2026 J. Chem. Eng. Data **2007,** *52,* 2026−2031

Liquid−Liquid Equilibria of Aqueous Biphasic Systems Containing Selected Imidazolium Ionic Liquids and Salts

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Liquid−liquid equilibrium data have been determined for imidazolium ionic liquid ([C_4mim]Cl, [C_6mim]Cl, [C_4mim]Br, [C_6mim]Br, [C_8mim]Br, [C_{10}mim]Br) + salt (KOH, K_2HPO_4, K_2CO_3, K_3PO_4) aqueous biphasic systems at $T = 298.15$ K, and in part at $T = (308.15$ to $318.15)$ K. Factors affecting the binodal curves such as nature of ionic liquids and salts and temperature are also studied. The binodal curves are fitted to a three-parameter equation, and the tie-lines were described by the Othmer−Tobias and Bancroft equations. It is found that an increase in temperature caused no significant expansion of the two-phase area. However, the binodal curves became more close to the origin with an increase in alkyl chain length of the ionic liquids (ILs), and the ionic liquids with the Br^- anion are easier to form two phases compared to those with the Cl^- anion. These data are expected to be useful for the development and design of the extraction process using ILs based on aqueous biphasic systems.

Introduction

Aqueous biphasic systems (ABSs), introduced in 1956 by Albertsson,[1] have been recognized as an economical and efficient downstream processing method. Because the bulk of both phases consists of water, ABSs offer a gentle biocompatible environment over conventional extraction using organic solvents.[2,3] Without a doubt, the application of ABSs that has attracted the most interest in biotechnology is their successful usage for recovery and purification of many biological materials such as proteins, enzymes, and nucleic acids.[4−8]

In recent years, room-temperature ionic liquids (ILs), 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.[9,10] IL-based, aqueous two-phase systems were reported in 2003 by Rogers and co-workers for the first time.[11] These new ABSs have many advantages shared by ILs and ABSs, such as low viscosity, little emulsion formation, no need of using volatile organic solvent, quick phase separation, high extraction efficiency, and gentle biocompatible environment, and have been successfully used to separate testosterone, epitestosterone, opium alkaloids, and bovine serum albumin.[12−14]

Rogers and his co-workers[15] reported the phase diagrams for aqueous biphasic systems based on ionic liquids of tetra-*n*-butylammonium chloride (N_{4444}Cl), tetra-*n*-butylphosphonium chloride (P_{4444}Cl), 1-butyl-3-methylimidazolium chloride ([C_4mim]Cl), 1-butyl-2,3-dimethylimidazolium chloride ([C_4mmim]Cl), and *N*-butylpyridinium chloride ([C_4py]Cl) and the salts K_3PO_4, K_2HPO_4, K_2CO_3, $(NH_4)_2SO_4$, and KOH. The partitioning of straight chained alcohols between the phases and Gibbs energy of methylene transfer (ΔG_{CH_2}) were also determined for [C_4mim]Cl + salt aqueous biphasic systems. Berthod et al.[16] studied the liquid-phase retention of [C_4mim]Cl + K_2HPO_4 and PEG1000 + K_2HPO_4 aqueous biphasic systems in countercurrent chromatography columns. The [C_4mim]Cl-rich upper phase was found to have a polarity significantly lower than the corresponding PEG rich upper phase because of the much less polar character of imidazolium compared to PEG, and all compounds with an octanol/water partition coefficient higher than 0.02 ($\log P_{IL/W} > -1.7$) will partition preferably to the IL upper phase.

However, systematic studies of liquid−liquid equilibrium for imidazolium ILs + salt aqueous biphasic systems are very limited in the literature. Such information is very useful for the design of an extraction process. In this paper, we report the liquid−liquid equilibrium data for selected ILs ([C_4mim]Cl, [C_6mim]Cl, [C_4mim]Br, [C_6mim]Br, [C_8mim]Br, [C_{10}mim]Br) + salts (KOH, K_2HPO_4, K_2CO_3, K_3PO_4) aqueous biphasic systems. The binodal curves were fitted to a three-parameter equation, and the tie-lines were described by using the Othmer−Tobias and Bancroft equations. These data provide a possible basis for the prediction of phase compositions when such data are not available.

Experimental Section

Materials. Ionic liquids [C_4mim]Cl, [C_6mim]Cl, [C_4mim]Br, [C_6mim]Br, [C_8mim]Br, and [C_{10}mim]Br were prepared as described elsewhere.[17] Commercially available *N*-methylimidazolium (Linhai Kaile Chemical Company, C. P.) and a series of alkyl halides (Shanghai Hushi Chemical Factory, C. P.) were distilled twice before use. All other reagents were of analytical grade, and double distilled deionized water was used in the experiments.

