Novel Ionic Liquids Composed of Only Azole Ions

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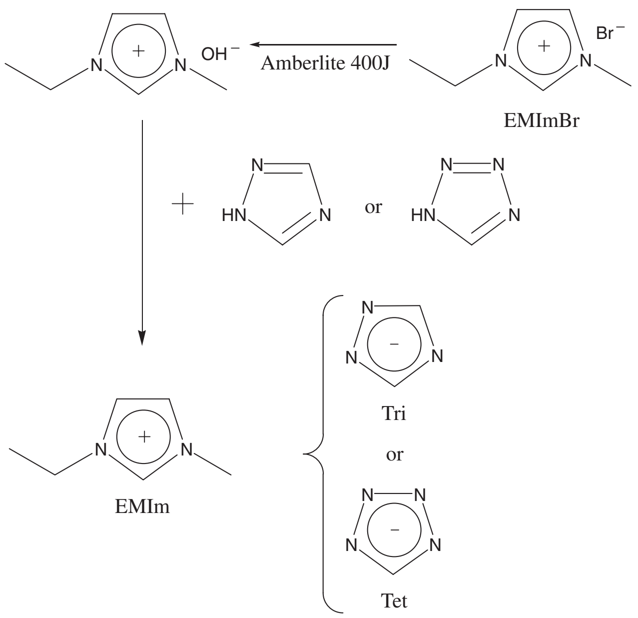
Novel ionic liquids (ILs) composed of azole type cation and anion were prepared. Triazole and tetrazole were coupled with 1-ethyl-3-methylimidazolium hydroxide. Obtained tetrazole salt was liquid at room temperature showing only glass transition temperature at −89 °C. The ionic conductivity reached to 8.9×10^{-3} S cm^{-1} at room temperature reflecting low viscosity of 42.5 cP at 25 °C. This is the first report on the ILs based on only azole type ions.

ILs[1] are defined molten salt at room temperature, and expected as novel solvents due to their unique characteristics such as non-volatility, high ionic conductivity, etc. ILs have been investigated as alternative electrolyte solutions for lithium ion battery,[2] fuel cell,[3] capacitor,[4] and dye-sensitized solar cell.[5] A large number of ILs was prepared and characterized in this decade, most of them were based on halogenated counter anions such as PF_6^-, BF_4^-, and $(CF_3SO_2)_2N^-$ ($TFSI^-$). Halogens have been used to reduce negative charge density by their electron withdrawing effect. These ILs have low melting point (Tm) reflecting their weak electrostatic interaction attributable to the negative charge delocalization. Although some halogen-free anions were also used to form ILs, there were few reports on these anions like nitrate or acetate.[6] It was semi-empirically believed that organic salts based on halogen-free counter anions were difficult to prepare IL. These salts showed poor properties even if they formed IL.

On the other hand, azole compounds such as imidazole were frequently used to prepare cations for excellent ILs because positive charge delocalization on the azole ring weakened electrostatic interaction in spite of small molecular weight. We expected that excellent ILs could also be obtained by using charge-delocalized azole type anion without halogenated anion. These salts with azole type anions had already been reported. Lithium 4,5-dicyano-1,2,3-triazolate was reported as electrolyte due to charge delocalization and interfacial stability.[7] Also similar salts were prepared for capacitor.[8] However there was no report about ILs containing azole type anions in spite that there were lots of ILs containing azole type cations.[9] It should be noted here that these azole type ILs contained only three kinds of element, C, H, and N. Preparation of the ILs, those are free from halogens, O, P, and S, is significant to prepare "green" materials.

1-Ethyl-3-methylimidazolium bromide (EMImBr) was prepared by the quarternization of methylimidazole with ethyl bromide as already reported.[10] Bromide anion of EMImBr was converted into hydroxide by anion exchange resin (Amberlite-400J), and neutralized with 1,2,4-triazole (Tri) or 1,2,3,4-tetrazole (Tet) as shown in Scheme 1. Each aqueous solution was concentrated with rotary evaporator and residual liquid was mixed with diethyl ether to extract the target salt. The extracted compounds were further washed with ethyl acetate twice and dried under reduced pressure at room temperature for two days. The obtained compounds were liquid state at room temperature and their structures were characterized by using ^{1}H NMR spectroscopy.[11]



Scheme 1. Synthesis of the ILs based on only azole ions.

