JOURNAL OF CHEMICAL & ENGINEERING DATA

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Influence of Some Ionic Liquids Containing the Trifluoromethanesulfonate Anion on the Vapor−Liquid Equilibria of the Acetone + Methanol System

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ABSTRACT: Isobaric vapor−liquid equilibria (VLE) for the binary systems acetone + 1-butyl-3-ethylimidazolium trifluoromethanesulfonate ([beim][triflate]), methanol + [beim][triflate], acetone + 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate ([bmpyr][triflate]), and methanol + [bmpyr][triflate] as well as the VLE for the acetone + methanol + [beim][triflate] and acetone + methanol + [bmpyr][triflate] ternary systems have been obtained at 100 kPa using a recirculating still. The addition of both ionic liquids to the solvent mixtures produced an important salting-out effect, and the azeotrope tended to disappear for small amounts of ionic liquid. The experimental binary data sets were independently fitted with the electrolyte nonrandom two-liquid (NRTL) model, and the parameters of the Mock's model were estimated for each binary system. These parameters were used to predict the ternary VLE, which agreed very well with the experimental ones.

INTRODUCTION

Ionic liquids (ILs) are chemicals composed entirely of ions, 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 temperature (mainly below 373 K). They have a liquidus range of 300 K, are outstandingly good solvents for a wide range of inorganic, organic, and polymeric materials, and have no effective vapor pressure. Because of their structure and ionic interactions, some ILs present other interesting properties such as relatively low viscosity, nonflammability, and high thermal stability up to 450 K or higher and are much less corrosive than conventional high point melting salts. These special characteristics have converted ILs into chemicals of high scientific and commercial interest.[1,2]

The use of ILs in separation technology, mainly in special distillation of azeotropic or close-boiling mixtures, is promising. 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 like inorganic salts, its practically nonvolatile character prevents them from going out 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] suggesting using ILs for the separation of azeotropic mixtures, the number of studied systems has augmented appreciably, 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. At the best of our understanding, there are not complete isothermal VLE data (p, x, y) in the literature for systems made up of two solvents and one IL.

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 binary and ternary systems composed of acetone, methanol, 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.

The VLE of the acetone (1) + methanol (2) system show, at atmospheric pressure, a minimum boiling point homogeneous azeotrope at an acetone mole fraction of $x_1 \approx 0.78$. To break it, many salts have been used, not always successfully. Only lithium nitrate,[8] zinc chloride,[9] sodium iodide,[10] lithium[11] and calcium[12] bromides, and sodium[13] and potassium[14] thiocyanates have been reported to be effective in breaking this azeotrope. To the best of our knowledge, only three ILs have been used for breaking the acetone + methanol azeotrope: Seiler et al.[3] and Kurzin et al.[15] studied the effect at isothermal conditions of 1-ethyl-3-methylimidazolium tetrafluoroborate ([emim][BF_4]) at T = 328.15 K and n-butylpyridinium hexafluorophosphate ([bpy][PF_6]) at T = 313.15 K, respectively, reporting only $x-y$ data, whereas Orchillés et al.[16] used 1-ethyl-3-methylimidazolium trifluoromethanesulfonate [emim][triflate] at isobaric conditions (p = 100 kPa) and reported $T-x-y$ data. Consequently, one of the aims of this work is to determine at what composition, if any, [beim][triflate] and [bmpyr][triflate] are capable of breaking the acetone + methanol azeotrope and compare their effect with those produced by other ILs.

Special Issue: Kenneth N. Marsh Festschrift

Received: March 29, 2011
Accepted: May 12, 2011
Published: May 18, 2011

Table 1. Specifications of Chemical Samples

chemical name	source	mass fraction purity	purification method	final water mass fraction	analysis method
acetone	Merck	0.995	none	no detected	GC[c]
methanol	Riedel-de Haën	0.998	none	no detected	GC[c]
[beim][triflate][a]	Solvent Innovation	0.98	vacuum desiccation	0.0005	KF[d]
[bmpyr][triflate][b]	Solvent Innovation	0.98	vacuum desiccation	0.0005	KF[d]

[a] [beim][triflate] = 1-butyl-3-ethylimidazolium trifluoromethanesulfonate. [b] [bmpyr][triflate] = 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate. [c] GC = gas—liquid chromatography. [d] KF = Karl Fischer titration.

