Separation of 2-propanol and water azeotropic system using ionic liquids as entrainers

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Abstract

2-propanol and water form an azeotropic mixture of the minimum boiling point at constant pressure. In this work, three ionic liquids (ILs), namely 1-ethyl-3-methylimidazolium acetate ([EMIM][OAc]), 1-butyl-3-methylimidazolium acetate ([BMIM][OAc]) and 1-ethyl-3-methylimidazolium bromide ([EMIM][Br]), were used as entrainers to separate the azeotropic mixture by the method of extractive distillation. Isobaric vapor-liquid equilibrium (VLE) data for the ternary systems of 2-propanol + water + [EMIM][OAc], 2-propanol + water + [BMIM][OAc], and 2-propanol + water + [EMIM][Br] were measured at 101.3 kPa. The results demonstrate that the relative volatility of 2-propanol to water is dramatically enhanced with the addition of ILs at areas of 2-propanol molar fraction higher than 0.2. As the amounts of ILs increase, the azeotropic point is pulled up and the azeotropy is even eliminated gradually. The separation effect (namely the effect of ILs on enhancement of the relative volatility) of the three ILs follows the order: [EMIM][OAc] > [BMIM][OAc] > [EMIM][Br]. Moreover, The experimental VLE data were well correlated with the nonrandom two-liquid model (NRTL).

Keywords: vapor-liquid equilibrium, ionic liquids, 2-propanol, water, NRTL model

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1. Introduction

2-propanol is an important chemical product and raw material. Due to its excellent physico-chemical properties, 2-propanol finds its use in various areas, such as used as an intermediate or a solvent in pharmaceutical industry [1], applications in biofuels [2], and other engineering applications [3][4]. Generally, there are two commercial routes to produce 2-propanol, namely direct hydration and indirect hydration of propylene. [5] Therefore, it becomes necessary to separate 2-propanol from water. However, a separation problem occurs because 2-propanol and water form a minimum azeotrope at 2-propanol mass fraction of 87.4%, and the azeotropic temperature is 353.45 K at 101.3 kPa. [6]

Due to the inefficiency of conventional distillation for azeotrope separation, it is indispensable to turn to special distillations, such as extractive distillation, pressure swing distillation, azeotropic distillation, salt adding distillation and so on. [7] In this study, the extractive distillation separation method draws our attention, for its high-efficiency separation capacity for binary azeotropes and other close boiling point mixtures. Extractive distillation, by adding a third solvent (namely entrainer) to the separated mixtures, achieves the goal of valid separation.[8] Hence, the selection of entrainers should be paid more attention. Traditional entrainers such as salts [9] and organic solvents [10] have been applied to separate the azeotropic mixture, but they have the disadvantages of corrosivity, pollution to the environment and difficulty in recycling.

In this work, ionic liquids (ILs) are proposed as entrainers because of their attractive advantages, such as non-volatility, non-flammability, high chemical and thermal stability, convenient recycling and tailorable structures.[11] During the past years, the isobaric or isothermal vapor-liquid equilibrium data for 2-propanol and water containing ionic liquids have been reported. Various ionic liquids have been investigated to test their abilities to break the azeotropy, including 1-ethyl-3-methylimidazole tetrafluoroborate [12], 1-butyl-3-methylimidazole tetrafluoroborate [6], 1-butyl-3-methylimidazole chloride [13] and 1-butyl-3-methylimidazole acetate [14]. The ILs [EMIM][OAc], [BMIM][OAc] have also been used to

separate the mixture[15], but the experiment conclusion only can be made at the **2-propanol- rich region**. In this study, the ILs [EMIM][OAc], [BMIM][OAc], [EMIM][Br] were utilized to separate the azeotropic mixture of 2-propanol and water. The VLE data expanded to **water- rich region** were measured at 101.3 kPa and were correlated with the non-random two liquid (NRTL) model. By analyzing the results, we tried to find the potential entrainers for the system.

2. Experimental section

2.1. Material

2-propanol (mass fraction $\geq 99.7\%$) used in this work was provided by Sinopharm Group without further purification. Water used in this work was ultrapure water produced by Water purification system (Direct-Q3UV). The ILs, [EMIM][OAc], [BMIM][OAc], and [EMIM][Br] were synthesized in our lab, and the mass purities of them were determined by Liquid Chromatography. The ILs were dried in a vacuum desiccator at 373 K for 24 h before experiment with the purpose of making the moisture content down to 0.003 (mass fraction) checked by Karl Fischer titration. Specifications of the chemicals utilized in this work are listed in Table 1.

