Supplementary Material

Expanding chemical space of ionic liquid based aqueous biphasic systems with thiocyanate

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Tables

Mixture points composition and partition data

Table S1. Partition coefficient of MV and BV on top and bottom phases of all ABS under study.

ABS	MV				BV			
	Kavg	**Kstdev**	**logKavg**	**logKstdev**	**Kavg**	**Kstdev**	**logKavg**	**logKstdev**
9.6% NaSCN 17.6% $[C_2C1im]Cl$] 15.0% $(NH_4)_2SO_4$ (1:1) Moles	3.663	0.033	0.564	0.004	32.827	1.423	1.516	0.019
14.2% NaSCN 12.7% $[C_2C1im]Cl$ 14.9% $(NH_4)_2SO_4$ (1:2) Moles	3.303	0.411	0.517	0.054	9.862	0.890	0.993	0.039
10.3% NaSCN 19.4% $[C_4C1im]Cl$ 8.0% $(NH_4)_2SO_4$ (1:1) Moles	1.783	0.075	0.251	0.018	14.060	1.368	1.146	0.043
15.8% NaSCN 15.1% $[C_4C1im]Cl$ 8.0% $(NH_4)_2SO_4$ (1:2) Moles	2.481	0.138	0.394	0.025	40.796	17.940	1.564	0.205
5.6% NaSCN 12.2% $[N_{2222}]Cl$ 15.9% $(NH_4)_2SO_4$ (1:1) Moles	2.226	0.066	0.347	0.013	37.197	2.730	1.570	0.032
9.1% NaSCN 9.2% $[N_{2222}]Cl$ 15.9% $(NH_4)_2SO_4$ (1:2) Moles	2.946	1.327	0.443	0.181	175.220	11.528	2.243	0.029
7.9% NaSCN 21.7% $[N_{3333}]Cl$ 6.0% $(NH_4)_2SO_4$ (1:1) Moles	0.818	0.013	-0.087	0.007	23.080	2.472	1.362	0.047
12.4% NaSCN 16.9% $[N_{3333}]Cl$ 6.3% $(NH_4)_2SO_4$ (1:2) Moles	2.311	0.035	0.364	0.006	33.943	1.765	1.530	0.023

Table S2. Partition coefficient of TEMPO and WS-TEMPO on top and bottom phases of all ABS under study.

ABS	TEMPO				WS-TEMPO			
	Kavg	**Kstdev**	**logKavg**	**logKstdev**	**Kavg**	**Kstdev**	**logKavg**	**logKstdev**
9.6% NaSCN 17.6% $[C_2C1im]Cl$] 15.0% $(NH_4)_2SO_4$ (1:1) Moles	4.816	1.049	0.677	0.095	2.954	0.086	0.470	0.013
14.2% NaSCN 12.7% $[C_2C1im]Cl$ 14.9% $(NH_4)_2SO_4$ (1:2) Moles	3.334	0.341	0.522	0.045	2.548	0.451	0.403	0.077
10.3% NaSCN 19.4% $[C_4C1im]Cl$ 8.0% $(NH_4)_2SO_4$ (1:1) Moles	2.827	0.178	0.450	0.027	2.179	0.051	0.338	0.010
15.8% NaSCN 15.1% $[C_4C1im]Cl$ 8.0% $(NH_4)_2SO_4$ (1:2) Moles	4.079	0.250	0.610	0.027	3.811	0.317	0.579	0.036
5.6% NaSCN 12.2% $[N_{2222}]Cl$ 15.9% $(NH_4)_2SO_4$ (1:1) Moles	4.798	0.046	0.681	0.004	2.759	0.032	0.441	0.005
9.1% NaSCN 9.2% $[N_{2222}]Cl$ 15.9% $(NH_4)_2SO_4$ (1:2) Moles	7.085	0.573	0.850	0.035	22.248	4.162	1.342	0.087
7.9% NaSCN 21.7% $[N_{3333}]Cl$ 6.0% $(NH_4)_2SO_4$ (1:1) Moles	4.645	0.321	0.666	0.030	2.410	0.069	0.382	0.012
12.4% NaSCN 16.9% $[N_{3333}]Cl$ 6.3% $(NH_4)_2SO_4$ (1:2) Moles	4.171	0.044	0.620	0.005	2.417	0.024	0.383	0.004

Table S3. Partition coefficient of $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$ on top and bottom phases of all ABS under study.

