

## Using Ionic Liquids To Break the Ethanol–Ethyl Acetate Azeotrope

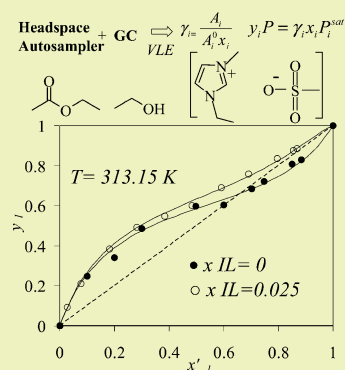
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## Supporting Information

**ABSTRACT:** Systems that form azeotropes or have relative volatilities close to 1.0 represent very little energy and capital intensive separations. Ionic liquids (ILs) can serve as nonvolatile entrainers to break azeotropes and enable a more energy efficient and environmentally friendly process. Here, six ILs have been investigated for their ability to break the ethanol + ethyl acetate azeotrope at 313.15 K. Three of the ILs investigated, 1-ethyl-3-methyl-imidazolium methanesulfonate [emim][MeSO<sub>3</sub>], 1-ethyl-3-methyl-imidazolium methylsulfate [emim][MeSO<sub>4</sub>], and 1-butyl-3-methyl-imidazolium trifluoromethanesulfonate [bmim][CF<sub>3</sub>SO<sub>3</sub>] are excellent entrainer candidates. In fact, the ethanol + ethyl acetate azeotrope can be broken over the entire composition range by adding as little as 2.5 mol percent of either [emim][MeSO<sub>3</sub>] or [emim][MeSO<sub>4</sub>] to the binary organic mixture, which is less IL than what is needed to break any azeotropic system discussed in literature to date. The other three ILs, 1-ethyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide [emim][Tf<sub>2</sub>N], 1-hexyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide [hmim][Tf<sub>2</sub>N], and 1-butyl-1-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)imide [bmpyr][Tf<sub>2</sub>N], are limited in their ability to break this azeotrope. The difference between these two groups correlates with the infinite dilution activity coefficients of the ethyl acetate and ethanol in each of the ILs. Both polarity and hydrogen bonding are important in determining the preferential affinity of the ethanol for the ILs, which raises the ethyl acetate/ethanol relative volatility. In addition, the experimental binary and ternary vapor–liquid equilibrium data have been fit to the Non Random Two Liquid (NRTL) activity coefficient model, which is able to predict and correlate the amount of IL needed to break the azeotrope in these ternary vapor–liquid equilibrium systems.

**KEYWORDS:** Headspace autosampler, Azeotropic mixture, Extractive distillation, Entrainers, NRTL



## INTRODUCTION

Separating mixtures into their individual components has always been an important part of chemical engineering. Separating systems that form azeotropes or have relative volatilities close to 1.0 are particularly challenging and can be very energy and capital intensive. The use of ionic liquids (ILs) in separation processes is an area of research that has developed over the past few years. ILs have many potential uses, including CO<sub>2</sub> capture from post-combustion flue gas,<sup>1</sup> but they can also be used as entrainers in extractive distillation. Extractive distillation is of particular interest for separating azeotropic mixtures or mixtures with relative volatility close to one. There are many ways to attempt to separate these mixtures; some of the more common are extractive distillation, salt distillation, pressure-swing distillation, homogeneous and heterogeneous azeotropic distillation, and reactive distillation.<sup>2</sup> Since the components are generally unreactive and we want to purify both components, the focus lies with the first three options. However, pressure swing distillation can be expensive to operate, depending on the sizes of the two columns and pressure difference needed, the third component added in extractive distillation may either be difficult to separate at the end, and a salt added could precipitate out of the system as composition changes, causing physical damage to the system. ILs used as entrainers have the potential to allow for easy and

effective separation of azeotropic mixtures while reducing the energy costs needed to run the process.

Several properties of ILs make them an attractive option for entrainers in extractive distillation. The nonvolatility of ILs allows for their easy removal and recycle after the separation has been completed. The high thermal stability and chemical diversity of ILs means that they will not degrade under normal distillation conditions, and a specific IL can be chosen to give the optimal results for a given system. Finally, an IL can pass through process equipment without damaging the system, where a standard salt or other entrainer might precipitate out of solution and harm process equipment.

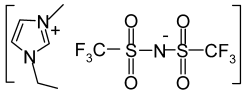
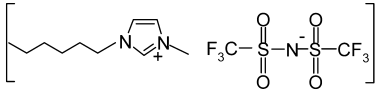
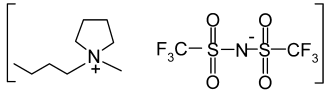
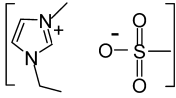
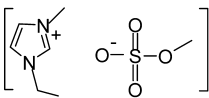
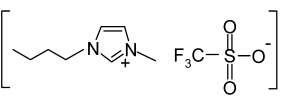


Several different studies have explored the use of ILs in separation processes. The review by Pereiro et al.<sup>3</sup> analyzes azeotropic systems using an IL as a separating agent in extractive distillation, liquid–liquid extraction, and supported liquid membranes. In the extractive distillation process, most of the ILs studied are able to eliminate the azeotrope at a specific IL content. In that review, the smallest content of IL that was able to break any azeotrope was found for the water–ethanol azeotrope at 101.3 kPa. An IL content of 5 mol percent was

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Table 1. Description of Reagents Used in This Work

Ionic liquid	Supplier	Purity / %	CASRN*	ppm of water
[emim][Tf <sub>2</sub> N] 	Iolitec	99	174899-82-2	50
[hmim][Tf <sub>2</sub> N] 	This lab	99	382150-50-7	50
[bmpyrr][Tf <sub>2</sub> N] 	Iolitec	99	223437-11-4	50
[emim][MeSO <sub>3</sub> ] 	Iolitec	99	145022-45-3	200
[emim][MeSO <sub>4</sub> ] 	Iolitec	99	516474-01-4	50
[bmim][CF <sub>3</sub> SO <sub>3</sub> ] 	Aldrich	≥98	174899-66-2	5000
Ethyl acetate 	Alfa	>99.5	141-78-6	100
Ethanol 	Aesar	99.5	64-17-5	100

\*CASRN: Chemical Abstract Service registry number.

able to break this azeotrope with any of five ILs: 1-methyl-3-methylimidazolium dimethylphosphate [mmim][(Me)<sub>2</sub>PO<sub>4</sub>], 1-ethyl-3-methylimidazolium diethylphosphate [emim]-[(Et)<sub>2</sub>PO<sub>4</sub>], 1-butyl-3-methylimidazolium bromide [bmim]-[Br], 1-butyl-3-methylimidazolium chloride [bmim][Cl], or 1-butyl-3-methylimidazolium hexafluorophosphate [bmim]-[PF<sub>6</sub>].<sup>4</sup> Several other ILs, including 1-ethyl-3-methylimidazo-

lium trifluoromethanesulfonate and 1-ethyl-3-methylimidazolium dicyanamide, can also break the water–ethanol azeotrope with mole fractions just above 0.05.<sup>5,6</sup> Subsequently, researchers have discovered ILs to break acetone–methanol,<sup>7</sup> ethyl tert butyl ether–ethanol,<sup>8</sup> and methyl acetate–methanol<sup>9</sup> with relatively low compositions (~0.05 mole fractions). The review by Lei et al.<sup>10</sup> in 2014 reports an extensive database of

the vapor liquid equilibria and infinite dilution activity coefficients of mixtures containing ILs.

