Isobaric Vapor–Liquid Equilibrium for Ternary Mixtures of Acetone + Methanol + Ionic Liquids at 101.3kPa

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Abstract

In order to avoid the pollution and the corrosion of inorganic anions, such as BF_4^- , SO_4^{2-} and Cl^- , three ionic liquids (ILs) with different organic anions (1-methylimidazolium acetate [MIM]Ac, 1-methylimidazolium 2-hydroxypropionate [MIM]HPr and 1-methyl imidazolium propionate [MIM]Pr) were studied as entrainers for separating acetone + methanol azeotropic mixture. Isobaric vapor-liquid equilibrium (VLE) data for the ternary system containing ILs were measured at 101.3kPa by using an all-glass dynamic recirculating still. The experimental data are well correlated by using the nonrandom two-liquid (NRTL) model. The separation ability of the three ILs follows the order: [MIM]Ac > [MIM]HPr > [MIM]Pr.

Keywords: vapor-liquid equilibrium; ionic liquid; acetone; methanol; NRTL model

1. Introduction

Acetone and methanol are two important raw materials in the modern chemical industry. The acetone + methanol mixture presents a minimum azeotrope at acetone mole fraction of 78%, and the azeotropic temperature is 55.5°C at 101.3kPa. Thus, it is difficult to separate this azeotropic system by common distillation. Several special distillation methods have been used to separate azeotropic mixtures, such as extractive distillation, salt adding distillation, and pressure swing distillation [1-5]. Because of the advantages of flexible selection of the entrainers, weak corrosiveness, low energy consumption and so on, extractive distillation has been widely applied to the separation of azeotropic or close-boiling mixtures. In the process of extractive distillation, it is essential to select a suitable entrainer with high stability, low toxicity,

good solubility and high selectivity.

In recent years, ionic liquids (ILs) have been widely used as entrainers of extractive distillation since they showed the excellent abilities to separate azeotropic mixtures by Seiler et al [6-17]. ILs are composed of organic cations and inorganic or organic anions. ILs have many unique properties, such as negligible vapor pressure, good thermal stability, environmental friendliness. Arlt et al. [18] reported the isothermal vapor–liquid equilibrium (VLE) data for the ternary system of acetone + methanol + ILs (1-ethyl-3-methylimidazolium tetra-fluoroborate [EMIM][BF₄] and N-butylpyridinium hexafluoro-phosphate [BPY][PF₆]) in 2002. Since then, several ionic liquids (e.g., 1-ethyl-3-methylimidazolium trifluoromethanesulfonate [emim][triflate], 1-butyl-3-ethylimidazolium trifluoromethanesulfonate [beim][triflate] 1-ethyl-3-methylimidazolium dicyanamide [EMIM][DCA], 1-ethyl-3-methylimidazolium diethylphosphate [EMIM] [DEP], and 1-ethyl-3-methylimidazolium hydrogen sulfate, [EMIM] [HSO₄] [12,13,19-21]) have been investigated as solvents to separate this binary azeotropic system. The isothermal or the isobaric VLE data of these ternary systems containing ILs were obtained, and the azeotropic phenomenon for acetone + methanol system were totally broken at the mole fractions of ILs from 0.022 to 0.079. Li et al.[22,23] studied the influence of five ILs (monoethanolamine chloride [HMEA][Cl], monoethanolamine acetate [HMEA][OAC], 1-ethyl-3-methylimidazole acetate [EMIM][OAC], 1-ethyl-3-methylimidazolebromine [EMIM][Br] and 1-butyl-3-methylimidazole bromine [BMIM][Br]) on the VLE data of this binary system. The results showed that, the shorter the alkyl chain length on the imidazole ring of the IL cation is, the better the separation capacity.

In this work, the ILs investigated are three ILs with organic anions 1-methylimidazolium acetate [MIM]Ac, 1-methylimidazolium 2-hydroxypropionate [MIM]HPr, and 1-methylimidazolium propionate[MIM]Pr. The three ILs are without pollution and corrosion like the ILs containing inorganic anions such as BF₄⁻, SO₄²⁻ and Cl⁻. They are also inexpensive and with short alkyl chain on the imidazole ring of the IL cations. The isobaric vapor–liquid equilibrium (VLE) data for the ternary systems of acetone + methanol containing different ILs were measured at 101.3 kPa, and the effects of the ILs on the separation performance of the acetone and methanol system were discussed.

