1004 *J. Chem. Eng. Data* **2009,** *54,* 1004–1008

Vapor−Liquid Equilibria for the Ternary System Ethanol + Water + 1-Butyl-3-methylimidazolium Methylsulfate and the Corresponding Binary Systems at 101.3 kPa

Noelia Calvar, Begoña González, Elena Gómez, and Ángeles Domínguez*

Departamento de Ingeniería Química de la Universidad de Vigo, 36310 Vigo, Spain

In this work, isobaric ternary vapor−liquid equilibria for the ionic liquid 1-butyl-3-methylimidazolium methylsulfate ($BMimMSO_4$) + ethanol + water and for the corresponding binary systems containing the ionic liquid were carried out at 101.3 kPa. Vapor−liquid equilibria data of binary systems were correlated using the e-NRTL and NRTL equations. The ternary system was correlated using the NRTL equation. A study of the evolution of the ethanol + water azeotrope composition with different amounts of ionic liquid was made.

Introduction

Ionic liquids (ILs) are relatively new components that are attracting increasing interest in their application on industrial processes. One of those processes is their use as entrainers for separation of azeotropic mixtures.

Experimental data of phase equilibria of systems involving ILs are necessary to obtain information about the influence of the structure of the IL on its physical and solvent properties. This information is important for developing predictive models. VLE (vapor−liquid equilibria) data permit checking the potential of models which are applied for the description of the real behavior of systems with ionic liquids.

Models such as the Margules equation, Wilson equation, NRTL equation, and UNIQUAC equation are used[1,2] in the literature in studies of mixtures containing ionic liquids. Although the NRTL model[3] is theoretically developed for systems involving nonelectrolytes, it usually leads to good correlations for systems containing ILs.[4–8] Although it is less common, the e-NRTL model is also used. The e-NRTL model[9–11] is an extension of the NRTL model that considers the fact that ILs are organic salts that present ionic character that has also been studied in the literature.[12,13] In any case, perhaps for the lack of models specifically created for systems with ILs and for its relative simplicity, the most used model is the NRTL model.

This work is part of a systematic study to determine vapor−liquid equilibria (VLE) data of ternary mixtures containing the azeotropic mixture ethanol + water plus an ionic liquid[14–16] and to test the different thermodynamic models usually used in VLE studies. In the previous works, the ionic liquids were 1-butyl-3-methylimidazolium chloride (BMimCl), 1-hexyl-3-methylimidazolium chloride (HMimCl), and 1-ethyl-3-methylimidazolium ethylsulfate ($EMimESO_4$).

In the present study, VLE of the ternary mixture ethanol (1) + water (2) + $BMimMSO_4$ (3) and the constituent binary mixtures containing ILs have been determined at 101.3 kPa. In addition to the determination of experimental VLE data, a comparison of the correlation models commonly used for the treatment of these experimental data, the NRTL and the e-NRTL models, was made for the binary systems, and the experimental data of the ternary mixture were correlated using the NRTL model. A study of the evolution of the ethanol + water azeotrope composition with different amounts of IL was made.

Experimental

Materials. Ethanol was purchased from Merck. It was degassed ultrasonically and dried over molecular sieves type 0.4 nm. Its purity was more than 99.8 %. Water was bidistilled and deionized. The ionic liquid used in this work, 1-butyl-3-methylimidazolium methylsulfate ($BMimMSO_4$), was synthesized in our laboratory, following the previously published procedure.[17] It was dried by heating at $T = 343.15$ K and stirring under high vacuum ($2 \cdot 10^{-1}$ Pa) for 48 h always prior to their use. To ensure its purity, NMR measurements were made, and no differences were found with Pereiro et al.[18] The water mass fraction was determined using a 787 Karl Fischer Titrinio and a Ti Stand 703 stirrer, and it was lower than 0.04 %. The physical properties of chemicals used were compared with literature values.[19−21]

Density and viscosity of ethanol, water, and $BMimMSO_4$ were measured and compared with the literature, as presented in a previous work.[17] The viscosity values for pure $BMimMSO_4$ are lower than those reported in the literature. As a consequence, we repeated the synthesis twice, and the density and viscosity obtained were very similar. We did not find any explanation for this difference, except for the difference which exists between the water content of ionic liquid or nonvolatile impurities in their samples or our samples. Widegren et al.[22] studied the effect of water in the viscosity of pure ionic liquids at 298.15 K, and they found that the addition of a mass fraction of water of $1 \cdot 10^{-4}$ decreased the viscosity by approximately 1 %.

