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Phase Diagrams for Aqueous Two-Phase Systems Containing the 1-Ethyl-3-methylimidazolium Tetrafluoroborate/1-Propyl-3-methylimidazolium Tetrafluoroborate and Trisodium Phosphate/Sodium Sulfite/Sodium Dihydrogen Phosphate at 298.15 K: Experiment and Correlation

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ABSTRACT: Liquid—liquid equilibrium data have been determined for 1-ethyl-3-methylimidazolium tetrafluoroborate ([Emim]BF_4)/1-propyl-3-methylimidazolium tetrafluoroborate ([Pmim]BF_4) + trisodium phosphate (Na_3PO_4)/sodium sulfite (Na_2SO_3)/sodium dihydrogen phosphate (NaH_2PO_4) aqueous two-phase systems at $T = 298.15$ K, respectively. Two empirical equations were used to correlate binodal data. The Othmer-Tobias and Bancroft as well as Setschenow-type equations were used to correlate the tie-line data. The results show that good agreement was obtained with the experimental data. The effect of salt on the phase forming ability has been studied based on the effective excluded volume (EEV) values from fitting the binodal data to the binodal model. The binodal curves and EEV both indicate that the salting-out effect of the three salts follow the order $Na_3PO_4 > Na_2SO_3 > NaH_2PO_4$, which can also be related to the Gibbs free energy of hydration of the ions ($\Delta_{hyd}G$) and [Pmim]BF_4 is easier to be excluded the IL-rich phase than [Emim]BF_4.

INTRODUCTION

Liquid—liquid extraction (LLE), also called solvent extraction, has often been a favored choice of the process engineer for separation of two or more components due to their unequal solubilities in two immiscible liquid phases. However, some shortcomings such as the emulsion formation, the use of toxic organic solvents, and the generation of large amounts of pollutants make LLE time-consuming and environmentally unfriendly. At the same time, aqueous two-phase systems (ATPSs) with advantages as short processing time and a biocompatible environment[1] set foot into the research field of vision. ATPSs were usually formed as a result of mutual incompatibility of two polymers or one polymer and one salt above a certain concentration. Up to now, ATPSs have been successfully used for separation, enrichment, and purification for heavy metal ions,[2] drugs,[3] proteins,[4,5] small organic molecules,[6] cell organelles,[7] and antibiotics.[8,9]

A new type of ATPS based on ionic liquids (ILs) has been investigated since Gutowski and co-workers[10] for the first time reported ionic liquid + salt aqueous two-phase systems (ILATPSs). These new ATPSs have many advantages shared by ILs and ATPSs, such as little emulsion formation, no need to use a volatile organic solvent, quick phase separation, high extraction efficiency, and gentle biocompatible environment.[11] ILATPSs have been successfully used in the separation, concentration, and purification of proteins,[12] heavy metal ions,[13] organic molecules,[14] and antibiotics.[15] Real data on the properties and equilibrium of phase systems are necessary for the design of extraction processes and also for the development of models to predict phase partitioning. In recent years, imidazolium tetrafluoroborate ILATPSs have been studied extensively. For instance, 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF_4) + sugars (sucrose, glucose, xylose, fructose, and maltose) ATPSs have been reported by different research groups.[16−20] Moreover, Chen et al.[21] have researched 1-alkyl-3-methyl imidazolium tetrafluoroborate ([$C_n$mim][BF_4], $n = 2$ to 10) + glucose ATPSs. In a previous work,[22−25] our team has systematically investigated the liquid—liquid phase behavior of some ILATPSs formed by [Bmim]BF_4 + salt (Na_3PO_4, Na_2CO_3, Na_2SO_4, Na_2SO_3, $(NH_4)_2SO_4$, NaH_2PO_4, NaCl, $Na_3C_6H_5O_7$, $Na_2C_4H_4O_6$, $NaC_2H_3O_2$, and $(NH_4)_3C_6H_5O_7$). However, the liquid—liquid equilibrium data for 1-ethyl-3-methylimidazolium tetrafluoroborate ([Emim]BF_4)/1-propyl-3-methylimidazolium tetrafluoroborate ([Pmim]BF_4) + inorganic salt ATPSs were not reported.

This work is devoted to studying the phase behaviors of ILATPSs based on [Emim]BF_4/[Pmim]BF_4 + Na_3PO_4/Na_2SO_3/NaH_2PO_4 at $T = 298.15$ K, respectively. Here, these systems have not been previously published. Suitable equations were used to correlate the binodal data and the tie-line data for the investigated systems. Results obtained from the correlations are in good agreement with the experimental data. The location of the plait point for the studied systems was also estimated by extrapolation. The effect of salt on the phase forming ability has been studied based on the effective excluded volume (EEV) values from fitting the binodal data to the binodal model and the phase-forming ability of [Pmim]BF_4 is better than [Emim]BF_4.

EXPERIMENTAL SECTION

Materials. [Emim]BF_4 and [Pmim]BF_4 (99 % by mass fraction) were obtained from Cheng Jie Chemical Co., Ltd.