In this work, six ILs have been investigated for their ability to break the ethanol + ethyl acetate azeotrope at 313.15 K: [emim][Tf<sub>2</sub>N], [hmim][Tf<sub>2</sub>N], [bmpyrr][Tf<sub>2</sub>N], [emim]-[MeSO<sub>3</sub>], [emim][MeSO<sub>4</sub>], and [bmim][CF<sub>3</sub>SO<sub>3</sub>]. Previous studies to identify an appropriate IL entrainer to eliminate this particular azeotrope have found that relatively high IL concentrations are required. For example, at 101.32 kPa, IL mole fractions of 0.2, 0.3, 0.1, and 0.1 are necessary using 1-ethyl-3-methylimidazolium tetrafluoroborate [emim][BF<sub>4</sub>],<sup>11</sup> 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF<sub>4</sub>],<sup>12</sup> 1-methyl-3-octylimidazolium tetrafluoroborate [omim][BF<sub>4</sub>],<sup>12</sup> and 1-ethyl-3-methylimidazolium acetate [emim][Ac],<sup>13</sup> respectively. In addition, Orchillés et al.<sup>14</sup> have reported that, at a slightly lower pressure of 100 kPa, 0.2 mole fraction of [emim][F<sub>3</sub>CSO<sub>3</sub>] is necessary to eliminate this azeotrope. In this work, we show that just a mole fraction of 0.025 of either [emim][MeSO<sub>3</sub>] or [emim][MeSO<sub>4</sub>] is enough to break the azeotrope at 313.15 K. To our knowledge, this is the most effective IL for breaking an azeotrope, in terms of the lowest composition of entrainer needed, shown in the literature.

Infinite dilution activity coefficient data, at least in part, was used to select ILs for this study, and the relationship between infinite dilution activity coefficient and ease of breaking the azeotrope is analyzed. Prediction of vapor–liquid equilibrium for ternary mixtures is also essential in designing separation systems that would use ILs to perform extractive distillation. To this end, the Non-Random Two-Liquid (NRTL) activity coefficient model<sup>15</sup> has been used to fit interaction energies to the different ethanol–IL and ethyl acetate–IL binary systems. These data are then used to predict the ternary system vapor–liquid equilibrium. In cases where the binary mixture was not miscible, data from the ternary system was used to fit binary parameters to that mixture for further analysis.

## ■ EXPERIMENTAL AND THEORETICAL METHODS

Table 1 shows the supplier, purity, Chemical Abstract Service registry number, and maximum water content of the reagents used in this work, which includes six ILs and two organic components. A Karl Fischer Autotitrator was used to measure the water content in all reagents when each set of mixtures was prepared.

[Hmim][Tf<sub>2</sub>N] was synthesized in the laboratory following the procedure described in Widegren and Magee<sup>16</sup> with 1-methyl-3-hexyl-imidazolium bromide [hmim][Br] as intermediate. The remaining ILs were obtained from Iolitec or Sigma-Aldrich. NMR spectra were generated for each ILs before use in order to verify the purity. Also, the ILs were allowed to equilibrate on a vacuum line at moderate temperature for 48 h in order to remove excess moisture before being used to make the samples for analysis.

The binary and ternary vapor–liquid equilibrium data were obtained using a Teledyne Tekmar HT3 Static Headspace Autosampler connected to a Varian 450-GC gas chromatograph. The procedure used here allows for calculation of the vapor compositions that are in equilibrium with a given liquid phase composition. The binary and ternary mixtures were prepared by weighing the appropriate amount of each compound into a 9 mL vial. Samples were prepared in a dry nitrogen environment to reduce contamination (especially by water). Components were added in order of increasing volatility to reduce evaporation from the mixture. A Mettler

Toledo XS205 balance with an accuracy of ±0.00001 g was used in the nitrogen chamber, and each vial was sealed, in the chamber, with a septum and aluminum cap using a Supelco adjustable hand crimper.

After mixing the sealed vials and verifying that the mixture forms a single liquid phase, the vials were inserted into the headspace autosampler. The autosampler lowers the vials into an oven, where the mixture is allowed to equilibrate to a defined temperature before a sample is taken from the vapor phase in the headspace to be analyzed by gas chromatography. The autosampler used a loop method with “constant heat time” activated, so each sample sits in the oven for the same amount of time. The platen/sample temperature was 313.15 K with an uncertainty of ±0.5 K. The sample was equilibrated for 60 min. Then the mixer was turned off, and the sample was allowed to equilibrate for an additional min. The oven valve and transfer line temperatures were set to 453.15 K to eliminate any condensation, and the standby flow rate was 125 mL min<sup>-1</sup>. While taking the sample, the vial was pressurized to 137.9 kPa with helium in 0.20 min, and depressurized to 110.3 kPa, filling the 1 mL loop in 2 min. The sample was injected into the gas chromatograph in 0.20 min.

A 25 m long capillary CP Pora bond Q fused silica column, with 0.32 mm internal diameter and 0.45 μm film thickness was used in the Varian gas chromatograph. A flame ionization detector (FID) was used to detect the compounds as they eluted from the column. The injector of the gas chromatograph was set to 503.15 K with a split ratio of 40. The oven was set to 453.15 K, and a makeup helium flow of 29 mL min<sup>-1</sup> carried the sample through the column, with everything eluting in under 8 min. The FID was set to 523.15 K with a hydrogen flow of 30 mL min<sup>-1</sup> and an air flow of 300 mL min<sup>-1</sup> for the combustion process.

In addition to the mixtures, pure samples of each solvent (ethyl acetate and ethanol) were analyzed by the headspace autosampler and gas chromatograph to generate reference values for the peak areas. From the peak areas obtained by analyzing the vapor phase in equilibrium with a liquid mixture of known composition, the activity coefficient  $\gamma_i$  of component  $i$  in the mixture can be determined by the equation:

$$\gamma_i = \frac{A_i}{A_i^0 x_i} \quad (1)$$

where  $A_i$  is the peak area of the component  $i$  in the vapor phase;  $A_i^0$  is the peak area of the pure component as reference in the vapor phase;  $x_i$  is the mole fraction of component  $i$  in the liquid phase mixture.<sup>17</sup> Since the headspace is only a small volume within the closed vial and the sample temperature is well below the boiling point of the mixture, it is assumed that the composition of the liquid phase does not change as the system comes to equilibrium. The pressure of the mixture is then obtained from the equation:

$$P = \sum_i \gamma_i x_i P_i^{\text{sat}} \quad (2)$$

where  $P_i^{\text{sat}}$  is the vapor pressure of pure component at the temperature of the sample taken from the DIPPR database.<sup>18</sup> For all of the mixtures analyzed in this work, except the binary ethanol–ethyl acetate mixtures, one of the compounds in the binary or ternary mixtures is an IL, which has negligible vapor pressure and is not present in the vapor phase. In using eq 2, the vapor pressure,  $P_i^{\text{sat}}$ , for the IL is set to zero.

