Electronic Supplementary Data

Improved recovery of ionic liquids from contaminated aqueous streams using aluminium-based salts

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1. Results

The experimental solubility data obtained, at 298 K and at atmospheric pressure, are presented in Tables S1 and S2. Figure S1 depicts the gathered results in molality units. It should be remarked that for the salt $AlK(SO_4)_2$ the concentrations reported were calculated without the contribution of the water complexed with the salt.

Table S1. Experimental mass fraction data for the system composed of ionic liquid (1) + $Al_2(SO_4)_3$ (2) + H_2O (3) at 298 K.

[C$_2$mim][CF$_3$SO$_3$] M_w = 260.23					
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
12.997	27.292	27.011	15.625	34.456	10.650
13.985	26.307	27.543	15.183	34.757	10.415
14.961	25.337	28.056	14.869	35.173	10.164
15.741	24.571	28.564	14.493	35.537	9.964
16.570	23.764	29.051	14.143	35.855	9.766
17.707	22.861	29.646	13.790	35.988	9.522
18.762	22.000	30.060	13.454	36.289	9.389
19.830	21.129	30.415	13.178	36.580	9.177
20.783	20.361	30.874	12.882	37.464	8.948
21.386	19.901	31.349	12.567	37.720	8.752
22.278	19.228	31.746	12.305	38.376	8.495
23.044	18.613	32.111	12.039	38.663	8.239
23.697	18.057	32.633	11.745	39.826	7.911
24.117	17.617	32.802	11.538	40.385	7.202
25.149	16.972	32.980	11.377	42.004	6.656
25.849	16.512	33.377	11.152	44.480	6.048
26.462	16.055	33.975	10.857		
[C$_4$mim][CF$_3$SO$_3$] M_w = 288.28					
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
4.151	27.119	17.233	11.710	26.368	7.931
5.162	25.205	17.598	11.538	27.239	7.678
6.264	23.134	18.224	11.106	28.220	7.347
6.767	22.060	18.530	10.868	29.226	7.045
8.727	19.385	18.945	10.753	30.307	6.729
9.873	17.908	19.466	10.530	31.766	6.400
10.666	16.970	19.985	10.316	33.136	5.992
11.398	16.264	20.469	10.152	34.565	5.555
12.069	15.550	20.865	9.857	36.370	5.178
12.599	15.053	21.567	9.700	38.470	4.742

14.160	13.784	22.186	9.398	40.565	4.122
14.676	13.333	22.889	9.191	44.066	3.620
15.177	13.131	23.355	8.827	48.718	2.819
15.872	12.621	24.076	8.621	51.022	2.065
16.346	12.230	24.809	8.430	57.809	1.074
16.672	12.114	25.555	8.194		
[C_4mim][Tos] M_w = 310.42					
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
7.659	27.371	16.398	20.827	35.211	10.339
8.613	26.487	17.750	19.966	37.797	9.288
9.448	25.775	18.819	19.343	39.529	8.942
10.347	25.038	20.745	18.143	42.944	7.621
11.217	24.364	22.789	16.923	45.492	6.956
12.192	23.633	24.732	15.859	48.439	6.224
13.127	22.995	27.420	14.272	51.902	5.310
14.167	22.275	29.885	12.959		
15.204	21.608	32.373	11.735		
[C_4mim][$N(CN)_2$] M_w = 205.26					
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
8.893	26.678	21.133	16.414	35.688	7.255
11.229	24.349	22.458	15.449	37.576	6.234
12.870	22.789	23.644	14.584	39.024	5.807
13.926	21.837	24.318	14.159	40.387	5.179
15.222	20.784	25.877	13.069	41.762	4.611
16.141	20.063	27.194	12.199	43.816	3.989
16.842	19.531	28.687	11.195	45.372	3.289
17.502	19.034	29.765	10.577	47.133	2.543
18.244	18.487	31.021	9.862	49.885	1.851
19.318	17.686	33.106	8.621	58.498	0.800
20.140	17.111	34.005	8.216		
[C_8py][$N(CN)_2$] M_w = 258.36					
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
1.430	35.132	12.491	12.294	20.066	8.014
2.116	30.754	12.777	12.150	20.542	7.801
2.608	28.773	13.124	11.995	21.190	7.636
3.071	26.845	13.413	11.741	21.704	7.433
3.469	25.118	13.717	11.482	22.204	7.222
3.929	24.058	14.028	11.217	22.821	7.000
4.712	22.543	14.227	11.117	23.577	6.744
5.510	20.994	14.387	10.974	24.323	6.483
5.811	19.245	14.550	10.839	25.007	6.200
7.167	17.499	14.799	10.745	25.953	5.949

