J. Chem. Eng. Data **2009,** *54,* 2470–2473

Phase Diagram of [Amim]Cl + Salt Aqueous Biphasic Systems and Its Application for [Amim]Cl Recovery[†]

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In this study, binodal curves and tie line data of [Amim]Cl + salt (K_3PO_4, K_2HPO_4, K_2CO_3) + water aqueous biphasic systems (ABS) were measured and correlated satisfactorily with the Merchuk equation and Othmer−Tobias and Bancroft equations, respectively. [Amim]Cl could be recovered from aqueous solutions using the ABS, and the recovery efficiency could reach 96.80 %. The recovery efficiency was influenced by the concentrations of the salts and their Homeister series: $K_3PO_4 > K_2HPO_4 > K_2CO_3$. Our method provides a new and effective route for the recovery of hydrophilic IL using [Amim]Cl + salt + water ABS from aqueous solutions.

Introduction

Aqueous biphasic systems (ABS) are formed when two mutually incompatible polymer/polymer, polymer/salt, or salt/salt systems are dissolved in water above a certain critical concentration. These systems comprise mass fractions of water of (80 to 90) % in equilibrium phases, each phase containing mainly one of the compounds and a small amount of the other. So ABS have been widely used in separation science.[1−5] Ionic liquids (ILs) have been gaining great exposure due to their potential use as green solvents and possible replacements for traditional volatile organic compounds (VOCs). Rogers et al. first reported that 1-butyl-3-methylimidazolium chloride ([C_4mim]Cl) + K_3PO_4 + water can be used to form ABS.[6] These new types of ABS have many advantages, such as low viscosity, little emulsion formation, quick phase separation, high extraction efficiency, and gentle biocompatible environment. Recently, more ABS based on ionic liquids have been successfully used in the separation of biological particles,[7,8] metal ion species,[9] microsolid particles,[10] and small organic molecules.[11]

On one hand, it is important to design ABS for separation using the phase diagram. On the other hand, the new type of ABS could be used to recycle or concentrate hydrophilic ILs from aqueous solution. Bridges et al. 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 ABS.[12] Pei et al. studied liquid−liquid equilibrium data for selected imidazolium ionic liquid + salt ABS.[13] Wu and co-workers reported the phase diagrams for 1-butyl-3-methylimidazolium tetrafluoroborate ([C_4mim]BF_4) + saccharides + water ABS.[14,15] 1-Allyl-3-methylimidazolium chloride ([Amim]Cl) is a new and highly efficient direct solvent for the dissolution and regeneration of cellulose.[16] The regenerated cellulose could be precipitated from the IL solution by the addition of water. So there were many [Amim]Cl aqueous solutions. However, data for the phase diagram and recovery of the [Amim]Cl + salt + water systems have not been reported at present.

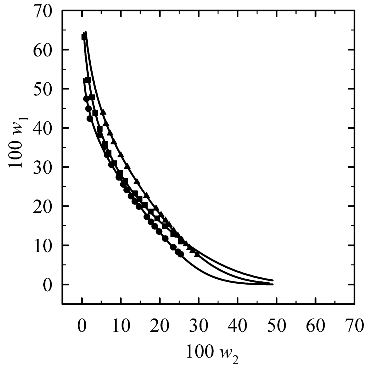

Figure 1. Phase diagram for [Amim]Cl (1) + salt (2) + water (3) ABS: ●, K_3PO_4; ■, K_2HPO_4; ▲, K_2CO_3. "w_1" and "w_2" are the mass fraction of [Amim]Cl and salt, respectively. The binodal curves determined by the cloud point method at room temperature (●). The binodal curves were fitted by least-squares regression to the Merchuk equation (—). Refs 6, 12 to 15, and 17.

In our previous work, phase diagrams of salt ([C_4mim]Cl, [C_6mim]Cl, [C_8mim]Cl) + salt (K_2CO_3, K_3PO_4) + water ABS were determined.[17] In this paper, we studied [Amim]Cl + salt (K_3PO_4, K_2HPO_4, K_2CO_3) + water ABS phase diagrams. In addition, we utilized this ABS for recovery of ILs from aqueous solutions and discussed the factors of the recovery efficiency.

