Fluctuation for aqueous solution of phosphonium-based ionic liquid, [P$_{4444}$]CF$_3$COO near the LCST by small-angle X-ray scattering

Ayako Nitta and Takeshi Morita*

Chiba University Graduate School of Advanced Integration Science,
1-33 Yayoi-cho, Inage-ku, Chiba, 263-8522, Japan

1 Introduction
Aqueous solution of phosphonium-based ionic liquid tetrabutylphosphonium trifluoroacetate, [P$_{4444}$]CF$_3$COO, shows phase separation with the lower critical solution temperature (LCST) at 29.2 °C at $x_{IL} = 0.025$, where $x_{IL}$ indicates the mole fraction of [P$_{4444}$]CF$_3$COO [1]. Figure 1 shows the structure of [P$_{4444}$]CF$_3$COO and the phase diagram of the aqueous solution [1]. We have studied the aggregation of [P$_{4444}$]CF$_3$COO near the critical point from mesoscopic view point.

![Figure 1. The structure of tetrabutylphosphonium trifluoroacetate, [P$_{4444}$]CF$_3$COO and the phase diagram of aqueous solution of [P$_{4444}$]CF$_3$COO [1].](image)

Fluctuations are the variation from global average for particle and for concentration defined as $(\langle \Delta N \rangle^2)/\bar{N}$ and $\bar{N}((\Delta x)^2)$, 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$_3$COO near the critical point by small-angle X-ray scattering (SAXS) method [4].

2 Experimental
[P$_{4444}$]CF$_3$COO was synthesized and was dried under vacuum for 2 days. We mixed [P$_{4444}$]CF$_3$COO with ultra pure H$_2$O (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 °C.

The SAXS experiments were 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$_3$COO, $v_{IL}$, and H$_2$O, $v_W$, were 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, $\kappa_T$, 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 pump. Temperature was controlled by circulator. The pressure dependence of density was approximated by the second order function. Then we obtained $\kappa_T$ 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$_3$COO at $T$= 28 °C. The solid lines show the fitting curve to evaluate the value at scattering parameter, $s=0$.](image)

Figure 3 shows the concentration dependence of partial molar volumes of (a)[P$_{4444}$]CF$_3$COO, $v_{IL}$, and (b) H$_2$O, $v_W$. At lower concentration region, $v_{IL}$ becomes smaller. It suggests that H$_2$O molecules make hydrogen shell and infill void of bulky [P$_{4444}$]CF$_3$COO. In dilute region the
significant large hydration number of \([\text{P}_{4444}]^+\) was reported as 72 and the large hydration shell of \([\text{P}_{4444}]^+\) was suggested [7].

$$G_{ij} = \int \left( g_{ij}(r) - 1 \right) 4\pi r^2 dr$$

where \(g_{ij}(r)\) is the partial distribution function. The individual density fluctuation of component i, \((\Delta N_i)^2)/\bar{N}_i\), is described as,

$$\frac{(\Delta N_i)^2}{\bar{N}_i} = \left( \frac{N_i}{V} \right) G_{ii} + 1$$

We can calculate \(G_{ii}\) using \(\bar{N}((\Delta x_{1i})^2)\) as,

$$G_{ii} = -\frac{1}{(N_i/V)} \kappa_T k_B T + \frac{V_i^2}{x_i} \left( N_i((\Delta x_{1i})^2) \right)$$

Figure 3. The concentration dependence of partial molar volumes of (a) [P_{4444}]CF_3COO, \(v_W\), and (b) water, \(v_W\), at \(T = 20, 25\) and \(28^\circ C\).

SAXS intensity at \(s = 0\), \(I(0)\), is described by \(\bar{N}((\Delta x_{1i})^2)\), \(v_W\), \(v_W\) and \(\kappa_T\) as,

$$I(0) = \frac{Z}{\bar{N}} \kappa_T k_B T \left( \frac{N_i}{V} \right) (v_{1i} - v_W)^2 (Z_{1i} - Z_W)^2 \bar{N}((\Delta x_{1i})^2)$$

\(Z_i\) is the number of electrons of component i, \(i = \text{IL} \text{ or } W\). \(\text{IL}\) corresponds to \([\text{P}_{4444}]\text{CF}_3\text{COO}\) and \(W\) corresponds to \(\text{H}_2\text{O}\). \(\bar{Z} = x_{1i}Z_{1i} + x_WZ_W\). \(k_B\) is the Boltzmann constant. Then \((\Delta N)^2)/\bar{N}\) is obtained by,

$$\frac{(\Delta N)^2}{\bar{N}} = \left( \frac{N_i}{V} \right) \kappa_T k_B T + \left( \frac{N_i}{V} \right) (v_{1i} - v_W)^2 \bar{N}((\Delta x_{1i})^2)$$

Figure 4 shows the results of (a) \(\bar{N}((\Delta x_{1i})^2)\) and (b) \((\Delta N)^2)/\bar{N}\) of the aqueous solution of \([\text{P}_{4444}]\text{CF}_3\text{COO}\). Both fluctuations increase on approaching to the critical point. \((\Delta N)^2)/\bar{N}\) shows particularly large value.

Figure 5 shows the contour maps of the individual fluctuations of (a) \([\text{P}_{4444}]\text{CF}_3\text{COO}, (\Delta N_{1i})^2)/\bar{N}_{1i}\), and (b) \(\text{H}_2\text{O}, (\Delta N_{2i})^2)/\bar{N}_{2i}\), described on the phase diagram. Fluctuations of both components increase toward the critical point. At the critical concentration, \(x_{1\text{IL}} = 0.025\), the increase from 25 to 28 \(^\circ C\) is more remarkable than that from 20 to 25 \(^\circ C\). From figure 5(a), \([\text{P}_{4444}]\text{CF}_3\text{COO}\) aggregates toward phase separation. \(\text{H}_2\text{O}\) in figure 5(b), shows ten times larger fluctuation than that of \([\text{P}_{4444}]\text{CF}_3\text{COO}\). Combine the results of fluctuations and concentration dependence of the partial molar volumes, we suggest the aggregates of \([\text{P}_{4444}]\text{CF}_3\text{COO}\) contain a large number of water molecules.

Figure 3. The concentration dependence of partial molar volumes of (a) [P_{4444}]CF_3COO, \(v_W\), and (b) water, \(v_W\), at \(T = 20, 25\) and \(28^\circ C\).

SAXS intensity at \(s = 0\), \(I(0)\), is described by \(\bar{N}((\Delta x_{1i})^2)\), \(v_W\), \(v_W\) and \(\kappa_T\) as,

$$I(0) = \frac{Z}{\bar{N}} \kappa_T k_B T \left( \frac{N_i}{V} \right) (v_{1i} - v_W)^2 (Z_{1i} - Z_W)^2 \bar{N}((\Delta x_{1i})^2)$$

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*moritat@faculty.chiba-u.jp

References
*moritat@faculty.chiba-u.jp