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Isobaric Vapor−Liquid Equilibria for the Extractive Distillation of Ethanol + Water Mixtures Using 1-Ethyl-3-methylimidazolium Dicyanamide

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ABSTRACT: Isobaric vapor−liquid equilibria (VLE) for the binary systems ethanol + 1-ethyl-3-methylimidazolium dicyanamide ([emim][DCA]) and water + [emim][DCA] as well as the VLE for the ternary system ethanol + water + [emim][DCA] have been obtained at 100 kPa using a recirculating still. The effect of [emim][DCA] on the ethanol + water system has been compared with that produced by another ionic liquid reported in the literature on the basis of the variation of solvent activity coefficients in ionic liquid (IL) + molecular solvent binary systems. From the results, [emim][DCA] appears as one of the best entrainers for the extractive distillation of the ethanol + water mixtures, causing the azeotrope to disappear at 100 kPa for ionic liquid mole fractions as low as 0.019. The experimental data were fitted with the Mock's electrolyte nonrandom two-liquid (NRTL) model, with a good agreement.

INTRODUCTION

Ionic liquids (ILs) are salts with a very low melting point, mainly below 100 °C. They are 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, dicyanamide, acetate, alkylsulfate, hexafluorophosphate, tetrafluoroborate, trifluoromethanesulfonate, and so forth. 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 have no effective vapor pressure, are liquid in a wide range of temperatures, 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 "green" solvents replacing organic volatile solvents and extraction media for separation processes.[3] Applications as catalysts for organic and organometallic synthesis,[4,5] lubricants, thermofluids, plasticizers, and electrically conductive liquids in electrochemistry have also been reported.[2]

The use of ILs as an entrainer in the extractive distillation of azeotropic or close-boiling mixtures is promising. Usually, the IL interacts more strongly with one of the two solvents, and preferential solvation may take place, modifying the relative volatility, and therefore improving the separation or producing the azeotrope disappearance. Even in cases where this effect is not too notable, the greater solubility of some ILs in low-polar solvents allows a larger IL concentration in the mixture and therefore a stronger salt effect.

In addition, 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 as inorganic salts, its practically nonvolatile character prevents its presence in distillate streams, and it can be totally removed from the solvents by flash distillation of the column bottom stream.

The vapor−liquid equilibria (VLE) of the ethanol + water system is, by far, the most studied one because of its industrial importance and the availability of both components. It shows, at atmospheric pressure, a minimum boiling point homogeneous azeotrope at an ethanol mole fraction of 0.90. In spite of the advantages of ILs as entrainers mentioned above, only five research teams placed at the Technical University of Berlin (Germany),[6−10] the Beijing University of Chemical Technology (China),[11−19] the University of Vigo (Spain),[20−24] the University of Valencia (Spain),[25] and the Zhejiang University of Technology (Hangzhou, China)[26−28] have studied their use to break this azeotrope. The ILs used contained mainly a dialkylimidazolium cation and [Cl],[9,10,12,19−21,26−28] [Br],[11,12] $[PF_6]$,[12] $[BF_4]$,[6−10,26] [Ac],[26] $[MeSO_4]$,[23] $[EtSO_4]$,[17,22,24] $[Me_2PO_4]$,[12−14,16,18] $[Et_2PO_4]$,[12,15] [DCA],[26] and [TfO][25] as anions, although, depending on the concentration, only some of them are able to break the azeotrope. Many of these studies are limited to determine the vapor pressure[11−19] or the activity coefficients[6−10] of ethanol and water in ILs, and the works reporting complete isobaric VLE data ($T−x−y$) for the ternary system containing ILs are not so numerous.[20−28] We have not found in the literature complete isothermal VLE data ($p−x−y$) for ternary systems containing ILs.

