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Measurement and Prediction of Vapor Pressure of Binary and Ternary Systems Containing 1-Ethyl-3-methylimidazolium Ethyl Sulfate

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Vapor pressure data were measured for water, methanol, and ethanol as well as their binary mixtures in the presence of the ionic liquid (IL) 1-ethyl-3-methylimidazolium ethyl sulfate ([EMIM][ES]) at different temperatures and IL-content ranging from mass fraction of (0.10 to 0.70) using a quasi-static ebulliometer method. The vapor pressure data of the IL-containing binary systems were correlated by the NRTL equation with an average absolute relative deviation (ARD) within 0.0068. The binary NRTL parameter was used for the prediction of vapor pressure of ternary systems with fair accuracy. Furthermore, the isobaric vapor−liquid equilibrium data for water + ethanol and methanol + ethanol binary mixtures at 101.3 kPa and mass fraction of [EMIM][ES] of 0.5 were predicted. It is shown that the relative volatility of ethanol in both binaries is enhanced and that the azeotrope of the water + ethanol mixture was eliminated completely since the interaction energy between different solvents and IL follows the order water > methanol ≫ ethanol, manifested by the infinite dilution activity coefficients of the solvent in the IL [EMIM][ES].

Introduction

Room temperature ionic liquids (ILs) are a new kind of molten electrolyte. Their electric conductivity in organic solvents is higher than typical inorganic salts in the same solvents,[1] implying that the IL is easier to be dissociated into ions in organic solvents due to its relatively low lattice energy arising from its high asymmetry and low ratio of charge to ionic size. Therefore, IL in a solvent mainly occurred as ionic clusters in a solvated form. Considering the interaction difference between ions and different solvent, for example, a hydrogen bond may be formed between the H-atom at the C2 position of the imidazolium ring of an IL and an electron donor of the solvent (e.g., oxygen atom of hydroxyl group)[2,3] and preferential solvation may take place, which gives rise to the variation of relative volatility and even removal of azeotropic phenomena for a binary solvent mixture.[4,5] Therefore, ILs may be used as a new kind of entrainer in an extractive/salt distillation process for the separation of azeotropic or close-boiling mixtures. Some vapor−liquid equilibria (VLE) data have been reported for the IL-containing systems accordingly (see refs 6−9, for example).

In screening a feasible IL entrainer in an extractive/salt distillation process, some factors with respect to the IL should be taken into account; for example, cost, stability, toxicity, corrosiveness, and potential risk to the environment and ecosphere. For the representative ILs reported, the cation basically falls into three types (i.e., imidazolium, pyridinium, and phosphonium), while the anion is numerous (e.g., halide (X), metallic halide complex ($[M_mX_n]$), $[PF_6]^-$, $[BF_4]^-$, $[NTf_2]^-$, $[OTf]^-$, alkylsulfate, and dialkylphosphate, etc.)[10] Among these anions, the halides are highly corrosive to steel,[11,12] $[M_mX_n]$ is sensitive to moisture,[13] $[PF_6]$ is subject to hydrolysis,[14] and $[NTf_2]$ and [OTf] type ILs are expensive. In contrast, ILs with alkylsulfate and dialkylphosphate anions are probable for practical applications because they can be produced in a one-pot reactor under mild conditions with very high yield. More importantly, they are biodegradable, less toxic, and greener than other ILs.[12] For this reason, VLE data for several dialkylphosphate IL-containing systems have been measured in our laboratory.[4,5,8,9] As a continuous work in this series, vapor pressure data for three binary and three ternary systems composed of water, methanol, ethanol, and [EMIM][ES] (1-ethyl-3-methylimidazolium ethyl sulfate) were determined using a quasi-static ebulliometer apparatus. The experimental VLE data of binary systems were correlated with a NRTL model, and the resulting model parameters were used to predict the vapor pressure of ternary systems.

