

ELECTRONIC SUPPLEMENTARY INFORMATION

Understanding the Fundamentals of Acid-induced Ionic Liquid-based Aqueous Biphasic System

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Electronic supplementary information (ESI)

Table S1 and S2: Experimental binodal data for HCl-[P₄₄₄₁₄]⁺Cl⁻-H₂O system at 8°C, 13°C, 16°C, 25°C, 36°C, 45°C, 50°C and 56°C and at atmospheric pressure

Table S3. Experimental binodal data in wt % units and mol/kg of solvent units for HNO₃, H₂SO₄ and HCl based AcABS at 25°C and at atmospheric pressure.

Table S4. Number of moles of [P₄₄₄₁₄]⁺ cation and Cl⁻ anion present in the upper phase for all mixture points in HNO₃-[P₄₄₄₁₄]⁺Cl⁻-H₂O system.

Table S5. Number of moles of [P₄₄₄₁₄]⁺ cation and Cl⁻ anion present in the upper phase for all mixture points in H₂SO₄-[P₄₄₄₁₄]⁺Cl⁻-H₂O system.

Figure S1: Binodal curves of HCl-[P₄₄₄₁₄]⁺Cl⁻-H₂O system at 8°C, 13°C, 16°C and 24°C and at atmospheric pressure

Table S1. Experimental binodal data for HCl-[P₄₄₄₁₄]Cl-H₂O system at various temperatures and at atmospheric pressure.

8°C		13°C		16°C		25°C	
IL wt %	HCl wt %	IL wt %	HCl wt %	IL wt %	HCl wt %	IL wt %	HCl wt %
34.508	16.698	60.481	14.123	60.075	14.551	55.801	13.971
33.439	16.922	56.805	14.379	54.893	14.362	53.807	14.097
32.549	17.107	51.808	14.672	52.451	14.534	49.546	14.146
31.446	17.410	48.458	14.934	50.474	14.860	47.861	14.299
30.511	17.673	44.431	15.592	47.542	15.046	45.167	14.763
29.261	17.759	42.119	15.630	45.767	15.211	42.152	15.292
28.291	17.962	40.543	15.935	44.628	15.359	41.518	15.428
27.665	18.129	39.074	16.244	42.839	15.509	37.636	15.940
26.613	18.309	36.888	16.522	41.158	15.748	32.089	17.317
25.247	18.624	35.390	16.797	39.567	15.937	30.357	17.566
24.269	18.848	34.412	17.022	37.849	16.227	28.492	17.936
23.299	19.041	32.462	17.401	36.314	16.518	27.973	17.933
22.544	19.201	30.827	17.666	34.718	16.811	25.937	18.486
21.756	19.259	29.837	17.883	32.689	17.437	22.221	18.940
21.303	19.387	28.834	18.170	31.833	17.396	18.896	19.622
20.578	19.557	28.220	18.249	29.596	17.875	15.096	20.208
20.107	19.590	27.554	18.350	40.663	15.657	12.880	20.682
19.659	19.748	26.789	18.526	38.799	15.996	10.945	21.121
18.778	19.861	25.485	18.850	37.220	16.161	8.895	21.580
17.782	20.024	24.747	18.813	36.247	16.316	6.950	21.932
16.926	20.128	23.090	19.169	35.132	16.569	5.797	22.331
15.722	20.385	22.163	19.266	33.491	16.922	3.969	22.952
14.707	20.614	20.718	19.427	32.036	17.201	2.995	23.289
13.790	20.696	19.030	19.766	30.521	17.429	1.931	23.593
12.775	20.977	18.780	19.758	29.917	17.577	0.986	24.228
12.050	21.083	16.791	20.034	28.052	17.943	0.924	24.314
11.299	21.265	15.043	20.416	27.360	18.179	0.145	28.770
10.556	21.448	13.933	20.585	26.193	18.409	0.289	27.776
9.798	21.649	12.882	20.799	25.335	18.554	0.372	26.723
8.949	21.809	11.789	21.007	24.210	18.834	0.541	25.857
8.365	21.937	10.860	21.213	23.808	18.923	0.706	25.161
8.205	21.971	10.309	21.306	21.966	19.283		
8.002	21.999	9.918	21.421	20.275	19.595		
				19.069	19.836		
				17.599	20.203		
				17.351	20.111		
				15.997	20.348		
				15.732	20.397		
				14.973	20.538		

Table S2. Experimental binodal data for HCl-[P₄₄₄₁₄]Cl-H₂O system at various temperatures and at atmospheric pressure.

