# Experimental Vapor−Liquid Equilibria for the Ternary System Ethanol + Water + 1-Ethyl-3-methylpyridinium Ethylsulfate and the Corresponding Binary Systems at 101.3 kPa: Study of the Effect of the Cation

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A study on the isobaric vapor−liquid equilibria of the ternary system containing the ionic liquid 1-ethyl-3-methylpyridinium ethylsulfate ($EMpyESO_4$) and the azeotropic mixture ethanol + water is presented in this work. Experimental isobaric vapor−liquid equilibrium of the ternary system ethanol + water + $EMpyESO_4$ was determined at 101.3 kPa, together with the vapor−liquid equilibria of the binary systems ethanol + $EMpyESO_4$ and water + $EMpyESO_4$. The experimental data obtained from the binary vapor−liquid equilibria were correlated using the NRTL and e-NRTL equations. The NRTL equation was also used to correlate the experimental vapor−liquid equilibrium of the ternary system. With the parameters obtained from these correlations, the evolution of the azeotrope ethanol + water with different amounts of ionic liquid can be studied. The results obtained were compared with the isobaric vapor−liquid equilibria data of the system containing this azeotropic mixture with the ionic liquid 1-ethyl-3-methylimidazolium ethylsulfate.

## Introduction

In the latest years, ionic liquids (ILs) have been investigated as separation agents for industrial mixtures. This interest is related to the new advantages that these compounds present, such as their negligible vapor pressure at normal temperature and pressure conditions, thermal stability, and their capability as solvents.

The ionic liquids are relatively new compounds, and the information about their physical and solvent properties is still scarce. Experimental phase equilibrium data are required for developing thermodynamic models and for understanding their thermodynamic behavior. Vapor−liquid equilibria (VLE) data permit checking the potential of $G^E$ models which are used for the description of the nonideal behavior of systems containing ILs. The ILs based on imidazolium and pyridinium cations are two main groups of these substances. There are a number of workers who have studied the VLE of binary and ternary systems of imidazolium-based ILs. However, for systems containing pyridinium-based ILs, these studies are scarce.

In previous papers,[1−4] binary and ternary systems involving the ionic liquids 1-butyl-3-methylimidazolium chloride (BMimCl), 1-hexyl-3-methylimidazolium chloride (HMimCl), 1-ethyl-3-methylimidazolium ethylsulfate ($EMimESO_4$), and 1-butyl-3-methylimidazolium methylsulfate ($BMimMSO_4$) and the binary mixture ethanol + water have been reported. In this work, the pyridinium-based ionic liquid 1-ethyl-3-methylpyridinium ethylsulfate ($EMpyESO_4$) was studied, making it possible to compare the behavior of the evolution of the azeotrope with ionic liquids with different cations. No literature data about isobaric vapor−liquid equilibria of ternary systems containing a pyridinium-based ionic liquid have been found.

Wilson, NRTL, and UNIQUAC equations have been used for the correlation of systems involving ionic liquids in several studies.[5,6] In these works, it is stated that the NRTL equation[7] gives the best empirical description of activity coefficients, being the most commonly used model. Although this model is theoretically developed for systems involving nonelectrolytes, it usually leads to good correlations for systems containing ILs.[8−15] Nevertheless, there is an extension of the NRTL model that considers the fact that ILs are organic salts that present ionic character, the e-NRTL model.[16−18] This model has also been used in the literature,[19,20] although it is less common. In any case, perhaps for the lack of models specifically created for systems with ILs and for its relative simplicity, the NRTL model is the most used. A comparison of the correlation models commonly used for the treatment of vapor−liquid equilibria experimental data, the NRTL and the e-NRTL models, was carried out in this work for the studied mixtures.