Experimental Section

Materials. The chemical reagents used in this study were ethanol, methanol, redistilled water, and IL [EMIM][ES]. AR grade methanol and ethanol with purity of 0.997 were purchased from Beijing Red Star Reagents Company, China. The IL used was prepared and purified in the laboratory according to literature procedures,[12] and the purity was more than 0.98 in terms of NMR analysis. Furthermore, the IL was treated before use by vacuum evaporation to remove the residual volatile impurities, and the mass fraction of water was 5.2×10^{-4} as measured by the Karl Fischer method (CBS-1A).

Apparatus and Procedure. Details of the experimental apparatus, its working principle, and the operation procedure have been described elsewhere.[9] The apparatus was composed of a working ebulliometer filled with liquid mixture and a reference one filled with a pure liquid, sharing the same equilibrium pressure. The equilibrium pressure of the reference system was determined by the boiling point of the pure liquid in the reference ebulliometer in terms of the temperature−pressure relation represented by Antoine equation.[15] The equilibrium temperatures of the ebulliometers were measured using

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Table 1. Vapor Pressure Data of Binary System Water (1) + [EMIM][ES] (2)[a]

T/K	P^{exp}/kPa	P^{NRTL}/kPa	γ_1^{exp}	$\gamma_1^{\mathrm{exp}} - \gamma_1^{\mathrm{NRTL}}$
		$x_1 = 0.9915$		
316.93	8.843	8.891	0.9937	−0.0054
328.27	15.566	15.648	0.9939	−0.0053
335.25	21.593	21.682	0.9952	−0.0041
344.29	32.228	32.358	0.9953	−0.0040
348.27	38.203	38.309	0.9966	−0.0027
352.99	46.426	46.523	0.9973	−0.0021
358.06	56.897	56.979	0.9980	−0.0014
363.71	70.899	70.884	0.9996	0.0002
		$x_1 = 0.9683$		
318.06	9.018	9.110	0.9788	−0.0100
325.10	12.858	12.977	0.9804	−0.0091
332.58	18.414	18.558	0.9825	−0.0077
339.37	25.062	25.265	0.9828	−0.0079
345.48	32.753	32.980	0.9844	−0.0068
351.71	42.577	42.800	0.9865	−0.0051
356.54	51.819	52.020	0.9881	−0.0038
364.69	71.142	71.353	0.9895	−0.0029
		$x_1 = 0.9291$		
321.47	9.988	10.023	0.9502	−0.0034
327.87	13.708	13.763	0.9521	−0.0039
334.76	18.953	19.054	0.9533	−0.0050
343.69	28.279	28.412	0.9566	−0.0045
349.08	35.550	35.758	0.9570	−0.0056
354.16	43.748	44.102	0.9563	−0.0077
359.21	53.509	53.955	0.9573	−0.0080
366.60	71.023	71.668	0.9583	−0.0087
		$x_1 = 0.8489$		
325.55	10.030	9.991	0.8532	0.0033
334.18	15.148	15.181	0.8565	−0.0018
340.27	20.028	20.100	0.8607	−0.0031
346.15	25.941	26.075	0.8644	−0.0044
352.47	33.899	34.109	0.8685	−0.0054
357.64	41.547	42.144	0.8653	−0.0125
364.54	54.343	55.310	0.8673	−0.0154
369.29	65.276	66.268	0.8727	−0.0133

[a] ARD(P) = 0.0062, rmsd = 0.0073 where ARD(P) = $(\sum_{i=1}^{n} |P^{\mathrm{NRTL}} - P^{\mathrm{exp}}|/P^{\mathrm{exp}})/n$ and rmsd = $\sqrt{[\sum_{i=1}^{n} (P^{\mathrm{cal}}/P^{\mathrm{exp}} - 1)^2]/n}$.

two-channel four-wire 25 Ω calibrated platinum resistance thermometers (type CST6601) with an uncertainty of 0.02 K. 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, and the total uncertainty was within 0.11 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 concentration variation of the solution. The uncertainty of the mole fraction in the liquid phase prepared by weighing was estimated within 0.002.

