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Isobaric Vapor−Liquid Equilibria of 1-Propanol + Water + Trifluoromethanesulfonate-Based Ionic Liquid Ternary Systems at 100 kPa

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ABSTRACT: Isobaric vapor−liquid equilibria (VLE) for the 1-propanol + 1-butyl-3-ethylimidazolium trifluoromethanesulfonate ([beim][triflate]), water + [beim][triflate], 1-propanol + 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate ([bmpyr][triflate]), and water + [bmpyr][triflate] binary systems, as well as the VLE for the 1-propanol + water + [beim][triflate] and 1-propanol + water + [bmpyr][triflate] ternary systems have been obtained at 100 kPa using a recirculating still. The salting-out effect on the 1-propanol produced by the [bmpyr][triflate] was stronger than that produced by the [beim][triflate], although for the IL concentrations used in this study the effect was not enough to break the azeotrope, unlike of that produced by the 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([emim][triflate]). The electrolyte nonrandom two-liquid (NRTL) model was used for fitting successfully the experimental data.

INTRODUCTION

Ionic liquids (ILs) are typically salts made up of relatively large organic cations and inorganic or organic anions. As a consequence of their asymmetric structure and ionic interactions, they are liquid below 100 °C and present no effective vapor pressure. In addition to this, they have other interesting properties such as relatively low viscosity and good stability up to 200 °C and can be used as "green" solvents replacing volatile organic compounds. These special characteristics have converted ILs into chemicals of high commercial interest.[1−4]

The use of ILs in separation technology is becoming an important alternative for separation of azeotropic or close-boiling mixtures, mainly in cases where the IL interacts more strongly with one solvent modifying the relative volatility, and therefore improving the separation, so as to finally cause the azeotrope to disappear. Moreover, they present obvious advantages over classical entrainers or inorganic salts. Compared with classical liquid entrainers, the zero vapor pressure of IL allow us to totally recover, by flash distillation, and reuse them in the reflux stream free of the least volatile solvent. Related to inorganic salts, it can be said that the problems of corrosion and managing associated with the use of fused salts are avoided. Besides, ILs usually have a higher solubility in organic solvents than inorganic salts, which allows us to use greater concentrations of electrolyte.

Nevertheless, there are limited investigations on vapor−liquid equilibria (VLE) with ILs. Among them, we should point out those from Seiler et al.[5,6] and Lei et al.[7] since in them the use of ILs for separation of azeotropic mixtures was suggested for the first time.

Furthermore, in most cases, the studies on the VLE of IL-containing systems are uncompleted because they are limited to determine the vapor pressure and/or the activity coefficients of one or two solvents in ILs. For ternary systems containing ILs, there are not too many works reporting complete isobaric VLE data (T, x, y).

As a continuation of our research line consisting of the use of ILs to modify the VLE of solvent mixtures, we present in this paper the isobaric VLE for the binary and ternary systems composed of 1-propanol, water, 1-butyl-3-ethylimidazolium trifluoromethanesulfonate ([beim][triflate], CAS Registry No. 145022-48-6), and 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate ([bmpyr][triflate], CAS Registry No. 367522-96-1), at 100 kPa. It is worth noting that only 8 references for the [beim][triflate] and 89 for the [bmpyr][triflate] are recorded in the CAPLUS database of Chemical Abstracts Service (CAS),[8] whereas for the 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]), perhaps the most studied IL, there are more than 3500 references.

The 1-propanol (1) + water (2) system forms, at atmospheric pressure, a minimum boiling point azeotrope at $x_1 \approx 0.43$, which causes the 1-propanol separation by distillation from spent aqueous solutions to be unfeasible. Some salts[9−12] have been demonstrated to be effective in breaking the azeotrope, and until now, only Zhang et al.[13] and Orchillés et al.[14] have used ILs to break the 1-propanol + water azeotrope. The two ILs investigated in this work, as well as that used in a previous work,[14] have the same anion ([triflate]$^-$) although the cation has a different size and structure. In recent research[15] we found that, in the extractive distillation of the acetone + methanol system, the size and structure of the cation did not seem to be an important factor in its behavior as entrainer. Consequently, another of the aims of this work is to determine if the cation interacts in a different manner on 1-propanol and water.

