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

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In this work, experimental data of isobaric vapor−liquid equilibria for the ternary system ethanol + water + 1-butyl-3-methylimidazolium chloride ([C_4mim][Cl]) and for the corresponding binary systems containing the ionic liquid (ethanol + [C_4mim][Cl] and water + [C_4mim][Cl]) were measured at 101.3 kPa. Vapor−liquid equilibria experimental data of binary and ternary systems were correlated by the NRTL equation. NRTL parameters have been used to predict the evolution of the ethanol−water azeotrope composition with different amounts of ionic liquid.

Introduction

Ionic liquids (ILs) are substances formed by ions, and they show a negligibly vapor pressure at normal temperature and pressure conditions. This and other properties, such as their relatively low viscosities, their thermal stability, and their capability as solvents, make the ILs a new alternative for different processes. The use of IL in separation processes is one of the multiple alternatives.

The prediction of the ideal IL for each separation process is nowadays impossible since there is not enough information about the influence of the structure of IL in its physical and solvent properties. We have to take into account that there are about 10^{18} possible ionic liquids by combination of ions.[1] Besides, experimental phase equilibrium data are required for developing thermodynamic models and for understanding their thermodynamic behavior.

As said previously, ILs are becoming an important alternative to separate azeotropic mixtures. In this work, we study the possibility of separating the azeotropic mixture ethanol−water ($y_{1(\mathrm{az})} \approx 0.90$) using an IL, 1-butyl-3-methylimidazolium chloride ([C_4mim][Cl]), as proposed by Jork et al.[2]

Experimental data of isobaric vapor−liquid equilibria (VLE) for the ternary system ethanol + water + [C_4mim][Cl] and for the corresponding binary systems containing the ILs (ethanol + [C_4mim][Cl] and water + [C_4mim][Cl]) were carried out at 101.3 kPa. The binary system ethanol + water was not experimentally determined since it is a widely studied system.[3] Experimental results of the binary and ternary systems were correlated using the NRTL equation.[4] With the parameters obtained in the correlation, we can study the behavior of the ternary system under different conditions.

Experimental Section

Chemicals. Ethanol was supplied by Merck and degassed ultrasonically, dried over molecular sieves type 0.4 nm, and kept in an inert argon atmosphere. Its purity was more than 99.8 %. Water was bi-distilled and deionized. The IL used in this work was synthetised in our laboratory. It was dried by heating (343.15 K to 353.15 K) and stirring under high vacuum ($2 \cdot 10^{-1}$ Pa) for 48 h. To determine its molecular structure and purity, a NMR and a positive FABMS (fast atom bombardment mass spectroscopy) were made.[5] The water content was 10^{-4} w/w determined by a 756 Karl Fisher coulometer.

Table 1. Comparison of Data with Literature Data for Pure Liquids at 298.15 K

	ρ/g·cm^{-3}		$10^{-3}\ \eta$/Pa·s		T_B/K	
component	exptl	lit.[a]	exptl	lit.[a]	exptl	lit.[b]
ethanol	0.78545	0.78546	1.082	1.082	351.43	351.443
water	0.99710	0.99705	0.890	0.890	373.15	373.150

[a] Ref 6. [b] Ref 7.

Density (ρ), viscosity (η), and boiling point (T_B) of ethanol and water used in this work were measured and compared with the literature (Table 1). These two components were analyzed by gas chromatography also. The IL used is not present in this table since it is solid at room temperature.[8]

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

The liquid-phase composition of binary mixtures was determined by density using a Anton Paar DSA-5000 densimeter, with an uncertainty of $\pm\ 2 \cdot 10^{-6}$ g·cm^{-3}. The vapor-phase density was also measured to ensure that only ethanol or water was evaporated. The liquid-phase composition of ternary system was measured by density and refractive index, and the vapor-phase composition was measured by density. To measure refractive indices, an Abbemat-HP Dr. Kernchen automatic refractometer with an uncertainty of $\pm\ 4 \cdot 10^{-5}$ was used. Physical properties of these binary and ternary systems were determined in a previous work.[9]

Results and Discussion

Experimental isobaric VLE data of the binary systems ethanol + [C_4mim][Cl] and water + [C_4mim][Cl] are reported in Tables