Apparatus and Procedure. A glass Fischer Labodest apparatus model 602/D was used for the VLE determinations. The equilibrium vessel is a dynamic recirculating still, and it is equipped with a Cottrell pump. A thermometer Yokogawa model 7563, with an uncertainty of ± 0.01 K, was used to measure the equilibrium temperature. The pressure was maintained and measured with a digital pressure controller Ruska model 7218 with an uncertainty of 0.001 kPa.

---

* To whom correspondence should be addressed. E-mail: admguez@uvigo.es. Tel.: +34 986 812 422. Fax: +34 986 812 382.

10.1021/je800828y CCC: $40.75

The initial sample for the binary VLE was the pure solvent (ethanol or water), and then IL was added for each experimental point. For the ternary VLE, the initial sample was a binary mixture. When equilibrium was reached, vapor and liquid samples were obtained, and different amounts of solvents or IL were then added, to cover the whole composition range. In the range of low composition of solvents, the temperature becomes instable, and the IL could decompose. So, the experimental VLE are carried out as long as the equilibrium temperature is stable. For the binary system ethanol (1) + BMimMSO$_4$ (2), x_2 reaches a composition of 0.43 approximately, corresponding to a mass fraction $w_2 \approx 0.81$ at a temperature of $T = 373.70$ K, and for the binary system water (1) + BMimMSO$_4$ (2), x_2 reaches 0.54 approximately, corresponding to $w_2 \approx 0.94$ at a temperature of $T = 374.12$ K. In the ternary system ethanol (1) + water (2) + BMimMSO$_4$ (3), the mass fraction of IL reached, w_3, was approximately 0.79 at a temperature of $T = 365.97$ K.

The liquid phase composition of the binary systems was determined by density measurements, using the density−composition curves determined in a previous work.[17] The density of the condensed vapor phase was also measured to ensure that only ethanol or water is present in the vapor phase. To determine the liquid phase composition of the ternary systemm, it is necessary to know at least two physical properties of the ternary mixture. In this case, the density and refractive index physical properties were determined for both liquid and condensed vapor phases. The physical properties of the ternary system and the constituent binary systems containing ionic liquid were determined and published in a previous work.[17] From these published data, isolines of density and refractive index were calculated, and the composition of the liquid and condensed vapor phase can be determined. The composition of the vapor phase, formed by a binary mixture ethanol + water, was determined by density using the density−composition curve of this binary mixture, determined in our laboratory and not published since it is a widely studied system. The mole fraction uncertainty of the technique for the determination of liquid and vapor composition is ± 0.001.

The densities of pure liquids and mixtures were measured with a densimeter (Anton Paar DSA-5000). The uncertainty in experimental measurement has been found to be lower than $\pm 2.6 \cdot 10^{-5}$ g·cm^{-3}. To measure refractive indices, an automatic refractometer (Abbemat-HP Dr. Kernchen) with an uncertainty in the experimental measurements of $\pm 4 \cdot 10^{-5}$ was used.

Results and Discussion

VLE for the binary systems ethanol (1) + BMimMSO$_4$ (2) and water (1) + BMimMSO$_4$ (2) as well as the VLE for the ternary system ethanol (1) + water (2) + BMimMSO$_4$ (3) have been determined at 101.3 kPa, and the results are summarized in Tables 1 to 3. No literature isobaric VLE data have been found for the studied systems or other systems containing this ionic liquid.

For the correlation of experimental data of VLE, NRTL and e-NRTL models are usually used. The NRTL model[3] has proved to be a good model for the correlation of VLE of systems containing IL. The e-NRTL model is an extension of the NRTL model which Chen et al.[9] derived as a model for single-solvent + electrolyte systems. Mock et al.[10,11] extended it to mixed-solvent + electrolyte systems.

