Phase Behavior of (1-Alkyl-3-methyl Imidazolium Tetrafluoroborate + 6-(Hydroxymethyl)oxane-2,3,4,5-tetrol + Water)

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Phase behavior of 1-alkyl-3-methyl imidazolium tetrafluoroborate ([C_n mim][BF₄], n=2 to 10), 6-(hydroxymethyl)oxane-2,3,4,5-tetrol and water has been determined at temperatures in the range of (242.15 to 308.15) K. Binodal curves, tie-lines, and the slope of the tie-line (STL) for [C_3 mim][BF₄]/[C_4 mim][BF₄] + glucose + H₂O systems were obtained at different temperatures of T=(278.15, 288.15, 298.15, and 308.15) K. Results show that, as the temperature decreases, the two-phase area expands and the STL increases. Binodal curves were correlated using an empirical equation, and tie-lines were correlated according to the Othmer—Tobias and Bancroft equations. These equations satisfactorily represented the experimental data. The molecular structure is used as an argument to describe the phase-forming mechanism.

Introduction

Aqueous biphasic systems (ABS's) are well-known as green separation systems and are potentially able to replace conventional organic compounds. ABS's are usually composed of aqueous solutions of two water-soluble polymers or by addition of an inorganic salt (e.g., sulfate or phosphate), at a high concentration, to a solution of a polymer. However, polymer—polymer ABS's have a relatively high cost, a high viscosity, and require a relatively long time to result in for phase splitting. For electrolyte—polymer systems, the properties strongly limit their applications in biotechnology owing to high salt concentrations, which may cause the denaturation of sensitive biological structures.

Ionic liquids (ILs) are the latest molecular class that has attracted attention for green chemistry applications owing to their unique properties: extremely low vapor pressure, nonflammability, excellent solvent power for organic and inorganic compounds, and relative ease of structure modification to elicit the desired physical properties. ILs have been applied to biocatalysis, electrochemistry, and separation. IL-based ABS's were reported by Rogers and co-workers in 2003¹ and more recent work reported in refs 2 to 6. However, these ABS's are based on IL with salt where the IL tends to be concentrated in the upper phase with some salt contamination, which makes the system more complex. Recently, alternative ABS's based on ILs, carbohydrate, and water have been reported.7-11 This system is more environmentally benign and is potentially used in biological engineering, pharmaceuticals, and polluted water treatment.

In this work, we report the phase behaviors of 1-alkyl-3-methyl imidazolium tetrafluoroborate ($[C_n mim][BF_4]$, n = 2 to 10), with 6-(hydroxymethyl)oxane-2,3,4,5-tetrol (glucose) and water. Binodal curves, tie-lines, and the slope of the tie-line

(STL) for $[C_3 mim][BF_4]/[C_4 mim][BF_4] + glucose + H_2O$ ABS's were obtained at T = (278.15 to 308.15) K. Binodal curves were correlated using an empirical equation, and the tielines were correlated according to the Othmer–Tobias and Bancroft equations. Results obtained from the correlations are in good agreement with the experimental data.

Experimental Section

Reagents and Chemicals. [C_nmim][BF₄] (n = 2 to 10) was synthesized according to procedures reported in the literature, and the composition was verified by H NMR. The IL was dried under vacuum at T = 353.15 K for a time of 48 h before use. The water content of IL after drying was measured by Karl Fischer titration (Metrohm KF 787) and was less than $2 \cdot 10^{-4}$. Residual chloride in IL was $2 \cdot 10^{-3}$ mol·dm⁻³, which was determined by the method reported by Seddon et al. Glucose was purchased from Beijing Chemistry Reagent Company, dried under vacuum at T = 353.15 K for 48 h, and used without further purification. The water used was twice-distilled.

Procedures. The binodal curves were determined by a titration method according to literature 14 at T=(278.15, 288.15, 298.15, and 308.15) K. The experiment on tie-lines was conducted with the apparatus similar to the reported work. A glass vessel with a volume of 50 cm^3 was used to conduct the phase equilibrium determinations. The glass vessel was fitted with an external jacket through which water or ethanol was circulated to form a thermostat with a temperature stability of ± 0.1 K. The fluid mixture was prepared gravimetrically in a sealed glass vessel that was stirred for 3 h and then was set in the thermostat with a desired temperature for a time of 24 h to permit thorough separation. Preliminary experiments showed that this time was sufficient to achieve the equilibrium of two transparent liquid phases with a well-defined interface. After separation

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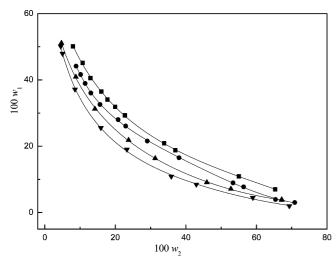


