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# Physicochemical Properties of Ionic Liquids Containing *N*-alkylamine-Silver(I) Complex Cations or Protic *N*-alkylaminium Cations

Masayasu Iida<sup>1</sup> and Hua Er<sup>2</sup>

<sup>1</sup>*Division of Materials Science, Graduate School of Humanities and Sciences, Nara Women's University, Kita-uoya-nishi-machi, Nara 630-8506,*

<sup>2</sup>*School of Chemistry and Chemical Engineering, Beifang Ethnic University, Ningxia 750021,*

<sup>1</sup>*Japan*

<sup>2</sup>*P. R. China*

## 1. Introduction

Metal-containing ionic liquids are expected to behave as functional materials that combine the unique properties of ionic liquids with additional magnetic, electric, catalytic or emission properties. (Abbott *et al.* 2008; Nockemann *et al.*, 2006, 2009; Scheeren *et al.*, 2006) Ionic liquids of metal complexes which contain metal ions in their molecular structures (metallo-ILs) are particularly applicable in many fields as task-specific soft materials with many possibilities for molecular design. (Lee *et al.*, 2004; Lin *et al.*, 2005; Binnemans, 2007) The first systematic studies of metallo-ILs have been performed for the mixtures of 1-ethylpyridinium bromide and aluminum(III) chloride (Hurley & Wier, 1951). Since then the halogenoaluminate(III) and the alkylhalogenoaluminate(III) ionic liquids have been the most extensively studied systems (Hussey, 1988). The conventional metallo-ILs can be formed by the complexation reactions of simple anionic species with neutral compounds such as:  $\text{AlCl}_3 + \text{EMICl} \rightarrow \text{EMI}^+\text{AlCl}_4^-$ , where  $\text{EMI}^+$  is 1-ethyl-3-methyl-imidazolium cation. These ionic liquids provide a useful extension to the range of solvents that are available for synthetic chemistry (Welton, 1999).

Numerous transition metal chlorides have been shown to form well-defined anionic complexes in basic haloaluminate ionic liquids. When transition metals are bound to neutral ligands in ILs to form transition-metal complex cations, the salts tend to have higher melting points compared with conventional ILs. (Lee *et al.*, 2004; Lin & Vasam, 2005) However, for such kinds of metallo-ILs there are potential applications in a wide range of fields due to their affinity for anionic surfaces which are present abundantly in nature (Israelachvili, 1992) and for carbon surfaces rich in  $\pi$ -electron density by virtue of cation- $\pi$  interactions. (Ma & Dougherty, 1997; Fukushima *et al.*, 2003; Zhang & Cui, 2009)

On the other hand, protic ionic liquids (PILs) have recently attracted attention for their variable proton activities (Yoshizawa *et al.*, 2003; Belieres & Angell, 2007; Angell *et al.*, 2007; Greaves & Drummond, 2008). Although the first room-temperature ionic liquid is ethylammonium nitrate (= EAN) which is the simplest PIL, a large part of the ILs hitherto

studied treats aprotic ILs (AILs). PILs generally have larger polarities and can dissolve metal salts to a larger extent than common AILs. Studies on PILs have been increasing and revealed the attractive features. PIL is also an interesting subset of ILs as follows. They generally form hydrogen-bonded networks, have larger polarity, and generally incorporate metal salts to a larger extent in comparison with AILs due to the more hydrophilic character. The PILs have advantages of potential application in organic synthesis, fuel cells, biological fields, and self-assembly media for amphiphiles. (Greaves, 2006, 2008)

In the present review, we refer to the systems of metallo-ILs having alkylamine or alkylethylenediamine ligands which are the structurally most simple and neutral amphiphilic ligands. Furthermore, alkylamines or alkylethylenediamines can provide protic ionic liquids. We here focus on the physicochemical properties of ionic liquids of *N*-alkylethylenediamines containing silver(I) ion or proton and compare the effects of alkylchains on the physicochemical properties between the silver(I)-ILs and the PILs. We emphasize the difference in the physicochemical properties between the alkylamines and alkylethylenediamines; the latter is more advantageous to incorporate metal ions to the polar domains in the ILs than the former.

## 2. Alkylammonium and metallo-alkylamine ionic liquids

The most extensively studied PIL is EAN, whose property is close to that of water. EAN also forms a strong hydrogen-bonded network structure and is miscible in water and other polar organic solvents. The alkylammonium PILs are solvents available for the self-organization of amphiphiles. Studies on the micellar formation in EAN for cationic surfactants (Evans *et al.*, 1982; Evans & Wennerström, 1999) revealed that the CMCs in EAN are about a factor of 5-10 higher than those in water and that the aggregation numbers are about a factor of 4 smaller. Self-organization of amphiphilic molecules in various solvents including EAN is explained on the basis of cohesive energy. The Gordon parameter (*G*) defined as  $\gamma/V_m^{1/3}$  [J/m<sup>3</sup>], where  $\gamma$  is the surface tension and the  $V_m$  molar volume, is a measure of cohesive energy density of solvents and therefore indicates the driving force for self-assembly. PILs composing of alkylammonium ions other than EAN have also been studied as self-assembly media for amphiphiles. (Greaves *et al.*, 2006, 2008) The *G* value decreases with an increase in the alkyl chain lengths and the driving force for aggregation also decreases. It has been clarified that the alkylammonium PILs are the solvents with the lowest *G* value (552 J/m<sup>3</sup>) which can still self-assemble amphiphiles.

