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Low-melting zwitterion: effect of oxyethylene units on thermal properties and conductivity[†]

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An imidazolium-based zwitterion containing two oxyethylene units was obtained as a colorless liquid at room temperature. The equimolar mixture of the liquid zwitterion and lithium bis(trifluoromethylsulfonyl)amide showed an ionic conductivity of over 10^{-4} S cm⁻¹ at 80 °C, which was higher than those of mixtures composed of analogous solid zwitterions.

Ever since air- and water-stable ionic liquids (ILs) were reported in the early 1990's,¹ ILs have been studied over a wide range of areas including electrochemical applications.² Especially for battery applications, ILs have been considered as promising materials to replace volatile and flammable electrolyte solutions because of their desirable properties such as non-volatility, non-flammability, wide electrochemical window, and high conductivity of over 10^{-2} S cm⁻¹ at room temperature.³ A number of ILs composed of aliphatic and alicyclic ammonium cations have already been reported as lithium battery electrolytes due to their high electrochemical stability toward lithium.⁴ However, those ILs tend to have higher melting points and viscosity values than imidazoliumbased ILs.⁵ This tendency results in a significant decrease in the conductivity of ILs. Angell et al., Matsumoto et al., and Sato et al.⁶ have proposed that the introduction of an ether oxygen into cations and anions is an useful methodology for the preparation of low-melting and low-viscosity quaternary ammonium ILs. In addition to this, even alkali metal salts having multiple ether units can be obtained as liquids at room temperature.⁷

Ohno *et al.* have designed and synthesized the zwitterion structures in which both cation and anion units attach to the parent molecules.⁸ A number of studies have been aimed at developing electrolyte materials for lithium batteries and fuel cells.⁹ Zwitterions can dissolve many kinds of inorganic salts^{8b,10} and can promote lithium ion transport in polymer electrolytes,¹¹ that is, zwitterions can act as solvents or as ion dissociators. Furthermore, when a zwitterion was added to a IL/lithium salt mixture as a salt dissociator, the coulombic

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efficiency of the electrolyte system was significantly improved.¹² These results clearly show that zwitterions can act as excellent target ion conductors and can promote target ion transport in electrolyte solutions. Most zwitterions, however, have melting points above 100 $^{\circ}C^{8b,13}$ because of a decrease in the motional freedom of each ion and strong molecular interactions. It is quite difficult to depress the inherent melting points of zwitterions. Although the addition of lithium bis(trifluoromethylsulfonyl)amide (LiN(Tf)2) or 1,1,1-trifluoro-N-(trifluoromethylsulfonyl)methanesulfoneamide (HN(Tf)₂) to zwitterions results in a liquid at room temperature,^{8b,9b,13,14} the equimolar mixtures of such zwitterions and LiN(Tf)₂ gradually crystallize after a few weeks. The ionic conductivities of the solid mixtures are quite low. The crystallization of zwitterion/LiN(Tf)2 mixtures will be prevented by lowering the melting points of the zwitterions.

In this study, we have synthesized zwitterions containing oxyethylene (OE) units: 3-(1-(2-methoxyethyl)-1H-imidazol-3-ium-3-yl)propane-1-sulfonate (OE1imps) and 3-(1-(2-(2-methoxyethyl)-1H-imidazol-3-ium-3-yl)propane-1-sulfonate (OE2imps), for lowering their melting points, as shown in Fig. 1. 3-(1-Butyl-1H-imidazol-3-ium-3-yl)propane-1-sulfonate (Bimps) is also synthesized with butylimidazole and 1,3-propanesultone for comparison.⁸ The effects of OE units on the thermal and physical properties are investigated.

These zwitterions were characterized by FAB-MS, ¹H NMR, ¹³C NMR, and elemental analyses (see ESI†). Bimps and OE1imps containing one OE unit were obtained as white solids at room temperature, whereas OE2imps containing two OE units was a high-viscosity liquid at room



Bimps

Fig. 1 Structures of zwitterions synthesized in this study.

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Fig. 2 (a) DSC traces on their second heating $(10 \text{ }^{\circ}\text{C min}^{-1})$ for the zwitterions. Dashed arrows indicate the T_g values of the zwitterions. (b) Expanded T_g signals of the zwitterions.

temperature. Fig. 2 shows DSC diagrams of the zwitterions on their second heating trace (10 $^{\circ}$ C min⁻¹). Bimps with a butyl group on the side chain showed a glass transition temperature (T_{g}) at 11 °C, a crystallization temperature (T_{c}) at 73 °C, and a melting point (T_m) at 170 °C. OE1imps with an ether unit on the side chain showed a $T_{\rm g}$ at 7 °C, a $T_{\rm c}$ at 72 °C, and a $T_{\rm m}$ at 175 °C. The $T_{\rm m}$ of OE1imps was almost the same as that of Bimps. OE1imps also showed an endothermic peak at 166 °C before melting, which suggested that the crystal was transformed into a different crystal form. The solid-solid phase transition for OE1imps suggests that the OE unit enhances the motional freedom of zwitterions even in the solid phase. Similar behavior was also observed for the ammonium-type zwitterions containing an OE unit on the side chain of cations.¹⁵ In contrast, OE2imps showed only a T_{σ} at -32 °C, demonstrating that two OE units were effective in lowering the crystallinity of zwitterions. This fact suggests that the large enhancement of motional freedom by the introduction of two OE units depressed the molecular interaction of zwitterions. Although the introduction of alkyl chains would also be effective in lowering the crystallinity of zwitterions, it is known that zwitterions with long alkyl chains show a liquid crystalline thermotropic behavior.16

We also measured the decomposition temperature (T_d) of zwitterions by measurement with a thermogravimetric apparatus. While both Bimps and OE1imps showed T_d values at 330 °C, the T_d of OE2imps was 320 °C. The zwitterions were thermally stable up to around 300 °C (see ESI†). We found that attaching OE units to the zwitterions depressed the crystallinity without reducing their thermal stability.

