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A critical assessment of the mechanisms governing the formation of aqueous biphasic systems composed of protic ionic liquids and polyethylene glycol

Ana Filipa M. Cláudio[1], *Jorge F. B. Pereira*[2*], *Parker D. McCrary*[3], *Mara G. Freire*[1], *João A. P. Coutinho*[1] *and Robin D. Rogers*[3,4]

[1] Chemistry Department, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal.

[2] Department of Bioprocess and Biotechnology, School of Pharmaceutical Sciences, UNESP – Univ Estadual Paulista, 14801-902 – Araraquara, SP, Brazil.

[3] Department of Chemistry, The University of Alabama, Tuscaloosa, AL 35487, USA.

[4] Department of Chemistry, McGill University, 801 Sherbrooke St. West, Montreal, QC Canada H3A 0B8.

*Corresponding author

E-mail address: jfbpereira@fcfar.unesp.br

Synthesis of PILs

Synthesis of N-propylammonium acetate, [C_3NH_3][OAc]

Glacial acetic acid (300 mmol, 18.015 g) was placed in a 100 mL vial. N-propylamine (300 mmol, 17.733 g) was added. A yellow viscous oil was obtained with no mass loss for essentially a 100% yield. ^{1}H NMR (360 MHz, *DMSO-d6*) δ ppm: 9.37 (s, 3H, -NH_3^+), 3.03 (t, 2H, -CH_2-N), 2.09 (s, 3H, CH_3-COO^-), 1.92 (m, 2H, -CH_2-,), 1.19 (t, 3H, CH_3-).

Synthesis of N-butylammonium acetate, [C_4NH_3][OAc]

Glacial acetic acid (300 mmol, 17.155 mL) was placed in a 100 mL vial. N-butylamine (300 mmol, 29.650 mL) was added. A yellow viscous oil was obtained with no mass loss for essentially a 100% yield. TGA: $T_{5\%\ onset}$ = 106 ºC. DSC: No thermal transitions were observed. ^{1}H NMR (360 MHz, *DMSO-d6*) δ ppm: 8.24 (s, 3H, -NH_3^+), 2.67 (t, 2H, -CH_2-N), 1.69 (s, 3H, CH_3-COO^-), 1.49 (m, 2H, -CH_2-,), 1.31 (m, 2H, -CH_2-), 0.86 (t, 3H, CH_3-).

Synthesis of N-hexylammonium acetate, [C_6NH_3][OAc]

Glacial acetic acid (300 mmol, 17.155 mL) was placed in a 100 mL vial. N-hexylamine (300 mmol, 39.635 mL) was added. A clear crystalline solid was obtained with no mass loss for essentially a 100% yield. DSC: T_m = 326 K. ^{1}H NMR (360 MHz, *DMSO-d6*) δ ppm: 7.80 (s, 3H, -NH_3^+), 2.66 (t, 2H, -CH_2-N), 1.72 (s, 3H, CH_3-COO^-), 1.49 (m, 2H, -CH_2-), 1.27 (m, 6H), 0.88 (t, 3H, CH_3-).

Synthesis of N-octylammonium acetate, [C_8NH_3][OAc]

Glacial acetic acid (300 mmol, 17.155 mL) was placed in a 100 mL vial. N-octylamine (300 mmol, 49.565 mL) was added. A clear crystalline solid was obtained with no mass loss for essentially a 100% yield. DSC: T_m = 321 K. ^{1}H NMR (360 MHz, *DMSO-d6*) δ ppm: 7.16 (s, 3H, -NH_3^+), 2.64 (t, 2H, -CH_2-N), 1.73 (s, 3H, CH_3-COO^-), 1.46 (m, 2H, -CH_2-), 1.25 (m, 8H, -CH_2-CH_2-CH_2-CH_2-), 0.87 (t, 3H, CH_3-).