8.021	16.258	14.965	10.609	26.741	5.603
8.579	15.619	15.159	10.470	27.991	5.351
9.137	15.072	15.411	10.361	29.329	5.040
9.515	14.714	15.605	10.218	30.624	4.655
9.816	14.397	15.876	10.106	32.098	4.245
10.147	14.091	16.239	10.035	34.384	3.886
10.416	13.852	16.714	9.761	37.033	3.423
10.736	13.661	17.180	9.402	40.237	2.934
11.032	13.392	17.506	9.243	45.576	2.385
11.326	13.134	17.848	9.089	49.903	1.855
11.578	12.985	18.313	8.992	59.041	1.000
11.828	12.844	19.028	8.655		
12.072	12.646	19.635	8.210		

$[C_7H_7mim][C_2H_5SO_4]$ M_w = 298.36

100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
10.211	31.136	30.872	14.733	30.872	14.733
12.491	29.191	31.694	14.183	31.694	14.183
13.403	27.885	32.268	13.743	32.268	13.743
15.218	26.299	33.052	13.228	33.052	13.228
17.315	24.811	33.922	12.730	33.922	12.730
18.807	23.490	34.556	12.303	34.556	12.303
20.350	22.323	35.371	11.865	35.371	11.865
21.674	21.304	35.676	11.568	35.676	11.568
22.614	20.381	36.504	11.167	36.504	11.167
24.219	19.344	37.062	10.844	37.062	10.844
25.128	18.620	37.561	10.542	37.561	10.542
26.252	17.853	38.080	10.229	38.080	10.229
27.457	17.115	38.619	9.942	38.619	9.942
28.487	16.412	39.209	9.672	39.209	9.672
29.221	15.849	39.791	9.376	39.791	9.376
29.763	15.348	40.360	9.096		

$[P_{i(444)1}][Tos]$ M_w = 385.52

100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
6.968	19.962	11.100	16.959	18.869	13.064
7.075	19.880	11.342	16.754	19.319	12.935
7.188	19.790	11.501	16.713	19.807	12.776
7.351	19.618	11.749	16.545	20.590	12.261
7.533	19.424	11.913	16.520	21.113	12.097
7.667	19.328	12.204	16.305	21.651	11.925
7.810	19.225	12.397	16.245	22.581	11.360
8.013	18.999	12.705	16.032	23.227	11.122
8.164	18.892	12.906	15.970	23.926	10.854

