

Supplementary Information

Development of back-extraction and recyclability routes for ionic-liquid-based aqueous two-phase systems

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Table ESI 1 - Experimental binodal curve weight fraction data for the system composed of IL (1) + Na₂CO₃ (2) + H₂O (3) at 25 °C.

[C ₄ C ₁ im]Cl		<i>M_w</i> = 174.67	
100 <i>w</i> ₁	100 <i>w</i> ₂	100 <i>w</i> ₁	100 <i>w</i> ₂
41.5686	2.7448	17.6325	11.1366
33.8129	3.4842	17.1680	11.4377
31.6037	4.1522	16.2135	11.8527
29.7255	4.7229	15.7151	12.2075
27.9213	5.2768	15.2083	12.6092
26.4494	5.7408	14.6020	13.0224
21.6418	8.5535	13.9959	13.4519
21.4602	8.7218	13.5542	13.8842
21.2026	8.8995	12.9253	14.3009
21.0781	9.0387	12.1602	14.8002
20.3252	9.2895	11.3515	15.6770
20.0526	9.4711	10.6257	16.347
19.6790	9.6508	9.6719	17.0539
19.2390	9.8723	8.9252	17.7982
18.9163	10.1031		
18.6455	10.3356		
18.2303	10.5977		
17.8413	10.8986		

Table ESI 2 - Experimental binodal curve weight fraction data for the system IL (1) + Na₂CO₃ (2) + H₂O (3) at 25 °C.

[C ₄ C ₁ im]Br		<i>M_w</i> = 219.12	
100 <i>w</i> ₁	100 <i>w</i> ₂	100 <i>w</i> ₁	100 <i>w</i> ₂
54.2209	1.0403	25.1323	7.5559
43.5259	1.9326	25.0794	7.6346
40.7441	2.7053	24.7936	7.7474
38.9069	3.0232	24.4843	7.8606
36.7123	3.5645	24.3996	7.9359
34.6201	4.1330	24.0745	8.0517
32.7974	4.6233	23.7818	8.1745
30.6967	5.3405	23.7366	7.9943
29.6785	5.9084	23.4933	8.2982
28.9369	6.1090	23.4091	8.3880
28.8525	5.9602	23.1185	8.5104
28.6895	6.1857	22.7874	8.6320
28.5344	6.2507	22.6845	8.7219
28.2709	6.3293	22.3022	8.8708
28.1514	6.3908	21.9961	9.0123
27.9954	6.4596	21.8626	9.1158
27.9532	6.5134	21.4521	9.2726
27.7712	6.5841	21.0757	9.4302
27.4581	6.6757	20.9641	9.5530
27.2692	6.7493	20.4825	9.7292
27.0218	6.8274	20.3238	9.8454
26.7601	6.9120	19.8410	10.0186
26.6194	6.7931	19.6278	10.1505
26.5169	6.9988	19.3013	10.0365
26.2721	7.0850	19.2336	10.3253
26.0593	7.1737	19.0984	10.4598
25.8182	7.2699	18.5577	10.6761
25.7645	7.3357	18.3669	10.8284
25.4555	7.4433	17.8136	11.0498

Table ESI 3 - Experimental binodal curve weight fraction data for the system IL (1) + Na₂CO₃ (2) + H₂O (3) at 25 °C.

[C ₄ C ₁ im][CF ₃ SO ₃]		<i>M_w</i> = 288.29	
100 <i>w</i> ₁	100 <i>w</i> ₂	100 <i>w</i> ₁	100 <i>w</i> ₂
58.9369	0.5251	12.3581	4.9527
46.6759	0.9357	12.1267	5.0106
41.1924	1.3199	11.8316	5.0380
36.7950	1.5719	11.5288	5.1886
33.4487	1.8126	11.2373	5.4466
30.3788	1.9947	10.9951	5.5822
28.2656	2.1829	10.7535	5.7030
26.4296	2.3234	10.5791	5.7388
24.7731	2.4562	10.3457	5.8492
23.4476	2.6361	10.1093	5.9773
22.3581	2.7502	9.8735	6.0971
21.6889	2.8767	9.6516	6.2015
20.9211	2.9976	9.3961	6.3742
20.0825	3.1342	9.1583	6.4113
19.1542	3.2638	8.8820	6.6308
18.3742	3.3627	8.4951	6.8046
17.8552	3.5112	8.2052	7.0313
17.4708	3.5511	7.8085	7.2156
17.0490	3.6614	7.4196	7.4844
16.6749	3.7400	7.0476	7.6781
16.2784	3.8453	6.5897	8.0802
15.9471	3.9148	6.1945	8.4482
15.5332	4.0633	5.9031	8.7237
15.1625	4.1672	5.3406	9.3439
14.7753	4.2657	4.9597	9.7789
14.4170	4.3257	4.6125	10.1868
14.0847	4.3991	4.2332	10.5345
13.8757	4.5048	4.0543	10.7645
13.5659	4.6004	3.7890	11.0993
13.3061	4.6845	3.2141	12.1690
12.8665	4.8088	2.3114	14.1020
12.6119	4.8898		

