

Electronic Supplementary Information

Mechanisms ruling the partition of solutes in ionic-liquid-based aqueous biphasic systems – the multiple effects of ionic liquids

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1. Experimental

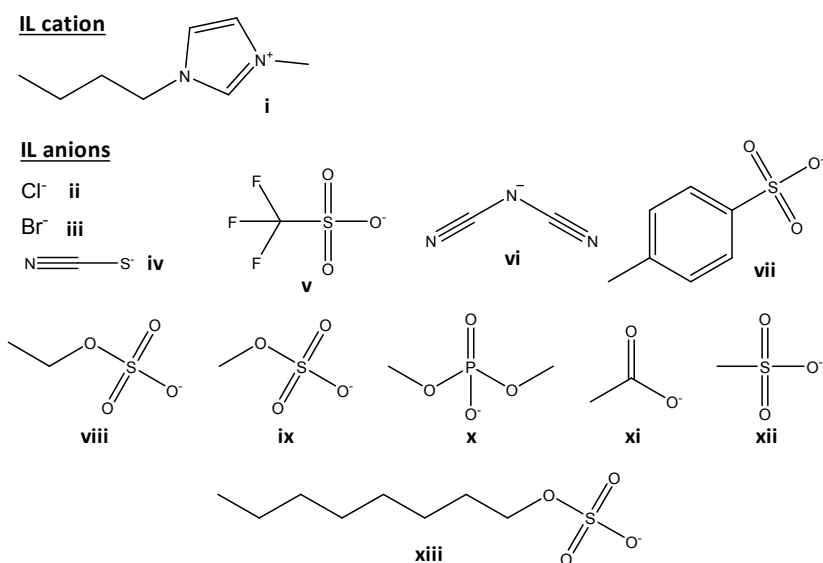


Fig. S1 ILs cation and anions chemical structures: (i) [C₄C₁im]⁺; (ii) Cl⁻; (iii) Br⁻; (iv) [SCN]⁻; (v) [CF₃SO₃]⁻; (vi) [N(CN)₂]⁻; (vii) [TOS]⁻; (viii) [C₂H₅SO₄]⁻; (ix) [CH₃SO₄]⁻; (x) [DMP]⁻; (xi) [CH₃CO₂]⁻; (xii) [CH₃SO₃]⁻; (xiii) [C₈H₁₇SO₄]⁻.

2. Phase diagrams and TLs

Table S1. Experimental weight fraction data for the system composed of [C₄C₁im][CF₃SO₃] (1) + K₂CO₃ (2) + H₂O (3) at 25 °C.

[C ₄ C ₁ im][CF ₃ SO ₃]					
100 w ₁	100 w ₂	100 w ₁	100 w ₂	100 w ₁	100 w ₂
56.00	0.93	18.64	4.82	14.92	6.13
47.81	1.65	18.55	5.03	14.70	6.04
40.19	2.03	18.08	4.90	14.65	6.19
37.49	2.36	18.00	5.10	14.42	6.09
34.16	2.60	17.69	5.01	14.30	6.45
31.97	2.89	17.61	5.23	13.92	6.28
26.63	3.45	17.11	5.09	13.80	6.67
26.44	3.78	17.04	5.27	13.53	6.54
25.06	3.58	16.67	5.16	13.42	6.88
23.14	3.90	16.53	5.53	12.52	7.07
23.00	4.18	16.29	5.45	11.57	7.55
22.01	4.00	16.24	5.58	10.98	7.91
21.86	4.33	16.10	5.53	10.67	8.13
21.06	4.17	16.05	5.68	10.31	8.39
20.95	4.43	15.80	5.59	9.92	8.63
20.72	4.38	15.72	5.82	9.06	9.49
20.61	4.61	15.59	5.78	8.20	10.25
19.91	4.46	15.53	5.96	7.35	10.92
19.79	4.73	15.16	5.83	6.36	12.05
19.36	4.62	15.12	5.97	5.60	13.05
19.21	4.97	14.99	5.92	4.80	14.09

Table S2. Experimental weight fraction data for the system composed of [C₄C₁im][SCN] (1) + K₂CO₃ (2) + H₂O (3) at 25 °C.

[C ₄ C ₁ im][SCN]					
100 w ₁	100 w ₂	100 w ₁	100 w ₂	100 w ₁	100 w ₂
59.72	1.41	19.89	7.38	8.63	10.46
58.06	1.37	19.83	8.18	8.36	11.68
57.41	1.91	19.72	7.75	8.10	11.32
52.66	1.76	19.45	8.03	7.97	11.96
52.05	2.31	19.35	7.61	7.79	11.70
49.31	2.19	19.34	8.27	7.66	12.34
44.06	2.89	19.23	7.86	7.49	12.07
43.49	3.49	19.03	8.14	7.40	12.52
40.89	3.28	18.93	8.36	7.30	12.35
40.24	4.03	18.81	7.69	7.22	12.74
38.06	3.81	18.71	7.92	7.07	12.47
37.76	4.17	18.56	8.19	7.02	12.75
37.03	3.81	18.47	8.39	6.93	12.59
36.07	3.98	18.30	7.74	6.85	12.98
35.38	4.86	18.18	8.26	6.78	12.84
34.09	4.68	18.16	8.05	6.71	13.18
33.75	5.14	18.08	8.50	6.59	12.95
32.54	4.95	17.88	7.93	6.54	13.27
32.14	5.51	17.77	8.35	6.45	13.10
30.69	5.26	17.77	8.19	6.40	13.43
30.41	5.68	17.67	8.59	6.29	13.20
29.47	5.50	17.39	8.45	6.21	13.66
29.22	5.88	17.37	8.01	6.10	13.41
27.97	5.62	17.30	8.65	6.03	13.80
27.59	6.23	17.30	8.20	5.93	13.57
26.52	5.99	17.07	8.53	5.86	14.03
26.32	6.31	17.06	8.08	5.74	13.74
26.20	6.48	16.98	8.75	5.67	14.18
25.64	6.15	16.95	8.36	5.60	14.02
25.39	6.56	16.73	8.62	5.56	14.27
25.36	6.79	16.65	8.83	5.48	14.07
24.80	6.41	16.42	8.10	5.42	14.45
24.59	6.97	16.28	8.46	5.34	14.23
24.54	6.86	16.12	8.55	5.30	14.50
23.89	6.68	16.03	8.79	5.19	14.20
23.75	6.93	15.83	8.68	5.12	14.71
23.33	7.14	15.76	8.19	5.04	14.49
23.19	6.77	15.75	8.87	4.98	14.89
23.04	7.03	15.62	8.56	4.89	14.61
22.53	6.88	15.47	8.72	4.84	14.98
22.20	7.51	15.40	8.93	4.75	14.71
22.12	7.33	15.23	8.34	4.66	15.39
21.96	7.63	14.94	8.66	4.57	15.12
21.57	7.49	14.78	9.10	4.52	15.57
21.45	7.74	14.18	8.73	4.46	15.39
21.32	7.21	14.00	9.24	4.42	15.72
21.15	7.54	13.47	8.89	4.32	15.35
21.03	7.59	13.26	9.54	4.23	16.01
20.89	7.87	11.83	9.91	4.16	15.72
20.53	7.32	10.69	10.12	4.10	16.15
20.50	7.73	10.30	9.75	4.06	15.97
20.41	7.57	10.06	10.69	4.02	16.31
20.37	7.98	9.43	10.02	3.97	16.12
19.99	7.83	9.18	11.12		

Table S3. Experimental weight fraction data for the system composed of [C₄C₁im][TOS] (1) + K₂CO₃ (2) + H₂O (3) at 25 °C.

[C ₄ C ₁ im][TOS]					
100 w ₁	100 w ₂	100 w ₁	100 w ₂	100 w ₁	100 w ₂
56.11	2.34	19.92	11.35	11.89	14.19
50.88	2.98	19.52	11.13	11.76	14.03
49.93	3.85	19.34	11.48	11.70	14.22
47.46	3.66	19.19	11.39	11.63	14.13
46.91	4.20	19.01	11.75	11.57	14.32
45.99	4.12	18.68	11.54	11.43	14.16
45.54	4.57	18.47	11.97	11.35	14.40
44.54	4.47	18.13	11.75	11.23	14.24
44.04	4.98	17.96	12.12	11.17	14.42
42.08	4.76	17.63	11.89	11.11	14.34
41.46	5.43	17.47	12.23	11.06	14.51
40.60	5.31	17.18	12.03	10.93	14.35
40.05	5.92	17.01	12.41	10.82	14.71
38.45	5.68	16.73	12.19	10.71	14.55
37.89	6.33	16.58	12.53	10.65	14.72
36.48	6.09	16.30	12.32	10.53	14.55
35.98	6.69	16.16	12.64	10.47	14.76
35.30	6.57	16.04	12.54	10.42	14.69
34.74	7.25	15.92	12.83	10.36	14.89
33.49	6.99	15.69	12.65	10.24	14.71
33.02	7.60	15.55	12.98	10.18	14.89
31.88	7.34	15.33	12.79	10.13	14.82
31.48	7.87	15.21	13.07	10.07	15.02
31.03	7.76	14.98	12.87	9.97	14.87
30.66	8.27	14.87	13.13	9.92	15.07
29.76	8.02	14.65	12.93	9.82	14.91
29.42	8.50	14.53	13.24	9.76	15.12
28.95	8.37	14.31	13.04	9.66	14.96
28.57	8.91	14.18	13.38	9.61	15.13
27.69	8.64	13.98	13.19	9.56	15.05
27.37	9.12	13.85	13.54	9.51	15.23
26.57	8.85	13.66	13.36	9.45	15.14
26.20	9.42	13.57	13.58	9.39	15.36
25.56	9.19	13.41	13.42	9.25	15.13
25.20	9.76	13.30	13.73	9.20	15.31
24.56	9.51	13.13	13.55	9.16	15.24
24.18	10.13	13.02	13.88	9.12	15.41
23.58	9.88	12.85	13.70	9.04	15.27
23.17	10.57	12.74	14.04	9.00	15.42
22.36	10.20	12.50	13.78	8.96	15.35
22.11	10.64	12.43	13.97	8.92	15.51
21.58	10.39	12.37	13.90	8.82	15.35
21.22	11.04	12.29	14.12	8.78	15.50
20.73	10.79	12.16	13.96	8.74	15.43
20.54	11.15	12.09	14.16	8.70	15.60
20.13	10.93	11.96	14.00	8.62	15.46

Table S4. Experimental weight fraction data for the system composed of [C₄C₁im][N(CN)₂] (1) + K₂CO₃ (2) + H₂O (3) at 25 °C.

