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

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Isobaric vapor−liquid equilibria for the binary systems 1-propanol + water, 1-propanol + 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([emim][triflate]), and water + [emim][triflate] as well as the vapor−liquid equilibria for the 1-propanol + water + [emim][triflate] ternary system have been obtained at 100 kPa using a recirculating still. Electrolyte NRTL fitting parameters for the 1-propanol + water and water + [emim][triflate] systems were calculated. The measured ternary data were correlated using Mock's electrolyte NRTL model which reproduces reasonably well the experimental values. The results show that the addition of [emim][triflate] to 1-propanol + water produced an important salting-out effect, and the model predicts that at 100 kPa the azeotrope disappears when the mole fraction of ionic liquid in the liquid phase is greater than 0.34.

Introduction

Ionic liquids (ILs) are substances consisting primarily of relatively large organic cations and inorganic or organic anions. In contrast to conventional salts, their properties can be tailored, and thus they can have melting points around ambient but present no effective vapor pressure and high polar character.[1] Apart from that, some ionic liquids 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, e.g., azeotropic or close-boiling mixtures, is promising. Arlt and co-workers[3−8] suggested for the first time the use of ILs for separation of azeotropic mixtures, reporting the effect of different ionic liquids on several azeotropic systems. 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. What is more, 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 this way, ILs may be used as a new kind of entrainer in extractive/salt distillation processes. Moreover, the use of an IL presents obvious advantages over classical entrainers or inorganic salts. First, its practically nonvolatile character prevents its presence in distillate streams. Second, because of its greater solubility, a higher concentration of electrolyte can exist along the distillation column. Finally, the IL can be totally removed from the solvents by flash distillation of the column bottoms stream, and a pure IL liquid stream can be easily added to the reflux stream avoiding the problems associated with the handling of fused or solid salts.

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 or gases in ILs. As far as we know, only Zhao et al.[9,10] (ethanol + water, ethanol + methanol), Calvar et al.[11−13] (ethanol + water), Orchillés et al.[14−16] (acetone + methanol, methyl acetate + methanol, ethyl acetate + ethanol), and Zhang et al.[17,18] (water + 2-propanol, water + 1-propanol) have reported complete isobaric vapor−liquid equilibria data (T, x, y) for ternary systems containing ILs. We have not found complete isothermic vapor−liquid equilibria data (P, x, y) for ternary systems containing ILs in the literature.

As a continuation of our recently started research 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 paper the isobaric vapor−liquid equilibria for binary and ternary systems composed of 1-propanol, water, and 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([emim][triflate]) at 100 kPa.

The 1-propanol (1) + water (2) system shows, at atmospheric pressure, a minimum boiling point azeotrope at $x_1 \approx 0.43$. To break it, many salts have been used, not always successfully. Only calcium chloride,[19] calcium nitrate,[20] lithium nitrate,[21] and lithium chloride[22] have been reported to be effective in breaking this azeotrope. Only Zhang et al.[18] have used two ionic liquids to break the 1-propanol + water azeotrope. Using the IL 1-ethyl-3-methylimidazolium tetrafluoroborate ([emim][BF_4]), they have reported the breaking of the 1-propanol + water azeotrope with a mass fraction of the IL in the liquid phase of 0.700. However, the same authors also report[18] that by using the same mass fraction of 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]) the azeotrope could not be broken, but a larger amount of this IL would be required to achieve this effect. Consequently, one of the aims of this work is to determine if [emim][triflate] is also capable of breaking the 1-propanol + water azeotrope.

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10.1021/je800436u CCC: $40.75

Experimental Section

Materials. The solvents used were 1-propanol (Merck, GR grade, minimum mass fraction 99.5 %) and distilled water (Merck, HPLC grade). No impurities were detected by GC, using the same procedure and conditions described below for liquid mixtures. These chemicals were used without further purification. 1-Ethyl-3-methylimidazolium trifluoromethanesulfonate was 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 $x_w < 0.05$ %.

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 observed.