36°C		45°C		50°C		56°C	
IL wt %	HCl wt %	IL wt %	HCl wt %	IL wt %	HCl wt %	IL wt %	HCl wt %
62.713	13.672	62.034	13.922	67.466	11.929	67.768	11.727
60.588	13.815	57.785	13.799	63.195	12.359	63.687	11.673
58.298	14.089	54.666	13.586	59.433	12.681	60.133	11.624
54.480	13.836	51.334	13.345	55.012	12.363	57.826	11.417
51.379	13.732	48.496	13.845	49.105	11.487	55.117	11.353
47.810	13.939	46.315	13.857	46.563	11.314	50.269	10.814
45.592	14.128	44.278	13.709	45.271	11.120	46.130	10.294
43.376	14.090	41.983	13.539	41.973	10.841	41.829	9.567
42.446	14.404	39.903	13.193	40.556	10.730	37.560	8.681
39.701	14.674	38.298	13.085	38.955	10.686	35.356	8.516
37.738	14.437	37.419	13.201	37.285	10.509	33.417	8.284
36.910	14.629	35.822	13.134	36.250	10.517	32.105	8.119
35.869	14.610	32.950	13.126	35.279	10.361	30.906	7.986
34.436	15.096	32.377	12.261	33.022	10.444	29.557	7.887
33.673	15.234	27.259	12.524	31.876	10.424	24.356	5.847
32.601	15.226	21.558	12.049	30.885	10.365	21.710	5.604
31.707	15.208	15.666	13.335	29.766	10.318	14.199	5.743
31.366	15.369	11.074	13.192	28.474	10.165	4.542	6.174
30.482	15.351	8.090	14.906	26.046	9.255	3.534	7.432
29.790	15.396	6.929	15.074	23.753	9.033	2.621	7.164
28.782	15.592	5.211	16.744	22.396	8.740	2.089	8.419
27.900	15.802	2.731	17.591	21.844	8.804	1.617	8.315
27.262	16.010	1.693	18.625	19.924	8.943		
23.188	16.262	1.069	19.691	18.810	8.846		
19.927	16.374	0.771	20.345	17.932	9.0405		
15.378	17.2399			16.802	9.411		
11.537	17.835			15.713	9.0144		
8.490	19.129			15.080	8.934		
3.982	21.288			14.318	9.643		
3.489	21.180			13.896	9.866		
2.583	21.720			13.438	9.958		
1.990	22.174			8.407	9.8724		
1.550	22.747			5.154	10.388		
				0.923	12.573		

Table S3. Experimental binodal data in wt % units and mol/kg of solvent units for HNO₃, H₂SO₄ and HCl based AcABS systems at 25°C and at atmospheric pressure.