**Table 2.** NRTL<sup>20</sup> Parameters and Deviation from Experimental Data ( $\sigma$ ) in Equilibrium Pressure ( $P$ ) and Vapor Phase Molar Fraction ( $y$ ) for the Ethyl Acetate–Ethanol Binary System

NRTL ( $\alpha = 0.2988$ )						
component 1	component 2	$\Delta g_{12}/\text{J mol}^{-1}$	$\Delta g_{21}/\text{J mol}^{-1}$	$T/\text{K}$	$\sigma_p$	$\sigma_{y1}$
ethanol	ethyl acetate	1039.8	1948.2	313.15	0.034	0.019
				323.15	0.058	0.028
				333.15	0.022	0.034

$$\sigma_p = \sqrt{(1/n_p) \sum_i (P_i^{\text{exp}} - P_i^{\text{theo}}/P_i^{\text{exp}})^2} \quad \sigma_y = \sqrt{(1/n_y) \sum_i (y_i^{\text{exp}} - y_i^{\text{theo}})^2}$$

The standard uncertainties in the activity coefficients have been obtained using the different peak areas of pure component samples run through the gas chromatograph. These uncertainties were calculated as  $u(\gamma_{\text{ethyl acetate}}) = 0.03$  and  $u(\gamma_{\text{ethanol}}) = 0.07$ . The standard uncertainties in pressure and vapor phase composition were propagated from the uncertainties in the activity coefficients and liquid mole fractions. In this way, these were calculated as  $u(P) = 0.1$  kPa and  $u(y_i) = 0.001$ . Finally, the relative volatility  $\alpha_{12}$  of ethyl acetate (1) in ethanol (2) has been calculated by the following equation:

$$\alpha_{12} = \frac{y_1/x_1'}{y_2/x_2'} \quad (3)$$

where  $x_1'$  and  $x_2'$  are the modified mole fractions, which ignore the presence of IL and of ethyl acetate and ethanol in the liquid phase, respectively, and  $y_1$  and  $y_2$  are mole fractions of ethyl acetate and ethanol in the vapor phase, respectively. These modified liquid mole fractions are computed by

$$x_i' = \frac{x_i}{1 - x_3} \quad (4)$$

where  $x_3$  is the mole fraction of IL in the ternary mixture.

### VAPOR LIQUID EQUILIBRIUM MODELING

The Non-Random Two Liquid model (NRTL) is an activity coefficient model which has been used to correlate and predict vapor–liquid equilibria for the binary and ternary systems studied in this work. This model has been proposed by Renon and Prausnitz<sup>15</sup> and combines the two-liquid theory from Scott<sup>19</sup> with the idea of local composition, as employed by the Wilson model. In these models, it is assumed that individual molecules will arrange themselves in order to reduce energy, and the local composition that a molecule sees is a function of a parameter  $\alpha$  describing the nonrandomness of the system and the interaction energy  $\Delta g_{ij} = (g_{ij} - g_{jj})$  between molecules  $i$  and  $j$ .

The vapor phase for both the binary and ternary mixtures containing IL was assumed to be ideal because of the low system pressure. Also, ethanol and ethyl acetate are the only components present in the vapor phase since the ILs have negligible vapor pressure. This application of the model also assumes that, in the liquid phase, the cation and anion of the IL are completely associated with each other, allowing them to be treated as a single molecule. Saturation pressures for ethyl acetate and ethanol have been taken from DIPPR database,<sup>18</sup> and since the IL has a negligible vapor pressure, its saturation pressure has been set to zero.

The nonrandomness parameter and interaction energies for the ethanol–ethyl acetate binary mixture reported in the literature<sup>20</sup> at 313.15 K are shown in Table 2 in the Results and

Discussion section. However, we use the parameters fit to the data obtained here in the modeling of the ternary systems.

The vapor–liquid equilibrium data for ethyl acetate–ethanol and organic–IL binary mixtures that formed a single liquid phase over the entire composition range have been used to determine the binary interaction parameters for these systems by minimizing the following objective function:

$$\min_{\Delta g_{12}, \Delta g_{21}} \text{obj} = \frac{1}{n_p} \sum_i \left( \frac{P_i^{\text{exp}} - P_i^{\text{calc}}}{P_i^{\text{exp}}} \right)^2 \quad (5)$$

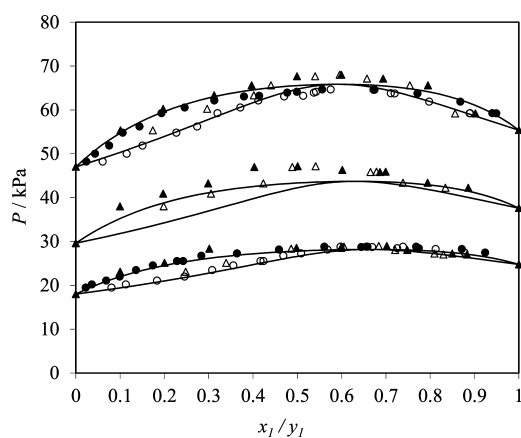
where exp represents the experimental data, and calc represents the calculated pressure from the NRTL parameters. The parameter fit described above was done using a program written by Simoni et al.,<sup>21</sup> which uses a fixed  $\alpha$  value and minimized the objective function by varying  $\Delta g_{12}$  and  $\Delta g_{21}$ .

The ternary mixtures were modeled using the parameters fit to the vapor–liquid equilibrium data for ethyl acetate–ethanol binary mixtures and the binary organic–IL mixtures obtained in this work. For four of the ILs, [emim][Tf<sub>2</sub>N], [hmim][Tf<sub>2</sub>N], [bmpyr][Tf<sub>2</sub>N], and [bmim][CF<sub>3</sub>SO<sub>3</sub>], the best-fit parameters were obtained for both solvent–IL binary mixtures. However, this could not be done for the systems involving [emim]-[MeSO<sub>3</sub>] and [emim][MeSO<sub>4</sub>]. This is because the binary mixtures of ethyl acetate with [emim][MeSO<sub>3</sub>] and [emim]-[MeSO<sub>4</sub>] form a two phase liquid system. Therefore, vapor–liquid equilibrium data could not be used to fit the binary parameters using the NRTL model. Fortunately, the ternary mixtures with these ILs and both organics were miscible over most of the composition range, so the binary parameters for the ethyl acetate–[emim][MeSO<sub>3</sub>] and ethyl acetate–[emim]-[MeSO<sub>4</sub>] binaries were obtained by fitting the vapor–liquid equilibrium data from the ternary system to the NRTL model. The previously determined parameters for the binary mixture of ethanol with the IL were fixed, and the interaction energies for ethyl acetate with the IL were varied for the best fit, as determined by the error in both pressure and vapor phase mole fraction, in order to minimize:

$$\min_{\Delta g_{12}, \Delta g_{21}} \text{obj} = \frac{1}{n_p} \sum_i \left( \frac{P_i^{\text{exp}} - P_i^{\text{calc}}}{P_i^{\text{exp}}} \right)^2 + \frac{1}{n_y} \sum_i (y_{1,i}^{\text{exp}} - y_{1,i}^{\text{calc}})^2 \quad (6)$$

