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Phase Behavior for the Aqueous Two-Phase Systems Containing the Ionic Liquid 1-Butyl-3-methylimidazolium Tetrafluoroborate and Kosmotropic Salts

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Liquid−liquid equilibria (LLE) for the aqueous 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF_4) + kosmotropic salt (Na_3PO_4, Na_2CO_3, Na_2SO_4, NaH_2PO_4, NaCl) systems have been determined experimentally at T= 298.15 K and in part at T = (313.15 to 333.15) K. The binodal curves are fitted to an empirical nonlinear expression developed by Merchuk, and the tie lines were described by the Othmer−Tobias and Bancroft equations. Factors affecting the binodal curves such as salts and temperature are also studied. It was found that the salting-out ability of different salts may also be related to the Gibbs energy of hydration of the ions, and the order of salting-out ability of the anions follows the Hofmerister series for the strength of the kosmotropic salts. It was also demonstrated that the two-phase area was expanded with a decrease in temperature. [Bmim]BF_4 could be recovered from aqueous solution using the aqueous two-phase system (ATPS), and the recovery efficiency could reach 98.77 %. The recovery efficiency was influenced by the concentrations of the salts and their Homeister series: Na_3PO_4 > Na_2CO_3 > Na_2SO_4 > NaH_2PO_4 > NaCl. These data are exposed to be useful for the development and design of the extraction process using ILs based on the ATPS. This proposed method also provided an effective route for the recovery of hydrophilic IL from aqueous solutions.

Introduction

Aqueous two-phase systems (ATPSs), introduced in 1956 by Albertsson,[1] have been recognized as an economical and efficient downstream processing method. An ATPS usually composed of two or more polymers, a polymer and a salt,[1−3] or two surfactants (including quaternary ammonium surfactants and anionic surfactants)[4,5] is considered to be environmentally friendly because there is no use of traditional volatile organic solvents in the whole process. ATPSs have been widely used in the separation, concentration, and fractionation of biological solutes and particles such as cells and proteins.[1,6] ATPSs have also been studied for applications including the selective distribution and separation of metal ion species,[7] dyes, drug molecules, small organic species,[8−11] nano- and microsolid particulates,[12,13] and as green reaction media.[14−16] In recent years, room-temperature ionic liquids, as a class of potential green solvents, have found wide application in chemistry and biochemistry including chemical synthesis, biocatalytic transformation, electrochemical device designs, and analytical and separation processes.[17−19] A new type of ATPS based on ionic liquids (ILs) has been investigated since Gutowski and coworkers[20] demonstrated that the addition of potassium phosphate to an aqueous solution of a hydrophilic IL produces ATPSs. These new ATPSs (ILATPSs) have been successfully used to separate testosterone,[21] epitestosterone,[21] opium alkaloids,[22] and bovine serum albumin.[23] The ILATPSs also have been demonstrated for extraction of antibiotics such as penicillin G,[24,25] amoxicillin, and ampicillin.[26]

It is important to design ILATPS for separation and concentration using the phase diagram. Rogers and his co-workers[27] described the phase diagrams for chaotropic salts (imidazolium-, pyridium-, quaternary ammonium-, and phosphonium-based chloride salts) + kosmotropic salts (K_3PO_4, K_2HPO_4, K_2CO_3, KOH, and $(NH_4)_2SO_4$) + water aqueous biphasic systems (ABS). Pei et al.[28] studied the liquid−liquid equilibrium data for imidazolium ionic liquid ([C_4mim]Cl, [C_6mim]Cl, [C_4mim]Br, [C_6mim]Br, [C_8mim]Br, and [C_{10}mim]Br) + salt (KOH, K_2HPO_4, K_2CO_3, and K_3PO_4) ABS at T = 298.15 K and in part at T = (308.15 to 318.15) K. Chen and his coworkers[29] measured the binodal curves and tie line data of [Amim]Cl + salt (K_3PO_4, K_2HPO_4, and K_2CO_3) + water ABS and correlated satisfactorily with the Merchuk equation and Othmer−Tobias and Bancroft equations, respectively. Wu and his co-workers[30,31] reported the phase diagrams for the 1-butyl-3-methylimidazolium tetrafluoroborate ([C4mim]BF_4) + saccharides + water ABS.

1-Butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF_4) is a common and useful IL, and BF_4^- is more chaotropic than Cl^-. Consequently, it seems reasonable to consider [Bmim]BF_4 as a chaotropic IL in this work. On the basis of this, it is not difficult to understand that it is easy to form ATPS for [Bmim]BF_4 when mixed with kosmotropic salt solutions.[31] However, data for the phase diagram and recovery of the [Bmim]BF_4 + salt + water systems have not been reported at present.