[C ₄ C ₁ im][N(CN) ₂]					
100 w ₁	100 w ₂	100 w ₁	100 w ₂	100 w ₁	100 w ₂
38.42	5.23	16.85	10.04	6.51	14.10
38.13	5.56	16.79	10.18	6.46	13.98
36.65	5.34	16.67	10.11	6.41	14.27
36.24	5.85	16.64	9.82	6.30	14.03
34.98	5.64	16.55	10.39	6.25	14.35
34.51	6.23	16.31	10.24	6.14	14.10
33.36	6.03	16.26	10.36	6.02	14.77
32.86	6.69	16.04	10.22	5.89	14.44
31.79	6.48	15.91	10.55	5.83	14.77
31.39	7.02	15.61	10.35	5.79	14.66
30.32	6.78	15.54	10.53	5.73	14.99
28.47	7.11	15.50	10.41	5.65	14.77
28.11	7.66	15.44	10.47	5.60	15.04
26.91	7.33	14.27	10.51	5.52	14.81
26.55	7.89	13.55	10.89	5.43	15.40
25.73	7.64	12.79	11.32	5.35	15.17
25.47	8.06	11.94	11.32	5.30	15.46
24.50	7.75	11.39	11.66	5.26	15.35
24.27	7.79	10.85	11.82	5.23	15.58
24.19	8.29	10.53	11.47	5.19	15.46
23.59	8.08	10.28	12.39	5.14	15.75
23.31	8.58	9.87	11.89	5.07	15.54
22.74	8.37	9.74	12.41	5.04	15.75
22.57	8.16	9.48	12.09	5.01	15.65
22.54	8.75	9.37	12.54	4.98	15.89
21.97	8.53	9.24	12.36	4.94	15.78
21.82	8.82	9.13	12.82	4.87	16.27
21.32	8.63	8.90	12.49	4.77	15.94
21.05	9.16	8.76	13.09	4.71	16.38
20.76	8.65	8.53	12.76	4.66	16.19
20.33	8.85	8.43	13.21	4.61	16.56
20.11	9.31	8.22	12.88	4.55	16.36
19.75	9.14	8.12	13.29	4.49	16.77
19.51	9.62	8.04	13.16	4.44	16.58
19.23	9.01	7.93	13.66	4.38	17.00
19.11	9.42	7.68	13.22	4.28	16.61
19.00	9.66	7.59	13.65	4.22	17.08
18.62	9.47	7.51	13.50	4.16	16.82
18.49	9.76	7.42	13.93	4.10	17.24
18.16	9.58	7.27	13.65	4.04	16.96
18.03	9.88	7.19	14.05	3.98	17.42
17.82	9.50	7.13	13.93	3.91	17.12
17.77	9.73	7.06	14.28	3.86	17.55
17.63	10.03	6.74	13.65	3.82	17.37
17.38	9.89	6.67	14.06		
17.22	10.26	6.56	13.83		

Table S5. Experimental weight fraction data for the system composed of [C₄C₁im][C₂H₅SO₄] (1) + K₂CO₃ (2) + H₂O (3) at 25 °C.

[C ₄ C ₁ im][C ₁ H ₅ SO ₄]					
100 w ₁	100 w ₂	100 w ₁	100 w ₂	100 w ₁	100 w ₂
43.44	6.38	27.23	12.06	18.58	15.80
41.65	6.12	26.88	11.91	18.40	15.65
40.99	6.81	26.52	12.42	18.02	16.36
40.11	6.66	25.82	12.09	17.70	16.07
39.57	7.25	25.44	12.65	17.37	16.69
38.80	7.11	25.10	12.48	17.08	16.40
38.26	7.70	24.58	13.25	16.64	17.27
37.63	7.57	23.96	12.92	16.48	17.11
37.12	8.14	23.56	13.55	16.29	17.49
36.39	7.98	23.24	13.37	16.02	17.20
35.87	8.58	22.87	13.97	15.75	17.74
35.20	8.42	22.31	13.63	15.53	17.48
34.76	8.93	21.83	14.41	15.26	18.04
34.12	8.77	21.36	14.10	15.03	17.77
33.59	9.40	21.06	14.59	14.92	18.00
33.02	9.25	20.83	14.42	14.82	17.87
32.63	9.72	20.58	14.85	14.70	18.12
31.57	9.40	20.36	14.70	14.60	18.00
30.74	10.47	20.13	15.10	14.45	18.32
30.30	10.32	19.92	14.94	14.36	18.20
29.92	10.81	19.76	15.22	14.28	18.37
29.43	10.63	19.55	15.05	14.19	18.26
29.04	11.15	19.24	15.61	14.11	18.44
28.58	10.97	19.04	15.45	14.00	18.30
28.26	11.41	18.91	15.70	13.84	18.67
27.83	11.23	18.72	15.54	13.75	18.55

Table S6. Experimental weight fraction data for the system composed of [C₄C₁im][CH₃SO₄] (1) + K₂CO₃ (2) + H₂O (3) at 25 °C.

[C ₄ C ₁ im][CH ₃ SO ₄]					
100 w ₁	100 w ₂	100 w ₁	100 w ₂	100 w ₁	100 w ₂
36.98	8.67	20.87	15.41	15.49	18.58
35.06	9.70	20.59	15.88	15.30	18.35
30.32	11.19	20.28	15.65	15.03	18.90
29.67	10.95	20.03	16.07	14.86	18.69
29.11	11.69	19.71	15.81	14.56	19.33
28.53	11.46	19.20	16.70	14.39	19.11
28.08	12.07	18.93	16.46	14.25	19.43
27.47	11.81	18.69	16.88	14.11	19.24
26.96	12.52	18.46	16.67	13.97	19.54
26.42	12.26	18.22	17.10	13.83	19.34
25.55	13.51	17.97	16.87	13.69	19.66
25.05	13.25	17.72	17.33	13.56	19.47
24.57	13.95	17.49	17.10	13.28	20.10
24.12	13.70	17.25	17.54	13.17	19.94
23.73	14.28	17.01	17.31	13.05	20.22
23.30	14.02	16.63	18.05	12.92	20.02
22.90	14.65	16.45	17.86	12.80	20.29
22.47	14.37	16.25	18.25	12.69	20.11
21.82	15.40	16.06	18.04	12.56	20.39
21.50	15.17	15.87	18.42	12.45	20.21
21.20	15.65	15.68	18.20		

Table S7. Experimental weight fraction data for the system composed of [C₄C₁im]Br (1) + K₂CO₃ (2) + H₂O (3) at 25 °C.

[C ₄ C ₁ im]Br					
100 w ₁	100 w ₂	100 w ₁	100 w ₂	100 w ₁	100 w ₂
61.89	1.04	24.25	13.29	14.45	18.79
59.64	1.00	23.92	13.10	14.33	18.63
58.26	2.13	23.51	13.74	14.22	18.86
54.71	2.00	23.26	13.60	14.10	18.69
53.57	2.99	23.10	13.84	13.88	19.17
50.55	2.82	22.84	13.68	13.79	19.04
49.65	3.66	22.58	14.10	13.69	19.27
47.12	3.47	22.26	13.91	13.59	19.13
46.26	4.32	21.70	14.82	13.51	19.32
44.90	4.19	21.19	14.47	13.42	19.19
43.82	5.29	20.82	15.08	13.23	19.60
41.95	5.06	20.57	14.90	13.14	19.46
41.30	5.77	20.33	15.32	13.06	19.63
40.42	5.65	20.09	15.13	12.97	19.49
39.96	6.16	19.74	15.74	12.81	19.87
39.02	6.01	19.53	15.58	12.71	19.72
38.04	7.12	19.30	15.98	12.64	19.89
37.25	6.97	19.09	15.80	12.55	19.75
36.70	7.60	18.81	16.29	12.37	20.20
35.96	7.44	18.60	16.11	12.29	20.07
35.55	7.92	18.49	16.31	12.21	20.27
34.87	7.77	18.31	16.15	12.12	20.12
34.50	8.22	18.02	16.68	12.05	20.30
33.82	8.06	17.83	16.51	11.96	20.16
32.90	9.21	17.66	16.83	11.78	20.60
32.27	9.03	17.47	16.66	11.72	20.48
31.90	9.49	17.17	17.24	11.66	20.63
31.37	9.33	16.99	17.07	11.58	20.49
30.85	10.00	16.87	17.30	11.49	20.71
30.30	9.82	16.74	17.17	11.41	20.57
29.80	10.48	16.65	17.36	11.24	21.02
29.31	10.31	16.50	17.21	11.16	20.87
28.65	11.20	16.29	17.64	11.09	21.04
28.22	11.03	16.13	17.47	11.03	20.92
27.90	11.48	15.94	17.85	10.95	21.11
27.47	11.30	15.79	17.69	10.88	20.97
27.07	11.85	15.58	18.12	10.74	21.36
26.72	11.70	15.43	17.94	10.68	21.23
26.54	11.95	15.32	18.18	10.60	21.43
26.19	11.80	15.18	18.02	10.54	21.30
25.87	12.25	14.98	18.45	10.48	21.47
25.51	12.09	14.86	18.30	10.43	21.36
24.95	12.92	14.78	18.48		
24.61	12.74	14.66	18.34		

Table S8. Experimental weight fraction data for the system composed of [C₄C₁im][DMP] (1) + K₂CO₃ (2) + H₂O (3) at 25 °C.