Experimental Procedure. A phase diagram is constituted by a binodal curve and tie-lines. The binodal curve represents the borderline between the one-phase and two-phase regions. The tie-line describes the compositions of the two phases in equilibrium. Determination of the binodal curves was carried out by a turbidometric titration method.[11] Stock aqueous salts solutions were prepared with different mass fractions. A few grams of pure ILs were weighed into a test tube, and a known mass of water was added and then mixed. The mixture was clear at first; however, after a certain amount of the salt solution was added, one further drop made the mixture turbid, and two

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10.1021/je700315u CCC: $37.00

Table 1. Binodal Data of the [C_4mim]Br (1) + Salt (2) + H_2O (3) Systems at Various Mass Fractions of the Components at T = 298.15 K

[C_4mim]Br + K_3PO_4		[C_4mim]Br + K_2HPO_4		[C_4mim]Br + K_2CO_3		[C_4mim]Br + KOH	
w_1	w_2	w_1	w_2	w_1	w_2	w_1	w_2
0.4125	0.0393	0.4353	0.0430	0.3920	0.0617	0.3315	0.1378
0.3533	0.0574	0.2961	0.0932	0.3208	0.0937	0.2744	0.1663
0.3095	0.0763	0.2498	0.1202	0.2786	0.1127	0.2345	0.1917
0.2712	0.0957	0.1935	0.1624	0.2474	0.1316	0.2050	0.2052
0.2339	0.1153	0.1612	0.1841	0.2122	0.1526	0.1833	0.2184
0.2082	0.1306	0.1439	0.1989	0.1809	0.1681	0.1615	0.2320
0.1857	0.1456	0.1235	0.2141	0.1602	0.1824	0.1453	0.2445
0.1670	0.1553	0.1118	0.2256	0.1418	0.1944	0.1301	0.2552
0.1501	0.1657	0.0999	0.2373	0.1313	0.2007	0.1185	0.2654
0.1266	0.1879	0.0891	0.2474	0.1226	0.2085	0.1075	0.2739
0.1129	0.1979	0.0776	0.2601	0.1143	0.2141	0.0975	0.2829
0.1005	0.2066	0.0597	0.2827	0.1042	0.2240	0.0889	0.2912
0.0903	0.2140	0.0489	0.2979	0.0955	0.2304	0.0818	0.2997
0.0789	0.2240	0.0400	0.3119	0.0872	0.2366	0.0726	0.3115
0.0693	0.2321	0.0335	0.3242	0.0790	0.2457	0.0643	0.3221
0.0614	0.2406	0.0312	0.3293	0.0701	0.2553	0.0570	0.3309
0.0548	0.2482	0.0284	0.3355	0.0624	0.2640	0.0508	0.3418
0.0479	0.2563	0.0262	0.3411	0.0508	0.2791	0.0413	0.3593
				0.0420	0.2923		

Table 2. Binodal Data of the [C_6mim]Br (1) + Salt (2) + H_2O (3) Systems at Various Mass Fractions of the Components at T = 298.15 K

[C_6mim]Br + K_3PO_4		[C_6mim]Br + K_2HPO_4		[C_6mim]Br + K_2CO_3		[C_6mim]Br + KOH	
w_1	w_2	w_1	w_2	w_1	w_2	w_1	w_2
0.4550	0.0395	0.3142	0.1280	0.4374	0.0524	0.3970	0.0972
0.3961	0.0550	0.1967	0.1439	0.2509	0.1184	0.2735	0.1473
0.3226	0.0747	0.1492	0.1729	0.1942	0.1478	0.1992	0.1783
0.2658	0.0954	0.1209	0.1939	0.1531	0.1693	0.1568	0.2039
0.2285	0.1111	0.0999	0.2099	0.1282	0.1852	0.1375	0.2163
0.1962	0.1249	0.0834	0.2236	0.1077	0.1980	0.1204	0.2274
0.1753	0.1370	0.0759	0.2311	0.0909	0.2120	0.1082	0.2377
0.1607	0.1450	0.0693	0.2385	0.0804	0.2220	0.0985	0.2451
0.1467	0.1511	0.0630	0.2454	0.0739	0.2265	0.0888	0.2546
0.1365	0.1565	0.0581	0.2514	0.0697	0.2307	0.0813	0.2613
0.1222	0.1662	0.0523	0.2583	0.0637	0.2378	0.0739	0.2662
0.1113	0.1726	0.0483	0.2648	0.0592	0.2432	0.0682	0.2742
0.1016	0.1794	0.0454	0.2689	0.0558	0.2459	0.0631	0.2801
0.0915	0.1870	0.0419	0.2736	0.0505	0.2532	0.0593	0.2844
0.0830	0.1936	0.0395	0.2779	0.0466	0.2578	0.0549	0.2907
0.0762	0.1985	0.0370	0.2813	0.0437	0.2621	0.0513	0.2954
0.0697	0.2048	0.0349	0.2850	0.0402	0.2666	0.0480	0.3005
0.0642	0.2100	0.0329	0.2887	0.0370	0.2723	0.0419	0.3114
0.0593	0.2143	0.0302	0.2941	0.0319	0.2807	0.0370	0.3201
0.0548	0.2194			0.0282	0.2878	0.0324	0.3292

Table 3. Binodal Data of the [C_8mim]Br (1) + Salt (2) + H_2O (3) Systems at Various Mass Fractions of the Components at T = 298.15 K

