Miscibility and phase behavior of water–dicarboxylic acid type ionic liquid mixed systems

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Tetra-*n*-butylphosphonium type ionic liquids with fumarate anion and maleate anion exhibit different physico-chemical properties and different solubility to water in their *cis* and *trans* conformations; fumarate showed the usual upper critical solution temperature (UCST) behavior, whereas maleate had highly unusual lower critical solution temperature (LCST) behavior after mixing with water.

Ionic liquids (ILs)[1] are organic salts designed to melt below 100 °C, or at room temperature, and have remarkable properties such as low volatility and low flammability because of their negligible vapor pressure.[2] Their physical, chemical, and electro-chemical properties can be tuned to specific tasks by exploiting the diversity of component organic ions. In view of these characteristics, ILs have been proposed and studied as reaction media,[3] ionic conductors,[4] and in other innovative applications. Since the polarity of ILs and their compatibility with other compounds vary widely with ionic structure, immiscible-ILs to other solvents may be prepared. Numerous papers have been published on the phase-separation behavior of systems such as IL/water,[5] IL/alcohol,[6] IL/K_2PO_4/water[7] and IL/super critical CO_2.[8] Seddon and co-workers recently reported a mixture of two immiscible ILs.[9] We have recently reported novel hydrophobic ILs having unusual lower critical solution temperature (LCST) behavior.[10] These findings suggest that ILs should act not only as alternatives to volatile organic solvents, but also as novel solvents for processing.

In general, hydrophobic ILs have been prepared with fluorine-containing anions, such as hexafluorophosphate (PF_6), bis(trifluoromethanesulfonyl)amide (Tf_2N) and their derivatives. The delocalization of negative charge and high water-shedding quality due to the fluorine atom give rise to lower solubility in water. In spite of their utility for preparation of hydrophobic ILs, some drawbacks remain, such as generation of HF by hydrolysis. Moreover, taking into account both degradation and disposal after use, halogen-free and hydrophobic ILs are preferable.

We have previously synthesized a series of halogen-free ILs, and studied the relation between ionic structure and various characteristics. Such compounds include azolate,[11] carboxylate,[12] phosphate[13] and sulfate.[14] In particular, we have synthesized ILs from dicarboxylic acids, for which the properties have scarcely been studied. We found in a series of studies that the physico-chemical properties of ILs from dicarboxylic acid anions having a double bond depend strongly on their *cis* and *trans* conformations. Tetra-*n*-butylphosphonium type ILs with these dicarboxylic acid anions were hydrophobic ILs having normal upper critical solution temperature (UCST) behavior but unusual LCST behavior according to conformation. This is the first example of halogen-free and hydrophobic ILs allowing control of phase behavior according to their conformation. In the present paper, we describe the effect of conformation on the physico-chemical properties and the solubility to water of these ILs.

The ILs examined (Fig. 1) were prepared by mixing tetra-*n*-butylphosphonium hydroxide ($[P_{4444}][OH]$) aqueous solution, a gift from Hokko Chem. Ind., with commercially available acids. For tetra-*n*-butylphosphonium fumarate ($[P_{4444}]$[fumarate]), after removal of water by evaporation, the resulting product was repeatedly recrystallized from ethyl acetate–ethanol solution. In contrast, tetra-*n*-butylphosphonium succinate ($[P_{4444}]$[succinate]) and maleate ($[P_{4444}]$[maleate]) were extracted from aqueous solution by dichloromethane, and purified further by passing them through a short column filled with neutral activated alumina. The structure of the resulting ILs was confirmed by ^{1}H and ^{13}C NMR spectroscopy (JEOL ECX 400 instruments)†. The products obtained were dried under pressure at 80 °C for 24 h. The water content of these ILs was confirmed as below 0.1 wt% by Karl–Fischer coulometric titration (Kyoto Electronics, MKC-510N).

Table 1 shows the physico-chemical properties of the ILs prepared. Of these, $[P_{4444}]$[fumarate] was solid at room temperature. Differential scanning calorimetry (DSC) measurements revealed that $[P_{4444}]$[fumarate] has a melting temperature (T_m) of 89.9 °C. In contrast, $[P_{4444}]$[succinate] was a highly viscous room temperature IL (RTIL) with a glass transition temperature (T_g) of −52.3 °C. In the DSC trace of $[P_{4444}]$[succinate], no melting and freezing behavior was observed even when this IL was slowly cooled and heated at 1 °C min^{-1}. This suggests that $[P_{4444}]$[succinate] was in a stable supercooled state. The melting

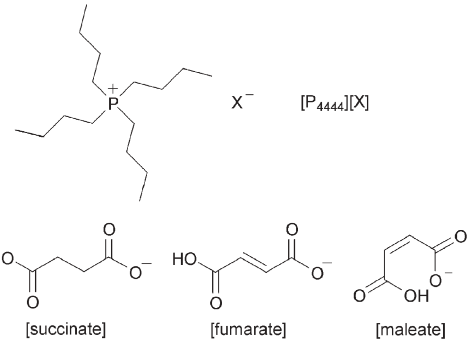

Fig. 1 Chemical structure of ionic liquids examined.