In our work, we reported liquid−liquid equilibrium (LLE) data for the aqueous [Bmim]BF_4 + kosmotropic salts (Na_3PO_4, Na_2CO_3, Na_2SO_4, NaH_2PO_4, NaCl) ATPSs. The obtained results are necessary for the design and optimization of extraction processes. The binodal curves were fitted to a three-parameter equation, and the tie lines were described by using the Othmer−Tobias and Bancroft equation. These data provide a possible basis for the prediction of phase composition when such data are not available. In addition, we utilized this ATPS

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Table 1. Binodal Curve Data for the [Bmim]BF_4 (1) + Salt (2) + Water (3) ATPS at 298.15 K

[Bmim]BF_4 + Na_3PO_4		[Bmim]BF_4 + Na_2CO_3		[Bmim]BF_4 + Na_2SO_4		[Bmim]BF_4 + NaH_2PO_4		[Bmim]BF_4 + NaCl	
100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1
0.21	76.75	0.54	67.51	0.69	60.18	0.84	56.96	2.55	72.98
0.26	72.92	0.66	61.65	1.25	48.00	1.48	48.49	2.79	68.36
0.31	68.67	0.74	59.61	1.42	43.61	1.63	47.23	2.82	65.24
0.37	63.01	0.93	53.10	1.69	39.28	1.81	45.07	3.03	63.38
0.39	62.27	1.53	44.22	2.06	35.33	1.98	43.02	3.16	61.25
0.41	60.09	1.67	41.69	2.12	33.51	2.29	40.04	3.97	53.76
0.49	56.04	2.12	35.93	2.63	28.09	2.54	37.64	4.78	48.07
0.66	51.97	2.31	32.92	2.87	26.30	2.80	34.97	5.42	45.01
0.91	47.54	2.76	27.26	5.45	17.45	2.93	33.50	6.54	36.81
1.09	43.37	3.98	22.22	6.47	15.17	3.53	29.16	7.11	33.91
1.28	38.57	4.79	17.81	7.15	13.82	3.79	27.34	8.02	31.51
1.32	37.89	6.01	13.95	7.90	12.57	4.63	24.06	8.63	29.07
1.64	32.86	7.10	11.18	8.55	11.18	5.65	20.25	9.37	27.11
1.81	30.55	8.16	9.38	9.61	9.33	5.95	19.18	9.89	25.43
2.23	26.17	8.77	8.57	13.10	6.92	6.48	18.03		
2.67	23.69	9.97	7.35	18.91	3.95	6.92	17.56		
3.15	20.83	11.00	6.34	22.99	2.43	8.67	14.29		
3.97	17.37	14.02	4.24			11.60	11.85		
		15.42	3.45			14.43	9.47		
		17.08	2.70			17.35	7.73		

for recovery of ILs from aqueous solutions and discussed the factors of the recovery efficiency.

Experimental Section

Material. [Bmim]BF_4 was purchased from Chengjie Chemical Co., Ltd. (Shanghai, China) with a quoted purity of greater 0.99 mass fraction and was used without further purification. Water content in the IL was determined by the use of the Karl Fischer method to be 0.009 mass fraction, which was in good agreement with the value quoted by the suppliers, approximately less than 0.01 mass fraction. $Na_3PO_4 \cdot 12H_2O$, Na_2CO_3, $NaH_2PO_4 \cdot 2H_2O$, Na_2SO_4, and NaCl were analytical grade reagents and purchased from Sinopharm Chemical Reagent Co., Ltd. (Nanjing, China). All other reagents were of analytical grade, and double distilled deionized water was used in the experiments.

Experimental Procedure. The binodal curves were determined by the cloud point method.[1] From the stock, an IL [Bmim]BF_4 solution of known mass fraction was taken into the vessel. A salt solution of known mass fraction was then added dropwise to the vessel until the mixture became turbid or cloudy. The composition of this mixture was noted. Then, water was added dropwise to the vessel to get a clear one-phase system, and the procedure was repeated and so on. The vessel was immersed in a jacketed glass vessel, and the temperature of the system was determined at T = (298.15, 313.15, and 333.15) K to within ± 0.05 K by a DC-2008 water thermostat (Shanghai Hengping Instrument Factory, China). The composition of the mixture for each point on the binodal curve was calculated by mass using an analytical balance (BS124S, Beijing Sartorius Instrument Co., China) with an uncertainty of $\pm\ 1.0 \cdot 10^{-7}$ kg.

Determination of the tie lines included a series of ATPSs formed by mixing appropriate amounts of [Bmim]BF_4, salt, and water in the vessel which were placed in a thermostatted bath. The system was vigorously stirred for at least 1 h, and the phase separation occurred quickly after cessation of the stirring process. However, an 802 centrifuge (Shanghai Surgery Instrument Factory, China) operated at 2000 rpm was still used for a period of 10 min in each test to ensure a complete phase separation. The systems were then placed again into the thermostatted bath. After reaching phase equilibrium, visual estimates of the top and bottom volumes were made. The mass fraction of NaH_2PO_4 and Na_2CO_3 in the top and bottom phases was determined by titration with sodium hydroxide and hydrochloric acid, respectively, using indicators and a pH-3C meter (Shanghai Lida Instrument Plant, China). The standard deviation of the salt mass fraction of the method was ± 0.05 %. The mass fraction of [Bmim]BF_4 in both the top phase and the bottom phase was determined by a UV−vis spectrometer model UV-2450 (Shimadzu Corporation, Japan). The mass fraction of water was then calculated. A mass balance check was made between the initial mass of each component and the amounts in the top and bottom phases on the basis of equilibrium compositions.