[C ₄ C ₁ im][DMP]					
100 w ₁	100 w ₂	100 w ₁	100 w ₂	100 w ₁	100 w ₂
49.50	5.08	24.49	15.69	13.14	24.13
46.87	4.81	23.35	17.29	13.00	23.87
44.87	6.74	22.86	16.93	12.56	24.76
42.56	6.39	22.32	17.71	12.30	24.25
41.53	7.44	21.88	17.36	11.84	25.21
40.54	7.26	20.70	19.12	11.73	24.97
39.56	8.30	20.32	18.77	11.52	25.41
38.64	8.10	19.99	19.28	11.31	24.95
37.81	9.00	19.61	18.91	10.86	25.93
36.97	8.80	18.64	20.44	10.76	25.69
35.97	9.91	18.37	20.14	10.58	26.09
35.17	9.69	18.10	20.58	10.49	25.86
34.03	10.99	17.81	20.25	10.25	26.42
33.38	10.78	17.26	21.17	10.08	25.98
32.47	11.84	16.99	20.85	9.66	26.99
31.80	11.60	16.32	21.99	9.59	26.79
30.95	12.63	16.10	21.69	9.44	27.14
30.43	12.41	15.73	22.34	9.29	26.72
29.71	13.26	15.54	22.06	8.95	27.59
29.70	13.31	15.06	22.92	8.81	27.16
29.10	13.04	14.86	22.61	8.56	27.79
28.93	12.91	14.45	23.37	8.44	27.39
27.82	14.32	14.29	23.10	8.10	28.29
27.19	13.99	14.11	23.43	7.90	27.58
26.07	15.47	13.94	23.14	7.44	28.89
25.64	15.22	13.58	23.84	7.22	28.06
25.03	16.04	13.42	23.57		

Table S9. Experimental weight fraction data for the system composed of [C₄C₁im][CH₃CO₂] (1) + K₂CO₃ (2) + H₂O (3) at 25 °C.

[C ₄ C ₁ im][CH ₃ CO ₂]					
100 w ₁	100 w ₂	100 w ₁	100 w ₂	100 w ₁	100 w ₂
45.49	2.80	23.25	14.30	15.80	5.59
43.72	2.69	22.87	14.88	15.73	19.85
42.57	3.93	22.70	14.77	15.72	5.82
41.00	3.78	22.31	15.38	15.63	19.71
39.94	4.98	22.12	15.25	15.59	5.78
38.66	4.82	21.80	15.75	15.53	5.96
37.79	5.84	21.59	15.60	15.50	19.95
37.22	5.75	21.34	16.00	15.41	19.83
36.27	6.89	21.15	15.86	15.16	5.83
35.27	6.70	20.63	16.70	15.16	20.31
34.50	7.64	20.45	16.56	15.12	5.97
34.03	7.54	20.22	16.94	15.09	20.21
33.31	8.44	20.04	16.79	14.99	5.92
32.85	8.32	19.75	17.28	14.97	20.43
32.30	9.02	19.62	17.16	14.92	6.13
31.91	8.92	19.38	17.55	14.90	20.33
31.35	9.64	19.25	17.42	14.70	6.04
30.53	9.39	18.84	18.11	14.65	6.19
29.90	10.22	18.69	17.97	14.42	6.09
29.61	10.12	18.49	18.31	14.30	6.45
29.06	10.86	18.37	18.19	13.92	6.28
28.30	10.58	18.17	18.54	13.80	6.67
27.28	11.99	18.06	18.43	13.53	6.54
27.00	11.87	17.85	18.79	13.42	6.88
26.48	12.60	17.72	18.66	12.77	6.55
26.19	12.46	17.34	19.34	12.62	7.06
25.71	13.15	17.22	19.20	12.30	6.88
25.19	12.88	17.04	19.53	12.20	7.26
24.34	14.14	16.92	19.39	11.91	7.09
23.87	13.86	15.96	19.69		
23.48	14.44	15.87	19.58		

Table S10 Experimental weight fraction data for the system composed of [C₄C₁im][CH₃SO₃] (1) + K₂CO₃ (2) + H₂O (3) at 25 °C.

[C ₄ C ₁ im][CH ₃ SO ₃]					
100 w ₁	100 w ₂	100 w ₁	100 w ₂	100 w ₁	100 w ₂
44.88	6.11	28.99	13.25	21.46	17.70
43.60	7.36	28.13	14.33	20.89	18.55
41.86	7.07	27.74	14.13	20.64	18.33
40.76	8.20	27.39	14.58	20.40	18.71
39.89	8.02	27.04	14.39	20.22	18.55
38.95	9.01	26.33	15.32	19.98	18.92
38.25	8.84	26.00	15.13	19.80	18.75
37.34	9.82	25.66	15.57	19.55	19.15
36.67	9.65	25.37	15.39	19.35	18.96
35.74	10.67	25.03	15.85	18.89	19.69
34.62	10.33	24.74	15.68	18.75	19.55
33.91	11.15	24.06	16.63	18.58	19.82
33.38	10.97	23.78	16.44	18.44	19.67
32.70	11.76	23.46	16.90	18.25	19.97
32.21	11.59	23.19	16.71	18.09	19.79
31.62	12.29	22.83	17.23	17.75	20.34
31.12	12.10	22.58	17.04	17.60	20.17
30.46	12.90	22.24	17.54	17.43	20.45
30.01	12.71	22.02	17.36	17.30	20.29
29.43	13.45	21.67	17.88		

Table S11. Experimental weight fraction data for the system composed of [C₄C₁im]Cl (1) + K₂CO₃ (2) + H₂O (3) at 25 °C.

[C ₄ C ₁ im]Cl					
100 w ₁	100 w ₂	100 w ₁	100 w ₂	100 w ₁	100 w ₂
48.27	3.21	25.43	12.99	18.77	17.28
46.94	3.13	25.26	12.90	18.62	17.55
45.98	4.09	24.92	13.40	18.51	17.46
44.08	3.92	24.72	13.29	18.33	17.78
43.38	4.66	24.48	13.63	18.20	17.66
42.35	4.55	24.29	13.52	18.05	17.94
38.38	5.91	23.99	13.96	17.95	17.84
37.66	6.74	23.79	13.85	17.76	18.19
36.39	6.51	23.52	14.26	17.68	18.11
35.35	7.75	23.35	14.15	17.39	18.62
34.08	7.47	23.07	14.59	17.29	18.51
33.20	8.57	22.89	14.47	17.17	18.73
32.86	8.48	22.59	14.94	17.07	18.62
32.40	9.06	22.25	14.72	16.90	18.93
31.76	8.88	21.99	15.12	16.80	18.83
30.97	9.91	21.83	15.01	16.58	19.25
30.42	9.73	21.39	15.73	16.42	19.07
29.99	10.31	21.23	15.61	16.24	19.41
29.73	10.22	21.00	16.00	16.16	19.31
29.29	10.81	20.76	15.82	15.96	19.69
28.77	10.62	20.54	16.18	15.87	19.58
28.41	11.12	20.41	16.08	15.73	19.85
28.14	11.02	20.24	16.37	15.63	19.71
27.82	11.46	20.12	16.28	15.50	19.95
27.60	11.37	19.81	16.79	15.41	19.83
27.23	11.88	19.68	16.68	15.16	20.31
27.01	11.78	19.47	17.03	15.09	20.21
26.70	12.22	19.35	16.92	14.97	20.43
26.35	12.06	19.18	17.21	14.90	20.33
26.00	12.57	19.06	17.10		
25.79	12.47	18.89	17.39		

Table S12. Experimental weight fraction data for the system composed of [C₄C₁im][CF₃SO₃] (1) + Na₂SO₄ (2) + H₂O (3) at pH 7, 25 °C.

