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Ionic Liquids as Entrainers in Extractive Distillation: Isobaric Vapor−Liquid Equilibria for Acetone + Methanol + 1-Ethyl-3-methylimidazolium Trifluoromethanesulfonate

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Isobaric vapor−liquid equilibria for the binary systems acetone + methanol, acetone + 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([emim][triflate]), and methanol + [emim][triflate] as well as the vapor−liquid equilibrium for the acetone + methanol + [emim][triflate] ternary system have been obtained at 100 kPa using a recirculating still. The addition of the ionic liquid to the solvent mixture produced an important salting-out effect, and the azeotrope tended to disappear for small contents of ionic liquid. The experimental binary data sets were independently fitted with the electrolyte NRTL model, and the parameters of Mock's model were estimated for each binary system. These parameters were used to predict the ternary vapor−liquid equilibrium which agreed very well with the experimental one.

Introduction

Generally, the term "ionic liquid" (IL) stands for a class of chemicals composed entirely of ions with very low melting points (mainly below 100 °C). Typically, ionic liquids comprise an organic greatly asymmetric substituted cation (imidazolium, pyridinium, pyrrolidinium, quaternary ammonium, tetraalkylphosphonium, etc.) and an inorganic weak anion (halide, nitrate, acetate, trifluoromethanesulfonate, tetrafluoroborate, hexafluorophosphate, etc.). These cations, substituents, and anions can be virtually varied at will to change their chemical and physical properties.[1]

Because of their structure and ionic interactions, they present unique properties:[2] they have a liquidus range of 300 °C, are outstandingly good solvents for a wide range of inorganic, organic, and polymeric materials, exhibit Bronsted, Lewis, and Franklin acidity as well as superacidity, have no effective vapor pressure, and are thermally stable up to 200 °C.

Although ILs have been known for 100 years, it is only during the past decade that the interest in ILs has increased dramatically. Applications as "green" solvent replacing volatile organic compounds, catalyst in chemical reactions, extraction media for separation processes, lubricants, thermofluids, plasticizers, and electrically conductive liquids in electrochemistry have been reported.[3]

Ionic liquids, when dissolved in solvent mixtures, like inorganic salts, are dissociated in ions which interact with the components of the liquid mixture modifying its chemical potential. 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 ILs in low-polar solvents allows a greater electrolyte concentration in the mixture and therefore a stronger salt effect.

From the viewpoint of separation processes, when an ionic liquid is used as an entrainer in extractive distillation of hardly separating solvent mixtures, it is withdrawn as the column bottom's effluent with the heavier components, from which the ionic liquid can be easily and completely separated by flash distillation because it presents a null vapor pressure. Moreover, unlike inorganic salts, ILs are liquids at work temperatures and can be easily recirculated and mixed with the reflux stream introducing none of the less-volatile components at the top of the distillation column. Because of that, the choice of an ionic liquid azeotrope breaker could have significant processing advantages over the use of solid inorganic salts or liquid entrainers to shift or break azeotropes.[4]

Arlt and co-workers[5−7] were the first group that suggested ionic liquids as selective compounds for separation of azeotropic mixtures.[8,9] They reported the effect of various ionic liquids on ethanol + water,[8−10] acetone + methanol,[8] water + acetic acid,[8] tetrahydrofurane + water,[9−11] methanol + trimethylborate,[12] and 1-hexene + *n*-hexane[13] azeotropic systems. Nevertheless, even though the use of ionic liquids as solvents or entrainers in separation technology is promising, thermodynamic data are rare and currently only a few investigations on vapor−liquid equilibria have been accomplished.

Most works on the vapor−liquid equilibrium of IL-containing systems are limited to determining the vapor pressure and/or activity coefficients of one or two solvents in ILs. Among them, we should cite here those presented by Anthony et al.,[14] Heintz and co-workers,[15−20] Lee and co-workers,[21,22] Gmehling and co-workers,[23−26] Abusen et al.,[27] Orchillés et al.,[28] and Banerjee et al.[29] Likewise, the results of Arlt and co-workers quoted before[8−13] were obtained using headspace chromatography techniques at constant temperature. Only Zhao et al.[30] have reported complete isobaric vapor−liquid equilibria ($T-x'-y$) for the ethanol−water system containing different ILs.