Figure 1. Binodal curves for $\{[C_3mim][BF_4](1) + glucose(2) + H_2O(3)\}$ as a function of mass fraction w_2 . \blacksquare , T = 308.15 K; \bullet , T = 298.15 K; \blacktriangle , $T = 288.15 \text{ K}; \, \mathbf{v}, \, T = 278.15 \text{ K}; \, -, \, \text{eq } 1.$

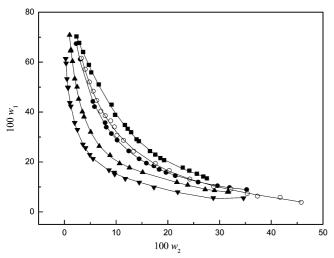


Figure 2. Binodal curves for $\{[C_4mim][BF_4](1) + glucose(2) + H_2O(3)\}$ as a function of mass fraction w_2 . \blacksquare , T = 308.15 K; \bullet , T = 298.15 K; \blacktriangle , T = 288.15 K; \triangle , T = 278.15 K; \bigcirc , literature data; 9 -, eq 1.

of the two phases, samples of both phases were collected with a long pinhead syringe and analyzed after dilution with water.

Analysis. The concentration of IL was determined by high performance liquid chromatography (HPLC), a Agilent 1100 series HPLC with cation exchange column⁸ (Zorbax Scx 250 \times 4.6 mm, inner diameter 5 μ m, Agilent). The concentration of water in both phases was determined by Karl Fischer titration (Metrohm KF 787). The concentration of glucose was obtained by the difference. The accuracy of the analysis method was verified by comparing this work with the published work. 16 For example, the mass fraction solubility of $[C_8 \text{mim}][BF_4]$ in water at T = 298.15 K is 0.0133, which is consistent with the reported value of (0.018 ± 0.005) . ¹⁶ All experiments were repeated twice, and the repeatability was about \pm 0.001.

Results and Discussion

In this work, it was found that $([C_3mim][BF_4]/[C_4mim][BF_4]$ + glucose + H₂O) forms ABS's in the temperature range of $(242.15 \text{ to } 373.15) \text{ K. } ([C_2 \text{mim}][BF_4] + \text{glucose} + H_2O) \text{ forms}$ solid at a temperature of about 245 K and [C_nmim][BF₄] (with

Table 1. Binodal Curves Data for the {[C₃mim][BF₄]/[C₄mim][BF₄] (1) + Glucose (2) + H_2O (3)} System at Temperatures T

T = 278.15 K		T = 288.15 K			98.15 K	-			
$100 \ w_1$	100 w ₂	$100 \ w_1$	100 w ₂	$100 \ w_1$	$100 \ w_2$	$100 \ w_1$	100 w ₂		
$[C_3 \text{mim}]BF_4(1) + Glucose(2) + H_2O(3)$									
58.98	4.47	67.16	3.92	65.42	3.94	8.01	50.13		
42.95 8.48		45.95	9.09	56.39	7.74	10.76	45.14		
35.85	10.88	31.30	16.34	38.04	16.55	12.95	40.55		
23.28	19.01	23.76	21.86	11.45	38.93	16.04	36.51		
15.91	25.53	8.80	40.90	22.92	26.10	17.80	34.07		
8.56	37.14	52.77	7.11	15.65	32.60	19.95	31.88		
5.02	47.92	14.23	31.24	13.05	36.04	22.72	29.30		
4.52	4.52 50.14		3.71	70.86	3.03	33.85	20.88		
69.35	1.98	4.72	51.13	10.17	41.66	65.33	7.01		
				8.86	44.16	55.05	10.90		
				29.08	21.55	37.02	18.81		
				20.80	28.02				
				53.38	8.95				
	[(C ₄ mim]BF	$F_4(1) + G$	lucose (2)	$+ H_2O$ (3)			
5.55	34.63	7.95	31.58	8.92	35.22	13.43	27.55		
5.61	28.80	8.09	31.73	9.73	31.92	14.14	26.87		
7.97	21.92	8.58	29.03	10.45	29.60	15.27	25.62		
9.82	17.31	8.98	27.23	11.96	25.84	16.54	24.17		
11.79	14.46	10.75	23.85	14.54	21.43	17.74	22.88		
13.34	11.77	11.84	21.75	15.82	19.64	20.74	19.26		
15.11	9.71	15.83	15.14	16.98	18.33	21.54	18.56		
15.80	9.66	17.70	12.57	18.44	17.29	22.91	17.56		
16.79	8.62	19.40	10.67	19.55	15.84	24.33	16.55		
21.31	5.54	22.69	8.84	21.25	14.45	28.30	14.39		
22.90	4.91	26.30	6.73	24.38	12.44	29.06	13.96		
25.66	4.09	31.98	5.08	28.74	10.18	31.89	12.90		
27.09	3.57	38.12	3.79	31.37	9.07	33.26	12.24		
32.93	2.52	40.10	3.47	33.94	8.09	34.79	11.67		
35.73	1.99	45.19	2.75	35.71	7.87	38.84	9.80		
42.32	1.22	50.10	2.46	42.15	5.81	42.97	9.13		
43.71	1.05	53.34	2.00	44.25	5.49	51.08	6.63		
49.69	0.71	60.33	1.55	61.16	3.06	55.87	5.19		
49.92	0.66	64.55	1.20	67.42	2.26	58.88	4.70		
53.30	0.49	64.90	1.26			64.05	3.60		
59.53	0.33	70.82	1.00			67.67	2.87		
61.37	0.25					70.24	2.32		

