Novel Alkali Metal Ionic Liquids: *N*-Ethylimidazolium Alkali Metal Sulfates

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Novel ionic liquids containing alkali metal ions as component were prepared by the neutralization of *N*-ethylimidazole with various kinds of hydrogensulfates ($MHSO_4$; M = Li, Na, or K). All salts were obtained as transparent viscous liquids at room temperature. These ionic liquids showed ionic conductivity higher than 10^{-4} S cm^{-1} at room temperature, reflecting low glass transition temperature of below −60 °C. This is the first report on alkali metal salts which are inherently liquid state at room temperature.

Ionic liquids have vigorously been investigated as a new class of ion conductive material in recent years,[1–5] owing to their remarkable properties such as high ionic conductivity at ambient temperature, low viscosity without any solvent, non-volatility, and excellent thermal stability. Although some ionic liquid systems show excellent ionic conductivity of over 10^{-2} S cm^{-1} at room temperature, their high ionic conductivity was derived from the migration of component ions of the ionic liquid. Furthermore, there is no report on the preparation of the ion conductive matrix for target carrier ion such as H^+, Li^+, and Na^+ by using these ionic liquids. Therefore, we have prepared zwitterionic salts[6] and various ionic liquid-type polymers[7–13] to overcome this drawback. The ionic liquid-type polymer having flexible spacer between vinyl group and ionic liquid moiety showed high ionic conductivity of about 10^{-4} S cm^{-1} which is almost comparable to that of corresponding ionic liquid monomer at room temperature. However, when lithium salt was added to ionic liquid-type polymers in order to generate target carrier ions, their ionic conductivity decreased monotonously with increasing the amount of added salt.[12] Similar tendency was also observed in simple ionic liquid systems.[14] When pure ionic liquids based on target carrier ions were prepared, these ionic liquids are expected as advanced ion conductive materials without salt addition.

Most ionic liquids are generally consisted of monovalent cation and anion, whereas there is few numbers of ionic liquids based on multivalent ions.[15,16] It is believed to be difficult to form ionic liquid with multivalent ions owing to their very strong electrostatic interaction. In this paper, we report novel ionic liquids based on alkali metal ion such as Li^+, Na^+, and K^+. These salts were prepared by the neutralization of *N*-ethylimidazole with various kinds of hydrogensulfates ($MHSO_4$; M = Li, Na, or K). These salts were obtained as liquid at room temperature. This is the first report on the preparation of pure ionic liquids based on alkali metal ions.

Lithium hydrogensulfate ($LiHSO_4$) was purchased from Mitsuwa Chemicals Co., Ltd. Sodium hydrogensulfate ($NaHSO_4$) and potassium hydrogensulfate ($KHSO_4$) were purchased from Kanto Chemical Co., Inc. *N*-Ethylimidazole was purchased from Tokyo Kasei Co., Ltd. $NaHSO_4$ and $KHSO_4$ were dried in vacuo before use. Other reagents were used as received.

Aqueous solution of *N*-ethylimidazole was slowly mixed with equimolar amount of $NaHSO_4$ or $KHSO_4$ on an ice bath. The mixtures were stirred at room temperature for a week. $LiHSO_4$ was mixed with an excess amount of *N*-ethylimidazole on an ice bath under dry nitrogen gas, and the mixture was stirred at room temperature for a day. The aqueous solution was then dehydrated with a rotary evaporator. Unreacted $MHSO_4$ was removed by filtration. The obtained salts were dried in vacuo at 100 °C for 1 h, and then dried at 60 °C at least a day. The structure of these ionic liquids was confirmed by ^{1}H-NMR spectroscopy (JEOL α-500 NMR spectrometer) and elemental analysis.[17] In addition, the existence of alkali metal ion was confirmed by flame reaction. The structure of the obtained ionic liquids is shown in Chart 1.

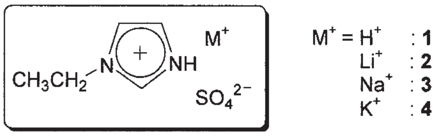

Chart 1. Structure of *N*-ethylimidazolium alkali metal sulfates.

Karl-Fischer moisture titrator (MKS-210; Kyoto electronics) was used to detect the amount of water content of these ionic liquids. The ionic liquid **2** was revealed to contain the highest amount of water; 0.76 wt% due to stronger hydration force of lithium cation. Other salts contained water less than 0.37 wt%.

The ionic conductivity of the obtained salts was measured with the complex-impedance method using an impedance analyzer (Schlumberger Solartron 1260 impedance/gain-phase analyzer) with a frequency range from 10 Hz to 5 MHz. The dynamic ionic conductivity measurement system was developed in our laboratory.[18] All measurements were carried out in a glove box filled with dry nitrogen gas in the temperature range 10 °C to 60 °C at a cooling rate of 2.5 °C min^{-1}.

