Effects of constituent ions of a phosphonium-based ionic liquid on molecular organization of H2O as probed by 1-propanol: tetrabutylphosphonium and trifluoroacetate ions

Morita, Takeshi; Miki, Kumiko; Ayako, Nitta; Ohgi, Hiroyo; Westh, Peter

Published in:
Physical Chemistry Chemical Physics

DOI:
10.1039/C5CP02329G

Publication date:
2015

Document Version
Publisher's PDF, also known as Version of record

Citation for published version (APA):

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain.

Take down policy
If you believe that this document breaches copyright please contact rucforsk@kb.dk providing details, and we will remove access to the work immediately and investigate your claim.

Download date: 04. Oct. 2023
Effects of constituent ions of a phosphonium-based ionic liquid on molecular organization of H2O as probed by 1-propanol: tetrabutylphosphonium and trifluoroacetate ions†

Takeshi Morita,†a Kumiko Miki,†b Ayako Nitta,†c Hiroyo Ohgi†a and Peter Westh†c

Aqueous solutions of tetrabutylphosphonium trifluoroacetate, [P4444]CF3COO, exhibit a liquid–liquid phase transition with a lower critical solution temperature. Herein, we characterized the constituent ions, [P4444]+ and CF3COO−, in terms of their effects on the molecular organization of H2O on the basis of 1-propanol probing methodology devised by Koga et al. The resulting characterization of the hydrophobicity/hydrophilicity is displayed on a two-dimensional map together with previous results, for a total of four cations and nine anions of typical ionic liquid (IL) constituents. The results indicate that [P4444]+ is the most significant amphiphile with strong hydrophobic and equally strong hydrophilic contributions among the group of constituent cations of ILs studied so far. The hydration number for [P4444]+ was evaluated to be nH = 72, which is three times larger than that of a typical imidazolium-based cation, [C4 mim]+. Self-aggregation of [P4444]+ was found to occur in an aqueous solution of [P4444]CF3COO above 0.0080 mole fraction of the IL.

Introduction

Ionic liquids (ILs) have gained considerable attention as they have radically changed the concept of the nature of liquids.1–5 ILs consisting entirely of ions have been increasingly proposed as alternatives to conventional organic solvents. Recent studies have focused on mixed systems composed of ILs and other molecular liquids, rather than neat ILs, for use as functional materials.6–12 In particular, thermoresponsive phase behaviour of aqueous solutions of ILs has been extensively investigated in relation to phase transitions with lower critical solution temperatures (LCSTs)6,12,13 as well as upper critical solution temperatures (UCSTs).13b,c,d,f,m,14

A UCST behaviour is understandable; a strong attraction in terms of enthalpy between species would cause phase separation at low temperatures, while at higher temperatures the total entropic effect drives the system to a random mixture. This transition is caused because the mixing entropic contribution in the mixing Gibbs energy generally becomes more dominant as the temperature (T) increases. Since the enthalpy–entropy compensation is operative particularly in aqueous solutions, the temperature could tip the balance of ΔmixH and TΔmixS terms, where ΔmixH and ΔmixS are the change of the mixing enthalpy and entropy, respectively. However, an LCST behaviour is not as simple to explain. The present aqueous solution of [P4444]CF3COO exhibits LCST-type phase behaviour with the critical point at 29.2 °C and 0.025 mole fraction of the IL.7 The chemical structure of [P4444]CF3COO is shown in Fig. 1.

It has been suggested that LCST behaviour depends on the balance of hydrophilicity and hydrophobicity of the IL constituent ions. Kohno et al.15 reported that LCST-type phase behaviours of aqueous solutions of ILs strongly depend on the “hydrophilicity” of each constituent cation and anion. Their analysis was based on a one-dimensional scale with hydrophilicity and hydrophobicity at the extreme ends. The miscibility of imidazolium-based ILs with