EXPERIMENTAL SECTION

Materials. The solvents used were acetone (Merck, GR grade, minimum mass fraction 0.995) and methanol dried (Riedel-de Haën, Analytical Reagent, minimum mass fraction 0.998). No impurities were detected by gas chromatography (GC), using the same procedure and conditions described below for analysis of liquid mixtures. These chemicals were used without further purification. [beim][triflate] and [bmpyr][triflate] were supplied by Solvent Innovation (Purum, minimum mass fraction 0.98). Because of their hygroscopic character, they were desiccated at 0.2 Pa overnight prior to use. The water mass fraction in the ILs determined by Karl Fisher titration was $x_\mathrm{w} < 0.0005$. The specifications of used chemicals are summarized in Table 1.

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

Apparatus and Procedures. VLE measurements were made with an all-glass dynamic recirculating still (Pilodist, modified Labodest model). The apparatus has been described in a previous paper.[8] 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 solvent + IL systems was obtained from an initial sample of solvent + IL with the highest IL concentration at which different quantities of solvent were added. For the ternary systems, several acetone + IL mixtures of known composition were prepared, and different quantities of a mixture of methanol + 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. For the solvent + IL binary systems, the IL mole fraction content in the liquid phase was gravimetrically determined after the solvent was separated from a known mass of sample (≈ 2.5 g) by evaporation at 393 K until constant weight. A Mettler AE200 analytical balance with a standard uncertainty of $1\cdot10^{-4}$ g was used to weigh the samples. In this way, the combined standard uncertainty of the mole fraction of solvent and IL in the liquid phase was 0.0001. As the vapor pressure of ILs is zero, the vapor phase was made up of pure solvent, and it was not analyzed.

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

x_3	T/K	x_3	T/K	x_3	T/K
0.0000	329.00	0.1983	335.32	0.3424	343.11
0.0146	329.41	0.2090	335.74	0.3504	343.66
0.0283	329.77	0.2210	336.24	0.3587	344.25
0.0450	330.21	0.2334	336.76	0.3672	344.89
0.0606	330.62	0.2467	337.52	0.3776	345.41
0.0759	331.06	0.2542	337.88	0.3871	346.24
0.0884	331.38	0.2661	338.42	0.3971	346.87
0.1036	331.89	0.2775	339.02	0.4054	347.46
0.1173	332.27	0.2871	339.53	0.4146	348.22
0.1313	332.77	0.2969	340.12	0.4196	348.78
0.1447	333.23	0.3071	340.66	0.4291	349.54
0.1573	333.67	0.3175	341.41	0.4439	350.70
0.1712	334.23	0.3246	341.84	0.4484	350.90
0.1842	334.66	0.3336	342.46		

[a] Standard uncertainties u are $u(T) = 0.01$ K, $u(p) = 0.05$ kPa, and the combined expanded uncertainty U_c is $U_\mathrm{c}(x_3) = 0.0001$ (0.95 level of confidence).

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

x_3	T/K	x_3	T/K	x_3	T/K
0.0000	337.42	0.1531	342.68	0.2978	350.26
0.0108	337.79	0.1652	343.26	0.3086	350.65
0.0204	338.07	0.1752	343.62	0.3191	351.40
0.0327	338.46	0.1863	344.18	0.3291	352.15
0.0444	338.80	0.1974	344.74	0.3432	352.94
0.0560	339.12	0.2083	345.24	0.3563	354.01
0.0683	339.45	0.2185	345.72	0.3682	354.68
0.0807	339.99	0.2286	346.30	0.3816	355.90
0.0920	340.33	0.2397	346.93	0.3952	357.03
0.1014	340.77	0.2522	347.63	0.4026	357.60
0.1094	341.02	0.2656	348.34	0.4184	358.88
0.1201	341.40	0.2752	349.03	0.4270	359.58
0.1314	341.85	0.2841	349.25	0.4365	360.45
0.1426	342.29	0.2920	349.87	0.4466	361.17

[a] Standard uncertainties u are $u(T) = 0.01$ K, $u(p) = 0.05$ kPa, and the combined expanded uncertainty U_c is $U_\mathrm{c}(x_3) = 0.0001$ (0.95 level of confidence).

