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Effect of the Ionic Liquid Triethylmethylammonium Dimethylphosphate on the Vapor Pressure of Water, Methanol, Ethanol, and Their Binary Mixtures

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ABSTRACT: Vapor pressure data were measured for binary and ternary systems containing water, methanol, ethanol, and a halogen-free ionic liquid (IL) triethylmethylammonium dimethylphosphate ([N_{1222}][DMP]) with IL content ranging from mass fractions of (0.1 to 0.5) at varying temperatures, using a quasi-static ebulliometer. The vapor pressure data of IL-containing binary systems were well-correlated by the nonrandom two-liquid (NRTL) equation with an overall average absolute relative deviation (AARD) of 0.0088, and the resulting binary parameters were used to predict the vapor pressure of three ternary systems with an overall AARD less than 0.0169. Further, the isobaric vapor−liquid equilibrium (VLE) data for ternary systems {water + ethanol + [N_{1222}][DMP]} and {methanol + ethanol + [N_{1222}][DMP]} with IL mass fractions of 0.1, 0.3, and 0.5 at 101.3 kPa were predicted, respectively. It is demonstrated that the relative volatilities of ethanol to water and ethanol to methanol are enhanced. Therefore, a separation of the azeotrope of {water + ethanol} mixture can be sufficiently facilitated by the addition of [N_{1222}][DMP] at a specified content.

INTRODUCTION

Special distillation[1] (e.g., extractive or salt distillation) is widely used to facilitate the separation of azeotropes and close boiling mixtures, in which an entrainer (a salt or a solvent) is employed to modify the relative volatility and make the separation more efficient. However, salt distillation has some shortcomings, such as the limited solubility of salts in some solvents and the corrosiveness of the salt solution for the facilities. In contrast, the organic entrainer may lead to contamination of the overhead product and a higher energy cost due to its partial vaporization/condensation in the distillation column. It is therefore of great interest to explore a new kind of liquid entrainer which have the merits of both but with limited volatility and corrosiveness.

An ionic liquid (IL), a neoteric compound comprising an organic bulk cation and an inorganic or organic anion, might be one of such candidates due to its unique properties, for instance, nonvolatility, tunable solubility for both polar and apolar substances, and a remarkable salt effect, and so forth.[2] As green and potential eco-friendly solvents, ILs have drawn increasing attention in the past decade and have been extensively applied in the chemical industry fields.[3] The industrial applications of ILs as entrainers for extractive distillation have been proposed by Gmehling and Krummen[4] and Arlt et al.[5] Presently, a number of studies have been conducted for the salt effect of ILs on the VLE of mixtures with azeotropic point or close boiling temperature, for example {propanol + water},[6,7] {ethylacetate + ethanol},[8,9] and {ethanol + water}[10−15] mixtures, which is helpful for better understanding intermolecular interactions between IL and solvent and screening suitable ILs entrainers for special rectification.

Among various ILs reported, the alkylimidazolium-based ILs have been comprehensively investigated. However, some ILs with fluoro-substituted anions, such as tetrafluoroborate ([BF_4]$^-$) and hexafluorophosphate ([PF_6]$^-$), are susceptible to hydrolyzation;[16] some halide-based ILs are apt to be corrosive, and more importantly, certain imidazolium-based ILs are too expensive to be applied commercially. Therefore, cheap and halogen-free ILs are worthy of development. The ILs based on dialkylphosphate anions are of potential applications[17] and worthy of development for their good stability and hydrophilicity, less toxicity and corrosiveness, and more importantly their low cost and ease of production for industrial applications.[18] Toward this end, a novel halogen-free IL, triethylmethylammonium dimethylphosphate ([N_{1222}][DMP]), is presented herein.

In view of the great importance of vapor pressure data of IL-containing systems in assessing intermolecular interactions between IL and solvent, screening appropriate entrainer for special rectification as well as developing thermodynamic models specific to IL-containing systems, the effects of [N_{1222}][DMP] on the VLE of water, methanol, and ethanol, as well as their binary mixtures at differing temperatures, were investigated in this work. The experimental vapor pressure data for the binary systems were correlated using the nonelectrolyte nonrandom two-liquid (NRTL) model, and the resulting binary parameters were used to predict the vapor pressure of ternary systems with favorable accuracy. Besides, the isobaric VLE data for ternary systems {water + ethanol + [N_{1222}][DMP]} and {methanol + ethanol + [N_{1222}][DMP]} with IL mass fractions of 0.1, 0.3, and 0.5 at 101.3 kPa were predicted, respectively.

The structure and synthesis route of [N_{1222}][DMP] studied in this work is depicted in Figure 1.

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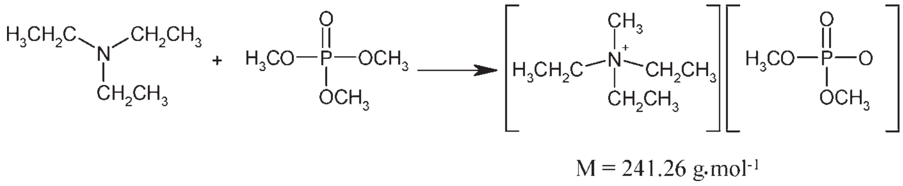

Figure 1. General synthesis route for the IL triethylmethylammonium dimethylphosphate.

