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Isobaric Vapor−Liquid Equilibria for Ethyl Acetate + Ethanol + 1-Ethyl-3-methylimidazolium Trifluoromethanesulfonate at 100 kPa

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Isobaric vapor−liquid equilibria for the binary systems ethyl acetate + ethanol, ethyl acetate + 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([emim][triflate]), and ethanol + [emim][triflate] as well as the vapor−liquid equilibria for the ethyl acetate + ethanol + [emim][triflate] ternary system have been obtained at 100 kPa using a recirculating still. NRTL fitting parameters for the ethyl acetate + ethanol and ethanol + [emim][triflate] systems were calculated. The measured ternary data were correlated using the Mock electrolyte NRTL model, which reproduces reasonably well the experimental values. The results suggest that the addition of [emim][triflate] to the ethyl acetate + ethanol mixture produced an important salting-out effect, and the azeotrope disappears when the mole fraction of ionic liquid in the liquid phase is greater than 0.20.

Introduction

Ionic liquids (IL) are typically salts composed of relatively large organic cations and inorganic or organic anions. Because of their asymmetric structure and ionic interactions, they are liquids below 100 °C and present very low vapor pressures and a highly polar character caused by coulomb forces.[1] These special characteristics have converted ILs into chemicals of high commercial interest.[2] As indicated by Heintz,[1] ILs can be used as “green” solvents replacing volatile organic compounds as catalysts in chemical reactions and as extraction media. New applications of ILs are being continuously reported.

Ionic liquids, when dissolved in solvent mixtures, interact with the components of the liquid phase modifying its chemical potential, just like other ionic chemicals such as inorganic salts do. In cases where an IL interacts more strongly with one solvent in a mixture, azeotropes could be broken and improved separations might be achieved. Even when this effect is not too intense, the greater solubility of some ILs in low-polar solvents allows a greater solute concentration in the mixture and therefore a stronger salt effect.

Arlt and co-workers were the first group that suggested using ILs for separation of azeotropic mixtures. They reported the effect of various ionic liquids on several azeotropic binary systems.[3−8] Nevertheless, even though the use of ILs as solvents or entrainers in separation technology is promising, thermodynamic data are rare. Currently, only a few investigations on vapor−liquid equilibria have been accomplished.

In most cases, the studies on the vapor−liquid equilibria of IL-containing systems are incomplete because they are limited to determining the vapor pressure and/or activity coefficients of one or two solvents in ILs. As far as we know, only Zhao et al.[9,10] (ethanol + water + IL system and ethanol + methanol + IL system), Calvar et al.[11] (ethanol + water + IL system), Orchillés et al.[12,13] (acetone + methanol + IL system and methyl acetate + methanol + IL system), and Zhang et al.[14,15] (water + 2-propanol + IL system) have reported complete isobaric vapor−liquid equilibria data (T, x, y) for ternary systems containing ILs, all published in the last year. We have not found complete isothermal vapor−liquid equilibria data (P, x, y) for ternary systems containing ILs in the literature.

Following a research line recently started which consists of the use of ILs to modify the vapor−liquid equilibria of solvent mixtures that are difficult to separate by distillation, we present in this work isobaric vapor−liquid equilibria for ethyl acetate + ethanol + 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([emim][triflate]) binary and ternary systems at 100 kPa.

The ethyl acetate (1) + ethanol (2) system shows, at atmospheric pressure, a minimum boiling point azeotrope at $x_1 \approx 0.54$. To break it, various salts have been used, not always successfully. Thus, vapor−liquid equilibria measurements with potassium acetate,[16,17] calcium chloride,[18−21] copper(II) chloride,[20] lithium chloride,[17,21,22] sodium iodide,[23] lithium nitrate,[24] and magnesium perchlorate[20] have been reported, but they do not break the azeotrope even at saturation conditions because of the very low salt solubility in ethyl acetate. Takamatsu and Ohe[21] have measured the effect of lithium chloride on the isothermal vapor−liquid equilibria for the ethyl acetate + ethanol system at 313.15 K, and they assert that lithium chloride at mole fraction > 0.06 can break the azeotrope. Their affirmation is a theoretical extrapolation from a modified solvation model, and there is no evidence that the azeotrope disappears although it is displaced. Only zinc chloride[16] has been reported to be effective in breaking the ethyl acetate + ethanol azeotrope, although we suspect it can be due to the water content of the salt, which might increase the solubility of this salt in ethyl acetate. Consequently, one of the aims of this work is to determine if [emim][triflate] is also capable of breaking the ethyl acetate + ethanol azeotrope.

