Extraction of Biofuels and Biofeedstocks from Aqueous Solutions

Using Ionic Liquids

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Abstract

The production from biomass of chemicals and fuels by fermentation, biocatalysis, and related techniques implies energy-intensive separations of organics from relatively 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) 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 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.

1. Introduction

Biomass-based routes to fuels and chemicals have been suggested as alternatives to the fossil-fuel-based routes that are commonly used in industry today. Methanol, ethanol, 1-propanol, 1-butanol, and various other organic compounds can be produced biologically, and thus can be considered as biofuel candidates, as biofeedstocks for production of other chemicals, and as bio-based solvents for various applications. For example, ethanol can be used as a fuel, as a solvent in the chemical industry, and as a starting material for many other compounds, including ethylene and its derivatives. Likewise, 1-butanol can be used as a feedstock and has uses as a solvent in many applications, such as re-crystallization processes used in the pharmaceutical industry. Furthermore, there is growing interest in 1-butanol as a biofuel. Compared to ethanol, it has a significantly higher energy density (only about 10% less than gasoline). It is also more hydrophobic than ethanol, leading to reduced concerns about fuel system and pipeline corrosion.

Ethanol and 1-butanol are synthesized using fermentation of biomass (sugars, starch, cellulose, etc.) using yeasts or bacteria as the biological agents. Current bioethanol production is based on fermentation with the yeast *Saccharomyces cerevisiae*, though there is also current interest in use of strains of the bacterium *Zymomonas mobilis* (Rogers et al., 2007). Because the current biological agents have a limited tolerance for ethanol, a typical fermentation broth will have no more than about 16 wt% ethanol (Fischer et al., 2008). Improved fermentation agents are being developed (Alper et al., 2006) with higher ethanol tolerance. Biobutanol has historically been based on fermentation with the bacteria *Clostridium acetobutylicum* or *Clostridium biejerinckii*. These have limited tolerance to 1-butanol and so a typical fermentation broth currently contains about 1.3 wt% 1-butanol (Fischer et al., 2008). However, significant

progress is being made in increasing this tolerance level. For example, Zhao et al. (2009) have recently described the evolution of a mutant strain of *C. biejerinckii* that improves the butanol concentration to about 3 wt%. Furthermore, yeast-based fermentation processes for 1-butanol are now being developed (Steen et al., 2008; Boles, 2009), and this may lead to tolerance of much higher levels of 1-butanol, via the same mechanisms a high tolerance for ethanol is achieved. These fermentation processes for bio-based alcohol production ultimately yield a broth consisting mostly of water, the target alcohol, and perhaps other organic compounds. Separation processes are needed for these relatively dilute aqueous solutions.

Conventionally, separation of alcohols from water has been done using distillation, with multiple columns often required to achieve desired purity. If the separation achievable using conventional distillation is limited due to a homogeneous azeotrope (as in the case of ethanol), then additional water may be removed using techniques such as drying over zeolites, freeze drying, use of membranes, or use of an entrainer in an azeotropic distillation scheme. If the alcohol and water are not completely miscible and form a heterogeneous azeotrope (as in the case of 1-butanol), then this can be exploited in the separation process, but two columns are still required. In general, the separation of alcohols from water by distillation is energetically costly, and much room for improvement exists. Thus, there has been significant interest in alternative separation methods, including membrane technology and liquid-liquid extraction, which could be less energetically costly than distillation, and thus potentially more attractive economically. Our focus here is on the potential use of ionic liquids (ILs) for separating alcohol/water mixtures with simple liquid-liquid extraction (Chapeaux et al., 2008; Fadeev and Meagher, 2001).

ILs are organic salts with low melting points (below 100 ℃). Many are liquid at room temperature. They are typically composed of a poorly coordinating, bulky organic cation, and an

organic or inorganic anion. ILs have many interesting and unique properties, among which is an exceedingly low vapor pressure. At normal process operating conditions, ILs essentially do not evaporate. Thus, there has been considerable interest in the use of ILs as industrial solvents to replace volatile organic compounds (VOCs) and thus eliminate a source of air pollution, as well as hazards due to inhalation and explosion (Welton, 1999; Wasserscheid and Keim, 2000; Brennecke and Maginn, 2001). Also, ILs are stable as liquids over a very wide temperature range (e.g., -70ºC to 400ºC) (Fredlake et al., 2004). Both of these properties (negligible vapor pressure, large liquidus range) will facilitate the recovery and reuse of ILs in the context of liquid-liquid extraction, and thus provide economic benefits (e.g., extremely low solvent loss and make-up requirement). By changing the anion, cation and/or cation substituents, an essentially endless variety of ILs can be created. Thus, it may be possible to "design" or "tune" ILs that preferentially select desired compounds from water. In this study, we consider the feasibility of using ILs as liquid-liquid extraction solvents for separating organic compounds from relatively dilute aqueous solutions. As an example, we will focus on the extraction of 1-butanol.

As a first step in this feasibility study, we will determine, based on experimental observations, distribution coefficients and selectivities for multicomponent liquid-liquid extraction of 1-butanol from water using three different ILs, namely 1-(6-hydroxyhexyl)-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide ([HOhmim][Tf_2N]), 1-hexyl-3-methylimidazolium tris(pentafluoroethyl) trifluorophosphate ([hmim][eFAP]), and 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([hmim][Tf_2N]). We will also do a simple equipment design calculation (Hunter-Nash method) to estimate the number of equilibrium stages needed for sample separation problems.

