Double-stimuli-responsive (temperature and pH) aqueous biphasic systems comprising ionic liquids

Ana F.C.S. Rufino,† Joana M. Bola,† Emanuel V. Capela,† João A.P. Coutinho,† Francisca A. e Silva,† Mara G. Freire†*

†CICECO-Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal.

*Corresponding author

Tel: +351-234-401422; Fax: +351-234-370084; E-mail address: maragfreire@ua.pt

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Supporting Information

MATERIALS AND METHODS

Synthesis of ILs

Three choline-based Ionic liquids (ILs) were synthesized by us according to previously reported protocols,[1,2] namely [Ch][C_3O_2], [Ch][C_2O_3] and [Ch][C_3O_3]. All aqueous solutions were prepared with distilled water. For the synthesis of ILs, the corresponding acid (i.e., propionic, glycolic and lactic acid) was added dropwise to choline bicarbonate in a molar ratio of 1.1:1. The mixtures were left in agitation overnight at ambient temperature. The removal of the water formed in the reaction was performed in a rotary evaporator. The IL was washed with ethyl acetate to remove any acid in excess. The removal of solvents was performed by a rotary evaporator at 50°C. The IL was dried under vacuum for 5 days at 70°C. ILs purity was determined by proton and carbon nuclear magnetic resonance (^{1}H and ^{13}C NMR) spectroscopy using a Bruker Avance 300 spectrometer at 300.13 MHz. NMR results are presented in Table S1. The water content of the ILs was confirmed to be lower than 5 wt% using a Metrohm 831 Karl Fischer coulometer with the analyte Hydranal® - Coulomat AG.

Determination of the liquid-liquid phase diagrams

Original and derived equations proposed by Merchuk et al.[3] are:

$$[PPG] = A\exp\left(B[IL]^{0.5} - C[IL]^3\right) \qquad (S1)$$

$$[PPG] = A\exp\left(B[IL]^C\right) \qquad (S2)$$

$$[PPG] = A\exp\left(B[IL]\right) \qquad (S3)$$

$$[PPG] = A\exp\left(B[IL]^D - C[IL]^3\right) \qquad (S4)$$

$$[PPG] = A.\exp\left(B[IL]^{0.5} - C[IL]^D\right) \qquad (S5)$$

where, [PPG] and [IL] denote the weight percent of PPG 400 and IL, respectively. *A*, *B*, *C* and *D* represent the constants obtained through the fitting of the experimental data.

Determination of the stimulus-responsive region extent

The extent of the stimulus-responsive region was determined following the strategy represented in **Figure S1** by the following equation:

$$Extent = \sqrt[2]{([IL]_{lower} - [IL]_{upper})^2 + ([PPG]_{lower} - [PPG]_{upper})^2} \qquad (S6)$$

where, [PPG] and [IL] denote the weight percentage of PPG 400 and IL in the mixture composition considered, respectively. The subscripts “lower” and “upper” represent the lower and upper extremes of the condition for which the extent is being calculated.

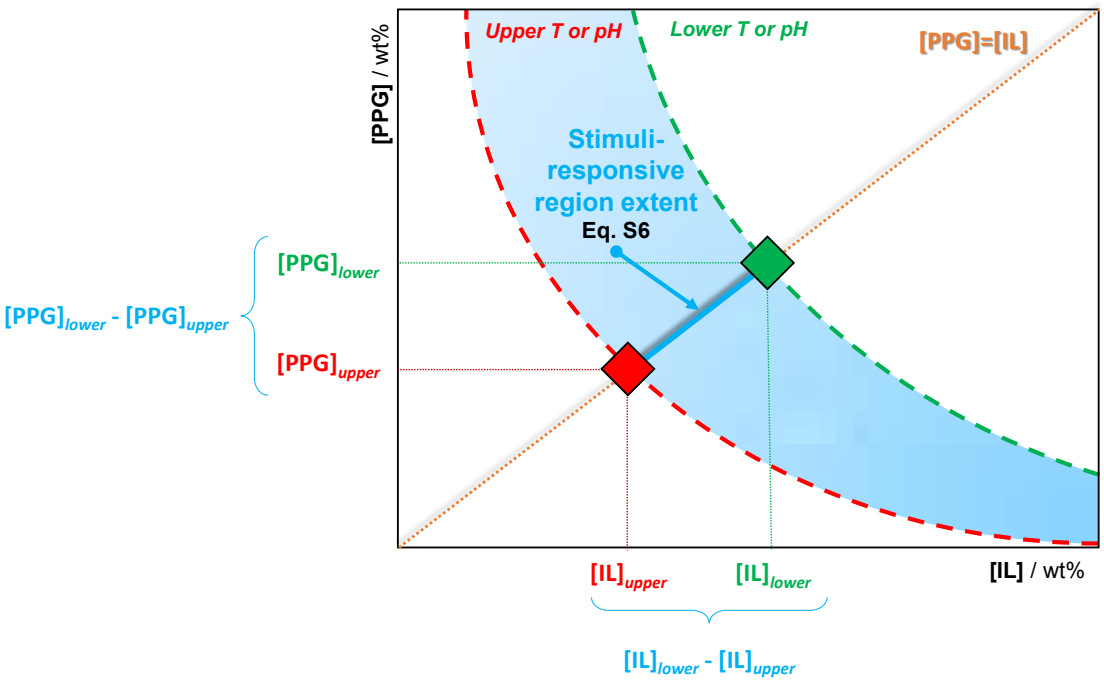


Figure S1 Schematic representation of the strategy adopted to determine the stimuli-responsive region extent: binodal curves obtained by the **Equations S1** to **S5** at the upper extreme of temperature or pH (red dashed line); binodal curves obtained by the **Equations S1** to **S5** at the lower extreme of temperature or pH (green dashed line); [IL]=[PPG] (orange dotted line); intersections between [IL]=[PPG] and binodal curves (red and green diamonds); stimuli-responsive region extent obtained by **Equation S6** (blue line).

RESULTS AND DISCUSSION

NMR Spectra of ILs

Table S1 Characterization of the synthesized ILs by NMR.

[Ch][C_3O_2]	**NMR ^{1}H (D_2O)**: 0.90 ppm (3H), 2.03 ppm (2H), 3.04 ppm (9H), 3.40 ppm (2H), 3.90 ppm (2H). **NMR ^{13}C (D_2O)**: 10.09 ppm (1C), 30.56 ppm (1C), 53.78 ppm (3C), 55.52 ppm (1C), 67.33 ppm (1C), 184.6 ppm (1C).
[Ch][C_3O_3]	**NMR ^{1}H (D_2O)**:1.20 ppm (3H), 3.08 ppm (10H), 3.40 ppm (2H), 3.90 ppm (3H). **NMR ^{13}C (D_2O)**: 19.98 ppm (1C), 53.80 ppm (3C), 55.52 ppm (1C), 67.35 ppm (1C), 68.40 ppm (1C), 182.40 ppm (1C).
[Ch][C_2O_3]	**NMR ^{1}H (D_2O)**: 3.09 ppm (9H), 3.40 ppm (2H), 3.85 ppm (2H), 3.94 ppm (2H). **NMR ^{13}C (D_2O)**: 53.80 ppm (3C), 55.53 ppm (1C), 60.92 ppm (1C), 67.35 ppm (1C), 179.4 ppm (1C).

Determination and characterization of ABS

Table S2 Experimental binodal data in weight percent (wt%) for the system composed of PPG 400 (1) + [Ch][C_2O_2] (2) + H_2O at pH 5.

pH 5					
25°C		**35°C**		**45°C**	
wt% 1	wt% 2	wt% 1	wt% 2	wt% 1	wt% 2
52.0526	6.6426	51.0081	3.6049	27.5181	1.0767
47.8649	7.4957	46.7639	4.5152	25.4878	1.4700
43.7978	8.6392	45.0800	5.1454	23.8206	1.9095
40.9635	10.0001	42.7463	5.2336	22.0939	2.4169
37.3311	10.8796	40.2729	5.6657	20.6231	2.7290
34.6332	11.8666	37.5205	6.0088	19.2640	3.5281
31.7785	13.2073	34.6189	6.5817	18.2740	4.0330
29.5765	14.4997	32.3465	7.1192	17.3336	4.6342
27.2302	15.3243	29.5743	7.6899	16.4276	5.4392
24.9395	17.0156	26.9419	8.4327	15.4217	6.9250
23.0502	18.6604	24.6685	9.6446	14.3297	7.6687
21.2834	20.1731	22.9234	10.6736	13.5598	8.9581
19.7638	21.6609	21.2764	11.7752	13.0102	9.9626
18.3446	22.6849	19.9849	13.1358	12.3283	10.9318
16.7054	24.6228	18.5646	13.8819	11.7257	11.8872
15.0980	26.7074	17.2963	15.0760		
		16.3440	16.1855		
		15.4950	17.3430		
		14.6650	18.3165		
		13.8015	19.3505		
		13.0711	20.5484		
		12.4223	21.5111		
		11.7741	22.4448		
		10.9206	23.4543		

Table S3 Experimental binodal data in weight percent (wt%) for the system composed of PPG 400 (1) + [Ch][C_2O_2] (2) + H_2O at pH 6.

pH 6					
25°C		**35°C**		**45°C**	
wt% 1	wt% 2	**wt%** 1	wt% 2	wt% 1	wt% 2
52.0383	4.7381	54.3955	2.5685	28.0663	1.0184
50.2980	5.0294	50.1224	2.9133	25.2986	1.8359
48.1989	5.2603	46.9557	3.2654	23.3208	2.3241
46.3469	5.5107	44.2337	3.6631	22.0002	2.5702
43.2140	5.9020	40.9815	3.7016	20.9085	2.8445
40.1971	6.2748	36.9974	4.1600	19.9327	3.1111
36.7778	6.7993	32.3655	4.7013	19.1201	3.3126
33.7471	7.5014	29.1148	5.3553	18.2332	3.5465
29.8559	8.2534	26.6254	5.9382	17.3395	3.9310
26.2272	9.6302	24.1082	6.5921	16.6737	4.2998
23.3128	10.9918	22.5823	7.5943	16.0391	4.6608
21.2540	12.5110	20.6872	8.1594	15.4314	5.0646
18.6970	13.2674	19.3304	8.9148	14.6468	5.4374
16.8440	15.2847	17.9818	9.6636	14.1187	5.6541
15.5629	16.1710	16.8677	10.3958	13.6146	6.0033
14.2039	17.0038	15.9546	11.1625	13.1623	6.3083
13.1303	18.0570	15.1517	11.7043	12.8101	6.6319
12.2751	18.9410	14.3029	12.3037	12.4234	6.9815
11.3491	20.1141	13.6020	12.8985	11.9718	7.1964
10.5844	20.7047	12.9544	13.5505		
9.8620	21.6936	12.2986	14.0171		
9.2370	22.6766	11.9768	14.6336		
8.6549	23.1520	11.4514	15.2497		
7.8561	23.7956	10.9823	15.7096		
		10.5461	16.2302		
		10.1255	16.6569		
		9.7639	17.2141		

Table S4 Experimental binodal data in weight percent (wt%) for the system composed of PPG 400 (1) + [Ch][C_2O_2] (2) + H_2O at pH 7.

pH 7					
25°C		**35°C**		**45°C**	
wt% 1	wt% 2	wt% 1	wt% 2	wt% 1	wt% 2
50.8678	3.8621	53.9272	1.9830	26.6820	0.6715
47.5811	4.5922	50.8829	2.1297	24.4373	1.0617
43.9977	5.4179	47.4662	2.6915	23.1565	1.4061
39.7212	5.8783	43.9468	2.9342	21.9719	1.6919
33.2348	6.3692	42.4763	3.2551	20.7468	1.9104
29.3248	7.7650	37.2310	3.3614	19.7253	2.2576
26.7109	8.9502	33.7856	3.7911	18.7702	2.6620
24.5690	10.0395	30.7088	4.0976	17.7827	3.0583
22.1818	10.8645	27.8331	4.7873	16.8953	3.4068
20.5197	11.9963	25.7969	5.4243	16.1645	3.6420
18.9642	13.0186	23.7174	5.7646	15.4728	3.9142
17.5809	13.7658	22.3942	6.4472	14.9074	4.1568
16.2120	14.6278	20.7684	7.1423	14.3427	4.5308
15.1945	15.8063	19.5002	7.8080	13.8234	4.8720
14.2040	16.4422	18.1627	8.5467	13.3428	5.2423
13.2327	17.1058	17.2184	9.3120	12.7482	5.6771
12.3935	17.9372	15.9818	9.7470	12.2663	5.9587
11.7017	18.5970	15.1370	10.3811	11.8502	6.2347
11.1514	19.3881	14.3074	10.9913	11.4816	6.4868
		13.4053	11.2989	11.0331	6.7965
		12.6023	11.7285		
		12.0660	12.3320		
		11.5299	12.9239		
		11.0093	13.4232		
		10.5500	14.1489		
		10.0701	14.5280		
		9.6537	15.0153		
		9.2062	15.6174		
		8.7834	16.5466		
		8.3760	17.1798		