ABS	$K_3[Fe(CN)_6]$				$K_4[Fe(CN)_6]$			
	Kavg	**Kstdev**	**logKavg**	**logKstdev**	**Kavg**	**Kstdev**	**logKavg**	**logKstdev**
9.6% NaSCN 17.6% $[C_2C1im]Cl$] 15.0% $(NH_4)_2SO_4$ (1:1) Moles	3.400	0.157	0.531	0.020	0.533	0.065	-0.275	0.053
14.2% NaSCN 12.7% $[C_2C1im]Cl$ 14.9% $(NH_4)_2SO_4$ (1:2) Moles	1.592	0.110	0.201	0.030	0.596	0.009	-0.225	0.006
10.3% NaSCN 19.4% $[C_4C1im]Cl$ 8.0% $(NH_4)_2SO_4$ (1:1) Moles	1.784	0.000	0.251	0.000	0.410	0.017	-0.388	0.018
15.8% NaSCN 15.1% $[C_4C1im]Cl$ 8.0% $(NH_4)_2SO_4$ (1:2) Moles	1.750	0.256	0.238	0.064	0.419	0.034	-0.379	0.035
5.6% NaSCN 12.2% $[N_{2222}]Cl$ 15.9% $(NH_4)_2SO_4$ (1:1) Moles	4.507	0.791	0.650	0.077	0.511	0.026	-0.292	0.022
9.1% NaSCN 9.2% $[N_{2222}]Cl$ 15.9% $(NH_4)_2SO_4$ (1:2) Moles	2.590	0.098	0.413	0.016	0.102	0.011	-0.993	0.047
7.9% NaSCN 21.7% $[N_{3333}]Cl$ 6.0% $(NH_4)_2SO_4$ (1:1) Moles	0.926	0.054	-0.034	0.025	0.442	0.040	-0.355	0.039
12.4% NaSCN 16.9% $[N_{3333}]Cl$ 6.3% $(NH_4)_2SO_4$ (1:2) Moles	0.533	0.013	-0.273	0.011	0.079	0.007	-1.101	0.037

Reagent prices

Table S4. Reagent prices, purities, and suppliers used for the cost analysis. Values correspond to the lowest catalogue prices available on 10/12/2025 and include purchased mass, total cost, price per kilogram, purity, and supplier. These data were used to estimate the cost impact of partially substituting the ionic liquid with NaSCN.

Compound	Mass (g)	Price (€)	Price(€/kg)	Purity	Supplier
Demin Water	800000	€ 622.60	€ 0.78	-	ReAgent
$(NH_4)_2SO_4$	50000	€ 1,380.00	€ 27.60	99.0%	Sigma-Aldrich
NaSCN	25000	€ 1,010.00	€ 40.40	98.5%	Supelco
$[N_{3333}]Cl$	50	€ 182.00	€ 3,640.00	98.0%	Sigma-Aldrich
$[N_{2222}]Cl$	100	€ 123.00	€ 1,230.00	98.0%	Sigma-Aldrich
$[C_4mim]Cl$	250	€ 461.00	€ 1,844.00	98.0%	Sigma-Aldrich
$[C_2mim]Cl$	1000	€ 528.00	€ 528.00	95.0%	Sigma-Aldrich

Binodal curves

Table S5. $[C_2mim][SCN] + (NH_4)_2SO_4$

IL (1) + $(NH_4)_2SO_4$ (2) + H_2O (3) at 298.15 K		
100 w1	**100 w2**	**100 w3**
63.25623	3.34169	33.40209
52.43363	5.24515	42.32122
45.17154	5.72202	49.10645
42.22090	6.64334	51.13575
39.28177	8.01060	52.70763
37.38170	8.66361	53.95469
34.64912	9.72296	55.62791
32.54005	10.66531	56.79465
30.64655	11.73332	57.62013
28.72727	12.43451	58.83821
27.12705	13.12870	59.74425
26.05350	13.76349	60.18302
23.33443	15.13710	61.52847
22.02602	15.71466	62.25931
20.83211	16.33021	62.83768