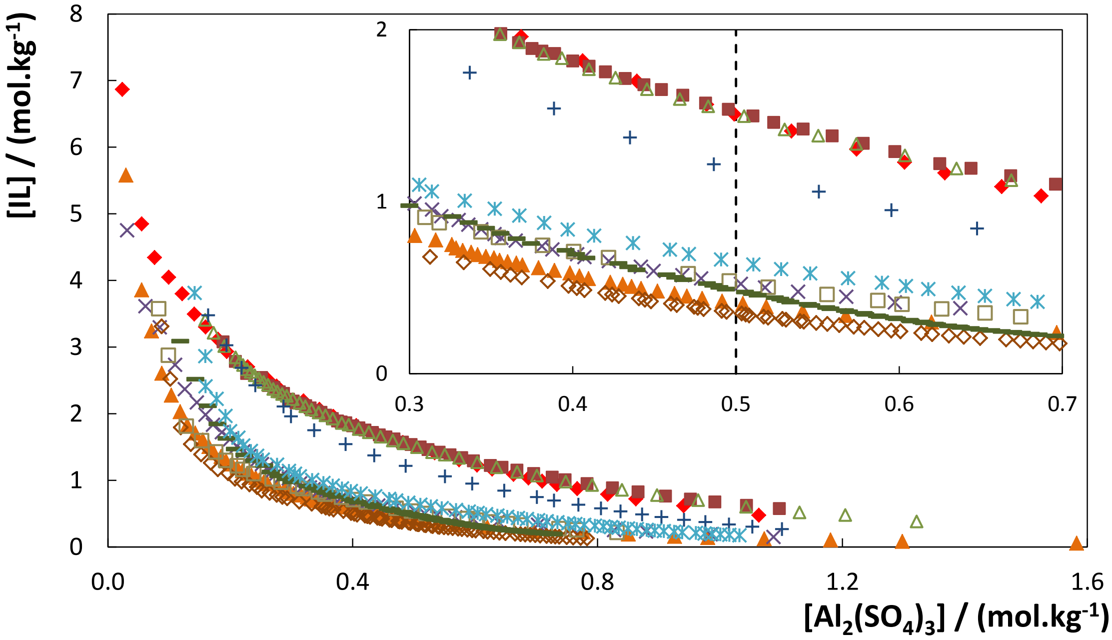
8.321	18.769	13.238	15.748	24.584	10.614
8.487	18.650	13.460	15.697	25.307	10.322
8.650	18.491	13.827	15.436	26.060	10.045
8.838	18.344	14.061	15.362	27.360	9.312
9.028	18.177	14.316	15.282	28.252	9.040
9.199	18.055	14.559	15.201	29.179	8.705
9.381	17.917	14.954	14.942	30.242	8.352
9.500	17.890	15.212	14.853	32.040	8.047
9.690	17.737	15.487	14.749	33.353	7.583
9.895	17.577	15.915	14.457	34.777	7.094
10.029	17.547	16.207	14.356	36.186	6.634
10.234	17.391	16.512	14.264	38.604	6.231
10.358	17.356	16.820	14.164	41.588	5.788
10.571	17.200	17.382	13.795	44.969	5.303
10.718	17.187	17.762	13.674	49.247	4.675
10.959	17.003	18.160	13.538	54.358	3.894
$[P_{4444}]Br$ M_w = 339.34					
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
4.190	21.128	9.087	15.820	15.425	11.634
4.379	20.908	9.273	15.633	15.948	11.205
4.552	20.640	9.394	15.578	16.318	11.019
4.721	20.419	9.596	15.367	16.692	10.857
4.888	20.147	9.726	15.314	17.105	10.679
5.013	20.010	9.938	15.097	17.990	10.235
5.136	19.862	10.078	15.032	18.723	9.663
5.274	19.694	10.295	14.812	19.803	9.111
5.453	19.465	10.444	14.759	20.319	8.885
5.611	19.288	10.600	14.696	20.930	8.628
5.776	19.099	11.300	14.113	23.349	7.690
5.950	18.921	11.475	14.021	24.120	7.339
6.113	18.747	11.639	13.965	24.936	6.956
6.293	18.547	11.929	13.695	25.743	6.636
6.540	18.184	12.128	13.604	27.239	6.299
6.752	17.955	12.467	13.293	28.329	5.788
6.977	17.745	12.704	13.197	29.943	5.443
7.203	17.508	12.912	13.101	32.009	4.952
7.408	17.351	13.261	12.778	34.363	4.431
7.675	17.053	13.486	12.674	37.818	3.917
7.810	16.919	13.740	12.565	46.099	3.370
8.042	16.733	14.148	12.232	52.891	2.920
8.299	16.527	14.432	12.107	23.349	7.690
8.457	16.372	14.740	11.973	24.120	7.339

8.732	16.160	11.300	14.113		
8.904	15.985	11.475	14.021		
$[P_{4444}]Cl$ M_w = 294.89					
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
4.829	26.091	9.462	20.463	19.113	12.385
5.033	25.786	9.818	20.089	19.805	11.959
5.226	25.503	10.198	19.700	20.535	11.573
5.410	25.246	10.530	19.388	21.320	11.168
5.586	25.016	10.948	18.983	22.028	10.757
5.786	24.743	11.321	18.653	22.866	10.252
6.079	24.308	11.742	18.254	23.793	9.696
6.292	24.042	12.165	17.882	24.460	9.478
6.549	23.709	12.655	17.451	25.142	9.200
6.789	23.416	13.047	17.132	26.653	8.642
7.011	23.151	13.491	16.786	27.850	7.969
7.283	22.823	14.040	16.291	28.731	7.707
7.539	22.526	14.650	15.730	29.809	7.406
7.815	22.213	15.186	15.296	30.945	7.036
8.063	21.954	15.741	14.874	32.596	6.803
8.303	21.695	16.364	14.382	33.846	6.398
8.574	21.403	17.015	13.883	36.683	6.171
8.894	21.028	17.528	13.587	39.580	5.731
9.190	20.719	18.289	13.006	41.527	5.178
$[P_{4441}][CH_3SO_4]$ M_w = 358.52					
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
7.253	22.156	16.210	14.507	26.822	8.406
8.475	20.764	17.251	13.872	28.281	7.543
9.010	20.136	19.481	12.616	29.473	7.005
10.616	18.751	20.295	12.054	30.426	6.748
11.226	18.252	21.115	11.548	31.807	6.168
11.904	17.641	22.125	10.820	33.864	5.682
12.643	17.074	22.834	10.526	36.390	4.975
13.240	16.723	23.926	9.819	39.395	4.193
14.166	15.977	24.590	9.574	50.781	3.265
15.269	15.097	25.836	8.819	56.178	2.762