A large decrease of over 40 °C in T_g for OE2imps was observed as compared with those of Bimps and OE1imps.

Although such low T_g values will be desirable in the transport properties such as fluidity and conductivity for ILs,¹⁷ OE2imps showed low fluidity at room temperature. The low fluidity of zwitterions could be explained from the viewpoint of "fragility", an indicative parameter for temperature dependence of log(viscosity) on T_g/T , which is between 0 and 1.17,18 Glass-forming liquids are defined as strong or fragile on the basis of the plot. Strong liquids show a linear increase in log(viscosity) with T_g/T , while fragile liquids maintain much lower viscosity values than strong liquids over a wide temperature range. The fragility of ILs has been studied by many researchers¹⁹ since Angell et al.¹⁷ reported the parameter at 2003. In general, ILs are very fragile liquids. For instance, the plot of 1-butyl-3-methylimidazolium bis-oxalato-orthoborate overlaps that of an extremely fragile melt CKN (40Ca(NO₃)₂:60KNO₃) almost exactly in the plot. In this study, no viscosity data of OE2imps was obtained due to the limitation of our viscosity measurement apparatus. The fragility of liquid zwitterions will be discussed elsewhere.

The zwitterions were mixed with an equimolar amount of LiN(Tf)₂ in order to investigate their dissociator ability. Fig. 3 shows the ionic conductivities of zwitterion/LiN(Tf)2 mixtures as a function of temperature. The lithium salt content is 50 mol% for all the mixtures. The mixtures were obtained as high-viscosity liquids at room temperature for all the zwitterions. After addition of the lithium salt, the $T_{\rm m}$ of the mixtures with Bimps and OE1imps disappeared. This behavior is due to the formation of an ionic liquid-like moiety by the coupling of the imidazolium cation and the added N(Tf)₂ anion.^{13,20} This interpretation will be supported by the results that the $T_{\rm d}$ of the equimolar mixtures rose to 390 °C, which was equal to the values of traditional ILs composed of N(Tf)₂ anions.²¹ Bimps/LiN(Tf)₂ and OE1imps/LiN(Tf)₂ mixtures showed $T_{\rm g}$ at -18 and -12 °C, respectively. The $T_{\rm g}$ of OE2imps/LiN(Tf)₂ mixture was -27 °C, which was almost the same as that of pristine OE2imps.



Fig. 3 Ionic conductivities of zwitterion/LiN(Tf_2) mixtures as a function of temperature. The lithium salt content is 50 mol% for all the mixtures.

A curved relationship in the Arrhenius plots was observed for all the mixtures used in the present study. In general, an ion conductive process is expressed by the Vogel–Fulcher– Tamman (VFT) equation,²² which empirically explains the temperature dependence of viscosity in amorphous materials. The best fitting results are also depicted as the solid lines in Fig. 3. Thus, the temperature dependence of the ionic conductivity for all the mixtures obeyed the VFT equation quite well.

The OE1imps/LiN(Tf)₂ mixture showed the ionic conductivity of 9.2×10^{-5} S cm⁻¹ at 80 °C, which was almost identical to that of Bimps/LiN(Tf)₂ mixture. The ionic conductivity of OE2imps/LiN(Tf)2 mixture was 3.8×10^{-4} S cm⁻¹ at 80 °C, which was 4 times higher than that of OE1imps/LiN(Tf)₂ mixture. It is known that there is a good correlation between ionic conductivity values and T_{g} values for ILs.²³ The higher conductivity of the OE2imps/ LiN(Tf)₂ mixture should be mainly attributed to the T_{g} of -27 °C, which is the lowest among the mixtures. In addition, OE units attached to the imidazolium cations will be effective not only in lowering the crystallinity of zwitterions but also in enhancing the dissociation of lithium salts and the mobility of lithium ions in the matrix. The lithium transference number (t_{Li+}) and the electrochemical stability are important properties for applying zwitterions as electrolyte materials. Recently, the t_{Li+} values were determined by an electrochemical technique to be over 0.5 for the equimolar mixtures of LiN(Tf)₂ and the zwitterions containing dissociable anion structures such as sulfonate, amide, and borate anions.^{13,14} It has been suggested that zwitterions act as excellent ion conductive matrices, in which the target ions such as lithium cations preferentially migrate. It is, however, well known that poly(ethylene oxide) solubilizes lithium salts, which is attributable to a large polarity on the ether oxygen. OE units would trap lithium cations through ion-dipole interactions. Those investigations are now in progress and will be reported elsewhere.

In conclusion, the zwitterion containing two OE units on the imidazolium cation was obtained as a viscous liquid at room temperature. In addition, the equimolar mixture of the liquid zwitterion and $\text{LiN}(\text{Tf})_2$ maintained a liquid state even after a few months and showed higher ionic conductivity than those of other mixtures based on the solid zwitterions. Ether groups were effective not only in lowering the crystallinity of zwitterions but also in improving the ionic conductivity. Low-melting and low-viscosity zwitterions will be an interesting matrix for electrochemical applications.

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