ChemComm
www.rsc.org/chemcomm

Anhydrous proton transport system based on zwitterionic liquid and HTFSI

Masahiro Yoshizawa and Hiroyuki Ohno*
Department of Biotechnology, Tokyo University of Agriculture & Technology, 2-24-16 Nakacho, Koganei, Tokyo 184-8588, Japan. E-mail: ohnoh@cc.tuat.ac.jp; Fax: +81-42-388-7024; Tel: +81-42-388-7024

Received (in Cambridge, UK) 18th March 2004, Accepted 14th June 2004
First published as an Advance Article on the web 21st July 2004

Novel binary ionic liquids based on zwitterionic liquid and HTFSI for anhydrous proton transport were prepared and showed ionic conductivity of about 10^{-2} S cm^{-1} at 150 °C and a zwitterionic liquid content of 60 mol%.

Salts which are molten at room temperature, called ionic liquids (ILs),[1,2] have attracted the attention of many researchers because of their excellent properties such as existence in a liquid-state over a wide temperature range, relatively low viscosity, non-volatility, non-flammability, high ion content, high ionic conductivity at room temperature, and so on. Current topics concerning these unique salts are divided into two categories, one is neoteric solvents as environmentally benign reaction media,[1,2] and the other is electrolyte solutions for electrochemical applications.[3]

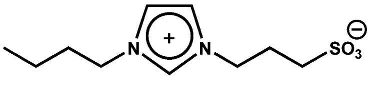
Recently, ILs have been studied as proton transfer media under water-free conditions with a view to fuel cell applications.[4–10] Most of these ILs are called “Brønsted acid–base ILs”.[7,8] Brønsted acid–base ILs can be obtained by simple couples of a wide variety of tertiary amines with various acids. There are many systems showing melting points (Tm) below 100 °C and high ionic conductivity of over 10^{-2} S cm^{-1} at 130 °C. Since they have activated protons, they can be used as proton conductors for the fuel cell electrolyte in a wide temperature range.

Generally, the very high ionic conductivity of IL systems is attributed to the high mobility of the IL itself. In applications such as the fuel cell, where conduction of only single ion species (*e.g.* protons) is required, no migration of IL component ions is favorable. A new matrix should be designed to inhibit the migration of the component ions. One possibility is to prepare an IL based on a zwitterionic liquid (ZIL),[11] that is one in which both cation and anion are tethered. We have already confirmed that the mixture of ZIL and LiTFSI is liquid at ambient temperature.[11,12] Both a high lithium transference number and excellent thermal stability were observed in the system.

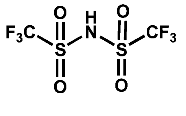
In the present study, novel binary ILs based on ZIL and HTFSI are prepared for anhydrous proton transport. 1-(1-Butyl-3-imidazolio)propane-3-sulfonate (BIm3S)† was adopted as a ZIL. Thermal properties and ionic conductivities of mixtures were also investigated.

The mixture of BIm3S and bis(trifluoromethanesulfonyl)imide (HTFSI) was a less viscous and colorless liquid at room temperature, especially in the presence of a less than equimolar amount of BIm3S. Table 1 summarizes thermal properties of novel binary ILs based on BIm3S and HTFSI. Although BIm3S and HTFSI showed their Tm at 56 °C and 179 °C, respectively, the mixture showed only a glass transition temperature (Tg). The Tg of the mixture increased with increasing BIm3S fraction. Interestingly, the decomposition temperature (Td) of the mixture also increased with increasing BIm3S fraction. In addition, the Td of these mixtures exceeded 300 °C despite the sublimation of HTFSI.[7] When the BIm3S mole fraction was 60%, the maximum Td was obtained at 347 °C, which is higher than that of pristine BIm3S. It is a similar tendency to that for ZIL/LiTFSI mixtures.[12] The combination of imidazolium cation and TFSI anion might be responsible for the formation of a thermally stable couple. In other words, since ZIL can promote dissociation of added acids, the mixture could generate activated protons. This hypothesis agrees with the results reported by Davis *et al.* and Shreeve *et al.*[13] They confirmed that ZIL/acid mixtures act as an acidic catalyst for esterification of alcohols and acetate derivatives. Furthermore, the thermal stability of the mixture was enough for the application of fuel cell electrolyte at ZIL excess condition.