Results and Discussion

The vapor pressure data for three binary systems of water, methanol, and ethanol with [EMIM][ES] and three ternary systems of water + methanol, water + ethanol, and ethanol + methanol with [EMIM][ES] at IL mass fraction from 0.10 to 0.70 (mole fraction from 0.0085 to 0.3126) were measured and listed in Tables 1 to 6, 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 equation:[16]

$$\gamma_i = y_i \hat{\phi}_i P / (x_i \phi_i^{\mathrm{s}} P_i^{\mathrm{s}}) \tag{1}$$

Table 2. Vapor Pressure Data of Binary System Methanol (1) + [EMIM][ES] (2)[a]

T/K	P^{exp}/kPa	P^{NRTL}/kPa	γ_1^{exp}	$\gamma_1^{\mathrm{exp}} - \gamma_1^{\mathrm{NRTL}}$
		$x_1 = 0.9852$		
291.66	11.684	11.787	0.9897	−0.0087
299.14	17.400	17.541	0.9905	−0.0080
304.28	22.581	22.753	0.9911	−0.0075
308.71	28.062	28.252	0.9920	−0.0066
313.71	35.592	35.784	0.9934	−0.0053
318.45	44.233	44.415	0.9947	−0.0040
322.57	53.123	53.302	0.9957	−0.0031
327.74	66.303	66.487	0.9961	−0.0027
		$x_1 = 0.9451$		
292.00	11.213	11.315	0.9717	−0.0089
295.26	13.371	13.492	0.9724	−0.0087
302.87	19.786	20.011	0.9713	−0.0111
307.75	25.181	25.476	0.9718	−0.0113
314.46	34.639	35.019	0.9733	−0.0107
319.77	44.019	44.554	0.9729	−0.0118
325.29	56.146	56.711	0.9756	−0.0098
329.17	66.186	66.832	0.9763	−0.0095
		$x_1 = 0.8806$		
294.24	11.210	11.254	0.9240	−0.0037
300.06	15.229	15.326	0.9250	−0.0059
304.34	18.911	19.057	0.9260	−0.0071
310.83	25.922	26.194	0.9266	−0.0097
317.71	35.615	36.124	0.9262	−0.0132
321.94	43.163	43.678	0.9302	−0.0111
327.98	55.934	56.719	0.9306	−0.0131
331.77	65.500	66.471	0.9313	−0.0138
		$x_1 = 0.7597$		
298.28	10.617	10.437	0.8195	0.0139
301.76	12.716	12.538	0.8212	0.0115
307.97	17.313	17.195	0.8224	0.0057
313.20	22.240	22.186	0.8244	0.0021
318.56	28.533	28.527	0.8280	0.0002
323.07	34.955	34.998	0.8312	−0.0010
327.83	43.000	43.114	0.8344	−0.0022
333.16	53.789	54.036	0.8375	−0.0039

[a] ARD(P) = 0.0084, rmsd = 0.0093.

where P and P_i^{s} are the vapor pressure of liquid mixture and pure component i at system temperature, respectively. The latter can be calculated by the Antoine equation with Antoine constants taken from the literature as shown in Table 8.[15] y_i and x_i represent the mole fraction of component i in the vapor and liquid phases, respectively. $\hat{\phi}_i$ is the fugacity coefficient of

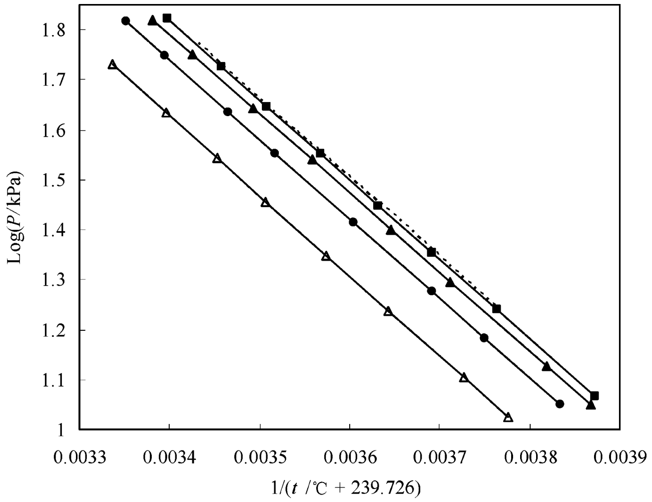

Figure 1. Experimental and correlative vapor pressure data of binary system methanol (1) + [EMIM][ES] (2) at different mass fraction of [EMIM][ES]: - - -, pure methanol; —, calculated by NRTL equation. Symbols are experimental data at different mass fraction of [EMIM][ES]: ■, 0.10; ▲, 0.30; ●, 0.50;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