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Table 1 Physico-chemical properties of ionic liquids prepared

				Kamlet–Taft parameters[c]		
Anion	T_g[a]	T_m[a]	T_{decomp}[b]	α	β	π^*
[succinate]	−52.3	[d]	276	0.60	0.90	1.04
[fumarate]	−32.1	89.9	265	0.15[e]	0.98[e]	1.01[e]
[maleate]	[d]	35.0	264	0.24	0.81	1.03

[a] Temperature (°C) at signal peak. [b] Temperature (°C) for 10% weight loss. [c] Measured at 25 °C. [d] Not detected. [e] At 95 °C.

temperature of $[P_{4444}]$[maleate] was 35 °C; this IL was obtained as a RTIL. Consequently, $[P_{4444}]$[maleate] also forms supercooled liquids. Since the rotation angle between a carboxyl acid group and the carboxylate anion moiety of fumarate is restricted, they form intermolecular hydrogen bonds. Conversely, for maleate, intramolecular hydrogen bonding and proton exchange between the carboxylic acid group and carboxylate anion moiety is suggested by the results of a neutron scattering,[15] X-ray crystallographic analysis[16] and molecular dynamics calculations.[17]

The polarities of these ILs were estimated using the Kamlet–Taft parameters (α value: hydrogen bond acidity, β value: hydrogen bond basicity, π^*: dipolarity) by a reported procedure.[18] These ILs have almost identical π^* values and higher β values than common ILs. In general, β is governed by the nature of the anions. These dicarboxylic acid anions are the conjugate bases of weak acids. Consequently, these ILs had higher β values than common ILs, as also seen in Table 1. The value for these ILs depends strongly on the anion structure. $[P_{4444}]$[succinate] has a higher α value (0.6), whereas the $[P_{4444}]$ cation does not act as a proton donor. This might be due to the hydroxyl group of the succinate anion. Although $[P_{4444}]$[maleate] has a carboxylic acid moiety, the α value of $[P_{4444}]$[maleate] was 0.24, which is lower than that of $[P_{4444}]$[succinate]. Since T_m for $[P_{4444}]$[fumarate] was 89.9 °C, the Kamlet–Taft parameters for $[P_{4444}]$[fumarate] were tentatively determined by absorption measured at 95 °C. $[P_{4444}]$[fumarate] has the lowest α value (0.15). These results might be due to the intra- and inter-molecular hydrogen bonds. As above, the maleate anion does not partake of intermolecular hydrogen bonding with other maleate anions; the intramolecular hydrogen bond leads to delocalization of negative charge, and the resulting weakening of the electrostatic interactions with $[P_{4444}]$ cation helps to lower the T_m of $[P_{4444}]$[maleate]. The thermal degradation temperatures (T_{decomp}) of these ILs were around 260 °C. This could be due to the high thermal stability of the $[P_{4444}]$ cation.[19]

We investigated the solubility of the ILs in water. $[P_{4444}]$[succinate] was readily soluble in water, but $[P_{4444}]$[fumarate] was less soluble. The low proton donor properties of $[P_{4444}]$[fumarate] might be responsible for the low solubility of this IL in water. To solubilize fumaric acid and sodium fumarate in water, it is necessary to apply heat to break the strong intermolecular hydrogen bonds. When the mixture of $[P_{4444}]$[fumarate] and water was heated and cooled, $[P_{4444}]$[fumarate] dissolved completely in water at high temperatures, and $[P_{4444}]$[fumarate] separated from water at low temperatures. The change between homogeneously mixed phase and phase separation was reversible. Fig. 2 shows the relation between the phase transition temperatures (T_c), which is the lowest temperature to give a clear solution, and the quantity of water added. Fig. 2, left, shows a convex curve giving an UCST of 62.2 °C at a water content of 50 (mol/mol), which is the highest temperature at which two phases can coexist in the $[P_{4444}]$[fumarate]–water system. A convex curve of this type is seen in many liquid/liquid systems. The UCST-type phase separation of the $[P_{4444}]$[fumarate] and water system would be in correspondence with the general solubility behavior. The phase behavior of $[P_{4444}]$[maleate] was totally different from $[P_{4444}]$[fumarate], however. Upon cooling the two-phase system (water/$[P_{4444}]$[maleate] = 20 (by mol)), the volume fraction of the IL phase increased gradually to reach a homogeneous phase, suggesting the increase of water solubility to the IL by cooling. The mixture of $[P_{4444}]$[maleate] and water showed phase separation with a LCST as seen in Fig. 2, right. The temperature–water content phase diagram for the $[P_{4444}]$[maleate]/water mixture gave a concave curve, with lowest T_c at 21.7 °C for a water content of 20 (mol/mol). This LCST type phase transition was also observed after cooling or heating the mixture at least some dozen times.

