Vapor Pressure Measurement and Correlation or Prediction for Water, 1-Propanol, 2-Propanol, and Their Binary Mixtures with [MMIM][DMP] Ionic Liquid

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This work presents vapor pressure data for water, 1-propanol, and 2-propanol as well as their binary mixtures in the presence of ionic liquid (IL) 1,3-dimethylimidazolium dimethylphosphate ([MMIM][DMP]) at different temperatures and IL content ranging from mass fraction 0.10 to 0.70 using a quasi-static ebulliometer method. Activity coefficients of these solvents in the IL have been determined from the vapor pressure data of binary systems and correlated by the nonrandom two-liquid (NRTL) equation with an average relative deviation (ARD) within 0.013. The resulting binary NRTL parameters were used for the prediction of vapor pressure of ternary systems with fair accuracy. Furthermore, the isobaric vapor−liquid equilibrium data for ternary systems water + 1-propanol + [MMIM][DMP] and water + 2-propanol + [MMIM][DMP] at different IL mass fractions were predicted. It is shown that the relative volatility of 1-propanol and 2-propanol is enhanced and that the azeotrope of water + 1-propanol and water + 2-propanol mixtures is eliminated completely.

Introduction

Room temperature ionic liquids (RTILs), as the name implies, are a new kind of molten electrolyte at temperatures lower than 373 K and possess many attractive properties, such as negligible vapor pressure, solubility of a wide range of organic and inorganic compounds, wide electrochemical window, and tunability of properties through the change in the combination of cation and anion. ILs have been considered as the separating agent in extractive distillation.[1,2] The most important reason why ILs are promising for the application of separation processes is that they have no detectable vapor pressure, which decreases the risk of worker exposure and the loss of solvent to the atmosphere. Additionally, ILs are easily regenerated from volatile compounds by distillation.

Vapor−liquid equilibria (VLE) data for azeotropic or close-boiling systems containing ILs are essential for a better understanding of the thermodynamic behavior of such systems, for the development of thermodynamic models, and for separation design purpose. Meanwhile, in screening feasible IL entrainers in an extractive or salt distillation process for the separation of azeotropic or close-boiling mixtures, some factors with respect to the IL should be taken into account, for example, its cost, stability, toxicity, and corrosiveness, as well as its potential risk to the environment and ecosphere. ILs with dialkylphosphate anions are probable for practical applications because they can be produced in an one-pot reactor under mild conditions with very high yield. More importantly, they are biodegradable, less toxic, and greener than other ILs.[3]

For these reasons, VLE data for several dialkylphosphate IL-containing systems have been measured.[4−8] The results show that the kind of ILs can enhance the relative volatility of ethanol in water + ethanol and ethanol + methanol mixtures and eliminate completely the azeotrope of the both binaries. In this paper, we study the possibility of separating the azeotropic mixtures water + 1-propanol and water + 2-propanol using an IL, 1,3-dimethylimidazolium dimethylphosphate ([MMIM][DMP]). For this purpose, vapor pressure data for three binary and two ternary systems composed of water, 1-propanol, 2-propanol, and [MMIM][DMP] were determined by a quasi-static method. The experimental vapor pressure data of binary systems were correlated with the nonrandom two-liquid (NRTL) model, and the resulting model parameters were used to predict the vapor pressure data of ternary systems and the isobaric vapor−liquid equilibrium data for ternary systems water + 1-propanol + [MMIM][DMP] and water + 2-propanol + [MMIM][DMP].

Experimental Section

Materials. 1-Propanol and 2-propanol were purchased from Beijing Red Star Reagents Company, China. The purities of these compounds were 99.7 % according to specification. The IL used was prepared and purified in the laboratory according to literature procedures,[6] and its purity was more than 98 % in terms of NMR analysis. Before used, the IL was subjected to vacuum evaporation at 353 K over 12 h to remove possible traces of solvents and moisture. The water mass fraction was within $5.2 \cdot 10^{-4}$ as measured by the Karl Fischer method (CBS-1A).

