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Using 1-Ethyl-3-methylimidazolium Trifluoromethanesulfonate as an Entrainer for the Extractive Distillation of Ethanol + Water Mixtures

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Isobaric vapor−liquid equilibria (VLE) for the ethanol + water + [emim][triflate] ternary system have been obtained at 100 kPa using a recirculating still. The ethanol + water binary system was also obtained. Furthermore, data were simulated with the Mock's electrolyte nonrandom two-liquid (NRTL) model, using the solvent−solvent interaction parameters obtained from VLE data of the ethanol + water system and taking the solvent−ionic liquid (IL) interaction parameters for the other binary systems from previous works. The agreement between experimental and calculated data is very good, showing the predictive capacity of the model. The addition of [emim][triflate] produces the disappearance of the ethanol + water azeotrope when the mole fraction of ionic liquid in the liquid phase is greater than 0.023 at 100 kPa. The effect of [emim][triflate] on the ethanol + water system has been compared with that produced by other ionic liquids reported in the literature.

Introduction

Ionic liquids (ILs), a new class of organic molten salts, have been considered a novel replacement for many traditional organic compounds because of their negligible volatility, low melting points, favorable solubility, and high polar character.[1] Apart from that, some ILs possess other interesting properties such as relatively low viscosity and good stability up to 200 °C or higher and are much less corrosive than conventional high melting salts. These special characteristics have converted ILs into chemicals of high commercial interest.[2]

The use of ILs in separation technology, mainly in special distillation processes, for example, azeotropic or close-boiling mixtures, is promising. Thus, in cases where an IL interacts more strongly with one solvent, preferential solvation may take place, modifying the relative volatility, and therefore improved separation or azeotrope disappearance might be achieved. Moreover, in cases where this effect is not too evident, the greater solubility of some ILs in low-polar solvents allows a larger solute concentration in the mixture and therefore a stronger salt effect.

In addition, by using ILs, obvious advantages over classical entrainers or inorganic salts can be achieved. Similarly to classical entrainers, a pure IL liquid stream can be easily added to the reflux stream, and a higher concentration of electrolyte can exist along the distillation column because of its great solubility: whereas, in the same way as inorganic salts, its practically nonvolatile character prevents its presence in distillate streams, and it can be totally removed from the solvents by flash distillation of the column bottom stream.

Since the early works of Seiler et al.,[3,4] Jork et al.,[5] Beste et al.,[6] and Lei et al.[7] suggested using ILs for the separation of azeotropic mixtures, the number of studied systems has augmented appreciablely, as it can be seen at the International Union of Pure and Applied Chemistry (IUPAC) Ionic Liquid Database,[8] although in most cases the studies on the vapor−liquid equilibria (VLE) of IL-containing systems are limited to determine the vapor pressure and/or activity coefficients of one or two solvents or gases in ILs, and the works reporting complete isobaric VLE data (*T*, *x*, *y*) for ternary systems containing ILs are not so numerous. We have not found complete isothermal VLE data (*p*, *x*, *y*) for these systems in the literature.

As a continuation of our research, which consists of the use of ILs to modify the VLE of solvent mixtures that are difficult to separate by distillation, we present in this paper the isobaric VLE for the ternary system composed of ethanol, water, and 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([emim][triflate]) at 100 kPa. Moreover, the vapor pressure of ethanol and water and the isobaric VLE for the ethanol + water system at 100 kPa have been also determined.

The VLE of the ethanol (1) + water (2) system is, by far, the most studied one because of its industrial importance and the availability of both components. In the Dortmund Data Bank[9] there are 127 references of 245 data sets reported for this system. It shows, at atmospheric pressure, a minimum boiling point homogeneous azeotrope at an ethanol mole fraction of $x_1 \approx 0.90$. To break it, many entrainers have been used. Among them, inorganic salts have been used successfully because of the polarity of both solvents makes it easier to dissolve the salt in the liquid mixture, exerting a noticeable salt effect on it. In the database EVLM'2003[10] there are 102 references reported using 46 inorganic salts to move or break the ethanol + water azeotrope. Because of the advantages mentioned above, several ILs have been also used as entrainers to move or break the ethanol + water azeotrope: [emim][Cl],[11] [bmim][Cl],[4,11−14] [hmim][Cl],[15,16] [bmim][Br],[12] [emim][OAc],[11] [bmim][OAc],[11] [emim][BF_4],[4,11] [bmim][BF_4],[4,11] [bmim][PF_6],[12] [emim][$EtSO_4$],[17,18] [bmim][$MeSO_4$],[19] [mmim][Me_2PO_4],[12,20] [emim][Me_2PO_4],[21] [emim][Et_2PO_4],[12] [eeim][Et_2PO_4],[22] [emim][$N(CN)_2$],[11] and [bmim][$N(CN)_2$],[11] although, depending on concentration, only some of them achieve that.

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Consequently, one of the aims of this work is to determine at what composition, if any, [emim][triflate] is capable of breaking the ethanol + water azeotrope and compare its effect with that produced by other ILs.

Experimental Section

Materials. The solvents used were absolute ethanol (Merck, GR grade, minimum mass fraction 99.9 %) and distilled water (Merck, HPLC grade). No impurities were detected by GC, using the same procedure and conditions described below for analysis of liquid mixtures. These chemicals were used without further purification. 1-Ethyl-3-methylimidazolium trifluoromethanesulfonate was supplied by Solvent Innovation (Purum, minimum mass fraction 98 %). Because of its hygroscopic character, it was desiccated at 0.2 Pa overnight prior to use. The water mass fraction in the IL determined by Karl Fisher titration was $x_w < 0.0005$.