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 ternary system composed of ethanol, water, and 1-ethyl-3-methylimidazolium dicyanamide ([emim][DCA]) at 100 kPa in the whole range of composition. This ternary system was studied

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Table 1. Specifications of Chemical Samples

chemical name	source	mass fraction purity	purification method	final water mass fraction	analysis method
ethanol	Merck	0.999	none	no detected	GC[c]
water	Merck	*b*	none		
[emim][DCA][a]	IoLiTec	0.98	vacuum desiccation	0.0005	KF[d]

[a] [emim][DCA] = 1-ethyl-3-methylimidazolium dicyanamide. [b] Conductivity at 298.15 K: $\sigma \leq 1\ \mu\mathrm{S \cdot cm^{-1}}$. [c] GC = gas chromatography. [d] KF = Karl Fischer titration.

by Ge et al.[26] at different IL mass fractions, but keeping unchanged the mole fraction of ethanol calculated on IL-free basis at 0.95. Moreover, we have also determined the boiling points of ethanol + [emim][DCA] and water + [emim][DCA] binary mixtures at 100 kPa at several IL concentrations.

Table 2. VLE Data for Ethanol (1) + [emim][DCA] (3) at 100 kPa[a]

x_3	T/K	x_3	T/K	x_3	T/K
0.0000	351.21	0.1597	356.39	0.2934	362.82
0.0146	351.58	0.1791	357.14	0.3036	363.41
0.0155	351.60	0.1912	357.70	0.3221	364.45
0.0298	351.95	0.2031	358.32	0.3596	366.66
0.0313	351.98	0.2033	358.24	0.3732	367.56
0.0449	352.28	0.2148	358.85	0.3832	368.21
0.0466	352.34	0.2248	359.20	0.3941	368.83
0.0566	352.67	0.2465	360.28	0.4037	369.45
0.0719	353.15	0.2479	360.50	0.4377	371.70
0.0976	353.93	0.2534	360.69	0.4453	372.13
0.1095	354.46	0.2628	361.25	0.4534	372.83
0.1209	354.77	0.2737	361.75	0.4782	374.50
0.1339	355.28	0.2854	362.43	0.4927	375.43

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

■ EXPERIMENTAL SECTION

Materials. The solvents used were absolute ethanol (Merck, guaranteed reagent (GR) grade) and distilled water (Merck, high-performance liquid chromatography (HPLC) grade). No impurities were detected by GC, using the same procedure and conditions described below for the analysis of liquid mixtures. These chemicals were used without further purification. 1-Ethyl-3-methylimidazolium dicyanamide (Purum) was supplied by Ionic Liquids Tecnologies (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 $x_w < 0.0005$. 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 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 an entrainer were observed.

Apparatus and Procedure. VLE measurements were made with an all-glass dynamic recirculating still (Pilodist, modified Labodest model). The apparatus has been described in a previous paper.[29] 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 IL concentrated solution at which different quantities of ethanol or water were added until a very diluted solution was achieved. For the ternary system, several ethanol + IL mixtures of distinct composition were taken, and different quantities of another mixture of water + IL 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 constant temperature was reached (30 min or longer) were the equilibrium conditions assumed.

Sample Analysis. The IL content in the liquid phase was gravimetrically determined after the volatile components were separated from a known mass of sample (≈2.5 g) by evaporation at 398 K until constant mass. Ethanol and water contained in the liquid and condensed vapor phases were analyzed using a Varian Star 3400 CX gas chromatograph with a thermal conductivity detector (TCD). The chromatographic column (2 m × 3.2 mm) was packed with Porapak QS. The carrier gas was helium flowing at 30 $\mathrm{cm^3 \cdot min^{-1}}$, and the operating conditions were as follows: injector temperature of 523 K, oven temperature of 423 K, and detector temperature of 493 K.

For the samples of the liquid phase, the whole of the IL was retained by a trap located between the injector and the chromatographic column. In this way, the result of the analysis was not affected by the presence of the IL, as we were able to experimentally verify. The trap was periodically cleaned to prevent the IL from coming into the column. A calibration curve was obtained from a set of gravimetrically prepared standard solutions, which allowed us to quantify the amounts of water and ethanol in the samples. Thus it is that the combined standard uncertainty of the mole fraction of the components in the liquid and vapor phases was 0.001.

