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Extraction of Biofuels and Biofeedstocks Using Ionic Liquids

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ABSTRACT Biomass production of chemicals and fuels by fermentation, biocatalysis, and related techniques implies energy-intensive separations of organics from dilute aqueous solutions, and may require use of hazardous materials as entrainers to break azeotropes. We consider the design feasibility of using ionic liquids as solvents in liquid-liquid extractions for separating organic compounds from dilute aqueous solutions. As an example, we focus on the extraction of 1-butanol from a dilute aqueous solution. We have recently shown [Chapeaux et al. (2008), *Green Chemistry*, 10, 1301] that 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide shows significant promise as a solvent for extracting 1-butanol from water. We will consider here two additional ionic liquids, 1-(6-hydroxyhexyl)-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide and 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluoro-phosphate, as extraction solvents for 1-butanol. Preliminary design feasibility calculations will be used to compare the

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three ionic liquid extraction solvents considered. The ability to predict the observed ternary liquid-liquid equilibrium behavior using selected excess Gibbs energy models, with parameters estimated solely using binary data and pure component properties, will also be explored

KEYWORDS *Ionic liquids, 1-Butanol, Extraction, Liquid-Liquid Equilibrium, Excess Gibbs Energy Models*

Introduction

1-Butanol is used as a feedstock for making many common chemicals. It is also used as solvent in many applications, such as re-crystallization processes in the pharmaceutical industry. Furthermore, there is growing interest in 1-butanol as a fuel. For any current and potential use of 1-butanol, it is important to look to renewable sources for its synthesis. Thus, there is much current research focused on the fermentation of biomass, resulting in a broth composed of mainly water and alcohols, from which 1-butanol can be separated. Conventionally, separating alcohols and water requires a series of distillation columns. This method is energetically costly, and much room for improvement exists. It has been shown that ionic liquids (ILs) have the potential for separating alcohol/water mixtures with simple liquid-liquid extraction (Fadeev and Meagher, 2001; Chapeaux et al., 2008), which could be less energetically costly than distillation.

ILs are salts with a melting point below 100°C, and which are usually composed of a poorly coordinating, bulky organic cation, and an organic or inorganic anion. Some of the properties that make them advantageous for this application are a negligible vapor pressure, which allows for recovery and reuse of the IL; a large liquid range, which allows for ease of separation; and, finally, a tunability that allows the creation of ILs that preferentially select alcohols from water.

In this study we will determine, based on experimental observations, the distribution coefficients, selectivities, and number of equilibrium stages for multicomponent liquid-liquid extraction of 1-butanol from water using 1-(6-hydroxyhexyl)-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide ([HOhmim][Tf₂N]) and 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluoro-phosphate ([hmim][eFAP]), and compare these results to previously published results for 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([hmim][Tf₂N]) (Chapeaux et al, 2008).

Predicting an IL's capability as a separation solvent is important as experimental observation of every system of interest is time consuming. Clearly, a model that predicts ternary liquid-liquid equilibrium (LLE) behavior *a priori* is desired; however, at the present time models based on first principles are

both computationally expensive and inaccurate for multicomponent LLE. For example, COSMO-RS has been applied to predictions of binary LLE upper critical solution temperature behavior and of a ternary LLE system, but without satisfactory results (Freire et al., 2007; Jork et al., 2005). More recently, COSMO-RS has been modified for LLE (COSMO_LL), yielding better ternary predictions involving ILs, but still with much room for improvement (Banerjee et al., 2008). Molecular descriptor and group contribution methods, e.g., NRTL-SAC (NRTL Segment Activity Coefficient) and UNIFAC (Dortmund), respectively, also provide qualitatively inaccurate predictions in many cases (Chen et al., 2008; Chapeaux et al., 2008).

In this work, we use a semi-predictive method in which activity coefficient models are used to make ternary LLE predictions based on only binary and pure component data. It was shown previously (Chapeaux et al., 2008; Simoni et al., 2008) that ternary systems containing ILs and water were more difficult to qualitatively predict using this approach. In such systems, it is likely that there are different degrees of ionic dissociation in different phases. To account for this, we have developed a novel asymmetric framework in which different activity coefficient models are used in different liquid phases. Although ILs most likely partially ionize, as a first approximation, we assume the IL is *completely dissociated* in a dilute aqueous phase and completely paired (molecular) in an alcohol/IL-rich phase (Simoni et al., 2009a,b). We will apply this modeling approach here to one of the ternary systems investigated experimentally, namely [hmim][Tf₂N]/1-butanol/water.