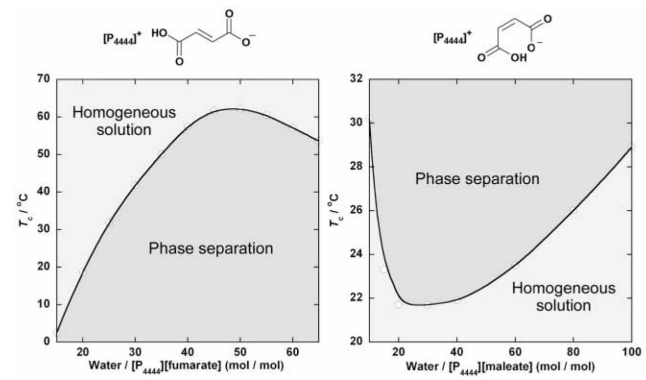

Fig. 2 Water content dependence of T_c for ionic liquids/water mixtures.

Raman spectroscopy (JASCO NRS-1000 spectrometer with a Kaiser Optical halographic super-notch filter and a liquid N_2-cooled CCD detector) was performed to investigate the interaction between water molecules and $[P_{4444}]$[maleate]. As seen in Fig. 3, the peaks assigned to C–H and C=O shifted according to the water content. This strongly suggests that water molecules hydrated to

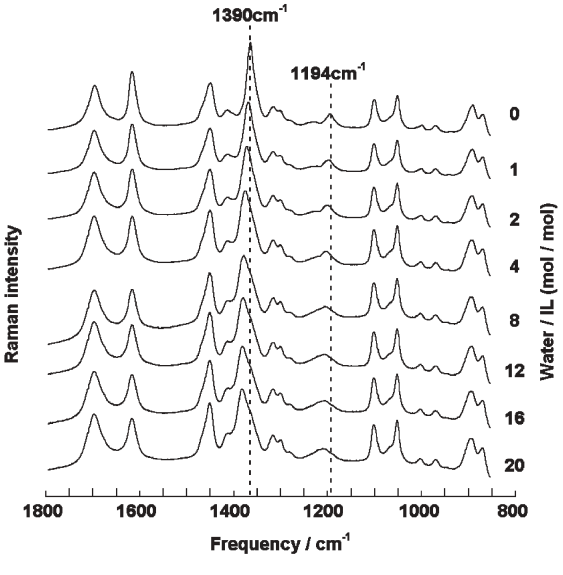

Fig. 3 Raman spectra of $[P_{4444}]$[maleate] containing water.

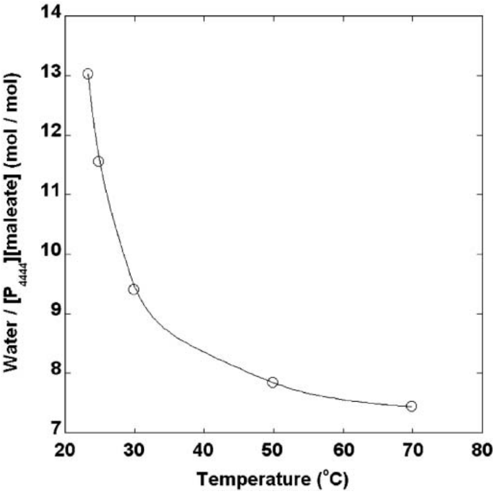

Fig. 4 Temperature dependence of the number of miscible water molecules per ion pair.

$[\mathrm{P_{4444}}]$[maleate] mainly on the C–H and C=O moiety of maleate anion.

Next, we investigated the temperature dependence of the water content in the $[\mathrm{P_{4444}}]$[maleate] rich phase (Fig. 4). One ion pair of $[\mathrm{P_{4444}}]$[maleate] was found to contain 7–13 water molecules; and the water content of the $[\mathrm{P_{4444}}]$[maleate] rich phase fell exponentially with temperature. These results show that the number of water molecules which $[\mathrm{P_{4444}}]$[maleate] retains is governed by the solution temperature. The water molecules hydrated to $[\mathrm{P_{4444}}]$[maleate] were released gradually upon heating, and $[\mathrm{P_{4444}}]$[maleate] was finally separated from the water phase.

