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Aqueous Biphasic Systems of Hydrophilic Ionic Liquids + Sucrose for Separation

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In this work, we proposed a new aqueous biphasic system (ABS) composed of hydrophilic ionic liquids (ILs, namely, 1-allyl-3-methylimidazolium chloride, [Amim]Cl, 1-allyl-3-methylimidazolium bromide, [Amim]Br, and 1-butyl-3-methylimidazolium tetrafluoroborate, [Bmim]BF_4) and sucrose, forming an upper IL-rich phase and a lower sucrose-rich phase. The effects of IL structure on the phase equilibrium were investigated. It was found that the formation of ABS could be promoted by the increase of the side-chain length of ILs, but the effect was weaker than that of the anion. On the basis of phase diagrams we described, it was concluded that the chaotropicity decreased in the order [Bmim]BF_4 > [Amim]Br > [Amim]Cl. This is consistent with IL + salt systems with which they were compared; however, the proposed systems are more environmentally benign for separating ILs from the aqueous phase.

Introduction

Aqueous biphasic systems (ABS) have been widely used as a powerful technique for purification, extraction, and enrichment.[1–3] Recently, more aqueous biphasic systems[4–6] based on ionic liquids (ILs) have been investigated since Rogers and coworkers[7] demonstrated that the addition of potassium phosphate to an aqueous solution of a hydrophilic IL produces a salting-out effect, whereby they proposed this salting-out effect has the potential for handling a challenge of ILs due to their nonvolatility, i.e., separating hydrophilic ILs from water. However, as far as we know, there is no report on the IL recycle with this system because the introduction of the potassium ion complicates the recycling process since hydrophilic ILs dissociate into ions.

Taking this into account, we investigated the covalent compound replacing inorganic salts. Here, interestingly, a novel and environmentally benign ABS was produced by addition of sucrose to an aqueous solution of ILs (1-allyl-3-methylimidazolium chloride, [Amim]Cl, 1-allyl-3-methylimidazolium bromide, [Amim]Br, and 1-butyl-3-methylimidazolium tetrafluoroborate, [Bmim]BF_4). In this work, we investigated the phase diagrams of IL + sucrose systems in detail. In addition, for the first time, we utilized this novel ABS for separating hydrophilic ILs from aqueous solutions. As a contribution to develop efficient IL separation, this novel ABS was used as an instructive example to separate and recycle hydrophilic ILs from aqueous solutions.

Experimental

Materials. The sucrose, chlorobutane, allyl bromide, allyl chloride, 1-methylimidazole, ethyl acetate, acetone, and $NaBF_4$ were all purchased from Shanghai Chemical Reagents Company. They are of analytical grade and were used as received. Doubly distilled water was used in all experiments.

Synthesis of ILs. [Amim]Cl, [Amim]Br, and [Bmim][BF_4] were prepared based on the reported procedures.[8–10] [Bmim]BF_4 was dried under vacuum at 373.15 K for 24 h. The purity of the ILs was verified in terms of NMR analysis (> 99 %). The water content of all ILs (< 0.5 %) was determined by Karl Fischer titration (ZSD-2 KF with a precision of 0.05 %, Cany Precision Instruments Co., Ltd.), and any residual water in the ILs was used in constructing the phase diagrams.

Preparation of Phase Diagrams. The binodal curve was determined by the cloud-point method at room temperature. An IL solution of known concentration by weight was prepared in a test tube. A sucrose solution of known mass fraction was then added dropwise to the tube. The tube was shaken, and the resulting solution was visually examined. If there was no phase separation (seen by turbidity), another known portion of sucrose was added and so on until a phase change was observed. The composition of this mixture was noted by mass using an analytical balance with a precision of 10^{-7} kg. Then, water was added dropwise to the vessel to get a clear one-phase system, and more sucrose solution was added again to form the ABS. The above procedure was repeated, and so on.