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Table 1. Experimental (Liquid + Liquid) Equilibrium Mass Fractions w (Binodal Curve Data) ATPSs for [Emin]BF_4 (1) + Na_3PO_4/Na_2SO_3/NaH_2PO_4 (2) + H_2O (3) at Temperature T = 298.15 K and Pressure p = 0.1 MPa[a]

Na_3PO_4		Na_2SO_3		NaH_2PO_4	
100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1
0.06	75.65	1.28	61.44	2.17	65.86
0.15	72.55	1.30	60.94	2.80	61.54
0.23	68.81	1.68	58.35	3.08	58.95
0.28	66.75	1.94	56.17	3.75	56.03
0.33	64.75	2.17	54.04	4.38	53.40
0.47	61.36	2.51	51.61	4.94	51.07
0.62	58.16	2.90	49.43	5.47	48.89
0.86	54.46	3.27	47.21	5.94	46.89
1.16	50.23	3.58	45.36	6.68	44.47
1.59	46.02	3.88	43.46	7.34	42.29
1.91	43.06	4.33	41.31	8.11	39.94
2.23	40.85	4.89	38.99	8.84	37.86
2.57	38.39	5.48	36.28	9.49	36.00
2.88	36.86	5.79	34.94	10.06	34.31
3.25	35.43	6.17	33.13	10.73	32.47
3.54	33.72	6.88	30.26	11.33	30.84
3.82	32.47	7.18	29.03	11.96	29.42
4.07	31.53	7.38	28.07	13.01	26.75
4.44	29.99	7.64	27.06	13.72	25.70
4.63	29.25	8.08	25.59	14.40	23.88
4.83	28.46	8.45	24.38	15.27	22.19
5.06	27.62	8.77	23.33	16.3	20.53
5.45	26.45	9.10	22.38	17.13	19.16
5.76	25.04	9.59	21.12	17.85	17.97
6.13	24.20	9.57	21.06	19.06	16.46
6.57	23.01	10.68	18.27	20.20	15.05
7.16	21.39	11.43	16.54	21.42	13.90
7.63	19.91	11.91	15.50	22.14	13.20
8.05	18.70	13.06	13.61	22.82	12.60
		13.43	13.03	23.42	12.08
		14.29	11.87	23.94	11.72
		15.21	10.67	24.90	11.00
				26.36	9.98

[a] Standard uncertainties u are $u(w)$ = 0.001, $u(t)$ = 0.05 K, and $u(p)$ = 10 kPa.

Table 2. Experimental (Liquid + Liquid) Equilibrium Mass Fractions w (Binodal Curve Data) ATPSs for [Pmin]BF_4 (1) + Na_3PO_4/Na_2SO_3/NaH_2PO_4 (2) + H_2O (3) at Temperature T = 298.15 K and Pressure p = 0.1 MPa[a]

Na_3PO_4		Na_2SO_3		NaH_2PO_4	
100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1
0.11	77.69	3.12	50.75	2.10	65.86
0.24	76.01	3.45	48.15	2.48	63.12
0.52	71.53	3.67	46.09	2.56	61.34
0.69	68.45	3.80	44.71	3.11	58.06
0.94	64.95	3.99	43.14	3.35	56.14
1.16	61.52	4.30	41.25	4.24	51.50
1.49	57.54	4.38	40.03	4.26	51.49
1.67	54.81	4.58	38.97	4.78	49.26
1.92	51.63	4.74	37.33	5.09	47.57
2.12	49.49	4.88	36.33	5.50	45.77
2.36	46.89	5.09	34.93	5.89	43.86
2.48	45.16	5.29	33.62	6.19	42.63
2.70	42.93	5.48	32.42	6.65	40.37
2.71	42.69	5.67	31.39	7.41	37.51
2.88	40.75	5.83	30.30	8.31	33.07
3.05	38.91	6.09	28.58	9.58	29.07
3.19	38.04	6.26	27.59	10.46	26.47
3.19	37.34	6.52	26.60	11.97	22.37
3.35	35.65	6.76	25.64	12.51	21.40
3.51	34.17	7.03	24.68	13.88	18.91
3.55	33.95	7.41	23.08	14.26	18.14
3.75	32.35	7.92	21.45	15.14	16.64
3.90	31.09	8.03	21.16	16.72	14.77
3.99	30.64	8.66	18.94	17.53	13.86
4.25	28.48	9.07	18.21	18.47	12.94
4.39	27.67	9.81	16.17	19.45	12.00
4.62	25.71	10.29	15.40	20.26	11.25
4.82	24.67	11.04	14.04	21.18	10.54
5.28	21.62	11.41	13.30	22.29	9.80
		12.07	12.63	23.41	9.04
		13.08	11.20	25.01	8.11
		13.82	10.47	27.22	7.02
				29.96	5.97

[a] Standard uncertainties u are $u(w)$ = 0.001, $u(t)$ = 0.05 K, and $u(p)$ = 10 kPa.