Methodology

Experimental

1-Butanol (71-36-3, 99.8+% purity, reagent grade, 600 ppm water) was purchased from Sigma-Aldrich and used as received. The water was deionized by a Millipore purification system (>18 M Ω -cm resistivity). [HOhmim][Tf₂N] was made and purified according to previously described methods (Bonhote et al., 1996; Cammarata et al., 2001; Crosthwaite et al., 2004; Crosthwaite et al., 2005; Fredlake et al., 2004). [hmim][eFAP] was received from Merck KGaA and used as received. All the ILs used were dried under vacuum (~1.3 Pa) for 24 hr at 70°C.

All experimental procedures have been described in other publications. (Chapeaux et al., 2008; Chapeaux et al., 2009b). In short, we mixed IL, water and 1-butanol in a vial, and then allowed the phases to separate. We analyzed all three components in each phase using high-performance liquid chromatography, gas chromatography, Karl-Fischer titration, and UV-Vis spectroscopy.

Modeling

In the asymmetric framework, we assume that the IL is *completely dissociated* in dilute aqueous phases (high average dielectric constant), and that the IL is *completely associated*, or molecular, as ion pairs in IL or solvent-rich phases (low average dielectric constant). Accordingly, we use electrolytic and conventional activity coefficient models to represent the dissociated and molecular phases, respectively, in particular the electrolyte-NRTL (eNRTL) (Chen et al., 2004) and NRTL models. Note that a complete, general formulation of this asymmetric framework, together with discussion of standard state definitions and phase stability analysis, for general mixed-salt/mixed-solvent systems will be presented elsewhere (Simoni et al., 2009a).

The degree of dissociation depends on the ability of the phase's components (mixed solvent) to screen the electrostatic forces of the ions. This implies that the molecular state of the electrolyte depends on its concentration and on the dielectric constant of the mixed solvent. The asymmetric framework uses a composite Gibbs free energy surface, in which model domains are defined by IL concentration and the dielectric constant of the mixed solvent (1-butanol/water in this case). In order for a phase to be considered as dissociated, the observable mole fraction of electrolyte (IL) must be less than some critical value (0.10 is used here) and the average mixed-solvent dielectric constant must be greater than some critical value (50 is used here). Otherwise, a phase will be treated as molecular.

The models used contain two energetic binary interaction parameters for each pair of components. These are determined based on *binary* data and are the only adjustable model parameters. Furthermore, we make the key assumption that these parameters are the same in both the dissociated-phase and molecular-phase models that are combined in the asymmetric framework. This follows from the assumption of Chen et al. (2004), based on local electroneutrality and the symmetry of interaction energies, that short-range cation-solvent and anion-solvent interaction energies are the same. For immiscible binaries, the binary parameters are determined from mutual solubility data by solving the equal chemical potential conditions for binary LLE. For miscible binaries, vapor-liquid equilibrium (VLE) data is used for parameter estimation. Details of the procedures used to determine binary parameters are given by Simoni et al. (2007; 2009a).

In using the asymmetric framework to compute multicomponent LLE, one must ensure the resultant equilibrium phases are thermodynamically stable. The conditions for phase stability in the context of the mixed-salt, mixed-solvent asymmetric model have been developed by Simoni et al. (2009a), based on an extension of tangent plane analysis (Baker et al., 1982; Michelsen, 1982). To implement this, we use an approach, similar to that described by Tessier et al. (2000), based on rigorous global optimization, accomplished using an interval-Newton approach.

Results

Experimental

Based on our experimental observations of the phase behavior of the ternary IL/1-butanol/water systems, we calculated the selectivity (S) and distribution coefficient (D) for 1-butanol in each of the three systems considered. These quantities are defined by

$$D = \frac{n_{\text{Alcohol}}^{\beta}}{n_{\text{Alcohol}}^{\alpha}} \quad (1)$$

$$S = \frac{\frac{n_{\text{Alcohol}}^{\beta}}{n_{\text{Alcohol}}^{\alpha}}}{\frac{n_{\text{H}_2\text{O}}^{\beta}}{n_{\text{H}_2\text{O}}^{\alpha}}} \quad (2)$$

where n_i^{β} indicates moles of i in the IL-rich phase and n_i^{α} in the aqueous phase. A multistage liquid-liquid extraction calculation was performed using the Hunter-Nash method (Seader and Henly, 1998) to determine the number of equilibrium stages required, based on the assumptions: 1) feed composition of 5 wt% of 1-butanol in water, 2) pure IL as the solvent, 3) equal feed and solvent mass flow rates, and 4) requiring 99 wt% water in the final raffinate.

