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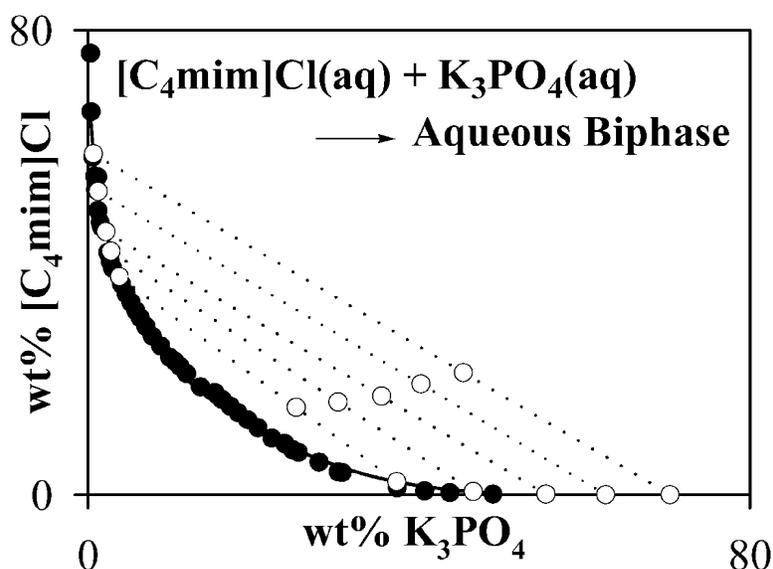### JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

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Controlling the Aqueous Miscibility of Ionic Liquids: Aqueous Biphasic Systems of Water-Miscible Ionic Liquids and Water-Structuring Salts for Recycle, Metathesis, and Separations

Keith E. Gutowski, Grant A. Broker, Heather D. Willauer, Jonathan G. Huddleston, Richard P. Swatloski, John D. Holbrey, and Robin D. Rogers*

Center for Green Manufacturing and Department of Chemistry, The University of Alabama, Tuscaloosa, Alabama 35487

Received March 16, 2003; E-mail: rdrogers@bama.ua.edu

Ionic liquids (ILs)[1] have been gaining exposure for their potential use as green solvents and possible replacements for traditional volatile organic solvents (VOCs) for a variety of applications. Examples include organic synthesis,[2] biphasic catalysis, separation and extraction processes,[3] and dissolution of biomaterials.[4] We have investigated the use of water-immiscible room-temperature ILs in place of VOCs for the separation of neutral organic molecules and metal ions.[5] However, the number of water-immiscible ILs is currently limited to a few cation/anion combinations, most notably with fluorinated anions which can be expensive and environmentally nonbenign.

Here we demonstrate that 1-butyl-3-methylimidazolium chloride, [C$_4$mim]Cl, a hydrophilic IL, can be induced to form aqueous biphasic systems (ABS) when contacted with concentrated solutions of the water-structuring salt, K$_3$PO$_4$, forming an upper IL-rich phase and a lower K$_3$PO$_4$-rich phase, both of which are aqueous. These new ABS can be utilized to recycle or concentrate hydrophilic ILs from aqueous solution, to carry out metathesis in the formation of new IL salts, and for separations, including reactive separations.

The mutual coexistence curve for the [C$_4$mim]Cl/K$_3$PO$_4$ system was determined by the cloud point method[6] at room temperature (Figure 1) and shows that aqueous biphasic systems can be formed over a large composition range from monophasic, aqueous solutions of [C$_4$mim]Cl upon addition of K$_3$PO$_4$. Using an empirical mathematical description of the coexistence curve[7] (least squares approximation and by application of the lever-arm rule), we determined binodal tie line relationships from volume and density data collected for each phase. This method uses a material balance to compute the tie lines so that the overall system composition bisects the tie line in the same proportion as the ratio of the measured masses of the phases formed.