EXPERIMENTAL SECTION

Materials. The chemical reagents used in this work were distilled−deionized water, ethanol, methanol, ether, triethylamine (TEA), and trimethylphosphate (TMP). TEA (Beijing Yili Chemical Co., Ltd., China) with the purity $w \geq 0.99$, TMP (Sinopharm Chemical Reagent Co., Ltd., China) with the purity $w \geq 0.99$, and ether (Beijing Chemical Reagents Company, China) with the purity $w \geq 0.995$ were all analytical reagent grade commercial products and used without further purification. Ethanol and methanol (both of them purchased from Beijing Red Star Co. Ltd., China) were all dried for 48 h prior to use with commercial molecular sieves ZMS-5. The purities of ethanol and methanol were all $w \geq 0.997$ as analyzed by gas chromatography (Shimadzu GC2010 equipped with a flame ionization detector (FID) and FFAP capillary column). [N_{1222}][DMP] was prepared and purified in the laboratory. The IL was subjected to vacuum evaporation at 95 °C over 12 h to remove possible traces of moisture prior to utilization.

IL Synthesis and Characterization. The IL [N_{1222}][DMP] was synthesized according to the method described in the literature,[19] that is, using TEA as the starting material to produce ammonium salts via the quaternization of TEA with a stoichiometric amount of TMP. For instance, 50.60 g (0.5 mol) of TEA and 70.04 g (0.5 mol) of TMP were placed in a 250 mL round flat-bottom flask equipped with a reflux condenser and a magnetic stirrer, and a demixing phenomenon was observed. The flask was mounted in a silicon oil bath, while the mixture was reacted for 12 h at 110 °C under rapidly and duratively stirred, the crude product was extracted twice by anhydrous ether with approximately half volume of the product to withdraw the unreacted materials and then transferred the IL to the rotatory evaporator (under vacuum condition, at 95 °C for 12 h) to remove all remaining volatile components, for example, ether and moisture. No crystallization or solidification was observed when the liquid sample was cooled down to room temperature. The resulting IL is a light-yellow transparent liquid at ambient temperature with a yield of 97.4 %.

The water content of [N_{1222}][DMP] was $w \leq 634 \cdot 10^{-6}$ as measured by the Karl Fischer titrator (CBS-1A). The purity was confirmed by ^{1}H and ^{13}C NMR spectra, indicating the absence of other impurities in the final product. The ^{1}H and ^{13}C NMR spectra for [N_{1222}][DMP] were recorded on a Bruker 600 MHz spectrometer at 300 K using deuterated dimethyl sulfoxide (DMSO-d_6) and deuterated water (D_2O) as solvents, respectively. The chemical shifts of hydrogen were referenced to DMSO-d_6 (δ_H = 2.50). Chemical shifts of ^{1}H NMR and ^{13}C NMR were reported in parts per million (ppm, δ) as follows: δ_H (600 MHz, DMSO-d_6, 300 K): 3.30 (q, 6H, N−(CH_2)$_3$−), 3.26 (d, 6H, −(O−CH_3)$_2$), 2.91 (s, 3H, N−CH_3), 1.19 (t, 9H, N−(C−CH_3)$_3$); δ_C (600 MHz, D_2O, 300 K): 55.74 (3C, N−(CH_2)$_3$−), 52.49 (2C, −(O−CH_3)$_2$), 46.49 (1C, N−CH_3), 7.50 (3C, N−(C−CH_3)$_3$).

Apparatus and Procedure. The details of the experimental apparatus and the operation procedure are described elsewhere.[10] The experimental apparatus is composed of two ebulliometers[20] in series with a buffer, namely, a working ebulliometer filled with liquid mixture and a reference one filled with pure water, sharing the same equilibrium pressure. The equilibrium pressure of the system was determined by the boiling temperature of pure water in the reference ebulliometer in terms of the temperature−pressure relation represented by Antoine equation.[21] The equilibrium temperature was measured by two four-wire 25 Ω calibrated platinum resistance thermometers (type CST 6501, viz. Pt 25 sensor precalibrated by the National Institute of Metrology (NIM), China) with an uncertainty of ± 0.02 K, connected to a two-channel standard digital indicator (type CST 6502) with a fluctuation of $\pm 1 \cdot 10^{-5}$ Ω. The uncertainty of the vapor pressure arising from the uncertainty of temperature measurement was estimated within ± 0.04 kPa, and the vapor pressure reproducibility for a replicate sample was less than ± 0.07 kPa. The condensers were cooled with chilling glycol aqueous solution at 275.15 K to minimize the vapor phase loss during the measurement and hence the concentration variation of the solution. All solutions were prepared gravimetrically by an electronic balance (type AR2130, Ohaus Corp., USA) with a readability of 0.001 g. The uncertainty of the mole fraction of the components in the mixtures was estimated to be within 0.0001. The reliability assessment of the apparatus was carried out in our previous work.[10] It was shown that the experimental apparatus was reliable and applicable for the measurement of vapor pressure for IL-containing systems.

RESULTS AND DISCUSSION

Binary Systems. Vapor pressure data for three binary systems {water (1) + [N_{1222}][DMP] (2)}, {ethanol (1) + [N_{1222}][DMP] (2)}, and {methanol (1) + [N_{1222}][DMP] (2)} with IL mass fractions of (w_2 = 0.1, 0.2, 0.3, and 0.5) at varying temperatures were measured and are listed in Tables 1 to 3, respectively.