■ RESULTS AND DISCUSSION

Experimental Data. Boiling temperatures for ethanol (1) + [emim][DCA] (3) and water (2) + [emim][DCA] (3) were measured at 100 kPa, and the experimental results are reported in Tables 2 and 3, 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 ethanol (1) + water (2) + [emim][DCA] (3) ternary system, at 100 kPa, were obtained by keeping the IL mole fraction nearly constant in each of the three series at $x_3 \approx 0.056$, 0.133, and 0.225. These values are shown in

Table 3. VLE Data for Water (2) + [emim][DCA] (3) at 100 kPa[a]

x_3	T/K	x_3	T/K	x_3	T/K
0.0000	372.77	0.0801	375.73	0.1793	381.21
0.0049	373.08	0.0899	376.16	0.1862	381.62
0.0101	373.26	0.0989	376.59	0.1939	382.20
0.0189	373.58	0.1082	377.00	0.2019	382.72
0.0278	373.86	0.1184	377.56	0.2091	383.36
0.0349	374.11	0.1276	377.98	0.2175	384.01
0.0447	374.42	0.1371	378.56	0.2240	384.47
0.0531	374.69	0.1478	379.20	0.2384	385.70
0.0622	375.02	0.1562	379.70	0.2467	386.45
0.0707	375.38	0.1650	380.28	0.2669	388.19

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

Table 4. VLE Data for Ethanol (1) + Water (2) + [emim][DCA] (3) at 100 kPa[a]

x_3	x'_1	y_1	T/K	x_3	x'_1	y_1	T/K
0.053	0.000	0.000	374.69	0.135	0.561	0.745	356.82
0.057	0.036	0.202	369.03	0.134	0.633	0.784	356.41
0.057	0.080	0.336	364.77	0.133	0.682	0.812	356.12
0.058	0.135	0.442	361.41	0.132	0.754	0.851	355.76
0.057	0.204	0.520	358.71	0.132	0.823	0.889	355.55
0.057	0.271	0.568	357.01	0.130	0.877	0.921	355.44
0.057	0.338	0.609	355.90	0.129	0.917	0.945	355.27
0.057	0.390	0.636	355.16	0.128	0.959	0.972	355.12
0.057	0.444	0.662	354.63	0.127	1.000	1.000	354.97
0.056	0.507	0.684	354.08	0.224	0.000	0.000	384.47
0.056	0.583	0.724	353.55	0.232	0.033	0.140	381.22
0.055	0.654	0.762	353.19	0.233	0.067	0.253	378.36
0.055	0.716	0.796	352.91	0.233	0.114	0.355	375.07
0.054	0.775	0.835	352.75	0.229	0.178	0.467	371.27
0.054	0.840	0.877	352.57	0.231	0.251	0.559	368.36
0.054	0.901	0.919	352.49	0.226	0.336	0.638	365.62
0.053	0.953	0.960	352.46	0.226	0.414	0.697	364.00
0.053	1.000	1.000	352.55	0.226	0.485	0.739	362.83
0.128	0.000	0.000	377.98	0.226	0.560	0.783	361.84
0.135	0.036	0.163	373.49	0.225	0.636	0.820	361.11
0.136	0.076	0.293	370.22	0.224	0.707	0.856	360.56
0.137	0.132	0.409	366.59	0.223	0.780	0.889	360.15
0.137	0.208	0.513	363.18	0.222	0.840	0.918	359.88
0.136	0.288	0.575	360.82	0.220	0.888	0.942	359.64
0.136	0.372	0.636	358.98	0.218	0.923	0.959	359.47
0.136	0.443	0.679	357.94	0.216	0.957	0.977	359.32
0.135	0.501	0.714	357.40	0.215	1.000	1.000	359.25

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

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}
ethanol (1)	water (2)	0.330[a]	−311.48[a]	5744.1[a]
ethanol (1)	[emim][DCA] (3)	0.750	7034.1	−2054.2
water (2)	[emim][DCA] (3)	0.827	9557.0	−2613.0

[a] From Orchilles et al.[25]

Table 4 where x_3 is the mole fraction of IL in the liquid phase, x'_1 is the mole fraction of ethanol in the liquid phase expressed on an IL-free basis, y_1 is the mole fraction of ethanol in the vapor phase, and T is the equilibrium temperature.