Table S6. $[C_4mim][SCN] + (NH_4)_2SO_4$

IL (1) + $(NH_4)_2SO_4$ (2) + H_2O (3) at 298.15 K		
100 w1	**100 w2**	**100 w3**
44.81216	4.23539	50.95244
39.85680	5.12362	55.01958
37.13862	5.65858	57.20280
35.15789	6.30210	58.54000
33.33333	6.92562	59.74104
31.06014	7.31377	61.62610
29.55752	7.89918	62.54330
28.30508	8.18715	63.50777
27.15447	8.49596	64.34957
26.24411	8.68156	65.07433
25.30303	8.92689	65.77008
24.10972	9.60596	66.28431
22.38606	10.12303	67.49091
20.84894	10.63404	68.51702
19.82588	10.61299	69.56113
19.29149	10.76704	69.94147
18.72197	10.87630	70.40173
18.12590	11.16507	70.70903
17.66573	11.32782	71.00646
17.08149	11.50989	71.40862
16.68887	11.59888	71.71225
15.86447	12.09877	72.03675
15.24650	12.17408	72.57942
14.36765	12.58445	73.04790
13.68479	13.00099	73.31422
13.03669	13.40499	73.55832
12.31261	13.63357	74.05383
11.58382	14.11019	74.30600
10.98443	14.72257	74.29300
10.33203	15.06879	74.59918
9.45818	15.64385	74.89796
8.48146	16.44704	75.07150
7.45980	17.53528	75.00492
6.42308	18.93964	74.63729

Table S7. Binodal ([C_2mim]Cl + NaSCN) + $(NH_4)_2SO_4$

IL–Cl + NaSCN (1:2) (1) + $(NH_4)_2SO_4$ (2) + H_2O (3) at 298.15 K		
100 w1	**100 w2**	**100 w3**
35.21863	11.78888	52.99249
33.74317	12.08894	54.16789
31.88468	12.80400	55.31131
30.31915	13.39451	56.28634
28.92272	13.90918	57.16810
27.62864	14.38283	57.98854
26.07319	15.13159	58.79522
24.90756	15.48376	59.60867
23.59873	16.13201	60.26926
22.70221	16.48139	60.81641
21.57833	17.08428	61.33738
20.56049	17.61913	61.82038
19.61355	18.02267	62.36378
18.79756	18.46798	62.73446
18.03797	18.87832	63.08371
17.20455	19.38971	63.40574
16.40469	19.85215	63.74315
15.52483	20.40713	64.06804
14.77862	20.95208	64.26930
14.07675	21.50983	64.41343
12.95908	21.59768	65.44324
12.32125	22.16834	65.51041
11.69692	22.76120	65.54188
11.07292	23.37613	65.55095
10.32177	24.23022	65.44801
9.70022	24.89539	65.40439
9.07532	25.65380	65.27088
8.36626	26.56359	65.07015

Table S8. Binodal ([C_4mim]Cl + NaSCN) + $(NH_4)_2SO_4$

IL–Cl + NaSCN (1:2) (1) + $(NH_4)_2SO_4$ (2) + H2O (3) at 298.15 K					
100 w1	**100 w2**	**100 w3**	**100 w1**	**100 w2**	**100 w3**
45.28186	4.27486	50.44327	13.35623	12.60178	74.04199
43.34311	4.48056	52.17633	12.99683	12.76335	74.23981
40.62672	4.78322	54.59006	12.79432	12.86297	74.34271
38.19121	5.84334	55.96544	12.54669	13.13137	74.32194
36.13692	5.88195	57.98113	12.21286	13.23919	74.54795
34.77647	6.24543	58.97810	11.98702	13.41712	74.59586
33.52995	6.56733	59.90273	11.65248	13.53579	74.81174
32.36969	6.81426	60.81605	11.45736	13.72564	74.81700
31.30030	7.04766	61.65204	11.12114	13.96848	74.91038
30.29930	7.21682	62.48388	10.92549	14.13174	74.94277
29.41879	7.34229	63.23892	10.60563	14.36248	75.03189
28.54384	7.51109	63.94507	10.27959	14.58466	75.13575
27.79240	7.66017	64.54743	13.35623	12.60178	74.04199
27.08944	7.84856	65.06200	12.99683	12.76335	74.23981
26.36461	8.05338	65.58201			
25.71329	8.21716	66.06955			
25.05934	8.38887	66.55179			
24.51078	8.52440	66.96482			
23.93135	8.72539	67.34326			
23.36390	8.87344	67.76267			
22.83684	8.99542	68.16775			
22.35330	9.13241	68.51430			
21.82516	9.28372	68.89111			
21.35221	9.38375	69.26404			
20.86392	9.48612	69.64996			
20.42565	9.60824	69.96611			
19.98918	9.73913	70.27169			
19.41161	10.10017	70.48822			
18.80407	10.15135	71.04458			
18.28303	10.46524	71.25173			
17.57432	10.75564	71.67004			
17.18205	10.71134	72.10661			
16.87600	10.84101	72.28299			
16.44049	11.13212	72.42739			
15.87199	11.34999	72.77802			
15.31289	11.60652	73.08059			
14.87520	11.75095	73.37385			
14.61341	11.86921	73.51738			
14.38023	11.94510	73.67467			
14.01214	12.25513	73.73273			
13.64728	12.35808	73.99464			