(Shanghai, China). and used without further purification. $Na_3PO_4 \cdot 12H_2O$, Na_2SO_3, and $NaH_2PO_4 \cdot 2H_2O$ were supplied from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) with a quoted purity of greater than 99 % mass fraction. The ionic liquids and salt were used without further purification. Double-distilled deionized water was used for the preparation of solutions.

Apparatus and Procedures. The binodal curves were determined by titration method at T = 298.15 K. A few grams of pure ILs were weighed into a vessel, and a known mass of water was added and then mixed. The mixture was clear at first. Then a salt solution of known mass fraction was added to the vessel until the mixture become turbid or cloudy. Adding a few drops of water made the mixture clear again, and then the above procedure was repeated to obtain sufficient data for the construction of a phase diagram. The vessel was immersed in a Solar-type heating temperature magnetic stirrer (Gongyi Yuhua Instrument Co., Ltd. China) with an uncertainty of ± 0.05 K. The composition of the mixture was determined by mass using an analytical balance (BS124S, Beijing Saiduolisi Instrument Co., Ltd. China) with an uncertainty of $\pm 1.0 \cdot 10^{-7}$ kg.

For determination of the tie-lines, a series of ILATPSs with three different total compositions were prepared in vessels which were placed in a thermostatted bath for 48 h until they separated into two clear phases. The temperature was controlled to within ± 0.05 K. After a clear phase separation was reached, the volume of top and bottom phases were recorded accurately, and the top phases were taken out carefully by a rubber dropper. The mass of the top phase was determined by analytical balance and the bottom phase was obtained by the subtraction method.

The mass fraction of ILs was determined by UV−vis spectrometer model UV-2450 (Shimadzu Corporation, Japan) at 211 nm. The mass fraction of NaH_2PO_4 and Na_2SO_3 in the top and bottom phases was determined by titration with sodium hydroxide and sulfuric acid, respectively, and the mass fraction of water in both phases was calculated according to the material balance equation of the top and bottom phase.

Table 3. Values of Parameters of eq 3 for the [Emim]BF_4/Pmim]BF_4 (1) + Na_3PO_4/Na_2SO_3/NaH_2PO_4 (2) + H_2O (3) ATPSs at 298.15 K

salt	*a*	*b*	10^5c	R^2	sd[a]
		[Emin]BF_4 (1) + salt (2) + H_2O (3)			
Na_3PO_4	86.5385	−0.4979	19.3876	0.99947	0.39
Na_2SO_3	103.2784	−0.4408	20.9018	0.99691	0.83
NaH_2PO_4	116.3529	−0.3754	3.8482	0.99747	0.81
		[Pmin]BF_4 (1) + salt (2) + H_2O (3)			
Na_3PO_4	93.6033	−0.4118	448.0000	0.99042	1.49
Na_2SO_3	228.3121	−0.8359	0.6842	0.99855	0.43
NaH_2PO_4	136.9872	−0.4832	3.6750	0.99454	1.37

[a] sd = $\{\Sigma_{i=1}^{N}(100\,w_1^{\text{calcd}} - 100\,w_1^{\text{exptl}})^2/N\}^{0.5}$, where w_1^{exptl} is the experimental mass fraction of [Emim]BF_4/[Pmim]BF_4 in Tables 1 and 2, w_1^{calcd} is the corresponding data calculated using eq 3. *N* represents the number of binodal data.

Table 4. Values of Parameters of eq 4 for the [Emim]BF_4/Pmim]BF_4 (1) + Na_3PO_4/Na_2SO_3/NaH_2PO_4 (2) + H_2O (3) ATPSs at 298.15 K

salt	*a*	*b*	*c*	*d*	R^2	sd[a]
		[Emin]BF_4 (1) + salt (2) + H_2O (3)				
Na_3PO_4	4.4707	−0.5305	0.0236	−0.0032	0.99941	0.39
Na_2SO_3	4.3171	−0.0571	−0.1075	−0.00058	0.99964	0.28
NaH_2PO_4	4.4467	−0.0976	−0.0587	−0.00022	0.99945	0.37
		[Pmin]BF_4 (1) + salt (2) + H_2O (3)				
Na_3PO_4	4.3697	0.0290	−0.2322	−0.0052	0.99971	0.26
Na_2SO_3	4.1693	0.5252	−0.4019	0.0095	0.99951	0.25
NaH_2PO_4	4.2515	0.1850	−0.1684	0.0018	0.99945	0.43

[a] sd = $\{\Sigma_{i=1}^{N}(100\,w_1^{\text{calcd}} - 100\,w_1^{\text{exptl}})^2/N\}^{0.5}$, where w_1^{exptl} is the experimental mass fraction of [Emim]BF_4/[Pmim]BF_4 in Tables 1 and 2, w_1^{calcd} is the corresponding data calculated using eq 4. *N* represents the number of binodal data.

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

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

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

where w_1^{t} and w_2^{t} represent the equilibrium compositions (in mass fraction) of ILs (1) and salt (2) in the top phase, respectively. w_1^{b} and w_2^{b} represent the equilibrium compositions (in mass fraction) of ILs (1) and salt (2) in bottom phases, respectively.

