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

A. Vicent Orchillés, Pablo J. Miguel, Ernesto Vercher, and Antoni Martínez-Andreu*

Departamento de Ingeniería Química, Escuela Técnica Superior de Ingeniería, Universitat de València,
46100 Burjassot, Valencia, Spain

Isobaric vapor−liquid equilibria (VLE) for the binary systems methyl acetate + methanol and methyl acetate + 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([emim][triflate]) as well as the VLE for the methyl acetate + methanol + [emim][triflate] ternary system have been obtained at 100 kPa using a recirculating still. 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, together with those early obtained for methanol + [emim][triflate], were used to predict the ternary VLE, which agreed reasonably with the experimental values. The results suggest that the addition of [emim][triflate] to the methyl acetate + methanol mixture produced an important salting-out effect, and the azeotrope disappears when the mole fraction of ionic liquid in the liquid phase is greater than 0.129.

Introduction

During the past decade, much research has focused on ionic liquids (IL). ILs have very low vapor pressures, are liquids below 100 °C, present a highly polar character caused by coulomb forces acting between the ions in the liquid state, and are outstandingly good solvents for a wide range of materials.[1,2] Applications as "green" solvent replacing volatile organic compounds, catalyst in chemical reactions, extraction media, and others have been reported.[2]

ILs may be also used for separation processes in order to modify and improve distillation, evaporation, and pervaporation processes performance. In cases where an IL interacts more strongly with one solvent in a mixture, azeotropes may be broken, and improved separations might be achieved. Arlt and co-workers were the first group that suggested ILs as selective compounds for separation of azeotropic mixtures.[3] They reported the effect of various ionic liquids on ethanol + water,[3,4] acetone + methanol,[3] water + acetic acid,[3] tetrahydrofurane + water,[4,5] methanol + trimethylborate,[6] and 1-hexene + *n*-hexane[7,8] azeotropic systems. Nevertheless, even though the use of ILs as solvents or entrainers in separation technology is promising, thermodynamic data are rare. Currently, only a few investigations on vapor−liquid equilibria (VLE) have been accomplished.

Most works on the VLE 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.,[9] Heintz and co-workers,[10−16] Lee and co-workers,[17,18] Gmehling and co-workers,[19−22] Abusen et al.,[23] Orchillés et al.,[24] Zhao et al.,[25] and Banerjee et al.[26,27] Likewise, the results of Arlt and co-workers quoted before[3−8] were obtained using headspace chromatography techniques at constant temperature in which the system pressure is not available. As far as we know, only Zhao et al.[28,29] (ethanol + water + IL system, ethanol + methanol + IL system), Calvar et al.[30] (ethanol + water + IL system), Orchillés et al.[31] (acetone + methanol + IL system), and Zhang et al.[32] (water + 2-propanol + IL system) have reported complete isobaric VLE data (T, x, y) for ternary systems containing ILs. We have not found complete isothermic VLE data (P, x, y) for ternary systems containing ILs in the literature.

Recently we started a research line consisting of the use of ILs to modify the VLE of solvent mixtures that are difficult to separate by distillation. In this work isobaric VLE data for methyl acetate + methanol + 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([emim][triflate]) binary and ternary systems are presented at 100 kPa.

The methyl acetate (1) + methanol (2) system shows, at atmospheric pressure, a minimum boiling point azeotrope at $x_1 \approx 0.66$. In order to break it, various salts have been used, not always successfully. Thus, VLE measurements with sodium acetate,[33,34] potassium acetate,[34−37] mercury(II) chloride,[34] and calcium chloride[36,38] have been determined at saturation conditions, but they do not break the azeotrope. Moreover, although some authors have reported that lithium chloride[36,37,39] and lithium nitrate[40] can break the azeotrope because these salts present an important salting-out effect, there is a problem because the solubility of these salts decreases dramatically when the methyl acetate mole fraction increases, and there is no evidence that it disappears although the azeotrope is displaced. Only zinc chloride,[35] calcium nitrate,[36] and sodium thiocyanate[41] have been reported to be effective in breaking the methyl acetate + methanol azeotrope. Consequently, one of the aims of this work is to determine if [emim][triflate] is also capable of breaking the methyl acetate + methanol azeotrope.

Experimental Section

Materials. The solvents used were methyl acetate (Fluka, puriss., p.a., minimum mass fraction 99.5 %) and dried methanol (Riedel-de Haën, analytical reagent, minimum mass fraction 99.8 %). No impurities were detected by GC, using the same procedure and conditions described below for liquid mixtures. These chemicals were directly used without further purification. The IL used was 1-ethyl-3-methylimidazolium trifluoromethanesulfonate supplied by Solvent Innovation (purum, minimum mass fraction 98 %). It was selected because of its complete

---

* Corresponding author. Fax: +34 963 544 898. E-mail: antoni.martinez@uv.es.

10.1021/je600518s CCC: $37.00

miscibility in both solvents, its low melting point (T_m < 264 K) that makes it easy to use it, and its high decomposition temperature (T_d > 623 K) that allows us to recover it from column bottoms and reuse it. Because of its hygroscopic character, it was desiccated at 0.2 Pa overnight prior to use. The water mass fraction in the IL determined by Karl Fisher titration was x_w < 0.05 %.

The IL, after being used in the VLE apparatus, was recovered from the liquid mixture by heating under high vacuum (393 K, 0.2 Pa) for 48 h in order to remove the volatile solvents. So, the same IL without observing any change in its properties was used.