The effect of IL on the nonideality of a solution can be expressed by the activity coefficient of component i, γ_i, which can be calculated by the following phase equilibrium equation:

$$\gamma_i = y_i \hat{\varphi}_i^{v} p/(x_i \varphi_i^{S} p_i^{S}) \qquad (1)$$

where p and p_i^{S} are vapor pressure of the system and pure component i at system temperature, respectively, and the latter can be calculated by the Antoine equation. y_i and x_i represent mole fraction of component i in the vapor phase and liquid phase, respectively. $\hat{\varphi}_i^{v}$ is the fugacity coefficient of component i in the vapor mixture, and φ_i^{S} is the fugacity coefficient of pure component i in its saturated state.

Table 1. Experimental and Calculated Vapor Pressure Data of the Binary System {Water (1) + $[N_{1222}][DMP]$ (2)} with Fixed IL Mass Fractions of w_2 = 0.1, 0.2, 0.3, and 0.5

T/K	p^{exp}/kPa	p^{cal}/kPa	γ_1^{exp}	γ_1^{cal}
		$x_1 = 0.9918$		
327.20	14.83	14.86	0.9947	0.9966
334.51	20.92	20.97	0.9941	0.9969
341.69	28.84	28.94	0.9939	0.9972
348.47	38.51	38.65	0.9936	0.9974
354.66	49.62	49.81	0.9937	0.9975
361.53	64.95	65.22	0.9935	0.9977
368.64	84.82	85.18	0.9938	0.9979
373.33	100.54	100.94	0.9941	0.9980
		$x_1 = 0.9817$		
325.68	13.52	13.49	0.9865	0.9841
334.94	20.93	20.94	0.9855	0.9858
341.23	27.75	27.77	0.9861	0.9868
349.09	38.87	38.88	0.9876	0.9878
356.79	53.12	53.19	0.9876	0.9888
363.13	68.00	68.07	0.9886	0.9895
369.34	85.72	85.81	0.9890	0.9901
373.98	101.36	101.49	0.9893	0.9906
		$x_1 = 0.9690$		
332.27	17.79	17.82	0.9597	0.9618
338.80	23.99	24.07	0.9611	0.9644
345.30	31.85	32.02	0.9617	0.9668
352.40	42.90	43.15	0.9636	0.9691
358.42	54.57	54.97	0.9638	0.9709
364.84	69.86	70.44	0.9647	0.9727
370.32	85.67	86.36	0.9662	0.9741
374.92	101.16	101.94	0.9677	0.9752
		$x_1 = 0.9305$		
335.18	17.25	17.52	0.8475	0.8606
341.97	23.45	23.94	0.8513	0.8690
348.83	31.60	32.37	0.8560	0.8769
354.92	40.73	41.80	0.8607	0.8833
361.29	52.48	54.05	0.8636	0.8896
367.56	66.96	68.90	0.8701	0.8953
374.10	85.31	87.84	0.8748	0.9008
378.92	101.30	104.38	0.8779	0.9046

For an IL-containing binary system, that is, {solvent (1) + IL (2)}, the vapor phase is fully composed of solvent vapor due to the negligible volatility of IL, and thus $y_1 = 1$. Considering the fact that the vapor phase composition for such binary system and for the pure solvent is the same, and the pressure difference between them $(p - p_1^S)$ is relatively small, the assumption of an ideal behavior is adopted for the vapor at a low pressure; therefore, the fugacity coefficient ratio (viz., φ_i^v/φ_i^S) appears to be unity,[21] and eq 1 can be simplified as:

$$\gamma_1 = p/(p_1^S x_1) \tag{2}$$

From eq 2, the experimental activity coefficient of the solvent in an IL-containing binary liquid mixture, γ_1^{exp}, can be calculated from the vapor pressure data.

Table 2. Experimental and Calculated Vapor Pressure Data of the Binary System {Ethanol (1) + $[N_{1222}][DMP]$ (2)} with Fixed IL Mass Fractions of w_2 = 0.1, 0.2, 0.3, and 0.5

T/K	p^{exp}/kPa	p^{cal}/kPa	γ_1^{exp}	γ_1^{cal}
		$x_1 = 0.9792$		
316.43	20.56	20.60	0.9929	0.9949
322.06	27.21	27.21	0.9952	0.9951
328.61	37.10	37.10	0.9955	0.9954
333.69	46.74	46.73	0.9959	0.9956
338.70	58.24	58.22	0.9960	0.9958
343.54	71.56	71.53	0.9963	0.9959
348.50	87.66	87.69	0.9957	0.9961
352.31	101.96	102.11	0.9948	0.9962
		$x_1 = 0.9544$		
309.47	13.78	13.74	0.9787	0.9760
317.48	20.89	20.80	0.9817	0.9776
324.83	29.94	29.80	0.9834	0.9789
331.00	39.92	39.73	0.9847	0.9799
338.98	56.80	56.61	0.9844	0.9811
344.28	71.12	70.88	0.9852	0.9818
349.29	87.18	87.04	0.9840	0.9824
353.17	101.31	101.58	0.9803	0.9829
		$x_1 = 0.9244$		
312.94	15.59	15.41	0.9532	0.9423
320.88	23.31	23.05	0.9564	0.9457
327.63	32.20	31.89	0.9577	0.9484
333.73	42.54	42.21	0.9581	0.9507
340.02	56.01	55.66	0.9587	0.9528
345.40	70.23	69.89	0.9592	0.9545
350.44	86.14	85.90	0.9588	0.9561
354.57	101.23	101.20	0.9575	0.9573
		$x_1 = 0.8397$		
316.01	14.16	14.10	0.8142	0.8110
323.36	20.63	20.46	0.8263	0.8196
332.05	30.90	31.00	0.8264	0.8289
338.61	41.64	41.74	0.8335	0.8355
345.54	56.04	56.34	0.8376	0.8420
351.23	71.00	71.33	0.8432	0.8471
356.32	85.90	87.46	0.8361	0.8514
360.70	101.22	103.68	0.8346	0.8549

