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1-Ethyl-3-methylimidazolium Dicyanamide as a Very Efficient Entrainer for the Extractive Distillation of the Acetone + Methanol System

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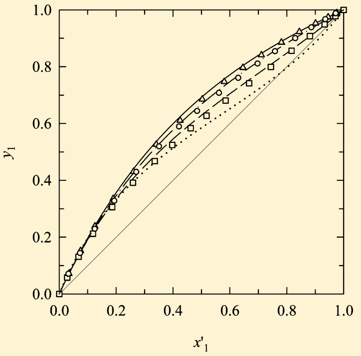
ABSTRACT: Isobaric vapor−liquid equilibria (VLE) for the ternary system acetone + methanol +1-ethyl-3-methylimidazolium dicyanamide ([emim][DCA]) as well as the two solvent + IL binary systems have been obtained at 100 kPa using a recirculating still. The addition of [emim][DCA] to the solvent mixture produced a salting-out effect greater than that produced by other ionic liquids, showing that this ionic liquid is, until now, the best IL tested as an entrainer for the extractive distillation of the acetone + methanol mixtures, causing the azeotrope to disappear for an ionic liquid mole fraction as low as 0.031, at 100 kPa. This behavior can be explained on the basis of the influence of the IL concentration on the activity coefficient of each solvent in the binary mixtures. The electrolyte nonrandom two-liquid (NRTL) model was used for fitting successfully the experimental data.



■ INTRODUCTION

Ionic liquids (ILs) are salts made up of an organic greatly asymmetric substituted cation such as imidazolium, pyridinium, pyrrolidinium, tetraalkylphosphonium, quaternary ammonium, and so forth and an anion such as halide, hexafluorophosphate, tetrafluoroborate, trifluoromethanesulfonate, acetate, dicyanamide, alkylsulfate, and so forth, their main feature being a very low melting point, mainly below 100 °C. 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, ILs exhibit unique properties: they are liquid in a wide range of temperatures, have no effective vapor pressure, are outstandingly good solvents for a wide range of inorganic, organic, and polymeric materials, and have a high thermal stability.[2] They are often used as a "green" solvent replacing volatile organic solvents, extraction media for separation processes,[3] and entrainers for extractive distillation.[4] Applications as catalysts for organic and organometallic synthesis,[5,6] lubricants, thermofluids, plasticizers, and electrically conductive liquids in electrochemistry have also been reported.[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. Moreover, 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.,[4,7] Jork et al.,[8] Beste et al.,[9] and Lei et al.[10] 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 have been 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 is 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, and 1-ethyl-3-methylimidazolium dicyanamide ([emim][DCA], CAS Registry No. 370865-89-7), 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, only five ILs have been used. Seiler et al.[7] and Kurzin et al.[11] have 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]-

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$[PF_6]$) at T = 313.15 K, respectively, using the headspace gas chromatography, and reporting only x−y data. Orchillés et al. have used 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([emim][triflate]),[12] 1-butyl-3-ethylimidazolium trifluoromethanesulfonate ([beim][triflate]),[13] and 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate ([bmpyr][triflate])[13] at isobaric conditions (p = 100 kPa) and reported T−x−y data. In addition to this, Kato et al.[14] have measured the vapor pressures for acetone and methanol with the ionic liquids 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([emim][NTf_2]), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim][NTf_2]), and 1,3-dimethylimidazolium dimethylphosphate ([mmim][DMP]) at 353.15 K with a static apparatus. Consequently, one of the aims of this work is to determine at what composition, if any, [emim][DCA] is capable of breaking the acetone + methanol azeotrope and compare its effect with those produced by other ILs.

■ EXPERIMENTAL SECTION

Materials. The solvents used were acetone (Merck, SupraSolv grade) and dried methanol (Sigma-Aldrich, analytical reagent grade). 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. 1-Ethyl-3-methylimidazolium dicyanamide (Purum) was supplied by Ionic Liquids Technologies (IoLiTec). Because of its hygroscopic character, it was vacuum-dried prior to use. The water mass fraction in the IL determined by Karl Fischer titration was $w_w < 0.0005$. The specifications of chemicals used are summarized in Table 1.

