

A New Family of Zwitterionic Liquids Arising from a Phase Transition of Ammonium Inner Salts Containing an Ether Bond

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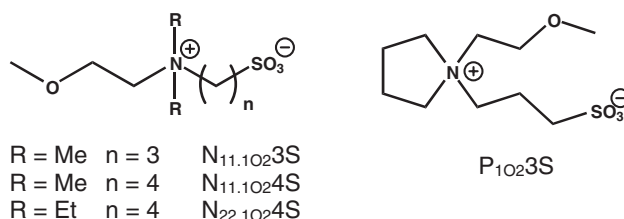
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Aliphatic and alicyclic ammonium inner salts containing an ether bond were prepared as a new family of zwitterionic liquids. Ether bond is not only effective for lowering melting points of ammonium-type zwitterions but also interesting to realize unique solid–solid transition.

Ever since air- and water-stable ionic liquids (ILs) were reported in the early 1990's, ILs have been studied over a wide range of areas including designer solvents and electrochemical applications.¹ Most IL studies use imidazolium cation-based ILs due to their low melting point (T_m), low viscosity, and high ionic conductivity as compared with those of salts composed of other organic cations. However, ammonium salts containing an ether bond have low T_m or glass transition temperature (T_g), and accordingly, they have a low viscosity and high ionic conductivity that are equal to those of imidazolium systems.^{2–4} As with organic salts,⁵ even alkali metal salts are obtained as liquid at room temperature by the effect of multiple ether units.⁶ On the other hand, some of ammonium salts containing an ether bond show plastic crystal behavior due to a solid–solid transition accompanied by the rotational motion of ions.^{2b} In addition, MacFarlane et al. showed that several ionic plastic crystals have high ionic conductivity when doped with lithium cations.⁷

Recently, we reported on a new generation of ILs: zwitterionic liquids (ZILs)⁸ in which both cation and anion were tethered in the same molecule. Because ILs, a liquid matrix for transporting target ions such as lithium and proton, can also migrate along the potential gradient. To overcome this drawback, we designed ZILs as a solvent for electrochemical applications. In fact, these ZILs have been studied with the aim of developing electrolyte materials for lithium battery⁹ and fuel cell.¹⁰ In addition, researchers have reported that ZIL/acid mixtures act as an acidic catalyst for esterification of alcohols and acetate derivatives.¹¹ Also, ZIL/silver salt complexes act as carriers for facilitated transport membranes through which isoprene is separated from a mixture with *n*-pentane.¹² The number of studies on ZILs are increasing, as are studies of typical ILs. However, the T_m of ZILs is generally much higher than those of common ILs. Higher T_m of ZILs should be based on the decrease of freedom of the component ions. Although the addition of LiTFSI or HTFSI to ZIL results in a liquid at room temperature,^{8,10} it is very difficult to lower the T_m of ZIL itself. Here we describe our preparation of low-molecular-weight aliphatic and alicyclic ammonium inner salts containing an ether bond and show that the result is a new family of ZILs with lower T_m . Scheme 1 shows the structure and abbreviations of the ammonium inner salts containing an ether bond. In the case of ZILs, imidazolium cation derivatives have lower T_m values than aliphatic and alicyclic ammonium systems. In contrast, most ammonium derivatives decompose before melting. Moreover, aliphatic and alicyclic ammonium



Scheme 1. Structure and abbreviations of ammonium inner salts containing an ether bond.

um cations should be useful for electrochemical applications because of their wide range of possible electrochemical potentials as compared with those of imidazolium cations.^{3b}

These zwitterions containing an ether bond prepared were obtained as a white solid at room temperature. All the zwitterionic liquids synthesized were characterized by ¹H NMR and elemental analyses.¹³ Figure 1 shows DSC heating traces (10 °C min⁻¹) for ZILs containing an ether bond. All the ZILs had a T_m below 200 °C, which is lower than that of ammonium zwitterions without an ether bond. For example, in the case of triethylamine as the cation, the zwitterions decomposed at 284.7 °C ($n = 3$) or 293.5 °C ($n = 4$) before melting.¹⁴ Among the four ZILs, N_{11.1023S} had the lowest T_m of 161 °C, which is equal to that of imidazolium systems. This low value is obviously the effect of the ether bond because most of the ammonium zwitterions decomposed around 300 °C before melting as mentioned above.

The compounds, N_{11.1024S} and N_{22.1024S} have a solid–solid transition as indicated by the data in Figure 1. It is known that zwitterions with long alkyl chains show liquid crystalline thermotropic behavior.¹⁵ Here, N_{11.1024S}, a crystalline sample obtained by recrystallization from acetonitrile, had an endothermic peak at 125 °C, which suggests that the crystal was transformed into a different crystal form. The sample then melted at 197 °C to form an isotropic liquid phase. In contrast, a crystalline sample of N_{22.1024S} had an endothermic peak at 169 °C, indicating a solid–solid transition of crystal forms, and then melted at 183 °C. Although N_{11.1024S} and N_{22.1024S} have a similar structure, their solid–solid transition temperatures are significantly different. This difference likely arises from the steric hindrance of the ethyl group on the ammonium cation. We confirmed the reproducibility of this unique behavior for both samples through cyclic heating and cooling analyses. These results showed that N_{11.1024S} and N_{22.1024S} exhibited polymorphism. Each crystal structure determined by X-ray diffraction will be reported elsewhere. After cooling N_{11.1023S} and P_{1023S} at 10 °C min⁻¹, these compounds had T_g values of 14 and 10 °C, respectively, on their second heating trace. This differs from N_{11.1024S} and N_{22.1024S}; moreover, no solid–solid transition was found. Thus, N_{11.1023S} and P_{1023S} formed an amorphous phase. These results suggest