Experimental Section

Materials. The solvents used were ethyl acetate (Merck, GR grade, minimum mass fraction 99.5 %) and absolute ethanol (Merck, GR grade, minimum mass fraction 99.9 %). No impurities were detected by GC, using the same procedure and

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conditions described below for liquid mixtures. These chemicals were used directly without further purification. The IL used was 1-ethyl-3-methylimidazolium trifluoromethanesulfonate supplied by Solvent Innovation (Purum, minimum mass fraction 98 %). It was selected because of its complete miscibility in both solvents, its low melting point ($T_m < 264$ K) that makes it easy to use it, and its high decomposition temperature ($T_d > 623$ K) that allows us to recover it from column bottoms and reuse it. 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 $w_w < 0.05$ %.

The IL, after being used in the VLE apparatus, was recovered from the liquid mixture by heating under a high vacuum (393 K, 0.2 Pa) for 48 h to remove the volatile solvents. So, the same IL without observing any change in its properties was used.

Apparatus and Procedure. Vapor−liquid equilibrium measurements were made with an all-glass dynamic recirculating still (Pilodist, modified Labodest model), equipped with a Cottrell circulation pump,[25] which ensures that both liquid and vapor phases are in intimate contact during boiling and in contact with the temperature-sensing element. The apparatus has been described in a previous paper.[26] 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 ethyl acetate + ethanol system was obtained from an initial sample of pure ethyl acetate at which different quantities of ethanol were added, whereas for the binary solvent + IL systems, ethyl acetate or ethanol was added to an IL concentrated solution until a very diluted solution was achieved. For the ternary system, several ethyl acetate + IL mixtures of distinct composition were taken, and different quantities of a mixture of ethanol + IL having a slightly higher concentration than the original one were added. A Mettler AE200 analytical balance with a standard uncertainty of 0.0001 g was used to prepare the samples. 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 393 K until constant mass. Ethyl acetate and ethanol contained in the liquid and condensed vapor phases were analyzed by using a Varian Star 3400 CX gas chromatograph with a thermal conductivity detector (TCD). The chromatographic column (2 m × 0.125 in.) was packed with Porapak QS. The carrier gas was helium flowing at 30 $\text{cm}^3 \cdot \text{min}^{-1}$, and the operating conditions were as follows: injector and oven temperatures of 473 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 ethanol and ethyl acetate 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. Experimental Antoine Coefficients and Standard Deviations for Ethyl Acetate and Ethanol

	temperature range	Antoine coefficients[a]			$\sigma(P°)$[b]
component	K	A	B	C	kPa
ethyl acetate	310 to 359	14.2283	2799.54	−58.92	0.046
ethanol	321 to 359	16.8316	3758.56	−43.78	0.018

[a] Antoine equation: $\ln P°/\text{kPa} = A - B/(T/\text{K} + C)$. [b] $\sigma(P°) = [\Sigma (P°_{\text{exptl}} - P°_{\text{calcd}})^2/(N - 3)]^{1/2}$.