Since experimental observation of the ternary liquid-liquid equilibrium (LLE) for every system of possible interest is time consuming, the ability to *predict* an IL's potential as an extraction solvent is an important capability in our feasibility analysis. Clearly, a model that predicts ternary 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, show some promise, but also provide qualitatively inaccurate predictions in many cases (Chapeaux et al., 2008; Chen et al., 2008).

As part of this study, we will demonstrate a recently developed semi-predictive method in which activity coefficient models are used to make ternary LLE predictions based on only binary and pure component data. We have shown previously (Chapeaux et al., 2008; Simoni et al., 2008) that LLE for ternary systems containing ILs and water were more difficult to predict than nonaqueous systems when using this approach. In aqueous systems involving ILs, 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, we assume, as a first approximation, that the IL is *completely dissociated* in a dilute aqueous phase and completely paired (*molecular*) in an organic- or IL-rich phase (Simoni et al., 2009a,b). Results (Simoni et

al., 2009b) for one of the ternary systems of interest here, [HOhmim][Tf$_2$N]/1-butanol/water, suggest that this is a promising approach for modeling systems of this type. Thus, we will apply this approach here to predict the LLE for the other two systems of interest, [hmim][Tf$_2$N]/1-butanol/water and [hmim][eFAP]/1-butanol/water, and compare the results to experimental observations and to predictions obtained from conventional (symmetric) activity coefficient models, namely the NRTL, UNIQUAC and electrolyte-NRTL (eNRTL) models.

2. Methodology

2.1 Experimental

Details of all experimental procedures have been described elsewhere (Chapeaux et al., 2008; Chapeaux et al., 2009a). 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.

2.2 Equipment Design

Using the experimentally determined ternary diagrams for the IL/1-butanol/water systems of interest, we will do a simple equipment design calculation to estimate the number of equilibrium stages needed for sample 1-butanol/water separation problems. For this purpose, we will use the standard Hunter-Nash method for design of countercurrent liquid-liquid extraction processes, as described in detail by Seader and Henley (1998). These sample calculations are based on the following specifications: 1) pure IL as the solvent, 2) equal feed and solvent mass flow rates, 3) 99 wt% water in the final raffinate, and 4) feed composition of either 5 wt% or 20 wt% 1-butanol in water. This provides for only a preliminary design of a liquid-liquid extraction

process. No attempts have been made to determine an optimal solvent to feed ratio, or to optimize the design in any way. The feed compositions of 5 and 20 wt% 1-butanol are significantly higher than what is currently achieved in the standard bacterial fermentation process. However, as discussed above, rapid progress is being made in engineering the biological agents used for producing 1-butanol, and thus concentrations much higher than those currently achieved can be expected in the future, and we believe that this is reasonable range of feed compositions to consider.

2.3 Modeling

In the asymmetric modeling framework used, 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 alcohol-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 and Song, 2004) and NRTL (Renon and Prausnitz, 1968) 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 is presented elsewhere (Simoni et al., 2009a).

The degree of dissociation depends on the ability of the phase's non-IL 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 the 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.

In the modeling results presented below, we present predictions for both conventional symmetric models and the new asymmetric NRTL/eNRTL model. The symmetric models studied are NRTL, UNIQUAC (Abrams and Prausnitz, 1975) and eNRTL. All of these models contain two energetic binary interaction parameters, θ_{ij} and θ_{ji}, for each pair of components. These are determined based on *binary* data and are the only fully adjustable model parameters. For the asymmetric NRTL/eNRTL model we make the key assumption that these binary interaction 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 completely miscible binaries, vapor-liquid equilibrium (VLE) data is used for parameter estimation. However, if VLE data is unavailable we resort to other binary data (LLE at different temperatures or excess enthalpy data). Details of the procedures used to determine the fully adjustable binary parameters as well as a presentation of the models themselves are given by Simoni et al. (2007, 2008, 2009a).

In addition to the fully adjustable binary interaction parameters, there are also model parameters that take on fixed values, depending on the system in question. The NRTL-based models use the standard nonrandomness parameter values (Sørensen and Arlt, 1979-1980; Renon and Prausnitz, 1969) of $\alpha_{ij} = \alpha_{ji} = 0.2$ for immiscible binaries, and $\alpha_{ij} = \alpha_{ji} = 0.3$ for completely

miscible binaries (Renon and Prausnitz, 1968), unless excess enthalpy data is used for fitting the interaction parameters, in which case the larger value of $\alpha_{ij} = \alpha_{ji} = 0.8$ is used (Simoni et al., 2009b). The symmetric eNRTL and asymmetric NRTL/eNRTL models contain parameters that are related to the distance of closest ionic approach (ρ and σ). For the symmetric eNRTL model (Chen and Song, 2004) we fix ρ to the standard, dimensionless value of 14.9. For the asymmetric NRTL/eNRTL model, ρ and σ are fixed according to a priority list (Simoni et al., 2009b) that takes into account the physical relationship between these parameters (Pitzer, 1977; Pitzer and Li, 1983), and the ability to obtain stable binary interaction parameter solutions from a given set of values. In the results below for the NRLT/eNRTL model, we report the ρ and σ values used for each example.

