

Fluctuations and Mixing State of an Aqueous Solution of the Ionic Liquid Tetrabutylphosphonium Trifluoroacetate around the Critical Point

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Aqueous solutions of ionic liquids have unique mixing states. Fluctuations are useful for understanding the inhomogeneity of the mixing states. In this study, an aqueous solution of tetrabutylphosphonium trifluoroacetate, ($[P_{4,4,4,4}]CF_3COO$), which exhibits a lower-critical-solution-temperature-type phase transition, was investigated. Focussing on the concentration and temperature range near the critical point, the fluctuations were evaluated by combining three kinds of experimentally obtained data: small-angle X-ray scattering intensity, partial molar volumes, and isothermal compressibility. Using Kirkwood–Buff integrals, individual density fluctuations of water and $[P_{4,4,4,4}]CF_3COO$ were calculated, and these suggested that a large number of water molecules hydrated $[P_{4,4,4,4}]CF_3COO$ ion pairs, and the hydrated ion pairs aggregated near the critical point. The relationship between the mesoscopic fluctuations and the macroscopic phase transition was clarified by drawing counter maps of the fluctuations in the phase diagrams.

Manuscript received: 31 July 2018.

Manuscript accepted: 22 October 2018.

Published online: 16 November 2018.

Introduction

Ionic liquids (ILs) are a novel type of liquid composed of only cations and anions that have melting points below 373 K.^[1,2] They can show unique properties^[3–5] such as non-volatility, non-flammability, high thermal and chemical stability, high solubility in a large number of solutes, and good electrical conductivity. Furthermore, ILs have anomalous kinetic behaviours associated with freezing and melting processes.^[6,7] In recent years, there has been extensive activity investigating these special characteristics of ILs.

As a small amount of impurity tends to change the properties of a pure IL rather drastically, solubility in other solvents is important.^[8–10] The liquid–liquid equilibrium properties of binary or ternary mixtures of ILs and alcohols or water have been reported.^[11–14] In particular, aqueous solutions of ILs have been studied for biochemical reactions and chemical extraction media.^[15] Water itself has unique characteristics due to its three-dimensional hydrogen bonding. Thus, mixtures of these two unique materials have attracted increasing attention recently.

The solubility of ILs in water depends not only on the characteristics of the constituent ions, but also on the combination of cations and anions of the ILs. Some aqueous solutions of ILs show temperature-dependent reversible phase separation.^[15–17] For example, an aqueous solution of 1-butyl-3-methylimidazolium tetrafluoroborate, $[C_4mim]BF_4$, was observed to exhibit phase separation with an upper critical solution temperature (UCST).^[16,17] However, tetrabutylphosphonium trifluoroacetate, $[P_{4,4,4,4}]CF_3COO$, exhibited phase separation with a lower critical

solution temperature (LCST). The latter system is the target of the present study, and its critical point is observed at $x_{IL} = 0.025$ and at $T = 302.35$ K,^[18] where x_{IL} is the mole fraction of $[P_{4,4,4,4}]CF_3COO$ and T is the absolute temperature.

In general, fluctuations, which are a local deviation from the average, are a fundamental and important concept for describing the structure and properties of a disordered system. For instance, the mixing states of aqueous solutions of molecular liquids have sometimes been discussed in terms of fluctuations.^[19–27] In particular, it has been reported that mixtures with a temperature-dependent phase separation exhibit large fluctuations near the critical point.^[28,29] Moreover, in order to discuss the solution structure around the critical point, a mesoscopic viewpoint is indispensable, because the scale at which the fluctuations are discussed expands as the critical point is approached.

The objective of the present study is to quantitatively understand the mixing states of aqueous solutions of ILs exhibiting phase separation in terms of fluctuations as the probe. As mentioned above, it is thought that mesoscopic fluctuations gradually increase and finally lead to macroscopic phase separation. In the previous studies,^[20,28] the structural fluctuations in aqueous solutions of molecular liquids (2-butoxyethanol or acetonitrile) with an LCST or UCST-type phase separation were studied around the critical point. Targeting aqueous solutions of ILs, we have reported preliminary results on the mixture of $[P_{4,4,4,4}]CF_3COO$ and water as our first sample.^[30] In the present paper, adding to the previous results, we present comprehensive results on the mixing state of an aqueous solution of $[P_{4,4,4,4}]$

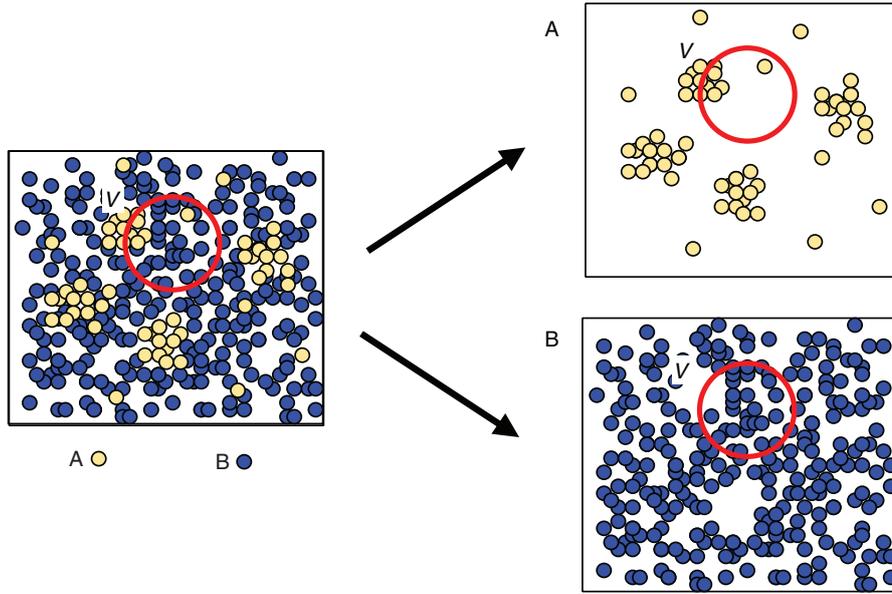


Fig. 1. Conceptual diagram of the fluctuations of an A-B binary system. The density fluctuation of the system (shown on the left side) is divided into the individual density fluctuation of each component (shown on the right side) by KBIs.