Binary Systems. For comparison purposes, the binary VLE have been correlated using the NRTL and the e-NRTL models. In these correlations, the nonrandomness parameters α are also adjusted, obtaining better results than fixing them as constants. When these models are used for systems constituted by a solvent + salt, the equilibrium condition has to do only with the solvent, which is the component that is present in both phases. These correlations were made by minimizing the following objective function

Table 1. Vapor−Liquid Equilibrium Data for the Ethanol (1) + BMimMSO$_4$ (2) System at 101.3 kPa

T/K	x_1	γ_1
351.44	1.000	1.000
351.67	0.980	1.012
351.88	0.966	1.018
352.14	0.943	1.032
352.56	0.923	1.037
352.97	0.904	1.042
353.66	0.884	1.037
354.43	0.862	1.032
355.37	0.835	1.028
356.85	0.804	1.009
360.43	0.735	0.964
362.98	0.693	0.930
368.33	0.629	0.845
373.70	0.565	0.780

Table 2. Vapor−Liquid Equilibrium Data for the Water (1) + BMimMSO$_4$ (2) System at 101.3 kPa

T/K	x_1	γ_1
373.15	1.000	1.000
373.48	0.931	1.061
373.59	0.901	1.092
373.74	0.848	1.154
373.83	0.817	1.194
373.84	0.758	1.288
373.89	0.740	1.317
373.90	0.704	1.382
373.93	0.664	1.465
373.94	0.650	1.495
374.09	0.605	1.598
374.09	0.550	1.759
374.10	0.507	1.908
374.12	0.455	2.125

$$\mathrm{OF} = \sum_j h|y_1 - y_{1,\mathrm{calc}}| + \sum_j k|T - T_{\mathrm{calc}}| \qquad (1)$$

where y_1 is the experimental solvent mole fraction in the vapor phase ($y_1 = 1$ for binary systems); $y_{1,\mathrm{calc}}$ is the calculated solvent mole fraction in the vapor phase; T is the experimental equilibrium temperature; T_{calc} is the calculated equilibrium temperature; and h and k are the weighting factors. The calculated parameters, Δg and α, and root-mean-square deviations (rmsd), ΔT and Δy, for both correlation models are summarized in Table 4. The vapor pressures of the components were calculated using the Antoine equation.

Figure 1a shows the boiling temperature diagram of the experimental and calculated data, and Figure 1b shows the experimental and calculated activity coefficients for both binary systems and both correlation models. As can be seen in Figure 1b, ethanol has smaller activity coefficients than water. This could be related to the fact that ethanol has a stronger interaction with the IL than water. It can be observed that in the case of the binary system containing water, the activity coefficients present a positive deviation of Raoult's law, with $\gamma > 1$. Similar behavior can be observed in other binary systems containing an ionic liquid.[23,24] It is noticeable that the temperature increases very little with the increase of the composition of ionic liquid in the mixture. This behavior is also present in the literature[24]

Table 3. Vapor−Liquid Equilibrium Data for the Ethanol (1) + Water (2) + BMimMSO$_4$ (3) System at 101.3 kPa

T/K	x_1	x_2	y_1	γ_1	γ_2
357.00	0.174	0.818	0.567	2.622	0.973
357.56	0.167	0.818	0.536	2.532	1.018
359.28	0.150	0.817	0.508	2.504	1.012
360.19	0.141	0.817	0.509	2.583	0.976
361.25	0.128	0.817	0.501	2.684	0.951
362.24	0.119	0.811	0.496	2.767	0.931
363.16	0.106	0.811	0.461	2.778	0.962
365.20	0.070	0.811	0.459	3.888	0.894
361.67	0.122	0.759	0.545	3.014	0.919
359.30	0.183	0.707	0.600	2.422	0.951
356.79	0.270	0.629	0.655	1.971	1.017
358.39	0.256	0.619	0.656	1.957	0.965
360.30	0.237	0.611	0.655	1.971	0.912
362.19	0.209	0.601	0.661	2.099	0.847
363.24	0.197	0.585	0.682	2.206	0.785
365.97	0.175	0.553	0.694	2.297	0.719
362.42	0.261	0.487	0.741	1.868	0.791
359.82	0.375	0.403	0.787	1.519	0.868
358.07	0.492	0.334	0.808	1.271	1.012
355.84	0.589	0.263	0.842	1.205	1.154
354.62	0.678	0.201	0.864	1.125	1.368
355.63	0.369	0.563	0.666	1.533	1.149
357.45	0.227	0.729	0.586	2.043	1.026
359.12	0.153	0.814	0.525	2.547	0.986
360.21	0.118	0.855	0.482	2.923	0.981
361.61	0.090	0.888	0.430	3.245	0.985
362.88	0.070	0.911	0.393	3.628	0.974
364.84	0.051	0.934	0.325	3.853	0.982
360.35	0.097	0.888	0.455	3.340	0.989
355.85	0.239	0.748	0.574	2.020	1.095
355.16	0.293	0.695	0.591	1.745	1.164
356.45	0.275	0.684	0.596	1.783	1.109
355.41	0.330	0.630	0.625	1.621	1.166
354.60	0.391	0.573	0.653	1.477	1.225
353.78	0.470	0.498	0.684	1.328	1.326
353.00	0.563	0.411	0.724	1.210	1.448
352.47	0.643	0.335	0.762	1.137	1.570
353.31	0.630	0.320	0.782	1.153	1.451
354.40	0.605	0.308	0.801	1.179	1.312
354.98	0.423	0.511	0.691	1.423	1.204
354.27	0.470	0.466	0.711	1.354	1.268
352.38	0.515	0.428	0.740	1.385	1.343