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,[23] 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.[24] 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 1-propanol + water system was obtained from an initial sample of pure 1-propanol at which different quantities of water were added, whereas for the binary solvent + IL systems, 1-propanol or water was added to an IL concentrated solution until a very diluted solution was achieved. For the ternary system, several water + IL mixtures of known composition were prepared, and different quantities of a mixture of 1-propanol + IL were added trying to keep the scheduled mole fraction of IL in each series. 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 408 K until constant mass. 1-Propanol 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 m × 3.2 mm) 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 water and 1-propanol 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. Antoine Coefficients Derived from the Present Vapor Pressure Measurements and Mean Absolute Deviations for 1-Propanol and Water

		Antoine coefficients[a]			
component	ΔT/K	A	B	C	$\sigma(P°)^b$/kPa
1-propanol	332 to 378	15.7038	3241.07	−77.83	0.037
water	331 to 382	15.6197	3387.08	−65.30	0.024

[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 1-Propanol (1) + Water (2) at 100 kPa

x_1	y_1	T/K	x_1	y_1	T/K
0.000	0.000	372.81	0.440	0.432	360.49
0.008	0.139	368.64	0.484	0.446	360.52
0.014	0.213	366.69	0.524	0.462	360.57
0.028	0.297	364.09	0.573	0.478	360.77
0.048	0.353	362.46	0.618	0.499	360.98
0.075	0.373	361.56	0.669	0.526	361.33
0.111	0.383	361.15	0.726	0.566	361.98
0.150	0.388	360.99	0.773	0.606	362.66
0.192	0.393	360.85	0.820	0.658	363.61
0.233	0.397	360.73	0.873	0.727	364.92
0.269	0.401	360.65	0.916	0.796	366.20
0.311	0.408	360.59	0.956	0.882	367.77
0.352	0.414	360.53	0.977	0.927	368.56
0.396	0.422	360.51	1.000	1.000	369.87

Results and Discussion

Vapor Pressures of 1-Propanol and Water. Vapor pressures of 1-propanol and water were measured in the range (330 to 390) K to test the performance of the apparatus. In Table 1, besides the Antoine coefficients for both solvents derived from our experimental data, the standard deviations between experimental and calculated vapor pressure data are shown. Regarding 1-propanol, our vapor pressure data and those reported in the literature[25,26] agree on average within 0.33 %. For water, the agreement with the literature values[27−29] is within 0.28 %.

1-Propanol + Water. Vapor−liquid equilibrium for the 1-propanol (1) + water (2) binary 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 1-propanol in the liquid and vapor phases, respectively, and T is the equilibrium temperature. The experimental results for this binary system show a good thermodynamic consistency according to the Van Ness test[30] modified by Fredenslund.[31] The test gave a mean absolute deviation between calculated and measured mole fractions of 1-propanol in the vapor phase of $\delta y = 0.0046$, which shows that the values are thermodynamically consistent.

To compare our experimental values with those existing in the literature obtained at 101.32 kPa, we have reduced our data to this pressure using the NRTL model as it will be described later. At this pressure, our data are in agreement within the experimental accuracy with those reported by Smirnova,[32] Kojima et al.,[33] Dawe et al.,[34] and Iliuta et al.,[19] although they disagree with those reported by Murti and van Winkle,[35] Dobroserdov and Il'ina,[36] and Lin et al.[37]

This system shows at 100 kPa a minimum boiling point azeotrope at $x_1 = 0.431$ and $T = 360.49$ K, which can be

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

x_3	T/K	x_3	T/K	x_3	T/K
0.0000	369.86	0.0778	371.09	0.2016	373.39
0.0081	370.05	0.0822	371.22	0.2164	373.69
0.0106	370.13	0.0948	371.37	0.2238	373.83
0.0143	370.15	0.0989	371.48	0.2390	374.18
0.0186	370.29	0.1128	371.69	0.2554	374.64
0.0230	370.30	0.1139	371.76	0.2705	374.95
0.0279	370.43	0.1275	371.95	0.2777	375.25
0.0345	370.46	0.1325	372.02	0.2859	375.41
0.0397	370.56	0.1421	372.25	0.2969	375.63
0.0477	370.65	0.1557	372.48	0.3027	375.73
0.0521	370.77	0.1634	372.66	0.3210	376.39
0.0627	370.90	0.1780	372.96	0.3354	376.63
0.0660	371.02	0.1782	372.85	0.3455	377.04