Finally, UNIQUAC requires for each pure component i, a "size" (relative volume) parameter r_i and "shape" (relative area) parameter q_i. For the IL species, these parameters were calculated using the IL and IL-segment values determined by Banerjee et al. (2005), Nebig et al. (2007), and other standard sources (Gmehling et al., 1993; Anderson and Prausnitz, 1978). For 1-butanol and water, these parameters were also taken from a standard source (Hansen et al., 1991). Traditionally, the reference species used in determining the relative area parameter q_i has been the van der Waals $-CH_2-$ group (Abrams and Prausnitz, 1975). However, as explained by Abreu et al. (1999), this choice may make it impossible to find suitable binary parameter values for modeling binary LLE with UNIQUAC, especially when there are components of greatly different sizes and shapes. To alleviate this problem, Abreu et al. (1999) suggest using water as an alternative reference species. Following suit, we choose water as an alternative reference species, but use it only when using the $-CH_2-$ group does not lead to suitable binary parameter values. A coordination number of $Z = 10$ is used for all UNIQUAC calculations.

In using the asymmetric model to compute multicomponent LLE, one must ensure that 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.

3. Results

3.1 Experimental and Design Calculations

Detailed experimental results for the ternary phase behavior of the three IL/1-butanol/water systems of interest at a temperature of 295 K are given by Chapeaux et al. (2008; 2009a). We use these results in the calculations reported here, and as a basis for comparison to the model predictions (Figs. 1-6). Two quantities often considered when assessing the potential of an extraction solvent are the distribution coefficient D and the selectivity S. Here, the distribution coefficient gives the ratio of moles of 1-butanol (BuOH) in the IL-rich phase to moles of 1-butanol in the water-rich phase. That is,

$$D = \frac{n^{\beta}_{BuOH}}{n^{\alpha}_{BuOH}},$$ (1)

where the superscript β is used to represent the IL-rich phase and α to represent the water-rich phase. The selectivity gives the BuOH to water ratio in the IL-rich phase relative to the same ratio in the water-rich phase. That is,

$$S = \frac{n^{\beta}_{BuOH} \big/ n^{\beta}_{H_2O}}{n^{\alpha}_{BuOH} \big/ n^{\alpha}_{H_2O}} . \tag{2}$$

Clearly it is desirable to have high values of both *D* and *S*. We also use the experimental equilibrium curve to perform a simple Hunter-Nash calculation of the number of stages *N* required for the sample separation problem specified in Section 2.2.

Table 1 shows the results for selectivity, distribution coefficient, and number of stages for each of the three ILs considered and for both 5 and 20 wt% 1-butanol in the feed mixture. For the dilute case, we can see that [hmim][eFAP] provides the highest selectivity (300) with nearly the highest distribution coefficient (6) while requiring the fewest number of stages (3). [hmim][eFAP] is extremely hydrophobic (Chapeaux et al., 2009b), and therefore repels water more than it attracts alcohol. The results for [HOhmim][Tf$_2$N] indicate that adding a hydroxyl on the cation chain attracts more water than alcohol and therefore reduces the selectivity, the distribution coefficient, and increases the number of stages necessary. At least based on phase equilibrium, it appears that selected ILs may be quite good solvents for extraction of 1-butanol from water.

3.2 Modeling

Experimentally (Chapeaux et al., 2008; Chapeaux et al., 2009a), the ternary systems [hmim][Tf$_2$N] (1)/1-butanol (2)/water (3) and [hmim][eFAP] (1)/1-butanol (2)/water (3) at 295 K, both exhibit Type 2 ternary LLE behavior (Figs. 1 and 3, respectively). 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 IL (1)/water (3) (Chapeaux et al., 2009a; Chapeaux et al., 2007) and 1-butanol (2)/water (3) (Sørensen and Arlt, 1979-1980) at 295 K were used to

calculate model parameters for these two binaries for each system. For the NRTL-based models, $\alpha_{13} = \alpha_{23} = 0.2$ for these immiscible binaries. For the completely miscible IL (1)/1-butanol (2) binary systems, there are no VLE data available at the temperature of the systems. Therefore, to estimate the model parameters for these binaries, other types of binary data were sought. For the [hmim][Tf$_2$N] (1)/1-butanol (2) binary, LLE data at lower temperatures (Łachwa et al., 2006) were used with $\alpha_{12} = 0.3$ for the NRTL-based models, and the resulting parameter solutions (from solving the equal chemical potential conditions) were linearly regressed and extrapolated to the system temperature. For the [hmim][eFAP] (1)/1-butanol (2) binary, only excess enthalpy data is available (Chapeaux and Brennecke, 2009), so this data was used to fit model parameters using $\alpha_{12} = 0.8$ for the NRTL-based models, as prescribed previously (Simoni et al., 2009b). For the [hmim][Tf$_2$N] and [hmim][eFAP] systems the parameter estimation results are given in Tables 2 and 3 respectively. Modeling results for the third system considered, [HOhmim][Tf$_2$N] (1)/1-butanol (2)/water (3), have been described in detail elsewhere (Simoni et al., 2009b). All predictions of ternary LLE reported here are based on parameters determined from binary and pure component data only.

