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Fluctuation for aqueous solution of phosphonium-based ionic liquid, $[P_{4444}]CF_3COO$ near the LCST by small-angle X-ray scattering

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1 Introduction

Aqueous solution of phosphonium-based ionic liquid tetrabutylphosphonium trifluoroacetate, $[P_{4444}]CF_3COO$, shows phase separation with the lower critical solution temperature (LCST) at 29.2 ºC at x_{IL}= 0.025, where x_{IL} indicates the mole fraction of $[P_{4444}]CF_3COO$ [1]. Figure 1 shows the structure of $[P_{4444}]CF_3COO$ and the phase diagram of the aqueous solution [1]. We have studied the aggregation of $[P_{4444}]CF_3COO$ near the critical point from mesoscopic view point.

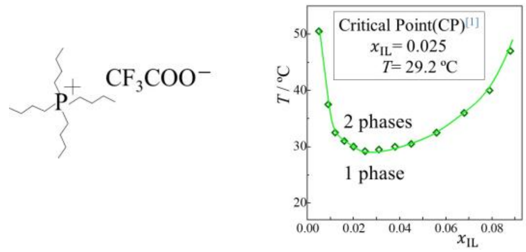

Figure 1. The structure of tetrabutylphosphonium trifluoroacetate, $[P_{4444}]CF_3COO$ and the phase diagram of aqueous solution of $[P_{4444}]CF_3COO$ [1].

Fluctuations are the variation from global average for particle and for concentration defined as $\langle(\Delta N)^2\rangle/\overline{N}$ and $\overline{N}\langle(\Delta x)^2\rangle$, respectively, where N is the number of particles, x is mole fraction, and overlines and brackets mean average value. Fluctuations are calculated by combination of scattering intensity at 0 angle, partial molar volumes and isothermal compressibility [2, 3]. We evaluated the fluctuations for the aqueous solution of $[P_{4444}]CF_3COO$ near the critical point by small-angle X-ray scattering (SAXS) method [4].

2 Experimental

$[P_{4444}]CF_3COO$ was synthesized and was dried under vacuum for 2 days. We mixed $[P_{4444}]CF_3COO$ with ultra pure H_2O (Milli-Q, Millipore) and the concentration of the mixture was determined by measuring their mass. All experiments were performed at x_{IL}= 0.012-0.079 along isotherms at T= 20, 25 and 28 ºC.

The SAXS experiments ware performed at beamline BL-6A. The X-ray wavelength was 1.5 Å. The distance from sample to detector was set at 2 m and its correct value was determined by calibration using AgBh diffraction pattern. The exposure time was 300 s. The scattered intensities were detected by 2-D semiconductor detector, PILATUS 1M (DECTRIS). The 2-D images of intensity were converted to 1-D intensity data versus scattering parameter by the program Fit2D [5]. The intensity of transmitted X-rays was monitored simultaneously by photodiode detector attached on beam stopper. We can obtain the absorption coefficient using the in-situ apparatus [6]. The sample holder was made of stainless steel and sealed by O-ring. Single crystal diamond windows were attached. The sample length was 1.6 mm. Temperature was controlled by circulator and monitored by thermocouple.

Partial molar volumes of $[P_{4444}]CF_3COO$, v_{IL} , and H_2O, v_{W}, ware evaluated by differentiation of density of the aqueous solution by concentration. Concentration dependence of the density was measured using the vibration tube density meter, DMA 4500 (Anton Paar). Temperature was controlled at set temperatures automatically. We adapted graphical fitting curve on measured data without any model fitting for differentiation.

Isothermal compressibility, κ_T, was also evaluated by differentiation of the density by pressure. Pressure dependence of the density was measured using the vibration tube density meter supportable for high pressure, DMA HP (Anton Paar). Measured pressure range was from 0.1 to 8 MPa. The pressure was controlled by pushing sample using pomp. Temperature was controlled by circulator. The pressure dependence of density was approximated by the second order function. Then we obtained κ_T at 0.1 MPa.