Apparatus and Procedure. A detailed description of the equipment and the measurement procedure can be found in literature.[8] The apparatus is composed of a working ebulliometer filled with liquid mixture and a reference one filled with a pure liquid (such as water). The equilibrium temperatures of the two ebulliometers were measured using two-channel four-wire 25

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Table 1. Vapor Pressure Data of the Binary System Water (1) + [MMIM][DMP] (2)

T/K	P/kPa	P^{NRTL}/kPa	γ_1^{exp}	γ_1^{NRTL}
		$x_1 = 0.9911$		
329.215	16.236	16.312	0.9915	0.9961
338.913	25.394	25.494	0.9926	0.9965
346.990	36.093	36.192	0.9940	0.9968
353.535	47.352	47.443	0.9950	0.9970
359.060	59.162	59.110	0.9980	0.9971
364.383	72.914	72.538	1.0024	0.9972
369.074	87.100	86.405	1.0054	0.9974
373.030	100.776	99.757	1.0076	0.9974
		$x_1 = 0.9664$		
328.936	15.045	15.004	0.9548	0.9522
338.650	23.528	23.582	0.9543	0.9564
346.576	33.254	33.381	0.9558	0.9595
352.987	43.412	43.645	0.9566	0.9617
359.121	55.445	55.837	0.9569	0.9637
364.782	68.977	69.511	0.9580	0.9654
370.206	84.737	85.133	0.9624	0.9669
374.804	100.434	100.576	0.9667	0.9681
		$x_1 = 0.9250$		
330.756	13.834	13.500	0.8416	0.8212
339.860	20.960	20.761	0.8417	0.8337
347.585	29.328	29.302	0.8440	0.8433
356.167	41.905	42.104	0.8489	0.8530
363.087	55.141	55.590	0.8532	0.8602
368.733	68.680	69.118	0.8601	0.8656
374.860	85.822	86.805	0.8613	0.8712
379.411	101.270	102.252	0.8667	0.8751
		ARD(P)[a] = 0.007, rmsd = 0.009		

[a] $\mathrm{ARD}(P) = (\sum_{i=1}^{n}|P^{\mathrm{NRTL}} - P|/P)/n$; $\mathrm{rmsd} = ([\sum_{i=1}^{n}(P^{\mathrm{NRTL}}/P - 1)^2]/n)^{1/2}$.

Ω calibrated platinum resistance thermometers (type CST6601) with an uncertainty of ± 0.02 K. The reference system and the working system share the same equilibrium pressure. The equilibrium pressure of the reference system was determined by the temperature−pressure relation represented by the Antoine equation[9] at system temperature. 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 within ± 0.07 kPa. The vapor phase condensers of the ebulliometers were cooled with chilling glycol aqueous solution at 275 K to minimize the vapor phase loss during the measurement and hence the composition variation of the solution. The uncertainty of the mole fraction in the liquid phase prepared by weighting was estimated within 0.002.

Results and Discussion

Binary Systems. The experimental vapor pressure data for three binary systems of water + [MMIM][DMP], 1-propanol + [MMIM][DMP], and 2-propanol + [MMIM][DMP] at IL mass fractions from 0.10 to 0.70 (mole fraction from 0.0089 to 0.3869) were measured and listed in Tables 1 to 3, respectively.

For an IL-containing binary system, that is, solvent (1) + IL (2), the experimental activity coefficients of solvent, γ_1, were calculated using the following equation:[10]

$$\gamma_1 = P y_1 \hat{\phi}_1^{\mathrm{v}}/(P_1^{\mathrm{s}} x_1) \tag{1}$$

where P andP_1^{s} are vapor pressure of liquid mixture and pure solvent at system temperature, respectively. y_1 and x_1 represent the mole fraction of solvent in the vapor phase and liquid phase, respectively. φ_1^{v} is the fugacity coefficient of solvent in the vapor mixture.

