

Mutually immiscible ionic liquids†

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This work presents the novel discovery of room-temperature ionic liquids that are mutually immiscible, some of which are also immiscible with solvents as diverse as water and alkanes; an archetypal biphasic system is trihexyltetradecylphosphonium chloride with 1-alkyl-3-methylimidazolium chloride (where the alkyl group is shorter than hexyl).

Ionic liquids have been attracting considerable interest because of their novel properties, such as tuneable solubility and very low vapour pressure.¹ By adjusting the structure of ionic liquids, it is possible to control their physical and chemical properties² and hence they have become known as “Designer Solvents”.³ Properties such as a defined density, melting point, viscosity, or solubility in water or other molecular solvents can be selected by changing either the anion or cation. An example is the solubility of 1-alkyl-3-methylimidazolium tetrafluoroborates⁴ in water, where for alkyl groups smaller than pentyl, these ionic liquids are completely miscible with water at 25 °C, and for longer alkyl chain lengths, they form a separate ionic phase and become increasingly less soluble in water.

We have found that mixtures of some hydrophilic ionic liquids and some specific hydrophobic ionic liquids gave rise to two distinct phases, particularly when there was a large difference in the structures of either the cation or the anion. Commercially-available phosphonium-based ionic liquids, such as trihexyltetradecylphosphonium chloride [P(C₆H₁₃)₃(C₁₄H₂₉)]Cl (or [P_{6 6 6 14}][NTf₂])⁵ and 1-alkyl-3-methylimidazolium chlorides [C_nmim]Cl⁶ (where the alkyl group is shorter than hexyl) form such biphasic systems when mixed. Furthermore, in some cases, hydrophobic ionic liquids were found to be partially soluble in each other at ambient temperatures. An example of this is a mixture of 1-ethyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}amide, [C₂mim][NTf₂],⁷ and [P_{6 6 6 14}][NTf₂].⁸ Knowing that these ionic liquids are also immiscible with light alkanes¹ such as pentane, it was possible to prepare a stable tetraphasic solvent system, consisting of layers of pentane, [P_{6 6 6 14}][NTf₂], water, and [C₂mim][NTf₂] (Fig. 1). The miscibility of [P_{6 6 6 14}][NTf₂] and [C₂mim][NTf₂] was found to be temperature dependant, with [C₂mim][NTf₂] being more soluble in the less dense [P_{6 6 6 14}][NTf₂] phase than [P_{6 6 6 14}][NTf₂] was in the denser [C₂mim][NTf₂] phase. The biphasic solubility region is shown in Fig. 2.

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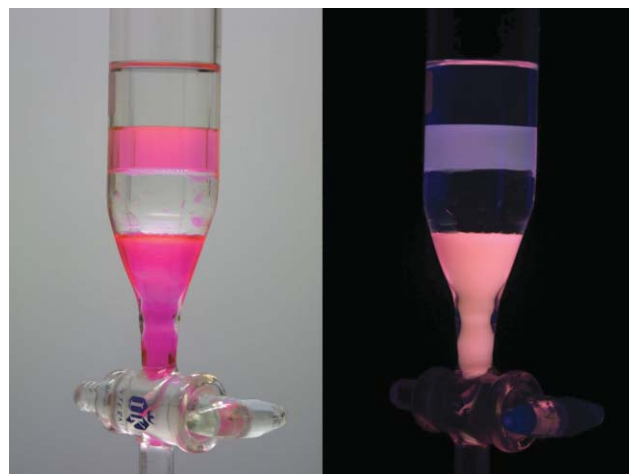


Fig. 1 A stable tetraphasic mixture of (from top to bottom): pentane, [P_{6 6 6 14}][NTf₂], water and [C₂mim][NTf₂]. The pink colouration is due to rhodamine B dye, which is soluble in the ionic layers. The figure on the left was taken in daylight and the figure on the right was taken under illumination from UV light (254 nm).

When two different ionic liquids (each consisting of different anions and cations) are mixed, a four-ion mixture is created and some of these were also found to give rise to biphasic mixtures at room temperature. Some examples of these include [C₂mim][OSO₂CH₃] (OSO₂CH₃ is also known as methane sulfonate)⁹ and [P_{6 6 6 14}][NTf₂], or [C₂mim][OSO₂CH₃] and [P_{6 6 6 14}][PO₂(C₈H₁₇)₂] (PO₂(C₈H₁₇)₂ is also known as diisooctylphosphinate or bis-(2,4,4-trimethylpentyl)-phosphinate).¹⁰ It was

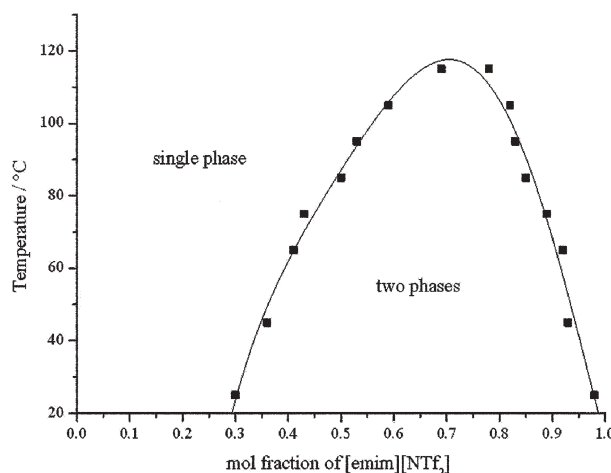


Fig. 2 Temperature-composition diagram for the binary system [C₂mim][NTf₂] + [P_{6 6 6 14}][NTf₂].

