Electronic Supplementary Material (ESI) for Green Chemistry.

Electronic Supporting Information

Switchable (pH-Driven) Aqueous Biphasic Systems formed by Ionic Liquids as Integrated Production-Separation Platforms

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Materials

Potassium citrate tribasic monohydrate, $K_3C_6H_5O_7.H_2O$ (≥ 99 wt% pure), was from Sigma–Aldrich, citric acid monohydrate, $C_6H_8O_7.H_2O$ (100 wt% pure), from Fisher Scienti c, and potassium hydroxide, KOH (pure), from Pronalab.

The ionic liquids (ILs) used were 1-butyl-3-methylimidazolium chloride, $[C_4C_1im]Cl$ (99 wt%); 1-butyl-3-methylpyridinium chloride, $[C_4C_1py]Cl$ (> 98 wt%); 1-butyl-1-methylpiperidinium chloride, $[C_4C_1pip]Cl$ (99 wt%); tetrabutylphosphonium chloride, $[P_{4444}]Cl$ (98 wt%); 1-butyl-3-methylimidazolium bromide, $[C_4C_1im]Br$ (99 wt%); and 1-butyl-2,3-dimethylimidazolium chloride, $[C_4C_1C_1im]Cl$ (98wt%). The chemical structures of the investigated ILs are depicted in Fig. S1. All imidazolium-, pyridinium-, and pyrrolidinium-based ILs were purchased from Iolitec. The $[P_{4444}]Cl$ was kindly supplied by Cytec Industries Inc. Before use, each IL was dried for a minimum of 24h, at moderate temperature (60 °C), under constant agitation and vacuum.

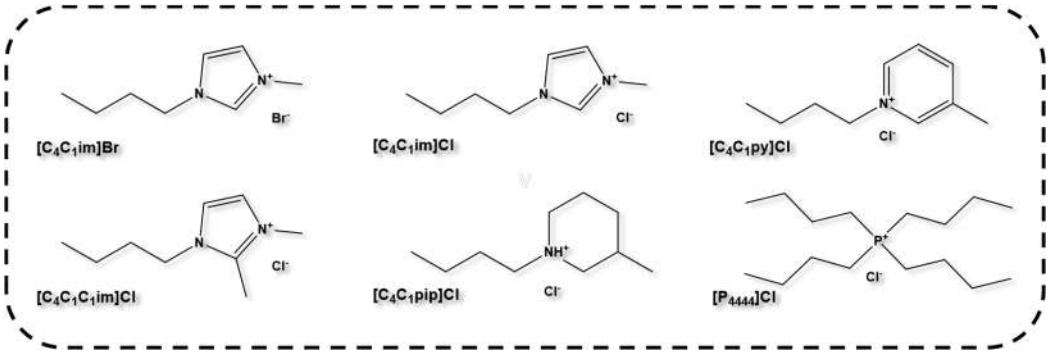


Fig. S1. Chemical structures of the ILs investigated.

For the production of 5-hydroxymetilfurfural (HMF) it was used D-(-)-fructose (purity ≥ 98 wt%) from Panreac. Pure HMF (purity ≥ 99 wt%) from Sigma-Aldrich was used as a standard and to establish the calibration curve required for HMF quantification by HPLC. The following solvents were additional used for HPLC analysis: methanol (purity ≥ 99.99 wt%) from Fisher Chemical, and ultra-pure water (purity ≥ 99.99 wt%) from Merck. Syringe filters (0.45 μm) acquired at GE healthcare Whatman were used.

Experimental Procedure

Determination of the ABS phase diagrams. The binodal curves were determined through the cloud point titration method (previously described by us[1]) at (25 ± 1) °C and atmospheric pressure, using aqueous solutions of salt at around 50 wt% and aqueous solutions of the different hydrophilic ILs with concentrations ranging from 60 wt% to 90 wt%. It was carried out the addition of the salt aqueous solution to the IL aqueous solution, and *vice-versa*, to determine the phase diagrams. All the additions were carried out under constant stirring. The ternary system compositions were determined by weight quanti cation within ± 10^{-4} g.

The determination of the tie-lines (TLs) was carried out by a gravimetric approach initially proposed by Merchuk et al.[2]. Ternary mixtures composed of ionic liquid + $K_3C_6H_5O_7/C_6H_8O_7$ + water at the biphasic region were gravimetrically prepared within ± 10^{-4} g, vigorously agitated, and left under equilibrium for 12 h at (25 ± 1) °C. Both phases were then separated and individually weighted. Each TL was determined through the relationship between the top phase composition, the overall system composition, and weight of the two phases.[3]

The pH of each aqueous phase was determined at (25 ± 1) °C using an HI 9321 Microprocessor pH meter (HANNA instruments).

Production and separation of HMF. Fructose (0.30 g), an aqueous solution of citric acid at 50 wt% (0.75 g, pH ≈ 1.5) and ionic liquid (1 g) were added to a glass reaction vial, and left for reaction under a constant temperature of 80 °C, during 80 min. The reaction system was cooled down to room temperature, and potassium hydroxide was added up to a pH ≈7 (with the simultaneous formation of two phases, IL-based ABS). The amounts of HMF and fructose in the two phases were analysed by HPLC. Each procedure has been repeated at least for three times.

Quantification of HMF and fructose by HPLC. The quanti cation of HMF and fructose in both aqueous phases was carried out by HPLC. Blank control samples were used to evaluate the possible interferences of the salt and ILs in the quanti cation. An HPLC-DAD (DIONEX ultimate 3000 DAD) was used for the quantification of HMF, and HPLC analyses were performed with an analytical C18 reversed-phase column (250 × 4.60 mm 10 µ), SPHERISORB S10 ODS 2. The mobile phase consisted of a mixture of methanol and water (1:4, v:v). The separation was conducted in isocratic mode, at a flow rate of 0.6 mL·min ^{1} and using an injection volume of 20 µL. DAD was set at 284 nm. Each sample was analysed at least in duplicate. The column oven was operated at a controlled temperature of 35 °C. Calibration curves were previously prepared using the pure/standard HMF dissolved in ultra-pure water. At the described conditions, HMF displays a retention time of 6.9 min.

The quantification of fructose in each phase was carried out by HPLC-RID (Gilson Model 131). HPLC analyses were performed with a sugar-alcohol column (250 × 4.60 mm 8 µ), REZEX RCU-USP, from Phenomenex. The mobile phase consisted of 100% of ultra-pure water. The separation was conducted in isocratic mode, at a flow rate of 0.1 mL·min ^{1} and using an injection volume of 20 µL. Each sample was analysed at least in duplicate. The column oven was operated at a controlled temperature of 60 °C. Calibration curves were prepared using the pure/standard fructose sample dissolved in ultra-pure water. At the described conditions, fructose displays a retention time of 17.7 min.