n = 5 to 9) is partially soluble with water at ambient temperature. The mutual solubility of IL and water can be lowered by the addition of glucose.

Binodal Curves. Binodal curves for ([C₃mim][BF₄]/ $[C_4 \text{mim}][BF_4]$ (1) + glucose (2) + H₂O) were determined at temperatures of (278.15, 288.15, 298.15, and 308.15) K and are shown in Figures 1 and 2; the results are listed in Table 1. The data reported in the literature⁹ for ($[C_4 mim][BF_4]$ + glucose + H₂O) at room temperature are also shown in Figure 2. From Figure 2, it is clear that the results obtained in this work are consistent with the literature values. Figure 2 also shows that the two-phase area expands with decreasing temperature. This phenomenon has been observed for other ABS's composed of $([C_4mim][BF_4] + fructose + H_2O)^{8,10}$ and in aqueous twopolymer systems¹⁷ and is contrary to that observed in singlepolymer systems. 18 The two-phase area of ([C₃mim][BF₄] + glucose $+ H_2O$) is less than ($[C_4mim][BF_4] + glucose + H_2O$). In the experiment, it was found that the top phase is not always glucose-rich and the bottom phase is not always IL-rich. As the concentration of glucose increases, phase inversion occurs so that the glucose-rich phase is beneath the IL-rich phase. This phenomenon is essential information for the design of separation process with phase tunable IL-based ABS's.

The binodal curves data for ([C₃mim][BF₄]/[C₄mim][BF₄] + glucose + H_2O) were correlated with a nonlinear empirical eq 1^8

Table 2. Values of Parameters of Eq 1 for $([C_3mim][BF_4]/[C_4mim][BF_4] + Glucose + H_2O)$ at Temperatures T

T/K	а	b	С	d	e	SD	R^2					
$[C_3 mim][BF_4] + Glucose + H_2O$												
278.15	99.3223	-29.4337	2.9928	-0.01736	0.0001	0.4976	0.9996					
288.15	90.6001	-21.9488	1.7971	-0.0094	0.0001	0.2910	0.9999					
298.15	124.1526	-41.5259	5.3255	-0.04613	0.0002	0.2640	0.9998					
308.15	96.3172	-19.4761	1.1311	0.0005	-0.0000	0.2964	0.9997					
	$[C_4 mim][BF_4] + Glucose + H_2O$											
278.15	80.5595	-43.8773	8.8339	-0.1696	0.0019	0.5819	0.9992					
288.15	128.7286	-72.7347	14.3952	-0.2472	0.0025	0.6098	0.9994					
298.15	136.4746	-57.8110	8.3436	-0.0857	0.0006	0.4458	0.9995					
308.15	79.2740	4.94825	-7.6878	0.2411	-0.0030	0.4664	0.9995					

$$w_1 = a + bw_2^{0.5} + cw_2 + dw_2^2 + ew_2^3$$
 (1)

where w_1 and w_2 represent the mass fraction of IL and glucose, respectively. In eq 1, a, b, c, d, and e are coefficients, and the numerical values, listed in Table 2, are obtained by adjustment to the measured values.