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Table 2. Vapor−Liquid Equilibrium Data for Ethanol (1) + [C$_4$mim][Cl] (2) System at 101.3 kPa

T/K	x_1	γ_1	T/K	x_1	γ_1
351.44	1.0000	1.000	366.16	0.7951	0.722
351.97	0.9826	0.997	370.21	0.7635	0.652
352.99	0.9562	0.984	377.00	0.7119	0.554
354.18	0.9276	0.968	386.30	0.6442	0.452
356.04	0.8926	0.937	398.67	0.5581	0.357
358.91	0.8581	0.874	412.61	0.4816	0.278
361.61	0.8298	0.817			

Table 3. Vapor−Liquid Equilibrium Data for Water (1) + [C$_4$mim][Cl] (2) System at 101.3 kPa

T/K	x_1	γ_1	T/K	x_1	γ_1
373.15	1.0000	1.000	376.01	0.9433	0.958
373.30	0.9991	0.996	376.37	0.9379	0.952
373.48	0.9954	0.993	376.84	0.9330	0.941
373.59	0.9915	0.993	377.67	0.9199	0.927
373.74	0.9865	0.993	379.05	0.9078	0.896
373.93	0.9827	0.990	381.09	0.8896	0.852
374.09	0.9801	0.987	383.67	0.8697	0.799
374.19	0.9781	0.985	386.78	0.8431	0.744
374.36	0.9746	0.983	388.22	0.8295	0.721
374.54	0.9703	0.981	391.19	0.8118	0.669
374.77	0.9660	0.977	394.00	0.7879	0.631
374.99	0.9638	0.972	405.82	0.7191	0.482
375.22	0.9601	0.968	407.30	0.7104	0.467
375.43	0.9548	0.966	421.97	0.6318	0.348
375.63	0.9506	0.963	441.11	0.5403	0.249

Table 4. NRTL Correlation Parameters, Δg (J·mol^{-1}) and α, and Root-Mean-Square Deviations for the Binary Systems Ethanol (1) + [C$_4$mim][Cl] (2) and Water (1) + [C$_4$mim][Cl] (2) at 101.3 kPa

parameters						ΔT/K	Δy_1
Ethanol + [C$_4$mim][Cl]							
Δg_{12}	−1687.95	Δg_{21}	−9820.96	α	0.168	0.63	0.023
Water + [C$_4$mim][Cl]							
Δg_{12}	−3604.88	Δg_{21}	−11772.27	α	0.189	0.20	0.007

2 and 3. These experimental data were correlated using the NRTL equation.[4] To simplify, the IL was treated like a non-dissociating component, and the assumption of an ideal behavior of the vapor phase was assumed. The correlation was made by minimizing the following objective function:

$$\mathrm{OF} = \sum_{j=1}^{n_p} \sum_{i=1}^{n_c} (y_{ij}^{\mathrm{exp}} - y_{ij}^{\mathrm{calc}})^2 \tag{1}$$

where y is the mole fraction of the vapor phase, n_c is the number of components, and n_p is the number of experimental data.

The correlation parameters are given in Table 4 together with the root-mean-square (rms) deviations. These are calculated from the values of the property and the number of experimental data, represented by z_{exp} and n_p, respectively:

$$\sigma = \{\sum_{i}^{n_p} (z_{\mathrm{exp}} - z_{\mathrm{calc}})^2/n_p\}^{1/2} \tag{2}$$

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. As can be seen in Figure 1b, the activity coefficients of ethanol and water in the binary systems studied are less than one ($\gamma_1 < 1$), showing a negative deviation from Raoult's law. This behavior indicates that intermolecular attraction forces between different molecules (EtOH + [C$_4$mim][Cl] and H$_2$O + [C$_4$mim][Cl]) are stronger than between equal molecules. In Figure 1c, the excess molar Gibbs energies (G^E/RT) calculated from the NRTL equation for both binary systems plotted against mole fraction are presented.