CF_3COO , applying the concept of fluctuations with data obtained with the small-angle X-ray scattering (SAXS) technique.

The solution was treated as a binary mixture of $[\text{P}_{4,4,4,4}]$ CF_3COO and water in the concentration range of $x_{\text{IL}} = 0.01$ – 0.06 , based on the assumption that the cation and the anion form a pair in aqueous solution. We have reported the concentration dependence of the electric conductivity for an aqueous solution of $[\text{P}_{4,4,4,4}]\text{CF}_3\text{COO}$.^[31] The isotherm of the molar conductivity as a function of the square root of IL concentration showed a linear relationship up to $x_{\text{IL}} = 0.0080$, suggesting that the constituent ions, $[\text{P}_{4,4,4,4}]^+$ and CF_3COO^- , associated with each other to form ion pairs above the 0.0080 mole fraction. Although we should consider the specific pairing behaviour of the cation and the anion, such as H_2O -mediated ion pairing,^[32,33] for precise discussion about the pairing structure, it was acceptable to treat the solution as a binary mixture of $[\text{P}_{4,4,4,4}]\text{CF}_3\text{COO}$ and water in an adaptation for evaluating the fluctuation parameters.

Theoretical Method

Fluctuations in Binary Systems

The theory of fluctuations in a binary system is briefly summarized here. Let us consider a binary solution system with components A and B. A snapshot of a schematic molecular distribution is shown on the left-side in Fig. 1. The number of molecules N in volume V denoted by a circle fluctuates depending on the position of the circle. The mean square ranging over the system, $\langle (\Delta N)^2 \rangle = \langle (N - \bar{N})^2 \rangle$, is the number fluctuation for the fixed volume V . With division by \bar{N} , we obtain the density fluctuation, $\langle (\Delta N)^2 \rangle / \bar{N}$, as the intensive value of the system. Note that here N is the number of molecules without distinguishing between A and B (see the left side of Fig. 1). The concentration fluctuation, $\bar{N} \langle (\Delta x)^2 \rangle$, expresses the contrast between components A and B. It is defined as the mean square difference of the concentration derived from the global average, where $\Delta x = x - \bar{x}$ and x is the mole fraction of component A. The correlation term between the density fluctuation and the concentration

fluctuation, $\langle (\Delta N)(\Delta x) \rangle$, is also defined as the cross term of the density deviation and the concentration deviation.

Bhatia and Thornton showed that the zero-angle X-ray scattering intensity, $I(0)$, can be formulated in terms of the fluctuations as:^[34,35]

$$I(0)/\bar{N} = \bar{Z}^2 \langle (\Delta N)^2 \rangle / \bar{N} + (Z_A - Z_B)^2 \bar{N} \langle (\Delta x)^2 \rangle + 2\bar{Z}(Z_A - Z_B) \langle (\Delta N)(\Delta x) \rangle \quad (1)$$

and the scattering parameter s is defined by $4\pi \sin\theta/\lambda$, where λ is the wavelength of the X-rays, and 2θ is the scattering angle; Z_A and Z_B are the total number of electrons in the A- and the B-type molecules respectively, and they correspond to the scattering amplitudes of X-rays at $s = 0$; and \bar{Z} is the averaged number of electrons:

$$\bar{Z} = xZ_A + (1-x)Z_B. \quad (2)$$

These fluctuations are also expressed using thermodynamic quantities,^[19,34] all of which are related to the second derivatives of the Gibbs energy G :^[19,36]

$$\bar{N} \langle (\Delta x)^2 \rangle = \bar{N} kT / \left(\frac{\partial^2 G}{\partial x^2} \right)_{T,p}, \quad (3)$$

$$\frac{\langle (\Delta N)^2 \rangle}{\bar{N}} = \left(\frac{\bar{N}}{V} \right) kT \kappa_T + \left\{ \frac{\bar{N}}{V} (v_A - v_B) \right\}^2 \bar{N} \langle (\Delta x)^2 \rangle, \quad (4)$$

$$\langle (\Delta N)(\Delta x) \rangle = - \left\{ \frac{\bar{N}}{V} (v_A - v_B) \right\} \bar{N} \langle (\Delta x)^2 \rangle, \quad (5)$$

where k is the Boltzmann constant, T is the thermodynamic temperature, κ_T is the isothermal compressibility of the mixture, and v_A and v_B are the partial molar volumes of components of A and B respectively. The quantities κ_T , v_A , and v_B are all second derivatives of G .^[36]

From Eqns 1, 4, and 5, $I(0)$ can be written as:

$$\frac{I(0)}{\bar{N}} = \bar{Z}^2 \left(\frac{\bar{N}}{\bar{V}} \right) kT \kappa_T + \left\{ \bar{Z}(v_A - v_B) \frac{\bar{N}}{\bar{V}} - (Z_A - Z_B) \right\}^2 \bar{N} \langle (\Delta x)^2 \rangle. \quad (6)$$

Thus, the density fluctuation, the concentration fluctuation, and their correlation term are determined by a combination of $I(0)$, κ_T , v_A , and v_B , which can be measured experimentally. Of course, it is possible to determine the three kinds of fluctuations using only the thermodynamic measurements, as shown in Eqns 3–5. However, it is usually difficult to accurately determine the value of $\left(\frac{\partial^2 G}{\partial x^2} \right)_{T,p}$. Eqn 6 shows that it is possible to replace the troublesome measurement of G and its double differentiation with an SAXS experiment.

