

Electronic Supplementary Information

One-step extraction and concentration of estrogens for an adequate monitoring of wastewaters using ionic-liquid-based aqueous biphasic systems

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ILs that were not able to form ABS with $\text{KNaC}_4\text{H}_4\text{O}_6$: 1-butyl-3-methylimidazolium chloride ($[\text{C}_4\text{mim}]\text{Cl}$), 1-butyl-3-methylpyridinium chloride ($[\text{C}_4\text{mpy}]\text{Cl}$), 1-butyl-3-methylpiperidinium chloride ($[\text{C}_4\text{mpip}]\text{Cl}$), 1-butyl-3-methylpyrrolidinium chloride ($[\text{C}_4\text{mpyr}]\text{Cl}$), tributyl(methyl)phosphonium chloride ($[\text{Bu}_3\text{MeP}]\text{Cl}$), tetrapropylammonium chloride ($[\text{Pr}_4\text{N}]\text{Cl}$), 1-butyl-3-methylimidazolium tetrafluoroborate ($[\text{C}_4\text{mim}][\text{BF}_4]$), 1-butyl-3-methylimidazolium ethylsulfate ($[\text{C}_4\text{mim}][\text{C}_2\text{H}_5\text{SO}_4]$) and 1-butyl-3-methylimidazolium methylsulfate ($[\text{C}_4\text{mim}][\text{CH}_3\text{SO}_4]$).

Table S 1. Experimental weight fraction data for the system composed of IL (1) + $\text{KNaC}_4\text{H}_4\text{O}_6$ (2) + H_2O (3) at 25 °C and atmospheric pressure.

[C ₄ mim][N(CN) ₂]					
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
61.750	1.320	28.667	10.709	15.225	17.243
56.785	2.068	27.764	10.976	14.451	17.599
52.198	3.012	26.971	11.233	13.675	18.017
48.179	3.712	26.520	11.504	13.125	18.438
45.859	4.445	25.696	11.816	13.006	18.879
44.162	4.759	24.966	12.158	12.329	19.390
42.144	5.441	24.350	12.467	11.085	20.563
40.377	6.030	24.009	12.675	10.278	21.194
38.800	6.529	23.300	13.027	9.703	21.767
37.248	7.038	22.858	13.311	8.534	22.479
36.082	7.413	21.507	13.813	7.496	23.868
34.664	7.835	20.487	14.246	7.044	25.091
33.763	8.227	19.652	14.646	6.059	26.706
32.247	8.934	19.061	15.067	4.809	29.670
30.480	9.567	18.373	15.393	3.636	31.787
29.821	9.818	17.467	15.845	2.390	36.170
29.326	10.222	16.930	16.212		
28.904	10.471	16.154	16.688		

Table S 2. Experimental weight fraction data for the system composed of IL (1) + KNaC₄H₄O₆ (2) + H₂O (3) at 25 °C and atmospheric pressure.

[C ₄ mim][SCN]		[C ₄ mim]Br		[C ₄ mim][CF ₃ CO ₂]	
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
42.840	4.614	66.333	1.090	61.899	2.860
38.031	5.528	58.845	3.038	41.211	10.370
36.609	6.016	49.023	6.062	40.575	10.657
35.344	6.416	39.785	10.175	39.915	10.954
32.819	7.338	37.712	11.639	39.229	11.258
31.791	7.701	36.577	12.095	38.597	11.593
30.678	8.006	36.051	12.517	37.139	12.093
29.039	8.673	34.790	13.159	36.693	12.410
27.331	9.167	34.170	13.668	35.829	12.800
25.639	9.730	33.493	14.199	35.275	13.168
24.571	10.283	32.914	14.727	34.122	14.045
23.874	10.511	31.599	15.511	33.276	14.684
22.434	11.197	30.619	16.169	31.637	15.350
21.844	11.374	29.619	16.931	30.803	15.872
21.124	11.787	28.373	17.826	30.297	16.203
20.168	12.134	27.758	18.517	29.430	16.765
19.488	12.489	26.412	19.524	27.350	17.989
19.081	12.550	24.905	20.691	26.622	18.544
18.713	12.742	23.936	21.639	25.492	19.272
18.143	12.994	22.324	22.943	24.127	20.130
17.554	13.305	21.084	24.104	23.261	20.886
17.219	13.411	18.997	25.786	15.232	26.320
16.674	13.754	17.691	27.108	10.780	31.193
15.765	14.154				
15.373	14.394				
14.332	14.954				
13.407	15.514				
12.802	15.685				
12.061	16.134				
11.057	16.737				
9.865	18.047				
9.128	18.753				
8.400	19.534				
7.935	20.026				