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

x_3	T/K	x_3	T/K	x_3	T/K
0.0000	372.81	0.1091	375.60	0.2482	380.90
0.0029	372.95	0.1190	375.87	0.2635	381.75
0.0069	373.13	0.1298	376.21	0.2836	382.56
0.0143	373.37	0.1413	376.56	0.3010	383.81
0.0251	373.67	0.1546	376.99	0.3199	384.89
0.0367	373.94	0.1699	377.55	0.3359	385.70
0.0489	374.19	0.1868	378.25	0.3561	387.14
0.0603	374.44	0.2016	378.84	0.3741	388.41
0.0725	374.71	0.2167	379.51	0.3971	389.81
0.0874	375.05	0.2327	380.15	0.4145	391.10
0.0988	375.34				

interpolated from the experimental data. These data agree very well within the experimental accuracy with those reported by Gabaldón et al.[38] and Vercher et al.,[20] both obtained at 100 kPa. What is more, the azeotropic point at 101.32 kPa extrapolated from our experimental data ($x_1 = 0.431$, $T = 360.92$ K) agrees with those reported in the literature[39] obtained at this pressure.

Solvent + IL Binary Systems. Boiling temperatures for 1-propanol (1) + [emim][triflate] (3) and water (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.

The boiling point elevation produced by [emim][triflate] on 1-propanol and water can be compared with those produced on other solvents. When the IL mole fraction is $x_3 = 0.35$, the temperature rise is about 14 K for methanol[14] and water, 12 K for acetone,[14] 9 K for ethanol,[16] 7 K for 1-propanol, 5 K for methyl acetate,[15] and less than 1.5 K for ethyl acetate.[16]

1-Propanol + Water + [emim][triflate] System. Vapor−liquid equilibria for the 1-propanol (1) + water (2) + [emim][triflate] (3) system, at 100 kPa, were obtained by keeping the IL mole fraction constant in each of the four series at $x_3 \approx 0.055$, 0.10, 0.19, and 0.30. These values are shown in Table 5, where x_1' is the mole fraction of 1-propanol in the liquid phase expressed on an IL-free basis; y_1 is the mole fraction of 1-propanol in the vapor phase; and T is the equilibrium temperature.

Modeling the Phase Equilibrium. As indicated in previous papers,[14−16] we have used 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[40] for liquid-phase activity coefficients. Chen et al.[41] derived a model for single-solvent + electrolyte systems, and later Mock et al.[42,43] extended it to mixed-solvent + electrolyte systems, by neglecting the long-range interaction contribution term.

Table 5. Vapor−Liquid Equilibrium Data for 1-Propanol (1) + Water (2) + [emim][triflate] (3) at 100 kPa