### RESULTS AND DISCUSSION

**Binary Mixtures: Ethyl Acetate–Ethanol.** The ethyl acetate–ethanol binary system is well-known azeotropic system. The vapor–liquid equilibrium (VLE) data for this binary mixture was measured at 313.15, 323.15, and 333.15 K in order to validate the experimental apparatus and method. As shown in Figure 1, there is good agreement between the



**Figure 1.** Comparison of the experimental vapor–liquid equilibrium data for the ethyl acetate (1) + ethanol (2) binary system obtained in this work ( $\blacktriangle P_x$ ,  $\triangle P_y$ ), those available in the literature ( $\bullet P_x$ ,  $\circ P_y$ )<sup>20</sup> and the best fit NRTL model (lines). From bottom to top, the temperatures are (313.15, 323.15, 333.15) K.

experimental values available in literature<sup>20</sup> and those obtained in this study. Table S1 in the Supporting Information contains the experimental data obtained in this work. Figure 1 also shows the fit of the NRTL equation to the binary data, which shows the agreement of the experimental data with the NRTL model.

As mentioned above, the nonrandomness parameter and interaction energies for the ethanol–ethyl acetate binary mixture reported in the literature<sup>20</sup> are shown in Table 2. Note that the  $\Delta g_{12}$  and  $\Delta g_{21}$  values are independent of temperature. The temperature dependence is introduced in the model through the  $\tau_{ij}$  parameters ( $\tau_{ij} = \Delta g_{ij}/RT$ ). Table 2 also reports the deviation in pressure and in vapor phase composition between the literature experimental data and their NRTL modeling at three different temperatures.<sup>20</sup> Note that for the purposes of modeling the ternary systems herein, we have fit our experimental ethyl acetate + ethanol data using  $\alpha = 0.30$ , and those results are shown in Table 3.

**Binary Mixtures: Ethyl Acetate–IL and Ethanol–IL.** The binary VLE was measured at 313.15 K for ethyl acetate with the four ILs ([emim][Tf<sub>2</sub>N], [hmim][Tf<sub>2</sub>N], [bmpyrr]-[Tf<sub>2</sub>N], and [bmim][CF<sub>3</sub>SO<sub>3</sub>]) for which the binary

combination is completely miscible. Binary VLE was measured for all six of the IL with ethanol at 313.15 K. Tables S2 and S3 in the Supporting Information show the VLE data for the binary mixtures involved in this work.

Since the vapor phase is either pure ethyl acetate or pure ethanol (since the ILs are essentially nonvolatile), a good way to present the data is in terms of the activity coefficients of the ethyl acetate or ethanol in the liquid phase. This is what is shown in Figure 2 for the binary ethyl acetate–IL and ethanol–IL vapor liquid equilibrium data and the best fit NRTL model at 313.15 K.

The activity coefficients of ethyl acetate in [bmpyrr][Tf<sub>2</sub>N], [hmim][Tf<sub>2</sub>N], and [emim][Tf<sub>2</sub>N] indicate a negative deviation from ideality, while the mixture with [bmim]-[CF<sub>3</sub>SO<sub>3</sub>] indicates a positive deviation. Generally, activity coefficients less than one indicate attractions between the species. For the activity coefficient of ethanol in binary mixtures with ILs, positive deviation is observed with [bmpyrr][Tf<sub>2</sub>N] and [hmim][Tf<sub>2</sub>N], and negative deviation is found for the other four ILs. The lowest values for the activity coefficient of ethanol were found in the mixtures with [emim][MeSO<sub>3</sub>], [emim][MeSO<sub>4</sub>], and [bmim][CF<sub>3</sub>SO<sub>3</sub>].

The parameters obtained from this correlation process with the standard deviation in pressure between the experimental data and the best fit NRTL model for each data set are shown in Table 3. Recall that since [emim][MeSO<sub>3</sub>] and [emim]-[MeSO<sub>4</sub>] are not miscible with ethyl acetate, it was impossible to obtain vapor–liquid equilibrium data for those two systems, and thus, the binary NRTL parameters could not be determined from the binary mixtures for these systems. Those binary parameters will be determined from the ternary data, as described below.

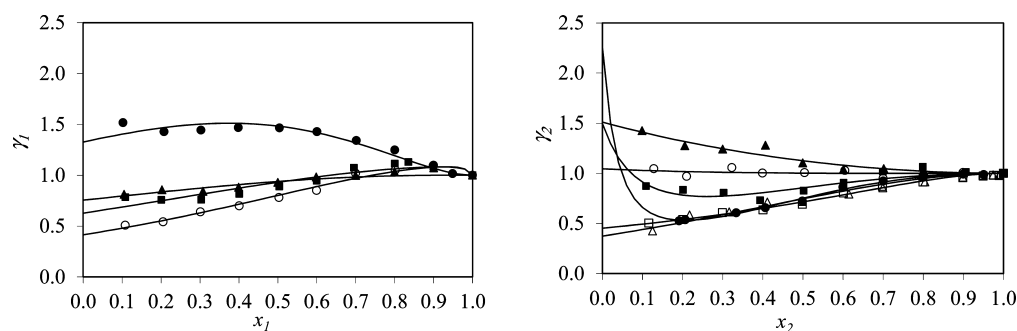
In determining the best-fit NRTL parameters, the nonrandomness parameter  $\alpha$  was varied to find the value that resulted in NRTL modeling results that were the closest to the experimental data in terms of the objective function shown in eq 5. The nonrandomness parameter was only varied between 0.1 and 0.3 because  $\alpha$  begins to lose its physical significance outside of this range, as described by Renon and Prausnitz.<sup>15</sup> For all of the data sets in this work, setting  $\alpha$  to 0.3 gave the best fit of the NRTL model to the experimental data.