EXPERIMENTAL SECTION

Materials. The chemicals used were 1-propanol (Merck, GR grade) and distilled water (Merck, HPLC grade). No impurities

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Table 1. Specifications of Chemical Samples

chemical name	source	mass fraction purity	purification method	final water mass fraction	analysis method
1-propanol	Merck	0.995	none	no detected	GC[d]
water	Merck	c	none		
[beim][triflate][a]	Solvent Innovation	0.98	vacuum desiccation	0.0005	KF[e]
[bmpyr][triflate][b]	Solvent Innovation	0.98	vacuum desiccation	0.0005	KF[e]

[a] [beim][triflate] = 1-butyl-3-ethylimidazolium trifluoromethanesulfonate. [b] [bmpyr][triflate] = 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate. [c] Conductivity at 298.15 K: $\sigma \leq 1\ \mu\text{S}\cdot\text{cm}^{-1}$. [d] GC = gas–liquid chromatography. [e] KF = Karl Fischer titration.

were detected by gas chromatography (GC), using the same procedure and conditions described below for the liquid mixtures. These solvents were directly used without further purification. The ILs were supplied by Solvent Innovation (Purum grade). Because of their hygroscopic character, they were desiccated at 0.2 Pa overnight prior to use. The water mass fraction in the IL determined by Karl Fischer titration was $x_w < 0.0005$. The chemical specifications of the materials used are reported in Table 1.

After using the liquid mixtures in the VLE apparatus, their solvents were removed by heating and stirring under a high vacuum (408 K, 0.2 Pa) for 48 h to recover the IL. Thus, the IL was reused provided that no changes in its behavior as an entrainer were observed.

Apparatus and Procedure. VLE measurements were made with an all-glass dynamic recirculating still (Pilodist, modified Labodest model), equipped with a Cottrell circulation pump,[16] 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.[17] 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 highest standard uncertainty for temperature measurements was 0.1 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 solvent + IL systems was obtained from an IL concentrated solution at which different quantities of 1-propanol or water were added until a very diluted solution was achieved. For the ternary system, several water + IL mixtures of distinct composition were taken, and different quantities of a mixture of 1-propanol + IL having a slightly higher concentration than the original one were added, trying to keep the scheduled IL mole fraction in each series. A Mettler AE200 analytical balance with a standard uncertainty of 0.0001 g was used to prepare the samples. Only when a 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 separating the volatile components 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 (2.44 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 and oven temperatures, 473 K, and detector temperature, 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 verify experimentally. 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.

Table 2. Vapor–Liquid Equilibrium Data for 1-Propanol (1) + [beim][triflate] (3) at 100 kPa[a]

x_3	T/K	x_3	T/K	x_3	T/K
0.0000	369.8	0.1559	373.2	0.3138	378.9
0.0115	370.1	0.1678	373.5	0.3242	379.7
0.0215	370.2	0.1792	373.9	0.3333	380.3
0.0338	370.5	0.1920	374.3	0.3466	380.8
0.0494	370.7	0.2046	374.7	0.3582	381.5
0.0635	371.0	0.2196	375.2	0.3734	382.3
0.0809	371.3	0.2428	376.1	0.3881	383.0
0.0974	371.7	0.2593	376.7	0.3961	383.8
0.1120	372.0	0.2743	377.1	0.4024	383.9
0.1258	372.3	0.2859	377.9	0.4096	384.6
0.1392	372.7	0.3057	378.5	0.4156	385.0

[a] Standard uncertainties u are: $u(T) = 0.1$ K, $u(p) = 0.05$ kPa, and the combined expanded uncertainty U_c is $U_c(x_3) = 0.0001$ (0.95 level of confidence).

■ RESULTS AND DISCUSSION

Experimental Data. Boiling temperatures for 1-propanol (1) + [beim][triflate] (3), water (2) + [beim][triflate] (3), and 1-propanol (1) + [bmpyr][triflate] (3), and water (2) + [bmpyr][triflate] (3) were measured at 100 kPa, and the experimental results are reported in Tables 2 to 5, respectively. In these tables, x_3 is the mole fraction of IL in the liquid phase, and T is the equilibrium temperature.