The other nonadjustable parameter values were assigned as follows: For the asymmetric NRTL/eNRTL model, the ρ and σ values for the [hmim][Tf$_2$N] and [hmim][eFAP] systems were set at 5 and $1 \cdot 10^{-9}$ m and 5 and $5 \cdot 10^{-10}$ m, respectively, as prescribed by the procedure given previously by Simoni et al. (2009b). For the electrostatic portion of the eNRTL model, the molecular weight, density and dielectric constant are needed for 1-butanol/water mixtures, which make up the mixed-solvent dielectric continuum of the model. These were calculated from the pure component values as described by Simoni et al. (2009a,b). Finally, for the UNIQUAC model, the reference species for the surface area parameter, q_i is water for both systems. Table 4

lists the r_i and q_i values of UNIQUAC for the components of these systems when using water as the reference species for q_i.

Fig. 1 shows the ternary LLE predicted (Chapeaux et al., 2008) by the conventional symmetric NRTL, UNIQUAC and eNRTL models for the [hmim][Tf$_2$N]/1-butanol/water system, with comparison to experimental data (Chapeaux et al., 2008). For NRTL and UNIQUAC the IL is assumed to be molecular, and for eNRTL the IL is assumed to undergo complete ionic dissociation over the entire composition range. Fig. 2 shows the ternary LLE predicted by the new asymmetric NRTL/eNRTL model for the same system. For all of the predictions, the model parameters are obtained from binary data only, as described above. Comparison to the experimental data indicates that all of the predictions are quite good, in terms of both the phase envelope and the slope of the tie lines. A quantitative comparison yields average absolute deviation (AAD) values of 0.0198 for NRTL, 0.00878 for UNIQUAC, 0.0324 for eNRTL, and 0.0095 for the asymmetric NRTL/eNRTL model. Here

$$\text{AAD} = \frac{1}{N} \sum_{k=1}^{TL} \sum_{j=1}^{2} \sum_{i=1}^{3} \left| x_{i,k,\text{exp}}^{(j)} - x_{i,k,\text{calc}}^{(j)} \right|, \text{ where } x_{i,k,\text{calc}}^{(j)} \text{ is the calculated mole fraction of component } i$$

in phase j based on the midpoint of tie line k, and $x_{i,k,\text{exp}}^{(j)}$ is the corresponding experimental value. $TL = 15$ is the number of tie lines used for the comparison, and $N = (2)(3)(TL)$ is the number of terms in the summation.

Type 2 diagrams are generally considered to be the easiest type to predict when phase equilibrium data (VLE or extrapolated LLE) is used to predict the parameters for the miscible binary (Simoni et al., 2008). It is clear that, for this particular system, the standard (symmetric) NRTL, UNIQUAC and eNRTL models provide reasonably accurate predictions, and the asymmetric NRTL/eNRTL approach also produces accurate results. However, this asymmetric approach has been tested on more difficult problems and, in such cases, found to be superior to

conventional symmetric models (Simoni et al., 2009b). This is also the case in the following example.

Figs. 3-5 shows the ternary LLE predicted by the conventional symmetric NRTL, UNIQUAC and eNRTL models for the [hmim][eFAP]/1-butanol/water system. Fig. 6 shows the ternary LLE predicted by the asymmetric NRTL/eNRTL model for the same system. Again, the model parameters are obtained from binary data only, as described above. In this case, the symmetric model predictions shown in Figs. 3-5 produce qualitatively incorrect results. All three models predict a spurious three-phase region. This is largely due to using excess enthalpy data, which is quite endothermic, in the parameter estimation for the [hmim][eFAP]/1-butanol binary. As a result, the UNIQUAC and eNRTL models predict this binary to have a spurious miscibility gap, as shown in Figs. 4 and 5. The NRTL model correctly predicts that this binary is completely miscible; however, it still predicts the existence of a three-phase region with a two-phase envelope emanating from the IL/1-butanol side of the three-phase region and terminating in a plait point. On the other hand, in Fig. 6, we see that the asymmetric NRTL/eNRTL model correctly predicts a Type 2 diagram. Although the NRTL/eNRTL predictions show some deviation from the experimental tie lines, this proves to be a vast qualitative improvement in ternary LLE prediction for this system. A similar conclusion has been obtained for the [HOhmim][Tf$_2$N]/1-butanol/water system, as described in detail by Simoni et al. (2009b).

4. Concluding Remarks

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 some ILs are solvents capable of liquid-liquid extraction of 1-butanol from water, with selectivities ranging

from 30 to 300, and high distribution coefficients. From this standpoint, [hmim][eFAP] appears to be an especially good solvent for this separation.

We also have shown that we can use a semi-predictive method, based on a novel asymmetric framework, to model IL/1-butanol/water 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.

Detailed design studies, including economic analysis and life cycle analysis, are now needed. These studies must account for the fact that the separation problem is likely to be more complex than just separation of 1-butanol and water, since there may be various other compounds in the fermentation broth. Since, as noted above, the development of biological processes for 1-butanol is currently a very active research area, the exact nature of this separation problem is unclear. The design and tuning of even better ILs for this separation is possible and may be needed. In this context, the use of predictive and semi-predictive models for LLE can play an important role in studying separation process design issues.

Acknowledgements

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Table 1: Distribution coefficient (D), selectivity (S) and number of stages (N) for IL/water/1-butanol systems with 5 and 20 wt% 1-butanol in the feed mixture.

IL	5 wt% 1-butanol			20 wt% 1-butanol		
	D	S	N	D	S	N
[hmim][Tf$_2$N]	6	90*	4*	3.7	50	6
[HOhmim][Tf$_2$N]	1.5	40	5	3.8	33	7
[hmim][eFAP]	5	300	3	3.5	110	5

*Chapeaux et al., 2008

Table 2: Binary interaction parameters (J/mol) estimated from binary data for the system [hmim][Tf$_2$N] (1)/1-butanol (2)/water (3) at 295 K.

