NOVEL IONIC LIQUIDS COMPOSED OF ONLY HETERO CYCLES

Hiroyuki Ohno*, Mayu Kameda, Kenta Fukumoto, Wataru Ogihara, and Masahiro Yoshizawa

Department of Biotechnology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan
Tel & Fax: +81-42-388-7024
e-mail: ohnoh@cc.tuat.ac.jp

ABSTRACT

We prepared novel ionic liquids containing halogen-free anions. Heterocyclic anions were selected to prepare ionic liquid with low melting point and viscosity. Salts were prepared by neutralization between 1-ethyl-3-methylimidazolium hydroxide and corresponding heterocyclic acids. Some of sulfide salts having heterocyclic structure became ionic liquid and showed relatively low glass transition temperature (Tg). On the other hand, the salts containing azolate anion such as triazolate, became excellent ionic liquids, they showed the Tg at -80 °C by the effect of negative charge delocalization. The ionic liquid containing azole anion showed high ionic conductivity of 8.9 x 10^{-3} S cm^{-1} at room temperature reflecting low Tg and low viscosity (42.5 cP at room temperature). This paper reports the preparation and characteristics of novel ionic liquids composed of halogen-free heterocyclic anions and cations.

INTRODUCTION

There are a lot of studies to improve the characteristics of ionic liquids (ILs) for the application to reaction media (1) or ion conductive materials (2). Although many works on ILs have been reported, development of structural variation of ILs was limited. Most of ILs are based on halogenated counter anions such as PF_6^-, BF_4^-, trifluoromethanesulfonate, and bis(trifluoromethanesulfonyl)imide (TFSI) (3). These halogenated anions have delocalized negative charges stabilized by strong electron withdrawing effect of halogens. These halogenated anions have the effect to lower melting point (T_m) and viscosity by weakened electrostatic interaction with cations. Additionally, strong hydrophobicity of halogenated anion, especially fluorinated anion, is one of attractive points for the use as water-insoluble ILs.

However, development of halogen-free ILs should also be important from the viewpoint that ILs was expected as eco-friendly materials. Development of halogen-free IL system is highly significant for the investigation of the correlation between structure and properties of ILs. Because, there are not so many excellent anions whose charge was delocalized without the aid of halogen.

These are only a few works about halogen-free ILs, for instance, nitrate or acetate.
Organic salts containing halogen-free anion is believed to be rather difficult to form IL at ambient temperature due to insufficient acidity. In order to prepare halogen-free ILs, we first focused on a strong electron withdrawing effect of sulfur atom. Lowering surface charge density should weaken the electrostatic interaction among the component ions of ILs.

Also, we attempted to use heterocyclic compounds as counter anion also to realize negative charge delocalization. Positive charge has already been expanded on heterocyclic structure of onium cation such as imidazolium. Azole compounds were frequently used as organic cations because of effective charge delocalization. Charge delocalized anions showed also be prepared from π-conjugated heteroaromatic molecules. Salts based on azolate anion have already been reported. Lithium 4,5-dicyano-1,2,3-triazolate was expected as highly dissociable salt and generate lithium ion as one of excellent electrolyte materials (5).

In this work, novel ILs were prepared by using heterocyclic anions whose negative charge was delocalized. Their characteristic thermal properties and ionic conductivity suggest the possibility of halogen-free heterocyclic anions as components of ILs.

EXPERIMENTAL

Preparation

The starting material, 1-ethyl-3-methylimidazolium bromide (EMImBr) was prepared according to our previous work (3). The bromide anion of EMImBr was converted into hydroxide anion by using anion exchange resin (Amberlite-400J) in an aqueous solution. Then it was neutralized with desired acidic compounds as shown in Scheme 1. Reaction mixtures were concentrated by rotary evaporator and residual compounds were washed with appropriate organic solvent to remove unreacted reagents. Precipitates were dried under reduced pressure at room temperature or 60 °C during 48 hours. The structure of the obtained salts was confirmed with 1H NMR.

Methods

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. Thermal stability of the salts was investigated by TG/DTA 120 (Seiko Instruments Inc.) with heating rate of 10 °C min⁻¹ from 25 to 450 °C.