The only data found in the literature related to the binary ethyl acetate–IL or ethanol–IL systems discussed above shows

**Table 3.** Best-Fit NRTL Parameters for Ethyl Acetate–Ethanol, Ethanol–IL, and Ethyl Acetate–IL Binary Systems and Deviation from Experimental Data ( $\sigma$ ) in Equilibrium Pressure (P) at 313.15 K

		NRTL ( $\alpha = 0.3$ )		
component 1	component 2	$\Delta g_{12}/\text{J mol}^{-1}$	$\Delta g_{21}/\text{J mol}^{-1}$	$\sigma_p$
ethyl acetate	ethanol	1217.6	2052.8	0.020
	[emim][Tf <sub>2</sub> N]	45348	−1459.0	0.059
	[hmim][Tf <sub>2</sub> N]	44289	−2561.0	0.032
	[bmpyrr][Tf <sub>2</sub> N]	4466.6	−3402.9	0.034
	[bmim][CF <sub>3</sub> SO <sub>3</sub> ]	9872.1	−2430.3	0.045
ethanol	[emim][Tf <sub>2</sub> N]	−4452.7	8487.1	0.058
	[hmim][Tf <sub>2</sub> N]	−1468.8	1855.0	0.031
	[bmpyrr][Tf <sub>2</sub> N]	1239.5	−1.4761	0.033
	[emim][MeSO <sub>3</sub> ]	3343.2	−4374.2	0.022
	[emim][MeSO <sub>4</sub> ]	−461.36	−2074.2	0.049
	[bmim][CF <sub>3</sub> SO <sub>3</sub> ]	−5370.4	12084	0.017

$$\sigma_p = \sqrt{(1/n_p) \sum_i (P_i^{\text{exp}} - P_i^{\text{calc}}/P_i^{\text{exp}})^2}$$



**Figure 2.** Activity coefficient of ethyl acetate (1) and ethanol (2) plotted against mole fraction of ethyl acetate or ethanol in binary mixtures with the ionic liquids discussed in this work:  $\blacktriangle$  [bmpyrr][Tf<sub>2</sub>N],  $\circ$  [hmim][Tf<sub>2</sub>N],  $\blacksquare$  [emim][Tf<sub>2</sub>N],  $\square$  [emim][MeSO<sub>3</sub>],  $\triangle$  [emim][MeSO<sub>4</sub>],  $\bullet$  [bmim][CF<sub>3</sub>SO<sub>3</sub>]. The symbols correspond to the experimental data, while the lines are the NRTL correlations.

the vapor pressure of ethanol in binary mixtures with [emim][Tf<sub>2</sub>N] and [hmim][Tf<sub>2</sub>N] at 353.15 K.<sup>22</sup>

The ILs investigated in this study were chosen, at least in part, based on infinite dilution activity coefficients ( $\gamma_i^\infty$ ). The limited experimental data available in the literature for  $\gamma_i^\infty$  values of ethyl acetate and ethanol in the ILs discussed in this work are shown in Table 4. These values provide a quantification of the interactions between the IL and either the ethyl acetate or the ethanol without the presence of ethyl acetate–ethyl acetate or ethanol–ethanol interactions. While the actual separations are done in ternary mixtures at finite concentrations, binary  $\gamma_i^\infty$  values can be used to guide the selection of the entrainers for extractive distillation,<sup>23</sup> as was done here.

As shown in Table 4, there is a large difference between the activity coefficients of ethanol and ethyl acetate in [emim]-[MeSO<sub>3</sub>], which suggests that it may be an excellent entrainer to break the azeotrope formed by these two compounds. This is borne out by the ternary results presented below. The large value of the infinite dilution activity coefficient of ethyl acetate in [emim][MeSO<sub>3</sub>] shows a strong tendency for ethyl acetate to prefer the vapor phase as opposed to remaining in the liquid mixture. The opposite is true for ethanol, where the  $\gamma_2^\infty$  value below 1.0 indicates favorable IL–ethanol interactions. This has been attributed to the formation of a hydrogen bonding complex between ethanol and [emim][MeSO<sub>3</sub>].<sup>28</sup> The high value of  $\gamma_1^\infty$  for ethyl acetate in [emim][MeSO<sub>3</sub>] is consistent with the observation of a liquid–liquid phase separation of the binary mixture. The infinite dilution activity coefficients of ethyl acetate and ethanol in [emim][MeSO<sub>4</sub>] are not available in literature, but similarities in molecular structure suggest that they may be close to those of [emim][MeSO<sub>3</sub>].

The fact that there is little difference between the infinite dilution activity coefficients of ethyl acetate and ethanol in [emim][Tf<sub>2</sub>N] and that the value for ethanol is actually a bit larger than the value for ethyl acetate suggests that this IL would not be a good choice as an entrainer for this azeotropic mixture, as is demonstrated by the ternary results presented below.

Like [emim][MeSO<sub>3</sub>], the infinite dilution activity coefficient of the ethanol in the [bmim][CF<sub>3</sub>SO<sub>3</sub>] shows an attraction of ethanol for the liquid phase, as opposed to ethyl acetate, which will favor the vapor phase. The difference between the infinite dilution activity coefficients of the two organics in [bmim]-[CF<sub>3</sub>SO<sub>3</sub>] is significantly less than the difference between these values for [emim][MeSO<sub>3</sub>], but since the value for ethyl acetate is larger than the value for ethanol, the IL should work well to

**Table 4.** Infinite Activity Coefficient of Ethyl Acetate (1) and Ethanol (2) in Different Ionic Liquids

	$\gamma_1^\infty$	T/K	$\gamma_2^\infty$	T/K
[emim][Tf <sub>2</sub> N]	0.886 <sup>24</sup>	313.15	2.14 <sup>25</sup>	293.15
	0.9 <sup>24</sup>	323.15	1.93 <sup>25</sup>	303.15
	0.91 <sup>24</sup>	333.15	1.525, <sup>24</sup> 1.77 <sup>25</sup>	313.15
	0.924 <sup>24</sup>	343.15	1.411, <sup>24</sup> 1.62 <sup>25</sup>	323.15
			1.29 <sup>24</sup>	333.15
			1.187 <sup>24</sup>	343.15
[hmim][Tf <sub>2</sub> N]	n.a. <sup>a</sup>		1.82 <sup>26</sup>	293.15
			1.60 <sup>22</sup>	303.15
			1.47 <sup>22,26</sup>	313.15
			1.36 <sup>22</sup>	323.15
			1.27, <sup>22</sup> 1.23 <sup>26</sup>	333.15
[bmpyrr][Tf <sub>2</sub> N]	n.a.		1.03 <sup>26</sup>	353.15
			1.84 <sup>22</sup>	303.15
			1.73 <sup>22</sup>	313.15
			1.63, <sup>22</sup> 1.73 <sup>27</sup>	323.15
			1.50, <sup>22</sup> 1.57 <sup>27</sup>	333.15
[emim][MeSO <sub>3</sub> ]			1.43 <sup>27</sup>	343.15
	7.32 <sup>28</sup>	318.15	0.489 <sup>29</sup>	308.15
	7.29 <sup>28</sup>	323.15	0.513, <sup>28</sup> 0.483 <sup>29</sup>	318.15
	7.22 <sup>28</sup>	333.15	0.479 <sup>29</sup>	328.15
	7.17 <sup>28</sup>	343.15	0.474 <sup>29</sup>	338.15
[emim][MeSO <sub>4</sub> ]			0.47 <sup>29</sup>	348.15
			0.467 <sup>29</sup>	358.15
	n.a.		0.449 <sup>30</sup>	323.15
			0.398 <sup>30</sup>	333.15
			0.349 <sup>30</sup>	343.15
[bmim][CF <sub>3</sub> SO <sub>3</sub> ]			0.303 <sup>30</sup>	353.15
	1.889 <sup>31</sup>	303.15	1.07 <sup>32</sup>	298.15
	1.938 <sup>31</sup>	313.15	1.01 <sup>32</sup>	308.15
	1.962 <sup>31</sup>	323.15	1.085 <sup>31</sup>	313.15
	2.015 <sup>31</sup>	333.15	0.958 <sup>32</sup>	318.15
	2.068 <sup>31</sup>	343.15	0.911 <sup>32</sup>	328.15
	2.106 <sup>31</sup>	353.15	0.871 <sup>32</sup>	338.15
	2.143 <sup>31</sup>	363.15	0.832 <sup>32</sup>	348.15
		0.798 <sup>32</sup>	358.15	
		0.768 <sup>32</sup>	368.15	

