Polar and Low Viscosity Ionic Liquid Mixtures from Amino Acids

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(Received July 1, 2008; CL-080649; E-mail: ohnoh@cc.tuat.ac.jp)

Amino acid ionic liquids, composed of tetrabutylphosphonium ([P_{4444}]) cation and both asparagic acid ([Asp]) and lysine ([Lys]) anions, are polar and of low viscosity because of perturbation of the ordered Asp anion alignment.

Room-temperature ionic liquids (RTILs) are attracting much attention because of their potential possibility to show remarkable properties, including negligible vapor pressure, high thermal stability, and high ionic conductivity.[1] In particular, RTILs have potential to dissolve several materials as well as "designer solvents." Properties such as viscosity, melting point, density, refractive index, and miscibility can be tuned by using suitable anions and cations.[2–4]

We have previously reported that amino acids were used as anions to prepare RTILs by coupling them with suitable imidazolium cations.[5] Those amino acid derived RTILs (AAILs) are halogen-free designer liquids. Since amino acid residues may extensively and easily be modified, AAILs are expected to be platform for novel functional materials. For the use of RTILs as solvents, polarity is one of very important parameters. Since it is not possible to measure the dielectric constant of conductive materials, the polarity of many ILs has been evaluated via the Kamlet–Taft parameters determined by solvatochromism of three different dye molecules.[6,7] We have already shown,[5] for example, that the polarity of AAILs is higher than that of ILs containing anions such as Cl^- and Br^-. Mixing of two distinct (and miscible) RTILs is one of simple methods to prepare ionic liquids having moderate properties in between two constituents. We unexpectedly found the increase in the polarity by mixing two different AAILs. There are a few papers on the increase in the ionic conductivity or polarity of some IL mixtures.[8–10] Although interaction among component ions is an important factor to influence the properties of ionic liquids, no detailed discussion on this has been reported so far. In the present study, we have analyzed the influence of the composition of AAIL mixtures on the Kamlet–Taft parameters in relation to the preparation of polar and less viscous AAILs.

Figure 1 shows the Kamlet–Taft parameters as a function of mixing composition for each binary mixture. For [emim][Ala] + [emim][Val], all polarity parameters (α, β, and π^* values) vary linearly with the mixing ratio. In contrast, in the [emim][Asp] + [emim][Lys] and the [emim][Glu] + [emim][Lys] systems, the α and π^* values changed nonlinearly (convex upwards) with mixing composition (see Figure 1) showing the maximum π^* value. The π^* value of both of pure [emim][Asp] and [emim][Lys] is about 1.1, but the mixture ([emim][Asp] + [emim][Lys] (1:3 by mol)) shows much higher value, 1.36. This strongly suggests that the mixtures are highly polar liquids. The π^* value of known polar IL (mainly chloride salts) to date is approximately 1.0.[7] Two mixed systems ([emim][Asp] + [emim][Lys] and [emim][Glu] + [emim][Lys]), which exhibited unexpectedly large π^* values, contained amino acids having carboxylic acid and amino residues, respectively. This finding suggests us to consider that it should be important to examine the effect of hydrogen bonding between side groups of amino acid anions on the polarity of the mixture. However, the mixture of [emim][Asp] and [emim][Lys] has a serious drawback, high viscosity. To solve this problem we have examined other AAILs having relatively low viscosity.

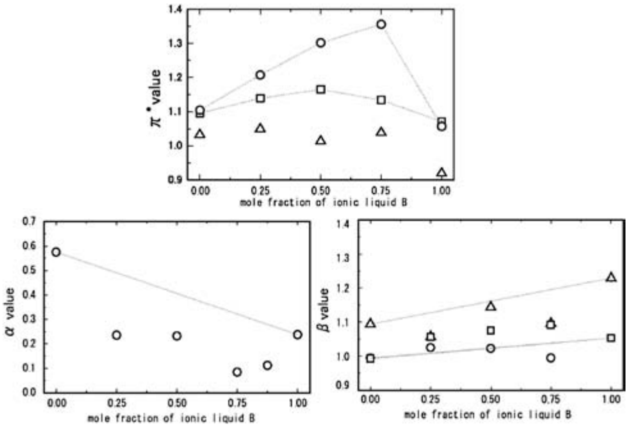

Figure 1. Kamlet–Taft parameters for the AAIL mixtures (A + B). [emim][Ala] + [emim][Val] (△), [emim][Asp] + [emim][Lys] (○), [emim][Glu] + [emim][Lys] (□).

