

Supporting Information

A Critical Assessment on the Formation of Ionic-Liquid-Based Aqueous Two-Phase Systems in Acidic Media

Ana Filipa M. Cláudio¹, Ana M. Ferreira¹, Shahla Shahriari², Mara G. Freire^{1} and João A. P. Coutinho¹*

¹Departamento de Química, CICECO, Universidade de Aveiro, 3810-193 Aveiro, Portugal

²Department of Chemical Engineering, Shahr-e-Qods Branch, Islamic Azad University,
Iran

*Corresponding author

Tel: +351-234-370200; Fax: +351-234-370084.

E-mail address: maragfreire@ua.pt (M. G. Freire).

Table S1. Initial weight fraction compositions used in the determination of the phase diagrams and indication of the possibility of forming liquid-liquid equilibrium systems.

IL + Na ₂ SO ₄ + Water system	Weight fraction composition / (wt %)		LLE
	IL	Na ₂ SO ₄	
[C ₂ mim][CH ₃ SO ₄]	59.94	24.89	✗
[C ₂ mim][CF ₃ SO ₃]	59.17	24.89	✓
[C ₄ mim]Cl	79.61	24.89	✗
	78.38	24.89	✗
	69.70	24.89	✗
	79.43	24.17	✗
	70.05	24.17	✗
	63.73	24.08	✗
	49.69	24.08	✗
[C ₄ mim]Br	59.40	24.89	✓
[C ₄ mim][CH ₃ CO ₂]	62.06	24.89	✗
[C ₄ mim][CF ₃ SO ₃]	59.41	24.98	✓
[C ₄ mim][N(CN) ₂]	60.45	24.98	✓
[C ₄ mim][HSO ₄]	60.05	24.98	✗
[C ₄ mim][CH ₃ SO ₄]	59.46	24.98	✓
[C ₄ mim][C ₂ H ₅ SO ₄]	60.83	24.98	✓
[C ₄ mim][TOS]	59.43	24.98	✓
[C ₄ mim][SCN]	59.29	24.48	✓
[C ₄ mim][CF ₃ CO ₂]	59.84	23.85	✓
[C ₄ mim][OctylSO ₄]	59.27	24.15	✓
[C ₆ mim]Cl	61.52	24.89	✗
[C ₇ mim]Cl	59.27	24.98	✓
[amim][C ₂ H ₅ SO ₄]	63.51	24.89	✗
[C ₇ H ₇ mim]Cl	78.64	24.98	✗
	60.68	24.50	✓
[C ₇ H ₇ mim][C ₂ H ₅ SO ₄]	60.36	24.50	✓
[C ₄ mim][DMP]	58.74	24.98	✗
[C ₄ mpyr]Cl	59.85	24.98	✗
	46.60	24.98	✗
[C ₄ mpip]Cl	59.19	24.98	✗

[C ₄ mpy]Cl	59.58	24.89	✘
[C ₈ py][N(CN) ₂]	60.42	24.98	✓

✘: a liquid-liquid two-phase system was not observed

✓: a liquid-liquid two-phase system was observed

Table S2. Weight fraction binodal data for the ternary systems with the ILs (1) [C₄mim]Br and [C₇mim]Cl, Na₂SO₄ (2) and water (3) at 298 K.

[C ₄ mim]Br $M_w = 219.12$		[C ₇ mim]Cl $M_w = 216.75$	
100 w_1	100 w_2	100 w_1	100 w_2
54.0393	2.2450	49.1640	4.5704
50.0374	2.9426	46.0364	5.4667
46.3758	3.5181	42.2129	6.7470
42.6690	4.3629	36.0936	8.9788
40.7340	4.9203		
39.1392	5.3432		
34.1860	7.1392		

Table S3. Weight fraction binodal data for the ternary systems with the ILs (1) [C₄mim][CF₃SO₃] and [C₇H₇mim]Cl, Na₂SO₄ (2) and water (3) at 298 K.