The NRTL model for nonelectrolyte solution[22] is employed to describe activity coefficients in this work. By representing the activity coefficients with the NRTL model, the experimental vapor pressure data are fitted using a Levenberg−Marquardt algorithm[23] through minimizing the following objective function (OF):

$$\mathrm{OF}(p) = \min\left(\sum_{i=1}^{n}(p^{cal}/p^{exp} - 1.0)^2/n\right)^{1/2} \tag{3}$$

$$\mathrm{AARD}(p) = \sum_{i=1}^{n}|p^{cal}/p^{exp} - 1.0|/n \tag{4}$$

The resulting NRTL binary parameters α_{ij} and $(g_{ij} - g_{jj})$ and the correlation accuracy in terms of average absolute relative

Table 3. Experimental and Calculated Vapor Pressure Data of the Binary System {Methanol (1) + $[N_{1222}][DMP]$ (2)} with Fixed IL Mass Fractions of w_2 = 0.1, 0.2, 0.3, and 0.5

T/K	p^{exp}/kPa	p^{cal}/kPa	γ_1^{exp}	γ_1^{cal}
		$x_1 = 0.9855$		
299.20	17.43	17.50	0.9901	0.9938
304.65	22.98	23.06	0.9905	0.9941
311.42	31.88	32.02	0.9900	0.9945
318.87	44.85	45.11	0.9892	0.9949
324.75	58.04	58.42	0.9887	0.9952
329.53	71.04	71.51	0.9888	0.9954
334.72	87.84	88.43	0.9889	0.9956
338.25	100.81	101.75	0.9865	0.9957
		$x_1 = 0.9679$		
300.08	17.51	17.59	0.9679	0.9723
305.71	23.20	23.38	0.9665	0.9739
312.22	31.73	32.03	0.9662	0.9755
317.81	41.03	41.48	0.9663	0.9767
323.02	51.67	52.29	0.9661	0.9778
329.23	67.34	68.23	0.9662	0.9790
335.28	86.17	87.43	0.9660	0.9801
339.27	100.93	102.44	0.9663	0.9807
		$x_1 = 0.9462$		
297.98	15.02	14.74	0.9470	0.9291
304.55	20.98	20.68	0.9466	0.9333
311.51	29.34	29.10	0.9453	0.9374
317.64	38.96	38.76	0.9457	0.9407
324.12	51.79	51.77	0.9443	0.9439
330.66	68.40	68.46	0.9460	0.9469
336.17	85.49	85.76	0.9462	0.9492
340.33	100.75	101.15	0.9470	0.9508
		$x_1 = 0.8828$		
305.48	17.73	16.73	0.8187	0.7727
312.48	24.88	23.77	0.8208	0.7840
319.42	34.25	33.07	0.8227	0.7943
324.80	43.44	42.25	0.8243	0.8018
330.17	54.58	53.47	0.8258	0.8089
335.72	68.56	67.57	0.8278	0.8158
341.24	85.29	84.55	0.8294	0.8222
345.52	100.41	100.03	0.8302	0.8270

deviation (AARD; eq 4) for binary systems studied are listed in Table 4. It is showed that the experimental vapor pressure can be well-correlated by NRTL equation with an overall AARD of 0.0088 and the maximum AARD of 0.0125 for the system of {methanol (1) + $[N_{1222}][DMP]$ (2)}. The Antoine constants of vapor pressure for ethanol, methanol, and water are taken from literature[21] and listed in Table 5.

The overall goodness of fit in comparison with the experimental ones for system {ethanol (1) + $[N_{1222}][DMP]$ (2)} is schematically presented in Figure 2. It is seen that the $\ln(p/\text{kPa})$ against $1/(T/\text{K} - 41.68)$ for a given concentration is linear over the pressure and temperature range studied, which is similar to the vapor pressure behavior of the pure solvent. The Antoine constant $C = -41.68$ is equal to that of the pure ethanol. For other binary systems in the presence of $[N_{1222}][DMP]$, the same trends are followed.

It is apparent that the IL always decreases the vapor pressure of solvent due to its diluting effect and affinity to the solvent, and the higher the IL content is, the lower the solvent vapor pressure is. Nevertheless, the degrees of the nonideality for IL-containing systems studied are different and can be reflected by the activity coefficient of component, which is obtained as an intermediate in the fitting process of vapor pressure. As can be seen from Tables 1 to 3, the activity coefficients of three pure solvents (namely, water, methanol, and ethanol) are always less than unity, thus presenting a negative deviation from the Raoult's law.

Ternary Systems. Vapor pressure data measurement for three ternary systems, namely, {water (1) + methanol (2) + $[N_{1222}][DMP]$ (3)}, {water (1) + ethanol (2) + $[N_{1222}][DMP]$ (3)}, and {methanol (1) + ethanol (2) + $[N_{1222}][DMP]$ (3)}, with a fixed IL mass fraction of w_3 = 0.3 and component 2 (ethanol or methanol) mass fractions of (w'_2 = 0.1,

Table 5. Antoine Constants of Vapor Pressure of Pure Compounds[21]

compound	Antoine constants[a]			
	A	B	C	ΔT/K
water	11.6834	3816.44	− 46.13	284 to 441
methanol	11.9673	3626.55	− 34.29	257 to 364
ethanol	12.2917	3803.98	− 41.68	270 to 369

[a] The Antoine equation is adopted as the form: $\ln(p^s/\text{bar}) = A - B/(T/\text{K} + C)$, where p^s is the saturated vapor pressure in bar, and T is the equilibrium temperature in K. One bar = $1 \cdot 10^5$ Pa.