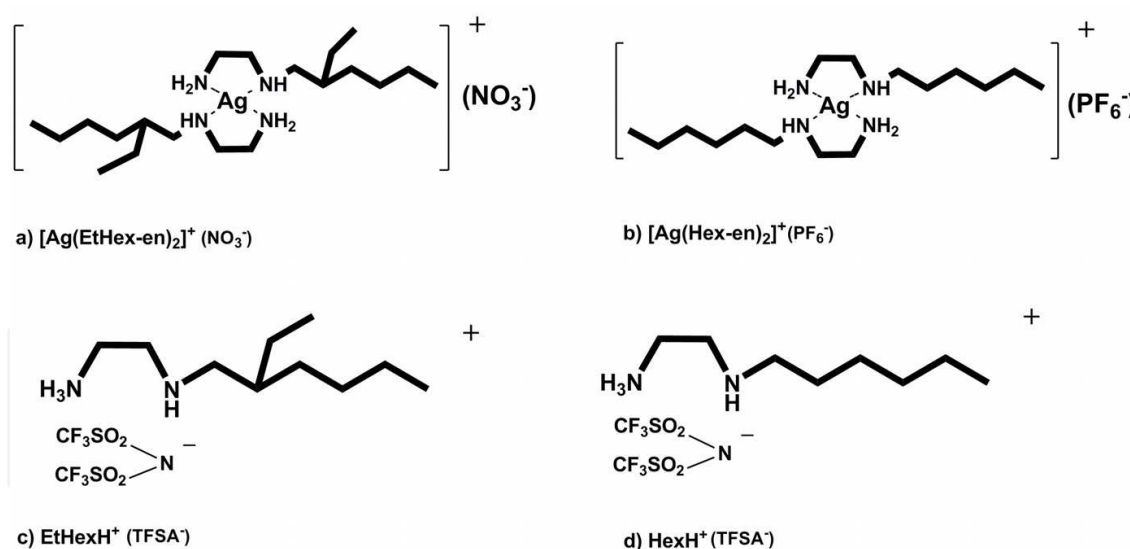
The alkylamine-silver(I) cationic complexes with NO<sub>3</sub><sup>-</sup> and BF<sub>4</sub><sup>-</sup> have been prepared and it was found that they form liquid crystals having bilayer structure of a U-shaped geometry for the cations at near room temperature. (Albéniz *et al.*, 2000) Low melting points of this kind of the complexes are advantageous to form room-temperature ionic liquids using proper counter anions. The ionic liquids of [Ag(H<sub>2</sub>N-R)<sub>2</sub>](TFSA) and [Zn(H<sub>2</sub>N-R)<sub>4</sub>](TFSA)<sub>2</sub> (R = Methyl, Ethyl, Propyl, or *t*-Butyl; TFSA = bis(trifluoromethanesulfonyl)amide anion) have been first prepared (Huang *et al.*, 2006). These metallo-ILs have been utilized in the electrodepositions of silver and zinc, respectively, and have tunable specific functionalities as well as the physicochemical properties by changing both organic ligands and central metal ions.

*N*-alkylethylenediamines have two amines and are more favorable for an incorporation of Lewis acids such as proton and transition metal ions into the ILs in comparison with *N*-alkylamines. Therefore, it is of interest to compare the IL systems containing protic *N*-

alkylethylenediaminium (PIL) with those containing metal(I) *N*-alkylethylenediamine complexes (metallo-IL).

### 3. Silver(I)-alkylethylenediamine ILs and alkylethylenediaminium PILs

Bis(*N*-alkylethylenediamine)silver(I) nitrates (alkyl = hexyl, octyl, dodecyl, and hexadecyl) have been prepared by our research group and the X-ray crystallographic analysis for the dodecyl complex has been performed. (Manna *et al.*, 2001; Iida *et al.*, 2004) These surfactants are structurally similar to gemini-type surfactants which have been extensively studied and showed a variety of aggregation phenomena due to multi-alkyl chains and bulky headgroup. (Zana & Xia, 2003) As the metallosurfactants have additional properties due to containing transition metals, multi-chained metallosurfactants are oriented to a wide range of potential applications such as metallomesogens, optoelectronic devices, magnetic resonance imaging, homogeneous catalysis, and nanoparticles. Physicochemical properties of *N*-alkylethylenediamine metal complexes in solution have been studied and it has been clarified that they behave as components of various aggregates in solution such as reverse micelles, microemulsions, and ionic liquid crystals. (Er *et al.*, 2003, 2007) It is characteristic that the W/O microemulsions (or reverse micelles) provided homogeneous and uniformly sized silver(0) or palladium(0) nanoparticles by the reaction with aqueous NaBH<sub>4</sub> solution. It was clarified that the dodecyl and octyl complexes form lyotropic or thermotropic liquid crystals. The octyl complex has a transition from the crystal to the thermotropic liquid crystal at 48 °C, whereas the hexyl complex is melt at 44 °C without a formation of liquid crystal.



Scheme 1. Room temperature ionic liquids containing alkylethylenediamines

From these low-melting points, room-temperature ionic liquids or room-temperature ionic liquid crystals are expected to form by properly controlling structural conditions.

#### 3.1 Formation of room-temperature ionic liquids of alkylethylenediamine silver(I) complexes

An introduction of ethyl-branch in the ligand or an exchange of the counter anion by PF<sub>6</sub> (Scheme 1) was very effective on lowering the melting point of [Ag(Hex-en)<sub>2</sub>]NO<sub>3</sub>. The

complexes of  $[\text{Ag}(\text{EtHex-en})_2]\text{NO}_3$  (EtHex-en = 2-ethylhexylethylenediamine) and  $[\text{Ag}(\text{Hex-en})_2]\text{PF}_6$  were newly synthesized. The Hex-en and EtHex-en were prepared by the reactions between the alkylbromides and ethylenediamine (1:5 molar ratio) and then by the distillation under around 1 kPa. The EtHex complex was prepared by the reaction of  $\text{AgNO}_3$  with the ligand in 1: 1.9 molar ratio at 0 °C. The purities of the silver(I) complexes were confirmed by CHN elemental analyses and  $^{13}\text{C}$  NMR spectra. With considering the water content (determined by a Karl-Fisher titration), the elemental analyses gave satisfactory results.

The appearance of the EtHex-en complex at solid state (around - 60 °C) was pale-yellowish transparent, glassy, and the observation by polarizing microscopy (PM) clarified the solid to be isotropic, while the  $[\text{Ag}(\text{Hex-en})_2]\text{PF}_6$  was devitrified at solid state. The DSC curve (with Shimadzu DSC-50 attached LTC-50 apparatus for low-temperature measurements at a constant rate of 10 K min<sup>-1</sup>) for  $[\text{Ag}(\text{EtHex-en})_2]\text{NO}_3$  described in Fig. 1(a) shows that the glass transition at - 54 °C and small endothermic peak ( $\Delta H = - 1.5$  kJ mol<sup>-1</sup>) at - 30 °C were observed; the latter may be ascribed to the enthalpy relaxation. On the other hand,  $[\text{Ag}(\text{Hex-en})_2]\text{PF}_6$  shows a sharp and endothermic peak corresponding to 18 kJ mol<sup>-1</sup> enthalpy change. (Fig. 1(b)) For comparison, DSC curves for  $[\text{Ag}(\text{Hex-en})_2]\text{NO}_3$  and  $[\text{Ag}(\text{oct-en})_2]\text{NO}_3$  are described together. (Figs. 1(c) and (d))

