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Electronic Supplementary Information

Hydrogen bond basicity of ionic liquids and molar entropy of hydration of salts as major descriptors in the formation of aqueous biphasic systems

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1. Aqueous Biphasic Systems (ABS) Database

Table S1. Hydrogen-bonding interaction energies, E_{HB}, and molality of the IL/salt at saturation solubility of each ABS.

Name of IL	Abbreviation of IL	E_{HB} (kJ/mol)	K_3PO_4	REF	K_2HPO_4	REF	$K_3C_6H_5O_7$	REF	Na_2SO_4	REF	Na_2CO_3	REF	$KNaC_4H_4O_6$	REF
Tetrabutylammonium bromide	$[N_{4444}]Br$	-3.77	0.60	1	0.69	1	0.65	*a*	0.67	*a*	0.77	*a*	0.77	*a*
Tetrabutylphosphonium bromide	$[P_{4444}]Br$	-3.79	0.42	2	---		---		---		---		---	
Triisobutylmethylphosphonium tosylate	$[P_{i(444)1}][TOS]$	-4.53	0.51	2	---		---		---		---		---	
Tetrabutylammonium chloride	$[N_{4444}]Cl$	-4.81	0.67	3	0.76	1	0.87	4	0.64	5	0.73	6	0.90	7
Tetrabutylphosphonium chloride	$[P_{4444}]Cl$	-4.82	0.64	3	0.74	*a*	0.77	4	0.74	*a*	0.72	6	0.86	7
1-Butyl-3-methylimidazolium tetrafluoroborate	$[C_4C_1im][BF_4]$	-5.52	---		---		---		0.62	8	0.65	9	---	
1-Butyl-1-methylpiperidinium chloride	$[C_4C_1pip]Cl$	-6.75	0.96	*a*	1.07	*a*	1.43	4	1.19	*a*	1.04	6	1.49	*a*
1-Butyl-1-methylpyrrolidinium chloride	$[C_4C_1pyr]Cl$	-6.99	0.96	3	1.14	*a*	1.51	4	1.28	*a*	1.10	6	1.5	*a*
1-Butyl-3-methylimidazolium triflate	$[C_4C_1im][CF_3SO_3]$	-7.00	0.43	10	0.54	11	0.45	4	0.54	12	0.54	13	0.56	*a*
1-Ethyl-3-methylimidazolium triflate	$[C_2C_1im][CF_3SO_3]$	-7.23	0.70	10	---		---		0.89	12	---		---	
1-Butyl-3-methylimidazolium thiocyanate	$[C_4C_1im][SCN]$	-8.20	0.60	*a*	0.72	*a*	0.62	4	0.79	12	0.71	14	0.84	7
1-Octylpyridinium dicyanamide	$[C_8py][N(CN)_2]$	-8.80	---		---		---		---		---		---	
1-Butyl-3-methylimidazolium octylsulfate	$[C_4C_1im][C_8H_{17}SO_4]$	-9.06	---		---		---		0.71	12	---		---	
1-Butyl-3-methylimidazolium methylsulfate	$[C_4C_1im][CH_3SO_4]$	-9.33	0.63	15	1.13	11	1.22	*a*	1.13	12	1.0	14	---	
1-Butyl-3-methylimidazolium ethylsulfate	$[C_4C_1im][C_2H_5SO_4]$	-9.51	0.83	15	1.03	11	---		1.02	12	0.93	14	---	
1-Ethyl-3-methylimidazolium methylsulfate	$[C_2C_1im][CH_3SO_4]$	-9.68	1.02	10	---		---		---		---		---	
1-Hexyl-3-methylimidazolium dycianamide	$[C_6C_1im][N(CN)_2]$	-9.70	---		---		---		---		---		0.59	7
1-Ethyl-3-methylimidazolium ethylsulfate	$[C_2C_1im][C_2H_5SO_4]$	-9.83	0.93	10	---		---		---		---		---	
1-Butyl-3-methylimidazolium dycianamide	$[C_4C_1im][N(CN)_2]$	-9.87	0.63	10	0.84	11	0.71	4	0.87	12	0.79	14	0.93	7
1-Ethyl-3-methylimidazolium dycianamide	$[C_2C_1im][N(CN)_2]$	-10.15	0.89	*a*	1.10	*a*	1.08	*a*	1.19	*a*	---		1.35	7
1-Benzyl-3-methylimidazolium ethylsulfate	$[C_7H_7C_1im][C_2H_5SO_4]$	-10.21	---		---		---		0.94	12	---		---	
1-Butyl-3-methylimidazolium trifluoroacetate	$[C_4C_1im][CF_3CO_2]$	-11.43	0.79	10	1.03	11	1.01	4	1.29	12	---		1.23	7
1-Butyl-3-methylimidazolium tosylate	$[C_4C_1im][TOS]$	-11.49	0.65	15	0.82	11	---		0.84	12	0.76	14	0.95	7
1-Butyl-3-methylimidazolium bromide	$[C_4C_1im]Br$	-11.66	0.89	10	1.14	11	1.17	4	1.39	12	1.08	14	1.33	7
1-Butyl-3-methylpyridinium chloride	$[C_4C_1py]Cl$ (1,3)	-11.83	1.01	*a*	1.19	*a*	1.44	4	1.26	*a*	1.10	6	---	
1-Ethyl-3-methylimidazolium bromide	$[C_2C_1im]Br$	-12.09	1.06	10	---		---		---		---		---	
1-Butyl-3-methylimidazolium methanesulfonate	$[C_4C_1im][CH_3SO_3]$	-13.28	0.99	10	1.21	11	1.66	4	---		1.09	14	---	
1-Ethyl-3-methylimidazolium methanesulfonate	$[C_2C_1im][CH_3SO_3]$	-13.69	1.37	10	---		---		---		---		---	
1-Methyl-3-tetradecylimidazolium chloride	$[C_{14}C_1im]Cl$	-13.77	0.88	16	---		---		---		---		---	
1-Dodecyl-3-methylimidazolium chloride	$[C_{12}C_1im]Cl$	-13.86	0.93	16	---		---		---		---		---	
1-Decyl-3-methylimidazolium chloride	$[C_{10}C_1im]Cl$	-13.95	0.97	16	1.85	*a*	1.35	4	---		---		---	
1-Methyl-3-octylimidazolium chloride	$[C_8C_1im]Cl$	-14.14	0.97	16	1.20	*a*	1.40	4	1.19	15	---		1.45	*a*
1-Heptyl-3-methylimidazolium chloride	$[C_7C_1im]Cl$	-14.28	0.95	16	---		1.42	4	1.32	12	---		---	
1-Hexyl-3-methylimidazolium chloride	$[C_6C_1im]Cl$	-14.28	0.93	16	1.18	17	1.49	4	---		1.10	18	1.55	*a*
1-Butyl-3-methylimidazolium chloride	$[C_4C_1im]Cl$	-14.52	1.02	10	1.26	17	1.64	4	---		1.21	14	---	