Table 4. Binary Correlation Parameters, Δg and α, and Root-Mean-Square Deviations, ΔT, Δy, and $\Delta\gamma$, for the Binary Systems Ethanol (1) + BMimMSO$_4$ (2) and Water (1) + BMimMSO$_4$ (2) at 101.3 kPa

	Ethanol (1) + BMimMSO$_4$ (2)			
NRTL	Δg_{12}/J·mol^{-1}	12151.62	ΔT/K	0.25
	Δg_{21}/J·mol^{-1}	−5154.57	Δy	0.009
	α	0.48	$\Delta\gamma$	0.007
e-NRTL	Δg_{12}/J·mol^{-1}	−15915.74	ΔT/K	0.24
	Δg_{21}/J·mol^{-1}	9074.04	Δy	0.009
	α	−0.18	$\Delta\gamma$	0.009
	Water (1) + BMimMSO$_4$ (2)			
NRTL	Δg_{12}/J·mol^{-1}	2243.93	ΔT/K	0.24
	Δg_{21}/J·mol^{-1}	1935.24	Δy	0.009
	α	0.44	$\Delta\gamma$	0.010
e-NRTL	Δg_{12}/J·mol^{-1}	1747.37	ΔT/K	0.21
	Δg_{21}/J·mol^{-1}	1914.39	Δy	0.007
	α	−1.28	$\Delta\gamma$	0.008

for other binary systems with ionic liquids. The mole fraction of ionic liquid reaches approximately $x_1 = 0.55$, which is equivalent to $w_1 = 0.95$ in weight fraction, but the temperature only increases 1 K. Because of this unusual behavior, the experimental vapor−liquid equilibrium of the binary system water (1) + BMimMSO$_4$ (2) was carried out twice, and similar results were achieved. As can be observed in Table 4 and Figure 1, NRTL and e-NRTL models correlate satisfactorily the experimental data, giving very similar deviations.

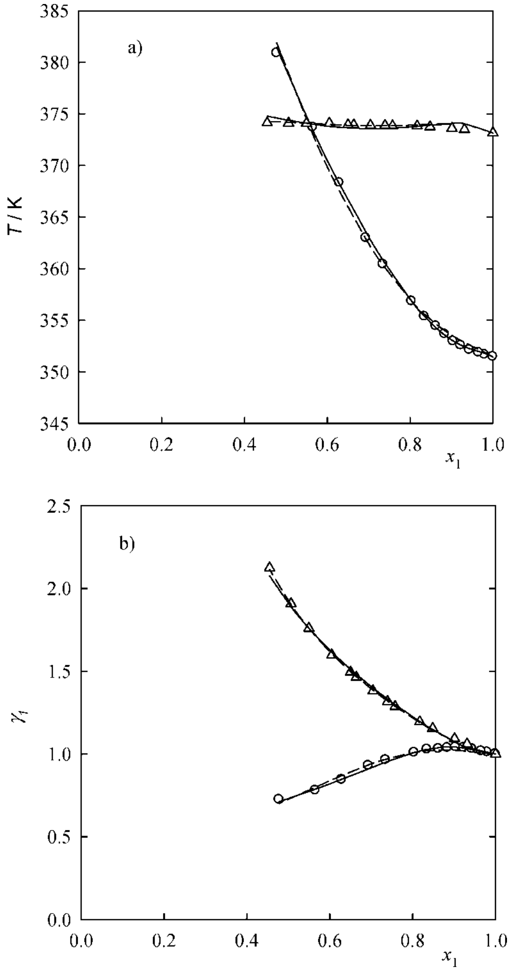

Figure 1. (a) Boiling temperature diagram and (b) activity coefficient diagram of experimental VLE data: ○, EtOH (1) + BMimMSO$_4$ (2); Δ, H$_2$O (1) + BMimMSO$_4$ (2); and calculated correlation curves: —, NRTL; and — —, e-NRTL.