Table 1

Overviews of the chemical samples

Chemical name	Source	purity	Purification method	Analysis method
2-propanol	SinopharmGroup	0.997	None	GC ^a
[BMIM][OAc]	Synthesized own	0.990	Vacuum desiccation	LC ^c KF ^b
[EMIM][OAc]	Synthesized own	0.990	Vacuum desiccation	LC ^c KF ^b
[EMIM][Br]	Synthesized own	0.990	Vacuum desiccation	LC ^c KF ^b

^a GC = gas chromatography.

^b KF = Karl Fisher titration.

^c LC = liquid chromatography.

2.2. Apparatus and procedure

In this work, an all-glass dynamic recirculating still (NGW, Wertheim, Germany), which has been described in detail in the previous literature[16] [17], was used to conduct the experiment. The pressure of

the apparatus was kept at 101.3 kPa by controlling a gas buffer connected with the still. A manometer with an uncertainty of 0.1 kPa was used to measure the pressure of the apparatus. A precise and calibrated thermometer with an uncertainty of 0.01 K was used to measure the temperature of the apparatus. The experiment was performed in the way that the binary mixture of water and defined mole fraction of ILs were added in batches into the other mixture of 2-propanol and the same mole fraction of IL continuously, with the purpose of changing the mole fraction of 2-propanol from zero to unity and keeping the mole fraction of IL in each series constant in the ternary system. Only when the temperature was constant for more than 30 min, was the VLE assumed.

Both the vapor and liquid phases were detected by a gas chromatograph (Model 7890A, Agilent Technologies) equipped with a 30 m, 0.32 mm i.d., and 0.25 μm Agilent 19091J-413 capillary column and a TCD detector for which the carrier gas is N_2 . The operating conditions were as follows: the temperatures of oven, injector, and detector were 373, 473, and 473 K, respectively. The samples were injected into the headspace sampler (G1888 Network. headspace Sampler Agilent Technologies) before being injected into the GC. Due to the non-volatility of ILs, only the peaks of 2-propanol and water were observed. A digital balance (CAV264C OHAUS America) with a standard uncertainty of 0.001 g was used to measure the content of ILs by weighting the sample before and after vaporizing the volatile component in a vacuum desiccator. And the standard uncertainty of the content of the component in the liquid and vapor phase is 0.001(mole fraction).

3. Results and discussion

3.1. Experimental data

With the purpose of verifying the reliability of the still used in this work, the binary VLE data of 2-propanol and water were determined at 101.3 kPa. The VLE data, listed in Table 2, were compared with the data calculated by the NRTL model and the data from literature [12]. As shown in Fig.1, the VLE data of 2-propanol and water system measured in this work agree well with the literature and the calculated data,

indicating that the still used in the work is reliable.

Table 2

The isobaric VLE data for the binary system of 2-propanol (1) + Water (2) at 101.3 kPa.

T (K)	x_1	y_1
365.42	0.023	0.307
358.73	0.049	0.433
356.22	0.078	0.502
354.91	0.126	0.522
354.34	0.248	0.544
354.15	0.373	0.554
353.82	0.448	0.574
353.43	0.562	0.624
353.36	0.625	0.645
353.32	0.675	0.674
353.45	0.747	0.710
353.76	0.825	0.790
353.88	0.865	0.831
354.65	0.948	0.928

Standard uncertainty $u(x_1) = u(y_1) = \pm 0.001$, $u(T) = \pm 0.01$ K

Fig. 1 Comparison of isobaric VLE data for the binary system of 2-propanol (1) + water (2) at 101.3 kPa: ●, this work; ■, ref [12]; solid line, the correlated data using the NRTL model.

As mentioned above, the relative volatility α_{12} is considered as an important indicative quantity to evaluate the separation effect of an entrainer, and is defined as

$$\alpha_{12} = \frac{y_1/x_1}{y_2/x_2} \quad (1)$$

where $x_1(x_2)$ and $y_1(y_2)$ are the mole fractions of component 1(2) in the liquid phase and vapor phase, respectively.