Model	θ_{12}	θ_{21}	θ_{13}	θ_{31}	θ_{23}	θ_{32}
NRTL	−5222.6	9210.2	702.08	21820	−2566.9	12505
UNIQUAC	−377.54	1049.6	6951.4	1582.83	1842.0	2413.5
eNRTL	−5456.4	10477	−2707.1	21287	−2566.9	12505
NRTL/eNRTL	−5222.6	9210.2	167.35	11807	−2566.9	12505

Table 3: Binary interaction parameters (J/mol) estimated from binary data for the system [hmim][eFAP] (1)/1-butanol (2)/water (3) at 295 K.

Model	θ_{12}	θ_{21}	θ_{13}	θ_{31}	θ_{23}	θ_{32}
NRTL	1867.3	2005.7	19113	23225	−2566.9	12505
UNIQUAC	9884.3	926.23	19611	−1415.2	1842.0	2413.53
eNRTL	2017.0	2135.6	15381	17980	−2566.9	12505
NRTL/eNRTL	1867.3	2005.7	18690	6843.4	−2566.9	12505

Table 4: Pure component size and shape parameters for UNIQUAC model with water as q_i reference species.

IL(1) used	q_1	r_1	q_2	r_2	q_3	r_3
[hmim][Tf$_2$N]	8.30	12.51	2.62	3.92	1.00	0.92
[hmim][eFAP]	8.19	16.72	2.62	3.92	1.00	0.92

