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

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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 hydrophobic/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 n₁ = 72, which is three times larger than that of a typical imidazolium-based cation, [C₄mim]⁺. 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).13a,c,d,p,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-phase behaviour 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

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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.16,17 The origin of LCST- and UCST-type phase transitions of mixtures of thiophene with two ILs, [C4C1mim]SCN and [C6C1mim][NTf2], was investigated using NMR spectroscopy and molecular dynamics simulations by Batista et al.18

Koga et al.19–21 devised a method by which an individual ion 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 [P4444][CF3COO] to seek a deeper insight.

A differential thermodynamic approach to characterize the effects of a solute on the molecular organization of H2O was devised by Koga et al.19 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 H2O-rich regions. In Mixing Scheme I, the hydrogen bonds of H2O are bond-percolated throughout the entire bulk of H2O. 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,19,20a a brief description is given here. This methodology is based on the finding that, within Mixing Scheme I, the effects of separate solutes on H2O are additive.19 Thus, we study a ternary system, 1P–S–H2O, where S is the test sample whose effect on H2O is being examined. In the ternary system of 1P–S–H2O, the thermodynamic signature of 1P, $E_{1P}^S$ (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 H2O. $H_{1P}^S$ is the enthalpic 1P–1P interaction in a complex ternary system and is defined as,

$$H_{1P}^S = \sum (\partial H^S_{1P}/\partial n_{1P}) = (1 - x_{1P}) (\partial H_{1P}^S/\partial x_{1P}),$$  

where

$$E_F^P = \sum (\partial H^S_{1P}/\partial n_{1P}),$$  

and $H^S$ 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 H2O, respectively. We directly measure the extra partial molar enthalpy of 1P, $H_{1P}^S$. To do so, we perturb the ternary system by increasing $n_{1P}$ to $n_{1P} + \delta n_{1P}$, with a fixed initial mole fraction of S, $x_S^0 = n_S/(n_S + n_W)$, and measure the $H^F$ response, $\delta H^F$. We approximate the $H_{1P}^S$ by differentiating the data set ($x_{1P}, H_{1P}^S$) using the far right of eqn (1).

Fig. 2 shows a schematic representation of the changes in the $H_{1P}^S$ 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, $x_S^0$, 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 $x_S^0$ is taken as the hydrophobicity index, while that towards the south (i.e. to the negative direction of the $H_{1P}^S$ axis) is the hydrophilicity index. Fig. 2(a) shows a typical change in $H_{1P}^S$ for hydration centres such as in Na+ and Cl− ion pairs.22,23 Upon addition of the salt, the $H_{1P}^S$ pattern is compressed to the west. This compression indicates that, upon addition of the Na+ and Cl− ion pair, the available H2O molecules for 1P to interact with are reduced. We thus interpret this westward shift to be due to hydration of the ions. From the westward shift of point X as a function of $x_S^0$, the hydration number, $n_{H}$, can be evaluated for Na+ and Cl−. It must be stressed that at the starting point, $x_{1P} = 0$, the value of $H_{1P}^S$ remains the same even in the presence of Na+ and Cl−. This invariance and the fact that the value of $H_{1P}^S$ at point X also remains the same led to the following suggestions: (1) Na+ and Cl− ions are hydrated by a number of H2O molecules, (2) the hydrating H2O molecules are unavailable to interact with 1P and (3) the bulk H2O molecules away from the hydration shells are unperturbed by Na+ and Cl− even in the presence of the ions. This finding can be utilized to characterize individual ions. For a given test ion, we chose the counter ion Na+ or Cl− and applied the 1P probing on the combined salt. Namely, we used tetra- butylphosphonium chloride, [P4444]Cl, and sodium trifluoroacetate, NaCF3COO, to characterize [P4444]+ and CF3COO−, respectively.

Fig. 2(b) shows the behaviour of the hydrophobic solute. For a solute almost equally hydrophobic as 1P such as 2-propanol,24 the $H_{1P}^S$ pattern shifts parallel to the west, as shown in the figure. This parallel shift is expected when compared to the case in which 1P was added as S to $x_S^0$ (i.e. S = 1P). For a hydrophobe that is stronger (or weaker) than the probing 1P, such as tert-butanol25 (or ethanol26), the westward shift is greater (or lesser), reflecting a larger (or smaller) $n_H$. This westward shift of point X indicates that a hydrophobe is hydrated by H2O molecules, making them unavailable to interact with 1P, as was the case for the hydration centre. In addition, the value of $H_{1P}^S$ at point X shifts northward (or southward), reflecting the fact that the ability of tert-butanol (or ethanol) to reduce the hydrogen bond probability of bulk H2O away from the hydration shell is greater (or lesser) than 1P, as studied earlier.19 Furthermore, the hydrogen bonding within the hydration shells is more organized than it is in bulk H2O.