Table S5 Experimental binodal data in weight percent (wt%) for the system composed of PPG 400 (1) + [Ch][C_3O_2] (2) + H_2O at pH 5.

pH 5					
25°C		**35°C**		**45°C**	
wt% 1	wt% 2	wt% 1	wt% 2	wt% 1	wt% 2
46.8748	7.0431	51.7672	4.3445	27.0211	1.2872
38.7754	9.3292	47.5769	5.1275	25.4250	1.8141
34.3940	12.0066	43.9050	5.7056	24.0638	1.9822
31.9112	13.0886	39.1480	6.0865	23.2466	2.1519
29.9347	13.7039	36.3332	6.8151	22.3075	2.4617
28.1129	14.5778	32.7036	7.4210	21.4659	2.6792
26.2945	15.0336	29.7389	7.3150	19.8649	2.9566
24.0011	16.3037	27.5069	7.9003	19.1356	3.1785
		25.2873	8.2126	18.5677	3.3970
		23.3341	8.8655	18.0011	3.6902
		21.6867	9.5448	17.3521	4.0084
		20.1110	10.0594	16.7390	4.3281
		18.9815	10.9605	16.2325	4.5517
		17.9115	11.5225	15.7795	4.7595
		16.9674	12.3731	15.2088	4.9812
		16.1825	13.1372	14.6253	5.1674
		15.4700	13.8933	14.2597	5.3778
		14.4415	14.5823	13.8824	5.5604
				13.5060	5.8128
				12.9972	6.0251

Table S6 Experimental binodal data in weight percent (wt%) for the system composed of PPG 400 (1) + [Ch][C_3O_2] (2) + H_2O at pH 6.

pH 6					
25°C		**35°C**		**45°C**	
wt% 1	wt% 2	wt% 1	wt% 2	wt% 1	wt% 2
53.1110	5.4635	50.9619	3.2328	27.0953	0.8379
51.3104	5.7345	45.0929	3.7895	25.5875	1.1053
49.3779	6.1263	41.1726	4.1655	23.9249	1.4562
47.3136	6.6051	37.8511	4.8215	22.4859	1.5828
44.5544	7.1340	33.3357	4.9943	21.1085	1.9189
42.4386	7.5000	30.4648	5.3938	20.1135	2.3122
39.7190	8.0903	28.2761	5.8685	19.2489	2.6437
37.0040	8.6146	26.2328	6.5708	18.2689	3.1673
35.1156	8.9502	24.7881	7.2378	17.5985	3.4865
31.8809	9.6800	23.2926	7.7205	16.8821	3.8749
30.0298	10.2268	21.8843	8.2112	16.1325	4.2508
28.1598	10.8279	20.7804	8.5727	15.3804	4.5147
26.4585	11.4299	19.8303	9.1191	14.8387	4.8553
24.7215	12.0755	18.9846	9.6364	14.3270	5.1507
23.2494	12.6942	18.1705	10.0812	13.8571	5.5395
21.7161	13.3782	17.4129	10.5879	13.4631	5.8142
20.3161	14.0558	16.6903	11.0183	13.0066	6.1329
18.9173	14.7680	16.0155	11.4695	12.5561	6.4419
17.7476	15.5089	15.4641	11.8253	12.1939	6.7110
16.5792	16.1302	14.8904	12.2325	11.8900	6.9628
		14.3567	12.6155		
		13.8739	13.0515		
		13.4035	13.5741		
		12.9607	13.9188		

Table S*7* Experimental binodal data in weight percent (wt%) for the system composed of PPG 400 (1) + [Ch][C_3O_2] (2) + H_2O at pH 7.

pH 7					
25°C		**35°C**		**45°C**	
wt% 1	wt% 2	wt% 1	wt% 2	wt% 1	wt% 2
51.0836	5.1028	53.9515	2.5165	27.2335	0.7168
47.9513	5.7016	50.7921	2.9743	25.5018	1.0673
45.0270	6.2915	47.5000	3.2701	23.8809	1.3527
41.1596	6.9643	45.9192	3.5120	22.7674	1.7173
38.1563	7.2852	42.9734	3.8557	20.4727	2.0850
35.1216	7.6491	41.0063	4.0133	19.3463	2.5785
32.0942	8.3232	38.9292	4.1509	18.1925	3.1946
29.9256	9.1064	34.1494	4.4272	17.1036	3.6365
26.9320	9.7614	31.8043	4.7062	16.4705	4.2326
25.1829	10.8957	29.7871	5.3178	15.7935	4.6403
23.2269	11.4934	27.9141	5.7368	15.2976	5.0609
21.2135	12.0826	25.5866	6.0610	14.6954	5.3865
19.7625	13.0315	23.8861	6.7504	14.1544	5.6911
18.3189	13.9869	22.4848	7.3711	13.6623	6.0892
17.2077	14.8245	21.0216	8.1203	12.9221	6.4191
15.9720	15.5128	19.7887	8.7383	12.5584	6.8038
15.0257	16.4302	18.6528	9.2530	12.1683	7.2149
14.1246	17.0703	17.6980	9.6986	11.7959	7.5328
13.2340	17.6448	16.6762	10.1712	11.4163	7.7915
12.4682	18.2054	15.7511	10.7202		
		14.8810	11.3177		
		14.2179	11.8907		
		13.4606	12.5021		
		12.7531	12.9190		

Table S8 Experimental binodal data in weight percent (wt%) for the system composed of PPG 400 (1) + [Ch][C_3O_3] (2) + H_2O at pH 4.

pH 4					
25°C		**35°C**		**45°C**	
wt% 1	wt% 2	wt% 1	wt% 2	wt% 1	wt% 2
48.3805	8.1294	49.8890	4.2937	27.0467	1.2430
42.8362	10.0296	44.6675	5.8546	23.4174	2.4815
37.3550	11.9395	39.7215	6.7231	21.3587	3.9666
31.5866	14.5502	35.4386	7.7968	18.9820	5.1510
26.2592	17.4088	32.1220	9.0281	16.8761	6.6091
22.5516	21.5894	29.7298	10.2205	15.6556	8.0787
19.8779	23.9944	26.9896	11.2427	14.5717	9.4543
16.8850	26.4863	24.7029	12.7533	13.6372	10.7088
13.9486	30.2170	22.6621	14.0027	12.8886	12.0303
		20.8237	15.4467	12.1266	12.9250
		19.1008	17.0357	11.3053	14.0891
		17.6666	18.7151	10.2947	16.4539
				9.5066	18.2928

Table S9 Experimental binodal data in weight percent (wt%) for the system composed of PPG 400 (1) + [Ch][C_3O_3] (2) + H_2O at pH 5.

pH 5					
25°C		**35°C**		**45°C**	
wt% 1	wt% 2	wt% 1	wt% 2	wt% 1	wt% 2
50.3539	5.2264	44.4720	3.9500	28.1804	0.9660
46.2283	6.3775	37.6959	4.2262	25.4555	1.5042
41.7916	7.4113	34.1929	5.3057	23.3908	2.0004
38.0003	8.0868	29.9877	5.9303	20.8479	2.2834
34.8356	9.4835	25.9930	6.4766	19.3339	3.3002
31.5141	10.1195	23.3341	8.3285	17.9862	3.9649
28.5320	11.2705	21.3065	9.5424	16.8947	4.5569
26.4381	12.9115	19.7957	10.3073	15.9957	5.2910
24.2008	13.8370	18.5764	11.1781	15.1746	5.8496
22.1841	14.5286	17.3767	12.0323	14.3415	6.5712
20.6405	16.0372	16.5371	12.9296	13.6554	7.0732
19.4217	17.1636	15.6634	13.5786	12.9911	7.4788
18.2014	18.0737	14.8526	14.2264	12.5974	7.9471
17.1147	18.8624	14.1338	14.7434	12.1492	8.5688
16.1578	19.5385	13.5004	15.5693	11.7601	9.0503
15.1319	20.3603	12.8892	16.0956	11.2909	9.9207
14.2832	21.1499				

Table S10 Experimental binodal data in weight percent (wt%) for the system composed of PPG 400 (1) + [Ch][C_3O_3] (2) + H_2O at pH 6.

pH 6					
25°C		**35°C**		**45°C**	
wt% 1	wt% 2	wt% 1	wt% 2	wt% 1	wt% 2
52.9398	3.9883	52.5304	2.3406	29.1393	0.6379
49.1621	4.9168	46.4562	3.0707	25.8100	1.0703
44.9005	5.7412	40.9653	3.6506	23.1114	1.5259
41.8368	6.3083	36.5482	4.1252	21.7396	1.8936
39.0403	6.9270	32.8556	4.4404	20.4634	2.2067
36.1647	7.5312	29.1867	5.0834	19.5272	2.6215
33.1985	8.3297	26.9028	6.0466	18.5394	2.9742
30.6613	8.9103	24.3635	6.6844	17.7458	3.2806
28.1640	9.7504	23.0489	7.3564	17.1270	3.5332
25.7912	10.5269	21.6780	8.0209	16.4110	3.9443
23.7907	11.6279	20.1298	8.5110	15.8207	4.3357
22.0288	12.5375	19.1388	9.1474	15.2346	4.6974
20.2462	13.5833	18.4091	9.6800	14.4310	5.0581
18.7633	14.5741	17.6382	10.1735	13.9706	5.4129
17.4505	15.3704	16.9766	10.6925	13.5463	5.7789
16.2469	16.1062	16.3220	11.1280	13.0803	6.2104
15.2239	17.0086	15.7345	11.5428	12.6020	6.6197
14.3771	17.7542	15.1736	11.9943	12.0997	6.8646
13.5973	18.3405	14.6944	12.2792	11.7539	7.2239
12.8285	18.9972	14.1987	12.6777	11.4036	7.5568

Table S11 Experimental binodal data in weight percent (wt%) for the system composed of PPG 400 (1) + [Ch][C_3O_3] (2) + H_2O at pH 7.

pH 7					
25°C		**35°C**		**45°C**	
wt% 1	wt% 2	wt% 1	wt% 2	wt% 1	wt% 2
52.9855	3.6741	50.8602	2.4249	30.0736	0.5431
47.7791	4.4453	47.8575	2.7991	26.5332	0.7381
44.8707	5.1595	42.4436	2.9316	23.8353	0.8662
41.3538	5.7254	39.4671	3.5613	22.5006	1.2796
38.5893	6.3112	34.7226	3.8562	21.2215	1.5639
36.4363	6.8183	31.7006	4.2925	19.8854	1.9450
34.2671	7.1604	29.1653	4.7424	19.0883	2.1903
31.9993	7.6465	26.7982	5.0619	18.3815	2.4432
29.9607	8.3590	25.1342	5.9860	17.7181	2.8757
28.1584	9.0329	23.6922	6.5403	17.0103	3.0604
26.4148	9.7718	22.3208	7.0024	16.3109	3.5713
24.8581	10.4785	21.3717	7.5145	15.7144	4.0981
22.8939	10.9574	20.4247	7.9391	15.0855	4.4688
21.7153	11.5315	19.4981	8.3489	14.3160	5.1947
20.8692	12.3856	18.7039	8.7239	13.9533	5.4903
19.8893	13.0531	17.9323	9.0741	13.5849	5.8528
18.9883	13.5014	17.3816	9.4639	13.2250	6.0315
18.2071	13.8897	16.7927	9.8217	12.9019	6.2923
17.4959	14.4949	16.2089	10.2253	12.6083	6.5239
16.8207	14.7779	15.5856	10.4581	12.3114	6.8632