Experimental Results

Fig. S2 depicts the speciation curves of citric acid as a function of the pH. The experimental weight fraction data for the determined phase diagrams are provided in Tables S1-S11. Fig. S3. depicts the phases diagrams at different pH vales for the ILs investigated. Table S12 presents the regression of the experimental binodal data for the systems studied, and Table S12 shows the information on the experimental tie-lines, along with their respective length (TLL). Fig. S4 depicts the phases diagrams for the different ILs at a fixed pH.

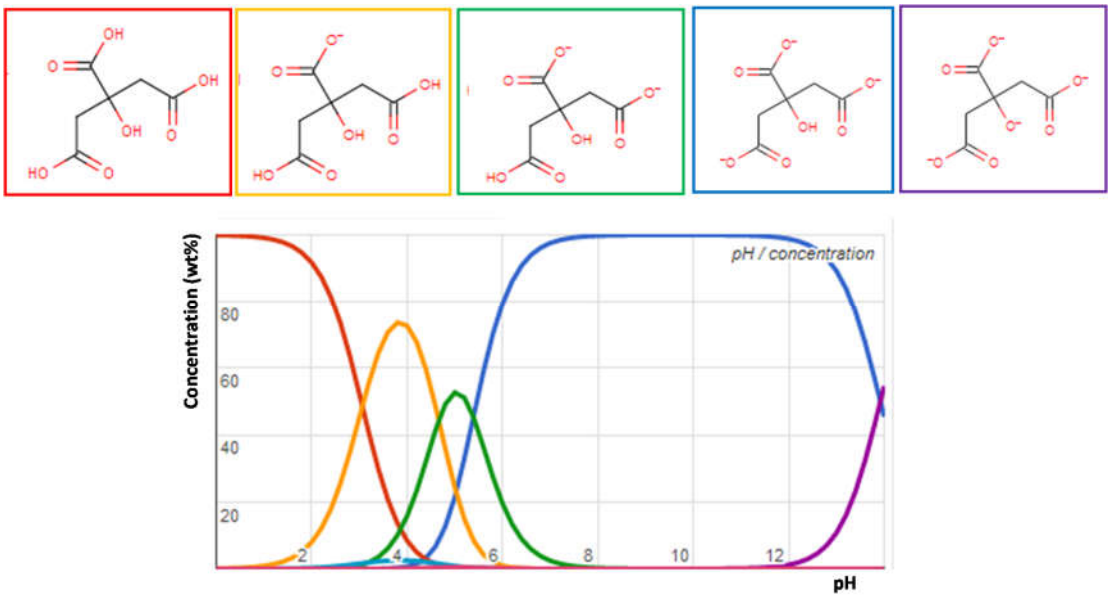


Fig. S2. Speciation curves of citric acid as a function of pH.[3]

Table S1. Experimental weight fraction data for the systems composed of $[C_4C_1im]Cl$ (1) + salt (2) + H_2O (3) at 25 °C and at atmospheric pressure.

pH≈9		pH≈8		pH≈7	
100 w1	100 w2	100 w1	100 w2	100 w1	100 w2
16.0591	39.9485	16.3947	39.7533	14.7563	42.5266
17.9726	37.6514	18.1351	37.5613	16.5634	40.2903
19.6938	35.5432	20.6379	34.6574	18.1753	38.2234
21.1447	33.6433	22.9777	32.3000	20.4143	35.8728
22.9233	31.5002	24.8409	30.2236	22.3989	33.6556
25.3400	28.4100	26.5139	28.3980	23.6100	32.1799
28.3300	25.8100	28.5845	26.3586	25.3891	30.4357
30.9800	23.1000	29.8132	24.9234	26.9197	28.8631
32.3000	21.8400	31.7043	23.2323	28.1425	27.4771
33.7700	20.5200	33.1419	21.8759	29.3640	26.1079
34.9000	19.3900	33.9817	20.9766	30.5421	24.8985
35.9100	18.5100	35.0461	19.9804	31.6398	23.8687
37.4900	17.0100	36.1685	19.0202	32.9935	22.6317
39.0000	15.8200	36.8758	18.3354	33.8930	21.7312
42.9530	13.7150	37.8069	17.5496	34.7234	20.9158
49.4490	9.4070	38.6094	16.8158	35.8402	19.9569
54.4870	6.5200	39.3870	16.1450	36.5202	19.2637
58.9900	4.3630	40.6013	15.3096	37.6967	18.3265
62.7670	2.9200	41.4766	14.6329	38.7095	17.4915
68.6300	1.5800	42.2971	14.0321	39.5328	16.7724
		43.2780	13.3493	40.2287	16.1767
		44.3115	12.6948	41.1063	15.5093
		44.9843	12.1720	41.7192	14.9869
		45.7937	11.6260	42.4183	14.4346
		46.4473	11.1761	43.2104	13.8353
		46.9252	10.8470	43.8263	13.3640
		47.6044	10.4271	44.6029	12.8143
		48.2284	10.0283	45.1577	12.4218
		48.7219	9.7110	45.7855	11.9815
		49.3645	9.3324	46.3013	11.6199
		49.9221	9.0053	46.6216	11.3363
		50.4147	8.7071	47.0996	11.0136
		51.0178	8.3643	47.6565	10.6718
		55.9191	6.2504	48.0247	10.4504
		62.8618	2.9875	48.5419	10.1118
		71.7474	1.5942	49.1112	9.7797
				49.6217	9.4639
				50.0253	9.2153
				50.3852	8.9873

Table S2. Experimental weight fraction data for the systems composed of $[C_4C_1C_1im]Cl$ (1) + salt (2) + H_2O (3) at 25 °C and at atmospheric pressure.