Table 4. NRTL Parameters for Binary IL-Containing Systems Fitted Herein and Taken From Literature

binary system	α_{12}	$g_{12} - g_{22}$ J·mol^{-1}	$g_{21} - g_{11}$ J·mol^{-1}	AARD(p)
water (1) + $[N_{1222}][DMP]$ (2)[a]	0.5493	4058.122	− 7494.543	0.0091
methanol (1) + $[N_{1222}][DMP]$ (2)[a]	0.4436	− 3578.034	− 6799.365	0.0125
ethanol (1) + $[N_{1222}][DMP]$ (2)[a]	0.4649	32.210	− 5224.169	0.0049
water (1) + methanol (2)[b]	0.3008	3587.834	− 976.656	
water (1) + ethanol (2)[b]	0.3008	5615.836	− 511.156	
methanol (1) + ethanol (2)[c]	0.3009	281.731	− 295.208	
overall AARD				0.0088

[a] NRTL parameters fitted in this work. [b] Taken from ref 24. [c] Taken from ref 25.

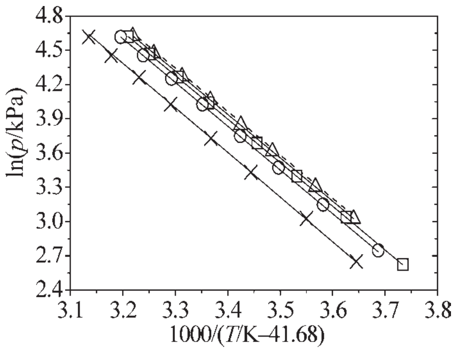

Figure 2. Experimental and correlative vapor pressure data for binary system {ethanol (1) + $[N_{1222}][DMP]$ (2)} at different mass fraction of $[N_{1222}][DMP]$ as a function of inverse temperature. Legend: - - -, pure solvent; —, calculated by NRTL equation. Symbols are experimental data at different mass fraction of $[N_{1222}][DMP]$: △, $w_2 = 0.1$; □, $w_2 = 0.2$; ○, $w_2 = 0.3$; ×, $w_2 = 0.5$.

0.3, 0.5, 0.7, and 0.9), at varying temperatures were carried out. The results are listed in Tables 6 to 8, respectively. Here w'_2 denotes the mass fraction of component 2 for the ternary system of {solvent (1) + solvent (2) + IL (3)} on an IL-free basis.

Under low pressures, the vapor phase is approximately ideal; hence, the vapor pressure for a ternary system {solvent (1) + solvent (2) + IL (3)} can be calculated by eq 5, and the vapor-phase mole fraction of component i, y_i, at equilibrium can be calculated with eq 6 considering the nonvolatility of IL ($p_3^S = 0$).

$$p = \sum_{i=1}^{2} x_i \gamma_i p_i^S \tag{5}$$

$$y_i = \frac{x_i \gamma_i p_i^S}{\sum_{j=1}^{2} x_j \gamma_j p_j^S} \tag{6}$$

Based on eqs 5 and 6, vapor pressures for three ternary systems investigated were predicted by the NRTL model using the fitted and literature parameters shown in Table 4. The predicted accuracy was expressed in terms of AARD (see eq 4) and the root-mean-square deviation (rmsd) shown as follows:

$$\text{rmsd}(p) = \left(\sum_{i=1}^{n} (p^{\text{cal}}/p^{\text{exp}} - 1.0)^2/n \right)^{1/2} \tag{7}$$

The calculated system pressures as well as the activity coefficients of components in IL-containing ternary systems are presented in Tables 6 to 8. It is seen that the agreement between the experimental and the predicted values is fairly good as manifested by AARD and rmsd given in Table 9. In addition, Figure 3 demonstrates the favorable goodness of the experimental and predicted results for ternary system {water (1) + ethanol (2) + $[N_{1222}][DMP]$ (3)}, and the same trend for other ternary systems are followed and thus not presented herein.

Table 6. Experimental and Predicted Vapor Pressure Data of the Ternary System {Water (1) + Methanol (2) + $[N_{1222}][DMP](3)$} with a Fixed IL Mass Fraction of $w_3 = 0.3$