2. Experimental

2.1. Materials

The chemicals used in this work were acetone (Sinopharm Group, minimum wt 99.5%), methanol (Sinopharm Group, minimum wt 99.5%), and ionic liquids (Lanzhou yulu fine chemical co. LTD, minimum wt 99.0%). The organic solvents were checked by gas chromatograph. The water contents were measured by Karl Fischer titration. The three ILs were analyzed by liquid chromatography, and dried in

a vacuum drying oven at 393K overnight before experiment. Specifications of the chemical samples in this study are summarized in Table 1.

Table.1 Specifications of the chemical samples

Chemical name	CAS RN	source	Water content	purity	Purification method	Analysis method
acetone	67-64-1	Sinopharm Group	none	0.995	none	GC ^a
methanol	67-56-1	Sinopharm Group	none	0.995	none	GC ^a
[MIM]Ac ^d	none	Yulu Group	<5000ppm	0.990	Vacuum desiccation	KF ^b LC ^c
[MIM]Pr ^e	none	Yulu Group	<5000ppm	0.990	Vacuum desiccation	KF ^b LC ^c
[MIM]HPr ^f	none	Yulu Group	<5000ppm	0.990	Vacuum desiccation	KF ^b LC ^c

^aGC = gas chromatography.

^bKF =Karl Fischer titration.

^cLC =liquid chromatography.

^d[MIM]Ac=1-methylimidazolium acetate

^e[MIM]Pr=1-methylimidazolium propionate

^f[MIM]HPr=1-methylimidazolium 2-hydroxypropionate

2.2. Apparatus and procedures

All vapor-liquid equilibrium (VLE) experiments were conducted in an all-glass dynamic recirculating still (NGW, Wertheim, Germany) described by Hunsmann[24]. The temperature was detected by a calibrated thermometer with a standard uncertainty of 0.01 K. The equilibrium pressure was kept constant at 101.3kPa via a gas buffer, and determined by a manometer with a standard uncertainty of 0.1kPa. Each sample for the VLE experiment was gravimetrically prepared with an electronic balance (CAV264C OHAUS America), and the standard uncertainty is 0.1mg.

The mole fractions of acetone and methanol were measured by using headspace sampler (G1888 headspace sampler, Agilent Technologies) and the gas chromatograph (model network 7890A, Agilent Technologies) described in the previous literatures [22, 23]. After the temperature was stable for one hour, the condensed vapor and liquid phase samples taken from the dynamic recirculating still were inserted into the

headspace sampler and tested by the gas chromatography (GC). The original reactants (1-methylimidazole, acetic acid, propionic acid and 2-hydroxyl propionic acid) were not found in the liquid and vapor phases by GC and liquid chromatography (LC). Due to its negligible vapor pressure, the IL content was gravimetrically determined by the mass difference after vaporizing the volatile components from a known mass of sample until constant mass. Each experiment was replicated at least three times, and the standard uncertainty of the mole composition is 0.001.

3. Results and discussion

3.1 Experimental data

The VLE data for ternary systems of acetone (1) and methanol (2) containing [MIM]Ac (3), [MIM]HPr (3) and [MIM]Pr (3) were measured at 101.3kPa to examine the separation effects of ILs on acetone and methanol mixture. The mole fractions of ILs were kept nearly constant in series of 0.060, 0.080 and 0.100 in the liquid phase. The VLE data are listed in Tables 2-4, where T presents the equilibrium temperature, x_i and y_i are mole fractions of component i in the liquid and vapor phase, respectively. x_1' presents the mole fraction of acetone in the liquid phase expressed on an IL-free basis, γ_i is the activity coefficient of component i, α_{12} is the relative volatility of acetone to methanol.

Since the VLE data are measured at low total pressure of 101.3KPa, the assumption of ideal vapor-phase can be made. The equation (1) is simply written as follows:

$$y_i P = x_i \gamma_i P_i^\circ \quad (1)$$

Where P is the total pressure, and P_i° is the saturated vapor pressure of component i at VLE temperature, which is calculated by Antoine equation (2). The Antoine equation is described as follows:

$$\log P_i^\circ = A - \frac{B}{T + C} \quad (2)$$

Where A, B and C are the Antoine parameters taken from previous literature [23]. The Antoine parameters are presented in Table 5. The relative volatility α_{12} is calculated by the following equation (3).

$$\alpha_{12} = \frac{y_1/x_1}{y_2/x_2} = \frac{\gamma_1}{\gamma_2} \times \frac{P_1^\circ}{P_2^\circ} \quad (3)$$

Table.2. Vapor-Liquid Equilibrium Data of the Ternary System Acetone (1) + Methanol (2) + [MIM]Ac (3) at 101.3kPa