pH≈9		pH≈8		pH≈7	
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
17.5639	39.8362	20.7075	36.3945	22.4236	35.3274
20.0557	37.4146	22.5899	34.4799	23.3368	33.4880
21.6310	35.2678	23.9211	32.5651	26.1175	30.6571
23.6885	33.0411	25.0982	30.8423	27.8648	28.8437
25.6583	31.0179	27.2221	28.6135	28.7956	27.7530
26.5884	29.8473	28.9819	27.0687	29.9169	26.9052
27.6666	28.4244	30.3432	25.5562	30.7609	25.6530
29.1333	26.8809	32.8459	23.5999	32.6215	23.9410
30.6602	25.3975	33.3921	22.6689	34.7080	22.2041
31.9121	24.1263	33.9155	21.9135	35.4705	21.1840
32.9990	22.9993	35.1220	20.7665	36.1866	20.3259
33.8364	22.0619	36.6756	19.5156	37.4028	19.2026
35.7135	20.6511	37.1041	18.8897	38.4585	18.3004
36.7707	19.6852	38.2027	17.9040	39.3304	17.5438
37.4674	18.9073	39.3748	17.0284	39.8576	16.9852
38.2935	18.1959	40.0938	16.4192	40.3881	16.5001
39.1099	17.4737	40.3612	16.1345	41.2282	15.8913
39.6331	16.9411	41.1552	15.4867	41.7614	15.4316
40.3374	16.3041	42.1021	14.8585	42.5672	14.7401
40.9630	15.7582	42.7267	14.3328	43.0529	14.3983
41.8435	15.1113	43.3789	13.8474	43.5522	13.9208
42.6419	14.5066	44.3593	13.2308	44.0532	13.5694
43.1248	14.0310	44.7070	12.8436	44.7276	13.0196
43.9949	13.4263	45.1969	12.4955	45.1257	12.7364
44.7581	12.8835	45.7177	12.0789	45.7717	12.2850
45.8031	12.2799	46.0371	11.8184	46.4527	11.7919
46.4520	11.8184	46.5260	11.4930	47.1620	11.3652
47.0710	11.3796	47.1892	11.0339	48.2544	10.6519
47.5449	11.0071	47.8669	10.5941	48.7955	10.2831
48.1635	10.6226	48.3715	10.2174	49.1995	9.9937
48.6019	10.3021	49.0378	9.7943	49.8791	9.5702
49.0689	9.9799	49.7889	9.3565	50.7905	9.0487
49.5037	9.6697	50.2905	9.0643	51.9121	8.4121
50.0581	9.3561	50.7832	8.7779	52.5663	7.9932
50.5745	9.0419	51.1282	8.5133	53.2454	7.6860
42.4123	14.5350	51.6471	8.2342	53.7612	7.4004
49.8258	9.1656	52.0449	7.9955	54.4843	7.0120
53.1731	7.3481	52.4355	7.7726		
56.8969	5.3008	59.8442	4.8006		
59.9870	3.7771	80.7466	1.5373		

Table S3. Experimental weight fraction data for the systems composed of $[C_4C_1pip]Cl$ (1) + salt (2) + H_2O (3) at 25 °C and at atmospheric pressure.

pH≈9		pH≈8		pH≈7		pH≈6	
		100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
11.8779	42.0814	18.5918	34.7445	19.1288	34.2900	27.7645	27.8446
13.2137	40.2890	20.8318	32.2317	21.7665	31.4809	29.1664	25.8716
13.8002	39.4154	22.1675	30.4867	23.7906	29.1489	30.3075	24.5749
15.1159	37.6963	24.0414	28.4860	25.3628	27.2222	32.1771	22.5954
16.1873	36.2783	25.6902	26.6967	27.2252	25.2342	33.3385	21.3135
17.2135	34.8857	27.5645	24.7879	29.2963	23.1948	34.8580	19.8117
18.8257	33.2705	28.9116	23.3592	30.9309	21.5805	38.9572	16.7164
19.6583	32.2197	30.4896	21.8523	32.7478	19.8526	40.0301	15.6677
20.9142	30.8794	31.2913	20.9193	33.9099	18.7602	41.2147	14.5968
21.5887	29.9564	32.4779	19.8362	35.3521	17.4506	42.6312	13.4330
22.7780	28.7832	33.6068	18.7931	36.9450	16.1302	43.9236	12.4418
23.7344	27.7078	34.9018	17.6500	37.9718	15.2572	45.4226	11.3171
24.6492	26.7513	36.1462	16.5798	39.0318	14.3832	47.8643	9.6811
25.5752	25.7733	38.5627	14.5789	40.3601	13.3873	64.4868	1.6150
26.5109	24.8309	39.4598	13.8450	41.5498	12.4932		
27.4363	23.9149	40.5345	13.0524	42.3966	11.8384		
28.9490	22.3683	41.7785	12.1531	43.5867	11.0112		
29.6948	21.6456	44.0910	10.6062	45.2099	9.9857		
30.3373	20.9788	44.7628	10.0927	46.5449	9.1533		
30.9753	20.3619	45.9167	9.3553	47.7960	8.3586		
31.4895	19.8072	46.8941	8.7397	50.9636	6.6636		
32.2745	19.1440	48.9936	7.6139	56.2140	3.5958		
33.5724	17.9547	49.5723	7.0979	63.3822	2.2685		
34.2235	17.3762	53.5122	5.0866				
34.4711	17.1436	68.5290	1.7860				
34.9649	16.6948						
35.4650	16.3068						
35.9407	15.9036						
36.3142	15.5403						
37.4033	14.7061						
37.7808	14.3866						
38.2987	13.9777						
38.5338	13.7857						
38.9518	13.4665						
39.4754	13.1443						
39.8736	12.8322						
40.4423	12.4411						
44.2930	10.1380						
51.2880	6.5760						

Table S4. Experimental weight fraction data for the systems composed of $[C_4C_1py]Cl$ (1) + salt (2) + H_2O (3) at 25 °C and at atmospheric pressure.

pH≈9		pH≈8		pH≈7		pH≈6	
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w1	100 w2
10.3520	43.9106	16.1550	35.7374	21.5230	31.5972	20.1890	37.1099
10.9390	42.6182	17.3005	34.1121	24.1622	28.7340	21.8798	33.9768
12.1725	40.3244	19.1243	32.1241	26.6534	26.1362	21.9294	33.8754
12.7275	39.2124	20.1184	30.6920	28.9522	23.8002	23.3702	32.1461
13.2595	38.3247	21.5311	29.0830	30.9445	21.8262	24.2277	31.3730
13.7627	37.2681	23.4651	27.3004	31.9832	20.8481	26.4111	28.9153
15.1317	35.7952	24.1238	26.2884	37.4705	16.3452	28.2444	26.8664
16.2410	34.3927	25.2560	25.1026	40.8486	13.8405	29.8631	25.0636
16.6722	33.5235	26.3273	23.9771	45.7694	10.5323	31.2613	23.5228
17.7926	32.4672	27.3393	22.9533	48.1000	9.1209	32.9111	21.9934
18.2788	31.8734	28.2592	22.0161	50.9472	7.4900	34.2906	20.6312
18.5719	31.1133	29.4633	20.9673	53.3648	6.2672	35.6823	19.2698
19.5507	30.0672	30.2357	20.2155			36.7937	18.1956
20.8888	28.6347	30.9456	19.4711			37.9766	17.1577
21.7727	27.7161	31.9261	18.6081			39.2486	16.0311
22.0155	27.1612	32.7787	17.8515			40.2094	15.2015
22.8139	26.3470	33.5242	17.1840			41.2908	14.3338
23.5572	25.5278	34.3287	16.5383			42.2571	13.5635
24.2755	24.8298	35.0301	15.9536			42.9198	13.0848
24.9947	24.1091	35.8603	15.3058			43.9808	12.3111
25.6083	23.4746	36.7579	14.8650			45.1592	11.4777
26.1681	22.8390	37.1963	14.5139			46.2131	10.7239
26.7165	22.2807	37.8043	14.0119			47.5453	9.8649
27.1404	21.7079	42.6186	12.0786			48.9056	9.0284
27.6823	21.1891	45.2390	10.4194			74.1362	1.2936
28.1828	20.6464	47.2672	9.2849				
28.4209	20.3486	49.6622	7.8631				
29.2571	19.7281	51.2425	7.1452				
29.6596	19.2829	53.0469	6.3009				
29.9995	18.8759	54.7933	5.5007				
30.7441	18.3101	56.6343	4.6833				
31.0773	17.9129	58.4954	3.8977				
31.4224	17.5977	75.3583	0.9350				
31.9635	17.1619						
32.2555	16.8272						
32.8425	16.3991						
33.6176	15.7280						
34.6460	14.8366						
35.9625	13.8039						
36.6668	13.2573						