Table ESI 4 - Experimental binodal curve weight fraction data for the system IL (1) + Na₂CO₃ (2) + H₂O (3) at 25 °C.

[C ₄ C ₁ im][Tos]		<i>M_w</i> = 310.41	
100 <i>w</i> ₁	100 <i>w</i> ₂	100 <i>w</i> ₁	100 <i>w</i> ₂
57.3652	0.5025	17.7665	7.9328
52.8729	1.0083	17.1123	8.1812
50.2719	1.4740	16.5756	8.3350
46.8319	1.8548	16.1571	8.4741
43.8677	2.1973	15.8679	8.5062
41.2055	2.5384	15.5303	8.6788
39.5563	2.8726	15.2691	8.7066
37.9644	3.1765	14.8557	8.8412
36.5667	3.4404	14.5043	8.9444
35.2517	3.7086	14.0640	9.1129
34.0685	3.9617	13.7777	9.2001
32.8756	4.2070	13.4321	9.2895
31.7533	4.4290	13.1092	9.3899
30.6989	4.6457	12.8118	9.5103
29.6873	4.8315	12.5396	9.5941
28.7210	5.0308	12.2040	9.7272
27.8568	5.2428	11.9233	9.8289
27.0347	5.4084	11.6630	9.9175
25.8563	5.7380	11.3803	10.0240
24.8234	6.0458	11.1197	10.1295
24.0312	6.2520	10.9098	10.1967
23.5112	6.3953	10.7066	10.2677
22.8714	6.4770	10.4937	10.3212
21.9371	6.7994	10.1962	10.4561
21.3760	6.8994	9.9446	10.5771
20.8126	6.9828	9.7530	10.6417
19.8566	7.3520	9.5732	10.7011
19.1461	7.6070	9.3527	10.8048
18.7196	7.6718	9.1326	10.9120
18.1262	7.8599	8.9117	11.0122

Table ESI 5 - Experimental binodal curve weight fraction data for the system IL (1) + Na₂CO₃ (2) + H₂O (3) at 25 °C.

[C ₄ C ₁ im][N(CN) ₂]		<i>M_w</i> = 205.26	
100 <i>w</i> ₁	100 <i>w</i> ₂	100 <i>w</i> ₁	100 <i>w</i> ₂
58.1355	0.5314	10.9585	8.4131
46.3029	1.0808	10.3874	8.6958
43.0437	1.5243	9.9456	8.9195
39.3171	1.9075	8.6763	9.5047
36.8240	2.2299	8.2716	9.6982
35.2820	2.6118	7.0401	10.9784
33.4039	2.9138	6.4002	11.3677
31.5455	3.1914	6.0076	11.7067
30.4086	3.5053	5.7014	11.9091
29.0804	3.7255	5.3682	12.1738
28.0708	3.9743	5.0286	12.4841
27.1252	4.2167	4.6106	12.9570
25.9573	4.3788	4.2774	13.3195
25.2356	4.5768	4.0067	13.6105
24.1137	4.9603	3.7075	13.9382
11.6377	8.3191	3.2060	14.6330

Table ESI 6 - Experimental binodal curve weight fraction data for the system IL (1) + Na₂CO₃ (2) + H₂O (3) at 25 °C.

[C ₄ C ₁ im][CH ₃ SO ₄]		<i>M_w</i> = 250.31	
100 <i>w</i> ₁	100 <i>w</i> ₂	100 <i>w</i> ₁	100 <i>w</i> ₂
58.3891	0.6235	21.1986	9.1483
51.8037	1.1862	20.0978	9.5335
47.2774	1.6513	20.0140	9.5075
44.5902	2.1058	19.2806	9.9064
42.2038	2.5064	18.7416	10.2303
39.4376	2.7865	17.4138	10.7167
36.7473	3.5306	16.5185	11.1740
34.2947	4.2091	16.0771	11.3784
32.1816	4.7978	14.6286	12.4267
30.2834	5.2988	13.4974	13.0855
27.1611	6.4613	12.2575	13.7570
25.3860	7.3928	10.8772	14.4752
24.6929	7.6518	9.3208	15.3280
24.0892	7.6839	8.6768	15.9816
23.8875	7.9413	6.9578	16.9676
23.0976	8.2541	6.0643	17.8269
22.7187	8.5059	5.2666	18.6825
21.7896	8.8399		

Table ESI 7 - Experimental binodal curve weight fraction data for the system IL (1) + Na₂CO₃ (2) + H₂O (3) at 25 °C.