---

Fig. 1 Chemical structure of tetrabutylphosphonium trifluoroacetate, [P4444]CF3COO. Aqueous solution of the IL exhibits an LCST-type phase transition. In the present study, [P4444]Cl and NaCF3COO were used for characterization of the individual constituent ions, [P4444]+ and CF3COO−, respectively.
water was evaluated from estimated partition coefficients in octanol–water systems. The origin of LCST- and UCST-type phase transitions of mixtures of thiophene with two ILs, \([C_6C_{11}mim][SCN]\) and \([C_6C_{11}mim][NTf_2]\), was investigated using NMR spectroscopy and molecular dynamics simulations by Batista et al. Koga et al. devised a method by which an individual component can be characterized in terms of a two-dimensional (2D) hydrophilicity and hydrophobicity scale. This technique is known as the 1-propanol (1P)-probing methodology. By this method, “amphiphiles” with hydrophobic and hydrophilic contributions can be quantitatively assessed. Here, we applied this method to characterize the constituent ions of \([P_{4444}]CF_3COO\) to seek a deeper insight.

A differential thermodynamic approach to characterize the effects of a solute on the molecular organization of H\(_2\)O was devised by Koga et al. They realized that aqueous solutions consist of three composition regions in each of which the mixing scenario on the molecular level is qualitatively different. The mixing scenario is identified by the term “mixing scheme” instead of solution structure, since the word “structure” implies a stable, ordered molecular arrangement. The mixing schemes are labelled as I, II or III from the H\(_2\)O-rich regions. In Mixing Scheme I, the hydrogen bonds of H\(_2\)O are bond-percolated throughout the entire bulk of H\(_2\)O. The transition to Mixing Scheme II from I is regarded as a loss of bond percolation when the hydrogen bond probability is reduced to the percolation threshold. The 1P-probing methodology is applicable only in the region of Mixing Scheme I.

Although the 1P-probing methodology was described in detail elsewhere, a brief description is given here. This methodology is based on the finding that, within Mixing Scheme I, the effects of separate solutes on H\(_2\)O are additive. Thus, we study a ternary system, 1P–S–H\(_2\)O, where S is the test sample whose effect on H\(_2\)O is being examined. In the ternary system of 1P–S–H\(_2\)O, the thermodynamic signature of 1P, \(E^P\) (defined below), is evaluated. Modification to its \(x_{1P}\)-dependence pattern due to the presence of S is used to characterize the effect of S on H\(_2\)O. \(E^P\) is the enthalpic 1P–1P interaction in a complex ternary system and is defined as,

\[
E^P = N(\delta H^P / \delta n_{1P}) = (1 - x_{1P}) (\delta H^P / \delta x_{1P}),
\]

where

\[
H^P = (\delta H^P / \delta n_{1P}),
\]

and \(H^P\) is the total excess enthalpy in the \((p, T, n_{1P}, n_S, n_W)\) variable system, \(N = n_{1P} + n_S + n_W\) and \(x_{1P} = n_{1P} / N\). The subscripts 1P, S and W signify 1-propanol, test sample S and H\(_2\)O, respectively. We directly measure the excess partial molar enthalpy of 1P, \(H^P\). To do so, we perturb the ternary system by increasing \(n_{1P}\) to \(n_{1P} + \delta n_{1P}\), with a fixed initial molar fraction of S, \(x_S = n_S / (n_S + n_W)\), and measure the \(H^P\) response, \(\delta H^P\). We approximate the quotient \(\delta H^P / \delta n_{1P}\) to the partial derivative in eqn (2), and evaluate \(H^P\) by differentiating the data set \((x_{1P}, H^P)\) using the far right of eqn (1).