## Experimental Section

***Chemicals.*** Ethanol was purchased from Merck with purity higher than 99.8 %, and it was degassed ultrasonically and dried over molecular sieves type 0.4 nm. Water was bidistilled and deionized. 1-Ethyl-3-methylpyridinium ethylsulfate ($EMpyESO_4$) was synthesized in our laboratory using the method described in a previous paper.[21] To reduce the water content to negligible, vacuum ($2 \cdot 10^{-1}$ Pa) and moderate temperature (343.15 K) were applied to the IL for several days, always immediately prior to its use. The water concentration ($<7 \cdot 10^{-4}$ mass fraction) was checked by Karl Fischer titration. To ensure its purity, the final product was checked by nuclear magnetic resonance (NMR) spectroscopy. Its purity was found to be

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10.1021/je900998f

**Table 1. Experimental Pure Component Data and Literature Values at $T = 298.15$ K**

| | $\rho$/g·cm$^{-3}$ | | $10^3\eta$/Pa·s | |
|---|---|---|---|---|
| component | exptl | lit. | exptl | lit. |
| ethanol | 0.78546 | 0.78546[a] | 1.082 | 1.082[a] |
| water | 0.99705 | 0.99705[b] | 0.890 | 0.890[b] |
| EMpyESO$_4$ | 1.22226 | n.a. | 161.4 | 150[c] |

[a] From ref 22. [b] From ref 23. [c] From ref 24.

higher than 99 % mass fraction. The ionic liquid was kept in bottles under an inert atmosphere in a glovebox.

***Experimental Method.*** Density and viscosity of ethanol, water, and EMpyESO$_4$ were measured and compared with literature values[22−24] (Table 1). The results show that there is a good agreement between experimental and literature data; the small differences between experimental and literature data for viscosity of EMpyESO$_4$ may be due to the presence of water or nonvolatile impurities in our samples or their samples.

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. For the pressure measurement, a digital pressure controller Ruska model 7218 with an uncertainty of 0.001 kPa was used.

The procedure for the determination of the experimental binary and ternary VLE and for the calculation of the composition of the phases was explained in detail in previous papers.[1−4] Briefly, 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 ILs were then added. The phase composition of the binary systems was determined by density measurements, and the liquid phase composition of the ternary system was calculated by means of the density and refractive index. The vapor phase of the ternary system, formed by a binary mixture ethanol + water, was measured by density. The mole fraction uncertainty of the technique for the determination of liquid and vapor compositions is ± 0.001. Physical properties of these binary and ternary systems were determined in a previous work.[21,25]

In the range of low composition of solvents, the temperature becomes instable, and the IL could decompose[24] ($T_{\text{start}} = 486$ K); therefore, the experimental VLE are carried out as long as the equilibrium temperature is stable. For the binary system ethanol (1) + EMpyESO$_4$ (2), $x_2$ reaches a mole composition of 0.48 approximately, corresponding to a mass fraction $w_2 \approx 0.83$ at $T = 385.52$ K, and for the binary system water (1) + EMpyESO$_4$ (2), $x_2$ reaches 0.28 approximately, corresponding to $w_2 \approx 0.68$ at $T = 393.47$ K. In the ternary system ethanol (1) + water (2) + EMpyESO$_4$ (3), the mass fraction of IL reached, $w_3$, was approximately 0.77 at $T = 371.50$ K.

The densities of pure liquids and mixtures were measured with a densimeter (Anton Paar DSA-5000), and the uncertainty in experimental measurements has been found to be lower than $3 \cdot 10^{-5}$ 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. Kinematic viscosities of pure chemicals were determined using an automatic viscosimeter (Lauda PVS1) with three Ubbelhode capillary microviscosimeters of $0.53 \cdot 10^{-3}$ m, $0.70 \cdot 10^{-3}$ m, and $1.26 \cdot 10^{-3}$ m diameter (the uncertainty in experimental measurement is (± 0.01, ± 0.03, and ± 0.2) mPa·s, respectively). The capillary is maintained in a D20KP LAUDA thermostat with an uncertainty of 0.01 K. The capillaries are calibrated and credited by the company. The equipment has a control unit PVS1 (Processor Viscosity System) that is a PC-controlled instrument for the precise measurement of the fall time, using standardized glass capillaries, with an uncertainty of 0.01 s.

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

| $T$/K | $x_1$ | $\gamma_1$ |
|---|---|---|
| 351.44 | 1.000 | 1.000 |
| 352.01 | 0.983 | 0.995 |
| 352.45 | 0.971 | 0.990 |
| 353.00 | 0.955 | 0.985 |
| 353.88 | 0.926 | 0.982 |
| 355.06 | 0.893 | 0.973 |
| 356.18 | 0.864 | 0.963 |
| 357.89 | 0.831 | 0.937 |
| 360.49 | 0.789 | 0.895 |
| 362.17 | 0.765 | 0.868 |
| 364.30 | 0.731 | 0.840 |
| 366.36 | 0.706 | 0.808 |
| 368.87 | 0.670 | 0.778 |
| 371.35 | 0.640 | 0.747 |
| 374.55 | 0.605 | 0.707 |
| 378.64 | 0.576 | 0.648 |
| 385.52 | 0.524 | 0.569 |