[C ₄ mim][CF ₃ SO ₃] $M_w = 288.29$				[C ₇ H ₇ mim]Cl $M_w = 208.69$	
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
55.9574	1.7420	15.1997	6.4856	52.1187	3.4585
49.4163	2.1839	14.4891	6.9713	46.5538	4.8036
42.6622	2.5451	12.2491	7.8038	40.8953	6.1407
34.8741	3.1113	11.5476	8.2326	37.6422	7.2163
32.6968	3.3737	11.0102	8.5085	33.4692	8.8851
30.5625	3.6435	10.0308	9.1107		
29.0106	3.7196	9.3828	9.5904		
27.7697	3.9934	8.8289	10.1775		
26.0803	4.1160	7.7806	11.0171		
24.7855	4.3262	7.1237	11.6274		
23.4750	4.3606	6.7579	12.1002		
22.8571	4.5089	5.8257	13.2419		
21.6940	4.7606	5.2346	13.9924		
20.6162	5.0007	4.6460	14.9558		
19.2576	5.3606	4.2967	15.4922		
17.9431	5.6416	3.8793	16.2220		
16.7055	5.9138	3.5031	16.9919		
16.0429	6.1503				

Table S4. Weight fraction binodal data for the ternary system with the IL (1) [C₄mim][TOS], Na₂SO₄ (2) and water (3) at 298 K.

[C ₄ mim][TOS] $M_w = 310.42$					
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
55.1134	2.1965	19.3974	11.2545	11.2386	14.6425
52.3394	2.6370	19.0500	11.4263	10.8706	14.8501
49.0955	2.8920	18.5964	11.5308	10.5177	15.0144
47.6123	3.1879	18.2917	11.6676	10.3712	15.1164
45.5860	3.4124	17.9707	11.8142	10.1745	15.2113
44.3467	3.7432	17.6109	12.0100	10.0096	15.3772
43.0472	4.0834	17.4088	12.0376	9.8803	15.4039
40.4762	4.7220	17.1820	12.1230	9.6622	15.5324
38.3937	5.2297	16.8909	12.2817	9.4526	15.6658
36.5879	5.6003	16.4149	12.4691	9.2542	15.7874
35.8001	5.7930	16.2235	12.4916	9.0369	15.9254
35.0292	6.0081	15.9246	12.6629	8.6186	16.1558
34.1439	6.3172	15.7350	12.7080	8.3261	16.3428
33.3922	6.5271	15.5763	12.7441	8.0952	16.4750
32.5639	6.7218	15.4164	12.8053	7.9051	16.5861
31.9451	6.9343	15.1744	12.9359	7.5276	16.8535
31.2862	7.1026	15.0058	12.9715	7.2816	17.0011
30.6430	7.2707	14.7916	13.0911	6.9570	17.2276
30.0079	7.3962	14.5786	13.2072	6.6214	17.5031
29.4015	7.5716	14.3603	13.3118	6.2816	17.7352
28.8451	7.7471	14.2303	13.3293	6.0770	17.9045
28.3121	7.9154	13.9992	13.4720	5.9626	18.0061
26.5392	8.5570	13.8788	13.4957	5.7514	18.2244
25.8754	8.8774	13.6864	13.5946	5.4535	18.4622
25.5197	8.9404	13.3823	13.7201	5.2532	18.6667
24.9577	9.1554	13.2580	13.7511	5.1007	18.7947
24.4377	9.3715	13.1571	13.7965	4.9191	18.9523
24.0474	9.4984	12.9707	13.9066	4.8301	19.0611
23.5909	9.6437	12.8544	13.9330	4.6437	19.2740
22.8076	9.8880	12.6924	14.0296	4.3385	19.5714
22.2451	10.1692	12.5264	14.1223	4.0870	19.8312
21.2068	10.4920	12.4110	14.1580	3.8341	20.2070
20.8417	10.6302	12.2465	14.2600	3.6212	20.4269
20.4646	10.7767	12.1334	14.2944	3.4326	20.6973
20.0577	10.9956	11.7681	14.3944	3.2827	20.8456
19.7507	11.0861	11.4662	14.5194		

Table S5. Weight fraction binodal data for the ternary system with the IL (1) [C₄mim][N(CN)₂], Na₂SO₄ (2) and water (3) at 298 K.