Table S9. Binodal ($[N_{2222}]Cl$ + NaSCN) + $(NH_4)_2SO_4$

IL–Cl + NaSCN (1:2) (1) + $(NH_4)_2SO_4$ (2) + H_2O (3) at 298.15 K					
100 w1	**100 w2**	**100 w3**	**100 w1**	**100 w2**	**100 w3**
40.95774	6.58413	52.45814	7.99287	20.08514	71.92199
38.32541	7.07490	54.59969	7.74209	20.40232	71.85559
34.83401	7.63344	57.53255	7.54842	20.60433	71.84726
32.95481	8.17046	58.87473	7.30727	20.89282	71.79991
31.32665	8.49336	60.17999	7.08305	21.14111	71.77584
29.58731	8.87366	61.53903	6.83654	21.52075	71.64271
28.15701	9.27790	62.56509	6.59617	21.82973	71.57410
26.88745	9.65522	63.45734	6.38350	22.14187	71.47463
25.67469	9.95894	64.36638	6.14542	22.56446	71.29012
24.63911	10.30606	65.05483	5.91956	22.91873	71.16171
23.69504	10.63130	65.67366	5.75564	23.18170	71.06267
22.62480	11.20061	66.17459	5.56694	23.54811	70.88495
21.72216	11.41391	66.86392	5.39080	23.82916	70.78004
20.61371	12.01849	67.36781	5.16938	24.24782	70.58280
19.92495	12.20652	67.86853	4.91188	24.75272	70.33540
19.27330	12.34681	68.37989	4.55831	25.49740	69.94428
18.30823	12.87067	68.82110	4.24863	26.31019	69.44119
17.61298	13.14258	69.24444	3.94358	27.02945	69.02697
17.09601	13.27639	69.62760	3.60343	27.86244	68.53413
16.39114	13.72530	69.88356			
16.08068	13.90260	70.01672			
15.62424	13.97033	70.40543			
15.10594	14.26802	70.62603			
14.55720	14.63454	70.80826			
14.05480	14.98376	70.96143			
13.73117	15.05605	71.21278			
13.26571	15.39444	71.33985			
12.87363	15.62928	71.49708			
12.48537	15.89683	71.61779			
12.08476	16.15996	71.75529			
11.63021	16.59390	71.77589			
11.30219	16.79478	71.90302			
10.99941	17.02223	71.97836			
10.70785	17.21331	72.07884			
10.34731	17.58540	72.06729			
10.00026	17.93935	72.06039			
9.74729	18.07021	72.18250			
9.43872	18.36629	72.19498			
9.15746	18.66124	72.18130			
8.87672	18.91976	72.20352			
8.56555	19.31151	72.12295			
8.26726	19.70352	72.02922			