The SAXS method is a powerful tool for observing structures at nanoscopic and mesoscopic levels, and it has often been used in the structural analysis of nanomaterials and macromolecules such as proteins in solution.^[37,38] Bhatia and Thornton formulated the importance of SAXS in material science by its novel use for studying fluctuations. For details of the relation between fluctuations and SAXS intensity, see the original papers^[34,35] and the review.^[19]

Density Fluctuations for Each Component

The relation between fluctuations and the Kirkwood–Buff integrals (KBIs) is summarized briefly. KBIs are defined by:^[39]

$$G_{ij} = \int (g_{ij} - 1) 4\pi r^2 dr, \quad (7)$$

where i or j corresponds to A or B, g_{ij} is the correlation function, and r is the inter-particle distance between i - and j -components. KBIs are expressions for fluctuation that are important in solution chemistry.^[40,41] To express fluctuations explicitly, KBIs have been formulated using the concentration fluctuation, $\bar{N} \langle (\Delta x)^2 \rangle$:^[42]

$$G_{AA} = - \left(\frac{V}{N_A} \right) + \kappa_T kT + \left(\frac{v_B}{x_A} \right)^2 \left(\frac{\bar{N}}{\bar{V}} \right) \cdot \bar{N} \langle (\Delta x)^2 \rangle, \quad (8)$$

$$G_{BB} = - \left(\frac{V}{N_B} \right) + \kappa_T kT + \left(\frac{v_A}{x_B} \right)^2 \left(\frac{\bar{N}}{\bar{V}} \right) \cdot \bar{N} \langle (\Delta x)^2 \rangle, \quad (9)$$

$$G_{AB} = \kappa_T kT + \left(\frac{v_A v_B}{x_A x_B} \right) \left(\frac{\bar{N}}{\bar{V}} \right) \cdot \bar{N} \langle (\Delta x)^2 \rangle. \quad (10)$$

Usually, KBIs for various solutions are obtained using thermodynamic quantities only.^[41] However, KBIs can be obtained more accurately and more easily using SAXS data combined with Eqns 8–10, as pointed out in the simple determination of the concentration fluctuation.

It is possible to describe various thermodynamic quantities using KBIs.^[43] The individual density fluctuation of component i , $\frac{\langle (\Delta N_i)^2 \rangle}{\bar{N}_i}$, can be expressed using KBIs as follows:^[34,42]

$$\frac{\langle (\Delta N_i)^2 \rangle}{\bar{N}_i} = \left(\frac{\bar{N}_i}{\bar{V}} \right) G_{ii} + 1. \quad (11)$$

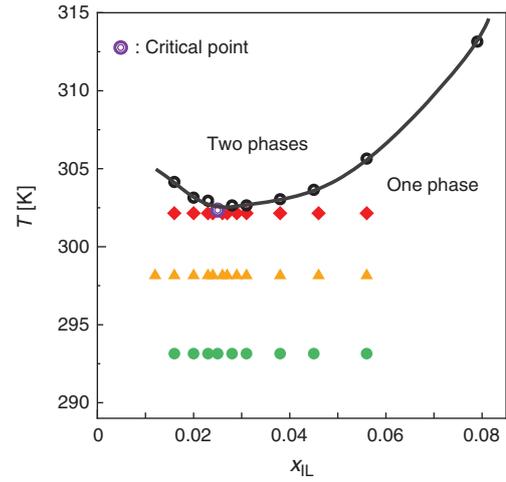


Fig. 2. Phase diagram of an aqueous solution of tetrabutylphosphonium trifluoroacetate, $[P_{4,4,4,4}]CF_3COO$. The black line is the phase boundary and the purple symbol indicates the critical point at $x_{IL} = 0.025$ and $T = 302$ K. The red diamonds, orange triangles, and green circles represent the observed points for SAXS measurements at 293, 298, and 302 K respectively.

Unlike the density fluctuation defined in Eqns 1 and 4, the individual density fluctuation considers each component of a binary system. Fig. 1 shows a schematic view of these density fluctuations.

Experimental

$[P_{4,4,4,4}]CF_3COO$ was prepared by direct neutralization of aqueous solutions of the tetrabutylphosphonium hydroxide (Hokko Chemical Industry Co.) with trifluoroacetic acid (Wako Pure Chemical Co.). The structure and the purity of the salt were confirmed by 1H NMR and elemental analyses. The $[P_{4,4,4,4}]CF_3COO$ was mixed with ultrapure water (Milli-Q, Millipore) to the desired concentration gravimetrically. All the experiments were performed for $x_{IL} = 0.000$ – 0.079 along isotherms at $T = 293$, 298 , and 301 K within 1 week of preparing the mixtures. The data points were plotted on the solution phase diagram,^[18] as shown in Fig. 2.