Table S12 Experimental binodal data in weight percent (wt%) for the system composed of PPG 400 (1) + [Ch][C_2O_3] (2) + H_2O at pH 3.

pH 3					
25°C		**35°C**		**45°C**	
wt% 1	wt% 2	wt% 1	wt% 2	wt% 1	wt% 2
47.0843	8.0792	43.6079	3.4607	30.0274	1.1144
35.2865	11.1036	33.4381	7.5830	23.6628	1.8346
24.0550	17.7162	24.4446	10.8759	16.6339	5.1564
17.1762	25.8776	17.8555	16.5824	13.2317	11.2340
12.9369	31.7364	12.8649	24.3085	10.6148	14.0661
		9.2674	29.6595	8.6778	20.6185

Table S13 Experimental binodal data in weight percent (wt%) for the system composed of PPG 400 (1) + [Ch][C_2O_3] (2) + H_2O at pH 4.

pH 4					
25°C		**35°C**		**45°C**	
wt% 1	wt% 2	wt% 1	wt% 2	wt% 1	wt% 2
51.6117	5.1634	40.6904	4.2990	24.7092	1.2555
44.2285	6.5446	36.1927	5.5286	22.2734	2.4483
38.2132	8.4454	30.4091	6.1288	20.6575	3.0724
34.3607	10.3301	26.3852	7.3571	19.4427	3.6091
29.6854	11.9131	23.4970	8.7713	18.3534	4.2692
26.3085	13.4601	21.2252	10.1050	17.2859	4.8418
23.6850	15.2502	19.5372	11.4266	16.2936	5.4958
21.2674	17.3772	18.1494	12.6293	15.4553	6.0556
19.1828	18.3592	16.8208	13.5454	14.7260	6.6233
17.3293	20.1251	15.6445	14.6275	14.0259	7.4008
15.8272	21.6498	14.6447	15.5982	13.3186	7.8947
14.1696	23.1806	13.7964	16.3318	12.7422	8.5617
13.0464	24.6301	13.0639	17.3125	12.2935	9.1422
10.5013	27.2553	12.4398	18.0910	11.8747	9.8389
9.5167	28.2245	11.9065	18.7438	11.3166	10.2448
		11.2744	19.4416	10.8856	10.8121
		10.6947	20.2689	10.4423	11.3970

Table S14 Experimental binodal data in weight percent (wt%) for the system composed of PPG 400 (1) + [Ch][C_2O_3] (2) + H_2O at pH 5.

pH 5					
25°C		**35°C**		**45°C**	
wt% 1	wt% 2	wt% 1	wt% 2	wt% 1	wt% 2
44.1557	6.1333	44.1460	3.4740	27.0451	0.6775
40.1281	7.0954	39.0186	3.7437	24.3166	1.2696
36.4031	8.0001	34.6534	4.4653	21.8823	1.9762
33.1068	8.7872	30.7600	5.0127	20.4320	2.4837
29.4944	9.7076	27.5912	5.6900	19.0647	3.1972
27.2580	10.7327	25.2529	6.5080	17.8752	3.5280
24.9963	11.8764	23.3240	7.3543	16.8665	4.1828
23.0563	12.8369	21.4663	8.1530	15.9685	4.7033
21.1971	13.8795	20.1407	8.9645	15.2308	5.2069
19.7276	14.8662	18.7077	9.6748	14.6365	5.4650
18.3711	16.0214	17.6509	10.2456	14.0173	5.8880
17.2781	16.9912	16.5705	11.0764	13.4871	6.2112
16.1661	17.7762	15.4260	11.7607	12.8472	6.9158
15.2486	18.4783	14.6517	12.3623	12.1715	7.3913
14.4919	19.3388	13.9638	13.0401	11.6296	7.9056
13.7357	20.0480	13.2132	13.5753	11.1928	8.4247
13.0309	20.5402	12.5558	14.2863	10.7625	8.7209
12.3732	21.2126	12.1003	14.6592	10.4021	9.2065
11.7760	21.8062	11.4734	15.2594	10.0361	9.6103
				9.6094	9.9694

Table S15 Experimental binodal data in weight percent (wt%) for the system composed of PPG 400 (1) + [Ch][C_2O_3] (2) + H_2O at pH 6.

pH 6					
25°C		**35°C**		**45°C**	
wt% 1	wt% 2	wt% 1	wt% 2	wt% 1	wt% 2
53.9349	3.6708	51.8471	2.3360	23.0465	1.1130
51.3538	4.1625	46.2965	2.7390	21.3714	1.6761
47.3901	4.5269	40.8127	3.0008	20.3095	2.1107
43.1681	5.6504	37.1580	3.2756	19.4021	2.3687
39.9403	6.2553	34.5715	3.5172	18.0773	2.5725
36.0062	6.7294	30.4354	4.0702	17.4585	2.8532
31.9501	7.4952	27.2917	4.5872	16.7045	3.1258
29.6889	8.2654	25.5003	5.1053	16.0732	3.6224
27.7612	9.1421	23.7715	5.6409	15.4852	4.0343
25.9524	10.1806	22.1628	6.4198	14.7743	4.3115
24.2398	10.7851	20.0709	6.8545	14.1576	4.7331
22.7445	11.2533	18.9754	7.5163	13.6180	5.1508
21.4482	11.7269	17.9028	8.0710	13.0245	5.5436
20.5018	12.5279	16.9464	8.5340	12.5321	5.8989
19.5224	13.2292	16.0634	8.9872	12.0250	6.1774
18.5154	13.9485	15.3824	9.5122	11.6437	6.6683
17.6441	14.4196	14.7001	10.0694	11.2110	6.9907
16.9750	15.0645	14.0692	10.5560	10.8391	7.3312
		13.4841	11.1595		
		12.8559	11.6218		

Table S16 Correlation parameters used to describe the experimental binodal data of the system composed of PPG 400 + [Ch][C_2O_2] + H_2O at pH 7.

T	Eq.	$A \pm \sigma$	$B \pm \sigma$	$C \pm \sigma$	R^2
25°C	(S2)	$2.24 \times 10^2 \pm 2.03 \times 10^2$	$-8.01 \times 10^{-1} \pm 8.46 \times 10^{-1}$	$4.43 \times 10^{-1} \pm 2.40 \times 10^{-1}$	0.9917
35°C	(S2)	$5.27 \times 10^2 \pm 3.71 \times 10^2$	$-1.87 \times 10^0 \pm 1.21 \times 10^0$	$2.79 \times 10^{-1} \pm 1.23 \times 10^{-1}$	0.9932
45°C	(S2)	$3.39 \times 10^1 \pm 1.51 \times 10^0$	$-3.12 \times 10^{-1} \pm 4.10 \times 10^{-2}$	$6.66 \times 10^{-1} \pm 5.21 \times 10^{-2}$	0.9990

Table S17 Correlation parameters used to describe the experimental binodal data of the system composed of PPG 400 + [Ch][C_2O_2] + H_2O at pH 6.

T	Eq.	$A \pm \sigma$	$B \pm \sigma$	$C \pm \sigma$	R^2
25°C	(S3)	$8.02 \times 10^1 \pm 5.41 \times 10^0$	$-1.05 \times 10^{-1} \pm 8.26 \times 10^{-3}$	-	0.9828
35°C	(S3)	$6.87 \times 10^1 \pm 5.75 \times 10^0$	$-1.34 \times 10^{-1} \pm 1.41 \times 10^{-2}$	-	0.9580
45°C	(S2)	$3.84 \times 10^1 \pm 4.98 \times 10^0$	$-2.91 \times 10^{-1} \pm 1.08 \times 10^{-1}$	$7.09 \times 10^{-1} \pm 1.42 \times 10^{-1}$	0.9939

Table S18 Correlation parameters used to describe the experimental binodal data of the system composed of PPG 400 + [Ch][C_2O_2] + H_2O at pH 5.

T	Eq.	$A \pm \sigma$	$B \pm \sigma$	$C \pm \sigma$	R^2
25°C	(S2)	$1.39 \times 10^2 \pm 3.91 \times 10^1$	$-3.28 \times 10^{-1} \pm 1.61 \times 10^{-1}$	$5.83 \times 10^{-1} \pm 1.15 \times 10^{-1}$	0.9988
35°C	(S2)	$6.11 \times 10^2 \pm 5.54 \times 10^1$	$-1.73 \times 10^0 \pm 1.71 \times 10^0$	$2.66 \times 10^{-1} \pm 1.67 \times 10^{-1}$	0.9923
45°C	(S2)	$9.03 \times 10^1 \pm 4.94 \times 10^1$	$-1.16 \times 10^0 \pm 5.35 \times 10^{-1}$	$2.24 \times 10^{-1} \pm 7.96 \times 10^{-2}$	0.9982

Table S19 Correlation parameters used to describe the experimental binodal data of the system composed of PPG 400 + [Ch][C_3O_2] + H_2O at pH 7.

T	Eq.	$A \pm \sigma$	$B \pm \sigma$	$C \pm \sigma$	R^2
25°C	(S2)	$3.76 \times 10^{2} \pm 3.35 \times 10^{2}$	$-9.85 \times 10^{-1} \pm 8.47 \times 10^{-1}$	$4.26 \times 10^{-1} \pm 1.88 \times 10^{-1}$	0.9963
35°C	(S2)	$1.04 \times 10^{3} \pm 1.03 \times 10^{3}$	$-2.30 \times 10^{0} \pm 2.81 \times 10^{0}$	$2.53 \times 10^{-1} \pm 2.17 \times 10^{-1}$	0.9897
45°C	(S1)	$3.89 \times 10^{1} \pm 1.37 \times 10^{0}$	$-4.21 \times 10^{-1} \pm 2.57 \times 10^{-2}$	$8.01 \times 10^{-5} \pm 3.37 \times 10^{-5}$	0.9968

Table S20 Correlation parameters used to describe the experimental binodal curve of the system composed of PPG 400 + [Ch][C_3O_2] + H_2O at pH 6.

T	Eq.	$A \pm \sigma$	$B \pm \sigma$	$C \pm \sigma$	$D \pm \sigma$	R^2
25°C	(S2)	$1.22 \times 10^{2} \pm 2.59 \times 10^{2}$	$-2.01 \times 10^{-1} \pm 9.86 \times 10^{-2}$	$8.29 \times 10^{-1} \pm 1.43 \times 10^{-1}$	-	0.9985
35°C	(S3)	$7.15 \times 10^{1} \pm 6.44 \times 10^{0}$	$-1.37 \times 10^{-1} \pm 1.35 \times 10^{-2}$	-	-	0.9588
45°C	(S4)	$8.93 \times 10^{1} \pm 4.78 \times 10^{1}$	$-1.23 \times 10^{0} \pm 1.46 \times 10^{0}$	$4.25 \times 10^{-4} \pm 2.93 \times 10^{-4}$	$2.17 \times 10^{-1} \pm 2.04 \times 10^{-1}$	0.9978

Table S21 Correlation parameters used to describe the experimental binodal curve of the system composed of PPG 400 + [Ch][C_3O_2] + H_2O at pH 5.

T	Eq.	$A \pm \sigma$	$B \pm \sigma$	$C \pm \sigma$	R^2
25°C	(S1)	$1.00 \times 10^{2} \pm 5.02 \times 10^{1}$	$-2.81 \times 10^{-1} \pm 1.87 \times 10^{-1}$	$6.56 \times 10^{-5} \pm 5.92 \times 10^{-5}$	0.9905
35°C	(S3)	$9.79 \times 10^{1} \pm 1.19 \times 10^{1}$	$-1.50 \times 10^{-1} \pm 1.67 \times 10^{-2}$	-	0.9651
45°C	(S2)	$3.99 \times 10^{1} \pm 6.55 \times 10^{0}$	$-3.15 \times 10^{-1} \pm 1.37 \times 10^{-1}$	$7.03 \times 10^{-1} \pm 1.69 \times 10^{-1}$	0.9954

Table S22 Correlation parameters used to describe the experimental binodal curve of the system composed of PPG 400 + [Ch][C_3O_3] + H_2O at pH 7.