[C₄C₁im][C₂H₅SO₄] <i>M_w</i> = 264.34	
100 <i>w</i>₁	100 <i>w</i>₂
56.0389	1.3267
46.4982	1.8268
42.7100	2.2663
42.3962	2.3461
40.4017	2.7351
39.8626	2.8412
38.2985	3.1658
37.5963	3.2923
36.3380	3.6025
35.6026	3.6550
34.6297	3.9434
33.7541	4.0097
33.0694	4.2463
31.6452	4.5088
31.3679	4.7005
29.4695	5.2065
29.1288	5.3571
27.4429	5.8683
25.0642	6.7764
23.0263	7.5406
20.9146	8.3904
18.6279	9.4119
16.6004	10.3254
15.0900	10.9978

Table ESI 8 - Experimental binodal curve weight fraction data for the system IL (1) + Na₂CO₃ (2) + H₂O (3) at 25 °C.

[C₄C₁im][CH₃SO₃] <i>M_w</i> = 234.32	
100 <i>w</i>₁	100 <i>w</i>₂
59.8275	0.8609
51.1588	1.5589
46.4396	2.1021
41.1512	3.0933
38.9643	3.5091
35.2406	4.1796
29.0885	6.5779
28.6078	6.7650
28.0315	6.9753
27.4624	7.2021
27.2356	7.3840
26.6466	7.6229
25.6137	7.9427
24.8803	8.2496
24.4730	8.5130
24.0387	8.7897
23.5263	9.0822
22.9153	9.3990
21.8185	9.8402
21.2968	10.1957
20.0177	10.7019
19.2782	11.1303
18.4369	11.6393
17.6831	12.1221
16.7535	12.6871
15.6861	13.3252
14.4370	14.0348
13.1331	14.8093
11.6447	15.6779
10.9920	16.4220
9.6110	17.4998

Table ESI 9 - Experimental binodal curve weight fraction data for the system IL (1) + Na₂CO₃ (2) + H₂O (3) at 25 °C.

[C₄C₁im][DMP]		<i>M_w</i> = 264.26	
100 <i>w</i>₁		100 <i>w</i>₂	
51.0129		2.1654	
39.0398		3.1601	
30.4151		5.7636	
26.1655		8.1431	
25.1673		8.6170	
24.5557		8.9799	
23.7187		9.3166	
22.8384		9.7203	
21.7289		10.142	
20.7462		10.5989	
20.3837		10.9228	
19.7759		11.2644	
18.9063		11.7658	
17.9718		12.348	
16.3242		13.0001	
15.8280		13.3776	
15.1060		13.8780	
14.8047		14.2688	
14.1880		14.6226	
13.7644		14.9138	
13.2904		15.2268	
12.8028		15.8362	
12.4509		16.8557	

Table ESI 10 - Experimental binodal curve weight fraction data for the system IL (1) + Na₂CO₃ (2) + H₂O (3) at 25 °C.

[C ₄ C ₁ im][SCN]		<i>M_w</i> = 194.28	
100 <i>w</i> ₁	100 <i>w</i> ₂	100 <i>w</i> ₁	100 <i>w</i> ₂
57.9075	0.6895	13.2912	6.5732
45.1559	1.2152	12.9852	6.6164
40.7561	1.731	12.5707	6.7694
37.0598	2.1233	12.1637	6.9182
34.6914	2.456	11.9797	6.9772
32.6315	2.7802	11.6512	7.0721
30.8838	3.0285	11.4758	7.1383
29.2392	3.2959	11.3162	7.1911
28.1632	3.5803	11.1235	7.2818
26.8227	3.7867	10.8863	7.2945
25.6083	3.9339	10.5895	7.4079
24.4904	4.0842	10.3153	7.5033
23.8002	4.2951	10.0514	7.5996
22.8518	4.434	9.8008	7.7173
22.0041	4.5935	9.4608	7.8675
21.4721	4.7324	9.218	7.9593
20.6338	4.8335	9.0053	8.0322
20.0719	5.0181	8.7019	8.1469
19.3236	5.1156	8.4585	8.2771
18.8838	5.2572	8.2192	8.4224
17.0508	5.6959	7.9605	8.4982
16.672	5.8164	7.7137	8.677
16.1487	5.8649	7.4217	8.7826
15.8101	5.9925	7.1263	8.9695
15.3753	6.0378	6.7841	9.0885
15.0651	6.1277	3.4462	10.6489
14.7718	6.2273	2.7371	12.3003
14.3945	6.2659	2.4921	13.2349
14.1381	6.3525	2.0324	15.0699
13.8845	6.4362	1.4917	16.4997
13.6425	6.5249	1.0236	19.6763