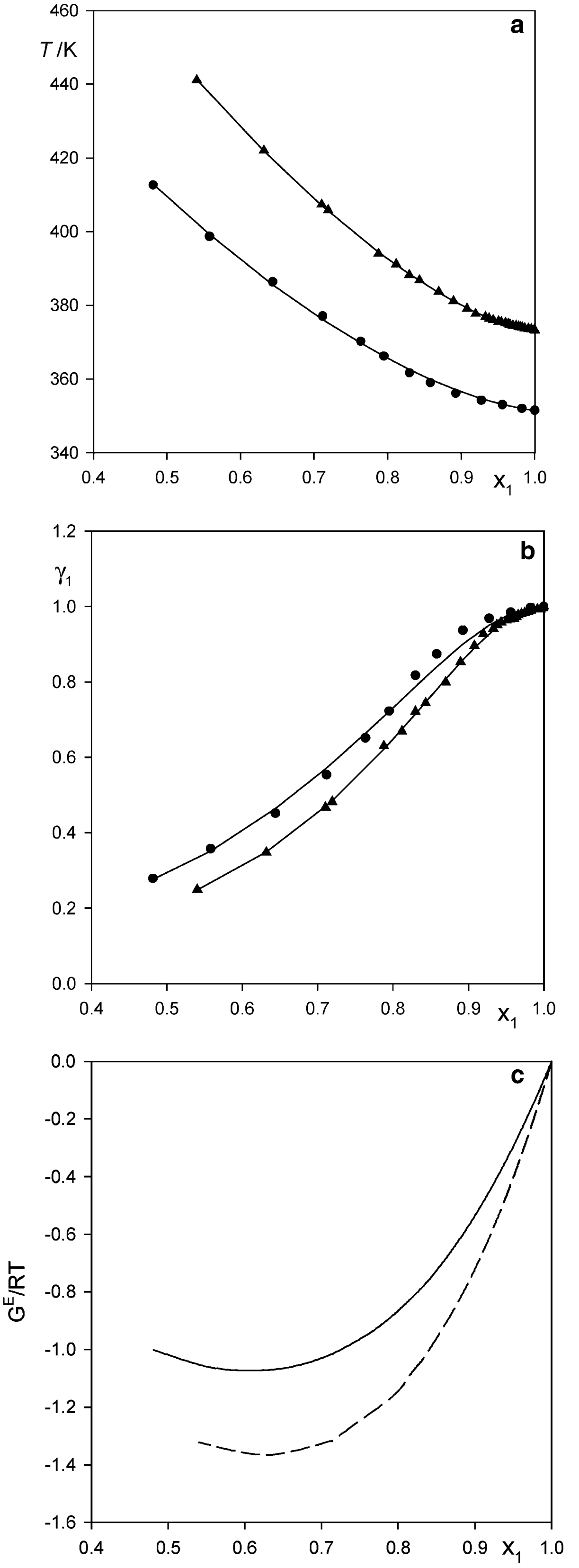

Figure 1. (a) Boiling temperature diagram and (b) activity coefficients diagram of experimental VLE data (○, EtOH + [C$_4$mim][Cl]; △, H$_2$O + [C$_4$mim][Cl]) and calculated correlation curve (−, NRTL) for both binary systems. (c) Excess molar Gibbs energies calculated from NRTL for the binary systems: −, EtOH + [C$_4$mim][Cl]; − −, H$_2$O + [C$_4$mim][Cl].

Table 5. Vapor−Liquid Equilibrium Data for the Ternary System Ethanol (1) + Water (2) + $[C_4mim][Cl]$ (3) at 101.3 kPa