1-Ethyl-3-methylimidazolium chloride	$[C_2C_1im]Cl$	-14.99	1.15	[10]	1.46	[17]	---		---	1.44	[6]	---
1-Benzyl-3-methylimidazolium chloride	$[C_7H_7C_1im]Cl$	-15.47	0.95	[19]	---		---		---	---		---
1,3-Dimethylimidazolium chloride	$[C_1C_1im]Cl$	-15.49	1.35	[16]	---		---		---	---		---
1-Butyl-3-methylimidazolium dimethylphosphate	$[C_4C_1im][DMP]$	-15.58	0.91	[15]	1.11	[11]	1.73	[4]	---	1.06	[14]	---
1-Butyl-3-methylimidazolium acetate	$[C_4C_1im][CH_3CO_2]$	-19.83	1.07	[10]	1.20	[11]	1.82	[4]	---	---		---
1-Ethyl-3-methylimidazolium acetate	$[C_2C_1im][CH_3CO_2]$	-20.21	1.13	[10]	---		---		---	---		---
Cholinium chloride	$[N_{111(2OH)}]Cl$	-27.11	1.28	[3]	2.09	[a]	---		---	---		---
1-Methylimidazolium chloride	$[C_1im]Cl$	-27.14	1.36	[19]	---		---		---	---		---
1-(2-Hydroxyethyl)-3-methylimidazolium chloride	$[OHC_2C_1im]Cl$	-30.36	1.48	[19]	---		---		---	---		---

[a] Phase diagrams determined in this work.

2. Phase Diagrams

Table S2. Experimental weight fraction data for the binodal curves of the systems composed of IL (1) + K_3PO_4 (2) + H_2O at 298 K and atmospheric pressure.