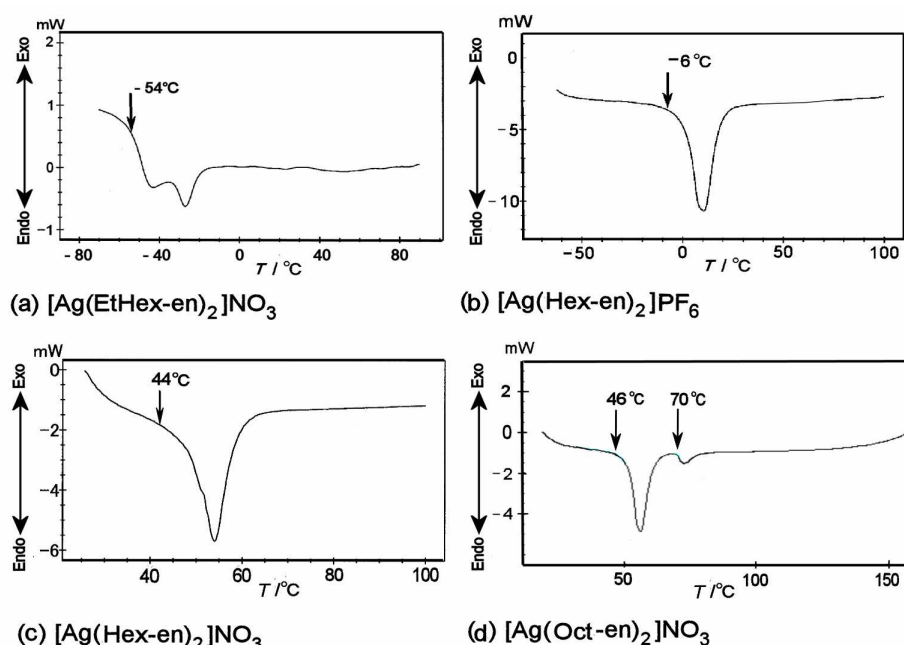


Fig. 1. DSC curves of (a)  $[\text{Ag}(\text{EtHex-en})_2]\text{NO}_3$  at - 80–200 °C, (b)  $[\text{Ag}(\text{Hex-en})_2]\text{PF}_6$  at - 80–200 °C, (c)  $[\text{Ag}(\text{Hex-en})_2]\text{NO}_3$  at 25–200 °C, and (d)  $[\text{Ag}(\text{Oct-en})_2]\text{NO}_3$  at 25–200 °C

The Hex-en complex of the nitrate shows the melting at 44 °C ( $\Delta H = - 34$  kJ mol<sup>-1</sup>) and the Oct-en complex of the nitrate ( $\Delta H = - 32$  kJ mol<sup>-1</sup> for 46 °C and  $\Delta H = - 2.7$  kJ mol<sup>-1</sup> for 70 °C) shows the formation of liquid crystals in the range of 46–70 °C. These DSC results show that the structural ordering in the solid state is in the order,  $[\text{Ag}(\text{oct-en})_2]\text{NO}_3 > [\text{Ag}(\text{Hex-en})_2]\text{NO}_3 > [\text{Ag}(\text{Hex-en})_2]\text{PF}_6 > [\text{Ag}(\text{EtHex-en})_2]\text{NO}_3$ .

The glassy structure of  $[\text{Ag}(\text{EtHex-en})_2]\text{NO}_3$  in the solid state was directly observed by wide angle X-ray diffraction (WAXD) in the range of  $2\theta = 10$ –60 °. The WAXD was measured with a 0.8 kW generator of  $\text{Cu}_{K\alpha}$  radiation (Panalytical X'Pert Pro). The samples were placed on a horizontal cell in vacuo and measured by using a reflection method. The WAXD profiles for

[Ag(EtHex-en)<sub>2</sub>]<sub>2</sub>NO<sub>3</sub> and [Ag(Hex-en)<sub>2</sub>]<sub>2</sub>PF<sub>6</sub> at two temperatures (– 58 and 25 °C) are shown in Fig. 2(a) and 2(b), respectively. In both systems the profiles show amorphous structures, whereas the Hex-en complex is less amorphous than the EtHex-en complex and several sharp peaks additionally appear. The sharper peaks due to the crystalline portions appear more clearly in the Hex-en complex. This result explains the larger and simpler endothermic peak in the DSC curve for the Hex-en complex in comparison with the EtHex-en complex.

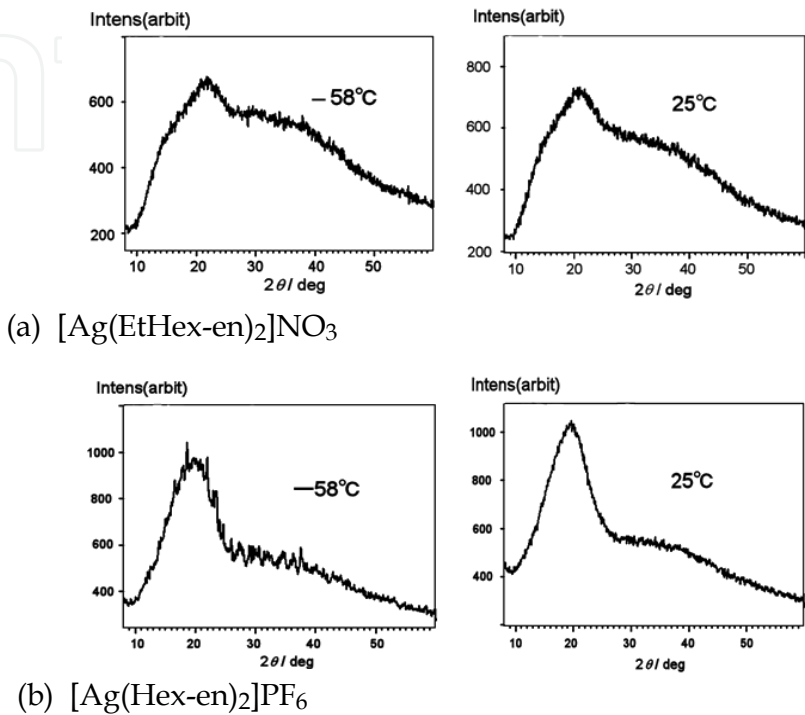


Fig. 2. WAXD profiles of (a) [Ag(EtHex-en)<sub>2</sub>]<sub>2</sub>NO<sub>3</sub>·0.3H<sub>2</sub>O and (b) [Ag(Hex-en)<sub>2</sub>]<sub>2</sub>PF<sub>6</sub> at –58 and 25°C.

