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Isobaric Vapor−Liquid and Liquid−Liquid Equilibria for Chloroform + Methanol + 1-Ethyl-3-methylimidazolium Trifluoromethanesulfonate at 100 kPa

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Isobaric vapor−liquid equilibria for the binary system chloroform + methanol as well as the vapor−liquid equilibria for the chloroform + methanol + [emim][triflate] ternary system have been obtained at 100 kPa using a recirculating still. The ternary ionic liquid (IL) system presents an immiscibility zone at high chloroform composition, which increases with the temperature. Liquid−liquid equilibria for this system have also been determined. The measured ternary vapor−liquid equilibrium data were correlated using the Mock's electrolyte nonrandom two-liquid (NRTL) model which reproduces reasonably well the experimental values and predicts the total disappearance of the azeotrope when the mole fraction of ionic liquid in the liquid phase is 0.25. The immiscibility does not affect the use of [emim][triflate] as the entrainer for the complete chloroform + methanol separation.

Introduction

During the past few years, ionic liquids (ILs) have received special attention mainly because of their possible contribution in environmentally friendly processes.[1−3] Applications as "green" solvents in extraction media, catalysts in chemical reactions, entrainers for separation of azeotropic mixtures, and others have been reported.[4,5]

The use of ILs presents advantages over those of solvents or inorganic salts in distillation processes. This is so because ILs have practically no vapor pressure and are typically less corrosive than molten salts and thus more easily handled.

It was Arlt and co-workers[6−8] who first suggested adding ILs to improve the separation of azeotropic mixtures. Since then, the use of ILs is well-informed, although only for isobaric systems. In this way, the works of Arce et al.,[5] Calvar et al.,[9,10] Zhang et al.,[11,12] and Orchillés et al.[13,14] should be mentioned. As far as we know, complete isothermal vapor−liquid equilibrium (VLE) data (P, x, y) have not been reported in the literature.

In a previous work[15] we presented the effect of 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([emim][triflate]) on the vapor−liquid equilibria for the system chloroform + ethanol which is difficult to separate by distillation because of the presence of an azeotrope. There, a small immiscibility zone for the ternary system was detected at the highest chloroform composition, which became more evident with temperature. As a continuation work, we present here the isobaric vapor−liquid equilibria for the chloroform + methanol + [emim][triflate] binary and ternary systems at 100 kPa.

The chloroform (1) + methanol (2) system shows, at atmospheric pressure, a minimum boiling point azeotrope at $x_1 \approx 0.65$. For this system, lithium chloride,[16,17] potassium acetate,[17] calcium chloride,[17] and sodium iodide[18] have been used as entrainers although the low solubility of the salts at greater chloroform composition hinders any azeotrope breaking effect. Thus, one of the aims of this work is to determine the immiscibility zone for the chloroform (1) + methanol (2) + [emim][triflate] (3) system, as well as to test the capability of this IL to break the azeotrope. Until now, we have not found a paper reporting the breakage of this azeotrope by an IL or a salt.

Experimental Section

Materials. The chemicals used were chloroform (Merck, HPLC grade, minimum mass fraction 0.998), dried methanol (Riedel-de Haën, analytical reagent, minimum mass fraction 0.998), and the ionic liquid 1-ethyl-3-methylimidazolium trifluoromethanesulfonate supplied by Solvent Innovation (purum, minimum mass fraction 0.98). It was selected because of its solubility in both solvents, its low melting point ($T_m < 264$ K) that makes it easier to use it, and its high decomposition temperature ($T_d > 623$ K). Prior treatment of the IL before use and its recovering procedure after being used were given elsewhere.[15]

Apparatus and Procedure. An all-glass dynamic recirculating still (Pilodist, modified Labodest model) was used for the VLE measurement. The apparatus is equipped with a Cottrell circulation pump[19] and has been described in previous papers.[14,20] The standard uncertainties for pressure and temperature measurements were 0.05 kPa and 0.01 K, respectively.

