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Liquid–liquid equilibria of aqueous biphasic systems of ionic liquids and dipotassium hydrogen phosphate at different temperatures: Experimental study and thermodynamic modeling

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ABSTRACT

The phase diagrams of the {1-butyl-3-methylimidazolium nitrate ([Bmim][NO_3]) / 1-hexyl-3-methylimidazolium nitrate ([Hmim][NO_3]) + dipotassium hydrogen phosphate (K_2HPO_4)}c aqueous biphasic systems (ABS) and the binodal curves of {1-octyl-3-methylimidazolium nitrate ([Omim][NO_3]) + K_2HPO_4} ABS have been determined experimentally at T = (288.15, 298.15, and 308.15) K. The Merchuk equation with three dependent-temperature adjustable parameters was used for reproducing and predicting the binodal curves. The effect of the alkyl chain length of ionic liquids (ILs) was studied. It was found that the two-phase formation in the investigated ABS is decreased with decreasing the alkyl chain length of IL in the order: [Hmim][NO_3] > [Omim][NO_3] > [Bmim][NO_3]. Moreover, the effect of temperature on the binodal curves and tie-lines was also discussed. It was shown that the biphasic region expanded with a decrease in temperature, whereas the absolute value of slope of the tie-lines slightly decreased with an increase in temperature. Finally, the liquid–liquid equilibrium (LLE) data for the studied systems are correlated by using the NRTL thermodynamic model, and good agreement was obtained between the correlation and the experimental data.

1. Introduction

Aqueous biphasic systems (ABS) have been applied as an alternative to conventional extraction methods for the separation and purification of several biological compounds such as amino acids [1,2], proteins [3,4], metallic ions [5], dye molecules [6], small organic species [7,8] and pharmaceutical [9]. These systems, which were usually composed by mixing two or more polymers, a polymer and a salt [10], were for the first time introduced by Albertsson [11] in 1956. ABS compared to traditional liquid–liquid extraction methods, due to the absence of volatile organic compounds (VOCs), are known as an environmentally friendly media [12,13]. In recent years, ionic liquids (ILs) due to their "green" and unique characteristics such as negligible volatility, non-flammability, low melting point, high chemical and thermal stability, excellent solvation for organic and inorganic compounds, and a number of feasible variation in cation and anion specifications [14], have attracted a lot of attention for used in the analytical and separation processes. For the first time, Rogers et al. [15], in 2003, investigated a new kind of ABS, in which the ILs were used as an alternative to polymers in traditional ABS [16]. This new ABS based on IL (IL-based ABS), can be formed by the dissolution of a hydrophilic IL and a kosmotropic salt in water at appropriate concentrations, which formed an upper IL-rich phase and lower salt-rich phase [17]. IL-based ABS combine the advantages of the traditional ABS with IL, such as quick phase separation, little emulsion formation, low viscosity, no need of using VOC, effective extraction, and gentle biocompatible environment [18]. Moreover, these systems have been successfully used to separate amino acids [19,20], proteins [21–23], pharmaceuticals [24–26], and alkaloids [27–29].

Up to now, different types of IL-based ABS have been widely investigated. Sheng et al. [14] studied the phase behavior of ether-functionalized IL 1-(2-methoxyethyl)-3-methylimidazolium bromide ([EOMiM]Br) and salt (K_2CO_3, K_2HPO_4, K_3PO_4) ABS, at T = (288.15, 298.15, and 308.15) K. Han and his coworkers [30] investigated IL-based ABS composed of hydrophilic IL ([$C_n$mim][BF_4], n = 2, 3, 4) and ammonium tartrate at different temperatures. Zafarani-Moattar and Hamzehzadeh [17] reported the liquid–liquid equilibrium (LLE) data of ABS formed by an imidazolium-based IL ([C_4mim]Br) and a salt (K_3PO_4, K_2HPO_4) at T = 298.15 K. They studied the effect of types of salt on the binodal and tie lines; furthermore, the extended NRTL model has been used for the correlation of the tie lines.

The LLE data and phase diagram of ABS with different compositions are necessary for the design and optimization of extraction process and the development of thermodynamic models of ABS. In present study, we examined the inorganic salt dipotassium hydrogen phosphate (K_2HPO_4) as a salting-out agent to form ABS with the hydrophilic nitrate-based ILs. These nitrate-based ILs are halogen free and thus more environment friendly [31]. The binodal curves and the LLE data

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Table 1
The purities and suppliers of the chemicals.