Because the phase-forming components are ionic, the tie lines describe the initial component compositions. In solution, a series of distribution equilibria may exist, and so it is important to characterize the compositions of the two phases. The distributions of the component ions of the biphasic system were determined using partitioning of radiotracers to determine the speciation within the biphasic systems. A series of five stock systems, with compositions within the upper region of the phase diagram, were prepared with [C$_4$mim]Cl/K$_3$PO$_4$/H$_2$O compositions of 25/15/60, 30/16/54, 35/17/48, 40/19/41, and 45/21/34 wt %, respectively. The distributions of ^{14}C-labeled [C$_4$mim]$^+$ cations, and ^{32}P-labeled [PO$_4$]$^{3-}$ and ^{36}Cl-labeled Cl$^-$ anions, were determined directly by scintillation counting of the activity of equal aliquots of each phase in independent experiments; the results are shown in Figure 2 (along with phase diagram-determined distributions).

The distribution ratios in Figure 2 show the partitioning of the system components (except potassium) at equilibrium after biphase
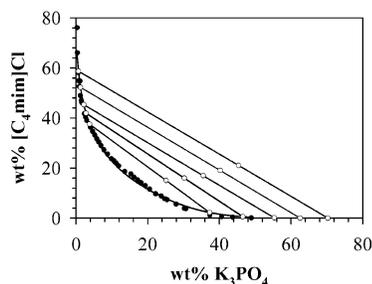

Figure 1. The mutual coexistence curve for the aqueous [C$_4$mim]Cl/K$_3$PO$_4$ system. System compositions below the coexistence curve are monophasic; compositions above the curve are biphasic. Tie lines (○) relate upper and lower phase compositions.
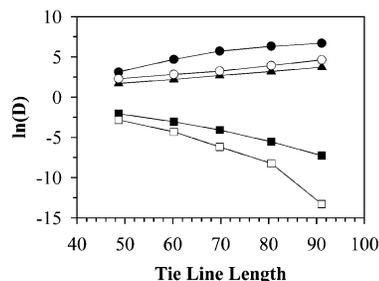

Figure 2. Plot of the natural log of the distribution ratio as a function of tie line length for ^{36}Cl (▲), ^{14}C (●), and ^{32}P (■) tracer species and for [C$_4$mim]Cl (○) and K$_3$PO$_4$ (□) as determined from the phase diagram.

formation. As the tie line length increases, [C$_4$mim]$^+$ and Cl$^-$ distribution ratios increase, consistent with the observation that the upper phase is rich in aqueous [C$_4$mim]Cl, although it must be noted that the distribution ratios for the imidazolium and chloride ions are not exactly 1:1, indicating that equilibria of ions exist in the two phases, as might be expected. In addition, as the tie line length increases, the distribution ratio for [PO$_4$]$^{3-}$ decreases, indicating a preference for the lower phase. To maintain the charge balance, it can be concluded that the K$^+$ cations are also concentrated in the lower phase.

Addition of the water-structuring salt K$_3$PO$_4$ to an aqueous solution of [C$_4$mim]Cl in proportions dictated by the binodal in the phase diagram produces a salting-out effect leading to the formation of a biphasic system consisting of a [C$_4$mim]Cl-rich upper phase and a K$_3$PO$_4$-rich lower phase. In this respect, this two-phase system resembles those formed, for example, in poly(ethylene glycol) (PEG)/salt aqueous biphasic systems (ABS).[8−10] Here, the efficiency of separation is governed by the Gibb's free energy of hydration of the salt, where K$_3$PO$_4$ results in very efficient separations at relatively low concentrations of PEG and salt due to its very negative ΔG_{hyd} of -3750 kJ/mol.[11] An important trend is

that the IL salt becomes more concentrated in the upper phase as the concentration of K₃PO₄ increases, as well as there being less phosphate contamination in the upper phase.

The water-structuring nature of the $[PO_4]^{3-}$ anion results in electroconstriction of the water surrounding these anions, thus increasing the hydrogen bond network of the water in this phase and requiring more energy for cavity formation around the bulky organic $[C_4mim]^+$ cation. At a certain concentration of $[PO_4]^{3-}$, this results in the more hydrophobic cation and the less water-structuring anion (Cl^-) forming a separate aqueous phase. Increased K₃PO₄ concentrations enhance phase separation. This is exactly analogous to what we observe in the formation of PEG/salt ABS. This phenomenon is probably a solvophobic one;[12] according to Weingärtner, kosmotropic (i.e., water-structuring) salts increase the dielectric constant of the aqueous phase, thus forcing the low dielectric $[C_4mim]^+$ cations to the upper phase with concurrent transfer of chloride anions.