Synthesis of N-triethylammonium acetate, [$C_2C_2C_2NH$][OAc]

Glacial acetic acid (300 mmol, 17.157 mL) was placed in a 100 mL vial. N-triethylamine (300 mmol, 41.823 mL) was added drop-wise. An orange oil was obtained with no mass loss for essentially a 100% yield. ^{1}H NMR (360 MHz, *DMSO-d6*) δ ppm: 13.17 (s, 1H, -NH^+), 3.46 (m, 8H, -CH_2-N, -CH_2-N, -CH_2-N), 2.24 (t, 3H, CH_3-COO^-), 1.57 (m, 9H, CH_3-, CH_3-, CH_3-).

Synthesis of N-dipropylammonium acetate, [$C_3C_3NH_2$][OAc]

Glacial acetic acid (300 mmol, 17.157 mL) was placed in a 100 mL vial. N-dipropylamine (300 mmol, 41.134 mL) was added drop-wise. A clear crystalline solid was obtained with no mass loss for essentially a 100% yield. DSC: T_m = 326 K. ^{1}H NMR (360 MHz, *DMSO-d6*) δ ppm: 11.67 (s, 2H, -NH_2^+), 3.24 (m, 4H, -CH_2-N, -CH_2-N,), 2.23 (s, 3H, CH_3-COO^-), 2.06 (m, 4H, -CH_2-, -CH_2-), 1.28 (t, 6H, CH_3-, CH_3-).

Synthesis of ammonium butanoate, [NH_4][But]

Butanoic acid (300 mmol, 27.550 mL) was placed in a 100 mL vial. Ammonium in water (25%w/w) (300 mmol, 22.458 mL) was added drop-wise. A transparent viscous oil was observed with no mass loss for essentially a 100% yield. ^{1}H NMR (360 MHz, *DMSO-d6*) δ ppm: 9.20 (s, 4H, -NH_4^+), 2.48 (t, 2H, CH_2-COO^-), 1.85 (m, 2H, -CH_2-), 1.20 (m, 3H, CH_3-).

Synthesis of N-propylammonium butanoate, [C_3NH_3][But]

Butanoic acid (300 mmol, 27.550 mL) was placed in a 100 mL vial. N-propylamine (300 mmol, 24.663 mL) was added drop-wise. A yellow viscous oil was obtained with no mass loss for essentially a 100% yield. ^{1}H NMR (360 MHz, *DMSO-d6*) δ ppm: 9.54 (s, 3H, -NH_3^+), 3.05 (t, 2H, -CH_2-N), 2.26 (t, 2H, CH_2-COO^-), 1.96 (m, 2H, -CH_2-,), 1.79 (m, 2H, -CH_2-), 1.19 (m, 3H, CH_3-), 1.15 (m, 3H, CH_3-).

Synthesis of N-hexylammonium butanoate, [C_6NH_3][But]

Butyric acid (300 mmol, 27.550 mL) was placed in a 100 mL vial. N-hexylamine (300 mmol, 39.634 mL) was added drop-wise. A white viscous oil was obtained with no mass loss for essentially a 100% yield. ^{1}H NMR (360 MHz, *DMSO-d6*) δ ppm: 9.45 (s, 3H, -NH_3^+), 3.08 (t, 2H, -CH_2-N), 2.27 (t, 2H, CH_2-COO^-), 1.95 (m, 2H, -CH_2-,), 1.81 (m, 2H, -CH_2-), 1.57 (m, 6H, -CH_2-CH_2-CH_2-), 1.16 (m, 6H, CH_3-, CH_3-).

Synthesis of N-octylammonium butanoate, [C_8NH_3][But]

Butyric acid (300 mmol, 27.550 mL) was placed in a 100 mL vial. N-octylamine (300 mmol, 49.565 mL) was added. A clear crystalline solid was observed with no mass loss for essentially a 100% yield. DSC: T_m = 305 K. ^{1}H NMR (360 MHz, *DMSO-d6*) δ ppm: 9.42 (s, 3H, -NH_3^+), 3.07 (t, 2H, -CH_2-N), 2.33 (t, 2H, CH_2-COO^-), 1.94 (m, 2H, -CH_2-,), 1.81 (m, 2H, -CH_2-), 1.56 (m, 10H, -CH_2-CH_2-CH_2-CH_2-CH_2-), 1.15 (m, 6H, CH_3-, CH_3-).