Ternary System. From the binary adjustable parameters obtained in the correlations of the constituent binary systems, we can study the behavior of the VLE of the ethanol (1) + water (2) + BMimMSO$_4$ (3) ternary system. In our system, nine binary adjustable parameters must be determined for each model (NRTL and e-NRTL), from which six are energy parameters and three are nonrandomness factors.

The parameters of the binary system ethanol (1) + water (2) have been taken from the literature.[25] The other necessary parameters have been determined in this work. Using these binary parameters previously determined, we can study the behavior of the ternary system using the NRTL and e-NRTL models. Similar calculation of the behavior of ternary systems using the binary NRTL correlation parameters has already been reported by several authors.[26–28] The deviations obtained (rms) using the binary parameters for the prediction of the ternary system are $\Delta T = 1.56$ and $\Delta y = 0.190$ for the NRTL parameters and $\Delta T = 4.41$ and $\Delta y = 0.076$ for the e-NRTL parameters. It can be observed that while NRTL gives smaller deviations for the temperature the e-NRTL gives smaller deviations for the vapor composition. The pseudobinary representations of the $x'y$ and $Tx'y$ diagrams obtained from the NRTL correlation of the binary systems are plotted in Figure 2. To verify that the prediction considering the mole fraction of IL = 0 (binary system) is satisfactory, experimental data of the binary system ethanol (1) + water (2) from the literature[25] are also plotted. In

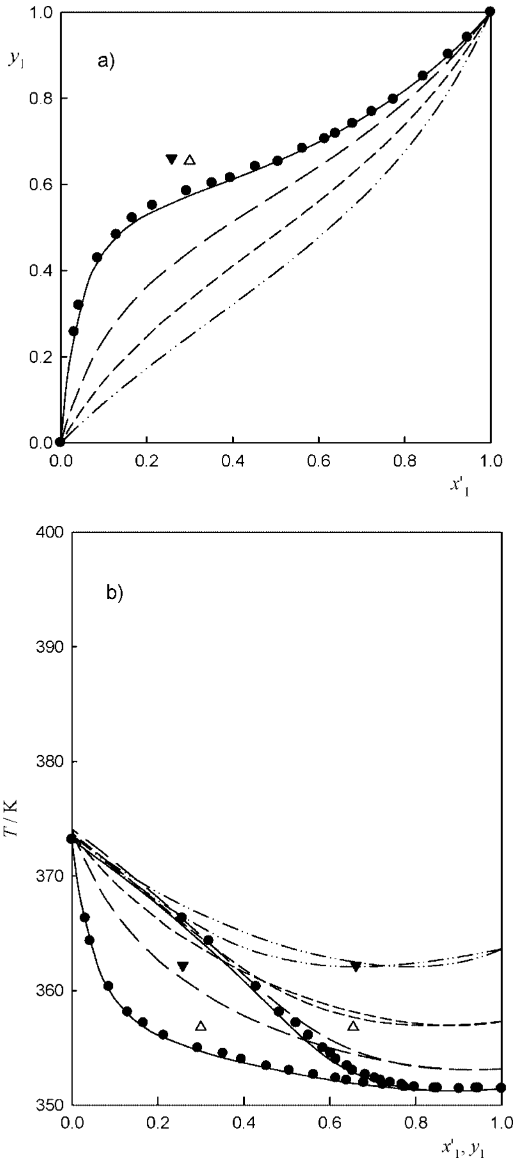

Figure 2. (a) $x'y$ and (b) $Tx'y$ diagrams of the ternary system ethanol (1) + water (2) + BMimMSO$_4$ (3) from the NRTL parameters obtained from the correlation of the binary systems, at IL mole fractions of —, 0 %; — —, 10 %; - -, 20 %; and — ••—••, 30 %. ●, experimental VLE data from ref 24; △, experimental ternary point $x_1 = 0.270$, $x_3 = 0.101$; ▼, experimental ternary point $x_1 = 0.209$, $x_3 = 0.190$.