Table 1. Specifications of Chemical Samples

chemical name	source	mass fraction purity	purification method	final water mass fraction	analysis method
acetone	Merck	0.998	none	no detected	GC[b]
methanol	Sigma-Aldrich	0.998	none	no detected	GC[b]
[emim][DCA][a]	IoLiTec	0.98	vacuum desiccation	0.0005	KF[c]

[a] [emim][DCA] = 1-ethyl-3-methylimidazolium dicyanamide. [b] GC = gas chromatography. [c] KF = Karl Fischer titration.

After using the liquid mixtures in the VLE apparatus, their solvents were removed by heating and stirring under vacuum (398 K, 0.2 kPa) for 48 h to recover all of the IL. Thus, the IL was reused provided that no changes in its behavior as entrainer were produced.

Apparatus and Procedures. Vapor−liquid equilibrium measurements were made with an all-glass dynamic recirculating still (Pilodist, modified Labodest model). The apparatus has been described in a previous paper.[15] 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 the temperature measurements was 0.05 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 system, several acetone + IL mixtures of known composition were prepared, and different quantities of another 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 398 K until constant weight. A Mettler AE200 analytical balance with a standard uncertainty of $1 \cdot 10^{-4}$ 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 effective vapor pressure of ILs is zero, the vapor phase was made up of pure solvent, and it was not analyzed.

For the ternary system, the IL content in the liquid phase was gravimetrically determined as previously stated. 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 m × 3.2 mm) 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 temperature, 523 K; oven temperature, 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) + [emim][DCA] (3) and methanol (2) + [emim][DCA] (3) binary systems were obtained at 100 kPa, and the results are reported in Tables 2 and 3, respectively. In these tables, x_3 is the IL mole fraction in the liquid phase and T the equilibrium temperature.

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

x_3	T/K	x_3	T/K	x_3	T/K
0.0000	329.00	0.1822	332.38	0.4600	342.23
0.0149	329.32	0.2017	332.82	0.4885	343.92
0.0319	329.71	0.2222	333.24	0.5169	345.90
0.0534	330.14	0.2356	333.63	0.5212	346.31
0.0738	330.44	0.2538	334.07	0.5292	346.85
0.0926	330.76	0.3308	336.22	0.5413	347.93
0.1113	331.09	0.3756	337.97	0.5453	348.24
0.1305	331.43	0.4045	339.14	0.5509	348.71
0.1479	331.72	0.4190	339.91	0.5639	349.68
0.1648	332.05	0.4438	341.25		

[a] Standard uncertainties u are $u(T)$ = 0.05 K and $u(p)$ = 0.05 kPa, and the combined standard uncertainty u_c is $u_c(x_3)$ = 0.0001.

Furthermore, VLE for the acetone (1) + methanol (2) + [emim][DCA] (3) ternary system, at 100 kPa, were obtained

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

x_3	T/K	x_3	T/K	x_3	T/K
0.0000	337.42	0.1651	344.73	0.2798	352.29
0.0079	337.69	0.1758	345.49	0.2887	352.85
0.0160	337.93	0.1855	345.95	0.2993	353.65
0.0259	338.25	0.1967	346.75	0.3153	355.00
0.0356	338.58	0.2084	347.49	0.3433	357.03
0.0833	340.57	0.2178	348.09	0.3638	358.73
0.0923	341.01	0.2294	348.76	0.3745	359.59
0.1013	341.38	0.2370	349.36	0.3852	360.58
0.1110	341.94	0.2447	349.79	0.3986	361.71
0.1219	342.39	0.2541	350.50	0.4201	363.55
0.1336	342.99	0.2629	351.09	0.4294	364.30
0.1441	343.55	0.2716	351.73	0.4628	367.34
0.1557	344.17				

[a] Standard uncertainties u are $u(T) = 0.05$ K and $u(p) = 0.05$ kPa, and the combined standard uncertainty u_c is $u_c(x_3) = 0.0001$.

by keeping the IL mole fraction nearly constant in each of the three series reported at $x_3 \approx 0.057$, 0.136, and 0.228. These data are shown in Table 4, where 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.