Calculation of the Vapor−Liquid Phase Equilibrium. The electrolyte nonrandom two-liquid (NRTL) model worked just as well for correlating the VLE results reported in Table 4 as it was in previous papers dealing with ILs.[25,30,31] This model is an extension of the nonrandom two-liquid local composition proposed by Renon and Prausnitz[32] for liquid-phase activity coefficients. Chen et al.[33] derived a model for single solvent + electrolyte systems, and later Mock et al.[34,35] extended it to mixed solvent + electrolyte systems, by neglecting the long-range interaction contribution term.

The model makes it possible to generate expressions for the liquid-phase activity coefficients of ethanol (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,[36] 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.

The 1−2 binary ethanol−water parameters were taken from a previous work,[25] and their values are reported in Table 5. The parameters corresponding to the 1−3 and 2−3 binary interactions are usually obtained by adjusting the VLE data of the corresponding binary systems like those shown in Tables 2 and 3. However, in this case, the solvent−IL interaction parameters obtained in this way suffered from a total lack of predictability of the ternary system. Consequently, the model was applied by taking into account the (1−2) binary parameters shown in Table 5, whereas those corresponding to the (1−3) and (2−3) binary systems were obtained by adjusting the VLE data of Table 4 through the minimization of the objective function F

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

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

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

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.[25] 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

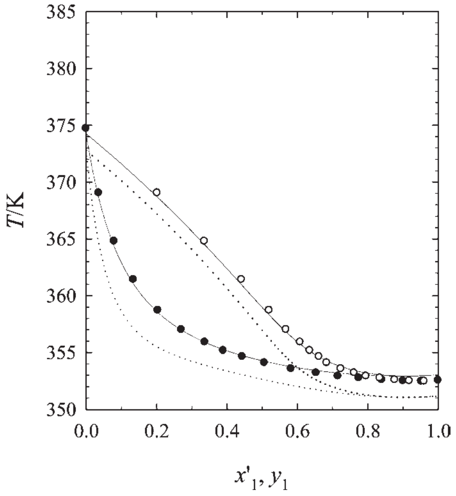

Figure 1. Temperature—composition diagram for ethanol (1) + water (2) + [emim][DCA] (3) at 100 kPa, with a mole fraction of IL $x_3 \approx 0.056$. ●, x'_1 experimental; ○, y_1 experimental; solid lines, calculated; dotted lines, calculated for the IL-free system.

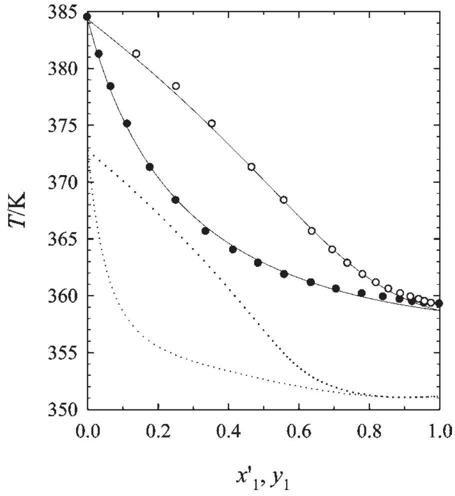

Figure 3. Temperature—composition diagram for ethanol (1) + water (2) + [emim][DCA] (3) at 100 kPa, with a mole fraction of IL $x_3 \approx 0.225$. ●, x'_1 experimental; ○, y_1 experimental; solid lines, calculated; dotted lines, calculated for the IL-free system.