T/K	x_1	x_2	y_1	γ_1	γ_2
398.50	0.2036	0.4278	0.7666	0.983	1.004
393.63	0.2625	0.3849	0.8138	0.882	1.301
382.86	0.2019	0.5424	0.6578	1.608	1.315
376.07	0.1002	0.7018	0.4912	4.060	1.284
374.33	0.0886	0.7450	0.4553	4.866	1.287
373.11	0.1133	0.7163	0.4998	3.969	1.398
367.16	0.1866	0.6479	0.5984	2.969	1.921
362.62	0.2986	0.5601	0.6863	2.187	2.636
360.42	0.3667	0.5036	0.7210	1.932	3.191
359.25	0.4170	0.4608	0.7416	1.775	3.650
357.44	0.4932	0.4000	0.7695	1.607	4.514
356.04	0.5795	0.3298	0.7939	1.443	5.787
372.77	0.0381	0.8394	0.3314	11.952	1.208
367.91	0.0863	0.7980	0.4423	6.253	1.517
364.56	0.1323	0.7578	0.5373	4.600	1.810
361.19	0.2048	0.6960	0.5956	3.362	2.241
359.04	0.2759	0.6321	0.6435	2.704	2.682
357.41	0.3482	0.5681	0.6766	2.279	3.182
356.17	0.4205	0.5040	0.6998	1.978	3.767
354.66	0.5073	0.4264	0.7374	1.738	4.730
352.92	0.5723	0.3697	0.4466	1.649	5.853
353.43	0.4021	0.5575	0.6732	2.300	3.802
355.74	0.2841	0.6853	0.6103	2.977	2.818
355.44	0.2259	0.7479	0.5788	3.788	2.614
357.82	0.1666	0.8124	0.5348	4.690	2.189
357.85	0.1339	0.8479	0.5254	5.829	2.095
359.45	0.1032	0.8825	0.5014	7.120	1.891
352.47	0.7319	0.2106	0.8540	1.312	10.463
354.25	0.6867	0.2175	0.8591	1.305	9.429
358.62	0.6354	0.2348	0.8639	1.193	7.341
362.54	0.5723	0.2592	0.8650	1.145	5.714
369.00	0.5084	0.2749	0.8635	1.021	4.228
379.75	0.3854	0.3304	0.8533	0.933	2.400
390.27	0.3482	0.3327	0.8386	0.738	1.677
353.55	0.7974	0.1399	0.9000	1.155	15.073
357.42	0.7141	0.1644	0.9010	1.111	10.992
361.12	0.6167	0.2197	0.9022	1.119	7.117
363.28	0.0969	0.8328	0.4597	6.578	1.729
360.47	0.1491	0.7837	0.5464	4.744	2.047
357.47	0.2588	0.6816	0.6128	3.059	2.646
358.34	0.1911	0.7616	0.5635	4.008	2.288
359.26	0.1461	0.8146	0.5313	5.065	2.064
360.54	0.1083	0.8589	0.4858	6.513	1.862
362.06	0.0831	0.8910	0.4444	8.022	1.693
363.91	0.0599	0.9212	0.4002	10.397	1.526
365.65	0.0458	0.9407	0.3442	12.778	1.399
367.57	0.0323	0.9580	0.2799	16.887	1.279

Table 5 summarizes experimental VLE data of ternary system ethanol + water + $[C_4mim][Cl]$. To correlate the experimental phase equilibrium data of this system, the NRTL equation was used treating the IL like a nondissociating component and assuming ideal behavior of the vapor phase. In this case, the objective function to minimize is defined by

$$\mathrm{OF} = \sum_{i=1}^{n_p} (T^{\mathrm{exp}} - T^{\mathrm{calc}}) \tag{4}$$

This objective function was chosen because of the wide temperature range studied.

The correlation parameters and the rms deviations calculated in the correlation of the VLE ternary experimental data are shown in Table 6. With these parameters obtained from the correlation of the VLE experimental data of the ternary system, we can predict the behavior of the ternary system depending on the quantity of IL present in the mixture. In Figure 2, the predicted VLE containing the azeotropic system EtOH + H_2O and the IL $[C_4mim][Cl]$ are presented in a pseudobinary way. In this figure, the liquid-phase composition of the low-boiling component is the amount of this substance in the volatile part of the liquid phase. The IL concentration is stated for each curve separately. In Figure 2a, we present the *xy* diagram, and Figure 2b shows the *Txy* diagram. VLE experimental data of the binary system EtOH + H_2O were obtained from literature.[3]

Table 6. NRTL Correlation Parameters, Δg ($J\cdot mol^{-1}$) and α, Obtained from the Correlation of Vle Experimental Data of the Ternary System and Root-Mean-Square Deviations for the Ternary System Ethanol (1) + Water (2) + $[C_4mim][Cl]$ (3) at 101.3 kPa

parameters	Δg_{12}	−4393.85	Δg_{23}	7403.72	α_{12}	0.094
	Δg_{13}	−24.31	Δg_{31}	−12 484.39	α_{13}	0.098
	Δg_{21}	9835.19	Δg_{32}	−19 489.62	α_{23}	0.093
rms	ΔT	1.18	Δy	0.06		

As can be observed in these figures, the addition of $[C_4mim]$-$[Cl]$ to this binary azeotropic mixture leads to a noticeable

