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Properties of protic ionic liquids composed of *N*-alkyl (= hexyl, octyl and 2-ethylhexyl) ethylenediaminum cations with trifluoromethanesulfonate and trifluoroacetate anion

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ABSTRACT

Protic ionic liquids (PILs) composed of *N*-alkyl (= hexyl, octyl and 2-ethylhexyl) ethylenediaminum cation with trifluoromethanesulfonate (TFS) or trifluoroacetate (TFA) anion such as HOct(TFA), HEtHex(TFA), HHex(TFS), HOct(TFS) and HEtHex (TFS) were newly synthesized and HHex(TFA) was synthesized according to the method from a literature. Among them, HHex(TFA), HEtHex(TFA) and HEtHex (TFS) are room temperature ionic liquids. The PILs with TFS exhibit more thermostable than the PILs with TFA and their decomposition temperatures are about 250 °C and 150 °C, respectively. The physical properties such as density, viscosity and electric conductivity of the PILs were studied in the temperature range of (293.15 to 353.15) K. Temperature dependence of the viscosity and the conductivity was discussed using the Arrhenius equation. The relationship between the molar conductivity and the fluidity was described on the basis of the Walden rule. The results show that the PILs with TFS have a larger ionic mobility compared to the PILs with TFA.

1. Introduction

Ionic liquid (IL) is a melt salt in which the ions are poorly interacting with each other and results in liquid below 100 °C or even at room temperature [1]. ILs are generally classified into the two major subclasses: aprotic ionic liquids (AILs) and protic ionic liquid (PILs). PILs are formed by proton transfer from a strong Brønsted acid (HA) to a Brønsted base (B) (eq 1) [2–4]. In this study, trifluoromethanesulfonic acid (HTFS, CF_3SO_3H) and trifluoroacetic acid (HTFA, CF_3COOH) are used as strong Brønsted acids, and then *N*-alkylethylenediamines (Hexylethylenediamine, Hex-en; Ethylhexylethylenediamine, EtHex-en; Octylethylenediamine, Oct-en) are as Brønsted bases.

$$B + HA \rightarrow HB^+ + A^- \quad (1)$$

PILs have been found to be a suitable electrolyte in a fuel cells due to the presence of the active proton [3–7] and to be useful as solvents for a number of acid catalyzed reactions including a Diels-Alder reaction [8,9] because they behave as a Brønsted acid. PILs are generally more hydrophilic and dissolve metal salts to a larger extent than AILs [3,4,10]. Especially, alkylethylenediamines have a chelate amine and have larger affinity for Lewis acids compared to alkylamines [11–13]. Therefore, in comparing with the PILs composed of *N*-alkylamines, PILs composed of alkylethylenediamines are expected to have wider applications in the studies of fuel cells, the extraction of metal ions [11–13] and the absorption of CO_2 [14,15]. The fairly low melting point, greater thermal stability, higher fluidity and good electric conductivity are the important parameters that are relevant to their possible applications [16,17].

The physicochemical properties such as melting point, density, dynamic viscosity and electric conductivity of HHex (TFA) [11,18], HOct (TFA), HEtHex (TFA), HHex (TFS), HOct (TFS) and HEtHex(TFS) which are illustrated in Scheme 1 are discussed in this study. The important parameters such as molecular volume, standard molar entropy and lattice energy were estimated by the empirical equations. The Arrhenius equation is used to fit the temperature dependency of the dynamic viscosities and electric conductivities. The ionicity is discussed by the Walden plots through the relationship between the molar conductivity and the fluidity of PILs.

We herein focus on the properties of the PILs in a comparison between the TFA and TFS counter anions, on the effect of ethyl branch, and on the length of alkyl chain.

2. Experimental section

2.1. Materials

The chemicals for the preparation of *N*-alkylethylenediamnes: Ethylenediamine (>99%,CAS 107-15-3) was supplied from Tianjin

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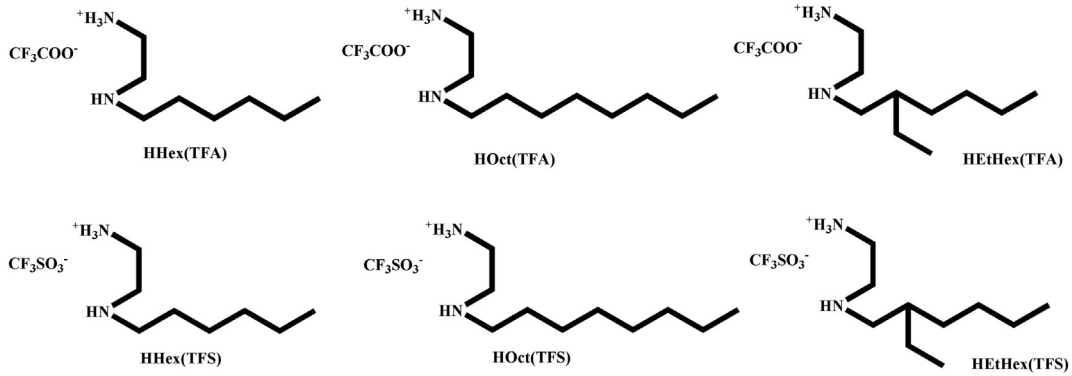

Scheme 1.

Kemiou Chemical Reagent Co. Ltd.; *n*-hexylbromide ($C_6H_{13}Br$, >99%, CAS 111-25-1), 2-ethylhexylbromide ($C_8H_{17}Br$, >98%, CAS 18908–66-2) and *n*-octylbromide ($C_8H_{17}Br$, >99%, CAS 111-83-1) were supplied from Nanjing Duolun Chem. Co. Ltd.