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Figure 1: Predicted ternary LLE for [hmim][Tf$_2$N]/1-Butanol/Water at 295 K (in mol fraction) from symmetric NRTL, UNIQUAC and eNRTL models, compared to experimental measurements (Chapeaux et al., 2008).
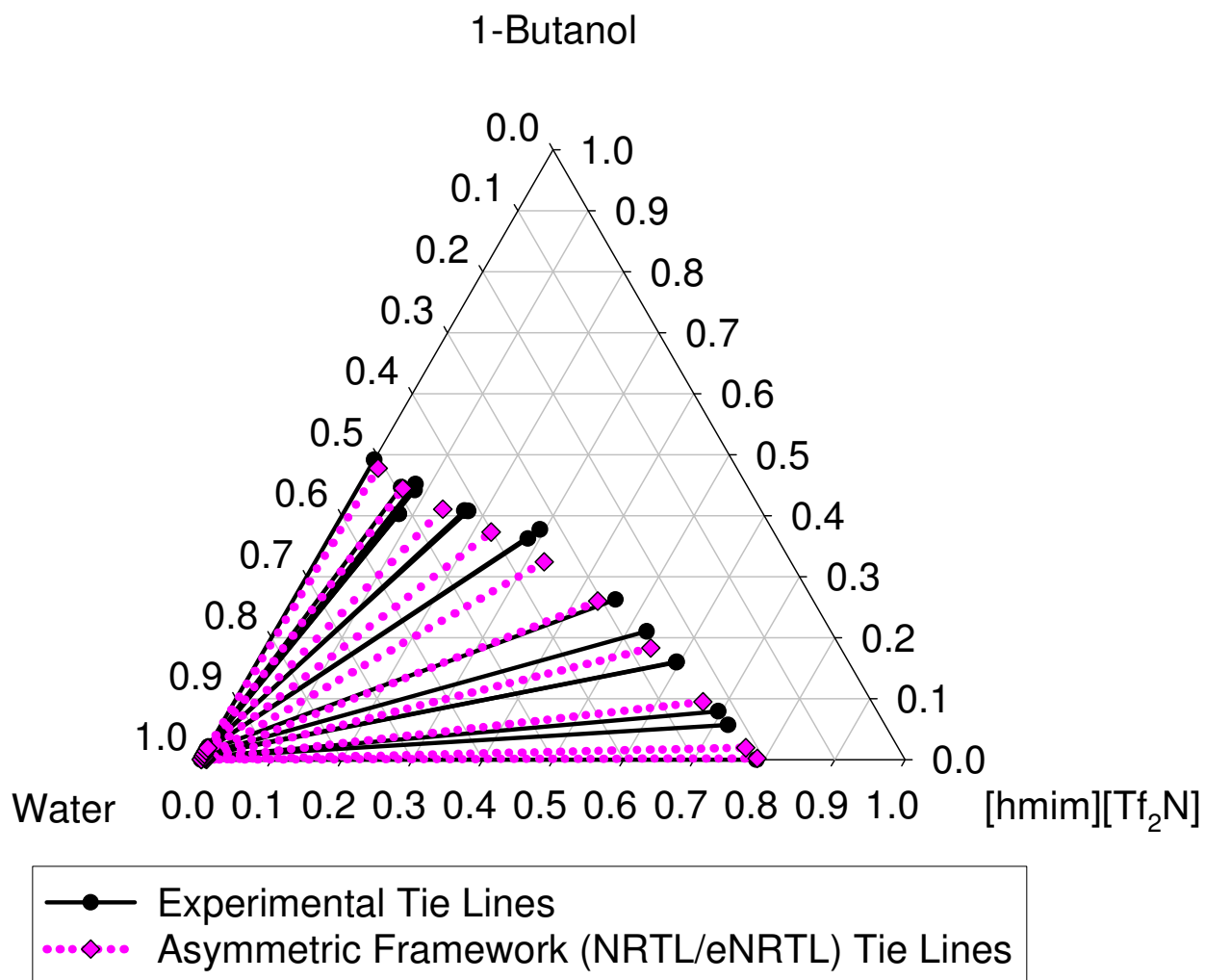