Table 3. Vapor Pressure Data of Binary System Ethanol (1) + [EMIM][ES] (2)[a]

T/K	P^{exp}/kPa	P^{NRTL}/kPa	γ_1^{exp}	$\gamma_1^{\mathrm{exp}} - \gamma_1^{\mathrm{NRTL}}$
		$x_1 = 0.9788$		
299.82	8.514	8.477	1.0044	0.0043
309.12	14.234	14.186	1.0035	0.0034
315.58	19.901	19.861	1.0022	0.0021
321.28	26.388	26.369	1.0008	0.0007
326.63	34.054	34.057	1.0000	−0.0001
332.21	44.000	44.007	0.9999	−0.0002
337.70	56.084	56.102	0.9998	−0.0003
342.13	67.782	67.819	0.9995	−0.0006
		$x_1 = 0.9229$		
298.99	7.742	7.626	1.0162	0.0152
306.41	11.681	11.563	1.0111	0.0101
313.87	17.287	17.171	1.0078	0.0068
320.94	24.548	24.475	1.0040	0.0030
326.82	32.469	32.426	1.0023	0.0013
332.60	42.304	42.274	1.0017	0.0007
337.59	52.691	52.706	1.0007	−0.0003
342.96	66.174	66.255	0.9989	−0.0021
		$x_1 = 0.8369$		
300.55	7.718	7.576	1.0215	0.0188
311.00	13.526	13.434	1.0097	0.0069
317.30	18.685	18.572	1.0090	0.0061
322.92	24.612	24.486	1.0081	0.0051
328.62	32.084	32.038	1.0045	0.0015
333.58	40.123	40.130	1.0029	−0.0001
339.52	51.997	52.054	1.0020	−0.0011
345.43	66.579	66.712	1.0011	−0.0020
		$x_1 = 0.6874$		
305.35	8.385	8.143	1.0327	0.0298
314.52	13.612	13.260	1.0302	0.0266
321.14	18.711	18.465	1.0175	0.0134
326.74	24.248	24.144	1.0088	0.0043
331.63	30.278	30.259	1.0054	0.0006
335.42	35.663	35.840	1.0000	−0.0050
338.76	41.105	41.470	0.9963	−0.0089
345.75	54.978	55.657	0.9933	−0.0122

[a] ARD(P) = 0.0059, rmsd = 0.0094.

Table 4. Experimental and Predictive Vapor Pressure Data of Ternary System Water (1) + Ethanol (2) + [EMIM][ES] (3)[a]

T/K	P^{exp}/kPa	P^{NRTL}/kPa	γ_1^{NRTL}	γ_2^{NRTL}
		$x_1 = 0.8307$, $x_2 = 0.0813$		
308.27	8.360	8.775	0.9461	3.8544
317.67	13.528	14.223	0.9511	3.7387
324.54	18.813	19.829	0.9544	3.6590
330.77	24.984	26.436	0.9572	3.5900
336.67	32.638	34.322	0.9596	3.5276
341.52	40.227	42.212	0.9614	3.4781
346.21	48.919	51.247	0.9631	3.4319
350.66	58.751	61.259	0.9646	3.3894
		$x_1 = 0.7205$, $x_2 = 0.1880$		
302.37	7.507	7.775	0.9907	2.5973
313.71	13.598	14.239	0.9969	2.5371
320.20	18.672	19.674	0.9999	2.5044
326.48	25.225	26.526	1.0025	2.4739
332.47	33.053	34.856	1.0048	2.4458
337.45	41.146	43.370	1.0065	2.4231
342.36	50.690	53.386	1.0081	2.4014
346.84	61.230	64.185	1.0094	2.3821
		$x_1 = 0.5626$, $x_2 = 0.3302$		
300.88	7.384	7.653	1.0508	1.7976
311.17	12.914	13.413	1.0592	1.7754
318.83	19.147	19.799	1.0645	1.7595
324.22	24.722	25.721	1.0678	1.7488
330.37	33.063	34.244	1.0712	1.7368
335.07	40.996	42.253	1.0736	1.7279
339.84	50.456	51.949	1.0758	1.7191
344.39	61.139	62.885	1.0777	1.7109
		$x_1 = 0.3394$, $x_2 = 0.5312$		
301.49	8.144	8.121	1.1207	1.3157
310.37	12.989	13.198	1.1346	1.3084
317.47	18.752	19.024	1.1445	1.3028
323.20	24.832	25.215	1.1517	1.2984
329.06	32.683	33.221	1.1585	1.2941
333.93	40.838	41.427	1.1637	1.2906
338.66	50.208	50.987	1.1683	1.2873
343.38	61.278	62.277	1.1727	1.2840