[C ₄ mim][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	100 <i>w</i> ₁	100 <i>w</i> ₂
59.2507	0.5991	19.3120	9.2399	10.5544	13.2900
54.8690	1.1009	18.9342	9.4514	10.2598	13.3806
51.8550	1.6138	18.4497	9.6099	10.1166	13.4258
47.9001	1.9655	17.9810	9.7746	10.0147	13.5064
45.7296	2.3546	17.7649	9.8481	9.8187	13.6411
43.2478	2.6726	17.5410	9.9005	9.6239	13.7901
41.4875	3.0222	17.3206	9.9768	9.3697	13.9669
39.7641	3.3222	17.1234	10.0482	9.0471	14.1683
38.7154	3.6490	16.9255	10.1182	8.8929	14.2606
37.4124	3.9044	16.6287	10.2968	8.7105	14.4260
35.9524	4.1705	16.2728	10.4175	8.3211	14.7223
34.7078	4.4181	16.0995	10.4923	8.0822	14.8679
33.9512	4.6701	15.9253	10.5539	7.8427	15.0854
32.7114	4.9416	15.7515	10.6159	7.4506	15.4000
31.9583	5.1872	15.5882	10.6604	7.1248	15.6940
31.2631	5.3689	15.3151	10.8452	6.7903	16.0136
30.3312	5.4886	15.1581	10.9127	6.5486	16.2837
29.6970	5.7078	14.9995	10.9872	6.4309	16.3862
29.1123	5.8740	14.8507	11.0481	6.3199	16.5247
28.5183	6.1085	14.6931	11.0881	6.1377	16.7014
27.9697	6.3166	14.4710	11.2360	5.9503	16.9071
27.1516	6.4626	14.1961	11.3348	5.7490	17.1101
26.5973	6.6612	14.0631	11.3673	5.3191	17.9163
25.5167	7.0438	13.9227	11.4104	5.2314	17.8581
25.0388	7.2168	13.7166	11.5710	5.1330	17.9955
24.5804	7.4327	13.4617	11.6521	5.0040	18.2019
24.1565	7.5785	13.1654	11.8092	4.7432	18.5431
23.7470	7.7101	12.8565	11.9486	4.5561	18.8122
23.3335	7.8485	12.6568	12.0365	4.4179	19.0152
22.9589	8.0339	12.4205	12.1512	4.3237	19.1583
22.2747	8.2669	12.2737	12.2618	4.1728	19.4197
21.6125	8.5008	11.9127	12.4634	3.9017	19.8292
20.9677	8.7064	11.7399	12.5114	3.7390	20.1007
20.6801	8.7899	11.6039	12.5993	3.6139	20.3203
20.3732	8.8735	11.3870	12.7199	3.4851	20.5542
19.8287	9.0598	11.1653	12.8373	3.3498	20.8181
19.5651	9.1478	10.9648	12.9529		

Table S6. Weight fraction binodal data for the ternary systems with the ILs (1) [C₈py][N(CN)₂] and [C₂mim][CF₃SO₃], Na₂SO₄ (2) and water (3) at 298 K.