The IL, after being used in the VLE apparatus, was recovered from the liquid mixture by heating under a high vacuum (408 K, 0.2 Pa) for 48 h to remove the volatile solvents. The IL was reused noting that no changes in its behavior as an entrainer were produced.

Apparatus and Procedure. Vapor−liquid equilibrium measurements were made with an all-glass dynamic recirculating still (Pilodist, modified Labodest model). The apparatus has been described in a previous paper.[23] The equilibrium temperature was measured with a Fluke 1502A digital thermometer and a Pt-100 probe. The temperature probe was calibrated against the ice and steam points of distilled water. The standard uncertainty for temperature measurements was 0.01 K. The apparatus pressure was kept constant by means of a vacuum pump and an electrovalve modified by an on−off pressure controller whose standard uncertainty is 0.05 kPa.

Every experimental point of the binary ethanol + water system was obtained from an initial sample of pure ethanol at which different quantities of water were added, whereas for the ternary system, several water + IL mixtures of known composition were prepared, and different quantities of a mixture of ethanol + IL were added trying to keep the scheduled mole fraction of IL in each series. Only when constant temperature was reached (30 min or longer) were the equilibrium conditions assumed.

Sample Analysis. The IL mole fraction content in the liquid phase was gravimetrically determined after the volatile components were separated from a known mass of sample (≈ 2.5 g) by evaporation at 408 K until constant mass. A Mettler AE200 analytical balance with a standard uncertainty of $1 \cdot 10^{-4}$ g was used to weigh the samples. Ethanol and water contained in the liquid and condensed vapor phases were analyzed using a Varian Star 3400 CX gas chromatograph with a thermal conductivity detector (TCD). The chromatographic column (2.44 m × 3.2 mm) was packed with HayeSep P. The carrier gas was helium flowing at 30 $\text{cm}^3 \cdot \text{min}^{-1}$, and the operating conditions were as follows: injector temperature of 453 K, oven temperature of 423 K, and detector temperature of 493 K.

For the samples of the liquid phase, the whole of the IL was retained by a trap located between the injector and the chromatographic column. In this way, the result of the analysis was not affected by the presence of the IL, as we were able to experimentally verify. The trap was periodically cleaned to prevent the IL from coming into the column. A calibration curve was obtained from a set of gravimetrically prepared standard solutions, which allowed us to quantify the amounts of water and ethanol in the samples. In this way, the combined standard uncertainty of the mole fraction of the components in the liquid and vapor phases was 0.001.

Table 1. Variation of the Vapor Pressure p_S of Pure Ethanol with Temperature *T*

T/K	p_S/kPa	T/K	p_S/kPa	T/K	p_S/kPa	T/K	p_S/kPa
325.48	33.02	335.17	51.30	344.41	76.08	351.76	102.37
326.03	33.91	335.84	52.80	344.93	77.68	352.07	103.64
326.48	34.57	336.28	53.85	345.30	78.95	352.45	105.17
326.93	35.30	336.81	55.13	345.77	80.44	352.79	106.59
327.33	36.03	337.31	56.32	346.17	81.82	353.15	108.08
327.80	36.78	337.86	57.69	346.75	83.74	353.50	109.58
328.26	37.60	338.32	58.87	347.17	85.17	353.79	110.80
328.73	38.43	338.97	60.49	347.51	86.38	354.14	112.36
329.18	39.16	339.47	61.82	347.91	87.78	354.46	113.75
329.62	40.01	339.99	63.19	348.29	89.17	354.82	115.35
330.11	40.90	340.47	64.47	348.62	90.34	355.15	116.81
330.62	41.88	340.82	65.48	349.03	91.82	355.51	118.44
331.16	42.91	341.18	66.45	349.36	93.08	355.85	120.01
331.66	43.92	341.68	67.91	349.67	94.24	356.22	121.68
332.17	44.92	342.01	68.92	350.05	95.68	356.54	123.23
332.68	45.93	342.53	70.35	350.44	97.16	356.81	124.46
333.15	46.87	343.05	71.88	350.82	98.63	357.16	126.16
333.86	48.35	343.54	73.35	351.17	100.02	357.48	127.68
334.55	49.93	343.97	74.68	351.51	101.38	357.89	129.67