The experimental binodal curves were fitted by least-squares regression according to the following equation¹:

$$[\text{IL}] = A \exp[(B \times [\text{Salt}]^{0.5}) - (C \times [\text{Salt}]^3)] \quad (1)$$

where [IL] and [Salt] are the ionic liquid and the inorganic salt weight fraction percentages, respectively, and *A*, *B* and *C* are fitted constants obtained by the regression of the experimental data. The regression parameter values and corresponding standard deviations are provided in Table ESI 11.

Table ESI 11 - Parameters *A*, *B* and *C* of eq. 1 (and respective standard deviations, σ , and correlation coefficients, R^2) for the [C₄C₁im]-based ILs + Na₂CO₃ + H₂O systems at 25 °C.

IL + Na ₂ CO ₃ + H ₂ O	<i>A</i> ± σ	<i>B</i> ± σ	10 ⁵ (<i>C</i> ± σ)	<i>R</i> ²
[C ₄ C ₁ im]Cl	67.40 ± 1.06	0.372 ± 0.007	8.1±0.4	0.999
[C ₄ C ₁ im]Br	78.00 ± 0.62	0.39 ± 0.004	10±0.3	0.999
[C ₄ C ₁ im][CF ₃ SO ₃]	126.00 ± 2.57	1026 ± 0.017	40±20	0.996
[C ₄ C ₁ im][TOS]	80.05 ± 0.83	0.413 ± 0.007	70±1.7	0.998
[C ₄ C ₁ im][N(CN) ₂]	85.99 ± 1.71	0.555 ± 0.013	50±3.6	0.996
[C ₄ C ₁ im][CH ₃ SO ₄]	80.23 ± 0.48	0.408 ± 0.003	10±0.4	0.999
[C ₄ C ₁ im][CH ₃ SO ₃]	86.39 ± 0.80	0.417 ± 0.050	8.1±0.6	0.999
[C ₄ C ₁ im][DMP]	72.49 ± 2.51	0.346 ± 0.014	9.4±0.9	0.995
[C ₄ C ₁ im][C ₂ H ₅ SO ₄]	97.00 ± 3.06	0.521 ± 0.019	6.6±4.3	0.997
[C ₄ C ₁ im][SCN]	97.71 ± 1.72	0.653 ± 0.012	100±5.0	0.997

The correlation coefficients obtained for all systems are close to unity indicating that the fitting described by eq. (1) can be used to predict data in a given region of the phase diagram where no experimental results are available.

For the determination of each tie-line (TL), a ternary mixture composed of Na₂CO₃ + water + ionic liquid at the biphasic region was prepared, vigorously stirred, and left to equilibrate for at least 12 h at 25 °C, aiming for a complete separation of the coexisting aqueous phases. The phases were further separated and individually weighed. The ternary systems compositions were determined by weight quantification of all components within ± 10⁻⁴ g.

Each TL was determined through the relationship between the weight of the top phase and the overall weight by the lever-arm rule¹, and for which the following system of four equations (eqs. 2 to 5) and four unknown values ($[\text{IL}]_{\text{T}}$, $[\text{IL}]_{\text{B}}$, $[\text{Salt}]_{\text{T}}$ and $[\text{Salt}]_{\text{B}}$) was solved:

$$[\text{IL}]_{\text{T}} = A \exp[(B \times [\text{Salt}]_{\text{T}}^{0.5}) - (C \times [\text{Salt}]_{\text{T}}^3)] \quad (2)$$

$$[\text{IL}]_{\text{B}} = A \exp[(B \times [\text{Salt}]_{\text{B}}^{0.5}) - (C \times [\text{Salt}]_{\text{B}}^3)] \quad (3)$$