The tie line length, TLL, and the slope of the tie line, S, at different compositions and temperatures were also calculated, respectively, using eqs 1 and 2 as follows[15]

$$\text{TLL} = [(w_1^{\text{t}} - w_1^{\text{b}})^2 + (w_2^{\text{t}} - w_2^{\text{b}})^2]^{0.5} \tag{1}$$

$$S = (w_1^{\text{t}} - w_1^{\text{b}})/(w_2^{\text{t}} - w_2^{\text{b}}) \tag{2}$$

where w_1^{t}, w_1^{b}, w_2^{t}, and w_2^{b} represent the equilibrium mass fraction of [Bmim]BF_4 (1) and salt (2) in the top, t, and bottom, b, phases, respectively.

Recovery of [Bmim]BF_4 from Aqueous Solutions. From the stock, IL aqueous solutions of known concentration by weight were taken into the vessel. A salt of known mass fraction was then added and mixed in a vorticity mixture apparatus for 5 min until the salt dissolved thoroughly. After 5 min of centrifuge operated at 2000 rpm, the sample was then placed into the thermostatted bath until the phase separated thoroughly. Finally, the concentration by weight of [Bmim]BF_4 in the top phase was analyzed by a UV−vis spectrometer. The UV detection wavelength was set at 211 nm. The recovery efficiency (100R/%) of [Bmim]BF_4 is calculated as the following expression

$$R = \frac{C_{\text{t}} \times V_{\text{t}}}{C_{\text{aq}} \times V_{\text{aq}}} \tag{3}$$

where C_{t} and C_{aq} are the concentrations by weight ($\text{g} \cdot \text{L}^{-1}$) of [Bmim]$BF_4$ in the top phase of ATPS and the IL aqueous solution and V_{t} and V_{b} are the volumes (L) of the top phase of ATPS and the IL aqueous solution, respectively.

Results and Discussion

Phase Diagram. The binodal curve data for [Bmim]BF_4 (1) + salt (2) (Na_3PO_4, Na_2CO_3, Na_2SO_4, NaH_2PO_4, NaCl)

Table 2. Values of Parameters of Equation 4 for $[Bmim]BF_4$ (1) + Salt (2) + Water (3) at 298.15 K[a]

system	*a*	*b*	*c*	sd
$[Bmim]BF_4 + Na_3PO_4$	118.274	−1.001	$1.180 \cdot 10^{-3}$	1.51
$[Bmim]BF_4 + Na_2CO_3$	110.901	−0.940	$4.451 \cdot 10^{-5}$	1.85
$[Bmim]BF_4 + Na_2SO_4$	132.477	−0.898	$5.566 \cdot 10^{-5}$	2.01
$[Bmim]BF_4 + NaH_2PO_4$	115.942	−0.725	$6.785 \cdot 10^{-5}$	1.65
$[Bmim]BF_4 + NaCl$	205.471	−0.668	$1.638 \cdot 10^{-5}$	1.09

[a] $sd = \{\Sigma_{i=1}^{n} (w_i^{calcd} - w_i^{exptl})^2/n\}^{0.5}$, where *n* is the number of binodal data.

Table 3. Binodal Curve Data for $[Bmim]BF_4$ (1) + Na_2CO_3 (2) + Water (3) ATPS at Different Temperatures

T/K = 313.15		*T*/K = 333.15	
100 w_2	100 w_1	100 w_2	100 w_1
0.54	67.51	1.11	62.70
0.66	61.65	1.16	53.79
0.74	59.61	1.79	47.37
0.93	53.10	2.21	42.11
1.53	44.22	2.58	37.51
1.67	41.69	3.06	33.32
2.12	35.93	3.40	30.15
2.31	32.92	4.21	25.11
2.76	27.26	4.64	22.62
3.98	22.22	5.37	19.67
4.79	17.81	7.01	15.17
6.01	13.95	7.69	13.03
7.10	11.18	8.85	10.97
8.16	9.38	9.94	9.49
8.77	8.57	10.45	8.74
9.97	7.35	11.47	7.49
11.00	6.34	13.35	5.75
14.02	4.24	14.85	4.51
15.42	3.45	16.43	3.55
17.08	2.70	18.10	2.74

Table 4. Binodal Curve Data for $[Bmim]BF_4$ (1) + NaH_2PO_4 (2) + Water (3) ATPS at Different Temperatures

T/K = 313.15		*T*/K = 333.15	
100 w_2	100 w_1	100 w_2	100 w_1
0.85	69.66	1.19	63.12
1.22	60.95	2.97	47.87
1.78	54.64	4.52	41.96
2.46	52.11	5.14	38.24
3.89	40.68	6.28	33.69
4.25	37.71	6.88	32.51
5.51	30.43	8.03	28.16
5.58	29.04	8.32	26.58
6.29	25.46	9.67	24.40
6.58	24.41	10.81	22.02
7.85	20.43	12.76	16.95
10.46	15.41	14.31	14.48
13.12	12.59	15.18	14.12
17.41	8.97	16.58	11.93
20.12	7.30	17.32	10.98
		19.42	10.00
		18.72	9.66
		20.16	9.18

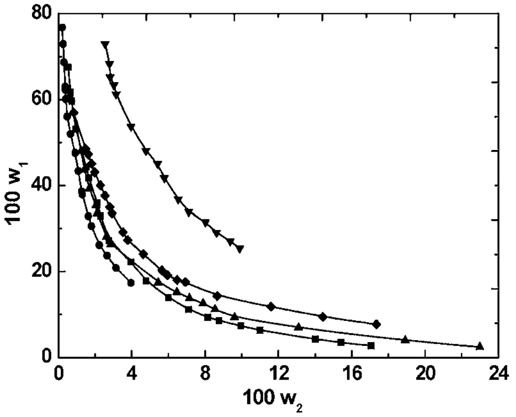

Figure 1. Binodal curves of $[Bmim]BF_4$ (1) + salt (2) ATPS at *T* = 298.15 K: ▼, NaCl; ◆, NaH2PO4; ▲, Na2SO4; ■, Na_2CO_3; ●, Na_3PO_4.