Apparatus and Procedure. VLE measurements were made with an all-glass dynamic recirculating still (Fischer, Labodest model), equipped with a Cottrell circulation pump,[42] which ensures that both liquid and vapor phases are in intimate contact during boiling and in contact with the temperature-sensing element. The apparatus has been described in a previous paper.[31] The equilibrium temperature was measured with a Fluke 1502A digital thermometer and a Pt-100 probe. The temperature probe was calibrated against the ice and steam points of distilled water. The standard uncertainty for temperature measurements was 0.01 K. The apparatus pressure was kept constant by means of a vacuum pump and an electrovalve modified by an on−off pressure controller whose standard uncertainty is 0.05 kPa.

Every experimental point of the binary methyl acetate + methanol system was obtained from an initial sample of pure methyl acetate at which different quantities of methanol were added; whereas for the methyl acetate + IL system, methyl acetate was added to a concentrated solution until a very diluted solution was achieved. For the ternary system, several methyl acetate + 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. 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 mass. Methyl acetate and methanol contained in the liquid and condensed vapor 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 detector temperature of 493 K.

For the samples of the liquid phase, the whole 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 in order 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 methanol and methyl acetate in the samples. In this way, 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. To test the performance of the equilibrium apparatus vapor pressure of methyl acetate was measured in the range (304 to 338) K. The Antoine coefficients for methyl acetate obtained from our experimental data and those obtained for methanol in a previous work[43] as well as the mean absolute deviations between experimental and calculated vapor pressure data are shown in Table 1. As far as methyl acetate is concerned, our vapor pressure data and those reported in the literature[44−46] agree on average within 0.13 %. For methanol, the agreement with the literature values[46,47] is within 0.3 %.

Table 1. Experimental Antoine Coefficients and Mean Absolute Deviations for Methyl Acetate and Methanol

	temperature range	Antoine coefficients[a]			$\delta P^{\circ b}$
component	K	*A*	*B*	*C*	kPa
methyl acetate	304 to 338	14.6947	2898.84	−42.37	0.022
methanol[c]	315 to 345	16.4847	3563.73	−37.42	0.014

[a] Antoine equation: $\ln P^\circ/\text{kPa} = A - B/(T/\text{K} + C)$. [b] $\delta P^\circ = (1/N)\Sigma|P^\circ_{\text{exptl}} - P^\circ_{\text{calcd}}|$. [c] From ref 43.

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

x_1	y_1	T/K	x_1	y_1	T/K	x_1	y_1	T/K
0.000	0.000	337.41	0.412	0.537	327.20	0.768	0.727	326.54
0.033	0.100	335.44	0.443	0.556	326.92	0.788	0.743	326.63
0.069	0.192	333.70	0.486	0.575	326.71	0.808	0.757	326.74
0.109	0.269	332.14	0.534	0.599	326.54	0.829	0.775	326.89
0.150	0.328	330.89	0.583	0.620	326.42	0.852	0.796	327.07
0.193	0.372	329.95	0.624	0.642	326.35	0.875	0.818	327.28
0.235	0.413	329.18	0.655	0.656	326.32	0.921	0.871	327.90
0.278	0.447	328.53	0.683	0.676	326.35	0.967	0.940	328.82
0.321	0.485	327.99	0.720	0.695	326.39	1.000	1.000	329.72
0.368	0.513	327.55	0.749	0.713	326.46			

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

x_3	T/K	x_3	T/K	x_3	T/K	x_3	T/K
0.0000	329.72	0.1577	330.61	0.2681	332.36	0.3634	335.04
0.0193	329.89	0.1779	330.84	0.2815	332.72	0.3767	335.55
0.0374	329.94	0.1959	331.07	0.2982	333.11	0.3933	336.25
0.0591	330.00	0.2107	331.30	0.3082	333.38	0.4096	336.85
0.0846	330.11	0.2289	331.58	0.3204	333.79	0.4258	337.35
0.1105	330.23	0.2397	331.78	0.3344	334.09	0.4307	337.55
0.1346	330.40	0.2555	332.14	0.3474	334.55	0.4318	337.55

VLE for the binary systems methyl acetate (1) + methanol (2) and methyl acetate (1) + [emim][triflate] (3) were measured at 100 kPa. The results are shown in Tables 2 and 3, respectively. The VLE for the binary system methanol (2) + [emim][triflate] (3) at 100 kPa was determined in a previous work.[31] VLE for the methyl acetate (1) + methanol (2) + [emim][triflate] (3) ternary system, at 100 kPa also, was obtained by trying to keep constant the IL mole fraction in each of the six series shown in Table 4. The experimental data for the methyl acetate (1) + methanol (2) system at 100 kPa show a minimum boiling point azeotrope at $x_1 = 0.663$ and $T = 326.32$ K, which can be interpolated from the experimental values. In order to compare these 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 NRTL model as described later. Despite the observed dispersion in the VLE data reported in the literature for this system, our data agree very well with those reported by Vasil'eva et al.[48] and Topphoff et al.[40] within the experimental accuracy. Our azeotropic point at 101.325 kPa ($x_1 = 0.660$, $T = 326.69$ K) is in complete agreement with those reported by Vasil'eva et al.[48] ($x_1 = 0.660$, $T = 326.66$ K) and Gmehling[49] ($x_1 = 0.6618$, $T = 326.65$ K), but it differs by 0.25 K from those reported by Mato et al.[50] ($x_1 = 0.670$, $T = 326.95$ K) and Iliuta et al.[41] ($x_1 = 0.668$, $T = 327.0$ K).