The viscosity of AAILs is strongly affected by the cation structure.[5] We have already reported that [P_{4444}][amino acid] is less viscous than [emim][amino acid].[5c] Accordingly, we prepared new AAIL mixtures with [P_{4444}] cation instead of [emim].[5c] As expected, [P_{4444}] cation was better to prepare ILs with amino acid. Thus prepared [P_{4444}][Asp] was then mixed with [P_{4444}][Lys] to prepare polar and less viscous ionic liquids. The polarity of this mixture was also evaluated with solvatochromic dyes. As expected, the π^* value of the mixture changed nonlinearly (convex, upwards) versus composition. Furthermore, there was little increase in the viscosity of [P_{4444}][Asp] upon adding [P_{4444}][Lys] as shown in Figure 2. Very high π^* value (1.17) and relatively low viscosity (0.5P) were successfully observed by mixing [P_{4444}][Asp] with [P_{4444}][Lys] (by 1:4). Regardless of cation structure, the mixture of AAILs having Asp and Lys anions had very high π^* value. It is necessary to consider packing of Asp and Lys anions in the mixtures to understand the increase of π^* value after mixing.

We believe that the crystal structure of [P_{4444}][Asp] should be obtained through the packing study of the crystal, but unfortunately the [P_{4444}][Asp] could not be crystallized.

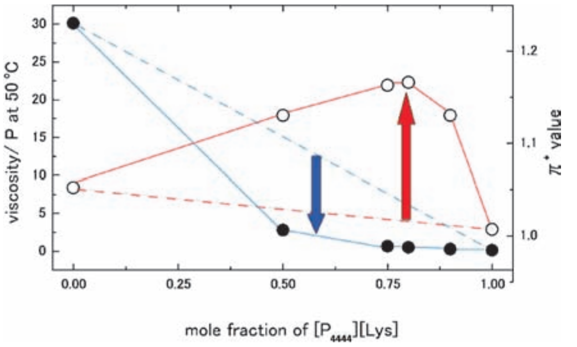

Figure 2. Effect of $[P_{4444}]$[Lys] fraction on the π^* value (○) and viscosity (●) at 50 °C for the mixtures ($[P_{4444}]$[Asp] + $[P_{4444}]$[Lys]).

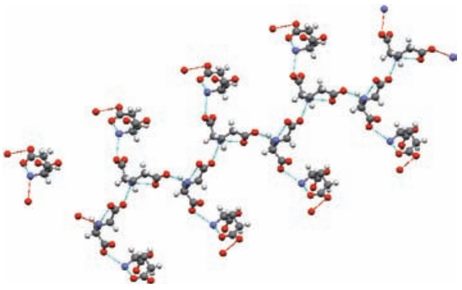

Figure 3. Glu layer in crystalline $[P_{4444}]$[Glu].

Instead, we could analyze the crystal structure of $[P_{4444}]$[Glu] by single-crystal X-ray diffraction measurement. The melting point of $[P_{4444}]$[Glu] was 101.7 °C, and accordingly this is not a room-temperature ionic liquid, but $[P_{4444}]$[Glu] is useful to analyze crystals at ambient temperature. The understanding of the crystal structure of $[P_{4444}]$[Glu] should be useful to estimate the ion packing of $[P_{4444}]$[Asp] considering the similarity in structure between these two salts. $[P_{4444}]$[Glu] crystal was analyzed with R-AXIS RAPID.[11] Successive Glu anion layers were found in the crystal stabilized by hydrogen bonds among anions as shown in Figure 3. There are two types of hydrogen bonds, intermolecular hydrogen bonds and intramolecular ones. These hydrogen bonds contribute to lower the mobility of ions. On the other hand, $[P_{4444}]$[Asp] is liquid but its viscosity is still high (7400 cP at 50 °C). From the viewpoint of crystal structure of $[P_{4444}]$[Glu], crystallization of $[P_{4444}]$[Asp] was suppressed because of weaker interaction among Asp anions. The $[P_{4444}]$[Asp] is expected to have high electron density, because Asp was strongly suggested to exist as triple ion containing two dissociated carboxylic acid residues and one protonated amino group.[12] Although this high electron density would make $[P_{4444}]$[Asp] polar, the π^* value was unchanged.

In the $[P_{4444}]$[Asp] + $[P_{4444}]$[Lys] mixed system, the fraction of Asp anions interacted with Lys anions increased compared to pure $[P_{4444}]$[Asp]. There should be another hydrogen bond between the amine group(s) of Lys and the carboxylic group of Asp, but as explained above it is possible that these bonds do not form anion layers. Even in the molten state, there could remain an aggregation via hydrogen bonds. The electron density around the *N*,*N*-diethyl-4-nitroaniline dye would then increase upon adding $[P_{4444}]$[Lys]. The mixture is accordingly considered to show higher π^* value and lower viscosity than those for $[P_{4444}]$[Asp].

In conclusion, we succeeded in improving polarity of amino acid ionic liquids by adding another amino acid ionic liquid having hydrogen-bonding ability. Especially, well-regulated network of Asp anions would effectively be disturbed, and viscosity decreased without lowering polarity even in the molten state.

J. K. acknowledges the financial support of the Japan Society for the Promotion of Science (Research Fellowship for Young Scientists). This study was supported by KAKENHI, a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology (Nos. 17205020 and 17073005).

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