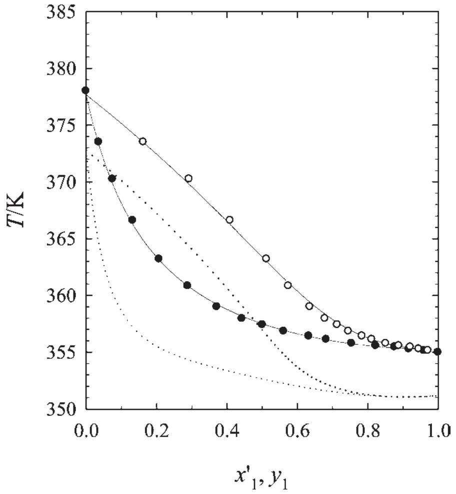

Figure 2. Temperature—composition diagram for ethanol (1) + water (2) + [emim][DCA] (3) at 100 kPa, with a mole fraction of IL $x_3 \approx 0.133$. ●, x'_1 experimental; ○, y_1 experimental; solid lines, calculated; dotted lines, calculated for the IL-free system.

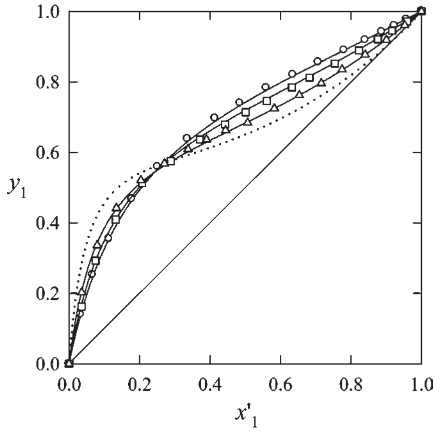

Figure 4. Salting effect of [emim][DCA] on the VLE of the ethanol (1) + water (2) system at 100 kPa for several IL mole fractions. △, $x_3 \approx 0.056$; □, $x_3 \approx 0.133$; ○, $x_3 \approx 0.225$; solid lines, calculated at the same IL mole fractions; dotted line, calculated for the IL-free system.

ethanol + water + [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 0.003, whereas the mean absolute deviation of equilibrium temperature was 0.2 K. In Figures 1, 2, and 3, the calculated and experimental VLE of the ethanol + water + [emim][DCA] points are plotted on a $(T-x'_1-y_1)$ diagram for $x_3 \approx 0.056$, 0.133, and 0.225, respectively. Apparently, the model is able to properly reproduce the experimental VLE data.

The [emim][DCA] produces a strong crossover effect between salting-in and salting-out in the ethanol + water system, as observed in Figure 4, where the different solid lines, which represent the $(y_1-x'_1)$ equilibrium, separate from the diagonal for $x'_1 > 0.27$, while they are closer to it for $x'_1 < 0.27$, as the IL mole fraction increases. This effect, which is seldom found with inorganic salts, is very common with ILs, and it has been pointed out in a lot of papers, as many in the ethanol + water + IL[8,13,16−21,24,25,27,28] systems as in other IL-containing systems.[30,31,37−40]

With the smallest mole fraction of [emim][DCA] used in this study ($x_3 = 0.056$), the azeotrope has already disappeared. From the electrolyte NRTL model, the mole fraction of [emim][DCA] at which the disappearance of the azeotrope for ethanol + water at 100 kPa occurs is estimated to be $x_3 = 0.019$.

The effect produced by the [emim][DCA] on the VLE of the ethanol + water system can be compared with that produced by other ILs reported in the literature. Ge et al.[26] claimed that [emim][Cl], [emim][Ac], and [bmim][Ac] produce the greatest salt effect on this system because they can break the ethanol + water azeotrope at IL mole fractions of $x_3 = 0.016$, 0.013, and 0.014, respectively. All of these x_3 values are smaller than that calculated in this work for the [emim][DCA] ($x_3 = 0.019$). However, Orchilles et al.[25] affirm that a good VLE behavior is not the only requirement demanded for a good entrainer.