For the ternary systems, the IL content in the liquid phase was gravimetrically determined as is previously said. Acetone and methanol 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.

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

x_3	T/K	x_3	T/K	x_3	T/K
0.0000	329.00	0.1853	334.06	0.3210	340.04
0.0126	329.31	0.2006	334.61	0.3320	340.60
0.0258	329.65	0.2144	335.21	0.3433	341.07
0.0435	330.06	0.2334	335.81	0.3551	341.67
0.0601	330.46	0.2447	336.33	0.3648	342.57
0.0766	330.86	0.2585	336.81	0.3768	343.19
0.0934	331.27	0.2663	337.23	0.3837	343.90
0.1111	331.73	0.2807	337.77	0.3953	344.38
0.1318	332.34	0.2867	338.07	0.4070	345.13
0.1491	332.85	0.2922	338.57	0.4122	345.62
0.1633	333.28	0.3052	339.12	0.4223	346.27
0.1745	333.69	0.3125	339.45		

[a] Standard uncertainties u are $u(T)$ = 0.01 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 Methanol (2) + [bmpyr][triflate] (3) at 100 kPa[a]

x_3	T/K	x_3	T/K	x_3	T/K
0.0000	337.42	0.1702	342.71	0.3252	350.47
0.0130	337.82	0.1818	343.24	0.3374	351.40
0.0248	338.11	0.1946	343.75	0.3513	352.10
0.0402	338.49	0.2096	344.42	0.3554	352.63
0.0552	338.84	0.2228	345.12	0.3623	353.17
0.0667	338.96	0.2352	345.70	0.3747	353.77
0.0787	339.19	0.2472	346.18	0.3850	354.73
0.0897	339.52	0.2579	346.87	0.3983	355.69
0.1032	340.19	0.2675	347.37	0.4101	356.52
0.1153	340.52	0.2786	347.92	0.4191	357.27
0.1265	340.99	0.2898	348.54	0.4288	358.20
0.1369	341.29	0.3010	349.22	0.4376	358.88
0.1481	341.93	0.3156	349.94	0.4519	360.08
0.1596	342.38				

[a] Standard uncertainties u are $u(T)$ = 0.01 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 6. Vapor−Liquid Equilibrium Data for Acetone (1) + Methanol (2) + [beim][triflate] (3) at 100 kPa[a]

x_3	x'_1	y_1	T/K	x_3	x'_1	y_1	T/K
0.056	0.000	0.000	339.12	0.229	0.000	0.000	346.30
0.057	0.032	0.061	338.18	0.233	0.026	0.049	345.40
0.057	0.072	0.129	337.08	0.234	0.069	0.121	344.74
0.056	0.121	0.200	335.88	0.236	0.118	0.188	344.10
0.055	0.181	0.282	334.68	0.233	0.175	0.259	343.00
0.055	0.250	0.358	333.51	0.235	0.259	0.364	341.87
0.055	0.325	0.428	332.51	0.235	0.343	0.449	340.86
0.055	0.396	0.506	331.71	0.234	0.430	0.532	339.83
0.056	0.459	0.557	331.11	0.232	0.513	0.606	338.94
0.055	0.519	0.601	330.71	0.231	0.593	0.672	338.32
0.055	0.588	0.652	330.32	0.230	0.675	0.741	337.76
0.055	0.665	0.711	330.05	0.229	0.754	0.807	337.35
0.055	0.742	0.771	329.88	0.227	0.837	0.875	336.87
0.055	0.821	0.835	329.86	0.224	0.906	0.930	336.55
0.055	0.883	0.889	329.97	0.220	0.907	0.929	336.28
0.056	0.935	0.936	330.11	0.218	0.949	0.964	336.10
0.054	0.972	0.972	330.25	0.215	0.979	0.986	335.97
0.054	1.000	1.000	330.40	0.211	1.000	1.000	336.08

[a] Standard uncertainties u are $u(T)$ = 0.01 K, $u(p)$ = 0.05 kPa, and the combined expanded uncertainty U_c are $U_c(x'_1)$ = 0.001, $U_c(x_3)$ = 0.001, and $U_c(y_1)$ = 0.001 (0.95 level of confidence).