Table 2. Vapor Pressure Data of the Binary System 1-Propanol (1) + [MMIM][DMP] (2)

T/K	P/kPa	P^{NRTL}/kPa	γ_1^{exp}	γ_1^{NRTL}
		$x_1 = 0.9708$		
333.635	20.354	20.254	0.9994	0.9945
338.495	25.756	25.652	0.9989	0.9949
344.055	33.341	33.269	0.9976	0.9954
349.713	42.918	42.889	0.9966	0.9960
355.775	55.621	55.679	0.9955	0.9966
361.332	69.901	70.061	0.9949	0.9972
366.936	87.180	87.566	0.9934	0.9978
370.757	100.935	101.465	0.9931	0.9983
		$x_1 = 0.8961$		
330.478	15.244	14.779	0.9496	0.9206
337.904	21.980	21.378	0.9500	0.9240
345.631	31.556	30.734	0.9522	0.9273
353.900	45.281	44.341	0.9506	0.9308
359.885	58.267	57.067	0.9529	0.9333
364.536	70.313	68.938	0.9538	0.9351
369.607	85.754	84.150	0.9550	0.9372
373.797	100.631	98.727	0.9569	0.9388
		$x_1 = 0.7871$		
343.306	19.076	19.578	0.7286	0.7478
349.250	25.182	25.801	0.7361	0.7542
357.220	36.070	36.688	0.7401	0.7625
363.347	46.131	47.470	0.7469	0.7686
368.688	57.380	58.913	0.7536	0.7738
374.178	71.200	72.977	0.7600	0.7790
378.875	85.632	87.121	0.7699	0.7833
382.701	100.449	100.306	0.7883	0.7872
		$x_1 = 0.6131$		
349.026	11.094	12.003	0.4204	0.4549
357.418	16.251	17.672	0.4300	0.4676
365.949	24.282	25.601	0.4554	0.4801
374.409	34.880	36.223	0.4739	0.4921
381.830	48.399	48.357	0.5028	0.5024
387.587	61.624	59.949	0.5244	0.5102
394.777	78.786	77.571	0.5279	0.5197
401.916	99.563	99.096	0.5315	0.5290
		ARD(P) = 0.022, rmsd = 0.030		

Vapor pressure P_1^{s} of pure compounds can be calculated with the Antoine equation

$$\ln(P_i^{\mathrm{s}}/\mathrm{kPa}) = A - \frac{B}{(T/\mathrm{K} + C)} \tag{2}$$

where A, B, and C are Antoine coefficients. The Antoine constants for 1-propanol, 2-propanol, and water were those given in literature[9] and summarized in Table 4. The assumption of an ideal behavior is adopted for the vapor at a low pressure. Therefore, the fugacity coefficient is equal to unity. Equation 1 could be written as

$$\gamma_1 = P y_1/(P_1^{\mathrm{s}} x_1) \tag{3}$$

It should be noted that the IL does not appear in the vapor phase due to its nonvolatility. The vapor pressure of IL is safely assumed to be zero, thus $y_1 = 1$. Therefore, eq 3 can be simplified as follows:

$$\gamma_1 = P/(P_1^{\mathrm{s}} x_1) \tag{4}$$

According to eq 4, the experimental activity coefficients of the solvent in an IL-containing binary system can be calculated from the vapor pressure data, which were noted as γ_1^{exp} and listed

Table 3. Vapor Pressure Data of the Binary System 2-Propanol (1) + [MMIM][DMP] (2)