[C_8mim]Br + K_3PO_4		[C_8mim]Br + K_2HPO_4		[C_8mim]Br + K_2CO_3		[C_8mim]Br + KOH	
w_1	w_2	w_1	w_2	w_1	w_2	w_1	w_2
0.3965	0.0621	0.3238	0.0942	0.4264	0.0717	0.4013	0.0990
0.3474	0.0766	0.2691	0.1225	0.3037	0.1110	0.2799	0.1438
0.2966	0.0946	0.2221	0.1433	0.2276	0.1398	0.2055	0.1774
0.2631	0.1083	0.1931	0.1563	0.2026	0.1540	0.1601	0.2051
0.2329	0.1189	0.1670	0.1722	0.1815	0.1671	0.1274	0.2243
0.2111	0.1285	0.1414	0.1878	0.1615	0.1794	0.1072	0.2387
0.1891	0.1382	0.1157	0.2078	0.1449	0.1906	0.0917	0.2494
0.1701	0.1510	0.0964	0.2226	0.1216	0.2036	0.0782	0.2630
0.1505	0.1589	0.0819	0.2351	0.1046	0.2163	0.0680	0.2756
0.1361	0.1658	0.0704	0.2465	0.0917	0.2258	0.0598	0.2849
0.1231	0.1736	0.0607	0.2580	0.0808	0.2361	0.0534	0.2935
0.1102	0.1821	0.0529	0.2681	0.0712	0.2460	0.0474	0.3013
0.1003	0.1897	0.0486	0.2745	0.0643	0.2528	0.0434	0.3062
0.0912	0.1962	0.0431	0.2816	0.0583	0.2598	0.0391	0.3138
0.0820	0.2022	0.0383	0.2894	0.0530	0.2654	0.0360	0.3191
0.0745	0.2084	0.0368	0.2921	0.0483	0.2718	0.0334	0.3231
0.0643	0.2182	0.0323	0.3004	0.0445	0.2774		
0.0572	0.2257	0.0294	0.3050	0.0412	0.2825		
0.0459	0.2383	0.0268	0.3108	0.0383	0.2875		
0.0423	0.2434			0.0350	0.2913		

Table 4. Binodal Data of the [C_{10}mim]Br (1) + Salt (2) + H_2O (3) Systems at Various Mass Fractions of the Components at T = 298.15 K

[C_{10}mim]Br + K_2HPO_4		[C_{10}mim]Br + K_2CO_3		[C_{10}mim]Br + KOH	
w_1	w_2	w_1	w_2	w_1	w_2
0.2125	0.1465	0.2657	0.1188	0.3016	0.1395
0.1381	0.1953	0.2035	0.1444	0.2350	0.1541
0.1137	0.2110	0.1426	0.1802	0.1612	0.1958
0.0906	0.2283	0.1268	0.1910	0.1260	0.2187
0.0727	0.2440	0.1162	0.1977	0.1032	0.2327
0.0632	0.2546	0.1078	0.2022	0.0810	0.2521
0.0571	0.2615	0.0989	0.2096	0.0744	0.2568
0.0514	0.2696	0.0895	0.2158	0.0673	0.2633
0.0484	0.2736	0.0831	0.2206	0.0613	0.2695
0.0450	0.2794	0.0773	0.2255	0.0569	0.2741
0.0435	0.2815	0.0716	0.2311	0.0531	0.2788
0.0423	0.2829	0.0657	0.2349	0.0495	0.2837
0.0398	0.2873	0.0612	0.2405	0.0457	0.2890
0.0353	0.2950	0.0565	0.2451	0.0417	0.2961
0.0333	0.2986	0.0526	0.2491	0.0390	0.2996
0.0318	0.3016	0.0501	0.2525	0.0369	0.3027
0.0304	0.3043	0.0464	0.2578	0.0345	0.3072
0.0293	0.3061	0.0429	0.2627	0.0324	0.3101
0.0276	0.3097	0.0407	0.2665	0.0305	0.3139
0.0255	0.3139	0.0385	0.2699	0.0291	0.3163
		0.0365	0.2729	0.0274	0.3195
		0.0342	0.2768	0.0258	0.3223
		0.0324	0.2797	0.0244	0.3257
		0.0306	0.2828	0.0232	0.3281

Table 5. Binodal Data of the [C_6mim]Cl (1) + Salt (2) + H_2O (3) Systems at Various Mass Fractions of the Components at T = 298.15 K

[C_6mim]Cl + K_3PO_4		[C_6mim]Cl + K_2HPO_4		[C_6mim]Cl + K_2CO_3		[C_6mim]Cl + KOH	
w_1	w_2	w_1	w_2	w_1	w_2	w_1	w_2
0.3994	0.0530	0.3554	0.0790	0.4398	0.0600	0.3379	0.1610
0.3423	0.0691	0.2156	0.1534	0.3765	0.0856	0.2438	0.2158
0.2796	0.0967	0.1618	0.1954	0.3097	0.1127	0.2052	0.2375
0.2079	0.1354	0.1372	0.2163	0.2589	0.1374	0.1741	0.2584
0.1873	0.1490	0.1124	0.2392	0.2234	0.1558	0.1525	0.2750
0.1676	0.1623	0.0955	0.2561	0.1923	0.1749	0.1325	0.2914
0.1516	0.1713	0.0776	0.2762	0.1697	0.1903	0.1167	0.3019
0.1367	0.1829	0.0704	0.2841	0.1502	0.2049	0.1013	0.3171
0.1244	0.1922	0.0636	0.2933	0.1345	0.2162	0.0907	0.3273
0.1143	0.1996	0.0587	0.3001	0.1218	0.2261	0.0814	0.3370
0.1058	0.2062	0.0552	0.3052	0.1109	0.2338	0.0719	0.3473
0.0949	0.2161	0.0517	0.3107	0.0977	0.2459	0.0660	0.3549
0.0859	0.2239	0.0478	0.3165	0.0876	0.2556	0.0607	0.3613
0.0778	0.2314	0.0440	0.3231	0.0782	0.2655	0.0557	0.3680
0.0712	0.2387	0.0405	0.3293	0.0714	0.2716	0.0499	0.3769
0.0652	0.2452	0.0362	0.3373	0.0651	0.2788	0.0435	0.3875
0.0577	0.2533	0.0337	0.3422	0.0587	0.2858	0.0399	0.3939
0.0520	0.2604	0.0310	0.3479	0.0531	0.2927	0.0375	0.3983
0.0483	0.2646			0.0485	0.2989		
				0.0445	0.3044		