Since the experimental data were measured at 101.3 kPa, the assumption of the ideal vapor phase could

be made. After neglecting the fugacity coefficients and the Poynting correction, the VLE equation can be simplified as:

$$y_i P = x_i \gamma_i P_i^s \quad (2)$$

where y_i and x_i represent the mole fraction of components i in the vapor phase and the liquid phase, respectively, P is the total pressure of 101.3 kPa, γ_i is the activity coefficient of component i in the liquid phase, P_i^s is the saturated vapor pressure of component i at equilibrium temperature which can be calculated using the Antoine equation:

$$\log P_i^s = A_i - \frac{B_i}{t + C_i} \quad (3)$$

where P_i^s is the saturated vapor pressure of component i at equilibrium temperature in mmHg, t is the equilibrium temperature in °C, and A_i , B_i , and C_i are the Antoine parameters of i . The Antoine parameters of 2-propanol [18] and water from the Aspen Plus are listed in Table 3.

Table 3

Antoine parameters for 2-propanol and water.

Component	Antoine parameters			Temperature range	
	A_i	B_i	C_i	Min/(°C)	Max/(°C)
2-propanol	8.1182	1580.92	219.62	0	133
Water	7.96681	1668.21	228	60	150

The VLE data for the 2-propanol (1) + water (2) + [EMIM][OAc] (3), 2-propanol (1) + water (2) + [BMIM][OAc] (3), 2-propanol (1) + water (2) + [EMIM][Br] (3) ternary systems measured at 101.3 kPa are listed in Tables 4-6, where x_3 represents the mole fraction of ILs in the liquid phase, x_1 represents the mole fraction of 2-propanol in the liquid phase containing ILs, x_1' represents the mole fraction of 2-propanol in the liquid phase on an IL-free basis, y_1 is the mole fraction of 2-propanol in the vapor phase, T is the equilibrium temperature, α_{12} is the relative volatility of 2-propanol to water calculated by the equation (1). The VLE data were measured by keeping the mole fractions of ILs nearly constant at 0.1, 0.2, and 0.3, respectively.

Table 4

Isobaric VLE data for ternary system of 2-propanol (1) + water (2) + [EMIM][OAc] (3) at 101.3 kPa.

T (K)	x_3	x_1	x_1'	y_1	α_{12}	T (K)	x_3	x_1	x_1'	y_1	α_{12}
$x_3 \approx 0.1$											
357.08	0.124	0.876	1.000	1.000		358.67	0.124	0.366	0.418	0.758	4.361
356.67	0.121	0.858	0.976	0.977	1.044	360.08	0.127	0.340	0.389	0.745	4.589
356.37	0.123	0.796	0.908	0.937	1.507	362.38	0.126	0.263	0.301	0.686	5.073
356.04	0.127	0.726	0.832	0.907	1.969	364.16	0.126	0.200	0.229	0.619	5.470
355.66	0.124	0.627	0.716	0.866	2.563	366.56	0.120	0.136	0.154	0.516	5.857
355.84	0.127	0.569	0.652	0.849	3.000	369.95	0.109	0.046	0.052	0.257	6.306
356.14	0.126	0.485	0.555	0.816	3.556	373.55	0.112	0.000	0.000	0.000	
357.17	0.124	0.427	0.487	0.789	3.939						
$x_3 \approx 0.2$											
360.26	0.202	0.798	1.000	1.000		363.35	0.196	0.324	0.403	0.785	5.409
359.03	0.207	0.780	0.984	0.992	2.016	365.54	0.192	0.218	0.270	0.688	5.962
358.74	0.194	0.728	0.903	0.962	2.719	367.51	0.192	0.160	0.198	0.609	6.309
358.58	0.200	0.666	0.832	0.941	3.220	370.43	0.192	0.128	0.158	0.550	6.513
358.77	0.200	0.572	0.715	0.906	3.842	372.73	0.191	0.080	0.099	0.424	6.700
359.97	0.196	0.478	0.594	0.866	4.417	375.53	0.193	0.043	0.053	0.282	7.018
361.53	0.194	0.392	0.486	0.825	4.986	376.28	0.213	0.000	0.000	0.000	
$x_3 \approx 0.3$											
359.77	0.316	0.684	1.000	1.000		366.65	0.298	0.298	0.424	0.837	6.976
359.73	0.286	0.667	0.934	0.985	4.640	369.37	0.297	0.225	0.320	0.777	7.404
359.67	0.288	0.634	0.891	0.976	4.975	371.14	0.296	0.185	0.263	0.729	7.538
359.75	0.291	0.581	0.820	0.960	5.268	373.04	0.299	0.153	0.219	0.683	7.684
360.02	0.289	0.524	0.738	0.941	5.662	375.96	0.300	0.090	0.129	0.540	7.926
360.55	0.292	0.481	0.679	0.927	6.003	377.16	0.300	0.060	0.086	0.429	7.985
361.32	0.296	0.439	0.624	0.913	6.323	379.25	0.299	0.000	0.000	0.000	
362.82	0.296	0.381	0.541	0.887	6.660						

Standard uncertainty $u(x_1') = u(x_1) = u(y_1) = \pm 0.001$ $u(T) = \pm 0.01$ K.