T/K	P/kPa	P^{NRTL}/kPa	γ_1^{exp}	γ_1^{NRTL}
		$x_1 = 0.9708$		
317.341	16.832	17.104	0.9898	1.0058
324.261	24.337	24.565	0.9992	1.0085
332.024	35.611	36.072	0.9987	1.0116
338.007	47.121	47.805	0.9998	1.0143
343.105	59.198	60.212	0.9996	1.0167
347.838	72.654	74.059	0.9998	1.0191
352.377	87.726	89.766	0.9983	1.0215
356.066	101.869	104.511	0.9977	1.0236
		$x_1 = 0.8961$		
316.402	14.437	13.959	0.9672	0.9352
325.260	22.869	22.255	0.9672	0.9413
333.239	33.802	33.017	0.9695	0.9469
339.310	44.731	43.914	0.9691	0.9514
345.028	57.668	56.822	0.9700	0.9557
350.294	72.116	71.408	0.9694	0.9598
355.052	87.776	87.183	0.9702	0.9637
358.667	101.485	101.040	0.9709	0.9667
		$x_1 = 0.7871$		
324.277	14.941	14.991	0.7560	0.7585
332.836	23.100	23.129	0.7688	0.7697
341.816	35.256	35.443	0.7773	0.7814
348.988	48.578	48.914	0.7853	0.7907
354.658	61.855	62.418	0.7909	0.7981
359.125	74.635	75.201	0.7984	0.8045
363.015	87.832	88.045	0.8079	0.8098
366.603	102.082	101.484	0.8197	0.8148
		$x_1 = 0.6131$		
333.981	11.149	11.296	0.4513	0.4573
342.619	16.446	17.278	0.4492	0.4720
348.812	23.043	23.072	0.4818	0.4824
355.800	31.660	31.522	0.4963	0.4941
362.591	42.945	42.117	0.5154	0.5055
370.120	58.353	57.240	0.5281	0.5181
377.929	78.826	77.524	0.5400	0.5311
384.177	99.599	97.823	0.5514	0.5416

ARD(P) = 0.014, rmsd = 0.018

Table 4. Antoine Coefficients *A*, *B*, and *C* in Equation 2[9]

	Antoine coefficients		
component	A	B	C
1-propanol	16.0353	3415.56	−70.7330
2-propanol	16.4089	3439.60	−63.4170
water	16.5700	3984.92	−39.7240

Table 5. NRTL Parameters Fitted for IL-Containing Binary Systems for the Vapor Pressure Prediction of the IL-Containing Ternary Systems

		$g_{12} - g_{22}$	$g_{21} - g_{11}$
system	α	J·mol^{-1}	J·mol^{-1}
water + [MMIM][DMP][4]	0.4116	5065.44	−9565.90
1-propanol + [MMIM][DMP]	0.1473	202060	−9138.41
2-propanol + [MMIM][DMP]	0.1059	218635	−9744.88
water + 1-propanol[13]	0.4770	7896.70	1648.80
water + 2-propanol[14]	0.3000	6900.81	77.4900

in Tables 1 to 3, respectively. As it can be observed in these tables, the activity coefficients of water, 1-propanol, and 2-propanol in the binary systems studied are less than one ($\gamma < 1$), showing a negative deviation from the Raoult's law. The result usually indicates that intermolecular attraction forces between different molecules, that is, solvent−IL, are stronger than between similar ones, that is, solvent−solvent.

The experimental vapor pressure data were then correlated using the NRTL equation.[11] To simplify, the IL was treated as a nondissociating component, and the assumption of an ideal behavior of the vapor phase was employed. For the binary water + [MMIM][DMP] system, the experimental vapor pressure data were predicted using the available NRTL parameters taken from the literature[6] as listed in Table 5. The vapor pressure (P^{NRTL}) and activity coefficients (γ^{NRTL}) can be calculated through the NRTL equation and listed in Table 1. As shown in Table 1, the parameters closely reflect the experimental vapor pressure data with the ARD of 0.007. It can be concluded from the results that the experimental procedure for measuring the vapor pressure data was considered to be reliable. The parameters for the binary systems 1-propanol + [MMIM][DMP] and 2-propanol + [MMIM][DMP], α_{ij} and ($g_{ij} - g_{jj}$), were obtained by fitting the experimental vapor pressure data in the whole temperature and composition range using the least-squares method and listed in Table 5. As can be shown in Tables 2 and 3, the experimental vapor pressure can be well-correlated by NRTL equation with average relative deviation (ARD) of 0.022 and 0.014, respectively. The results showed that the NRTL model satisfactorily represents the vapor pressure data for the binary systems.