Our research group has been working for 15 years on the effect of different inorganic salts on the vapor−liquid equilibrium of hardly separating solvent mixtures, mainly alcohols + water. Currently, we have started a new research line using ionic liquids instead of inorganic salts so as to modify the vapor−liquid equilibrium of solvent mixtures resulting in difficult

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Table 1. Vapor−Liquid Equilibrium Data for Acetone (1) + Methanol (2) at 100 kPa

x_1	y_1	T/K
0.000	0.000	337.41
0.015	0.034	336.90
0.029	0.063	336.45
0.057	0.119	335.60
0.097	0.188	334.52
0.137	0.247	333.58
0.176	0.303	332.72
0.214	0.348	332.05
0.254	0.388	331.45
0.292	0.423	330.95
0.331	0.456	330.48
0.372	0.489	330.06
0.412	0.518	329.70
0.449	0.546	329.39
0.491	0.576	329.10
0.531	0.603	328.86
0.574	0.630	328.66
0.617	0.662	328.43
0.659	0.690	328.31
0.697	0.718	328.20
0.727	0.739	328.15
0.743	0.751	328.13
0.760	0.765	328.13
0.781	0.781	328.13
0.800	0.797	328.14
0.820	0.813	328.15
0.841	0.830	328.18
0.862	0.850	328.23
0.883	0.870	328.29
0.930	0.918	328.49
0.972	0.964	328.75
1.000	1.000	329.01

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

x_3	T/K
0.0157	329.45
0.0263	329.69
0.0395	330.01
0.0544	330.34
0.0700	330.69
0.0832	331.01
0.1004	331.38
0.1150	331.73
0.1282	332.05
0.1448	332.55
0.1585	332.85
0.1721	333.25
0.1867	333.75
0.2010	334.15
0.2124	334.65
0.2240	334.95
0.2359	335.35
0.2481	335.85
0.2596	336.30
0.2702	336.65
0.2769	337.05
0.2866	337.45
0.2945	337.95
0.3095	338.45
0.3236	339.15
0.3435	340.25
0.3532	340.60
0.3636	341.21
0.3686	341.45
0.3791	342.05
0.3908	342.77
0.4022	343.45
0.4105	343.55
0.4125	344.05
0.4282	344.95
0.4349	345.45
0.4399	345.95
0.4513	346.45
0.4609	347.25
0.4722	347.95
0.4876	348.95

separation by distillation.

In this work, complete isobaric vapor−liquid equilibria data for acetone + methanol + 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([emim][triflate]) binary and ternary systems are presented at 100 kPa. In a previous work,[31] we studied the effect of an inorganic salt (lithium nitrate) on the vapor−liquid equilibrium of the acetone + methanol mixture.

Experimental Section

Materials. The chemicals used were acetone (Merck, GR grade, minimum 99.5 wt %), dried methanol (Riedel-de Haën, Analytical Reagent, minimum 99.8 wt %), and the ionic liquid 1-ethyl-3-methylimidazolium trifluoromethanesulfonate supplied by Solvent Innovation (Purum, minimum 98 wt %).

Because of its hygroscopic character, the ionic liquid was desiccated at 10^{-3} Torr of vacuum overnight. No impurities were detected by GC. The solvents were directly used without further purification.

Apparatus and Procedure. The equilibrium apparatus used to obtain the experimental data was an all-glass dynamic recirculating still manufactured by Fischer (Labodest model). In this apparatus, the vaporization ensues via an electrical immersion heater. Because of the regular circulation of both phases and the simultaneous mixing of the back-flowing circulation streams in a special mixing chamber (Cottrell pump),[32] a quick adjustment of the equilibrium will be obtained. Before entering the separation chamber, the vapor−liquid mixture passes an extended contact line, which guarantees an intense phase exchange. The construction of the separation chamber prevents an entrainment of liquid particles into the vapor phase.

The still is capable of handling pressures from (0.25 to 400) kPa and temperatures up to 523 K. The apparatus pressure was kept constant by means of a vacuum pump and an electrovalve modified by an on−off pressure controller. The equilibrium pressure was measured with a Fischer vacuum probe, whereas the boiling point was measured with a Fluke 1502A digital thermometer and a Pt-100 probe. The standard uncertainties for pressure and temperature measurements were 0.01 kPa and 0.01 K, respectively.