Table S5. Experimental weight fraction data for the systems composed of $[P_{4444}]Cl$ (1) + salt (2) + H_2O (3) at 25 °C and at atmospheric pressure.

pH≈9					
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
5.3948	31.9074	11.0171	25.1436	29.1193	11.6832
5.4979	31.7579	11.2365	24.9242	29.9589	11.3385
5.5927	31.6088	11.5073	24.5869	30.8292	10.9785
5.6934	31.4443	11.6487	24.4848	32.7905	10.1775
5.7746	31.3460	11.8039	24.4161	34.4216	9.7388
5.8626	31.2440	12.0945	24.0175	35.5912	9.1585
5.9770	31.0747	12.2515	23.9305	37.2858	8.7838
6.0899	30.8912	12.4937	23.6946	39.2541	8.2486
6.2028	30.7388	12.6651	23.5927	41.7165	7.7237
6.3186	30.5726	12.9623	23.2558	45.0090	7.1845
6.4329	30.4180	13.0995	23.1312	48.7886	6.7607
6.5407	30.2694	13.2689	23.0590		
6.6636	30.0961	13.5524	22.7698		
6.7980	29.9059	13.7589	22.6892		
6.9469	29.6917	14.1365	22.3069		
7.0262	29.6338	14.3801	22.1978		
7.1624	29.4611	14.7046	21.8403		
7.2862	29.3033	15.0868	21.4970		
7.4572	29.0782	15.3047	21.4193		
7.5971	28.8946	15.6354	21.1153		
7.7403	28.7135	16.0217	20.7685		
7.8911	28.5028	16.3874	20.4539		
7.9884	28.4275	16.7671	20.0977		
8.1354	28.2129	17.1680	19.7297		
8.2793	28.0402	17.7517	19.3876		
8.4275	27.8636	18.4587	18.9242		
8.5682	27.7119	19.0499	18.3418		
8.7140	27.5760	19.9655	17.6546		
8.8988	27.3352	20.3343	17.4617		
9.0417	27.2270	21.0431	16.9084		
9.2235	26.9862	21.6530	16.4435		
9.3407	26.9228	22.3247	15.8673		
9.5300	26.6785	22.8310	15.6092		
9.7514	26.4223	23.3095	15.3755		
9.9206	26.2841	23.7648	15.1701		
10.0740	26.1489	24.2746	14.9452		
10.3403	25.7647	25.7977	13.7085		
10.4598	25.7122	26.4988	13.3945		
10.6775	25.4512	27.6162	12.5410		
10.8818	25.2190	28.4037	12.0422		

Table S6. Experimental weight fraction data for the systems composed of $[P_{4444}]Cl$ (1) + salt (2) + H_2O (3) at 25 °C and at atmospheric pressure.

pH≈8					
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
57.5547	5.1133	21.9022	16.7962	11.3907	25.1182
51.3753	5.7210	21.0825	17.4168	11.1177	25.4472
47.5050	6.4933	20.0351	18.1653	10.8229	25.6632
43.0923	7.0668	18.9056	18.9747	10.5643	25.9218
40.1382	7.7242	18.4039	19.2313	10.2648	26.2606
38.2240	8.4985	17.8655	19.6852	10.0261	26.4734
35.8977	9.0434	17.1444	20.3577	9.8045	26.7087
34.5148	9.7294	16.2847	21.0846	9.5972	26.8828
33.2760	10.2711	15.2364	21.7508	9.1832	27.2877
32.3099	10.6881	14.7070	22.2491	9.0141	27.4496
31.2601	11.0874	14.4866	22.3586	8.8087	27.6920
29.6716	12.1152	13.9772	22.8716	8.4320	28.1528
28.6393	12.4888	13.6519	23.0838	8.3148	28.2237
27.3283	13.2994	13.2699	23.4331	8.2061	28.2859
25.9506	14.2791	13.0134	23.6562	7.9859	28.5354
25.1962	14.5425	12.7424	23.8372	7.7987	28.7652
24.1979	15.3099	12.3581	24.1644	7.6536	28.9181
23.6382	15.6013	12.0469	24.5081	7.4963	29.1136
23.1173	15.8606	11.7097	24.8224	7.3494	29.2819

Table S7. Experimental weight fraction data for the systems composed of $[P_{4444}]Cl$ (1) + salt (2) + H_2O (3) at 25 °C and at atmospheric pressure.