T/K	x ₃	x ₂	x ₁ '	y ₁	γ ₁	γ ₂	α ₁₂	T/K	x ₃	x ₂	x ₁ '	y ₁	γ ₁	γ ₂	α ₁₂
337.84	0.061	0.888	0.054	0.129	1.912	0.977	2.567	331.34	0.079	0.417	0.547	0.671	1.247	1.018	1.684
336.34	0.059	0.841	0.106	0.226	1.797	0.973	2.451	331.16	0.081	0.364	0.604	0.708	1.203	1.042	1.591
335.03	0.058	0.790	0.161	0.311	1.698	0.971	2.34	331.04	0.082	0.317	0.655	0.743	1.171	1.058	1.526
334.07	0.062	0.741	0.210	0.374	1.629	0.977	2.248	330.93	0.083	0.271	0.704	0.773	1.134	1.096	1.426
333.12	0.057	0.697	0.261	0.431	1.548	0.982	2.142	330.93	0.081	0.216	0.765	0.815	1.101	1.118	1.357
332.49	0.061	0.644	0.314	0.482	1.474	0.992	2.027	331.01	0.080	0.169	0.816	0.851	1.071	1.148	1.285
331.77	0.062	0.585	0.376	0.536	1.405	1.006	1.914	331.21	0.079	0.115	0.875	0.894	1.042	1.195	1.200
331.39	0.060	0.539	0.427	0.574	1.339	1.018	1.807	331.72	0.081	0.022	0.976	0.977	1.005	1.328	1.037
331.02	0.061	0.484	0.485	0.616	1.283	1.036	1.707	339.58	0.098	0.851	0.057	0.141	1.973	0.935	2.734
330.73	0.062	0.434	0.537	0.651	1.237	1.063	1.608	337.77	0.101	0.799	0.111	0.247	1.872	0.936	2.625
330.50	0.059	0.386	0.590	0.686	1.190	1.083	1.519	336.26	0.102	0.746	0.169	0.338	1.764	0.936	2.500
330.31	0.060	0.339	0.639	0.720	1.159	1.110	1.447	335.12	0.097	0.706	0.218	0.405	1.693	0.929	2.436
330.25	0.062	0.292	0.689	0.754	1.132	1.136	1.382	334.16	0.102	0.652	0.274	0.464	1.605	0.942	2.294
330.19	0.068	0.229	0.754	0.792	1.096	1.223	1.243	333.45	0.101	0.604	0.328	0.517	1.527	0.942	2.193
330.22	0.061	0.188	0.800	0.831	1.075	1.210	1.231	332.83	0.099	0.548	0.392	0.571	1.440	0.946	2.070
330.41	0.062	0.132	0.859	0.873	1.046	1.286	1.126	332.49	0.098	0.501	0.445	0.612	1.376	0.954	1.967
330.94	0.059	0.044	0.953	0.955	1.010	1.328	1.048	332.08	0.101	0.444	0.506	0.655	1.317	0.972	1.853
338.71	0.082	0.867	0.056	0.134	1.941	0.960	2.637	331.80	0.099	0.397	0.559	0.691	1.266	0.985	1.761
337.14	0.078	0.822	0.108	0.236	1.831	0.950	2.542	331.59	0.102	0.343	0.618	0.729	1.220	1.007	1.662
335.69	0.081	0.767	0.165	0.325	1.738	0.953	2.431	331.54	0.099	0.300	0.667	0.760	1.178	1.021	1.584
334.73	0.080	0.723	0.214	0.387	1.650	0.954	2.321	331.51	0.102	0.252	0.719	0.794	1.144	1.046	1.501
333.79	0.079	0.675	0.267	0.446	1.569	0.958	2.213	331.53	0.101	0.196	0.782	0.836	1.105	1.066	1.423
333.11	0.082	0.623	0.321	0.499	1.500	0.968	2.103	331.71	0.104	0.145	0.838	0.872	1.072	1.120	1.312
332.46	0.081	0.566	0.384	0.554	1.420	0.974	1.990	332.07	0.099	0.095	0.895	0.915	1.035	1.121	1.262
331.99	0.082	0.517	0.437	0.596	1.365	0.985	1.898	332.74	0.102	0.001	0.999	0.999	0.994	1.214	1.114
331.58	0.083	0.462	0.496	0.635	1.300	1.009	1.769								

Standard uncertainty u (x₁) = u (y₁) = 0.001, u (T) = 0.01K

Table.3. Vapor-Liquid Equilibrium Data of the Ternary System Acetone (1) + Methanol (2) + [MIM] **HPr (3) at 101.3kPa**