x_3	x_1'	y_1	T/K
0.0550	0.000	0.000	374.28
0.0543	0.009	0.059	372.38
0.0538	0.030	0.189	369.25
0.0533	0.079	0.301	365.30
0.0550	0.157	0.373	363.42
0.0559	0.238	0.410	362.60
0.0558	0.334	0.445	362.14
0.0566	0.434	0.481	362.08
0.0576	0.523	0.516	362.32
0.0583	0.604	0.554	362.71
0.0592	0.680	0.603	363.40
0.0597	0.752	0.663	364.30
0.0594	0.820	0.724	365.37
0.0581	0.879	0.784	366.51
0.0587	0.928	0.846	367.86
0.0590	0.961	0.901	369.02
0.0589	0.980	0.945	369.82
0.0627	1.000	1.000	370.90
0.1015	0.000	0.000	375.27
0.1004	0.024	0.107	372.67
0.1024	0.058	0.198	370.54
0.1009	0.106	0.279	367.41
0.0990	0.164	0.346	365.32
0.0991	0.240	0.401	364.23
0.0996	0.323	0.439	363.67
0.0992	0.403	0.473	363.45
0.0985	0.483	0.511	363.53
0.0983	0.571	0.563	363.93
0.0983	0.658	0.616	364.58
0.0981	0.737	0.678	365.51
0.0974	0.798	0.728	366.47
0.0987	0.851	0.778	367.53
0.1003	0.897	0.841	368.62
0.1030	0.935	0.882	369.76
0.1041	0.966	0.936	370.51
0.0989	1.000	1.000	371.48
0.2069	0.000	0.000	378.88
0.2010	0.023	0.081	376.61
0.1980	0.054	0.158	375.05
0.1956	0.093	0.232	372.30
0.1925	0.146	0.304	370.18
0.1910	0.211	0.371	368.51
0.1909	0.284	0.427	367.48
0.1904	0.361	0.478	367.02
0.1908	0.450	0.527	366.77
0.1903	0.542	0.585	366.97
0.1897	0.624	0.640	367.56
0.1887	0.699	0.694	368.11
0.1882	0.761	0.740	368.91
0.1863	0.829	0.799	369.75
0.1883	0.883	0.848	370.68
0.1877	0.923	0.893	371.54
0.1886	0.955	0.932	372.28
0.1782	1.000	1.000	372.85
0.3010	0.000	0.000	383.81
0.3164	0.013	0.036	383.33
0.3165	0.029	0.081	382.06
0.3120	0.066	0.166	379.78
0.3158	0.126	0.270	377.54
0.3142	0.184	0.344	375.79
0.3143	0.248	0.405	374.19
0.3136	0.326	0.465	373.08
0.3113	0.403	0.522	372.46
0.3061	0.471	0.577	372.10
0.3029	0.548	0.633	372.14
0.3000	0.628	0.690	372.25
0.2988	0.705	0.741	372.62
0.2940	0.768	0.794	372.96
0.2951	0.837	0.848	373.74
0.2945	0.894	0.896	374.29
0.2955	0.956	0.951	374.97
0.2969	1.000	1.000	375.63

The model produces expressions for the liquid-phase activity coefficients of 1-propanol (1) and water (2) in a binary or ternary

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}
1-propanol	water	0.510	1864.8	7981.5
1-propanol	[emim][triflate]	0.631	7882.2	−808.2
water	[emim][triflate]	0.870	7555.9	−1254.2

system containing [emim][triflate] (3). These equations have been reported in a previous paper.[20] According to the proposed method, we must determine the nine binary adjustable parameters for all the solvent + solvent and solvent + electrolyte pairs in the system to represent the phase equilibrium of mixed-solvent + electrolyte systems.

The 1−2 binary solvent−solvent parameters were obtained from the vapor−liquid equilibria data of the 1-propanol (1) + water (2) system shown in Table 2, whereas those corresponding to the 2−3 binary solvent−IL were obtained from the vapor−liquid equilibria data of the water (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

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

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.

Regarding the parameters related to the 1−3 binary solvent−IL pair, we have to stress that they could not be estimated from the vapor−liquid equilibria data of the 1-propanol (1) + [emim][triflate] (3) binary system because the experimental data shown in Table 3 are poorly fitted by the electrolyte NRTL model. The same was found for the ethyl acetate + [emim][triflate] and methyl acetate + [emim][triflate] binary systems.[15,16] Perhaps, due to the fact that these systems show significant positive deviations for the activity coefficients, neglecting the long-range interaction contribution term may not be totally right.

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 1-propanol (1) + water (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 the (1−3) binary system were obtained by minimization of the objective function F_2

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

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.

Following this procedure, the parameters of the model could be determined, and their values are reported in Table 6. These parameters were obtained by assuming ideal behavior for the vapor phase and iteratively solving the equilibrium conditions expressed in eq 3 for the solvent.

$$y_i P = X_i \gamma_i P_i^{\text{o}} \tag{3}$$

where, 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 of solvent i calculated as if total dissociation of electrolytes had happened; 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. The vapor pressures of pure solvents were calculated using the Antoine coefficients given in Table 1.