[a] ARD(P) = 0.037, rmsd = 0.040.

component i in the vapor mixture, and ϕ_i^{s} is the fugacity coefficient of pure component i in its saturated state.

For an IL-containing binary system [i.e., solvent (1) + IL (2)], the vapor phase is fully composed of solvent due to the negligible volatility of IL,[17] and thus $y_1 = 1$. Since the vapor-phase composition for such binary system and for the pure solvent is same and the pressure difference between them is relatively small, the fugacity coefficient correction can be cancelled out. Therefore, eq 1 can be simplified as follows:

$$\gamma_1 = P/(P_1^{\mathrm{s}} x_1) \tag{2}$$

According to eq 2, the experimental activity coefficient of the solvent in an IL-containing binary liquid mixture can be

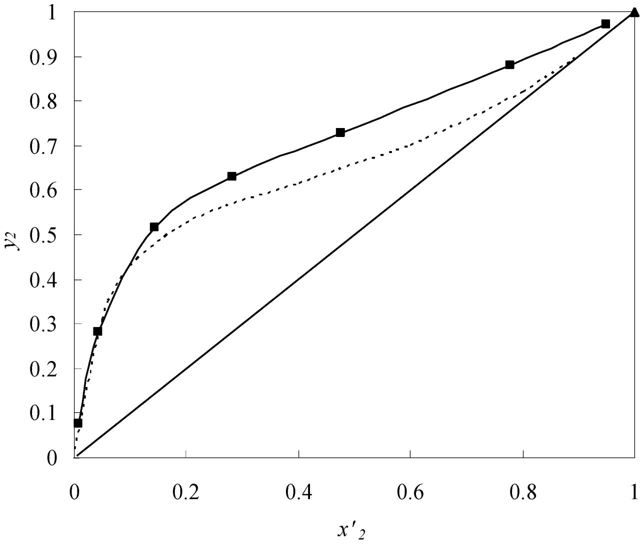

Figure 2. Isobaric VLE diagram for water (1) + ethanol (2) + [EMIM]-[ES] (3) ternary systems at atmospheric pressure: - - -, IL-free mixture of water and ethanol; ■, water + ethanol mixture at mass fraction of [EMIM]-[ES] of 0.50.

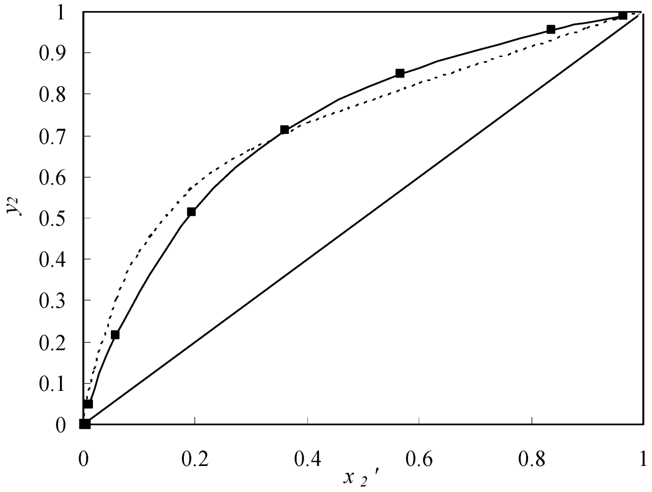

Figure 3. Isobaric VLE diagram for water (1) + methanol (2) + [EMIM]-[ES] (3) ternary systems at atmospheric pressure: - - -, IL-free mixture of water and methanol; ■, water + methanol mixture at mass fraction of [EMIM][ES] of 0.50.