T/K	p^{exp}/kPa	p^{cal}/kPa	γ_1^{cal}	γ_2^{cal}
		$x_1 = 0.1567, x_2 = 0.7931$		
307.46	21.37	22.01	1.1404	0.9821
314.25	29.59	30.52	1.1577	0.9841
320.59	39.47	40.83	1.1723	0.9857
325.34	48.60	50.34	1.1824	0.9867
329.84	58.90	61.02	1.1914	0.9877
334.27	70.76	73.32	1.1997	0.9885
338.39	83.41	86.60	1.2069	0.9893
342.84	99.05	103.10	1.2142	0.9900
		$x_1 = 0.4135, x_2 = 0.5424$		
303.35	14.41	15.01	1.0846	1.0943
311.55	21.78	22.55	1.0979	1.0929
318.52	30.26	31.28	1.1078	1.0917
324.68	40.00	41.26	1.1156	1.0907
329.74	49.93	51.34	1.1214	1.0897
336.05	64.92	66.75	1.1280	1.0886
341.29	80.00	82.31	1.1328	1.0876
346.95	99.54	102.42	1.1376	1.0866
		$x_1 = 0.6149, x_2 = 0.3457$		
305.86	13.52	13.86	1.0374	1.2411
314.05	20.49	20.76	1.0455	1.2366
321.93	29.41	29.96	1.0522	1.2323
327.76	38.18	38.80	1.0565	1.2292
333.55	49.30	49.68	1.0602	1.2262
339.24	62.37	62.77	1.0636	1.2234
345.65	80.65	80.84	1.0669	1.2202
351.07	98.86	99.37	1.0693	1.2176
		$x_1 = 0.7772, x_2 = 0.1873$		
313.66	15.25	15.52	1.0011	1.4175
320.87	21.82	21.89	1.0054	1.4116
328.59	31.01	31.06	1.0093	1.4054
336.07	43.01	42.86	1.0126	1.3995
341.71	54.27	54.09	1.0148	1.3951
347.48	68.32	68.01	1.0167	1.3906
352.21	82.05	81.56	1.0182	1.3871
357.25	99.01	98.42	1.0196	1.3833
		$x_1 = 0.9107, x_2 = 0.0569$		
317.92	12.38	12.35	0.9703	1.5916
324.52	17.08	17.03	0.9734	1.5891
332.03	24.30	24.11	0.9765	1.5857
338.62	32.57	32.24	0.9789	1.5822
345.09	43.01	42.38	0.9810	1.5784
352.19	57.15	56.46	0.9830	1.5739
359.89	76.70	75.95	0.9850	1.5687
366.88	99.02	98.22	0.9866	1.5638

To show the salt effect of $[N_{1222}][DMP]$ on the distillation separation of azeotrope {water + ethanol} and close boiling mixture {methanol + ethanol}, the isobaric VLE data for ternary systems {water + ethanol + $[N_{1222}][DMP]$} and {methanol + ethanol + $[N_{1222}][DMP]$} with IL mass fractions of 0.1, 0.3, and 0.5 at 101.3 kPa were predicted by the NRTL model on the basis of fitted NRTL and literature parameters, respectively.

The results for VLE diagrams are plotted in Figures 4 and 5 on a salt-free basis, and compared with the VLE curve in the absence

Table 7. Experimental and Predicted Vapor Pressure Data of the Ternary System {Water (1) + Ethanol (2) + $[N_{1222}][DMP](3)$} with a Fixed IL Mass Fraction of $w_3 = 0.3$

T/K	p^{exp}/kPa	p^{cal}/kPa	γ_1^{cal}	γ_2^{cal}
		$x_1 = 0.2066, x_2 = 0.7272$		
318.21	20.47	20.43	1.2453	1.0681
323.22	26.22	26.15	1.2630	1.0674
329.00	34.47	34.40	1.2821	1.0667
333.57	42.44	42.40	1.2962	1.0661
338.85	53.51	53.55	1.3114	1.0653
344.36	67.61	67.76	1.3261	1.0646
349.45	83.14	83.53	1.3388	1.0639
354.16	100.60	100.76	1.3497	1.0632
		$x_1 = 0.4953, x_2 = 0.4519$		
313.45	15.86	15.67	1.1477	1.3912
318.70	20.72	20.47	1.1569	1.3856
325.95	29.28	29.13	1.1682	1.3780
333.55	41.57	41.35	1.1785	1.3703
339.30	53.40	53.25	1.1854	1.3648
344.88	67.51	67.46	1.1914	1.3596
350.08	83.26	83.41	1.1964	1.3549
354.76	100.56	100.39	1.2004	1.3508
		$x_1 = 0.6873, x_2 = 0.2687$		
315.91	16.84	16.73	1.0590	1.9026
322.52	23.33	23.22	1.0647	1.8862
329.67	32.73	32.52	1.0700	1.8692
335.13	41.81	41.59	1.0735	1.8565
340.43	52.69	52.36	1.0765	1.8446
346.35	67.44	67.06	1.0795	1.8316
352.37	85.70	85.41	1.0822	1.8188
356.36	99.85	99.73	1.0838	1.8106
		$x_1 = 0.8242, x_2 = 0.1381$		
314.01	13.58	13.46	0.9925	2.7715
321.18	19.51	19.27	0.9969	2.7302
328.19	27.27	26.88	1.0006	2.6911
335.72	38.28	37.75	1.0041	2.6507
340.64	47.45	46.69	1.0061	2.6251
347.13	62.15	61.14	1.0085	2.5923
353.87	81.14	79.97	1.0107	2.5594
359.22	99.28	98.12	1.0123	2.5340
		$x_1 = 0.9268, x_2 = 0.0403$		
323.96	15.95	16.51	0.9643	4.0946
331.37	22.76	23.40	0.9677	3.9987
337.81	30.58	31.23	0.9703	3.9191
343.89	39.87	40.55	0.9726	3.8468
350.04	51.51	52.23	0.9747	3.7766
356.13	65.53	66.47	0.9766	3.7098
362.18	82.56	83.70	0.9783	3.6458
367.16	98.95	100.51	0.9796	3.5951

Table 8. Experimental and Predicted Vapor Pressure Data of the Ternary System {Methanol (1) + Ethanol (2) + $[N_{1222}][DMP](3)$} with a Fixed IL Mass Fraction of $w_3 = 0.3$