Tie-Lines. Tie-lines data for ($[C_3mim][BF_4]/[C_4mim][BF_4]$) (1) + glucose (2) + H₂O) are listed in Table 3 and, at T=298.15 K, shown in Figure 3. The tie-line compositions were fit to equations given by Othmer–Tobias, eq 2, and Bancroft, eq 3:^{7,19–21}

$$\frac{1 - w_1^{\mathrm{I}}}{w_1^{\mathrm{I}}} = k_1 \left(\frac{1 - w_2^{\mathrm{G}}}{w_2^{\mathrm{G}}} \right)^n \tag{2}$$

and

$$\frac{w_3^{G}}{w_2^{G}} = k_2 \left(\frac{w_3^{I}}{w_1^{I}}\right)^r \tag{3}$$

where k_1 , k_2 , n, and r are adjustable parameters obtained by regression analyses. In eqs 1 and 2, $w_1^{\rm I}$ is the mass fraction of IL in the IL-rich phase and $w_2^{\rm G}$ the mass fraction of glucose in the glucose-rich phase, and $w_3^{\rm G}$ and $w_3^{\rm I}$ are the mass fractions of water in the glucose-rich phase and IL-rich phase, respectively. Linearized forms of eqs 2 and 3 were used to determine the adjustable parameters, and these are listed in Table 4 where the subscripts 1 and 2 refer to the use of eqs 2 and 3, respectively.

STL was determined from

$$STL = \Delta w(glucose)/\Delta w(IL)$$
 (4)

where $\Delta w(\text{glucose})$ and $\Delta w(\text{IL})$ are the differences in the mass fraction of glucose and IL between the two phases, respectively. STLs obtained as a function of temperatures are shown in Figure 4 and the data listed in Table 3. Figure 4 shows that STL decreases with increasing temperature. From Figure 4, it can be seen that STL of ([C₃mim][BF₄] + glucose + H₂O) is less than that of the [C₄mim][BF₄] ABS; that is, the mutual solubility of the [C₃mim][BF₄]-rich phase and glucose-rich phase is better. This phenomena concurs with the two-phase area of ([C₃mim][BF₄] + glucose + H₂O) that is less than that of ([C₄mim][BF₄] + glucose + H₂O).

Phase-Forming Mechanism. At infinite dilution the IL dissociates in H_2O albeit with weak hydration. As the concentration of IL increases, the ions attract to form H_2O -mediated clusters, 22 and when the cluster size is sufficiently large, that is, the case for ILs (with n > 4), they phase-separate.

Raman spectroscopy has been used to study the hydrogen interactions between glucose and water.²³ At high concentrations sugar and water dissociate owing to interactions between sugar and sugar although the tendency for glucose molecules

Table 3. Tie-lines Data and STLs for $\{[C_3mim][BF_4]/[C_4mim][BF_4](1) + Glucose (2) + H_2O (3)\}$ at Temperatures T

T	IL-rich	phase	glucose-r	ich phase		
K	$100 \ w_1$	100 w ₂	100 w ₁	100 w ₂	STL	average of STI
	[0	C ₃ mim][E	$3F_{4}(1) +$	Glucose (2	$(2) + H_2O$	3)
278.15	89.70	0.50	5.24	44.39	-0.5197	
	86.81	0.63	5.54	41.19	-0.4991	
	84.20	1.08	6.18	39.61	-0.4938	
	78.11	1.10	8.22	35.40	-0.4908	
	72.30	1.57	10.45	31.83	-0.4892	-0.4985
288.15	85.40	1.07	8.52	43.01	-0.5455	
	82.11	1.17	9.34	40.45	-0.5398	
	77.10	1.45	11.68	37.36	-0.5489	
	71.64	1.69	12.95	34.06	-0.5515	
	61.54	4.60	16.63	29.38	-0.5518	-0.5475
298.15	84.32	1.22	7.60	45.27	-0.5742	
	79.22	1.83	9.12	41.68	-0.5684	
	74.23	2.36	11.63	38.12	-0.5712	
	68.83	3.58	13.19	34.85	-0.5620	
	63.64	4.01	17.72	31.66	-0.6021	-0.5756
308.15	82.33	5.62	5.55	53.86	-0.6283	
	74.72	6.13	10.71	44.90	-0.6057	
	66.62	7.23	12.83	38.31	-0.5778	
	60.03	8.14	19.93	32.24	-0.6259	-0.6094
	[0	C ₄ mim][E	$3F_4$ (1) +	Glucose (2	$(2) + H_2O$	3)
278.15	56.34	0.39	10.08	19.60	-0.4152	,
	68.04	0.14	8.43	22.50	-0.3752	
	76.40	0.10	7.14	25.20	-0.3624	
	79.95	0.13	6.52	26.80	-0.3633	
	87.83	0.14	5.86	31.20	-0.3789	
	92.14	0.13	5.51	34.95	-0.4019	-0.3828
288.15	60.63	1.00	11.70	22.30	-0.4354	
	73.40	0.96	9.25	26.80	-0.4028	
	76.80	0.89	8.45	28.60	-0.4055	
	81.20	0.72	8.22	30.90	-0.4136	
	86.40	0.62	7.03	34.10	-0.4218	
	91.75	0.71	5.24	39.88	-0.4528	-0.4220
298.15	60.90	2.76	12.40	25.01	-0.4588	
	71.30	2.02	10.37	29.80	-0.4559	
	77.50	1.92	8.95	33.24	-0.4569	
	85.70	1.91	7.01	39.72	-0.4805	
	89.14	1.90	6.22	42.87	-0.4941	-0.4692
308.15	56.44	4.93	15.00	25.20	-0.4891	
	65.57	3.48	11.80	29.70	-0.4876	
	70.70	2.28	9.90	32.57	-0.4981	
	81.09	1.76	8.07	39.64	-0.5188	
	87.60	1.65	5.51	45.14	-0.5298	
	91.48	1.49	5.36	50.87	-0.5734	-0.5161
	, 1		2.23	20.07	0.0.751	0.0101