For the binary 1-propanol + [MMIM][DMP] system, the variation trend of vapor pressure with temperature at different compositions of IL content was shown in Figure 1, while the

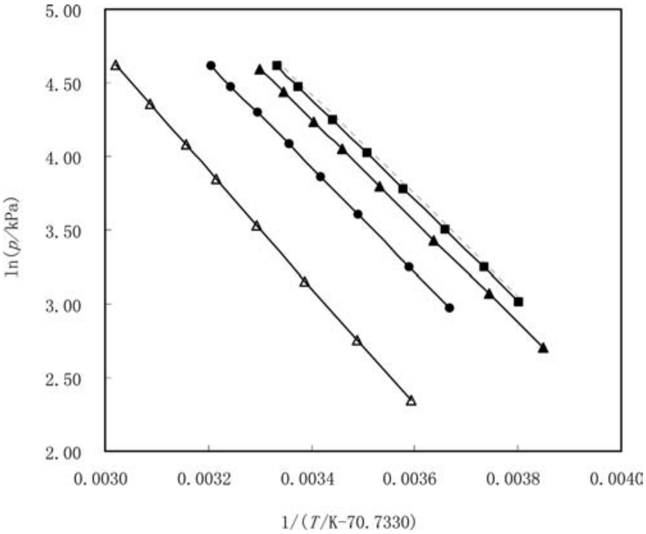

Figure 1. Experimental and correlative vapor pressure data of the binary system 1-propanol (1) + [MMIM][DMP] (2) at different mass fractions of [MMIM][DMP]. Legend: ----, pure 1-propanol; —, calculated by NRTL equation. Symbols are experimental data at different mass fractions of [MMIM][DMP]: ■, 0.10; ▲, 0.30; ●, 0.50; △, 0.70.

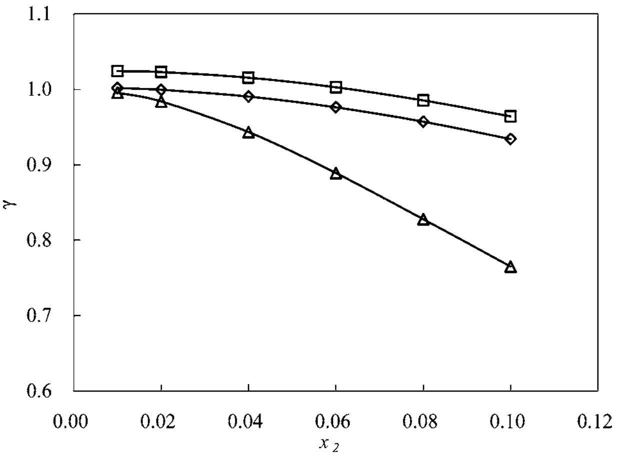

Figure 2. Predicted activity coefficients of water, 1-propanol, and 2-propanol in [MMIM][DMP] at different mole fractions of [MMIM][DMP] and 350 K. Legend: △, water; ◇, 1-propanol; □, 2-propanol.

Table 6. Experimental and Predictive Vapor Pressure Data of the Ternary System Water (1) + 1-Propanol (2) + [MMIM][DMP] (3)

T/K	P/kPa	P^{NRTL}/kPa	γ_1^{NRTL}	γ_2^{NRTL}
$x_1 = 0.2472$, $x_2 = 0.6669$				
331.458	20.304	19.952	1.1232	1.1831
337.477	27.196	26.844	1.1578	1.1805
343.101	35.142	35.006	1.1886	1.1781
349.476	46.605	46.691	1.2218	1.1754
355.004	58.938	59.316	1.2492	1.1732
359.551	71.053	71.730	1.2706	1.1714
364.590	86.898	87.943	1.2934	1.1694
368.665	101.152	103.176	1.3110	1.1678
$x_1 = 0.5509$, $x_2 = 0.3853$				
322.085	15.296	14.590	1.1064	1.6804
329.351	22.025	21.239	1.1279	1.6732
336.582	31.137	30.249	1.1472	1.6662
344.240	43.988	43.116	1.1656	1.6589
350.196	56.805	56.057	1.1786	1.6533
355.768	71.558	70.959	1.1897	1.6482
360.776	87.386	87.042	1.1990	1.6437
364.850	102.156	102.260	1.2060	1.6400
$x_1 = 0.7303$, $x_2 = 0.2189$				
320.289	15.049	13.873	1.0747	2.4010
327.543	21.627	20.179	1.0845	2.4002
335.088	31.079	29.172	1.0932	2.3981
342.052	42.531	40.277	1.1002	2.3952
347.885	54.759	52.134	1.1054	2.3922
353.881	70.238	67.244	1.1100	2.3885
359.086	86.431	83.168	1.1136	2.3849
363.362	101.953	98.489	1.1162	2.3817
$x_1 = 0.8488$, $x_2 = 0.1091$				
317.104	13.002	11.492	1.0124	3.8737
325.851	20.266	18.132	1.0186	3.8842
334.284	30.308	27.378	1.0235	3.8872
341.614	42.173	38.390	1.0271	3.8847
348.325	56.227	51.530	1.0299	3.8788
353.956	70.856	65.286	1.0319	3.8715
359.309	87.510	81.075	1.0336	3.8627
363.231	101.681	94.552	1.0347	3.8552
$x_1 = 0.9329$, $x_2 = 0.0311$				
320.486	13.551	12.147	0.9610	7.5657
327.956	19.615	17.694	0.9652	7.5261
335.678	28.248	25.559	0.9689	7.4687
343.525	40.001	36.390	0.9723	7.3964
351.180	55.100	50.440	0.9752	7.3149
357.363	70.552	64.864	0.9772	7.2426
362.916	87.266	80.603	0.9789	7.1736
367.081	101.831	94.379	0.9801	7.1199