The VLE for the binary chloroform + methanol system was obtained by adding different quantities of methanol at an initial sample of pure chloroform. For the ternary system, several chloroform + IL mixtures of known composition were prepared, and different quantities of a mixture of methanol + IL were added with a suitable composition so that the IL mole fraction in each series was as constant as possible. 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. For the ternary system, the mass fraction of IL reached, w_3, was approximately 0.80 at 350.95 K.

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Table 1. VLE Data for Chloroform (1) + Methanol (2) at 100 kPa

x_1	y_1	T/K	x_1	y_1	T/K
0.0000	0.0000	337.41	0.5521	0.6231	326.29
0.0231	0.0629	336.29	0.5977	0.6354	326.22
0.0413	0.1078	335.51	0.6347	0.6454	326.17
0.0584	0.1431	334.80	0.6685	0.6544	326.17
0.0805	0.1916	333.97	0.7128	0.6656	326.21
0.1081	0.2463	332.99	0.7452	0.6769	326.27
0.1382	0.2991	332.00	0.7821	0.6893	326.41
0.1767	0.3558	330.86	0.8178	0.7060	326.60
0.2218	0.4127	329.74	0.8562	0.7268	326.91
0.2702	0.4647	328.73	0.8857	0.7453	327.27
0.3218	0.5066	327.92	0.9131	0.7688	327.85
0.3685	0.5374	327.30	0.9407	0.8012	328.67
0.4203	0.5648	326.93	0.9629	0.8408	329.77
0.4642	0.5861	326.64	0.9805	0.9123	331.45
0.5092	0.6059	326.42	1.0000	1.0000	333.96

Liquid−liquid ternary equilibrium data were obtained by preparing mixtures in the immiscibility zone and placing them inside of test tubes. The tested tubes were maintained at constant temperature after being stirred, and samples were taken from both phases which were analyzed as described below. The temperature was controlled with a thermostatted bath with an uncertainty in their measurements of 0.1 K, and the pressure remained at 100 ± 3 kPa. More details of this experimental procedure are given elsewhere.[15]

Sample Analysis. The IL mole fraction in the liquid phase was gravimetrically determined after separating the volatile components at 393 K until constant mass. Chloroform and methanol in the liquid and condensed vapor phases were analyzed by gas chromatography in a thermal conductivity detector (TCD). Details of the chromatographic column and procedure can be seen in a previous paper.[14] It was possible to quantify the amounts of chloroform and methanol in the samples from a calibration curve obtained with a set of gravimetrically prepared standard solutions. In this way, the combined standard uncertainty of the mole fractions of the components in the liquid and vapor phases was 0.001.

Results and Discussion

Chloroform + Methanol Binary System. Table 1 presents the experimental results of the VLE for the chloroform (1) + methanol (2) binary system at 100 kPa. In this table x_1 and y_1 are the mole fraction of chloroform in the liquid and vapor phases, respectively, and T is the equilibrium temperature. The experimental data show a minimum boiling point azeotrope at $x_1 = 0.649$ and $T = 326.17$ K, which can be interpolated from the experimental values. The system shows a good thermodynamic consistency according to the Van Ness et al. test[21] modified by Fredenslund et al.[22] The test gave a mean absolute deviation between calculated and measured mole fractions of chloroform in the vapor phase of $\delta y = 0.0025$, showing that the values are thermodynamically consistent.

To compare our experimental values with those existing in the literature, in most cases obtained at 101.32 kPa, we have reduced our data to this pressure using the nonrandom two-liquid (NRTL) model as will be described later. Our data agree very well with those reported by Vasil'eva et al.[23] and Hiaki et al.[24] As far as the azeotropic point is concerned, our data calculated at 101.32 kPa ($x_1 = 0.649$, $T = 326.52$ K) are in complete agreement with those reported by Vasil'eva et al.[23] ($x_1 = 0.653$, $T = 326.50$ K) and Hiaki et al.[24] ($x_1 = 0.648$, $T = 326.48$ K) but differ by 0.2 K from those reported by Nagata[25] ($x_1 = 0.653$, $T = 326.73$ K) or Tanaka[26] ($x_1 = 0.650$, $T = 326.65$ K).