Table 5

Isobaric VLE data for ternary system of 2-propanol (1) + water (2) + [BMIM][OAc] (3) at 101.3 kPa.

T (K)	x_3	x_1	x_1'	y_1	α_{12}	T (K)	x_3	x_1	x_1'	y_1	α_{12}
$x_3 \approx 0.1$											
356.84	0.102	0.898	1.000	1.000		358.01	0.120	0.289	0.328	0.675	4.259
355.68	0.112	0.741	0.834	0.875	1.398	358.82	0.114	0.253	0.286	0.642	4.467
355.64	0.115	0.668	0.755	0.846	1.777	359.82	0.116	0.218	0.247	0.606	4.691
355.66	0.112	0.580	0.653	0.814	2.329	360.94	0.113	0.162	0.183	0.526	4.956
355.86	0.118	0.484	0.549	0.781	2.935	363.90	0.114	0.074	0.084	0.331	5.398
356.18	0.119	0.426	0.484	0.756	3.305	365.91	0.115	0.037	0.042	0.200	5.706
356.64	0.118	0.385	0.436	0.734	3.569	373.15	0.120	0.000	0.000	0.000	
357.24	0.117	0.325	0.368	0.700	4.007						
$x_3 \approx 0.2$											
357.76	0.236	0.764	1.000	1.000		362.24	0.234	0.230	0.300	0.665	4.632
357.55	0.232	0.686	0.893	0.949	2.230	363.13	0.230	0.191	0.248	0.613	4.803
357.25	0.234	0.617	0.805	0.916	2.642	365.12	0.230	0.174	0.226	0.586	4.846
357.31	0.235	0.557	0.728	0.888	2.962	367.14	0.231	0.141	0.183	0.529	5.014
357.34	0.238	0.471	0.618	0.847	3.422	368.57	0.235	0.097	0.127	0.428	5.143
357.55	0.231	0.439	0.571	0.827	3.591	372.63	0.234	0.056	0.073	0.295	5.314
358.06	0.232	0.379	0.493	0.792	3.916	374.35	0.234	0.030	0.039	0.182	5.482
359.12	0.230	0.333	0.432	0.759	4.141	377.25	0.233	0.000	0.000	0.000	
361.03	0.232	0.276	0.359	0.712	4.414						
$x_3 \approx 0.3$											
356.84	0.341	0.659	1.000	1.000		356.64	0.342	0.315	0.479	0.807	4.548
355.94	0.343	0.608	0.925	0.976	3.300	357.24	0.341	0.273	0.414	0.768	4.686
355.68	0.340	0.567	0.859	0.955	3.484	358.01	0.343	0.204	0.310	0.687	4.880
355.64	0.338	0.506	0.766	0.925	3.768	358.82	0.343	0.174	0.265	0.643	5.000
355.66	0.341	0.468	0.710	0.907	3.983	359.82	0.342	0.126	0.191	0.545	5.073
355.86	0.338	0.435	0.657	0.887	4.098	363.00	0.339	0.087	0.132	0.439	5.146
356.18	0.341	0.374	0.568	0.851	4.344	364.64	0.336	0.000	0.000	0.000	

Standard uncertainty $u(x_1') = u(x_1) = u(y_1) = \pm 0.001$, $u(T) = \pm 0.01$ K.

Table 6

Isobaric VLE data for ternary system of 2-propanol (1) + water (2) + [EMIM][Br] (3) at 101.3 kPa.