3 Results and discussion

Figure 2 shows the SAXS profiles. Scattering intensities of mixture increase toward scattering parameter, s= 0. At x_{IL} = 0.025, the critical concentration, the scattering intensity significantly increased. We evaluated the scattering intensities at s= 0 with fitting curves.

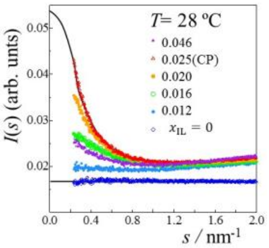

Figure 2. The SAXS profiles of aqueous solution of $[P_{4444}]CF_3COO$ at T= 28 ºC. The solid lines show the fitting curve to evaluate the value at scattering parameter, s= 0.

Figure 3 shows the concentration dependence of partial molar volumes of (a)$[P_{4444}]CF_3COO$, v_{IL}, and (b) H_2O, v_{W}. At lower concentration region, v_{IL} becomes smaller. It suggests that H_2O molecules make hydrogen shell and infill void of bulky $[P_{4444}]CF_3COO$. In dilute region the significant large hydration number of $[P_{4444}]^+$ was reported as 72 and the large hydration shell of $[P_{4444}]^+$ was suggested [7].

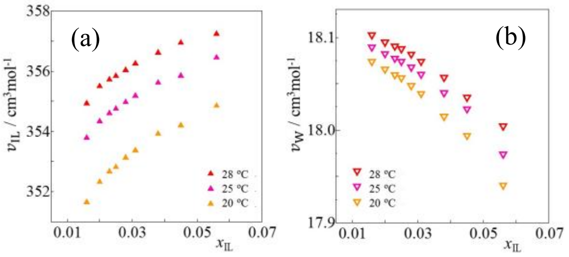

Figure 3. The concentration dependence of partial molar volumes of (a)$[P_{4444}]CF_3COO$, v_{IL}, and (b)water, v_{W}, at *T*= 20, 25 and 28 °C.

SAXS intensity at *s*= 0, *I*(0), is described by $\bar{N}\langle(\Delta x_{\mathrm{IL}})^2\rangle$, v_{IL}, v_{W} and κ_T as,

$$\frac{I(0)}{\bar{N}} = \bar{Z}^2\left(\frac{\bar{N}}{V}\right)\kappa_T k_{\mathrm{B}} T + \left\{\bar{Z}\frac{\bar{N}}{V}(v_{\mathrm{IL}} - v_{\mathrm{W}}) - (Z_{\mathrm{IL}} - Z_{\mathrm{W}})\right\}^2 \bar{N}\langle(\Delta x_{\mathrm{IL}})^2\rangle$$

Z_{i} is the number of electrons of component i, i= IL or W. IL corresponds to $[P_{4444}]CF_3COO$ and W corresponds to H_2O. $\bar{Z}$ is the average number of electrons defined as $\bar{Z} = x_{\mathrm{IL}}Z_{\mathrm{IL}} + x_{\mathrm{W}}Z_{\mathrm{W}}$. k_{B} is the Boltzmann constant. Then $\langle(\Delta N)^2\rangle/\bar{N}$ is obtained by,

$$\frac{\langle(\Delta N)^2\rangle}{\bar{N}} = \left(\frac{\bar{N}}{V}\right)\kappa_T k_{\mathrm{B}} T + \left\{\frac{\bar{N}}{V}(v_{\mathrm{IL}} - v_{\mathrm{W}})\right\}^2 \bar{N}\langle(\Delta x_{\mathrm{IL}})^2\rangle$$

Figure 4 shows the results of (a) $\bar{N}\langle(\Delta x_{\mathrm{IL}})^2\rangle$ and (b)$\langle(\Delta N)^2\rangle/\bar{N}$ of the aqueous solution of $[P_{4444}]CF_3COO$. Both fluctuations increase on approaching to the critical point. $\langle(\Delta N)^2\rangle/\bar{N}$ shows particularly large value.