these figures, the liquid phase composition is represented on an IL-free basis. The IL concentration is stated for each curve separately for $x_3 = (0, 10, 20, \text{and } 30)$ %. Different experimental points are also included to test the goodness of the predictions. These experimental points represent $x_3 \approx 0.1$ ($x_1 = 0.270$, $x_3 = 0.101$) and $x_3 \approx 0.2$ ($x_1 = 0.209$, $x_3 = 0.190$). As can be seen in Figure 2, with these parameters the VLE of the binary system ethanol (1) + water (2) and the temperatures in the nearest of the $x'_1 = 0$ (binary system water + IL) are correctly predicted, but these parameters are not capable of reproducing the behavior of the experimental VLE of the ternary system.

For the treatment of the experimental data of the vapor−liquid equilibrium of the ternary system ethanol (1) + water (2) + BMimMSO$_4$ (3), the NRTL model was used. The calculated parameters and deviations of this correlation are summarized in Table 5, and the pseudobinary representations of the $x'y$ and $Tx'y$ diagrams are plotted in Figure 3. The considerations for this figure were already mentioned, and the experimental points shown are the same as that in Figure 2. The deviations presented in Table 5 are referred to the experimental data obtained in the VLE of the ternary system. With this correlation, the predicted temperature in the nearest of the $x'_1 = 0$ (binary system water + IL) is not adequate, probably due to the unusual behavior of the VLE of the binary system water (1) + BMimMSO$_4$ (2), although the prediction of the behavior of the VLE of the ternary system is acceptable, as can be observed in Figure 3 and Table 5.

In Figure 3a, we can observe that the addition of the ionic liquid BMimMSO$_4$ to this binary azeotropic mixture leads to the break of the binary azeotrope ethanol + water, producing a salting-out effect near the azeotropic point.

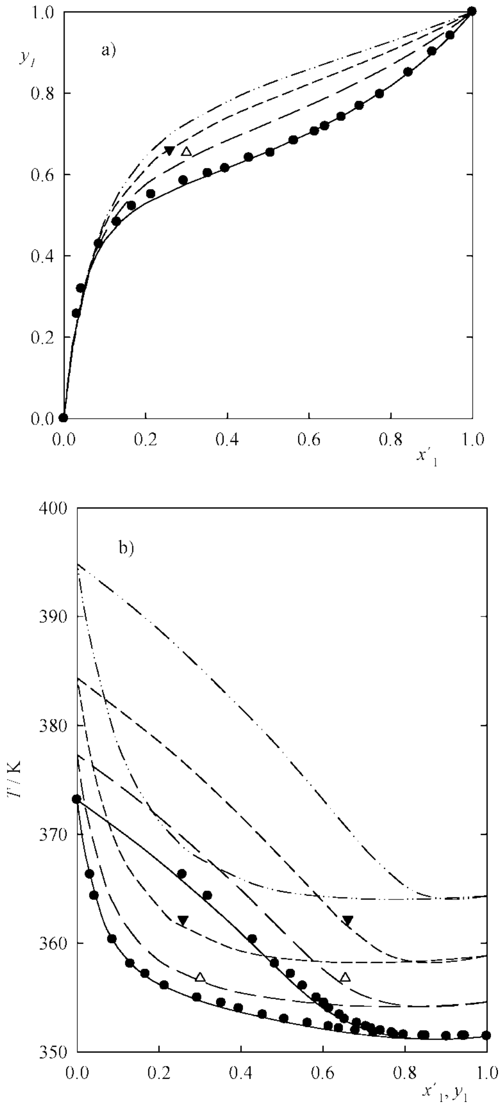

Figure 3. (a) $x'y$ and (b) $Tx'y$ diagrams of the ternary system ethanol (1) + water (2) + BMimMSO$_4$ (3) from the NRTL ternary correlation, at IL mole fractions of —, 0 %; — —, 10 %; - -, 20 %; and — ••—••, 30 %. ●, experimental VLE data from ref 24; △, experimental ternary point $x_1 = 0.270$, $x_3 = 0.101$; ▼, experimental ternary point $x_1 = 0.209$, $x_3 = 0.190$.