Table 2. Mole Fraction Compositions of the Experimental Tie-Line Ends for the Ternary System Chloroform (1) + Methanol (2) + [emim][triflate] (3) at (293.15 and 313.15) K

	[emim][triflate]-rich phase			chloroform-rich phase		
T/K	x_1	x_2	x_3	y_1	y_2	y_3
293.15	0.8052	0.0000	0.1948	0.9981	0.0000	0.0019
	0.8038	0.0112	0.1851	0.9943	0.0035	0.0022
	0.8021	0.0170	0.1809	0.9921	0.0056	0.0023
	0.8018	0.0291	0.1691	0.9909	0.0066	0.0025
	0.7981	0.0344	0.1675	0.9893	0.0080	0.0027
	0.7972	0.0451	0.1577	0.9868	0.0103	0.0029
	0.7963	0.0520	0.1517	0.9847	0.0121	0.0032
	0.7953	0.0642	0.1406	0.9805	0.0158	0.0037
	0.7937	0.0680	0.1384	0.9774	0.0184	0.0042
	0.7967	0.0769	0.1263	0.9742	0.0210	0.0048
	0.7971	0.0839	0.1190	0.9706	0.0238	0.0056
	0.7990	0.0889	0.1121	0.9648	0.0284	0.0068
	0.8030	0.0905	0.1065	0.9607	0.0313	0.0079
	0.8206	0.0951	0.0843	0.9460	0.0406	0.0134
	0.8099	0.0957	0.0944	0.9542	0.0354	0.0104
313.15	0.7868	0.0000	0.2132	0.9982	0.0000	0.0018
	0.7815	0.0154	0.2032	0.9951	0.0029	0.0020
	0.7799	0.0210	0.1992	0.9909	0.0070	0.0021
	0.7790	0.0271	0.1939	0.9906	0.0072	0.0022
	0.7754	0.0370	0.1876	0.9875	0.0101	0.0024
	0.7757	0.0439	0.1804	0.9843	0.0131	0.0026
	0.7742	0.0523	0.1735	0.9816	0.0156	0.0029
	0.7724	0.0580	0.1696	0.9791	0.0178	0.0031
	0.7692	0.0700	0.1608	0.9751	0.0214	0.0035
	0.7698	0.0732	0.1571	0.9715	0.0244	0.0041
	0.7698	0.0869	0.1433	0.9645	0.0302	0.0053
	0.7742	0.0955	0.1303	0.9587	0.0343	0.0070
	0.7773	0.1011	0.1216	0.9544	0.0379	0.0077
	0.7825	0.1049	0.1126	0.9474	0.0429	0.0097
	0.7950	0.1099	0.0951	0.9318	0.0535	0.0147

Solvent + [emim][triflate] Binary System. Boiling temperatures for chloroform (1) + [emim][triflate] (3) and methanol (2) + [emim][triflate] (3) were reported in previous papers.[13,15] In the case of chloroform + IL binary system, it was observed that for $x_3 < 0.235$ the boiling temperature of solution remained constant[15] which was associated with the presence of immiscibility between both components.

Chloroform + Methanol + [emim][triflate] System. [emim][triflate] has been said not to be completely miscible in chloroform, so an immiscible region for the ternary system is supposed to occur. In this way, liquid−liquid equilibria for the chloroform (1) + methanol (2) + [emim][triflate] (3) system, were measured at (293.15 and 313.15) K, following the experimental procedure reported before. The experimental results are presented in Table 2 and are plotted in Figures 1 and 2, where only the chloroform-