Table S2. Experimental mass fraction data for the system composed of ionic liquid (1) + $AlK(SO_4)_2$ (2) + H_2O (3) at 298 K.

[C$_4$mim][CF$_3$SO$_3$] M_w = 288.28					
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
28.905	4.312	37.099	3.018	42.396	2.287
29.415	4.219	37.411	2.964	42.723	2.247
29.673	4.121	37.923	2.903	42.959	2.212
29.892	4.088	38.256	2.850	43.333	2.170
30.915	3.954	38.553	2.807	43.651	2.133
31.427	3.857	39.024	2.743	43.815	2.115
32.003	3.759	39.327	2.698	44.303	2.053
32.568	3.669	39.574	2.671	44.534	2.024
33.145	3.585	39.872	2.625	45.107	1.961
33.694	3.502	40.335	2.553	45.618	1.902
34.260	3.412	40.856	2.499	46.095	1.851
34.823	3.331	41.097	2.458	46.450	1.821
35.737	3.203	41.441	2.409	54.621	1.010
35.991	3.163	41.812	2.365	61.240	0.612
36.696	3.073	42.046	2.329	65.196	0.424
[C$_8$py][N(CN)$_2$] M_w = 258.36					
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
22.417	4.613	30.612	3.349	35.460	2.649
22.861	4.513	31.045	3.282	36.387	2.291
23.444	4.389	31.466	3.213	38.301	2.075
23.990	4.297	31.815	3.165	40.321	1.865
24.660	4.192	32.092	3.113	42.313	1.678
25.713	4.022	32.543	3.051	43.970	1.527
26.170	3.941	33.052	2.984	45.465	1.408
27.023	3.831	33.541	2.922	46.850	1.304
27.560	3.752	33.750	2.875	48.893	1.151
28.050	3.672	34.266	2.811	61.431	0.501
28.392	3.610	34.673	2.759	64.680	0.390
29.675	3.486	34.780	2.732	67.666	0.293
29.967	3.425	35.014	2.695		