Viscosity measurement of the ILs was carried out with DV-I+ viscometer (Brookfield) with temperature controlled apparatus.

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 1 MHz. The dynamic ionic conductivity measurement system was developed in our laboratory (6). All measurements were carried out in a glove box filled with dry nitrogen gas atmosphere in the temperature range 10 °C to 60 °C at a cooling rate of 2.5 °C min⁻¹.
RESULTS AND DISCUSSION

Sulfide containing ILs

Among seven sulfide salts, five became liquid at room temperature, and these were confirmed as IL. Anion structure of these salts is shown in Table 1. Cation structure for all the salts was fixed to be 1-ethyl-3-methylimidazolium cation to compare the effect of anion structure.

These five sulfide salt type ILs showed no $T_m$ and showed only glass transition temperature ($T_g$) at around $-60$ to $-40 \, ^\circ\text{C}$. In particular, IL a showed low $T_g$ at $-69 \, ^\circ\text{C}$. Although these $T_g$ value are relatively high compared to that of ILs containing halogenated anion, these are excellent ILs as halogen-free ILs. On the other hand, salts c and e, which were solid at room temperature, showed $T_m$ at $110 \, ^\circ\text{C}$ and $61 \, ^\circ\text{C}$, respectively. It is known that IL formed super-cooled liquid above their $T_g$ owing to high viscosity. However, since these sulfide salt type ILs have not been crystallized in a refrigerator for over six months, it is difficult to conclude that these ILs were in a super-cooled condition. Thermal stability of these salts is not so good. The decomposition temperature ($T_d$) of these sulfide salt type ILs was around $200 \, ^\circ\text{C}$. This was inferior to that of ILs having halogenated anions such as EMImBF$_4$ or EMImTFSI. Thermal properties of salts are also summarized in Table 1.

Five different ILs in this system showed good ionic conductivity reflecting relatively low $T_g$. IL a showed the highest ionic conductivity of $4.6 \times 10^{-3}$ S cm$^{-1}$ at room temperature due to low $T_g$ at $-69 \, ^\circ\text{C}$. The discussion about the relation between ionic conductivity and $T_g$ clearly leads the tendency that IL having lower $T_g$ shows higher ionic conductivity. This behavior was also observed in general IL systems (7).

Azolate type IL system

We prepared halogen-free ILs by using sulfide anion in combination with heterocyclic structure in the previous section. Although some of them became ILs at room temperature, their properties is not favorable value compared with that of general halogenated ILs. Therefore we prepared novel ILs composed of anion, which has delocalized negative charge on the heterocycle ring. The heterocyclic anions were derived from 1,2,4-triazole and 1,2,3,4-tetrazole. We also tried to prepare salts of imidazole as anion. It was however impossible to do so from the viewpoint of acidity. The acidity of imidazole is weaker than that of triazole or tetrazole, and the dissociation of imino group (=NH) on the heterocycle was not expected under the ordinary condition.

Anion structure of these two salts is shown in Table 2. Both of the obtained salts, h and I, were confirmed as ILs and showed no $T_m$ in the temperature range for DSC measurement. These two ILs showed quite low $T_g$ at $-76 \, ^\circ\text{C}$ and $-86 \, ^\circ\text{C}$, respectively. These $T_g$ was as low as that of halogenated ILs such as EMImTFSI, and $20 \, ^\circ\text{C}$ lower than that of the sulfide salt type ILs in the previous section. This result was attributable to weak electrostatic interaction owing to delocalization of negative charge of the azole anions. TG/DTA measurement revealed that IL h was stable until $207 \, ^\circ\text{C}$ without any decomposition. On the other hand, thermal stability of i was not conducted because of...
the fear of explosive characteristics.

The viscosity of azole anion type ILs was measured. Temperature dependence of viscosity in temperature range from 10 to 60 °C is shown in Fig. 1. The viscosity of h and I at room temperature is 60 and 42 cP, respectively, comparable to that of general halogenated IL. Viscosity is also one of parameter to show the degree of interaction among constituents. This result supports that the delocalized charge of heterocyclic anion is effective to form room temperature IL.