Table S10. Binodal ($[N_{3333}]Cl$ + NaSCN) + $(NH_4)_2SO_4$

IL–Cl + NaSCN (1:2) (1) + $(NH_4)_2SO_4$ (2) + H_2O (3) at 298.15 K					
100 w1	**100 w2**	**100 w3**	**100 w1**	**100 w2**	**100 w3**
54.99613	1.01935	43.98452	10.19968	8.00317	81.79715
48.63014	2.02161	49.34825	10.08093	8.10816	81.81091
44.31960	2.63864	53.04176	9.90652	8.16819	81.92530
41.08796	2.97703	55.93501	9.73803	8.26993	81.99204
38.17204	3.43039	58.39756	9.59200	8.32909	82.07891
35.62469	3.84177	60.53355	9.46540	8.42118	82.11341
33.52219	4.17988	62.29793	9.29806	8.45509	82.24685
31.12670	4.44064	64.43266	9.21001	8.54056	82.24943
29.20609	4.70797	66.08594	9.07348	8.60761	82.31891
26.92454	4.99046	68.08500	8.93869	8.63035	82.43096
24.70424	5.18946	70.10630	8.84956	8.73814	82.41230
22.88108	5.37195	71.74697	8.70632	8.79231	82.50138
21.26385	6.01937	72.71678	8.55628	8.95797	82.48575
20.45520	5.91684	73.62796	8.43030	8.98233	82.58736
19.96064	6.26708	73.77228	8.27602	9.12939	82.59458
18.83789	6.26372	74.89839	8.08288	9.22958	82.68754
18.40332	6.15024	75.44645	7.93473	9.35011	82.71516
17.81681	6.23443	75.94876	7.75787	9.45106	82.79107
17.30863	6.36770	76.32367	7.56526	9.60310	82.83164
16.78090	6.47516	76.74393	7.44781	9.75938	82.79281
16.08518	6.47775	77.43707	7.27832	9.83570	82.88598
15.60783	6.58356	77.80861	7.16593	9.88909	82.94499
15.15798	6.68328	78.15873	7.05275	9.99038	82.95687
14.72724	6.79942	78.47335	6.94037	10.10797	82.95166
14.32896	6.88917	78.78186	6.83415	10.20661	82.95923
13.83476	6.94685	79.21839	6.70444	10.43464	82.86092
13.52896	7.02886	79.44218	6.56982	10.48342	82.94676
13.17499	7.08915	79.73586	6.45513	10.54697	82.99790
12.85766	7.17839	79.96395	6.31223	10.70702	82.98074
12.53974	7.23332	80.22694	6.17499	10.86961	82.95541
12.24349	7.27561	80.48090	6.03844	11.01589	82.94567
12.07072	7.38990	80.53938	5.91076	11.15478	82.93446
11.80382	7.46517	80.73100	5.79829	11.32356	82.87816
11.62981	7.56415	80.80604	5.65827	11.42514	82.91659
11.41296	7.64746	80.93958	5.54125	11.56232	82.89643
11.19697	7.63481	81.16822	5.43312	11.67238	82.89450
11.04371	7.74740	81.20889	5.35041	11.83128	82.81831
10.81822	7.78974	81.39204	5.23985	12.00765	82.75250
10.63193	7.84071	81.52736			
10.43504	7.88306	81.68190			

Table S11. Binodal $[C_4mpyr]Cl$ + NaSCN + $(NH_4)_2SO_4$

IL–Cl + NaSCN (1:2) (1) + $(NH_4)_2SO_4$ (2) + H_2O (3) at 298.15 K		
100 w1	**100 w2**	**100 w3**
48.29659	3.15187	48.55154
44.22018	3.90107	51.87874
40.68655	4.52290	54.79055
37.77429	5.01392	57.21179
35.18248	5.38984	59.42768
32.80399	5.82373	61.37227
30.76596	6.24462	62.98942
29.10628	6.47116	64.42256
27.94743	6.95543	65.09714
26.44477	7.15185	66.40338
25.13908	7.42438	67.43654
24.14023	7.74353	68.11623
23.11381	7.97675	68.90944
22.11686	8.19536	69.68779
21.46037	8.46246	70.07717
20.83573	8.76926	70.39500
19.97789	8.79493	71.22717
19.48262	9.08332	71.43406
18.76947	9.16605	72.06448
18.31307	9.37868	72.30825
17.57414	9.59314	72.83272
16.91624	9.76729	73.31648
16.14560	10.02775	73.82665
15.52168	10.38709	74.09123
14.92876	10.65082	74.42041
14.29984	10.89017	74.80998
13.55456	11.28964	75.15581
12.58705	11.94568	75.46727
11.57541	12.49002	75.93457
10.77818	13.10215	76.11967
10.13883	13.55857	76.30260
9.59140	13.94577	76.46283
9.00149	14.55168	76.44683
8.54913	15.04972	76.40115
7.98366	15.71888	76.29746
7.36103	16.44303	76.19594