T (K)	x_3	x_1	x_1'	y_1	α_{12}	T (K)	x_3	x_1	x_1'	y_1	α_{12}
$x_3 \approx 0.1$											
355.24	0.116	0.884	1.000	1.000		357.10	0.116	0.364	0.412	0.724	3.744
354.95	0.113	0.854	0.963	0.938	0.581	360.00	0.118	0.288	0.326	0.681	4.414
354.37	0.117	0.784	0.888	0.876	0.891	362.10	0.114	0.208	0.235	0.608	5.049
354.10	0.111	0.736	0.828	0.842	1.107	364.47	0.115	0.159	0.180	0.544	5.435
353.74	0.115	0.654	0.739	0.817	1.577	368.30	0.112	0.101	0.114	0.432	5.911
353.95	0.110	0.614	0.690	0.804	1.843	369.05	0.104	0.076	0.085	0.361	6.081
353.97	0.110	0.562	0.631	0.790	2.200	369.45	0.114	0.046	0.052	0.258	6.339
354.70	0.116	0.513	0.580	0.780	2.567	371.45	0.115	0.020	0.023	0.133	6.516
355.56	0.112	0.454	0.511	0.759	3.014	372.22	0.116	0.000	0.000	0.000	
$x_3 \approx 0.2$											
357.21	0.199	0.801	1.000	1.000		356.45	0.206	0.313	0.394	0.748	4.565
356.10	0.198	0.746	0.930	0.939	1.159	357.86	0.206	0.203	0.256	0.656	5.542
355.85	0.203	0.686	0.861	0.911	1.652	360.04	0.206	0.150	0.189	0.583	5.999
355.83	0.208	0.645	0.814	0.893	1.907	362.22	0.205	0.088	0.111	0.446	6.448
355.57	0.209	0.570	0.721	0.862	2.417	364.25	0.209	0.055	0.070	0.338	6.783
355.50	0.201	0.496	0.621	0.829	2.959	367.15	0.207	0.032	0.040	0.226	7.008
355.36	0.206	0.416	0.524	0.800	3.634	368.24	0.205	0.000	0.000	0.000	
355.58	0.204	0.370	0.465	0.778	4.032						
$x_3 \approx 0.3$											
356.82	0.308	0.692	1.000	1.000		360.00	0.303	0.224	0.321	0.743	6.115
356.43	0.301	0.659	0.943	0.980	2.962	361.70	0.307	0.180	0.260	0.695	6.485
356.76	0.302	0.610	0.874	0.955	3.059	363.74	0.303	0.132	0.189	0.616	6.883
357.05	0.302	0.538	0.771	0.919	3.370	365.57	0.302	0.097	0.139	0.537	7.184
357.10	0.310	0.455	0.659	0.888	4.103	367.56	0.304	0.051	0.073	0.374	7.587
357.77	0.304	0.370	0.532	0.844	4.759	371.26	0.304	0.013	0.018	0.126	7.856
358.57	0.304	0.284	0.408	0.793	5.558	372.55	0.304	0.000	0.000	0.000	

Standard uncertainty $u(x_1') = u(x_1) = u(y_1) = \pm 0.001$, $u(T) = \pm 0.01\text{K}$.

3.2. Calculation of the Phase Equilibrium

The NRTL model proposed by Renon and Prausnitz [19] is frequently used for the experimental VLE data regression of the IL-containing system because it often fits the experimental data well. In this work, the NRTL model is also used to correlate the experimental VLE data. To calculate the ternary VLE data, nine parameters of the NRTL model should be determined, including six binary energy parameters and three non-randomness factors. The parameters for 2-propanol and water were obtained from literature [20]. The other six parameters were regressed by the NRTL model and experimental data and are listed in Table 7.

Table 7

Nonrandom factors and binary energy parameters for the NRTL model.

Component <i>i</i>	Component <i>j</i>	α_{ij}	$\frac{\Delta g_{i,j}}{J / \text{mol}}$	$\frac{\Delta g_{j,i}}{J / \text{mol}}$
2-propanol	Water	0.300 ^a	6900.81 ^a	77.49 ^a
2-propanol	[EMIM][OAc]	0.200	-5680.2	-985.6
Water	[EMIM][OAc]	0.26	-6580.2	-7000.2
2-propanol	[BMIM][OAc]	0.300	-6255.6	-1185.4
Water	[BMIM][OAc]	0.200	-5442.5	-6344.8
2-propanol	[EMIM][Br]	0.018	-2458.27	123.23
Water	[EMIM][Br]	0.455	-8990.65	20380.41

^a From ref. [20], $\Delta g_{i,j} = g_{ij} - g_{i,i}$, $\tau_{ij} = (g_{ij} - g_{i,i})/RT$

Figs. 2-4 shows the isobaric y_1-x_1' diagram for the 2-propanol (1) + water (2) + [EMIM][OAc] (3), [BMIM][OAc] (3) or [EMIM][Br] (3) ternary systems at 101.3 kPa on an IL-free basis. As can be seen, at areas of higher 2-propanol content, the addition of a small quantity of ILs can significantly increase the content of 2-propanol in the vapor phase, producing a salting-out effect. Moreover, the azeotropic point of 2-propanol and water shifts towards areas of higher 2-propanol contents, and can be totally eliminated with increasing the amount of ILs to a specific value. For [EMIM][OAc], the azeotrope is broken when its mole fraction is larger than 0.1, while the amount of [BMIM][OAc] and [EMIM][Br] needed is greater. According to the NRTL model, the minimum mole fractions of [EMIM][OAc], [BMIM][OAc] and [EMIM][Br] needed to break the azeotrope are 0.1184, 0.1503, 0.1989, respectively.