Figure 2: Predicted ternary LLE for [hmim][Tf$_2$N]/1-Butanol/Water at 295 K (in mol fraction) from asymmetric NRTL/eNRTL model, compared to experimental measurements.
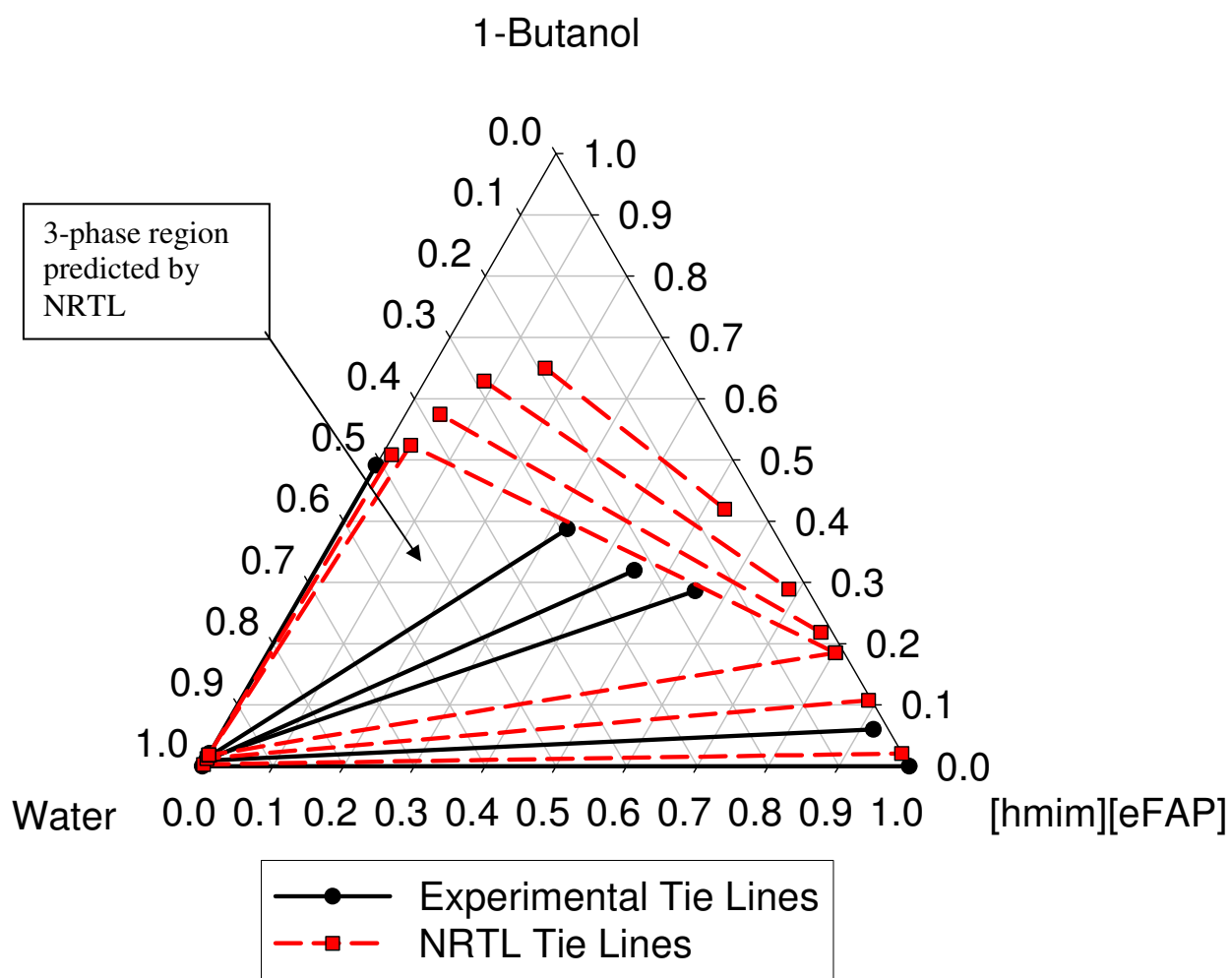
Figure 3: Predicted ternary LLE for [hmim][eFAP]/1-Butanol/Water at 295 K (in mol fraction) from the symmetric NRTL model, compared to experimental measurements.