Table 2. Variation of the Vapor Pressure p_S of Pure Water with Temperature *T*

T/K	p_S/kPa	T/K	p_S/kPa	T/K	p_S/kPa	T/K	p_S/kPa
333.02	19.55	346.11	35.15	358.65	58.78	371.52	95.59
333.56	20.05	346.61	35.90	359.19	60.08	371.94	97.02
334.08	20.55	347.15	36.75	359.62	61.09	372.36	98.48
334.59	21.05	347.62	37.50	360.26	62.64	372.78	100.03
335.15	21.60	348.15	38.32	360.74	63.82	373.16	101.39
335.64	22.10	348.22	38.47	361.20	64.95	373.59	103.00
336.11	22.60	348.65	39.18	361.61	65.98	374.00	104.48
336.66	23.15	349.17	40.04	362.13	67.33	374.39	105.94
337.12	23.65	349.68	40.88	362.71	68.85	374.82	107.57
337.65	24.22	350.22	41.85	363.17	70.05	375.18	108.97
338.13	24.75	350.66	42.59	363.72	71.54	375.60	110.58
338.60	25.30	351.18	43.50	364.28	73.07	376.10	112.55
339.12	25.90	351.67	44.39	364.75	74.38	376.46	113.99
339.62	26.45	352.13	45.28	365.34	76.08	376.86	115.58
340.15	27.10	352.64	46.19	365.84	77.53	377.21	117.02
340.63	27.70	353.13	47.14	366.34	78.95	377.57	118.54
341.25	28.45	353.65	48.15	366.86	80.58	377.92	119.94
341.67	29.00	354.12	49.06	367.35	82.03	378.29	121.58
342.13	29.60	354.63	50.07	367.83	83.48	378.65	123.07
342.71	30.33	355.13	51.10	368.33	85.04	378.99	124.48
343.17	30.95	355.71	52.36	368.80	86.54	379.33	126.01
343.73	31.72	356.14	53.24	369.27	88.07	379.71	127.64
344.21	32.40	356.65	54.34	369.69	89.44	380.00	128.92
344.73	33.15	357.13	55.42	370.03	90.54	380.36	130.53
345.22	33.85	357.69	56.64	370.62	92.52	380.74	132.25
345.66	34.50	358.16	57.69	371.09	94.12		

Table 3. Antoine Coefficients Derived from the Vapor Pressure Measurements and Standard Deviations for Ethanol and Water

		Antoine coefficients[a]			
component	ΔT/K	A	B	C	$\sigma(p_S)$[b]/kPa
ethanol	325 to 358	16.7596	3736.94	–43.72	0.022
water	333 to 381	16.1021	3678.09	–52.85	0.019

[a] Antoine equation: $\ln p_S/\text{kPa} = A - B/(T/\text{K} + C)$. [b] $\sigma(p_S) = [\sum(p_{S,\text{exp}} - p_{S,\text{calc}})^2/(N - 3)]^{1/2}$.

Results and Discussion

Vapor Pressures of Ethanol and Water. Vapor pressures of ethanol and water were measured in the range of (325 to 380) K to test the performance of the apparatus and ascertain the purity of both solvents. Tables 1 and 2 show the experimental values of vapor pressure of ethanol and water, respectively, and in Table 3 the Antoine coefficients for both solvents and the standard deviations of vapor pressure are reported. Regarding ethanol, our vapor pressure data and those reported in the

Table 4. VLE Data for Ethanol (1) + Water (2) at 100 kPa

x_1	y_1	T/K	x_1	y_1	T/K
0.000	0.000	372.81	0.498	0.661	352.67
0.002	0.035	371.86	0.543	0.678	352.34
0.005	0.080	370.68	0.587	0.699	352.05
0.014	0.149	368.88	0.630	0.716	351.81
0.021	0.234	366.61	0.676	0.744	351.58
0.038	0.325	363.82	0.724	0.772	351.42
0.067	0.402	360.95	0.770	0.799	351.24
0.103	0.468	358.62	0.816	0.831	351.13
0.152	0.515	356.92	0.853	0.860	351.05
0.214	0.553	355.65	0.892	0.893	351.04
0.266	0.573	354.89	0.923	0.920	351.04
0.314	0.594	354.29	0.939	0.937	351.06
0.354	0.608	353.83	0.962	0.960	351.10
0.403	0.624	353.39	0.977	0.976	351.14
0.449	0.639	353.03	1.000	1.000	351.19

Table 5. Estimated Values of Nonrandomness Factors, $\alpha_{i,j}$, and Energy Parameters, $\Delta g_{i,j}$ and $\Delta g_{j,i}$, for the Electrolyte NRTL Model

i component	j component	$\alpha_{i,j}$	$\Delta g_{i,j}$ J·mol^{-1}	$\Delta g_{j,i}$ J·mol^{-1}
ethanol	water	0.330[a]	–311.48[a]	5744.1[a]
ethanol	[emim][triflate]	0.350[b]	13663[b]	–4404.0[b]
water	[emim][triflate]	0.870[c]	7555.9[c]	–1254.2[c]

[a] From this work. [b] From ref 42. [c] From ref 43.

literature[24−27] agree on average within 0.16 %. For water the agreement with the literature values[28] is within 0.21 %.

Ethanol + Water System. Vapor−liquid equilibrium for the ethanol (1) + water (2) binary system was measured at 100 kPa, and the experimental results are shown in Table 4, where x_1 and y_1 are the mole fraction of ethanol in the liquid and vapor phases, respectively, and T is the equilibrium temperature. This system shows at 100 kPa a minimum boiling point azeotrope at $x_1 = 0.900$ and $T = 351.04$ K, which can be interpolated from the experimental data. The experimental results for this binary system show a good thermodynamic consistency according to the Van Ness test[29] modified by Fredenslund et al.[30] The test gave a mean absolute deviation between calculated and measured mole fractions of ethanol in the vapor phase of $\delta y = 0.006$, which shows that the values are thermodynamically consistent.

The nonrandom two-liquid (NRTL) local composition model proposed by Renon and Prausnitz[31] have been used to model the VLE of the ethanol (1) + water (2) system. The parameters, which are shown in Table 5, were obtained by minimization of the objective function F_1

$$F_1 = \sum_N (T_{\text{exp}} - T_{\text{calcd}})^2 \tag{1}$$

where T is the equilibrium temperature, the indices exp and calcd denote the experimental and calculated values, respectively, and the summations are extended to the whole range of data points.