phases occurred. The mass of the mixture was noted, and the composition of the two-phase system was determined by the ratio of the weight of a component added to the total weight of all components added. 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 glass tubes were immersed in a jacketed glass vessel, and the temperature of the system was maintained at T = (298.15, 308.15, and 318.15) K to within ± 0.05 K by a DC-2006 water thermostat (Shanghai Hengping Instrument Factory).

For determination of the tie-lines, a series of aqueous biphasic systems (ABSs) with three different total compositions were prepared in graduated glass tubes which were placed in a thermostated bath. The system was vigorously stirred for at least 1 h to attain equilibrium. The phase separation occurred quickly after cessation of the stirring process. However, a XYJ-802 centrifuge (Jiangsu Medical Instrument Factory) operated at 2000 rpm was still used for a period of 5 min in each test to ensure a complete phase separation. The systems were then placed again into the thermostated bath. After reaching phase equilibrium, visual estimates of the top and bottom volumes were made. The concentration of ILs in both the top phase and the bottom phase was determined by spectrophotometry at 210 nm. For the quantification of water content, the upper and lower phases were dried at 343 K under a vacuum, without decom-

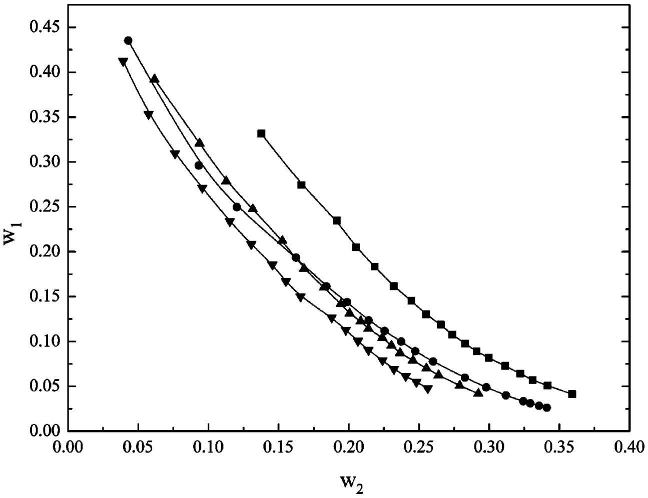

Figure 1. Binodal curves of [C_4mim]Br (1) + salt (2) aqueous biphasic systems at T = 298.15 K: ■, KOH; ●, K_2HPO_4; ▲, K_2CO_3; ▼, K_3PO_4.

position of components of ABSs, until constant mass was obtained. The content of salt 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) at different compositions was calculated by the equation[18]

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

where w_1^t, w_1^b, w_2^t, and w_2^b are the equilibrium mass fractions of ILs (1) and salt (2) in the top (t) and bottom (b) phases. The tie-line lengths are expressed in mass fractions.

Results and Discussion

Effect of Salts and ILs on Binodal Curves. The binodal data determined at 298.15 K for the salts (KOH, K_2HPO_4, K_2CO_3, K_3PO_4) + ILs ([C_4mim]Cl, [C_6mim]Cl, [C_4mim]Br, [C_6mim]Br, [C_8mim]Br, [C_{10}mim]Br) + H_2O are shown in Tables 1 to 5. As an example, the binodal curves of [C_4mim]Br + salts and ILs + K_2HPO_4 are plotted in Figures 1 and 2. The phase diagram provides information about (i) the concentration of phase-forming components required to form two phases, (ii) the concentration of phase components in the top and bottom phases, and (iii) the ratio of phase volumes. Figure 1 shows that ABSs can be formed by adding an appropriate amount of salts to an aqueous solution of [C_4mim]Br. As can be seen, the ability of the salts studied for phase separation follows the order: K_3PO_4 > K_2HPO_4 ≈ K_2CO_3 > KOH. The kosmotropic ions, PO_4^{3-}, HPO_4^{2-}, CO_3^{2-}, and OH^-, which exhibit stronger interaction with water molecules, are beneficial to the ABSs 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-} ($\Delta G_{\mathrm{hyd}} = -2765$ kJ·mol^{-1}) > CO_3^{2-} ($\Delta G_{\mathrm{hyd}} = -1315$ kJ·mol^{-1}) > OH^- ($\Delta G_{\mathrm{hyd}} = -430$ kJ·mol^{-1}).[19] This order follows the Hofmeister series for the strength of the kosmotropic salts. The most kosmotropic salt, K_3PO_4, results in a binodal closest to the origin, indicating that less salt is needed to form an aqueous biphasic system.