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
1-propanol + water	0.005	0.006	0.13	0.17
water + [emim][triflate]			0.01	0.08
1-propanol + water + [emim][triflate]	0.005	0.007	0.39	0.53

[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.

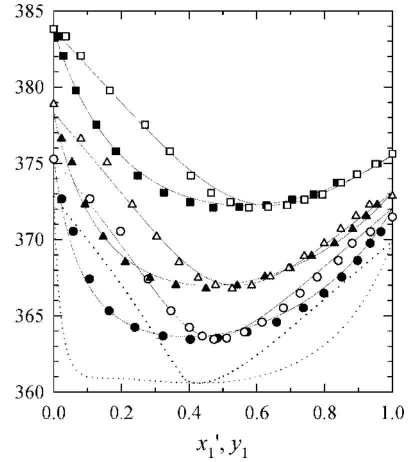

Figure 1. Temperature−composition diagram for 1-propanol (1) + water (2) + [emim][triflate] (3) at 100 kPa, with several mole fractions of IL: ●, x_1' experimental at $x_3 \approx 0.10$; ○, y_1 experimental at $x_3 \approx 0.10$; ▲, x_1' experimental at $x_3 \approx 0.19$; △, y_1 experimental at $x_3 \approx 0.19$; ■, x_1' experimental at $x_3 \approx 0.30$; □, y_1 experimental at $x_3 \approx 0.30$; solid lines, calculated; dotted lines, calculated for IL-free system.

With the electrolyte NRTL model and the parameters shown in Table 6, it was possible to calculate the composition in the vapor phase and equilibrium temperature for each composition in the liquid phase. In this way, the standard and mean absolute deviations between the experimental and calculated values of mole fraction in the vapor phase and equilibrium temperature for binary and ternary systems were calculated and are reported in Table 7.

In Figure 1, the calculated and experimental vapor−liquid equilibrium of the 1-propanol + water + [emim][triflate] points are plotted on a (T, x_1', y_1) diagram for $x_3 \approx 0.10$, 0.19, and 0.30, the experimental and calculated values for $x_3 \approx 0.05$ being omitted for clarity. The model is seen to be able to properly fit the experimental vapor−liquid equilibrium data. In this way, the ability of the model to reproduce the vapor−liquid equilibrium for this system is demonstrated.

In the presence of electrolytes, where their interaction with water and 1-propanol is related to several factors such as polarity, hydrogen bonding, etc., 1-propanol should be salted-out from the mixed solvent over the whole range of the liquid concentrations. However, we only note an appreciable salting-out effect when 1-propanol mole fractions in the liquid phase are higher than 0.2, whereas a sharp salting-in effect appears at lower compositions. This can be observed in Figure 2, where

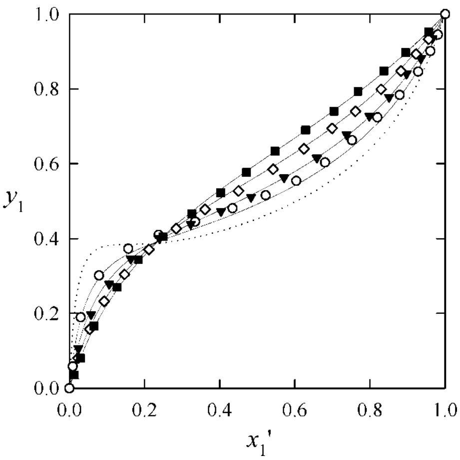

Figure 2. Salting effect of [emim][triflate] on vapor−liquid equilibrium of the 1-propanol (1) + water (2) system at 100 kPa for several IL mole fractions: ○, $x_3 \approx 0.05$; ▼, $x_3 \approx 0.10$; ◇, $x_3 \approx 0.19$; ■, $x_3 \approx 0.30$; solid lines, calculated at the same IL mole fractions; dotted line, calculated for IL-free system.