Fig. 1 shows temperature dependence of ionic conductivity for two ILs. The ionic conductivity at room temperature of IL h was about five times as high as that of IL I. This can be explained by the differences of $T_g$ and viscosity. The viscosity of these ILs at higher temperature is largely similar in spite of different conductivity, $T_g$ should be the main factor to affect the ionic conductivity in this IL system. The ionic conductivity of both ILs h and I is high comparable to that of halogen-containing IL such as EMImTFSI. These azolate anions have potential to design functional IL by introducing some substituent onto the ring.

CONCLUSION

In order to prepare halogen-free ILs, we synthesized several 1-ethyl-3-methylimidazolium salts containing acidic heterocyclic compounds. Some of the obtained salts were obtained as ILs with excellent properties. Ions having delocalized charge are quite effective to prepare excellent ionic liquids. Heteroaromatic anions should also be useful for this purpose.

ACKNOWLEDGEMENTS

The present work was supported by the Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan (No.14205136). Two authors (K. F. and W. O.) appreciated the financial support from 21st Century COE program of "Future Nano-materials" in Tokyo University of Agriculture and Technology.

REFERENCES

1. P. Wasserscheid, T. Welton, Ionic Liquids in Synthesis John Wiley & Sons Inc., (2003). R. D. Rogers, K. R. Seddon, Ionic Liquids: Industrial Applications for Green Chemistry (Acs Symposium Series, 818) Oxford Univ Press, (2002)
2. M. A. B. H. Susan, A. Noda, S. Mitsushima, M. Watanabe, Chem. Commun., 938 (2003). P. Wang, S. M. Zakeeruddin, P. Comte, I. Exnar, M. Grätzel, J. Am. Chem. Soc., 125, 1166 (2003)
3. A. B. McEwen, H. L. Ngo, K. LeCompte, J. L. Goldman, J. Electrochem. Soc., 146, 1687 (1999)
4. P. Walden, Bull. Acad. Imp. Sci. St. Petersburg, 1800 (1914). P. Bonhôte, A-P. Dias, N. Papageorgiou, K. Kalyanasundaram, and M. Grätzel, Inorg. Chem., 35, 1168
5. M. Egashira, B. Scrosati, M. Armand, S. Béranger, C. Michot, *Electrochem. Solid-State Lett.*, 6, A71 (2003).

6. H. Ohno, Y. Inoue, and P. Wang, *Solid State Ionics*, 62, 257 (1993).

7. H. Ohno and M. Yoshizawa, *Solid State Ionics*, 154-155, 303 (2002).
Scheme 1 Preparation of ionic liquids

Table 1 Properties of halogen-free ionic liquids

| Salt | Anion | T<sub>e</sub> (T<sub>m</sub>) / °C | T<sub>d</sub> / °C | σ<sub>i</sub> / mS cm<sup>-1</sup> at 25 °C |
|------|-------|-------------------------------|----------------|---------------------------------|
| a    | ![](image) | -69                           | 212            | 4.60                            |
| b    | ![](image) | -59                           | 220            | 1.50                            |
| c    | ![](image) | (110)                         | 187            | *                               |
| d    | ![](image) | -64                           | 215            | 0.52                            |
| e    | ![](image) | (61)                          | 221            | 0.022                           |
| f    | ![](image) | -50                           | 210            | 0.33                            |
| g    | ![](image) | -43                           | 192            | 0.32                            |

*: very poor ionic conductivity
Table 2 Properties of novel ionic liquids containing azole anion

| Salt | Anion | T_g / °C | T_d / °C | η / cP at 25 °C | σ_i / mS cm^{-1} at 25 °C |
|------|-------|----------|----------|-----------------|---------------------------|
| h    | ![Ion1] | -76      | 207      | 60.2            | 1.80                      |
| i    | ![Ion2] | -89      | -        | 42.5            | 8.90                      |

Figure 1. Temperature dependence of the ionic conductivity (closed) and viscosity (open) for h (circle) and i (square)