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

| $T$/K | $x_1$ | $\gamma_1$ |
|---|---|---|
| 373.15 | 1.000 | 1.000 |
| 373.48 | 0.996 | 0.992 |
| 373.80 | 0.990 | 0.987 |
| 374.10 | 0.984 | 0.982 |
| 374.37 | 0.977 | 0.980 |
| 374.68 | 0.969 | 0.977 |
| 375.12 | 0.959 | 0.972 |
| 375.43 | 0.953 | 0.968 |
| 376.01 | 0.943 | 0.959 |
| 376.64 | 0.929 | 0.952 |
| 377.44 | 0.916 | 0.938 |
| 378.61 | 0.900 | 0.917 |
| 380.39 | 0.876 | 0.887 |
| 382.77 | 0.843 | 0.850 |
| 385.40 | 0.810 | 0.810 |
| 388.73 | 0.769 | 0.765 |
| 393.47 | 0.719 | 0.703 |

## Results and Discussion

Experimental vapor−liquid equilibria for the binary systems ethanol (1) or water (1) + EMpyESO$_4$ (2) as well as the VLE for the ternary system ethanol (1) + water (2) + EMpyESO$_4$ (3) have been determined at 101.3 kPa, and the results are summarized in Tables 2 to 4.

For the correlation of experimental data of VLE, two models are usually used: the NRTL model[3] has proved to be a good model for the correlation of VLE of systems containing IL, although it is theoretically developed for systems involving nonelectrolytes. The e-NRTL model is an extension of the NRTL model which Chen et al.[16] derived as a model for single-solvent + electrolyte systems. Mock et al.[17,18] extended it to mixed-solvent + electrolyte systems, assuming that the local composition of cations (anions) around a central cation (anion) is zero, that the distribution of cations and anions around a central solvent molecule is such that the net local ionic charge is zero, and that the long-range interaction contribution can be neglected.

**Table 4. Vapor−Liquid Equilibrium Data for the Ethanol (1) + Water (2) + EMpyESO$_4$ (3) System at 101.3 kPa**

| $T$/K | $x_1$ | $x_2$ | $y_1$ | $\gamma_1$ | $\gamma_2$ |
|---|---|---|---|---|---|
| 371.50 | 0.112 | 0.659 | 0.503 | 2.1252 | 0.8005 |
| 366.76 | 0.204 | 0.593 | 0.631 | 1.7365 | 0.7862 |
| 361.99 | 0.302 | 0.512 | 0.710 | 1.5692 | 0.8578 |
| 359.21 | 0.413 | 0.433 | 0.754 | 1.3543 | 0.9562 |
| 357.24 | 0.495 | 0.370 | 0.791 | 1.2765 | 1.0294 |
| 357.44 | 0.301 | 0.613 | 0.649 | 1.7106 | 1.0351 |
| 358.43 | 0.196 | 0.741 | 0.577 | 2.2426 | 0.9917 |
| 359.91 | 0.135 | 0.816 | 0.515 | 2.7456 | 0.9748 |
| 361.55 | 0.097 | 0.865 | 0.455 | 3.1721 | 0.9698 |
| 363.15 | 0.073 | 0.897 | 0.400 | 3.5121 | 0.9685 |
| 363.98 | 0.068 | 0.893 | 0.397 | 3.6434 | 0.9475 |
| 365.10 | 0.068 | 0.879 | 0.381 | 3.3569 | 0.9472 |
| 366.18 | 0.065 | 0.867 | 0.373 | 3.2960 | 0.9338 |
| 367.32 | 0.067 | 0.845 | 0.374 | 3.0584 | 0.9167 |
| 368.36 | 0.070 | 0.823 | 0.383 | 2.8978 | 0.8931 |
| 362.38 | 0.150 | 0.750 | 0.521 | 2.2911 | 0.9510 |
| 363.98 | 0.152 | 0.736 | 0.519 | 2.1239 | 0.9164 |
| 365.51 | 0.147 | 0.724 | 0.510 | 2.0339 | 0.8957 |
| 360.58 | 0.243 | 0.640 | 0.612 | 1.7776 | 0.9681 |
| 357.88 | 0.343 | 0.553 | 0.672 | 1.5284 | 1.0523 |
| 355.07 | 0.503 | 0.416 | 0.742 | 1.2796 | 1.2288 |
| 356.00 | 0.330 | 0.614 | 0.610 | 1.5487 | 1.2125 |
| 357.18 | 0.230 | 0.728 | 0.572 | 1.9868 | 1.0735 |
| 358.41 | 0.168 | 0.799 | 0.530 | 2.4181 | 1.0218 |
| 361.62 | 0.090 | 0.889 | 0.429 | 3.2271 | 0.9848 |
| 359.07 | 0.128 | 0.852 | 0.487 | 2.8378 | 1.0196 |
| 357.21 | 0.182 | 0.798 | 0.539 | 2.3599 | 1.0535 |
| 355.47 | 0.272 | 0.711 | 0.584 | 1.8377 | 1.1415 |
| 356.04 | 0.290 | 0.670 | 0.604 | 1.7408 | 1.1284 |
| 354.61 | 0.400 | 0.561 | 0.656 | 1.4470 | 1.2396 |
| 355.83 | 0.282 | 0.689 | 0.600 | 1.7901 | 1.1184 |
| 354.36 | 0.384 | 0.592 | 0.638 | 1.4818 | 1.2472 |
| 355.08 | 0.372 | 0.585 | 0.645 | 1.5020 | 1.2039 |
| 353.43 | 0.530 | 0.437 | 0.706 | 1.2312 | 1.4262 |
| 354.76 | 0.488 | 0.450 | 0.714 | 1.2859 | 1.2774 |