Table 2. Vapor−Liquid Equilibrium Data for Ethyl Acetate (1) + Ethanol (2) at 100 kPa

x_1	y_1	T/K	x_1	y_1	T/K
0.000	0.000	351.21	0.624	0.593	344.80
0.021	0.048	350.45	0.666	0.621	344.91
0.043	0.091	349.74	0.690	0.637	345.04
0.074	0.147	348.85	0.717	0.657	345.18
0.121	0.212	347.82	0.744	0.679	345.37
0.168	0.272	347.02	0.767	0.699	345.57
0.217	0.317	346.39	0.790	0.720	345.80
0.260	0.358	345.89	0.818	0.740	346.05
0.303	0.392	345.53	0.835	0.759	346.27
0.355	0.428	345.18	0.851	0.774	346.51
0.402	0.458	344.98	0.875	0.803	346.88
0.448	0.486	344.82	0.900	0.833	347.36
0.493	0.514	344.73	0.937	0.888	348.13
0.540	0.542	344.71	0.975	0.951	349.10
0.584	0.568	344.73	1.000	1.000	349.89

Results and Discussion

Vapor Pressures of Ethyl Acetate and Ethanol. To test the performance of the equilibrium apparatus, the vapor pressures of ethyl acetate and ethanol were measured in the range (310 to 360) K. The Antoine coefficients for both solvents obtained from our experimental data, as well as the standard deviations between experimental and calculated vapor pressure data, are shown in Table 1. As far as ethyl acetate is concerned, our vapor pressure data and those reported in the literature[27−29] agree on average to within 0.35 %. For ethanol, the agreement with the literature values[29−31] is within 0.40 %.

Ethyl Acetate + Ethanol System. The vapor−liquid equilibrium for the ethyl acetate (1) + ethanol (2) system was measured at 100 kPa, and the experimental results are in Table 2, where x_1 and y_1 are the mole fraction of ethyl acetate in the liquid and vapor phases, respectively, and T is the equilibrium temperature. This system shows a minimum boiling point azeotrope at $x_1 = 0.542$ and $T = 344.71$ K, which can be interpolated from the experimental values. The experimental results for this binary system show a good thermodynamic consistency according to the Van Ness test[32] modified by Fredenslund.[33] The test gave a mean absolute deviation between calculated and measured mole fractions of ethyl acetate in the vapor phase of $\delta y = 0.0050$, which shows that the values are thermodynamically consistent.

To compare these values with those existing in the literature, in most cases obtained at 101.32 kPa, we have reduced our data to this pressure using the NRTL model as it is described later. The azeotropic point reduced to 101.325 kPa from our experimental data would take place at $x_1 = 0.539$ and $T = 345.09$ K.

As pointed out by Figurski and Malanowski,[29] there is a great dispersion in the vapor−liquid equilibrium data reported in the literature for this system as well as in the location of the azeotropic point, both for isothermal and isobaric data sets. The experimental data reported in the literature at 101.325 kPa[24,34−39]

Table 3. Vapor−Liquid Equilibrium Data for Ethyl Acetate (1) + [emim][triflate] (3) at 100 kPa

x_3	T/K	x_3	T/K	x_3	T/K
0.0000	349.84	0.2255	350.19	0.3525	351.20
0.0187	349.98	0.2478	350.26	0.3690	351.51
0.0468	350.02	0.2547	350.29	0.3833	351.85
0.0769	349.99	0.2695	350.34	0.4054	352.31
0.1133	350.04	0.2890	350.55	0.4090	352.36
0.1464	350.05	0.3106	350.73	0.4133	352.38
0.1748	350.07	0.3149	350.84	0.4155	352.50
0.2005	350.07	0.3349	351.00		

Table 4. Vapor−Liquid Equilibrium Data for Ethanol (2) + [emim][triflate] (3) at 100 kPa

x_3	T/K	x_3	T/K	x_3	T/K
0.0000	351.21	0.1192	353.39	0.2390	356.30
0.0133	351.51	0.1326	353.70	0.2562	356.83
0.0234	351.77	0.1529	354.17	0.2668	357.25
0.0242	351.70	0.1627	354.36	0.2885	357.90
0.0362	351.84	0.1875	354.98	0.2969	358.25
0.0393	352.00	0.1913	355.02	0.2999	358.39
0.0500	352.11	0.1985	355.19	0.3062	358.60
0.0540	352.23	0.2018	355.27	0.3113	358.74
0.0634	352.48	0.2100	355.54	0.3221	359.28
0.0683	352.44	0.2142	355.62	0.3235	359.25
0.0770	352.67	0.2191	355.83	0.3330	359.64
0.0865	352.84	0.2275	356.09	0.3331	359.75
0.1036	353.13	0.2282	356.04	0.3661	361.19
0.1172	353.34	0.2377	356.39	0.3766	361.75

present the azeotropic point at $x_1 = (0.519^{37}$ to $0.575^{35})$ and $T = (344.85^{34,37}$ to $345.25^{36,38})$ K. Our data, reduced at 101.325 kPa, fall within the reported range and agree very well within the experimental accuracy with those reported by Topphoff et al.[24] and Calvar et al.[39]