[C ₈ py][N(CN) ₂] <i>M_w</i> = 258.36				[C ₂ mim][CF ₃ SO ₃] <i>M_w</i> = 260.24	
100 <i>w</i> ₁	100 <i>w</i> ₂	100 <i>w</i> ₁	100 <i>w</i> ₂	100 <i>w</i> ₁	100 <i>w</i> ₂
57.5580	1.2385	15.1578	5.5323	53.3158	2.4638
43.6287	2.0683	15.0073	5.5637	49.4139	3.0753
39.1437	2.2653	14.8937	5.6462	44.4428	3.7831
33.8130	2.6257	14.7083	5.7134	43.1016	3.9712
31.2184	2.9191	14.5026	5.7610	41.2364	4.3877
28.7135	3.1255	14.3661	5.7754	39.5981	4.8028
27.4374	3.3485	14.2455	5.8154	38.1521	5.2062
26.1565	3.4498	14.1186	5.8513	36.4040	5.6931
25.4447	3.4785	13.9139	5.8647	34.7971	6.1124
25.1179	3.5793	13.8500	5.9203	33.4398	6.4554
24.4985	3.6185	13.6765	5.9861	32.2907	6.7684
24.0542	3.6921	13.3575	6.0368	30.7529	7.2544
23.7701	3.7390	13.2439	6.0828	29.6633	7.5532
23.2812	3.8205	13.1093	6.1252	28.3340	8.0048
22.8095	3.8829	12.8933	6.2292	27.4934	8.2396
22.2150	3.9714	12.6171	6.3006	26.6661	8.5056
21.7859	4.0411	12.4076	6.4226	25.5859	8.8881
21.4472	4.1088	11.8153	6.5740	24.8934	9.1017
20.0571	4.3784	11.5904	6.7487	23.9731	9.4298
19.7457	4.5182	11.0104	6.8955	23.3184	9.5977
19.3349	4.5297	10.7827	6.9758	22.5173	9.9069
19.0429	4.5861	10.4877	7.1538	21.9252	10.0743
18.8071	4.7018	9.9474	7.5127	21.1417	10.3506
18.3628	4.7188	9.4912	7.5706	20.3808	10.6432
18.0543	4.8616	9.2734	7.7176	19.5504	10.9968
17.6229	4.8907	8.9230	7.8876	18.9203	11.2141
17.4320	4.9866	8.5210	8.0841	18.1378	11.5603
17.1705	5.0127	8.2254	8.2800	17.6013	11.7560
17.0422	5.0789	7.9646	8.4414	17.0099	12.0153
16.8599	5.1180	7.7605	8.4937	16.4263	12.2785
16.7032	5.1333	7.2879	8.7874	15.7777	12.6050
16.5480	5.1933	6.8013	9.1839	15.1860	12.8932
16.4349	5.2182	6.0454	9.8807	14.6977	13.1162
16.3280	5.2782	5.5230	10.3016	14.0930	13.4521
16.1708	5.2916	5.2292	10.5481	12.5720	14.3292
16.0378	5.3457	4.7336	11.0829	11.5895	14.8978
15.8360	5.3427	4.2814	11.6575	10.8252	15.3583
15.7188	5.3703	3.8289	12.2741	9.4095	16.4006
15.4709	5.5858	3.4029	12.9468	8.1689	17.4210

Table S7. Weight fraction binodal data for the ternary systems with the ILs (1) [C₇H₇mim][C₂H₅SO₄], [C₄mim][CH₃SO₄] and [C₄mim][C₂H₅SO₄], Na₂SO₄ (2) and water (3) at 298 K.

[C ₇ H ₇ mim][C ₂ H ₅ SO ₄] <i>M_w</i> = 298.36		[C ₄ mim][CH ₃ SO ₄] <i>M_w</i> = 250.32		[C ₄ mim][C ₂ H ₅ SO ₄] <i>M_w</i> = 265.35	
100 <i>w</i> ₁	100 <i>w</i> ₂	100 <i>w</i> ₁	100 <i>w</i> ₂	100 <i>w</i> ₁	100 <i>w</i> ₂
53.3251	2.8555	53.3183	3.1271	56.8853	1.7503
50.0374	3.4612	46.1214	4.4358	41.9873	4.2498
46.1067	4.0318	40.6256	5.4312	39.0972	5.0302
44.4395	4.2513	38.7093	5.9070	36.8093	5.8472
43.1716	4.5200	37.2599	6.5209	34.5103	6.4383
41.4795	5.0534	34.6465	7.4609	33.3151	6.8799
40.5604	5.3062	33.4808	7.9653	30.8742	7.8076
39.5924	5.5147	32.3996	8.4007	29.5095	8.4032
38.3225	5.8618	31.3748	8.8180	27.6936	9.1974
37.5132	6.0479	30.0638	9.4826	26.3776	9.8560
36.2727	6.4353	28.6195	10.2025	25.0556	10.5662
33.7954	7.4438	27.5691	10.7060	22.2210	12.1135
32.3485	7.9584	26.4669	11.2814	18.6276	14.2831
30.7323	8.5199	24.8772	12.1464	17.3126	15.0240
29.6636	8.8972	23.2223	13.1486	15.7241	16.0192
28.7666	9.1631	22.0758	13.7757	14.2479	16.9511
27.3528	9.7434	20.8716	14.4885	12.3795	18.1727
26.4785	10.0547	19.5884	15.2581		
25.6092	10.3728	18.4211	15.9849		
24.3068	10.9243	17.4049	16.6016		
23.7376	11.0762	16.3759	17.2508		
22.7202	11.4954	15.4763	17.8197		
21.9493	11.8047	14.4705	18.4983		
20.8771	12.2551	13.6965	19.0167		
20.1465	12.5739	12.6420	19.7702		
19.4855	12.8456	11.6527	20.4815		
18.8382	13.1165	9.7585	21.9799		
18.1796	13.3200				
17.2887	13.7520				
16.8193	13.9515				
16.2200	14.2279				
15.6623	14.4678				
15.0916	14.7390				
14.5730	14.9957				
13.4582	15.6343				
12.7531	15.9859				
12.2490	16.2463				
10.5122	17.2697				