Fig. 2. Isobaric y_1-x_1' diagram for the 2-propanol (1) + water (2) + [EMIM][OAc] (3) ternary system at 101.3 kPa: dotted line, IL-free system; $\bullet$, $x_3 = 0.1$; $\blacksquare$, $x_3 = 0.2$; $\blacktriangle$, $x_3 = 0.3$; solid line, correlated using NRTL model.

Fig. 3. Isobaric y_1-x_1' diagram for the 2-propanol (1) + water (2) + [BMIM][OAc] (3) ternary system at 101.3 kPa: dotted line, IL-free system; $\bullet$, $x_3 = 0.1$; $\blacksquare$, $x_3 = 0.2$; $\blacktriangle$, $x_3 = 0.3$; solid line, correlated using NRTL model.

Fig. 4. Isobaric y_1-x_1' diagram for the 2-propanol (1) + water (2) + [EMIM][Br] (3) ternary system at 101.3 kPa: dotted line, IL-free system; $\bullet$, $x_3 = 0.1$; $\blacksquare$, $x_3 = 0.2$; $\blacktriangle$, $x_3 = 0.3$; solid line, correlated using NRTL model.

The relative activities (α_{12}) of 2-propanol to water containing different ILs are illustrated in Figs. 5-7. It is obvious that the addition of small amounts of ILs significantly enhance the relative volatility of 2-propanol to water at areas of higher 2-propanol contents. Moreover, the more the addition of ILs, the larger the relative volatilities of 2-propanol to water, consequently the easier the separation. At areas of higher 2-propanol contents, with the same amount of ILs, the sequence of the value of α_{12} varying with different ILs is: [EMIM][OAc] > [BMIM][OAc] > [EMIM][Br]. At areas of higher water contents, ILs show complex effects on the mixture of 2-propanol and water. In general, among the three ILs, [EMIM][OAc] produces the most obvious salting-out effect, followed by [BMIM][OAc] and [EMIM][Br], which is consistent with the result of literature[15].

Fig. 5. Relative activity a_{12} of 2-propanol (1) to water (2) at different mole fraction of [EMIM][OAc] at 101.3 kPa: $\circ$, $x_3 = 0$; $\bullet$, $x_3 = 0.1$; $\blacksquare$, $x_3 = 0.2$; $\blacktriangle$, $x_3 = 0.3$; solid lines, correlated using NRTL model.

Fig. 6. Relative activity a_{12} of 2-propanol (1) to water (2) at different mole fraction of [BMIM][OAc] at 101.3 kPa: $\circ$, $x_3 = 0$; $\bullet$, $x_3 = 0.1$; $\blacksquare$, $x_3 = 0.2$; $\blacktriangle$, $x_3 = 0.3$; solid lines, correlated using NRTL model.

Fig. 7. Relative activity a_{12} of 2-propanol (1) to water (2) at different mole fraction of [EMIM][Br] at 101.3 kPa: $\circ$, $x_3 = 0$; $\bullet$, $x_3 = 0.1$; $\blacksquare$, $x_3 = 0.2$; $\blacktriangle$, $x_3 = 0.3$; solid lines, correlated using NRTL model.

The effect of [EMIM][OAc], [BMIM][OAc] and [EMIM][Br] on the VLE behavior of the **2-propanol** and water system might be attributed to the different molecular interactions between ILs and solvents. Molecular interactions are mainly electrostatic interaction, hydrogen bonding and Vander Waals forces.[21] In this work, the hydrogen bond is discussed.[22] As water is a stronger hydrogen bond donator than **2-propanol** and the polarity of water is greater than that of **2-propanol**, the interaction of ILs with water is stronger than that with **2-propanol**, making **2-propanol** more volatile compared to the IL-free system [24]. While at areas of higher water contents, in spite of the stronger molecular interaction between water molecules and ILs, more and more 2-propanol molecules are also interacted, thus making relative volatility of **2-propanol** to water decreasing (at x'_1 below 0.2). To our knowledge, the anions of ILs play a key role in the molecular interactions of ILs with water.[23] Because the acetate ion can form a stronger hydrogen bond with water than bromide ion, the relative volatility of **2-propanol** to water containing ILs with acetate ion is superior to that containing ILs with bromide ion. And for [EMIM][OAc] and [BMIM][OAc], the difference lies in the cation of ILs. As we all know, the weaker the polarity of the cation, the weaker the hydrogen bond to be formed. [21] [25] As the $[\text{EMIM}]^+$ cation has a shorter alkyl chain than $[\text{BMIM}]^+$ cation, the polarity of [EMIM][OAc] is stronger than that of [BMIM][OAc], thus [EMIM][OAc] can form a stronger hydrogen