We can generalize the formation of ABS of this type by considering the use of other water-structuring salts to salt-out the IL ions from aqueous solution. ABS of $[C_4mim]Cl$ have been formed with a range of kosmotropic salts including KOH, K_2CO_3, Na_2HPO_4, and $Na_2S_2O_3$. Similarly, $[C_4mim]Cl$ is formed by metathesis and is concentrated in the upper phase of an ABS produced on addition of KCl to aqueous $[C_4mim]_3[PO_4]$. We have also formed ABS 1,3-dialkylimidazolium triflate and tetrafluoroborate ILs with $CaCl_2$ and NaCl solutions.

Solvophobic arguments point toward the generality of salting-out of hydrophilic ILs with bulky organic cations, as an anion pair, by addition, or formation of a salt containing a *more* kosmotropic anion. In addition, increasing the hydrophobic nature of the organic cations enhances the facility for phase separation. These observations might allow one to exploit some unique properties of these novel systems for separations and extraction, providing they possess sufficient chemical potential between phases, or perhaps IL reconcentration/recycling without the use of VOCs. For example, molten, anhydrous $[C_4mim]Cl$ has been used to dissolve cellulose[4] and the cellulose reconstituted by contact of the solution with water. The resulting $[C_4mim]Cl(aq)$ solution can be concentrated for reuse by a liquid/liquid contact with concentrated $K_3PO_4(aq)$, thus reducing the energy penalty of evaporating all of the water, although, as indicated in Figure 2, a small amount of undesirable speciation does occur.

The salting-out effect explained here has also been noticed in a few other IL systems. Dupont et al.[13] have noted that hydrophilic $[C_4mim][BF_4]$ phase-separates from aqueous solution in the presence of KCl (a more kosmotropic salt than the corresponding KBF₄). Additionally, Scurto et al.[14] have shown that CO_2 has the ability to induce separation of ILs and water. While this effect is described as a pressure phenomenon, salting-out due to the formation of carbonate in solution may also play a key role.

The ability to control the aqueous miscibility of ILs, particularly the hydrophilic type, is of particular importance in areas such as separations technology. Many of the current hydrophobic ILs have fluorine-containing anions that are expensive to produce and/or difficult to dispose of. By using the salting-out phenomenon to induce phase separation, we found that the potential to use nonfluorinated ILs in ABS may be realized as illustrated below.

Figure 3 shows the distribution ratios of a series of short chain alcohols in $[C_4mim]Cl/K_3PO_4$ ABS at various tie line lengths. The *D* values to the upper, $[C_4mim]Cl$-rich phase increase with increasing tie line length and with increasing number of carbons in the aliphatic chain. This is significant in that it shows the increase in free energy of transfer of a methylene group between the phases
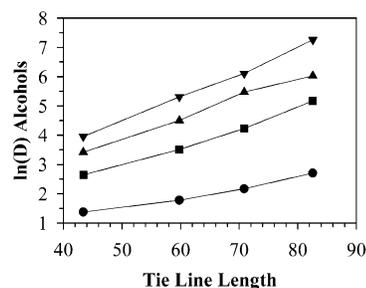

Figure 3. The natural log (ln) of the distribution ratios for methanol (●), propanol (■), butanol (▲), and pentanol (▼) in the $[C_4mim]Cl/K_3PO_4$ biphasic system at four different tie line lengths.

with tie line length. That is, the upper phase becomes increasingly hydrophobic as the divergence between the two phases increases, which allows fine-tuning of the separations in these ABS. Obviously, a sufficient chemical potential exists so as to allow the partitioning of the organic molecules between the phases, indicating potential use in separations applications.

Supporting Information Available: Experimental details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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JA0351802