Table 5. Ternary NRTL Correlation Parameters, Δ*g* and α, Obtained from the Correlation of VLE Experimental Data of the Ternary System Ethanol (1) + Water (2) + BMimMSO$_4$ (3) and Root-Mean-Square Deviations, Δ*T* and Δ*y*, at 101.3 kPa

parameters	Δg_{12}/J·mol^{-1}	1045.21	Δg_{23}/J·mol^{-1}	−14038.66	α_{12}	0.57
	Δg_{13}/J· mol^{-1}	−3995.68	Δg_{31}/J· mol^{-1}	263.88	α_{13}	−0.05
	Δg_{21}/J· mol^{-1}	4454.85	Δg_{32}/J· mol^{-1}	400 307.36	α_{23}	0.04
rmsd	ΔT	1.00	Δy	0.015		

Conclusions

Experimental VLE of the ternary system ethanol (1) + water (2) + $BMimMSO_4$ (3) at 101.3 kPa has been carried out in this study, as well as the constituent binary systems containing the IL, ethanol (1) + $BMimMSO_4$ (2), and water (1) + $BMimMSO_4$ (2).

The NRTL and e-NRTL correlation models have been tested in this paper. Both models give similar results for the binary systems, obtaining very satisfactory results. In the study of the prediction of the behavior of the VLE of the ternary system from the binary correlation parameters, the NRTL model shows a better prediction of the equilibrium temperature, and the e-NRTL model describes better the vapor composition behavior; however, neither is capable of representing adequately the experimental VLE of the ternary mixture.

The NRTL model was used to correlate the experimental data of the VLE of the ternary system, obtaining a good agreement with the ternary experimental data, but with serious discrepancies in the temperature in the nearest of the binary system water + IL. In a previous publication,[16] the differences between the deviations obtained in the study of the behavior of the ternary system using the parameters from the ternary correlation and the parameters from the correlation of the binary systems were very similar. In the present case, the prediction of the temperature in the nearest of the binary system containing water and ionic liquid is not satisfactory using the parameters from the ternary correlation, but the prediction of the behavior of the VLE of the ternary system gives better results than using the parameters obtained from the correlation of the binary systems.

From the study carried out in this work, it can be concluded that with the addition of $BMimMSO_4$ to the mixture ethanol + water the existing azeotrope can be broken, opening a new possibility as an entrainer for this IL.

Literature Cited

(1) 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.

(2) Sarafov, 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 sulphate and 1-methyl-3-octylimidazolium tetrafluoroborate. *J. Chem. Eng. Data* **2006**, *51*, 518–525.

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

(4) Arce, A.; Rodríguez, H.; Soto, A. Use of a green and cheap ionic liquid to purify gasolina octane boosters. *Green Chem.* **2007**, *9*, 247–253.

(5) 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.

(6) Zhang, L.; Han, J.; Wang, R.; Qiu, X.; Ji, J. Isobaric vapor-liquid equilibria for three ternary systems: water + 2-propanol + 1-ethyl-3-methylimidazolium tetrafluoroborate, water + 1-propanol + 1-ethyl-3-methylimidazolium tetrafluoroborate, and water + 1-propanol + 1-butyl-3-methylimidazolium tetrafluoroborate. *J. Chem. Eng. Data* **2007**, *52*, 1401–1407.

(7) Wang, J. F.; Li, C. X.; Wang, Z. H.; Li, Z. J.; Jiang, Y. B. Vapor pressure measurement for water, methanol, ethanol, and their binary mixtures in the presence of an ionic liquid 1-ethyl-3-methylimidazolium dimethylphosphate. *Fluid Phase Equilib.* **2007**, *255*, 186–192.

(8) Zhang, L.; Han, J.; Deng, D.; Ji, J. Selection of ionic liquids as entrainers for separation of water and 2-propanol. *Fluid Phase Equilib.* **2007**, *255*, 179–185.

(9) Chen, C. C.; Britt, H. I.; Boston, J. F.; Evans, L. B. Local composition model for excess Gibbs energy of electrolyte systems. Part 1: single solvent, single completely dissociated electrolyte systems. *AIChE J.* **1982**, *28*, 588–596.

(10) 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**, *1984* (1), 558–562.

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

(12) Orchillés, A. V.; Miguel, P. J.; Vercher, E.; Martínez-Andreu, A. Isobaric vapor-liquid equilibria for methyl acetate + methanol + 1-ethyl-3-methylimidazolium trifluoromethanesulfonate at 100 kPa. *J. Chem. Eng. Data* **2007**, *52*, 915–920.