[C_4C_1im][SCN]				[C_2C_1im][$N(CN)_2$]			
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
80.61	0.52	18.83	8.28	58.79	1.42	17.51	13.76
55.26	0.74	18.44	8.41	47.43	2.24	17.01	14.06
52.26	1.08	18.04	8.53	42.97	2.92	16.66	14.18
50.49	1.55	17.59	8.66	40.80	3.77	16.21	14.47
47.17	1.75	17.19	8.79	37.98	4.43	15.78	14.76
45.82	1.99	16.72	8.93	36.41	5.05	15.52	14.82
44.52	2.27	16.54	9.03	34.87	5.69	15.09	15.10
43.29	2.52	16.04	9.17	33.34	6.38	14.67	15.41
41.44	2.70	15.52	9.33	31.91	6.97	14.42	15.48
40.38	2.96	15.36	9.43	30.76	7.39	14.05	15.73
38.65	3.25	14.85	9.58	29.59	7.86	13.70	15.96
37.79	3.44	14.65	9.70	28.55	8.29	13.39	16.16
36.93	3.64	14.07	9.87	27.57	8.68	13.09	16.35
35.50	3.90	13.85	10.00	26.65	9.04	12.89	16.43
34.60	4.24	13.61	10.12	25.33	9.83	11.50	17.24
33.40	4.33	13.00	10.31	24.55	10.13	10.58	17.94
32.63	4.56	12.73	10.46	23.54	10.70	9.58	18.68
31.77	4.96	12.48	10.59	22.87	10.99	8.41	19.52
30.59	5.14	12.20	10.74	22.25	11.22	7.14	20.44
29.52	5.33	11.55	10.96	21.38	11.79	6.56	21.21
28.93	5.58	11.25	11.12	20.82	12.00	5.78	21.97
27.97	5.80	10.96	11.29	20.17	12.35	5.06	22.83
27.13	5.92	10.65	11.46	19.60	12.66	4.25	23.71
26.62	6.14	10.33	11.64	18.96	13.07	3.51	25.85
25.86	6.28	9.99	11.83	18.47	13.30	2.70	29.39
25.48	6.37	9.66	12.02	18.05	13.41	1.61	36.37
25.02	6.57	9.35	12.33				
24.31	6.70	8.99	12.54				
23.87	6.91	8.59	12.75				
23.24	7.00	7.75	13.19				
22.38	7.21	4.92	14.37				
22.09	7.30	4.52	14.83				
21.77	7.40	4.22	15.66				
21.26	7.52	3.78	16.36				
20.93	7.62	3.37	17.39				
20.57	7.72	2.91	18.49				
20.03	7.85	2.40	19.87				
19.64	7.97	1.93	22.94				
19.14	8.10	1.68	38.40				
18.97	8.19						

Table S3. Experimental weight fraction data for the binodal curves of the systems composed of IL (1) + K_3PO_4 (2) + H_2O at 298 K and atmospheric pressure.

[C_4C_1py]Cl				[C_4C_1pip]Cl			
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
59.98	0.648	11.19	21.786	58.60	0.63	17.90	14.83
44.42	1.002	10.62	22.37	46.38	0.95	17.33	15.32
39.10	3.460	10.13	22.86	42.64	1.29	16.61	15.89
35.29	4.866	9.69	23.32	38.95	2.13	16.37	16.29
33.68	5.510	9.21	23.85	37.09	3.06	15.72	16.89
31.72	6.602	8.86	24.20	35.65	3.73	14.90	17.56
30.14	7.405	8.58	24.45	34.10	4.49	14.03	18.28
28.57	8.272	8.17	24.92	32.34	5.56	13.66	18.81
27.03	9.192	7.79	25.37	31.20	5.97	12.68	19.62
25.45	10.194	7.44	25.78	30.26	6.33	11.64	20.55
24.14	11.052	7.14	26.12	28.91	7.12	11.15	21.22
22.78	12.013	6.84	26.49	27.88	7.65	9.97	22.24
21.25	13.243	6.55	26.86	26.63	8.53	9.42	23.06
19.95	14.265	6.25	27.23	25.65	9.11	8.85	23.95
18.92	15.017	5.96	27.61	24.68	9.70	7.32	25.31
17.89	15.80	5.67	28.01	23.45	10.65	6.56	26.38
16.81	16.70	5.56	28.09	22.62	11.19	5.78	27.53
15.86	17.53	5.30	28.45	21.73	11.84	4.91	28.74
14.91	18.40	5.02	28.85	21.09	12.19	3.98	30.12
14.09	19.13	4.76	29.26	20.10	13.03	3.10	32.65
13.41	19.70	4.48	29.71	19.41	13.54	2.07	35.31
12.76	20.32	4.24	30.08	18.56	14.32	0.94	38.56
12.28	20.74	4.00	30.47				
11.71	21.27						

Table S4. Experimental weight fraction data for the binodal curves of the systems composed of IL (1) + K_2HPO_4 (2) + H_2O at 298 K and atmospheric pressure.

[C_4C_1im][SCN]							
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
82.27	0.79	17.17	9.51	10.62	12.17	8.04	13.89
54.87	1.04	16.73	9.66	10.48	12.22	7.96	13.94
50.26	1.52	16.30	9.78	10.35	12.30	7.88	13.98
47.68	2.33	15.92	9.90	10.23	12.38	7.78	13.86
43.19	3.16	15.54	10.06	10.11	12.46	7.52	14.04
38.99	3.60	15.17	10.15	9.98	12.56	7.23	14.36
36.70	4.18	14.83	10.27	9.86	12.63	6.91	14.56
34.44	4.67	14.50	10.36	9.75	12.70	6.58	14.77
32.54	5.12	14.25	10.51	9.61	12.73	6.24	14.97
30.70	5.51	13.94	10.61	9.50	12.81	5.93	15.33
29.15	5.89	13.71	10.75	9.39	12.88	5.63	15.72
27.72	6.18	13.41	10.82	9.28	12.95	5.31	16.08
26.60	6.48	13.21	10.94	9.18	13.02	5.04	16.65
25.61	6.79	12.94	11.02	9.08	13.08	4.62	16.92
24.67	7.08	12.73	11.15	8.98	13.14	4.36	17.57
23.79	7.32	12.47	11.22	8.90	13.22	3.98	18.05
22.95	7.60	12.29	11.31	8.80	13.27	3.60	18.58
22.19	7.85	12.11	11.43	8.75	13.37	3.20	19.34
21.33	8.05	11.94	11.53	8.66	13.42	2.81	20.42
20.69	8.26	11.76	11.64	8.56	13.47	2.45	22.15
20.06	8.45	11.54	11.69	8.50	13.56	1.97	24.29
19.60	8.70	11.38	11.79	8.42	13.61	1.48	27.66
19.04	8.88	11.22	11.88	8.34	13.67	1.32	49.38
18.50	9.03	11.07	11.98	8.25	13.71		
18.00	9.17	10.88	12.02	8.20	13.80		
17.64	9.36	10.74	12.09	8.12	13.85		