DSC measurement was carried out with a DSC-6200 (Seiko Instruments Inc.) in the temperature range −150 °C to 200 °C at a heating rate of 10 °C min^{-1}.

All the obtained alkali metal salts were transparent viscous liquid at room temperature. These ionic liquids showed low glass transition temperature (Tg) of −60 to −70 °C (Table 1) and there was no melting point (Tm) in the range of measurement

Table 1. Properties of the *N*-ethylimidazolium alkali metal sulfates

No.	Tg/°C	σ_i/mS cm^{-1} at 30 °C	ion radii[a] of M^+/Å
1	−75	0.24	—
2	−60	0.10	0.60
3	−68	0.26	0.91
4	−67	0.27	1.33

[a] Ref. 19.

temperature, suggesting glass materials. However, their viscosity exceeded 1000 cP at room temperature, which was much higher than that of typical ionic liquids consist of only monovalent ions. The electrostatic interaction in these ionic liquids based on divalent anion is confirmed to be stronger than that of typical ionic liquid.

Ionic conductivity measurement of every ionic liquid was carried out. Figure 1 shows temperature dependence of the ionic conductivity for these alkali metal ionic liquids. In spite of higher viscosity, these ionic liquids showed relatively high ionic conductivity of approximately 10^{-4} S cm^{-1} at room temperature, reflecting low Tg. The ionic liquid **1** showed the lowest Tg of $-75\,^{\circ}$C among four ionic liquids, however the ionic liquid **4** showed the highest ionic conductivity of 2.7×10^{-4} S cm^{-1} at 30 °C. There are a few parameters to affect the ionic conductivity such as degree of dissociation, ion size, Tg, Tm, fragility, etc. To clarify this sequence, further investigation should be carried out to discuss about the salt dissociation behaviors in these systems. Electrochemical stability and target ion transport number have currently been investigating. Synthesis of the quaternary onium salts is now under progress. The present study proposes a new method to design the ionic liquids containing desired ions as component.

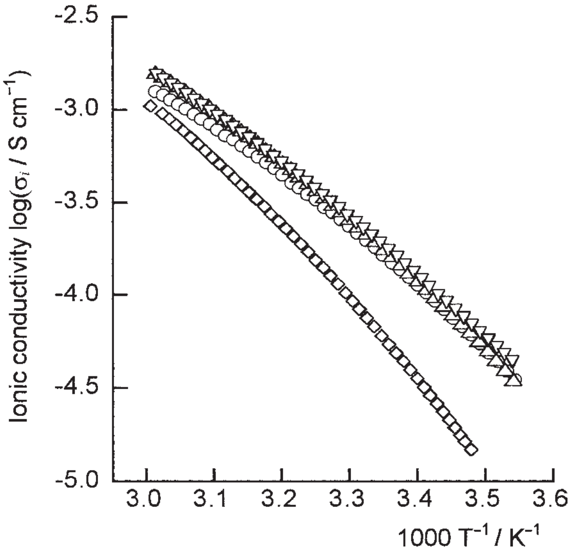

Figure 1. Temperature dependence of ionic conductivity for the *N*-ethylimidazolium alkali metal sulfates. **1**: (○), **2**: (◇), **3** (△), **4**: (▽).

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17 Compound **1**: ^{1}H NMR (DMSO) δ 1.37 (t, 3H), 4.16 (q, 2H), 7.63 (s, 1H), 7.75 (s, 1H), 9.07 (s, 1H). Anal. Calcd. for $C_5H_{10}N_2O_4S$: C, 30.92; H, 5.19; N, 14.42%, C/N, 2.144. Found C, 26.88; H, 5.67; N, 12.58%, C/N, 2.137. Compound **2**: ^{1}H NMR (DMSO) δ 1.33 (t, 3H), 4.06 (q, 2H), 7.31 (s, 1H), 7.50 (s, 1H), 8.48 (s, 1H). Anal. Calcd. for $C_5H_9LiN_2O_4S$: C, 30.01; H, 4.53; N, 14.00%, C/N, 2.144. Found C, 29.99; H, 6.94; N, 14.11%, C/N, 2.125. Compound **3** ^{1}H NMR (DMSO) δ 1.33 (t, 3H), 4.06 (q, 2H), 7.32 (s, 1H), 7.51 (s, 1H), 8.50 (s, 1H). Anal. Calcd. for $C_5H_9NaN_2O_4S$: C, 27.78; H, 4.20; N, 12.96%, C/N, 2.144. Found C, 32.13; H, 5.93; N, 15.05%, C/N, 2.135. Compound **4** ^{1}H NMR (DMSO) δ 1.33 (t, 3H), 4.06 (q, 2H), 7.31 (s, 1H), 7.50 (s, 1H), 8.48 (s, 1H). Anal. Calcd. for $C_5H_9KN_2O_4S$: C, 25.85; H, 3.91; N, 12.06%, C/N, 2.143. Found C, 32.01; H, 5.90; N, 15.06%, C/N, 2.125.

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