bond with water, making 2-propanol more volatile compare to [BMIM][OAc]. So [EMIM][OAc] has a better separation effect than [BMIM][OAc]. As a result, [EMIM][OAc] could be expected to have a potential application for the separation of 2-propanol and water.

4. Conclusions

The VLE data of the 2-propanol (1) + water (2) + [EMIM][OAc] (3), 2-propanol (1) + water (2) + [BMIM][OAc] (3), 2-propanol (1) + water (2) + [EMIM][Br] (3) ternary systems were measured at 101.3 kPa. All the three ILs produced a salting-out effect on 2-propanol at areas of higher 2-propanol content, enhancing the relative volatility of 2-propanol to water, and could eventually eliminate the azeotropic point with the increase of the amounts of ILs. [EMIM][OAc] has a better separation effect than the other two ILs, thus can be selected as a potential entrainer for the separation of the azeotropic mixture. In addition, the NRTL model can be applied to the IL-containing systems with good accuracy.

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List of symbols

Δg_{ij}	binary energy parameter of NRTL model
x_i	mole fraction of solvent i in the liquid phase
y_i	mole fraction of solvent i in the vapor phase
T	equilibrium temperature
P	total pressure in the equilibrium system
P_i^s	Saturated vapor pressure of component i

Greek letters

α_{12}	separation factor of component 1 to component 2
α_{ij}	non-randomness parameter of NRTL model
γ_i	activity coefficient of component i

References

- [1] A. A. Sizikov, A. Yu. Manakov, Double gas hydrate of isopropanol and methane. *Fluid Phase Equilib.* 371 (2014) 75-81.
- [2] B. Likozar, J. Levec, Transesterification of canola, palm, peanut, soybean and sunflower oil with methanol, ethanol, isopropanol, butanol and tert-butanol to biodiesel: Modelling of chemical equilibrium, reaction kinetics and mass transfer based on fatty acid composition. *Appl. Energy.* 123 (2014) 108-120.
- [3] X-Y. Wang, X-D. Li, G. Tang, L-X. Zhao, W-J. Zhang, T-G. Jiu, J-F. Fang, Improving efficiency of planar hybrid $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite solar cells by isopropanol solvent treatment. *Org. Electron.* 24 (2015) 205-211.
- [4] B. Burrichter, C. Pasel, M. Luckas, D. Bathen, Parameter study on the adsorptive drying of isopropanol in a fixed bed adsorber. *Sep. Purif. Technol.* 132 (2014) 736-743.
- [5] J. I. Kroschwitz, Kirk – Othmer Encyclopedia of Chemical Technology, 4th Edition. John Wiley & Sons, New York, USA 20 (1991) 216-240.
- [6] Q-S. Li, J-G. Zhang, Z-G. Lei, J-Q. Zhu, B-H. Wang and X-Q. Huang, Isobaric Vapor-Liquid Equilibrium for (Propan-2-ol + Water + 1-Butyl-3-methylimidazolium Tetrafluoroborate). *J. Chem. Eng. Data* 54 (2009) 2785-2788.
- [7] Z. Lei, B. Chen, Z. Ding, *Special Distillation Processes*. Elsevier: Amsterdam, 2005.
- [8] M. I. Zaretskii, V. V. Rusak, and E. M. Chartov, Extractive distillation in chemical technology: a review, *Coke and chemistry* 53 (2010) 36-40.
- [9] J. Bao. Y. M. Zhang, X. Jin, Vapor-Liquid Equilibria for the Isopropanol – Water - Mixed Solvent Containing Salt Systems. *J. Chem. Eng. Chin. Univ.* 19 (2005) 258-262.
- [10] A. Font, J. Asensi, F. Ruiz, and Vicente Gomis, Isobaric Vapor - Liquid and Vapor - Liquid - Liquid Equilibria Data for the System Water + Isopropanol + Isooctane. *J. Chem. Eng. Data.* 49 (2004) 765-767.
- [11] Alfredo Ortiz, Lara María Galán, Daniel Gorri, André B. de Haan and Inmaculada Ortiz, Reactive Ionic

Liquid Media for the Separation of Propylene / Propane Gaseous Mixtures. *Ind. Eng. Chem. Res.* 49 (2010) 7227-7233.