$$[\text{IL}]_{\text{T}} = \frac{[\text{IL}]_{\text{M}}}{\alpha} - \frac{1-\alpha}{\alpha} \times [\text{IL}]_{\text{B}} \quad (4)$$

$$[\text{Salt}]_{\text{T}} = \frac{[\text{Salt}]_{\text{M}}}{\alpha} - \frac{1-\alpha}{\alpha} \times [\text{Salt}]_{\text{B}} \quad (5)$$

where “T”, “B”, and “M” designate the top phase, the bottom phase and the mixture, respectively; $[\text{Salt}]$ and $[\text{IL}]$ represent the weight fraction of inorganic salt and ionic liquid, and α is the ratio between the mass of the top phase and the total mass of the mixture. The system solution results in the weight fraction percentage of the ionic liquid and inorganic salt in the top and bottom phases, and thus represents the TLs of each system.

The tie-line length (TLL) was determined using equation 6,

$$\text{TLL} = \sqrt{([\text{Salt}]_{\text{T}} - [\text{Salt}]_{\text{B}})^2 + ([\text{IL}]_{\text{T}} - [\text{IL}]_{\text{B}})^2} \quad (6)$$

and corresponds to the distance between the point in the binodal curve at the bottom phase composition to that at the top phase.

The calculated TLs, that is, the compositions of the coexisting phases, along with their respective length, are reported in Table ESI 12.

Table ESI 12 – Equilibrium phase compositions for IL + Na₂CO₃ + water ATPS at 25 °C and respective values of TLL.

IL + Na ₂ CO ₃ + H ₂ O	Weight fraction composition / (wt%)							TLL
	[IL] _{IL}	[Salt] _{IL}	[IL] _M	[Salt] _M	[IL] _{salt}	[Salt] _{salt}	α	
[C ₄ C ₁ im]Cl	28.98	5.01	20.23	11.93	2.44	25.98	0.67	33.82
	33.80	3.40	21.12	12.77	2.03	26.88	0.60	39.50
[C ₄ C ₁ im]Br	27.03	6.92	20.42	10.59	11.48	15.56	0.57	17.79
	36.71	3.68	25.20	9.88	5.79	20.33	0.63	35.12
	39.60	2.99	25.69	10.38	4.68	21.55	0.60	39.54
	42.47	2.41	25.90	11.31	3.23	23.47	0.58	44.53
	45.66	1.88	29.98	10.07	2.68	24.35	0.64	48.49
	47.35	1.63	30.65	10.43	2.08	25.47	0.63	51.16
	52.36	1.04	35.06	10.19	1.05	28.16	0.66	58.04
	54.66	0.83	34.89	11.10	0.89	28.76	0.63	60.59
[C ₄ C ₁ im][CF ₃ SO ₃]	34.45	1.61	26.93	3.37	4.98	8.51	0.74	30.27
	37.37	1.42	27.11	4.05	3.15	10.19	0.70	35.32
	83.61	0.17	20.08	9.89	1.42	12.75	0.23	83.14
	84.34	0.16	29.90	10.05	0.53	15.38	0.35	85.18
[C ₄ C ₁ im][TOS]	43.88	2.08	30.06	6.12	2.18	14.29	0.67	43.46
	46.23	1.74	30.16	7.03	0.54	16.77	0.65	48.09
[C ₄ C ₁ im][N(CN) ₂]	43.01	1.55	22.07	7.04	7.07	10.97	0.47	43.09
	52.78	0.77	19.97	9.95	1.83	15.02	0.36	52.90
	55.65	0.61	24.36	10.41	0.47	17.89	0.43	57.83
	58.07	0.50	30.42	9.99	0.10	20.39	0.52	61.28
	58.41	0.48	30.02	10.14	0.11	20.32	0.51	61.59
	61.60	0.36	34.79	9.96	0.02	22.41	0.56	65.40
	61.99	0.35	34.90	10.05	0.02	22.55	0.56	65.82
[C ₄ C ₁ im][CH ₃ SO ₄]	29.66	5.74	20.50	10.71	9.63	16.61	0.54	22.79
	36.98	3.57	27.82	8.56	4.83	21.09	0.72	36.61
	43.45	2.25	30.10	9.03	3.82	22.35	0.66	44.43
	45.64	1.91	29.88	9.94	2.94	23.65	0.63	47.91
	54.43	0.91	34.81	12.04	0.35	31.60	0.64	62.19
[C ₄ C ₁ im][C ₂ H ₅ SO ₄]	32.22	4.42	21.13	10.06	8.83	16.32	0.53	26.24
	38.23	3.17	26.69	9.30	4.88	20.88	0.65	37.76
	46.69	1.96	29.95	10.01	3.76	22.61	0.61	47.64
	47.37	1.89	30.08	10.13	3.70	22.72	0.60	48.39
[C ₄ C ₁ im][CH ₃ SO ₃]	39.28	3.55	29.96	8.98	3.33	24.51	0.74	41.61
[C ₄ C ₁ im][DMP]	29.45	6.41	21.96	12.09	1.70	27.46	0.73	34.83
	34.40	4.53	24.02	14.03	0.12	35.90	0.70	47.64
[C ₄ C ₁ im][SCN]	41.64	1.69	20.53	6.06	6.97	8.86	0.39	35.40
	47.35	1.22	20.44	7.11	3.09	10.90	0.39	45.31