Solvent + IL Binary Systems. Boiling temperatures for ethyl acetate (1) + [emim][triflate] (3) and ethanol (2) + [emim][triflate] (3) were also measured at 100 kPa, and the experimental results are reported in Tables 3 and 4, respectively. In these tables, x_3 is the mole fraction of [emim][triflate] in the liquid phase, and T is the equilibrium temperature.

In relation to the ethyl acetate + [emim][triflate] system, we wish to emphasize that, as seen in Table 3, the temperature rise at 100 kPa is imperceptible up to $x_3 = 0.20$, and it is only 2.6 K at $x_3 = 0.42$ (67.8 % mass fraction of IL). This unusual small ebullioscopic effect of the [emim][triflate] on ethyl acetate can be compared with those produced on other solvents. The temperature rise is about 20 K for acetone[12] and methanol,[12] 12 K for ethanol, 7 K for methyl acetate,[13] and less than 3 K for ethyl acetate.

This effect can be seen in Figure 1, where the vapor pressure correction factor proposed by Jaques and Furter,[40] defined as

$$\epsilon = \frac{P^*}{P^{\text{o}}} \tag{1}$$

has been drawn vs mole fraction of [emim][triflate] in solution. In eq 1, P^* is the vapor pressure of solution containing a salt and P^{o} is the vapor pressure of pure solvent, both at the same temperature. This correction factor ϵ is assumed independent of temperature. The relative vapor pressure depletion for acetone, methanol, and ethanol is similar and considerable but for ethyl acetate is very low. Methyl acetate shows a behavior similar to ethyl acetate, but less pronounced.

Ethyl Acetate + Ethanol + [emim][triflate] System. Vapor−liquid equilibria for the ethyl acetate (1) + ethanol (2) + [emim][triflate] (3) system, at 100 kPa as well, was obtained by trying to keep the IL mole fraction constant in each of the four series at $x_3 \approx 0.05$, 0.10, 0.20, and 0.30. We repeated some points in the series made at $x_3 \approx 0.20$ and checked that these points agreed very well with the previous ones, proving the reproducibility of the experimental procedure. These values are shown in Table 5, where x_3 is the mole fraction of [emim][triflate] in the liquid phase; x_1' is the mole fraction of ethyl acetate in the liquid phase expressed on an IL-free basis; y_1 is the mole fraction of ethyl acetate in the vapor phase; and T is the equilibrium temperature.

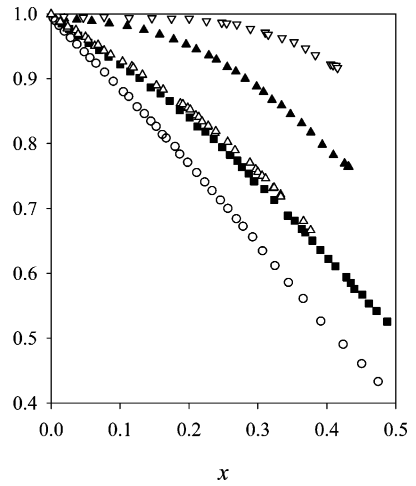

Figure 1. Vapor pressure correction factor ϵ for the [emim][triflate] + solvent binary systems, at 100 kPa, as a function of the mole fraction x of IL in the liquid phase. Solvent: △, ethanol; ▽, ethyl acetate; ■, methanol; ▲, methyl acetate; ○, acetone.