In addition, VLE data for the 1-propanol (1) + water (2) + [beim][triflate] (3) and 1-propanol (1) + water (2) + [bmpyr][triflate] (3) ternary systems, at 100 kPa, were obtained at IL mole fraction constants of $x_3 \approx 0.05$, 0.19, and 0.31. These values are shown in Tables 6 and 7, respectively, where x_3 is the mole fraction of IL in the liquid phase; 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.

Calculation of the Vapor–Liquid Phase Equilibrium. The electrolyte nonrandom two-liquid (NRTL) model has been just as well for correlating the VLE results reported in Tables 6 and 7 as it was in previous papers dealing with ILs.[18−20] This model is an extension of the nonrandom two-liquid local composition

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

x_3	T/K	x_3	T/K	x_3	T/K
0.0000	372.84	0.0869	373.75	0.2037	376.06
0.0033	373.00	0.1039	373.93	0.2144	376.48
0.0067	373.12	0.1177	374.12	0.2310	377.06
0.0141	373.25	0.1509	374.71	0.2388	377.50
0.0269	373.38	0.1649	375.02	0.2522	377.99
0.0414	373.45	0.1798	375.41	0.2641	378.52
0.0563	373.53	0.1916	375.71	0.2814	379.31
0.0715	373.64				

[a] Standard uncertainties u are: $u(T) = 0.05$ K, $u(p) = 0.05$ kPa, and the combined expanded uncertainty U_c is $U_c(x_3) = 0.0001$ (0.95 level of confidence).

Table 4. Vapor−Liquid Equilibrium Data for 1-Propanol (1) + [bmpyr][triflate] (3) at 100 kPa[a]

x_3	T/K	x_3	T/K	x_3	T/K
0.000	369.8	0.176	373.0	0.328	378.1
0.015	370.1	0.190	373.4	0.339	378.8
0.027	370.3	0.208	373.9	0.350	379.2
0.040	370.5	0.221	374.3	0.363	379.8
0.056	370.7	0.234	374.5	0.374	380.3
0.074	371.0	0.247	375.0	0.386	381.1
0.093	371.3	0.261	375.6	0.399	381.8
0.112	371.7	0.273	376.0	0.413	382.7
0.129	372.0	0.289	376.6	0.419	383.1
0.146	372.3	0.303	377.3	0.427	383.7
0.162	372.7	0.320	378.0	0.442	384.8

[a] Standard uncertainties u are: $u(T) = 0.1$ K, $u(p) = 0.05$ kPa, and the combined expanded uncertainty U_c is $U_c(x_3) = 0.0001$ (0.95 level of confidence).

Table 5. Vapor−Liquid Equilibrium Data for Water (2) + [bmpyr][triflate] (3) at 100 kPa[a]

x_3	T/K	x_3	T/K	x_3	T/K
0.000	372.84	0.136	374.95	0.302	380.87
0.003	372.96	0.153	375.29	0.314	381.58
0.007	373.10	0.171	375.82	0.334	382.31
0.012	373.21	0.186	376.22	0.355	383.60
0.023	373.40	0.204	376.81	0.374	384.94
0.037	373.58	0.221	377.35	0.402	386.82
0.053	373.69	0.237	377.96	0.433	388.81
0.071	373.89	0.253	378.75	0.466	391.57
0.104	374.32	0.277	379.50	0.512	394.81
0.120	374.66	0.288	380.15		

[a] Standard uncertainties u are: $u(T) = 0.05$ K, $u(p) = 0.05$ kPa, and the combined expanded uncertainty U_c is $U_c(x_3) = 0.0001$ (0.95 level of confidence).

proposed by Renon and Prausnitz[21] for liquid-phase activity coefficients. Chen et al.[22] derived a model for single-solvent + electrolyte systems, and later Mock et al.[23,24] extended it to mixed-solvent + electrolyte systems, by neglecting the long-range interaction contribution term.