Acquiring the SAXS Intensity Data

SAXS measurements were performed at the BL-6A and 10C stations in the Photon Factory (PF) at the National Laboratory of the High-Energy Accelerator Research Organization (KEK), Tsukuba. The scattering intensities of the aqueous solutions were measured using high-intensity X-rays of wavelength 1.50 \AA (8.27 keV) and a highly accurate detector in the PF to quantify the fluctuations.^[44] The X-rays were focussed and monochromated using a bent mirror and a monochromator. The monochromatic X-rays passed through three slits. The intensity of the incident X-rays was monitored using an ionization chamber placed before the sample holder. The transmitted X-rays were simultaneously detected by a photodiode set on the X-ray beam stop, which enabled the determination of the precise absorption coefficient of each sample so that the scattering intensity could be obtained on an absolute scale.^[45] The X-rays scattered by the sample materials were detected by a two-dimensional semiconductor detector, PILATUS 1M or 2M (Dectris). The distance from the sample to the detector was set at ~ 2 m, and an accurate value was determined using the diffraction pattern of silver behenate,

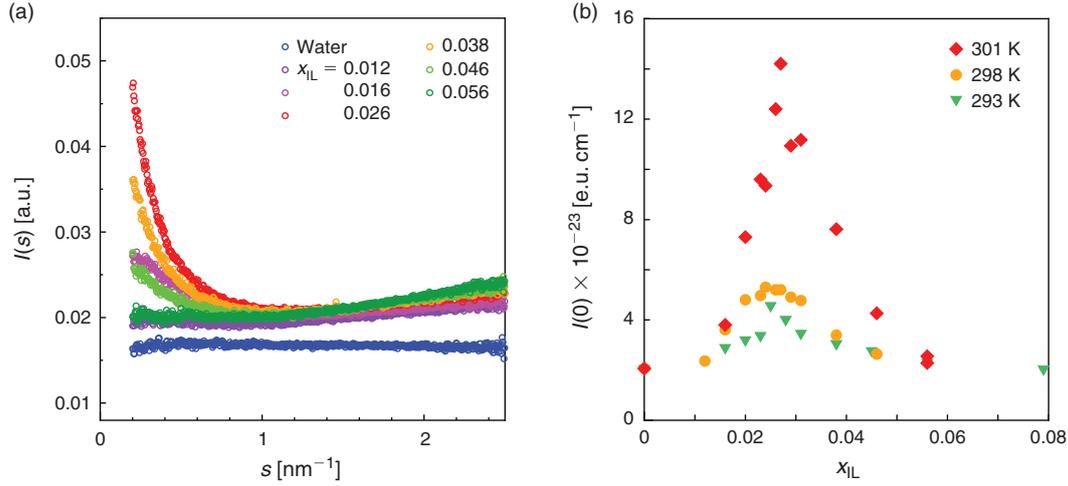


Fig. 3. (a) SAXS profiles of aqueous solutions of $[P_{4,4,4,4}]CF_3COO$ at 301 K. The blue symbols are the results for neat water. On adding $[P_{4,4,4,4}]CF_3COO$, the SAXS intensity, $I(s)$, increases towards $s = 0$, and at $x_{IL} = 0.026$, $I(s)$ shows the greatest increase. (b) Concentration dependence of the zero-angle scattering intensity, $I(0)$, at 293, 298, and 301 K. The unit ‘e.u.’ represents the units of electrons. $I(0)$ s peak near the critical concentration, $x_{IL} = 0.025$, at each temperature. In particular, $I(0)$ at 301 K sharply increases towards the critical concentration.

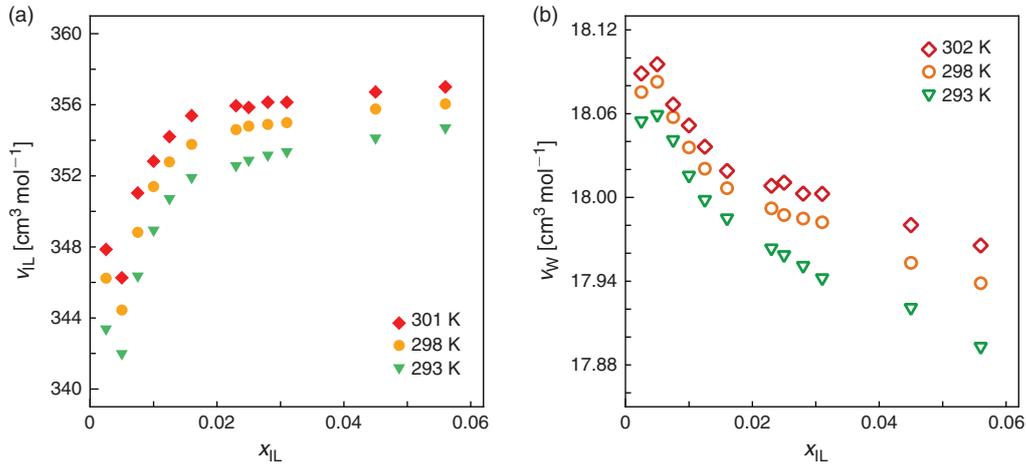


Fig. 4. Concentration dependence of the partial molar volumes of (a) $[P_{4,4,4,4}]CF_3COO$, v_{IL} ; and (b) water, v_W , at 293, 298, and 301 K.

AgBh. The sample holder was made of stainless steel (SUS 304),^[30] and the sample thickness was set to 1.6 mm. A pair of single-crystal diamond disks (Sumitomo Electric Hardmetal Co.) with a thickness of 0.3 mm and a diameter of 4.0 mm were used as X-ray windows. The temperature of the sample materials was controlled by circulating water through a rubber hose from a thermostatted bath and was monitored by a K-type thermocouple set at the sample holder.