RESULTS AND DISCUSSION

Binodal Data and Correlation. The binodal curve data of ATPSs based on [Emim]BF_4/[Pmim]BF_4 + Na_3PO_4/Na_2SO_3/NaH_2PO_4 are showed in Tables 1 and 2, respectively. The binodal data of this experiment were fitted by Merchuk[26]

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

where w_1 and w_2 are the mass factions of ILs and salt, respectively, and coefficients *a*, *b*, and *c* are fitting parameters. The parameters which were determined by least-squares regression of the cloud point data obtained from the correlation of experimental binodal data along with the correlation coefficient (R^2) and standard deviations (sd) are given in Table 3. This expression has been extensive to fitted PEG + salt ATPSs,[27] IL + salt ATPSs,[22,23] and IL + sugars ATPSs.[17] In order to get more accurate fitting, we also proposed a nonliner empirical expression[28] with four fitting parameters to correlate the binodal data, which has the following form:

$$w_1 = \exp(a + bw_2^{\,0.5} + cw_2 + dw_2^{\,2}) \tag{4}$$

Table 5. Experimental (Liquid + Liquid) Equilibrium Data for ATPSs [Emim]BF_4/[Pmim]BF_4 (1) + Na_2SO_3/NaH_2PO_4 (2) + H_2O (3) at the Temperature $T = 298.15$ K and Pressure $p = 0.1$ MPa[a]

	total system		top phase		bottom phase			
ATPSs	$100\,w_1$	$100\,w_2$	$100\,w_1$	$100\,w_2$	$100\,w_1$	$100\,w_2$	TLL	S
Na_2SO_3 + [Emim]BF_4	24.86	10.54	66.97	0.63	13.12	13.58	0.5539	−4.16
	41.78	8.31	72.14	0.25	11.25	16.00	0.6289	−3.87
	34.72	8.59	68.75	0.45	12.50	14.16	0.5790	−4.10
NaH_2PO_4 + [Emim]BF_4	32.37	13.11	65.36	2.23	19.88	16.92	0.4779	−3.10
	32.97	11.95	60.27	3.02	23.41	14.82	0.3870	−3.12
	35.25	13.05	69.12	1.79	17.22	18.76	0.5460	−3.06
Na_2SO_3 + [Pmim]BF_4	35.24	8.75	77.10	0.48	11.38	13.16	0.6693	−5.18
	31.83	10.65	83.50	0.33	9.86	15.29	0.7514	−4.92
	32.17	10.26	81.12	0.37	10.26	14.53	0.7226	−5.00
NaH_2PO_4 + [Pmim]BF_4	37.99	7.98	57.71	3.26	25.44	10.94	0.3317	−4.20
	37.76	8.95	64.90	2.25	21.17	12.80	0.4498	−4.15
	40.06	8.90	67.82	1.85	18.98	13.95	0.5032	−4.04

[a] Standard uncertainties *u* are $u(w) = 0.001$, $u(t) = 0.05$ K, and $u(p) = 10$ kPa.

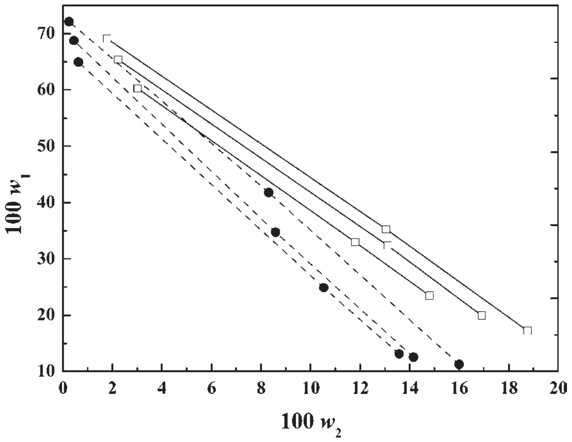

Figure 1. Tie-lines for the [Emim]BF_4 (1) + Na_2SO_3/NaH_2PO_4 (2) + H_2O (3) ATPSs at 298.15 K. ●, Na_2SO_3; □, NaH_2PO_4.

where w_1 is the mass fraction of ILs, w_2 is the mass fraction of salt, and the coefficients a, b, c, and d are fitting parameters. The parameters along with the correlation coefficient (R^2) and standard deviations (sd) are given in Table 4. This equation has successfully used for the correlation of binodal data of small molecular alcohols + salt.[29,30] On the basis of the obtained R^2 and sd in Tables 3 and 4, it can be concluded that eq 4 shows more satisfactory accuracy in binodal data fitting for the investigated systems. This is due to the fact that eq 4 has four fitting parameters.