Chemical name	Supplier	Mass fraction purity	Purification method
Dipotassium hydrogen phosphate	Merck	>=0.99	None
[Bmim][NO_3]	Synthesized in lab	>=0.98	None
[Hmim][NO_3]	Synthesized in lab	>=0.98	None
[Omim][NO_3]	Synthesized in lab	>=0.98	None

Table 2
Binodal data for the {[Bmim][NO_3] (1) + K_2HPO_4 (2) } ABS at different temperatures and $P = 101.3$ kPa.[a]

100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
$T = 288.15$ K							
56.72	3.35	27.83	11.16	14.54	18.03	7.25	23.63
54.17	3.68	26.70	11.56	13.81	18.43	7.66	23.39
51.66	4.13	26.22	11.82	13.50	18.66	7.15	23.81
49.45	4.52	25.59	12.11	13.32	18.83	6.92	23.95
48.16	4.79	24.66	12.55	12.77	19.14	6.81	24.19
47.16	5.07	23.78	12.87	12.42	19.34	6.68	24.37
45.82	5.32	23.18	13.25	12.27	19.53	6.46	24.60
44.22	5.66	22.65	13.47	12.02	19.73	6.29	24.76
42.95	6.06	21.97	13.76	11.52	20.03	6.02	25.07
41.57	6.42	21.57	13.95	11.39	20.19	5.83	25.21
40.12	6.82	21.11	14.17	11.07	20.32	5.64	25.44
39.14	7.13	20.69	14.39	10.75	20.64	5.37	25.73
37.73	7.56	20.39	14.67	10.44	20.83	5.19	25.93
36.27	7.99	19.81	14.97	10.25	20.96	5.02	26.17
35.49	8.24	19.25	15.23	10.15	21.14	4.86	26.32
34.83	8.43	18.68	15.58	9.97	21.25	4.69	26.57
33.96	8.76	18.27	15.84	9.60	21.57	4.54	26.76
33.23	8.96	17.57	16.13	9.42	21.73	4.37	26.98
32.53	9.28	17.26	16.35	9.18	21.94	4.17	27.17
31.86	9.47	16.79	16.67	8.82	22.27	4.05	27.35
30.94	9.82	16.35	16.92	8.54	22.53	3.96	27.57
30.11	10.11	16.12	17.10	8.25	22.79	3.82	27.76
29.55	10.29	15.65	17.37	8.19	22.89	3.71	27.96
29.15	10.51	15.23	17.56	7.93	23.08	3.55	28.12
28.65	10.69	14.79	17.80	7.75	23.23		
$T = 298.15$ K							
58.69	3.76	27.28	11.99	14.31	19.04	8.59	23.56
57.48	3.92	26.28	12.33	14.02	19.24	8.34	23.83
55.88	4.18	25.38	12.75	13.75	19.42	8.26	23.92
54.57	4.38	24.62	13.12	13.49	19.59	8.03	24.14
52.76	4.69	23.89	13.50	13.23	19.77	7.81	24.38
50.72	5.06	23.16	13.91	12.98	19.94	7.60	24.62
49.53	5.30	22.54	14.20	12.76	20.07	7.39	24.85
47.58	5.71	21.89	14.57	12.53	20.23	7.09	25.09
46.34	6.03	21.31	14.86	12.30	20.40	7.00	25.32
44.87	6.30	20.74	15.17	12.08	20.56	6.71	25.54
43.67	6.65	20.20	15.47	11.87	20.71	6.55	25.75
41.97	7.05	19.67	15.79	11.66	20.87	6.28	25.96
40.38	7.47	19.27	16.07	11.46	21.04	6.12	26.17
39.31	7.77	18.79	16.36	11.26	21.19	5.95	26.38
38.27	8.06	18.35	16.59	11.07	21.34	5.88	26.58
37.29	8.36	17.91	16.87	10.89	21.48	5.67	26.80
35.98	8.76	17.38	17.13	10.70	21.64	5.32	26.96
34.85	9.13	17.21	17.33	10.53	21.78	5.20	27.11
33.56	9.56	16.73	17.55	10.36	21.92	5.06	27.30
32.46	9.95	16.34	17.81	10.19	22.07	5.07	27.42
31.32	10.37	15.89	18.03	10.03	22.21	4.80	27.65
30.30	10.76	15.65	18.24	9.70	22.52	4.47	27.96
29.52	11.06	15.22	18.46	9.42	22.76		
28.87	11.32	14.91	18.65	9.13	23.02		
28.05	11.66	14.60	18.86	8.85	23.30		
$T = 308.15$ K							
57.67	4.47	31.91	10.90	17.66	17.96	9.89	24.11
55.91	4.76	31.14	11.19	17.43	18.22	9.65	24.35
54.14	5.04	30.32	11.51	16.74	18.55	9.42	24.57
53.14	5.26	29.71	11.76	16.46	18.80	9.18	24.81
51.95	5.43	28.99	12.05	16.08	18.98	8.96	25.05
50.32	5.74	27.99	12.47	15.58	19.33	8.84	25.27
49.46	5.91	27.15	12.81	15.33	19.51	8.55	25.48
48.32	6.15	26.41	13.27	15.01	19.85	8.36	25.70
46.68	6.50	25.90	13.48	14.47	20.15	8.17	25.95
45.61	6.84	24.73	13.96	14.15	20.45	7.88	26.14
44.27	7.06	24.22	14.33	13.63	20.76	7.70	26.37
42.82	7.41	23.64	14.62	13.35	21.01	7.51	26.59
42.16	7.62	22.95	14.93	12.97	21.35	7.31	26.81
41.24	7.83	22.48	15.22	12.80	21.54	7.02	27.11
40.00	8.17	21.90	15.50	12.56	21.80	6.83	27.33
39.06	8.43	21.39	15.86	12.29	21.94	6.68	27.52
38.30	8.75	20.98	16.06	11.93	22.28	6.51	27.74
37.31	9.06	20.48	16.35	11.65	22.46	6.35	27.95
36.36	9.34	20.01	16.62	11.35	22.71	6.21	28.12
35.34	9.59	19.57	16.87	11.04	23.01	6.04	28.35
34.60	9.86	18.96	17.27	10.65	23.32	5.89	28.56
33.60	10.13	18.47	17.54	10.37	23.61		
32.90	10.41	18.03	17.72	10.13	23.88		