Table S 3. Experimental weight fraction data for the system composed of IL (1) + $\text{KNaC}_4\text{H}_4\text{O}_6$ (2) + H_2O (3) at 25 °C and atmospheric pressure.

[C ₄ mim][TOS]		[C ₂ mim][N(CN) ₂]			
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
59.275	3.832	43.884	7.375	32.579	13.260
53.170	5.336	43.462	7.584	32.314	13.522
47.530	6.973	43.144	7.706	31.735	13.809
41.261	8.972	42.381	7.975	31.376	14.119
38.759	9.262	42.352	8.068	30.648	14.515
37.051	9.952	41.994	8.206	30.004	14.920
32.488	11.936	41.576	8.356	29.653	15.229
28.808	13.715	41.328	8.492	29.064	15.588
24.025	15.984	40.926	8.663	28.577	15.948
19.470	18.503	40.480	8.834	27.522	16.447
14.611	21.324	40.401	8.958	27.206	16.808
		39.897	9.157	26.822	17.181
		39.771	9.290	25.659	17.762
		39.279	9.470	25.134	18.218
		38.770	9.660	24.271	18.688
		38.619	9.791	23.704	19.177
		38.025	10.124	22.944	19.760
		37.480	10.344	22.371	20.240
		37.390	10.498	21.580	20.840
		36.842	10.735	20.141	21.674
		36.683	10.914	19.056	22.114
		36.082	11.186	17.690	22.940
		35.889	11.379	16.777	23.719
		35.171	11.675	16.470	24.333
		35.039	11.869	15.302	25.242
		34.348	12.156	12.423	27.069
		33.841	12.426	9.672	29.395
		33.643	12.651	8.377	31.415
		33.462	12.884		

Table S 4. Experimental weight fraction data for the system composed of IL (1) + KNaC₄H₄O₆ (2) + H₂O (3) at 25 °C and atmospheric pressure.

[C ₆ mim][N(CN) ₂]					
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
41.632	3.503	13.525	10.436	8.805	12.778
38.990	4.044	13.215	10.514	8.707	12.851
36.553	4.508	13.022	10.642	8.572	13.033
33.687	4.875	12.734	10.719	8.398	13.132
30.299	5.669	12.555	10.830	8.314	13.177
28.829	6.125	12.288	10.889	8.228	13.241
26.303	6.724	12.125	11.001	8.164	13.273
22.321	7.737	11.874	11.064	8.042	13.436
21.486	7.947	11.702	11.180	7.962	13.491
20.695	8.081	11.557	11.306	7.891	13.553
20.000	8.207	11.339	11.372	7.821	13.598
19.594	8.422	11.176	11.500	7.736	13.660
18.932	8.592	10.971	11.505	7.630	13.803
18.498	8.801	10.838	11.589	7.563	13.837
17.915	8.926	10.693	11.673	7.486	13.882
17.379	9.030	10.436	11.872	7.422	13.927
17.030	9.248	10.182	12.015	7.321	14.054
16.532	9.363	10.015	12.041	7.153	14.237
16.200	9.581	9.897	12.113	6.362	15.406
15.755	9.699	9.784	12.176	5.925	16.269
15.330	9.773	9.678	12.247	5.291	16.899
15.060	9.942	9.522	12.448	4.887	18.118
14.712	9.997	9.366	12.469	4.301	19.978
14.469	10.124	9.155	12.622	3.555	22.460
14.113	10.204	9.052	12.707		
13.753	10.291	8.904	12.709		

Table S 5. Experimental weight fraction data for the system composed of IL (1) + $\text{KNaC}_4\text{H}_4\text{O}_6$ (2) + H_2O (3) at 25 °C and atmospheric pressure.