Fig. 2 shows a schematic representation of the changes in the \(H^P\) pattern induced by the presence of various classes of solute, S. As shown in Fig. 2(a)–(d), the peak top is named point X, which marks the end of Mixing Scheme I. Upon addition of S, point X shifts depending on the nature of S. The shifts are in general linear to the initial mole fraction of S, \(x^0_{1P}\), within Mixing Scheme I. The slope of the westward shift (i.e. to the negative direction of \(x_{1P}\)) of point X per unit increase in \(x^0_{1P}\) is taken as the "hydrophobicity index" of the solute, S. As shown in Fig. 2(a)–(d), the peak top is named point X, which marks the end of Mixing Scheme I. Upon addition of S, point X shifts depending on the nature of S. The shifts are in general linear to the initial mole fraction of S, \(x^0_{1P}\), within Mixing Scheme I. The slope of the westward shift (i.e. to the negative direction of \(x_{1P}\)) of point X per unit increase in \(x^0_{1P}\) is taken as the "hydrophobicity index" of the solute, S. This finding, as well as others, led to the interpretation that hydrophiles form hydrogen bonds directly to the existing hydrogen bond network of H\(_2\)O and maintain the hydrogen bond connectivity of the network; thus, they act as impurities in the network. As such, they break the H donor/acceptor symmetry. Hence, the southward shift apparent in the figure is...
interpreted as a reduction of the net entropy-volume cross fluctuation.

Fig. 2(d) is for the amphiphilic solute. The effects seem to be a combination of those observed for hydrophobic and hydrophilic moieties. Their westward and southward components show contributions from hydrophobic and hydrophilic moieties, respectively. Typical IL constituent ions generally show amphiphilic responses to 1P-probing studies with strong hydrophobic and equally strong hydrophilic characteristics.27–30 These results fit into the special properties of ILs. Low melting points for ionic compounds can be related to the strength of hydrophobicity and/or hydrophilicity.20,30

With this pair of coordinates, the characterization of each species, including individual constituent ions, is displayed on a 2D map of hydrophobicity/hydrophilicity.

**Experimental**

**Titration calorimetry for 1P probing**

Tetrabutylphosphonium chloride, [P4444]Cl, (Aldrich, > 98%) was used as the sample for characterization of the cation, [P4444]+. Sodium trifluoroacetate, NaCF3COO, (Sigma-Aldrich, > 96%) was used as the sample for that of CF3COO−. Deionized H2O was prepared using a Milli-Q system (Millipore), with a resulting resistivity of 18.2 MΩ cm. Stock solutions were prepared using the purified H2O and the salts from freshly opened bottles. 1-Propanol (1P) (Sigma-Aldrich, Chromasolv for HPLC 99.9+%) was used as supplied. Due care was exercised not to contaminate the 1P with moisture from the atmosphere. The excess partial molar enthalpy, \( H_{EP} \), was determined using a TAM III semi-isothermal titration calorimeter (TA Instruments, New Castle, USA) at 25.0 ± 0.0001 °C and in the dynamic correction mode.31–33 A 1 mL stainless steel container was used as the cell. The initial volume of the sample solution was set at 750 μL and the exact amount was determined gravimetrically. The volume and duration of each titration of 1P were set at 10 μL and 10 s, respectively. The injection volume per titration was calibrated to 9.9483 μL and was used to calculate the concentration. The ratio of titrant over titrand was on the order of 10^2 and was well within the acceptable range for approximation of the differentiation. The interval of injection was set at 30 min. The averaged uncertainty of the titration measurements was estimated to be ±0.03 kJ mol⁻¹.

**Electric conductivity**

The IL, [P4444]CF3COO, was synthesized and used for conductivity measurements. It was prepared by direct neutralization of

---

**Fig. 2**. Induced changes of \( H_{EP} \) pattern in the presence of various types of solute S. [binary] represents the binary 1P–H2O system without test solute S. (a) Effects of the hydration centre on the pattern per unit increase in test sample S. Region of Mixing Scheme I is defined as \( x_{1P} = 0 \) to \( x_{1P} \) at point X, as described on the horizontal axis, (b) the effects of hydrophobes, (c) hydrophiles and (d) amphiphiles.
aqueous tetrabutyolphosphonium hydroxide solutions with trifluoroacetic acid. After evaporation, the product was added to a dichloromethane/water biphasic system and the resulting mixture was washed several times with distilled water. The required [P$_{4444}$]Cl$_3$COO was dissolved in dichloromethane phase, and was dried in vacuum for 24 h at 60 $^\circ$C prior to use. The structure and purity were confirmed by $^1$H NMR spectroscopy. The procedure of the synthesis has been described elsewhere in detail.\(^7\)

The electric conductivity of the aqueous solution was measured using an electrical conduction metre with automatic temperature compensation (Hanna instruments, DiST4). The measured concentration range was from 0.001127 to 0.04610 mole fraction of the IL.