Modeling the Vapor−Liquid Phase Equilibrium. We have used the electrolyte nonrandom two-liquid (NRTL) model[16] to model the VLE of the acetone (1) + methanol (2) + [emim][DCA] (3) ternary system. This model produces expressions for the liquid-phase activity coefficients of acetone (1) and methanol (2) in a binary or ternary system containing [emim][DCA] (3). These equations have been reported in a previous paper.[17] According to the proposed method, we need nine 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 acetone−methanol parameters were taken from a previous work,[15] and their values are reported in Table 5. The parameters corresponding to the 1−3 and 2−3 binary interactions were obtained by adjusting the VLE ternary data of Table 4 through the minimization of the objective function F

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

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][DCA]	0.140	29740.4	−12586.6
methanol	[emim][DCA]	0.142	31203.2	−14529.3

[a] From Vercher et al.[15]

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

x_3	x'_1	y_1	T/K	x_3	x'_1	y_1	T/K
0.058	0.000	0.000	339.40	0.138	0.564	0.706	333.85
0.058	0.028	0.058	338.52	0.137	0.631	0.759	333.29
0.058	0.068	0.131	337.43	0.136	0.699	0.809	332.84
0.059	0.119	0.212	336.24	0.135	0.761	0.852	332.49
0.059	0.186	0.306	334.87	0.135	0.832	0.898	332.16
0.059	0.259	0.392	333.67	0.133	0.888	0.936	331.94
0.058	0.336	0.468	332.55	0.132	0.937	0.965	331.68
0.058	0.397	0.525	331.86	0.130	0.974	0.986	331.54
0.057	0.462	0.583	331.24	0.129	1.000	1.000	331.42
0.057	0.518	0.627	330.79	0.229	0.000	0.000	348.76
0.057	0.585	0.680	330.42	0.237	0.034	0.071	348.06
0.056	0.667	0.741	330.13	0.236	0.075	0.152	346.85
0.056	0.744	0.800	329.97	0.235	0.125	0.238	345.60
0.055	0.817	0.856	329.91	0.230	0.190	0.335	343.91
0.055	0.881	0.908	329.92	0.231	0.261	0.431	342.47
0.054	0.933	0.949	330.00	0.232	0.341	0.526	341.01
0.054	0.971	0.978	330.06	0.230	0.425	0.611	339.69
0.053	1.000	1.000	330.13	0.230	0.503	0.685	338.56
0.134	0.000	0.000	342.99	0.228	0.580	0.747	337.54
0.136	0.034	0.069	341.97	0.228	0.646	0.797	336.74
0.137	0.075	0.142	341.15	0.226	0.710	0.841	336.02
0.139	0.127	0.227	340.03	0.225	0.781	0.886	335.28
0.140	0.196	0.326	338.66	0.225	0.844	0.923	334.62
0.140	0.272	0.428	337.31	0.223	0.901	0.953	334.13
0.140	0.353	0.517	336.16	0.221	0.946	0.975	333.71
0.139	0.423	0.587	335.21	0.221	0.976	0.989	333.45
0.139	0.487	0.642	334.52	0.220	1.000	1.000	333.29

[a] Standard uncertainties u are $u(T) = 0.05$ K and $u(p) = 0.05$ kPa, and the combined standard uncertainties u_c are $u_c(x'_1) = 0.001$, $u_c(x_3) = 0.001$, and $u_c(y_1) = 0.001$.

where γ_i is the activity coefficient of solvent *i*.

Following this procedure, we were able to obtain the binary parameters 1−3 and 2−3 by assuming ideal behavior for the vapor phase and iteratively solving the equilibrium conditions expressed in eq 2 for the molecular solvent

$$y_i p = X_i \gamma_i P_i^{\mathrm{o}} \tag{2}$$

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.[15] Results of the optimized binary parameters 1−3 and 2−3 are also summarized in Table 5.

With the electrolyte NRTL model and the parameters shown in Table 5, it was possible to reproduce the VLE of the acetone + methanol + [emim][DCA] system and compare it with the experimental data. Thus, the mean absolute deviation between the experimental and the calculated values of the mole fraction in the vapor phase was 0.006, whereas the mean absolute deviation of equilibrium temperature was 0.2 K. In Figure 1, the calculated and experimental VLE of the acetone + methanol + [emim][DCA] points are plotted on a (x'_1−y_1) diagram for x_3 ≈ 0.057, 0.136, and 0.228, respectively. In Figure 2, the same data are plotted on a (T−x'_1−y_1) diagram. Apparently, the model is able to properly reproduce the experimental VLE data.