Every experimental point of the binary acetone + methanol system was obtained from an initial sample of pure acetone at which different quantities of methanol were added, whereas for the acetone + IL and methanol + IL binary systems, acetone or methanol, respectively, was added to a concentrated solution until a very diluted solution was achieved. For the ternary system, several acetone + IL mixtures of distinct composition were taken and different quantities of a mixture of methanol + IL having a slightly higher concentration than the original one were added. The samples were prepared with a Mettler AE200 analytical balance with a standard uncertainty of 0.0001 g. Only when constant temperature was reached (30 min or longer) were the equilibrium conditions assumed.

Sample Analysis. Compositions of the condensed vapor (acetone + methanol) and liquid (acetone + methanol + IL) 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 $cm^3 \cdot min^{-1}$, and the operating conditions were as follows: injector and oven temperatures of 453 K and a detector

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

x_3	T/K
0.0030	337.58
0.0061	337.68
0.0117	337.87
0.0192	338.10
0.0281	338.36
0.0373	338.63
0.0480	338.94
0.0563	339.19
0.0649	339.42
0.0774	339.81
0.0903	340.21
0.1048	340.68
0.1126	340.90
0.1247	341.37
0.1352	341.69
0.1447	342.05
0.1523	342.30
0.1612	342.70
0.1669	342.88
0.1798	343.30
0.1866	343.69
0.1980	344.13
0.2110	344.67
0.2228	345.19
0.2334	345.67
0.2455	346.21
0.2564	346.70
0.2687	347.32
0.2782	347.78
0.2921	348.45
0.3065	349.35
0.3246	350.35
0.3442	351.55
0.3656	352.75
0.3912	354.55
0.4235	356.55
0.4504	358.35
0.4743	360.15

Table 4. Vapor−Liquid Equilibrium Data for Acetone (1) + Methanol (2) + [emim][triflate] (3) at 100 kPa

x_3	x'_1	y_1	T/K	x_3	x'_1	y_1	T/K
0.056	0.000	0.000	339.19	0.168	0.345	0.457	336.43
0.057	0.034	0.069	338.09	0.168	0.398	0.513	335.83
0.058	0.074	0.137	337.11	0.167	0.459	0.564	335.29
0.059	0.120	0.206	336.09	0.166	0.522	0.623	334.65
0.059	0.174	0.276	335.03	0.163	0.581	0.670	334.14
0.060	0.250	0.367	333.75	0.162	0.636	0.718	333.72
0.060	0.316	0.430	332.83	0.163	0.696	0.764	333.35
0.060	0.388	0.492	332.02	0.158	0.746	0.804	333.11
0.060	0.455	0.550	331.40	0.165	0.829	0.865	333.25
0.059	0.530	0.613	330.87	0.160	0.889	0.911	332.93
0.059	0.596	0.662	330.49	0.169	0.927	0.943	333.13
0.059	0.675	0.723	330.17	0.168	0.979	0.984	333.05
0.058	0.749	0.780	329.97	0.160	1.000	1.000	332.93
0.057	0.815	0.833	329.89	0.256	0.000	0.000	346.70
0.057	0.875	0.884	329.90	0.247	0.032	0.059	345.45
0.056	0.932	0.934	330.01	0.254	0.116	0.187	343.97
0.055	0.980	0.981	330.18	0.259	0.163	0.250	343.40
0.054	1.000	1.000	330.30	0.262	0.212	0.308	342.80
0.125	0.000	0.000	341.37	0.258	0.314	0.423	340.92
0.123	0.016	0.035	340.60	0.259	0.364	0.472	340.29
0.121	0.082	0.147	338.90	0.254	0.418	0.522	339.77
0.123	0.122	0.204	338.13	0.256	0.466	0.572	339.33
0.123	0.163	0.263	337.39	0.258	0.516	0.620	338.70
0.123	0.209	0.326	336.60	0.258	0.585	0.663	338.25
0.124	0.259	0.380	335.80	0.255	0.689	0.751	337.30
0.125	0.306	0.428	335.18	0.253	0.738	0.801	336.86
0.122	0.358	0.479	334.47	0.250	0.790	0.841	336.66
0.121	0.399	0.522	333.93	0.249	0.839	0.880	336.30
0.120	0.464	0.570	333.37	0.248	0.892	0.921	336.02
0.120	0.520	0.619	332.89	0.247	0.940	0.956	335.78
0.119	0.578	0.668	332.48	0.248	1.000	1.000	335.85
0.118	0.632	0.710	332.18	0.355	0.000	0.000	352.05
0.119	0.689	0.757	331.94	0.360	0.048	0.083	351.20
0.117	0.758	0.803	331.73	0.365	0.092	0.151	350.66
0.116	0.817	0.850	331.64	0.368	0.138	0.212	350.04
0.117	0.873	0.895	331.62	0.370	0.189	0.277	349.33
0.114	0.924	0.936	331.56	0.367	0.258	0.357	348.13
0.116	0.979	0.983	331.66	0.367	0.323	0.431	347.14
0.115	1.000	1.000	331.73	0.367	0.395	0.496	346.22
0.167	0.000	0.000	342.88	0.365	0.469	0.570	345.35
0.163	0.021	0.046	342.01	0.363	0.536	0.642	344.52
0.167	0.057	0.104	341.34	0.362	0.610	0.703	343.71
0.169	0.085	0.147	340.78	0.361	0.686	0.770	342.72
0.168	0.123	0.201	340.05	0.356	0.756	0.825	342.02
0.168	0.160	0.250	339.30	0.355	0.831	0.886	341.46
0.171	0.201	0.302	338.75	0.351	0.900	0.937	340.85
0.172	0.248	0.356	338.11	0.358	1.000	1.000	340.62
0.166	0.298	0.412	336.96				

