SANS Study on Morphology of Pyridinium-based Ionic Liquids in Molecular Liquids

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Room-temperature ionic liquids consist of organic cation and anion with a large size to reduce the electrostatic force between them. The cations often involve the positively charged aromatic rings, such as imidazolium and pyridinium. The aromatic rings are attached by an alkyl chain to increase the entropic effect to avoid crystallization of ionic liquids. Thus, the physicochemical properties of the ionic liquids depend on the charged aromatic-ring structure and the length of the alkyl chain of cation.

In the present investigation, the morphology of pyridinium-based ionic liquids in molecular liquid of water has been observed using small-angle neutron scattering (SANS) technique on the mesoscopic scale. In addition, the results of the pyridinium-based ionic liquids has been compared with those of imidazolium-based ionic liquids.

Pyridinium-based ionic liquids with the two different alkyl chain lengths, 1-hexylpyridinium bromide and 1-octylpyrininium bromide C_nPyBr (n represents the alkyl chain length, n = 6 and 8), synthesized in our laboratory were dissolved into D_2O at various concentrations. D_2O solutions of imidazolium-based ionic liquids C_nmImTFSA with the same alkyl lengths, C_nmImBr, was also prepared. Electro-conductivity measurements were made on the ionic liquid–D_2O solutions at 298.2 K to determine critical aggregation concentration (cac). According to the concentration, SANS experiments at 298.2 K were performed on the solutions using the SANS-U spectrometer. The camera lengths were set at 1 and 4 m. The accumulation times for the scattered neutrons at the camera lengths were 10 and 40 min, respectively. The transmittance of the solutions was determined at the camera length of 16 m for 100 s. The observed scattering intensities were corrected for the absorbance, background, and incoherent scatterings.

Fig. 1 indicates the SANS profiles of C_nPyBr–D_2O and C_nmImBr–D_2O solutions as a function of concentration. Both C_6PyBr and C_6mImBr systems do not show significant SANS intensities over the concentration range examined. Thus, the ionic liquids do not remarkably form aggregation in the D_2O solutions. This is consistent with no significant break point in the plots of the electro-conductivity against the concentration. On the contrary, the significant SANS intensities are observed for the profiles of both C_8PyBr and C_8mImBr systems above 200 mmol dm^{-3}. This concentration agrees with the cac determined from the electroconductivity. The profiles were fitted using Fuzzy sphere model to determine the geometry of the aggregates formed in the solutions. C_8PyBr and C_8mImBr forms spherical micelles with the mean radius of ~16 Å. However, the aromatic-ring dependence between C_8PyBr and C_8mImBr cannot be found in the present experiments.

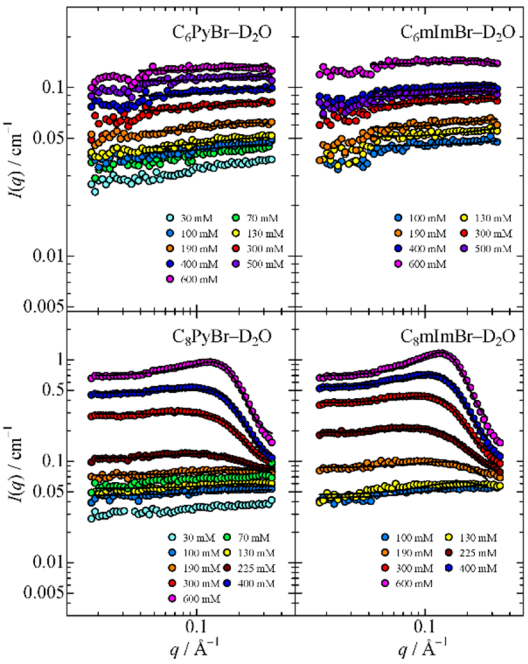

Fig. 1. SANS profiles of C_nPyBr–D_2O and C_nmImBr–D_2O solutions.