

Solvation of 1-butyl-3-methylimidazolium hexafluorophosphate in aqueous ethanol—a green solution for dissolving ‘hydrophobic’ ionic liquids

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Received (in Columbia, MO, USA) 1st July 2001, Accepted 28th August 2001

First published as an Advance Article on the web 27th September 2001

The relatively hydrophobic ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate has been found to be totally miscible with aqueous ethanol between 0.5 and 0.9 mol fraction ethanol, whereas the ionic liquid is only partially miscible with either pure water or absolute ethanol; the ability to dissolve 1-butyl-3-methylimidazolium hexafluorophosphate in a ‘green’ aqueous solvent system has important implications for cleaning, purification, and separations using ionic liquids.

Current interest in ionic liquids^{1,2} (IL) stems primarily from the heightened awareness of the potential applications for IL in Green Chemistry³ and the associated emphasis on clean manufacturing processes. We have investigated IL as clean, environmentally benign solvents as replacements for VOCs in liquid/liquid separations and extraction processes.^{4–9} From the ‘green’ perspective, an issue of primary importance is the separation and recovery of products from reaction systems, as well as the potential to recycle and reuse the reaction/separations media without generating secondary waste. There is concern about how to address issues such as cleaning and removal of *non-volatile* IL from surfaces or from solid products without using VOCs. For example, the commonly used ‘hydrophobic’ IL 1-butyl-3-methylimidazolium hexafluorophosphate, [C₄mim][PF₆],[†] is readily soluble in many common organic solvents but is relatively insoluble in most green solvents including water and sc-CO₂. Here, we demonstrate that [C₄mim][PF₆] can be solubilized in a green aqueous solvent system—ethanol/water.

In a traditional liquid/liquid separation processes, the principle of ‘like dissolves like’ forms the basis for the partitioning of solutes between the two phases; the less water-soluble the solute, the higher its affinity for the hydrophobic extracting phase. The partitioning of organic solutes in IL/water systems shows a correlation with the octan-1-ol/water partition coefficient.⁶ This is consistent with solvatochromatic studies^{10,11} which appear to show that IL have solvent characteristics similar to moderately polar organic molecules, but with some important and inherent differences.¹² The solvent parameters determined for IL can vary significantly depending on the experimental probe used, and depend upon the contributions from specific interactions between IL and solutes. Volume and hydrogen-bond acceptor terms appear to be most important to the overall solvating environment. In light of this, it is important to note that PF₆[−] is a poor hydrogen-bond acceptor and consequently ethanol and water should not partition in significant concentrations to [C₄mim][PF₆].

Dullius *et al.*¹³ have shown that tetrafluoroborate-containing IL display miscibility curves with water typical of a partially miscible two-component system with an upper thermal critical point and, at lower temperatures, the formation of a two-phase system containing IL-rich and aqueous-rich layers. Work by Friberg *et al.*¹⁴ has highlighted the complexity of the miscibility/solvation profile in [C₄mim][PF₆]/water/nonionic

surfactant systems and also noted that the IL exhibited only partial miscibility with hydrated ethanol.

During partitioning studies, we were intrigued by the variation in miscibility of IL with molecular solvents we had observed from simple bench tests, and in particular, the observation that [C₄mim][PF₆] was totally miscible with 80% aqueous ethanol and yet formed biphasic mixtures with both pure water and pure ethanol. This prompted a more detailed investigation of the phase behavior.

The ternary phase diagram for [C₄mim][PF₆] in contact with ethanol and water was determined by cloud-point titration¹⁵ at 25 °C and is shown in Fig. 1. [C₄mim][PF₆] is partially miscible with both pure water and with pure ethanol. Regions of biphasic coexistence extend along the [C₄mim][PF₆]/H₂O and [C₄mim][PF₆]/ethanol axes, respectively. The solubility limit of absolute ethanol in the IL was determined to be 10.1 wt% and the solubility of water was 1.2 wt%. The water content of saturated [C₄mim][PF₆] has been reported in the literature ranging from 1.2 to 2.3 wt%,^{7,16,17} corresponding to a mol fraction between 0.16 to 0.27. The region of complete miscibility of the three components, water, ethanol, and [C₄mim][PF₆], is shown between the two binodal curves and extends from the EtOH/H₂O axis.

To further our characterization of the ethanol/water solubility in [C₄mim][PF₆], the distribution of ethanol and water to the IL was determined (Fig. 2). Samples containing 2 mL of IL were contacted with an equal volume of aqueous ethanol solution labeled with a ¹⁴C-ethanol tracer.¹² The distribution of ethanol was determined from the radiotracer partitioning, and the water content of the IL phase was measured by Karl Fischer titration.¹² In the biphasic regions, the distribution of ethanol is

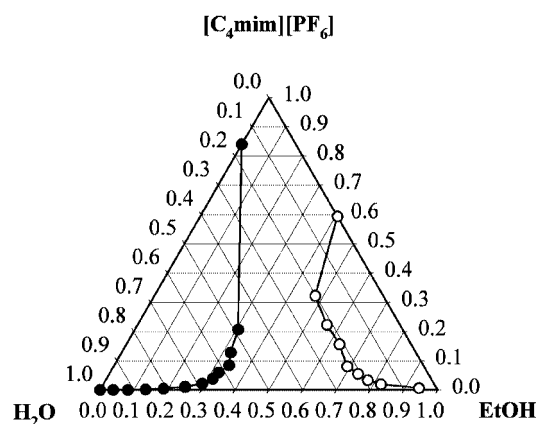


Fig. 1 Triangular phase diagram for ternary compositions of [C₄mim][PF₆], ethanol, and water determined at 25 °C and plotted as mol fraction. The region to the left of the binodal line, ● is biphasic with water- and [C₄mim][PF₆]-rich phases; the region to the right of the line ○ is biphasic comprising ethanol- and [C₄mim][PF₆]-rich phases. In the central region, the three components are totally miscible and form a single monophasic solution.