Hydrophilic-hydrophobic balance of a molecule is an important factor governing a self-aggregation behavior both in neat state and in solution. Therefore, in order to consider the formation of ILs we examined the solubilities of the respective complexes in various solvents. All of the four complexes well dissolved (class 1) in acetone, dichloromethane, ethylacetate, and 1,4-dioxane. The differences in the solubilities for the complexes were seen in some solvents and the results are listed in Table 1. The hydrophobicities of PF<sub>6</sub><sup>–</sup> and C8-alkyl chains clearly appeared in the cases of water and benzene, but the relationship is somewhat complicated in the other solvents.

	Water	Methanol	Ethanol	CHCl <sub>3</sub>	Diethyl Ether	Benzene
[Ag(Hex-en) <sub>2</sub> ] <sub>2</sub> NO <sub>3</sub>	1	1	1	2	3	3
[Ag(Hex-en) <sub>2</sub> ] <sub>2</sub> PF <sub>6</sub>	3	1	1	3	3	1
[Ag(Oct-en) <sub>2</sub> ] <sub>2</sub> NO <sub>3</sub>	3	3	3	2	2	1
[Ag(EtHex-en) <sub>2</sub> ] <sub>2</sub> NO <sub>3</sub>	3	1	1	3	1	1

1: > 10%; 2: 0.1-10%; 3: < 0.1%

Table 1. A classification of the solubilities of the bis (alkylethylenediamine)silver(I) complexes.



Dynamic properties of solutions are generally sensitive to the extent of the aggregation in the solution. Self-diffusions and electric conductivities are particularly important and fundamental in the studies on ionic liquid systems. (Tokuda *et al.*, 2004, 2005; Ueno *et al.*, 2010) As small amounts of water significantly affect the dynamic properties in the Ag-ILs, the self-diffusions of the silver complexes and water were measured with a change in the water content. The measurements were performed in the temperature range of 30 (or 40)–70 °C using  $^1\text{H}$  NMR PFG analysis with a JEOL FX-90 spectrometer operating at 90 MHz for the methylene-chain protons in the silver(I) complex. The diffusion coefficients as a function of temperature are given by Arrhenius plots in Fig. 3. Good linearities in the Arrhenius plots are obtained for the Hex-en complex (e), whereas the plots are curved for the EtHex systems at lower water content. Even in the case of the EtHex-en complex the linearities of the plots for both the complex and content water become better with an increase in the water content. Small diffusion coefficients of the EtHex complex at the lowest water content ( $W_0 = 0.3$ , Fig. 3 (a)(i)) mean the formation of strong self-assemblies of the complexes. The liquid at room temperature is regarded as a super-cooling liquid.

For the ILs the curvature of the Arrhenius plots are generally observed and the following Vogel-Tamman-Fulcher (VTF) equation (1) have been conveniently used to interpret the results.

$$D = D_0 \exp\left(-\frac{B}{T - T_0}\right) \quad (1)$$

where  $D_0$  and  $B$  are characteristic constants (VTF parameters) for a given system and a given property, and  $T_0$  is a reference temperature which should be the ideal glass transition temperature of the system independent of the studied property. In the present study, the data for the largest curvature system ( $[\text{Ag}(\text{EtHex-en})_2]\text{NO}_3$ ,  $W_0 = 0.3$ ) were used and the best fitting parameter of  $T_0$  was determined as 200 K. This value was used in the other systems to determine the other  $D_0$  and  $B$  parameters.

For the same  $T_0$  value (200 K), both the  $D_0$  and  $B$  values for  $[\text{Ag}(\text{EtHex-en})_2]\text{NO}_3$  were determined (Iida *et al.*, 2008); they decrease with an increase in the water content. As the  $B$  parameter is related with the apparent activation energy in the Arrhenius plot, the decrease with an increase in water is a reasonable result.

In the case of the Hex complex, the liquid is more fluid. The resultant diffusion coefficient is somewhat larger and the temperature dependency is smaller than the EtHex complex.

In relating with the self-diffusions, the electric conductivities for the two PILs were measured at  $25 \pm 1$  °C with a HORIBA B173, where  $0.01 \text{ mol dm}^{-3}$  KCl aqueous solution at 25 °C ( $\kappa = 1.41 \text{ mS cm}^{-1}$ ) was used as a standard. The electric conductivities were 31 and  $74 \mu\text{S cm}^{-1}$  for the  $[\text{Ag}(\text{EtHex-en})_2]\text{NO}_3$  and  $[\text{Ag}(\text{Hex-en})_2]\text{PF}_6$ , respectively. The larger electric conductivity for the Hex-en complex than that for the EtHex complex is consistent with the result of the self-diffusions. These very small values reflect the high viscosities. This type of ionic liquids is thus disadvantageous for an application to the field of electric conductivity.

A series of alkyethylenediamine-metal complexes form aggregates in solution such as microemulsions and lyotropic liquid crystals, and thus the present silver(I)-ILs are also expected to form organized nanostructures, which were investigated by small-angle X-ray scattering (SAXS). The SAXS was measured in the range  $2\theta = 1\text{--}10^\circ$  at room temperature with a 15-kW generator of  $\text{Cu}_{K\alpha}$  radiation (RIGAKU RINT-TRIII) The sample was put in a 0.4-mm cell interposed by a 0.02-mm Mylar film. The SAXS profiles are given as plots of

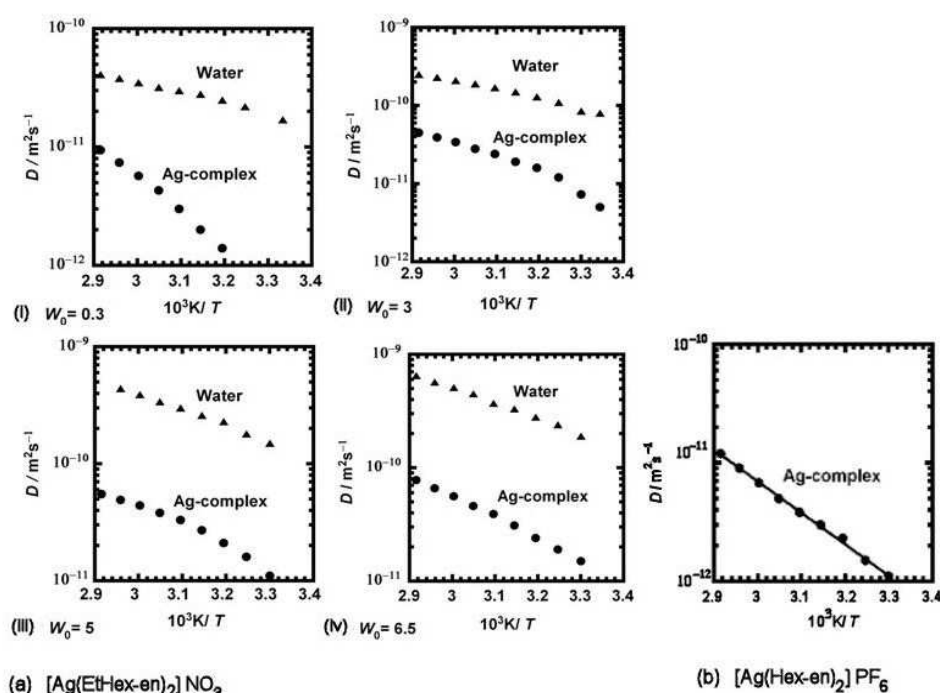


Fig. 3. Diffusion coefficients of the EtHex-en complex containing varying amounts of water (i–iv) and the Hex-en complex as a function of temperature shown as Arrhenius plots.