For the determination of the tie lines, samples were prepared by mixing desired masses of ILs, sucrose, and water in the test tube and maintained at room temperature. After the equilibrium was achieved, samples were withdrawn using syringes for determining the composition of the mixture. The amount of water in both phases was measured through a ZSD-2 Karl Fischer titrator. The concentration of ILs in both phases was determined with a UV spectrophotometer (UV–visible 1200 spectrometer) at a wavelength of 212 nm for [Amim]Cl and [Amim]Br and of 211 nm for [Bmim]BF_4.

Recycle. To separate the hydrophilic ILs from their aqueous solutions, sucrose was added to solutions with various concentrations of ILs until the ABS formed. The IL-rich phase (upper phase) was separated, followed by heating to crystallize the residual sucrose in this phase. Thus, ILs in the upper phase were obtained after filtering the crystal substance. The subsequent work is to separate the residual ILs in the sucrose-rich phase (bottom phase), to which after addition of ethyl acetate, a second IL-rich phase (middle phase) appears surprisingly, concomitant with the top phase rich in ethyl acetate and the bottom phase rich in sucrose. To test whether the recovered ILs contained sucrose, a qualitative detection was conducted through color-

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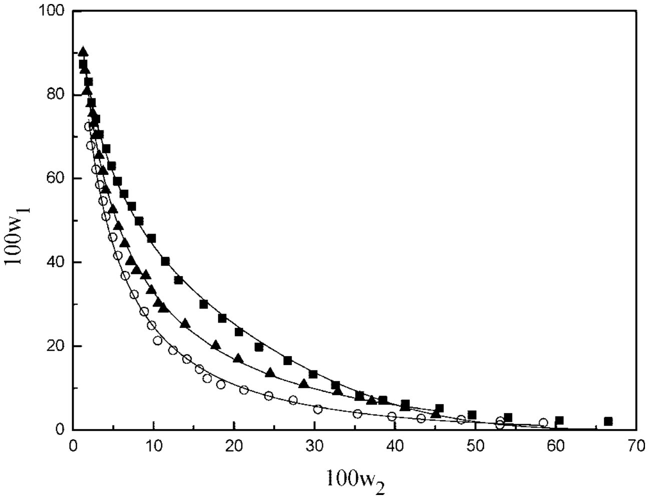

Figure 1. Phase diagram for the IL + sucrose + H_2O system: ■, [Amim]Cl; ○, [Bmim]BF_4; ▲, [Amim]Br.

reaction between resorcinol and sucrose in the presence of hydrochloride acid.[11]

Results and Discussion

Phase Diagram. The binodal curves for the various IL + sucrose systems are depicted in Figure 1. It shows that the distance between binodal curves and the origin is in the order of [Bmim]BF_4 < [Amim]Br < [Amim]Cl, implying less [Bmim]$^+$-based salt is needed to form an ABS. This is partially attributable to the fact that an increase in hydrophobicity of ILs by increasing the side chain length of cations could promote the formation of ABS.[6,12] But this is just a smaller effect on the observed effect, which is predominately due to the chaotropic order of anions (BF_4^- > Br^- > Cl^-), characterized by the order of the structural entropy (ΔS_{stru}) (BF_4^- (76.2) > Br^- (61.6) > Cl^- (36.6)).[13] Therefore, an overall chaotropic order can be established: [Bmim]BF_4 > [Amim]Br > [Amim]Cl, indicating their interactions with water molecules become stronger.

The binodal data for IL + sucrose + water systems are listed in Table 1. The data were fitted by least-squares regression, using the empirical nonlinear equation developed by Merchuk.[14]

$$w_1 = a \exp(bw_2^{0.5} - cw_2^3) \qquad (1)$$

where w_1 and w_2 represent the mass fraction of ILs and sucrose, respectively. Recently, the above equation has been successfully used for the correlation of binodal data of the aqueous [Bmim]Cl + K_3PO_4 system.[7]

The coefficients a, b, and c of eq 1, along with the values of the corresponding standard deviations (σ) and correlation coefficients (R^2) are given in Table 2. It is observed remarkably that the empirical equation is satisfactory for correlating the binodal curves of the investigated systems.