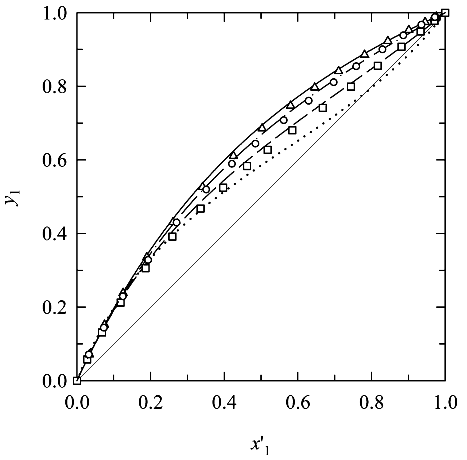

Figure 1. Composition diagram for acetone (1) + methanol (2) + [emim][DCA] (3) at 100 kPa for several IL mole fractions: dotted line, calculated for the IL-free system; dashed line, calculated for x_3 = 0.057; dashed−dotted line, calculated for x_3 = 0.136; solid line, calculated for x_3 = 0.228; □, experimental for x_3 ≈ 0.057; ○, experimental for x_3 ≈ 0.136; △, experimental for x_3 ≈ 0.228.

It is important to point out that small concentrations of [emim][DCA] 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 1 and 2. With the smallest mole fraction of [emim][DCA] used in this study (x_3 = 0.057), the azeotrope has already disappeared. From the electrolyte NRTL model, the mole fraction of [emim][DCA] at which the disappearance of the azeotrope for acetone + methanol at 100 kPa occurs is estimated to be x_3 = 0.031.

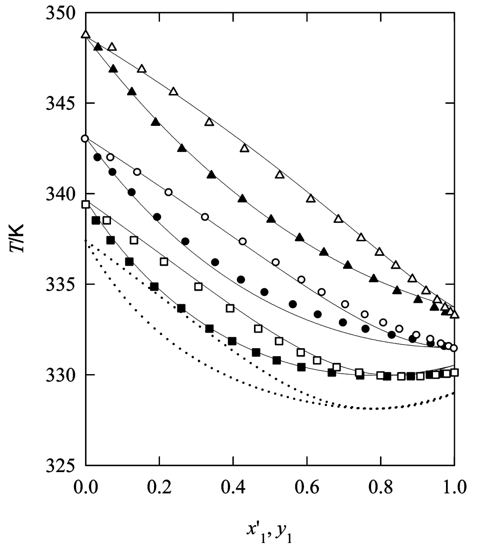

Figure 2. Temperature−composition diagram for acetone (1) + methanol (2) + [emim][DCA] (3) at 100 kPa for several IL mole fractions: ■, x'_1 experimental for x_3 ≈ 0.057; □, y_1 experimental for x_3 ≈ 0.057; ●, x'_1 experimental for x_3 ≈ 0.136; ○, y_1 experimental for x_3 ≈ 0.136; ▲, x'_1 experimental for x_3 ≈ 0.228; △, y_1 experimental for x_3 ≈ 0.228; solid lines, calculated with the e-NRTL model; dotted lines, calculated for the IL-free system.

In Figure 1 it can be also observed that [emim][DCA] produces a salting-out effect in the acetone + methanol system, which increases the relative volatility of the acetone over the methanol in the whole composition range. It is worth noting that all of the ILs studied up to now at isobaric conditions, [emim][triflate],[12] [beim][triflate],[13] and [bmpyr][triflate],[13] produce a crossover effect over the acetone + methanol system, which does not appear for [emim][DCA].

Table 6. 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.[7]
[emim][triflate][b]	0.078	isobaric, p = 100.00 kPa	Orchillés et al.[12]
[beim][triflate][c]	0.073	isobaric, p = 100.00 kPa	Orchillés et al.[13]
[bmpyr][triflate][d]	0.079	isobaric, p = 100.00 kPa	Orchillés et al.[13]
[emim][DCA][e]	0.031	isobaric, p = 100.00 kPa	this work

[a] [emim][BF_4] = 1-ethyl-3-methylimidazolium tetrafluoroborate. [b] [emim][triflate] = 1-ethyl-3-methylimidazolium trifluoromethanesulfonate. [c] [beim][triflate] = 1-butyl-3-ethylimidazolium trifluoromethanesulfonate. [d] [bmpyr][triflate] = 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate. [e] [emim][DCA] = 1-ethyl-3-methylimidazolium dicyanamide.