Table S12. $[C_4mpip]Cl + NaSCN + (NH_4)_2SO_4$

IL–Cl + NaSCN (1:2) (1) + $(NH_4)_2SO_4$ (2) + H_2O (3) at 298.15 K					
100 w1	**100 w2**	**100 w3**	**100 w1**	**100 w2**	**100 w3**
50.87843	0.87109	48.25048	6.51021	14.51160	78.97819
45.05289	2.01521	52.93190	6.13299	15.16453	78.70247
42.91642	2.74948	54.33410			
39.86784	3.47896	56.65320			
36.23624	4.00260	59.76116			
33.11985	4.40834	62.47181			
30.49705	4.74981	64.75314			
28.21512	5.22031	66.56457			
26.44266	5.46193	68.09541			
24.74368	5.65762	69.59870			
23.69110	5.96650	70.34240			
22.30437	6.15927	71.53635			
21.36323	6.37133	72.26544			
20.49830	6.52093	72.98077			
19.69532	6.68971	73.61496			
18.95288	6.84577	74.20135			
18.29669	6.91191	74.79140			
17.64563	7.06553	75.28885			
17.04733	7.19315	75.75952			
16.65516	7.44161	75.90323			
16.18239	7.58787	76.22975			
15.65744	7.69627	76.64629			
15.21648	7.82408	76.95944			
14.91246	8.02191	77.06563			
14.50611	8.14782	77.34607			
13.99845	8.48118	77.52037			
13.63979	8.56520	77.79501			
13.14213	8.86239	77.99548			
12.70621	9.16492	78.12887			
12.18445	9.36730	78.44825			
11.63613	9.69767	78.66620			
11.14189	9.98727	78.87084			
10.68162	10.32392	78.99447			
10.25205	10.62217	79.12578			
9.76926	10.96904	79.26170			
9.33953	11.39952	79.26096			
8.93276	11.67759	79.38965			
8.39907	12.29268	79.30825			
7.98060	12.78653	79.23287			
7.53539	13.27179	79.19282			
7.18967	13.66354	79.14679			
6.84245	14.11849	79.03906			

Table S13. [C_4mpy]Cl + NaSCN + $(NH_4)_2SO_4$

IL–Cl + NaSCN (1:2) (1) + $(NH_4)_2SO_4$ (2) + H_2O (3) at 298.15 K		
100 w1	**100 w2**	**100 w3**
48.95903	1.47950	49.56146
43.65269	2.44825	53.89905
40.16529	3.21422	56.62049
37.23187	4.02125	58.74688
33.97018	4.46740	61.56242
31.26072	5.02077	63.71851
28.80284	5.25463	65.94252
27.15084	5.62178	67.22738
25.29493	5.77541	68.92965
24.02769	6.07770	69.89461
22.85266	6.33040	70.81693
21.82635	6.62018	71.55348
20.73379	6.77611	72.49010
20.00000	7.06234	72.93766
19.21962	7.24926	73.53112
18.25238	7.43601	74.31161
17.75451	7.72003	74.52547
17.03271	7.85417	75.11312
16.43743	7.99361	75.56896
16.05727	8.18614	75.75659
15.37326	8.52568	76.10106
14.59459	8.86158	76.54383
14.07879	8.94233	76.97888
13.80420	9.10009	77.09570
13.28837	9.45163	77.26000
12.82773	9.75570	77.41657
12.34338	10.02975	77.62687
11.73535	10.40913	77.85552
11.20160	10.75062	78.04779
10.64544	11.03897	78.31559
10.22871	11.47117	78.30012
9.69415	11.92413	78.38172
9.07620	12.40334	78.52046
8.54531	12.92118	78.53352
7.98904	13.49730	78.51366
7.48921	14.06525	78.44554
7.10526	14.48931	78.40543
6.69299	15.03816	78.26886
6.37126	15.55251	78.07623
5.95929	16.02089	78.01982
5.64722	16.43656	77.91621