[C ₄ C ₁ im][CF ₃ SO ₃]					
100 w ₁	100 w ₂	100 w ₁	100 w ₂	100 w ₁	100 w ₂
56.34	1.15	21.73	4.15	13.75	6.61
52.39	1.07	21.51	4.32	13.59	6.53
50.96	1.60	21.20	4.26	13.30	6.83
46.50	1.46	20.97	4.43	13.13	6.74
45.48	1.88	20.64	4.36	12.85	7.04
42.83	1.77	20.41	4.54	12.70	6.97
41.52	2.34	20.13	4.48	12.44	7.25
38.31	2.16	19.89	4.67	12.29	7.16
37.60	2.50	19.58	4.60	12.01	7.46
35.67	2.37	19.35	4.78	11.88	7.38
35.14	2.64	19.07	4.72	11.60	7.70
34.28	2.58	18.86	4.89	11.49	7.62
33.64	2.91	18.59	4.82	11.19	7.95
31.67	2.74	18.42	4.97	11.06	7.86
31.11	3.05	18.20	4.91	10.69	8.27
30.07	2.95	18.00	5.08	10.59	8.19
29.50	3.28	17.79	5.02	10.32	8.51
28.46	3.16	17.54	5.23	10.20	8.41
28.09	3.39	17.32	5.17	9.79	8.90
27.14	3.27	17.10	5.37	9.70	8.81
26.85	3.46	16.86	5.29	9.37	9.21
26.35	3.39	16.65	5.48	9.28	9.11
25.92	3.67	16.42	5.40	8.87	9.62
25.06	3.54	16.14	5.66	8.79	9.54
24.74	3.76	15.93	5.59	8.40	10.03
24.33	3.70	15.70	5.80	8.33	9.95
24.07	3.88	15.47	5.71	7.88	10.52
23.63	3.80	15.19	5.98	7.82	10.44
23.34	4.01	15.00	5.91	7.38	10.99
22.92	3.94	14.71	6.19	7.33	10.92
22.71	4.09	14.52	6.12	6.74	11.69
22.31	4.02	14.26	6.38	6.70	11.62
22.05	4.21	14.06	6.29		

Table S13. Experimental weight fraction data for the system composed of [C₄C₁im][C₈H₁₇SO₄] (1) + Na₂SO₄ (2) + H₂O (3) at pH 7, 25 °C.

[C ₄ C ₁ im][C ₈ H ₁₇ SO ₄]					
100 w ₁	100 w ₂	100 w ₁	100 w ₂	100 w ₁	100 w ₂
64.50	1.59	26.58	7.23	14.77	10.18
61.36	1.51	26.15	7.11	14.68	10.11
58.43	2.40	25.23	7.57	14.38	10.31
55.86	2.29	24.93	7.48	14.25	10.21
53.98	2.89	24.44	7.72	13.93	10.43
51.67	2.76	24.00	7.59	13.81	10.34
49.44	3.51	23.24	7.98	13.44	10.59
47.95	3.40	22.96	7.88	13.35	10.52
46.04	4.07	22.38	8.19	13.11	10.70
44.73	3.95	22.16	8.10	13.03	10.63
43.94	4.24	21.77	8.31	12.80	10.79
43.07	4.15	21.54	8.22	12.67	10.68
41.97	4.56	21.09	8.46	12.28	10.97
41.04	4.46	20.93	8.40	12.17	10.87
40.03	4.84	20.60	8.58	11.78	11.17
39.12	4.73	20.39	8.50	11.68	11.08
37.72	5.28	19.92	8.76	11.38	11.30
37.26	5.22	19.69	8.66	11.31	11.24
36.71	5.44	19.26	8.91	11.09	11.41
36.12	5.35	19.09	8.83	10.99	11.31
35.53	5.59	18.72	9.04	10.66	11.57
34.84	5.48	18.52	8.94	10.58	11.49
33.96	5.84	18.04	9.23	10.31	11.71
33.47	5.76	17.87	9.14	10.25	11.64
32.66	6.10	17.51	9.36	10.05	11.80
32.16	6.01	17.34	9.27	10.00	11.74
31.40	6.34	16.88	9.56	9.76	11.93
30.93	6.25	16.71	9.47	9.71	11.87
30.45	6.46	16.39	9.67	9.51	12.03
30.01	6.37	16.25	9.58	9.44	11.94
29.09	6.79	15.84	9.84	9.15	12.19
28.64	6.68	15.68	9.75	9.10	12.13
28.05	6.96	15.27	10.01		
27.45	6.81	15.14	9.93		

Table S14. Experimental weight fraction data for the system composed of [C₄C₁im][SCN] (1) + Na₂SO₄ (2) + H₂O (3) at pH 7, 25 °C.

[C ₄ C ₁ im][SCN]					
100 w ₁	100 w ₂	100 w ₁	100 w ₂	100 w ₁	100 w ₂
47.22	1.47	30.47	4.51	19.07	7.76
46.35	1.44	30.10	4.45	18.91	7.69
45.55	1.74	29.58	4.71	18.51	7.93
44.88	1.72	29.31	4.66	18.37	7.87
44.34	1.92	28.69	4.97	17.92	8.14
43.79	1.90	28.39	4.91	17.81	8.09
43.35	2.07	27.89	5.16	17.55	8.25
42.76	2.04	27.57	5.10	17.43	8.20
42.40	2.18	26.98	5.40	17.12	8.40
41.92	2.16	26.71	5.35	17.00	8.34
41.53	2.31	26.21	5.61	16.75	8.50
40.98	2.28	25.97	5.56	16.65	8.45
40.68	2.40	25.46	5.82	16.25	8.71
40.13	2.37	25.24	5.77	16.13	8.64
39.53	2.62	24.68	6.07	15.82	8.84
38.93	2.58	24.37	5.99	15.72	8.79
38.32	2.84	23.79	6.30	15.61	8.87
37.81	2.80	23.58	6.25	15.55	8.83
37.49	2.94	23.14	6.49	15.42	8.91
37.08	2.91	22.92	6.43	15.32	8.85
36.53	3.15	22.39	6.72	15.08	9.01
36.02	3.10	22.17	6.65	15.01	8.97
35.31	3.42	21.69	6.92	14.79	9.11
34.83	3.37	21.50	6.86	14.68	9.04
34.22	3.64	21.00	7.14	14.31	9.29
33.83	3.60	20.86	7.09	14.10	9.15
33.43	3.79	20.52	7.29	13.44	9.61
32.98	3.73	20.40	7.24	13.16	9.42
32.33	4.04	20.04	7.45	12.10	10.19
31.91	3.98	19.88	7.39	11.68	9.83
31.19	4.32	19.51	7.61		
30.94	4.29	19.40	7.56		

Table S15. Experimental weight fraction data for the system composed of [C₄C₁im][TOS] (1) + Na₂SO₄ (2) + H₂O (3) at pH 7, 25 °C.

[C ₄ C ₁ im][TOS]					
100 w ₁	100 w ₂	100 w ₁	100 w ₂	100 w ₁	100 w ₂
53.420	2.118	37.556	4.830	27.40	8.02
51.385	2.038	37.242	4.789	26.98	7.90
49.601	2.567	36.926	5.071	25.09	8.87
48.667	2.519	36.346	4.991	24.60	8.70
47.775	2.790	35.348	5.431	23.10	9.66
46.872	2.737	34.979	5.375	22.67	9.48
44.671	3.420	33.430	6.004	20.16	10.78
43.941	3.365	33.033	5.933	19.70	10.54
42.190	3.920	31.468	6.642	17.53	11.89
41.527	3.903	31.078	6.560	17.10	11.60
41.486	3.854	30.905	6.798	15.29	12.91
41.142	3.867	30.38	6.68	14.94	12.61
39.606	4.463	29.04	7.41		
38.976	4.392	28.66	7.32		

Table S16. Experimental weight fraction data for the system composed of [C₄C₁im][N(CN)₂] (1) + Na₂SO₄ (2) + H₂O (3) at pH 7, 25 °C.

[C ₄ C ₁ im][N(CN) ₂]					
100 w ₁	100 w ₂	100 w ₁	100 w ₂	100 w ₁	100 w ₂
56.32	0.55	41.08	2.44	28.09	5.63
55.54	0.78	40.20	2.75	26.99	6.08
54.34	0.77	39.56	2.71	26.68	6.01
53.66	0.97	38.56	3.07	24.29	7.01
52.17	0.94	37.96	3.03	24.03	6.93
50.63	1.42	36.57	3.54	21.80	7.88
48.42	1.36	36.06	3.49	21.57	7.80
47.57	1.64	34.89	3.94	19.12	8.86
46.63	1.61	34.40	3.89	18.95	8.78
45.95	1.83	33.22	4.34	16.54	9.85
45.07	1.80	32.73	4.28	16.41	9.77
43.99	2.16	30.92	4.99	11.54	12.15
43.12	2.12	30.45	4.92		
42.04	2.49	28.50	5.71		

Table S17. Experimental weight fraction data for the system composed of [C₄C₁im][CH₃SO₄] (1) + Na₂SO₄ (2) + H₂O (3) at pH 7, 25 °C.