The effect produced by [emim][DCA] on the VLE of the acetone + methanol system can be compared with that caused by other ILs reported in the literature and shown in Table 6, on the basis of the minimum value of IL mole fraction x_3 needed to break the azeotrope. Although the data from Seiler et al.[7] are isothermal (T = 328.15 K), they can be compared with the isobaric data (p = 100.00 kPa) of Orchilles et al.[12,13] and those from this work, because in both conditions the acetone + methanol azeotrope happens at x'_1 ≈ 0.78. The data of Kurzin et al.[11] cannot be compared with the rest of data reported in Table 6 for two reasons. First, because at 313.15 K the azeotrope occurs at x'_1 ≈ 0.85 instead of x'_1 ≈ 0.78 (at p = 100 kPa or T = 328.15 K), making its breakage easier; and last, because although they claimed that [bpy][PF$_6$], at isothermal conditions (T = 313.15 K) breaks the acetone + methanol azeotrope at an IL molality $m_3 = 0.100$ mol·kg^{-1} ($x_3 \approx 0.006$), they only proved in their paper that, at this IL content, the azeotrope was moved from $x'_1 \approx 0.85$ to $x'_1 > 0.89$, without showing that the azeotrope had really disappeared. In Table 6, it can be observed that [emim][DCA] achieves the azeotrope breakage at a mole fraction much less than other ILs.

The great ability of [emim][DCA] to break the acetone + methanol azeotrope compared to other ILs can be explained on the basis of the different effects produced by adding IL at each solvent. In Figure 3, the activity coefficients of solvents acetone and methanol, in binary mixtures with [emim][DCA], [emim][triflate],[12] [beim][triflate],[13] or [bmpyr][triflate][13] against the IL mole fraction have been drawn. In this figure, it can be seen that the activity coefficient of acetone γ_1 follows the order [beim][triflate] < [bmpyr][triflate] < [emim][triflate] ≪ [emim][DCA], whereas the activity coefficient of methanol γ_2 follows the order [emim][DCA] ≪ [beim][triflate] < [bmpyr][triflate] < [emim][triflate]. Both effects lead to state that the addition of [emim][DCA] has the strongest effect on increasing γ_1 and the weakest effect on increasing γ_2, whereas for the rest of the ILs the effect on γ_1 and γ_2 is similar. As a result of that, the salting-out effect produced by these ILs on the VLE of the acetone + methanol system, which can be quantified by the quotient γ_1/γ_2, takes place in the order [emim][DCA] ≫ [emim][triflate] ≈ [beim][triflate] ≈ [bmpyr][triflate]. Moreover, the minimum value of x_3 needed to break the azeotrope just follows this order, as it can be seen in Table 6.

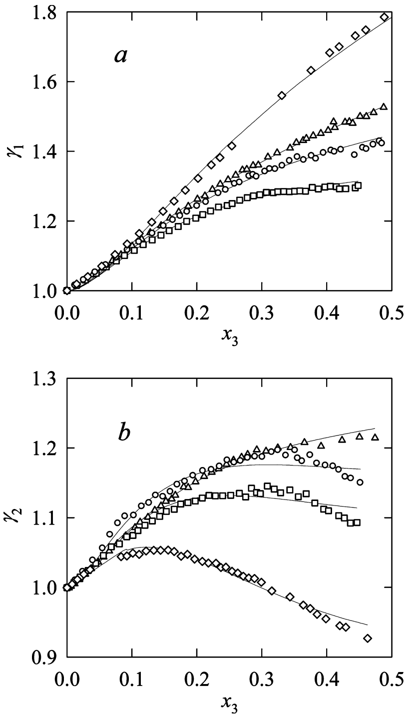

Figure 3. Variation of the activity coefficient of solvent γ_i with the mole fraction of IL x_3 in solvent + IL binary systems at 100.00 kPa. Solvent: (a) acetone (1); (b) methanol (2). IL: ◇, [emim][DCA]; △, [emim][triflate];[12] □, [beim][triflate];[13] ○, [bmpyr][triflate].[13] Solid lines, calculated with the electrolyte NTRL model.