T/K	x ₃	x ₂	x ₁ '	y ₁	γ ₁	γ ₂	α ₁₂	T/K	x ₃	x ₂	x ₁ '	y ₁	γ ₁	γ ₂	α ₁₂
337.79	0.061	0.888	0.054	0.131	1.942	0.976	2.613	331.25	0.079	0.417	0.547	0.670	1.251	1.023	1.681
336.28	0.059	0.841	0.106	0.228	1.813	0.971	2.477	331.09	0.081	0.364	0.604	0.707	1.204	1.049	1.582
334.89	0.058	0.790	0.161	0.313	1.720	0.974	2.368	330.91	0.082	0.317	0.655	0.740	1.169	1.074	1.500
333.93	0.062	0.741	0.210	0.372	1.625	0.985	2.226	330.90	0.080	0.274	0.702	0.771	1.134	1.096	1.427
333.13	0.059	0.695	0.261	0.432	1.554	0.981	2.150	330.85	0.081	0.216	0.765	0.813	1.100	1.134	1.338
332.36	0.061	0.644	0.314	0.483	1.488	0.994	2.043	330.93	0.080	0.169	0.816	0.849	1.072	1.173	1.260
331.72	0.062	0.585	0.376	0.537	1.411	1.006	1.923	331.10	0.079	0.115	0.875	0.892	1.041	1.220	1.175
331.39	0.057	0.542	0.425	0.574	1.343	1.013	1.823	331.70	0.081	0.022	0.976	0.976	1.006	1.372	1.006
330.89	0.061	0.484	0.485	0.617	1.290	1.041	1.710	339.39	0.098	0.851	0.057	0.144	1.909	0.942	2.800
330.63	0.058	0.438	0.535	0.649	1.237	1.064	1.608	337.78	0.101	0.799	0.111	0.251	1.793	0.935	2.682
330.48	0.059	0.386	0.590	0.685	1.191	1.089	1.514	336.27	0.103	0.745	0.169	0.342	1.720	0.936	2.544
330.34	0.061	0.338	0.640	0.718	1.158	1.119	1.434	335.15	0.102	0.701	0.219	0.409	1.621	0.935	2.461
330.21	0.062	0.292	0.689	0.752	1.131	1.144	1.371	334.22	0.097	0.657	0.272	0.467	1.541	0.933	2.341
330.20	0.063	0.234	0.750	0.791	1.094	1.206	1.257	333.53	0.101	0.604	0.328	0.521	1.451	0.937	2.226
330.28	0.061	0.188	0.800	0.828	1.070	1.231	1.205	332.86	0.102	0.545	0.393	0.574	1.384	0.950	2.079
330.47	0.062	0.132	0.859	0.871	1.041	1.303	1.106	332.39	0.099	0.500	0.445	0.612	1.318	0.959	1.969
331.02	0.061	0.042	0.955	0.954	1.006	1.417	0.978	332.05	0.101	0.444	0.506	0.655	1.257	0.973	1.853
338.67	0.078	0.871	0.055	0.136	1.975	0.955	2.697	331.84	0.099	0.397	0.559	0.687	1.217	0.995	1.731
336.89	0.080	0.820	0.109	0.240	1.874	0.959	2.582	331.64	0.101	0.344	0.617	0.728	1.182	1.009	1.655
335.53	0.081	0.767	0.165	0.328	1.764	0.954	2.465	331.47	0.099	0.300	0.667	0.762	1.143	1.016	1.597
334.48	0.083	0.72	0.215	0.391	1.677	0.962	2.345	331.42	0.102	0.252	0.719	0.791	1.107	1.061	1.480
333.73	0.079	0.675	0.267	0.451	1.588	0.953	2.251	331.48	0.101	0.196	0.782	0.834	1.078	1.085	1.401
333.00	0.082	0.623	0.321	0.501	1.508	0.967	2.119	331.52	0.100	0.149	0.834	0.870	1.049	1.112	1.331
332.39	0.081	0.566	0.384	0.555	1.425	0.974	1.997	331.61	0.099	0.095	0.895	0.913	1.021	1.171	1.229
331.93	0.082	0.517	0.437	0.596	1.369	0.985	1.904	331.90	0.102	0.001	0.999	0.999	1.015	1.255	1.114
331.49	0.078	0.467	0.493	0.636	1.303	1.000	1.791								

Standard uncertainty u (x₁) = u (y₁) = 0.001, u (T) = 0.01K

Table.4. Vapor-Liquid Equilibrium Data of the Ternary System Acetone (1) + Methanol (2) + [MIM]Pr (3) at 101.3kPa