Partial Molar Volume and Isothermal Compressibility

The partial molar volumes of the components and the isothermal compressibility were determined to give the second derivatives in Eqn 6. For this purpose, we determined the density of the present aqueous solution as a function of mole fraction and pressure using vibration tube density meters DMA 4500, DMA 4100, and DMA HP (Anton Paar). The pressure dependence of the density was adjusted using distilled pure water and nitrogen gas at all temperatures and pressures, according to the conditions for the measurement points. These volumetric data were differentiated using the concentration or pressure to obtain the partial molar volumes or isothermal compressibility respectively.

Results and Discussion

Fig. 3a shows the SAXS intensity, $I(s)$, versus the scattering parameter, s , of aqueous solutions of $[P_{4,4,4,4}]CF_3COO$ at 301 K. The profile of water, shown in blue, is flat in this s range. On adding $[P_{4,4,4,4}]CF_3COO$, the scattering intensity curves up towards $s = 0$. The intensity for $x_{IL} = 0.026$, which is closest to the critical concentration, has the largest increase. Beyond the critical concentration, scattering intensity decreases. The magnitude of the intensity at 293 and 298 K was considerably smaller than that at 301 K. Each value of $I(0)$ was obtained by extrapolating the corresponding fitted curve obtained in the range $0.2 < s < 1.0 \text{ nm}^{-1}$ to $s = 0$. The SAXS intensity of the system near the critical point follows the Ornstein–Zernike equation as follows:^[46]

$$I(s) = \frac{I(0)}{1 + \xi^2 s^2}, \quad (12)$$

where ξ is the correlation length. This equation is applicable to systems that have a large structural inhomogeneity, namely highly fluctuating systems. The inverse of $I(s)$ should be a linear

function of s^2 . In the study of aqueous solutions of acetonitrile, $I(0)$ values were well determined using Eqn 12 near the critical point.^[28] However, for the present aqueous solution of $[P_{4,4,4,4}]CF_3COO$, the SAXS intensities did not follow Eqn 12, even for $x_{IL} = 0.026$ and at 301 K, which is very close to the critical concentration and corresponds to a temperature only 1.0 K lower than the critical temperature. We decided that Eqn 12 was not suitable because it may have led to involving the characteristics of an unintended contribution to the ILs. Molecular dynamics simulation studies showed that most ILs have strong interactions among themselves in the pure state.^[47–49] The influence from the interaction is frequently observed in the X-ray scattering intensity as a broad peak, generally in an s region larger than the region shown in Fig. 3.^[50,51] The intensity of neat $[P_{4,4,4,4}]CF_3COO$ also showed an increase in the region of s larger than 2 nm^{-1} and a similar increase in intensity was observed in X-ray scattering intensity of its aqueous solution in $s > 1.2 \text{ nm}^{-1}$. Thus, to fit our data, instead of Eqn 12, we used the following equation:

$$I(s) = \frac{I(0)'}{1 + \xi^2 s^2} + \alpha. \quad (13)$$

The attempt was reasonably successful. $I(0)$ was obtained as the sum of $I(0)'$ and α , where α is the corrected term for the contribution from the base of the strong and broad peak due to the interference among ILs. Fig. 3b shows the concentration dependence for the zero-angle scattering intensities, $I(0)$, at 293, 298, and 301 K.

Fig. 4 shows the partial molar volumes of $[P_{4,4,4,4}]CF_3COO$, v_{IL} , and water, v_W , at 293, 298, and 301 K for $x_{IL} = 0.000–0.079$. v_{IL} and v_W have a minimum and a maximum respectively for $x_{IL} = 0.003$. In the concentration region $x_{IL} = 0.016–0.06$, v_{IL} increases with x_{IL} , whereas v_W decreases. This is because the ion pair $[P_{4,4,4,4}]CF_3COO$ has an ~ 20 times larger volume than that of a water molecule. Because $[P_{4,4,4,4}]CF_3COO$ is very bulky and has large steric hindrance, it requires a large space in solution. However, water molecules are likely to fill the voids formed by the ion-pair packing owing to their size difference.^[30]

The isothermal compressibility, κ_T is given as:

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_{T, x_i} = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial p} \right)_{T, x_i}. \quad (14)$$

where p is the sample pressure. κ_T was obtained by measuring the pressure dependence of the density, ρ , for an aqueous solution of $[P_{4,4,4,4}]CF_3COO$ at 293 and 301 K for the pressure range from 0.1 to 12.0 MPa in steps of 1.0 MPa. Fig. 5a shows the results at 301 K. The increase of density or the decrease of molar volume, V_m , with increasing pressure was too small to use the fitting functions introduced in a previous study.^[52] We approximated the pressure dependence of V_m by a straight line. Then, we calculated κ_T up to $p = 12 \text{ MPa}$ using the slope. Fig. 5b is an example of a linear fit at 301 K for $x_{IL} = 0.025$. Fig. 5c shows the concentration dependence of κ_T of an aqueous solution of $[P_{4,4,4,4}]CF_3COO$ at 293 and 301 K. The values of κ_T for 298 K were obtained by interpolation of the results between 293 and 301 K. This approximation by interpolation does not have a serious influence on the final results because the term including κ_T is quite small.