We expected the novel phase separation system arising upon mixing both IL/water mixtures to show UCST and LCST behavior. $[\mathrm{P_{4444}}]$[maleate] was mixed with an equimolar amount of $[\mathrm{P_{4444}}]$[fumarate] to give a homogeneous solution at room temperature. These two ILs were miscible due to their structural similarity. To this mixture, 5, 10, 20 and 50 times (by mol) of water were added. Although this solution was cooled or heated from −5 to 80 °C, it did not show UCST or LCST behavior, and the mixture was homogeneous at any temperature.

The series of halogen-free ILs examined here was readily prepared from easily obtained and inexpensive materials. Maleate and fumarate exhibit different physico-chemical properties and solubility to water in their *cis* and *trans* conformations. Furthermore, their UCST and LCST behavior were readily controllable by choosing the anion structure and specifying the amount of water added. Their equimolar mixture did not show any phase transition after mixing with water.

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Notes and references

† Starting from 50 g of $[\mathrm{P_{4444}}]$[OH] aqueous solution (41.6 wt% in water) and 8.73 g of maleic acid, 25.9 g of $[\mathrm{P_{4444}}]$[maleate] was obtained (yield: 92%). ^{1}H NMR (400 MHz; $\mathrm{D_2O}$; δ/ppm relative to DSS): 0.91 (12H, t, J = 7.32 Hz, $\mathrm{CH_2C}\mathit{H}_3$), 1.40–1.57 (16H, m, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 2.10–2.17 (8H, m, $\mathrm{C}\mathit{H}_2\mathrm{CH_2}$), 6.33 (2H, s, $\mathrm{C}\mathit{H}\mathrm{{=}C}\mathit{H}$). ^{13}C NMR (400 MHz; $\mathrm{D_2O}$; δ/ppm relative to DSS): 13.20 ($\mathrm{CH_2}\mathit{C}\mathrm{H_3}$), 18.00–18.48 (d, $\mathit{C}\mathrm{H_2CH_3}$), 23.30–23.99 ($\mathit{C}\mathrm{H_2CH_2}$), 135.55 ($\mathit{C}\mathrm{H{=}}\mathit{C}\mathrm{H}$), 171.09 ($\mathit{C}\mathrm{{=}O}$). Starting from 50 g of $[\mathrm{P_{4444}}]$[OH] aqueous solution (41.6 wt% in water) and 8.74 g of fumaric acid, 20.28 g of $[\mathrm{P_{4444}}]$[fumarate] was obtained (yield: 87%). ^{1}H NMR (400 MHz; $\mathrm{D_2O}$; δ/ppm relative to DSS): 0.91 (12H, t, J = 9.15 Hz, 5.03 Hz $\mathrm{CH_2C}\mathit{H}_3$), 1.40–1.57 (16H, m, 39.57, 19.60, 6.40 Hz, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 2.14 (8H, m, 15.40, 6.40 Hz, $\mathrm{C}\mathit{H}_2\mathrm{CH_2}$), 6.73 (2H, s, $\mathrm{C}\mathit{H}\mathrm{{=}C}\mathit{H}$). ^{13}C NMR (400 MHz; $\mathrm{D_2O}$; δ/ppm relative to DSS): 13.17 ($\mathrm{CH_2}\mathit{C}\mathrm{H_3}$), 18.00–18.48 (d, $\mathit{C}\mathrm{H_2CH_3}$), 23.29–23.98 ($\mathit{C}\mathrm{H_2CH_2}$), 135.14 ($\mathit{C}\mathrm{H{=}}\mathit{C}\mathrm{H}$), 171.00 ($\mathit{C}\mathrm{{=}O}$). Starting from 50 g of $[\mathrm{P_{4444}}]$[OH] aqueous solution (41.6 wt% in water) and 8.90 g of succinic acid, 24.94 g of $[\mathrm{P_{4444}}]$[succinate] was obtained (Yield: 88%). ^{1}H NMR (400 MHz; DMSO-$\mathrm{d_6}$; δ/ppm relative to TMS): 0.93 (12H, m, J = 16.24 Hz, $\mathrm{CH_2C}\mathit{H}_3$), 1.38–1.47 (16H, m, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 2.19 (8H, m, 18.30, 9.61 Hz, $\mathrm{C}\mathit{H}_2\mathrm{CH_2}$), 2.28 (4H, d, 1.37 Hz, $\mathrm{C}\mathit{H}_2\mathrm{C}\mathit{H}_2$). ^{13}C NMR (400 MHz; DMSO-$\mathrm{d_6}$; δ/ppm relative to TMS): 13.48 ($\mathrm{CH_2}\mathit{C}\mathrm{H_3}$), 18.56–19.02 (d, $\mathit{C}\mathrm{H_2CH_3}$), 23.70–24.10 ($\mathit{C}\mathrm{H_2CH_2}$), 32.03 ($\mathit{C}\mathrm{H_2CH_2}$), 177.25 ($\mathit{C}\mathrm{{=}O}$).

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