T	Eq.	$A \pm \sigma$	$B \pm \sigma$	$C \pm \sigma$	$D \pm \sigma$	R^2
25°C	(S2)	$1.26 \times 10^{2} \pm 3.14 \times 10^{1}$	$-3.87 \times 10^{-1} \pm 1.64 \times 10^{-1}$	$6.13 \times 10^{-1} \pm 1.16 \times 10^{-1}$	-	0.9981
35°C	(S3)	$6.75 \times 10^{1} \pm 6.22 \times 10^{0}$	$-1.54 \times 10^{-1} \pm 1.79 \times 10^{-2}$	-	-	0.9535
45°C	(S5)	$3.34 \times 10^{1} \pm 1.85 \times 10^{0}$	$-3.77 \times 10^{-1} \pm 2.69 \times 10^{-2}$	$-3.13 \times 10^{-2} \pm 3.15 \times 10^{-2}$	$-2.81 \times 10^{0} \pm 1.39 \times 10^{0}$	0.9970

Table S23 Correlation parameters used to describe the experimental binodal curve of the system composed of PPG 400 + [Ch][C_3O_3] + H_2O at pH 6.

T	Eq.	$A \pm \sigma$	$B \pm \sigma$	$C \pm \sigma$	$D \pm \sigma$	R^2
25°C	(S2)	$1.09 \times 10^{2} \pm 2.00 \times 10^{1}$	$-2.57 \times 10^{-1} \pm 1.02 \times 10^{-1}$	$7.20 \times 10^{-1} \pm 1.10 \times 10^{-1}$	-	0.9980
35°C	(S2)	$1.65 \times 10^{3} \pm 1.91 \times 10^{3}$	$-2.90 \times 10^{0} \pm 3.04 \times 10^{0}$	$1.93 \times 10^{-1} \pm 1.53 \times 10^{-1}$	-	0.9949
45°C	(S4)	$5.66 \times 10^{1} \pm 9.98 \times 10^{0}$	$-7.72 \times 10^{-1} \pm 1.75 \times 10^{-1}$	$-1.72 \times 10^{-4} \pm 9.64 \times 10^{-5}$	$-3.38 \times 10^{-1} \pm 6.61 \times 10^{-2}$	0.9996

Table S24 Correlation parameters used to describe the experimental binodal curve of the system composed of PPG 400 + [Ch][C_3O_3] + H_2O at pH 5.

T	Eq.	$A \pm \sigma$	$B \pm \sigma$	$C \pm \sigma$	$D \pm \sigma$	R^2
25°C	(S2)	$1.20 \times 10^{2} \pm 3.87 \times 10^{1}$	$-2.94 \times 10^{-1} \pm 1.82 \times 10^{-1}$	$6.46 \times 10^{-1} \pm 1.58 \times 10^{-1}$	-	0.9974
35°C	(S3)	$5.83 \times 10^{1} \pm 6.38 \times 10^{0}$	$-1.01 \times 10^{-1} \pm 1.36 \times 10^{-2}$	-	-	0.9530
45°C	(S4)	$6.78 \times 10^{1} \pm 5.80 \times 10^{1}$	$-8.82 \times 10^{-1} \pm 1.13 \times 10^{0}$	$-6.81 \times 10^{-5} \pm 6.11 \times 10^{-5}$	$-2.97 \times 10^{-1} \pm 2.87 \times 10^{-1}$	0.9954

Table S25 Correlation parameters used to describe the experimental binodal curve of the system composed of PPG 400 + [Ch][C_3O_3] + H_2O at pH 4.

T	Eq.	$A \pm \sigma$	$B \pm \sigma$	$C \pm \sigma$	R^2
25°C	(S1)	$1.65 \times 10^{2} \pm 2.74 \times 10^{1}$	$-4.38 \times 10^{-1} \pm 5.29 \times 10^{-2}$	$3.42 \times 10^{-6} \pm 1.23 \times 10^{-7}$	0.9981
35°C	(S2)	$1.31 \times 10^{2} \pm 7.59 \times 10^{1}$	$-4.47 \times 10^{-1} \pm 4.08 \times 10^{-1}$	$5.16 \times 10^{-1} \pm 2.21 \times 10^{-1}$	0.9962
45°C	(S2)	$3.51 \times 10^{1} \pm 2.83 \times 10^{0}$	$-2.28 \times 10^{-1} \pm 6.30 \times 10^{-2}$	$6.01 \times 10^{-1} \pm 8.03 \times 10^{-2}$	0.9983

Table S26 Correlation parameters used to describe the experimental binodal curve of the system composed of PPG 400 + [Ch][C_2O_3] + H_2O at pH 6.

T	Eq.	$A \pm \sigma$	$B \pm \sigma$	$C \pm \sigma$	R^2
25°C	(S2)	$1.61 \times 10^{2} \pm 9.27 \times 10^{1}$	$-5.46 \times 10^{-1} \pm 4.23 \times 10^{-1}$	$5.25 \times 10^{-1} \pm 1.98 \times 10^{-1}$	0.9956
35°C	(S3)	$6.68 \times 10^{1} \pm 7.45 \times 10^{1}$	$-1.65 \times 10^{-1} \pm 2.29 \times 10^{-2}$	-	0.9424
45°C	(S2)	$3.24 \times 10^{1} \pm 4.80 \times 10^{0}$	$-3.08 \times 10^{-1} \pm 1.27 \times 10^{-1}$	$6.37 \times 10^{-1} \pm 1.48 \times 10^{-1}$	0.9951

Table S27 Correlation parameters used to describe the experimental binodal curve of the system composed of PPG 400 + [Ch][C_2O_3] + H_2O at pH 5.

T	Eq.	$A \pm \sigma$	$B \pm \sigma$	$C \pm \sigma$	R^2
25°C	(S2)	$2.15 \times 10^{2} \pm 1.03 \times 10^{2}$	$-6.70 \times 10^{-1} \pm 3.32 \times 10^{-1}$	$4.71 \times 10^{-1} \pm 1.09 \times 10^{-1}$	0.9988
35°C	(S3)	$5.87 \times 10^{1} \pm 5.09 \times 10^{0}$	$-1.16 \times 10^{-1} \pm 1.21 \times 10^{-2}$	-	0.9659
45°C	(S2)	$3.19 \times 10^{1} \pm 1.34 \times 10^{0}$	$-2.30 \times 10^{-1} \pm 3.24 \times 10^{-2}$	$7.15 \times 10^{-1} \pm 4.89 \times 10^{-2}$	0.9993

Table S28 Correlation parameters used to describe the experimental binodal curve of the system composed of PPG 400 + [Ch][C_2O_3] + H_2O at pH 4.

T	Eq.	$A \pm \sigma$	$B \pm \sigma$	$C \pm \sigma$	R^2
25°C	(S1)	$1.38 \times 10^{2} \pm 9.27 \times 10^{0}$	$-4.37 \times 10^{-1} \pm 2.41 \times 10^{-2}$	$1.42 \times 10^{-5} \pm 4.86 \times 10^{-6}$	0.9988
35°C	(S2)	$8.00 \times 10^{2} \pm 1.10 \times 10^{3}$	$-2.11 \times 10^{0} \pm 3.08 \times 10^{0}$	$2.34 \times 10^{-1} \pm 2.25 \times 10^{-1}$	0.9934
45°C	(S2)	$3.07 \times 10^{1} \pm 1.71 \times 10^{0}$	$-1.73 \times 10^{-1} \pm 4.00 \times 10^{-2}$	$7.54 \times 10^{-1} \pm 7.89 \times 10^{-2}$	0.9983

Table S29 Correlation parameters used to describe the experimental binodal curve of the system composed of PPG 400 + [Ch][C_2O_3] + H_2O for pH 3.

T	Eq.	$A \pm \sigma$	$B \pm \sigma$	$C \pm \sigma$	R^2
25°C	(S3)	$7.14 \times 10^{1} \pm 1.85 \times 10^{1}$	$-5.75 \times 10^{-2} \pm 1.92 \times 10^{-2}$	-	0.9782
35°C	(S2)	$6.66 \times 10^{1} \pm 3.52 \times 10^{1}$	$-1.70 \times 10^{-1} \pm 2.91 \times 10^{-1}$	$7.22 \times 10^{-1} \pm 4.69 \times 10^{-1}$	0.9947
45°C	(S3)	$2.88 \times 10^{1} \pm 6.44 \times 10^{0}$	$-7.11 \times 10^{-2} \pm 3.69 \times 10^{-2}$	-	0.9126

Binodal curves representations: temperature and pH effect

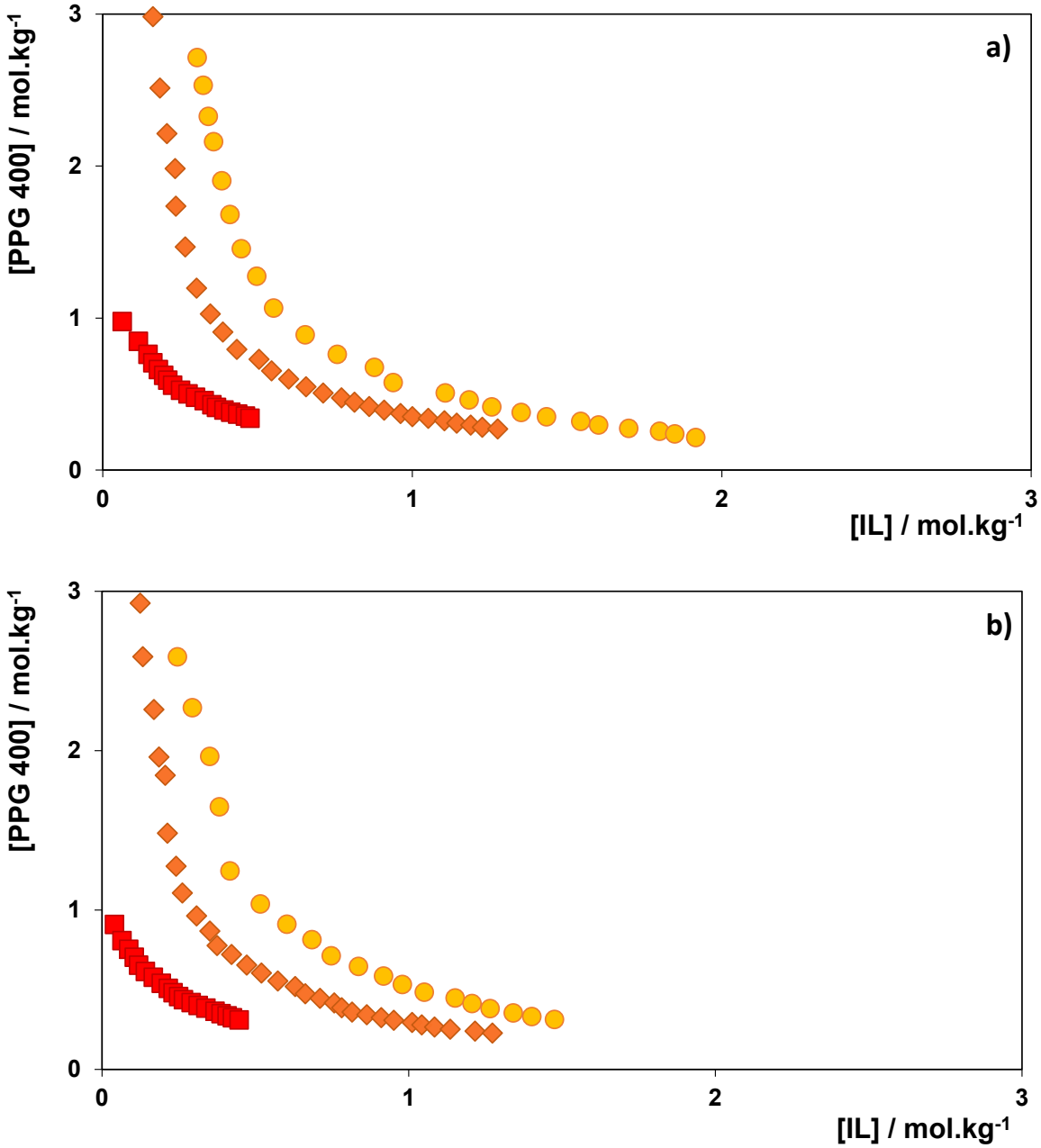


Figure S2 Binodal curves of the systems composed of PPG 400 + [Ch][C_2O_2] + H_2O at a) pH 6 and b) pH 7 at 25°C (●), 35°C (◆) and 45°C (■).

