Properties of Protic Ionic Liquids Composed of *N*-Hexylethylenediaminium and *N*-(2-Ethylhexyl)ethylenediaminium Cations with Bis(trifluoromethanesulfonyl)amide Anion

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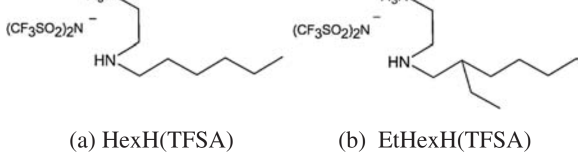
We have newly prepared protic ionic liquids (PIL) composed of monoprotic alkylethylenediaminium (alkyl = *N*-hexyl and *N*-2-ethylhexyl) cations coupled with bis(trifluoromethanesulfonyl)amide anion (=TFSA) at room temperature. It is in contrast to the monoprotic *N*-hexylethylenediaminium (=HexH)-TFSA salt which tends to crystallize on cooling that the monoprotic *N*-(2-ethylhexyl)ethylenediaminium (=EtHexH)TFSA salt assumes only a glassy state in solid. In the liquids, the HexH salt is more fluid than the EtHexH salt.

Protic ionic liquids (PILs) have recently attracted attention from the viewpoint of variable proton activities.[1,2] The oldest and most extensively studied protic ionic liquid (PIL) is ethylammonium nitrate (EAN) which has water-like properties and well dissolve a variety of electrolytes. PILs are generally more hydrophilic and dissolve metal salts to a larger extent than aprotic ionic liquids (AILs). Alkylethylenediamines have two amines and have larger affinity for Lewis acids compared to alkylamines. Therefore, it is significant to investigate the ionic liquid systems of alkylethylenediamines in relation to an interaction with Lewis acids including transition-metal ions. Our research group has recently studied *N*-alkylethylenediamine silver(I) complexes which provided room temperature ionic liquids and showed unique phase behavior.[3] The silver(I) ionic liquids are, however, gradually decomposed by light or heat and applications to wide fields are limited. As silver ion is a Lewis acid, the proton analogue is expected to form hydrophilic ionic liquids.

In the present study, we have newly isolated four PILs, monoprotic *N*-hexylethylenediaminium bis(trifluoromethanesulfonyl)amide (=HexH(TFSA)) (Scheme 1a), diprotic *N*-hexylethylenediaminium bis(trifluoromethanesulfonyl)amide (=$HexH_2(TFSA)_2$), monoprotic *N*-(2-ethylhexyl)ethylenediaminium bis(trifluoromethanesulfonyl)amide (=EtHexH(TFSA)) (Scheme 1b), and diprotic *N*-(2-ethylhexyl)ethylenediaminium bis(trifluoromethanesulfonyl)amide (=$EtHexH_2(TFSA)_2$).

Of these *N*-alkylethylenediaminium TFSA salts, monoprotic HexH(TFSA) and EtHexH(TFSA) were liquids at room temperature and were less viscous than the diprotic salts,[4] we thus studied here physical properties of the two monoprotic liquids of HexH(TFSA) and EtHexH(TFSA). We focused on a comparison of the properties between the *N*-2-ethylhexyl and *N*-hexyl PILs based on the molecular structures.



(a) HexH(TFSA) (b) EtHexH(TFSA)

Scheme 1.

The *N*-hexylethylenediamine (=Hex) and *N*-(2-ethylhexyl)-ethylenediamine (=EtHex) were prepared by the reactions between the alkyl bromides and ethylenediamine (1:5 molar ratio) according to the literature[5] followed by distillation under 1 kPa. The purities were confirmed by ^{13}C NMR spectra. Each PIL was prepared by neutralization of the *N*-alkylethylenediamines with HTFSA (supplied from Morita Chemicals) and then isolated by a repeat freeze–thaw method from diethyl ether solutions as a colorless (or pale yellowish) liquid. All of the ILs were dried under vacuum at room temperature for a day in the presence of P_2O_5. The CHN elemental analyses were performed with a Perkin-Elmer model 2400II.[6] The water contents were directly measured using Karl-Fisher titration, which gave the water content ($W_0 = [H_2O]/[PIL]$) as follows: 0.02 for HexH(TFSA), 0.02 for EtHexH(TFSA), 0.7 for $HexH_2(TFSA)_2$, and 0.9 for $EtHexH_2(TFSA)_2$. The monoprotic PILs as well as the diprotic PILs were somewhat hygroscopic and the former gradually absorbed moisture to around $W_0 = 0.1$–0.2. The water content slightly affected dynamic properties such as self-diffusions and electric conductivities.