The ionic conductivity of these mixtures was investigated for anhydrous proton transport. Fig. 1 shows isothermal ionic conductivities for BIm3S/HTFSI mixtures as a function of BIm3S content. The mixtures showed almost the same ionic conductivity, about 10^{-4} S cm^{-1} at room temperature until the BIm3S mole



BIm3S



HTFSI

Table 1 Thermal properties of BIm3S/HTFSI mixtures at various molar ratios

Mole fraction of BIm3S (%)	Tg/°C[a]	Tc/°C[a]	Tm/°C[a]	Td/°C[b]
0	—[c]	—[c]	56	*[d]
20	−60	—[c]	—[c]	*[d]
33.3	−60	—[c]	—[c]	115
50	−58	—[c]	—[c]	204
60	−49	—[c]	—[c]	347
66.7	−38	—[c]	—[c]	339
80	−29	—[c]	—[c]	334
100[e]	17	85	179	329

[a] Glass transition temperature (Tg), crystallization temperature (Tc), and melting temperature (Tm) were determined by using differential scanning calorimetry (DSC-6200; Seiko Instruments Inc.) at a scan rate of 10 °C min^{-1}. [b] Temperature of 10% weight loss during heating process from room temperature at 10 °C min^{-1} under dry nitrogen by using thermogravimetry (TG/DTA-220; Seiko Instruments Inc.). [c] Not detected. [d] Not measured. [e] Scan rate was 20 °C min^{-1}for both cooling and heating processes.

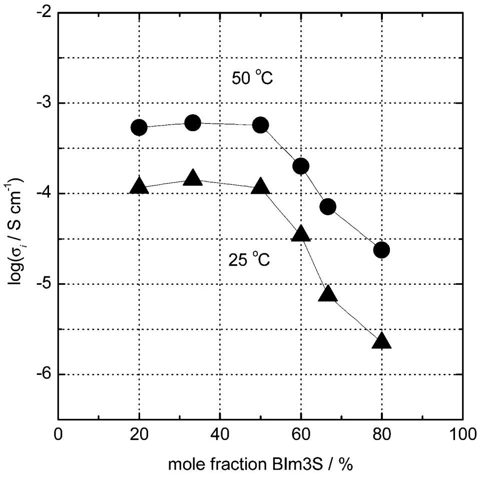


Fig. 1 Isothermal conductivities for BIm3S/HTFSI mixtures as a function of BIm3S content.

DOI: 10.1039/b404137b

fraction reached 50%. And then, the ionic conductivity gradually decreased with increasing BIm3S content. This behavior can be explained by the change of Tg of the mixture, that is, it is considered that the ionic conductivity is strongly affected by the carrier ion mobility. The ionic conductivity of ILs is also affected by viscosity. However, no viscosity data were obtained due to the limitations of our viscosity measurement apparatus.

The ionic conductivity of the mixture of BIm3S (60%) was measured in a wide temperature range as shown in Fig. 2. Although higher ionic conductivity was demonstrated at excess HTFSI condition as shown in Fig. 1, this was relatively unstable at higher temperature. Therefore, the mixture containing 60 mol% BIm3S was examined. The ionic conductivity increased continuously even in the range of over 100 °C and was about 10^{-2} S cm^{-1} at 150 °C, almost equal to that of other proton conductive systems. Temperature dependence of the ionic conductivity is shown as an upper convex curve. A curved relation was also seen in the Arrhenius plots. Such a tendency is observed for all mixtures used in the present study. Generally, an ion conductive process is expressed by the Vogel–Fulcher–Tamman (VFT) equation (eqn. 1)[14] which empirically explains the temperature dependence of viscosity in amorphous materials. The best fitting result is also depicted as the solid line in Fig. 2. The temperature dependence of the ionic conductivity for BIm3S/HTFSI obeyed the VFT equation quite well. All systems used in the present study also obeyed it (data not shown). There are two typical mechanisms of proton conduction *i.e.*, proton hopping (Grotthuss mechanism) and matrix transport (vehicle mechanism).[7,15] Since the ionic conductivity agrees with the VFT equation, the vehicle mechanism should mainly govern the proton conduction in this mixture. However, it is still necessary to study the proton conductive mechanism in the mixture.

$$\sigma = \sigma_0 \exp\left(\frac{-B}{T - T_0}\right) \qquad (1)$$

These ZIL/acid mixtures are expected to be thermally stable proton conductors under water-free conditions. The study of the mixtures for application in fuel cell electrolytes is in progress now.

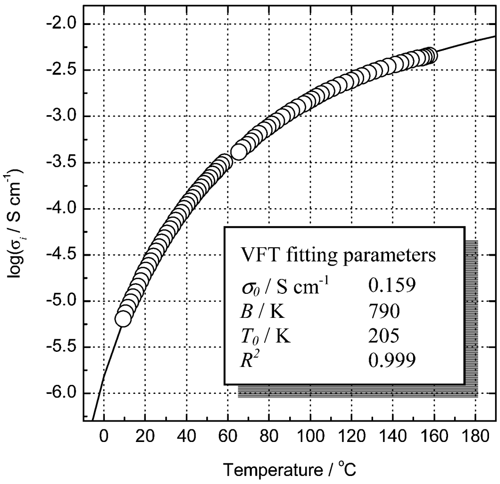


Fig. 2 Temperature dependence of the ionic conductivity for the BIm3S/HTFSI mixture (mole fraction of BIm3S is 60%).