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

x_3	x'_1	y_1	T/K	x_3	x'_1	y_1	T/K
0.055	0.000	0.000	338.84	0.235	0.000	0.000	345.70
0.058	0.026	0.049	338.11	0.237	0.032	0.058	344.82
0.058	0.065	0.114	337.06	0.240	0.073	0.121	344.32
0.057	0.114	0.188	335.89	0.241	0.111	0.177	343.57
0.056	0.175	0.272	334.58	0.241	0.161	0.253	342.61
0.056	0.250	0.352	333.49	0.244	0.243	0.349	341.66
0.056	0.326	0.445	332.54	0.241	0.339	0.450	340.29
0.057	0.401	0.510	331.76	0.238	0.425	0.534	339.11
0.057	0.472	0.566	331.22	0.234	0.502	0.601	338.23
0.056	0.530	0.613	330.84	0.232	0.573	0.666	337.59
0.056	0.598	0.664	330.42	0.231	0.648	0.726	337.00
0.056	0.678	0.721	330.14	0.227	0.721	0.783	336.47
0.056	0.755	0.780	329.91	0.227	0.793	0.843	336.04
0.056	0.825	0.841	329.89	0.223	0.855	0.891	335.70
0.055	0.889	0.892	329.93	0.221	0.908	0.931	335.48
0.055	0.937	0.937	330.04	0.219	0.950	0.963	335.25
0.055	0.974	0.973	330.16	0.215	0.979	0.985	335.12
0.054	1.000	1.000	330.32	0.212	1.000	1.000	335.13

[a] Standard uncertainties u are $u(T)$ = 0.01 K, $u(p)$ = 0.05 kPa, and the combined expanded uncertainty U_c are $U_c(x'_1)$ = 0.001, $U_c(x_3)$ = 0.001, and $U_c(y_1)$ = 0.001 (0.95 level of confidence).

The carrier gas was helium flowing at 30 $cm^3 \cdot min^{-1}$, and the operating conditions were as follows: injector and oven temperatures, 453 K; and detector temperature, 493 K. A calibration curve was obtained from a set of gravimetrically prepared standard solutions, which allowed us to quantify the amounts of methanol and acetone in the samples. Thus, the combined standard uncertainty of the mole fraction of components of the ternary systems in the liquid and vapor phase was 0.001.

RESULTS AND DISCUSSION

Experimental Data. Boiling temperatures for acetone (1) + [beim][triflate] (3), methanol (2) + [beim][triflate] (3), acetone (1) + [bmpyr][triflate] (3), and methanol (2) + [bmpyr][triflate] (3) binary systems have been obtained at 100 kPa, and the results are reported in Tables 2 to 5, respectively. In these tables, x_3 is the IL mole fraction in the liquid phase and T the equilibrium temperature.

Moreover, VLE for the acetone (1) + methanol (2) + [beim][triflate] (3) and acetone (1) + methanol (2) + [bmpyr][triflate] (3) ternary systems have been also obtained at 100 kPa, and the results are shown in Tables 6 and 7, respectively. In

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	$\alpha_{i,j}$	$\text{J}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{mol}^{-1}$
acetone	methanol	0.300[a]	924.2[a]	863.1[a]
acetone	[beim][triflate]	0.089	47999	−21701
methanol	[beim][triflate]	0.210	22389	−9498
acetone	[bmpyr][triflate]	0.038	107586	−51242
methanol	[bmpyr][triflate]	0.141	31627	−14037

[a] From Orchillés et al.[16]

Table 9. Average 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
acetone + [beim][triflate]			0.26	0.29
methanol + [beim][triflate]			0.19	0.24
acetone + [bmpyr][triflate]			0.19	0.22
methanol + [bmpyr][triflate]			0.12	0.16
acetone + methanol + [beim][triflate]	0.005	0.006	0.05	0.10
acetone + methanol + [bmpyr][triflate]	0.007	0.009	0.14	0.18

[a] $\delta y = (1/N)\Sigma|y_{\text{exptl}} - y_{\text{calcd}}|$. [b] $\sigma y = [1/(N-1)][\Sigma(y_{\text{exptl}} - y_{\text{calcd}})^2]^{1/2}$. [c] $\delta T = (1/N)\Sigma|T_{\text{exptl}} - T_{\text{calcd}}|$. [d] $\sigma T = [1/(N-1)][\Sigma(T_{\text{exptl}} - T_{\text{calcd}})^2]^{1/2}$.

these tables, x_3 is the IL mole fraction in the liquid phase, x'_1 the mole fraction of acetone in the liquid phase expressed on an IL-free basis, y_1 the mole fraction of acetone in the vapor phase, and T the equilibrium temperature.