We have compared our experimental values with those existing in the literature obtained at 101.32 kPa using the NRTL model. At this pressure, the results from the model are in agreement within the experimental accuracy with data reported by Stabnikov et al.,[32] Zemp and Francesconi,[33] Kurihara et al.,[34] Arce et al.,[35] and Iwakabe and Kosuge,[36] although they disagree with those reported by Yang and Wang[37] and Lei et al.[38] The azeotropic point at 101.32 kPa, extrapolated from the model ($x_1 = 0.902$, $T = 351.32$ K), agrees with the numerous ones reported in the literature[39] at this pressure, which range from $T = (351.15$ to $351.45)$ K and $x_1 = (0.890$ to $0.905)$.

Table 6. VLE Data for Ethanol (1) + Water (2) + [emim][triflate] (3) at 100 kPa

x_3	x_1'	y_1	T/K
0.054	0.000	0.000	374.28
0.054	0.011	0.078	372.15
0.052	0.034	0.195	368.80
0.052	0.084	0.366	364.10
0.053	0.147	0.457	360.57
0.053	0.221	0.525	358.13
0.053	0.304	0.582	356.37
0.054	0.393	0.626	354.97
0.054	0.476	0.668	354.03
0.054	0.553	0.705	353.40
0.054	0.625	0.741	353.01
0.054	0.688	0.777	352.71
0.054	0.740	0.807	352.48
0.054	0.792	0.840	352.37
0.055	0.848	0.878	352.23
0.056	0.901	0.917	352.28
0.057	0.943	0.952	352.30
0.054	1.000	1.000	352.23
0.101	0.000	0.000	375.45
0.097	0.022	0.123	372.19
0.096	0.048	0.218	369.36
0.096	0.093	0.340	365.75
0.096	0.145	0.419	362.89
0.096	0.203	0.492	360.58
0.099	0.261	0.547	358.94
0.099	0.337	0.598	357.32
0.099	0.422	0.647	355.80
0.100	0.519	0.693	354.95
0.099	0.601	0.743	354.13
0.099	0.687	0.789	353.80
0.098	0.761	0.834	353.46
0.098	0.825	0.872	353.26
0.100	0.875	0.908	353.16
0.102	0.924	0.939	353.12
0.105	0.960	0.969	353.25
0.104	1.000	1.000	353.13
0.217	0.000	0.000	379.51
0.217	0.019	0.076	377.44
0.214	0.040	0.160	375.09
0.211	0.081	0.271	371.74
0.209	0.133	0.369	368.52
0.205	0.180	0.447	365.93
0.210	0.248	0.510	364.13
0.211	0.302	0.564	362.64
0.213	0.376	0.624	360.89
0.214	0.449	0.679	359.46
0.216	0.532	0.727	358.45
0.216	0.612	0.778	357.60
0.218	0.692	0.822	357.19
0.217	0.766	0.860	356.74
0.221	0.832	0.900	356.49
0.222	0.887	0.931	356.27
0.222	0.931	0.957	356.22
0.219	1.000	1.000	355.83

Ethanol + Water + [emim][triflate] System. VLE for the ethanol (1) + water (2) + [emim][triflate] (3) system, at 100 kPa, were obtained by keeping the IL mole fraction nearly constant in each of the three series at $x_3 \approx 0.054$, 0.100, and 0.215. These values are shown in Table 6, where x_1' is the mole fraction of ethanol in the liquid phase expressed on an IL-free basis, y_1 is the mole fraction of ethanol in the vapor phase, and T is the equilibrium temperature.

Modeling the Phase Equilibrium. As indicated in previous papers,[40−44] we have used the electrolyte NRTL model to predict the VLE of the IL-containing ternary system. This model is an extension of the original NRTL model proposed by Renon and Prausnitz[31] for liquid-phase activity coefficients. Chen et al.[45] derived a model for single-solvent + electrolyte systems, and later Mock et al.[46,47] extended it to mixed-solvent + electrolyte systems, by neglecting the long-range interaction contribution term.

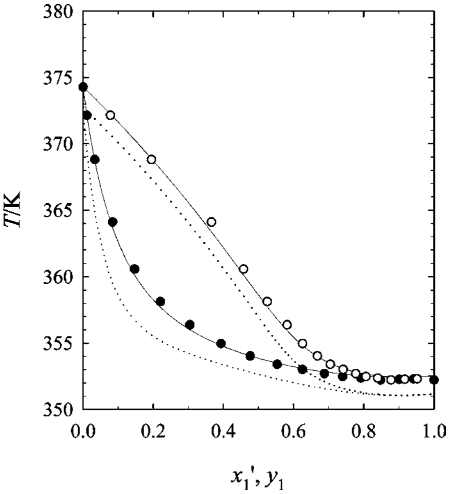

Figure 1. Temperature−composition diagram for ethanol (1) + water (2) + [emim][triflate] (3) at 100 kPa, with a mole fraction of IL $x_3 \approx 0.054$. ●, x_1' experimental; ○, y_1 experimental; solid lines, calculated; dotted lines, calculated for the IL-free system.

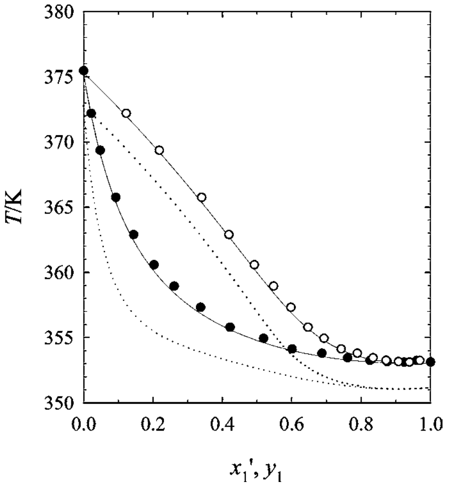

Figure 2. Temperature−composition diagram for ethanol (1) + water (2) + [emim][triflate] (3) at 100 kPa, with a mole fraction of IL $x_3 \approx 0.100$. ●, x_1' experimental; ○, y_1 experimental; solid lines, calculated; dotted lines, calculated for the IL-free system.