intensity versus  $q$  ( $4\pi\sin\theta/\lambda$ ), in which  $\lambda = 0.154$  nm. The SAXS profiles for the EtHex-en and Hex-en systems show a broad and large peak in a similar manner. Although the peak positions are almost the same of  $q = 3.2$  nm<sup>-1</sup>, which corresponds to the close alkyl-chain lengths of 2.0 nm, the half-width of the peak for the EtHex-en complex is 1.72° while that for the Hex-en complex is 2.47°. This significant difference means that the nanostructure observed by SAXS is more ordered in the EtHex-en complex than in the Hex-en complex. The result of SAXS is in contrast to that of WAXD, which shows that the nearby structure around each molecule is less ordered and the system is more easily vitrified. The formation of nanostructure in ionic liquid system has also been clarified for alkylimidazolium systems. (for example, Lopes & Pauda, 2006)

The ordering of the nanostructure containing silver ions will be conveniently monitored by this heavy metal using TEM (Transmission Electron Microscope). The encapsulated silver ions in the nanodomains of ILs will be expected to behave as an appropriate probe. Furthermore, one of the characteristic features of ionic liquids is non-volatility, which may make possible to directly observe the nanostructures using TEM under high vacuum (around 10<sup>-5</sup> Pa). Especially, silver(I) ions in the Ag-ILs are able to be monitored assembled in the polar regions of the ILs nanostructure and are partially reduced to silver(0) by light or heat promoted by the ethylenediamine headgroup. We have thus studied the Ag-ILs by TEM from the following two viewpoints. One is the direct observation of the nanostructures of Ag-ILs for the neat Ag-ILs and the other is the formation of silver(0) nanoparticles on the basis of the nanodomains of Ag-ILs.

The TEM measurements were performed at ambient temperature on a Hitachi H-800 electron microscope operating at 200 kV. A specimen for the TEM measurements was prepared by spreading an ionic liquid or a small-drop silver(0) sol directly onto a standard 200-mesh copper grid (coated with a thin amorphous carbon film) and letting the dry



completely in air. The size distribution for the Ag(0) nanoparticles prepared from was derived from histograms for about 800 particles. A thin liquid film of the Ag-ILs was made by about twice dilution with diethylether.

Fig. 4 shows the TEM images for the two Ag-ILs. The image for  $[\text{Ag}(\text{EtHex-en})_2]\text{NO}_3$  (Fig. 4(a)) indicates that the hydrophilic (black) regions and hydrophobic alkyl-chain (white) regions are present in the liquid state and form organized structures, such as microemulsions. On the other hand, a similar TEM image for  $[\text{Ag}(\text{Hex-en})_2]\text{PF}_6$  (Fig. 4(b)) shows that the organized structure is less clear. These characteristics in the TEM images are consistent with the results of the half-widths in the SAXS profiles. A formation of nanostructure, such as a W/O microemulsion in the EtHex liquid is comparable to the W/O microemulsion or lyotropic liquid crystals composed of  $[\text{Ag}(\text{Oct-en})_2]\text{NO}_3$  (Oct-en = *N*-octylethylenediamine) or  $[\text{Ag}(\text{Dod-en})_2]\text{NO}_3$  (Dod-en = *N*-dodecylethylenediamine). (Iida *et al.*, 2004) The use of alkylethylenediamine silver(I) and palladium(II) complexes to create silver(0) or palladium(0) nanoparticles has been successfully performed for the  $[\text{Ag}(\text{Tetd-en})_2]\text{NO}_3$  (Tetd-en = *N*-tetradecylethylenediamine)/water/heptane or  $[\text{Pd}(\text{Oct-en})_2]\text{Cl}_2$ /water/chloroform microemulsion system. (Manna *et al.*, 2001; Iida *et al.*, 2002) In the present Ag-IL, the silver(I) ions are condensed in very limited nanoregions surrounded by the alkyl chains without organic solvents; this characteristic property suggests potential applications to effectively obtain silver(0) nanoparticles from the present ionic liquid system.

The reaction of neat Ag-ILs with aqueous  $\text{NaBH}_4$  solution was performed for  $[\text{Ag}(\text{EtHex-en})_2]\text{NO}_3$  and for  $[\text{Ag}(\text{Hex-en})_2]\text{PF}_6$ ; the following contrast results have been obtained. The reaction of the EtHex derivative gave a yellow sol with an absorption peak of 409 nm, whereas that of the Hex derivative gave only colorless solution with precipitates of bulk silver metal.

The formation of silver(0) colloidal sol by the reaction of Ag-ILs with aqueous  $\text{NaBH}_4$  solution was subtly dependent on the alkyl-chain of the silver complex. The TEM images of the sol obtained were observed under some conditions (water content or the excess ligand content) of the Ag-ILs and the results are described in Fig. 5. The Ag-IL system gave well-uniformed nanoparticles compared to the previously reported the Tetd-en complex microemulsion system in spite of the shorter alkyl-chain length. The difference in the nanostructures of the Ag-ILs between the silver complexes was observed by SAXS, and the TEM observation of the Ag-ILs clarified the significant difference in the organization of polar region where the silver ions are encapsulated. The slight difference in the molecular structure of the Ag-IL results in the contrast reaction with aqueous  $\text{NaBH}_4$  solution. This government of the delicate condition in the formation of the silver(0) nanoparticles is also observed in the other reaction conditions. The effect of the presence of small amounts of water on the formation of silver(0) nanoparticles was examined.