**Table 5. Binary Correlation Parameters, $\Delta g$ (J·mol$^{-1}$) and α, and Root-Mean-Square Deviations for the Binary Systems Ethanol (1) + EMpyESO$_4$ (2) and Water (1) + EMpyESO$_4$ (2) at 101.3 kPa**

| | | | | |
|---|---|---|---|---|
| Ethanol + EMpyESO$_4$ | | | | |
| NRTL | $\Delta g_{12}$ | −4010.22 | $\Delta T$/K | 0.39 |
| | $\Delta g_{21}$ | −3205.55 | $\Delta y$ | 0.013 |
| | α | 0.09 | $\Delta\gamma$ | 0.008 |
| e-NRTL | $\Delta g_{12}$ | −4062.43 | $\Delta T$/K | 0.33 |
| | $\Delta g_{21}$ | 170.66 | $\Delta y$ | 0.011 |
| | α | 0.10 | $\Delta\gamma$ | 0.009 |
| Water + EMpyESO$_4$ | | | | |
| NRTL | $\Delta g_{12}$ | −3458.54 | $\Delta T$/K | 0.27 |
| | $\Delta g_{21}$ | −3577.73 | $\Delta y$ | 0.010 |
| | α | 1.00 | $\Delta\gamma$ | 0.008 |
| e-NRTL | $\Delta g_{12}$ | −2325.42 | $\Delta T$/K | 0.21 |
| | $\Delta g_{21}$ | −2279.12 | $\Delta y$ | 0.008 |
| | α | 1.10 | $\Delta\gamma$ | 0.007 |

***Binary Systems.*** The binary VLE experimental data have been correlated using NRTL and e-NRTL models. In these correlations, the binary parameters, $\Delta g$, are obtained, and 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

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

where $y_1$ is the solvent mole fraction in the vapor phase ($y_1 = 1$ for binary systems); $T$ is the equilibrium temperature; and $h$ and $k$ are the weighing factors. The calculated parameters and root-mean-square deviations for both correlation models are summarized in Table 5. The vapor pressures of pure ethanol and water were calculated using the Antoine equation.

Figure 1a shows the boiling temperature diagram of experimental data of the binary systems ethanol (1) or water (1) + EMpyESO$_4$ (2), together with the correlation obtained with NRTL and e-NRTL equations, and Figure 1b shows the experimental and calculated activity coefficients for both binary systems and both correlation models. In these figures, the binary systems ethanol (1) or water (1) + 1-ethyl-3-methylimidazolium ethylsulfate (EMimESO$_4$) (2), taken from the literature,[3] are also presented. It can be observed in Figure 1a that the temperature has a similar behavior in the systems containing both ILs with ethanol or water, although the addition of EMpyESO$_4$ to ethanol produces a slightly higher increase in the boiling temperature of the mixture. The activity coefficients of the solvent in the binary system ethanol (1) + EMimESO$_4$ (2) are higher than for the binary system with EMpyESO$_4$, while for the mixtures of the ILs with water, the behavior is similar, being slightly higher for the system containing the pyridinium-based IL (Figure 1b). As can be deduced from Table 5 and Figure 1, both models correlate satisfactorily the experimental data, both giving similar deviations.