Experimental Section

Materials. 1-Methyl imidazole was purchased from Linhai Kaile Chemical factory. Allyl chloride was purchased from J & K Chemical Ltd. 1-Allyl-3-methylimidazolium chloride ([Amim]Cl) was prepared, purified, and dried according to the literature.[16] The purity of the compound was verified through ^{1}H NMR and ^{13}C NMR (Bruker AV 400 NMR). ^{1}H NMR (400 MHz; DMSO; 25 °C): δ(ppm) = 3.883 (3H, s, N-CH3), 4.877−4.888 (2H, d, J = 4.4 HZ, N−CH2−CH═CH2), 5.277−5.354 (2H, m, N−CH2−CH═CH2), 5.992−6.075 (1H, m, N−CH2−CH═CH2), 7.771−7.787 (2H, s, N−CH−CH−N), 9.374 (1H, s, N−CH−N). ^{13}C NMR (100 MHz; CDCl3, 25 °C):

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[†] Part of the "William A. Wakeham Festschrift".

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10.1021/je900009a CCC: $40.75

δ (ppm) = 35.71 (N−CH3), 50.53 (N−CH2−CH=CH2), 120.00 (N−CH2−CH=CH2), 122.22 (N−CH2−CH=CH2), 123.66 (N−CH−CH−N), 131.87 (N−CH−CH−N), 136.76 (N−CH−N). The K_3PO_4, K_2HPO_4, and K_2CO_3 were analytical grade reagents and purchased from Beijing chemical reagent Co., Ltd., China. All the solutions were prepared from deionized water.

Preparation of Phase Diagrams. The binodal curves were determined by the cloud point method at room temperature. The binodal curves, tie lines, and tie line lengths of [Amim]Cl + salt + water ABS were referred to the references.[17,18] The binodal curves were fitted by least-squares regression to an empirical relationship developed by Merchuk[19] and shown as eq 1.

$$Y_A = a \exp(bX_A^{0.5} - cX_A^3) \qquad (1)$$

where Y_A and X_A are the concentrations of IL and salt. The constants a, b, and c were obtained by least-squares regression. The tie lines were determined by the application of the lever arm rule to the relationship between the mass phase composition and the overall system composition.[18] Tie line lengths (TLL) for the different compositions were calculated by the equivalent expression

$$\text{TLL} = [(Y_T - Y_B)^2 + (X_T - X_B)^2]^{1/2} \qquad (2)$$

where T and B are the points representing the top phase and the bottom phase, respectively, and Y and X are the concentrations of IL and salt.

Recovery of [Amim]Cl from Aqueous Solutions. From the stock, IL aqueous solutions of known concentration were taken into the vessel. A salt of known mass fraction was then added and mixed in a vorticity mixture apparatus for ten minutes until the salt dissolved thoroughly. Then the sample was allowed to stand 24 h until the phases separated. Finally, the concentration of [Amim]Cl in the bottom phase was analyzed by high-performance liquid chromatography (HPLC waters 515) equipped with a reverse-phase column (waters, sunfire C18) and a UV detector (waters 2487). The mobile phase consisted of methanol and water (60:40). The UV detection wavelength was set at 211 nm, and the retention time of [Amim]Cl was recorded at 1.414 min. The recovery efficiency (R) of [Amim]Cl is calculated as the following expression

$$R = \frac{C_{aq} \cdot V_o - C_b \cdot V_b}{C_{aq} \cdot V_o} \qquad (3)$$

where C_{aq} and C_b are the concentrations of [Amim]Cl in the IL aqueous solutions and the bottom phase of ABS and V_{aq} and V_b are the volumes of IL aqueous solution and bottom phase of ABS, respectively.