[C ₄ C ₁ im][CH ₃ SO ₄]					
100 w ₁	100 w ₂	100 w ₁	100 w ₂	100 w ₁	100 w ₂
50.60	2.17	42.89	3.68	32.10	7.31
50.42	2.16	42.41	4.02	31.84	7.25
50.37	2.21	42.29	3.82	31.66	7.49
50.10	2.25	41.80	4.15	31.34	7.66
50.00	2.19	41.75	3.96	31.25	7.40
49.74	2.24	41.42	4.22	30.96	7.57
49.70	2.31	41.27	4.10	30.63	7.91
49.27	2.29	41.19	4.20	30.18	7.79
49.21	2.38	41.01	4.35	30.15	8.09
48.95	2.42	40.45	4.29	29.81	8.00
48.76	2.35	40.30	4.50	29.73	8.27
48.61	2.47	39.98	4.60	29.59	8.52
48.57	2.41	39.77	4.44	29.40	8.18
48.46	2.50	39.70	4.71	29.00	8.35
48.32	2.45	39.59	4.56	28.48	8.86
48.21	2.49	39.34	4.82	28.16	9.12
48.12	2.56	39.24	4.66	28.01	8.72
47.66	2.54	38.95	4.77	27.70	9.38
47.53	2.65	38.78	4.96	27.66	8.96
47.28	2.71	38.52	5.08	27.40	9.68
47.01	2.62	38.29	4.90	27.28	9.24
46.83	2.68	38.09	5.02	26.86	9.49
46.83	2.79	37.96	5.24	26.35	10.02
46.40	2.86	37.61	5.37	25.95	9.87
46.32	2.76	37.43	5.17	25.80	10.37
46.02	2.83	37.16	5.31	25.48	10.81
45.94	2.93	37.10	5.50	25.30	10.17
45.73	2.99	36.75	5.63	24.77	11.20
45.48	2.90	36.73	5.45	24.77	10.51
45.41	3.07	36.36	5.81	24.29	10.98
45.33	2.97	36.34	5.57	24.04	11.64
45.27	3.27	35.81	6.01	23.52	11.39
45.13	3.32	35.77	5.72	23.29	12.10
44.99	3.15	35.33	6.16	22.77	11.83
44.92	3.04	35.22	5.91	22.49	12.60
44.80	3.30	35.21	6.27	21.98	12.31
44.67	3.42	34.96	6.09	20.77	13.33
44.55	3.12	34.82	6.20	20.20	12.97
44.24	3.52	34.69	6.49	20.19	14.26
44.24	3.19	34.10	6.38	19.24	13.59
44.14	3.38	33.94	6.70	19.02	14.91
43.90	3.62	33.48	6.61	18.56	14.55
43.70	3.48	33.40	6.95	16.18	16.15
43.51	3.73	32.88	7.14	15.58	15.55
43.40	3.58	32.77	6.82	14.82	17.22
42.96	3.88	32.47	7.05	14.22	16.53

Table S18. Experimental weight fraction data for the system composed of [C₄C₁im]Br (1) + Na₂SO₄ (2) + H₂O (3) at pH 7, 25 °C.

[C ₄ C ₁ im]Br					
100 w ₁	100 w ₂	100 w ₁	100 w ₂	100 w ₁	100 w ₂
56.58	1.45	34.29	5.73	26.62	9.83
45.19	2.94	33.47	6.49	26.07	9.63
41.51	3.78	33.38	6.52	25.53	10.51
41.07	3.74	32.66	6.38	25.00	10.30
40.19	4.14	32.05	7.11	24.26	11.27
39.86	4.32	31.45	6.98	23.76	11.04
39.83	4.10	30.51	7.81	21.95	12.57
38.78	4.57	29.88	7.65	21.28	12.19
38.32	4.52	29.55	8.33	19.69	14.12
37.16	5.11	29.04	8.19	18.91	13.56
36.57	5.03	27.98	9.10		
34.99	5.85	27.40	8.91		

Table S19. Experimental weight fraction data for the system composed of [C₄C₁im][TOS] (1) + K₃C₆H₅O₇ (2) + H₂O (3) at pH 7, 25 °C.

[C ₄ C ₁ im][TOS]					
100 w ₁	100 w ₂	100 w ₁	100 w ₂	100 w ₁	100 w ₂
80.84	1.88	33.98	12.32	22.76	17.29
56.21	5.16	32.99	12.73	22.11	17.82
52.56	6.00	32.10	13.08	21.29	18.14
49.45	6.75	31.24	13.46	20.93	18.28
47.39	7.60	30.40	13.87	20.61	18.36
44.84	8.17	28.90	14.55	20.27	18.49
43.21	8.82	28.24	14.86	19.93	18.62
41.63	9.44	26.91	15.48	19.48	18.91
40.20	10.03	26.32	15.77	19.16	19.04
38.84	10.57	25.23	16.23	18.89	19.15
37.10	10.90	24.23	16.65	18.62	19.24
35.98	11.44	23.70	16.85	18.23	19.57
34.99	11.86	23.21	17.08	17.71	20.14

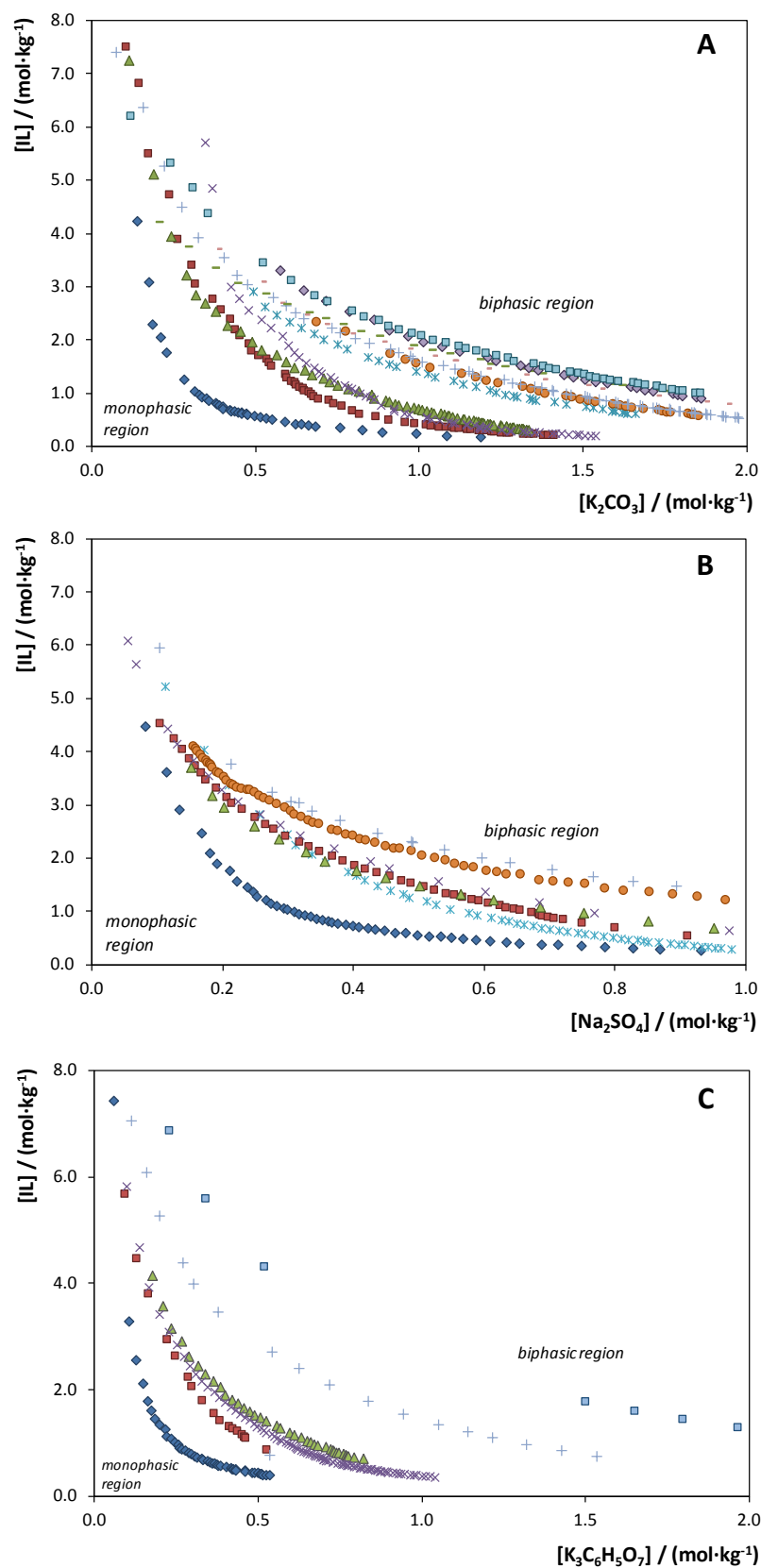


Fig. S2. Ternary phase diagrams composed of (A) [C₄C₁im]-based ILs + K₂CO₃ + H₂O, (B) [C₄C₁im]-based ILs + Na₂SO₄ + H₂O and (C) [C₄C₁im]-based ILs + K₃C₆H₅O₇ + H₂O: [C₄C₁im][CF₃SO₃] (●); [C₄C₁im][SCN] (○); [C₄C₁im][TOS] (⊕); [C₄C₁im][N(CN)₂] (⊗); [C₄C₁im][C₂H₅SO₄] (⊖); [C₄C₁im][C₈H₁₇SO₄] (⊕); [C₄C₁im][CH₃SO₄] (⊗); [C₄C₁im]Br (⊖); [C₄C₁im][DMP] (★); [C₄C₁im][CH₃CO₂] (→); [C₄C₁im][CH₃SO₃] (⊖); and [C₄C₁im]Cl (○).