Fig. 6 shows the density fluctuation, $\langle (\Delta N)^2 \rangle / \bar{N}$, the concentration fluctuation, $\bar{N} \langle (\Delta x)^2 \rangle$, and their cross-term, $\langle (\Delta N)(\Delta x) \rangle$, for the aqueous solution of $[P_{4,4,4,4}]CF_3COO$ at

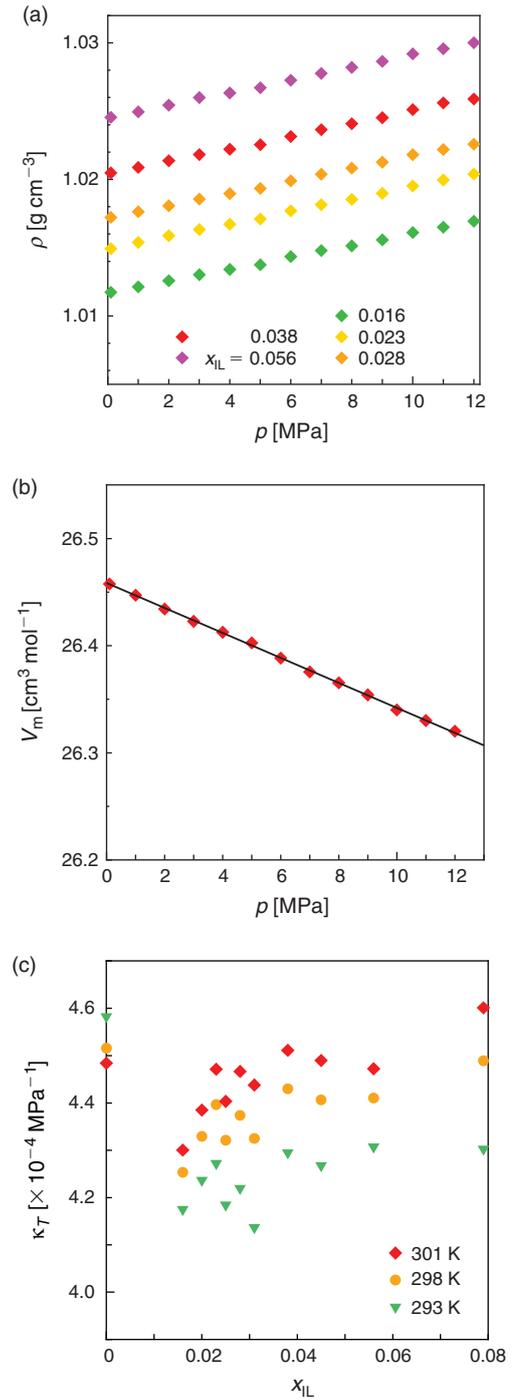


Fig. 5. Pressure dependence of (a) ρ and (b) V_m for the aqueous solution of $[P_{4,4,4,4}]CF_3COO$ at 301 K and $x_{IL} = 0.025$. The black solid line represents the fitted linear line. κ_T was determined using the slope up to 12.0 MPa. (c) Concentration dependence of κ_T for the aqueous solution of $[P_{4,4,4,4}]CF_3COO$ at 293 and 301 K. κ_T at 298 K was obtained by interpolating the values at 293 and 301 K.

293, 298, and 301 K against x_{IL} obtained from $I(0)$, v_{IL} and v_W , and κ_T . Both $\langle (\Delta N)^2 \rangle / \bar{N}$ and $\bar{N} \langle (\Delta x)^2 \rangle$ increase near the critical point and they have sharp peaks at 301 K. These results show the large fluctuations on approaching the critical point at 302 K and $x_{IL} = 0.025$.

Interestingly, the density fluctuation of the present mixture shows a much larger value than that for an aqueous solution of

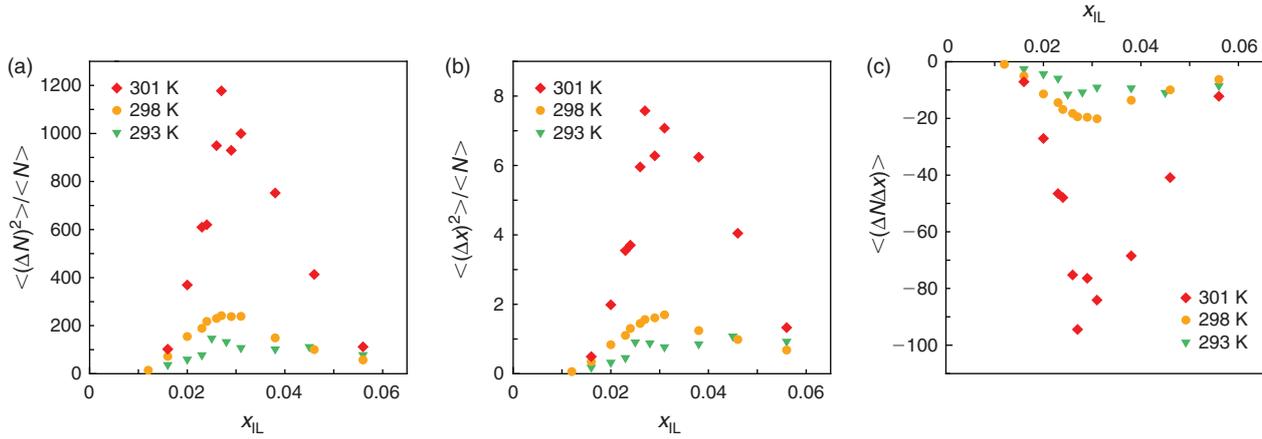


Fig. 6. Fluctuations of the aqueous solution of $[P_{4,4,4,4}]CF_3COO$ at 293, 298, and 301 K. (a) Density fluctuation, $\langle(\Delta N)^2\rangle/\bar{N}$; (b) concentration fluctuation, $\bar{N}\langle(\Delta x)^2\rangle$; and (c) the cross term of the density and concentration fluctuations, $\langle(\Delta N)(\Delta x)\rangle$.