HNO ₃ -[P ₄₄₄₁₄]Cl-H ₂ O wt %		HNO ₃ -[P ₄₄₄₁₄]Cl-H ₂ O mol/kg		H ₂ SO ₄ -[P ₄₄₄₁₄]Cl-H ₂ O wt %		H ₂ SO ₄ -[P ₄₄₄₁₄]Cl-H ₂ O mol/kg		HCl-[P ₄₄₄₁₄]Cl-H ₂ O mol/kg	
IL	HNO ₃	IL	HNO ₃	IL	H ₂ SO ₄	IL	H ₂ SO ₄	IL	HCl
28.612	1.703	0.657	0.270	34.814	18.684	0.800	1.905	1.282	3.833
24.160	1.797	0.555	0.285	32.712	19.373	0.752	1.975	1.236	3.867
12.028	1.803	0.276	0.286	30.687	19.727	0.705	2.011	1.139	3.881
7.687	1.924	0.177	0.305	28.593	19.935	0.657	2.033	1.010	3.923
14.985	1.928	0.344	0.306	26.946	20.188	0.619	2.0581	1.038	4.050
8.386	1.946	0.193	0.309	26.019	20.897	0.598	2.131	0.969	4.195
5.252	1.874	0.121	0.297	24.662	21.281	0.567	2.170	0.954	4.232
2.713	1.774	0.062	0.282	23.143	21.294	0.532	2.171	0.865	4.373
1.80	1.915	0.041	0.304	21.582	21.184	0.496	2.160	0.737	4.750
0.577	2.236	0.013	0.355	20.163	21.005	0.463	2.142	0.698	4.819
				19.098	20.867	0.439	2.128	0.655	4.920
				18.088	20.850	0.416	2.126	0.643	4.919
				16.248	20.691	0.373	2.110	0.596	5.071
				14.756	20.479	0.339	2.088	0.511	5.196
				13.629	20.541	0.313	2.094	0.434	5.383
				12.003	20.641	0.276	2.104	0.347	5.544
				10.369	20.792	0.239	2.120	0.296	5.674
				9.271	20.670	0.214	2.107	0.252	5.794
				7.255	20.777	0.167	2.118	0.204	5.920
				6.211	20.958	0.143	2.137	0.160	6.017
				4.143	20.858	0.095	2.127	0.133	6.126
				2.555	20.765	0.059	2.117	0.091	6.296
				1.885	21.448	0.043	2.187	0.069	6.389
				1.0073	23.419	0.023	2.388	0.044	6.472
				0.5956	24.618	0.014	2.510	0.023	6.646
				0.0501	26.408	0.0014	2.693	0.021	6.670
				0.0449	27.830	0.0010	2.837	0.003	7.892
				0.0385	29.949	0.0008	3.054	0.007	7.620
				0.0281	29.515	0.0006	3.0099	0.009	7.331
				0.0207	30.884	0.0004	3.149	0.012	7.093
								0.016	6.902

Table S4. Number of moles of $[P_{44414}]^+$ cation and Cl^- anion ($\pm 5\%$) present in the upper phase for all mixture points in HNO_3 - $[P_{44414}]Cl$ - H_2O system.

Mixture points	Mixture point	Upper phase	
		$[P_{44414}]^+$ (no. moles)	Cl^- (no. moles)
IL:acid ratio	$[P_{44414}]^+ / Cl^-$ (no. moles)		
1:2 (E)	4.69×10^{-3}	4.69×10^{-3}	1.72×10^{-3}
1:5 (F)	3.46×10^{-3}	3.38×10^{-3}	1.54×10^{-4}
1:20 (G)	3.52×10^{-3}	3.57×10^{-3}	6.80×10^{-5}

Table S5. Number of moles of $[P_{44414}]^+$ cation and Cl^- anion ($\pm 5\%$) present in the upper phase for all mixture points in H_2SO_4 - $[P_{44414}]Cl$ - H_2O system

Mixture points	Mixture point	Upper phase	
		$[P_{44414}]^+$ (no. moles)	Cl^- (no. moles)
IL:acid ratio	$[P_{44414}]^+ / Cl^-$ (no. moles)		
1:2 (H)	3.90×10^{-3}	3.74×10^{-3}	3.26×10^{-3}
1:5 (I)	4.78×10^{-3}	4.43×10^{-3}	2.45×10^{-3}
1:20 (J)	5.30×10^{-4}	3.89×10^{-4}	8.72×10^{-5}

Figure S1. Binodal curves of HCl - $[P_{44414}]Cl$ - H_2O system at $8^\circ C$ (●), $13^\circ C$ (▼), $16^\circ C$ (▲) and $25^\circ C$ (■) and at atmospheric pressure.