ARD(P) = 0.052, rmsd = 0.063

Table 7. Experimental and Predictive Vapor Pressure Data of the Ternary System Water (1) + 2-Propanol (2) + [MMIM][DMP] (3)

T/K	P/kPa	P^{NRTL}/kPa	γ_1^{NRTL}	γ_2^{NRTL}
$x_1 = 0.2472$, $x_2 = 0.6669$				
317.212	16.452	16.498	1.2731	1.1751
322.666	21.819	21.949	1.2989	1.1727
330.794	32.586	32.875	1.3338	1.1694
337.443	44.373	44.945	1.3594	1.1670
343.359	57.662	58.634	1.3799	1.1651
348.173	70.852	72.208	1.3952	1.1637
353.220	87.224	89.164	1.4099	1.1624
357.191	102.205	104.728	1.4206	1.1615
$x_1 = 0.5509$, $x_2 = 0.3853$				
311.361	13.038	12.903	1.0959	1.8214
318.489	19.053	18.896	1.1125	1.8031
327.197	29.430	29.290	1.1301	1.7821
335.362	43.119	43.074	1.1444	1.7636
341.624	56.852	57.026	1.1540	1.7503
347.323	72.646	72.838	1.1618	1.7387
351.669	86.839	87.220	1.1672	1.7302
355.734	102.115	102.735	1.1719	1.7225
$x_1 = 0.7303$, $x_2 = 0.2189$				
313.530	14.296	14.681	1.0145	2.9231
320.642	20.716	21.232	1.0231	2.8760
327.404	28.943	29.607	1.0303	2.8333
333.848	39.208	40.027	1.0364	2.7944
340.698	53.209	54.319	1.0420	2.7549
346.375	67.862	69.192	1.0462	2.7234
352.010	85.497	87.166	1.0499	2.6934
356.151	100.940	102.707	1.0523	2.6719
$x_1 = 0.8488$, $x_2 = 0.1091$				
312.791	13.362	13.292	0.9606	4.9619
321.525	20.879	20.764	0.9681	4.8060
328.684	29.662	29.292	0.9734	4.6859
334.958	39.680	39.022	0.9776	4.5859
343.024	56.530	55.384	0.9823	4.4640
348.407	70.765	69.212	0.9851	4.3867
353.323	86.243	84.238	0.9874	4.3187
357.258	100.525	98.1262	0.9892	4.2661
$x_1 = 0.9329$, $x_2 = 0.0311$				
319.258	13.794	13.964	0.9436	8.3865
327.383	20.918	20.713	0.9489	8.0202
334.755	29.619	29.047	0.9531	7.7130
343.277	43.445	42.040	0.9575	7.3847
349.287	56.092	53.880	0.9603	7.1690
354.644	69.742	66.666	0.9625	6.9868
359.795	84.827	81.249	0.9646	6.8201
364.314	100.969	96.1369	0.9662	6.6803

ARD(P) = 0.018, rmsd = 0.021

T, P, x diagrams for the other binary systems were not shown as they were very similar to Figure 1. It is obvious that the vapor pressure decreases with an increasing mole fraction of IL. Graphically speaking, it is true that the ln(P/kPa) against 1/(T/K + C) relation for a given concentration is linear over the pressure and temperature studied, which is similar to the vapor pressure behavior of the pure solvent.