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

x_3	$x_1'^a$	y_1	T/K	x_3	$x_1'^a$	y_1	T/K	x_3	$x_1'^a$	y_1	T/K	x_3	$x_1'^a$	y_1	T/K
0.051	0.000	0.000	338.65	0.113	0.437	0.586	329.42	0.172	0.000	0.000	343.03	0.250	0.507	0.667	333.40
0.052	0.021	0.067	337.45	0.115	0.494	0.629	328.93	0.173	0.020	0.057	341.88	0.251	0.572	0.712	332.85
0.057	0.038	0.113	336.35	0.112	0.560	0.670	328.58	0.177	0.045	0.116	340.81	0.248	0.640	0.760	332.30
0.052	0.055	0.155	335.55	0.114	0.619	0.709	328.45	0.177	0.077	0.195	339.37	0.249	0.700	0.801	332.10
0.057	0.092	0.234	334.39	0.112	0.679	0.748	328.38	0.178	0.119	0.266	337.83	0.246	0.756	0.834	331.80
0.052	0.103	0.253	333.96	0.113	0.738	0.786	328.44	0.179	0.179	0.355	336.05	0.243	0.810	0.872	331.66
0.053	0.166	0.346	332.01	0.110	0.805	0.834	328.63	0.180	0.245	0.435	334.30	0.239	0.866	0.907	331.53
0.059	0.313	0.477	329.14	0.106	0.871	0.885	328.97	0.180	0.312	0.494	333.21	0.240	0.916	0.942	331.62
0.059	0.396	0.548	328.30	0.106	0.939	0.942	329.52	0.182	0.378	0.556	332.19	0.240	0.962	0.973	331.73
0.059	0.454	0.592	327.85	0.111	1.000	1.000	330.23	0.182	0.439	0.605	331.48	0.240	1.000	1.000	331.78
0.059	0.535	0.633	327.52	0.141	0.000	0.000	341.79	0.180	0.507	0.651	330.90	0.289	0.000	0.000	348.35
0.059	0.605	0.674	327.32	0.141	0.017	0.050	340.83	0.181	0.572	0.697	330.42	0.295	0.018	0.050	347.57
0.058	0.672	0.713	327.31	0.142	0.039	0.107	339.70	0.180	0.636	0.739	330.13	0.297	0.043	0.110	346.36
0.057	0.733	0.752	327.43	0.142	0.070	0.175	338.31	0.179	0.695	0.779	329.95	0.302	0.074	0.183	345.02
0.056	0.786	0.788	327.62	0.143	0.108	0.248	336.87	0.176	0.751	0.815	329.87	0.298	0.119	0.254	343.53
0.056	0.838	0.829	327.93	0.143	0.160	0.328	335.21	0.174	0.807	0.853	329.85	0.303	0.176	0.351	341.87
0.055	0.894	0.879	328.43	0.144	0.221	0.401	333.66	0.170	0.863	0.892	329.95	0.304	0.234	0.422	340.40
0.055	0.941	0.928	329.02	0.145	0.287	0.466	332.30	0.173	0.915	0.931	330.23	0.307	0.290	0.484	339.22
0.055	0.979	0.973	329.62	0.146	0.358	0.533	331.30	0.174	0.963	0.967	330.52	0.309	0.352	0.540	338.11
0.055	1.000	1.000	330.01	0.146	0.437	0.595	330.41	0.178	1.000	1.000	330.84	0.313	0.408	0.593	337.56
0.107	0.000	0.000	340.66	0.147	0.503	0.641	329.83	0.234	0.000	0.000	345.50	0.311	0.472	0.645	336.64
0.108	0.017	0.053	339.63	0.147	0.569	0.686	329.47	0.233	0.020	0.056	344.23	0.317	0.532	0.697	335.90
0.109	0.037	0.106	338.57	0.148	0.629	0.726	329.27	0.235	0.045	0.116	343.34	0.315	0.598	0.741	335.44
0.109	0.067	0.171	337.31	0.147	0.688	0.764	329.23	0.236	0.079	0.186	342.00	0.311	0.659	0.781	334.87
0.109	0.102	0.241	335.89	0.147	0.741	0.798	329.19	0.238	0.123	0.264	340.40	0.308	0.721	0.825	334.23
0.110	0.152	0.320	334.22	0.147	0.794	0.837	329.29	0.243	0.178	0.355	338.80	0.306	0.782	0.865	333.83
0.111	0.207	0.392	332.80	0.144	0.847	0.873	329.42	0.243	0.247	0.430	337.22	0.300	0.847	0.905	333.32
0.112	0.261	0.449	331.69	0.144	0.903	0.918	329.73	0.249	0.307	0.493	336.25	0.296	0.903	0.939	333.17
0.112	0.322	0.491	330.66	0.146	0.956	0.960	330.15	0.243	0.382	0.561	335.00	0.298	0.957	0.972	333.13
0.113	0.377	0.545	329.95	0.146	1.000	1.000	330.51	0.248	0.442	0.614	334.10	0.298	1.000	1.000	333.11

[a] x_1' is the mole fraction of methyl acetate in the liquid phase expressed on an IL-free basis.

The experimental results for this binary system show a good thermodynamic consistency according to the Van Ness test[51] modified by Fredenslund.[52] The test gave a mean absolute deviation between calculated and measured mole fractions of methyl acetate in the vapor phase of $\delta y = 0.0027$, which shows that the values are thermodynamically consistent. No consistency test was used for IL-containing systems.