pH≈7					
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
6.7891	30.1625	12.1061	25.1963	38.5866	8.4976
6.8782	30.0836	12.2740	25.1079	41.1608	7.7125
6.9942	29.9324	12.5806	24.7897	43.8623	6.7416
7.0871	29.8433	12.9027	24.5157		
7.1796	29.7243	13.2231	24.2613		
7.2703	29.5901	13.5461	23.9753		
7.3761	29.4990	13.8776	23.7010		
7.4807	29.3996	14.2109	23.4382		
7.6123	29.2241	14.6087	23.0861		
7.7444	29.0704	14.9831	22.7630		
7.8074	29.0439	15.2195	22.6639		
7.8610	28.9736	15.6287	22.2673		
7.9287	28.9499	16.0507	21.9113		
8.0980	28.7172	16.3493	21.7874		
8.2263	28.6113	16.8117	21.3660		
8.3018	28.6086	17.3418	20.9465		
8.4850	28.3765	17.8555	20.5213		
8.6043	28.2238	18.1681	20.3472		
8.7466	28.0892	18.7362	19.9064		
8.8816	27.9928	19.1292	19.7115		
9.0161	27.8187	19.7536	19.1752		
9.1718	27.6760	20.3100	18.8208		
9.3336	27.5277	20.7504	18.6420		
9.4743	27.3823	21.5071	18.0248		
9.5719	27.3279	22.3061	17.4067		
9.7326	27.2039	22.9839	17.0111		
9.9034	27.0569	23.7585	16.5123		
10.0889	26.8950	24.3950	16.2060		
10.2366	26.7504	24.9565	15.8711		
10.4231	26.5817	26.0625	14.9920		
10.6205	26.4069	26.7792	14.6135		
10.8005	26.2040	27.5793	14.2128		
10.9003	26.1948	28.3617	13.7621		
11.1271	25.9765	29.1461	13.2893		
11.3244	25.8604	30.0949	12.8133		
11.4516	25.7708	32.1408	11.8075		
11.6962	25.5666	34.1085	10.3152		
11.8454	25.4751	35.0160	9.9361		
12.1061	25.1963	36.9793	9.3338		

Table S8. Experimental weight fraction data for the systems composed of $[P_{4444}]Cl$ (1) + salt (2) + H_2O (3) at 25 °C and at atmospheric pressure.

pH≈6					
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
41.5610	9.4338	17.6874	21.6882	10.0606	27.3306
39.8025	10.0148	16.8498	22.1895	9.8021	27.5614
38.1769	10.5583	16.2087	22.6783	9.5076	27.8837
36.8672	10.8672	15.4576	23.3484	9.3654	28.0262
35.4010	11.3902	15.0291	23.6087	9.1816	28.1641
33.8517	12.0940	14.5723	23.9605	9.0279	28.3228
32.6151	12.6011	14.0916	24.3544	8.9228	28.3978
31.0253	13.4039	13.5857	24.7420	8.6930	28.6809
29.8230	13.8782	13.0761	25.2134	8.4773	28.8730
28.5100	14.6504	12.9396	25.2058	8.3147	29.0162
27.1956	15.4978	12.6996	25.3586	8.1654	29.1964
25.8070	16.1369	12.4731	25.4425	7.9760	29.3996
24.6101	16.8965	12.2056	25.4959	7.7789	29.5979
23.4508	17.7110	11.8010	25.8939	7.6032	29.7881
22.3471	18.3558	11.5617	26.0623	7.3574	30.0296
21.4818	18.8986	11.2675	26.3211	7.1839	30.2386
20.5104	19.5391	11.0216	26.4946	6.9413	30.4722
19.6346	20.2063	10.7197	26.7594	6.7763	30.6786
19.1031	20.6049	10.4980	26.9721	6.6610	30.7860
18.3677	21.1999	10.2920	27.1530	6.5208	30.9234

Table S9. Experimental weight fraction data for the systems composed of $[P_{4444}]Cl$ (1) + salt (2) + H_2O (3) at 25 °C and at atmospheric pressure.

pH≈5					
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
57.7084	4.1732	18.3660	24.0994	9.9574	30.8217
52.3413	5.3498	17.4716	24.8313	9.6061	31.1558
41.1731	9.4540	16.5868	25.4299	9.2556	31.4689
38.4940	10.7645	15.6178	26.2426	8.9596	31.7383
36.2354	11.9482	14.8823	26.7742	8.6081	32.1045
34.3652	13.0916	14.1684	27.3257	8.3384	32.3654
32.2713	14.1512	13.6598	27.7164	8.0661	32.6489
29.5863	15.9934	13.0798	28.1534	7.5930	33.1546
27.3230	17.6217	12.4625	28.7098	7.1679	33.5836
25.3565	18.9943	12.0134	29.0412	6.8786	33.8693
23.5731	20.2839	11.5925	29.3615	6.5060	34.3004
21.8258	21.5693	11.1492	29.7298	6.1373	34.7029
20.5767	22.5930	10.7012	30.1348	5.7658	35.1614
19.4395	23.3356	10.3057	30.4901		

Table S10. Experimental weight fraction data for the systems composed of $[C_4C_1im]Br$ (1) + salt (2) + H_2O (3) at 25 °C and at atmospheric pressure.

pH≈9		pH≈8				pH≈7	
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
14.0588	31.4976	74.6692	1.7071	14.7402	31.1274	14.0554	34.0102
15.6686	29.9014	62.2292	3.5899			15.8671	32.1716
17.3798	28.2620	55.7952	4.5687			18.9328	29.3782
19.2837	26.5865	53.7379	5.4895			20.5407	28.0655
20.8123	25.3568	52.4385	6.0282			22.2259	26.6261
22.7626	23.7899	51.1184	6.5971			24.2693	24.9879
25.2484	21.8864	49.2717	7.6222			26.4308	23.3838
28.1199	19.8442	47.9687	8.3090			28.6680	21.6541
31.3557	17.4650	46.8307	8.7596			31.3276	19.7129
34.4359	15.4745	45.6325	9.3666			34.2345	17.5869
37.2668	13.7305	43.9663	10.2978			37.0418	15.7384
43.0663	9.7932	42.5776	11.0643			40.0378	13.7155
46.5773	7.9639	41.4969	11.7464			43.6035	11.3177
48.9797	7.2517	40.4967	12.3258			46.6277	9.6972
53.6390	5.3732	39.2647	13.0520			48.9873	8.5396
57.2031	4.3649	38.3023	13.6647			52.7198	6.5982
60.7843	3.2181	36.8416	14.6905			54.5368	5.9419
66.6892	1.9342	35.3456	15.7034			57.8177	4.2714
14.0588	31.4976	34.2934	16.4524			61.0892	2.7458
15.6686	29.9014	33.0183	17.3642			63.6529	1.8296
17.3798	28.2620	31.1062	18.8453			78.0200	0.4262
19.2837	26.5865	30.2517	19.3823			14.0554	34.0102
20.8123	25.3568	28.7960	20.4784			15.8671	32.1716
22.7626	23.7899	27.8623	21.1637			18.9328	29.3782
25.2484	21.8864	27.0973	21.7318			20.5407	28.0655
28.1199	19.8442	26.6466	22.0029			22.2259	26.6261
31.3557	17.4650	25.9514	22.5344			24.2693	24.9879
34.4359	15.4745	25.2505	23.0745			26.4308	23.3838
37.2668	13.7305	24.1415	23.9091			28.6680	21.6541
43.0663	9.7932	23.5451	24.3393			31.3276	19.7129
46.5773	7.9639	20.8741	25.2211			34.2345	17.5869
48.9797	7.2517	20.2310	25.7807			37.0418	15.7384
53.6390	5.3732	19.5592	26.3928			40.0378	13.7155
57.2031	4.3649	18.9190	26.9909			43.6035	11.3177
60.7843	3.2181	18.3783	27.4884			46.6277	9.6972
66.6892	1.9342	17.6814	28.1693			48.9873	8.5396
		17.0936	28.7205			52.7198	6.5982
		16.3846	29.4266			54.5368	5.9419
		15.5370	30.3036			57.8177	4.2714