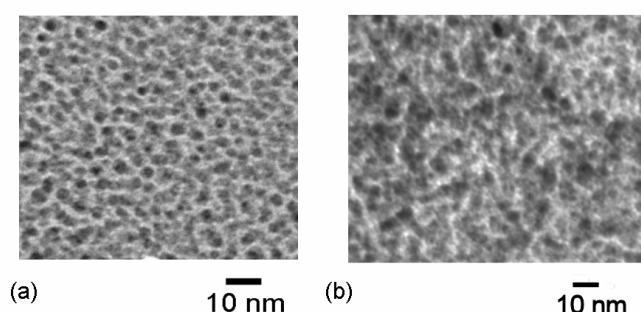


Fig. 4. TEM images of the direct observation of (a)  $[\text{Ag}(\text{EtHex-en})_2]\text{NO}_3$  and (b)  $[\text{Ag}(\text{Hex-en})_2]\text{PF}_6$  liquids.

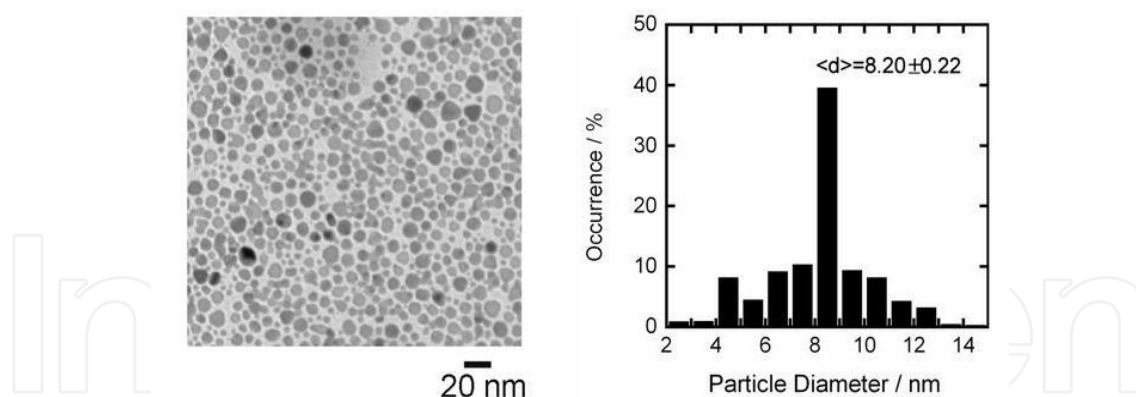


Fig. 5. TEM images and size distribution of silver(0) nanoparticles obtained by the reactions between the Ag-ILs and aqueous  $\text{NaBH}_4$  solution. neat  $[\text{Ag}(\text{EtHex-en})_2]\text{NO}_3$  ( $W_0 = 0.3$ )

Although the EtHex complex is sparingly soluble in water, this liquid incorporates a small amounts of water to form a transparent liquid. The EtHex complex was reacted with aqueous  $\text{NaBH}_4$  solution with varying  $W_0$  values. At higher water content, a similar deep-yellowish colloidal sol as for  $W_0 = 0.3$  was obtained and the resultant solution was observed by TEM after dried on the TEM grid. In the case of  $W_0 = 5$ , the sizes were somewhat larger and the distributions more polydispersed than those obtained from the liquid with  $W_0 = 0.3$ . This result may reflect the enlargement of the hydrophilic silver(I) domains with an increase in the water content. In order to stabilize the reversed-micellar structure in the  $[\text{Ag}(\text{EtHex-en})_2]\text{NO}_3$  liquid, the free ligand was added to the Ag-IL so that the ligand/silver molar ratio became 3:1. When this liquid was reacted with aqueous  $\text{NaBH}_4$  solution, the yellowish silver(0) sol was obtained as well. The TEM observation of the sol gave silver(0) nanoparticles having smaller sizes than in the neat system. This result indicates that the addition of the free ligand makes the hydrophilic core of Ag-IL smaller and stabilizes the reversed-micellar structure.

The characteristic difference in the reaction of the Ag-ILs with aqueous  $\text{NaBH}_4$  solution between  $[\text{Ag}(\text{EtHex-en})_2]\text{NO}_3$  and  $[\text{Ag}(\text{Hex-en})_2]\text{PF}_6$  was reflected in the ordering of the nanostructures of the Ag-ILs observed by the TEM images and the SAXS profiles.

### 3.2 Room-temperature PILs of alkylethylenediaminium coupled with TFSA anion.

As the silver(I) ion is a Lewis acid, a replacement of the silver(I) ion with proton may also have comparable properties of IL as well as PILs. (Scheme 1) The major structural differences between the Ag-ILs and the corresponding PIL are that the Ag-IL has a double-chain and the PIL has a single-chain, and that the latter can form hydrogen-bonding network structures.

Protic ionic liquids (PIL) composed of monoprotic alkylethylenediaminium (alkyl = hexyl and 2-ethylhexyl) cations coupled with bis(trifluoromethanesulfonyl)imide anion (= TFSA) at room temperature have been isolated. (Iida *et al.*, 2009) It is contrast that the monoprotic hexylethylenediaminium (= HexH)TFSA salt tends to be crystallized by cooling while the monoprotic 2-ethylhexylethylenediaminium (= EtHexH)TFSA salt assumed only a glassy state in the solid state. In the liquids, the HexH salt was more fluid than the EtHexH salt.

Protic ionic liquids (PILs) have recently attracted attention from a viewpoint of variable proton activities. PILs are generally more hydrophilic and dissolve metal salts to a larger extent than aprotic ionic liquids (AILs). Alkylethylene-diamines have two amines and have

larger affinity to Lewis acids compared to alkyl amines. Therefore, it is significant to investigate the ionic liquid systems of alkyl ethylenediamines in relation to an interaction with Lewis acids including transition metal ions. As shown in the previous section, alkyl-ethylenediamine silver(I) complexes provided room temperature ionic liquids and showed unique phase behavior. The silver(I) ionic liquids are, however, gradually decomposed by light and temperature and applications to wide fields are limited. As silver ion is a Lewis acid, the proton analogue is expected to form more hydrophilic ionic liquids than the Ag-ILs.

The following four PILs have been isolated: HexH(TFSA), diprotic hexylethylenediaminium bis(trifluoromethanesulfonyl)amide (= HexH<sub>2</sub>(TFSA)<sub>2</sub>), EtHexH(TFSA), diprotic 2-ethylhexylethylene-diaminium bis(tri-fluoromethanesulfonyl)amide (= EtHexH<sub>2</sub>(TFSA)<sub>2</sub>). Of these alkyl-diaminium TFSA salts, monoprotic HexH(TFSA) and EtHexH(TFSA) were liquids at room temperature and were less viscous than the diprotic salts; we have thus studied physical properties of the two monoprotic liquids of HexH(TFSA) and EtHexH(TFSA). We focused on a comparison of the properties between the 2-ethylhexyl and hexyl PILs based on the molecular structures.