<sup>a</sup>n.a.: not available.

break the azeotrope. This is because ethyl acetate has a higher volatility than ethanol over the majority of the composition range in the binary mixture, so increasing the relative volatility of ethyl acetate by adding [bmim][CF<sub>3</sub>SO<sub>3</sub>] should aid in the separation. However, increasing the volatility of ethanol by using [emim][Tf<sub>2</sub>N] should make it harder to separate the

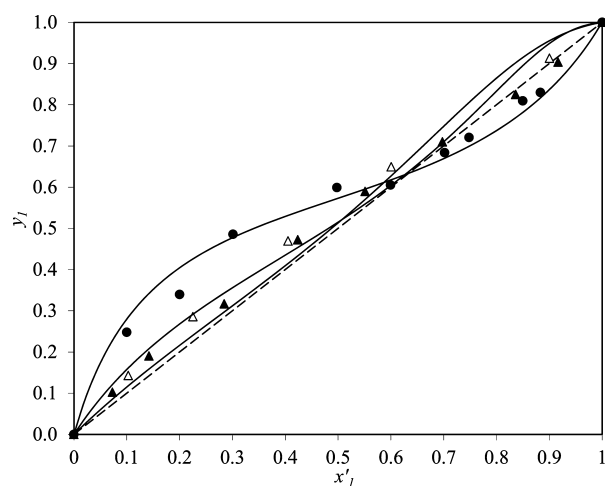
compounds. All of these trends are borne out in the ternary results.

As mentioned by Ge and Wang,<sup>31</sup> the infinite dilution activity coefficient of an organic in an IL is more dependent on the anion than the cation since the association is frequently between the anion and the organic compound. This is certainly true for the systems investigated here. As shown from Figure 2 and Tables S2 and S3 in the Supporting Information, the activity coefficient of ethyl acetate and ethanol in mixtures with ILs with the  $[\text{Tf}_2\text{N}]^-$  anion, over the full composition range, are all similar even though the cation of the IL is different.

### ■ TERNARY MIXTURES

Vapor–liquid equilibria for the ternary mixtures of ethyl acetate + ethanol + IL have been measured at 313.15 K. Each set of trials was run at constant mole fraction of IL, and trials were run up to (and slightly above) the amount of IL needed to break the azeotrope. These data are available in Tables S4–S9 in the Supporting Information.

Figure 3 shows the vapor–liquid equilibrium behavior for the ternary system with  $[\text{emim}][\text{Tf}_2\text{N}]$  for several of the IL



**Figure 3.** VLE for ethyl acetate (1) + ethanol (2) +  $[\text{emim}][\text{Tf}_2\text{N}]$  (3) at 313.15 K. The symbols correspond to experimental data while the lines are NRTL predictions: ●  $x_3 = 0$  (IL-free); ▲  $x_3 = 0.3$ ; △  $x_3 = 0.5$ .

concentrations (all of the data is provided in the Supporting Information). The vapor phase composition is plotted as a function of mole fraction of ethyl acetate in the ethyl acetate + ethanol in the liquid phase, which is designated  $x'_i$ . In other words, the amount of IL in the liquid phase has been ignored in calculating  $x'_i$ . Note that the vapor phase is composed only of

ethyl acetate and ethanol because the IL is nonvolatile. The data is plotted for different overall IL mole fractions in the liquid phase (i.e., different values of  $x_3$ ).

The addition of  $[\text{emim}][\text{Tf}_2\text{N}]$  pulls the data toward the  $x = y$  line for compositions both above and below the azeotropic composition. As a result, even though  $[\text{emim}][\text{Tf}_2\text{N}]$  is able to break the azeotrope at high IL concentrations ( $>0.5$  mole fraction IL), the relative volatility of ethyl acetate to ethanol is only slightly above 1.0 over the whole composition range. This means that a very large number of stages would be required to obtain relatively pure products.

The solid lines in Figure 3 are the NRTL model for the ternary system. Since all of the binary interaction parameters were determined from binary data, the model is a pure prediction. As such, it does a very good job of representing the ternary system. This is quantified in Table 5 in terms of the deviation in both composition and total pressure.

$[\text{Emim}][\text{Tf}_2\text{N}]$  and  $[\text{hmim}][\text{Tf}_2\text{N}]$  have very similar behavior; a mole fraction of 0.5 was required to break the azeotrope with both ILs. Increasing the length of the alkyl chain from two to six carbons in the cation of the IL had very little effect on the ternary vapor–liquid equilibrium. This also supports the argument that the anion has a greater effect on the ability of an IL to break an azeotrope, in agreement with Anderson et al.,<sup>33</sup> who explain in more detail the influence of the anion on the overall hydrogen bond basicity of ILs.

The third  $[\text{Tf}_2\text{N}]$ -based IL,  $[\text{bmpyrr}][\text{Tf}_2\text{N}]$ , requires an even a higher mole fraction ( $x_3 = 0.6$ ) to fully break the azeotrope. This IL breaks the azeotrope by reducing the volatility of ethyl acetate relative to ethanol, which is opposite compared to the two other  $[\text{Tf}_2\text{N}]$ -based IL systems. When the azeotrope disappears, the mole fraction of ethyl acetate is lower in the vapor phase than the liquid phase over the entire composition range, which is shown in Figure 4. Therefore, this IL salts out the ethanol rather than the ethyl acetate. Even though this is a slightly different behavior, the ILs with the bis(trifluoromethylsulfonyl)imide anion show very similar results in that they would not be good choices as an entrainer to aid in the separation of the ethyl acetate + ethanol azeotropic mixture.

By contrast,  $[\text{emim}][\text{MeSO}_3]$ ,  $[\text{emim}][\text{MeSO}_4]$ , and  $[\text{bmim}][\text{CF}_3\text{SO}_3]$  are excellent entrainers for breaking the ethyl acetate–ethanol azeotrope and facilitating easy separation.