Table S5. Experimental weight fraction data for the binodal curves of the systems composed of IL (1) + K_2HPO_4 (2) + H_2O at 298 K and atmospheric pressure.

[C_8C_1im]Cl		[$C_{10}C_1$im]Cl		[C_2C_1im][$N(CN)_2$]			
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
56.08	1.90	34.86	24.24	57.13	1.72	17.50	15.26
52.33	3.62	32.18	24.44	45.19	2.85	16.64	15.81
47.42	5.02	29.82	24.61	40.86	3.99	15.69	16.42
43.09	6.22	27.23	25.08	38.01	4.98	15.06	16.92
40.81	7.29	25.57	25.19	35.63	5.81	13.91	17.63
38.70	8.34	23.50	25.60	34.02	6.79	13.15	18.22
35.99	9.01	21.75	25.96	32.03	7.45	12.36	18.82
34.42	9.78	20.26	26.25	30.76	8.27	11.52	19.49
32.94	10.49	18.97	26.49	29.14	8.80	10.65	20.19
31.51	11.18	17.59	26.88	28.06	9.50	9.67	20.96
29.62	12.57	16.38	27.26	26.70	9.98	9.21	21.56
28.50	13.09	15.32	27.57	25.82	10.52	8.03	22.49
27.47	13.57	14.21	27.96	24.99	11.06	7.49	23.17
26.57	14.01	13.24	28.28	24.20	11.58	6.94	23.87
25.29	15.05	12.42	28.59	23.17	11.86	6.35	24.57
24.47	15.42	11.57	28.98	22.48	12.33	5.69	25.39
23.40	16.23	10.97	29.23	21.86	12.70	4.29	27.17
22.70	16.56	10.28	29.56	21.25	13.11	3.52	28.15
21.73	17.33	9.61	29.90	20.12	13.67	2.69	29.75
21.13	17.58	8.95	30.29	19.11	14.25	1.80	31.62
19.47	18.75	8.39	30.59	18.34	14.74	1.26	48.23
18.35	19.61	7.25	31.56				
17.07	20.62	5.77	32.56				
15.73	21.68	4.63	34.30				
14.25	22.85	3.50	36.24				
12.96	23.96	2.30	40.07				
11.95	24.99						
10.40	26.37						
9.19	27.61						
8.37	28.71						
6.90	30.22						
6.43	31.17						
4.70	32.92						
4.13	34.16						
3.59	35.48						
2.94	36.79						
2.26	38.33						
1.59	39.92						
1.00	48.45						

Table S6. Experimental weight fraction data for the binodal curves of the systems composed of IL (1) + K_2HPO_4 (2) + H_2O at 298 K and atmospheric pressure.

[C_4C_1pip]Cl				[C_4C_1py]Cl		[C_4C_1pyr]Cl	
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
75.20	1.35	17.49	15.30	22.11	13.755	20.12	13.46
46.61	1.82	17.24	15.51	20.90	14.641	19.18	14.21
41.19	2.59	16.98	15.70	19.88	15.383	18.34	14.84
37.75	3.42	16.73	15.88	18.83	16.202	17.08	16.31
35.90	4.17	16.52	16.05	17.35	17.758	16.40	16.81
34.22	4.89	16.13	16.53	16.54	18.354	15.74	17.33
32.71	5.55	15.89	16.73	15.82	18.901	14.85	18.40
31.52	6.08	15.67	16.88	14.79	20.068	14.33	18.99
30.23	6.62	15.45	17.05	14.26	20.378	13.87	19.36
29.40	7.29	15.07	17.55	13.72	20.722	13.18	20.22
28.46	7.70	14.88	17.69	12.92	21.692	12.79	20.47
27.51	8.16	14.69	17.82	12.48	21.924	12.19	21.20
26.66	8.57	14.49	17.98	11.84	22.704	11.84	21.41
25.98	9.10	14.31	18.16	11.49	22.846	11.68	22.05
25.12	9.42	14.11	18.32	10.97	23.540	11.04	22.67
24.54	9.92	13.86	18.66	10.64	24.42	10.52	23.69
24.00	10.35	14.03	19.00	10.15	25.14	9.67	24.45
23.27	10.61	13.57	19.44	9.69	25.89	8.86	25.22
22.79	10.95	13.17	19.86	9.18	26.67	8.16	26.52
22.36	11.32	12.68	20.32	7.98	27.88	7.24	27.45
21.85	11.64	12.00	20.90	7.41	28.81	6.42	28.94
21.42	11.98	11.44	21.41	3.85	32.88		
21.01	12.29	10.89	21.95	3.01	34.23		
20.62	12.63	10.27	22.53	2.21	37.51		
20.23	12.96	9.87	23.51				
19.87	13.23	9.14	24.17				
19.51	13.49	8.48	24.87				
19.17	13.75	8.16	43.28				
18.83	14.06	7.88	26.05				
18.50	14.33	7.10	26.91				
18.18	14.59	6.27	27.78				
17.91	14.81	5.27	46.69				