Table 6. Vapor−Liquid Equilibrium Data for 1-Propanol (1) + Water (2) + [beim][triflate] (3) at 100 kPa[a]

x_3	x_1'	y_1	T/K	x_3	x_1'	y_1	T/K
0.0537	0.000	0.000	373.50	0.1823	0.468	0.468	366.98
0.0532	0.010	0.055	371.99	0.1831	0.544	0.519	367.18
0.0526	0.034	0.147	369.44	0.1828	0.613	0.563	367.50
0.0524	0.087	0.258	366.07	0.1827	0.678	0.619	368.18
0.0522	0.142	0.317	364.35	0.1825	0.746	0.680	368.94
0.0425	0.191	0.353	363.21	0.1854	0.822	0.749	370.08
0.0523	0.281	0.380	362.50	0.1865	0.878	0.815	371.23
0.0429	0.330	0.410	362.19	0.1865	0.926	0.887	372.40
0.0531	0.443	0.441	362.11	0.1856	1.000	1.000	374.10
0.0534	0.512	0.473	362.26	0.3446	0.000	0.000	382.28
0.0536	0.577	0.507	362.53	0.3223	0.016	0.027	380.47
0.0542	0.640	0.543	363.03	0.3239	0.038	0.061	379.43
0.0556	0.704	0.587	363.62	0.3210	0.077	0.115	378.49
0.0553	0.773	0.650	364.67	0.3166	0.131	0.184	377.05
0.0561	0.841	0.735	366.04	0.3086	0.188	0.242	375.58
0.0567	0.894	0.796	367.49	0.3034	0.250	0.303	373.89
0.0569	0.937	0.871	368.76	0.3016	0.315	0.358	372.88
0.0565	1.000	1.000	371.15	0.2991	0.382	0.413	372.27
0.1983	0.000	0.000	375.92	0.3014	0.459	0.469	372.57
0.1912	0.022	0.051	374.56	0.3012	0.537	0.528	373.13
0.1861	0.046	0.095	373.35	0.2977	0.622	0.592	373.15
0.1910	0.088	0.168	371.79	0.2941	0.693	0.657	373.40
0.1873	0.137	0.226	370.32	0.2903	0.757	0.715	374.06
0.1835	0.192	0.280	368.93	0.2934	0.820	0.784	375.16
0.1837	0.252	0.329	367.86	0.2956	0.885	0.845	376.08
0.1824	0.316	0.369	367.09	0.2937	0.928	0.901	376.57
0.1816	0.383	0.412	366.88	0.2958	1.000	1.000	378.21

[a] Standard uncertainties u are: $u(T) = 0.05$ K and $u(p) = 0.05$ kPa. Combined expanded uncertainties $U_c(x_1') = U_c(x_3) = U_c(y_1) = 0.001$ (0.95 level of confidence).

The model makes it possible to generate expressions for the liquid-phase activity coefficients of 1-propanol (1) and water (2) in a binary or ternary system containing an IL (3), which is due to behave as an electrolyte. These equations have been reported in a previous paper,[10] and according to them, we must determine 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. Six of them are energy parameters (Δg_{12}, Δg_{21}, Δg_{13}, Δg_{31}, Δg_{23}, and Δg_{32}), the rest being nonrandomness factors ($\alpha_{12} = \alpha_{21}$, $\alpha_{13} = \alpha_{31}$, and $\alpha_{23} = \alpha_{32}$).

The 1−2 binary 1-propanol−water parameters were taken from a previous work,[14] whereas those corresponding to the 2−3 binary water−IL were obtained by adjusting to the model the VLE data of the water (2) + IL (3) binary systems shown in Tables 3 and 5 and are reported in Table 8. In all of those cases, the parameters were obtained by minimization of the objective function F_1:

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

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

Table 7. Vapor−Liquid Equilibrium Data for 1-Propanol (1) + Water (2) + [bmpyr][triflate] (3) at 100 kPa[a]