Table S8. Weight fraction binodal data for the ternary system with the IL (1) [C₄mim][SCN], Na₂SO₄ (2) and water (3) at 298 K.

[C ₄ mim][SCN] $M_w = 197.30$					
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
57.5738	0.8303	27.0777	5.9257	18.7073	8.2460
53.9628	1.1600	26.7329	6.0279	18.5045	8.3199
50.9712	1.4404	26.3934	6.1002	18.3465	8.3502
48.5957	1.7133	25.7872	6.3460	18.1373	8.4248
46.2918	1.9667	25.2506	6.4612	17.9912	8.4612
44.9986	2.1794	24.9732	6.5155	17.8621	8.4865
43.3866	2.4218	24.2380	6.5705	17.6217	8.5751
41.9224	2.6317	23.8769	6.6026	17.4784	8.6025
41.1097	2.8108	23.5712	6.6940	17.2918	8.6740
40.0127	2.9660	23.2450	6.8028	17.0928	8.7502
39.3305	3.1692	23.0628	6.8562	16.8122	8.8477
37.9443	3.3599	22.6677	7.0242	16.4956	8.9395
37.0014	3.5453	22.4352	7.0664	16.2992	8.9908
36.1788	3.7815	21.9488	7.3073	16.0377	9.1371
35.4258	3.9700	21.4429	7.4431	15.6756	9.2550
34.4680	4.1346	20.9500	7.5668	15.3430	9.3395
33.7604	4.3214	20.6933	7.6422	14.9245	9.5164
33.0829	4.4905	20.4880	7.6787	14.5155	9.6889
32.4038	4.6906	20.3089	7.7213	14.1601	9.7929
31.5563	4.8243	20.1169	7.7828	13.7544	9.9780
30.5506	5.1218	19.8958	7.8798	13.3260	10.1127
29.8752	5.2292	19.6628	7.9419	12.7376	10.3386
28.8476	5.5606	19.4473	8.0189	12.3677	10.5710
28.0485	5.6835	19.0982	8.0954		
27.5575	5.8476	18.8970	8.1739		

Table S9. Weight fraction binodal data for the ternary systems with the IL (1) [C₄mim][OctylSO₄] and [C₄mim][CF₃CO₂], Na₂SO₄ (2) and water (3) at 298 K.

[C ₄ mim][OctylSO ₄] <i>M_w</i> = 348.50				[C ₄ mim][CF ₃ CO ₂] <i>M_w</i> = 252.23	
100 <i>w</i> ₁	100 <i>w</i> ₂	100 <i>w</i> ₁	100 <i>w</i> ₂	100 <i>w</i> ₁	100 <i>w</i> ₂
50.4923	3.7322	27.6961	7.4667	52.0163	2.9569
48.8330	3.9844	27.2000	7.4998	50.0083	3.4104
47.5778	4.1861	26.7533	7.6143	47.4128	3.9047
46.0034	4.3229	26.4212	7.6527	46.1852	4.1153
45.0137	4.4907	26.0906	7.7589	44.2050	4.5090
43.2074	4.7404	25.6888	7.7814	42.1174	5.0320
42.2903	4.9300	25.1558	7.9939	40.0146	5.6424
40.9665	5.0396	24.8323	8.0256	38.2476	6.1923
40.2341	5.1995	24.5738	8.0619	37.1187	6.5210
39.4277	5.3508	24.2490	8.1319	35.4945	7.0556
37.8899	5.5494	23.9253	8.2085	33.3666	7.8645
37.1916	5.7023	23.6289	8.2789	31.4022	8.5822
36.5527	5.7813	23.3233	8.3292	28.4571	9.8569
35.9582	5.9066	22.7524	8.5529		
35.3766	6.0282	22.1483	8.6323		
34.6075	6.1082	21.8718	8.6771		
34.1392	6.1778	21.5108	8.8381		
33.7578	6.2388	20.9420	8.9397		
33.1989	6.3988	20.6728	8.9856		
32.6786	6.4804	20.1839	9.1524		
31.9347	6.5848	19.9185	9.1854		
31.4104	6.7138	19.4921	9.2927		
30.8496	6.7845	19.0831	9.4403		
30.4399	6.8696	18.6507	9.5428		
29.9646	6.9850	18.4249	9.5825		
29.4289	7.1115	18.1628	9.6761		
28.5336	7.2650	17.8320	9.7534		
28.1409	7.3259				

