

# Study on micro-solvent extraction mechanism using ionic liquid-water mixed solvents by SANS

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Aqueous mixed solvents of ionic liquids (ILs) were measured by small-angle neutron scattering (SANS) to elucidate the liquid structure on nanometer scale. The aqueous IL samples examined were prepared by weighting imidazolium based ionic liquid [C<sub>n</sub>mim+X<sup>-</sup>, X = Cl<sup>-</sup>, Br<sup>-</sup>, CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>, bis(trifluoromethylsulfonyl)amide (TFSA)] with the alkyl-chain length  $n = 4, 8$  and  $12$ . SANS measurements were carried out by using SANS-U spectrometer at 298 K and the scattering intensities for the samples were accumulated on the detector at the camera lengths of 1 and 4 m for 10 min and 1 h, respectively. Typical results are given below.

With regard to 1-butyl-3-methylimidazolium (C<sub>4</sub>mim<sup>+</sup>) ionic liquid system (IL concentration,  $m = 0 - 1$  mol kg<sup>-1</sup>), aqueous mixed solvents of C<sub>4</sub>mim<sup>+</sup>+Cl<sup>-</sup> and C<sub>4</sub>mim<sup>+</sup>+Br<sup>-</sup> show no scattering above the background over the whole  $Q$  range examined ( $0.01 < Q/\text{\AA}^{-1} < 0.35$ ). On the other hand, that of C<sub>4</sub>mim<sup>+</sup>+CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> shows a weak SANS profile based on a general Ornstein-Zernike function. This implies that a hydrophobic IL anion such as CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> is not easily solvated with water relative to Cl<sup>-</sup> and Br<sup>-</sup> anions, and then the CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> aggregates with hydrophobic C<sub>4</sub>mim<sup>+</sup> cation to form IL cluster.

With aqueous C<sub>8</sub>mim<sup>+</sup>+Br<sup>-</sup> system, No significant SANS profile is observed for the concentration  $m = 0.09$  mol kg<sup>-1</sup>, which is shown in Figure 1. The SANS intensity increases with increasing IL concentration up to 1 mol kg<sup>-1</sup>. Note that those for  $m = 0.46$  and  $0.97$  mol kg<sup>-1</sup> fall on the straight line with a  $I(Q) = Q^{-4}$  relationship on a range of  $Q = 0.15 - 0.25$  A<sup>-1</sup>, suggesting that the ionic liquids aggregate with each other to form the charged micelle in the so-

lutions. By assuming a spherical charged micelle, we analyzed the obtained data by using core-shell spherical model (form factor) with a Hyter-Penford structure factor for charged macroions. As seen in Figure 1, the observed  $I(Q)$  is in good agreement with the theoretical one (solid line), as the result, the core radius and shell thickness in the IL micelle were estimated to be 14.8 and 3.3 A, respectively, for  $m = 0.97$  mol kg<sup>-1</sup> and the same values were obtained for  $m = 0.46$  mol kg<sup>-1</sup>.

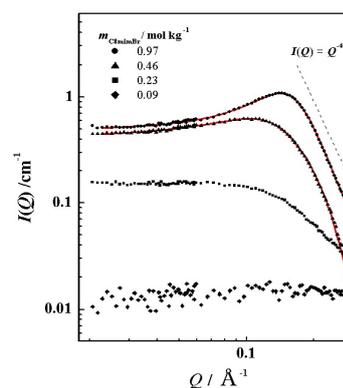


Fig. 1. SANS profiles observed for aqueous C<sub>8</sub>mimBr system. The solid lines correspond to the model fit results.