Electronic Supplementary Material (ESI) for RSC Advances



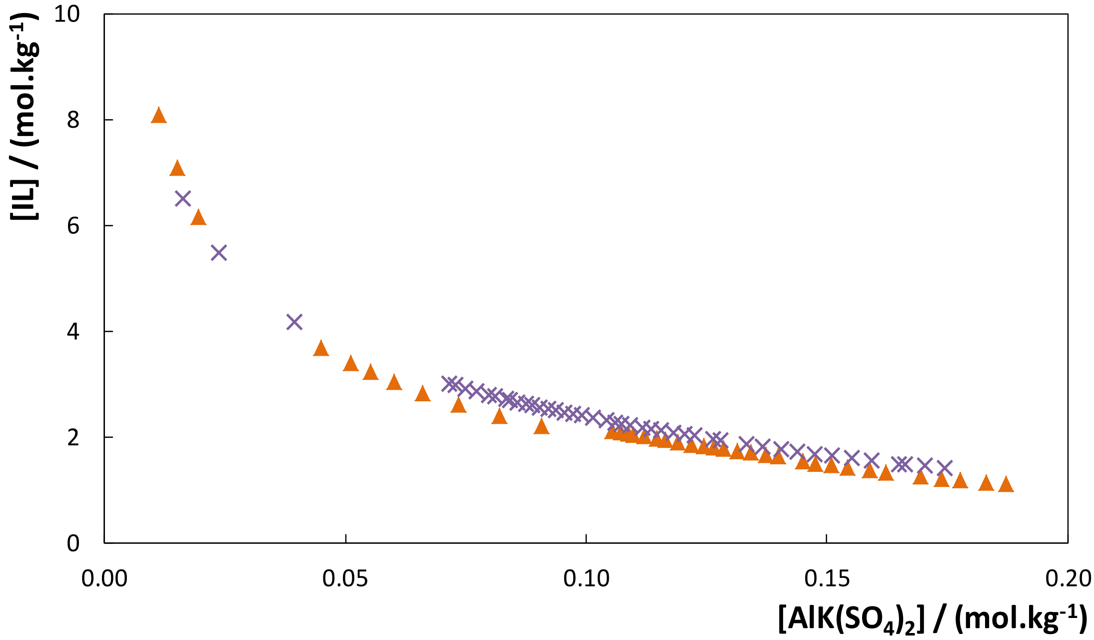


Fig. S1 Ternary phase diagrams for thesystems composed of ionic liquid + aluminium-based salt + water at 298 K and atmospheric pressure (molality units): ■, $[C_2mim][CF_3SO_3]$; ×, $[C_4mim][CF_3SO_3]$; ●, $[C_4mim][SCN]$; +, $[C_4mim][Tos]$; ◆, $[C_4mim][N(CN)_2]$;▲, $[C_8py][N(CN)_2]$; △, $[C_7H_7mim][C_2H_5SO_4]$; ▬, $[P_{i(444)1}][Tos]$; ◇, $[P_{4444}]Br$; ∗, $[P_{4444}]Cl$; □, $[P_{4441}][CH_3SO_4]$.

The consistency of the tie-line compositions was ascertained by the empirical correlations given by Othmer–Tobias[1] (eqn(S1)) and Bancroft[2] (eqn(S2)).

$$\left(\frac{1-[IL]_{IL}}{[IL]_{IL}}\right)=k_1\left(\frac{1-[Salt]_{Salt}}{[Salt]_{Salt}}\right)^n \qquad \text{(S1)}$$

$$\left(\frac{[H_2O]_{Salt}}{[Salt]_{Salt}}\right) = k_2\left(\frac{[H_2O]_{IL}}{[IL]_{IL}}\right)^r \qquad \text{(S2)}$$

where “IL” and “Salt” designate the ionic liquid rich-phase and the salt rich-phase, respectively; $[IL]$, $[Salt]$ and $[H_2O]$ represent, respectively, the weight fraction of ionic liquid, salt and water. The k_1, n, k_2 and r are fitting parameters. A linear dependency of the plots $\log\left(\frac{1-[IL]_{IL}}{[IL]_{IL}}\right)$ against $\log\left(\frac{1-[Salt]_{Salt}}{[Salt]_{Salt}}\right)$ and $\log\left(\frac{[H_2O]_{Salt}}{[Salt]_{Salt}}\right)$ against $\log\left(\frac{[H_2O]_{IL}}{[IL]_{IL}}\right)$ indicate an acceptable consistency of the results.

Table S3 Values of the fitting parameters of eqns (S1) and (S2) for the systems composed of ionic liquid + $Al_2(SO_4)_3$ + H_2O at 298 K, and respective correlation coefficients (R^2).

Ionic liquid	*Othmer – Tobias*, eqn (S1)			*Bancroft*, eqn (S2)		
	n	k_1	R^2	r	k_2	R^2
$[C_2mim][CF_3SO_3]$	1.3625	0.3385	0.9940	1.5451	0.3340	0.9920
$[C_4mim][CF_3SO_3]$	0.8348	0.1397	0.8129	0.9241	0.1305	0.8256
$[C_4mim][Tos]$	1.2994	0.6254	0.9911	1.2449	0.5726	0.9909
$[C_4mim][N(CN)_2]$	2.1597	0.3040	0.9175	0.4155	1.6808	0.9176
$[C_8py][N(CN)_2]$	0.1945	0.4004	0.9326	4.8194	89.5332	0.9298
$[C_7H_7mim][C_2H_5SO_4]$	1.2920	0.4474	0.9962	0.7072	1.8015	0.9970
$[P_{i(444)1}][Tos]$	1.9492	0.2628	0.9743	0.5051	2.0566	0.9740
$[P_{4444}]Br$	1.9628	0.1052	0.9985	2.0474	0.0969	0.9988
$[P_{4444}]Cl$	0.6422	0.5771	0.8135	0.6643	0.5414	0.8179
$[P_{4441}][CH_3SO_4]$	1.7494	0.2420	0.9020	0.4868	2.1296	0.9039