The ionic conductivity of the obtained ILs 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 1 MHz. The dynamic ionic conductivity measurement system was developed in our laboratory.[12] All the measurements were carried out in a glove box filled with dry N_2 atmosphere in the temperature range 10 to 60 °C at a cooling rate of 2.5 °C min^{-1}. DSC measurement was carried out with a DSC-6000 (Seiko Instruments Inc.) in the temperature range −150 to 200 °C at a heating rate of 10 °C min^{-1}. The thermal stability of the ILs was investigated by TG/DTA 220 (Seiko Instruments Inc.) with heating rate of 10 °C min^{-1} from 25 to 450 °C. The viscosity measurement of the ILs was carried out with DV-I + viscometer (Brookfield).

Thermal analysis revealed that EMImTri and EMImTet were liquids showing only glass transition temperature (T_g) as shown in Table 1. They showed very low T_g similar to those salts containing TFSI anion.[13] As shown in Table 1, Low T_g and vis-

Table 1. Thermal properties and viscosity of EMImTri and EMImTet

	T_g/°C	Td/°C	η/cP at 25 °C
EMImTri	−76	207	60.2
EMImTet	−89	—	42.5

—; Not measured

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cosity imply that azole type anions had potential to form excellent ILs. EMImTri showed no weight loss upto 200 °C. We did not carry out the thermal analysis at higher temperature of EMImTet because of explosive property.

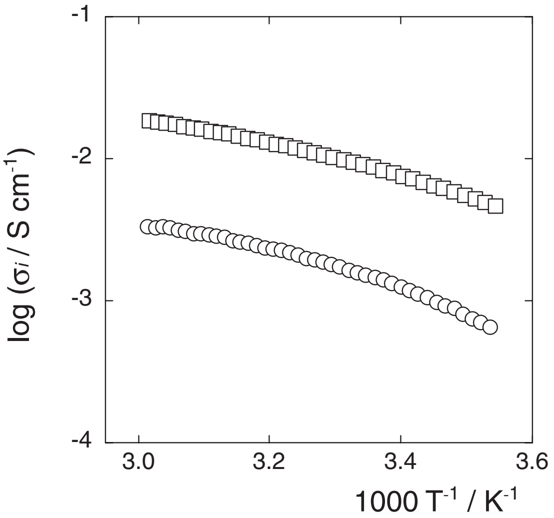

Figure 1. Temperature dependence of the ionic conductivity for EMImTri (○) and EMImTet (□).

The ionic conductivity of azole type ILs is shown in Figure 1. The ionic conductivity of EMImTet was five times higher than that of EMImTri at measured temperature range. This was attributable to both low T_g and low viscosity, the conductivity (8.9×10^{-3} S cm^{-1} at 25 °C) was comparable to that of general IL (EMImTFSI; 8.4×10^{-3} S cm^{-1} at 26 °C).[4] Since the properties of azoles change depending on the substituent group,[14] it should be effective to introduce some substituent groups such as cyano groups expecting negative charge delocalization and improvement of thermal stability. According to the strategy as mentioned in the present work, it is easy to expect ILs containing imidazole or pyrazole as anion species. We have already attempted to elaborate ILs with derivatives of imidazoles and pyrazoles, but failed.

Preparation of thermally or chemically stable salt based on azole type anion was not so easy, because there are only few acidic azole compounds just like triazole or tetrazole. These new azole type ILs may be used as not only electrolytes or solvents, but also explosives.[15]

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11 EMImTri: ^{1}H NMR (DMSO) δ 1.34 (t, 3H), 3.79 (s, 3H), 4.12 (q, 2H), 7.57 (s, 1H), 7.68 (s, 1H), 7.77 (s, 1H), 9.34 (s, 1H); EMImTet: ^{1}H NMR (DMSO) δ 1.35 (t, 3H), 3.81 (s, 3H), 4.15 (q, 2H), 7.70 (t, 1H), 7.79 (t, 1H), 8.22 (s, 1H), 9.22 (s, 1H).
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