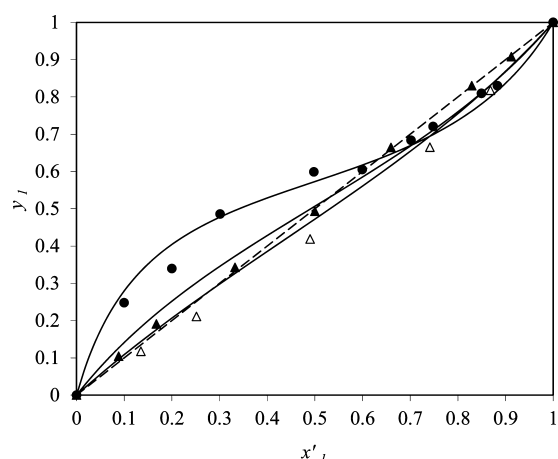
For  $[\text{emim}][\text{MeSO}_3]$  and  $[\text{emim}][\text{MeSO}_4]$ , a mole fraction of just 0.025 was sufficient to break the azeotrope. Figure 5 shows the behavior of the ternary system of ethanol, ethyl acetate, and  $[\text{emim}][\text{MeSO}_3]$  for several of the IL concentrations (all of the data is provided in the Supporting Information). The ethyl acetate–ethanol– $[\text{emim}][\text{MeSO}_4]$  ternary showed very similar results so that system is only

**Table 5.** Overall Deviation from Experimental Data ( $\sigma$ ) in Equilibrium Pressure ( $P$ ) and Vapor Phase Molar Fraction ( $y$ ) of Predicted NRTL Model for the Ternary Mixtures at 313.15K<sup>a</sup>

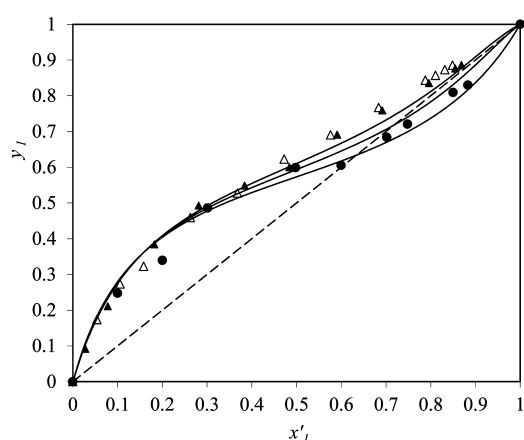
component 1	component 2	component 3	$\sigma_p$	$\sigma_{y_i}$
ethanol	ethyl acetate	$[\text{emim}][\text{Tf}_2\text{N}]$	0.108	0.035
		$[\text{hmim}][\text{Tf}_2\text{N}]$	0.083	0.037
		$[\text{bmpyrr}][\text{Tf}_2\text{N}]$	0.078	0.059
		$[\text{bmim}][\text{CF}_3\text{SO}_3]$	0.094	0.078

$$\sigma_y = \sqrt{(1/n_y) \sum_i (y_i^{\text{exp}} - y_i^{\text{calc}})^2}; \sigma_p = \sqrt{(1/n_p) \sum_i (P_i^{\text{exp}} - P_i^{\text{calc}}/P_i^{\text{exp}})^2}$$

<sup>a</sup>The parameters used are taken from Table 3.



**Figure 4.** VLE for ethyl acetate (1) + ethanol (2) + [bmpyrr][Tf<sub>2</sub>N] (3) at 313.15 K. The symbols correspond to experimental data while the lines are NRTL predictions: ●  $x_3 = 0$  (IL-free); ▲  $x_3 = 0.4$ ; △  $x_3 = 0.6$ .



**Figure 5.** VLE for ethyl acetate (1) + ethanol (2) + [emim][MeSO<sub>3</sub>] (3) at 313.15 K. The symbols correspond to experimental data while the lines are NRTL correlations: ●  $x_3 = 0$  (IL-free); ▲  $x_3 = 0.025$ ; △  $x_3 = 0.050$ .

shown in tabular form in the Supporting Information. The addition of [emim][MeSO<sub>3</sub>] (or [emim][MeSO<sub>4</sub>]) increases the volatility of ethyl acetate relative to ethanol. This means that it breaks the azeotrope but also pulls the vapor–liquid equilibrium line further away from the  $x = y$  line, which means that fewer stages would be needed for the separation. Recall that these two ILs are not miscible with ethyl acetate in the binary ethyl acetate–IL systems. However, adding just a very small amount of ethanol to the mixture generates a one phase

ternary system. Ethyl acetate and ethanol are completely miscible across the whole composition range and have similar dipole moments; ethanol is  $\mu = 1.69$  D<sup>18</sup> and ethyl acetate is  $\mu = 1.78$  D.<sup>18</sup> However, ethanol is also an effective hydrogen bond donor and acceptor. The ternary mixture becomes single phase due to the attractive interactions between the IL and the polar functional groups on the ethanol molecule<sup>23</sup> that are capable of hydrogen bonding with the IL. Over the composition range where the ternary mixture is a single liquid phase, the azeotrope could be broken using only 0.025 mole fraction of either [emim][MeSO<sub>3</sub>] or [emim][MeSO<sub>4</sub>]. The composition where a liquid–liquid phase split would occur is well past (i.e., higher ethyl acetate mole fraction) the composition at the azeotropic. Therefore, traditional distillation (without any complications from the formation of two liquid phases) can be used to separate and purify the ethyl acetate and ethanol when using [emim][MeSO<sub>3</sub>] or [emim][MeSO<sub>4</sub>] as the entrainer.

The lines shown in Figure 5 are from the NRTL model. In this case (and for [emim][MeSO<sub>4</sub>]), these are fits rather than predictions. This is because the ethyl acetate–IL binary interaction parameters could not be obtained from the binary VLE data (due to the liquid–liquid phase split in the binary system). Therefore, those parameters were fit to the ternary data, as described in the Modeling section. The ethyl acetate–[emim][MeSO<sub>3</sub>] and ethyl acetate–[emim][MeSO<sub>4</sub>] interaction energy parameters and deviations in pressure and vapor phase mole fraction for the corresponding ternary systems are reported in Table 6. As shown Tables S7 and S8 of the Supporting Information, the liquid–liquid immiscibility gap is smaller for the ethyl acetate–ethanol–[emim][MeSO<sub>3</sub>] ternary system than for the one containing [emim][MeSO<sub>4</sub>].

The final IL investigated is the same one previously shown by Orchillés et al.<sup>14</sup> to be an effective entrainer for the ethyl acetate–ethanol system. At a constant pressure of 101.3 kPa, which corresponds to temperatures between 344 and 351 K, they reported a minimum of 0.2 mole fraction of [emim]-[F<sub>3</sub>CSO<sub>3</sub>] needed to eliminate the ethyl acetate–ethanol azeotrope. Here, we found that a mole fraction of 0.1 [bmim][CF<sub>3</sub>SO<sub>3</sub>] was enough to break the azeotrope at 313.15 K. These data are shown in Figure 6. For this IL, the NRTL model is a pure prediction, with the goodness of fit shown in Table 5.