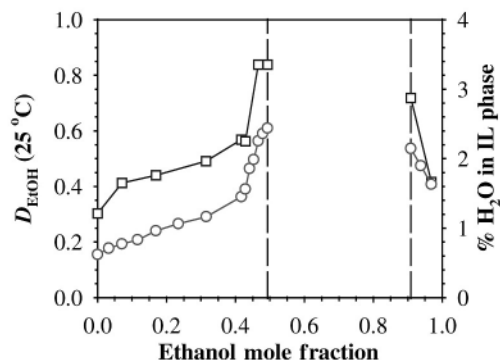


Fig. 2 The distribution ratios at 25 °C of ethanol ($D_{\text{EtOH}} = \circ$) and water content of the IL phase (\square) in 1:1 volume mixtures of $[\text{C}_4\text{mim}][\text{PF}_6]$ and aqueous ethanol as a function of initial mol fraction of ethanol in the aqueous phase prior to contact with the IL phase. The monophasic region is bounded by the vertical dashed lines.

less than 1, which indicates the tendency for ethanol to remain in the aqueous phase. For the two-component $[\text{C}_4\text{mim}][\text{PF}_6]$ /water system, the distribution ratio for the ethanol tracer between the IL and water is only 0.16. Successive increases in the mol fraction of ethanol cause an increase in ethanol distribution ratios up to a maximum of 0.61 at 0.5 mol fraction of ethanol in water. In the range 0.4–0.5 mol fraction, the distribution of ethanol to $[\text{C}_4\text{mim}][\text{PF}_6]$ and the water content of the IL increases dramatically, and for 0.5–0.9 mol fraction the system is monophasic, shown by the vertical lines in Fig. 2. Above 0.9 mol fraction, a biphasic mixture is once again obtained.

The solubility of both ethanol and water in the IL phase increases in the presence of the other component, leading to the large homogeneous region in the phase diagram. The D_{EtOH} and water content data shown in Fig. 2 indicate that ethanol and water are dissolved together in the IL. Both the D_{EtOH} and water content increase linearly with X_{EtOH} from 0 to 0.40, where a sharp rise in both is maintained until the miscibility region. At $X_{\text{EtOH}} = 0.90$ a biphasic region is again observed and D_{EtOH} and water content decrease with the addition of ethanol.

The liquid structure and association in ethanol/water compositions has been the subject of extensive study;¹⁸ when $X_{\text{EtOH}} < 0.2$, ethanol molecules cluster with the ethyl chains forming a hydrophobic core surrounded by water molecules. At $0.2 < X_{\text{EtOH}} < 0.8$, a sandwich-type cluster containing extended chains of hydrogen-bonded ethanol and water occurs. The interactions that could occur between the water/ethanol clusters and the IL to lead to the total miscibility region is not yet clear. Free-volume cavities, or void space within the IL matrix¹⁷ may allow ethanol and water to be dissolved together, whilst maintaining the bulk ethanol/water hydrogen-bonding structure with only weak interactions between the alkyl-groups of the IL and the hydrophobic ethyl-substituents of the water/ethanol chains.

A comparison of the vapor phase compositions above the $[\text{C}_4\text{mim}][\text{PF}_6]$ /water/ethanol mixtures with ethanol/water mixtures only was made using SPME/GC. No discernable differences in the ethanol/water composition of the gas vapor phase was observed. This adds to our supposition that ethanol/water compositions mix with the IL whilst maintaining the bulk ethanol/water hydrogen-bonded structure.

The observation that $[\text{C}_4\text{mim}][\text{PF}_6]$, regarded as a hydrophobic IL, can be dissolved in a 'green' aqueous solvent system has important implications for purification and separations from IL. As shown here, the addition of a solute or combination of solutes dramatically affects the solution behavior of IL, highlighting the need to fully understand these systems and instances in which their solution chemistry may vary from that of traditional organic solvents. At a practical level, these results show a method by which $[\text{C}_4\text{mim}][\text{PF}_6]$ can be dissolved and

cleaned from, for example, a reaction vessel or a solid product without using volatile chlorinated organic solvents. The IL can be recovered by distilling the water/ethanol azeotrope or by changing the solution composition to form a biphasic system.

This research was supported by the US Environmental Protection Agency's STAR program (grant number R-82825701-0). Additional support was provided to the Center for Green Manufacturing from the National Science Foundation Grant EPS-9977239 and the PG Research Foundation. The authors appreciate the chemicals supplied by Ozark Fluorine Specialties.

Notes and references

† The synthesis of 1-butyl-3-methylimidazolium hexafluorophosphate from $[\text{C}_4\text{mim}]\text{Cl}$ and HPF_6 (Ozark Fluorine Specialties) and the procedures used for the standard radiochemical assay utilized are described in ref. 12. The radiochemical assay of equal volumes of the two separated phases allows calculation of the distribution ratios directly from the activity of the two phases. ^{14}C -labeled ethanol was obtained from Sigma (St. Louis, MO). All aqueous solutions were prepared with deionized water that was purified with a Barnsted deionization system (Dubuque, IA) and polished to 18.3 M Ω cm. The water content of each ionic liquid or its mixtures was determined by Karl Fischer titration (Aquastar Karl Fischer titrator, EM Science, Gibbstown, NJ) with Composite 5 solution as the titrant in anhydrous methanol. The ternary composition diagram was determined by direct observation using the cloud-point titration method described in ref. 15.

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