Calculation of the Phase Equilibrium. As suggested in a previous work,[31] we tried to use the electrolyte NRTL model to predict the VLE of the IL-containing ternary system. This model is an extension of the nonrandom two-liquid local composition proposed by Renon and Prausnitz[53] from which Chen et al.[54] derived a model for single-solvent + electrolyte systems. Subsequent to that, Mock et al.[55,56] 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 methyl acetate (1) and methanol (2) in a binary or ternary system containing [emim][triflate] (3) can be derived. These equations have been reported in a previous paper.[57]

According to the proposed method, as long as we want to represent the phase equilibrium of mixed-solvent + electrolyte systems, we must determine the nine binary adjustable parameters for all of the solvent−solvent and solvent−electrolyte pairs in the system. These parameters were obtained from the VLE data by minimization of the objective function F:

$$F = \sum_j (T_{\text{exptl}} - T_{\text{calcd}})^2 \tag{1}$$

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.

In this way, the 1−2 binary solvent−solvent parameters were obtained from the VLE data of the methyl acetate (1) + methanol (2) system shown in Table 2, whereas those corresponding to the 1−3 binary solvent−IL were obtained from the VLE data of the methyl acetate (1) + [emim][triflate] (3) binary system shown in Table 3. The parameters corresponding to the 2−3 binary solvent−IL were taken from a previous paper.[31] 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.

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

i component	j component	$\alpha_{i,j}$	$\Delta g_{i,j}$/J·mol^{-1}	$\Delta g_{j,i}$/J·mol^{-1}
methyl acetate	methanol	0.300[a]	1466.6[a]	1617.8[a]
methyl acetate	[emim][triflate]	0.100[a]	40155.1[a]	−17225.9[a]
methanol	[emim][triflate]	0.389[b]	11950.6[b]	−4547.0[b]

[a] From this work. [b] From ref 31.

The parameters reported in Table 5 were used to predict the VLE of the methyl acetate (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:

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

In eq 2, y_i is the vapor-phase mole fraction of component 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 component i at equilibrium temperature. The vapor pressures of the pure solvents were calculated from the Antoine equation using the parameters given in Table 1.

The ability of the model to reproduce the VLE for this system can be seen in Figures 1 to 3 where, as an example, the

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
methyl acetate + methanol	0.002	0.003	0.02	0.03
methyl acetate + [emim][triflate]			0.26	0.36
methanol + [emim][triflate]			0.14	0.21
methyl acetate + methanol + [emim][triflate]	0.008	0.008	0.17	0.26

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

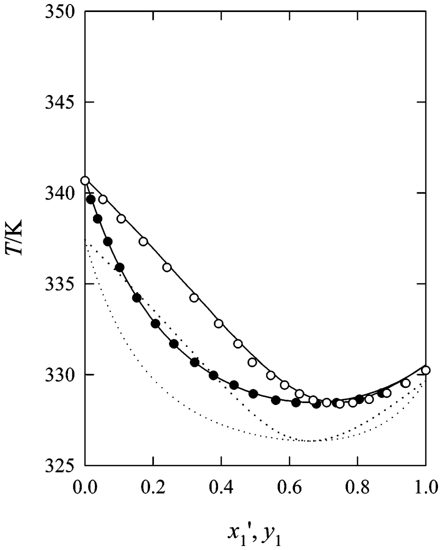

Figure 1. Temperature–composition diagram for methyl acetate (1) + methanol (2) + [emim][triflate] (3) at 100 kPa, with an IL mole fraction $x_3 = 0.110$: ●, x_1' experimental; ○, y_1 experimental; solid lines, calculated; dotted lines, calculated for IL-free system.

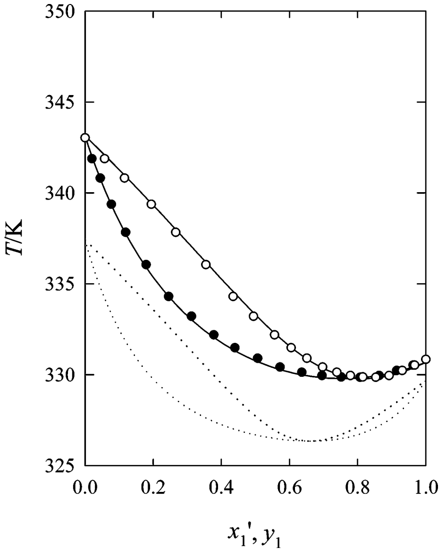

Figure 2. Temperature–composition diagram for methyl acetate (1) + methanol (2) + [emim][triflate] (3) at 100 kPa, with an IL mole fraction $x_3 = 0.177$: ●, x_1' experimental; ○, y_1 experimental; solid lines, calculated; dotted lines, calculated for IL-free system.

calculated and experimental VLE of the methyl acetate + methanol + [emim][triflate] ternary system are plotted on T, x, y diagrams for $x_3 = 0.110$, 0.177, and 0.304. These figures and the mean absolute deviations between the experimental and calculated values of vapor-phase composition and equilibrium temperature (also reported in Table 6) reveal that the proposed model is good enough to reasonably fit the experimental data.

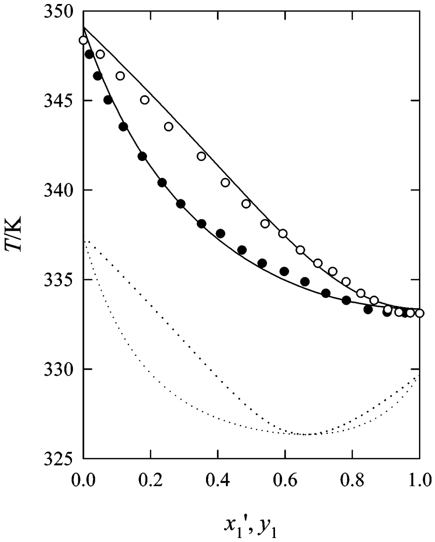

Figure 3. Temperature–composition diagram for methyl acetate (1) + methanol (2) + [emim][triflate] (3) at 100 kPa, with an IL mole fraction $x_3 = 0.304$: ●, x_1' experimental; ○, y_1 experimental; solid lines, calculated; dotted lines, calculated for IL-free system.