The comparison among the effect produced by several ILs can be better seen in Figure 4, where the experimental relative volatility α_{12} between acetone (1) and methanol (2) at constant IL mole fraction $x_3 \approx 0.23$ for [emim][triflate],[12] [beim][triflate],[13] [bmpyr][triflate],[13] and [emim][DCA] has been depicted in the whole range of solvent composition, at p = 100.00 kPa. Values of α_{12} have been obtained by using eq 3

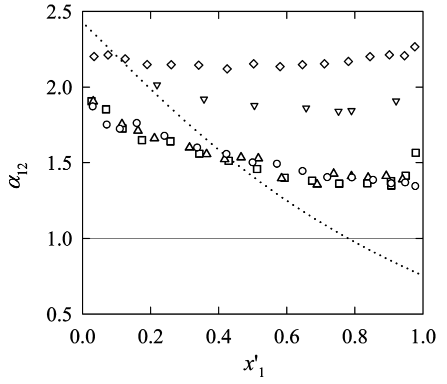

Figure 4. Variation of the relative volatility α_{12} between acetone (1) and methanol (2) with the acetone mole fraction x'_1 for different ILs: ◇, [emim][DCA] at x_3 = 0.228 and p = 100 kPa; △, [emim][triflate][12] at x_3 = 0.255 and p = 100 kPa; □, [beim][triflate][13] at x_3 = 0.228 and p = 100 kPa; ○, [bmpyr][triflate][13] at x_3 = 0.231 and p = 100 kPa; ▽, [emim][BF$_4$][7] at x_3 = 0.500 and T = 328.15 K; dotted line, calculated for the IL-free system.

$$\alpha_{12} = \frac{\gamma_1 P_1^{\circ}}{\gamma_2 P_2^{\circ}} \tag{3}$$

and the activity coefficients γ_i have been obtained from experimental VLE data by using eq 2.

In Figure 4, it can be observed that there are minimum differences in the behavior of the three ILs containing the [triflate] anion on the relative volatility of the mixture, matching all of the experimental points in the same line. On the contrary, the relative volatility in presence of [emim][DCA] is the greatest, and it presents a value nearly constant above 2.15. This constant value of the relative volatility in the whole range of solvent composition shows that [emim][DCA] at an IL mole fraction $x_3 \approx 0.228$ makes the behavior of the acetone + methanol system to be quasi-ideal.

In Figure 4, values of the relative volatility α_{12} between acetone (1) and methanol (2) in the presence of [emim][BF$_4$] at x_3 = 0.500, obtained from Seiler et al.[7] at T = 328.15 K have been also depicted. In spite of the mole fraction of [emim][BF$_4$] being much higher than that of [emim][DCA], its relative volatility does not come up to 2.0, and it is always less than that of [emim][DCA]. Therefore, the [emim][DCA] is the best IL tested up to now to break the azeotrope of the acetone + methanol system.

Nevertheless, Orchilles et al.[18] affirm that a good VLE behavior is not the only requirement demanded for a good entrainer. Other properties, such as melting point, viscosity, and decomposition temperature, play a very important role in the selection of an IL as entrainer. In this way, we can say that [emim][DCA] has all of the requirements demanded at an entrainer for the extractive distillation. It has a low melting point ($T_m \approx 261$ K) as well as a high thermal stability (decomposition temperature higher than 573 K), and a viscosity of 14.5 mPa·s at 298.15 K and 4.55 mPa·s at 353.15 K,[19] having one of the lowest viscosities for ILs. All of these properties make [emim][DCA] the best IL tested as an entrainer for the extractive distillation of acetone + methanol mixtures.

■ CONCLUSIONS

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

The electrolyte NRTL model is suitable to fit the VLE in the presence of an IL such as [emim][DCA]. From the parameters obtained, the ternary system has been reproduced with great precision. This confirms the extension of the model to ILs.

It has experimentally been proved that at 100 kPa the azeotrope of the acetone + methanol system has already disappeared at mole fractions of [emim][DCA] as low as 0.057, whereas the electrolyte NRTL model predicts a minimum value so that the azeotrope is broken at $x_3 = 0.031$.

The effect produced by the [emim][DCA] on the VLE of the acetone + methanol system is very higher than that produced by [emim][triflate], [beim][triflate], or [bmpyr][triflate] and reported in previous papers.[12,13] This effect can be explained on the basis of the different effects produced by adding the IL at each solvent. Moreover, [emim][DCA] has a low melting point and a large decomposition temperature. This, together with its very small viscosity, makes it possible for us to say that [emim][DCA] is the best IL tested as an entrainer to separate acetone + methanol mixtures by extractive distillation.

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