Modeling the Phase Equilibrium. As suggested in previous works,[12,13] we have tried to use the electrolyte NRTL model to predict the vapor−liquid equilibrium of the IL-containing ternary system. This model is an extension of the nonrandom two-liquid local composition proposed by Renon and Prausnitz[41] from which Chen et al.[42] derived a model for single-solvent + electrolyte systems. Subsequent to that, Mock et al.[43,44] extended it to mixed-solvent + electrolyte systems, by neglecting the long-range interaction contribution term.

In this way, expressions for the liquid-phase activity coefficients of ethyl acetate (1) and ethanol (2) in a binary or ternary system containing [emim][triflate] (3) can be derived. These equations have been reported in a previous paper.[45] According to the proposed method, as long as we want to represent the phase equilibrium of mixed-solvent + electrolyte systems, we must determine the nine binary adjustable parameters for all the solvent + solvent and solvent + electrolyte pairs in the system.

The 1−2 binary solvent−solvent parameters were obtained from the vapor−liquid equilibria data of the ethyl acetate (1) + ethanol (2) system shown in Table 2, and those corresponding to the 2−3 binary solvent−IL were obtained from the vapor−liquid equilibria data of the ethanol (2) + [emim][triflate] (3) binary system shown in Table 4. In both cases, the parameters were obtained by minimization of the objective function F_1

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

where T is the equilibrium temperature; the indices exptl and calcd denote the experimental and calculated values, respectively; and the summations are extended to the whole range of data points. All these six parameters are reported in Table 6.

The parameters corresponding to the 1−3 binary solvent−IL pair could not be estimated in the same way from the vapor−liquid equilibria data for the ethyl acetate (1) + [emim][triflate]

Table 5. Vapor−Liquid Equilibrium Data for Ethyl Acetate (1) + Ethanol (2) + [emim][triflate] (3) at 100 kPa

x_3	x_1'	y_1	T/K	x_3	x_1'	y_1	T/K
0.054	0.000	0.000	352.29	0.202	0.218	0.343	350.23
0.054	0.020	0.045	351.45	0.204	0.231	0.353	350.08
0.054	0.045	0.096	350.68	0.204	0.289	0.417	349.39
0.054	0.096	0.178	349.28	0.203	0.299	0.433	349.25
0.055	0.152	0.257	348.13	0.205	0.362	0.484	348.70
0.055	0.216	0.333	347.17	0.205	0.379	0.499	348.63
0.055	0.285	0.392	346.46	0.208	0.430	0.554	348.27
0.056	0.354	0.450	345.97	0.208	0.505	0.612	348.00
0.056	0.425	0.499	345.63	0.210	0.589	0.667	347.86
0.056	0.497	0.546	345.49	0.217	0.594	0.682	347.97
0.057	0.566	0.592	345.50	0.210	0.660	0.720	347.84
0.057	0.633	0.636	345.67	0.215	0.666	0.728	347.87
0.057	0.710	0.695	345.97	0.213	0.727	0.770	348.00
0.057	0.779	0.750	346.48	0.209	0.730	0.774	347.95
0.058	0.849	0.813	347.23	0.210	0.783	0.815	348.18
0.058	0.905	0.872	348.06	0.206	0.801	0.826	348.24
0.058	0.948	0.925	348.85	0.206	0.845	0.861	348.48
0.047	1.000	1.000	350.02	0.199	0.873	0.881	348.69
0.096	0.000	0.000	353.07	0.199	0.900	0.907	348.93
0.097	0.021	0.045	352.09	0.194	0.924	0.927	349.12
0.098	0.043	0.087	351.44	0.194	0.941	0.943	349.33
0.100	0.092	0.177	350.24	0.192	0.962	0.963	349.55
0.101	0.156	0.268	348.89	0.192	0.971	0.970	349.68
0.104	0.226	0.346	347.82	0.201	1.000	1.000	350.07
0.105	0.298	0.416	347.04	0.297	0.000	0.000	358.25
0.105	0.375	0.479	346.53	0.296	0.018	0.039	357.68
0.105	0.457	0.538	346.20	0.296	0.042	0.088	357.01
0.104	0.535	0.601	346.07	0.299	0.091	0.173	355.79
0.104	0.608	0.651	346.17	0.301	0.147	0.257	354.66
0.104	0.681	0.696	346.36	0.303	0.209	0.339	353.55
0.103	0.740	0.743	346.70	0.305	0.277	0.417	352.56
0.103	0.801	0.790	347.14	0.304	0.352	0.491	351.68
0.104	0.869	0.850	347.85	0.308	0.425	0.558	351.05
0.105	0.919	0.903	348.58	0.304	0.501	0.620	350.49
0.105	0.957	0.947	349.25	0.304	0.571	0.676	350.14
0.113	1.000	1.000	350.04	0.307	0.626	0.725	350.03
0.188	0.000	0.000	355.14	0.312	0.711	0.777	349.95
0.194	0.022	0.048	354.41	0.308	0.785	0.833	349.83
0.195	0.045	0.090	353.78	0.300	0.857	0.886	349.91
0.196	0.100	0.184	352.33	0.299	0.914	0.929	350.13
0.198	0.103	0.191	352.18	0.293	0.957	0.965	350.31
0.199	0.161	0.271	351.12	0.289	1.000	1.000	350.55
0.202	0.168	0.278	351.01				