The densities were measured at 25 °C using a micropipette and the results were 1.41 $g\,cm^{-3}$ for HexH(TFSA) and 1.32 $g\,cm^{-3}$ for EtHexH(TFSA).

As the diprotic chlorides for both the *N*-alkylethylenediamines were isolated as crystals, we determined the pK_a values by titration of both the diprotic chlorides (0.01 $mol\,dm^{-3}$) with aqueous NaOH solutions at approximately constant ionic strength (0.1 $mol\,dm^{-3}$, with addition of KCl). The pK_{a1} and pK_{a2} values obtained were 7.28 and 10.57 for Hex, and 7.30 and 10.42 for EtHex, respectively. As HTFSA is a strong acid, the relationship of $pK_a(\text{base}) - pK_a(\text{acid}) > 8$ for the monoprotic PILs holds well. That is, the transfer of the proton from the acid to the base was almost complete.[1b]

Hydrophilic–hydrophobic balance of a molecule is an important factor governing self-aggregation behavior both in neat state and in solution. The solubilities of HexH(TFSA) and EtHexH(TFSA) liquids in various solvents were tested and similarly classified into three categories as follows. They were more than 10% (w/v) in methanol, ethanol, acetone, dichloromethane, ethyl acetate, chloroform, diethyl ether, and 1,4-dioxane, from 0.1% (w/v) to 10% (w/v) in water (0.1% for both the PILs) and benzene (0.3% for HexH(TFSA) and 1% for EtHexH(TFSA)), and were less than 0.1% (w/v) in cyclohexane and hexane. Thus, the present ILs have moderate hydrophilic–hydrophobic characters.

Solid–liquid transition was observed by DSC in the temperature range of −100–150 °C (with a Shimadzu DSC-50 attached LTC-50 apparatus for low-temperature measurements). The samples (3–5 mg) were placed in aluminum pans and run at a

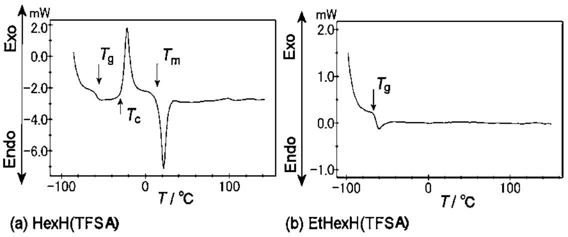


Figure 1. DSC curves of (a) HexH(TFSA) at −80–150 °C and (b) EtHexH(TFSA) at −100–150 °C.

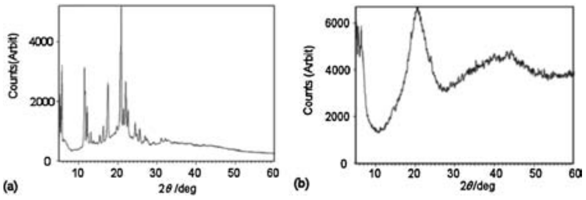


Figure 2. WAXD profiles of (a) HexH(TFSA) at −120 °C and (b) EtHexH(TFSA) at −120 °C.

rate of $10\,K\,min^{-1}$ under nitrogen gas at a flow rate of $20\,mL\,min^{-1}$. The results are described in Figure 1. For HexH(TFSA) a glass transition temperature (T_g), a crystallization temperature (T_c), and a melting point (T_m) are observed while in contrast for EtHexH(TFSA) only a glass transition is observed. Stronger tendency for HexH(TFSA) to crystallize is analogous to that for the corresponding silver(I) complexes.[3] The enthalpy change ($\Delta H = 9.4\,kJ\,mol^{-1}$) at T_m (10 °C) for the HexH(TFSA) salt is smaller than the general melting enthalpies. Similar differences in the DSC profiles have been observed in counter ion and alkyl chain effects in alkylammonium salts.[7] In the present PILs however, the liquids are present at lower temperature and the side-chain effect on the DSC profile more clearly appeared in comparison with the alkylammonium salts.