The present study was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Science, Sports and Technology, Japan (#14205136). The present study was carried out under the 21st Century COE program, Future Nano Materials.

Notes and references

† Synthetic procedure for BIm3S. BIm3S was synthesized according to previous reports.[11,13] 1-Butylimidazole (Aldrich, 98%) (4.85 g, 3.9×10^{-2} mol) was dissolved in acetone (100 ml), and then 1,3-propane sultone (Tokyo Kasei, > 99%) (4.76 g, 3.9×10^{-2} mol) was added to the solution. The solution was stirred under dry nitrogen at room temperature for 3 days. The insoluble zwitterion was separated by filtration. It was further purified by recrystallizing from acetonitrile twice to give 8.55 g (89%) as a white solid. ^1H NMR (DMSO-d_6, 500 MHz): δ 0.844 (t, 3H), 1.201 (m, 2H), 1.724 (m, 2H), 2.048 (m, 2H), 2.350 (t, 2H), 4.108 (t, 2H), 4.256 (t, 2H), 7.714 (s, 1H), 7.737 (s, 1H), 9.137 (s, 1H).

Elemental analysis calcd. for $C_{10}H_{18}N_2O_3S$: C, 48.75; H, 7.38; N, 11.37. Found: C, 48.59; H, 7.24; N, 11.44%. HTFSI (Morita Chemical Industries) was used as received.

1 (*a*) *Ionic Liquids: Industrial Applications for Green Chemistry*, R. D. Rogers and K. R. Seddon, Eds., ACS Symposium Series 818, American Chemical Society: Washington, DC, 2002; (*b*) *Ionic Liquids as Green Solvents: Progress and Prospects*, R. D. Rogers and K. R. Seddon, Eds., ACS Symposium Series 856, American Chemical Society: Washington, DC, 2003.

2 (*a*) T. Welton, *Chem. Rev.*, 1999, **99**, 2071; (*b*) *Ionic Liquids in Synthesis*, P. Wasserscheid and T. Welton, Eds., Wiley-VCH, Weinheim, 2003.

3 *Ionic Liquids: The Front and Future of Material Development*, H. Ohno, Ed., CMC, Tokyo, 2003.

4 M. Doyle, S. K. Choi and G. Proulx, *J. Electrochem. Soc.*, 2000, **147**, 34.

5 (*a*) M. Hirao, H. Sugimoto and H. Ohno, *J. Electrochem. Soc.*, 2000, **147**, 4168; (*b*) M. Yoshizawa, W. Ogihara and H. Ohno, *Electrochem. Solid-State Lett.*, 2001, **4**, E25; (*c*) H. Ohno and M. Yoshizawa, *Solid State Ionics*, 2003, **154–155**, 303.

6 M. Yoshizawa, W. Xu and C. A. Angell, *J. Am. Chem. Soc.*, 2003, **125**, 15411.

7 A. Noda, M. A. B. H. Susan, K. Kudo, S. Mitsushima, K. Hayamizu and M. Watanabe, *J. Phys. Chem. B*, 2003, **107**, 4024.

8 (*a*) M. A. B. H. Susan, A. Noda, S. Mitsushima and M. Watanabe, *Chem. Commun.*, 2003, 938; (*b*) M. A. B. H. Susan, M. Yoo, H. Nakamoto and M. Watanabe, *Chem. Lett.*, 2003, **32**, 836.

9 M. Yamada and I. Honma, *Electrochim. Acta*, 2003, **48**, 2411.

10 J. Sun, L. R. Jordan, M. Forsyth and D. R. MacFarlane, *Electrochim. Acta*, 2001, **46**, 1703.

11 (*a*) M. Yoshizawa, M. Hirao, K. Ito-Akita and H. Ohno, *J. Mater. Chem.*, 2001, **11**, 1057; (*b*) M. Yoshizawa, A. Narita and H. Ohno, *Aust. J. Chem.*, 2004, **57**, 139.

12 H. Ohno, M. Yoshizawa and W. Ogihara, *Electrochim. Acta*, 2003, **48**, 2079.

13 (*a*) A. C. Cole, J. L. Jensen, I. Ntai, K. L. T. Tran, K. J. Weaver, D. C. Forbes and J. H. Davis, Jr., *J. Am. Chem. Soc.*, 2002, **124**, 5962; (*b*) Y. R. Mirzaei, H. Xue and J. M. Shreeve, *Inorg. Chem.*, 2004, **43**, 361.

14 (*a*) H. Vogel, *Phys. Z.*, 1921, **22**, 645; (*b*) G. S. Fulcher, *J. Am. Ceram. Soc.*, 1925, **8**, 339; (*c*) G. Tamman and W. Hesse, *Z. Anorg. Allg. Chem.*, 1926, **156**, 245.

15 W. Münch, K.-D. Kreuer, W. Silvestri, J. Maier and G. Seifert, *Solid State Ionics*, 2001, **145**, 437.