***Ternary System.*** From the binary adjustable parameters obtained in the correlations of the constituent binary systems, the VLE of the ethanol (1) + water (2) + EMpyESO$_4$ (3) ternary system can be predicted. In a ternary system, nine binary adjustable parameters must be determined for each model, from which six are energy parameters and three are nonrandomness factors. The binary parameters of the binary system ethanol (1) + water (2) have been taken from the literature[26] ($\Delta g_{12} = 771.13$ J·mol$^{-1}$, $\Delta g_{21} = 4762.1$ J·mol$^{-1}$), and the other necessary parameters have been determined in this work. Using these binary parameters previously determined, we can predict the behavior of the ternary system using the NRTL and e-NRTL models. The deviations obtained using the binary parameters for the prediction of the ternary system are $\Delta T = 0.85$ and $\Delta y = 0.026$ from the NRTL parameters and $\Delta T = 3.21$ and $\Delta y = 0.025$ from the e-NRTL parameters. According to these deviations, NRTL parameters lead to better results in temperature. It is noteworthy that in the prediction of the behavior of ternary VLE from the parameters obtained from binary correlations in the systems previously published,[3,4] the parameters obtained from the NRTL model always gave the smaller temperature deviations.

To find out if it is worth correlating the ternary system separately or if it is enough with the prediction from binary parameters, the experimental data of the VLE of the ternary system ethanol (1) + water (2) + EMpyESO$_4$ (3) were correlated using the NRTL model. During the calculations, the pressure was fixed at 101.3 kPa, since experimental data were obtained in isobaric conditions. The calculated parameters and deviations of this correlation are summarized in Table 6, and the pseudobinary representations of the $x'y$ and $Tx'y$ diagrams are plotted in Figure 2a and Figure 3, respectively. In these figures, experimental data of the binary system ethanol + water from the literature[26] are also plotted to test the predictions considering the mole fraction of IL = 0 (binary system). In these figures, the liquid phase composition is presented in a free-ionic liquid basis way. The IL concentration is stated for each curve separately for $x_3$ = (0, 10, 20, and 30) %, and different experimental points are also included to test the goodness of the predictions.