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

			$\Delta g_{i,j}$	$\Delta g_{j,i}$
i component	j component	$\alpha_{i,j}$	J·mol^{-1}	J·mol^{-1}
acetone	methanol	0.300[a]	924.2[a]	863.1[a]
acetone	[emim][triflate]	0.335[b]	12765.9[b]	−4468.1[b]
methanol	[emim][triflate]	0.389[b]	11950.6[b]	−4547.0[b]

[a] From Vercher et al.[31] [b] From this work.

temperature of 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 measured mole fraction in the vapor phase was 0.001.

The IL mole fraction content in the liquid phase was gravimetrically determined after the volatile components were separated from a known mass of sample by evaporation at 393 K until constant weight. In this way, the combined standard uncertainty of the mole fraction of acetone, methanol, and [emim][triflate] was 0.001.

Results and Discussion

Experimental Data. Vapor−liquid equilibria for the binary systems acetone (1) + methanol (2), acetone (1) + [emim]-[triflate] (3), and methanol (2) + [emim][triflate] (3) as well as the vapor−liquid equilibrium for the acetone (1) + methanol (2) + [emim][triflate] (3) ternary system have been obtained at 100 kPa, and the results are shown in Tables 1 to 4. In these tables, x_i represents the component i mole fraction in the liquid phase and x'_1 represents the mole fraction of acetone in the liquid phase expressed on an IL-free basis. y_1 represents the mole fraction of acetone in the vapor phase, and T is the equilibrium temperature.

The acetone (1) + methanol (2) system shows a minimum point azeotrope at $x_1 = 0.781$ and $T = 328.13$ K, which can be interpolated from experimental data. These results are in accordance with those reported by Harper and Moore[33] and Freshwater and Pike[34] at the same pressure. Besides this, the system shows a good thermodynamic consistency according to the Van Ness test[35] modified by Fredenslund.[36] No consistency test was used for IL-containing systems.

Calculation of the Phase Equilibrium. Because of the fact that ionic liquids are organic salts and exhibit ionic character, electrolyte models have been used to correlate the vapor−liquid equilibrium of solvent + IL systems. So, Arlt and co-workers,[8,10,12] Heintz and co-workers,[15−17,19,20] and Gmehling and co-workers[23,24] have used the electrolyte NRTL model, and Gmehling and co-workers have also used the electrolyte UNIQUAC model[23−26] and the electrolyte Wilson model.[24] In

Table 6. 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
acetone + methanol	0.002	0.002	0.01	0.02
acetone + [emim][triflate]			0.19	0.14
methanol + [emim][triflate]			0.14	0.19
acetone + methanol + [emim][triflate]	0.008	0.008	0.13	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] $\sigma T = [1/(N-1)][\Sigma(T_{\text{exptl}} - T_{\text{calcd}})^2]^{1/2}$.