Table S11. Experimental weight fraction data for the systems composed of $[C_4C_1im]Br$ (1) + salt (2) + H_2O (3) at 25 °C and at atmospheric pressure.

pH≈7		pH≈6				pH≈5	
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
61.0892	2.7458	13.1289	40.9277	42.5059	13.0330	48.8255	11.8806
63.6529	1.8296	14.6369	37.8062	42.8610	12.7617	52.7982	9.5053
78.0200	0.4262	15.4353	36.7627	43.2331	12.5204	53.0294	9.3376
		16.6319	35.4319	43.5518	12.2803	53.3424	9.1489
		18.0233	34.0131	43.9026	12.0745	53.7521	8.8781
		18.6667	33.2197	44.2004	11.8618	54.2591	8.5404
		19.9499	32.0458	44.6306	11.5841	54.4792	8.3756
		21.4402	30.7913	45.0522	11.3258	54.8214	8.1616
		22.6211	29.6228	45.3365	11.1196	55.1614	7.9445
		23.4683	28.6192	45.8005	10.8714	55.7765	7.5528
		24.7265	27.5343	46.1277	10.6633	56.0490	7.3768
		26.1772	26.3980	46.4046	10.4826	56.3058	7.2228
		26.9795	25.6396	46.6931	10.2876	56.5910	7.0483
		27.5439	25.0612	46.9333	10.1271		
		28.6331	24.2187	47.2513	9.9269		
		29.3257	23.5222	47.4015	9.7540		
		30.4280	22.7180	47.7184	9.5641		
		30.9947	22.1325	48.0615	9.3802		
		31.6755	21.5690	48.3586	9.2140		
		32.4393	20.8683	48.6681	9.0465		
		32.8501	20.4090	48.9684	8.8754		
		33.3331	19.9721	49.2857	8.7043		
		34.0746	19.4849	49.6341	8.5348		
		34.4802	19.0562	50.0614	8.2920		
		35.3174	18.4711	50.8046	7.8751		
		35.6522	18.0907	51.1411	7.7314		
		36.3547	17.6037	51.3609	7.6091		
		36.7720	17.2347	51.6497	7.4731		
		37.5590	16.7515	52.0009	7.3234		
		37.8739	16.4092	52.2130	7.2098		
		38.4874	16.0096	52.5221	7.0811		
		38.7591	15.6990	52.9099	6.8869		
		39.2165	15.3895	53.5474	6.5863		
		39.5462	15.1067	54.4502	6.1986		
		40.0778	14.7448	54.9257	6.0009		
		40.5598	14.4099	54.9483	5.8978		
		40.9810	14.0989	56.2662	5.4754		
		41.3850	13.8069	58.0126	4.7360		
		41.8287	13.5066	69.9374	1.6121		