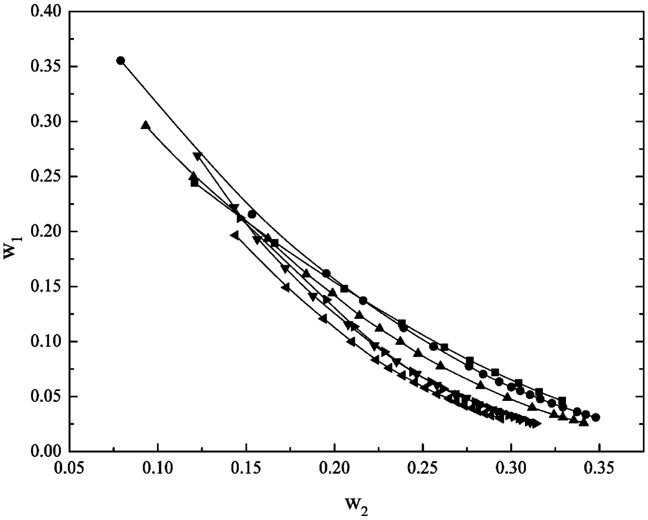

Figure 2. Binodal curves of IL (1) + K_2HPO_4 (2) aqueous biphasic systems at T = 298.15 K: ■, [C_4mim]Cl; ●, [C_6mim]Cl; ▲, [C_4mim]Br; ▼, [C_8mim]Br; solid triangle pointing right, [C_{10}mim]Br; solid triangle pointing left, [C_6mim]Br.

It can be seen from Figure 2 that in the presence of K_2HPO_4 the phase-forming ability of the ILs follows the order: [C_4mim]Br > [C_4mim]Cl, and [C_6mim]Br > [C_6mim]Cl. This can be explained by the different Gibbs energies of hydration of Cl^- and Br^- anions. The values of ΔG_{hyd} for Cl^- and Br^- are (−340 and −315) kJ·mol^{-1}, respectively.[19] Therefore, the ILs with the Cl^- anion hydrate more water molecules than those with the Br^- anion, resulting in difficulty in phase formation as salt was added. When the ILs contain different cations, the phase-forming ability follows the order: [C_6mim]Cl > [C_4mim]Cl, [C_6mim]Br > [C_8mim]Br ≈ [C_{10}mim]Br > [C_4mim]Br. In traditional PEG + salt aqueous biphasic systems, the binodal curves became closer to the origin with the increase in molecular weight of PEG. This may be caused by the increase in the incompatibility between the phase-forming components due to the more hydrophobic character of PEG with larger molecular weight. However, the phase-forming ability of the ILs with different alkyl chain length was not in accordance with the order of their hydrophobicity. [C_6mim]$^+$ has the best phase-forming ability. This anomalous behavior of [C_6mim]$^+$ has been observed by other researchers[20,21] in studying the polarity or melting point of ILs. The reason for this was not fully understood.

Effect of Temperature. As an example, the effect of temperature on phase separation of [C_4mim]Br + K_2HPO_4 + H_2O ABSs was examined at T = (298.15, 308.15, and 318.15) K.

Table 6. Binodal Data for [C_4mim]Br (1) + K_2HPO_4 (2) + H_2O (3) Systems at Different Temperatures

T/K = 308.15		T/K = 318.15	
w_1	w_2	w_1	w_2
0.4085	0.0514	0.4171	0.0487
0.3206	0.0864	0.3432	0.0801
0.2295	0.1374	0.2727	0.1146
0.1794	0.1730	0.2206	0.1481
0.1466	0.1975	0.1834	0.1734
0.1178	0.2222	0.1559	0.1929
0.0990	0.2394	0.1301	0.2164
0.0837	0.2548	0.1150	0.2282
0.0708	0.2697	0.1024	0.2391
0.0598	0.2837	0.0886	0.2559
0.0513	0.2963	0.0755	0.2709
0.0431	0.3098	0.0663	0.2823
0.0373	0.3207	0.0572	0.2944
0.0320	0.3319	0.0477	0.3091
		0.0405	0.3212

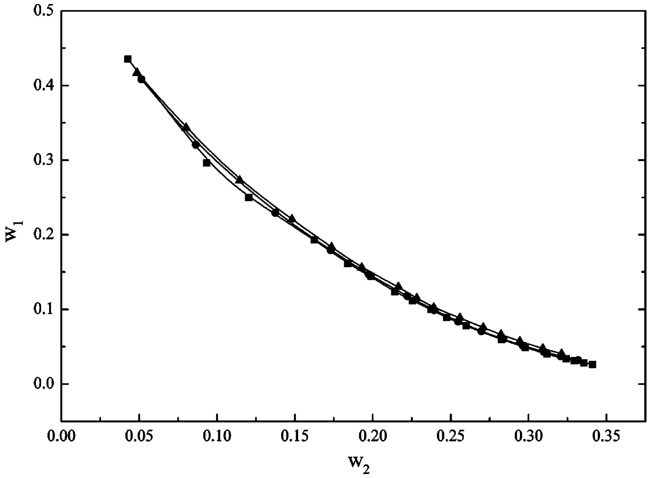

Figure 3. Effect of temperature on binodal curves of [C$_4$mim]Br (1) + K$_2$HPO$_4$ (2) aqueous biphasic systems: ■, 298.15 K; ●, 308.15 K; ▲, 318.15 K.