Fig. 2(c) shows the pattern change for the hydrophilic solute. This finding, as well as others,19 led to the interpretation that hydrophilic solvents form hydrogen bonds directly to the existing hydrogen bond network of H2O 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. 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.

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, [P₄4444]Cl, (Aldrich, > 98%) was used as the sample for characterization of the cation, [P₄4444]⁺. 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, H₁P, 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. 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, [P₄4444]CF₃COO, was synthesized and used for conductivity measurements. It was prepared by direct neutralization of
aqueous tetrabutylphosphonium 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 $[\text{P}_{4444}]\text{Cl}$ was dissolved in dichloromethane phase, and was dried in vacuum for 24 h at 60 °C prior to use. The structure and purity were confirmed by $^1\text{H}$ 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 $H^E_{1P}$ are deposited as Table S1 of the ESI,5 and are plotted in Fig. 3. A sigmoidal increase in $H^E_{1P}$ with an inflection point is evident as long as $x^S_0$ is appropriate for performing the 1P-probing methodology. As shown in Fig. 3, the $x_{1P}$-dependence pattern of $H^E_{1P}$ changes more rapidly for $S = \text{[P}_{4444}\text{]}\text{Cl}$ with increasing $x^S_0$ than it does for $S = \text{NaCF}_3\text{COO}$. The inflection point seems to disappear at $x^S_0 = 0.011$ for $S = \text{[P}_{4444}\text{]}\text{Cl}$ and at $x^S_0 = 0.055$ for $S = \text{NaCF}_3\text{COO}$. To see this behaviour more clearly, we took the derivative of $H^E_{1P}$ with respect to $x_{1P}$.

#### Evaluation of $H^E_{1P1P}$ from $H^E_{1P}$ data

With a good set of raw $H^E_{1P}$ data with an averaged uncertainty of $\pm 0.03 \text{ kJ mol}^{-1}$ and small increments in $x_{1P}$, the raw $H^E_{1P}$ 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.

$$H^E_{1P1P}(i) = \{1 - x_{1P}(i)\} \left\{\frac{\partial H^E_{1P}(i)}{\partial x_{1P}(i)}\right\}$$

$$\approx \frac{\{1 - x_{1P}(i)\} \left\{H^E_{1P}(i + 1) - H^E_{1P}(i)\right\}}{x_{1P}(i + 1) - x_{1P}(i - 1)\left\{x_{1P}(i) - x_{1P}(i - 1)\right\}}$$

$$+ \frac{\left\{H^E_{1P}(i) - H^E_{1P}(i - 1)\right\}}{x_{1P}(i) - x_{1P}(i - 1)\left\{x_{1P}(i + 1) - x_{1P}(i)\right\}}$$

(3)

The $x_{1P}$ interval of $x_{1P}(i)$ to $x_{1P}(i + 1)$, $\delta x_{1P}$, was approximately 0.003 in the present measurements. It is found that $\delta x_{1P} \approx 0.008$ in graphical evaluation normally exercised is appropriate to approximate the derivative of eqn (1) with the quotient $\partial H^E_{1P}/\partial n_{1P}$. In the present calculations, the total $\delta x_{1P}$ 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 $H^E_{1P1P}$ determined using eqn (3) and that determined using other evaluation methods. Fig. 4(a) shows comparison between the $H^E_{1P1P}$ 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 $H^E_{1P1P}$ 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 $H^E_{1P1P}$, leading to determination of the hydrophobicity and hydrophilicity indices.

#### Hydrophobicity/hydrophilicity obtained from the $H^E_{1P1P}$ pattern

Fig. 5 and 6 show the patterns of resulting $H^E_{1P1P}$ for $S = \text{[P}_{4444}\text{]}\text{Cl}$ and $S = \text{NaCF}_3\text{COO}$, respectively. The peak top of $H^E_{1P1P}$ appears...
at 0.049 of $x_{1P}$ for binary (1-propanol–H$_2$O) mixture. 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 $S = NaCF_3COO$, qualitatively indicating that the hydrophobicity of $[P_{4444}]Cl$ is much larger than that of NaCF$_3$COO. The starting point of $H_{1P1P}$ at $x_{1P} = 0$ shifts to the north (direction of larger $H_{1P1P}$) 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 $x_{1P}$ loci in Fig. 7(b) and 8(b) directly correspond to the hydrophilicity indices in the present evaluation. The hydrophilicity/hydrophobicity 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$_4$mim]$^+$. 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, 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. 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 CF$_3$COO$^-$ salt of [P$_{4444}$]$^+$ shows LCST, and that of the CH$_3$COO$^-$ salt does not.