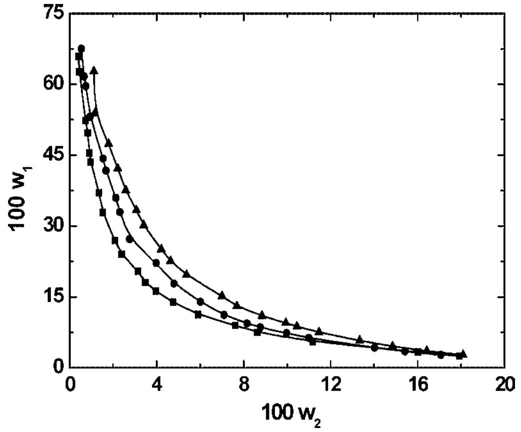

Figure 2. Effect of temperature on binodal curves of $[Bmim]BF_4$ (1) + Na_2CO_3 (2) ATPS: ▲, 333.15 K; ●, 313.15 K; ■, 298.15 K.

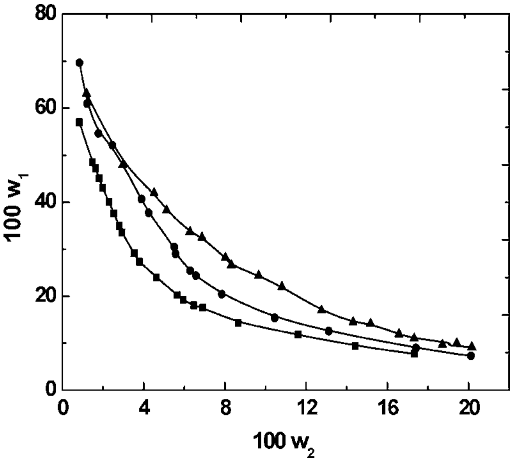

Figure 3. Effect of temperature on binodal curves of $[Bmim]BF_4$ (1) + NaH_2PO_4 (2) ATPS: ▲, 333.15 K; ●, 313.15 K; ■, 298.15 K.

+ water (3) ATPSs are given in Tables 1, 2, 3, and 4. The binodal curves for the various $[Bmim]BF_4$ + salt + water systems at different temperature are represented in Figures 1, 2, and 3. The data were fitted according to the empirical nonlinear expression developed by Merchuk[32]

$$w_1 = a \exp(bw_2^{0.5} - cw_2^3) \tag{4}$$

where w_1 and w_2 are the mass fractions of $[Bmim]BF_4$ and salt, respectively. The parameters for this equation were determined by least-squares regression of the cloud point data. Recently, the above equation has been successfully used for the correlation of binodal data of some aqueous PEG−salt[33,34] and IL−salt[28−31] ATPSs. Using eq 4, the coefficients *a*, *b*, and *c* obtained from the correlation of experimental binodal data along with the corresponding standard deviations (sd) are given in Tables 2 and 5. On the basis of the obtained standard deviations, we concluded that eq 4 can be satisfactorily used to correlate the binodal curves of the investigated systems.

Tie line compositions and average slopes (*S*) are listed in Table 6 and Figure 4. The tie line compositions are used for correlation by the Othmer−Tobias eq 5 and Bancroft eq 6

$$\left(\frac{1-w_1^{\mathrm{t}}}{w_1^{\mathrm{t}}}\right) = K\left(\frac{1-w_2^{\mathrm{b}}}{w_2^{\mathrm{b}}}\right)^n \qquad (5)$$

$$\left(\frac{w_3^{\mathrm{b}}}{w_2^{\mathrm{b}}}\right) = K_1\left(\frac{w_3^{\mathrm{t}}}{w_1^{\mathrm{t}}}\right)^r \qquad (6)$$

where w_1^{t} is the mass fraction of ILs in the top phase; w_2^{b} is the mass fraction of salt in the bottom phase; w_3^{b} and w_3^{t} are the mass fractions of water in the bottom and top phases, respectively; and K, n, K_1, and r are the fit parameters.

Recently, eqs 5 and 6 have been successfully used for the correlation of the tie line compositions of the imidazolium ionic liquids + salt or sucrose + water ATPSs.[18,30] A linear dependency of the plots $\log[(1-w_1^{\mathrm{t}})/w_1^{\mathrm{t}}]$ against $\log[(1-w_2^{\mathrm{b}})/w_2^{\mathrm{b}}]$ and $\log(w_3^{\mathrm{b}}/w_2^{\mathrm{b}})$ against $\log(w_3^{\mathrm{t}}/w_1^{\mathrm{t}})$ indicated an acceptable consistency of the results. The values of the parameters K, n, K_1, and r of equations with the corresponding correlation coefficient values (R) and standard deviations (δ) are given in Table 7, and it is indicated that eqs 5 and 6 can be satisfactorily used to correlate the tie line data of the investigated systems.