[12] Q-S. Li, J-G. Zhang, Z-G. Lei, J-J. Zhu and F-Y. Xing, Isobaric Vapor – Liquid Equilibrium for Ethyl Acetate + Ethanol + 1-Ethyl-3-methylimidazolium Tetrafluoroborate. *J. Chem. Eng. Data.* 2009 54 (2) 193-197.

[13] D-S. Deng ,Y-Z. Qiao, D-X. Ji, Y. Ge, L-Z. Zhang, Measurement and modeling of vapor-liquid equilibrium for ternary system water + 2-propanol +1-Butyl-3-methylimidazolium chloride. *Chin. J. Chem. Eng.* 22 (2014) 164-169.

[14] D-S. Deng, R-F. Wang, L-Z. Zhang, Y. Ge, J-B. Ji, Vapor-liquid equilibrium measurements and modelling for the ternary system (water +2 -propanol +1-butyl-3-methylimidazolium acetate). *Phys. Chem. Liq.* 50 (2012) 504-512.

[15] L-Zh. Zhang, J-Zh. Han, D-S. Deng, J-B. Ji, Selection of ionic liquids as entrainers for separation of water and 2-propanol. *Fluid Phase Equilib.* 255 (2007) 179-185.

[16] Z.-G. Zhang, D.-H. Huang, W.-X. Li, Entrainer selection for separating tetrahydrofuran/water azeotropic mixture by extractive distillation, *Sep. Purif. Technol.* 122 (2014) 73-77.

[17] Wenxiu Li, Dezhang Sun, Tao Zhang, Shangwu Dai, Fenjin Pan, Zhigang Zhang*, Separation of acetone and methanol azeotropic system using ionic liquid as entrainer, *Fluid Phase Equilib.* 383 (2014) 182–187.

[18] C. L. Yaws, H. C. Yang, To estimate Vapor pressure easily *Hydrocarbon Processing*, 1989, P65.

[19] H. Renon, J. M. Prausnitz, Local composition in thermodynamic excess functions for liquid mixtures. *AIChE J.* 14 (1968) 135-144.

[20] P. Marzal, J. B. Montón, M.A. Rodrigo, Isobaric vapor-liquid equilibria of the water + 2-propanol system at 30 , 60 ,and 100 kPa. *J. Chem. Eng. Data* 41 (1996) 608-611.

[21] J. Li, X. Yang, K. Chen, Sifting Ionic Liquids as Additives for Separation of Acetonitrile and Water

Azeotropic Mixture Using the COSMO-RS Method. *Ind. Eng. Chem. Res.* 51 (2012) 9376-9385.

[22] Mercedes Lo ´pez-Pastor, Mari´a Jose´ Ayora-Canada, Miguel Valca ´rcel, and Bernhard Lendl, Association of Methanol and Water in Ionic Liquids Elucidated by Infrared Spectroscopy Using Two-Dimensional Correlation and Multivariate Curve Resolution. *J. Phys. Chem. B* 110 (2006) 10896-10902.

[23] L C Cammarata, S G Kazarian, P A Salter, T Welton. Molecular states of water in room temperature ionic liquids. *Phys. Chem. Chem. Phys.* 3 (2001) 5192-5200.

[24] J. Dhanalakshmi, P. S. T. Sai, and A. R. Balakrishnan Study of Ionic Liquids as Entrainers for the Separation of Methyl Acetate–Methanol and Ethyl Acetate – Ethanol Systems Using the COSMO-RS Model. *Ind. Eng. Chem. Res.* 52 (2013) 16396-16405.

[25] Catarina M. S. S. Neves, Marta L. S. Batista, Ana Filipa M. Cla ´udio, Luı´s M. N. B. F. Santos, Isabel M. Marrucho, Mara G. Freire, and Joa˜o A. P. Coutinho, Thermophysical properties and water saturation of $[PF_6]^-$ based ionic liquids. *J. Chem. Eng. Data* 55 (2010) 5065-5073.