metal ions.
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