Table S7. Experimental weight fraction data for the binodal curves of the systems composed of IL (1) + K_2HPO_4 (2) + H_2O at 298 K and atmospheric pressure.

$[P_{4444}]Cl$		$[N_{111(2OH)}]Cl$	
100 w_1	100 w_2	100 w_1	100 w_2
39.00	3.52	20.83	29.25
34.51	4.78	22.15	27.68
30.25	5.63	23.53	26.11
27.55	6.49	25.15	24.25
25.26	7.17	26.60	22.83
22.77	8.72	28.61	20.57
21.51	9.31	30.46	18.70
20.75	10.00	32.60	16.64
19.70	10.51	35.11	14.21
18.77	10.94	37.98	11.44
17.93	11.29	40.08	10.09
17.36	11.86	42.56	8.37
16.60	12.22	45.36	6.54
15.96	12.50		
15.53	12.93		
14.95	13.17		
14.58	13.53		

Table S8. Experimental weight fraction data for the binodal curves of the systems composed of IL (1) + $K_3C_6H_5O_7$ (2) + H_2O at 298 K and atmospheric pressure.

$[C_4C_1im][CH_3SO_4]$		$[N_{111(2OH)}]Cl$	
100 w_1	100 w_2	100 w1	100 w2
43.19	13.42	72.96	1.16
39.84	15.41	66.68	2.51
35.37	18.84	59.42	4.23
33.02	20.39	54.24	6.20
30.41	22.33	50.54	8.34
28.18	23.86	42.73	12.62
26.54	24.90	38.00	14.45
25.04	25.92	30.99	18.29
23.51	27.13	19.58	22.62
22.03	28.20	11.36	26.65
20.94	28.95		
19.58	30.05		
18.36	31.09		
17.29	32.02		
16.34	32.82		
15.19	33.94		
14.15	34.93		
12.97	36.24		
11.77	37.55		
10.03	39.85		

Table S9. Experimental weight fraction data for the binodal curves of the systems composed of IL (1) + $K_3C_6H_5O_7$ (2) + H_2O at 298 K and atmospheric pressure.

$[N_{4444}]Br$				$[C_2C_1im][N(CN)_2]$			
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
52.94	2.24	14.06	18.96	57.38	2.50	18.53	22.92
49.23	3.78	13.83	19.16	54.00	3.96	17.92	23.32
45.13	4.78	13.53	19.25	50.89	5.29	17.16	24.00
41.81	5.81	13.23	19.30	45.73	7.40	16.63	24.36
38.76	6.72	12.90	19.73	43.51	8.33	15.97	24.95
36.55	7.48	12.63	19.79	41.41	9.17	15.51	25.26
34.61	8.24	12.28	20.11	39.54	9.96	14.93	25.78
33.04	8.69	11.94	20.42	37.80	10.75	14.51	26.07
31.87	9.46	11.63	20.73	35.32	12.30	13.99	26.54
30.05	9.97	11.14	21.06	33.25	13.65	13.36	27.24
29.14	10.68	10.86	21.33	31.99	14.18	12.91	27.68
27.90	11.13	10.55	21.50	30.20	15.38	12.49	28.08
26.82	11.57	10.39	21.53	28.63	16.44	12.00	28.62
25.80	12.00	10.14	21.78	27.71	16.84	11.90	28.79
25.06	12.63	10.01	21.85	26.29	17.74	10.60	30.32
24.16	13.05	9.89	21.97	25.09	18.57	9.17	31.93
23.31	13.38	9.68	22.17	24.01	19.33	7.61	33.71
22.46	13.71	9.30	22.55	23.35	19.61	6.76	35.20
21.91	14.12	8.59	23.12	22.39	20.28	4.75	37.53
20.92	14.82	8.22	23.58	21.50	20.89	3.64	39.32
20.20	15.04	7.49	24.25	20.65	21.52	2.57	43.66
19.58	15.25	7.14	24.73	19.90	22.01	1.46	48.84
18.79	15.91	6.76	25.22	19.17	22.47		
18.23	16.14	6.39	25.72				
17.73	16.32	5.61	26.90				
17.39	16.62	4.64	27.74				
16.92	16.77	4.24	28.75				
16.62	17.03	3.81	29.94				
16.02	17.55	3.27	31.07				
15.19	18.27	2.72	32.29				
14.89	18.46	2.27	35.72				
14.63	18.67	1.80	40.63				
14.30	18.76	1.07	49.21				

Table S10. Experimental weight fraction data for the binodal curves of the systems composed of IL (1) + Na_2SO_4 (2) + H_2O at 298 K and atmospheric pressure.

