ZWITTERIONIC LIQUID/ACID MIXTURES AS ANHYDROUS PROTON CONDUCTING SYSTEMS

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ABSTRACT

Novel binary ILs based on zwitterionic liquids (ZILs) and a super strong acid, bis((trifluoromethyl)sulfonyl)amide (HTFSI), are prepared for anhydrous proton transport. Although both the ZILs used in this study and HTFSI are solid at room temperature, the mixtures became viscous liquids, which show only a glass transition, \(T_g\), after mixing. The \(T_g\) of the mixtures decreased with increasing HTFSI content up to 50%. The \(T_g\) then remained at -60 °C in the range of excess HTFSI content. The mixtures were thermally stable over 300 °C when HTFSI content was less than 40%. The mixtures showed ionic conductivity around \(10^{-4}\) S cm\(^{-1}\) at room temperature when the HTFSI content was more than 50%. When HTFSI content was 40%, the mixture showed ionic conductivity of \(10^{-2}\) S cm\(^{-1}\) at 150 °C.

INTRODUCTION

It is well known that ionic liquids (ILs) show quite high ionic conductivity at room temperature without added solvents (1,2). Recently, ILs have been studied as proton transfer media under water-free condition in view of fuel cell applications (3-12). Most of these ILs are called “Brensted acid-base ILs” (8,9). Brensted acid-base ILs can be obtained by simple combination of a wide variety of tertiary amines with various acids. There are many systems showing melting points (\(T_m\)) below 100 °C and high ionic conductivity 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 over a wide temperature range.

Generally, the 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) (13,14), that is one in which both cation and anion are tethered. We have already confirmed that the mixtures of ZIL and LiTFSI are liquid at

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ambient temperature (13,14). 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

Materials

Synthesis of ZILs. Two ZILs, 1-(1-butyl-3-imidazolio)propane-3-sulfonate (BIm3S) and 1-(1-ethyl-3-imidazolio)propane-3-sulfonate (Elm3S), were prepared as shown in Figure 1. The synthetic procedure for BIm3S is described as an example of ZIL synthesis. 1-Butylimidazole (Aldrich, 98%) (4.85 g, 3.9 x 10^{-2} mol) was dissolved in acetone (100 ml), and then 1,3-propane sultone (Tokyo Kasei, >99%) (4.76 g, 3.9 x 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.

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\text{BIm3S} \quad \text{Elm3S}
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Figure 1. Structures of ZILs used in this report.

Preparation of the ZIL/HTFSI mixtures. Bis((trifluoromethyl)sulfonyl)amide (HTFSI) (Morita Chemical Industries) was used as received. The ZIL was mixed with certain amounts of HTFSI without solvent. After that, the mixtures were moderately heated with stirring.

Measurements

Thermal Analyses. Glass transition temperature (Tg), crystallization temperature (Tc), and melting temperature (Tm) were determined by using differential scanning calorimetry (DSC-6200; Seiko Instruments Inc.) at scan rate of 10 °C min^{-1}. Temperature of weight loss was obtained during heating from room temperature at 10 °C min^{-1} under a dry nitrogen by using thermogravimetry (TG/DTA-220; Seiko Instruments Inc.).

Electrochemical Measurements. Ionic conductivity of the obtained mixtures was measured with the complex-impedance method using an impedance analyzer (Solartron model 1260; Schlumberger). The conductivity measurements were performed in dry nitrogen gas atmosphere in the temperature range of +10 to +160 °C.
RESULTS AND DISCUSSION

Thermal behavior with respect to the mixtures of BIm3S and HTFSI has been analyzed. BIm3S showed Tg, Tc, and Tm at 17, 85, and 179 °C (scan rate was 20 °C min\(^{-1}\) both cooling and heating processes), whereas the Tm of HTFSI was 56 °C (Figure 2). These are solid at room temperature, respectively. Interestingly, these became viscous liquid at room temperature after mixing these materials. Figure 3 shows DSC traces of the mixtures of BIm3S and HTFSI. The Tm disappeared at all HTFSI mole fractions adopted in this study, and these mixtures showed only Tg below -20 °C. In addition, the Tg decreased with increasing the HTFSI content up to 50 %, then remained constant at around -60 °C. Such tendency was also observed in the mixtures of ZIL and LiTFSI (13,14). Therefore, it could be a result of the combination of the onium cation and the TFSI anion having the plasticizing effect. When other anion species were mixed with ZIL, those mixtures also became amorphous materials at room temperature. However, their Tg was higher than that of TFSI mixtures. These results reveal that the TFSI anion is a very useful choice to mix with ZILs in order to decrease the Tg for the mixtures.