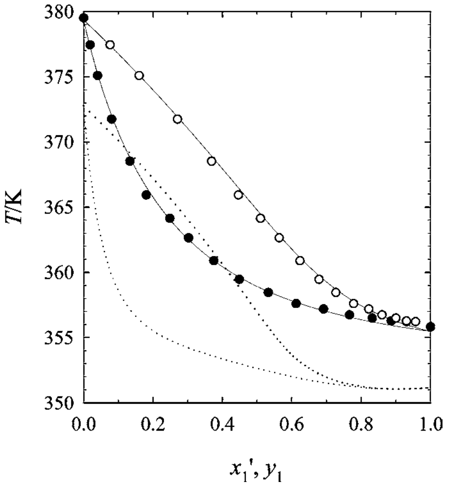

Figure 3. Temperature−composition diagram for ethanol (1) + water (2) + [emim][triflate] (3) at 100 kPa, with a mole fraction of IL $x_3 \approx 0.215$. ●, x_1' experimental; ○, y_1 experimental; solid lines, calculated; dotted lines, calculated for the IL-free system.

The model produces expressions for the liquid-phase activity coefficients of ethanol (1) and water (2) in a binary or ternary system containing [emim][triflate] (3). These equations have been reported in a previous paper.[48] According to the proposed method, we need the nine binary adjustable parameters for all of the solvent + solvent and solvent + electrolyte pairs in the system to represent the phase equilibrium of mixed-solvent + electrolyte systems.

As previously stated, the 1−2 binary solvent−solvent parameters were obtained from the VLE data of the ethanol (1) + water (2) system, which are reported in Table 5, whereas the parameters corresponding to the ethanol (1) + [emim][triflate] (3) and water (2) + [emim][triflate] (3) binary solvent−IL interactions were taken from our previous papers[42,43] in which the VLE of the ethanol (1) + [emim][triflate] (3) and water (2) + [emim][triflate] (3) binary systems were obtained and fitted to the electrolyte NRTL model. These parameters are also reported in Table 5.

With the electrolyte NRTL model and the parameters shown in Table 5, it was possible to simulate the VLE of the ethanol + water + [emim][triflate] system and compare it with the experimental data. Thus, the mean absolute deviation between the experimental and the calculated values of the mole fraction in the vapor phase was 0.004, whereas the mean absolute deviation of equilibrium temperature was 0.2 K.

In Figures 1, 2, and 3, the calculated and experimental VLE of the ethanol + water + [emim][triflate] points are plotted on a (T, x_1', y_1) diagram for $x_3 \approx 0.054$, 0.100, and 0.215. The model is seen to be able to properly predict the experimental VLE data. In this way, the ability of the model to reproduce the VLE for this system is demonstrated.

The [emim][triflate] produces a strong crossover effect[49] between salting-in and salting-out in the ethanol + water system, as observed in Figure 4, where the different solid lines, which represent the (y_1, x_1') equilibrium, separate from the diagonal for $x_1' > 0.3$, while they are closer to it for $x_1' < 0.3$, as the IL mole fraction increases. This effect, which is seldom found with inorganic salts, is very common with ILs, and it has been pointed out in many papers, as many in ethanol + water + IL[4,13−17,20,21] systems as in solvent + solvent + IL[40−44] systems.

With the smallest mole fraction of [emim][triflate] used in this study ($x_3 = 0.054$), the azeotrope has already disappeared. From the electrolyte NRTL model, the mole fraction of [emim][triflate] at which the disappearance of the azeotrope for ethanol + water at 100 kPa occurs is estimated to be $x_3 = 0.023$.

The effect produced by the [emim][triflate] on the VLE of the ethanol + water system can be compared with that produced by other ILs reported in the literature. From these works,[4,11−22] it can be deduced that [emim][Cl], [bmim][Cl], [emim][OAc], and [bmim][OAc] produce the greatest salt effect on this system. According Ge et al.,[11] these four ILs can break the ethanol + water azeotrope at an IL mole fractions of $x_3 = 0.016$, 0.020, 0.013, and 0.014, respectively. All of these x_3 values are smaller than that calculated in this work for the [emim][triflate] ($x_3 = 0.023$). However, [emim][Cl] and [bmim][Cl] have melting points about (358.1 and 340) K, respectively,[50] and high viscosities,[51] and therefore its use as entrainer does not present the advantages that ILs have over inorganic salts. Furthermore, [bmim][OAc] starts to decompose at 446 K, and it has a viscosity of 440 mPa·s at 298.15 K.[52] Although viscosity data of [emim][OAc] are not available, it must be higher than 200 mPa·s. The solution viscosities of these four ILs with water and ethanol are close to the acceptable distillation limit of 100 mPa·s, a barrier above which the number of required transfer units drastically increases and the manageability of the separa-