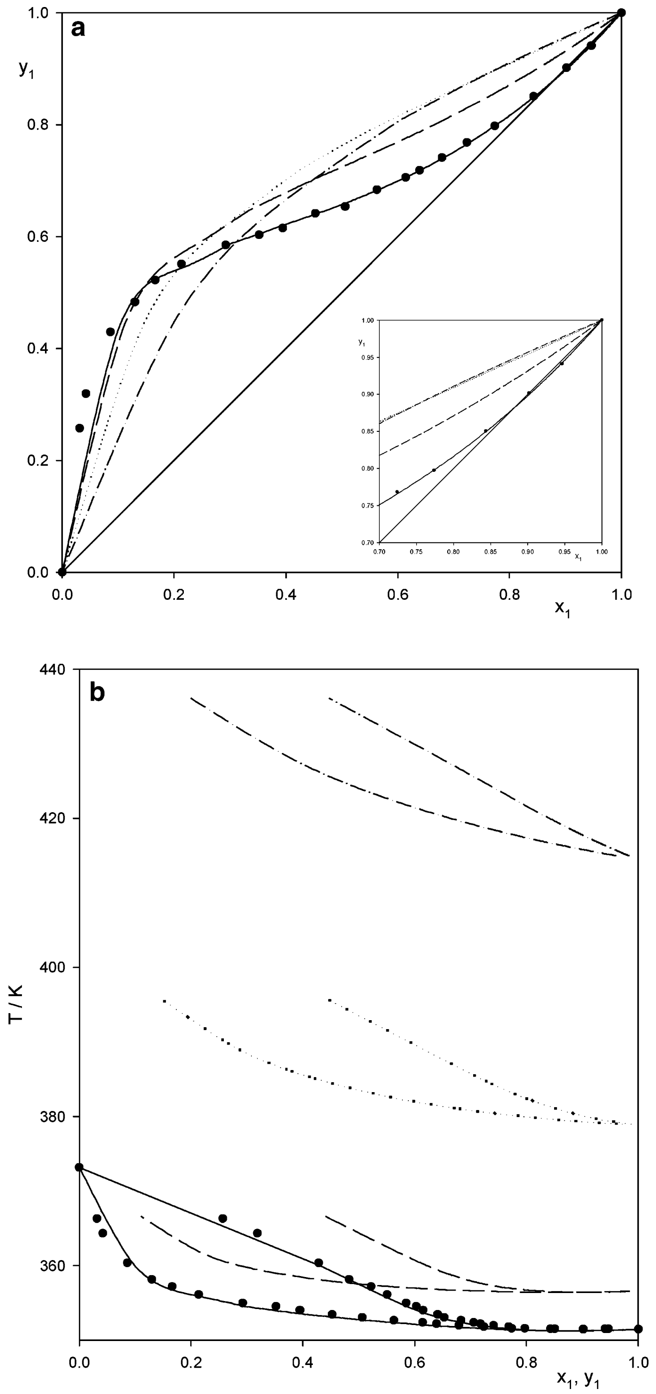

Figure 2. (a) *xy* diagram and (b) *Txy* diagram of the system ethanol (1) + water (2) + $[C_4mim][Cl]$ (3) at IL concentrations of mole fraction: —, 0 %; − −, 10 %; ···, 30 %; and − · −, 50 %. ●, experimental VLE data from ref 3.

increase in the molar vapor fraction of ethanol, breaking the azeotropic behavior of the system. This phenomena can be due to the interactions between water and [C_4mim][Cl], stronger than the interactions between ethanol and [C_4mim][Cl], decreasing the water activity. This study confirms the capability of this IL as an entrainer for the EtOH + H_2O separation.

Conclusions and Future Work

ILs are becoming a new alternative for separation processes. The studied IL is capable of breaking the binary azeotrope EtOH + H_2O, opening a new possibility as an entrainer for this system. It is noteworthy that, because of the nonvolatility of the IL, this can be regenerated by stripping, evaporation, or drying.

In future work, we will study the influence of [C_6mim][Cl] and [C_8mim][Cl] in the behavior of the azeotropic mixture EtOH + H_2O, making possible the comparison of the influence of different ILs, changing the chain length on the same system, and obtaining the correlation parameters.

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