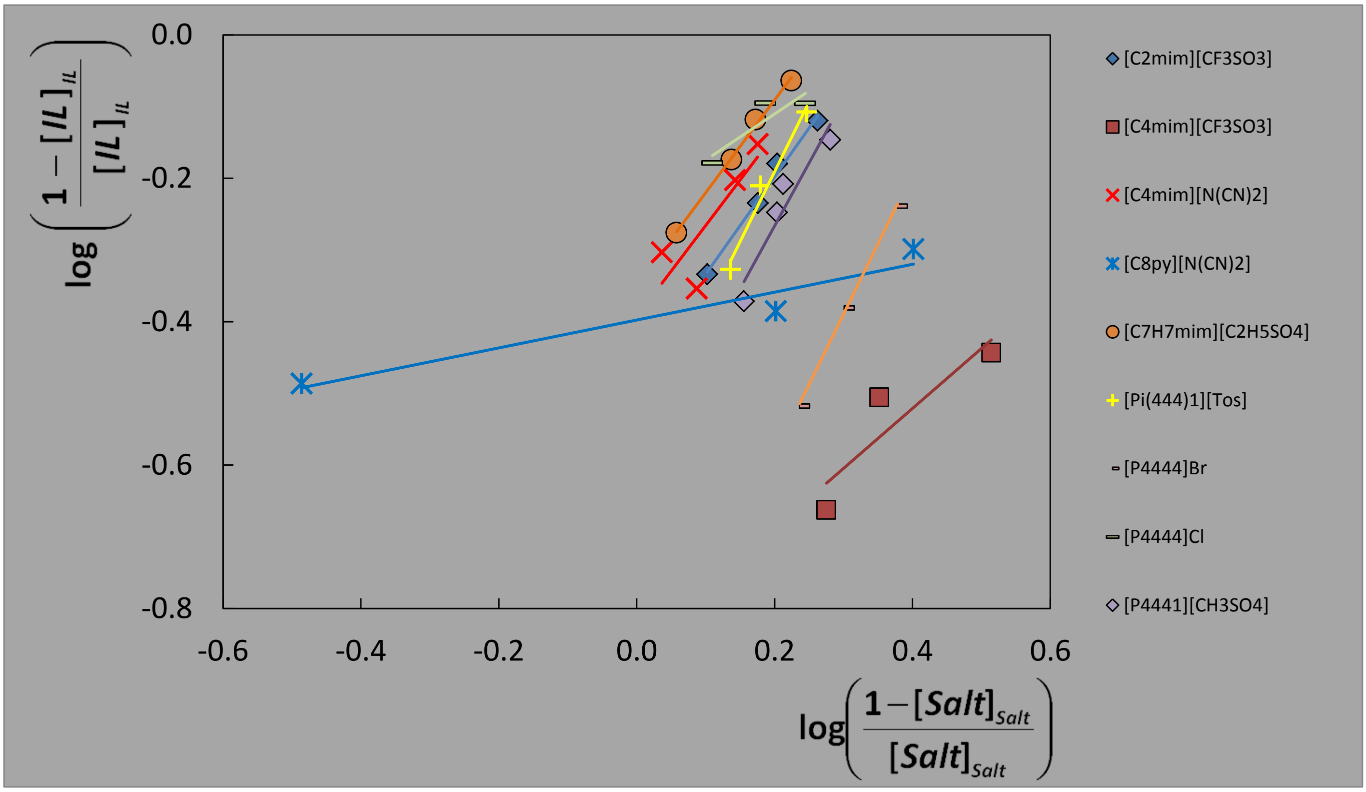


Fig. S2 Tie-lines correlation using the Othmer-Tobias correlation for each system composed of ionic liquid + $Al_2(SO_4)_3$ + H_2O.