[P_{4444}]Cl		[C_4C_1pip]Cl		[C_4C_1pyr]Cl		[C_4C_1py]Cl	
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
42.03	3.17	28.32	7.84	25.12	10.56	27.30	9.65
39.76	3.39	27.26	8.21	24.62	10.94	26.14	10.10
38.34	3.63	26.88	8.49	24.06	11.34	25.70	10.41
36.46	3.82	26.54	8.78	23.45	11.80	25.31	10.74
34.09	4.26	26.16	9.09	22.80	12.29	24.81	11.11
32.47	4.39	25.54	9.40	22.16	12.84	24.18	11.48
31.46	4.58	25.04	9.76	21.48	13.39	23.67	11.86
30.11	4.96	24.50	10.14	20.59	14.03	23.19	12.35
29.32	5.11	23.86	10.56	19.55	14.62	21.58	13.19
28.17	5.46	23.14	10.98	18.69	15.32	20.89	13.70
26.43	5.92	22.38	11.42				
25.15	6.37	21.52	11.97				
22.84	7.17	20.20	13.45				
21.38	7.77	19.11	14.13				
17.64	9.49	17.98	14.87				
17.26	9.86						
16.33	10.29						
16.02	10.59						
14.84	11.12						
14.43	11.48						
13.11	12.03						
12.60	12.46						
12.09	12.96						
11.38	13.52						
10.48	14.14						
8.97	15.40						
7.97	16.14						
6.87	17.04						
5.74	17.92						

Table S11. Experimental weight fraction data for the binodal curves of the systems composed of IL (1) + Na_2SO_4 (2) + H_2O at 298 K and atmospheric pressure.

[N_{4444}]Br				[C_2C_1im][N(CN)$_2$]			
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
57.85	0.40	20.20	7.58	58.18	0.46	8.87	28.20
51.57	0.71	19.83	7.82	51.35	1.53	8.44	29.30
47.27	1.16	19.02	8.14	44.78	3.21	8.11	29.94
43.72	1.52	18.18	8.50	38.67	4.86	7.70	31.16
41.96	1.74	17.63	8.80	13.95	18.66	7.41	31.83
40.39	1.94	17.05	9.12	12.98	20.88	7.12	32.54
38.40	2.46	15.94	9.56	12.38	21.55	6.86	33.10
36.16	3.00	15.24	9.97	11.62	23.16	6.62	33.54
34.76	3.22	14.50	10.39	11.14	23.71	6.40	34.11
32.67	3.80	13.66	10.85	10.52	25.22	6.13	35.04
31.12	4.17	12.73	11.32	10.14	25.60	5.93	35.51
29.40	4.62	12.39	11.63	9.62	26.85	5.69	36.35
27.62	5.15	11.30	12.18	9.15	27.99	5.32	37.43
25.92	5.67	10.13	12.79				
23.93	6.13	9.58	13.27				
23.45	6.32	8.98	13.78				
22.72	6.57	7.43	14.57				
22.19	6.81	6.71	15.21				
21.54	7.04	5.97	15.95				
20.89	7.31	5.14	16.77				

Table S12. Experimental weight fraction data for the binodal curves of the systems composed of IL (1) + Na_2CO_3 (2) + H_2O at 298 K and atmospheric pressure.

[N_{4444}]Br			
100 w_1	100 w_2	100 w_1	100 w_2
77.05	0.28	29.79	4.02
53.96	0.43	29.04	4.17
49.42	0.58	28.74	4.33
44.67	1.07	27.96	4.51
42.13	1.37	27.05	4.84
40.57	1.50	25.53	5.27
37.82	1.90	25.48	5.42
34.08	2.90	24.88	5.67
33.31	3.14	23.67	5.99
32.63	3.32	22.98	6.27
31.81	3.46	22.98	6.48
31.33	3.65	21.29	7.17
30.38	3.80		

Table S13. Experimental weight fraction data for the binodal curves of the systems composed of IL (1) + $KNaC_4H_4O_6$ (2) + H_2O at 298 K and atmospheric pressure.