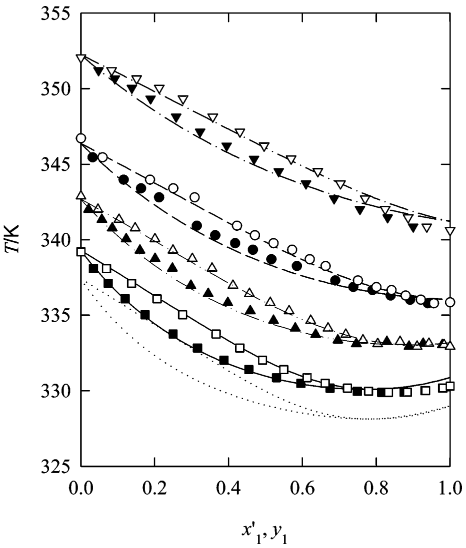

Figure 1. Experimental and calculated $T-x'_1-y_1$ diagrams for acetone (1) + methanol (2) + [emim][triflate] (3) at 100 kPa: dotted lines, T-x'_1-y_1 calculated IL-free system; solid lines, $T-x'_1-y_1$ calculated for $x_3 = 0.055$; dot-dot-dashed lines, $T-x'_1-y_1$ calculated for $x_3 = 0.165$; dashed lines, $T-x'_1-y_1$ calculated for $x_3 = 0.250$; dot-dashed lines, $T-x'_1-y_1$ calculated for $x_3 = 0.360$; ■, $T-x'_1$ experimental for $x_3 = 0.055$; □, $T-y_1$ experimental for $x_3 = 0.055$; ▲, $T-x'_1$ experimental for $x_3 = 0.165$; △, $T-y_1$ experimental for $x_3 = 0.165$; ●, $T-x'_1$ experimental for $x_3 = 0.250$; ○, $T-y_1$ experimental for $x_3 = 0.250$; ▼, $T-x'_1$ experimental for $x_3 = 0.360$; ▽, $T-y_1$ experimental for $x_3 = 0.360$.

this work, we have used the electrolyte NRTL model to correlate the vapor−liquid equilibrium of the binary system so as to predict the vapor−liquid equilibrium of the ternary system. This model is an extension of the nonrandom two-liquid local composition proposed by Renon and Prausnitz[37] from which Chen et al.[38] derived a model for single-solvent + electrolyte systems. Subsequent to that, Mock et al.[39,40] 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 acetone (1) and methanol (2) in a binary or ternary system containing [emim][triflate] (3) can be derived. These equations have been reported elsewhere.[41]

According to the proposed method, as long as we want to represent the phase equilibrium of mixed-solvent electrolyte systems, we must determine the binary adjustable parameters for all of the solvent−solvent and solvent−electrolyte pairs in the system. Provided that we have three pairs in our system (two solvents and one IL), there are nine binary parameters which have to be calculated. Six of them are energy parameters ($\Delta g_{1,2}$, $\Delta g_{2,1}$, $\Delta g_{1,3}$, $\Delta g_{3,1}$, $\Delta g_{2,3}$, and $\Delta g_{3,2}$), and the rest are nonrandomness factors ($\alpha_{1,2} = \alpha_{2,1}$, $\alpha_{1,3} = \alpha_{3,1}$, and $\alpha_{2,3} = \alpha_{3,2}$).

The 1−2 binary solvent−solvent parameters were taken from a previous paper.[31] On the other hand, the 1−3 and 2−3 binary solvent−IL parameters were determined from the binary vapor−liquid equilibrium data of Tables 2 and 3 and the NRTL electrolyte model by minimization of the objective function F

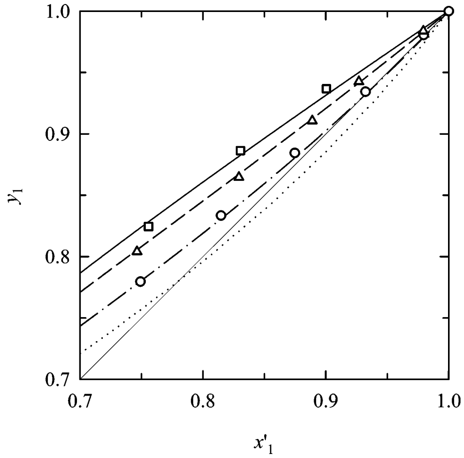

Figure 2. Experimental and calculated $y_1-x'_1$ diagrams for acetone (1) + methanol (2) + [emim][triflate] (3) at 100 kPa: dotted line, $y_1-x'_1$ calculated IL-free system; dot-dashed line, $y_1-x'_1$ calculated for $x_3 = 0.055$; dashed line, $y_1-x'_1$ calculated for $x_3 = 0.165$; solid line, $y_1-x'_1$ calculated for $x_3 = 0.360$; ○, $y_1-x'_1$ experimental for $x_3 = 0.055$; △, $y_1-x'_1$ experimental for $x_3 = 0.165$; □, $y_1-x'_1$ experimental for $x_3 = 0.360$.