In Fig. S2 the solubility curves are represented in molality units for a better understanding on the impact of the ILs chemical structure towards their ability to create two-phase systems. Since the ILs studied share a common cation, the results shown in Fig. S2 allow to appraise the effect of the IL anion nature on the ABS formation. In the phase diagrams depicted in Fig. S2 the biphasic region is located above the binodal curve, and the closer the binodal is to the axis the higher is the capability of a given IL to form ABS. According to Fig. S2 A, while considering the mixture compositions at the binodal curve where the IL concentration is equal to that of the salt, here designated as the molality of the IL at saturation solubility, $[IL]_{SS}$, the IL anion ability to form an ABS with K_2CO_3 is as follows: $[CF_3SO_3]^-$ (0.53 mol·kg⁻¹) > $[SCN]^-$ (0.79 mol·kg⁻¹) > $[N(CN)_2]^-$ (0.86 mol·kg⁻¹) ≈ $[TOS]^-$ (0.88 mol·kg⁻¹) >> $[C_2H_5SO_4]^-$ (1.14 mol·kg⁻¹) > $[CH_3SO_4]^-$ (1.21 mol·kg⁻¹) > Br^- (1.24 mol·kg⁻¹) > $[DMP]^-$ (1.31 mol·kg⁻¹) > $[CH_3CO_2]^-$ (1.38 mol·kg⁻¹) > $[CH_3SO_3]^-$ (1.39 mol·kg⁻¹) ≈ Cl^- (1.43 mol·kg⁻¹). Similarly, for Na_2SO_4 and $K_3C_6H_5O_7$, the following trends are observed (Fig. S2 B and C): $[CF_3SO_3]^-$ (0.51 mol·kg⁻¹) > $[C_8H_{17}SO_4]^-$ (0.69 mol·kg⁻¹) > $[SCN]^-$ (0.76 mol·kg⁻¹) > (0.83 mol·kg⁻¹) $[TOS]^-$ ≈ $[N(CN)_2]^-$ (0.83 mol·kg⁻¹) >> $[CH_3SO_4]^-$ (1.06 mol·kg⁻¹) > Br^- (1.13 mol·kg⁻¹) and $[CF_3SO_3]^-$ (0.45 mol·kg⁻¹) > $[SCN]^-$ (0.62 mol·kg⁻¹) > $[N(CN)_2]^-$ (0.71 mol·kg⁻¹) ≈ $[TOS]^-$ (0.76 mol·kg⁻¹) >> Br^- (1.16 mol·kg⁻¹) >> Cl^- (1.64 mol·kg⁻¹), respectively. Independently of the salt and pH conditions, the observed trends are in close agreement with previous studies using other inorganic or organic salts.¹⁻⁴ The effect of the ILs anion in ABS formation has been shown to be related with the ability of the IL anion to hydrogen-bond with water, *i.e.*, IL anions with a lower hydrogen bond donor ability more easily form ABS.⁵

Table S20. Correlation parameters used to describe the experimental binodal data by Eqn (4).

IL	A	B	10 ⁵ C
IL + K₂CO₃ + H₂O systems			
[C ₄ C ₁ im][CF ₃ SO ₃]	150 ± 11	-0.93 ± 0.04	3 ± 14
[C ₄ C ₁ im][SCN]	122 ± 6	-0.59 ± 0.03	38 ± 4
[C ₄ C ₁ im][TOS]	99 ± 3	-0.37 ± 0.06	26 ± 1
[C ₄ C ₁ im][N(CN) ₂]	219 ± 30	-0.73 ± 0.06	25 ± 3
[C ₄ C ₁ im][C ₂ H ₅ SO ₄]	110 ± 8	-0.37 ± 0.03	7.2 ± 0.9
[C ₄ C ₁ im][CH ₃ SO ₄]	124 ± 20	-0.40 ± 0.05	6 ± 1.
[C ₄ C ₁ im]Br	85 ± 1	-0.299 ± 0.008	7.3 ± 0.3
[C ₄ C ₁ im][DMP]	90 ± 4	-0.28 ± 0.02	4 ± 3
[C ₄ C ₁ im][CH ₃ CO ₂]	67 ± 2	-0.24 ± 0.01	4.6 ± 0.5
[C ₄ C ₁ im][CH ₃ SO ₃]	93 ± 6	-0.29 ± 0.02	4.5 ± 0.6
[C ₄ C ₁ im]Cl	82 ± 2	-0.303 ± 0.008	4.0 ± 0.3
IL + Na₂SO₄ + H₂O systems			
[C ₄ C ₁ im][CF ₃ SO ₃]	155 ± 8	-0.95 ± 0.03	5.0 ± 0.1
[C ₄ C ₁ im][C ₈ H ₁₇ SO ₄]	116 ± 4	-0.47 ± 0.02	55 ± 3
[C ₄ C ₁ im][SCN]	81 ± 1	-0.44 ± 0.01	49 ± 3
[C ₄ C ₁ im][TOS]	95 ± 3	-0.42 ± 0.02	17 ± 3
[C ₄ C ₁ im][N(CN) ₂]	78 ± 2	-0.40 ± 0.01	32 ± 5
[C ₄ C ₁ im][CH ₃ SO ₄]	83 ± 1	-0.345 ± 0.007	6.0 ± 0.7
[C ₄ C ₁ im]Br	88 ± 3	-0.38 ± 0.02	2 ± 2
IL + K₃C₆H₅O₇ + H₂O systems			
[C ₄ C ₁ im][TOS]	120 ± 3	-0.34 ± 0.01	5.5 ± 0.3

Table S21. Experimental data for Tl and TLLs of [C₄C₁im]-based ILs + K₂CO₃ + H₂O ABS. Tl used for the Gibbs free energy of transfer of a methylene group and Kamlet-Taft parameters determination are highlighted.

IL	Weight fraction composition / wt %								TLL
	[IL] _{IL}	[salt] _{IL}	pH _{IL}	[IL] _M	[salt] _M	[IL] _{salt}	[salt] _{salt}	pH _{salt}	
[C ₄ C ₁ im][CF ₃ SO ₃]	58.32	1.04	11.12	37.05	4.40	8.85	9.13	11.18	50.13
	89.16	0.31	11.18	16.99	10.00	6.16	11.45	11.24	83.74
[C ₄ C ₁ im][SCN]	52.42	2.07	10.36	19.39	10.31	4.96	13.91	11.53	48.91
	54.83	1.86	11.68	27.78	8.77	3.96	14.97	11.51	52.91
	56.25	1.74	11.21	19.77	12.38	1.23	17.79	11.30	57.31
[C ₄ C ₁ im][TOS]	45.96	4.19	---	26.85	10.27	6.29	16.81	---	41.62
	46.91	3.99	11.34	28.34	10.16	4.28	18.16	11.22	44.92
	50.46	3.31	12.22	26.85	12.01	1.37	21.40	12.07	52.32
	53.31	2.82	---	28.01	12.21	0.96	22.25	---	55.85
	55.81	2.43	11.48	29.55	12.25	0.67	23.05	11.81	58.87
[C ₄ C ₁ im][N(CN) ₂]	45.18	4.52	10.31	14.50	12.04	7.76	13.68	11.42	38.52
	60.81	3.04	12.15	29.08	10.80	3.01	17.18	12.14	59.51
[C ₄ C ₁ im][C ₂ H ₅ SO ₄]	52.30	3.90	11.05	29.08	13.44	9.50	21.49	11.20	46.28
	56.01	3.23	10.81	29.91	15.13	3.78	27.03	11.35	57.39
[C ₄ C ₁ im][CH ₃ SO ₄]	46.52	5.86	11.89	27.09	15.15	7.35	24.58	11.85	43.42
	52.53	4.55	12.19	28.17	15.54	6.66	25.26	11.89	50.32
	60.14	3.25	11.67	24.40	20.01	2.97	30.05	11.82	63.15
[C ₄ C ₁ im]Br	49.87	3.11	12.25	26.80	15.50	3.33	28.23	12.35	52.89
	58.43	1.54	12.50	30.45	16.80	1.16	32.78	12.57	65.24
[C ₄ C ₁ im][DMP]	29.26	13.31	12.36	21.73	18.68	7.76	28.66	12.82	26.42
	45.32	5.78	12.64	23.50	21.59	2.09	37.10	12.50	53.38
	47.16	5.16	12.38	25.97	20.82	1.46	38.93	12.58	56.82
[C ₄ C ₁ im][CH ₃ CO ₂]	39.19	4.92	12.09	29.60	14.86	0.19	45.29	12.36	56.13
	49.91	1.49	12.35	30.17	19.91	0.08	47.98	12.01	68.15
[C ₄ C ₁ im][CH ₃ SO ₃]	45.81	5.99	11.89	31.08	15.47	3.41	33.27	12.41	50.42
	51.10	4.36	12.18	31.75	16.99	1.84	36.52	12.02	58.83
[C ₄ C ₁ im]Cl	34.41	7.86	13.00	21.28	17.96	4.98	30.52	12.14	37.17
	43.10	4.46	12.68	21.94	19.92	3.11	33.67	12.66	49.53
	44.86	3.94	12.56	29.84	15.34	1.88	36.58	12.64	53.97

Table S22. Experimental data for Tl and TLLs of [C₄C₁im]-based ILs + Na₂SO₄ + H₂O ABS at pH 7. Tl used for the Gibbs free energy of transfer of a methylene group and Kamlet-Taft parameters determination are highlighted.