x_3	x_1'	y_1	T/K	x_3	x_1'	y_1	T/K
0.0546	0.000	0.000	373.73	0.1881	0.481	0.495	366.83
0.0538	0.010	0.061	372.03	0.1884	0.558	0.547	367.17
0.0531	0.032	0.165	369.20	0.1882	0.625	0.592	367.52
0.0529	0.086	0.267	365.74	0.1877	0.688	0.642	367.98
0.0528	0.141	0.329	364.00	0.1875	0.753	0.692	368.69
0.0529	0.212	0.363	362.97	0.1918	0.827	0.760	369.94
0.0527	0.281	0.391	362.39	0.1913	0.881	0.817	370.92
0.0533	0.372	0.422	362.07	0.1903	0.926	0.873	372.01
0.0534	0.452	0.453	362.02	0.1900	1.000	1.000	373.44
0.0536	0.525	0.482	362.11	0.3402	0.000	0.000	382.74
0.0537	0.590	0.518	362.56	0.3274	0.015	0.030	381.09
0.0538	0.652	0.556	363.05	0.3196	0.035	0.066	379.90
0.0537	0.707	0.597	363.63	0.3145	0.070	0.124	378.42
0.0535	0.773	0.658	364.66	0.3175	0.123	0.202	376.71
0.0553	0.848	0.746	366.10	0.3131	0.180	0.270	375.37
0.0560	0.898	0.810	367.43	0.3133	0.246	0.333	374.16
0.0567	0.937	0.870	368.70	0.3096	0.312	0.390	372.85
0.0565	1.000	1.000	371.13	0.3072	0.387	0.444	372.01
0.1963	0.000	0.000	376.39	0.3066	0.461	0.497	372.44
0.1941	0.022	0.057	374.99	0.3026	0.542	0.554	372.47
0.1910	0.045	0.108	373.53	0.3014	0.626	0.620	372.59
0.1898	0.084	0.185	371.79	0.2988	0.704	0.679	373.02
0.1896	0.136	0.247	370.18	0.2953	0.768	0.734	373.60
0.1903	0.195	0.307	368.76	0.2965	0.832	0.796	374.52
0.1871	0.258	0.358	367.61	0.2986	0.895	0.863	375.41
0.1863	0.319	0.400	367.14	0.2965	0.936	0.914	376.11
0.1880	0.391	0.442	366.90	0.2958	1.000	1.000	376.97

[a] Standard uncertainties u are: $u(T)$ = 0.05 K, and $u(p)$ = 0.05 kPa. Combined expanded uncertainties $U_c(x_1')$ = $U_c(x_3)$ = $U_c(y_1)$ = 0.001 (0.95 level of confidence).

Table 8. 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

			$\Delta g_{i,j}$	$\Delta g_{j,i}$
i component	j component	$\alpha_{i,j}$	J·mol^{-1}	J·mol^{-1}
1-propanol (1)	water (2)	0.510[a]	1864.8[a]	7981.5[a]
water (2)	[beim][triflate] (3)	0.759	9627.8	−455.9
water (2)	[bmpyr][triflate] (3)	0.620	10241.7	−1752.6
1-propanol (1)	[beim][triflate] (3)	0.738	7348.6	−1271.6
1-propanol (1)	[bmpyr][triflate] (3)	0.833	7116.8	−428.8

[a] From Orchillés et al.[14]

Table 9. 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
water + [beim][triflate]			0.055	0.07
water + [bmpyr][triflate]			0.17	0.12
1-propanol + water + [beim][triflate]	0.006	0.009	0.23	0.32
1-propanol + water + [bmpyr][triflate]	0.008	0.010	0.28	0.36

[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.

As far as the parameters related to the 1−3 binary 1-propanol−IL pairs are concerned, we have to stress that they were established from the experimental VLE data of the 1-propanol (1) + water (2) + IL (3) systems and the electrolyte NRTL model. We had to proceed in such a manner because the experimental data shown in Tables 2 and 4 were poorly fitted by the electrolyte NRTL model. The same was found for the ethyl acetate + [emim][triflate],[20] methyl acetate + [emim][triflate],[19] and 1-propanol + [emim][triflate][14] binary systems. Perhaps neglecting the long-range interaction contribution term in systems showing significant positive deviations for the activity coefficients is the fact responsible for this behavior.

Accordingly, the model was applied by taking into account the 1−2 and 2−3 binary parameters shown in Table 8, whereas those corresponding to the 1−3 binary system were obtained by minimization of the objective function F_2:

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

where γ_i is the activity coefficient of solvent i.

Following this procedure, we were able to obtain the binary parameters 1−3 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 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^{o}_i is the vapor pressure of solvent i at equilibrium temperature which was calculated by using the Antoine coefficients obtained with the same recirculating still.[14] Results for the optimized binary parameters 1−3 are also summarized in Table 8.