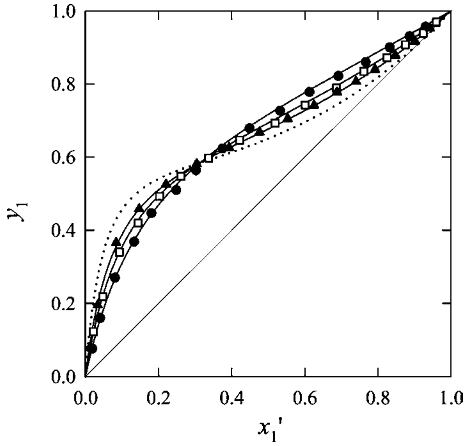

Figure 4. Salting effect of [emim][triflate] on VLE of the ethanol (1) + water (2) system at 100 kPa for several IL mole fractions. ▲, $x_3 \approx 0.054$; □, $x_3 \approx 0.100$; ●, $x_3 \approx 0.215$; solid lines, calculated at the same IL mole fractions; dotted line, calculated for the IL-free system.

tion becomes increasingly difficult.[4] Against this behavior, [emim][triflate] presents a melting point of 262.23 K,[53] a viscosity of 41 mPa·s at 298.15 K and 11 mPa·s at 348.15 K,[54] and a decomposition temperature higher than 613 K. When we have to use an IL as an entrainer in industrial extractive distillation columns, these properties, together with the important salt effect that it produces, make [emim][triflate] into a good entrainer for the ethanol + water system, even though its separation ability is lower and its price higher than other ILs.

Conclusions

In this work, vapor pressures of pure ethanol and water and VLE of ethanol + water and ethanol + water + [emim][triflate] at 100 kPa have been obtained with a recirculating still.

The electrolyte NRTL model is suitable to predict the VLE in the presence of an IL such as [emim][triflate]. From the parameters obtained of experimental data of binary systems, the ternary system has been reproduced with a great precision. This confirms the extension of the model to ILs.

It has been experimentally proved that at 100 kPa the azeotrope of the ethanol + water system has disappeared when the mole fraction of [emim][triflate] is $x_3 = 0.054$, and the electrolyte NRTL model predicts that it does the same when $x_3 = 0.023$.

The effect produced by the [emim][triflate] on the VLE of the ethanol + water system is slightly smaller than that produced by [emim][Cl], [bmim][Cl], [emim][OAc], or [bmim][OAc], and its price is noticeably higher. In spite of that, [emim][triflate] has the advantage of its smaller viscosity and melting point, as well as its larger decomposition temperature, which makes it in a very good entrainer for the ethanol + water system.

Literature Cited

(1) Heintz, A. Recent developments in thermodynamics and thermophysics of non-aqueous mixtures containing ionic liquids. A review. *J. Chem. Thermodyn.* **2005**, *37*, 525–535.

(2) Seddon, K. R. Ionic liquids for clean technology. *J. Chem. Technol. Biotechnol.* **1997**, *68*, 351–356.

(3) Seiler, M.; Jork, C.; Schneider, W.; Arlt, W. Ionic liquids and hyperbranched polymers-Promissing new classes of selective entrainers for extractive distillation. In *Proceedings of the International Conference on Distillation & Absorption 2002*; GVC-VDI: Düsseldorf, 2002.

(4) Seiler, M.; Jork, C.; Kavarnou, A.; Arlt, W.; Hirsch, R. Separation of azeotropic mixtures using hyperbranched polymers or ionic liquids. *AIChE J.* **2004**, *50*, 2439–2454.

(5) Jork, C.; Seiler, M.; Beste, Y. A.; Arlt, W. Influence of ionic liquids on the phase behavior of aqueous azeotropic systems. *J. Chem. Eng. Data* **2004**, *49*, 852–857.

(6) Beste, Y.; Eggersmann, M.; Schoenmakers, H. Extractive distillation with ionic fluids. *Chem. Ing. Tech.* **2005**, *77*, 1800–1808.

(7) Lei, Z.; Arlt, W.; Wasserscheid, P. Separation of 1-hexene and n-hexane with ionic liquids. *Fluid Phase Equilib.* **2006**, *241*, 290–299.

(8) IUPAC Ionic Liquid Database-(IL Thermo). NIST Standard Reference Database #147. http://ilthermo.boulder.nist.gov/ILThermo/mainmenu.uix (accessed December 1, 2009).

(9) *Dortmund Data Bank, Version 2009*; DDBST Software and Separation Technology GmbH: Oldenburg, Germany, 2009.

(10) Wichterle, I.; Linek, J.; Wagner, Z.; Kehiaian, H. V. *Vapor-Liquid Equilibrium in Mixtures and Solutions. Bibliographic Database EVLM'2003*; Electronic Data (ELDATA): Paris, France, 2004.

(11) Ge, Y.; Zhang, L.; Yuan, X.; Geng, W.; Ji, J. Selection of Ionic Liquids as Entrainers for Separation of Water and Ethanol. *J. Chem. Thermodyn.* **2008**, *40*, 1248–1252.

(12) Zhao, J.; Dong, C. C.; Li, C. X.; Meng, H.; Wang, Z. H. Isobaric vapor-liquid equilibria for ethanol-water system containing different ionic liquids at atmospheric pressure. *Fluid Phase Equilib.* **2006**, *242*, 147–153.

(13) Calvar, N.; González, B.; Gómez, E.; Domínguez, A. Vapor-Liquid Equilibria for the Ternary System Ethanol + Water + 1-Butyl-3-methylimidazolium Chloride and the Corresponding Binary Systems at 101.3 kPa. *J. Chem. Eng. Data* **2006**, *51*, 2178–2181.