[Bu ₄ N]Cl		[Bu ₄ P]Cl	
100 w_1	100 w_2	100 w_1	100 w_2
50.452	1.798	44.790	3.694
47.125	2.435	36.625	6.851
42.879	3.944	34.927	7.422
39.478	5.020	33.414	7.868
36.358	5.986	31.425	8.786
33.825	6.994	28.871	10.198
32.158	7.964	27.394	10.905
28.693	9.862	25.580	11.930
27.036	10.784	23.607	13.203
25.537	11.727	21.952	14.256
23.650	13.046	20.371	15.357
21.965	14.230	18.645	16.654
20.071	15.708	17.050	17.874
15.749	19.362	15.484	19.110
13.940	20.928	13.749	20.591
		12.257	21.893
		10.600	23.433

Table S 6. Correlation parameters used to describe the experimental binodal data by Eq. 1.

IL	$A \pm \sigma$	$B \pm \sigma$	$10^5(C \pm \sigma)$	R^2
[C ₄ mim]Br	86.5 ± 0.9	-0.237 ± 0.004	1.86 ± 0.12	0.9982
[C ₄ mim][CF ₃ SO ₃] ¹	102.4 ± 1.7	-0.464 ± 0.012	68.20 ± 6.10	0.9910
[C ₄ mim][CF ₃ CO ₂]	96.0 ± 1.0	-0.257 ± 0.004	2.71 ± 0.09	0.9990
[C ₄ mim][SCN]	111.2 ± 3.3	-0.441 ± 0.012	9.71 ± 0.52	0.9983
[C ₄ mim][TOS]	118.0 ± 4.1	-0.345 ± 0.014	5.14 ± 0.58	0.9982
[C ₂ mim][N(CN) ₂]	85.9 ± 0.9	-0.245 ± 0.003	3.17 ± 0.62	0.9995
[C ₄ mim][N(CN) ₂]	94.2 ± 1.4	-0.346 ± 0.006	6.61 ± 0.32	0.9970
[C ₆ mim][N(CN) ₂]	166.0 ± 8.0	-0.712 ± 0.021	16.59 ± 1.66	0.9918
[Bu ₄ P]Cl	84.3 ± 1.7	-0.322 ± 0.008	4.10 ± 0.24	0.9990
[Bu ₄ N]Cl	75.6 ± 1.0	-0.296 ± 0.006	3.82 ± 0.36	0.9987

Table S 7. Percentage extraction efficiencies of EE2 ($EE_{EE2}\%$) in IL-based ABS and respective mixture compositions.

IL	weight fraction percentage / wt %		$EE_{EE2}\% \pm \sigma$	Obs.
	$[IL]_M$	$[salt]_M$		
IL effect				---
[C ₄ mim][N(CN) ₂]	23.9	15.0	100.0 ± 0.2	
[C ₄ mim][TOS]	30.4	15.0	92.2 ± 0.6	
[C ₄ mim][SCN]	31.2	10.3	94.8 ± 1.0	
[C ₄ mim][CF ₃ SO ₃]	4.50	40.0	96.5 ± 0.6	
[Bu ₄ P]Cl	24.8	15.6	99.4 ± 0.2	
[Bu ₄ N]Cl	25.2	15.0	99.6 ± 0.3	
TLL effect				TLL
	29.9	12.3	100.0 ± 0.2	46.7
	29.9	13.5	100.0 ± 0.2	53.8
[C ₄ mim][N(CN) ₂]	29.9	15.1	100.0 ± 0.2	60.3
	30.0	19.9	100.0 ± 0.2	68.8
Concentration of EE2				CF^a
	30.0	19.9	100.0 ± 0.2	1.1
	21.4	25.0	100.0 ± 0.2	1.8
	13.1	29.9	100.0 ± 0.2	3.3
[C ₄ mim][N(CN) ₂]	6.09	34.0	100.0 ± 0.2	10.0
	2.69	36.00	---	~ 100
	2.43	36.15	---	~ 1000

^a CF – concentration factor

References

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