To exhibit the effect of the IL on the phase behavior of the three solvents, activity coefficients of these solvents in the IL were predicted by use of the available NRTL parameters with various mole fraction of IL at 350 K. The results were plotted in Figure 2. It is obvious that the activity coefficient of the three solvents decreases with an increasing mole fraction of IL and that the addition of IL has a slightly stronger effect on the decrease of activity coefficients of these solvents. It can be also observed that the interactions of IL with solvents are in the order of water > 1-propanol > 2-propanol.

Ternary Systems. The experimental vapor pressure data for two ternary systems of water + 1-propanol + [MMIM][DMP] and water + 2-propanol + [MMIM][DMP] at an IL mass fraction of 0.30 were measured and listed in Tables 6 and 7, respectively. The vapor phase is still approximately ideal; hence, the vapor pressure for a ternary system, that is, solvent (1) + solvent (2) + IL (3), can be calculated by eq 5. The vapor phase mole fraction of component i at equilibrium can be calculated with eq 6.

$$p = p_1^s x_1 \gamma_1 + p_2^s x_2 \gamma_2 \tag{5}$$

$$y_i = \frac{p_i^s x_i \gamma_i}{p_1^s x_1 \gamma_1 + p_2^s x_2 \gamma_2} \tag{6}$$

The binary NRTL parameters listed in Table 5 were used together to predict the vapor pressure of the two ternary systems water + 1-propanol + [MMIM][DMP] and water + 2-propanol + [MMIM][DMP] at varying liquid composition and temperature. The estimated values and ARD were listed in Tables 6 and 7, respectively. It is seen that the agreement between the

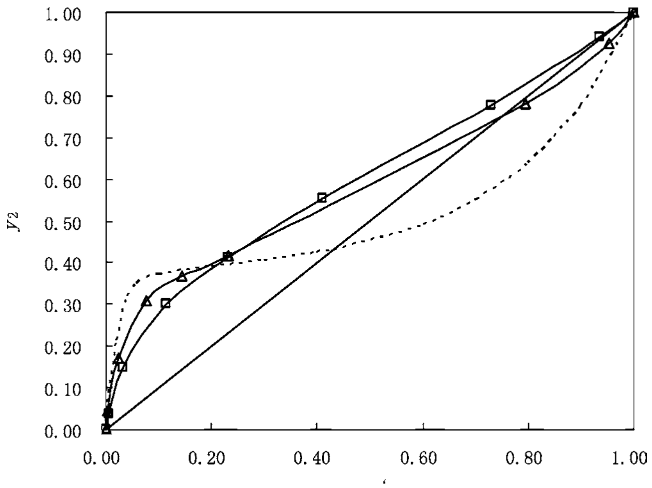

Figure 3. Isobaric VLE diagram for water (1) + 1-propanol (2) + [MMIM][DMP] (3) ternary systems at atmospheric pressure. Legend: ----, IL-free mixture of water and 1-propanol; △, water + 1-propanol mixture at a mass fraction of [MMIM][DMP] of 0.30; □, water + 1-propanol mixture at a mass fraction of [MMIM][DMP] of 0.50.