**Results and discussion**

The data of \(H_{IP}^E\) are deposited as Table S1 of the ESI,\(^8\) and are plotted in Fig. 3. A sigmoidal increase in \(H_{IP}^E\) with an inflection point is evident as long as \(x_0^S\) is appropriate for performing the IP-probing methodology. As shown in Fig. 3, the \(x_{IP}\) dependence pattern of \(H_{IP}^E\) changes more rapidly for \(S = [P_{4444}]\)Cl with increasing \(x_0^S\) than it does for \(S = NaCF_3COO\). The inflection point seems to disappear at \(x_0^S = 0.011\) for \(S = [P_{4444}]\)Cl and at \(x_0^S = 0.055\) for \(S = NaCF_3COO\). To see this behaviour more clearly, we took the derivative of \(H_{IP}^E\) with respect to \(x_{IP}\).

### Evaluation of \(H_{IP1IP}^E\) from \(H_{IP}^E\) data

With a good set of raw \(H_{IP}^E\) data with an averaged uncertainty of $\pm 0.03\ \text{kJ mol}^{-1}$ and small increments in \(x_{IP}\), the raw \(H_{IP}^E\) data themselves were used to calculate the derivative on the far right of eqn (1). In general, a numerical derivative directly using two neighbouring data points causes large noise, especially in applications with raw experimental data. In the present study, we originally utilized a differential method based on eqn (3) for calculation of the partial molar quantities with higher-order derivatives. We approximate the slope of the tangent at the \(i\)-th point as the weighted average of the slopes of the two adjacent arcs; one between the \((i - 1)\)-th and \(i\)-th data points and another between the \(i\)-th and \((i + 1)\)-th data points.

\[
H_{IP1IP}^E(i) = \left\{1 - x_{IP}(i)\right\}\left\{\frac{\partial H_{IP}^E(i)}{\partial x_{IP}(i)}\right\}
\approx \frac{1 - x_{IP}(i)}{x_{IP}(i + 1) - x_{IP}(i - 1)} \left\{H_{IP}^E(i + 1) - H_{IP}^E(i - 1)\right\}\left\{x_{IP}(i) - x_{IP}(i - 1)\right\}
+ \frac{H_{IP}^E(i) - H_{IP}^E(i - 1)}{x_{IP}(i + 1) - x_{IP}(i - 1)} \left\{x_{IP}(i + 1) - x_{IP}(i)\right\}
\tag{3}
\]

The \(x_{IP}\) interval of \(x_{IP}(i)\) to \(x_{IP}(i + 1)\), \(\Delta x_{IP}\), was approximately 0.003 in the present measurements. It is found that \(\Delta x_{IP} \approx 0.008\) in graphical evaluation normally exercised is appropriate to approximate the derivative of eqn (1) with the quotient \(\partial H_{IP}^E/\partial x_{IP}\). In the present calculations, the total \(\Delta x_{IP}\) for three neighbouring data points was approximately 0.006.

Certainty in evaluation of the partial molar quantities with higher-order derivatives is of particular importance in the present study. Fig. 4(a)-(c) show comparisons of \(H_{IP1IP}^E\) determined using eqn (3) and that determined using other evaluation methods. Fig. 4(a) shows comparison between the \(H_{IP1IP}^E\) pattern obtained using eqn (3) and that evaluated by the graphical method normally exercised. As shown in Fig. 4(b), combination of eqn (3) and the graphical evaluation shows improvement especially in the pre-peak region. The point X evaluated by the \(H_{IP1IP}^E\) pattern corresponds to each other regardless of the method. Fig. 4(c) shows comparison between eqn (3) and simple derivative using two neighbouring data points. As mentioned above, the calculation using eqn (3) is superior to the simple derivative using two alternating data points with regard to noise reduction, as shown in Fig. 4(c). Therefore, it is concluded that the calculation based on eqn (3) is the most certain for evaluation of partial molar quantities with higher-order derivatives in the present data set. Thus, calculation based on eqn (3) was utilized here for evaluation of \(H_{IP1IP}^E\), leading to determination of the hydrophobicity and hydrophilicity indices.