An example of the fitted data and the TLs obtained for this type of systems is illustrated in Fig. ESI 1.

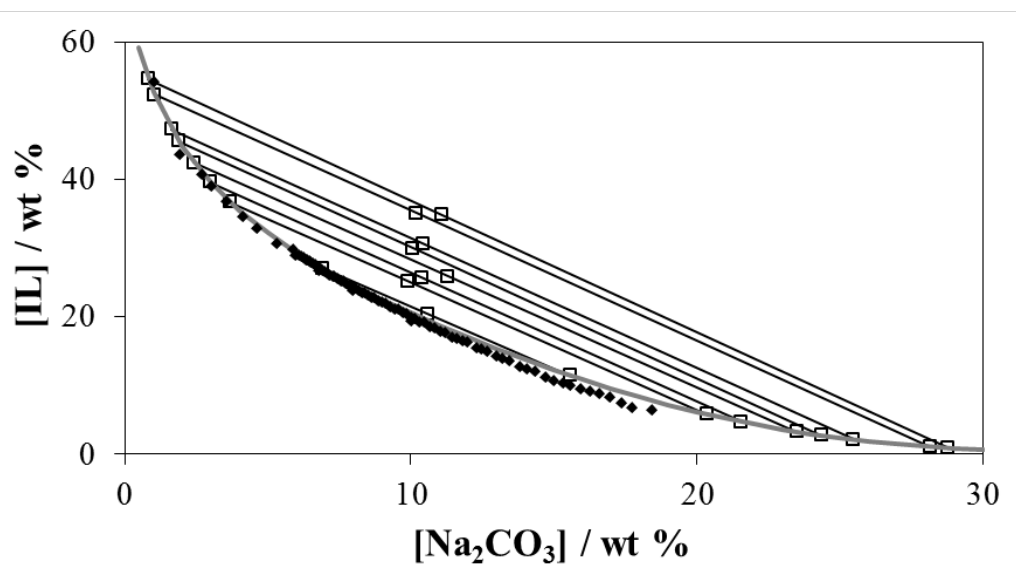


Fig. ESI 1. Ternary phase diagram for the ATPS composed of [C₄C₁im]Br + Na₂CO₃ + water at 25 °C: ♦, experimental solubility data; □, TL data, —, fitting by eq. 1.

Table ESI 13 - Experimental weight fraction composition and extraction efficiencies of gallic acid and pH of the coexisting phases of ATPS composed of ILs + Na₂CO₃ at 25 °C.

ionic liquid		% $EE_{\text{Salt}} \pm \sigma^a$	Weight fraction composition / (wt%)		pH _{IL}	pH _{salt}
			IL	Salt		
[C ₄ C ₁ im][N(CN) ₂]	20%	85.81 ± 1.04	20.19	10.38	11.39	11.43
	25%	87.97 ± 1.34	24.36	10.41	11.02	11.10
	30%	85.37 ± 2.85	30.02	10.14	11.39	11.47
	35%	80.26 ± 0.90	34.90	10.05	11.64	11.01
[C ₄ C ₁ im]Br	20%	48.40 ± 0.39	20.42	10.59	11.41	11.39
	25%	45.68 ± 0.34	25.20	9.88	10.99	10.86
	30%	41.65 ± 1.58	29.98	10.07	11.28	11.38
	35%	38.92 ± 3.09	35.06	10.19	10.99	11.07
[C ₄ C ₁ im][CF ₃ SO ₃]	20%	98.88 ± 0.03	20.08	9.89	11.26	11.28
	30%	95.16 ± 1.74	29.99	10.05	10.59	10.87
[C ₄ C ₁ im][C ₂ H ₅ SO ₄]	20%	45.79 ± 0.49	19.76	10.00	10.96	11.06
	30%	42.56 ± 2.36	29.95	10.01	9.93	9.92
[C ₄ C ₁ im][CH ₃ SO ₄]	20%	53.73 ± 0.12	20.50	10.63	11.19	11.31
	30%	45.94 ± 1.06	29.99	9.98	11.08	11.00

^a standard deviation

Table ESI 14 - Experimental weight fraction composition and extraction efficiencies of gallic acid and pH of the coexisting phases of ATPS composed of ILs + Na₂SO₄ at 25 °C.