[C_6C_1im]Cl		[C_4C_1pip]Cl		[C_4C_1pyr]Cl		[C_8C_1im]Cl	
100 w_1	100 w_2	100 w_1	100 w_1	100 w_2	100 w_2	100 w_1	100 w_2
41.37	11.42	37.11	73.59	1.22	16.73	73.59	1.22
40.69	11.90	36.31	66.46	2.43	17.41	66.46	2.43
39.51	12.53	35.37	62.38	3.50	18.12	62.38	3.50
38.55	13.09	34.90	53.59	7.09	18.89	53.59	7.09
37.89	13.56	34.34	44.20	11.24	19.74	44.20	11.24
37.17	14.06	33.74	41.89	12.43	21.19	41.89	12.43
36.06	14.85	32.41	39.76	13.60	22.61	39.76	13.60
35.25	15.50	31.66	37.53	14.91	23.45	37.53	14.91
34.30	16.22	30.84	35.69	16.12	24.76	35.69	16.12
32.78	17.17	28.32	33.54	17.56	25.75	33.54	17.56
32.16	17.84	25.53	31.02	19.27	26.81	31.02	19.27
30.92	18.83	25.05	28.48	21.10		28.48	21.10
29.53	19.90	23.58	26.05	23.01		26.05	23.01
28.05	21.07	21.88	23.85				
26.95	22.19	21.34	24.94				
25.22	23.69	19.16	26.88				
24.07	25.02						

Table S14. Experimental weight fraction data for the binodal curves of the systems composed of IL (1) + $KNaC_4H_4O_6$ (2) + H_2O at 298 K and atmospheric pressure.

$[C_4C_1im][CF_3SO_3]$				$[N_{4444}]Br$			
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
82.27	0.12	21.06	7.12	59.56	1.04	22.38	12.43
72.85	0.62	20.42	7.33	54.41	1.86	21.35	13.00
66.74	1.03	19.78	7.57	50.22	2.63	20.29	13.63
61.81	1.34	18.49	8.16	46.53	3.29	19.08	14.32
58.05	1.63	17.54	8.42	44.31	4.00	18.15	14.92
55.20	1.93	16.95	8.76	42.39	4.59	16.84	15.70
52.32	2.22	16.45	9.10	40.42	5.17	15.29	16.59
49.82	2.45	15.99	9.44	38.73	5.72	14.50	17.24
48.17	2.74	15.29	9.69	35.90	6.59	13.16	18.14
46.31	2.94	14.46	10.29	34.60	7.00	12.24	18.89
44.67	3.20	13.69	10.82	33.37	7.37	11.30	19.70
42.84	3.42	12.94	11.29	31.63	8.21	10.23	20.63
41.49	3.65	12.57	11.58	30.61	8.53	9.14	21.59
40.09	3.86	11.76	12.43	29.12	9.25	7.85	22.70
38.70	4.01	11.25	12.78	27.83	9.91	6.56	24.48
37.49	4.21	10.88	13.23	26.56	10.54	5.01	25.86
35.48	4.47	10.65	13.35	25.41	11.10	4.27	27.68
34.56	4.59	10.32	13.74	24.39	11.58	3.38	28.96
33.77	4.75	10.01	14.10	23.45	12.04	2.46	31.31
32.89	4.90	9.70	14.47	22.59	12.45	1.34	34.15
32.15	4.96	9.43	14.82				
31.41	5.10	9.17	15.13				
30.64	5.20	8.91	15.45				
30.18	5.31	8.66	15.77				
29.66	5.39	8.45	16.03				
29.10	5.53	9.11	15.11				
28.37	5.71	8.77	15.33				
27.94	5.82	5.69	18.31				
27.47	5.92	5.26	18.86				
27.02	6.01	4.87	19.84				
26.52	6.14	4.45	20.71				
26.11	6.24	4.07	22.23				
25.68	6.35	3.76	23.83				
24.97	6.17	3.16	25.31				
23.66	6.33	2.49	27.36				
22.92	6.58	1.68	29.78				
22.11	6.90	1.03	33.72				