With the electrolyte NRTL model and the parameters shown in Table 8, 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 9.

In Figures 1 and 2 the calculated and experimental VLE of the 1-propanol (1) + water (2) + [beim][triflate] (3) and 1-propanol (1) + water (2) + [bmpyr][triflate] (3) systems, respectively, are plotted on (T, x_1', y_1) diagrams for $x_3 \approx 0.05$ and 0.19. The model seems to be able to fit properly the experimental data. Accordingly, the ability of the model to reproduce the VLE for this system is demonstrated.

Figures 3 and 4 are composition diagrams (y_1, x_1') for the VLE of the 1-propanol (1) + water (2) + [beim][triflate] (3) and 1-propanol (1) + water (2) + [bmpyr][triflate] (3) systems, respectively. These plots show a displacement of azeotropic

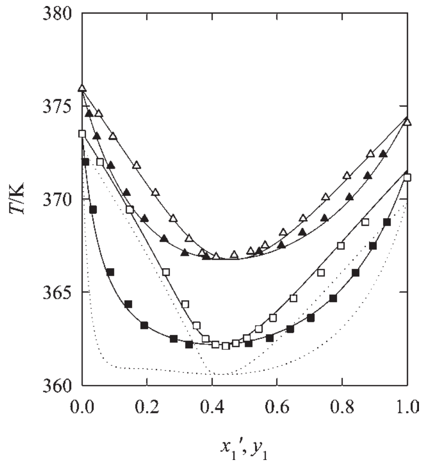

Figure 1. Temperature−composition diagram for 1-propanol (1) + water (2) + [beim][triflate] (3) at 100 kPa, with different mole fractions of IL: ■, x_1' experimental at $x_3 \approx 0.053$; □, y_1 experimental at $x_3 \approx 0.053$; ▲, x_1' experimental at $x_3 \approx 0.186$; △, y_1 experimental at $x_3 \approx 0.186$; solid lines, calculated; dotted lines, calculated for IL-free system.

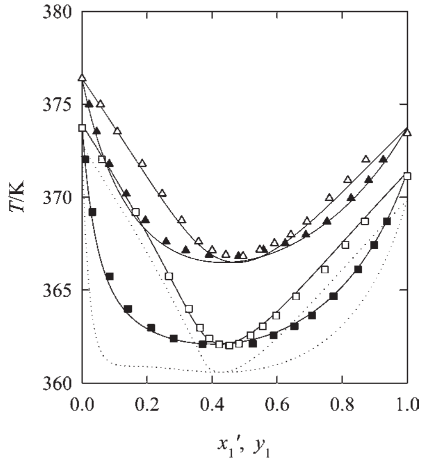

Figure 2. Temperature−composition diagram for 1-propanol (1) + water (2) + [bmpyr][triflate] (3) at 100 kPa, with different mole fractions of IL: ■, x_1' experimental at $x_3 \approx 0.054$; □, y_1 experimental at $x_3 \approx 0.054$; ▲, x_1' experimental at $x_3 \approx 0.190$; △, y_1 experimental at $x_3 \approx 0.190$; solid lines, calculated; dotted lines, calculated for IL-free system.

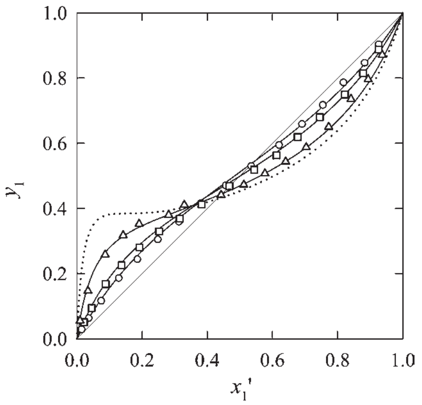

Figure 3. Composition diagram for the vapor−liquid equilibrium of the 1-propanol (1) + water (2) + [beim][triflate] (3) system at 100 kPa at several IL mole fractions: △, $x_3 \approx 0.053$; □, $x_3 \approx 0.186$; ○, $x_3 \approx 0.306$; solid lines, calculated at the same IL mole fractions; dotted line, calculated for the IL-free system.