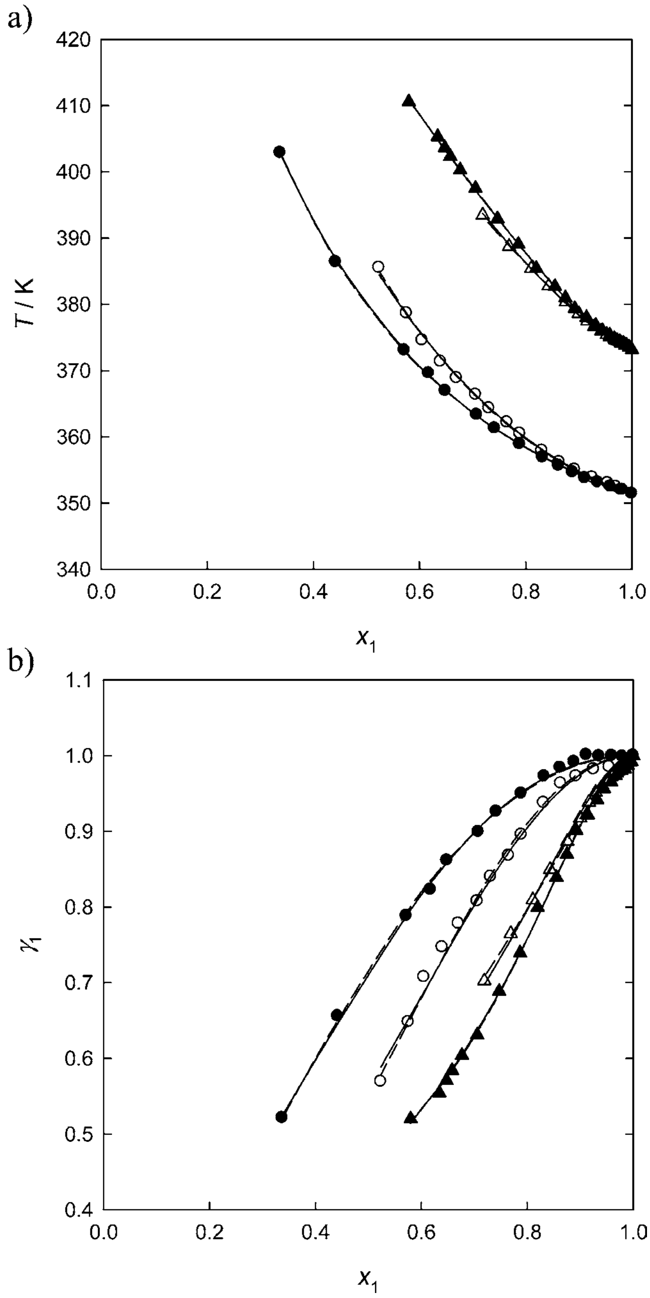

**Figure 1.** (a) Boiling temperature diagram and (b) activity coefficients diagram of VLE data: ○, EtOH (1) + EMpyESO$_4$ (2); Δ, $H_2O$ (1) + EMpyESO$_4$ (2); ●, EtOH (1) + EMimESO$_4$ (2) (ref 3); ▲, $H_2O$ (1) + EMimESO$_4$ (2) (ref 3), and calculated correlation curves: —, NRTL; and — —, e-NRTL.

**Table 6. Ternary NRTL Correlation Parameters, Δ*g* (J·mol$^{-1}$) and α, and Root-Mean-Square Deviations Obtained from the Correlation of VLE Experimental Data of the Ternary System Ethanol (1) + Water (2) + EMpyESO$_4$ (3) at 101.3 kPa**

| | | | | | | |
|---|---|---|---|---|---|---|
| parameters | $\Delta g_{12}$ | 3438.58 | $\Delta g_{23}$ | −6882.47 | $\alpha_{12}$ | −0.922 |
| | $\Delta g_{13}$ | 16973.85 | $\Delta g_{31}$ | −19609.12 | $\alpha_{13}$ | 0.035 |
| | $\Delta g_{21}$ | −4828.24 | $\Delta g_{32}$ | −14342.89 | $\alpha_{23}$ | −0.015 |
| rmsd | $\Delta T$ | 0.49 | $\Delta y$ | 0.029 | | |