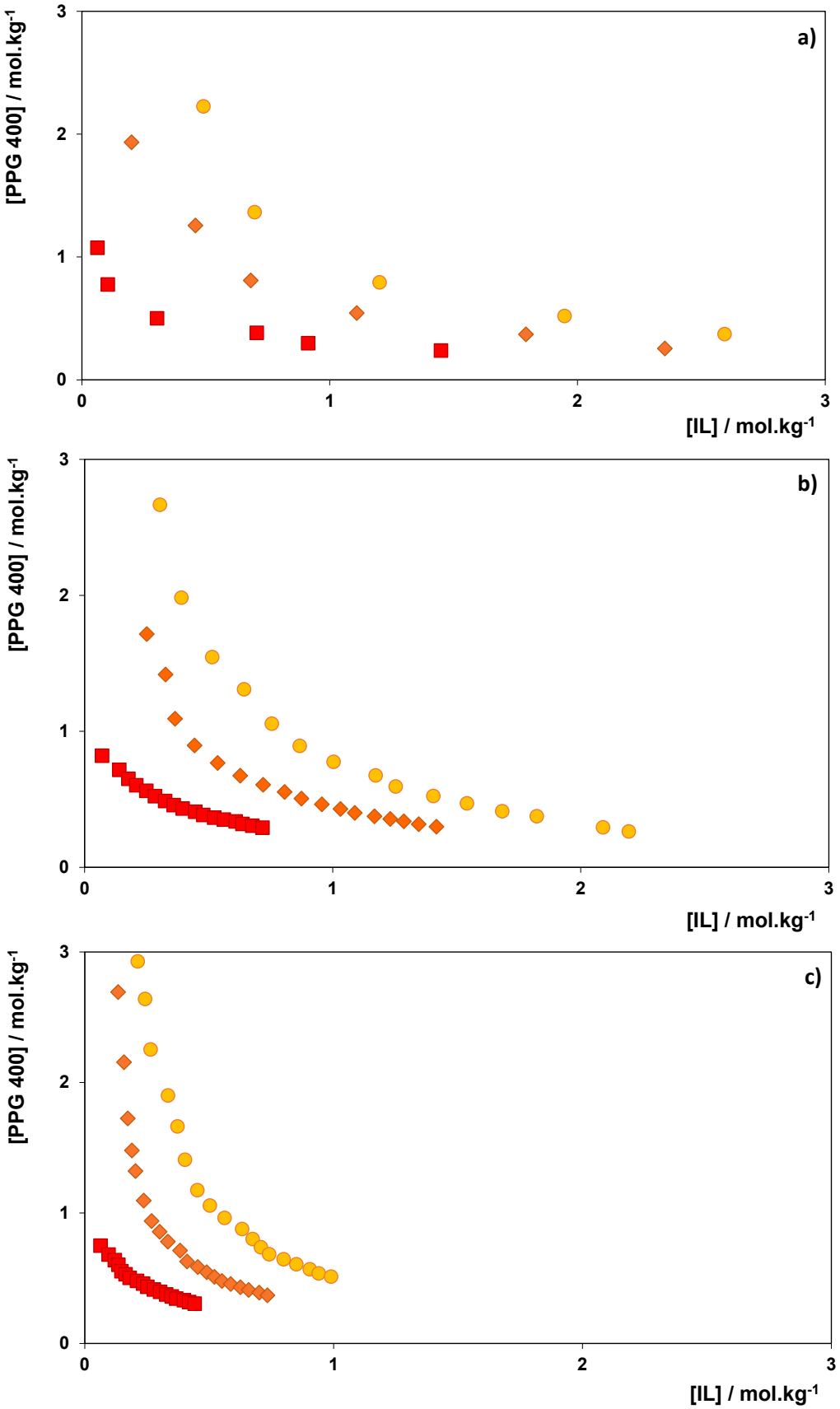


Figure S3 Binodal curves of the systems composed of PPG 400 + [Ch][C_2O_3] + H_2O at a) pH 3, b) pH 4 and *c*) pH 6 at 25°C (●), 35°C (◆) and 45°C (■).

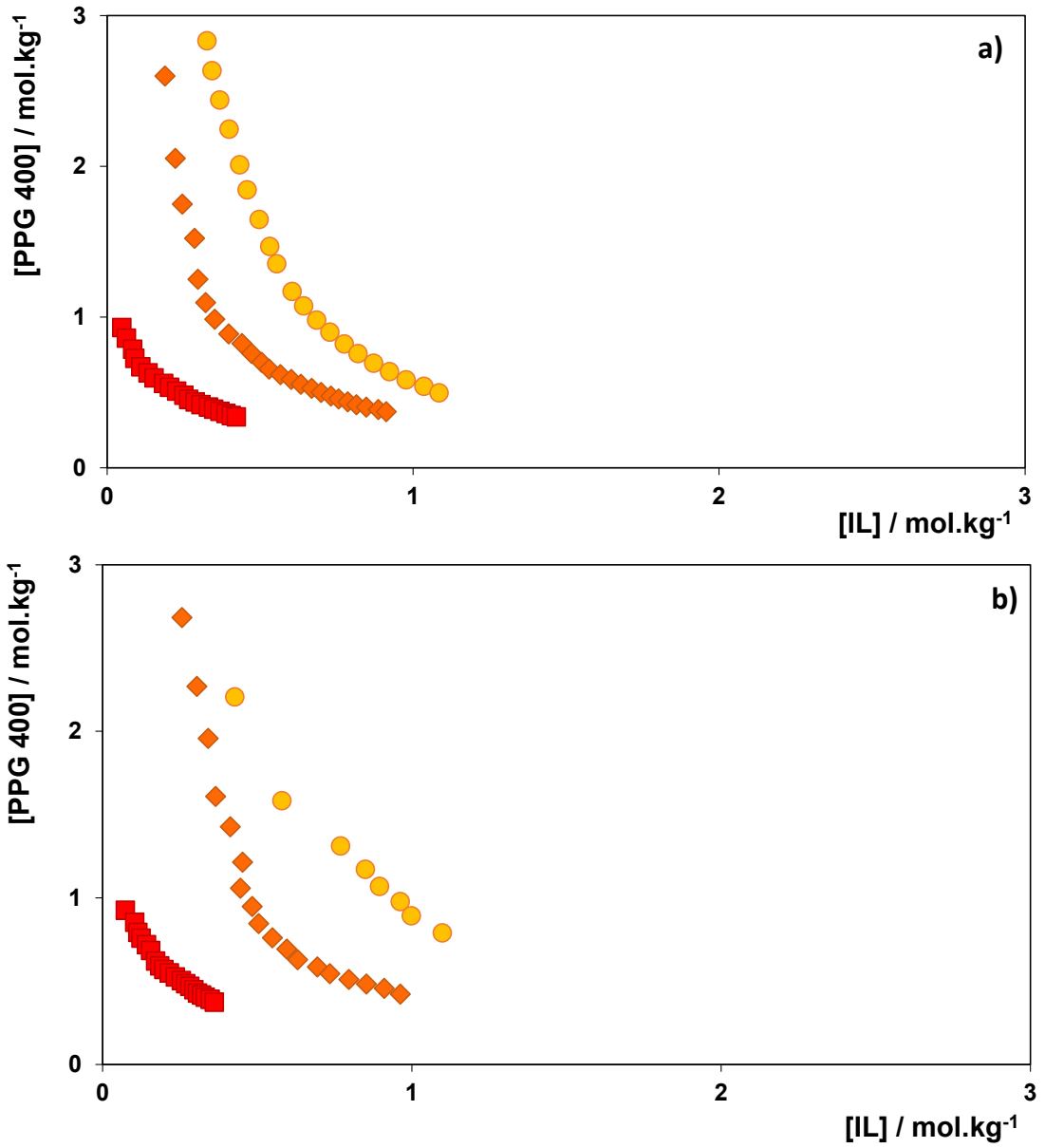


Figure S4 Binodal curves of the systems composed of PPG 400 + [Ch][C_3O_2] + H_2O at a) pH 6 and b) pH 7 at 25°C (●), 35°C (◆) and 45°C (■).

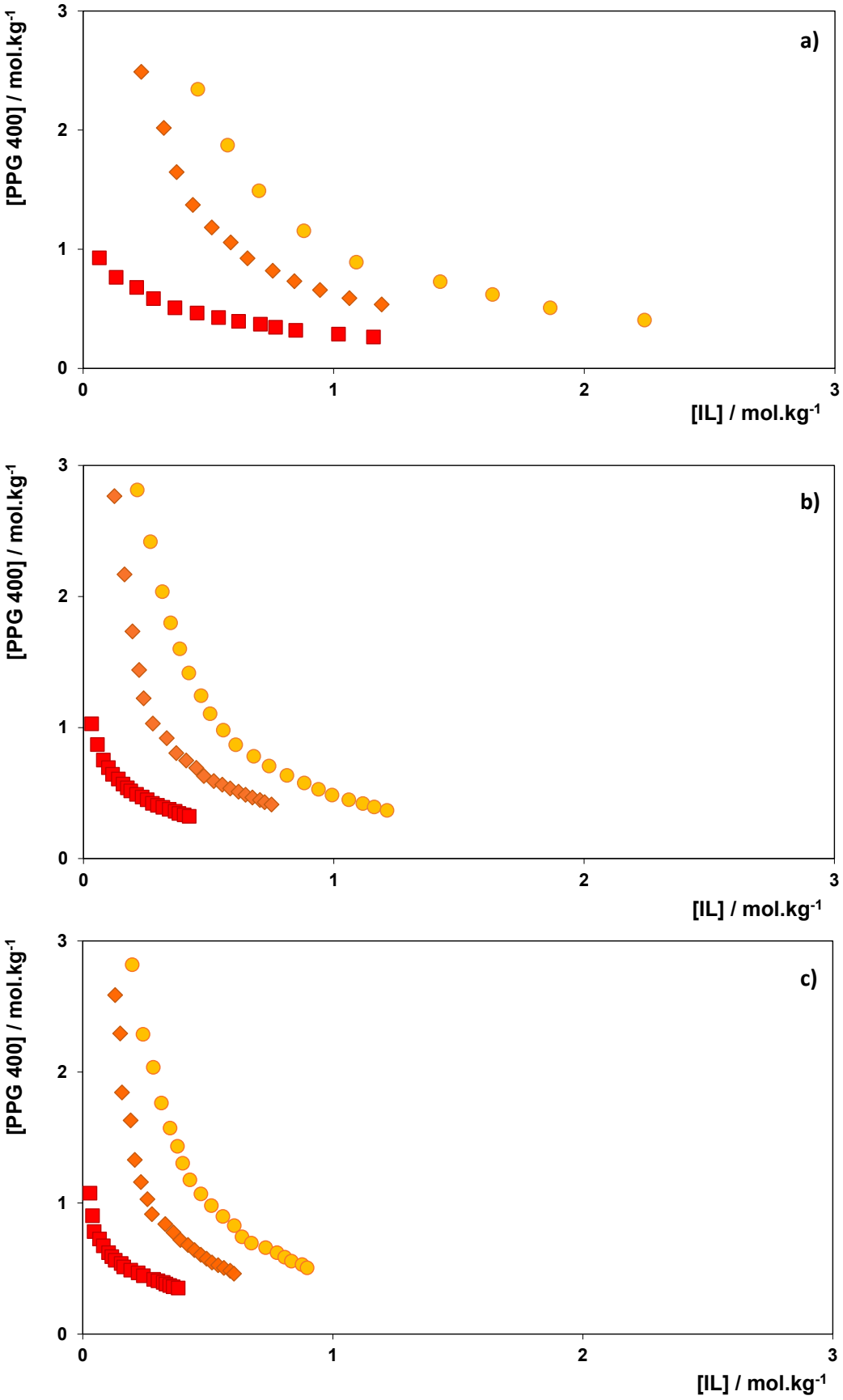


Figure S5 Binodal curves of the systems composed of PPG 400 + [Ch][C_3O_3] + H_2O at a) pH 4, b) pH 6 and c) pH 7 at 25°C (●), 35°C (◆) and 45°C (■).