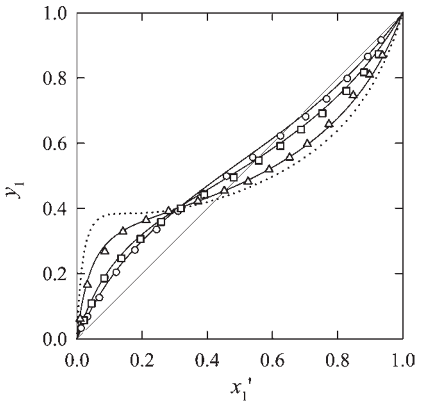

Figure 4. Composition diagram for the vapor−liquid equilibrium of the 1-propanol (1) + water (2) + [bmpyr][triflate] (3) system at 100 kPa at several IL mole fractions: △, $x_3 \approx 0.054$; □, $x_3 \approx 0.190$; ○, $x_3 \approx 0.309$; solid lines, calculated at the same IL mole fractions; dotted line, calculated for the IL-free system.

point toward higher values of $x_1' > 0.43$ as the IL mole fraction increases. Apart from this, a crossover effect[25] between salting-in and salting-out in the 1-propanol + water system takes place like that also observed when [emim][triflate] was used.[14] Nevertheless, for the IL mole fractions used in this study, it is evident that the salting-out effect produced at higher mole fractions of 1-propanol is far from breaking the azeotrope. Indeed, from the electrolyte NRTL model, we can calculate the IL mole fraction at which the azeotrope disappears, the values of x_3 being 0.72 and 0.52 for [beim][triflate] and [bmpyr][triflate], respectively. These values contrast with the 0.34 value that was found for 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([emim][triflate]).[14] In fact, the same can be seen in Figure 5, where the relative volatility α_{12} between 1-propanol (1) and water (2) in the presence of a constant mole fraction $x_3 \approx 0.31$ of [beim][triflate], [bmpyr][triflate], and [emim][triflate] has been depicted in the whole range of solvent composition. Both experimental and calculated values of α_{12} have been obtained using eq 4:

$$\alpha_{12} = \frac{\gamma_1 P_1^\circ}{\gamma_2 P_2^\circ} \qquad (4)$$

To calculate experimental α_{12} values, the activity coefficients γ_i have been obtained from experimental VLE data, using eq 3; the calculated values, γ_i, have been obtained from the electrolyte NRTL model, using the parameters of Table 8.

In all of the cases represented in Figure 5, the azeotrope is not broken, although [emim][triflate] shows a greater ability to break it. According to eq 4, the effect of the ILs on α_{12} can be depicted by their effect on the quotient γ_1/γ_2, and given that the ILs under investigation are composed of the same anion and different cations, the effect of the IL will also reflect the effect of the cation. This assertion can be confirmed by Figure 6, where the activity coefficients of solvents 1-propanol and water, in binary mixtures with [beim][triflate], [bmpyr][triflate], and [emim][triflate] against the IL mole fraction has been drawn. In this figure, it can be seen that the activity coefficient of

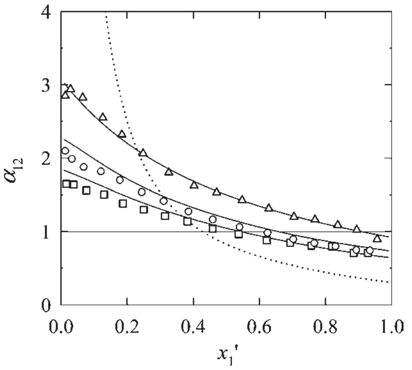

Figure 5. Variation of the relative volatility α_{12} between 1-propanol (1) and water (2) with the 1-propanol mole fraction x_1' at 100 kPa and $x_3 \approx 0.31$ for several ILs: experimental points, □, [beim][triflate]; ○, [bmpyr][triflate]; △, [emim][triflate]; solid lines, calculated at the same IL mole fraction; dotted line, calculated for the IL-free system.