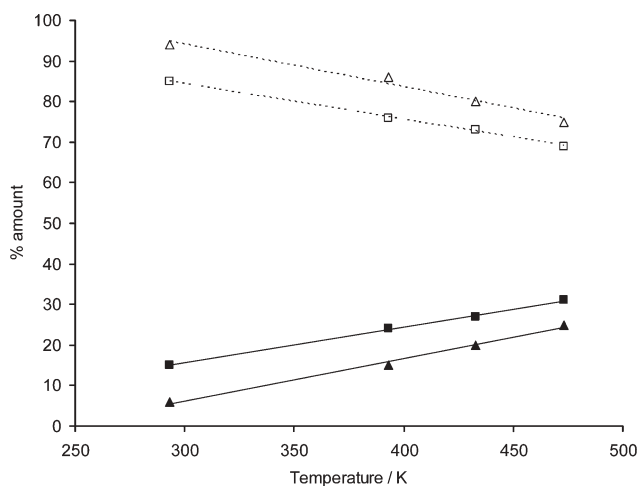


Fig. 3 The distribution of ions in the upper (less dense) phase of an equimolar mixture of $[C_2mim][OSO_2CH_3]$ and $[P_{6,6,6,14}][NTf_2]$. The dashed line represents $[P_{6,6,6,14}][NTf_2]$ and the solid line $[C_2mim][OSO_2CH_3]$, (Δ) for cations and (\square) for anions.

found that each ion behaves independently when mixed and biphasic solutions are formed. In the case of $[C_2mim][OSO_2CH_3]$ and $[P_{6,6,6,14}][NTf_2]$, the small $[C_2mim]^+$ cation prefers to associate with the small $[OSO_2CH_3]^-$ anion and the larger $[P_{6,6,6,14}]^+$ and $[NTf_2]^-$ ions associate with each other in the less dense phase. Fig. 3 shows how the composition of the upper phase varies with temperature (by 1H NMR spectroscopy).

Mixtures of $[P_{6,6,6,14}]Cl$ and $[C_nmim]Cl$ were found to be immiscible in the temperature range 298 to 458 K, where the alkyl group was pentyl or smaller; $[C_6mim]Cl$ was found to be miscible with $[P_{6,6,6,14}]Cl$ in all proportions. For the immiscible liquids, some of the imidazolium ions dissolved in the phosphonium phase and, to a much lesser extent, some of the phosphonium ions dissolved in the hydrophilic imidazolium layer. The composition of both layers was determined by 1H NMR analysis (Fig. 4).

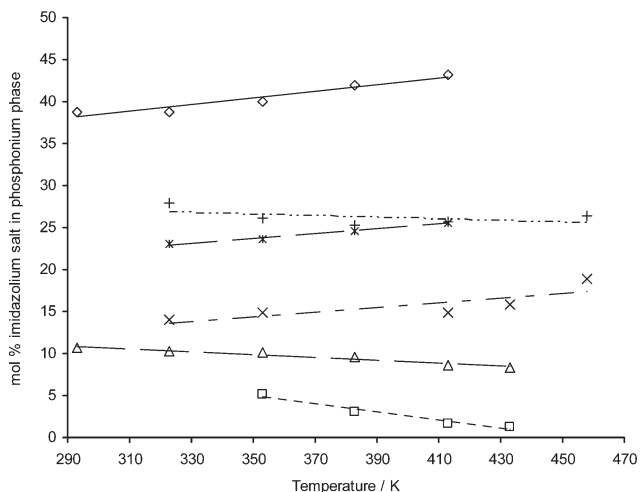


Fig. 4 The solubility of 1-alkyl-3-methylimidazolium chlorides in $[P_{6,6,6,14}]Cl$ at various temperatures. From top to bottom, the lines represent $[C_5mim]Cl$ (\diamond); $[s-C_4mim]Cl$ (+); $[C_4mim]Cl$ (*); $[C_3mim]Cl$ (\times); $[C_2mim]Cl$ (Δ); and $[C_1mim]Cl$ (\square).