Effect of Salts on Binodal Curves. The binodal data determined at 298.15 K for the salts (Na_3PO_4, Na_2CO_3, Na_2SO_4, NaH_2PO_4, and NaCl) + $[Bmim]BF_4$ ILATPSs are shown in Table 1 and Figure 1. The phase diagram provides information about the concentration of phase-forming components required to form two phases; the concentration of phase components in the top and bottom phases; and the ratio of phase volumes. Figure 1 shows that ILATPS can be formed by adding an appropriate amount of salts to an aqueous solution of $[Bmim]BF_4$. As can be seen, the ability of the salts studied for phase separation follows the order: $Na_3PO_4 > Na_2CO_3 > Na_2SO_4 > NaH_2PO_4 >$ NaCl. The kosmotropic ions, PO_4^{3-}, CO_3^{2-}, SO_4^{2-}, $H_2PO_4^-$, and Cl^-, which exhibit stronger interaction with water molecules, are beneficial to the ILATPS formation. This implies that anions with a higher valence are better salting-out agents than those with a lower valence because the higher valence anion hydrates more water molecules than the lower valence anion, thus decreasing the amount of water available to hydrate the ILs. The salting-out ability may also be related to the Gibbs energy of hydration of the ions. Considering the fact that these salts share a common cation but contain different anions, it is easy to see that the salting-out ability of the anions follows the order: PO_4^{3-} ($\Delta G_{\mathrm{hyd}} = -2765\ \mathrm{kJ\cdot mol^{-1}}$) > CO_3^{2-} ($\Delta G_{\mathrm{hyd}} = -1315\ \mathrm{kJ\cdot mol^{-1}}$) > HPO_4^{2-} ($\Delta G_{\mathrm{hyd}} = -1125\ \mathrm{kJ\cdot mol^{-1}}$) > Cl^- ($\Delta G_{\mathrm{hyd}} = -340\ \mathrm{kJ\cdot mol^{-1}}$).[35,36] This order follows the Hofmeister series for the strength of the kosmotropic salts.

Table 5. Values of Parameters of Equation [4] for $[Bmim]BF_4$ (1) + Salt (2) + Water (3) at Different Temperatures

system	T/K	a	b	c	sd
$[Bmim]BF_4$ + Na_2CO_3	313.15	131.426	−0.911	$-1.981\cdot 10^{-5}$	0.831
	333.15	146.090	−0.853	$-5.763\cdot 10^{-5}$	1.742
$[Bmim]BF_4$ + NaH_2PO_4	313.15	133.615	−0.651	$5.896\cdot 10^{-5}$	2.236
	333.15	118.520	−0.519	$-2.722\cdot 10^{-5}$	3.620

Table 6. Tie Line Data of $[Bmim]BF_4$ (1) + Salt (2) + Water (3) at 298.15 K

	total system		IL-rich phase		salt-rich phase			
ATPS	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	TLL	S
$[Bmim]BF_4$ + Na_2CO_3	10.11	30.78	0.48	68.34	17.80	2.91	67.68	−3.78
	12.01	30.20	0.47	68.67	19.89	2.58	68.88	−3.40
	14.52	31.35	0.44	69.58	24.05	2.25	71.35	−2.85
$[Bmim]BF_4$ + NaH_2PO_4	14.03	34.20	0.50	63.68	27.28	3.30	66.05	−2.25
	16.01	35.18	0.47	64.23	31.31	1.43	69.96	−2.04
	17.40	32.58	0.43	64.98	34.05	0.16	73.02	−1.93

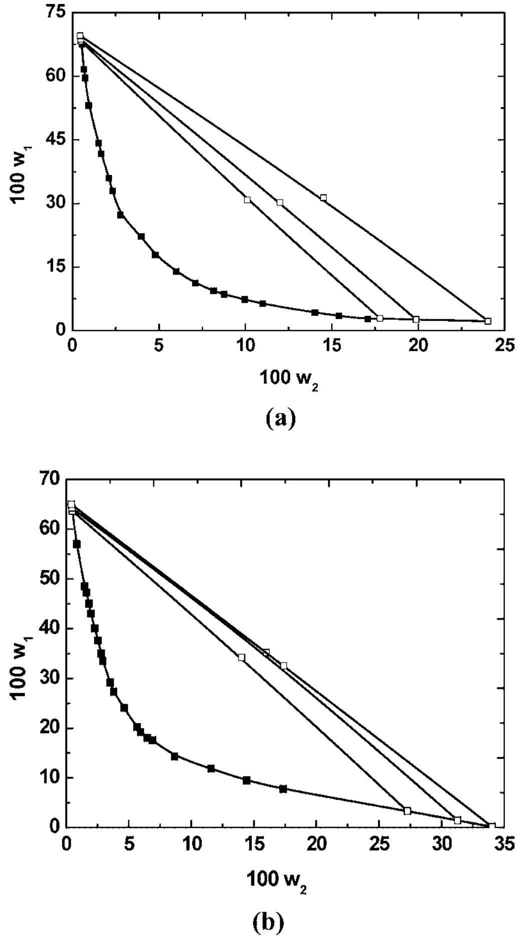

Figure 4. Phase diagram of the $[Bmim]BF_4$ (1) + salt (2) ATPS at 298.15 K: (a) Na_2CO_3; (b) NaH_2PO_4: ■, binodal curve data; □, tie line data.