T/K	p^{exp}/kPa	p^{cal}/kPa	γ_1^{cal}	γ_2^{cal}
		$x_1 = 0.1281, x_2 = 0.7993$		
309.09	14.20	13.95	0.6942	0.9819
316.17	20.39	20.09	0.7051	0.9837
321.82	26.56	26.52	0.7134	0.9850
328.48	36.23	36.29	0.7226	0.9864
334.00	46.38	46.54	0.7299	0.9874
341.07	62.72	63.18	0.7388	0.9887
347.32	80.84	81.81	0.7462	0.9896
352.54	99.14	100.69	0.7521	0.9904
		$x_1 = 0.3555, x_2 = 0.5770$		
306.40	14.96	14.58	0.7769	1.0386
312.74	20.43	20.19	0.7849	1.0385
320.42	29.55	29.36	0.7939	1.0383
326.92	39.43	39.69	0.8010	1.0380
333.20	51.86	52.42	0.8075	1.0378
338.95	66.01	66.95	0.8131	1.0375
344.43	82.26	83.80	0.8182	1.0372
349.27	99.20	101.52	0.8225	1.0369
		$x_1 = 0.5549, x_2 = 0.3825$		
302.98	14.36	14.32	0.8355	1.0791
310.22	20.66	20.76	0.8431	1.0773
318.12	30.17	30.48	0.8507	1.0754
325.19	41.62	42.20	0.8570	1.0738
331.14	53.83	54.80	0.8620	1.0724
336.21	66.53	67.92	0.8659	1.0713
341.83	83.40	85.45	0.8701	1.0700
346.31	99.27	102.03	0.8733	1.0690
		$x_1 = 0.7254, x_2 = 0.2158$		
300.11	14.01	14.04	0.8782	1.1095
306.58	19.54	19.62	0.8840	1.1066
313.03	26.61	26.97	0.8893	1.1039
319.59	36.10	36.70	0.8942	1.1012
325.73	47.42	48.37	0.8986	1.0988
331.54	60.73	62.15	0.9024	1.0966
337.83	78.43	80.64	0.9063	1.0943
343.72	98.74	101.92	0.9097	1.0922
		$x_1 = 0.8766, x_2 = 0.0680$		
301.01	16.44	16.45	0.9154	1.1320
308.10	23.41	23.55	0.9204	1.1276
315.05	32.37	32.87	0.9248	1.1236
321.17	42.75	43.50	0.9284	1.1202
326.55	53.92	55.12	0.9313	1.1173
331.00	64.96	66.62	0.9336	1.1151
336.51	81.17	83.58	0.9362	1.1124
341.62	99.08	102.33	0.9385	1.1100

of IL. As can be seen from Figure 4, the azeotropic point for {water + ethanol} mixture in $x'_2 = 0.894$ is shifted upward with the addition of $[N_{1222}][DMP]$, suggesting that the relative volatility of ethanol to water is improved, and more importantly the azeotropic phenomenon is completely eliminated at $[N_{1222}][DMP]$ mass fraction of approximate $w_3 = 0.3$. Figure 5 shows the variation trend of the relative volatility of ethanol to methanol with the concentration of $[N_{1222}][DMP]$. It is seen

Table 9. AARD and rmsd between Experimental and Predicted Vapor Pressure for Three Ternary IL-Containing Systems

ternary systems	AARD(p)	rmsd(p)
water (1) + methanol (2) + [N_{1222}][DMP] (3)	0.0187	0.0230
water (1) + ethanol (2) + [N_{1222}][DMP] (3)	0.0092	0.0120
methanol (1) + ethanol (2) + [N_{1222}][DMP] (3)	0.0151	0.0176
overall AARD or rmsd	0.0169	0.0203

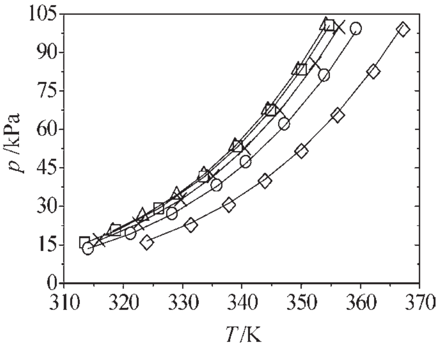

Figure 3. Experimental and predictive vapor pressure data for the ternary system {water (1) + ethanol (2) + [N_{1222}][DMP] (3)} with a fixed [N_{1222}][DMP] mass fraction of $w_3 = 0.3$ at varying temperatures. Legend: —, calculated by the NRTL equation. Symbols are experimental data at varying mass fractions of ethanol: △, $w'_2 = 0.9$; □, $w'_2 = 0.7$; ×, $w'_2 = 0.5$; ○, $w'_2 = 0.3$; ◇, $w'_2 = 0.1$. Here w'_2 denotes the mass fraction of ethanol for the ternary system of {water (1) + ethanol (2) + [N_{1222}][DMP] (3)} on IL-free basis.