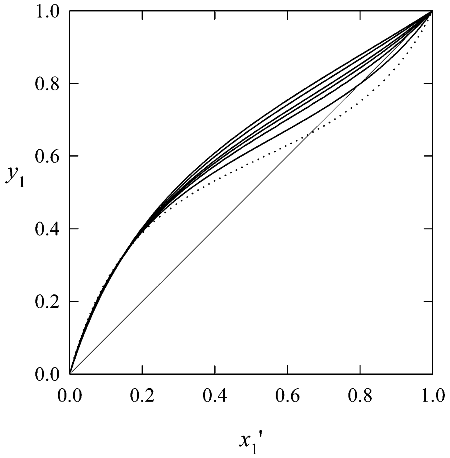

Figure 4. Salting-out effect of [emim][triflate] on vapor–liquid equilibrium of methyl acetate (1) + methanol (2) system at 100 kPa for several IL mole fractions: dotted line, calculated for IL-free system; solid lines, calculated at $x_3 = 0.056$, 0.110, 0.145, 0.177, 0.242, and 0.304. The higher IL mole fraction, the more separated curves from the diagonal line.

Methanol is more polar than methyl acetate. Hence, methyl acetate is expected to be salted-out from the mixed solvent over the whole range of the liquid concentration. However, the salting-out effect is only appreciable at methyl acetate mole fraction in the liquid-phase higher than 0.2. At lower compositions, the y_1, x_1' curve remains practically unchanged, whatever the IL concentration. This can be observed in Figure 4, where the different solid lines that represent the y_1, x_1' equilibrium separate from the diagonal as the IL mole fraction increases, but only for $x_1' > 0.2$. Hashitani and Hirata[35] reported the same behavior for the zinc chloride on the VLE of the methyl acetate

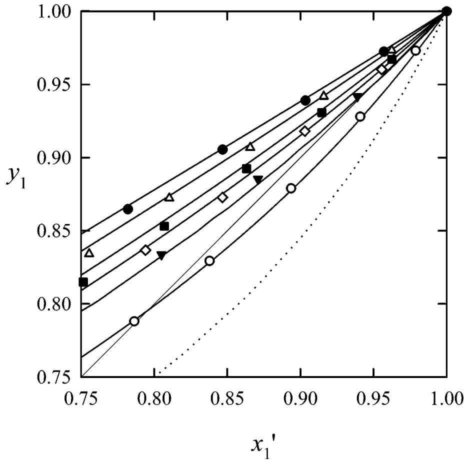

Figure 5. Composition diagram for methyl acetate (1) + methanol (2) + [emim][triflate] (3) at 100 kPa for several IL mole fractions: ○, $x_3 = 0.056$; ▼, $x_3 = 0.110$; ◇, $x_3 = 0.145$; ■, $x_3 = 0.177$; △, $x_3 = 0.242$; ●, $x_3 = 0.304$; solid lines, calculated at same IL mole fractions; dotted line, calculated for IL-free system.

+ methanol system at atmospheric pressure. This effect produces a very slight crossover effect[58] between salting-in and salting-out that is much less than that observed in the acetone + methanol system[31] with the same IL.

It is worth noting that small concentrations of [emim][triflate] produce a displacement of the azeotropic point of the methyl acetate + methanol system toward $x_1' > 0.663$ until the azeotrope disappears. Figure 5 shows that $x_3 = 0.056$ does not yet break the azeotrope, and at $x_3 = 0.110$ we are very closed to the limit from which the azeotrope disappears. From the NRTL electrolyte model, the disappearance of azeotropic point for the methyl acetate + methanol system at 100 kPa can be estimated to take place at a mole fraction of [emim][triflate] of $x_3 = 0.129$. This concentration is higher than that which was necessary when the same IL was used to break the azeotrope in the acetone + methanol system.[31]

If we compare the effect of [emim][triflate] with that produced by salts on methyl acetate + methanol azeotrope, it can be seen that both calcium nitrate[36] and sodium thiocyanate[41] break the azeotrope only at saturation conditions, although that is due to the low solubility of salts in methyl acetate and not because the ionic interactions are too weak. Only the zinc chloride can break the azeotrope at undersaturation conditions due to the great solubility of this salt in boiling methanol mass fraction of 91 % and methyl acetate mass fraction of 79 % at atmospheric pressure, as Hashitani and Hirata stated.[35] They also reported the disappearance of methyl acetate + methanol azeotrope at a salt mass fraction as low as 11 %, which represents a salt mole fraction from (0.03 to 0.06).

Conclusions

The electrolyte NRTL model is suitable to predict the VLE in the presence of an IL such as [emim][triflate]. In this way, this will allow us to extend the application of the model to the field of ionic liquids.

The addition of the IL [emim][triflate] to the methyl acetate + methanol mixture gives a noticeable salting-out effect on methyl acetate near the azeotropic point, although this effect is imperceptible at low methyl acetate concentrations. Even so, from VLE viewpoint, [emim][triflate] is as effective as zinc chloride in breaking the azeotrope of the methyl acetate + methanol system, although it takes place at an IL mole fraction of 0.129.