Table 5. Experimental and Predictive Vapor Pressure Data of Ternary System Water (1) + Methanol (2) + [EMIM][ES] (3)[a]

T/K	P^{exp}/kPa	P^{NRTL}/kPa	γ_1^{NRTL}	γ_2^{NRTL}
$x_1 = 0.6300$, $x_2 = 0.2835$				
299.40	8.180	7.751	0.9157	1.1299
307.97	12.866	12.083	0.9220	1.1272
315.30	18.311	17.290	0.9269	1.1249
321.89	24.984	23.507	0.9309	1.1228
328.23	33.107	31.203	0.9345	1.1208
333.43	41.341	38.996	0.9373	1.1192
337.97	50.099	47.094	0.9395	1.1178
342.74	60.923	57.093	0.9418	1.1164
$x_1 = 0.4915$, $x_2 = 0.4147$				
295.22	8.246	7.798	0.8970	1.0642
303.17	12.660	11.868	0.9046	1.0640
310.33	18.184	16.973	0.9108	1.0636
316.49	24.482	22.771	0.9158	1.0633
322.31	31.822	29.708	0.9201	1.0629
327.68	40.138	37.629	0.9239	1.0625
332.48	49.206	46.143	0.9270	1.0621
337.18	59.786	56.006	0.9300	1.0617
$x_1 = 0.2754$, $x_2 = 0.6196$				
291.87	8.282	8.227	0.8816	0.9870
300.22	13.124	12.878	0.8918	0.9896
307.23	18.662	18.364	0.8996	0.9914
313.81	25.593	25.215	0.9063	0.9930
320.06	34.116	33.626	0.9123	0.9943
324.96	42.423	41.775	0.9167	0.9953
330.31	53.212	52.506	0.9212	0.9962
334.59	63.468	62.702	0.9246	0.9970

[a] ARD(P) = 0.045, rmsd = 0.050.

calculated from the vapor pressure data, which are given as γ_1^{exp} and listed in Tables 1 to 3, respectively.

The NRTL parameters for three binary systems, α_{ij} and $(g_{ij} - g_{jj})$ as listed in Table 7, were obtained by fitting the experimental vapor pressure data in the whole temperature and composition range using the least-square method. As shown in Tables 1 through 3, the experimental vapor pressure can be well-correlated by the NRTL equation with average absolute relative deviation (ARD) within 0.0068 for the binary systems studied. Using the NRTL parameters obtained, the infinite dilution activity coefficients of solvent at varying temperatures in [EMIM][ES] were calculated, as shown in Table 9.

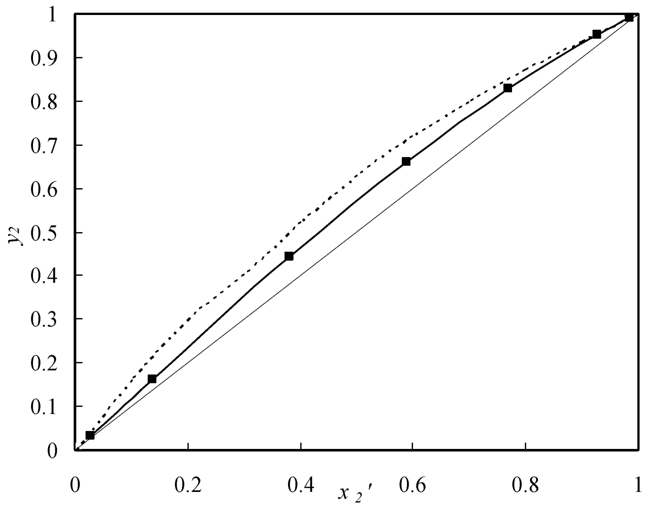

Figure 4. Isobaric VLE diagram for ethanol (1) + methanol (2) + [EMIM]-[ES] (3) ternary systems at atmospheric pressure: - - -, IL-free mixture of ethanol and methanol; ■, ethanol−methanol mixture at mass fraction of [EMIM][ES] of 0.50.