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

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.

All of the nine parameters considered are shown in Table 5, and in Table 6, the mean absolute deviations between the experimental and calculated values of the equilibrium temperature for binary systems can be seen.

The parameters reported in Table 5 were used to predict the vapor−liquid equilibrium of the acetone (1) + methanol (2) + [emim][triflate] (3) ternary system, in such a way that we were able to work out the composition in the vapor phase and the equilibrium temperature 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.

$$y_i P = X_i \gamma_i P^{\circ}_i \tag{2}$$

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.[31]

The ability of the model to reproduce the vapor−liquid equilibrium for this system can be seen in Figure 1 where the calculated and experimental vapor−liquid equilibrium of the acetone + methanol + [emim][triflate] ternary system is plotted on a $T-x'_1-y_1$ diagram for $x_3 = 0$, 0.055, 0.165, 0.250, and 0.360. This figure and the mean absolute deviations from Table 6 reveal that the proposed model successfully fits the experimental data, and only for the highest [emim][triflate] concentrations can small differences be appreciated, despite the fact that

Table 7. Minimum Value of Mole Fraction of Entrainer x_3 Which Is Needed to Break the Acetone + Methanol Azeotrope

entrainer	x_3	equilibrium conditions	ref
sodium iodide	0.015^a	isobaric, $P = 101.32$ kPa	Iliuta and Thyrion[44]
calcium bromide	0.021^a	isobaric, atmospheric pressure	Al-Asheh and Banat[48]
lithium nitrate	0.022^b	isobaric, $P = 100.00$ kPa	Vercher et al.[31]
sodium thiocyanate	0.030^a	isobaric, $P = 101.32$ kPa	Iliuta and Thyrion[45]
potassium thiocyanate	0.050^a	isobaric, $P = 101.32$ kPa	Iliuta et al.[46]
zinc chloride	0.050^a	isobaric, $P = 101.32$ kPa	Yan et al.[49]
[emim][triflate]	0.078^b	isobaric, $P = 100.00$ kPa	this work
lithium bromide	0.050^a	isotherm, $T = 343.75$ K	Yan et al.[47]
[emim][BF$_4$]	0.100^a	isotherm, $T = 328.15$ K	Seiler et al.[8]

[a] Experimental value, selected from a discrete set, in which it is observed that the azeotrope is broken. [b] Estimated value by modeling, from which the azeotrope is broken.

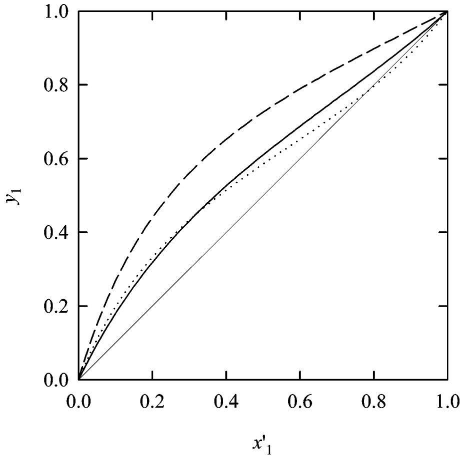

Figure 3. Salting-out effect of [emim][triflate] and lithium nitrate on the vapor−liquid equilibrium of the acetone (1) + methanol (2) system at 100 kPa for an electrolyte mole fraction of $x_3 = 0.120$: solid line, [emim][triflate]; dashed line, lithium nitrate; dotted line, salt-free system.

an [emim][triflate] mole fraction of 0.36 represents a mass fraction as high as 72−82%.