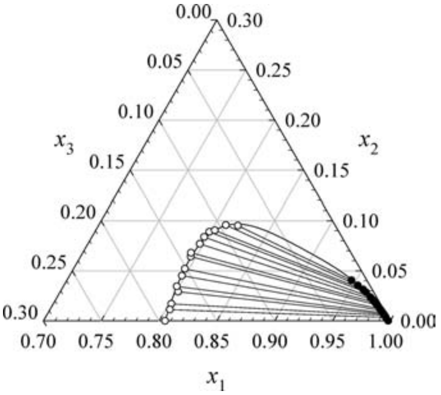

Figure 1. Liquid−liquid equilibrium data for the chloroform (1) + methanol (2) + [emim][triflate] (3) system at 293.15 K: ●, chloroform-rich phase; ○, [emim][triflate]-rich phase; solid straight line, experimental tie lines.

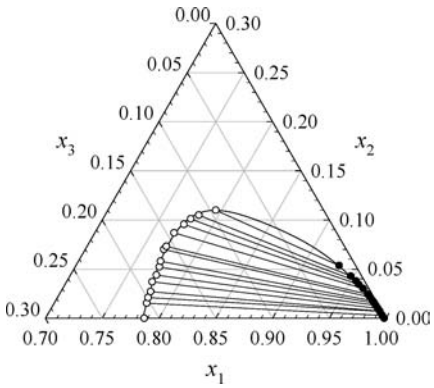

Figure 2. Liquid−liquid equilibrium data for the chloroform (1) + methanol (2) + [emim][triflate] (3) system at 313.15 K: ●, chloroform-rich phase; ○, [emim][triflate]-rich phase; solid straight line, experimental tie lines.

rich corner has been included for clarity. In these figures a small immiscible region can be seen, which expands with temperature, being placed at the highest chloroform compositions. The ternary system is completely miscible for $x_1 < 0.769$ or $x_2 > 0.110$ at temperatures lower than 313.15 K.

The VLE for the chloroform (1) + methanol (2) + [emim][triflate] (3) ternary system, at 100 kPa, was obtained by trying to maintain the IL mole fraction in each of the four series at $x_3 \approx 0.06$, 0.12, 0.23, and 0.35. Table 3 shows the experimental values of the VLE for the ternary system. In this table x_1' is the mole fraction of chloroform in the liquid phase expressed in an IL-free basis; y_1 is the mole fraction of chloroform in the vapor phase; T is the equilibrium temperature; and x_3 is the mole fraction of [emim][triflate] in the liquid phase.

The location of the liquid-phase compositions for the experimental points in every series is drawn on the ternary diagram of Figure 3, as well as the immiscibility area at (293.15 and 313.15) K. In this figure, it is observed that only very few points in two series remain inside the immiscibility area, whereas the series at the highest IL composition exhibits total liquid phase miscibility. Although total miscibility is predicted for the series at $x_3 \approx 0.23$, two points were taken in a region which showed heterogeneity in the liquid phase. This fact can be explained by taking into account that the equilibrium temperature in all of the series is higher than 313.15 K and, as known, the higher temperature, the higher area of the immiscible region. Despite the immiscibility found in some points, we had no problems with the samples taken with a syringe because they presented emulsification and therefore had a reproducible composition.

Calculation of the Vapor−Liquid Phase Equilibrium. As seen in previous papers,[13−15] the electrolyte NRTL model was proved to correlate well with the VLE results of systems containing [emim][triflate]. This model is an extension of the NRTL one proposed by Chen et al.[27] for single-solvent + electrolyte systems. Later, by neglecting the long-range interaction contribution term, Mock et al.[28] extended the model to mixed-solvent + electrolyte systems.