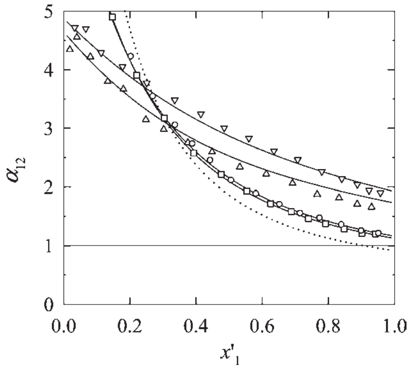

Figure 5. Variation of the relative volatility, α_{12}, between ethanol (1) and water (2) with the ethanol mole fraction x'_1 at 100 kPa for different ILs: Experimental points, □, [emim][triflate], x_3 = 0.054; ○, [emim][DCA], x_3 = 0.056; △, [emim][triflate], x_3 = 0.215; ▽, [emim][DCA], x_3 = 0.225; solid lines, calculated at the same IL mole fraction; dotted line, calculated for the IL-free system.

Other properties, as melting point, viscosity, and decomposition temperature of the entrainers, play a very important part in the selection of them. On this basis, they stated that [emim][triflate] could be a more appropriate entrainer for the separation of the ethanol + water mixture although it breaks the ethanol + water azeotrope at an IL mole fraction of x_3 = 0.023.

If a comparison is made between the salt effect produced by [emim][DCA] and that produced by [emim][triflate] on the ethanol + water system, it can be observed that [emim][DCA] achieves the azeotrope breakage at a slightly smaller IL mole fraction. In Figure 5, the relative volatility α_{12} between ethanol (1) and water (2) at two constant IL mole fractions $x_3 \approx 0.055$ and 0.22 has been depicted in the whole range of solvent composition. Both experimental and calculated values of α_{12} have been obtained by using eq 3:

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

To calculate experimental α_{12} values, the activity coefficients γ_i have been obtained from experimental VLE data by using eq 2, whereas the calculated values, γ_i, have been obtained from the electrolyte NRTL model, using the parameters of Table 5. In Figure 5, it can be observed that for both ILs and at the two IL mole fractions tested the azeotrope has disappeared. It can be also observed that at $x_3 \approx 0.055$ there are minimum differences in the behavior of both ILs, whereas at $x_3 \approx 0.22$ [emim][DCA] produces a greater salt effect than [emim][triflate]. Furthermore, although [emim][DCA] has a melting point similar to [emim][triflate] ($T_m \approx 261$ K) as well as a high thermal stability (decomposition temperature higher than 573 K), it has a viscosity of 14.5 mPa·s at 298.15 K and 4.55 mPa·s at 353.15 K,[41] which is several times lower than that of [emim][triflate].[42] All of these properties make [emim][DCA] one of the best ILs used as an entrainer for the extractive distillation of ethanol + water mixtures, even though its separation ability is lower and its price higher than those of other ILs.

CONCLUSIONS

In this work, VLE of ethanol + [emim][DCA], water + [emim][DCA], and ethanol + water + [emim][DCA] at 100 kPa have been obtained with 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 been experimentally proved that at 100 kPa the azeotrope of the ethanol + water system disappears when the mole fraction of [emim][DCA] is x_3 = 0.056, and the electrolyte NRTL model predicts that it does the same when x_3 = 0.019.

The effect produced by the [emim][DCA] on the VLE of the ethanol + water system is slightly smaller than that produced by [emim][Cl], [emim][Ac], or [bmim][Ac], and its price is noticeably higher. In spite of that, [emim][DCA] has the advantage of its smaller viscosity and melting point, as well as its larger decomposition temperature.

In comparison with [emim][triflate], it can be said that the behavior of [emim][DCA] presents minimum differences at $x_3 \approx 0.055$, whereas at $x_3 \approx 0.22$ [emim][DCA] produces a greater salt effect than [emim][triflate]. This, together with its lower viscosity makes it possible for us to say that [emim][DCA] may be a good entrainer to separate ethanol + water mixtures by distillation.

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