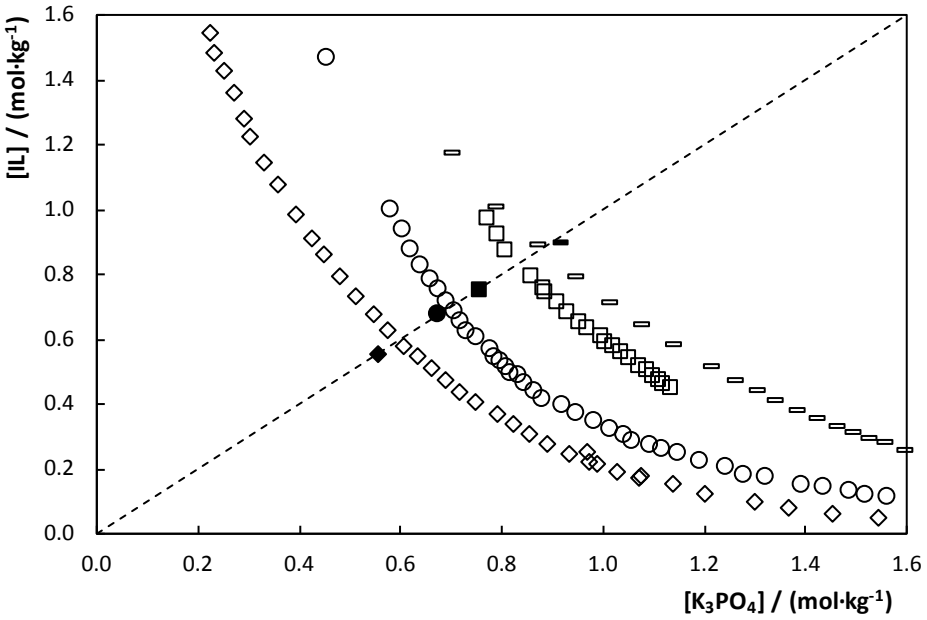

Fig. S1 Comparison between the experimental and predicted data: binodal curves (open symbols) and predicted $[IL]_{SS}$ (full symbols) of the ABS composed of K_3PO_4 and the ILs $[N_{4444}]Br$ (✹), $[C_2C_1im][CF_3SO_3]$ (●), $[C_4C_1im][C_2H_5SO_4]$ (🕘) and $[C_{14}C_1im]Cl$ (-).

3. References

1 M. Zawadzki, F. A. e Silva, U. Domańska, J. A. P. Coutinho and S. P. M. Ventura, *Green Chem.*, 2016, **18**, 3527–3536.

2 C. L. S. Louros, A. F. M. Cláudio, C. M. S. S. Neves, M. G. Freire, I. M. Marrucho, J. Pauly and J. A. P. Coutinho, *Int. J. Mol. Sci.*, 2010, **11**, 1777–1791.

3 H. Passos, A. C. A. Sousa, M. R. Pastorinho, A. J. A. Nogueira, L. P. N. Rebelo, J. A. P. Coutinho and M. G. Freire, *Anal. Methods*, 2012, **4**, 2664–2667.

4 H. Passos, A. R. Ferreira, A. F. M. Cláudio, J. A. P. Coutinho and M. G. Freire, *Biochem. Eng. J.*, 2012, **67**, 68–76.

5 S. Rocha, *Synthesis and characterization of chiral ionic liquids and their application in the development of aqueous biphasic systems*. Master Thesis. University of Aveiro, Aveiro, Portugal, 2016..

6 C. F. C. Marques, T. Mourão, C. M. S. S. Neves, Á. S. Lima, I. Boal-Palheiros, J. A. P. Coutinho and M. G. Freire, *Am. Inst. Chem. Eng. Biotechnol. Prog*, 2013, **29**, 645–654.

7 T. B. V Dinis, H. Passos, D. L. D. Lima, V. I. Esteves, J. A. P. Coutinho and M. G. Freire, *Green Chem.*, 2015, **17**, 2570–2579.

8 J. R. Trindade, Z. P. Visak, M. Blesic, I. M. Marrucho, J. A. P. Coutinho, J. N. Canongia Lopes and L. P. N. Rebelo, *J. Phys. Chem. B*, 2007, **111**, 4737–4741.

9 C. Li, J. Han, Y. Wang, Y. Yan, J. Pan, X. Xu and Z. Zhang, *J. Chem. Eng. Data*, 2010, **55**, 1087–1092.

10 S. P. M. Ventura, C. M. S. S. Neves, M. G. Freire, I. M. Marrucho, J. Oliveira and J. A. P. Coutinho, *J. Phys. Chem. B*, 2009, **113**, 9304–9310.

11 T. Mourão, A. F. M. Cláudio, I. Boal-Palheiros, M. G. Freire and J. A. P. Coutinho, *J. Chem. Thermodyn.*, 2012, **54**, 398–405.

12 A. F. M. Cláudio, A. M. Ferreira, S. Shahriari, M. G. Freire and J. A. P. Coutinho, *J. Phys. Chem. B*, 2011, **115**, 11145–11153.

13 S. Shahriari, C. M. S. S. Neves, M. G. Freire and J. A. P. Coutinho, *J. Phys. Chem. B*, 2012, **116**, 7252–7258.

14 A. F. M. Cláudio, C. F. C. Marques, I. Boal-Palheiros, M. G. Freire and J. A. P. Coutinho, *Green Chem.*, 2014, **16**, 259–268.

15 A. F. M. Cláudio, A. M. Ferreira, C. S. R. Freire, A. J. D. Silvestre, M. G. Freire and J. A. P. Coutinho, *Sep. Purif. Technol.*, 2012, **97**, 142–149.

16 M. G. Freire, C. M. S. S. Neves, J. N. C. Lopes, I. M. Marrucho, J. A. P. Coutinho and L. P. N. Rebelo, *J. Phys. Chem. B*, 2012, **116**, 7660–7668.

17 S. P. M. Ventura, S. G. Sousa, L. S. Serafim, Á. S. Lima, M. G. Freire and J. A. P. Coutinho, *J. Chem. Eng. Data*, 2011, **56**, 4253–4260.

18 F. J. Deive, M. A. Rivas and A. Rodríguez, *J. Chem. Thermodyn.*, 2011, **43**, 1153–1158.

19 C. M. S. S. Neves, S. P. M. Ventura, M. G. Freire, I. M. Marrucho and J. A. P. Coutinho, *J. Phys. Chem. B*, 2009, **113**, 5194–5199.