Results and Discussion

Phase Diagram. The binodal curve data for [Amim]Cl + salt (K_3PO_4, K_2HPO_4, and K_2CO_3) + water ABS are given in Table 1. The binodal curves for the various [Amim]Cl + salt + water systems are represented in Figure 1. The data were fitted according to the empirical relationship of Merchuk, and the parameters for this equation were determined by least-squares regression of the cloud point data. Gutowski has confirmed that the method can satisfactorily correlate binodal curves in [C_4mim]Cl + K_3PO_4 ABS.[6] Wu et al. have studied phase diagram data for [C_4mim]BF_4 + saccharide + water ABS using this method and obtained good results.[15] The coefficients a, b, and c of eq 1 along with the corresponding correlation coefficient values (R) and standard deviations (σ^a) are given in Table 2, which indicated that the empirical equation (eq 1) gave a rather good fit to the data for descriptive purposes.

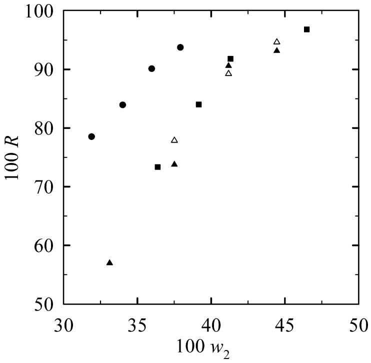

Figure 2. Effect of the mass percent of salts on recovery efficiency of [Amim]Cl. Experimental data: ●, K_3PO_4; ■, K_2HPO_4; ▲, K_2CO_3. Calculated data: Δ, K_2CO_3. "R" and "w_2" are recovery efficiency of [Amim]Cl and the mass fraction of salt, respectively. The recovery efficiency was determined by eq 3. Calculated data were determined by the Merchuk equation, the tie line slope, and the overall system composition.

Table 1. Binodal Curve Data for [AmimCl] (1) + Salt (2) + Water (3) ABS

AmimCl + K_3PO_4		AmimCl + K_2HPO_4		AmimCl + K_2CO_3	
100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1
1.19	47.42	0.66	63.23	5.46	43.91
1.72	44.89	1.56	52.22	6.19	41.02
2.06	42.36	2.58	47.83	7.24	38.58
4.57	38.16	3.44	43.82	8.21	36.32
5.87	35.23	4.58	39.74	10.01	33.01
6.49	33.13	5.92	35.91	11.67	30.09
7.61	30.58	6.87	33.68	14.14	26.18
9.50	27.35	8.33	30.97	16.61	22.66
10.66	25.53	9.81	28.52	19.05	19.42
11.51	24.14	11.17	26.43	20.36	17.77
12.62	22.57	13.61	23.28	21.50	16.36
13.61	21.20	14.80	21.85	22.46	15.16
14.67	19.89	16.18	20.28	23.56	13.81
16.70	17.28	17.70	18.64	24.67	12.51
17.76	16.00	19.37	16.90	25.65	11.42
18.71	14.85	21.40	14.89	26.77	10.26
19.84	13.52	23.46	12.90	27.69	9.34
21.41	11.72	25.48	10.99	28.46	8.59
23.50	9.50			29.66	7.54
24.70	8.35				
25.38	7.73				

Table 2. Parameters of Equation 1 for [Amim]Cl (1) + Salt (2) + Water (3) ABS

system	a	b	c	R	σ
1 AmimCl/K_3PO_4	62.74	−0.252	$5.22 \cdot 10^{-5}$	0.998	0.65
2 AmimCl/K_2HPO_4	81.11	−0.330	$1.74 \cdot 10^{-5}$	0.999	0.51
3 AmimCl/K_2CO_3	86.55	−0.294	$3.15 \cdot 10^{-5}$	0.999	0.20

Tie line compositions and average slopes (S) are listed in Table 3. The tie line compositions are used for correlation by the Othmer−Tobias eq 4 and Bancroft eq 5

$$\left(\frac{1 - W_1^t}{W_1^t}\right) = K\left(\frac{1 - W_1^b}{W_1^b}\right)^n \qquad (4)$$

Table 3. Tie Line Composition of [Amim]Cl (1) + Salt (2) + Water (3) ABS

[AmimCl] (1) + K_3PO_4 (2) + water (3)

	tie 1	tie 2	tie 3
100 w_1(mixture)	22.35	24.03	25.82
100 w_2(mixture)	19.85	23.86	27.60
100 w_1(top)	44.65	52.06	60.01
100 w_1(bottom)	0.92	0.15	0.029
100 w_2(top)	1.82	0.55	0.031
100 w_2(bottom)	37.17	43.72	48.40
R	0.49	0.46	0.43
TLL	56.23	67.52	77.05
S	−1.24	−1.20	−1.24