The electrolyte NRTL model makes it possible to obtain expressions for the liquid-phase activity coefficients of solvents in binary or ternary systems containing [emim][triflate], which behaves as an electrolyte. Those expressions were reported in a previous paper,[29] and in according with them, nine binary adjustable parameters are necessary to correlate the phase equilibrium of mixed-solvent + electrolyte systems. 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

Table 3. VLE Data for Chloroform (1) + Methanol (2) + [emim][triflate] (3) at 100 kPa

x_3	$x_1'^a$	y_1	T/K
0.0563	0.000	0.000	339.19
0.0579	0.033	0.086	337.65
0.0569	0.070	0.169	336.01
0.0557	0.112	0.243	334.38
0.0540	0.168	0.342	332.55
0.0544	0.229	0.416	330.96
0.0551	0.295	0.489	329.57
0.0554	0.367	0.554	328.43
0.0563	0.439	0.598	327.72
0.0563	0.502	0.627	327.28
0.0569	0.576	0.663	327.03
0.0573	0.650	0.690	327.00
0.0573	0.719	0.717	327.22
0.0582	0.797	0.753	327.78
0.0591	0.872	0.802	328.78
0.0576	0.919[b]	0.854	330.14
0.0580	0.962[b]	0.927	331.91
0.0583	1.000[b]	1.000	334.01
0.1126	0.000	0.000	340.90
0.1168	0.031	0.074	339.51
0.1215	0.068	0.154	338.08
0.1098	0.107	0.237	336.25
0.1106	0.161	0.324	334.55
0.1116	0.218	0.396	333.01
0.1127	0.284	0.474	331.49
0.1139	0.362	0.539	330.10
0.1148	0.438	0.597	329.12
0.1153	0.507	0.641	328.55
0.1170	0.580	0.680	328.20
0.1175	0.652	0.712	328.11
0.1178	0.734	0.759	328.32
0.1185	0.809	0.803	328.96
0.1184	0.876	0.846	329.93
0.1203	0.932[b]	0.909	331.41
0.1187	0.972[b]	0.959	332.76
0.1195	1.000[b]	1.000	334.00
0.2228	0.000	0.000	345.19
0.2231	0.027	0.064	343.57
0.2223	0.060	0.133	342.26
0.2248	0.095	0.203	341.19
0.2255	0.143	0.275	339.75
0.2283	0.195	0.352	338.38
0.2315	0.253	0.422	337.07
0.2332	0.315	0.480	335.81
0.2347	0.383	0.548	334.56
0.2356	0.460	0.607	333.48
0.2369	0.543	0.668	332.62
0.2393	0.632	0.727	332.02
0.2413	0.722	0.784	331.76
0.2421	0.809	0.840	331.85
0.2452	0.906	0.902	332.35
0.2428	0.961	0.949	332.98
0.2392	0.986[b]	0.980	333.51
0.2320	1.000[b]	1.000	333.99
0.3345	0.000	0.000	350.95
0.3322	0.028	0.069	349.22
0.3343	0.060	0.132	348.18
0.3347	0.093	0.195	347.22
0.3341	0.136	0.267	345.80
0.3363	0.186	0.331	344.65
0.3415	0.243	0.403	343.48
0.3433	0.308	0.473	342.31
0.3489	0.384	0.548	341.23
0.3514	0.464	0.613	340.09
0.3565	0.553	0.681	339.25
0.3582	0.645	0.746	338.44
0.3573	0.725	0.807	337.92
0.3588	0.813	0.870	337.57
0.3603	0.883	0.920	337.58
0.3606	0.940	0.956	337.58
0.3561	0.975	0.981	337.48
0.3520	1.000	1.000	337.48

[a] x_1' is the mole fraction of chloroform in the liquid phase expressed on an IL-free basis. [b] Because of the immiscibility, this value represents a bulk composition for the liquid phases.