The salt effect that [emim][triflate] produces on the methyl acetate + methanol system, just like that on the acetone + methanol system,[31] is less than that produced by an inorganic salt at the same mole fraction. However, due to its total miscibility with both solvents, a higher IL concentration can be achieved; therefore, the absolute salt effect can become very important.

The use of [emim][triflate] as an entrainer in the extractive distillation process of methyl acetate + methanol mixtures has advantages over the use of inorganic salts or liquids. Because of its total miscibility with both solvents, a great concentration of IL can be achieved, and then a greater salt effect is produced. Like the inorganic salts, its very low vapor pressure guarantees that all the IL will leave the distillation column with the bottoms stream. From this stream, made up of methanol and IL, the IL can be totally recovered by flash distillation, and the pure IL thus obtained can be used again.

Literature Cited

(1) Seddon, K. R. Ionic liquids for clean technology. *J. Chem. Technol. Biotechnol.* **1997**, *68*, 351−356.

(2) Heintz, A. Recent developments in thermodynamics and thermophysics of non-aqueous mixtures containing ionic liquids. A review. *J. Chem. Thermodyn.* **2005**, *37*, 525−535.

(3) Seiler, M.; Jork, C.; Schneider, W.; Arlt, W. Ionic liquids and hyperbranched polymers—Promising new classes of selective entrainers for extractive distillation. In *Proceedings of the International Conference on Distillation & Absorption 2002*; GVC-VDI: Düsseldorf, 2002.

(4) Seiler, M.; Jork, C.; Kavarnou, A.; Arlt, W.; Hirsch, R. Separation of azeotropic mixtures using hyperbranched polymers or ionic liquids. *AIChE J.* **2004**, *50*, 2439−2454.

(5) Jork, C.; Seiler, M.; Beste, Y. A.; Arlt, W. Influence of ionic liquids on the phase behavior of aqueous azeotropic systems. *J. Chem. Eng. Data* **2004**, *49*, 852−857.

(6) Beste, Y.; Eggersmann, M.; Schoenmakers, H. Extractive distillation with ionic fluids. *Chem. Ing. Tech.* **2005**, *77*, 1800−1808.

(7) Lei, Z.; Arlt, W.; Wasserscheid, P. Separation of 1-hexene and *n*-hexane with ionic liquids. *Fluid Phase Equilib.* **2006**, *241*, 290−299.

(8) Lei, Z.; Arlt, W.; Wasserscheid, P. Selection of entrainers in the 1-hexene/*n*-hexane system with a limited solubility. *Fluid Phase Equilib.* **2006**, doi:10.1016/j.fluid.2006.06.009.

(9) Anthony, J. L.; Maginn, E. J.; Brennecke, J. F. Solution thermodynamics of imidazolium-based ionic liquids and water. *J. Phys. Chem. B* **2001**, *105*, 10942−10949.

(10) Verevkin, S. P.; Vasiltsova, T. V.; Bich, E.; Heintz, A. Thermodynamic properties of mixtures containing ionic liquids. Activity coefficients of aldehides and ketones in 1-methyl-3-ethyl-imidazolium bis(trifluoromethylsulfonyl) imide using the transpiration method. *Fluid Phase Equilib.* **2004**, *218*, 165−175.

(11) Verevkin, S. P.; Safarov, J.; Bich, E.; Hassel, E.; Heintz, A. Thermodynamic properties of mixtures containing ionic liquids. *Fluid Phase Equilib.* **2005**, *236*, 222−228.

(12) Vasiltsova, T. V.; Verevkin, S. P.; Bich, E.; Heintz, A.; Bogel-Lukasik, R.; Domaska, U. Thermodynamic properties of mixtures containing ionic liquids. 7. Activity coefficients of aliphatic and aromatic esters and benzylamine in 1-methyl-3-ethylimidazolium bis(trifluoromethylsulfonyl) imide using the transpiration method. *J. Chem. Eng. Data* **2006**, *51*, 213−218.

(13) Heintz, A.; Verevkin, S. P.; Ondo, D. Thermodynamic properties of mixtures containing ionic liquids. 8. Activity coefficients at infinite dilution of hydrocarbons, alcohols, esters, and aldehydes in 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide using gas−liquid chromatography. *J. Chem. Eng. Data* **2006**, *51*, 434−437.

(14) Safarov, J.; Verevkin, S. P.; Bich, E.; Heintz, A. Vapor pressures and activity coefficients of *n*-alcohols and benzene in binary mixtures with 1-methyl-3-butylimidazolium octyl sulfate and 1-methyl-3-octylimidazolium tetrafluoroborate. *J. Chem. Eng. Data* **2006**, *51*, 518−525.

(15) Heintz, A.; Vasiltsova, T. V.; Safarov, J.; Bich, E.; Verevkin, S. P. Thermodynamic properties of mixtures containing ionic liquids. 9. Activity coefficients at infinite dilution of hydrocarbons, alcohols, esters, and aldehydes in trimethyl-butylammonium bis(trifluoromethylsulfonyl) imide using gas−liquid chromatography and static method. *J. Chem. Eng. Data* **2006**, *51*, 648−655.

(16) Sumartschenkowa, I. A.; Verevkin, S. P.; Vasiltsova, T. V.; Bich, E.; Heintz, A.; Shevelyova, M. P.; Kabo, G. J. Experimental study of

thermodynamic properties of mixtures containing ionic liquid 1-ethyl-3-methylimidazolium ethyl sulfate using gas−liquid chromatography and transpiration method. *J. Chem. Eng. Data* **2006**, *51*, 2138−2144.