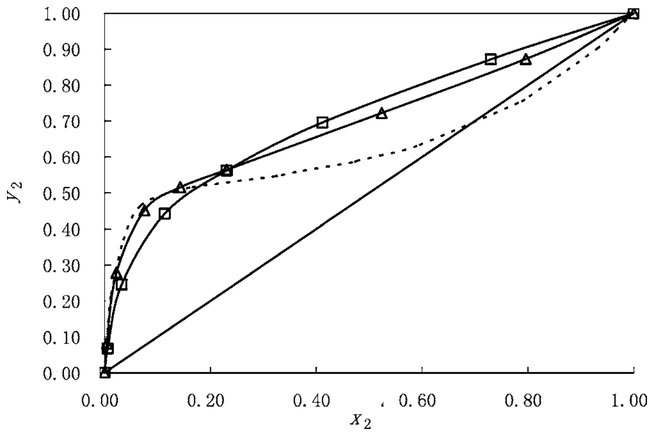

Figure 4. Isobaric VLE diagram for water (1) + 2-propanol (2) + [MMIM][DMP] (3) ternary systems at atmospheric pressure, Legend: ----, IL-free mixture of water and 2-propanol; △, water + 2-propanol mixture at a mass fraction of [MMIM][DMP] of 0.30; □, water + 2-propanol mixture at a mass fraction of [MMIM][DMP] of 0.50.

experimental and the predicted values is fairly good with an ARD of 0.052 and 0.018, respectively. From the point of view of practical application, the conventional NRTL model for nonelectrolyte solution is applicable for representing the vapor−liquid equilibrium of IL-containing multicomponent systems, as indicated by Shi et al. and Doker and Gmehling.[11,12]

To show the salt effect of [MMIM][DMP] on the distillation separation of the two binary mixtures, namely, water + 1-propanol and water + 2-propanol, isobaric VLE for such mixtures with mass fractions of [MMIM][DMP] of 0.3 and 0.5 were predicted in the whole concentration range. The results were plotted in Figures 3 and 4, respectively, on a salt-free basis and compared with the VLE curves in the absence of IL.

As can be seen from Figure 3, the azeotropic point for the water + 1-propanol binary mixture is shifted upward with the addition of IL, and even the azeotropic phenomena could be totally eliminated at the mass fraction of IL of 0.5. Figure 4 indicates that the azeotrope in the water + 2-propanol mixture can be completely eliminated at the mass fraction of IL of 0.3. The addition of IL to the two binary azeotropic mixtures leads to a noticeable increase in the mole fraction of solute in the vapor phase, breaking the azeotropic behavior of the two systems. This phenomena may be attributed to the interaction between water and [MMIM][DMP], which is stronger than the interaction between 1-propanol/2-propanol and [MMIM][DMP].

In addition, a complicated salt effect was observed for the VLE of the two systems. In the water-rich region, with the increase of the mass fraction of IL, more and more 1-propanol or 2-propanol molecules are bonded, and thus the relative volatility of 1-propanol or 2-propanol to water decreases. In the water-lean region, an increase of the IL content leads to a higher relative volatility of 1-propanol or 2-propanol and thus shows a salt-out effect for 1-propanol or 2-propanol. This may be attributed to the ions resulting from dissociation of IL have a stronger attraction to water than to 1-propanol or 2-propanol due to the polar difference of ion solvation energy, which leads to a preferential salvation of ions and enhancement of relative volatility of 1-propanol or 2-propanol.

Conclusions

The influence of the IL [MMIM][DMP] on the phase behavior of the aqueous azeotropic systems: 1-propanol + water and 2-propanol + water were investigated. Vapor pressure data for three binary and two ternary IL-containing systems at varying temperature and IL content were measured using a quasi-static method. The results indicate that the IL [MMIM][DMP] can reduce the vapor pressure of water, 1-propanol, and 2-propanol due to the affinity difference between [MMIM][DMP] and different solvents.

The vapor pressure data of binary systems can be well-correlated with the NRTL equation, and the NRTL parameters obtained can be applied for the prediction of vapor pressure of multicomponent systems and the isobaric VLE data with the mass fraction of [MMIM][DMP] of 0.3 and 0.5. It can be concluded that the addition of [MMIM][DMP] results in a increase of relative volatility of the low boiling component and eliminates the azeotropic system behavior in water + 1-propanol and water + 2-propanol mixtures. Therefore, the IL [MMIM]-[DMP] might be a favorable candidate as a solvent for the separation of the water + 1-propanol and water + 2-propanol mixtures by extractive distillation.

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