Table 1 shows the results for all three IL systems. We can see that [hmim][eFAP] provides the highest selectivity with almost the highest distribution coefficient. [hmim][eFAP] is extremely hydrophobic (Chapeaux et al 2009a), and therefore repels water more than it attracts alcohol. The results for [HOhmim][Tf₂N] indicate that adding a hydroxyl on the cation chain attracts more water than alcohol and therefore reduces the selectivity and the distribution coefficient.

Modeling

Experimentally (Chapeaux et al, 2008), the ternary system [hmim][Tf₂N]/1-butanol/water at 295 K exhibits Type 2 ternary LLE behavior (Figure 1).

TABLE 1

Distribution Coefficient (D), Selectivity (S) and Number of Equilibrium stages for IL/water/1-butanol

IL	D	S	Number of Stages
[hmim][Tf ₂ N]*	7.5	90	4
[HOhmim][Tf ₂ N]	1.5	40	5
[hmim][eFAP]	6	300	3

* Chapeaux et al., 2008

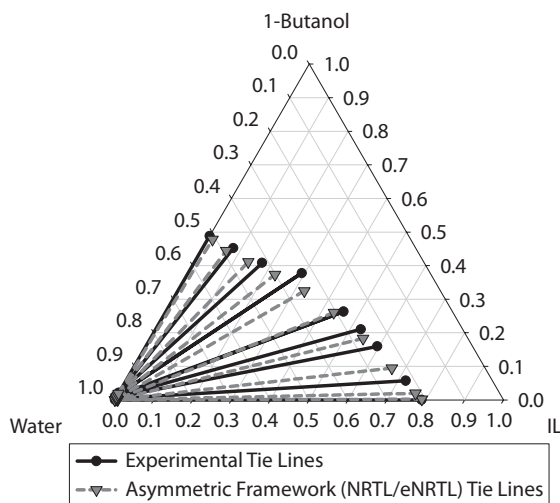


FIGURE 1

Predicted ternary LLE for [hmim][Tf₂N]/1-Butanol/Water at 295 K (in mol fraction), compared to experimental measurements (Chapeaux et al., 2008).

That is, there are two binary miscibility gaps and a single two-phase envelope that spans from one binary miscibility gap to the other. Mutual solubility data for [hmim][Tf₂N]/water (Chapeaux et al., 2007) and 1-butanol/water (Sørensen and Arlt, 1979-1980) at 295 K were used to calculate model parameters for these two immiscible binaries. For the completely miscible [hmim][Tf₂N]/1-butanol binary, there is no VLE data available at the system temperature. Therefore, to estimate the model parameters for this binary, LLE data for [hmim][Tf₂N]/1-butanol at lower temperatures (Łachwa et al., 2006) were linearly regressed and extrapolated to the system temperature.

Figure 1 shows the ternary LLE predicted by the asymmetric NRTL/eNRTL model, with the model parameters obtained from binary data only, as described above. Comparison to the experimental data indicates that this provides a prediction that is quite good, in terms of both the phase envelope and the slope of the tie lines. However, Type 2 diagrams are generally considered the easiest type to predict. In fact, for this particular system, the standard (symmetric) NRTL, UNIQUAC and eNRTL models also provide reasonably accurate predictions (Chapeaux et al., 2008). The asymmetric approach has also been tested on more difficult problems and, in such cases, found to be superior to conventional symmetric models (Simoni et al., 2009b).

Conclusions

Separating alcohols from fermentation broths is a critical step in producing the building blocks for renewable fuels and feedstocks. In this work, we have shown that ILs are apt solvents for liquid-liquid extraction of 1-butanol from water, with selectivities ranging from 40 to 300, and high distribution coefficients. From this standpoint, [hmim][eFAP] appears to be an especially a good solvent for this separation. Detailed design studies, including economic analysis and life cycle analysis, are now needed.

We also have shown that we can use a semi-predictive method, based on a novel asymmetric framework, to model IL/water/1-butanol systems. The asymmetric framework allows for the use of different excess Gibbs models in different phases. This framework, with the assumption that the IL is completely dissociated in a dilute aqueous phase and completely paired in an alcohol/IL-rich phase, allows for good predictions of ternary systems based solely on binary experimental data.

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