Table 6. 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}
ethyl acetate	ethanol	0.300	853.5	1860.3
ethyl acetate	[emim][triflate]	0.108	37608.3	−15617.1
ethanol	[emim][triflate]	0.350	13663.1	−4404.0

(3) system, since the abnormal small boiling point elevation produced by [emim][triflate] on ethyl acetate could not be fitted by the electrolyte NRTL model. Because of that, the parameters corresponding to the 1−3 binary solvent−IL pair had to be established from the experimental vapor−liquid equilibrium data of the ethyl acetate (1) + ethanol (2) + [emim][triflate] (3) system and the electrolyte NRTL model. Accordingly, the model was applied by taking into account the (1−2) and (2−3) binary parameters from the previous adjustments, whereas those corresponding to (1−3) binary system were obtained by minimization of the objective function F_2

$$F_2 = \sum_N \left(1 - \frac{\gamma_{1_{\text{calcd}}}}{\gamma_{1_{\text{exptl}}}}\right)^2 + \left(1 - \frac{\gamma_{2_{\text{calcd}}}}{\gamma_{2_{\text{exptl}}}}\right)^2 \tag{3}$$

where γ_i is the activity coefficient of solvent i; the indices exptl and calcd denote the experimental and calculated values, respectively; and the summations are extended to the whole range of data points.

Table 7. Mean Absolute Deviations, δy and δT, and Standard Deviations, σy and σT, between Experimental and Calculated Values of the Vapor-Phase Mole Fractions and the Equilibrium Temperatures

system	δy^a	σy^b	δT^c K	σT^d K
ethyl acetate + ethanol	0.003	0.005	0.03	0.04
ethanol + [emim][triflate]			0.17	0.23
ethyl acetate + ethanol + [emim][triflate]	0.002	0.003	0.33	0.40

[a] $\delta y = (1/N)\,\Sigma\,|y_{\text{exptl}} - y_{\text{calcd}}|$. [b] $\sigma y = [\Sigma\,(y_{\text{exptl}} - y_{\text{calcd}})^2/(N - m)]^{1/2}$. [c] $\delta T = (1/N)\,\Sigma\,|T_{\text{exptl}} - T_{\text{calcd}}|$. [d] $\sigma T = [\Sigma\,(T_{\text{exptl}} - T_{\text{calcd}})^2/(N - m)]^{1/2}$. N is the number of experimental points, and m is the number of parameters for the model.