Calculation of Phase Equilibrium. As indicated in previous papers,[16−22] we have used the electrolyte NRTL model to predict the VLE of the IL-containing ternary system. This model is an extension of the nonrandom two-liquid (NRTL) local composition proposed by Renon and Prausnitz[23] from which Chen et al.[24] derived a model for single-solvent + electrolyte systems, and later Mock et al.[25,26] extended it to mixed-solvent + electrolyte systems, by neglecting the long-range interaction contribution term.

The model produces expressions for the liquid-phase activity coefficients of acetone (1) and methanol (2) in a binary or ternary system containing [beim][triflate] (3) or [bmpyr][triflate] (3). These equations have been reported in a previous paper.[27] According to the proposed method, we need the binary adjustable parameters for all of the solvent + solvent and solvent + IL pairs in the systems to represent the phase equilibrium of mixed-solvent + electrolyte systems.

The 1−2 binary solvent−solvent parameters were taken from a previous paper.[16] On the other hand, the 1−3 and 2−3 binary solvent-IL parameters were determined from the binary VLE data of Tables 2 to 5 and the NRTL electrolyte model by minimization of the objective function F

$$F = \sum_j |T_{\text{exptl}} - T_{\text{calcd}}| \tag{1}$$

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

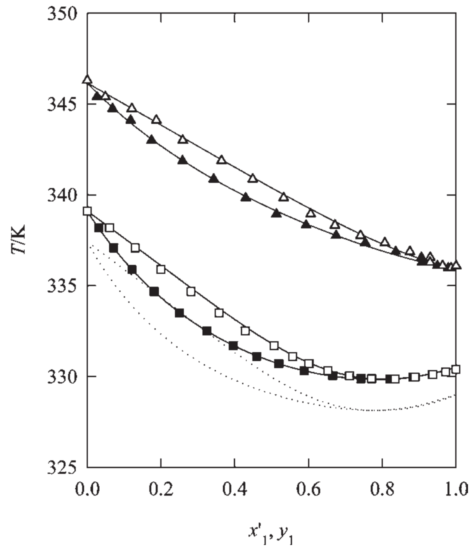

Figure 1. Temperature−composition diagram for acetone (1) + methanol (2) + [beim][triflate] (3) at 100 kPa for two IL mole fractions: ■, x'_1 experimental for $x_3 \approx 0.055$; □, y_1 experimental for $x_3 \approx 0.055$; ▲, x'_1 experimental for $x_3 \approx 0.228$; △, y_1 experimental for $x_3 \approx 0.228$; solid lines, calculated with the e-NRTL model; dotted lines, calculated IL-free system.

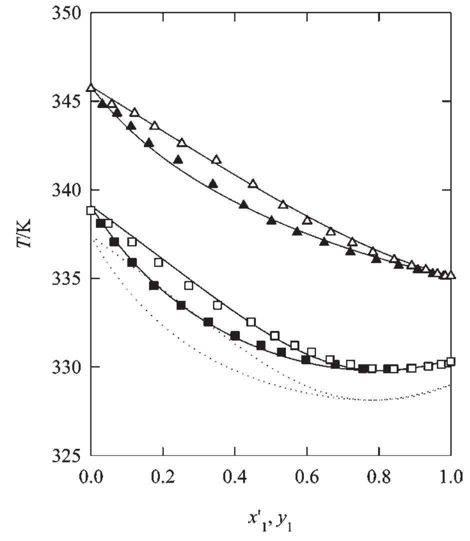

Figure 2. Temperature−composition diagram for acetone (1) + methanol (2) + [bmpyr][triflate] (3) at 100 kPa for two IL mole fractions: ■, x'_1 experimental for $x_3 \approx 0.056$; □, y_1 experimental for $x_3 \approx 0.056$; ▲, x'_1 experimental for $x_3 \approx 0.231$; △, y_1 experimental for $x_3 \approx 0.231$; solid lines, calculated with the e-NRTL model; dotted lines, calculated IL-free system.