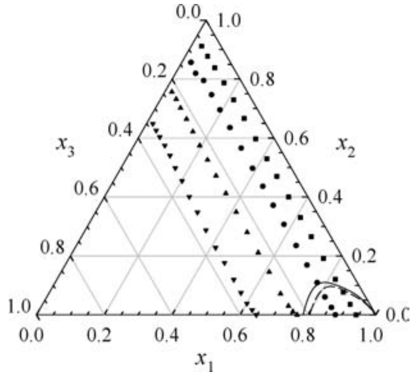

Figure 3. Location of the liquid-phase composition for the experimental points taken to determine the VLE for the chloroform (1) + methanol (2) + [emim][triflate] (3) system: ■, $x_3 = 0.06$; ●, $x_3 = 0.12$; ▲, $x_3 = 0.23$; ▼, $x_3 = 0.35$; solid line represents immiscible zone at 313.15 K; dashed line represents immiscible zone at 293.15 K.

Table 4. 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

i component	j component	$\alpha_{i,j}$	$\Delta g_{i,j}$ $\text{J}\cdot\text{mol}^{-1}$	$\Delta g_{j,i}$ $\text{J}\cdot\text{mol}^{-1}$
chloroform	methanol	0.159	7900.3	−2369.1
chloroform	[emim][triflate]	0.362	14081.3	−2710.4
methanol	[emim][triflate]	0.967	5503.2	−1273.8

$\Delta g_{3,2}$), and the rest are nonrandomness factors ($\alpha_{1,2} = \alpha_{2,1}$, $\alpha_{1,3} = \alpha_{3,1}$, $\alpha_{2,3} = \alpha_{3,2}$).

These parameters were obtained from the VLE data by minimization of the objective function F:

$$F = \sum_N h\left|T_{\text{exptl}} - T_{\text{calcd}}\right| + \sum_N k\left|y_{1,\text{exptl}} - y_{1,\text{calcd}}\right| \tag{1}$$

where T is the equilibrium temperature, y_1 is the vapor phase mole fraction of chloroform, the indices exptl and calcd denote the experimental and calculated values, respectively, h and k are weighting parameters, and the summations are extended to the whole range of data points.

In this way, the (1−2) binary solvent−solvent parameters were obtained from the VLE data of chloroform (1) + methanol (2) shown in Table 1.

As far as the binary solvent-[emim][triflate] parameters are concerned, they had to be determined from the experimental VLE data of the chloroform (1) + methanol (2) + [emim][triflate] (3) system and the electrolyte NRTL model. We proceeded in such a manner because the (1−3) binary parameters could not be estimated from the VLE data of the chloroform (1) + [emim][triflate] (3) binary system because of the immiscibility between these components at $x_3 < 0.235$ which resulted in a constant boiling point.

The parameters of the model are reported in Table 4 and were obtained by assuming ideal behavior for the vapor phase and searching the temperature so that the summations of the vapor phase mole fractions of solvents expressed by eq 2 were unity.

$$y_iP = X_i\gamma_iP_i^{\text{o}} \tag{2}$$

Table 5. Experimental Antoine Coefficients and Mean Absolute Deviations for Chloroform and Methanol

component	temperature range K	Antoine coefficients[a] A	B	C	σ (P°)[b] kPa
chloroform[c]	305 to 342	14.0135	2700.34	−46.93	0.033
methanol[d]	315 to 345	16.4847	3563.73	−37.42	0.014

[a] Antoine equation: $\ln P°/\text{kPa} = A - B/(T/\text{K} + C)$. [b] $\sigma (P°) = [\sum(P^{\text{o}}_{\text{exptl}} - P^{\text{o}}_{\text{calcd}})^2/(N-3)]^{1/2}$. [c] From ref 15. [d] From ref 20.