T/K	x ₃	x ₂	x ₁ '	y ₁	γ ₁	γ ₂	α ₁₂	T/K	x ₃	x ₂	x ₁ '	y ₁	γ ₁	γ ₂	α ₁₂
337.69	0.061	0.888	0.054	0.126	1.885	0.986	2.512	331.24	0.079	0.416	0.548	0.659	1.228	1.061	1.592
336.15	0.059	0.838	0.109	0.227	1.764	0.984	2.382	331.04	0.078	0.367	0.602	0.696	1.188	1.081	1.515
334.79	0.061	0.787	0.162	0.305	1.680	0.991	2.274	330.97	0.082	0.316	0.656	0.732	1.154	1.111	1.432
333.89	0.062	0.741	0.210	0.367	1.606	0.994	2.182	330.84	0.084	0.268	0.707	0.763	1.121	1.161	1.331
333.12	0.063	0.691	0.263	0.423	1.521	1.005	2.055	330.92	0.081	0.216	0.765	0.805	1.086	1.183	1.267
332.39	0.061	0.644	0.314	0.473	1.454	1.012	1.961	331.04	0.082	0.166	0.819	0.842	1.058	1.237	1.178
331.73	0.062	0.585	0.376	0.527	1.383	1.028	1.844	331.31	0.079	0.115	0.875	0.888	1.032	1.254	1.131
331.32	0.058	0.540	0.427	0.565	1.318	1.040	1.743	332.02	0.080	0.023	0.975	0.975	0.994	1.364	0.996
330.90	0.061	0.483	0.486	0.607	1.267	1.068	1.636	339.00	0.098	0.851	0.057	0.137	1.968	0.964	2.658
330.66	0.057	0.438	0.536	0.642	1.219	1.085	1.553	337.39	0.101	0.796	0.115	0.247	1.846	0.958	2.536
330.38	0.059	0.386	0.590	0.676	1.177	1.123	1.452	336.01	0.103	0.745	0.169	0.331	1.752	0.961	2.424
330.19	0.057	0.341	0.638	0.710	1.147	1.147	1.386	334.93	0.102	0.701	0.219	0.395	1.674	0.964	2.327
330.09	0.062	0.290	0.691	0.745	1.122	1.191	1.307	334.13	0.097	0.657	0.272	0.453	1.578	0.961	2.214
330.01	0.059	0.238	0.747	0.783	1.090	1.239	1.221	333.43	0.101	0.604	0.328	0.506	1.503	0.973	2.093
330.04	0.061	0.187	0.801	0.822	1.069	1.292	1.148	332.73	0.103	0.544	0.394	0.559	1.419	0.991	1.951
330.24	0.056	0.138	0.854	0.866	1.043	1.309	1.105	332.38	0.099	0.499	0.446	0.599	1.352	0.995	1.855
331.01	0.064	0.039	0.958	0.952	1.004	1.593	0.868	331.99	0.104	0.440	0.509	0.643	1.295	1.022	1.735
338.25	0.077	0.872	0.055	0.131	1.925	0.976	2.580	331.62	0.099	0.396	0.560	0.678	1.247	1.036	1.651
336.59	0.080	0.817	0.112	0.237	1.813	0.976	2.460	331.45	0.096	0.349	0.614	0.715	1.204	1.047	1.579
335.43	0.081	0.767	0.165	0.318	1.715	0.973	2.354	331.32	0.099	0.299	0.668	0.748	1.166	1.088	1.473
334.49	0.078	0.725	0.214	0.380	1.630	0.974	2.251	331.23	0.095	0.257	0.716	0.783	1.135	1.090	1.433
333.58	0.079	0.675	0.267	0.436	1.546	0.985	2.125	331.25	0.101	0.196	0.782	0.825	1.101	1.151	1.315
332.95	0.083	0.622	0.322	0.488	1.473	0.996	2.010	331.31	0.100	0.148	0.836	0.863	1.074	1.189	1.242
332.28	0.081	0.566	0.384	0.543	1.399	1.003	1.905	331.52	0.099	0.095	0.895	0.908	1.047	1.239	1.161
331.87	0.082	0.516	0.438	0.584	1.340	1.019	1.802	332.06	0.102	0.001	0.999	0.999	1.016	1.397	0.994
331.48	0.083	0.461	0.497	0.624	1.280	1.048	1.678								