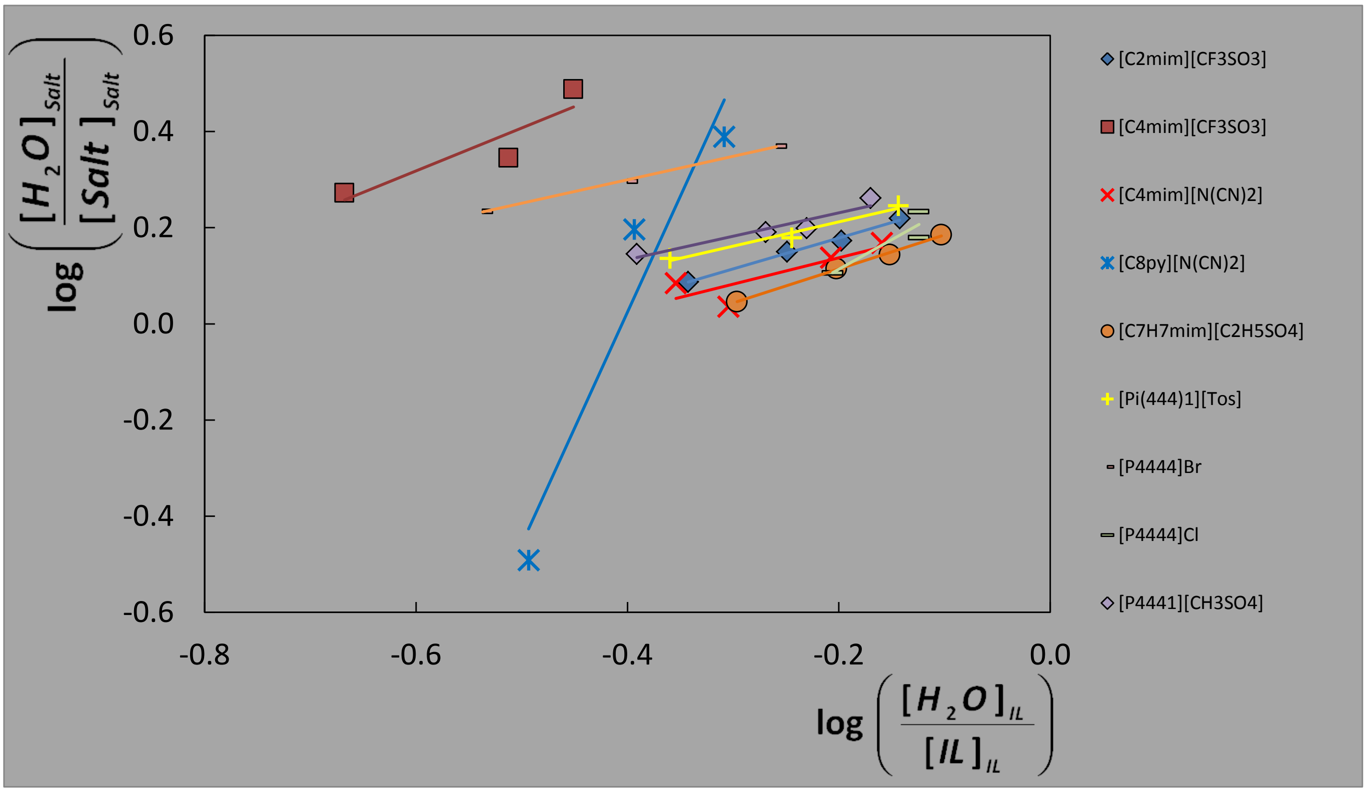


Fig. S3 Tie-lines correlation using the Bancroft correlation for each system composed of ionic liquid + $Al_2(SO_4)_3$ + H_2O.

Table S4 Critical point of each system composed of ionic liquid + $Al_2(SO_4)_3$ + H_2O at 298 K and respective values obtained from the fitting.

Ionic liquid	*f*	*g*	R^2	Critical Point / wt %	
				[*IL*]	[*Salt*]
$[C_2mim][CF_3SO_3]$	1.327	9.722	0.9926	14.32	28.72
$[C_4mim][CF_3SO_3]$	0.716	56.085	0.8568	1.49	57.15
$[C_4mim][Tos]$	1.268	-1.893	0.9895	17.88	20.79
$[C_4mim][N(CN)_2]$	2.034	-23.422	0.9292	19.72	16.68
$[C_8py][N(CN)_2]$	1.044	35.283	0.9747	3.13	38.55
$[C_7H_7mim][C_2H_5SO_4]$	1.273	5.979	0.9970	16.91	27.50
$[P_{i(444)1}][Tos]$	1.924	-13.816	0.9816	14.86	14.78
$[P_{4444}]Br$	1.846	8.992	0.9997	7.72	23.25
$[P_{4444}]Cl$	0.656	30.910	0.8203	35.03	6.29
$[P_{4441}][CH_3SO_4]$	1.714	-1.610	0.9193	12.05	19.04

Table S5 Experimental density (ρ) and viscosity (η) data of the coexisting phases in diverse ABS composed of 40 wt % of ionic liquid + 15 wt % of $Al_2(SO_4)_3$ + 45 wt % of H_2O in the temperature range between 298.15 K and 328.15 K.