IL + Na ₂ SO ₄ + water system	$EE\%_{GA} \pm \sigma^a$	Weight fraction composition / (wt%)		pH _{IL}	pH _{salt}
		IL	Na ₂ SO ₄		
[C ₄ C ₁ im][CF ₃ SO ₃]	88.90 ± 0.60	24.95	14.97	3.12	3.04
	89.93 ± 1.14	25.00	19.96	3.15	3.08
[C ₄ C ₁ im][CH ₃ SO ₄]	97.05 ± 0.06	24.69	14.52	1.88	1.57
[C ₄ C ₁ im][C ₂ H ₅ SO ₄]	98.53 ± 0.04	25.71	15.36	2.29	1.29
[C ₄ C ₁ im][N(CN) ₂]	93.37 ± 0.74	25.00	15.00	8.54	8.07
	94.56 ± 0.49	25.09	19.20	8.49	8.04
[C ₄ C ₁ im]Br	96.84 ± 0.15	24.96	15.22	5.43	5.22

^a standard deviation

Table ESI 15 - Experimental weight fraction composition, extraction efficiencies of gallic acid and pH values in ATPS corresponding to the two sequential cycles composed of 25 wt% of IL + 20 wt% of Na₂SO₄ and 20 wt% of IL + 10 wt% of Na₂CO₃ (at 25 °C).

ionic liquid	extraction	% $EE_{\text{Salt}} \pm \sigma^a$	Weight fraction composition / (wt%)		pH _{IL}	pH _{salt}
			IL	Salt		
[C ₄ C ₁ im][N(CN) ₂]	1 st to IL -rich phase	94.56 ± 0.47	25.09	19.20	7.40	7.69
	1 st to Na ₂ CO ₃ -rich phase (back extraction)	70.58 ± 0.74	19.94	9.96	11.20	11.34
	2 nd to IL-rich phase	50.06 ± 3.69	24.94	19.05	8.86	9.89
	2 nd to Na ₂ CO ₃ -rich phase (back extraction)	79.39 ± 4.20	19.98	10.01	11.34	11.75
[C ₄ C ₁ im][N(CN) ₂] adjusted pH	1 st to IL -rich phase	93.12 ± 0.17	24.98	19.49	7.54	7.49
	1 st to Na ₂ CO ₃ -rich phase (back extraction)	72.43 ± 1.22	19.70	9.85	11.72	11.74
	2 nd to IL-rich phase	96.70 ± 3.30	24.55	19.14	6.42	6.28
	2 nd to Na ₂ CO ₃ -rich phase (back extraction)	78.71 ± 1.99	20.05	9.91	11.13	11.33
[C ₄ C ₁ im][CF ₃ SO ₃]	1 st to IL -rich phase	89.93 ± 1.14	25.00	19.96	4.60	4.55
	1 st to Na ₂ CO ₃ -rich phase (back extraction)	98.67 ± 2.50	20.02	9.96	11.13	11.49
	2 nd to IL-rich phase	35.65 ± 4.95	24.95	19.58	8.55	8.45
	2 nd to Na ₂ CO ₃ -rich phase (back extraction)	91.05 ± 2.050	19.89	9.95	11.35	11.45
[C ₄ C ₁ im][CF ₃ SO ₃] adjusted pH	1 st to IL -rich phase	93.33 ± 3.67	25.13	19.95	3.97	3.34
	1 st to Na ₂ CO ₃ -rich phase (back extraction)	98.29 ± 1.71	20.00	9.92	11.12	11.05
	2 nd to IL-rich phase	95.49 ± 2.60	24.88	20.39	2.88	2.95
	2 nd to Na ₂ CO ₃ -rich phase (back extraction)	99.23 ± 0.80	19.61	9.95	11.42	11.34

Table ESI 16 - Experimental weight fraction composition and extraction efficiencies of syringic and vanillic acid in sequential ATPS composed of 25 wt% of IL + 20 wt% Na₂SO₄) and 20 wt% of IL + 10 wt% Na₂CO₃ at 25 °C.