[AmimCl] (1) + K_2HPO_4 (2) + water (3)

	tie 1	tie 2	tie 3	tie 4
100 w_1(mixture)	24.29	25.82	27.62	29.84
100 w_2(mixture)	22.71	26.42	30.15	33.73
100 w_1(top)	46.79	51.77	58.40	67.63
100 w_1(bottom)	2.68	0.89	0.32	0.15
100 w_2(top)	2.78	1.85	0.99	0.30
100 w_2(bottom)	41.86	50.03	56.01	59.99
R	0.49	0.49	0.47	0.44
TLL	58.93	70.07	80.00	90.09
S	−1.13	−1.06	−1.06	−1.13

[AmimCl] (1) + K_2CO_3 (2) + water (3)

	tie 1	tie 2	tie 3
100 w_1(mixture)	20.41	22.02	23.99
100 w_2(mixture)	19.89	24.93	30.11
100 w_1(top)	36.23	52.15	64.13
100 w_1(bottom)	8.94	1.93	0.42
100 w_2(top)	8.40	2.96	1.04
100 w_2(bottom)	28.23	39.58	47.18
R	0.42	0.40	0.37
TLL	33.71	62.15	78.65
S	−1.38	−1.37	−1.38

$$\left(\frac{W_3^{\mathrm{b}}}{W_2^{\mathrm{b}}}\right) = K_1\left(\frac{W_3^{\mathrm{t}}}{W_1^{\mathrm{t}}}\right)^r \tag{5}$$

where W_1^{t} is the mass fraction of ionic liquids 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.[20,21] Equations 4 and 5 are linearized by taking the logarithm on both sides of the equations to determine the fit parameters. Recently, eqs 4 and 5 have been successfully used for the correlation of the tie line compositions of the imidazolium ionic liquids + salt or sucrose + water ABS.[13,14] 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 (σ^a) are given in Table 4, and it is indicated that eq 4 and 5 can be satisfactorily used to correlate the tie line data of the investigated systems.

Recovery of [Amim]Cl from Aqueous Solutions. Because of the expensive price and unknown environmental pollution problem of ionic liquids, the recovery of ILs from aqueous solution is especially important. For large-scale industry application, the recovery and recycle of ILs are a basic challenge and need to be resolved. Gutowski and Rogers first proposed that ABS can be utilized to concentrate the hydrophilic ILs from aqueous solution,[6] but there were no data on the example. Wu et al. studied that $[C_4mim]BF_4$ was separated from water by $[C_4mim]BF_4$ + sugar ABS, but the recovery efficiency was only 74 %.[14] To overcome the problem, we studied recovery of ILs from water using IL + salt ABS. The effects of the percent mass of K_3PO_4, K_2HPO_4, and K_2CO_3 on the recovery efficiency of [Amim]Cl were studied, and the results were shown in Figure 2. The recovery efficiency of [Amim]Cl was found to increase with the increase of concentrations of the kosmotropic salts due to the salting-out effect. When the concentration of K_2HPO_4 was 46.48 %, the recovery efficiency could reach 96.80 %. When salt dissolved in 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 [Amim]Cl. The results were $K_3PO_4 > K_2HPO_4 > K_2CO_3$ on the same concentration of salts in our investigation, which agreed with the Homeister series (salting-out strength decreasing in the order: $K_3PO_4 > K_2HPO_4 > K_2CO_3$).[12] Therefore the stronger salting-out effect will bring the higher recovery efficiency of ILs.