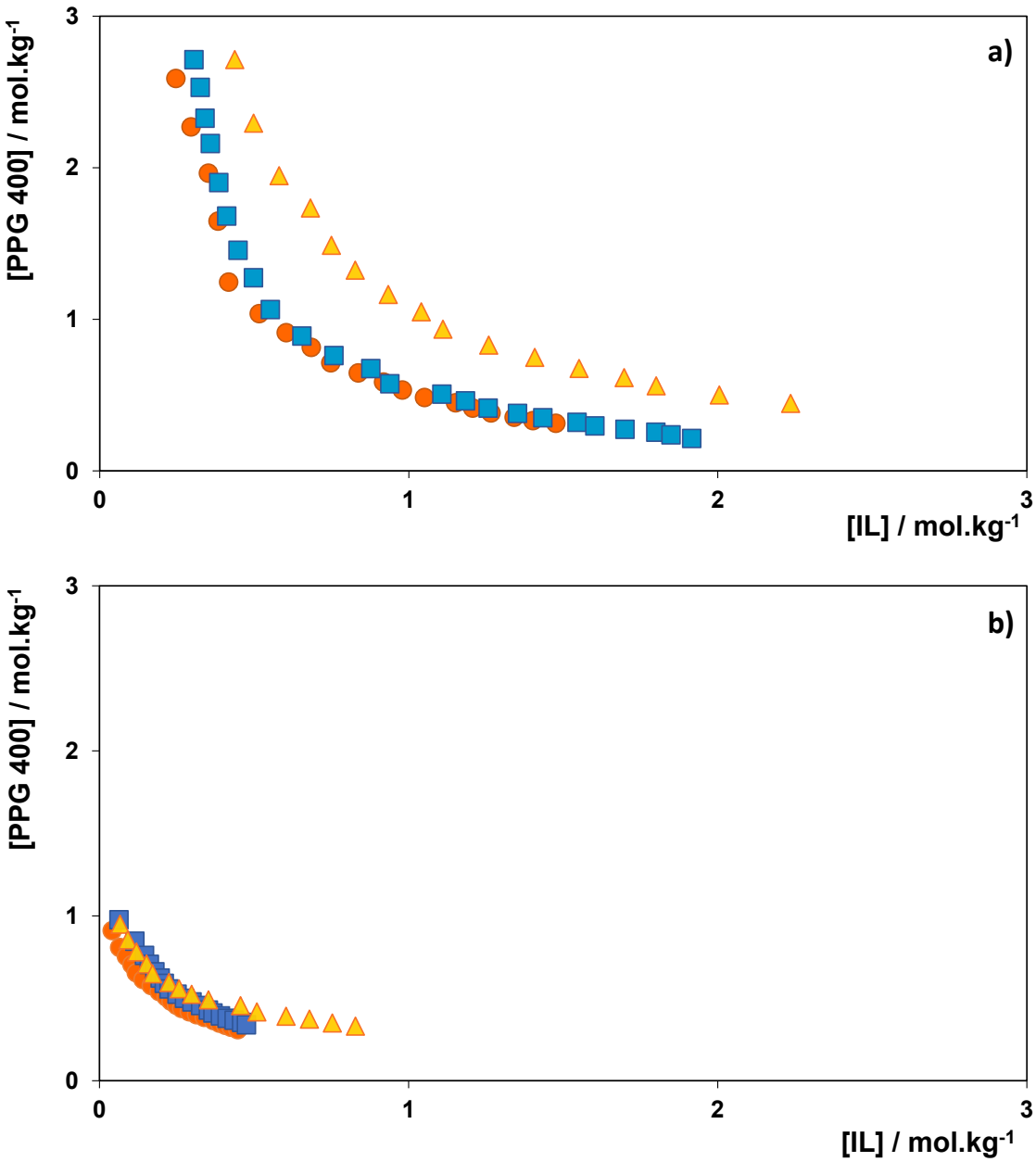


Figure S6 Binodal curves of the systems composed of PPG 400 + $[Ch][C_2O_2]$ + H_2O at pH 5 (▲), pH 6 (■) and pH 7 (●) at a) 25°C and b) 45°C.

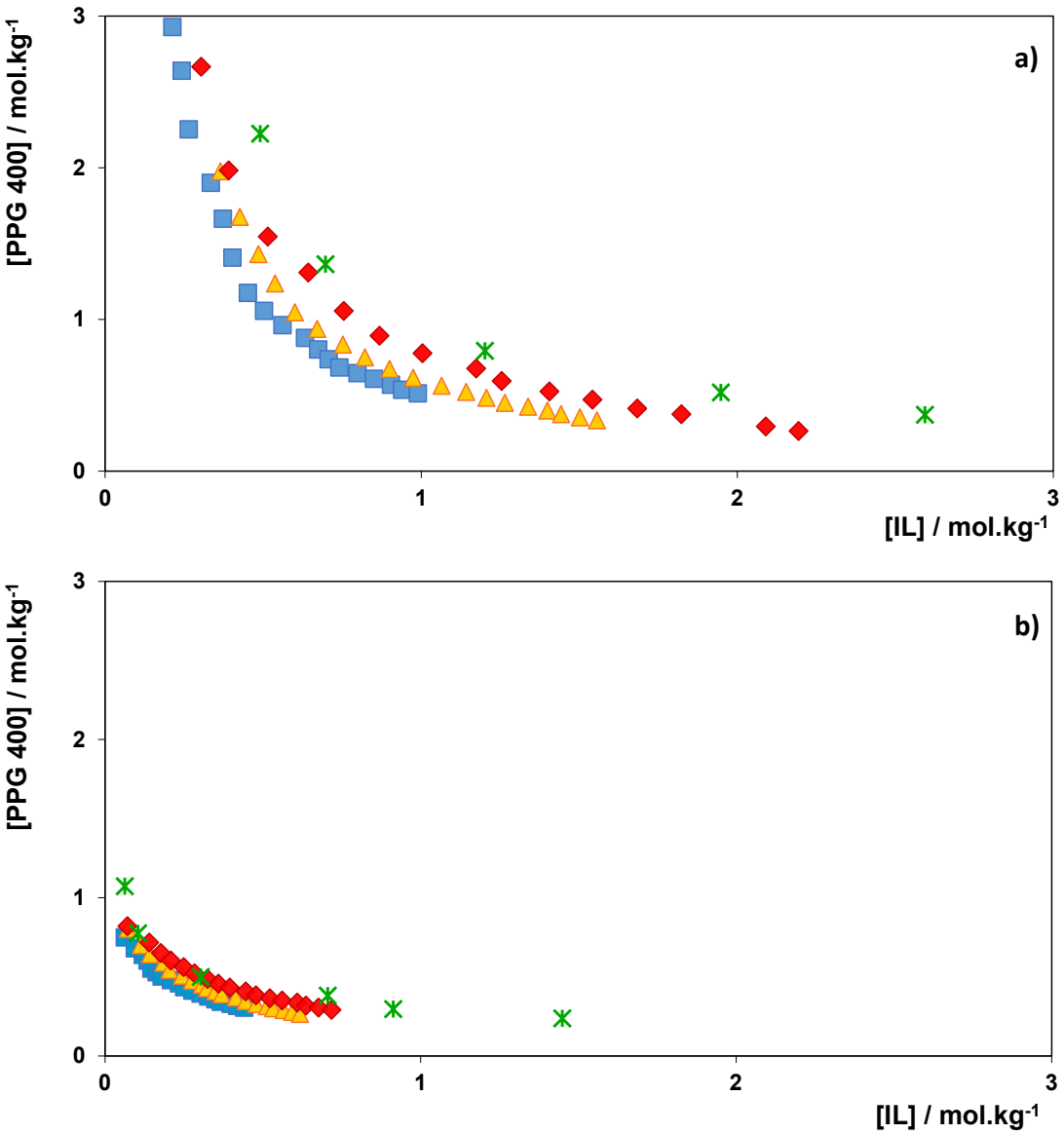


Figure S7 Binodal curves of the systems composed of PPG 400 + [Ch][C_2O_3] + H_2O at pH 3 (+), pH 4 (◆), pH 5 (▲) and pH 6 (■), at a) 25°C and b) 45°C.

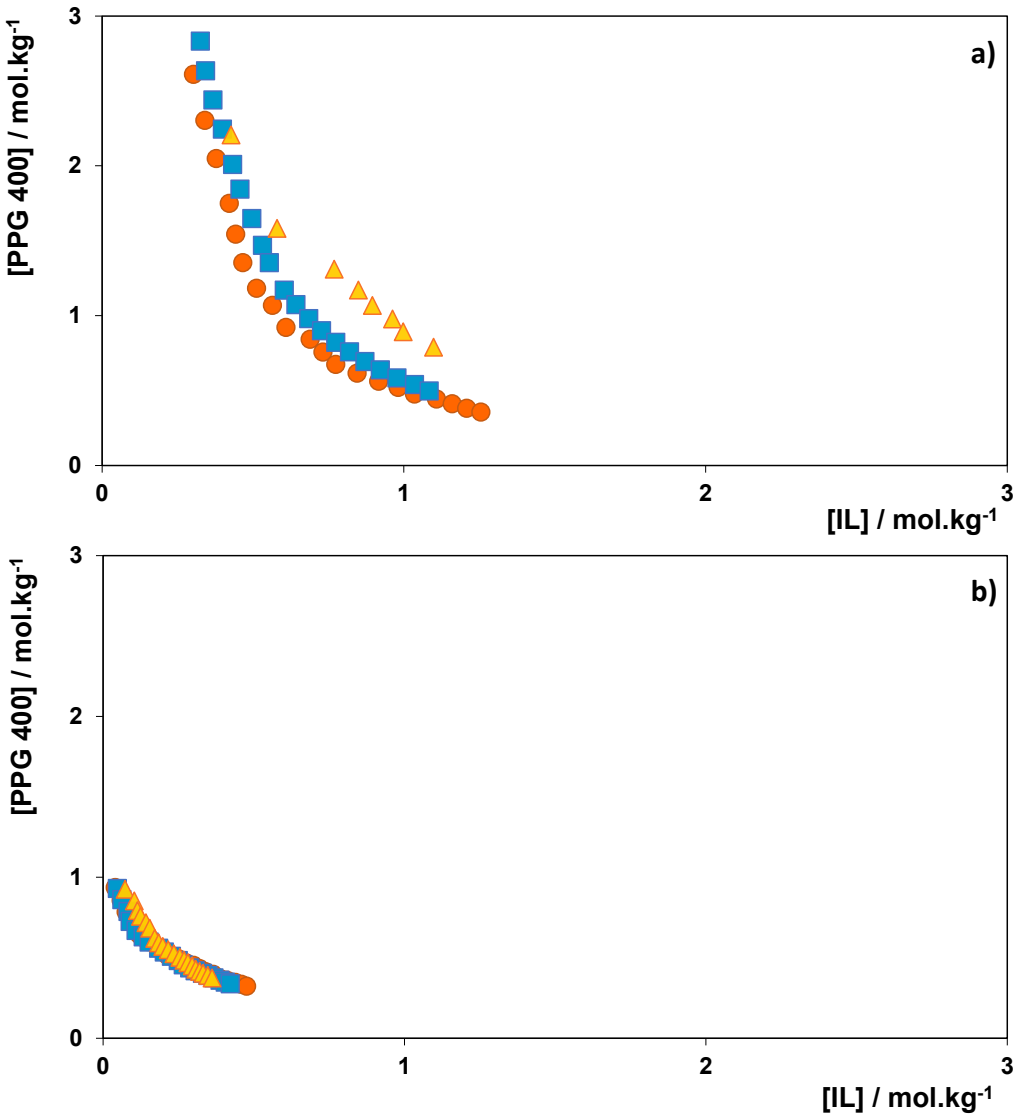


Figure S8 Binodal curves of the systems composed of PPG 400 + [Ch][C_3O_2] + H_2O at pH 5 (▲), pH 6 (■) and pH 7 (●) at a) 25°C and b) 45°C.