Figure 7 shows the relative volatility of ethyl acetate and ethanol in the ternary mixtures in order to represent the salting out effect of the ILs. The data are presented for the overall liquid composition at which each IL is able to break the ethyl acetate + ethanol azeotrope at 313.15 K. All of the ILs, except [bmpyrr][Tf<sub>2</sub>N], salt out the ethyl acetate. Since the polarity of ethanol and ethyl acetate are similar and ILs have effective

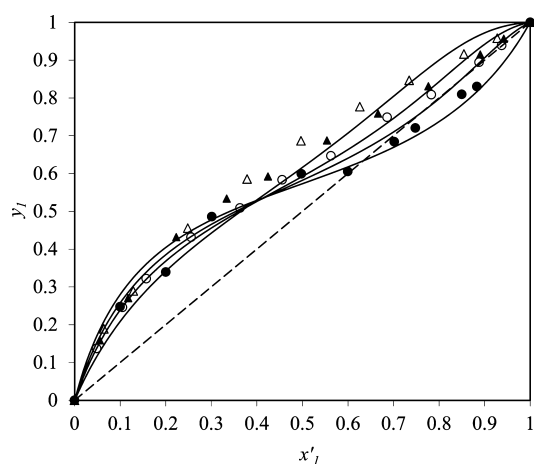
**Table 6.** NRTL Parameters at 313.15 K and Deviation from Experimental Data ( $\sigma$ ) in Equilibrium Pressure ( $P$ ) and Vapor Phase Mole Fraction ( $y$ ) from Fitting the Ternary Data for the Mixture of the Two Components below with Ethanol<sup>a</sup>

NRTL ( $\alpha = 0.3$ )					
component 1	component 2	$\Delta g_{12}/\text{J mol}^{-1}$	$\Delta g_{21}/\text{J mol}^{-1}$	$\sigma_p$	$\sigma_y$
ethyl acetate	[emim][MeSO <sub>3</sub> ]	20990	−3427.8	0.088	0.036
	[emim][MeSO <sub>4</sub> ]	16804	−4025.7	0.052	0.031

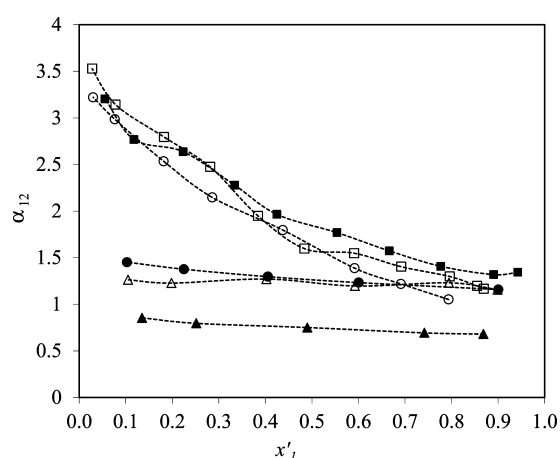
$$\sigma_y = \sqrt{(1/n_y) \sum_i (y_i^{\text{exp}} - y_i^{\text{calc}})^2}; \sigma_p = \sqrt{(1/n_p) \sum_i (P_i^{\text{exp}} - P_i^{\text{calc}}/P_i^{\text{exp}})^2}$$

<sup>a</sup>The deviations are calculated using the ternary data.





**Figure 6.** VLE for ethyl acetate (1) + ethanol (2) + [bmim][CF<sub>3</sub>SO<sub>3</sub>] (3) at 313.15 K. The symbols correspond to experimental data while the lines are NRTL predictions: ●  $x_3 = 0$  (IL-free); ○  $x_3 = 0.05$ ; ▲  $x_3 = 0.10$ ; △  $x_3 = 0.20$ .



**Figure 7.** Experimental relative volatility  $\alpha_{12}$  of ethyl acetate (1) and ethanol (2) in ternary mixtures with ionic liquid: ●  $x$  [emim][Tf<sub>2</sub>N] = 0.5; △  $x$  [hmim][Tf<sub>2</sub>N] = 0.5; ▲  $x$  [bmpyrr][Tf<sub>2</sub>N] = 0.6; □  $x$  [emim][MeSO<sub>3</sub>] = 0.025; ○  $x$  [emim][MeSO<sub>4</sub>] = 0.025; ■  $x$  [bmim][CF<sub>3</sub>SO<sub>3</sub>] = 0.1.

polarities similar to short chain alcohols,<sup>34</sup> this is the expected effect.<sup>12</sup> However, hydrogen bonding between the cation and the ethanol is clearly as important or more important than dipolar and electrostatic interactions. [bmpyrr]<sup>+</sup> is the only cation investigated that is not a good hydrogen-bond donor and [bmpyrr][Tf<sub>2</sub>N] is the only IL that salts out the ethanol, as shown by an  $\alpha_{12}$  value less than 1 over the entire composition range. All of the imidazolium cations possess an acidic proton in the C2 position that can readily hydrogen bond with ethanol. From Figure 7, it is shown that the magnitude of the salting out of ethyl acetate for the different ILs falls in the order of [emim][MeSO<sub>3</sub>] ( $x = 0.025$ ) > [bmim][CF<sub>3</sub>SO<sub>3</sub>] ( $x = 0.1$ ) > [emim][MeSO<sub>4</sub>] ( $x = 0.025$ ) > [emim][Tf<sub>2</sub>N] ( $x = 0.5$ ) > [hmim][Tf<sub>2</sub>N] ( $x = 0.5$ ).

## CONCLUSIONS

The addition of an entrainer to break azeotropes and improve relative volatilities is an effective way to reduce energy and capital costs for difficult separations. ILs are particularly attractive since they are nonvolatile (i.e., they will not

contribute to fugitive emissions) and tend to have good thermal stability. Here, we have observed six different ILs that can break the ethyl acetate + ethanol azeotrope at 313.15 K. From the results, it can be seen that ILs containing SO<sub>4</sub> and SO<sub>3</sub> groups are much better at breaking the azeotrope than the ILs containing SO<sub>2</sub> groups.

The most important result is that the azeotrope can be broken with only 2.5 mol % of [emim][MeSO<sub>3</sub>] or [emim][MeSO<sub>4</sub>] added to the ethyl acetate + mixture. This is the smallest known concentration of any IL known to break any azeotrope system.

In addition, the experimental binary and ternary vapor–liquid equilibria have been correlated and predicted with the Non-Random Two Liquid (NRTL) model with reasonable results. The NRTL composition and pressure values for the vapor–liquid equilibrium deviate a bit from the experimental data, but the IL composition needed to break the azeotrope is predicted quite well in all cases. This allows for prediction of how well an IL will work as an entrainer in extractive distillation of a given azeotrope before ternary data are gathered and analyzed.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.5b01175.

Vapor–liquid equilibria of binary and ternary mixtures involving the ethyl acetate, ethanol, and IL components. (PDF)

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### Notes

The authors declare no competing financial interest.

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