(13) 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.

(14) 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.

(15) Calvar, N.; González, B.; Gómez, E.; Domínguez, A. Study of the behaviour of the azeotropic mixture ethanol−water with imidazolium-based ionic liquids. *Fluid Phase Equilib.* **2007**, *259*, 51–56.

(16) Calvar, N.; González, B.; Gómez, E.; Domínguez, A. Vapor−liquid equilibria for the ternary system ethanol + water + 1-ethyl-3-methylimidazolium ethylsulfate and the corresponding binary systems containing the ionic liquid at 101.3 kPa. *J. Chem. Eng. Data* **2008**, *53*, 820–825.

(17) González, B.; Calvar, N.; Gómez, E.; Domínguez, A. Physical properties of the ternary system (ethanol + water + 1-butyl-3-methylimidazolium methylsulphate) and its binary mixtures at several temperatures. *J. Chem. Thermodyn.* **2008**, *40*, 1274–1281.

(18) Pereiro, A. B.; Verdía, P.; Tojo, E.; Rodríguez, A. Physical Properties of 1-Butyl-3-methylimidazolium Methyl Sulfate as a Function of Temperature *J. Chem. Eng. Data* **2007**, *52*, 377−380.

(19) Nikam, P. S.; Jadhav, M. C.; Hasan, M. Density and viscosity of mixtures of nitrobenzene with methanol, ethanol, propan-1-ol, propan-2-ol, butan-1-ol, 2-methylpropan-1-ol, and 2-methylpropan-2-ol at 298.15 and 303.15 K. *J. Chem. Eng. Data* **1995**, *40*, 931–934.

(20) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents*; Wiley: New York, 1986.

(21) Fernández, A.; Tordecilla, J. S.; García, J.; Rodríguez, F. Thermophysical properties of 1-ethyl-3-methylimidazolium ethylsulfate and 1-butyl-3-methylimidazolium methylsulfate ionic liquids. *J. Chem. Eng. Data* **2007**, *52*, 1979–1983.

(22) Widegren, J. A.; Laesecke, A.; Magee, J. W. The effect of dissolved water on the viscosities of hydrophobic room-temperature ionic liquids. *Chem. Commun.* **2005**, *12*, 1610–1612.

(23) Zhang, L.; Han, J.; Wang, R.; Qiu, X.; Ji, J. Isobaric vapor-liquid equilibria for three ternary systems: water + 2-propanol + 1-ethyl-3-methylimidazolium tetrafluoroborate, water + 1-propanol + 1-ethyl-3-methylimidazolium tetrafluoroborate, and water + 1-propanol + 1-butyl-3-methylimidazolium tetrafluoroborate. *J. Chem. Eng. Data* **2007**, *52*, 1401–1407.

(24) Orchillés, A. V.; Miguel, P. J.; Vercher, E.; Martínez-Andreu, A. Isobaric vapor-liquid equilibria for ethyl acetate + ethanol + 1-ethyl-3-methylimidazolium trifluoromethanesulfonate at 100 kPa. *J. Chem. Eng. Data* **2007**, *52*, 2325–2330.

(25) Arce, A.; Martínez-Ageitos, J.; Soto, A. VLE for water + ethanol + 1-octanol mixtures. Experimental measurements and correlations. *Fluid Phase Equilib.* **1996**, *122*, 117–129.

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

(27) Lladosa, E.; Montón, J. B.; Burguet, M. C. Isobaric vapor-liquid equilibria for binary and ternary mixtures of diisopropyl ether, 2-propyl alcohol, and 3-methyl-1-butanol. *J. Chem. Eng. Data* **2008**, *53*, 1897–1902.

(28) Sánchez-Russinyol, M. C.; Aucejo, A.; Loras, S. Isobaric vapor-liquid equilibrium for ternary mixtures of ethanol and methylcyclohexane with 3-methylpentane and tert-butyl alcohol at 101.3 kPa. *Fluid Phase Equilib.* **2007**, *261*, 104–110.

Received for review November 5, 2008. Accepted January 30, 2009. The authors are grateful to the Ministerio de Ciencia y Tecnología of Spain (project CTQ2004-00454) and to the Xunta de Galicia (Ángeles Alvariño program) for financial support.

JE800828Y