

# Effects of the ring structure of ionic liquid cation on complex formation equilibria

T. Takamuku<sup>a</sup>, M. Yamada<sup>a</sup>, K. Sasaki<sup>a</sup>

<sup>a</sup>Saga University

Room-temperature ionic liquids (ILs) attract much attention from various chemical fields. This is attributed to ILs' unique properties, negligible volatility, thermal stability, and high polarity. Particularly, ILs are one of the candidates for green solvents of metal ion extraction. Thus, the metal ion complex formation in ILs is essential to understand the mechanism of metal extraction using ILs.

We have clarified the complex formation equilibria of Ni<sup>2+</sup> with several molecular liquids (MLs), such as methanol, in imidazolium-based ILs. The mixing states of IL with ML play important roles to the complex formation. Especially, the hydrogen bonding of ML with the imidazolium ring H atoms affects the equilibria. Furthermore, the self-hydrogen bonding among ML molecules influences the complex formation. The stronger both the hydrogen bonds, the lower the complex stability. Small-angle neutron scattering (SANS) technique has been applied to observe the heterogeneous mixing of IL and ML on the mesoscopic scale.

In the present study, to clarify the solvent properties of IL with a different cation ring, the IL cation was replaced with pyridinium-based one. The mixing state of 1-alkylpyridinium bis(trifluoromethylsulfonyl)amide, C<sub>n</sub>PyTFSA (*n* represents the alkyl chain length), with deuterated formamide (FA-*d*<sub>2</sub>) was evaluated by SANS technique using SANS-U.

Fig. 1 shows the SANS profiles of C<sub>8</sub>PyTFSA–FA-*d*<sub>2</sub> mixture at the mole fraction  $x_{FA-d_2} = 0.89$  with lowering temperature. The SANS intensities strengthen with decreasing temperature, suggesting that the heterogenous mixing enhances by cooling. This is because the self-hydrogen bonds among FA molecules develop in the mixture with decreasing temperature. To quantitatively evaluate the heterogeneity, the profiles were fitted Ornstein-Zernike function. Fig. 2 displays the correlation

lengths  $\xi$  estimated for the solution at  $x_{FA-d_2} = 0.90$  as a function of temperature, together with those for the imidazolium-based IL system of C<sub>8</sub>mImTFSA for comparison. For both systems, the  $\xi$  value significantly increases with lowering temperature toward the phase separation temperature. The increase in the  $\xi$  value for the C<sub>8</sub>mImTFSA system begins at the lower temperature than the C<sub>8</sub>PyTFSA system. This reveals that the mixing state of the pyridinium system is less heterogeneous than the imidazolium one. One of the reasons for the lower heterogeneity of the former is the five sites of the pyridinium ring for the hydrogen bonding, while the imidazolium ring has three sites. FA molecules can more frequently interact with the pyridinium ring than the imidazolium one.

The complex formation of Ni<sup>2+</sup> with FA is exploring now. The effects of the mixing state of the C<sub>8</sub>PyTFSA–FA solvents on the equilibria will be discussed from the results.

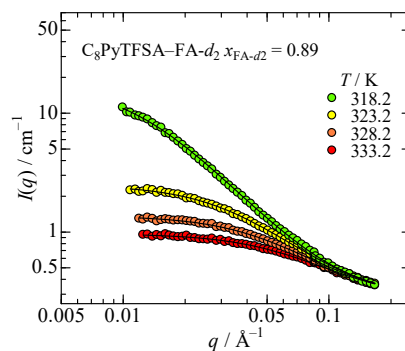


Fig.1 SANS profiles of C<sub>8</sub>PyTFSA–FA-*d*<sub>2</sub>.

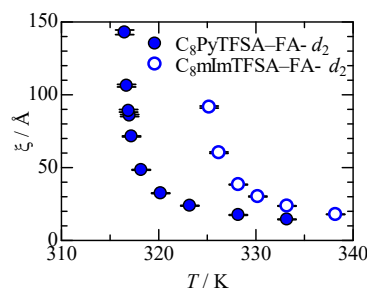


Fig. 2  $\xi$  values as a function of temperature.