Standard uncertainty $u(x_1) = u(y_1) = 0.001$, $u(T) = 0.01\text{K}$

Table.5. Antoine's Parameter for Pure Components

component	A	B	C
acetone	6.3565	1277.0	-35.920
methanol	7.0224	1474.1	-44.020

Parameter obtained from ref 23

Table.6. Binary Energy Parameters and Average Relative Deviations

component <i>i</i>	component <i>i</i>	$\alpha_{i,j}$	$\Delta g_{i,j}/(\text{J/mol})$	$\Delta g_{j,i}/(\text{J/mol})$	ARD
acetone	methanol	0.300	924.200	863.10	1.6%
acetone	[MIM]Ac	0.100	-3408.740	1829.08	0.6%
methanol	[MIM]Ac	0.680	-3533.450	-3325.60	
acetone	[MIM]HPr	0.100	-3491.880	3325.60	0.2%
methanol	[MIM]HPr	0.520	-2494.200	-3658.16	
acetone	[MIM]Pr	0.220	-6958.818	4157.00	0.7%
methanol	[MIM]Pr	0.690	-3325.600	-4073.86	

$$\Delta g_{i,j}=g_{i,j}-g_{j,i}, \tau_{ij}=(g_{i,j}-g_{j,i})/RT$$

3.2 Correlation of the phase equilibrium

In this work, the VLE data have been correlated by using the nonrandom two-liquid (NRTL) model, and regressed through minimizing the average relative deviations (ARD) function in the following equation (4) by levenberg-Marquardt method. There are six binary energy parameters and three nonrandom factors in the model. The nine parameters are obtained from the ternary VLE data in tables 2-4.

$$ARD(\%) = \frac{1}{n} \sum_n \sum_i \left| \frac{y_i^{\text{exptl}} - y_i^{\text{calcd}}}{y_i^{\text{exptl}}} \right| \times 100 \quad (4)$$

Where *n* denotes the number of experiment points, *y_i* is mole fraction of solvent *i* in the vapor phase, and the superscripts "exptl" and "calcd" represent experimental and calculated values, respectively. The binary interaction parameters and the average relative deviations (ARD) are shown in Table 6, and the experimental values and the correlated diagrams are drawn in Figs 1-15. As can be seen, the experimental values are **quite well** correlated by the NRTL model.

Figs 1-6 show the **y₁-x₁' diagrams** and the T-x₁'-y₁ diagrams for acetone (1) + methanol (2) + [MIM]Ac (3), [MIM]HPr (3) **or** [MIM]Pr (3) ternary systems on an IL-free basis, respectively. It can be seen that the addition of an IL makes the mole fraction of acetone in the vapor phase **increased**, and this effect is more notable with the increase of the content of the IL. The addition of an IL shifts upward the azeotropic point of acetone and methanol, and the azeotropy can be totally eliminated **by increasing** the mole fraction of the IL to a specific value. According to the NRTL model, the minimum mole contents of [MIM]Ac, [MIM]HPr and [MIM]Pr needed to eliminate the azeotropy are 0.067, 0.074 and 0.089, respectively. Therefore, [MIM]Ac has more remarkable azeotropy breaking capacity for acetone + methanol system than [MIM]HPr and [MIM]Pr. The VLE temperature also increases with the addition of an IL.

Fig.1. y - x' diagrams for acetone (1) + methanol (2) + [MIM]Ac (3) system in x - y diagram at 101.3kPa; dotted line, IL-free system; ■, $x_3=0.06$; ○, $x_3=0.08$; ▲, $x_3=0.1$; solid line, correlated using NRTL model.

Fig.2. y - x' diagrams for acetone (1) + methanol (2) + [MIM]HPr (3) system in x - y diagram at 101.3kPa; dotted line, IL-free system; ■, $x_3=0.06$; ○, $x_3=0.08$; ▲, $x_3=0.1$; solid line, correlated using NRTL model.

Fig.3. y - x' diagrams for acetone (1) + methanol (2) + [MIM]Pr (3) system in x - y diagram at 101.3kPa; dotted line, IL-free system; ■, $x_3=0.06$; ○, $x_3=0.08$; ▲, $x_3=0.1$; solid line, correlated using NRTL model.

Fig.4. T - x'_1 - y_1 diagrams for the ternary system of acetone (1) + methanol (2) + [MIM]Ac (3) at 101.3 kPa: dotted line, IL-free system; ▲, x'_1 ($x_3 = 0.06$); △, y_1 ($x_3 = 0.06$); ■, x'_1 ($x_3 = 0.08$); □, y_1 ($x_3 = 0.08$); ▼, x'_1 ($x_3 = 0.1$); ▽, y_1 ($x_3 = 0.1$); solid line, correlated using NRTL model.

Fig.5. T-x'-y₁ diagrams for the ternary system of acetone (1) + methanol (2) + [MIM]**HPr** (3) at 101.3 kPa: dotted line, IL-free system; ▲, x'₁ (x₃ = 0.06); △, y₁ (x₃ = 0.06); ■, x'₁ (x₃ = 0.08); □, y₁ (x₃ = 0.08); ▼, x'₁ (x₃ = 0.1); ▽, y₁ (x₃ = 0.1); solid line, correlated using NRTL model.