Table 6. Experimental and Predictive Vapor Pressure Data of Ternary System Ethanol (1) + Methanol (2) + [EMIM][ES] (3)

T/K	P^{exp}/kPa	P^{NRTL}/kPa	γ_1^{NRTL}	γ_2^{NRTL}
$x_1 = 0.1295$, $x_2 = 0.7444$				
296.00	11.432	11.130	1.0973	0.9004
299.03	13.348	13.085	1.0976	0.9025
304.38	17.682	17.269	1.0981	0.9060
310.21	23.475	23.075	1.0985	0.9095
315.81	30.513	30.129	1.0987	0.9128
320.50	37.631	37.379	1.0989	0.9153
325.47	46.790	46.627	1.0990	0.9179
330.38	57.630	57.571	1.0990	0.9203
$x_1 = 0.2745$, $x_2 = 0.5918$				
298.19	11.427	11.028	1.0997	0.8612
302.22	14.159	13.669	1.0996	0.8646
307.70	18.706	18.115	1.0993	0.8691
313.01	24.211	23.549	1.0989	0.8732
318.14	30.732	30.065	1.0985	0.8769
322.78	37.857	37.207	1.0981	0.8801
327.85	47.173	46.598	1.0977	0.8835
332.64	57.673	57.220	1.0972	0.8865
$x_1 = 0.4380$, $x_2 = 04197$				
300.50	11.416	10.766	1.0911	0.8048
301.83	11.973	11.563	1.0909	0.8063
310.18	18.303	17.853	1.0897	0.8152
316.16	24.419	23.993	1.0887	0.8212
321.83	31.746	31.368	1.0879	0.8266
326.86	39.651	39.455	1.0871	0.8311
331.63	48.761	48.677	1.0863	0.8352
335.28	56.765	56.908	1.0857	0.8383
$x_1 = 0.6238$, $x_2 = 0.2242$				
303.51	11.403	10.697	1.0633	0.7252
307.04	13.626	12.923	1.0628	0.7303
313.28	18.604	17.842	1.0618	0.7390
319.87	25.492	24.714	1.0608	0.7476
325.65	33.173	32.427	1.0599	0.7549
331.45	42.889	42.174	1.0590	0.7618
335.96	52.006	51.343	1.0583	0.7670
339.87	61.187	60.615	1.0578	0.7714

[a] ARD(P) = 0.022, rmsd = 0.027.

Table 7. NRTL Parameters Fitted for IL-Containing Binary Systems and Taken from the Literature[15] for the Vapor Pressure Prediction of the IL-Containing Ternary Systems

system	α	$(g_{12} - g_{22})$ J·mol^{-1}	$(g_{21} - g_{11})$ J·mol^{-1}
water + [EMIM][ES]	0.7364	37.910	−3868.0
ethanol + [EMIM][ES]	0.9465	1657.7	−1091.7
methanol + [EMIM][ES]	0.9332	30.840	−2588.4
ethanol + water[15]	0.3008	−510.82	5612.1
ethanol + methanol[15]	0.3053	1580.2	−1292.9
methanol + water[15]	0.3013	−172.12	768.56

Table 8. Antoine Vapor Pressure Constants of Pure Compounds[15]

component	Antoine constants[a] A	B	C
ethanol	8.1122	1592.864	226.184
methanol	8.08097	1582.271	239.726
water	8.07131	1730.63	233.426

[a] Antoine equation log p^{sat}/kPa = $A - B/(t/°\mathrm{C} + C)$ where p^{sat} is the saturated vapor pressure in Torr, and t is the equilibrium temperature in centigrade.