Table 7. Values of the Parameters of Equations [5] and [6] at 298.15 K[a]

systems	K	n	R	δ	K_1	r	R	δ
$[Bmim]BF_4$ + Na_2CO_3	0.3661	0.1551	0.9944	0.0011	644.5253	6.3539	0.9948	0.0068
$[Bmim]BF_4$ + NaH_2PO_4	0.4829	0.1726	0.9765	0.0022	41.6102	4.8922	0.9752	0.0109

[a] R, corresponding correlation coefficient values; δ, standard deviation.

Effect of Temperature on Binodal Curves. As an example, the effect of temperature on phase separation of $[Bmim]BF_4-Na_2CO_3$ and $[Bmim]BF_4-NaH_2PO_4$ ILATPS was examined at T = (298.15, 313.15, and 333.15) K, respectively. The results are shown in Figures 2 and 3. The locus for the experimental binodals demonstrates that the two-phase area is expanded with a decrease in temperature, which is attributed to the decrease in solubility of IL or the increase in the phase-forming ability in the studied system.[34] This is because the effects of a decrease in temperature on the structure of water is qualitatively similar to that of a kosmotropic (structure-making) ion and therefore can promote the phase-forming ability in the investigated system as a favorable factor for salting-out of IL. A possible reason is that the hydration sheath around the $[Bmim]BF_4$ in the aqueous $[Bmim]BF_4-Na_2CO_3$ and $[Bmim]BF_4-NaH_2PO_4$ ILATPS is more sensitive to temperature because of a decreased kosmotropicity of the CO_3^{2-} and $H_2PO_4^-$ ions.

Recovery of $[Bmim]BF_4$ from Aqueous Solutions. As the environmental impact of IL is still unknown, the removal of IL

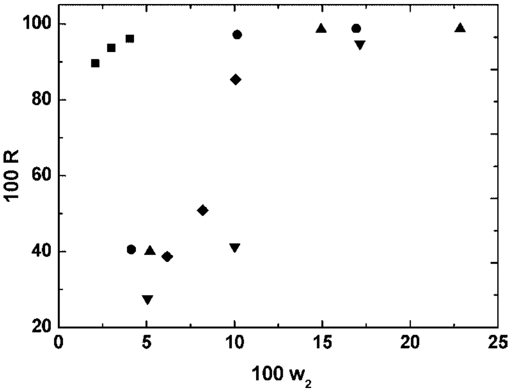

Figure 5. Effect of the mass fraction of salts on the recovery efficiency of $[Bmim]BF_4$: ■, Na_3PO_4; ●, Na_2CO_3; ▲, Na_2SO_4; ▼, NaH_2PO_4; ◆, NaCl.

from aqueous solution is especially important when dealing with wastewater streams. A few years ago, Rogers and his coworkers[20] proposed that ATPS could be utilized to recycle or concentrate hydrophilic ILs from aqueous solution, but there were no data on the example. Wu et al.[30] studied that $[C_4mim]BF_4$ was separated from water by $[C_4mim]BF_4$ + sugar ATPS, and the recovery efficiency was only about 74 %. Chen and his co-workers[29] used [Amim]Cl + salt (K_3PO_4, K_2HPO_4, K_2CO_3) ATPS, and the recovery efficiency could reach 96.80 %.

In our research, we studied recovery of IL from water using $[Bmim]BF_4$ + salt (Na_3PO_4, Na_2CO_3, Na_2SO_4, NaH_2PO_4, and NaCl) ILATPS. The effects of the mass fraction of Na_3PO_4, Na_2CO_3, Na_2SO_4, NaH_2PO_4, and NaCl on the recovery efficiency of $[Bmim]BF_4$ were shown in Figure 5. The recovery efficiency of $[Bmim]BF_4$ was found to increase with the increase of mass fraction of the kosmotropic salts due to the salting-out effect. When the mass fraction of Na_2CO_3 was 0.1694, the recovery efficiency could reach 98.77 %. When a salt is dissolved in an aqueous solution, and combined with water molecules, some hydrophilic ionic liquids separated from the water and formed the IL-rich phase. The results also showed that the different salts have different effects on the recovery of $[Bmim]BF_4$. The results were $Na_3PO_4 > Na_2CO_3 > Na_2SO_4 > NaH_2PO_4 >$ NaCl on the same mass fraction of salts in our investigation, which was related to the Gibbs energy of hydration of the ions, and this order agreed with the Hofmeister series for the strength of the kosmotropic salts. Therefore, the stronger salting-out effect will bring the higher recovery efficiency of ILs.