Table S10: pH values of the co-existing phases in IL- Na_2SO_4 -based ATPS at the biphasic composition of 25 wt % of IL + 15 wt % of Na_2SO_4 + 60 wt % of water (at 298 K), and the Na_2SO_4 speciation³¹ in aqueous solution.

IL+ Na_2SO_4 + water system		$[\text{HSO}_4^-]/[\text{H}_2\text{SO}_4]$	$[\text{SO}_4^{2-}]/[\text{HSO}_4^-]$
[C ₂ mim][CF ₃ SO ₃]	Na ₂ SO ₄ -rich phase	5.01×10^9	2.09×10^1
	IL-rich phase	1.23×10^9	5.13×10^0
[C ₄ mim][CF ₃ SO ₃]	Na ₂ SO ₄ -rich phase	2.63×10^9	1.10×10^1
	IL-rich phase	3.16×10^9	1.32×10^1
[C ₄ mim]Br	Na ₂ SO ₄ -rich phase	3.98×10^{11}	1.66×10^3
	IL-rich phase	6.46×10^{11}	2.69×10^3
[C ₄ mim][CH ₃ SO ₄]	Na ₂ SO ₄ -rich phase	8.92×10^7	3.72×10^{-1}
	IL-rich phase	1.82×10^8	7.59×10^{-1}
[C ₄ mim][C ₂ H ₅ SO ₄]	Na ₂ SO ₄ -rich phase	4.68×10^7	1.95×10^{-1}
	IL-rich phase	4.68×10^8	1.95×10^0
[C ₄ mim][OctylSO ₄]	Na ₂ SO ₄ -rich phase	7.95×10^9	3.31×10^1
	IL-rich phase	1.05×10^{10}	4.37×10^1
[C ₄ mim][N(CN) ₂]	Na ₂ SO ₄ -rich phase	2.82×10^{14}	1.17×10^6
	IL-rich phase	8.32×10^{14}	3.47×10^6
[C ₄ mim][TOS]	Na ₂ SO ₄ -rich phase	3.47×10^{11}	1.45×10^3
	IL-rich phase	5.13×10^{11}	2.14×10^3
[C ₄ mim][SCN]	Na ₂ SO ₄ -rich phase	4.68×10^{10}	1.95×10^2
	IL-rich phase	7.42×10^{10}	3.09×10^2
[C ₄ mim][CF ₃ CO ₂]	Na ₂ SO ₄ -rich phase	3.47×10^{10}	1.45×10^2
	IL-rich phase	3.63×10^{10}	1.51×10^2
[C ₇ mim]Cl	Na ₂ SO ₄ -rich phase	3.47×10^{10}	1.45×10^2

	IL-rich phase	3.39×10^{10}	1.41×10^2
[C ₇ H ₇ mim]Cl	Na ₂ SO ₄ -rich phase	1.05×10^{11}	4.37×10^2
	IL-rich phase	6.61×10^{10}	2.75×10^2
[C ₇ H ₇ mim][C ₂ H ₅ SO ₄]	Na ₂ SO ₄ -rich phase	2.69×10^8	1.12×10^0
	IL-rich phase	2.89×10^8	1.20×10^0
[C ₈ py][N(CN) ₂]	Na ₂ SO ₄ -rich phase	2.82×10^{13}	1.17×10^5
	IL-rich phase	2.09×10^{13}	8.71×10^5