(14) Geng, W.; Zhang, L.; Deng, D.; Ge, Y.; Ji, J. Experimental Measurement and Modeling of Vapor-Liquid Equilibrium for the Ternary System Water + Ethanol + 1-Butyl-3-methylimidazolium Chloride. *J. Chem. Eng. Data* **2009**, doi: 10.1021/je900723v.

(15) Calvar, N.; González, B.; Gómez, E.; Domínguez, A. Study of the behaviour of the azeotropic mixture ethanol-water with imidazolium-based ionic liquids. *Fluid Phase Equilib.* **2007**, *259*, 51–56.

(16) Zhang, L.; Ge, Y.; Ji, D.; Ji, J. Experimental Measurement and Modeling of Vapor-Liquid Equilibrium for Ternary Systems Containing Ionic Liquids: A Case Study for the System Water + Ethanol + 1-Hexyl-3-methylimidazolium Chloride. *J. Chem. Eng. Data* **2009**, *54*, 2322–2329.

(17) Wang, J. F.; Li, C. X.; Wang, Z. H. Measurement and Prediction of Vapor Pressure of Binary and Ternary Systems Containing 1-Ethyl-3-methylimidazolium Ethyl Sulfate. *J. Chem. Eng. Data* **2007**, *52*, 1307–1312.

(18) Calvar, N.; González, B.; Gómez, E.; Domínguez, A. Vapor-Liquid Equilibria for the Ternary System Ethanol + Water + 1-Ethyl-3-methylimidazolium Ethylsulfate and the Corresponding Binary Systems Containing the Ionic Liquid at 101.3 kPa. *J. Chem. Eng. Data* **2008**, *53*, 820–825.

(19) Calvar, N.; González, B.; Gómez, E.; Domínguez, A. Vapor-Liquid Equilibria for the Ternary System Ethanol + Water + 1-Butyl-3-methylimidazolium Methylsulfate and the corresponding Binary Systems at 101.3 kPa. *J. Chem. Eng. Data* **2009**, *54*, 1004–1008.

(20) Zhao, J.; Li, C.; Wang, Z. Vapor Pressure Measurement and Prediction for Ethanol + Methanol and Ethanol + Water Systems Containing Ionic Liquids. *J. Chem. Eng. Data* **2006**, *51*, 1755–1760.

(21) Wang, J. F.; Li, C. X.; Wang, Z. H.; Li, Z. J.; Jian, Y. B. Vapour pressure measurement for water, methanol, ethanol, and their binary mixtures in the presence of an ionic liquid 1-ethyl-3-methylimidazolium dimethylphosphate. *Fluid Phase Equilib.* **2007**, *255*, 186–192.

(22) Jiang, X. C.; Wang, J. F.; Li, C. X.; Wang, L. M.; Wang, Z. H. Vapour pressure measurement for binary and ternary systems containing water methanol ethanol and an ionic liquid 1-ethyl-3-ethylimidazolium diethylphosphate. *J. Chem. Thermodyn.* **2007**, *39*, 841–846.

(23) Vercher, E.; Orchillés, A. V.; Miguel, P. J.; González-Alfaro, V.; Martínez-Andreu, A. Isobaric vapor-liquid equilibria for acetone + methanol + lithium nitrate at 100 kPa. *Fluid Phase Equilib.* **2006**, *250*, 131–137.

(24) Figurski, G.; Malanowski, S. K. Vapor-liquid equilibrium studies of the ethanol + ethyl acetate system. *Fluid Phase Equilib.* **1988**, *148*, 161–169.

(25) Mund, W.; Heim, G. Vapor tensions of the system: ethyl alcohol-ethyl acetate. *Bull. Soc. Chim. Belg.* **1932**, *41*, 349–376.

(26) Ambrose, D.; Sprake, C. H. S. Thermodynamic properties of organic oxygen compounds XXV. Vapour pressures and normal boiling temperatures of aliphatic alcohols. *J. Chem. Thermodyn.* **1970**, *2*, 631–645.

(27) *NIST/TRC Table Database (Win Table). NIST Standard Reference Database 85*; Thermodynamic Research Center, Physical and Chemical Properties Division: Boulder, CO, 2004.

(28) Harvey, A. H. *NISTIR 5078. Thermodynamic Properties of Water: Tabulation from the IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific*

Use; NIST: Boulder, CO, 1998. http://www.nist.gov/srd/WebGuide/nist10v2.2/NISTIR5078.htm (accessed December 1, 2009).

(29) Van Ness, H. C.; Byer, S. M.; Gibbs, R. E. Vapor-liquid equilibrium: part I. An appraisal of data reduction methods. *AIChE J.* **1973**, *19*, 238–244.

(30) Fredenslund, A.; Gmehling, J.; Rasmussen, P. *Vapor-Liquid Equilibria Using UNIFAC*; Elsevier: Amsterdam, 1977.

(31) Renon, H.; Prausnitz, J. M. Local compositions in thermodynamic excess functions for liquid mixtures. *AIChE J.* **1968**, *14*, 135–144.

(32) Stabnikov, V. N.; Matyushev, B. Z.; Protsyuk, T. B.; Yushchenko, N. M. Equilibrium in the ethyl alcohol-water system at atmospheric pressure. *Kharchova Prom.* **1972**, *15*, 49–56.

(33) Zemp, R. J.; Francesconi, A. Z. Salt Effect on Phase Equilibria by a Recirculating Still. *J. Chem. Eng. Data* **1992**, *37*, 313–316.

(34) Kurihara, K.; Nakamichi, M.; Kojima, K. Isobaric vapor-liquid equilibria for methanol + ethanol + water and the three constituent binary systems. *J. Chem. Eng. Data* **1993**, *38*, 446–449.