Tie line compositions are listed in Table 3. The reliability of the tie line compositions was ascertained by the empirical correlation equations used elsewhere.[15]

$$\frac{1 - w_1^{\text{i}}}{w_1^{\text{i}}} = k_1\left(\frac{1 - w_2^{\text{s}}}{w_2^{\text{s}}}\right)^n \qquad (2)$$

$$\frac{w_3^{\text{s}}}{w_2^{\text{s}}} = k_2\left(\frac{w_3^{\text{i}}}{w_1^{\text{i}}}\right)^r \qquad (3)$$

Table 1. Binodal Curve Data for ILs (1) + Sucrose (2) + H_2O (3)

[Amim]Cl + sucrose		[Bmim]BF_4 + sucrose		[Amim]Br + sucrose	
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
87.26	1.25	72.44	1.96	90.08	1.25
83.14	1.96	67.91	2.22	85.87	1.50
78.10	2.34	62.24	2.86	80.86	1.75
74.22	2.87	58.55	3.33	77.84	2.25
70.57	3.27	54.62	3.74	75.50	2.45
67.17	4.12	50.96	4.10	73.10	2.60
63.05	4.83	46.02	4.94	70.25	2.80
59.43	5.53	41.69	5.59	65.45	3.25
56.37	6.36	36.85	6.51	61.75	3.75
53.45	7.33	32.32	7.62	57.21	4.10
49.86	8.22	28.26	8.88	52.50	4.95
45.77	9.74	24.97	9.79	48.53	5.65
40.24	11.52	21.33	10.55	44.46	6.45
35.82	13.12	19.04	12.44	40.23	7.15
29.98	16.23	16.92	14.18	38.05	7.90
26.61	18.57	14.56	15.71	36.84	9.05
23.35	20.64	12.29	16.68	33.30	9.75
19.81	23.14	10.86	18.40	30.26	10.61
16.54	26.67	9.57	21.25	28.86	11.24
13.33	29.87	8.14	24.34	25.23	13.93
10.71	32.65	7.05	27.37	20.04	17.75
8.22	35.62	4.96	30.46	16.88	20.52
7.01	38.54	3.81	35.37	13.50	24.50
6.22	41.27	3.21	39.65	10.81	28.68
5.18	45.56	2.75	43.27	9.04	32.90
3.63	49.57	2.45	48.24	7.83	35.63
2.93	54.07	2.08	53.12	6.92	37.13
2.33	60.45	1.76	58.46	5.28	41.27
1.98	66.56	1.23	53.05	3.58	45.09

Table 2. Values of Parameters of Equation 1

ABS	a	b	c	R^2	σ
[Amim]Cl + sucrose + H_2O	132.68	−0.3445	$1.00 \cdot 10^{-5}$	0.9980	1.30
[Amim]Br + sucrose + H_2O	160.06	−0.4994	$2.08 \cdot 10^{-6}$	0.9984	1.14
[Bmim]BF_4 + sucrose + H_2O	176.66	−0.6207	$1.74 \cdot 10^{-6}$	0.9980	1.04

Table 3. Tie Line Data for IL (1) + Sucrose (2) + H_2O (3)

	IL-rich phase		sucrose-rich phase	
ABS	100 w_1	100 w_2	100 w_1	100 w_2
[Amim]Cl + sucrose + H_2O	66.63	4.36	17.22	25.06
	71.38	3.14	14.16	28.24
	76.65	2.48	9.26	33.87
	80.56	2.12	5.50	40.78
[Amim]Br + sucrose + H_2O	56.72	3.55	13.30	16.04
	61.27	2.97	9.87	20.16
	66.68	2.33	7.15	26.24
	69.45	2.08	5.37	28.29
[Bmim]BF_4 + sucrose + H_2O	68.36	3.04	12.38	26.54
	73.28	2.51	9.57	31.13
	78.48	1.94	7.35	36.18
	82.66	1.62	5.86	40.07

where w_1^{i} is the mass fraction of ILs in the IL-rich phase; w_2^{s} is the mass fraction of sucrose in the sucrose-rich phase; w_3^{i} and w_3^{s} are the mass fractions of water in the IL-rich phase and sucrose-rich phase, respectively. k_1, k_2, n, and r represent fit parameters. Equations 2 and 3 are linearized by taking the logarithm on both sides of the equations to determine the fit parameters. The values of the parameters are given in Table 4, from which we can conclude that the eqs 2 and 3 can satisfactorily correlate the tie line data of the investigated systems.