Liquid−Liquid Equilibrium Data and Correlation. For most of the ILATPSs, the IL concentration in the bottom phase is very small, and in some cases, the IL is almost excluded completely from the phase. The opposite behavior is observed in the top phase. The total composition of the system has no significant effect upon the slope of the tie-lines, which implies that the tie-lines are parallel to each other. The tie-line compositions of [Emim]BF_4/[Pmim]BF_4 + Na_2SO_3/NaH_2PO_4 ATPSs at T = 298.15 K are collected in Table 5 and presented in Figures 1 and 2.

The tie lines data was fitted by the Othmer−Tobias and Bancroft equations[31] as follows:

$$\left(\frac{1 - w_1^t}{w_1^t}\right) = k_1\left(\frac{1 - w_2^b}{w_2^b}\right)^n \tag{5}$$

$$\frac{w_3^b}{w_2^b} = k_2\left(\frac{w_3^t}{w_1^t}\right)^r \tag{6}$$

In these questions w_1^t and w_3^t are the mass fractions of ILs (1) and H_2O (3) in the top phase, and w_2^b and w_3^b are the mass fractions of salt (2) and H_2O (3) in the bottom phase, respectively. k_1, n, k_2, and r represent the fit parameters which can be calculated from the intercept and slope of the linear relationship between $\log[(1 - w_2^t)/w_2^t]$ and $\log[(-w_2^b)/w_2^b]$ and between $\log\,[w_3^b/w_2^b]$ and $\log[w_2^t/w_1^t]$.The values of the parameters k_1, n, k_2, and r of equations with the corresponding correlation coefficient values (R^2) and standard deviations (sd) are given in Table 6. As can be seen, these equations can be satisfactorily used to correlate the tie-line data of the investigated systems.

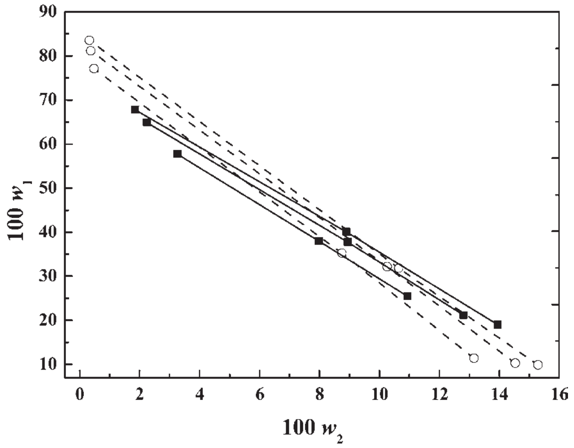

Figure 2. Tie-lines for the [Pmim]BF_4 (1) + Na_2SO_3/NaH_2PO_4 (2) + H_2O (3) ATPSs at 298.15 K.○, Na_2SO_3; ■, NaH_2PO_4.

Table 6. Values of Parameters of eqs 5 and 6 for the [Emim]BF_4/[Pmim]BF_4 (1) + Na_2SO_3/NaH_2PO_4 (2) + H_2O (3) ATPSs at T = 298.15 K

k_1	n	R^2	k_2	r	R^2	sd_1[a]	sd_2[a]
[Emim]BF_4 (1) + Na_2SO_3 (2) + H_2O (3)							
0.04991	1.4691	0.99902	6.5570	0.5589	0.99898	0.47	1.1
[Emim]BF_4 (1) + NaH_2PO_4 (2) + H_2O (3)							
0.05940	1.3761	0.99629	5.4498	0.5401	0.99674	0.02	0.08
[Pmim]BF_4 (1) + Na_2SO_3 (2) + H_2O (3)							
0.00407	2.2747	0.99560	9.3053	0.3934	0.99589	0.18	0.72
[Pmim]BF_4 (1) + NaH_2PO_4 (2) + H_2O (3)							
0.02533	1.6032	0.99633	6.9445	0.4488	0.99702	0.28	0.76

[a] sd= $\{\Sigma_{i=1}^{N}\,(100\,w_{i,j,\mathrm{cal}}^{\mathrm{top}} - 100\,w_{i,j,\mathrm{exp}}^{\mathrm{top}})^2 + (100\,w_{i,j,\mathrm{cal}}^{\mathrm{bot}} - 100\,w_{i,j,\mathrm{exp}}^{\mathrm{bot}})^2/2\,N\}^{0.5}$, where N is the number of tie lines and j = 1 and j = 2, sd^1 and sd^2 represent the mass percent standard deviations for [Emim]BF_4/[Pmim]BF_4 and salt, respectively.