Table 1 The enthalpy and entropy of dissolving 1-alkyl-3-methylimidazolium chlorides in the $[P_{6,6,6,14}]Cl$ rich phase

Alkyl group	$\Delta H/kJ mol^{-1}$	$\Delta S/J K^{-1} mol^{-1}$
C_1	-21.7	-100.3
C_2	-2.29	-39.1
C_3	1.03	-25.5
$s-C_4$	-1.14	-26.7
C_4	1.35	-20.3
C_5	1.51	-15.7

As the two phases are in equilibrium, the Van't Hoff isochore can be applied, and from a plot of the natural logarithm of the equilibrium constant, $\ln(K)$, versus the inverse of the absolute temperature, T^{-1} , the enthalpy and entropy of mixing (dissolving $[C_nmim]Cl$ in $[P_{6,6,6,14}]Cl$) can be determined. The solubility of the imidazolium salts increases with alkyl chain length. However, for 1,3-dimethyl-, 1-ethyl-3-methyl-, and 1-(1-methylpropyl)-3-methylimidazolium chlorides ($[C_1mim]Cl$, $[C_2mim]Cl$, and $[s-C_4mim]Cl$, respectively where $[s-C_4mim]^+$ is 1-(1-methylpropyl)-3-methylimidazolium), the solubility decreases with increasing temperature, whereas the solubility of 1-propyl-, 1-butyl-, and 1-pentyl-3-methylimidazolium chloride ($[C_3mim]Cl$, $[C_4mim]Cl$, and $[C_5mim]Cl$, respectively) increases with increasing temperature. The plots of $\ln(K)$ versus T^{-1} for the six mixtures gave in each case a straight line and the enthalpy (ΔH) and entropy (ΔS) of dissolution of the imidazolium chloride in the phosphonium chloride phase were obtained from the gradient ($-\Delta H/R$) and intercept ($\Delta S/R$). These values are reported in the Table 1. As can be seen, both the enthalpy and the entropy of dissolution increase rapidly as the alkyl chain length increases.

The most notable feature is the strongly negative entropy of mixing of $[C_1mim]Cl$ (and the corresponding exotherm). A plausible explanation for this is that the hydrogen bonding between the $[P_{6,6,6,14}]^+$ ion and chloride is relatively weak. The $[C_1mim]^+$ forms stronger hydrogen bonds as the imidazolium ion is introduced into the phosphonium chloride environment. The formation of new stronger hydrogen bonds results in the exotherm and an increase in the degree of ordering in the phosphonium layer (and hence a large entropy decrease). As the alkyl chain length increases, this introduces a degree of asymmetry and hence the entropy of dissolution is less negative. Interestingly, the dissolution of $[s-C_4mim]Cl$ is significantly more exothermic and has a lower entropy of dissolution than the isomeric $[C_4mim]Cl$. It should also be noted that $[s-C_4mim]Cl$ is a mixture of two enantiomers. This may account for the enthalpy and entropy differences. The solubilities of the phosphonium chloride in the imidazolium layer are very low, often below the detection limit of the NMR spectrometer, and are not detailed here.

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Notes and references

- Ionic Liquids in Synthesis*, ed. P. Wasserscheid and T. Welton, Wiley-VCH, Weinheim, 2003; M. J. Earle, J. M. S. S. Esperança, M. A. Gilea, J. N. C. Lopes, L. P. N. Rebelo, J. W. Magee, K. R. Seddon and J. A. Widegren, *Nature*, 2006, **439**, 831.
- M. Deetlefs, K. R. Seddon and M. Shara, *New J. Chem.*, 2006, **30**, 317.

- 3 M. Freemantle, *Chem. Eng. News*, 1998, **76**, 32.
- 4 J. D. Holbrey and K. R. Seddon, *J. Chem. Soc., Dalton Trans.*, 1999, 2133.
- 5 C. J. Bradaric, A. Downard, C. Kennedy, A. J. Robertson and Y. H. Zhou, *Green Chem.*, 2003, **5**, 143.
- 6 J. S. Wilkes, J. A. Levisky and M. L. Druelinger, *Inorg. Chem.*, 1982, **21**, 1263.
- 7 P. Bonhôte, A.-P. Dias, N. Papageorgiou, K. Kalyanasundaram and M. Gratzel, *Inorg. Chem.*, 1996, **35**, 1168; P. Bonhôte, A.-P. Dias, M. Armand, N. Papageorgiou, K. Kalyanasundaram and M. Gratzel, *Inorg. Chem.*, 1998, **37**, 166.
- 8 N. Ito, S. Arzhantsev, M. Heitz and M. Maroncelli, *J. Phys. Chem. B*, 2004, **108**, 5771.
- 9 A. J. Carmichael, M. Deetlefs, M. J. Earle, U. Fröhlich and K. R. Seddon, *Ionic Liquids as Green Solvents: Progress and Prospects*, in *ACS Symposium Series*, ed. R. D. Rogers and K. R. Seddon, American Chemical Society, Washington, 2003, vol. 856, p. 14.
- 10 C. J. Bradaric, A. Downard, C. Kennedy, A. J. Robertson and Y. H. Zhou, *Ionic Liquids as Green Solvents: Progress and Prospects*, in *ACS Symposium Series*, ed. R. D. Rogers and K. R. Seddon, American Chemical Society, Washington, 2003, vol. 856, p. 41.

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