to aggregate is not very significant.²⁴ The water molecules may be structured around the glucose and the hydrogen-bond between water reinforced. The interaction of first-shell water molecules with solute primarily is with glucose hydroxyl groups.

On the basis of this information, we speculate that, with the addition of glucose to homogeneous IL solution, a different water structure is formed owing to structural changes in the

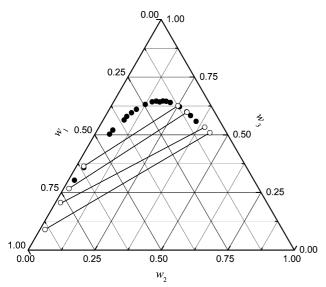


Figure 3. Ternary diagrams of $\{[C_4mim][BF_4](1) + glucose(2) + H_2O(1)\}$ (3)} at T = 298.15 K: \bullet , binodal curve; \bigcirc , tie-line; -, tie-lines.

Table 4. Values of Parameters of Eqs 2 and 3 for ([C₃mim][BF₄]/ $[C_4 mim][BF_4] + Glucose + H_2O)$ at Temperatures T

T/K	k_1	n	k_2	r	R_1	R_2	SD_1	SD_2			
$[C_3 mim][BF_4] + Glucose + H_2O$											
278.15	3.2210	0.4379	2.6639	0.3815	0.9982	0.9985	0.0064	0.0050			
288.15	2.9682	0.4605	2.2957	0.3904	0.9995	0.9977	0.0038	0.0065			
298.15	2.8354	0.5166	2.1210	0.4055	0.9977	0.9979	0.0077	0.0056			
308.15	2.7196	0.7467	1.9730	0.5000	0.9996	0.9969	0.0052	0.0118			
$[C_4 mim][BF_4] + Glucose + H_2O$											
278.15	4.5086	0.3600	3.9604	0.3382	0.9999	0.9996	0.0018	0.0035			
288.15	4.171	0.4217	3.5128	0.3763	0.9997	0.9996	0.0034	0.0036			
298.15	3.640	0.4911	3.1160	0.4381	0.9996	0.9996	0.0049	0.0038			
308.15	3.320	0.5236	2.7686	0.4559	0.9993	0.9984	0.0079	0.0104			

hydration shells of both IL and glucose. Therefore, two differently structured microphases of water originate in the homogeneous mixture (below the binodal). An increase in the amount of IL or glucose or both upsets the stability of this microemulsion and leads to coagulation of the droplets (turbidity) resulting in phase separation.

Conclusions

Phase diagrams for $([C_3mim][BF_4]/[C_4mim][BF_4] + glucose$ + H₂O) were reported at temperatures ranging from (278.15 to

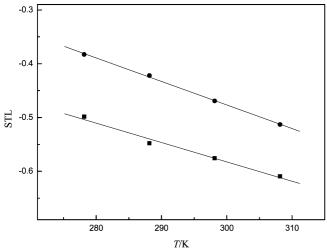


Figure 4. STLs for (IL + glucose + H_2O) as a function of temperatures $T. \blacksquare$, ([C₃mim][BF₄] + glucose + H₂O); \blacksquare , ([C₄mim][BF₄] + glucose + H₂O).

308.15) K, including binodal curves, tie-lines, and STL. It was found that with decreasing temperature the two-phase areas expanded and the STL increased. Binodal curves were correlated using an empirical equation, and the tie-lines were correlated according to both the Othmer-Tobias and the Bancroft equations. Results show that these equations can be satisfactorily represented in the experimental data of the systems investigated over the given temperatures studied.

Acknowledgment

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