PREPARATION OF ROOM TEMPERATURE IONIC LIQUIDS CONTAINING AMINO ACIDS

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Selection of component ions allows control of physical and chemical properties of room temperature ionic liquids (RTILs). Furthermore, these molten salts have been collecting considerable attention mainly as reaction solvents, extraction solvents, and electrolyte materials. Although extensive studies of ionic liquids have been performed, correlations between their structures and physico-chemical properties have not been summarized yet. Especially, information about the effect of anion structure is quite poor. Therefore, we focused on amino acids as component. Amino acids are important biomaterials that are known as structural unit of proteins, but are insoluble in most solvents except water. We have found preliminarily that some amino acids are effective to prepare ionic liquids with suitable cations[1]. Prepared ionic liquids from amino acids used as counter anion enable us to discuss the effect of anion structure on the properties of the corresponding salts.

In this study, we show some structure-property relationship of novel RTILs prepared by the coupling of imidazolium cations with natural amino acids. Through the preliminary studies of the combination of some onium cations with amino acids, 1-ethyl-3-methylimidazolium cation (Im) was found to be excellent to form transparent ionic liquids (amino acid ionic liquids) at room temperature with 20 natural amino acids (Fig.1). DSC measurement revealed that these amino acid ionic liquids exhibited no melting point but showed only glass transition temperature (T_g).

Although these amino acid ionic liquids were insoluble in ethers similar to general ionic liquids, they were miscible with various solvents such as methanol, acetonitrile, and even non-polar chloroform. RTILs composed of amino acids containing two carboxyl groups such as ImGlu and ImAsp were insoluble in chloroform, it became soluble by lowering the polarity of the side chain.

The structure of side chain influenced T_g of amino acid ionic liquids. Neutral amino acid such as Gly, Ala, Val, Leu and Ile, showed lower T_g than others when they formed ionic liquid. Increase in the length of alkyl side chain made gradual elevation of T_g. Even van der Waals force affect the T_g, these suggested that alkyl chain length of side chain is important factor in ionic liquids. Furthermore, similar relation was found between ImAsn and ImGln, or ImAsp and ImGlu having the same functional group. It was therefore concluded that the alkyl chain length were dominate factor of T_g regardless of functional group. Additionally, ionic liquids having carboxyl and amide group exhibited higher Tg than that of other amino acid ionic liquids. Especially ImAsp and ImGlu exhibited the highest T_g of 0 ^oC or more. Comparison of ImGlu, ImGln, and ImLys whose side chain length of anion was almost the same, T_g of ImGlu was 50 ^oC higher than that of ImLys. Since, this tendency was consistent with the above-mentioned solubility to various solvents, T_g might be influenced by the polarity of side chain.

Ionic conductivity of these amino acid ionic liquids was in the range of 10^{-4}-10^{-9} at 25 ^oC reflecting the T_g of amino acid ionic liquids (Fig.2). Mostly, salts with lower T_g showed higher ionic conductivity at the same temperature. This tendency agreed with that for many ionic liquids prepared by the neutralization with acids in our previous studies[2]. It is well known that ionic conductivity is a function of both number and mobility of carrier ions. It is therefore comprehensible that ionic liquids showing low T_g exhibited high ionic conductivity. On the other hand, some amino acid ionic liquids did not obey this relation. This characteristic ion conductive behavior will be discussed with some results by VFT equation and the polarity measurement using Kamlet-Taft parameter.

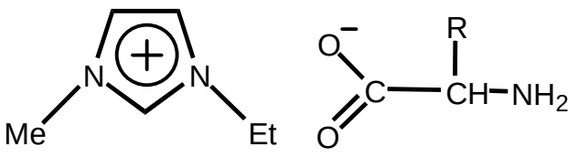

Fig. 1 Structure of amino acid ionic liquids.

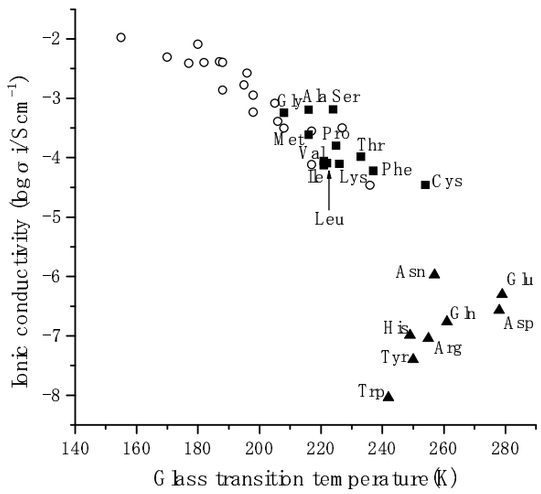

Fig. 2 Relation between ionic conductivity (at 298K) and glass transition temperature of amino acid ionic liquids. (▲,■; amino acid ionic liquids, ○; ionic liquids in our previous study)

Referencecs

1) K. Fukumoto, M. Yoshizawa, and H. Ohno, Proceedings of 70th meeting of the Electrochemical Society of Japan, 1L07 (2003)

2) M. Hirao, H. Sugimoto, and H. Ohno, *J. Electrochem. Soc.*, **147**, 4168 (2000).