(35) Arce, A.; Martínez-Ageitos, J.; Soto, A. VLE for water + ethanol + 1-octanol mixtures. Experimental measurements and correlations. *Fluid Phase Equilib.* **1996**, *122*, 117–129.

(36) Iwakabe, K.; Kosuge, H. Isobaric vapor-liquid-liquid equilibria with a newly developed still. *Fluid Phase Equilib.* **2001**, *192*, 171–186.

(37) Yang, B.; Wang, H. J. Vapor-Liquid Equilibrium for Mixtures of Water, Alcohols, and Ethers. *J. Chem. Eng. Data* **2002**, *47*, 1324–1329.

(38) Lei, Z.; Wang, H.; Zhou, R.; Duan, Z. Influence of salt added to solvent on extractive distillation. *Chem. Eng. J.* **2002**, *87*, 149–156.

(39) Gmehling, J.; Menke, J.; Krafczyk, J.; Fischer, K. *Azeotropic Data*; VCH: Weinheim, 1994.

(40) Orchillés, A. V.; Miguel, P. J.; Vercher, E.; Martínez-Andreu, A. Ionic liquids as entrainers in extractive distillation: isobaric vapor-liquid equilibria for acetone + methanol + 1-ethyl-3-methylimidazolium trifluoromethanesulfonate. *J. Chem. Eng. Data* **2007**, *52*, 141–147.

(41) Orchillés, A. V.; Miguel, P. J.; Vercher, E.; Martínez-Andreu, A. Isobaric vapor-liquid equilibria for methyl acetate + methanol + 1-ethyl-3-methylimidazolium trifluoromethanesulfonate at 100 kPa. *J. Chem. Eng. Data* **2007**, *52*, 915–920.

(42) Orchillés, A. V.; Miguel, P. J.; Vercher, E.; Martínez-Andreu, A. Isobaric vapor-liquid equilibria for ethyl acetate + ethanol + 1-ethyl-3-methylimidazolium trifluoromethanesulfonate at 100 kPa. *J. Chem. Eng. Data* **2007**, *52*, 2325–2330.

(43) Orchillés, A. V.; Miguel, P. J.; Vercher, E.; Martínez-Andreu, A. Isobaric vapor-liquid equilibria for 1-propanol + water + 1-ethyl-3-methylimidazolium trifluoromethanesulfonate at 100 kPa. *J. Chem. Eng. Data* **2008**, *53*, 2426–2431.

(44) Orchillés, A. V.; Miguel, P. J.; Vercher, E.; Martínez-Andreu, A. Isobaric vapor-liquid and liquid-liquid equilibria for chloroform + ethanol + 1-ethyl-3-methylimidazolium trifluoromethanesulfonate at 100 kPa. *J. Chem. Eng. Data* **2008**, *53*, 2642–2648.

(45) Chen, C. C.; Britt, H. I.; Boston, J. F.; Evans, L. B. Local composition model for excess Gibbs energy of electrolyte systems. Part I: single solvent, single completely dissociated electrolyte systems. *AIChE J.* **1982**, *28*, 588–596.

(46) Mock, B.; Evans, L. B.; Chen, C. C. Phase equilibria in multiple-solvent electrolyte systems: a new thermodynamic model. *Proc. Summer Comput. Simul. Conf.* **1984**, 558–562.

(47) Mock, B.; Evans, L. B.; Chen, C. C. Thermodynamic representation of phase equilibria of mixed-solvent electrolyte systems. *AIChE J.* **1986**, *32*, 1655–1664.

(48) Vercher, E.; Rojo, F. J.; Martínez-Andreu, A. Isobaric vapor-liquid equilibria for 1-propanol + water + calcium nitrate. *J. Chem. Eng. Data* **1999**, *44*, 1216–1221.

(49) Meranda, D.; Furter, W. F. Salt effects on VLE: some anomalies. *AIChE J.* **1974**, *20*, 103–108.

(50) Wilkes, J. S.; Levisky, J. A.; Wilson, R. A.; Hussey, C. L. Dialkylimidazolium Chloroaluminate Melts: A New Class of Room-Temperature Ionic Liquids for Electrochemistry, Spectroscopy, and Synthesis. *Inorg. Chem.* **1982**, *21*, 1263–1264.

(51) Seddon, K. R.; Stark, A.; Torres, M. J. Viscosity and Density Data of 1-Alkyl-3-methylimidazolium Ionic Liquids. In *Clean Solvents. Alternative Media for Chemical Reactions*; Abraham, M. A., Moens, L., Eds.; ACS Symposyum Series 819; American Chemical Society: Washington, DC, 2002; pp 34−49.

(52) Crosthwaite, J. M.; Muldoon, M. J.; Dixon, J. K.; Anderson, J. L.; Brennecke, J. F. Phase transition and decomposition temperatures, heat capacities and viscosities of pyridinium ionic liquids. *J. Chem. Thermodyn.* **2005**, *37*, 559–568.

(53) Wachter, P.; Schweiger, H. G.; Wudy, F.; Gores, H. J. Efficient determination of crystallisation and melting points at low cooling and heating rates with novel computer controlled equipment. *J. Chem. Thermodyn.* **2008**, *40*, 1542–1547.

(54) Rodríguez, H.; Brennecke, J. F. Temperature and Composition Dependence of the Density and Viscosity of Binary Mixtures of Water + Ionic Liquid. *J. Chem. Eng. Data* **2006**, *51*, 2145–2155.

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