Table 7. Parameters of Equation 2 for IL + Salt Aqueous Biphasic Systems at T = 298.15 K

	a	b	c	σ^a
[C$_4$mim]Br + K$_3$PO$_4$	−0.3241	−0.3211	0.0657	0.0022
[C$_4$mim]Br + K$_2$HPO$_4$	−0.2453	−0.2260	0.0244	0.0035
[C$_4$mim]Br + K$_2$CO$_3$	−0.3425	−0.3245	0.0601	0.0042
[C$_4$mim]Br + KOH	−0.2559	−0.2608	−0.0410	0.0046
[C$_6$mim]Br + K$_3$PO$_4$	−0.2935	−0.3691	0.0201	0.0024
[C$_6$mim]Br + K$_2$HPO$_4$	−0.0920	−0.1282	−0.1195	0.0054
[C$_6$mim]Br + K$_2$CO$_3$	−0.2596	−0.2996	0.0056	0.0048
[C$_6$mim]Br + KOH	−0.2428	−0.2762	−0.0359	0.0059
[C$_8$mim]Br + K$_3$PO$_4$	−0.2907	−0.3653	0.0096	0.0040
[C$_8$mim]Br + K$_2$HPO$_4$	−0.2256	−0.2601	−0.0215	0.0052
[C$_8$mim]Br + K$_2$CO$_3$	−0.2500	−0.2931	−0.0160	0.0037
[C$_8$mim]Br + KOH	−0.2454	−0.2809	−0.0378	0.0050
[C$_{10}$mim]Br + K$_2$HPO$_4$	−0.1516	−0.1987	−0.0809	0.0029
[C$_{10}$mim]Br + K$_2$CO$_3$	−0.1820	−0.2467	−0.0594	0.0028
[C$_{10}$mim]Br + KOH	−0.1450	−0.1988	−0.1071	0.0037
[C$_6$mim]Cl + K$_3$PO$_4$	−0.2784	−0.2927	0.0311	0.0020
[C$_6$mim]Cl + K$_2$HPO$_4$	−0.2403	−0.2186	0.0125	0.0022
[C$_6$mim]Cl + K$_2$CO$_3$	−0.3252	−0.3082	0.0387	0.0029
[C$_6$mim]Cl + KOH	−0.2878	−0.2628	−0.0385	0.0038

[a] $\sigma = \{\sum_{i=1}^{n} (w_1^{\text{calcd}} - w_1^{\text{exptl}})^2/n\}^{0.5}$, where n is the number of binodal data.

The results are shown in Table 6 and illustrated in Figure 3. It can be seen that the binodal curves are not sensitive to an increase of temperature. This is not in agreement with the fact that the binodal curves of PEG + salt ABSs are closer to the origin with an increase in temperature. A possible reason is that the hydration of [C$_4$mim]Br is not sensitive to temperature.

Presentation of Binodal Curves. From the binodal experimental data in Tables 1 to 5, the phase diagram of K$_2$HPO$_4$ + ILs is plotted in Figure 4a, 4b, and 4c. The liquid phase splits into two equilibrium immiscible liquid phases: a K$_2$HPO$_4$-rich bottom phase and an IL-rich upper phase. Once the two immiscible phases form, any addition of salt will alter the compositions of both immiscible phases (tie-lines). The binodal curves of IL + salt ABSs were fitted by a logarithmic expression which relates the mass fraction of ILs (w_1) to the mass fraction of K$_2$HPO$_4$ (w_2).