Each PIL was prepared by the neutralizations of the alkyl ethylenediamines 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. The CHN elemental analyses were performed with Perkin Elmer model 2400II. With considering the following water content, the elemental analyses gave satisfactory results. The water contents were directly measured using a Karl-Fisher titration, which gave the molar ratios of water ( $W_0$ ) to the respective IL molecules as follows: 0.02 for HexH(TFSA), 0.02 for EtHexH(TFSA), 0.7 for HexH<sub>2</sub>(TFSA)<sub>2</sub>•H<sub>2</sub>O, and 0.9 for EtHexH<sub>2</sub>(TFSA)<sub>2</sub>•H<sub>2</sub>O. The PILs were somewhat hygroscopic and gradually absorbed moisture to have around 0.1–0.2 molar water content. 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<sup>-3</sup> for HexH(TFSA) and 1.32 g cm<sup>-3</sup> for EtHexH(TFSA). The presence of the 2-ethyl branch will expand the assembled structure of the PIL and results in the lowering of the density.

As the diprotic chlorides for both the alkyl ethylenediamines were isolated as crystals, we determined the  $pK_a$  values by titration of both the diprotic chlorides (0.01 mol dm<sup>-3</sup>) with aqueous NaOH solutions at constant ionic strength (0.1 mol dm<sup>-3</sup>, with an 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 super acid ( $pK_a = -4$  (MacFarlane *et al.*, 2006)), a relationship of  $\Delta(pK_a(\text{base}) - pK_a(\text{acid})) > 8$  for the monoprotic PILs holds well. That is, the transfer of the proton from the acid to the base was almost complete. (Nuthakki *et al.*, 2007; Greaves & Drummond, 2008)

The solubilities of HexH(TFSA) and EtHexH(TFSA) liquids in various solvents were tested and 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 and benzene, and were less than 0.1% (w/v) in cyclohexane and hexane. Thus, the present PILs have moderate hydrophilic-hydrophobic balances. As these PILs have the same hydrophobic counter anion of TFSA, the difference in the hydrophilicity-hydrophobicity due to the alkyl chain of the cation was not clearly reflected in the solubilities of the PILs.

Melting was observed by DSC in the temperature range of  $-100$ – $150$  °C. The samples (3–5 mg) were placed in aluminum pans and run at a rate of  $10\text{ K min}^{-1}$  under nitrogen gas at a flow rate of  $20\text{ mL min}^{-1}$ . The results are described in Fig. 6. There is a contrast profile that for HexH(TFSA) a glass transition temperature ( $T_g$ ), a crystallization temperature ( $T_c$ ), and a melting point ( $T_m$ ) were observed while for EtHexH(TFSA) only a glass transition was observed. The larger trend of crystallization for HexH(TFSA) is analogous to that for the corresponding silver(I) complexes. In the latter case, the Hex salt showed a melting point where the enthalpy change ( $\Delta H = 9.4\text{ kJ mol}^{-1}$ ) was smaller than the general melting enthalpies, while for the EtHex salt the solid state was glassy and the glass transition was observed. Similar difference in the DSC profiles has been observed in the counterion and alkyl-chain effects on alkyl-ammonium salts. (Belieres & Angell, 2007) In the present PILs, however, the liquids are present at lower temperature and the difference in the alkyl chains is clearer than the alkyl-ammonium systems.

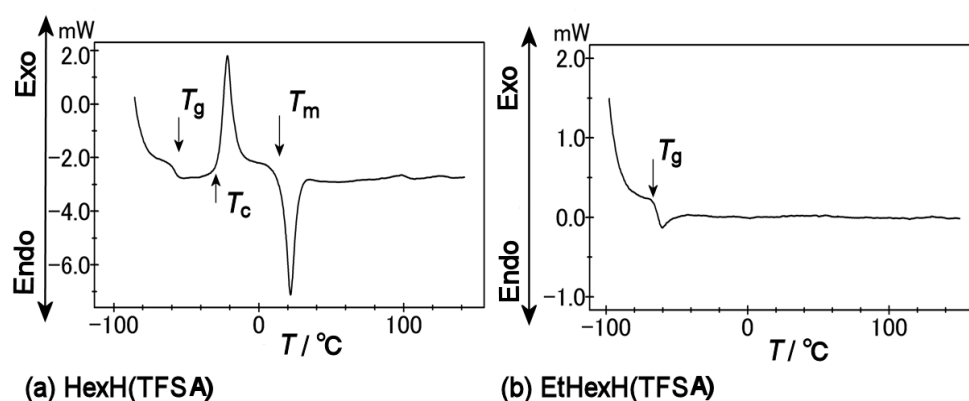


Fig. 6. DSC curves of (a) HexH(TFSA) at  $-80$ – $150$  °C and (b) EtHexH(TFSA) at  $-100$ – $150$  °C.

Wide-angle X-ray diffractions (WAXD) were measured at  $27$  °C and  $-120$  °C similarly to the methods for the Ag-ILs. The WAXD profiles for HexH(TFSA) and EtHexH(TFSA) at solid ( $-120$  °C) states are shown in Fig. 7. The profiles in the liquid states of both systems were close to that of EtHexH (TFSA) in the solid state at  $-120$  °C (Fig. 2 b)). On the other hand, HexH(TFSA) assumed an amorphous-based crystalline state at  $-120$  °C (Fig. 2(a)). The more ordered structure for the Hex silver(I) complex than for the EtHex silver(I) complex in

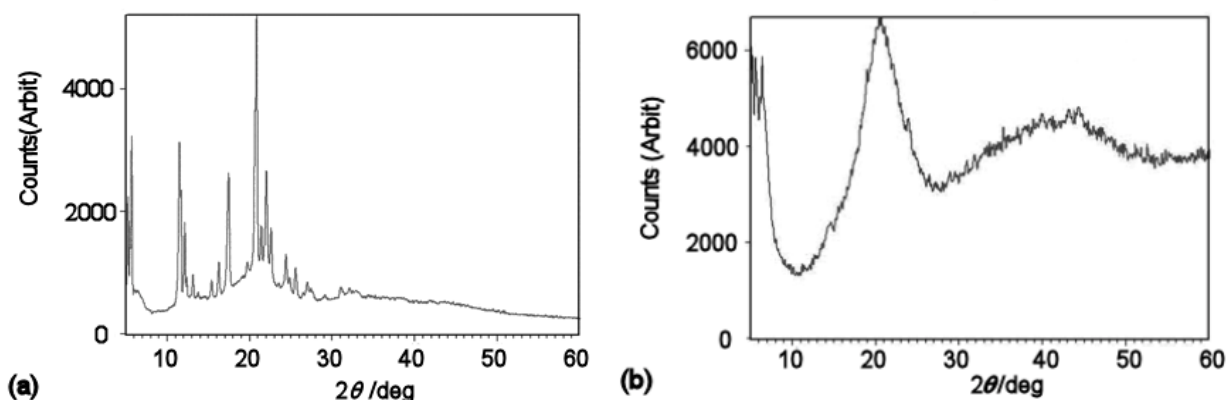


Fig. 7. WAXD profiles of (a) HexH(TFSA) at  $-120$  °C and (b) EtHexH(TFSA) at  $-120$  °C.