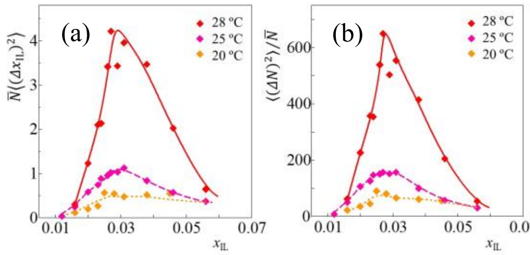

Figure 4. (a)The concentration fluctuation, $\bar{N}\langle(\Delta x_{\mathrm{IL}})^2\rangle$, and (b)the density fluctuation, $\langle(\Delta N)^2\rangle/\bar{N}$, of the aqueous solution of $[P_{4444}]CF_3COO$ at *T*= 20, 25 and 28 °C.

We can divide the fluctuation of entire system into the individual density fluctuations which are the fluctuations focusing on one component by using Kirkwood-Buff parameters. Kirkwood-Buff parameters for binary system composed of component i and j are defined as,

$$G_{\mathrm{ij}} = \int (g_{\mathrm{ij}}(r) - 1)4\pi r^2 \mathrm{d}r$$

where $g_{\mathrm{ij}}(r)$ is the partial distribution function. The individual density fluctuation of component i, $\langle(\Delta N_{\mathrm{i}})^2\rangle/\bar{N}_{\mathrm{i}}$, is described as,

$$\langle(\Delta N_{\mathrm{i}})^2\rangle/\bar{N}_{\mathrm{i}} = \left(\frac{N_{\mathrm{i}}}{V}\right)G_{\mathrm{ii}} + 1$$

We can calculate G_{ii} using $\bar{N}\langle(\Delta x_{\mathrm{IL}})^2\rangle$ as,

$$G_{\mathrm{ii}} = -\frac{1}{(N_{\mathrm{i}}/V)} + \kappa_T k_{\mathrm{B}} T + \frac{v_{\mathrm{j}}^2}{x_{\mathrm{i}}^2}\left(\frac{N}{V}\right)[\bar{N}\langle(\Delta x_{\mathrm{IL}})^2\rangle]$$

Figure 5 shows the contour maps of the individual fluctuations of (a)$[P_{4444}]CF_3COO$, $\langle(\Delta N_{\mathrm{IL}})^2\rangle/\bar{N}_{\mathrm{IL}}$, and (b)$H_2O$, $\langle(\Delta N_{\mathrm{W}})^2\rangle/\bar{N}_{\mathrm{W}}$, described on the phase diagram. Fluctuations of both components increase toward the critical point. At the critical concentration, x_{IL}= 0.025, the increase from 25 to 28 ºC is more remarkable than that from 20 to 25 ºC. From figure 5(a), $[P_{4444}]CF_3COO$ aggregates toward phase separation. H_2O in figure 5(b), shows ten times larger fluctuation than that of $[P_{4444}]CF_3COO$. Combine the results of fluctuations and concentration dependence of the partial molar volumes, we suggest the aggregates of $[P_{4444}]CF_3COO$ contain a large number of water molecules.

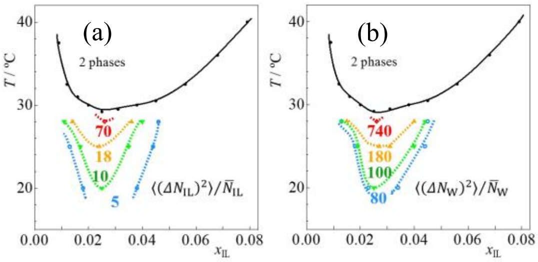

Figure 5. The contour maps of the individual fluctuations of (a)$[P_{4444}]CF_3COO$, $\langle(\Delta N_{\mathrm{IL}})^2\rangle/\bar{N}_{\mathrm{IL}}$, and (b)$H_2O$, $\langle(\Delta N_{\mathrm{W}})^2\rangle/\bar{N}_{\mathrm{W}}$, described on the phase diagram.

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