As shown in Table 9, the infinite activity coefficient for a specific solvent always increases with the increase of temperature, suggesting a decreasing interaction between solvent and IL species. Furthermore, the infinite activity coefficients for different solvent at a given temperature always follows the order ethanol ≫ methanol > water, implying that the IL [EMIM]-[ES] has a much stronger interaction to water and methanol than to ethanol. The mixture of ethanol and [EMIM][ES]

Table 9. Predicted Infinite Dilution Activity Coefficient of Solvent γ_1^∞ at Varying Temperature for Binary Mixtures of Solvent (1) + [EMIM][ES] (2)

	γ_1^∞					
solvent	T/K = 310	T/K = 320	T/K = 330	T/K = 340	T/K = 350	T/K = 360
water	0.2262	0.2370	0.2476	0.2579	0.2681	0.3079
methanol	0.3707	0.3823	0.3937	0.4046	0.4152	0.4599
ethanol	0.9290	0.9372	0.9448	0.9517	0.9580	0.9755

virtually shows an ideal solution behavior manifested by the closeness of activity coefficients to unity as seen in Table 3.

For the methanol + [EMIM][ES] system, the variation trend of vapor pressure with temperature at different IL content is shown in Figure 1, while the T, p, x diagrams for other binary systems were not shown as they were very similar to Figure 1. It is seen that the log(P/kPa) against 1/(t/°C + C) relation 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, and C is the corresponding Antoine constant for the pure solvent.

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 3. The vapor-phase mole fraction of component i (y_i) at equilibrium can be calculated with eq 4 considering the nonvolatility of IL:

$$p = \sum_{i=1}^{2} p_i^{s} x_i \gamma_i \tag{3}$$

$$y_i = \frac{p_i^{s} x_i \gamma_i}{\sum_j p_j^{s} x_j \gamma_j} \tag{4}$$

The vapor pressure for ternary systems water + ethanol + [EMIM][ES], water + methanol + [EMIM][ES], and ethanol + methanol + [EMIM][ES] at varying liquid compositions and temperatures was predicted using the binary NRTL parameters listed in Table 7 and compared with the experimental values as listed in Tables 4 through 6. It is seen that the agreement between the experimental and the predicted values is fairly good with average deviation ARD of 0.034 and the maximum deviation of −0.070. From the point of view of practical application, the conventional NRTL model for non-electrolyte solution is applicable for representing the VLE of IL-containing multicomponent systems, as indicated by refs 7 and 18.

In order to show the salt effect of the IL [EMIM][ES] on the distillation separation of three binary mixtures (namely, water + ethanol, water + methanol, and ethanol + methanol), isobaric VLE for such mixtures with mass fraction of [EMIM][ES] of 0.5 were predicted in the whole concentration range. The results are plotted in Figures 2 to 4, respectively, on a salt-free basis and compared with the VLE curves in the absence of IL. It is seen that the relative volatility of ethanol in both water + ethanol and methanol + ethanol mixtures were enhanced by the addition of the IL [EMIM][ES], and the azeotrope in the first mixture was eliminated. In contrast, a complicated salt effect was observed for the VLE of the water + methanol system manifested by a salting-in effect for methanol in the water-rich region and a salting-out effect in the water-lean region. This variation trend of relative volatility for different solvent components is consistent with the findings for the infinite dilution coefficients as well as the interaction order water + [EMIM][ES] > methanol + [EMIM][ES] ≫ ethanol + [EMIM]-[ES].

Conclusions

Vapor pressure data for three binary and three ternary IL-containing systems at varying temperature and IL content were measured using a quasi-static method. The results indicate that the IL [EMIM][ES] can reduce the vapor pressure of water, methanol, and ethanol but to different extents due to the affinity difference between [EMIM][ES] and different solvents. The vapor pressure data of binary systems can be well correlated with NRTL equation, and the NRTL parameters obtained can be applied for the prediction of vapor pressure of multicomponent systems with fair accuracy. The affinity between IL and solvents follows the order [EMIM][ES] + water > [EMIM]-[ES] + methanol ≫ [EMIM][ES] + ethanol, and hence the relative volatility of ethanol in water + ethanol and methanol + ethanol binary mixtures is enhanced, and even the azeotrope in the first mixture is exterminated.

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