Fig.6. T-x'-y₁ diagrams for the ternary system of acetone (1) + methanol (2) + [MIM]**Pr** (3) at 101.3 kPa: dotted line, IL-free system; ▲, x'₁ (x₃ = 0.06); △, y₁ (x₃ = 0.06); ■, x'₁ (x₃ = 0.08); □, y₁ (x₃ = 0.08); ▼, x'₁ (x₃ = 0.1); ▽, y₁ (x₃ = 0.1); solid line, correlated using NRTL model.

Fig.7. Separation factor of acetone (1) to methanol (2) at different mole fraction of [MIM]Ac at 101.3kPa: dotted line, IL-free system; ■, $x_3=0.06$; ○, $x_3=0.08$; ▲, $x_3=0.1$; solid line, correlated using the NRTL model.

Fig.8. Separation factor of acetone (1) to methanol (2) at different mole fraction of [MIM] **HPr** at 101.3kPa: dotted line, IL-free system; ■, $x_3=0.06$; ○, $x_3=0.08$; ▲, $x_3=0.1$; solid line, correlated using the NRTL model.

Fig.9. Separation factor of acetone (1) to methanol (2) at different mole fraction of [MIM]Pr at 101.3kPa: dotted line, IL- free system; ■, $x_3=0.06$; ○, $x_3=0.08$; ▲, $x_3=0.1$; solid line, correlated using the NRTL model.

As the separation ability of an entrainer can be expressed by the relative volatility, the relative volatilities of acetone to methanol for the ternary systems containing ILs ([MIM]Ac, [MIM]HPr or [MIM]Pr) are calculated and drawn in Figs 7-9. The relative volatility significantly increases with the addition of an IL. The more ILs are, the larger the relative volatility, consequently the easier the separation. The values of relative volatility are higher than 1 on the whole studied concentration range when the mole fractions of the three ILs are 0.1. The above results are consistent with the previous conclusions. It is worth noting that α_{12} produced by [MIM]HPr is obviously greater than that produced by [MIM]Ac at areas of higher methanol content. The complex effects of the two ILs on the mixture of acetone and methanol will be discussed in the later chapters.

The activity coefficients of acetone (γ_1) and methanol (γ_2) in the ternary systems with different mole fractions of ILs are plotted in Figs 10-15 to verify the effects of ILs on the solution non-ideality. It can be seen that γ_1 increase while γ_2 decrease with the increase of IL. This kind of change illustrates that ILs have repulsive forces to acetone and attractive forces to methanol, pushing acetone to the vapor phase, thus enhancing the relative volatility of acetone to methanol.

Fig.10. Activity coefficient of acetone γ_1 in relation with the mole fraction of acetone on an IL-free basis for the mixtures containing [MIM]Ac at 101.3kPa: dotted line, IL-free system; ■, $x_3=0.06$; ○, $x_3=0.08$; ▲, $x_3=0.1$; solid line, correlated using NRTL model.

Fig.11. Activity coefficient of acetone γ_1 in relation with the mole fraction of acetone on an IL-free basis for the mixtures containing [MIM]HPr at 101.3kPa: dotted line, IL-free system; ■, $x_3=0.06$; ○, $x_3=0.08$; ▲, $x_3=0.1$; solid line, correlated using NRTL model.

Fig.12. Activity coefficient of acetone γ_1 in relation with the mole fraction of acetone on an IL-free basis for the mixtures containing [MIM]Pr at 101.3kPa: dotted line, IL-free system; ■, $x_3=0.06$; ○, $x_3=0.08$; ▲, $x_3=0.1$; solid line, correlated using NRTL model.

Fig.13. Activity coefficient of methanol γ_2 in relation with the mole fraction of acetone on an IL-free basis for the mixtures containing [MIM]Ac at 101.3kPa: dotted line, IL-free system; ■, $x_3=0.06$; ○, $x_3=0.08$; ▲, $x_3=0.1$; solid line, correlated using NRTL model.

Fig.14. Activity coefficient of methanol γ_2 in relation with the mole fraction of acetone on an IL-free basis for the mixtures containing [MIM]**HPr** at 101.3kPa: dotted line, IL-free system; ■, $x_3=0.06$; ○, $x_3=0.08$; ▲, $x_3=0.1$; solid line, correlated using NRTL model.

Fig.15. Activity coefficient of methanol γ_2 in relation with the mole fraction of acetone on an IL-free basis for the mixtures containing [MIM]**Pr** at 101.3kPa: dotted line, IL-free system; ■, $x_3=0.06$; ○, $x_3=0.08$; ▲, $x_3=0.1$; solid line, correlated using NRTL model.