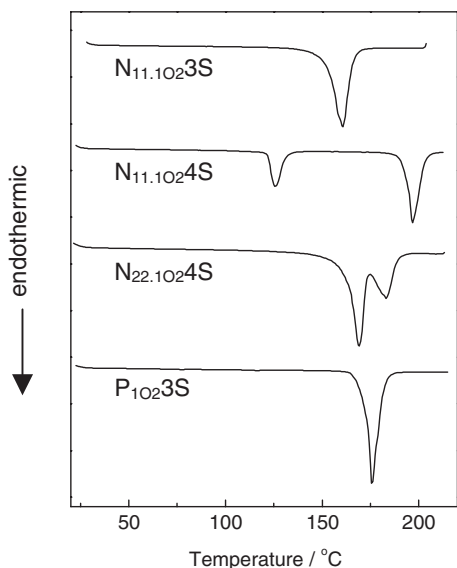


Figure 1. DSC heating traces ($10^{\circ}\text{C min}^{-1}$) for the ZILs.

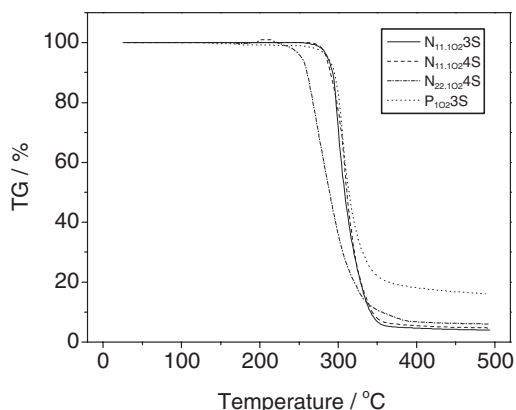


Figure 2. Thermogravimetric analyses of ZILs containing ether.

that the distance between cation and anion strongly affects the morphology change of ZILs. This agrees with the behavior found for zwitterionic thermotropic liquid crystals.¹⁵

We then determined the thermal stability of the ZILs. The thermogravimetric analyses of these new compounds are shown in Figure 2. Except for $\text{N}_{22.1024\text{S}}$, the ZILs (both with and without an ether bond) were thermally stable up to around 300°C . Therefore, adding an ether bond to ZILs decreased the T_m without reducing their thermal stability.

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- 13 Ether-containing ZILs were synthesized according to the previous reports.^{9,11} Corresponding tertiary amine (from Nisschimbo Ind. Inc.) was dissolved in acetone and then an equimolar amount of 1,3-propanesultone (Tokyo Kasei, >99%) or 1,4-butanedisultone (Tokyo Kasei, >99%) was added. The solution was stirred under dry nitrogen at room temperature for several days. Insoluble zwitterion was separated by filtration. The ZILs were further purified by recrystallization from acetonitrile. $\text{N}_{11.1023\text{S}}$. $^1\text{H NMR}$ ($\text{DMSO-}d_6$, 500 MHz): δ 1.913 (m, 2H), 2.385 (t, 2H), 2.983 (s, 6H), 3.233 (s, 3H), 3.384 (m, 2H), 3.449 (t, 2H), 3.684 (s, 2H). Elemental analysis Found: C, 42.57; H, 8.28; N, 6.29%. Calcd. for $\text{C}_8\text{H}_{19}\text{N}_1\text{O}_4\text{S}$: C, 42.64; H, 8.52; N, 6.22%. $\text{N}_{11.1024\text{S}}$. $^1\text{H NMR}$ ($\text{DMSO-}d_6$, 500 MHz): δ 1.525 (m, 2H), 1.699 (m, 2H), 2.395 (t, 2H), 2.966 (s, 6H), 3.236 (s, 3H), 3.260 (t, 2H), 3.429 (t, 2H), 3.674 (s, 2H). Elemental analysis Found: C, 44.86; H, 8.69; N, 5.78%. Calcd. for $\text{C}_9\text{H}_{21}\text{N}_1\text{O}_4\text{S}$: C, 45.16; H, 8.86; N, 5.85%. $\text{N}_{22.1024\text{S}}$. $^1\text{H NMR}$ ($\text{DMSO-}d_6$, 500 MHz): δ 1.134 (t, 6H), 1.572 (m, 2H), 1.677 (m, 2H), 2.405 (t, 2H), 3.189 (t, 2H), 3.242 (s, 3H), 3.256 (m, 4H), 3.367 (t, 2H), 3.644 (t, 2H). $\text{P}_{1023\text{S}}$. $^1\text{H NMR}$ ($\text{DMSO-}d_6$, 500 MHz): δ 1.917 (m, 2H), 1.998 (m, 4H), 2.418 (t, 2H), 3.252 (s, 3H), 3.435 (m, 8H), 3.697 (t, 2H). Elemental analysis Found: C, 47.73; H, 8.24; N, 5.64%. Calcd. for $\text{C}_{10}\text{H}_{18}\text{N}_2\text{O}_3\text{S}$: C, 47.77; H, 8.44; N, 5.57%.
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