Figures

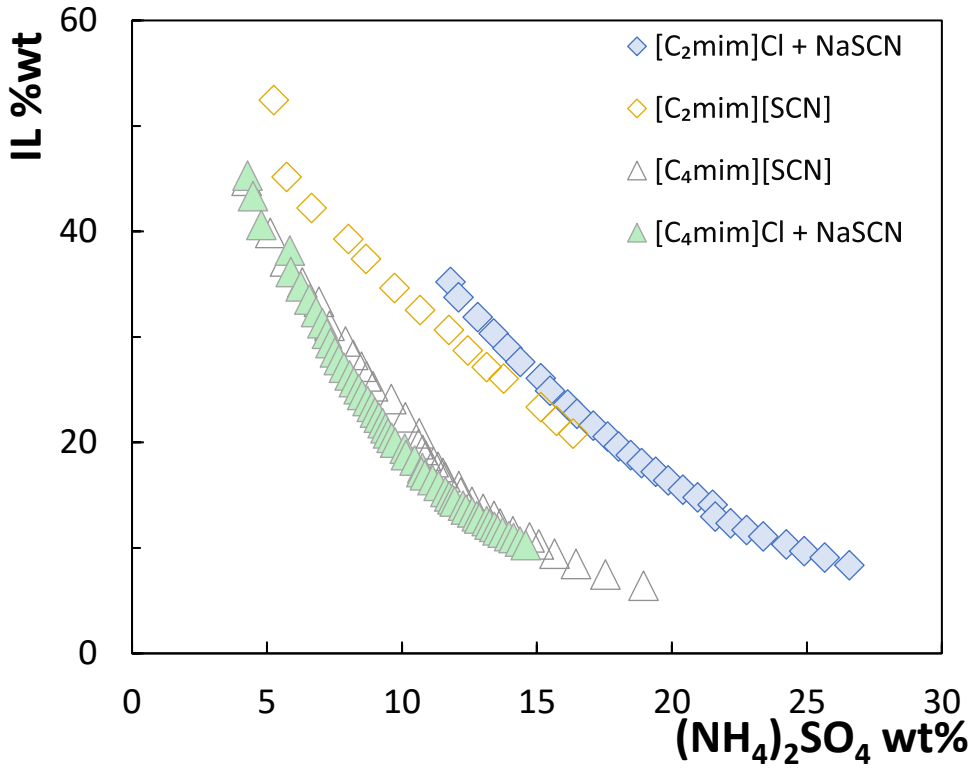

Figure S1. Comparison of binodal curves for imidazolium-based ionic liquids in the presence of NaSCN and for the corresponding SCN-based ionic liquids with $(NH_4)_2SO_4$ at 298 K (wt%). Experimental details are provided in the Supplementary Procedures section.

Supplementary Procedures

Comparison of binodal curves between [C_2mim]Cl/[C_4mim]Cl + NaSCN and [C_2mim]SCN/[C_4mim]SCN

To verify that the observed phase behavior arises from the dominant role of SCN^- rather than residual characteristics of the chloride precursors, ABS were also prepared using commercial thiocyanate ionic liquids (IL–SCN), namely [C_2mim][SCN] and [C_4mim][SCN]. The corresponding binodal curves (Figure S1) closely match those obtained for the IL–Cl/SCN systems, with only minor deviations at high IL contents, which may be attributed to experimental variability or residual NaCl in the mixtures. This close agreement indicates that, under the studied conditions, thiocyanate plays a dominant role in governing liquid–liquid demixing rather than acting as an inert co-solute. This behavior is consistent with the preferential partitioning of SCN^- into the IL-rich phase, as previously reported for related IL-based ABS upon NaSCN addition [1].
The ionic liquids used in this study were 1-ethyl-3-methylimidazolium chloride ([C_2mim]Cl, 98.0%, Iolitec) and 1-butyl-3-methylimidazolium chloride ([C_4mim]Cl, 99.0%, Iolitec), as well as their corresponding thiocyanate forms, 1-ethyl-3-methylimidazolium

thiocyanate ([C_2mim][SCN], 98.0%, Iolitec) and 1-butyl-3-methylimidazolium thiocyanate ([C_4mim][SCN], 98.0%, Iolitec). The inorganic salts sodium thiocyanate (NaSCN, 98.0%, Merck) and ammonium sulfate ($(NH_4)_2SO_4$, 99.5%, Panreac) were also used. All reagents were used as received.

Reference

[1] M.L. Alcantara, P. Navalpotro, G. Camilo, M. Prazeres, C.M.S.S. Neves, A.M. Ferreira, E. Ventosa, R. Marcilla, J.A.P. Coutinho, Tuning biphasic electrolytes for membrane-free redox flow batteries: influence of sodium thiocyanate on partition and viscosity, J. Mol. Liq. 439 (2025) 128767. https://doi.org/10.1016/J.MOLLIQ.2025.128767.