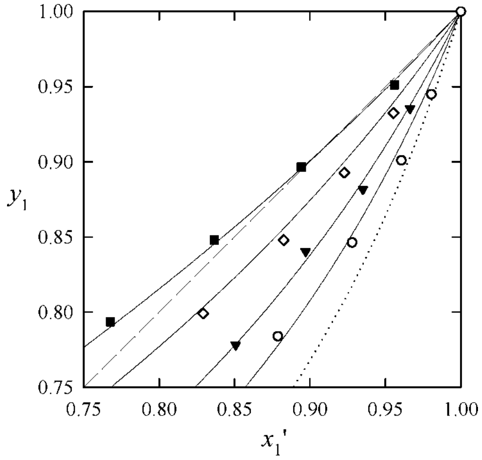

Figure 3. Composition diagram for 1-propanol (1) + water (2) + [emim][triflate] (3) at 100 kPa for several IL mole fractions: ○, $x_3 \approx 0.05$; ▼, $x_3 \approx 0.10$; ◇, $x_3 \approx 0.19$; ■, $x_3 \approx 0.30$; solid lines, calculated at the same IL mole fractions; dotted line, calculated for IL-free system.

the different solid lines, which represent the (y_1, x_1') equilibrium, separate from the diagonal for $x_1' > 0.2$, while they are closer to it for $x_1' < 0.2$, as the IL mole fraction increases. The [emim][triflate] produces a very strong crossover effect[44] between salting-in and salting-out in the 1-propanol + water system, higher than that observed in the acetone + methanol,[14] methyl acetate + methanol,[15] or ethyl acetate + ethanol systems[16] with the same IL.

It is worth noting that an increase of the [emim][triflate] mole fraction produces a displacement of the azeotropic point of the 1-propanol + water system toward $x_1' > 0.431$. Figure 3 shows that at $x_3 = 0.30$ the azeotrope has not been yet eliminated, and a larger amount of [emim][triflate] would be required to achieve this effect. From the electrolyte NRTL model, the mole fraction of [emim][triflate] at which the disappearance of the azeotrope for 1-propanol + water at 100 kPa occurs is estimated to be $x_3 = 0.34$. So, [emim][triflate] seems to be a better entrainer for the same system (1-propanol + water) than [emim][BF_4] or [bmim][BF_4] since Zhang et al.[18] achieved the breaking of the azeotrope with an [emim][BF_4] mass fraction of 0.700 ($x_3 \approx 0.41$), whereas the same mass fraction of [bmim][BF_4] ($x_3 \approx 0.38$) could not break the azeotrope.

When an inorganic salt is added to a mixture of 1-propanol + water, a minimum equilibrium temperature which differs from that corresponding to the azeotropic point is achieved,[19−22,45] the effect being more noticeable as the salt concentration increases. The same behavior is observed in Figure 1 although it is less evident than for calcium nitrate or calcium chloride.[45] As far we know, this effect may be related with the ability of the salt for breaking the azeotrope. The less salt concentration is needed to break the azeotrope, the larger temperature difference between the minimum and azeotropic point is observed.

Conclusions

The electrolyte NRTL model is suitable to predict the VLE in the presence of an IL such as [emim][triflate]. This allows the extension of the model to ionic liquids.

The addition of [emim][triflate] to the 1-propanol + water mixture gives a considerable salting-out effect on 1-propanol near the azeotropic point, but there is a salting-in effect at low 1-propanol mole fractions. The azeotropic point of the 1-propanol + water system is displaced toward upper values of x_1', i.e., the higher the IL mole fraction, the higher the relative volatility. Although this displacement is greater than for the acetone + methanol,[14] methyl acetate + methanol,[15] and ethyl acetate + ethanol[16] systems, the azeotrope could not be removed using a mole fraction of [emim][triflate] of 0.30, at 100 kPa. The electrolyte NRTL model predicts that the azeotrope for 1-propanol + water at 100 kPa disappears when the mole fraction of [emim][triflate] is $x_3 = 0.34$. Hence, the [emim][triflate] is a better entrainer than [emim][BF_4] or [bmim][BF_4] for the 1-propanol + water system.

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Received for review June 17, 2008. Accepted July 25, 2008. This research was supported by the Ministry of Education and Science of Spain and FEDER funds of the European Union, through Projects no. CTQ2004-02977/PPQ and CTQ2007-60831/PPQ.

JE800436U