It is worth noting that small concentrations of [emim][triflate] produce a displacement of the azeotropic point of the acetone + methanol system toward x'_1 values higher than 0.781 until the azeotrope disappears, as seen in Figure 2. As a matter of fact, it is seen in Table 4 that an x_3 mole fraction of 0.055 in IL is very closed to the limit from which the azeotrope disappears. From the NRTL electrolyte model, it can be estimated that the disappearance of the azeotropic point for the acetone + methanol system at 100 kPa takes place at $x_3 = 0.078$. This IL concentration is higher than that obtained when an inorganic salt was used, as can be seen in Table 7 where the minimum mole fraction of the electrolyte to break the acetone + methanol azeotrope is reported. As far as we know, only the action of an ionic liquid (1-ethyl-3-methylimidazolium tetrafluoroborate)[8] on the acetone + methanol system has been reported, but at isotherm conditions ($T = 328.15$ K). In this case, the azeotrope disappears at $x_3 = 0.100$.

It is a generally accepted fact that the variations of salt solubility in a mixed solvent with the system composition indicate that the salt interacts more strongly with one of solvents; that is, the salt effect is more pronounced, and thus using this salt as an entrainer in an extractive distillation, we can improve solvent separation. In accordance to this, [emim][triflate], which is totally miscible in acetone and methanol, should present a relative weak salt effect. However, what this great solubility in the mixture does is ensure an IL mole fraction in the liquid phase as high as one wants, and therefore, the salt effect, which is proportional to the amount of electrolyte that is present in solution, can be augmented. So, these unique properties of ILs combining the ionic properties of inorganic salts with its large solubility even in nonpolar solvents make them very suitable as entrainers in extractive distillation. For instance, the addition of lithium chloride in the acetone + methanol mixture at atmospheric pressure results in a very large increase in the acetone mole fraction of the vapor phase. However, the azeotrope of the mixed solvent system does not disappear even at saturation because the salt solubility in the mixture decreases dramatically as the acetone composition increases.[42] In this way, it is the decreased solubility of the inorganic salts in low-polar solvents that appears as its greatest handicap. Conversely, ILs do not present this sort of problem.

In the acetone + methanol + [emim][triflate] system, a crossover effect[43] between salting-in and salting-out of ILs on acetone is observed, such as in the case of sodium iodide, potassium iodide,[44] sodium thiocyanate,[45] or potassium thiocyanate.[46] On the contrary, this effect does not arise when lithium chloride,[42] lithium bromide,[47] lithium nitrate,[31] calcium bromide,[48] or zinc chloride[49] is used. Figure 3 shows the effect of [emim][triflate] and lithium nitrate[31] on the vapor−liquid equilibrium of the acetone + methanol system for an electrolyte mole fraction of $x_3 = 0.120$. The different behavior of the two electrolytes can be observed in it.

Conclusions

In this work, it has been confirmed that the electrolyte NRTL model, which has been extensively used with inorganic salts, is also suitable to predict the vapor−liquid equilibrium in the presence of an organic salt such as [emim][triflate]. In this way, this will allow us to extend the application of the model to the promising field of ionic liquids.

The addition of IL [emim][triflate] to acetone + methanol originates a noticeable salting-out effect on acetone near the azeotropic point and a slight salting-in effect at lower acetone concentrations (crossover effect), although this does not influence in any way the complete separation of these solvents. From the vapor−liquid equilibrium viewpoint, [emim][triflate] is as effective as other inorganic salts in breaking the azeotrope of the acetone + methanol system.

If we think about the extractive distillation process of acetone + methanol mixtures, the use of [emim][triflate] as the entrainer presents obvious advantages over inorganic salts. A great concentration of the electrolyte can be achieved in the liquid phase along the column because of its total miscibility with both solvents. Moreover, [emim][triflate] can be totally separated from methanol by flash distillation of the column bottom's stream, and a pure [emim][triflate] stream can be easily handled and mixed with the reflux stream to go back to the column top without introducing any additional amounts of methanol.

Compared with classic liquid entrainers, ionic liquids have two advantages: their ionic character, which produces heavier interactions with solvents and therefore a greater separating effect, and their zero vapor pressure which allows us to recover and reuse them free of a less-volatile component.

Furthermore, although wastage by evaporation is null, a considerable amount of ionic liquid is needed inside the column to break the azeotrope because of its large molecular mass. This fact and the high price of ionic liquids constitute the highest disadvantages. Nevertheless, we are confident the ionic liquids will come down in price when its demand augments, and what is more, one should not forget that the ionic liquid consumption in the distillation process is zero because its recovery is complete.

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