Ionic liquid	Antioxidant	Extraction	% $EE_{\text{Salt} \pm \sigma^a}$	Weight fraction composition / (wt%)	
				IL	Salt
[C ₄ C ₁ im][CF ₃ SO ₃]	Syringic acid	1 st to IL -rich phase	97.82 ± 0.25	25.00	20.15
		1 st to Na ₂ CO ₃ -rich phase (back extraction)	97.68 ± 0.28	20.04	9.72
[C ₄ C ₁ im][CF ₃ SO ₃]	Vanillic acid	1 st to IL -rich phase	97.29 ± 0.26	24.99	20.03
		1 st to Na ₂ CO ₃ -rich phase (back extraction)	97.40 ± 0.25	19.74	9.80

The amount of IL lost in each cycle was determined based on their recovery efficiencies and calculated according to,

$$\%R_{IL} = \frac{[IL]_{IL} \times w_{IL}}{[IL]_{IL} \times w_{IL} + [IL]_{salt} \times w_{salt}} \times 100 \quad (7)$$

where ‘‘IL’’ and ‘‘Salt’’ symbolize, respectively, the IL- and salt- rich phases, [Salt] and [IL] are the weight fraction percentage of inorganic salt and ionic liquid and w is the weight of each phase.

Table ESI 17 – Sodium content in the coexisting phases in sequential ATPS composed of 25 wt% of IL + 20 wt% Na₂SO₄ and 20 wt% of IL + 10 wt% Na₂CO₃ at 25 °C.

ATPS	[Sodium] by TL / (wt%)	[Sodium] by ICPOES / (wt%)	Relative deviation / (wt%)
[C ₄ C ₁ im][CF ₃ SO ₃] + Na ₂ CO ₃ top phase	12.88	13.86	0.08
[C ₄ C ₁ im][CF ₃ SO ₃] + Na ₂ CO ₃ bottom phase	0.17	0.17	-0.02
[C ₄ C ₁ im][CF ₃ SO ₃] + Na ₂ SO ₄ bottom phase	27.47	26.70	-0.03
[C ₄ C ₁ im][CF ₃ SO ₃] + Na ₂ SO ₄ top phase	0.67	0.68	0.01
[C ₄ C ₁ im][N(CN) ₂] + Na ₂ CO ₃ bottom phase	15.02	13.95	-0.07
[C ₄ C ₁ im][N(CN) ₂] + Na ₂ CO ₃ top phase	0.78	0.91	0.17
[C ₄ C ₁ im][N(CN) ₂] + Na ₂ SO ₄ bottom phase	33.96	33.43	-0.02
[C ₄ C ₁ im][N(CN) ₂] + Na ₂ SO ₄ top phase	1.16	1.23	0.06

Table ESI 18 – IL content in the coexisting phases in sequential ATPS composed of 25 wt% of IL + 20 wt% Na₂SO₄ and 20 wt% of IL + 10 wt% Na₂CO₃ at 25°C.

ATPS	[IL] by TL / (wt%)	[IL] by UV-Vis / (wt%)	Relative deviation / (wt%)
[C ₄ C ₁ im][CF ₃ SO ₃] + Na ₂ CO ₃ top phase	1.36	1.44	0.06
[C ₄ C ₁ im][CF ₃ SO ₃] + Na ₂ CO ₃ bottom phase	83.09	81.44	-0.02
[C ₄ C ₁ im][CF ₃ SO ₃] + Na ₂ SO ₄ bottom phase	0.79	0.76	-0.04
[C ₄ C ₁ im][CF ₃ SO ₃] + Na ₂ SO ₄ top phase	83.17	89.35	0.07
[C ₄ C ₁ im][N(CN) ₂] + Na ₂ CO ₃ bottom phase	1.83	1.77	-0.04
[C ₄ C ₁ im][N(CN) ₂] + Na ₂ CO ₃ top phase	52.71	56.24	0.07
[C ₄ C ₁ im][N(CN) ₂] + Na ₂ SO ₄ bottom phase	0.85	0.79	-0.06
[C ₄ C ₁ im][N(CN) ₂] + Na ₂ SO ₄ top phase	54.94	57.73	0.05

References:

1. J. C. Merchuk, B. A. Andrews and J. A. Asenjo, *J. Chromatogr. B*, 1998, **711**, 1-2.