Figure 2. DSC traces of (a) BIm3S and (b) HTFI at the second heating process.
Figure 4 summarizes the $T_g$ of the mixtures of ZIL and HTFSI as a function of HTFSI content. It includes the results for Elm3S for comparison. Both Blm3S and Elm3S showed almost the same $T_g$ values about 20 °C. After adding HTFSI, those mixtures showed almost the same $T_g$ as well, except for HTFSI content of 20%. Since these ZILs are similar structure, the effect of ZIL structure on $T_g$ would be expected to be only slight.

Next, the thermal stability of the mixtures was analyzed by means of thermogravimetry (Figure 5). Since HTFSI seems to sublime above its Tm (56 °C), the
thermal stability was not investigated (8). BIm3S was thermally stable up to over 300 °C. Surprisingly, the mixtures of BIm3S and HTFSI were thermally stable beyond that of pure BIm3S, when the HTFSI content was no more than 40 %. In the case when HTFSI was more than equimolar amount against BIm3S, the weight loss of the mixtures showed two steps. The first step, which should agree with the decomposition of excess HTFSI, was observed at around 100 °C. The second step started at almost same temperature with that of lower HTFSI contents. Elm3S also showed the same tendency concerning the thermal stability of the mixture with HTFSI. It is suggested that ZIL can considerably increase the thermal stability of HTFSI according to these results.

Figure 6 shows isothermal conductivities of the mixture of ZIL and HTFSI as a function of HTFSI content. The ionic conductivity of the mixtures increased with increasing HTFSI content up to 50 %. After that, they kept constant value around $10^{-4}$ S cm$^{-1}$ at room temperature. This tendency is consistent with that of Tg. In the case of Elm3S, the ionic conductivity dropped at HTFSI is 33.3 %. This could be caused from the crystallization of the mixture at this mixing ratio. In fact, the mixture showed Tm at 70 °C. Their ionic conductivity reached about $10^{-3}$ S cm$^{-1}$ at 50 °C when HTFSI was over 50 %. This value is equal to that of other IL systems (8-10). It can be pointed out that there are two typical mechanisms of proton conduction i.e., proton hopping (Grotthuss mechanism) and matrix transport (vehicle mechanism) even in IL systems (8,15). Thus far, there is no clear evidence concerning the proton conduction mechanism in the ZIL/HTFSI mixtures. We are in the process of measuring diffusion coefficients to clarify this.

![Figure 5. Thermogravimetric analyses of BIm3S and the mixtures.](image)
Figure 6. Isothermal conductivities of the mixtures of ZIL and HTFSI as a function of HTFSI mole fraction.

The ionic conductivity of the mixture of BIm3S and HTFSI (40%) was measured in a wide temperature range as shown in Figure 7. Although higher ionic conductivity was demonstrated at excess HTFSI condition as shown in Figure 6, these were relatively unstable at higher temperature. Therefore, the mixture containing 40 mol% HTFSI was examined. The ionic conductivity increased continuously even in the range above 100 °C and was about $10^{-2}$ S cm$^{-1}$ at 150 °C. It thus feasible that such mixtures could be applied to fuel cells.
CONCLUSIONS

Novel binary ILs based on a ZIL and HTFSI are prepared for anhydrous proton transport applications. Although ZILs used in this study and HTFSI are solid at room temperature, the mixtures are viscous liquids, which show only Tg. The Tg of the mixtures decreased with increasing HTFSI content up to 50 %. The Tg then remained constant at -60 °C at higher HTFSI content. Interestingly, the mixtures were thermally stable over 300 °C when the HTFSI content was less than 40 %. The mixtures showed the ionic conductivity around 10^{-4} S cm^{-1} at room temperature when HTFSI content was more than 50 %. This trend agrees with that of the Tg. When HTFSI content was 40 %, the ionic conductivity was obtained in the range of over 100 °C. In addition, the mixture showed ionic conductivity of 10^{-2} S cm^{-1} at 150 °C. It will be useful to apply to the electrolyte for fuel cell. We are in the process of measuring diffusion coefficients to clarify the proton conductive mechanism in these mixtures.

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