

Zwitterionic Liquid/Acid Mixtures as Anhydrous Proton Conducting Systems

Masahiro Yoshizawa¹, Maria Forsyth², Douglas R. MacFarlane¹, and Hiroyuki Ohno³

¹School of Chemistry and ²School of Physics and Materials Engineering, Monash University, Wellington Road, Clayton, Victoria 3800, AUSTRALIA

³Department of Biotechnology, Tokyo University of Agriculture & Technology 2-24-16 Nakacho, Koganei, Tokyo 184-8588, JAPAN

Introduction

It is well known that ionic liquids (ILs) show quite high ionic conductivity at room temperature without adding solvents.¹ Generally, very high ionic conductivity of IL systems is attributed to the high mobility of IL itself. In applications such as the fuel cell, where conduction of only single ion species (eg. protons) is required, the migration of IL component ions remains as a serious drawback. To overcome this drawback, 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),² 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.^{2,3} Both high lithium transference number and excellent thermal stability were observed in this system.

In this report, novel binary ILs based on ZIL and HTFSI are prepared for anhydrous proton transport. Thermal properties and ionic conductivity of ZIL/HTFSI mixtures are investigated.

Experimental

The synthetic procedure for 1-(1-Butyl-3-imidazolium)propane-3-sulfonate (BIm3S), which is adopted as a ZIL, is described. 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 two times to give 8.55 g (89 %) as a white solid. Bis(trifluoromethanesulfonyl)-imide (HTFSI) (Morita Chemical Industries) was used as received.

Results & Discussion

Figure 1 shows phase diagram of the mixture of BIm3S and HTFSI. BIm3S and HTFSI showed their T_m 's at 56 °C and 179 °C, respectively. However, the mixture showed only a glass transition temperature (T_g) over a wide range of BIm3S content. T_g of the mixtures was constant at about -60 °C until 50mol% BIm3S, and then increased with increasing BIm3S fraction. Interestingly, the decomposition temperature (T_d) of the mixture increased with increasing BIm3S fraction as shown in Figure 1. In addition, T_d of these mixtures exceeded 300 °C despite the sublimation of HTFSI.⁴ When BIm3S mole fraction was 60%, the maximum T_d was obtained at 347 °C, which is higher than that of pristine BIm3S. The combination of the imidazolium cation and the TFSI anion might be responsible for the formation of a thermally stable couple. In other words, since the ZIL can promote dissociation of added acids, the mixture could generate activated protons. Furthermore,

the thermal stability of the mixture was sufficient for application as a fuel cell electrolyte.

Figure 2 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 in the range of 20 – 50mol% BIm3S. After that, their ionic conductivity monotonously decreased with increasing BIm3S content. This behavior would reflect the increase in T_g at the same BIm3S content.

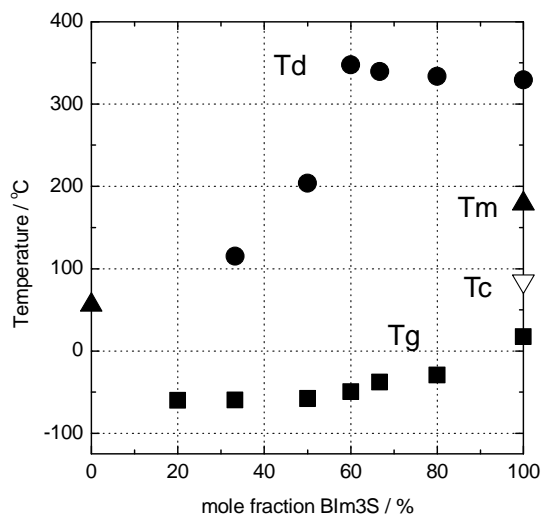


Figure 1 Phase diagram of the mixture of BIm3S and HTFSI.

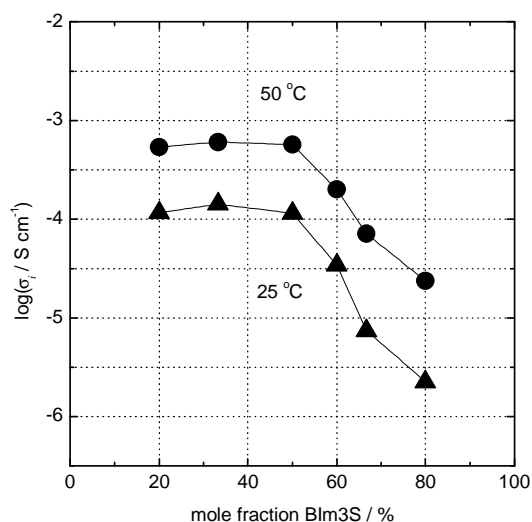


Figure 2 Isothermal conductivities for BIm3S/HTFSI mixtures as a function of BIm3S content.

References

1. *Ionic Liquids in Synthesis*, P. Wasserscheid and T. Welton, Eds., Wiley-VCH, Weinheim, 2003.
2. M. Yoshizawa, M. Hirao, K. Ito-Akita and H. Ohno, *J. Mater. Chem.*, 2001, **11**, 1057.
3. M. Yoshizawa, A. Narita and H. Ohno, *Aust. J. Chem.*, 2004, **57**, 139.
4. A. Noda, M. A. B. H. Susan, K. Kudo, S. Mitsushima, K. Hayamizu and M. Watanabe, *J. Phys. Chem. B*, 2003, **107**, 4024.