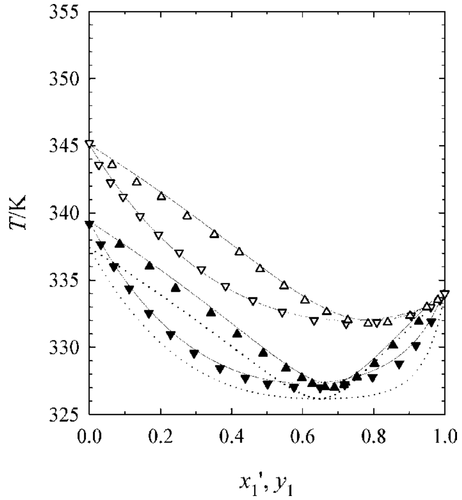

Figure 4. Temperature−composition diagram for chloroform (1) + methanol (2) + [emim][triflate] (3) at 100 kPa, at several mole fractions of IL: ▼, x_1' experimental at $x_3 = 0.06$; ▲, y_1 experimental at $x_3 = 0.06$; ▽, x_1' experimental at $x_3 = 0.23$; △, y_1 experimental at $x_3 = 0.23$; solid lines, calculated; dotted lines, calculated for the IL-free system.

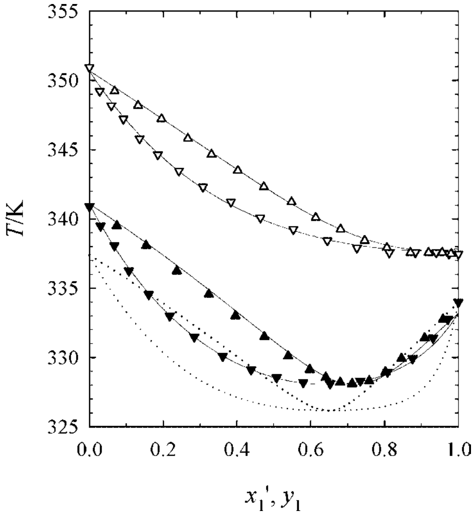

Figure 5. Temperature−composition diagram for chloroform (1) + methanol (2) + [emim][triflate] (3) at 100 kPa, at several mole fractions of IL: ▼, x_1' experimental at $x_3 = 0.12$; ▲, y_1 experimental at $x_3 = 0.12$; ▽, x_1' experimental at $x_3 = 0.35$; △, y_1 experimental at $x_3 = 0.35$; solid lines, calculated; dotted lines, calculated for the IL-free system.

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 solvent i resulting from the species that would exist if total dissociation of [emim][triflate] had happened; γ_i is the activity coefficient of component i obtained from the electrolyte NRTL model; and P_i^{o} is the vapor pressure of solvent i at equilibrium temperature that was calculated using the Antoine coefficients given in Table 5.

In Figures 4 and 5 the ability of the model to reproduce the VLE of this system can be seen. In these figures points of calculated and experimental VLE of the chloroform (1) + methanol (2) + [emim][triflate] (3) system are given on (T, x_1', y_1) diagrams for $x_3 = 0.06$, 0.12, 0.23, and 0.35. These figures and the deviations presented in Table 6 reveal that the model properly fits the experimental data and that the experimental

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
chloroform + methanol	0.003	0.005	0.07	0.14
chloroform + methanol + [emim][triflate]	0.007	0.009	0.19	0.27

[a] $\delta y = (1/N) \sum |y_{\text{exptl}} - y_{\text{calcd}}|$. [b] $\sigma y = [\sum (y_{\text{exptl}} - y_{\text{calcd}})^2/(N - m)]^{1/2}$. [c] $\delta T = (1/N) \sum |T_{\text{exptl}} - T_{\text{calcd}}|$. [d] $\sigma T = [\sum (T_{\text{exptl}} - T_{\text{calcd}})^2/(N - m)]^{1/2}$. N is the number of experimental points, and m is the number of parameters for the model.

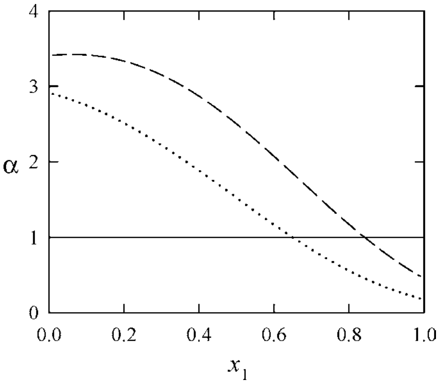

Figure 6. Relative volatility α at 100 kPa for the binary systems chloroform + methanol (dotted line) and chloroform + ethanol (dashed line) obtained from the NRTL model.