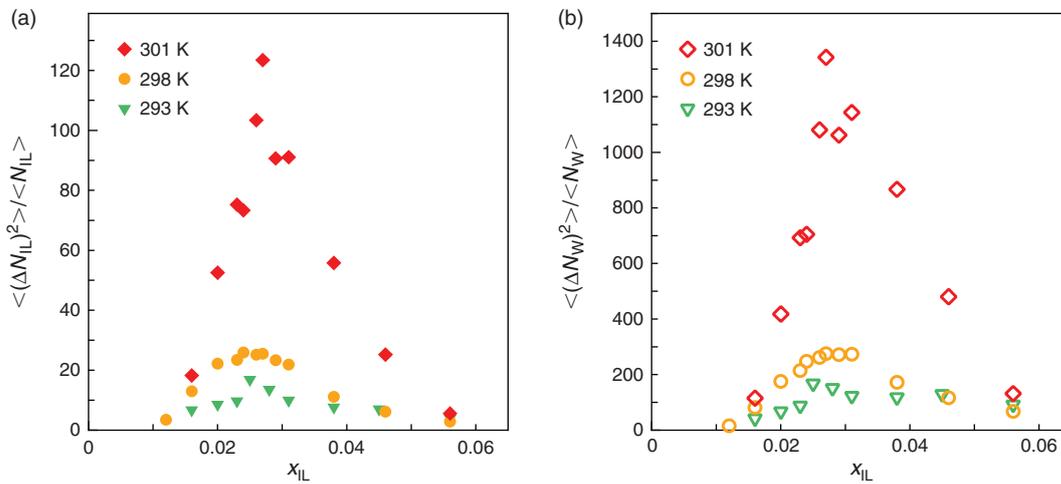


Fig. 7. Individual density fluctuations for (a) $[P_{4,4,4,4}]CF_3COO$, $\langle(\Delta N_{IL})^2\rangle/\bar{N}_{IL}$; and (b) water, $\langle(\Delta N_W)^2\rangle/\bar{N}_W$, as a function of x_{IL} at 293, 298, and 301 K.

acetonitrile studied previously,^[28] at the relevant critical mole fraction, it is ~ 1200 at 301 K, 1 K lower than the critical temperature, whereas it is ~ 85 for the aqueous solution of acetonitrile at 272 K.^[28]

Using the values of KBIs, the individual density fluctuations for $[P_{4,4,4,4}]CF_3COO$, $\langle(\Delta N_{IL})^2\rangle/\bar{N}_{IL}$, and for water, $\langle(\Delta N_W)^2\rangle/\bar{N}_W$, at 293, 298 and 301 K were calculated and are shown as the functions of x_{IL} in Fig. 7. Both components show large fluctuations near the critical point and a sharp change at 301 K. The individual density fluctuation for water is 10 times greater than that for $[P_{4,4,4,4}]CF_3COO$. The extremely large difference in the partial molar volumes between $[P_{4,4,4,4}]CF_3COO$ and water must be closely related to the large density fluctuations and also to the large individual density fluctuation of water. The correlation terms of those two individual density fluctuations, $\langle\Delta N_{IL}\Delta N_W\rangle/\bar{N}_{IL}$ or $\langle\Delta N_{IL}\Delta N_W\rangle/\bar{N}_W$, are positive for all the concentrations and temperatures, despite not being shown in Fig. 7. Such an observation is unique in our experience and these results indicate that the water molecules in the solution are distributed inhomogeneously near the critical point and there is a strong affinity between $[P_{4,4,4,4}]CF_3COO$ and water. In other

words, a large number of water molecules hydrate $[P_{4,4,4,4}]CF_3COO$, and ion pairs of $[P_{4,4,4,4}]CF_3COO$ make aggregates containing hydrating water molecules near the critical point.

Fig. 8 shows contour maps of the fluctuations drawn on the phase diagram of the aqueous solution of $[P_{4,4,4,4}]CF_3COO$. Near the critical point, the respective fluctuation functions show large values, and the solution tends towards macroscopic phase separation. There is a large difference in the partial molar volumes of $[P_{4,4,4,4}]CF_3COO$ and water. The difference increases with increase in concentration of $[P_{4,4,4,4}]CF_3COO$. As Eqn 6 shows, the term for the partial molar volume difference, $(v_{IL} - v_W)\bar{N}/V$, contributes to the fluctuations. In the region where ion pairs of $[P_{4,4,4,4}]CF_3COO$ are seen to aggregate, the total number of both $[P_{4,4,4,4}]CF_3COO$ and water molecules per unit volume, N , becomes much less than that in the water-rich region because of the large difference in partial molar volumes. Thus, the density fluctuation in aqueous solution is particularly sensitive to the distribution of the $[P_{4,4,4,4}]CF_3COO$ ion pair, when the total number N is considered. The individual density fluctuations indicate that the water molecules are largely localized near the $[P_{4,4,4,4}]CF_3COO$ ion pair, and this tendency will increase on approaching the critical point.