All of the parameters considered are shown in Table 8, and in Table 9, the average absolute deviations and the standard deviations between the experimental and calculated values of the equilibrium temperature for binary systems can be seen.

The parameters reported in Table 8 were used to predict the VLE of the acetone (1) + methanol (2) + [beim][triflate] (3) and the acetone (1) + methanol (2) + [bmpyr][triflate] (3) ternary systems, in such a way that we were able to work out the composition in the vapor phase and the equilibrium temperature

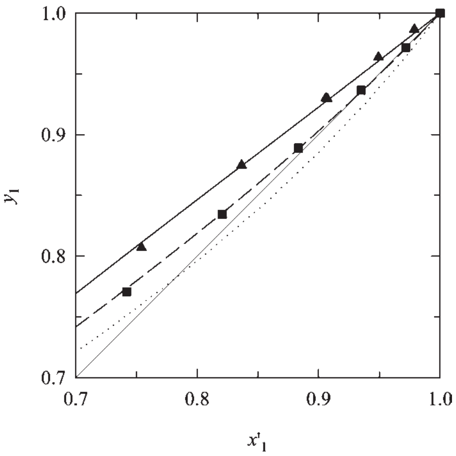

Figure 3. Composition diagram for acetone (1) + methanol (2) + [beim][triflate] (3) at 100 kPa for two IL mole fractions: dotted line, calculated for IL-free system; dashed line, calculated for $x_3 = 0.055$; solid line, calculated for $x_3 = 0.228$; ■, experimental for $x_3 \approx 0.055$; ▲, experimental for $x_3 \approx 0.228$.

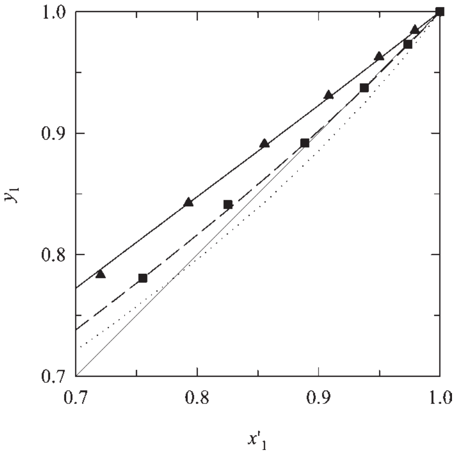

Figure 4. Composition diagram for acetone (1) + methanol (2) + [bmpyr][triflate] (3) at 100 kPa for two IL mole fractions: dotted line, calculated for IL-free system; dashed line, calculated for $x_3 = 0.056$; solid line, calculated for $x_3 = 0.231$; ■, experimental for $x_3 \approx 0.056$; ▲, experimental for $x_3 \approx 0.231$.

for each composition in the liquid phase. To do this, ideal behavior of the vapor phase was assumed, and the equilibrium conditions represented by eq 2 were considered.

$$y_i p = X_i \gamma_i P_i^{\circ} \qquad (2)$$

In eq 2, 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 component i based on the assumption of total dissociation of the IL, γ_i is the activity coefficient of component i obtained from the electrolyte NRTL model, and P_i° is the vapor pressure of solvent i at equilibrium temperature. The vapor pressures of the pure solvents were calculated by the Antoine equation using the parameters obtained with the same recirculating still.[16]

The ability of the model to reproduce the VLE for these systems can be seen in Figure 1, where the calculated and experimental VLE of the acetone + methanol + [beim][triflate] ternary system is plotted on a $T-x'_1-y_1$ diagram for $x_3 = 0$, 0.055, and 0.228, and in Figure 2, where the calculated and experimental VLE of the acetone + methanol + [bmpyr][triflate] ternary system is plotted on a $T-x'_1-y_1$ diagram for $x_3 = 0$, 0.056, and 0.231. These figures and the average absolute deviations and standard deviations reported in Table 9 reveal that the proposed model successfully fits the experimental data.