The Setschenow-type equation[32] has also been used to correlate the tie-line compositions of the [Emim]BF_4/[Pmim]BF_4 + Na_2SO_3/NaH_2PO_4 ATPSs

$$\ln\left(\frac{c_1^t}{c_1^b}\right) = k_{\mathrm{IL}}(c_1^b - c_1^t) + k_s(c_2^b - c_2^t) \tag{7}$$

where c_1, c_2, k_{IL}, and k_s represent the molality of the ILs, the molality of the salt, a parameter relating the activity coefficient of ILs to its concentration, and the salting-out coefficient, respectively. Superscripts "t" and "b" stand for the ILs-rich phase and salt-rich phase, respectively. If the first term on the right-hand side of this equation is small compared with the second term, then a Setschenow-type equation is obtained. This would imply that $k_{\mathrm{IL}} \ll k_s$ because the absolute values of $(c_1^b - c_1^t)$ exceed the $(c_2^b - c_2^t)$ values.[33] This equation was successfully used for the correlation of tie-line data for the IL + salt ATPSs.[34] The values of the salting-out coefficients, k_s, together with the corresponding intercepts, correlation coefficient values (R^2) and standard deviations (sd) are given in Table 7. On the basis of the standard deviations obtained, we conclude that the performance of eq 7 is fairly good in correlating the tie-line data of the systems investigated.

Table 7. Values of Parameters of eq 7 for the $[\mathrm{Emim}]\mathrm{BF}_4$/$[\mathrm{Pmim}]\mathrm{BF}_4$ (1) + Na_2SO_3/NaH_2PO_4 (2) + H_2O (3) ATPSs at T = 298.15 K

ATPSs	$10^{-3}\ k_s$ (g . mol^{-1})	intercept	R^2	$\delta(k_s)$[b]	δ(intercept)[c]	sd[a]
$[\mathrm{Emim}]\mathrm{BF}_4 + Na_2SO_3$	1.0106	0.59752	0.99999	61.87	0.070	0.26
$[\mathrm{Emim}]\mathrm{BF}_4 + NaH_2PO_4$	1.0302	−0.06837	0.99999	9.94	0.012	0.08
$[\mathrm{Pmim}]\mathrm{BF}_4 + Na_2SO_3$	1.2436	0.66428	0.99999	59.53	0.066	0.23
$[\mathrm{Pmim}]\mathrm{BF}_4 + NaH_2PO_4$	1.2369	0.02896	0.99999	18.66	0.016	0.13

[a] sd= $\{\Sigma_{i=1}^{3}\Sigma_{i=1}^{N}[(100\,w_{i,j,\mathrm{cal}}^{\mathrm{top}} - 100\,w_{i,j,\mathrm{exp}}^{\mathrm{top}})^2 + (100\,w_{i,j,\mathrm{cal}}^{\mathrm{bot}} - 100\,w_{i,j,\mathrm{exp}}^{\mathrm{bot}})^2/6N\}^{0.5}$, where N is the number of tie-lines and j is the number of components in each phase. [b] $\delta(k_s)$ is the standard deviation for the fitting parameters of "k_s". [c] δ(intercept) is the standard deviation for the fitting parameters of "intercept".

Table 8. Values of f, g, R^2, and Plaint Point of eq 8 for $[\mathrm{Emim}]\mathrm{BF}_4$/$[\mathrm{Pmim}]\mathrm{BF}_4$ (1) + Na_2SO_3/NaH_2PO_4 (2) + H_2O (3) ATPSs at T = 298.15 K

ATPSs	f	g	R^2	$\delta(f)$[a]	$\delta(g)$[b]	Plaint point 100 (w_1, w_2, w_3)
$[\mathrm{Emim}]\mathrm{BF}_4 + Na_2SO_3$	38.06076	2.14119	0.99931	3.46	0.24	(45.64, 3.55, 50.81)
$[\mathrm{Emim}]\mathrm{BF}_4 + NaH_2PO_4$	27.03853	2.25019	0.99965	1.85	0.11	(42.97, 7.08, 49.95)
$[\mathrm{Pmim}]\mathrm{BF}_4 + Na_2SO_3$	37.64173	2.99662	0.99999	0.73	0.05	(47.98, 3.45, 48.57)
$[\mathrm{Pmim}]\mathrm{BF}_4 + NaH_2PO_4$	20.68204	3.40663	0.99784	4.48	0.36	(41.87, 6.22, 51.92)

[a] $\delta(f)$ is the standard deviation for the fitting parameters of "f". [b] $\delta(g)$ is the standard deviation for the fitting parameters of "g".

The location of the plait point for the studied systems was also estimated by extrapolation from the auxiliary curve satisfactorily fitted with the following linear equation

$$w_1 = f + g w_2 \tag{8}$$

where f and g are the fitting parameters. For the investigated systems, the estimated values for the plait points along with the obtained fitting parameters for eq 8 and the corresponding correlation coefficients are shown in Table 8. As an example, The locus of the estimated plait point for the $[\mathrm{Emim}]\mathrm{BF}_4 + NaH_2PO_4$ ATPS along with the used procedure is illustrated in Figure 3.