The separation abilities of the three ILs for acetone and methanol should be attributed to the different intensities of the hydrogen bonds between them. The azeotropic phenomenon of methanol-acetone system is mainly due to the hydrogen bond between the hydroxyl group of methanol and the carbonyl group of acetone. The anions and imidazole rings of the three ILs can also form hydrogen bonds with hydroxyl group of methanol as hydrogen bonding acceptor and donator respectively, but the hydrogen bonds are stronger than that between methanol and acetone [22, 23]. Besides, it can be concluded from Figs.10-12 that all the three ILs have repulsive forces to acetone. Hence the addition of ILs can break the hydrogen bond between methanol and acetone. After the content of ILs is increased to a certain value, the azeotropic phenomenon of methanol-acetone system is eliminated.

According to the NRTL model, the separation abilities of the three ILs are $[MIM]Ac > [MIM]HPr > [MIM]Pr$. For $[MIM]Pr$ and $[MIM]Ac$, the hydrophobicity of $[MIM]Pr$ is stronger than that of $[MIM]Ac$ due to the longer alkyl chain length, so $[MIM]Pr$ produces weaker hydrogen bond with methanol than $[MIM]Ac$ [25].

The hydroxyl group of $[MIM]HPr$ can form hydrogen bonds with the hydroxyl group of methanol as hydrogen bonding acceptor and donator, and with the carbonyl group of acetone as hydrogen bonding donator. The hydrogen bond between the hydroxyl group of $[MIM]HPr$ and that of methanol is stronger than that between the hydroxyl group of $[MIM]HPr$ and the carbonyl group of acetone. Hence, the hydroxyl group on $[MIM]HPr$ can enhance the relative volatility of acetone to methanol, leading to the better separation effect of $[MIM]HPr$ than $[MIM]Pr$.

$[MIM]HPr$ and $[MIM]Ac$ show complex effects on mixture of acetone and methanol. At areas of higher methanol content, $[MIM]HPr$ shows the larger relative volatility than $[MIM]Ac$ due to the hydrogen bond between the hydroxyl group of $[MIM]HPr$ and the hydroxyl group of methanol. At areas of higher acetone content, the methanol molecules are surrounded by acetone molecules. The hydrogen bond between the hydroxyl group of $[MIM]HPr$ and the hydroxyl group of methanol is weakened by the hydrogen bond between acetone and $[MIM]HPr$ with the increase of acetone content. As a result of the integrative effect, the minimum mole content of $[MIM]HPr$ needed to eliminate the azeotropy is more than that of $[MIM]Ac$, showing the weaker separation ability than $[MIM]Ac$.

The minimum mole fractions of ILs with inorganic anions to totally break the azeotropy of acetone + methanol system are in the range of 0.022 to 0.079[12, 13, 19-23], so the separation ability of $[MIM]Ac$ is comparable to that of ILs with inorganic anions. In addition, the periods of validity for the three ILs are all more than 9 months by the VLE and liquid chromatography measurements. On the other hand, $[MIM]Ac$ is no pollution and corrosion of inorganic anions, such as BF_4^- , SO_4^{2-} and Cl^- . From this standpoint, $[MIM]Ac$ is a potential entrainer for the separation of acetone and methanol.

4. Conclusions

In this work, the isobaric VLE data for acetone and methanol in the presence of [MIM]Ac, [MIM]Pr or [MIM]HPr were measured. A remarkable salting out effect is produced by the addition of ILs. The VLE data are well correlated using NRTL model. The salting out effects of the three ILs with organic anions are [MIM]Ac > [MIM]HPr > [MIM]Pr. The minimum mole content of [MIM]Ac needed to eliminate the azeotropy is 0.067. The separation ability of [MIM]Ac is comparable to that of ILs with inorganic anions previously reported.

Nomenclature	
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
Δg_{ij}	Binary energy parameter of NRTL model
y_i^{cal}	Mole fraction of solvent i in the vapor phase calculated with the NRTL model
P	Total pressure in the equilibrium system
P_i^o	Saturated vapor pressure of component i at equilibrium temperature
Greek letters	
α_{12}	relative volatility of component 1 to component 2
α_{ij}	non-randomness parameter of NRTL model
γ_i	Activity coefficient of component i
γ_i^{exp}	The activity coefficient of component i measured by experimental data
γ_i^{cal}	The activity coefficient of component i calculated with the NRTL model

Acknowledgments

This work is financially supported by the National Science Foundation of China (Project No. 21576166), Program for Liaoning Excellent Talents in University (LR2012013) and Liaoning Province Science Foundation of China (Project No. 2014020140).

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