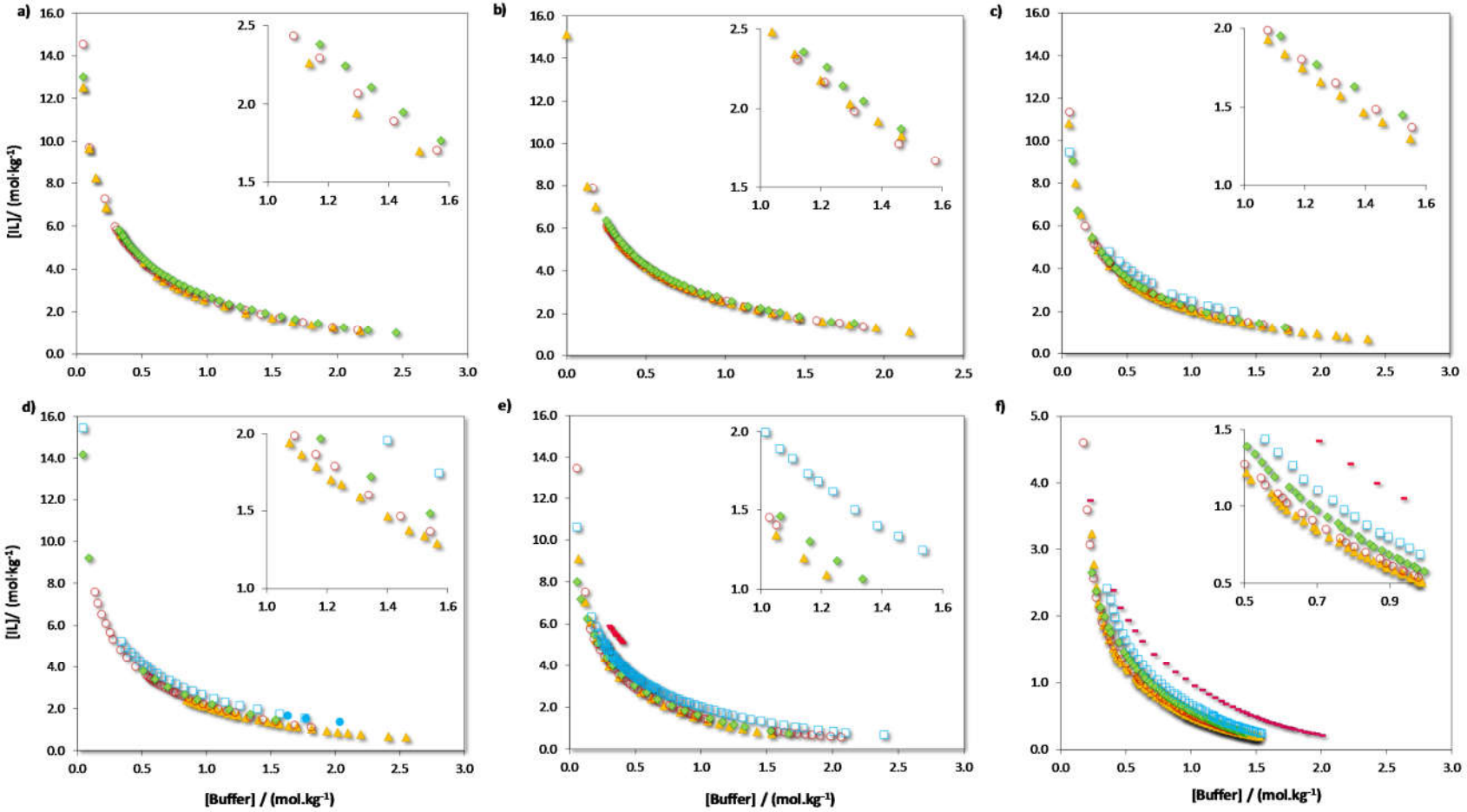


Fig. S3. Evaluation of the pH effect in the ternary phase diagrams composed of IL + water + $K_3C_6H_5O_7$/ $C_6H_8O_7$ at pH ≈ 9 (▲), pH ≈ 8 (○), pH ≈ 7 (◆), pH ≈ 6 (□) and pH ≈ 5 ( ). The ILs are: **(a)** [C_4C_1im]Cl, **(b)** [$C_4C_1C_1$im]Cl, **(c)** [C_4C_1pip]Cl, **(d)** [C_4C_1py]Cl, **(e)** [C_4C_1im]Br and **(f)** [P_{4444}]Cl.

Table S12. Values for the constants *A*, *B* and *C*, obtained by the regression of the experimental binodal data as described originally by Merchuk et al.[3] (and respective standard deviations, σ, and correlation coef cients, R^2).

IL	pH	$A \pm \sigma$	$B \pm \sigma$	$10^6(C \pm \sigma)$	R^2
$[C_4C_1C_1im]Cl$	9	86.8 ± 0.7	-0.181 ± 0.002	7.37 ± 0.25	0.9990
	8	103.8 ± 1.6	-0.235 ± 0.005	3.13 ± 0.68	0.9939
	7	86.7 ± 0.7	-0.178 ± 0.003	7.34 ± 0.34	0.9987
$[C_4C_1im]Cl$	9	88.7 ± 0.9	-0.197 ± 0.004	7.72 ± 0.47	0.9986
	8	88.7 ± 0.8	-0.178 ± 0.003	9.29 ± 0.37	0.9982
	7	91.8 ± 0.3	-0.201 ± 0.001	6.73 ± 0.06	1.0000
$[C_4C_1pip]Cl$	9	88.3 ± 0.4	-0.217 ± 0.001	8.07 ± 0.14	0.9996
	8	90.3 ± 0.9	-0.219 ± 0.003	6.62 ± 0.51	0.9986
	7	83.9 ± 0.9	-0.195 ± 0.004	8.56 ± 0.57	0.9983
	6	79.8 ± 0.8	-0.165 ± 0.004	9.88 ± 0.76	0.9985
$[C_4C_1py]Cl$	9	90.5 ± 1.4	-0.243 ± 0.004	7.18 ± 0.19	0.9996
	8	95.6 ± 1.0	-0.239 ± 0.004	8.36 ± 0.63	0.9978
	7	87.6 ± 0.9	-0.199 ± 0.004	9.71 ± 0.58	0.9995
	6	94.4 ± 0.4	-0.215 ± 0.001	5.01 ± 0.17	0.9997
$[C_4C_1im]Br$	9	93.1 ± 0.6	-0.237 ± 0.003	18.30 ± 0.57	0.9997
	8	90.8 ± 1.4	-0.218 ± 0.005	20.69 ± 0.87	0.9981
	7	85.6 ± 0.8	-0.192 ± 0.004	18.51 ± 0.79	0.9975
	6	90.7 ± 0.2	-0.204 ± 0.001	10.57 ± 0.11	0.9998
	5	76.3 ± 0.6	-0.107 ± 0.003	46.96 ± 1.91	0.9999
$[P_{4444}]Cl$	9	150.0 ± 4.6	-0.458 ± 0.010	20.69 ± 1.23	0.9964
	8	154.5 ± 5.3	-0.464 ± 0.012	17.76 ± 1.97	0.9953
	7	97.2 ± 1.0	-0.308 ± 0.003	34.64 ± 0.41	0.9996
	6	124.0 ± 3.6	-0.354 ± 0.009	31.75 ± 0.91	0.9995
	5	99.8 ± 1.4	-0.275 ± 0.005	26.10 ± 0.60	0.9990

Table S13. Weight fraction percentage (wt%) composition of the initial mixture and of the coexisting phases of IL-based ABS, and respective values of tie-line length (TLL) and pH values of each phase.

IL	Weight fraction composition / wt %								TLL
	$[IL]_{IL}$	$[salt]_{IL}$	pH_{IL}	$[IL]_{M}$	$[salt]_{M}$	$[IL]_{salt}$	$[salt]_{salt}$	pH_{salt}	
$[C_4C_1im]Cl$	53.04	7.13	9.32	25.25	35.03	5.77	54.58	9.30	66.98
$[C_4C_1C_1im]Cl$	47.88	10.76	8.93	25.02	34.90	9.78	51.00	8.67	55.42
$[C_4C_1pip]Cl$	55.91	4.46	9.26	25.13	34.75	4.40	55.15	9.34	72.27
	66.45	1.00	6.40	40.07	20.80	13.35	42.05	6.36	57.79
	62.07	2.00	6.19	33.18	24.83	18.12	36.73	6.29	56.02
$[C_4C_1py]Cl$	55.74	5.13	8.44	24.62	35.47	4.39	55.19	8.16	71.71
	54.52	6.56	6.24	32.86	24.75	23.28	32.80	6.20	40.80
	61.48	4.05	6.24	37.06	23.58	20.56	36.12	6.16	55.53
$[C_4C_1im]Br$	76.93	0.65	8.93	35.08	32.04	0.42	58.03	8.92	95.64
	51.51	7.57	6.00	33.54	21.54	20.82	31.42	5.93	38.87
	62.69	3.28	6.07	34.33	25.39	8.38	45.64	6.01	68.88
$[P_{4444}]Cl$	39.60	8.92	9.00	30.10	15.04	8.88	28.25	8.89	36.32
	72.93	3.06	9.34	24.97	35.03	0.58	51.29	9.14	86.95
	56.00	4.60	5.99	27.84	23.12	1.54	40.46	5.84	65.20
	63.15	3.28	5.62	33.29	21.97	1.13	42.11	5.90	73.17