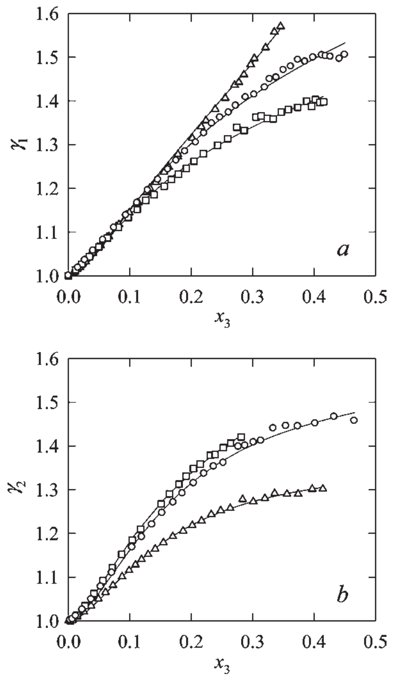

Figure 6. Variation of the activity coefficient of solvent γ_i with the mole fraction of IL x_3 in solvent + IL binary systems. Solvent: (a) 1-propanol (1); (b) water (2). IL: □, [beim][triflate]; ○, [bmpyr][triflate]; △, [emim][triflate]. Solid lines, calculated with the electrolyte NTRL model.

1-propanol γ_1 follows the order $[\text{beim}]^+ < [\text{bmpyr}]^+ < [\text{emim}]^+$, whereas the activity coefficient of water γ_2 follows the order $[\text{emim}]^+ < [\text{bmpyr}]^+ < [\text{beim}]^+$. Both effects lead to state that the addition of [emim][triflate] has the strongest effect on increasing γ_1 and the weakest effect on increasing γ_2, whereas the behavior of [beim][triflate] is just the opposite. As a result of that, the salting-out effect produced by the these ILs on the VLE of the 1-propanol + water system takes place in the order $[\text{emim}]^+ > [\text{bmpyr}]^+ > [\text{beim}]^+$, as it can be proved in Figure 5.

Zhang et al.,[13] by using ILs containing the tetrafluoroborate anion, found a similar result from activity coefficients after comparing the effect of $[\text{emim}]^+$ and 1-butyl-3-methylimidazolium ($[\text{bmim}]^+$) cations on water and 1-propanol, giving for $[\text{emim}]^+$ a stronger interaction with water than for $[\text{bmim}]^+$, whereas it had a weaker interaction with 1-propanol.

The systems studied here show a minimum equilibrium temperature slightly different from that corresponding to azeotropic point. This behavior was also observed with [emim][triflate] as well as with inorganic salts.[9−12,14,26] It was said that this effect could be related with the ability of the salt to break the azeotrope. The less salt concentration needed to break the azeotrope, the larger temperature difference between the minimum and azeotropic points was observed. The values reported in Table 8, corresponding to the parameters of the electrolyte NRTL model, support such an assumption, since the calculated difference with these parameters for $x_3 \approx 0.3$ is only (0.07 and 0.48) K for the systems with [beim][triflate] and [bmpyr][triflate], respectively, whereas it is 1.99 K for the system with [emim][triflate].

■ CONCLUSIONS

The electrolyte NRTL model has been also suitable to predict the VLE in the presence of [beim][triflate] and [bmpyr][triflate] ILs. In this way, this has allowed us to confirm the applicability of the model to the field of ILs.

The addition of [beim][triflate] and [bmpyr][triflate] to the 1-propanol + water mixture gives a salting-out effect on 1-propanol near the azeotropic point, but a salting-in effect at low 1-propanol concentrations, the azeotropic point of the 1-propanol + water system being displaced toward upper values of x_1'. Although this effect is important, we could not remove the azeotrope using a mole fraction of IL of 0.31, at 100 kPa.

In comparison with [emim][triflate], it can be said that $[\text{beim}]^+$ and $[\text{bmpyr}]^+$ cations produce a lower interaction with water than that produced by the $[\text{emim}]^+$ ion, which makes it easier to separate the components from the 1-propanol + water mixtures by adding [emim][triflate]. Thus, from the point of view of distillation process and not considering other physical properties, we say that [emim][triflate] may be a better entrainer than [bmpyr][triflate] or [beim][triflate] to separate 1-propanol + water mixtures by distillation.

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