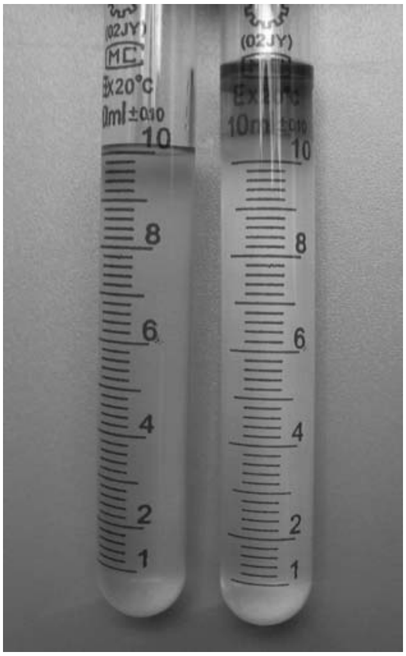

Figure 3. Photo of 10.00 mL of 10 % [Amim]Cl aqueous solutions (left) and 5.88 % [Amim]Cl + 41.18 % K_2CO_3 ABS after adding 7.00 g of K_2CO_3 (right).

The photo in Figure 3 illustrated the 10.00 mL 10% [Amim]Cl aqueous solutions (left) and the 5.88% [Amim]Cl/41.18% K_2CO_3 ABS after adding 7.00 g of K_2CO_3 (right). In this system, the top phase was [Amim]Cl-rich phase, and the bottom phase was K_2CO_3-rich phase. The two phases were then separated, and the recovery efficiency reached 90.58%. The top phase was dried in a vacuum oven at 70 °C until the water content under 0.5%, and at the same time K_2CO_3 in top phase

Table 4. Values of the Parameters of Equations 4 and 5

systems	K	n	R	σ^a	K_1	r	R	σ^a
1 [Amim]Cl/K_3PO_4	0.6289	1.3286	0.9917	0.025	1.4007	0.7112	0.9911	0.018
2 [Amim]Cl/K_2HPO_4	0.8478	1.1200	0.9539	0.060	1.1157	0.7939	0.9394	0.055
3 [Amim]Cl/K_2CO_3	0.4904	1.3858	0.9981	0.022	1.6445	0.7130	0.9967	0.018

was crystalled about 0.02 g. The recovered IL was examined by HPLC and NMR, and could be reused without the loss of its properties. The bottom phase was treated by the method of the patent.[22] The high solubility salts would be transformed to low solubility salts by reacting with corresponding acid, then the low solubility salts would be crystalled. The transformation was reversible by acids or alkalis. For example, 10.00 g 50% K_2CO_3 aqueous solutions were transformed to saturated $KHCO_3$ solutions by inlet the CO_2, then $KHCO_3$ was recovered about 6.28 g.

The phase diagram of the ABS is a "fingerprint" unique to others under a set of conditions, such as temperature, concentration of each component, and pH of the ABS. The phase diagram showed the concentration of phase-forming components, the equilibrium component concentration in the top and bottom phases, and the mass ratio of ABS.[10] It was found that the compositions of the two phases in random point of ABS could be calculated by the Merchuk equation and the tie line slope, then the recovery efficiency can be calculated by the above information. So we expand our research on the calculated recovery efficiency in [Amim]Cl + K_2CO_3 + water ABS, and the results were shown in Figure 2. It is observed remarkably that the experimental and calculated recovery efficiency were close to each other. The preliminary results are very promising.

Conclusions

Phase diagrams corresponding to aqueous biphasic systems of [Amim]Cl + salt (K_3PO_4, K_2HPO_4, K_2CO_3) + water have been determined. The binodal curves were fitted to the Merchuk equation, and tie lines were described using the Othmer−Tobias and Bancroft equations. The results showed that the empirical equations are satisfactory for correlating the investigated systems. It was found that the recovery efficiency could be promoted by the increase of the salting-out strength in the [Amim]Cl + salt + water ABS and could reach 96.80 % in the optimized conditions. Using this way, [Amim]Cl was effectively recovered from aqueous solution and almost completely recovered. It will promote the industrial application of ILs.

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Received for review January 4, 2009. Accepted February 24, 2009. This work was supported by the National Key Technology R&D Program of China (No. 2006BAC02A10), National High-tech R&D Program (No. 2007AA06Z202), Natural Science Foundation of China (No. 50574080), Hundred of Talent Program of Chinese Academy of Sciences, and the Distinguished Young Scholar Foundation of Jilin Province (No. 20060114).

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