Separation of ILs from Aqueous Solutions. As the environmental impact of ILs is still unknown, removal of ILs from water is especially important when dealing with wastewater streams. A few years ago, Rogers[7] and co-workers proposed that ABS can be utilized to recycle or concentrate hydrophilic ILs from aqueous solution, but to date, there is no example on the IL recycle with ABS.

Table 4. Values of Parameters of Equations 2 and 3

ABS	k_1	k_2	n	r	R_1^2	R_2^2	σ_1	σ_2
[Amim]Cl + sucrose + H_2O	0.161	4.456	1.010	0.775	0.993	0.993	0.020	0.016
[Amim]Br + sucrose + H_2O	0.234	6.847	0.718	1.260	0.998	0.998	0.007	0.011
[Bmim]BF_4 + sucrose + H_2O	0.130	4.093	0.680	1.275	0.996	0.996	0.011	0.016

Here, we found that ILs and sucrose could form a novel ABS, an upper IL-rich phase, and a lower sucrose-rich phase, which is illustrated in Figure 2a. The IL in the upper phase was removed, followed by adding a known volume of ethyl acetate, which surprisingly induces a second phase rich in ethyl acetate, as shown in Figure 2b. This can be explained with the most likely mechanism being the expansion of the sucrose-based liquid phase by the ethyl acetate, which decreases the dielectric constant, forcing a significant amount of the IL into a separate liquid phase.

The bottom phase is rich in sucrose; the next phase is rich in ILs and contains rare small amounts ethyl acetate due to their immiscibility; and the upper phase is mostly ethyl acetate (with a small amount of dissolved water). After purification, the recovered ILs (water content < 1 %) contain no sucrose, which was confirmed by the qualitative detection through color-reaction between resorcinol and sucrose in the presence of hydrochloride acid. But a bit depressed, the recoveries of ILs are not satisfying, just 74 % for [Bmim]BF_4, 65 % for [Amim]Br, and 63 % for [Amim]Cl.

This work is just an exploring study on the possibility of utilizing ABS to recycle ILs from aqueous solutions, and the recovery efficiency will be affirmed through optimizing varied conditions. Nevertheless, as a contribution to a better understanding of IL recycle and to the development of an efficient process, the separation of ILs using an ILs + sucrose ABS was studied as an instructive example.

Conclusions

For ABS of ILs + sucrose + water, binodal data and tie line data were measured and fitted satisfactorily with the Merchuk equation and the Othmer−Tobias and the Bancroft equations, respectively. In addition, the contamination of the aqueous phase with the ILs may require an additional downstream separation step. As one option, we have shown that ABS can be used successfully to separate hydrophilic ILs from water, but this method is relatively inefficient, and the highest recovery is 74 % for [Bmim]BF_4. Despite the recovery being dissatisfying, the potential use of ABS for recycling hydrophilic ILs and thus overcoming the challenge of cross-contamination of the aqueous and IL-rich phase has been demonstrated.

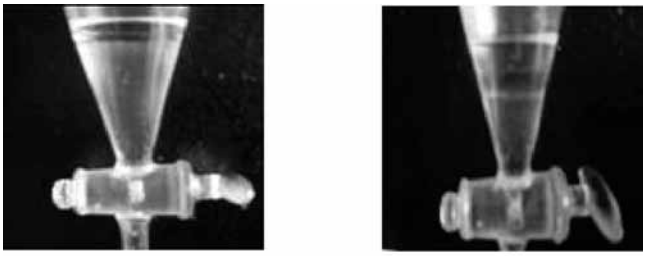
(a) (b)

Figure 2. Photo of phase behavior. (a) ILs + sucrose + H_2O; (b) after the addition of ethyl acetate to the sucrose-rich phase.

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