Synthesis of N-butylammonium propanoate, [C_4NH_3][Pro]

Propionic acid (300 mmol, 22.228 g) was placed in a 100 mL vial. N-butylamine (300 mmol, 21.942 g) was added drop-wise. A yellow viscous oil was obtained with no mass loss for essentially a 100% yield. ^{1}H

NMR (360 MHz, *DMSO-d6*) δ ppm: 9.39 (s, 3H, -NH_3^+), 3.09 (t, 2H, -CH_2-N), 2.34 (t, 2H, CH_2-COO^-), 1.92 (m, 2H, -CH_2-,), 1.63 (m, 2H, -CH_2-), 1.27 (m, 3H, CH_3-), 1.16 (m, 3H, CH_3-).

Synthesis of N-butylammonium butanoate, [C_4NH_3][But]

Butyric acid (300 mmol, 26.433 g) was placed in a 100 mL vial. N-butylamine (300 mmol, 21.942 g) was added drop-wise. A yellow viscous oil was obtained with no mass loss for essentially a 100% yield. ^{1}H NMR (360 MHz, *DMSO-d6*) δ ppm: 9.40 (s, 3H, -NH_3^+), 3.08 (t, 2H, -CH_2-N), 2.32 (t, 2H, CH_2-COO^-), 1.92 (m, 2H, -CH_2-,), 1.81 (m, 2H, -CH_2-), 1.64 (m, 2H, -CH_2-), 1.16 (m, 6H, CH_3-, CH_3-).

Synthesis of N-butylammonium hexanoate, [C_4NH_3][Hex]

Hexanoic acid (300 mmol, 34.848 g) was placed in a 100 mL vial. N-butylamine (300 mmol, 21.942 g) was added drop-wise. A. yellow viscous oil was obtained with no mass loss for essentially a 100% yield. ^{1}H NMR (360 MHz, *DMSO-d6*) δ ppm: 9.51 (s, 3H, -NH_3^+), 3.08 (t, 2H, -CH_2-N), 2.35 (t, 2H, CH_2-COO^-), 1.93 (m, 2H, -CH_2-,), 1.81 (m, 2H, -CH_2-), 1.65 (m, 2H, -CH_2-), 1.57 (m, 4H, -CH_2-CH_2-), 1.17 (m, 6H, CH_3-, CH_3-).

Characterization of PILs

Differential Scanning Calorimetry (DSC)

Characterization measurements of solids PILs were performed on a TA instruments Differential Scanning Calorimeter (DSC) 2920 Modulated DSC, TA Instruments, Inc. (New Castle, DE) cooled with a liquid nitrogen cryostat. The calorimeter for temperature and cell constants was calibrated using indium. Samples of each PIL or salt were carefully weighted and sealed in aluminium pans (5 – 15 mg), with a hole in the top to allow gases to escape, and heated at a rate of 5 °C/min up to 100 °C. Following the initial heating cycle the samples were cooled to -100 °C followed by a heating cycle to 100 °C at a rate of 5 °C/min. After each dynamic temperature ramp, a 5 min isotherm was employed to ensure the temperature equilibrium in the cell. The entire cycle was repeated twice and phase changes values determined. An empty aluminium pan was used as reference.

Proton and Carbon Nuclear Magnetic Resonance (^{1}H and ^{13}C NMR)

Nuclear Magnetic Resonance spectra were obtained utilizing a BrukerAvance NMR spectrometer (Karlsruhe, Germany) at 500 MHz for ^{1}H NMR spectroscopy and 125 MHz for ^{13}C NMR spectroscopy. Each PIL liquid at room temperature was loaded solvent-less in a flame-sealed capillary by using $CDCl_3$ as

the external lock. The PILs solid at room temperature were dissolved in DMSO-d_6 or D_2O-d_2, with TMS as the internal standard, for analysis.