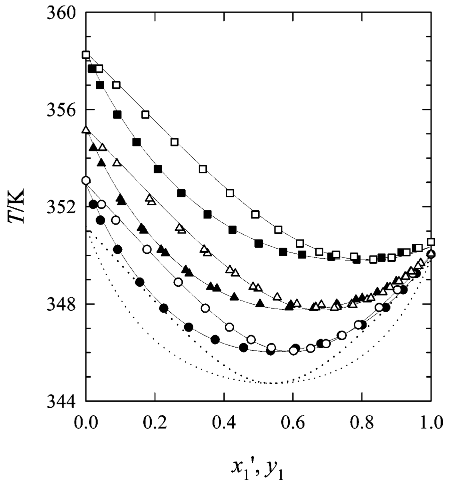

Figure 2. Temperature−composition diagram for ethyl acetate (1) + ethanol (2) + [emim][triflate] (3) at 100 kPa, with several mole fractions of IL: ●, x_1' experimental at $x_3 = 0.10$; ○, y_1 experimental at $x_3 = 0.10$; ▲, x_1' experimental at $x_3 = 0.20$; △, y_1 experimental at $x_3 = 0.20$; ■, x_1' experimental at $x_3 = 0.30$; □, y_1 experimental at $x_3 = 0.30$; solid lines, calculated; dotted lines, calculated for IL-free system.

Following this procedure, the parameters of the model reported in Table 6 could be determined. To obtain these parameters, ideal behavior of the vapor phase was assumed and the equilibrium conditions for the solvent, which are expressed in eq 4, were iteratively solved.

$$y_i P = X_i \gamma_i P_i^{\text{o}} \tag{4}$$

In eq 4, y_i is the vapor-phase mole fraction of solvent i; P is the total pressure in the system; X_i is the liquid-phase mole fraction based on the assumption of total dissociation of electrolytes; γ_i is the activity coefficient of component i obtained from the electrolyte NRTL model; and P_i^{o} is the vapor pressure of solvent i at equilibrium temperature. As far as the vapor pressures of pure solvents are concerned, they were calculated by using the Antoine coefficients given in Table 1.

With the electrolyte NRTL model and the parameters shown in Table 6, it is possible to work out the composition in the vapor phase and equilibrium temperature for each composition in the liquid phase. Thus, the standard and mean absolute deviations between the experimental and calculated values of molar fraction in the vapor phase and equilibrium temperature for binary and ternary systems were calculated and are reported in Table 7.

The ability of the model to reproduce the vapor−liquid equilibrium for this system can be seen in Figure 2 where the calculated and experimental vapor−liquid equilibrium of the ethyl acetate + ethanol + [emim][triflate] system are plotted

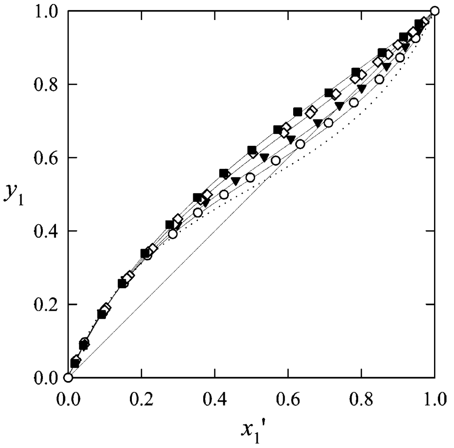

Figure 3. Salting-out effect of [emim][triflate] on vapor−liquid equilibrium of the ethyl acetate (1) + ethanol (2) system at 100 kPa for several IL mole fractions: ○, $x_3 = 0.05$; ▼, $x_3 = 0.10$; ◇, $x_3 = 0.20$; ■, $x_3 = 0.30$; solid lines, calculated at the same IL mole fractions; dotted line, calculated for IL-free system.

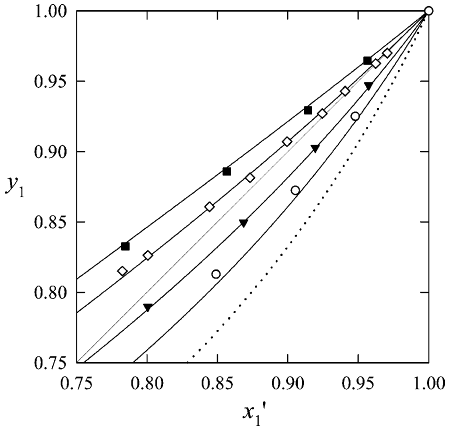

Figure 4. Composition diagram for ethyl acetate (1) + ethanol (2) + [emim][triflate] (3) at 100 kPa for several IL mole fractions: ○, $x_3 = 0.05$; ▼, $x_3 = 0.10$; ◇, $x_3 = 0.20$; ■, $x_3 = 0.30$; solid lines, calculated at the same IL mole fractions; dotted line, calculated for IL-free system.