**Self-aggregation behaviour of [P$_{4444}$]$^+$**

As shown in Fig. 7, the induced changes at $x_S^0 = 0.010$ for $S = [P_{4444}]Cl$ depart from the linear relationship defined in the lower $x_S^0$ region. This departure shifts to the upper side beyond the data error in the present evaluation. This departure hints at self-aggregation of the kind found in imidazolium-based ILs. For [C$_4$C$_1$mim]CF$_3$SO$_3$ and [C$_4$mim]Cl, similar plots are seen that show a break in the slopes at $x_S^0 = 0.006$ and 0.014, respectively. For aqueous solutions of [C$_4$mim]BF$_4$, 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 $x_S^0 = 0.010$ for the case shown in Fig. 7 could also be caused by self-aggregation of [P$_{4444}$]$^+$.

For further investigation of this issue, electric conductivity measurements were conducted for the aqueous solutions of [P$_{4444}$]CF$_3$COO. 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 $x_S^0$ for $S = [P_{4444}]Cl$. The slope following subtraction of the Cl$^-$ counterion contribution. (b) The loci of $H_{IP}$ at 25 °C. The slope corresponds to the hydrophilicity index, as Cl$^-$ is classified as the hydration centre. The hydrophilicity index of Cl$^-$ is zero.

2D map of hydrophobicity/hydrophilicity

Fig. 10 shows the 2D map of hydrophobicity/hydrophilicity for [P$_{4444}$]$^+$ and CF$_3$COO$^-$. In the map, H$_2$O 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).
Table 1 Hydrophobicity/hydrophilicity indices of [P4444]⁺ and CF3COO⁻ as probed by 1-propanol

<table>
<thead>
<tr>
<th>Ion</th>
<th>Class</th>
<th>Hydrophobicity n_i</th>
<th>Hydrophilicity (kJ mol⁻¹)</th>
<th>Applicable x_0 range</th>
<th>Aggregation⁹</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cations</td>
<td>[P4444]⁺</td>
<td>Amphiphile</td>
<td>−3.49</td>
<td>72</td>
<td>−5337</td>
<td>&lt;0.012</td>
</tr>
<tr>
<td>[C4mim]⁺</td>
<td>Amphiphile</td>
<td>−0.39</td>
<td>7</td>
<td>−1970</td>
<td>&lt;0.024</td>
<td>None</td>
</tr>
<tr>
<td>[C2mim]⁺</td>
<td>Amphiphile</td>
<td>−1.31</td>
<td>26</td>
<td>−3227</td>
<td>&lt;0.029</td>
<td>None</td>
</tr>
<tr>
<td>[C4C1mim]⁺</td>
<td>Amphiphile</td>
<td>−1.85</td>
<td>37</td>
<td>−6760</td>
<td>&lt;0.018</td>
<td>None</td>
</tr>
<tr>
<td>Anions</td>
<td>CF3COO⁻</td>
<td>Hydrophobe</td>
<td>−0.49</td>
<td>10</td>
<td>−767</td>
<td>&lt;0.055</td>
</tr>
<tr>
<td>CH3COO⁻</td>
<td>Hydrophobe</td>
<td>−0.22</td>
<td>3.7</td>
<td>0</td>
<td>&lt;0.05</td>
<td>None</td>
</tr>
</tbody>
</table>

⁹ Hydration number evaluated from the loci of point X. ⁹° Aggregation observed in the region of Mixing Scheme I.

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 cations²⁰,²¹ are [C2mim]⁺, [C4mim]⁺, [C4C1mim]⁺ and the present [P4444]⁺. The anions²⁰,²¹, are Cl⁻, CH₃COO⁻, Br⁻, BF₄⁻, [OTf]⁻, PF₆⁻, [NTf₂]⁻ and the present CF₃COO⁻. As evident from Fig. 10, [P4444]⁺ 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-*H₂O systems and estimated the *H₂O 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 *H₂O content in the IL-rich situation. In the 1P probing, hydrophilicity is only a part of the effects of the ion in question to *H₂O in the water-rich region, the other part being hydrophilicity. Saita et al.⁴⁷ suggested another one-dimensional scale based on salt effects of test ions fixed as [P4444]⁺ or CF₃COO⁻ counter ion on the LCST of [P4444]⁺CF₃COO⁻-*H₂O system. It is concluded that changes in the critical temperatures of IL-*H₂O 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 “hydrophilic” index. The hydrophilicity is defined on the basis of hydration of the solute with *H₂O molecules, namely the formation of the hydration shell in water-rich region. Hydrosphere in the 1P probing is defined as a solute that forms hydrogen bonds directly to the existing hydrogen bond network of *H₂O 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 Hᵣₛ. The most significant amphiphile among the IL constituent cations studied was [P₄444], which had strong hydrophobic and equally strong hydrophilic contributions. The hydration number was evaluated to be nₘ = 72, which was the largest value among the group of cations. Characterization of CF₃COO⁻ confirmed that it was a hydrophobe with a hydration number of nₘ = 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 [P₄444] in the aqueous solution of 0.07.49 For the present case, however, since we have not yet noted 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, nₘ = 58, and the aqueous solution of BE exhibits the LCST below 50 °C. 50,51

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Notes and references


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37 Private communication.