trend is also well-represented. Only for the immiscibility zone, small differences between experimental and calculated values can be appreciated. Perhaps the fact that in ternary systems there is not a unique set of model parameters so as to fit vapor−liquid−liquid equilibrium[30] might explain this situation. Furthermore, given that the original NRTL model has been successfully applied in systems involving ILs,[5,9−11] we have correlated our experimental data using the NRTL model proposed by Renon and Praustnitz,[31] with the mean absolute deviations for y_1 and T being 0.008 and 0.32 K, respectively. These deviations are of the same order as those shown in Table 6, and no significant differences between methods can be mentioned.

It is worth analyzing the displacement of azeotropic point with [emim][triflate] composition and comparing it with that which is produced on the chloroform + ethanol system. From experimental data of Table 3, the azeotrope is seen to have not yet disappeared at $x_3 = 0.23$, and in accordance to the model only when [emim][triflate] compositions higher than $x_3 = 0.25$ are reached does the azeotrope become extinct. However, in the chloroform + ethanol system, the azeotrope disappears at lower [emim][triflate] compositions ($x_3 = 0.20$).[15] This fact can be explained from Figure 6, where the relative volatility for the chloroform + ethanol system is observed to be higher than that for the chloroform + methanol system. Since methanol and ethanol exhibit similar dipole moment, it follows, therefore, that the chloroform + methanol system will need a bigger electrolyte concentration to break the azeotrope.

Furthermore, methanol is more polar than chloroform, and thus, it is expected to have a salting-out effect over chloroform at any composition. In Figure 7, however, the salting-out effect is only noticeable for chloroform compositions higher than 0.4, whereas a minor salting-in effect appears at lower compositions. This is what is known as crossover effect,[32] and that was also observed in the chloroform + ethanol + [emim][triflate] system.[15]

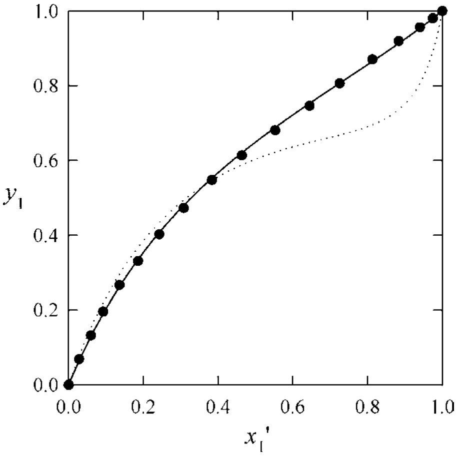

Figure 7. Salting-out effect of [emim][triflate] on VLE of the chloroform (1) + methanol (2) system at 100 kPa for an IL mole fraction $x_3 = 0.35$: ●, experimental value; solid line, calculated with the electrolyte NRTL model; dotted line, calculated for IL-free system.

Conclusions

In this work, vapor−liquid equilibria at 100 kPa and liquid−liquid equilibria at two temperatures for chloroform + methanol + [emim][triflate] system have been determined.

The ternary system of chloroform (1) + methanol (2) + [emim][triflate] (3) presents an immiscibility region placed at the highest chloroform compositions, which increases with the temperature. At 313.15 K the ternary system is totally miscible for $x_1 < 0.769$ or $x_2 > 0.110$.

The electrolyte NRTL model is suitable to predict the VLE in the presence of an IL such as [emim][triflate] whenever the ternary system is totally miscible. Although an immiscibility zone is present, the model is suitable outside of this zone.

The addition of [emim][triflate] to the chloroform + methanol mixture gives a considerable salting-out effect on chloroform near the azeotropic point, although a slight salting-in effect at low chloroform concentrations is produced. At 100 kPa, the azeotrope is removed at a mole fraction of [emim][triflate] of $x_3 = 0.25$.

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