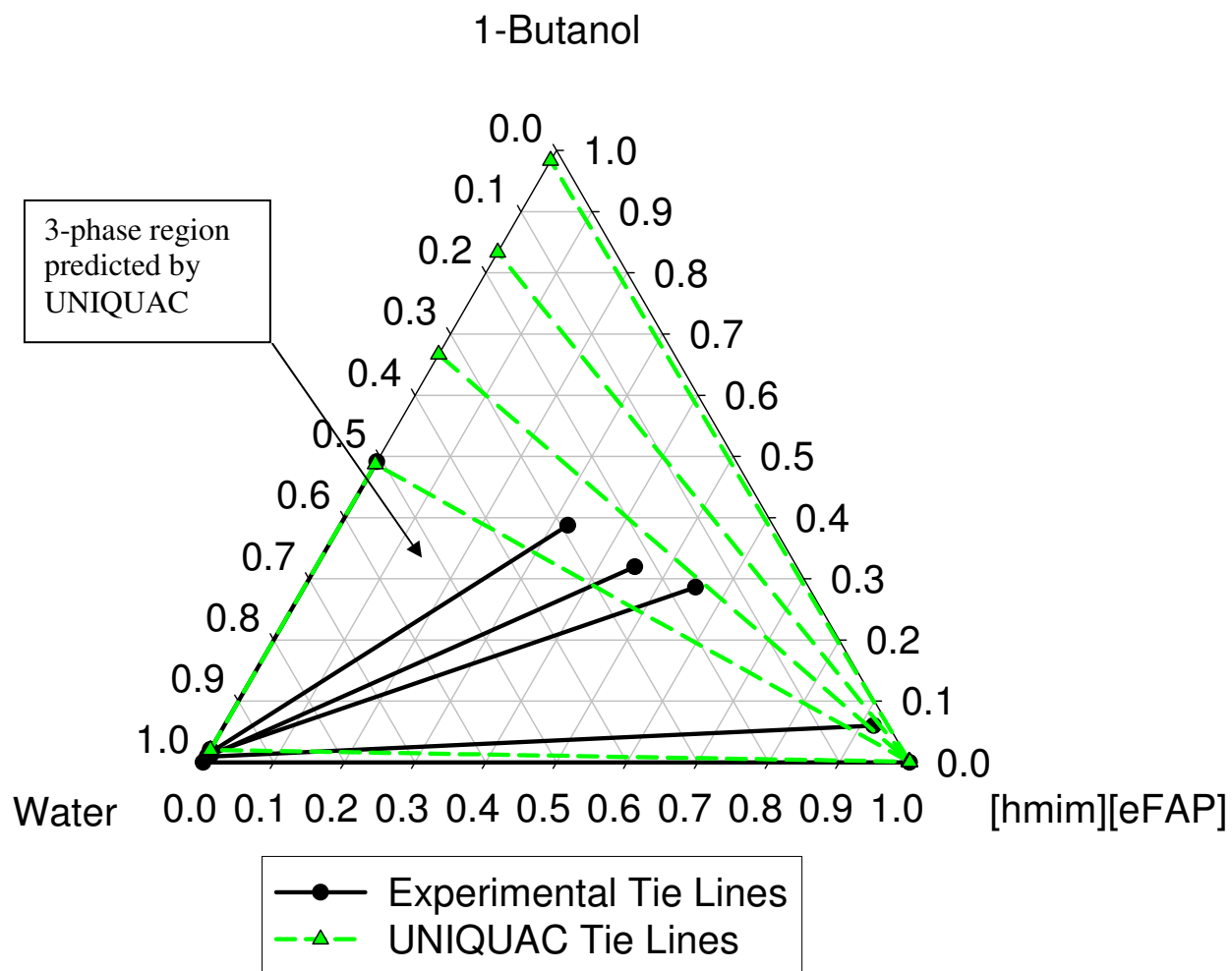
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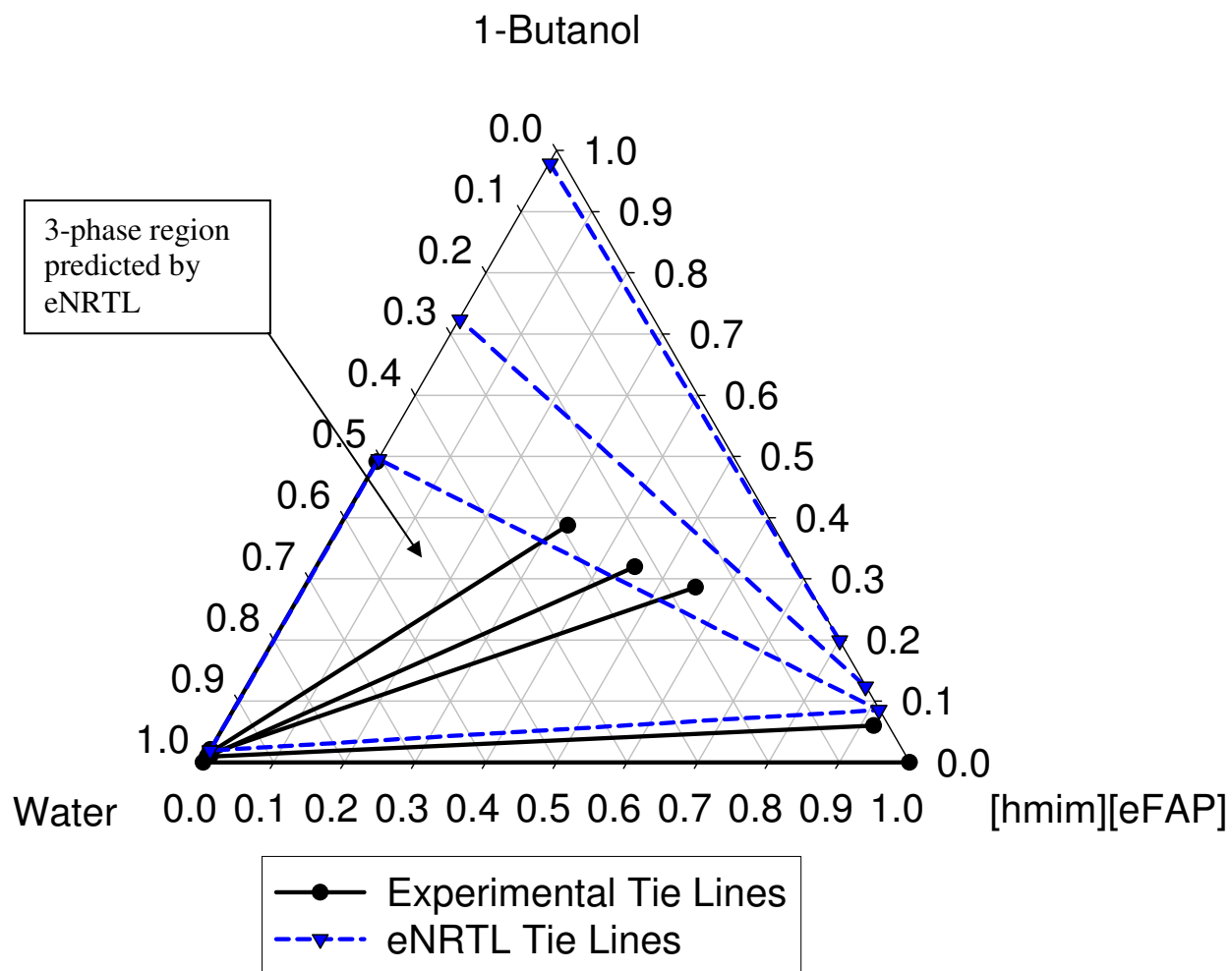
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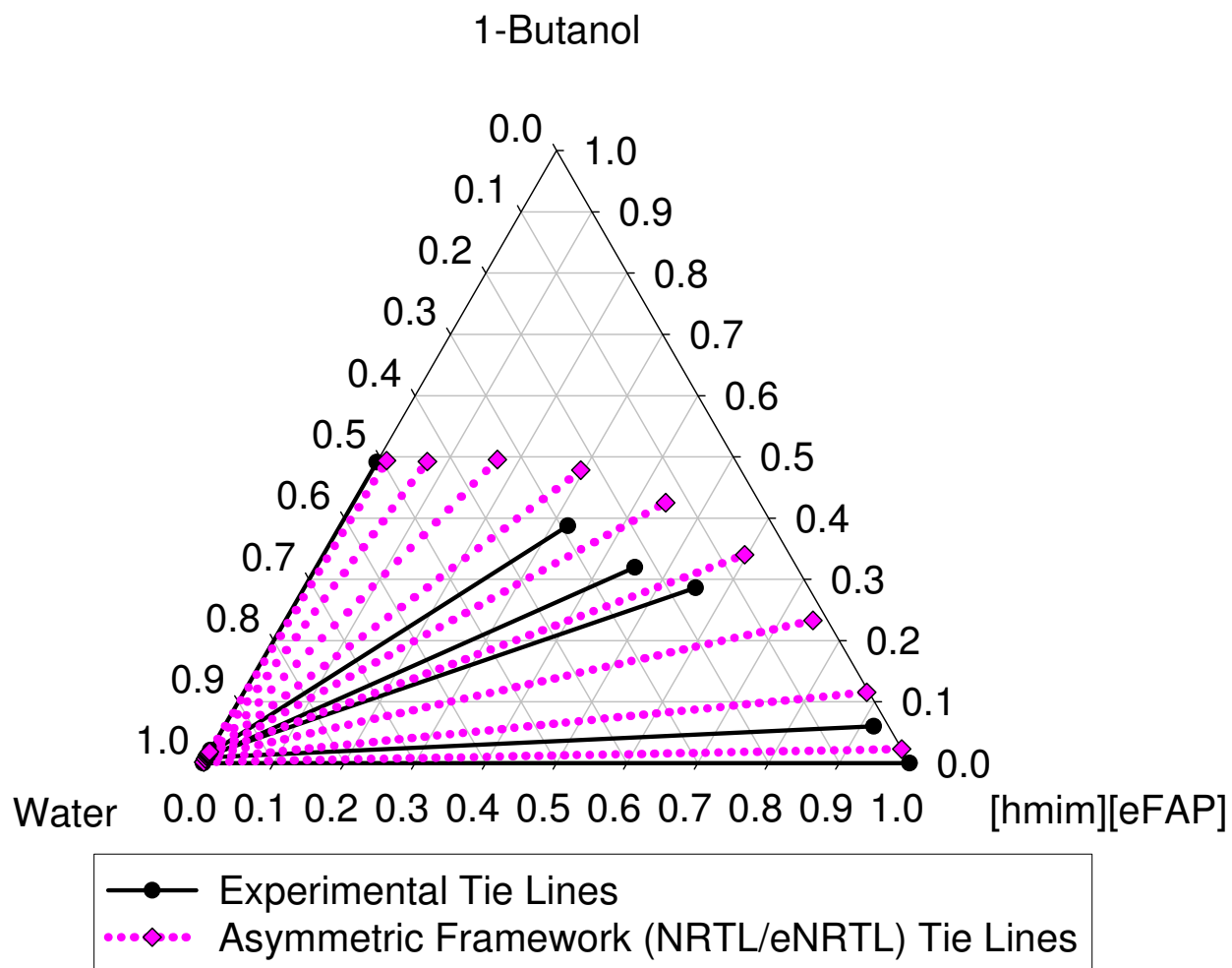
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