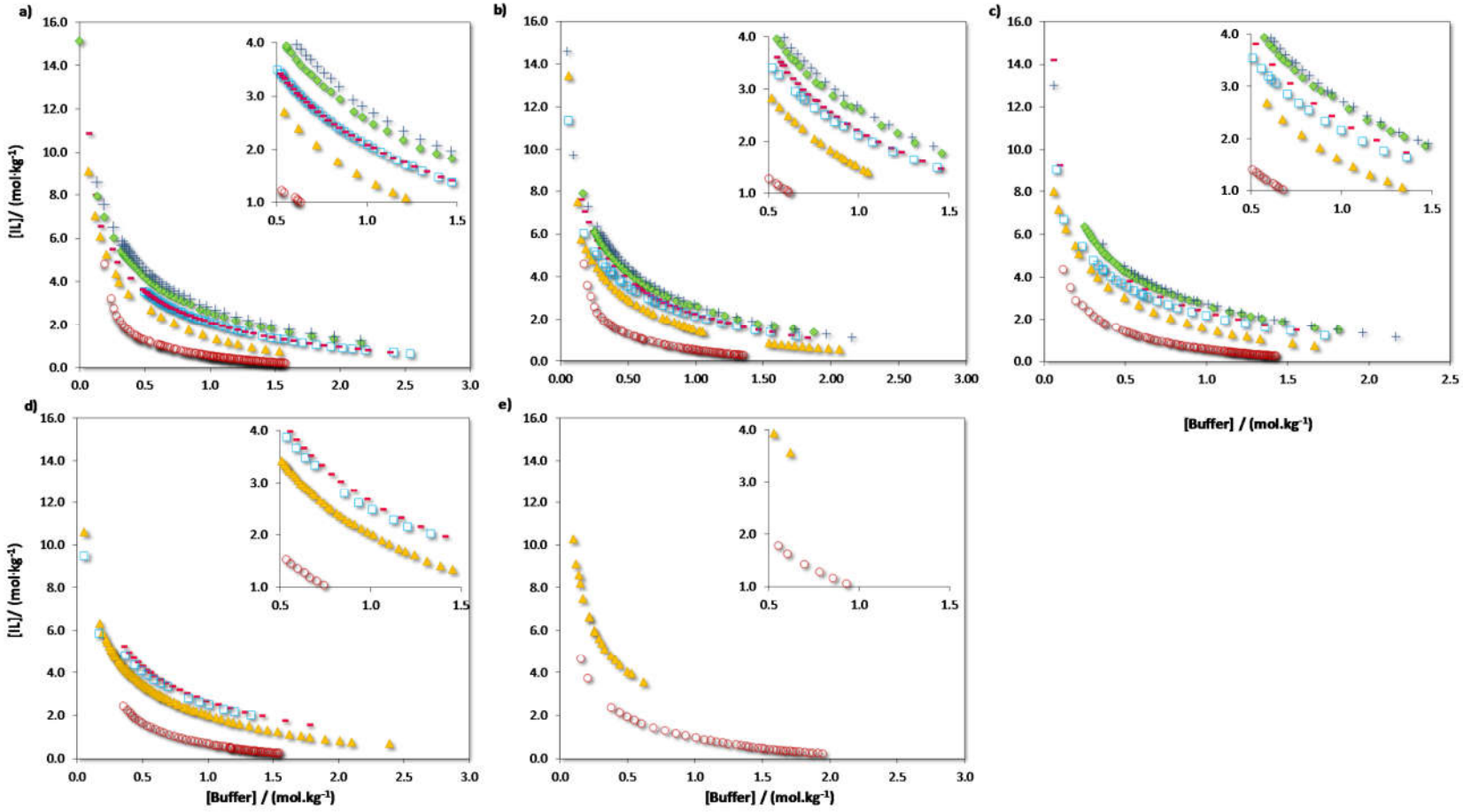


Fig. S4. Phases diagrams for the different IL-based ABS at fixed pH: pH ≈9 **(a)**; pH ≈8 **(b)**; pH ≈7 **(c)**; pH ≈6 **(d);** and pH ≈5 **(e)**. ILs investigated: $[P_{4444}]Cl$ (○), $[C_4C_1im]Br$ (▲), $[C_4C_1pip]Cl$ (□), $[C_4C_1py]Cl$ ( ), $[C_4C_1C_1im]Cl$ (◆) and $[C_4C_1im]Cl$ (+).

Table S14. Identification of the systems able (✓) or not able (×) to form two-phase systems as a function of the pH.

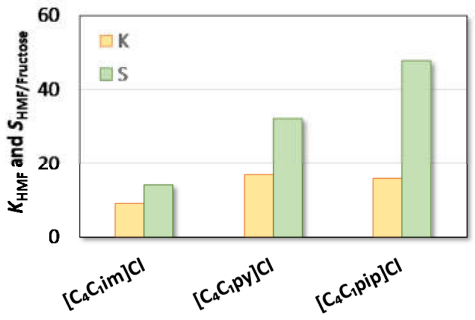
pH	9	8	7	6	5
$[C_4C_1im]Cl$	✓	✓	✓	×	×
$[C_4C_1C_1im]Cl$	✓	✓	✓	×	×
$[C_4C_1pip]Cl$	✓	✓	✓	✓	×
$[C_4C_1py]Cl$	✓	✓	✓	✓	×
$[C_4C_1im]Br$	✓	✓	✓	✓	✓
$[P_{4444}]Cl$	✓	✓	✓	✓	✓

Table S15. Production yields of HMF through fructose dehydration in presence (or not) of citric acid and ILs.

	[HMF] $g \cdot L^{-1}$	
	Without citric acid	**With citric acid**
H_2O	$(53.84 \pm 1.65) \times 10^{-5}$	2.28 ± 0.53
$[C_4C_1im]Cl$	$(64.61 \pm 7.88) \times 10^{-5}$	4.61 ± 0.46
$[C_4C_1py]Cl$	$(36.09 \pm 6.37) \times 10^{-5}$	4.85 ± 0.60
$[C_4C_1pip]Cl$	$(281.36 \pm 4.02) \times 10^{-5}$	6.37 ± 0.48

Table S16. Extraction efficiencies (*EE* %) of the systems studied for HMF and fructose.

	EE_{HMF} (IL-rich phase) %	$EE_{Fructose}$ (salt-rich phase) %
$[C_4C_1im]Cl$	92.50 ± 0.50	44.81 ± 3.13
$[C_4C_1py]Cl$	95.09 ± 1.09	50.70 ± 0.44
$[C_4C_1pip]Cl$	95.89 ± 0.45	58.73 ± 0.56



	K_{HMF}	$S_{HMF/Fructose}$
$[C_4C_1im]Cl$	8.87±0.50	13.94±0.07
$[C_4C_1py]Cl$	15.73±0.67	32.14±0.02
$[C_4C_1pip]Cl$	16.79±1.78	47.89±0.03

Fig. S5. Partition coefficients of HMF and selectivity values of the systems studied.

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