### Hydrophobicity/hydrophilicity obtained from the \(H_{IP1IP}^E\) pattern

Fig. 5 and 6 show the patterns of resulting \(H_{IP1IP}^E\) for \(S = [P_{4444}]\)Cl and \(S = NaCF_3COO\), respectively. The peak top of \(H_{IP1IP}^E\) appears...
at 0.049 of \( x_{1P} \) for binary (1-propanol–H\(_2\)O) mixture.\(^{19}\) The peak top shifts to the west (direction of smaller \( x_{1P} \)) as \( x_{0S} \) increases. Point X nearly disappears at \( x_{0S} = 0.0110 \) for S = [P\(_{4444}\)]Cl and \( x_{0S} = 0.0550 \) for S = NaCF\(_3\)COO, qualitatively indicating that the hydrophobicity of [P\(_{4444}\)]Cl is much larger than that of NaCF\(_3\)COO. The starting point of \( H_{E1P1P} \) at \( x_{1P} = 0 \) shifts to the north (direction of larger \( H_{E1P1P} \)) with increasing \( x_{0S} \). This northward shift also corresponds to the strong hydrophobicity of [P\(_{4444}\)]\(^+\). For NaCF\(_3\)COO, the equivalent shift at \( x_{1P} = 0 \) is lesser.

The degrees of the shifts are plotted in Fig. 7 and 8. The slopes of \( H_{E1P1P} \) loci in Fig. 7(b) and 8(b) directly correspond to the hydrophilicity indices in the present evaluation. The hydrophilicity indices of the counter ions of Na\(^+\) and Cl\(^-\) used in the present study are equal to zero, since these ions are classified as the hydration centre. As mentioned in Introduction, hydration centres such as Na\(^+\) and Cl\(^-\) unperturb the bulk H\(_2\)O molecules away from the hydration shells around the ions. Hydrophobicity/hydrophilicity indices and hydration numbers of [P\(_{4444}\)]\(^+\) and CF\(_3\)COO\(^-\) are listed in Table 1.

The results indicate that [P\(_{4444}\)]\(^+\) is an amphiphile with strong hydrophobic and equally strong hydrophilic contributions. [P\(_{4444}\)]\(^+\) forms a large hydration shell with a hydration number of \( n_H = 72 \), which is three times larger than that of typical imidazolium-based cation 1-butyl-3-methylimidazolium,\([C_4mim]\)^\(^+\).\(^{27}\) The value of a hydration number for CF\(_3\)COO\(^-\) was found to be \( n_H = 10 \). On the basis of earlier findings in 1P-probing studies on a series of carboxylates,\(^{36}\) one H\(_2\)O molecule out of the 10 H\(_2\)O molecules should be used for hydration of the –COO\(^-\) side and the remaining 9.0 H\(_2\)O molecules for the fluoroalkyl group, –CF\(_3\). This hydration number is much larger than that of the alkyl group in CH\(_3\)COO\(^-\); the hydration number for –CH\(_3\) in CH\(_3\)COO\(^-\) is estimated to be 2.7.\(^{36}\) The fact that the fluoroalkyl...
group is a stronger hydrophobe than the alkyl group could be related to this finding: an aqueous solution of the CF₃COO⁻ salt of [P₄₄₄₄]⁺ shows LCST, and that of the CH₃COO⁻ salt does not.