w_1, mass fraction of [Bmim][NO_3]. w_2, mass fraction of K_2HPO_4.
[a] Standard uncertainties, u, are $u(T) = \pm 0.01$ K, $u(P) = \pm 0.1$ kPa and $u(w) = 0.001$.

for the {[Bmim][NO_3] / [Hmim][NO_3] + K_2HPO_4} ABS were determined at $T = (288.15, 298.15, \text{and } 308.15)$ K. The effect of temperature on the phase diagrams was also studied. Furthermore, the effect of ILs cation side alkyl chain length (from butyl to octyl) on the binodal curves was investigated. For this purpose, the binodal curves for the {[Omim][NO_3] + K_2HPO_4} ABS were also determined at $T = (288.15, 298.15, \text{and } 308.15)$ K. Based on the experimental data, the binodal curves were correlated using Merchuk equation. Finally, the non-random two liquid (NRTL) equation [32] and asymmetric Pitzer–Debye–Huckel (PDH) equation [33], have been used for the correlation of the LLE data of the studied ABS.

2. Experimental

2.1. Material

The suppliers and purities of chemicals are represented in Table 1. The studied ILs were synthesized in our laboratory according to the procedure in the literature [34–36]. The explanation of the procedure is available in our previous works [37,38]. The structures of the synthesized ILs were checked with nuclear magnetic resonance (NMR) spectroscopy. The purified ILs were dried and degassed for 24 h at 343.15 K under a vacuum, and kept in bottle under argon gas. The water content in the dried ILs was determined by Karl Fischer method. The mass fraction of water was less than 0.006. This water content in the IL was taken into account during the preparation of the aqueous solutions for the treatment of the experimental data. Dipotassium hydrogen phosphate (≥99.0% mass fraction), was supplied by Merck and used without further purification. Double-distilled deionized water was used for the preparation of solutions.

2.2. Apparatus and procedure

A phase diagram includes a binodal curve and tie-lines. The binodal curves were determined visually through the cloud point method [39] at different temperatures and atmospheric pressure. A definite mass of pure IL was weighted into a glass vessel, and a known mass of water was added to obtain a clear mixture. The glass vessel was provided with an external jacket and the water was circulated at constant temperature by using a thermostat bath (Model: FP50-HL, Julabo Co., Germany). The temperature was controlled to within ±0.1 K. A salt solution of known mass fraction was added drop wise to the glass vessel until the mixture became turbid or cloudy. Adding a few drops of water made the mixture clear again, and the above procedure was repeated. The composition of the mixture for each point on the binodal curve