Conclusions

Liquid−liquid equilibrium data for the aqueous 1-butyl-3-methylimidazolium tetrafluoroborate ($[Bmim]BF_4$) + kosmotropic salt ILATPs were obtained at $T = 298.15$ K and in part at $T = (313.15$ and $333.15)$ K. The experimental binodal data were correlated with the Marchuk equation, and tie lines were described using the Othermer−Tobias and Bancroft equations. The results showed that empirical equations are satisfactory for correlating the investigated systems. The ability of the kosmotropic salts studied for phase separation follows the order: $Na_3PO_4 > Na_2CO_3 > Na_2SO_4 > NaH_2PO_4 >$ NaCl, which can be explained by Gibbs free energy of hydration of anions. The effect of temperature on the phase-forming ability of the studied systems was also explained on the basis of the hydration sheath around the $[Bmim]BF_4$ in the ATPSs which are more sensitive to temperature because of a decreased kosmotropicity of the CO_3^{2-} and $H_2PO_4^-$ ions. It was found that the recovery efficiency could be promoted by the increase of the salting-out strength in the $[Bmim]BF_4$ + salt + water ATPS and could reach 98.77 % in the optimum conditions. This method effectively recovered $[Bmim]BF_4$ from aqueous solution. It will overcome the unknown environmental pollution problems of ionic liquids and promote the industrial application of ILs.

Literature Cited

(1) Albertsson, P. Å. *Partition of Cell Particles and Macromolecules*, 3rd ed.; Wiley: New York, 1986.
(2) Walter, H.; Brooks, D. E.; Fisher, D. *Partitioning in Aqueous Two-Phase Systems: Theory, Methods, Uses, and Applications to Biotechnology*; Academic Press: New York, 1985.
(3) Zaslavsky, B. Y. *Aqueous Two-Phase Partitioning: Physical Chemistry and Bioanalytical Applications*; Marcel Dekker: New York,
1995.
(4) Xiao, J. X.; Sivars, U.; Tjerneld, F. Phase Behavior and Protein Partitioning in Aqueous Two-Phase Systems of Cationic-Anionic Surfactant Mixtures. *J. Chromatogr., B* **2000**, *743*, 327–338.
(5) Yin, H. Q.; Mao, M.; Huang, J. B.; Fu, H. L. Two-Phase Region in the DTAB/SL Mixed Surfactant System. *Langmiur* **2002**, *18*, 9198–9203.
(6) Chen, J.; Ma, G. X.; Li, D. Q. HPCPC Separation of Protein Using Polyethylene Glycol-Potassim Phosphate Aqueous Two-Phase. *Prep. Biochem. Biotechnol.* **1999**, *29*, 371–383.
(7) Rogers, R. D.; Bauer, C. B. Partitioning Behavior of Group 1 and Group 2 Cations in Poly (ethylene glycol)-Based Aqueous Biphasic System. *J. Chromatogr., B* **1996**, *680*, 237–241.
(8) Rogers, R. D.; Zhang, J. New Technologies for Metal Ion Separations Polyethylene Glycol-Based Aqueous Biphasic Systems and Aqueous Biphasic Extraction Chromatography. In *Ion Exchange and Solvent Extraction*; Marinsky, J. A., Marcus Y., Eds.; Marcel Dekker: New York, 1997; Vol. 13, Chapter 4, pp 141−193.
(9) Willauer, H. D.; Huddleston, J. G.; Rogers, R. D. Solvent Properties of Aqueous Biphasic Systems Composed of Polyethylene Glycol and Salt Characterized by the Free Energy of Transfer of a Methylene Group between the Phases and by a Linear Solvation Energy Relationship. *Ind. Eng. Chem. Res.* **2002**, *41*, 2591–2601.
(10) Rogers, R. D.; Willauer, H. D.; Griffin, S. T.; Huddleston, J. G. Partitioning of Small Organic Molecules in Aqueous Biphasic Systems. *J. Chromatogr., B* **1998**, *711*, 255–263.
(11) Willauer, H. D.; Huddleston, J. G.; Rogers, R. D. Solute Partitioning in Aqueous Biphasic System Composed of Polyethylene Glycol and Salt: the Partitioning of Small Neutral Organic Species. *Ind. Eng. Chem. Res.* **2002**, *41*, 1892–1904.
(12) Baxter, S. M.; Sperry, P. R.; Fu, Z. W. Partitioning of Polymer and Inorganic Colloids in Two-Phase Aqueous Polymer Systems. *Langmuir* **1997**, *13*, 3948–3952.
(13) Helfrich, M. R.; El-Kouedi, M.; Etherton, M. R.; Keating, C. D. Partitioning and Assembly of Metal Particles and their Bioconjugates in Aqueous Two-Phase System. *Langmuir* **2005**, *21*, 8478–8486.
(14) Chen, J.; Spear, S. K.; Huddleston, J. G.; Rogers, R. D. Polyethylene Glycol and Solutions of Polyethylene Glycol as Green Reaction Media. *Green Chem.* **2005**, *7*, 64–82.
(15) Chen, J.; Spear, S. K.; Huddleston, J. G.; Holbrey, J. D.; Swatloski, R. P.; Rogers, R. D. Application of Poly(ethylene glycol)-Based Aqueous Biphasic Systems as Reaction and Reactive Extraction Media. *Ind. Eng. Chem. Res.* **2004**, *43*, 5358–5364.
(16) Chen, J.; Spear, S. K.; Huddleston, J. G.; Holbrey, J. D.; Rogers, R. D. Application of Polyethylene Glycol-Based Aqueous Biphasic Reactive Extraction to the Catalytic Oxidation of Cyclic Olefins. *J. Chromatogr., B* **2004**, *807*, 145–149.
(17) Pandey, S. Analytical Applications of Room-Temperature Ionic Liquids: A Review of Recent Efforts. *Anal. Chim. Acta* **2006**, *556*, 38–45.
(18) Fukumoto, K.; Yoshizawa, M.; Ohno, H. Room Temperature Ionic Liquids from 20 Natural Amino Acids. *J. Am. Chem. Soc.* **2005**, *127*, 2398–2399.
(19) Anderson, J. L.; Armstrong, D. W.; Wei, G. T. Ionic Liquids in Analytical Chemistry. *Anal. Chem.* **2006**, *78*, 2892–2902.
(20) Gutowski, K. E.; Broker, G. A.; Willauer, H. D.; Huddleston, J. G.; Swatloski, R. P.; Holbrey, J. D.; Rogers, R. D. Controlling the Aqueous Miscibility of Ionic Liquids: Aqueous Biphasic Systems of Water-Miscible Ionic Liquids and Water- Structuring Salts for Recycle, Metathesis, and Separations. *J. Am. Chem. Soc.* **2003**, *125*, 6632–6633.
(21) He, C.; Li, S.; Liu, H.; Li, K.; Liu, F. Extraction of Testosterone and Epitestosterone in Human Urine Using Aqueous Two-Phase Systems of Ionic Liquid and Salt. *J. Chromatogr., A* **2005**, *1082*, 143–149.