Effective Excluded Volume (EEV) and Salting-out Effect of Salts. In the present paper, the scaled EEV of Na_3PO_4, Na_2SO_3, or NaH_2PO_4 was calculated using the model developed by Guan et al.[35] This binodal model based on the statistical geometry methods for aqueous polymer—polymer systems can also be used for the correlation of experimental binodal data for the studied systems. The binodal equation for the aqueous ionic liquid + salt systems can be written as our previous research,[36] using eqs 9 and 10 as follows:

$$\ln\left(V^*_{213}\frac{w_2}{M_2} + f_{213}\right) + V^*_{213}\frac{w_1}{M_1} = 0 \tag{9}$$

$$\ln\left(V^*_{213}\frac{w_2}{M_2}\right) + V^*_{213}\frac{w_1}{M_1} = 0 \tag{10}$$

where V^*_{213}, f_{213}, M_1, and M_2 are the scaled EEV of salt, the volume fraction of unfilled effective available volume after tight packing of salt molecules into the network of ionic liquid molecules in ionic liquid aqueous solutions, which includes the influence of the size of the water molecules, and molar masses of ionic liquid and salt, respectively. For the investigated systems, the V^*_{213} and f_{213} values obtained from the correlation of the experimental binodal data along with the corresponding correlation coefficients and standard deviations are given in Table 9. In the original application, eq 10 was used to correlate binodal data of polymer—polymer systems because of the marked difference in size between the two components. The f_{213} value will be very small and consequently can be neglected. From Table 9, we found that the parameter f_{213} was not so small as to be neglected for the investigated systems apart from $[\mathrm{Pmim}]\mathrm{BF}_4 + Na_2SO_3$ ATPSs, and thus eq 9 should be used to correlate binodal data. However, as for the $[\mathrm{Pmim}]\mathrm{BF}_4 + Na_2SO_3$ ATPSs, the standard deviation was no significant difference between these two equations in binodal data fitting, so a simplified eq 10 can be used.

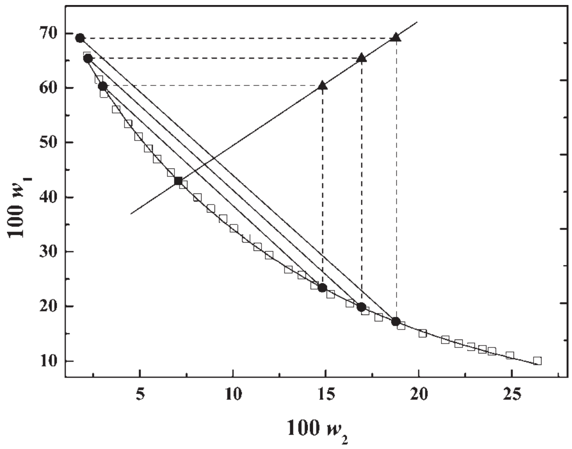

Figure 3. Binodal curve, tie-lines, and plait point for the $[\mathrm{Emim}]\mathrm{BF}_4$ (1) + NaH_2PO_4 (2) + H_2O (3) system at 298.15 K: □, binodal curve data; —, calculated binodal from eq 4; ●, tie-line data; —, tie-lines; ▲, auxiliary curve data; —, calculated from eq 8; ■, plait point.

The scaled EEV of inorganic salt in $[\mathrm{Emim}]\mathrm{BF}_4$ and $[\mathrm{Pmim}]\mathrm{BF}_4$ water component solvent is in the order Na_3PO_4 > Na_2SO_3 > NaH_2PO_4. On the basis of standard deviations presented in Tables 4 and 9, we conclude that in the correlation of the experimental binodal data, the binodal model, eq 9 or 10, with two or one parameters gives rather poor results. However, the values of fitted parameter, V^*_{213}, in the investigated systems

Table 9. Values of Parameters of eq 9 or 10 for the [Emim]BF_4/[Pmim]BF_4 (1) + Na_3PO_4/Na_2SO_3/NaH_2PO_4 (2) + H_2O (3) ATPSs at T = 298.15 K

salt	10^{-2} V^*_{213} ($g \cdot mol^{-1}$)	$10^2 f_{213}$	R^2	$\delta(V^*_{213})^b$	$\delta(f_{213})^c$	sd^a
			[Emim]BF_4 (1) + salt (2) + H_2O (3)			
Na_3PO_4	8.7611	3.65	0.99325	8.38	0.0023	1.38
Na_2SO_3	5.5509	12.31	0.99800	4.66	0.0044	0.68
NaH_2PO_4	2.4059	43.69	0.96901	18.95	0.0375	2.88
			[Pmim]BF_4 (1) + salt (2) + H_2O (3)			
Na_3PO_4	8.9950	2.38	0.96023	15.84	0.0044	3.09
Na_2SO_3	7.3088		0.98513	3.17		1.71
NaH_2PO_4	3.0208	37.11	0.93507	33.01	0.0552	4.79

[a] sd = $\{\sum_{i=1}^{N} (100\, w_1^{calcd} - 100\, w_1^{exptl})^2/N\}^{0.5}$, where w_1^{exptl} is the experimental mass fraction of [Emim]BF_4/[Pmim]BF_4 in Tables 1 and 2, w_1^{calcd} is the corresponding data calculated using eq 9 or 10. N represents the number of binodal data. [b] $\delta(V^*_{213})$ is the standard deviation for the fitting parameters of "V^*_{213}". [c] $\delta(f_{213})$ is the standard deviation for the fitting parameters of "f_{213}".