WAXD have been observed as described above. It is comparable that  $[\text{Ag}(\text{Hex-en})_2]\text{NO}_3$  is a crystal while  $[\text{Ag}(\text{EtHex-en})_2]\text{NO}_3$  is a viscous liquid at room temperature. The present WAXD explains the DSC profiles that HexH(TFSA) showed both glassy and melting transitions while EtHexH(TFSA) showed only a glassy transition. The introduction of 2-ethyl side-chain has a significant effect on disordering of the structures of the molecular assemblies for both the Ag-IL and the PIL. Thus the melting point of EtHexH(TFSA) was appreciably lowered and these ILs easily assume glassy states in solid.

The dynamic properties of the ILs were studied by the measurements of self-diffusions of the cations and the electric conductivities of the PILs. The measurements were followed by the above method. As both ILs are somewhat hygroscopic, the water content ( $W_0 = 0.01$ – $0.02$ ) of dried ILs was gradually changed to around  $W_0 = 0.2$  through the storage in a vial bottle for several days. We thus compared the self-diffusions of the cations in both the IL systems between  $W_0 = 0.02$  and  $0.2$ . Figure 8 shows Arrhenius plots for the self-diffusions in the range of  $25$ – $70$  °C. The result shows a better linearity even for the EtHex derivative compared to the Ag-ILs described above. This better linearity may be due to the TFSA anion which generally makes fluid ionic liquid systems. The self-diffusion coefficients for the HexH cation were slightly larger than those for the EtHexH cation. This trend is the same as that for the Ag-ILs. As the linearities of the Arrhenius plots were good, the apparent activation energies were obtained as follows. For the HexH and EtHexH cations, the apparent activation energies were  $46.3 \pm 0.8$  kJ mol<sup>-1</sup> and  $45.8 \pm 0.8$  kJ mol<sup>-1</sup>, respectively, at  $W_0 = 0.02$ . At higher water content ( $W_0 = 0.2$ ), the self-diffusions slightly increase and the difference between the HexH and EtHexH cations increases. Larger fluidity of the HexH cation was more clearly detected at  $W_0 = 0.2$ . The apparent activation energies were obtained for the HexH and EtHexH cations as  $41.6 \pm 0.9$  kJ mol<sup>-1</sup> and  $42.7 \pm 0.7$  kJ mol<sup>-1</sup>, respectively.

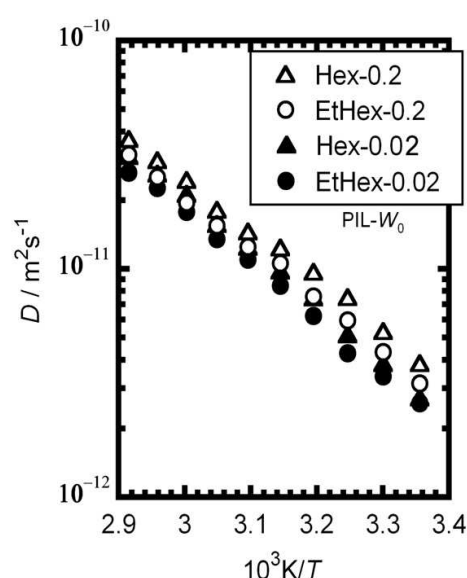


Fig. 8. Diffusion coefficients of HexH and EtHexH cations for  $W_0 = 0.02$  and  $0.2$ .



In relating with the self-diffusions, the electric conductivities for the two PILs were measured at  $25 \pm 1$  °C in a similar manner as for the Ag-ILs. The electric conductivities were  $250 \mu\text{S cm}^{-1}$  for HexH(TFSA) ( $W_0 = 0.02$ ) and  $210 \mu\text{S cm}^{-1}$  for EtHexH(TFSA) ( $W_0 = 0.02$ ). The absolute values of the electric conductivities of the PILs are much larger than those of the Ag-ILs due to both the smaller molecular interactions and the smaller molecular weights. The larger electric conductivity for the Hex PIL than that for the EtHex PIL is consistent with the result of the self-diffusions as observed for the Ag-ILs. Further consideration of the iconicity which can be estimated from the self-diffusions, electric conductivities, and densities (Tokuda, 2004, 2005; Ueno, 2010) will be discussed in a nearly publishing paper.

#### 4. Conclusion

There are particular meanings of the treatment of a series of bis(alkyl-en)metal complexes. As a development of the molecular structures of these silver(I) complexes offers a variety of molecular assemblies, the formation of ionic liquids can be regarded as one of the categories for various kinds of molecular assemblies. In the 2-ethylhexyl derivative of Ag-ILs, the organized nanostructures like W/O microemulsions are more effectively formed compared to the hexyl derivative. Uniformly-sized silver(0) nanoparticles were created by the reaction of the 2-ethylhexyl derivative with aqueous  $\text{NaBH}_4$  solution but the hexyl derivative did not give silver(0) colloids. Such a selectivity for the formation of silver(0) nanoparticles depending on the alkylchains and disuse of organic solvents are the advantages of the methodology using Ag-ILs for the synthesis of silver(0) nanoparticles.

A direct comparison of physicochemical properties between the Ag-ILs and PILs of alkylethylenediamines using the same counteranion is particularly important to understand the structural specificities in the formation of these unique ILs. Although the 2-ethylhexyl derivative of the Ag-IL forms more ordered nanostructures than the hexyl derivative and is advantageous to form silver(0) sols, in both the Ag-IL and PIL systems the former derivative tends to assume vitreous states. Wider alkyl-chain systems containing the same TFSA anion have been intensively studied and a comparison between the Ag-ILs and PILs has been performed to understand the structural effects of the cations on the physicochemical properties. The results will be published in near future.

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