Table 10. Minimum Value of Mole Fraction of IL x_3 Needed for Breaking the Acetone + Methanol Azeotrope

ionic liquid	x_3	equilibrium conditions	ref
[emim][BF$_4$][a]	0.100	isotherm, $T = 328.15$ K	Seiler et al.[3]
[bpy][PF$_6$][b]	0.006	isotherm, $T = 313.15$ K	Kurzin et al.[15]
[emim][triflate][c]	0.078	isobaric, $P = 100.00$ kPa	Orchillés et al.[16]
[beim][triflate]	0.073	isobaric, $P = 100.00$ kPa	this work
[bmpyr][triflate]	0.079	isobaric, $P = 100.00$ kPa	this work

[a] [emim][BF$_4$] = 1-ethyl-3-methylimidazolium tetrafluoroborate. [b] [bpy][PF$_6$] = n-butylpyridinium hexafluorophosphate. [c] [emim][triflate] = 1-ethyl-3-methylimidazolium trifluoromethanesulfonate.

It is worth noting that small concentrations of [beim][triflate] or [bmpyr][triflate] produce a displacement of the azeotropic point of the acetone + methanol system toward x'_1 values higher than 0.78 until the azeotrope disappears, as seen in Figures 3 and 4, respectively. As a matter of fact, it is seen in Tables 6 and 7 that a mole fraction of $x_3 \approx 0.06$ in both ILs is very closed to the limit from which the azeotrope disappears, whereas at $x_3 \approx 0.23$ the azeotrope is really disappeared. From the NRTL electrolyte model, the mole fraction of IL at which the disappearance of the azeotrope for the acetone + methanol at $p = 100$ kPa occurs has been estimated to be $x_3 = 0.073$ for the [beim][triflate] and $x_3 = 0.079$ for the [bmpyr][triflate]. These values are reported in Table 10, and they prove that the effect produced on the VLE of the acetone + methanol system by both ILs is very similar. This similarity in the behavior of both ILs used in this work can be also observed comparing jointly Figures 1 and 2 or Figures 3 and 4. In Table 10, the mole fraction of [emim][triflate] at which the azeotrope disappears for the acetone + methanol at 100 kPa is also reported from a previous paper,[16] and this value ($x_3 = 0.078$) is practically identical to that estimated for [beim][triflate] and [bmpyr][triflate]. From these facts, it can be concluded that the size and structure of the IL cation do not seem to be important in its behavior as entrainer in the extractive distillation of the acetone + methanol system, and all of the salt effects produced by the IL must be due to the triflate anion.

In Table 10 it can be also observed that the [emim][BF$_4$] at isothermal conditions ($T = 328.15$ K) breaks the acetone + methanol azeotrope at $x_3 = 0.100$[3] and that the [bpy][PF$_6$], at isothermal conditions too ($T = 313.15$ K), breaks it at an IL molality $m_3 = 0.100\ \mathrm{mol \cdot kg^{-1}}$ ($x_3 \approx 0.006$);[15] although in these last conditions the azeotrope occurs at $x'_1 \approx 0.85$ instead of $x'_1 \approx 0.78$ (at $p = 100$ kPa or $T = 313.15$ K), making its breakage easier.

■ CONCLUSIONS

In this work, vapor pressures of acetone + [beim][triflate], methanol + [beim][triflate], acetone + [bmpyr][triflate], and methanol + [bmpyr][triflate] binary systems and VLE of acetone + methanol + [beim][triflate] and acetone + methanol + [bmpyr][triflate] ternary systems at 100 kPa have been obtained in a recirculating still.

It has been confirmed that the electrolyte NRTL model is suitable to predict the VLE in the presence of an IL such as

[beim][triflate] or [bmpyr][triflate]. From the parameters obtained of experimental data of binary systems, the ternary system has been reproduced with great precision. This confirms the extension of the electrolyte NRTL model to ILs.

The addition of [beim][triflate] or [bmpyr][triflate] to acetone + methanol system originates a noticeable salting-out effect on acetone near the azeotropic point, which leads to the displacement and breakage of the azeotropic point.

The effect produced by the addition of either of the two ILs used in this work is practically identical at that produced by the [emim][triflate] and reported in a previous paper.[16] From these facts it can be concluded that the size and structure of the IL cation do not seem an important factor in its behavior as entrainer in the extractive distillation of the acetone + methanol system, and all of the salt effects produced by the IL is due to the triflate anion.

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Funding Sources

This research was supported by the Ministry of Education and Science of Spain and FEDER funds of the European Union, through Project Nos. CTQ2007-60831/PPQ and CTQ2010-18848/PPQ.

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