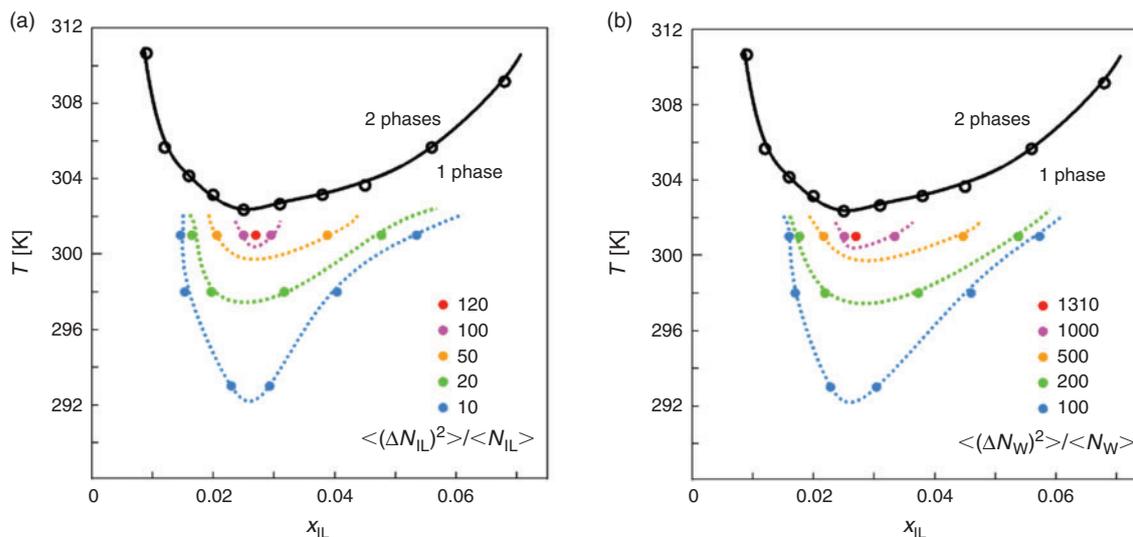


Fig. 8. Contour maps of fluctuations drawn in the phase diagram of the aqueous solution of $[P_{4,4,4,4}]CF_3COO$. (a) The individual density fluctuation for $[P_{4,4,4,4}]CF_3COO$, $\langle(\Delta N_{IL})^2\rangle/\overline{N_{IL}}$; and (b) the individual density fluctuation for water, $\langle(\Delta N_W)^2\rangle/\overline{N_W}$.

For an aqueous solution of $[C_4mim]BF_4$, which shows an UCST-type phase separation, a large concentration fluctuation was reported near its critical point, $x_{IL} = 0.08$, $T = 277$ K.^[21] The increases in fluctuations towards the critical point were also observed for the aqueous IL solution. However, one of KBIs, G_{IL-W} , which indicates the correlation between $[C_4mim]BF_4$ and water, is negative. The result suggests that the IL and water molecule interactions are repulsive,^[21] contrary to the present case where G_{IL-W} is positive, although the result is not shown in this paper. In the mixture below the LCST, therefore, it is considered that $[P_{4,4,4,4}]CF_3COO$ clusters are hydrated by a larger number of water molecules. Hence, it is proposed that $[P_{4,4,4,4}]CF_3COO$ aggregates with a large number of hydration water molecules, and $[P_{4,4,4,4}]CF_3COO$ and water do not completely separate under any circumstances. Approaching the critical point, the aggregation increases sharply. In a recent investigation, it was found that 7–14 water molecules exist per $[P_{4,4,4,4}]CF_3COO$ ion pair, even in the separated IL-rich phase above the LCST, and that the number of water molecules in the IL-rich phase decreases with increasing temperature.^[18] It was argued that a mixture that has a tendency for phase separation with an LCST shows an entropic attraction stronger than the enthalpic repulsion.^[36]

Conclusion

Using the SAXS method, fluctuations for the aqueous solution of $[P_{4,4,4,4}]CF_3COO$ around the critical point were determined in the concentration range $x_{IL} = 0.016$ – 0.056 at 293, 298, and 301 K. Fluctuations were calculated using three kinds of experimental data: the zero-angle scattering intensity, the partial molar volume of each component, and the isothermal compressibility. The individual fluctuations of $[P_{4,4,4,4}]CF_3COO$ and water suggest that a large number of water molecules hydrate $[P_{4,4,4,4}]CF_3COO$, and ion pairs of $[P_{4,4,4,4}]CF_3COO$ form aggregates containing hydrating water molecules near the critical point.

In the extremely dilute region, the various ions composing ILs have been characterized by the 1-propanol-probing methodology.^[36] It is suggested that the large hydration number around $[P_{4,4,4,4}]^+$, $n_H = 72$, is related to the LCST behaviour in

the aqueous solution of $[P_{4,4,4,4}]CF_3COO$.^[31] In addition, using differential thermodynamics,^[36] there is a critical point for the phase separation at $x_{IL} = 0.025$ in which there are two types of aggregations, namely water-rich and $[P_{4,4,4,4}]CF_3COO$ -rich aggregates.^[53] This proposition correlates with large individual fluctuations for each component and aggregate of $[P_{4,4,4,4}]CF_3COO$ containing water.

Conflicts of Interest

The authors declare no conflicts of interest.

Acknowledgements

The authors would like to express their appreciation to Dr Y. Koga at the University of British Columbia for fruitful discussions about the mixing state of aqueous solutions. This work was partially supported by JSPS KAKENHI (grant nos 25248003 and 24550009). The SAXS experiment in this work was performed under the approval of the PF Program Advisory Committee (proposals 2014G688, 2014G689, and 2015G119).

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