Novel Ionic Liquids Composed of Only Heterocycles

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INTRODUCTION

Since delocalized charge considerably helps to lower the melting point (Tm) of the salts, π-conjugated cations were frequently used. Similarly, introduction of halogens such as fluoride and chloride are used to lower the negative charge density. Therefore, most of general ionic liquids contain halogenated counter anions. Some halogen-free anions were also used to form salts with relatively low Tm, there were a few reports about the ionic liquids based on these anions[1)]. It is important to design halogen free ionic liquids from the viewpoint of green chemistry. We had prepared novel ionic liquids by using sulfur-based anion such as thiol or dithiocarboxylic acid expecting small surface charge density of sulfur[2)].

For this purpose, we prepared new ionic liquids composed of heterocycles having sulfur-based anion having heterocycle. Negative charge should be delocalized in the heterocycles like imidazolium cation in which positive charge was delocalized. These heterocyclic anions were characterized to have only C, H, and N atoms.

EXPERIMENTAL

1-Ethyl-3-methylimidazolium bromide (EMIBr) was prepared as already reported[2)]. Bromide anion of EMIBr was converted into the hydroxide by anion exchange resin (Amberlite-400J), and neutralized with each heterocyclic compound. Their structure (**a**-**g**) was confirmed by ^{1}H-NMR spectroscopy.

Ionic conductivity measurements were carried out using a Schlumberger Solartron 1260 impedance/gain phase analyzer with a frequency range from 10 Hz to 1 MHz. DSC measurements were carried out with a DSC-120 (SEIKO Instruments Inc). The temperature was swept from -150 to 200 ^{o}C at a heating rate of 10 ^{o}C min^{-1}. The thermal stability of the ionic liquids was investigated by TG/DTA 220 (SEIKO Instruments Inc) with heating rate of 10 ^{o}C min^{-1} from 25 to 450 ^{o}C.

RESULTS AND DISCUSSION

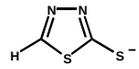
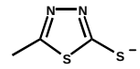
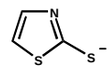
All salts listed in Table 1 were obtained as liquid at room temperature. These ionic liquids showed only glass transition temperature (Tg). They were totally amorphous having no Tm. However, decomposition temperature (Td) of these ionic liquids was inferior to that of general ionic liquids based on halogenated anions such as bis(trifluoromethanesulfonylimide). Reflecting low Tg, these ionic liquids showed good ionic conductivity around 10^{-3} S cm^{-1} at room temperature. As expected, the delocalization of negative charge of anion structure is effective to decrease their Tg and increase their ionic conductivity owing to the weakened electrostatic interaction.

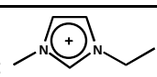
In systems containing sulfur (**a-e**) as anion, their Tg tended to decrease with increasing acidity of the starting materials. This tendency was also observed in general ionic liquid systems[1a)]. Hence in order to design excellent ionic liquid by using sulfur-containing anions, it is necessary to use more acidic compound to prepare counter anion.

Salt **f** and **g** showed very low Tg similar to general ionic liquids containing TFSI anion. Especially, salt **g** shows the lowest Tg at -89 ^{o}C and displayed the best ionic conductivity, 8.9×10^{-3} S cm^{-1} at 25^{o}C. These results suggested that these azole type anions were effective to prepare ionic liquids. This successful ionic liquid preparation pushed up to prepare new salts containing novel anion from imidazole, but in vain due to insufficient acidity of imidazoles.

Here, we first demonstrated the possibility of preparation of the excellent ionic liquids by only heterocycles, in other words, those composed of only C, H, and N atoms.

Table 1 Tg, Td, and ionic conductivity of EMI-based ionic liquids containing novel anions.

Salt	Anion	Tg / ^{o}C	Td / ^{o}C	σ_i / mS cm^{-1} at 25 ^{o}C
a		–69	212	4.60
b		–59	220	1.50
c		–64	215	0.52
d		–50	210	0.33
e		–43	192	0.32
f		–76	207	1.80
g		–89	–	8.90

EMI: 

REFERENCES

1) (a) P. Walden, *Bull. Acod. Imp. Sci. St. Petersburg*, 1914, 1800, (b) H. Ohno and M. Yoshizawa, *Solid State Ionics*, 154-155, 303 (2002).
2) M. Kameda, K. Fukumoto, and H. Ohno, *Abstract of 84th Annual meeting, Chem. Soc. Japan*, Vol. 1, 354 (2004).
3) P. Bonhote, A-P. Dias, M. Armand, N. Papageorgiou, K. Kalyanasundaram, and M. Gratzel, *Inorg. Chem.*, 35, 1168 (1996).