IL	Weight fraction composition / wt %						TLL
	[IL] _{IL}	[salt] _{IL}	[IL] _M	[salt] _M	[IL] _{salt}	[salt] _{salt}	
[C ₄ C ₁ im][CF ₃ SO ₃]	52.55	1.30	35.13	3.93	11.19	7.54	41.82
[C ₄ C ₁ im][C ₈ H ₁₇ SO ₄]	45.70	3.74	28.11	7.97	5.51	13.40	41.34
	50.17	3.11	30.12	7.93	4.08	14.19	47.40
[C ₄ C ₁ im][SCN]	62.93	1.71	49.55	5.11	0.84	17.49	64.06
	46.37	1.56	34.06	5.00	5.91	12.85	42.01
[C ₄ C ₁ im][TOS]	60.77	0.41	30.23	8.01	3.10	14.76	59.43
	44.35	3.33	32.76	8.00	4.35	19.5	43.14
[C ₄ C ₁ im][N(CN) ₂]	50.01	2.39	31.32	9.76	3.04	20.92	50.49
	53.07	1.98	45.10	5.19	1.91	22.57	55.15
[C ₄ C ₁ im][CH ₃ SO ₄]	54.44	1.81	40.18	7.97	0.87	24.95	58.35
	41.68	2.42	31.69	6.40	1.95	18.40	42.82
[C ₄ C ₁ im]Br	49.08	1.37	39.42	5.06	1.11	19.83	51.41
	37.24	5.35	30.16	10.10	3.19	28.20	41.01
[C ₄ C ₁ im]Cl	46.32	2.90	26.39	14.84	2.71	29.04	50.84
	32.91	6.51	28.14	9.96	11.00	22.33	27.02
[C ₄ C ₁ im]Br	35.28	5.65	28.17	10.82	9.12	24.67	32.34
	40.32	4.14	29.73	11.50	6.79	28.01	41.15

3. DNP-amino-acids partition coefficients and $\Delta G(CH_2)$ determination

Table S23. Partition coefficients of DNP-amino-acids in [C₄C₁im]-based ILs + K₂CO₃ + H₂O ABS at 25 °C.

DNP-AA	[C ₄ mim][CF ₃ SO ₃]	[C ₄ mim][SCN]	[C ₄ mim][N(CN) ₂]	[C ₄ mim]Br	[C ₄ mim][DMP]	[C ₄ mim]Cl
DNP-Gly	7.1 ± 0.2	28.4 ± 0.7	57 ± 1	73 ± 2	434 ± 19	215 ± 9
DNP-Ala	8.8 ± 0.4	34 ± 2	79 ± 3	91 ± 8	785 ± 42	350 ± 16
DNP-Val	12.9 ± 0.5	65 ± 4	161 ± 6	184 ± 12	1588 ± 128	600 ± 38
DNP-Leu	21.2 ± 0.5	81 ± 4	360 ± 20	382 ± 19	2252 ± 144	707 ± 55

Table S24. Partition coefficients of DNP-amino-acids in [C₄C₁im]-based ILs + Na₂SO₄ + H₂O ABS at pH 7 and 25 °C.

DNP-AA	[C ₄ mim][CF ₃ SO ₃]	[C ₄ mim][SCN]	[C ₄ mim][N(CN) ₂]	[C ₄ mim][TOS]	[C ₄ mim]Br
DNP-Gly	5.0 ± 0.1	9.9 ± 0.2	12.9 ± 0.4	19 ± 2	56 ± 4
DNP-Ala	6.3 ± 0.4	13.2 ± 0.9	16.6 ± 0.3	28 ± 1	82 ± 4
DNP-Val	8.9 ± 0.2	17.8 ± 0.9	22.7 ± 0.7	34 ± 1	93 ± 7
DNP-Leu	12 ± 1	22.0 ± 0.6	28.6 ± 0.8	64 ± 10	150 ± 27

Table S25. Partition coefficients of DNP-amino-acids in [C₄C₁im]-based ILs + K₃C₆H₅O₇ + H₂O ABS at 25 °C.

DNP-AA	[C ₄ mim][CF ₃ SO ₃]	[C ₄ mim][SCN]	[C ₄ mim][N(CN) ₂]	[C ₄ mim][TOS]	[C ₄ mim]Br	[C ₄ mim]Cl
DNP-Gly	9.97 ± 0.05	7.1 ± 0.2	13.6 ± 0.2	11.2 ± 0.5	15.2 ± 0.4	13.0 ± 0.4
DNP-Ala	14.9 ± 0.2	8.79 ± 0.09	15.5 ± 0.2	11.9 ± 0.6	19.2 ± 0.6	17.2 ± 0.5
DNP-Val	30.5 ± 0.1	14.1 ± 0.2	22.5 ± 1.1	15.8 ± 0.7	23 ± 1	22.2 ± 0.4
DNP-Leu	50 ± 4	18.1 ± 0.4	27.3 ± 0.8	19 ± 1	30 ± 1	27.5 ± 0.5

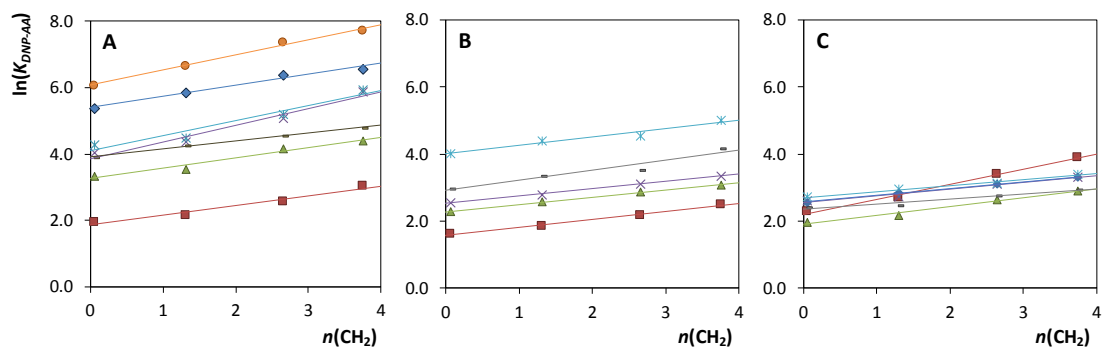


Fig. S3. Logarithm of the partition coefficients for the homologous series of DNP-amino-acids in ABS composed of $[C_4C_1im]$ -based ILs and (A) K_2CO_3 , (B) Na_2SO_4 and (C) $K_3C_6H_5O_7$ as a function of the number of equivalent methylene groups, $n(CH_2)$: $[C_4C_1im][CF_3SO_3]$ (\circ); $[C_4C_1im][SCN]$ (\odot); $[C_4C_1im][N(CN)_2]$ (\otimes); $[C_4C_1im][TOS]$ (\star); $[C_4C_1im]Br$ (\ominus); $[C_4C_1im]Cl$ (\star); $[C_4C_1im][DMP]$ (\otimes).

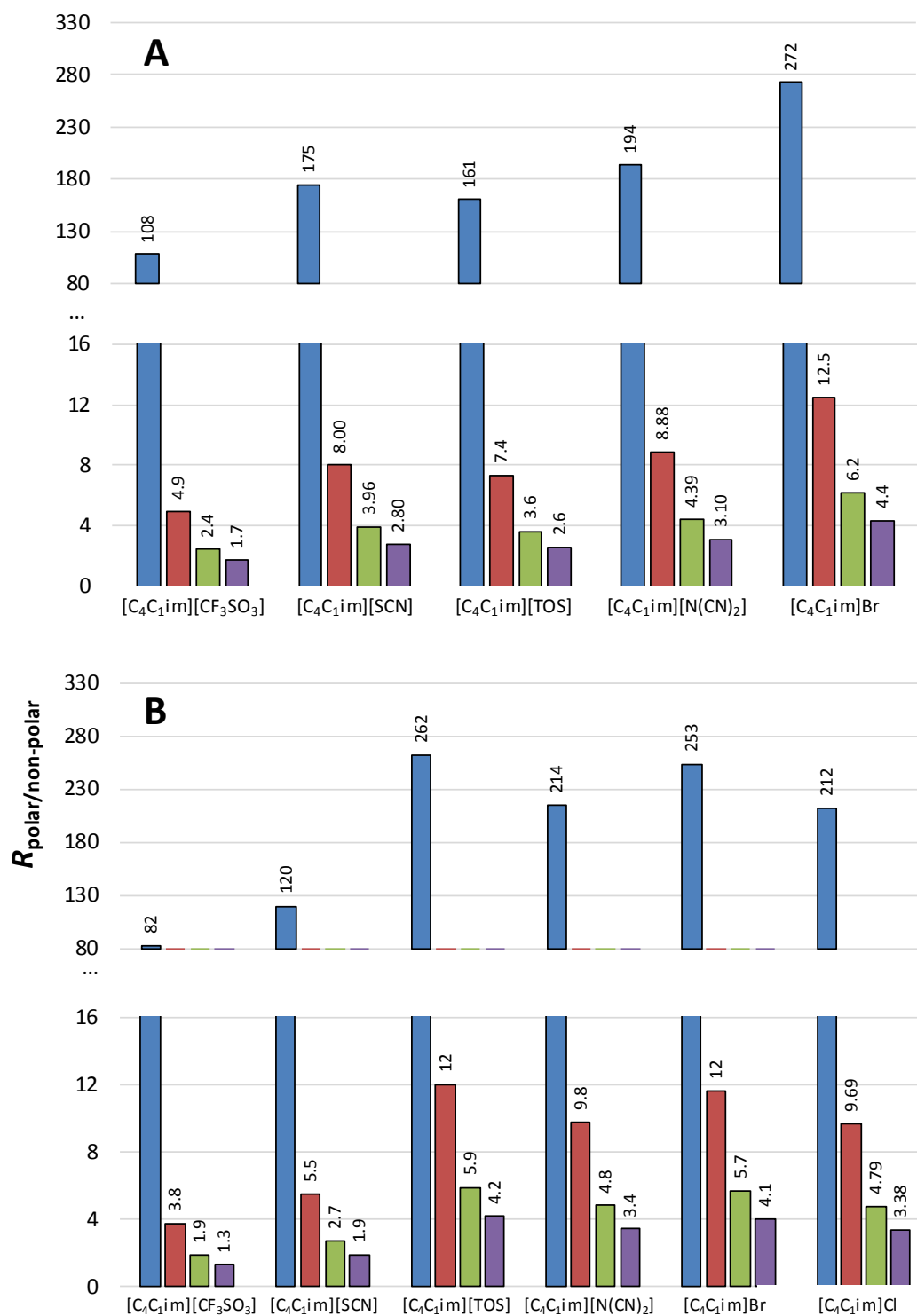


Fig. S4. Ratio of the contribution of polar (*i.e.* polar/hydrogen bonding interactions) and non-polar groups (*i.e.* hydrophobic interactions), $R_{polar/non-polar}$, of DNP-amino-acids (DNP-glycine – blue bars; DNP-valine – red bars; DNP-alanine – green bars and DNP-leucine – purple bars) on their partition in (A) Na_2SO_4 - and (B) $\text{K}_3\text{C}_6\text{H}_5\text{O}_7$ -based ABS.