$$w_1 = a \ln(w_2 + c) + b \tag{2}$$

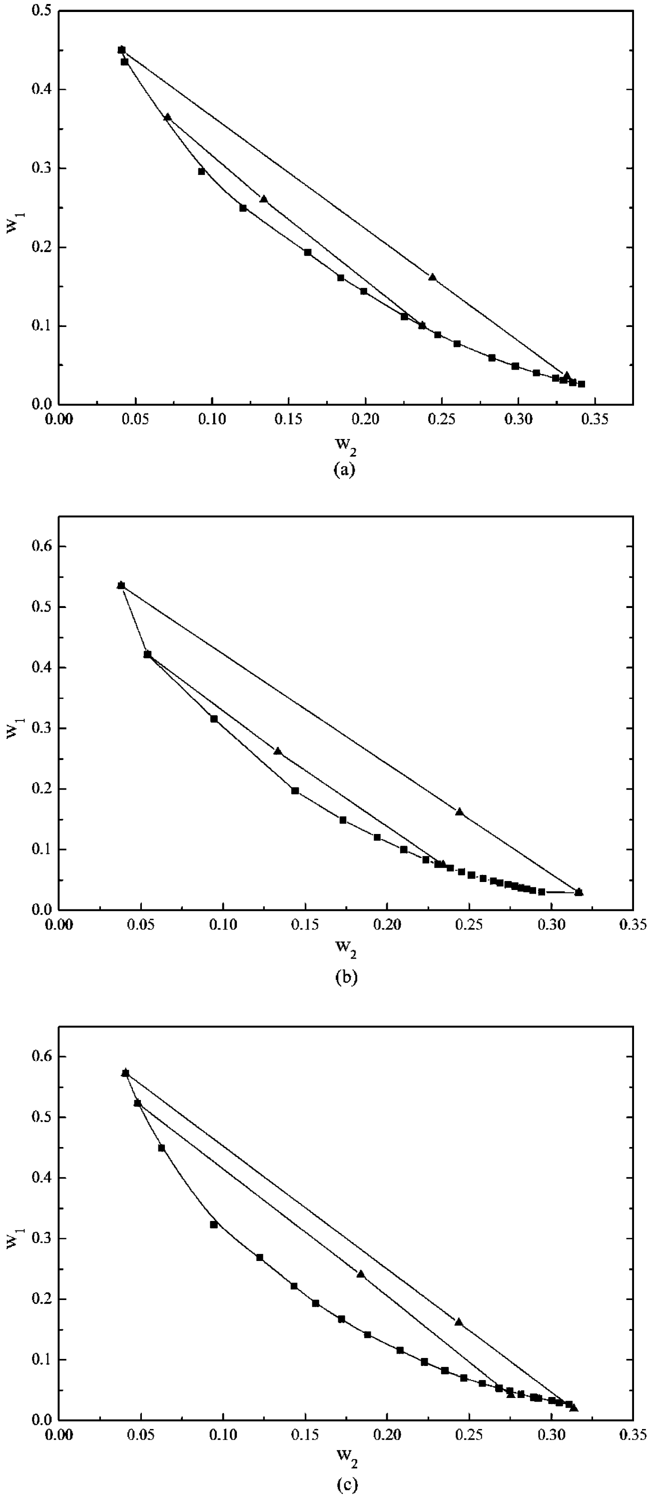

Figure 4. Phase diagram of the IL (1) + K$_2$HPO$_4$ (2) aqueous biphasic systems at T = 298.15 K: (a) [C$_4$mimBr]; (b) [C$_6$mimBr]; (c) [C$_8$mimBr]; ■, binodal; ▲, total composition.

This equation has been used to fit the results of aqueous two-phase systems based on PEG.[22] To obtain the parameters a, b, and c in eq 2 by nonlinear regression, a previous estimation of these values is necessary. From eq 2, we obtain

$$\frac{dw_1}{dw_2} = \frac{a}{c + w_2} \tag{3}$$

This equation can be transformed into

$$\frac{dw_2}{dw_1} = \frac{c}{a} + \frac{w_2}{a} \tag{4}$$

Table 8. Phase Compositions and the Tie-Line Length (TLL) for the IL (1) + K_2HPO_4 (2) + H_2O (3) Aqueous Biphasic Systems at T = 298.15 K

total system		salt-rich phase		IL-rich phase			total system		salt-rich phase		IL-rich phase		
w_1	w_2	w_1	w_2	w_1	w_2	TLL	w_1	w_2	w_1	w_2	w_1	w_2	TLL
			[C_4mim]Cl + K_2HPO_4							[C_4mim]Br + K_2HPO_4			
0.3633	0.1842	0.0556	0.4635	0.5642	0.0018	0.6869	0.3241	0.2485	0.0442	0.4415	0.6341	0.0347	0.7166
0.3218	0.1968	0.0317	0.4577	0.5234	0.0153	0.6615	0.3428	0.2181	0.0426	0.4251	0.6245	0.0237	0.7069
0.1940	0.2951	0.0275	0.4472	0.5001	0.0152	0.6403	0.1931	0.2950	0.0197	0.4145	0.5909	0.0206	0.6939
0.2073	0.2632	0.0246	0.4314	0.4790	0.0128	0.6178	0.3646	0.1854	0.0535	0.3920	0.5973	0.0309	0.6527
0.2760	0.2107	0.0376	0.4272	0.4871	0.0190	0.6072	0.3237	0.1967	0.0369	0.3860	0.5776	0.0289	0.6480
0.2228	0.2266	0.0368	0.4007	0.4344	0.0284	0.5448	0.2065	0.2626	0.0225	0.3879	0.5525	0.0267	0.6414
0.2401	0.1835	0.0496	0.3651	0.3860	0.0442	0.4649	0.2754	0.2116	0.0309	0.3795	0.5457	0.0259	0.6245
0.1613	0.2447	0.0330	0.3625	0.3589	0.0632	0.4425	0.2217	0.2263	0.0275	0.3653	0.5240	0.0098	0.6107
0.2605	0.1331	0.0578	0.3286	0.3403	0.0562	0.3925	0.3885	0.1473	0.0558	0.3593	0.5525	0.0428	0.5890
							0.4137	0.1060	0.0555	0.3372	0.5324	0.0276	0.5710
							0.2602	0.1338	0.0886	0.2374	0.3642	0.0710	0.3220
			[C_6mim]Br + K_2HPO_4							[C_8mim]Br + K_2HPO_4			
0.3248	0.2471	0.0339	0.4287	0.7154	0.0031	0.8035	0.3242	0.2470	0.0352	0.4128	0.7326	0.0126	0.8041
0.3425	0.2184	0.0276	0.4118	0.6836	0.0087	0.7700	0.1936	0.2951	0.0197	0.3873	0.6857	0.0336	0.7541
0.3626	0.1853	0.0302	0.3847	0.6638	0.0046	0.7388	0.2064	0.2639	0.0202	0.3602	0.6667	0.0256	0.7279
0.1947	0.2934	0.0294	0.3934	0.6542	0.0152	0.7303	0.3437	0.2175	0.0499	0.3729	0.6920	0.0332	0.7264
0.2078	0.2629	0.0189	0.3725	0.6212	0.0229	0.6964	0.3629	0.1853	0.0421	0.3488	0.6755	0.0260	0.7107
0.3206	0.1963	0.0458	0.3586	0.6380	0.0088	0.6879	0.3236	0.1970	0.0399	0.3430	0.6688	0.0193	0.7074
0.2761	0.2102	0.0315	0.3514	0.6127	0.0157	0.6712	0.2652	0.2028	0.0291	0.3240	0.6402	0.0102	0.6870
0.3841	0.1474	0.0491	0.3405	0.6284	0.0066	0.6686	0.2230	0.2260	0.0397	0.3165	0.6212	0.0292	0.6486
0.2224	0.2268	0.0304	0.3385	0.5934	0.0107	0.6514	0.1612	0.2437	0.0191	0.3136	0.5733	0.0407	0.6177
0.1612	0.2441	0.0291	0.3167	0.5356	0.0379	0.5782	0.2404	0.1839	0.0411	0.2753	0.5609	0.0367	0.5720
0.4135	0.1064	0.0650	0.2882	0.5672	0.0261	0.5664	0.2620	0.1341	0.0673	0.2045	0.4220	0.0762	0.3772
0.2405	0.1833	0.0492	0.2904	0.5271	0.0226	0.5478							
0.2616	0.1334	0.0578	0.2341	0.4221	0.0541	0.4063							