(22) Li, S.; He, C.; Liu, H.; Li, K.; Liu, F. Ionic liquid-based Aqueous Two-Phase System, A Sample Pretreatment Procedure Prior to Highperformance Liquid Chromatography of Opium Alkaloids. *J. Chromatogr., B* **2005**, *826*, 58–62.

(23) Du, Z.; Yu, Y.; Wang, J. Extraction of Proteins from Biological Fluids by Use of an Ionic Liquid/Aqueous Two-Phase System. *Chem.—Eur. J.* **2007**, *13*, 2130–2137.

(24) Liu, Q. F.; Yu, J.; Li, W. L.; Hu, X. S.; Xia, H. S.; Liu, H. Z.; Yang, P. Partitioning Behavior of Penicillin G in Aqueous Two Phase System Formed by Ionic Liquids and Phosphate. *Sep. Sci. Technol.* **2006**, *41*, 2849–2858.

(25) Jiang, Y. Y.; Xia, H. S.; Guo, C.; Mahmood, I.; Liu, H. Z. Phenomena and Mechanism for Separation and Recovery of Penicillin in Ionic Liquids Aqueous Solution. *Ind. Eng. Chem. Res.* **2007**, *46*, 6303–6312.

(26) Soto, A.; Arce, A.; Khoshkbarchi, M. K. Partition of Antibiotics in A Two- Liquid Phase System Formed by Water and A Room Temperature Ionic Liquid. *Sep. Purif. Technol.* **2005**, *44*, 242–246.

(27) Bridges, N. J.; Gutowski, K. E.; Rogers, R. D. Investigation of Aqueous Biphasic Systems Formed from Solutions of Chaotropic Salts with Kosmotropic Salts (salt- salt ABS). *Green Chem.* **2007**, *9*, 177–183.

(28) Pei, Y.; Wang, J.; Liu, L.; Wu, K.; Zhao, Y. Liquid-Liquid Equilibria of Aqueous Biphasic Systems Containing Selected Imidazolium Ionic Liquids and Salts. *J. Chem. Eng. Data* **2007**, *52*, 2026–2031.

(29) Deng, Y. F.; Long, T.; Zhang, D. L.; Chen, J.; Gan, S. C. Phase Diagram of [Amim]Cl + Salt Aqueous Biphasic Systems and Its Application for [Amim]Cl Recovery. *J. Chem. Eng. Data*, submitted.

(30) Wu, B.; Zhang, Y. M.; Wang, H. P. Aqueous biphasic systems of hydrophilic ionic liquids + sucrose for separation. *J. Chem. Eng. Data* **2008**, *53*, 983–985.

(31) Wu, B.; Zhang, Y. M.; Wang, H. P. Phase behavior for ternary systems composed of ionic liquid + saccharides + water. *J. Phys. Chem. B* **2008**, *112*, 6426–6429.

(32) Merchuk, J. C.; Andrews, B. A.; Asenjo, J. A. Aqueous Two-Phase Systems for Protein Separation: Studies on Phase Inversion. *J. Chromatogr., B* **1998**, *711*, 285–293.

(33) Zafarani-Moattar, M. T.; Hamzehzadeh, S. Liquid-Liquid Equilibria of Aqueous Two-Phase Systems Containing Poly (ethylene glycol) and Sodium Succinate or Sodium Formate. *Calphad* **2005**, *29*, 1–6.

(34) Huddleston, J. G.; Willauer, H. D.; Rogers, R. D. Phase Diagram Data for Several PEG + Salt Aqueous Biphasic Systems at 25 °C. *J. Chem. Eng. Data* **2003**, *48*, 1230–1236.

(35) Marcus, Y. Thermodynamics of Salvation of Ions: Part 6. The Standard Partial Molar Volumes of Aqueous Ions at 298.15 K. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 713–718.

(36) Marcus, Y. Thermodynamics of Salvation of Ions. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 2995–2999.

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