**Self-aggregation behaviour of [P₄₄₄₄]⁺**

As shown in Fig. 7, the induced changes at \( x^0 \) = 0.010 for \( S = [P₄₄₄₄]Cl \) depart from the linear relationship defined in the lower \( x^0 \) region. This departure shifts to the upper side beyond the data error in the present evaluation. This departure hints the self-aggregation of the kind found in imidazolium-based ILs. For [C₄C₁mim]CF₃SO₃ and [C₄mim]Cl, similar plots are seen that show a break in the slopes at \( x^0 = 0.006 \) and 0.014, respectively. For aqueous solutions of [C₄mim]BF₄, this similar behaviour was interpreted as self-aggregation of cations through NMR spectroscopy, electric conductivity, small-angle neutron scattering, density, speed of sound and surface tension. Thus, we suggest that departure of the induced change at \( x^0 = 0.010 \) for the case shown in Fig. 7 could also be caused by self-aggregation of [P₄₄₄₄]⁺.

For further investigation of this issue, electric conductivity measurements were conducted for the aqueous solutions of [P₄₄₄₄]CF₃COO. The obtained conductivity was converted to molar conductivity according to the Kohlrausch empirical relation. Fig. 9 shows the isotherm of the molar conductivity as a function of the square root of IL concentration. The linear portion represents the usual behaviour of ionic solutions in the dilute region. This linearity seems to start to deviate at approximately 0.0080, as the case for imidazolium-based ILs. Considering the larger hydrophobicity (hydration number) of [P₄₄₄₄]⁺ compared to those of [C₄mim]⁺ and [C₄C₁mim]⁺, the breakpoint or aggregation of [P₄₄₄₄]⁺ might be expected at a much lower concentration; however, this was not observed. This discrepancy could be related to the difference in the aggregation mechanisms of imidazolium-based and phosphonium-based cations. The imidazolium ions have an ionic head and alkyl tail, while phosphonium-based ions have an ionic centre and four alkyl tails extending in random directions. Wang et al. suggested that the aggregation aspect of [P₄₄₄₄]CF₃COO in aqueous solution can be described in terms of microemulsion-like aggregation at the mesoscale level in higher concentration ranges near the critical point.

**2D map of hydrophobicity/hydrophilicity**

Fig. 10 shows the 2D map of hydrophobicity/hydrophilicity for [P₄₄₄₄]⁺ and CF₃COO⁻. In the map, H₂O defines the origin (0,0). 1-Propanol used as the probe is necessarily plotted at (−1,0). Relative to these points, ions with greater hydrophobic contributions spread to the west (negative horizontal direction)
and those with greater hydrophilic contributions spread to the south (negative vertical direction). A total of four cations and nine anions of typical IL constituents are plotted in Fig. 10. The cations\(^{20,21}\) are \([C_4\text{ mim}]^+, [C_4\text{ mim}]^+, [C_4C_1\text{ mim}]^+\) and the present \([P_{4444}]^+\). The anions\(^{20,21,30}\) are \(\text{Cl}^-, \text{CF}_3\text{COO}^-, \text{Br}^-, \text{BF}_4^-, \text{OTf}^-, \text{PF}_6^-, \text{NTf}_2^-\) and the present \(\text{CF}_3\text{COO}^-\). As evident from Fig. 10, \([P_{4444}]^+\) shows the most significant amphiphilicity, with strong hydrophobic and equally strong hydrophilic contributions, among the constituent cations of the ILs studied. Furthermore, the IL constituent ions are located farther from the origin than are the typical inorganic small ions. Our recent study on normal ions (i.e. non-IL forming ions) shows that anions are located farther from the origin than cations.\(^{46}\)

Kohno et al.\(^{15}\) took advantage of the phase separation of IL–H\(_2\)O systems and estimated the H\(_2\)O content in the IL phase. They then determined the hydration number per mole of IL and defined it as the hydrophilicity of the IL. They concluded that the LCST behaviour strongly depended on the evaluated “hydrophilicity” indices. We point out that their hydrophilicity concept is based on the H\(_2\)O content in the IL-rich situation. In the 1P probing, hydrophilicity is only a part of the effects of the ion in question to H\(_2\)O in the water-rich region, the other part being hydrophobic. Saita et al.\(^{47}\) suggested another one-dimensional scale based on salt effects of test ions fixed as \([P_{4444}]^+\) or \(\text{CF}_3\text{COO}^-\) counter ion on the LCST of \([P_{4444}]\text{CF}_3\text{COO}^-\text{H}_2\text{O}\) system. It is concluded that changes in the critical temperatures of IL–H\(_2\)O systems are clearly related to the “hydrophilicity” of the target ions.