Ionic liquid	**Phase**	***T*** **K**	***ρ*** **g.cm^{-3}**	***η*** **mPa.s**
			$Al_2(SO_4)_3$	
$[C_4mim][CF_3SO_3]$	IL – rich phase	298.15	1.2374	3.7387
		308.15	1.2296	2.8957
		318.15	1.2215	2.3083
		328.15	1.2132	1.8999
	Salt – rich phase	298.15	1.2899	12.128
		308.15	1.2842	8.5076
		318.15	1.2780	6.1348
		328.15	1.2710	4.5322
$[C_8py][N(CN)_2]$	IL – rich phase	298.15	1.0105	11.372
		308.15	1.0040	8.1779
		318.15	0.9935	5.9367
		328.15	0.9812	4.5779
	Salt – rich phase	298.15	1.2630	8.8931
		308.15	1.2576	6.4328
		318.15	1.2517	4.7492
		328.15	1.2450	3.5907
$[C_7H_7mim][EtSO_4]$	IL – rich phase	298.15	1.1642	6.9866
		308.15	1.1573	5.0923
		318.15	1.1502	3.8604
		328.15	1.1430	3.0241
	Salt – rich phase	298.15	1.3061	15.242
		308.15	1.3006	10.478
		318.15	1.2944	7.4514
		328.15	1.2876	5.4609
$[C_4mim][N(CN)_2]$	IL – rich phase	298.15	1.0415	4.5958
	Salt – rich phase	298.15	1.3135	17.177
		308.15	1.3076	11.664
		318.15	1.3010	8.2411
$[C_2mim][CF_3SO_3]$	IL – rich phase	298.15	1.2394	3.7823
		308.15	1.2314	2.9436
		318.15	1.2233	2.361
		328.15	1.2151	1.9244
	Salt – rich phase	298.15	1.2911	12.214
		308.15	1.2855	8.5628
		318.15	1.2793	6.177
		328.15	1.2723	4.5755
$[C_4mim][Tos]$	IL – rich phase	298.15	1.1355	9.3852
		308.15	1.1284	6.5792
		318.15	1.1211	4.8017
		328.15	1.1137	3.6367
	Salt – rich phase	298.15	1.2969	15.568

		308.15	1.2912	10.582
		318.15	1.2848	7.4506
		328.15	1.2777	5.3999
$[P_{4444}]Br$	IL – rich phase	298.15	1.0591	19.382
		308.15	1.0515	12.462
		318.15	1.0439	8.5298
		328.15	1.0362	6.1428
	Salt – rich phase	298.15	1.2696	8.1799
		308.15	1.2643	5.9425
		318.15	1.2587	4.4584
		328.15	1.2524	3.4339
$[P_{4444}]Cl$	IL – rich phase	298.15	0.9999	12.795
		308.15	0.9929	8.4367
		318.15	0.9857	5.9034
		328.15	0.9784	4.3341
	Salt – rich phase	298.15	1.2928	13.02
		308.15	1.2876	9.1173
		318.15	1.2819	6.5977
		328.15	1.2757	4.8988
$[P_{i(444)1}][Tos]$	IL – rich phase	298.15	1.0709	14.363
		308.15	1.0638	9.5221
		318.15	1.0566	6.6981
		328.15	1.0493	4.9375
	Salt – rich phase	298.15	1.2802	10.527
		308.15	1.2750	7.5126
		318.15	1.2692	5.5288
		328.15	1.2628	4.1661
$[P_{4441}][CH_3SO_4]$	IL – rich phase	298.15	1.0495	10.385
		308.15	1.0420	7.0628
		318.15	1.0346	5.0561
		328.15	1.0271	3.7836
	Salt – rich phase	298.15	1.3045	14.579
		308.15	1.2991	10.117
		318.15	1.2933	7.2546
		328.15	1.2866	5.3356

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