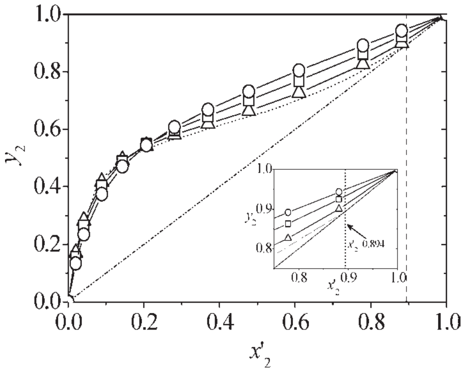

Figure 4. Predicted isobaric VLE diagram ($y_2 - x'_2$) for the ternary system {water (1) + ethanol (2) + [N_{1222}][DMP] (3)} at $p = 101.3$ kPa with [N_{1222}][DMP] mass fraction of: △, $w_3 = 0.1$; □, $w_3 = 0.3$; ○, $w_3 = 0.5$, respectively. Legend: - - -, IL-free system of {water (1) + ethanol (2)}; — - - —, $y_2 = x'_2$; — — —, $x'_2 = 0.894$; —, calculated by the NRTL equation. Here x'_2 represents mole fraction of component 2 for ternary system {water (1) + ethanol (2) + [N_{1222}][DMP] (3)} on an IL-free basis.

that the relative volatility of ethanol to methanol is increased steadily with the increase of IL concentration, and at a mass fraction of about $w_3 = 0.5$ the ethanol can be reversed from a heavy component to a light one in the ethanol-rich region due to the salt effect of [N_{1222}][DMP].

In summary, the relative volatilities of ethanol to water and ethanol to methanol can be actually enhanced by the addition of

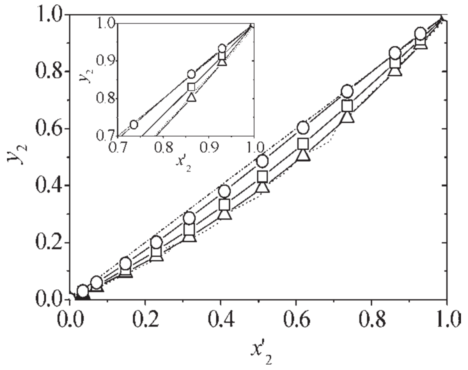

Figure 5. Predicted isobaric VLE diagram ($y_2 - x'_2$) for the ternary system {methanol (1) + ethanol (2) + [N_{1222}][DMP] (3)} at $p = 101.3$ kPa with [N_{1222}][DMP] mass fraction of: △, $w_3 = 0.1$; □, $w_3 = 0.3$; ○, $w_3 = 0.5$, respectively. Legend: - - -, IL-free system of {methanol (1) + ethanol (2)}; — - - —, $y_2 = x'_2$; —, calculated by the NRTL equation. Here x'_2 represents mole fraction of component 2 for ternary system {methanol (1) + ethanol (2) + [N_{1222}][DMP] (3)} on an IL-free basis.

[N_{1222}][DMP], and the hardly separating system of {water + ethanol + methanol} mixture can be sufficiently facilitated at a specified content of IL, whereby both methanol and water are separated from the bottom of the distillation tower.

■ CONCLUSIONS

Vapor pressure measurement for binary and ternary systems containing water, methanol, ethanol, and their binary systems with a halogen-free IL [N_{1222}][DMP] at varying temperatures and IL content were conducted using a quasi-static approach. The data of binary systems were well-correlated by the nonelectrolyte NRTL model, and the resulting binary parameters can be applied for the vapor pressure prediction of the corresponding ternary systems with fairly good accuracy. The results indicate that the vapor pressure of solvents studied shows a negative deviation from the Raoult's law, and the relative volatilities of both ethanol to water and ethanol to methanol are remarkably enhanced by the addition of [N_{1222}][DMP], indicating that [N_{1222}][DMP] might be used as an entrainer for the efficient separation of {water + ethanol} mixture by special rectification.

■ APPENDIX A. NRTL MODEL FOR NONELECTROLYTE MIXTURES

The NRTL[22] model is a so-called local composition model based on the hypothesis of Wilson that the local concentration around a molecule will be different from the bulk concentration. This model has been widely used in modeling both VLE[26] and liquid−liquid equilibria (LLE)[27] containing a variety of ILs.

For a multicomponent system, the excess Gibbs free energy is:

$$\frac{G^E}{RT} = \sum_{i=1}^{c} x_i \frac{\sum_{j=1}^{c} x_j \tau_{ji} G_{ji}}{\sum_{k=1}^{c} x_k G_{ki}} \tag{A1}$$

and $G_{ij} = \exp(-\alpha_{ij}\tau_{ij})$; $\tau_{ij} = (g_{ij} - g_{jj})/RT = \Delta g_{ij}/RT$; $\alpha_{ij} = \alpha_{ji}$, $(i \neq j)$; where c is the number of components; x represents the mole fraction; R is the gas constant; T is the absolute temperature; G_{ij} is a dimensionless interaction parameter depending on the energy interaction parameter (g_{ij}) and the nonrandomness factor (α_{ij}); g_{ij} is both composition- and temperature-independent that characterizes the interaction of species i and j; α_{ij} is composition-independent and related to the nonrandomness in the mixture ($\alpha_{ij} = 0$ corresponds to complete randomness, or an ideal solution).

From eq A1 the activity coefficient can be deduced as follows:

$$\ln \gamma_i = \frac{\sum_{j=1}^{c} x_j \tau_{ji} G_{ji}}{\sum_{k=1}^{c} x_k G_{ki}} + \sum_{j=1}^{c} \left(\frac{x_j G_{ij}}{\sum_{k=1}^{c} x_k G_{kj}} \left(\tau_{ij} - \frac{\sum_{l=1}^{c} x_l \tau_{lj} G_{lj}}{\sum_{k=1}^{c} x_k G_{kj}} \right) \right) \tag{A2}$$

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