In the present 1P-probing methodology, the hydration number of the species in question is evaluated from “hydrophobicity” index. The hydrophobicity is defined on the basis of hydration of the solute with H\(_2\)O molecules, namely the formation of the hydration shell in water-rich region. Hydrophile in the 1P probing is defined as a solute that forms hydrogen bonds directly to the existing hydrogen bond network of H\(_2\)O, discussed in detail in Introduction. As shown in Fig. 10, the typical constituent ions are classified as “amphiphiles” with strong hydrophobic and equally strong hydrophilic contributions. Thus, the present
two-dimensional scale covers the ranking of “hydrophilicity” from the one-dimensional scale and might lead to a deeper understanding on the effects of molecular organization of H₂O.

Conclusions

The constituent ions of [P₄444]CF₃COO were characterized in terms of their effects on the molecular organization of H₂O using the 1P-probing methodology. A differential method based on the weighted average of two slopes was utilized to calculate \( S^{1P}_{ii} \). The most significant amphiphile among the IL constituent cations studied was \([P_{4444}]^+ \), which had strong hydrophobic and equally strong hydrophilic contributions. The hydration number was evaluated to be \( n_H = 72 \), which was the largest value among the group of cations. Characterization of \( CF_3COO \) confirmed that it was a hydrophobe with a hydration number of \( n_H = 10 \), out of which one H₂O molecule hydrated the –COO⁻ side and the remaining 9.0 H₂O molecules the fluoroalkyl group, –CF₃. The self-aggregation behaviour of \([P_{4444}]^+ \) in the aqueous solution of \([P_{4444}]CF_3COO \) was revealed above 0.0080 mole fraction of the IL.

It is suggested that the formation of the large hydration shell around \([P_{4444}]^+ \) evaluated in the present study causes loss in excess entropy of mixing. Hence, this entropic loss must have bearing to the present LCST behaviour as mentioned in Introduction. Koga et al. sorted out the occurrence of phase separation with an LCST as well as a UCST in terms of signs of \( H^{1P}_{ii} \) and \( S^{1P}_{ii} \) as the third derivative of \( G^{1P} \) in the binary system(i–H₂O) system. Although their argument was based on a necessary but not sufficient condition, it was applied to the \([C₄mim]BF₄–H₂O \) system and the \( H^{1P}_{ii} \) and \( S^{1P}_{ii} \) for \( i = [C₄mim]BF₄ \) was found to be negative, which is appropriate for the UCST at 4 °C and \( x_i = 0.07. \) For the present case, however, since we have not yet determined \( H^{1P}_{ii} \) and \( S^{1P}_{ii} \) for \( i = [P_{4444}]CF_3COO \), we will postpone the detailed discussions about the occurrence of LCST for aqueous solution of the present IL. As shown in Fig. 10, 2-butoxyethanol (BE) was found to form an analogously large hydration shell around the molecule, \( n_H = 58, \) and the aqueous solution of BE exhibits the LCST below 50 °C.\(^{50,51}\)

Acknowledgements

We would like to express deepest appreciation to Dr Y. Koga at the University of British Columbia for his discussion about the 1P-probing experiment and critical reading of the manuscript. We are deeply grateful to Prof. H. Ohno, Dr Y. Kohno and Dr S. Saita at Tokyo University of Agriculture and Technology for preparation of the ionic liquid used in this study, measurements of the electric conductivity and fruitful discussion. T.M. is grateful to Prof. K. Nishikawa for cooperation of the experiment. This work was partially supported by Grant-in-Aid for Scientific Research (JPSP KAKENHI) [No. 24550009]. T.M. thanks MEXT, Japan, for Grants for Excellent Graduate Schools for the financial support for his stay at Roskilde University.

Notes and references