LCST behavior of Ionic liquid-water mixture

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Ionic liquid has hydrophilic and hydrophobic parts similar to a surfactant. Mixtures of ionic liquids and water behave differently from simple electrolyte solutions. Ionic liquids that phase-separate from water can be applied to material separation operations and the design of heterogeneous reaction phases. Ionic liquid, tetrabutylphosphonium *p*-toluenesulfonate (Fig. 1) ($[P_{4444}]^+[TsO]^-$)-water mixture shows lower critical solution temperature (LCST) behaviors [1]. As well as temperature-sensitive polymers with LCST, ionic liquids with LCST are also expected for some applications.

In the one-phase state at temperatures below the LCST, when a simple electrolyte, such as NaCl, is added to the mixture, the mixture is separated into two phases (ionic liquid-rich phase and water-rich phase). In order to molecularly clarify the phase separation mechanism of ionic liquid-water mixture and the effect of salt on it, we measured the SANS of the mixture of $[P_{4444}]^+[TsO]^-$ and D_2O with and without NaCl.

The mole fraction of water of the mixture, F_W, is defined as $F_W = n_w / (n_w + n_{IL})$ where n_w and n_{IL} are mole of water and the ionic liquid, respectively. The list of the measured samples is as follows:

F_W = 0.94, 0.96, 0.98, and 0.99 without salt

F_W = 0.95, 0.98, and 0.99 with salt *

(*) NaCl was added to the mixture. The concentration of NaCl is 0.75 mol per 1 kg of ionic liquid-water mixture.

At room temperature, the sample solution is in one phase. The sample solutions are sealed in a quartz cell with a 1 or 2 mm sample thickness. A temperature controller equipped with a beamline is used. The SANS was measured at a few temperature points from 25°C to 55°C less than LCST.

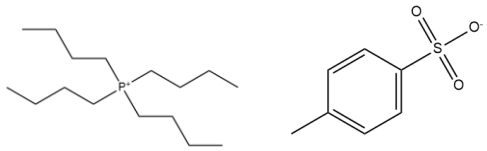

Figure 1. Structure of tetrabutylphosphonium *p*-toluenesulfonate

Figure 2(a) shows the SANS profile of the mixture without salt at F_W = 0.98. The LCST of the mixture without salt is ~53°C [1]. When the temperature approaches LCST, the scattering intensity gradually becomes larger due to microscopic segregation. Figure 2(b) indicates the SANS profile of the mixture with salt. The microscopic segregation takes place at a lower temperature than that without salt.

The microscopic structure will be investigated by wide-angle X-ray scattering to reveal the phase separation mechanism of the mixture.

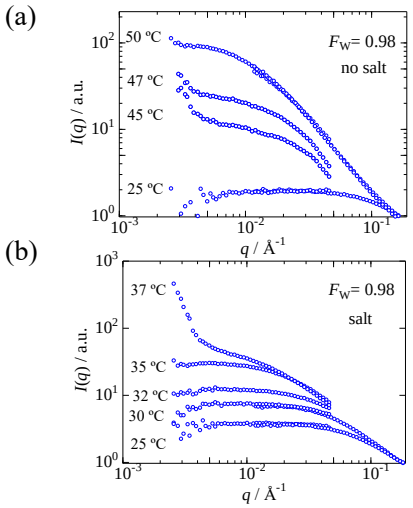

Figure 2. SANS profiles of the ionic liquid-water mixture (a) without / (b) with NaCl.

[1] Y. Kohno, H. Arai, S. Saita and H. Ohno, Aust. J. Chem., 2011, 64, 1560.