The chemicals for the preparation of PILs: Trifluoromethanesulfonic acid (HTFS, >99%, CAS 1493-13-6) and trifluoroacetic acid (HTFA, >99%, CAS 76-05-1) were supplied from Nanjing Duolun Chem. Co. Ltd., Diethyl ether (>99.5%, CAS 60-29-7) was supplied from Beijing Chem. Work.

The water content of the chemicals was <0.05% and all chemicals were used as received.

2.2. Synthesis and characterization of the PILs

N-alkyl (hexyl, ethylhexyl and octyl)ethylenediamines were prepared by the reactions between alkylbromides (*n*-hexylbromide, 2-ethylhexylbromide and *n*-octylbromide) and ethylenediamine (1:5 molar ratio) according to previously published procedures [19]. The PILs were synthesized by a simple neutralization reaction of the bases *N*-alkylethylenediamines with acids HTFS and HTFA (1:1 molar ratio) in diethyl ether, mixed for 4 h and then isolated by a complete evaporation of diethyl ether as a pale yellowish liquid or solid at room temperature. All the isolated PILs were treated with freeze-drying before measurements. The purity of PILs was confirmed by the measurements of ^{13}C NMR spectra and CHN elemental analyses. ^{13}C NMR spectra was confirmed with Bruker 400 MHz spectrometer [18] (see the supporting information) and CHN elemental analyses were carried out with a Vario EL instrument (Elementar Analysensysteme GmbH, Germany). The results of the CHN elemental analyses (%) are as follows: Anal. Found: C 46.43, H 7.90, N 10.67; Calcd for HHex(TFA)(=258.28): C 46.50, H 8.20, N 10.85. Anal. Found: C 50.69, H 8.47, N 9.80; Calcd for HOct(TFA) (=286.34): C 50.34, H 8.80, N 9.78. Anal. Found: C 50.62, H 8.55, N 9.66; Calcd for HEtHex (TFA) (=286.34): C 50.34, H 8.80, N 9.78. Anal. Found: C 36.83, H 7.34, N 9.39; Calcd for HHex (TFS) (=294.35): C 36.72, H 7.19, N 9.52. Anal. Found: *C*41.11, H 7.94, N 8.67; Calcd: for HOct (TFS) (=322.40): C 40.98, H 7.82, N 8.69. Anal. Found: C 40.74, H 8.07, N 8.52; Calcd for HEtHex (TFS) (=322.40): C 40.98, H 7.82, N 8.69. The differences between the calcd and anal. values are within ±0.5% point.

The PILs used here were freeze dried for 24h at −54 °C using a Christ Alpha 1–2 LD plus freeze dryer. Although we tried to remove all traces of water and solvent, 0.19–0.68% (w/w) water still remained. The water content was the average of the three times measurement using a METLER Toledo V20 volumetric type of Karl Fischer titrator. The values (%) are 0.68, 0.25, 0.56, 0.37, 0.19 and 0.55 for HHex (TFA), HOct (TFA), HEtHex (TFA), HHex (TFS), HOct (TFS) and HEtHex (TFS), respectively.

The solubility of PILs in various solvents was tested and similarly classified into three categories as follows: [1] >10% (w/v), [2] 0.1% to 10% (w/v), [3] <0.1% (w/v). For water, methanol, ethanol, acetone, propanol, butyl-alcohol, chloroform, ethyl ether and benzene, all the PILs were grouped into class [1] and for cyclohexane, the solubility of HEtHex (TFA) was also classified into [1]; HEtHex (TFS) was grouped into class [2] for cyclohexane (1.2%), hexane (0.3%) and petroleum ether (0.4%); All the PILs except for HEtHex (TFS) were grouped into class [3] for cyclohexane, hexane and petroleum ether. This result indicates that these PILs have moderate hydrophilic-hydrophobic balance.

2.3. Thermogravimetric analysis (TGA)

Thermal decomposition was observed using a TA instrument (Model TGA Q50) thermogravimetric analyzer under a nitrogen atmosphere at a.

heating rate of 10 °C/min in the temperature range from room temperature to 500 °C for PILs with TFA and from room temperature to 700 °C for PILs with TFS.

2.4. Phase transitions

Phase transition behavior was analyzed by a differential scanning calorimeter (DSC; TA Instruments' DSC Q20) in the temperature range from −80 °C to 120 °C. The samples (2-3mg for the solid sample and 5-10mg for the liquid sample) for DSC measurements were sealed in aluminum pans and at a heating rate of 10 °C/ min under a nitrogen atmosphere.

2.5. Density

The densities were measured using an Ostwald-type picnometer in the temperature range of $T =$ (293.15 to 353.15) K. The values were recorded every 5 K variation. The temperature was controlled by a thermostatic silicon oil bath with stability of ±0.1 °C. The uncertainty is $\pm 0.0002\ g \cdot cm^{-3}$ for density. The attaining thermal equilibrium time in the cell was 30 min. Each data point of the density is the average value of three times measurements. The values are listed in Tables 1 and 2.

2.6. Dynamic viscosity

The viscosities were measured using a Lovis 2000M microviscometer(Anton Paar, Austria) with a φ 2.5mm glass capillary in the temperature range of $T =$ (293.15 to 353.15) K according to Eq. 2. The temperature was controlled to within ±0.1 °C to the set point. The values were recorded every 5 K variation. The uncertainty is ±1% for the viscosity. The viscometer was calibrated before measurement using standard calibration oils provided by the suppliers.

$$\eta = k(\rho_b - \rho_s)\Delta t \quad (2)$$

where η is the dynamic viscosity, ρ_s and ρ_b are the density of the PIL and the steel ball, respectively, k is the constant value and Δt is the rolling time of the steel ball. The values of viscosity are also listed in Tables 1 and 2.