on a (T, x_1', y_1) diagram for $x_3 = 0.10$, 0.20, and 0.30, the experimental and calculated values for $x_3 = 0.05$ being omitted for clarity. This figure reveals that the proposed model can properly fit the experimental vapor−liquid equilibrium data.

In Figure 2, the different influence of [emim][triflate] on the boiling points of the solvents can also be observed. At $x_1' = 0$ (pure ethanol), the higher the IL mole fraction the higher the boiling point, whereas at $x_1' = 1$ (pure ethyl acetate), the boiling point remains practically unchanged regardless of the IL mole fraction. As a result of this, when x_3 augments, the (T, x_1', y_1) curves go up by the left of the diagram remaining anchored to the right y-axis. Consequently, the minimum temperature raises and the azeotrope point moves to higher temperatures and higher x_1' values until it disappears.

Ethanol is more polar than ethyl acetate. Hence, ethyl acetate is supposed to be salted-out from the mixed solvent over the whole range of the liquid concentration. However, the salting-out effect is only appreciable at ethyl acetate mole fractions in the liquid phase higher than 0.2. At lower compositions, the (y_1, x_1') curve remains practically unchanged, regardless of the IL concentration. This can be observed in Figure 3, where the different solid lines that represent the (y_1, x_1') equilibrium separate from the diagonal as the IL mole fraction increases, but only for $x_1' > 0.2$. The [emim][triflate] produces a very slight crossover effect[46] between salting-in and salting-out in the ethyl acetate + ethanol system similar to that observed in the methyl acetate + methanol system,[13] but it is much less than that observed in the acetone + methanol system[12] with the same IL.

It is worth noting that small concentrations of [emim][triflate] produce a displacement of the azeotropic point of the ethyl acetate + ethanol system toward $x_1' > 0.542$ until the azeotrope disappears. Figure 4 shows that at $x_3 = 0.10$ the azeotrope has not been broken, and at $x_3 = 0.20$ we are exactly in the limit from which the azeotrope disappears. At $x_3 = 0.30$, the azeotrope has totally disappeared. From the electrolyte NRTL model, the mole fraction of [emim][triflate] at which the disappearance of the azeotrope for ethyl acetate + ethanol at 100 kPa occurs can be estimated, which results to be $x_3 = 0.20$. This concentration is higher than that necessary when the same IL was used to break the azeotrope in the acetone + methanol[12] and methyl acetate + methanol[13] systems.

Conclusions

The addition of [emim][triflate] to the ethyl acetate + ethanol mixture gives a considerable salting-out effect on ethyl acetate near the azeotropic point, this effect being unnoticeable at low ethyl acetate concentrations. At 100 kPa, the azeotrope is removed when the mole fraction of [emim][triflate] is higher as 0.20. This IL is also capable of breaking the azeotrope of the acetone + methanol[12] or methyl acetate + methanol[13] system.

The salt effect that [emim][triflate] produces on the ethyl acetate + ethanol system is less than that produced by zinc chloride,[16] which presents a breaking effect on the ethyl acetate + ethanol azeotrope at $x_3 = 0.075$. However, the use of [emim][triflate] as an entrainer in the extractive distillation process of ethyl acetate + ethanol mixtures has clear advantages over the use of inorganic salts or conventional entrainers. Although the relative salt effect can be lower, its total miscibility with both solvents allows us to use a great concentration of IL, and therefore a greater salt effect is produced.

Furthermore, its very low vapor pressure, similar to inorganic salts, guarantees that all the IL will leave the distillation column with the bottom stream without polluting the top stream and will easily separate from it.

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