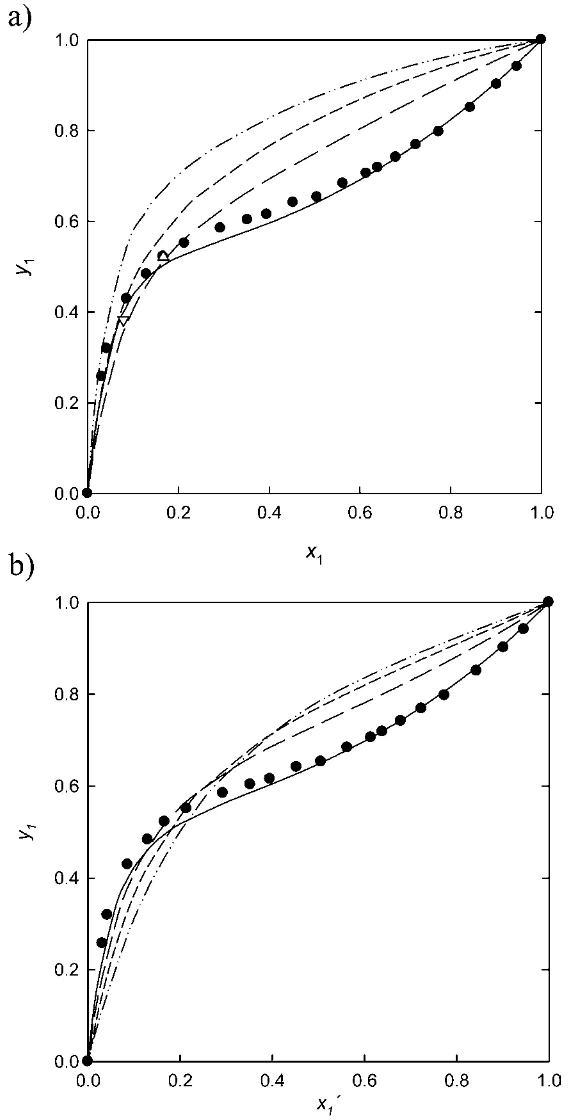

**Figure 2.** *x*′*y* diagrams of the ternary systems: (a) ethanol (1) + water (2) + EMpyESO$_4$ (3), Δ, experimental ternary point $x_1 = 0.150$, $x_3 = 0.100$; ▽, experimental ternary point $x_1 = 0.070$, $x_3 = 0.107$; and (b) ethanol (1) + water (2) + EMimESO$_4$ (3) (ref 3), from the NRTL ternary correlation, at IL mole fractions of —, 0 %; — —, 10 %; - - -, 20 %; and — • • — • •, 30 %. ●, experimental VLE data for the binary mixture ethanol (1) + water (2) (ref 26).

From Figure 2a, it can be deduced that the addition of EMpyESO$_4$ to this binary azeotropic mixture leads to the breaking of the binary azeotrope ethanol + water, producing a remarkable salting-out effect in the nearest of the azeotropic point and a salting-in effect at low concentrations of ethanol and ionic liquid, while for higher concentrations of ionic liquid, the salting-in effect is not present. It is remarkable that 10 % in mole fraction of ionic liquid is enough to break the azeotrope, and considering that the decomposition temperature of EMpyESO$_4$ is 486 K,[24] this concentration of ionic liquid can be used as an entrainer. In Figure 2b, the *x*′*y* diagram for the ternary system ethanol (1) + water (2) + EMimESO$_4$ (3) is represented to facilitate the comparison between the behavior of the VLE of ternary systems where the difference is the cation of the ionic liquid. It is important to mention that the NRTL model also gave satisfactory results for this ternary mixture. In these figures, it can be observed that in the ternary system containing the imidazolium-based ionic liquid there are important salting-in and salting-out effects, while the pyridinium-based ionic liquid leads to higher changes in the volatility of the solvents.

## Conclusions

In this work, the experimental determination of the VLE of the ternary system ethanol (1) + water (2) + EMpyESO$_4$ (3) at

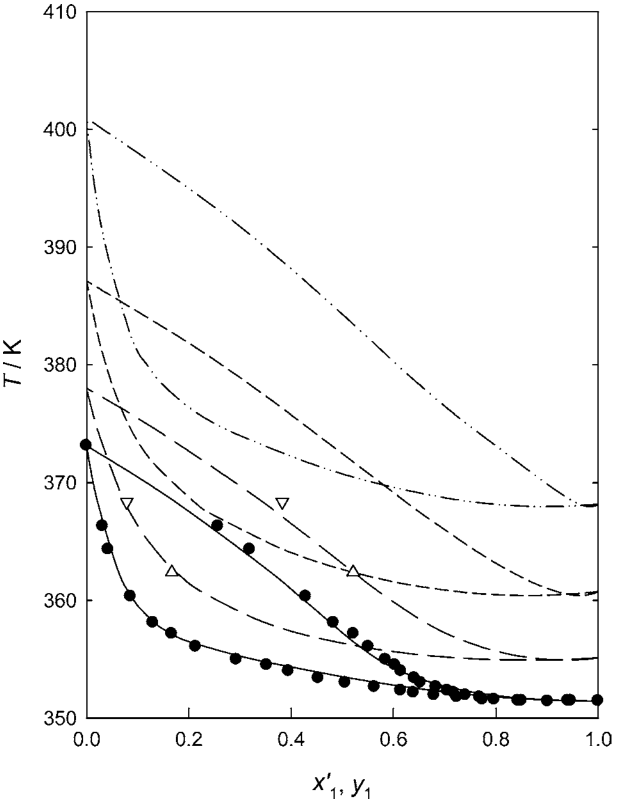

**Figure 3.** *Tx′y* diagrams of the ternary system ethanol (1) + water (2) + EMpyESO$_4$ (3), Δ, experimental ternary point $x_1 = 0.150$, $x_3 = 0.100$; ▽, experimental ternary point $x_1 = 0.070$, $x_3 = 0.107$; from the NRTL ternary correlation, at IL mole fractions of —, 0 %; — —, 10 %; - - -, 20 %; and — •• — ••, 30 %. ●, experimental VLE data for the binary mixture ethanol (1) + water (2) (ref 26).