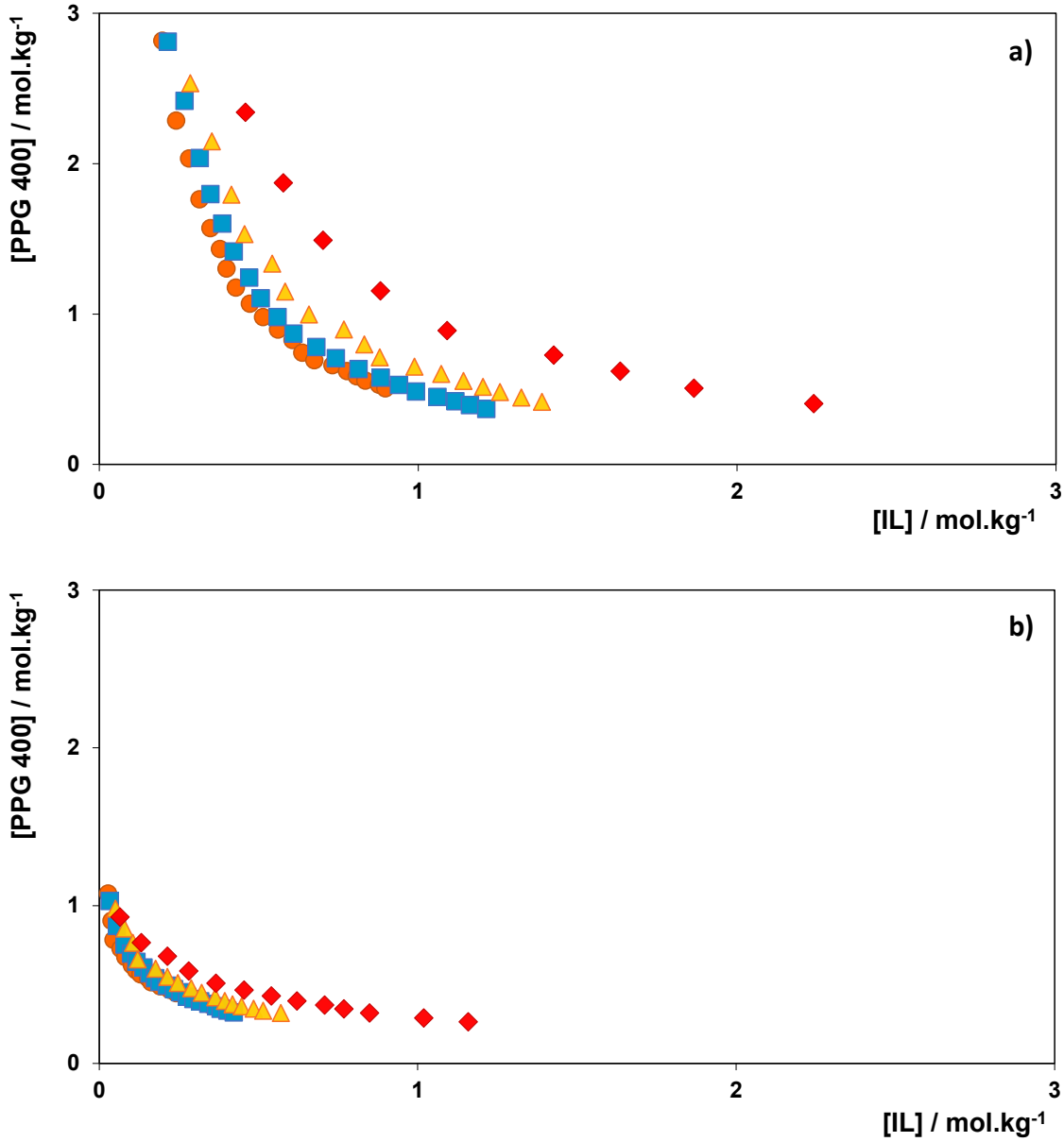
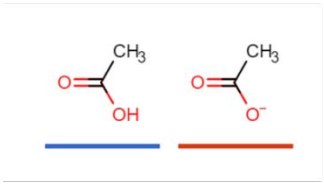


Figure S9 Binodal curves of the systems composed of PPG 400 + [Ch][C_3O_3] + H_2O at pH4 (◆), pH 5 (▲), pH 6 (■) and pH 7 (●) at a) 25°C and b) 45°C.

Speciation curves of acids

All speciation curves were acquired through Marvin version 22.18, ChemAxon (https://www.chemaxon.com).



pH	5	25.9 %	74.1%
	6	3.38 %	96.62 %
	7	0.35 %	99.65 %

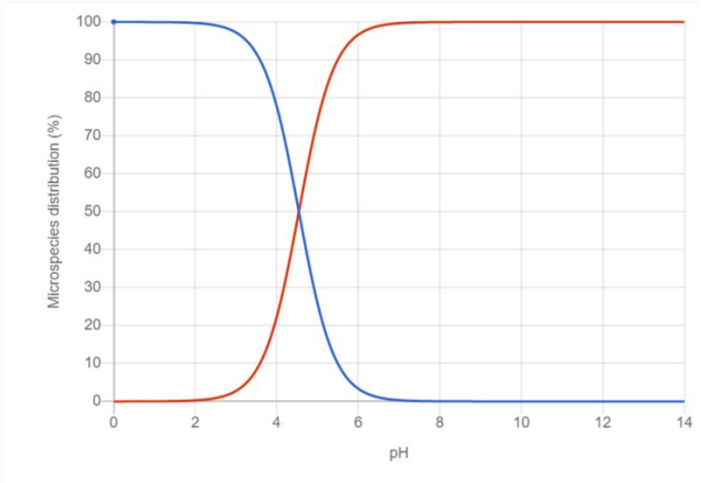
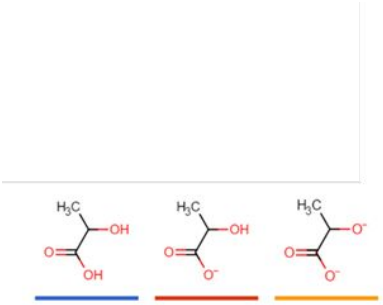


Figure S10 Speciation curves of acetic acid as a function of pH and microspecies distribution (data retrieved from the Chemaxon).[4]



pH	4	37.87 %	62.13 %	0 %
	5	5.74 %	94.26 %	0 %
	6	0.61 %	99.39 %	0 %
	7	0.06 %	99.94 %	0 %

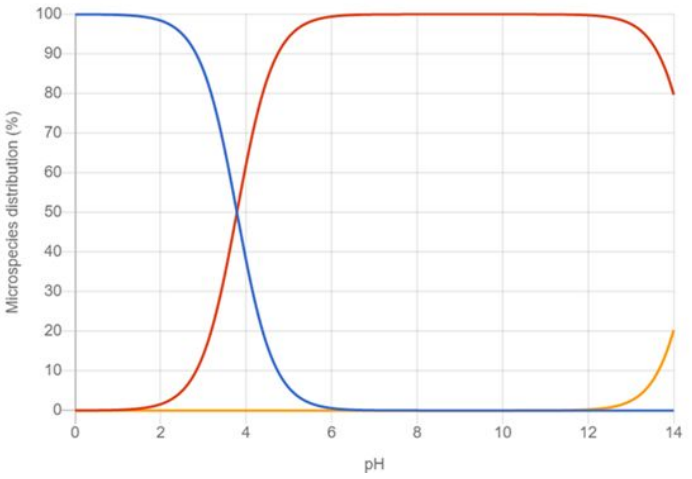
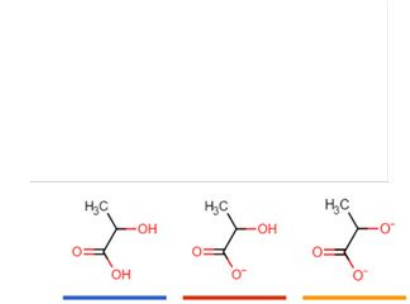


Figure S11 Speciation curves of lactic acid as a function of pH and microspecies distribution (data retrieved from the Chemaxon).[4]



pH	3	77.06 %	22.94 %	0 %
	4	25.15 %	74.85 %	0 %
	5	3.25 %	96.75 %	0 %
	6	0.33 %	99.67 %	0 %

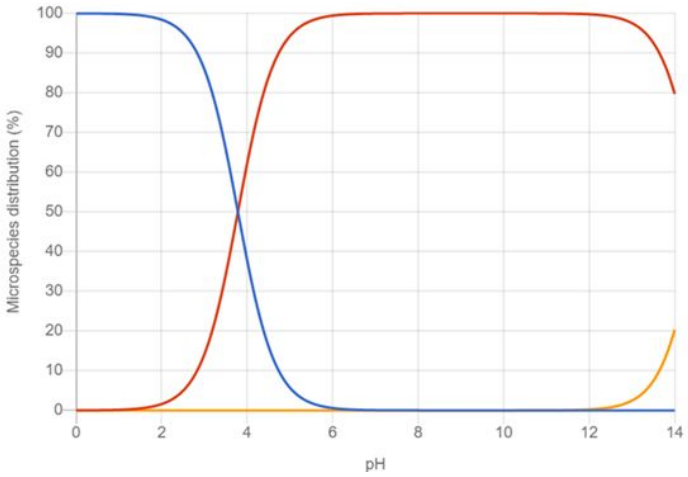
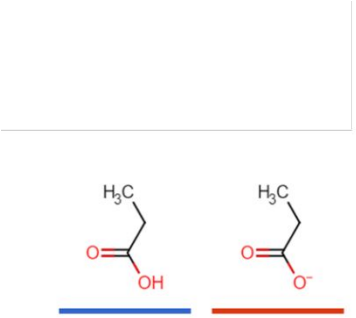


Figure S12 Speciation curves of glycolic acid as a function of pH and microspecies distribution (data retrieved from the Chemaxon).[4]



pH	5	36.24 %	63.76 %
	6	5.38 %	94.62 %
	7	0.57 %	99.43 %

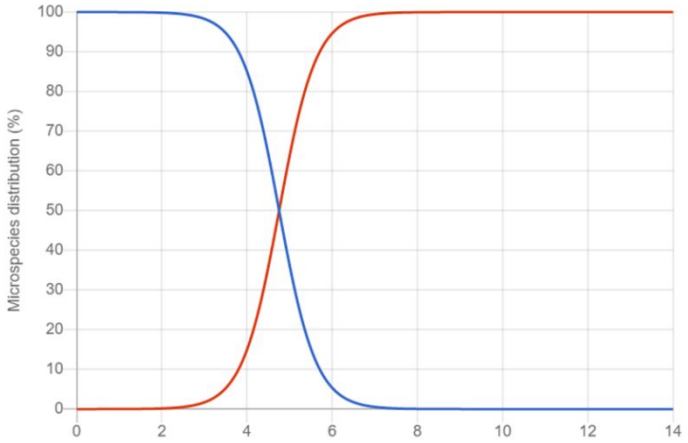


Figure S13 Speciation curves of propionic acid as a function of pH and microspecies distribution (data retrieved from the Chemaxon).[4]

Binodal curves representations: IL effect

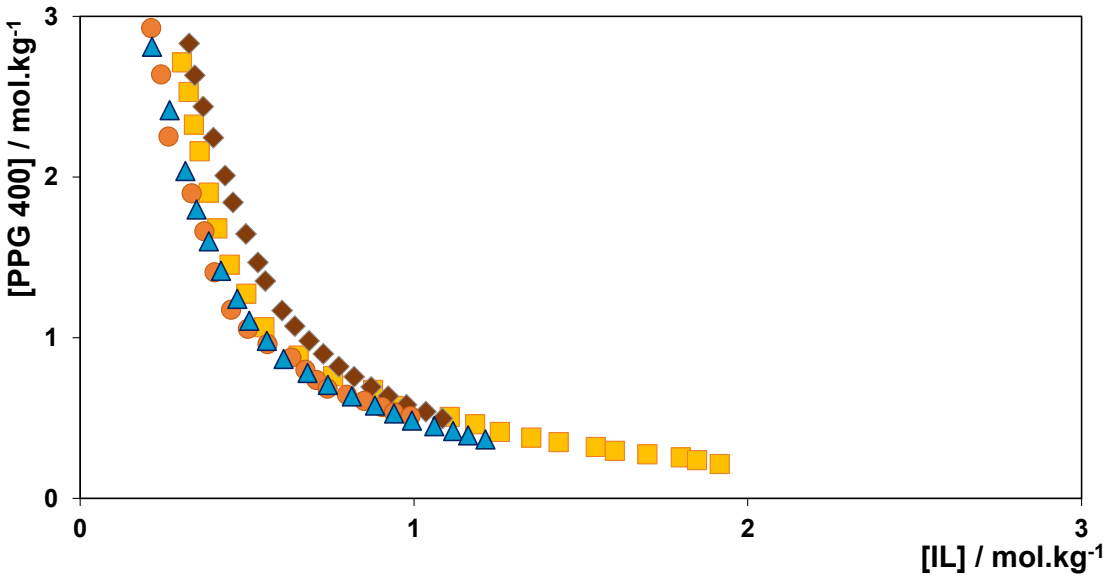


Figure S14 Binodal curves of the systems composed of PPG 400 + IL + H_2O at 25 °C and pH 6: [Ch][C_2O_2] (■); [Ch][C_3O_2] (◆); [Ch][C_2O_3] (●); [Ch][C_3O_3] (▲).