Table 9. Parameters of Equations 5 and 6 for IL + K_2HPO_4 Aqueous Biphasic Systems at T = 298.15 K

IL	k	n	σ^a	k_1	r	σ^a
[C4mim]Cl	0.684	1.554	0.027	1.222	0.694	0.008
[C_4mim]Br	0.440	1.162	0.030	1.969	0.791	0.021
[C_6mim]Br	0.288	1.261	0.037	2.597	0.780	0.019
[C_8mim]Br	0.231	1.296	0.033	3.116	0.765	0.017

[a] σ, standard deviation.

A plot of dw_2/dw_1 against w_2 will give a straight line, and thus the initial values of a and c can be calculated. Once the initial values of a and c are determined, b is estimated from eq 2. The nonlinear regression started with these initial parameters, and the final results are listed in Table 7. It can be seen that the binodal curves can be well described by eq 2.

Tie-Lines. The phase compositions determined for the systems K_2HPO_4 + IL are collected in Table 8 and illustrated in Figures 4a, 4b, and 4c. For most of the systems, 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. A similar phenomenon was observed for the PEG + phosphate ABSs.

For most of the systems, 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, thus allowing us to know the phase compositions for any given total composition. The empirical equations, proposed by Othmer−Tobias[23] (eq 5) and Bancroft[18] (eq 6) for the assessment and correlation of the tie-lines for PEG/salt ABSs[18,23−27]

$$[(1 - w_1^t)/w_1^t] = k[(1 - w_2^b)/w_2^b]^n \tag{5}$$

$$(w_3^b/w_2^b) = k_1(w_3^t/w_1^t)^r \tag{6}$$

have been used to correlate the tie-line data determined in the present work. In these equations, w_1^t and w_3^t are the mass fractions of ILs and water in the top phase, and w_2^b and w_3^b are the mass fractions of salt and water in the bottom phase, respectively. k, n, k_1, and r represent the fit parameters which can be calculated from the intercept and slope of the linear relationship between $\log[(1 - w_1^t)/w_1^t]$ and $\log[(1 - w_2^b)/w_2^b]$ and between $\log[w_3^b/w_2^b]$ and $\log[w_3^t/w_1^t]$. The values of these parameters obtained by linear least-square regression are given in Table 9. It is clear that the tie-line data can be presented adequately by the Othmer−Tobias and Bancroft equations.

Conclusions

In this work, we determined liquid−liquid equilibrium data for selected imidazolium ionic liquid ([C_4mim]Cl, [C_6mim]Cl, [C_4mim]Br, [C_6mim]Br, [C_8mim]Br, [C_{10}mim]Br) + salt (KOH, K_2HPO_4, K_2CO_3, K_3PO_4) aqueous biphasic systems at 298.15 K. It was shown that the two-phase area is not expanded with increasing temperature. The phase-forming ability of the ILs follows the order: [C_6mim]Cl > [C_4mim]Cl, [C_6mim]Br > [C_8mim]Br ≈ [C_{10}mim]Br > [C_4mim]Br, [C_4mim]Br > [C_4mim]Cl, and [C_6mim]Br > [C_6mim]Cl. The ability of the salts studied for phase separation follows the order K_3PO_4 > K_2HPO_4 ≈ K_2CO_3 > KOH, which can be explained by Gibbs free energy of hydration of the anions. The data of binodal curves and tie-lines were adequately described by using three-parameter, Othmer−Tobias, and Bancroft equations, respectively.

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Received for review June 4, 2007. Accepted July 9, 2007. The authors thank the financial support from the National Natural Science Foundation of China (No. 20273019 and No. 20573034).

JE700315U