101.3 kPa has been carried out, as well as of the constituent binary systems containing this ionic liquid, ethanol (1) or water (1) + EMpyESO$_4$ (2).

The NRTL and e-NRTL equations were used for the correlation of the binary systems, giving both models similar and 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, while the accuracy of the prediction of the vapor phase is similar for both models. To correlate the experimental data of the VLE of the ternary system, the NRTL model was tested, obtaining a good agreement with the ternary experimental data and improving the results obtained when the parameters from the correlation of the binary systems are used for the prediction of the behavior of the ternary system.

Comparing the results obtained with this pyridinium-based ionic liquid with the ones obtained with the imidazolium-based EMimESO$_4$, the ionic liquid studied in this work achieves higher changes in the volatility of the solvents, although both ionic liquids are capable of breaking the azeotrope.

From the study carried out in this work, it can be concluded that the azeotrope present in the mixture ethanol + water can be broken with the addition of EMpyESO$_4$, opening a new possibility as an entrainer for this IL.

## Literature Cited

(1) 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.

(2) 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.

(3) 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.

(4) Calvar, N.; González, B.; Gómez, E.; Domínguez, A. Vapour-liquid equilibria for the ternary system ethanol + water + 1-butyl-3-methylimidazolium methylsulfate and the corresponding binary systems at 101.3 kPa. *J. Chem. Eng. Data* **2009**, *54*, 1004–1008.

(5) 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.

(6) 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.

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

(8) 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.

(9) 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.

(10) 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.

(11) 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.

(12) 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.

(13) Zhang, L.; Ge, Y.; Ji, D.; Ji, J. Experimental measurement and modelling of vapor-liquid equilibrium for ternary systems containing ionic liquids: a case study for the system water + ethanol + 1-hexyl-3-methylimidazolium chloride. *J. Chem. Eng. Data* **2009**, *54*, 2322–2329.

(14) Li, Q.; Zhang, J.; Lei, Z.; Zhu, J.; Wang, B.; Huang, X. Isobaric vapor-liquid equilibrium for (propan-2-ol + water + 1-butyl-3-methylimidazolium tetrafluoroborate). *J. Chem. Eng. Data* **2009**, *54*, 2785–2788.

(15) Li, Q.; Zhang, J.; Lei, Z.; Zhu, J.; Zhu, J.; Huang, X. Selection of ionic liquids as entrainers for the separation of ethyl acetate and ethanol. *Ind. Eng. Chem. Res.* **2009**, *48*, 9006–9012.

(16) 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.

(17) 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.

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

(19) 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.

(20) 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.

(21) González, B.; Calvar, N.; Gómez, E.; Macedo, E. A.; Domínguez, A. Synthesis and physical properties of 1-ethyl 3-methylpyridinium ethylsulfate and its binary mixtures with ethanol and water at several temperatures. *J. Chem. Eng. Data* **2008**, *53*, 1824–1828.

(22) Nikam, P. S.; Jadhav, M. C.; Hasan, M. Density and viscosity of mixtures of nitrobenzene with methanol, ethanol, propan-1-ol, propan-

2-ol, putan-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.

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

(24) Crosthwaite, J. M.; Muldoon, M. J.; Dixon, J. K.; Anderson, J. L.; Brennecke, J. F. Phase transition and decomposition temperatures, heat capacities and viscosities of pyridinium ionic liquids. *J. Chem. Thermodyn.* **2005**, *37*, 559–568.

(25) Calvar, N.; Gómez, E.; González, B.; Domínguez, A. Experimental determination, correlation, and prediction of physical properties of the ternary mixtures ethanol and 1-propanol + water + 1-ethyl-3-methylpyridinium ethylsulfate at 298.15K. *J. Chem. Eng. Data* **2009**, *54*, 2229–2234.

(26) 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.

Received for review November 24, 2009. Accepted March 23, 2010. The authors are grateful to the Ministerio de Ciencia y Tecnología of Spain (project CTQ 2007-61272), to the scholarships from Fundação para a Ciência e a Tecnologia (FCT, Portugal) (ref SFRH/BDP/37775/2007 and ref SFRH/BDP/48210/2008), and to the LSRE financing by FEDER/POCI/2010, for financial support.

JE900998F