Wide-angle ($2\theta = 10$–$60°$) X-ray diffractions (WAXD) were measured at 25 and −120 °C with a 0.8-kW generator of Cu $K\alpha$ radiation (PANalytical X'Pert Pro). The samples were placed on a horizontal cell in vacuo and measured by a reflection. The WAXD profiles for HexH(TFSA) and EtHexH(TFSA) in solid (−120 °C) states are shown in Figure 2. The profiles in the liquid states of both systems at 25 °C were close to that of EtHexH (TFSA) in the solid sate at −120 °C (Figure 2b). On the other hand, HexH(TFSA) assumed an amorphous-based crystalline state at −120 °C (Figure 2a). The more ordered structure of the Hex silver(I) complex than of the EtHex silver(I) complex in WAXD has also been reported by our research group.[3a] It is comparable that the Hex silver(I) nitrate is a crystal at room temperature while the EtHex silver(I) nitrate is a viscous liquid at room temperature. The present WAXD result explains the DSC profiles that HexH(TFSA) showed both glassy and melting transitions while EtHexH(TFSA) showed only a glassy transition.

The dynamic properties of the ILs were studied by the measurements of self-diffusion of the cations. Self-diffusion was measured using ^1H NMR PFG analysis with a JEOL FX-90 spectrometer operating at 90 MHz. The procedure followed a previously reported method.[3] As both ILs are somewhat hygroscopic, the water content ($W_0 = 0.01$–0.02) of dried ILs gradually changed to around $W_0 = 0.2$ after storage in a vial for several days. We thus compared the self-diffusion of the cations in both the IL systems between $W_0 = 0.02$ and 0.2. Figure 3 shows Arrhenius plots for the self-diffusion in the range of 25–70 °C. The self-diffusion coefficients for the HexH cation were slightly larger than those for the EtHexH cation. Slight curvature is observed and the apparent activation energies for the HexH cation and the EtHexH cation at $W_0 = 0.02$ were 46.3 ± 0.8 and $45.8 \pm 0.8\,kJ\,mol^{-1}$, respectively. At higher water content ($W_0 = 0.2$), self-diffusion slightly increases and the difference between the HexH and EtHexH cations increases and the apparent activation energies for the HexH and EtHexH cations were 41.6 ± 0.9 and $42.7 \pm 0.7\,kJ\,mol^{-1}$, respectively. Greater fluidity of the HexH cation was more clearly detected at $W_0 = 0.2$.

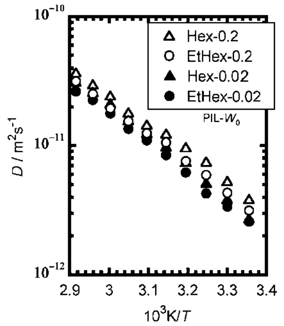


Figure 3. Diffusion coefficients of HexH and EtHexH cations for $W_0 = 0.02$ and 0.2.

In relation to self-diffusion, the electric conductivities for the two PILs were measured at 25 ± 1 °C with a HORIBA B173, where $0.01\,mol\,dm^{-3}$ KCl aqueous solution at 25 °C ($\kappa = 1.41\,mS\,cm^{-1}$) was used as a standard. The electric conductivities were $250\,\mu S\,cm^{-1}$ for HexH(TFSA) ($W_0 = 0.02$) and $210\,\mu S\,cm^{-1}$ for EtHexH(TFSA) ($W_0 = 0.02$). The larger conductivity for HexH(TFSA) than for EtHexH(TFSA) also reflects a larger fluidity of the former PIL.

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References and Notes

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4 Both the diprotic PILs were liquid and crystalline mixtures at room temperature and therir DSC profioles were more complicated than the monoprotic PILs.

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6 Anal. Found: C, 28.40; H, 5.13; N, 9.82%. Calcd for HexH(TFSA) ($C_{10}H_{21}N_3O_4S_2F_6$): C, 28.23; H, 4.98; N, 9.88%. Anal. Found: C, 20.26; H, 3.12; N, 7.63%. Calcd for $HexH_2(TFSA)_2{\cdot}H_2O$ ($C_{12}H_{24}N_4O_9S_4F_{12}$): C, 19.89; H, 3.34; N, 7.73%. Anal. Found: C, 31.40; H, 5.42; N, 9.12%. Calcd for EtHexH(TFSA) ($C_{12}H_{25}N_3O_4S_2F_6$): C, 31.78; H, 5.56; N, 9.27%. Anal. Found: C, 22.24; H, 3.89; N, 7.59%. Calcd for $EtHexH_2(TFSA)_2{\cdot}H_2O$ ($C_{14}H_{28}N_4O_9S_4F_{12}$): C, 22.34; H, 3.75; N, 7.44%.

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