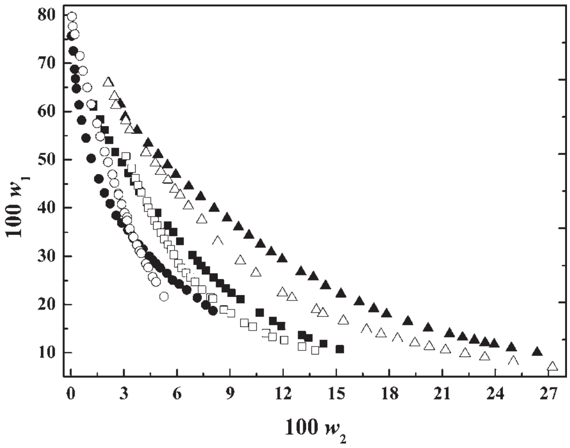

Figure 4. Binodal curves plotted in mass fraction for the [Emim]BF_4/Pmim]BF_4 (1) + Na_3PO_4/Na_2SO_3/NaH_2PO_4 (2) + H_2O (3) ATPSs at 298.15 K. ●, [Emim]BF_4 + Na_3PO_4 ATPS; ■, [Emim]BF_4 + Na_2SO_3 ATPS; ▲, [Emim]BF_4 + NaH_2PO_4 ATPS; ○, [Pmim]BF_4 + Na_3PO_4 ATPS; □, [Pmim]BF_4 + Na_2SO_3 ATPS; Δ, [Pmim]BF_4 + NaH_2PO_4 ATPS.

with a specific ionic liquid, should be related to the salting-out strength of the salt. To examine more closely the relation between the EEV values and salting-out strength, the binodals of the investigated systems are plotted in Figure 4 where the concentration of the two components is expressed in mass fraction. As shown in Figure 4, the salting-out effect of salts are in the same order as EEV, which indicate that increase in EEV is reflected by a decrease in the concentration of salt required for the formation of ATPSs.

The salting-out effect can also be related to the Gibbs free energy of hydration of the ions (ΔG_{hyd}).[37,38] In this work, the salts considered share a common cation (Na^+) but contained different anions of increasing charge. The anion with higher charge (with the same size[39]) has better salting-out effect because the higher charge anion hydrates more water than the lower charge anion. Also, it was found that better salting-out of ILs is observed when the ions of the salt have a more negative Gibbs free energy (ΔG_{hyd} PO_4^{3-}, -2765 $kJ \cdot mol^{-1}$ > SO_3^{2-}, -1301 $kJ \cdot mol^{-1}$ > $H_2PO_4^-$, -1125 $kJ \cdot mol^{-1}$).[40−42]

Phase-Separation Abilities of ILs. The effect of ILs on the phase-forming ability for the investigated systems is also illustrated in Figure 4. We can see that the binodal curve of [Pmim]BF_4 + Na_2SO_3 ATPS is shorter because there is a spot of solid in turbid when the [Pmim]BF_4 with high mass fraction. This may be caused by the solvent properties of [Pmim]BF_4. As shown in Figure 4, the phase-forming ability of [Pmim]BF_4 is better than [Emim]BF_4 in ILs + Na_2SO_3/NaH_2PO_4 ATPSs. It also can be seen from Table 9 that the scaled EEV of Na_2SO_3/NaH_2PO_4 in [Pmim]BF_4−water component solvent is higher than that in [Emim]BF_4−water component solvent. For the same salt in different component solvents, the increase of EEV indicates that the corresponding IL is easier to be excluded from the salt-rich phase to the IL-rich phase, that is to say, the phase-separation ability of IL increases with the increase of EEV. This can be due to the phase-forming ability of ILs increases with an increase of alkyl chain length in these systems. This is similar to PEG + salt ATPSs.[43] However, when the mass fraction of [Pmim]BF4 exceeds 32.35%, the phase-separation ability of [Emim]BF_4 is higher than [Pmim]BF_4 in [Emim]BF_4/[Pmim]-BF_4 + Na_3PO_4 ATPSs; when the mass fraction of [Pmim]BF_4 is below 32.35%, the phase-separation ability is just the reverse. At the present time, the reason for this was not fully understood.

■ CONCLUSION

Liquid−liquid equilibrium data have been determined for [Emim]BF_4/[Pmim]BF_4 + Na_3PO_4/Na_2SO_3/NaH_2PO_4 ATPSs at T = 298.15 K, respectively. Two empirical equations were used to correlate binodal data. The Othmer-Tobias and Bancroft as well as Setschenow-type equations were used to correlate tie-line data. The results indicate that the calculation method and corresponding tie-line data are reliable. The effect of salt on the phase forming ability has been studied based on the effective excluded volume (EEV) values from fitting the binodal data to the binodal model, and the salting-out effect are in the order of Na_3PO_4 > Na_2SO_3 > NaH_2PO_4, and the phase-separation ability of ILs is in the order [Pmim]BF_4 > [Emim]BF_4.

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