4. Kamlet-Taft parameters

Table S26. Kamlet-Taft parameters of water and pure ILs.

Solvent	π^*	α	β
water	1.26 ^(a)	1.36 ^(a)	0.15 ^(a)
[C ₄ C ₁ im][CF ₃ SO ₃]	0.98 ^(b)	0.39 ^(a)	0.48 ^(b)
[C ₄ C ₁ im][SCN]	^(d)	0.39 ^(a)	^(d)
[C ₄ C ₁ im][N(CN) ₂]	0.60 ^(c)	0.40 ^(a)	1.05 ^(c)
[C ₄ C ₁ im][DMP]	0.96 ^(b)	^(d)	1.12 ^(b)

^a parameters determined in this work; ^b parameters from ref.⁵; ^c parameters from ref.⁶; ^d it was not possible to determine the parameters due to the IL color or high viscosity.

5. Relations between the various parameters studied.

Table S27. Correlation of the solvent properties *E* and *C* obtained through partitioning of DNP-amino acids with the experimental Kamlet-Taft parameters data (Table 2) in all studied IL-based ABS.

Parameter	Equation	n ^a	r ^{2a}	F ^a	SD ^a	p Values ^a
E	$E = 0.2_{\pm 0.1} - 0.7_{\pm 1} \Delta\pi - 0.2_{\pm 0.8} \Delta\alpha + 0.06_{\pm 2} \Delta\beta$	16	0.14	0.65	0.1	0.1; 0.6; 0.8; 1.0
C	$C = 1.7_{\pm 0.6} + 26_{\pm 8} \Delta\pi - 6_{\pm 4} \Delta\alpha + 37_{\pm 10} \Delta\beta$	16	0.58	5.6	0.6	0.01; 0.006; 0.2; 0.02

^a n – number of experimental points; r – correlation coefficient; F – ratio of variance; SD – standard deviation; p - statistic p-value based on the null hypothesis

Table S28. Correlation of the experimental partition data given in Tables S23-S25 in the [C₄C₁im][SCN]- and [C₄C₁im][N(CN)₂]-based ABS with the experimental solvent properties for the same ABS given in Table 2.

Solute/parameter	Equation	n ^a	r ^{2a}	F ^a	SD ^a	p Values ^a	Outliers
DNP-Gly	$\ln K = 0.1_{\pm 0.1} - 25_{\pm 1} \Delta \pi^* - 7.7_{\pm 0.5} \Delta \alpha$	5	0.9971	348.7	0.06	0.5; 0.002; 0.05	[C ₄ C ₁ im][SCN]-Na ₂ SO ₄
DNP-Ala	$\ln K = 0.3_{\pm 0.2} - 27_{\pm 2} \Delta \pi^* - 7_{\pm 1} \Delta \alpha$	5	0.9900	99.3	0.12	0.3; 0.006; 0.02	[C ₄ C ₁ im][SCN]-Na ₂ SO ₄
DNP-Val	$\ln K = 0.48_{\pm 0.07} - 39_{\pm 2} \Delta \pi^* - 7.1_{\pm 0.4} \Delta \alpha - 9_{\pm 2} \Delta \beta$	5	0.9996	937	0.04	0.1; 0.03; 0.03; 0.1	[C ₄ C ₁ im][SCN]-Na ₂ SO ₄
DNP-Leu	$\ln K = 0.33_{\pm 0.05} - 57_{\pm 1} \Delta \pi^* - 7.0_{\pm 0.3} \Delta \alpha - 24_{\pm 1} \Delta \beta$	5	0.9999	2717	0.03	0.1; 0.01; 0.02; 0.04	[C ₄ C ₁ im][SCN]-Na ₂ SO ₄
E	$E = 0.05_{\pm 0.01} - 7.6_{\pm 0.5} \Delta \pi^* - 5.1_{\pm 0.5} \Delta \beta$	5	0.9954	215.2	0.01	0.06; 0.004; 0.01	[C ₄ C ₁ im][SCN]-Na ₂ SO ₄
C	$C = 0.20_{\pm 0.09} - 23.4_{\pm 0.8} \Delta \pi^* - 7.2_{\pm 0.4} \Delta \alpha$	5	0.9981	518.2	0.05	0.2; 0.001; 0.003	[C ₄ C ₁ im][SCN]-Na ₂ SO ₄

^a n – number of experimental points; r – correlation coefficient; F – ratio of variance; SD – standard deviation; p - statistic p-value based on the null hypothesis

Table S29. Correlation of the experimental partition data given in Tables S23-S25 in the [C₄C₁im][SCN]-; [C₄C₁im][N(CN)₂]- [C₄C₁im][TOS]- and [C₄C₁im][CF₃SO₃]-based ABS with the experimental solvent properties for the same ABS given in Table 2.

Solute/parameter	Equation	n ^a	r ^{2a}	F ^a	SD ^a	p Values ^a	Outliers
DNP-Gly	$\ln K = -16_{\pm 3} - 20_{\pm 3} \Delta \pi^* - 8_{\pm 2} \Delta \alpha - 1.5_{\pm 0.2} E_{\text{HB}} - 2.1_{\pm 0.4} E_{\text{MF}} - 1.2_{\pm 0.2} V_{\text{dW}}$	11	0.9562	21.8	0.23	0.003; 0.0005; 0.01; 0.0008; 0.003; 0.003	[C ₄ C ₁ im][CF ₃ SO ₃]-K ₂ CO ₃
DNP-Ala	$\ln K = -15_{\pm 3} - 23_{\pm 3} \Delta \pi^* - 7_{\pm 2} \Delta \alpha - 1.5_{\pm 0.2} E_{\text{HB}} - 2.0_{\pm 0.4} E_{\text{MF}} - 1.2_{\pm 0.3} V_{\text{dW}}$	11	0.9478	18.2	0.26	0.006; 0.0006; 0.03; 0.002; 0.005; 0.006	[C ₄ C ₁ im][CF ₃ SO ₃]-K ₂ CO ₃
DNP-Val	$\ln K = -30_{\pm 8} - 57_{\pm 16} \Delta \pi^* - 10_{\pm 3} \Delta \alpha - 36_{\pm 17} \Delta \beta - 2.5_{\pm 0.5} E_{\text{HB}} - 3.7_{\pm 0.8} E_{\text{MF}} - 2.2_{\pm 0.5} V_{\text{dW}}$	11	0.9495	12.5	0.31	0.02; 0.02; 0.03; 0.1; 0.009; 0.01; 0.01	[C ₄ C ₁ im][CF ₃ SO ₃]-K ₂ CO ₃
DNP-Leu	$\ln K = -39_{\pm 5} - 79_{\pm 9} \Delta \pi^* - 12_{\pm 2} \Delta \alpha - 49_{\pm 11} \Delta \beta - 3.0_{\pm 0.3} E_{\text{HB}} - 4.5_{\pm 0.5} E_{\text{MF}} - 2.8_{\pm 0.3} V_{\text{dW}}$	10	0.9882	41.7	0.19	0.003; 0.004; 0.008; 0.02; 0.002; 0.003; 0.003	[C ₄ C ₁ im][CF ₃ SO ₃]-K ₂ CO ₃ ; [C ₄ C ₁ im][TOS]-K ₂ CO ₃
E	$E = -4.0_{\pm 0.9} - 14_{\pm 2} \Delta \pi^* - 14_{\pm 2} \Delta \beta - 0.30_{\pm 0.06} E_{\text{HB}} - 0.4_{\pm 0.1} E_{\text{MF}} - 0.28_{\pm 0.06} V_{\text{dW}}$	11	0.9170	11.0	0.04	0.005; 0.001; 0.002; 0.004; 0.007; 0.007	[C ₄ C ₁ im][SCN]-K ₂ CO ₃ ;
C	$C = -16_{\pm 2} - 20_{\pm 2} \Delta \pi^* - 8_{\pm 2} \Delta \alpha - 1.5_{\pm 0.2} E_{\text{HB}} - 2.1_{\pm 0.3} E_{\text{MF}} - 1.2_{\pm 0.2} V_{\text{dW}}$	11	0.9726	35.5	0.18	0.0009; 0.0002; 0.006; 0.0003; 0.008; 0.01	[C ₄ C ₁ im][CF ₃ SO ₃]-K ₂ CO ₃

^a n – number of experimental points; r – correlation coefficient; F – ratio of variance; SD – standard deviation; p - statistic p-value based on the null hypothesis

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