(17) Kim, K. S.; Shin, B. K.; Lee, H.; Ziegler, F. Refractive index and heat capacity of 1-butyl-3-methylimidazolium bromide and 1-butyl-3-methylimidazolium tetrafluoroborate, and vapor pressure of binary systems for 1-butyl-3-methylimidazolium bromide + trifluoroethanol and 1-butyl-3-methylimidazolium tetrafluoroborate + trifluoroethanol. *Fluid Phase Equilib.* **2004**, *218*, 215−220.

(18) Kim, K. S.; Park, S. Y.; Choi, S.; Lee, H. Vapor pressures of the 1-butyl-3-methylimidazolium bromide + water, 1-butyl-3-methylimidazolium tetrafluoroborate + water, and 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate + water systems. *J. Chem. Eng. Data* **2004**, *49*, 1550−1553.

(19) Kato, R.; Krummen, M.; Gmehling, J. Measurement and correlation of vapor−liquid equilibria and excess enthalpies of binary systems containing ionic liquids and hydrocarbons. *Fluid Phase Equilib.* **2004**, *224*, 47−54.

(20) Döker, M.; Gmehling, J. Measurement and prediction of vapor−liquid equilibria of ternary systems containing ionic liquids. *Fluid Phase Equilib.* **2005**, *227*, 255−266.

(21) Kato, R.; Gmehling, J. Measurement and correlation of vapor−liquid equilibria of binary systems containing the ionic liquids [EMIM][$(CF_3SO_2)_2N$], [BMIM][$(CF_3SO_2)_2N$], [MMIM][$(CH_3)_2PO_4$] and oxygenated organic compounds respectively in water. *Fluid Phase Equilib.* **2005**, *231*, 38−43.

(22) Kato, R.; Gmehling, J. Systems with ionic liquids: measurement of VLE and γ^∞ data and prediction of their thermodynamic behavior using original UNIFAC, mod. UNIFAC(Do) and COSMO-RS(Ol). *J. Chem. Thermodyn.* **2005**, *37*, 603−619.

(23) Abusen, Z. R.; Zhao, J.; Li, C.; Wang, Z. Determination of vapor pressures for binary and ternary mixtures containing ionic liquid 1-propyl-3-methylimidazolium bromide. *Chin. J. Chem. Eng.* **2005**, *13*, 791−795.

(24) Orchillés, A. V.; González-Alfaro, V.; Vercher, E.; Martínez-Andreu, A. Vapor pressures of ionic liquid 1-butyl-3-methylimidazolium octylsulfate [BMIM] [$OcOSO_3$] in water and 1-propanol. In *Proceedings of the 10th Mediterranean Congress of Chemical Engineering*; SEQIIQ: Barcelona, 2005.

(25) Zhao, J.; Jiang, X.; Li, C.; Wang, Z. Vapor pressure measurement for binary and ternary systems containing a phosphoric ionic liquid. *Fluid Phase Equilib.* **2006**, *247*, 190−198.

(26) Banerjee, T.; Singh, M. K.; Khanna, A. Prediction of binary VLE for imidazolium based ionic liquid systems using COSMO-RS. *Ind. Eng. Chem. Res.* **2006**, *45*, 3207−3219.

(27) Banerjee, T.; Khanna, A. Infinite dilution activity coefficients for trihexyltetradecyl phosphonium ionic liquids: measurements and COSMO-RS prediction. *J. Chem. Eng. Data* **2006**, *51*, 2170−2177.

(28) Zhao, J.; Dong, C. C.; Li, C. X.; Meng, H.; Wang, Z. H. Isobaric vapor−liquid equilibria for ethanol−water system containing different ionic liquids at atmospheric pressure. *Fluid Phase Equilib.* **2006**, *242*, 147−153.

(29) Zhao, J.; Li, C.; Wang, Z. Vapor pressure measurement and prediction for ethanol + methanol and ethanol + water systems containing ionic liquids. *J. Chem. Eng. Data* **2006**, *51*, 1755−1760.

(30) Calvar, N.; González. B.; Gómez, E.; Domínguez, A. Vapor−liquid equilibria for the ternary system ethanol + water + 1-butyl-3-methylimidazolium chloride and the corresponding binary systems at 101.3 kPa. *J. Chem. Eng. Data* **2006**, *51*, 2178−2181.

(31) Orchillés, A. V.; Miguel, P. J.; Vercher, E.; Martínez-Andreu, A. Ionic liquids as entrainers in extractive distillation: isobaric vapor−liquid equilibria for acetone + methanol + 1-ethyl-3-methylimidazolium trifluoromethanesulfonate. *J. Chem. Eng. Data* **2007**, *52*, 141−147.

(32) Zhang, L. Z.; Deng, D. S.; Han, J. Z.; Ji, D. X.; Ji, J. B. Isobaric vapor−liquid equilibria for water + 2-propanol + 1-butyl-3-methylimidazolium tetrafluoroborate. *J. Chem. Eng. Data* **2007**, *52*, 199−205.

(33) Utkin, O. V.; Krivashov, A. V.; Serafimov, L. A. Effect of sodium acetate on liquid−vapor equilibrium in methyl acetate−water and methyl acetate−methanol systems. *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **1970**, *13*, 486−489.

(34) Park, W. K.; Do, K. S.; Bae, H. K.; Shim, H. S. Salt effect in vapor−liquid equilibrium for methyl acetate−methanol system. *Yongu Pogo−Yongnam Taehakkyo Kongop Kisul Yonguso* **1973**, *1*, 33−39.

(35) Hashitani, M.; Hirata, M. Salt effect in vapor−liquid equilibrium. Acetic ester−alcohol with potassium acetate and zinc chloride. *J. Chem. Eng. Jpn.* **1969**, *2*, 149−153.