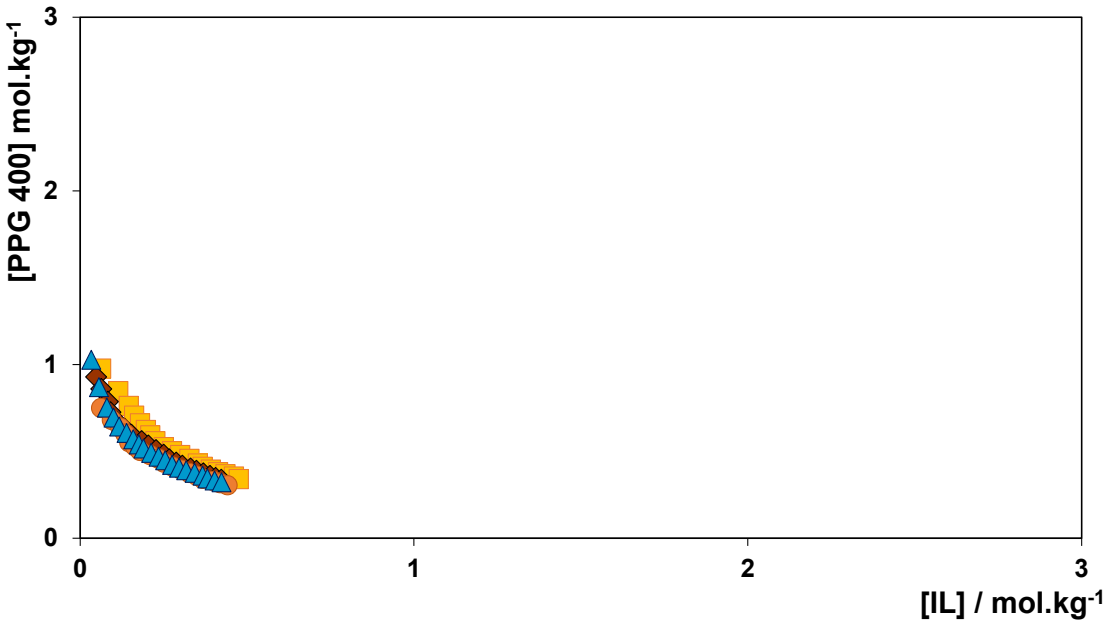


Figure S15 Binodal curves of the systems composed of PPG 400 + IL + H_2O at 45 °C and pH 6: [Ch][C_2O_2] (■); [Ch][C_3O_2] (◆); [Ch][C_2O_3] (●); [Ch][C_3O_3] (▲).

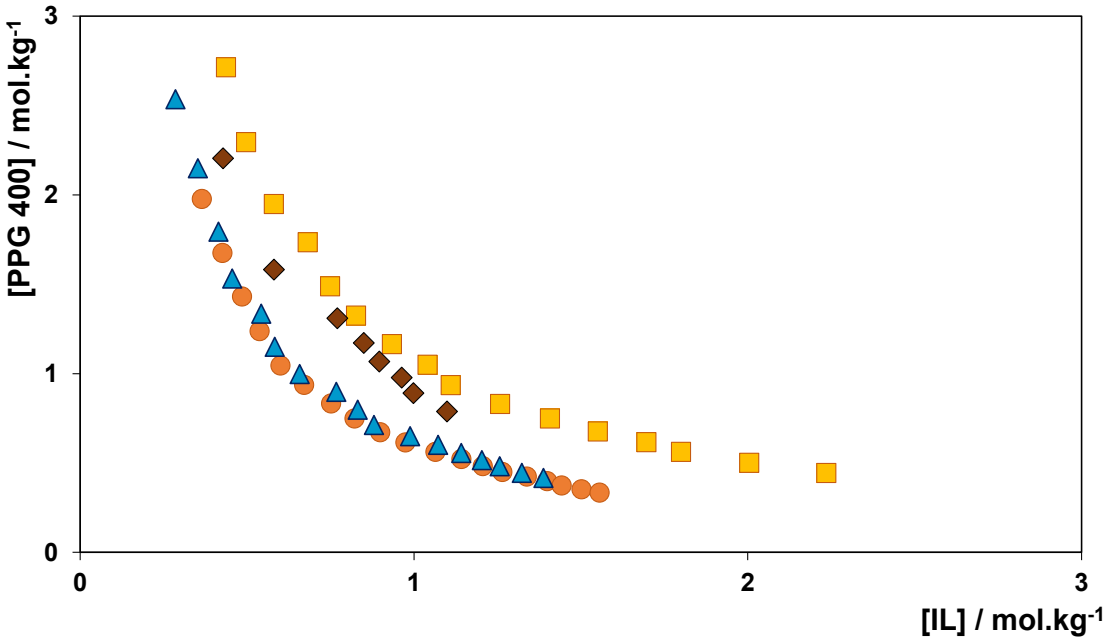


Figure S16 Binodal curves of the systems composed of PPG 400 + IL + H_2O at 25 °C and pH 5: [Ch][C_2O_2] (■); [Ch][C_3O_2] (◆); [Ch][C_2O_3] (●); [Ch][C_3O_3] (▲).

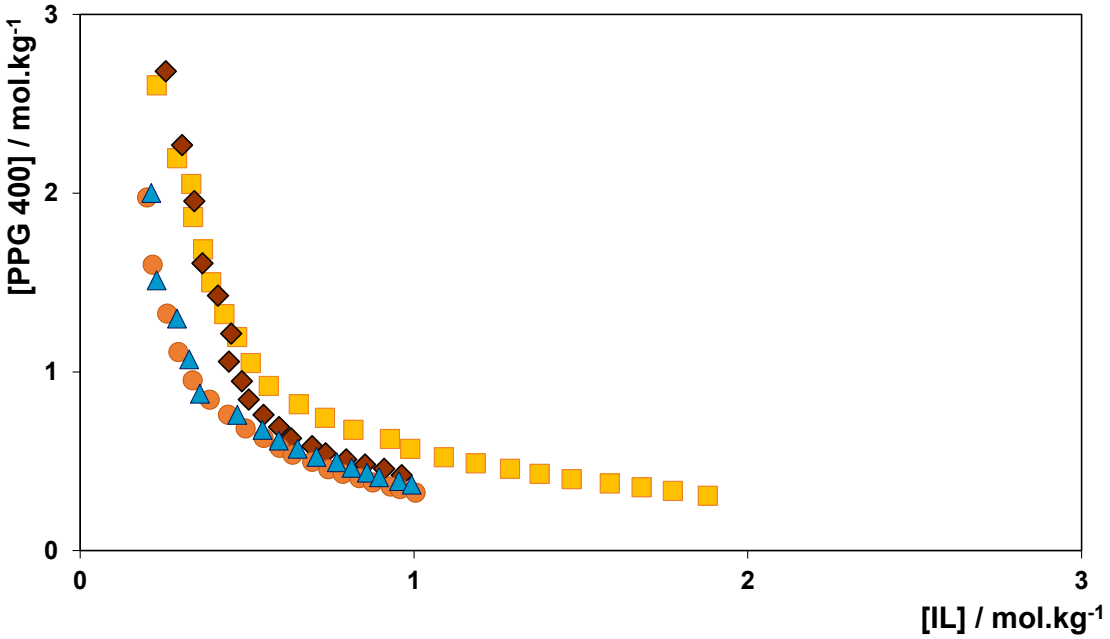


Figure S17 Binodal curves of the systems composed of PPG 400 + IL + H_2O at 35 °C and pH *5*: [Ch][C_2O_2] (■); [Ch][C_3O_2] (◆); [Ch][C_2O_3] (●); [Ch][C_3O_3] (▲).

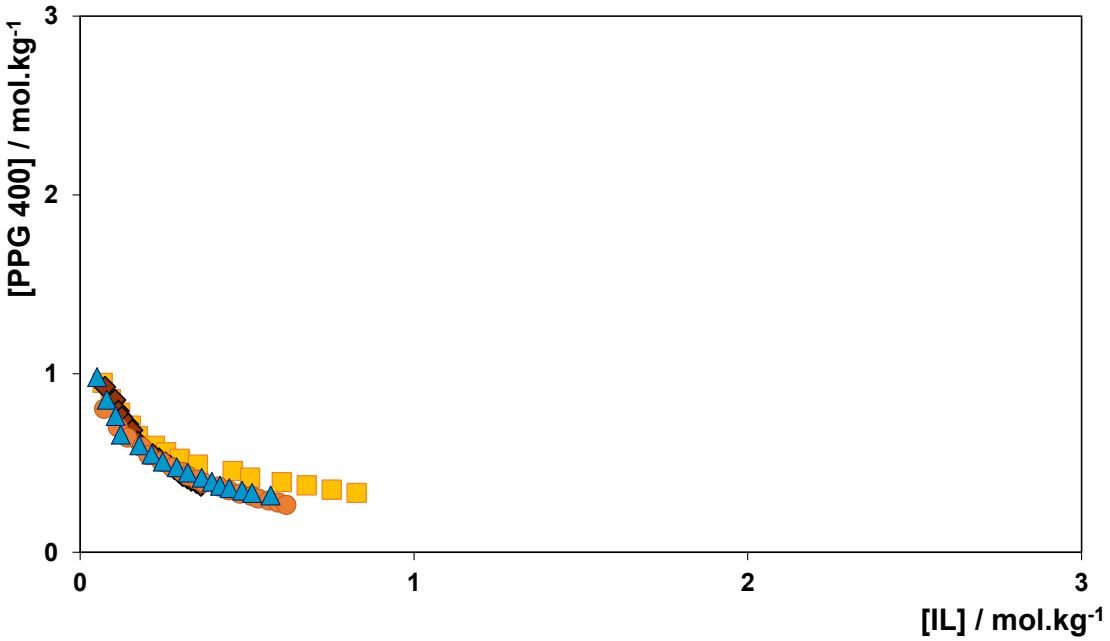


Figure S18 Binodal curves of the systems composed of PPG 400 + IL + H_2O at 45 °C and pH 5: [Ch][C_2O_2] (■); [Ch][C_3O_2] (◆); [Ch][C_2O_3] (●); [Ch][C_3O_3] (▲).

Partition of dyes

Table S30 Extraction efficiencies of Sudan III ($EE_{Sudan\ III}$, %) and E133 (EE_{E133}, %) obtained with the double-responsible ABS composed of [Ch][C_2O_2].

Stimulus	EE_{E133}%	$EE_{Sudan\ III}$%
Temperature	98.02 ± 1.36	100
pH	94.08 ± 1.68	96.32 ± 9.57

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(3) Merchuk, J. C.; Andrews, B. A.; Asenjo, J. A. Aqueous Two-Phase Systems for Protein Separation: Studies on Phase Inversion. *J. Chromatogr. B Biomed. Sci. Appl.* **1998**, *711* (1–2), 285–293. DOI: 10.1016/S0378-4347(97)00594-X

(4) Marvin Version 22.18, ChemAxon, https://www.chemaxon.com (Accessed October 2022).