(36) Martin, M. C.; Cocero, M. J.; Mato, F. Salt effect on the vapor−liquid equilibrium of methyl acetate + methanol at 298.15 K. *J. Chem. Eng. Data* **1994**, *39*, 538−540.

(37) Wang, S.; Cai, C. Vapor−liquid equilibrium data for methyl acetate−methanol systems containing salt. *Shiyou Huagong* **1993**, *22*, 444−450.

(38) Hashitani, M.; Hirata, M. Salt effect of calcium chloride in vapor−liquid equilibrium of the alcohol−acetic ester systems. *J. Chem. Eng. Jpn.* **1968**, *1*, 116−119.

(39) Rath, P.; Naik, S. C. Effect of lithium chloride on vapour−liquid equilibria of methyl acetate−methanol. *J. Inst. Eng. (India), Chem. Eng. Div.* **1992**, *73*, 22−24.

(40) Topphoff, M.; Kiepe, J.; Gmehling, J. Effects of lithium nitrate on the vapor−liquid equilibria of methyl acetate + methanol and ethyl acetate + ethanol. *J. Chem. Eng. Data* **2001**, *46*, 1333−1337.

(41) Iliuta, M. C.; Thyrion, F. C.; Landauer, O. M. Salt effect on the isobaric vapor−liquid equilibrium of the methyl acetate + methanol system. *J. Chem. Eng. Data* **1996**, *41*, 713−717.

(42) Walas, S. M. *Phase Equilibria in Chemical Engineering*; Butterworth: London, 1985.

(43) Vercher, E.; Orchillés, A. V.; Miguel, P. J.; González-Alfaro, V.; Martínez-Andreu, A. Isobaric vapor−liquid equilibria for acetone + methanol + lithium nitrate at 100 kPa. *Fluid Phase Equilib.* **2006**, *250*, 131−137.

(44) Polak, J.; Mertl, I. Saturated vapor pressure of methyl acetate, ethyl acetate, propyl acetate, methyl propionate, and ethyl propionate. *Collect. Czech. Chem. Commun.* **1965**, *30*, 3526−3528.

(45) Ambrose, D.; Ellender, J. H.; Gundry, H. A.; Lee, D. A.; Townsend, R. Thermodynamic properties of organic oxygen compounds LI. The vapour pressures of some esters and fatty acids. *J. Chem. Thermodyn.* **1981**, *13*, 795−802.

(46) *NIST/TRC Table Database* (*Win Table*). NIST Standard Reference Database 85. Thermodynamic Research Center, Physical and Chemical Properties Division: Boulder, CO, 2004.

(47) Ambrose, D.; Sprake, C. H. S. Thermodynamic properties of organic oxygen compounds XXV. Vapour pressures and normal boiling temperatures of aliphatic alcohols. *J. Chem. Thermodyn.* **1970**, *2*, 631−645.

(48) Vasil'eva, I. I.; Marinichev, A. N.; Susarev, M. P. Study of liquid−vapor equilibrium in acetone−methyl acetate, methyl acetate−methanol, methyl acetate−chloroform, and chloroform−methanol systems at 35 and 55° C and at normal pressure. *Deposited Doc. (VINITI 3400-83)*, 1983.

(49) Gmehling, J. Unpublished data. Reported in Gmehling, J.; Menke, J.; Krafczyk, J.; Fischer, K. *Azeotropic Data, Part I*; VCH: Weinheim, 1994.

(50) Mato, F.; Cepeda, E. Vapor−liquid equilibrium of binary mixtures of alcohols and acetic acid esters. I. Systems with methanol, ethanol, n-propanol and isopropanol at 760 mmHg. *An. Quim. Ser. A* **1984**, *80*, 338−342.

(51) Van Ness, H. C.; Byer, S. M.; Gibbs, R. E. Vapor−liquid equilibrium: part I. An appraisal of data reduction methods. *AIChE J.* **1973**, *19*, 238−244.

(52) Fredenslund, A.; Gmehling, J.; Rasmussen, P. *Vapor−Liquid Equilibria Using UNIFAC*; Elsevier: Amsterdam, 1977.

(53) Renon, H.; Prausnitz, J. M. Local compositions in thermodynamic excess functions for liquid mixtures. *AIChE J.* **1968**, *14*, 135−144.

(54) Chen, C. C.; Britt, H. I.; Boston, J. F.; Evans, L. B. Local composition model for excess Gibbs energy of electrolyte systems. Part I: single solvent, single completely dissociated electrolyte systems. *AIChE J.* **1982**, *28*, 588−596.

(55) Mock, B.; Evans, L. B.; Chen, C. C. Phase equilibria in multiple−solvent electrolyte systems: a new thermodynamic model. *Proc. Summer Comput. Simul. Conf.* **1984**, 558−562.

(56) Mock, B.; Evans, L. B.; Chen, C. C. Thermodynamic representation of phase equilibria of mixed−solvent electrolyte systems. *AIChE J.* **1986**, *32*, 1655−1664.

(57) Vercher, E.; Rojo, F. J.; Martínez-Andreu, A. Isobaric vapor−liquid equilibria for 1-propanol + water + calcium nitrate. *J. Chem. Eng. Data* **1999**, *44*, 1216−1221.

(58) Meranda, D.; Furter, W. F. Salt effects on VLE: some anomalies. *AIChE J.* **1974**, *20*, 103−108.

Received for review November 14, 2006. Accepted January 31, 2007. This research was supported by the Ministry of Education and Science of Spain and FEDER funds of the European Union, through Project CTQ2004-02977/PPQ.

JE600518S