Water content

The water content of all PILs was measured by Karl-Fischer titration and was taken into account during the preparation of each aqueous solution, and considered in the determination of the ternary phase diagrams.

pH determination

The pH (± 0.02) of the initial aqueous solutions (in the monophasic region) used for the determination of the phase diagrams by the titration method was measured at 298 K (± 1 K) using a SevenMultiTM (Mettler Toledo Instruments). The calibration of the pH meter was carried out using three buffers (pH values of 4.00, 7.00 and 9.00).

Results.

Table S1. Weight fraction data for the ternary system composed of [NH_4][OAc] (1) + PEG-2000 (2) + H_2O (3) at 323, 333 and 343 K.

323 K		333 K		343 K	
100 w_1	**100 w_2**	**100 w_1**	**100 w_2**	**100 w_1**	**100 w_2**
19.0571	59.0356	31.8562	32.5450	19.6689	40.9864
51.5801	10.3637	33.2813	28.7897	29.7063	22.7502
42.4561	19.4022	21.8826	48.0073	33.8448	14.5015
25.8337	45.8007	29.9584	35.2604	41.4202	7.3336
33.3135	32.6215	15.6463	60.4096	23.3809	35.8684
20.7325	55.2423	20.4122	50.4708	15.5315	51.0040
31.3605	35.4428	15.9597	59.6877		
45.7692	16.9321	29.9025	15.9597		

Table S2. Weight fraction data for the ternary system composed of [C_3NH_3][OAc] (1) + PEG-2000 (2) + H_2O (3) at 323, 333 and 343 K.

323 K		333 K		343 K	
100 w_1	**100 w_2**	**100 w_1**	**100 w_2**	**100 w_1**	**100 w_2**
32.2480	49.1876	54.4534	22.2790	19.1924	66.5731
48.7869	30.8830	39.8820	39.8191	28.6930	52.9489
43.4732	37.1139	34.2976	47.0872	40.1807	38.4052
45.5030	34.6845	24.8649	59.1303	54.1432	22.0215
39.1158	42.8019	19.5682	67.7146	59.7344	15.7777
18.6792	69.3159	46.8797	32.4126	32.5506	47.8970
26.9044	57.6662			48.4868	27.9201

Table S3. Weight fraction data for the ternary system composed of $[C_4NH_3][OAc]$ (1) + PEG-2000 (2) + H_2O (3) at 323, 333 and 343 K.

323 K		**333 K**		**343 K**	
100 w_1	**100 w_2**	**100 w_1**	**100 w_2**	**100 w_1**	**100 w_2**
65.9414	16.9135	10.6869	83.7239	10.3043	84.3595
55.5276	28.4606	18.4168	71.9734	19.9640	70.0576
46.6962	38.1847	26.0215	61.8665	25.6261	62.6943
36.4099	50.6936	34.4792	50.7473	35.1369	50.6468
22.9590	66.7180	43.2017	40.6064	41.7378	42.0525
68.4997	14.4647	50.0500	32.4593	49.8343	32.3990
60.5142	22.9462	56.6482	25.1271	58.3393	23.3316
50.7237	34.2265	65.4270	15.1698	58.8078	22.5009
41.6359	44.4263	73.6368	8.4188	68.6284	11.3153

Table S4. Weight fraction data for the ternary system composed of $[C_6NH_3][OAc]$ (1) + PEG-2000 (2) + H_2O (3) at 313, 323, 333 and 343 K.

313 K		323 K		333 K		343 K	
100 w_1	**100 w_2**	**100 w_1**	**100 w_2**	**100 w_1**	**100 w_2**	**100 w_1**	**100 w_2**
65.1880	12.8578	58.7432	23.3052	34.1934	51.7310	62.2475	21.2028
51.0630	27.7721	47.7775	35.3478	64.0178	18.8446	51.8040	32.3903
27.9260	50.3323	42.3815	40.8861	30.5686	56.2230	43.8880	41.0582
15.6300	66.8714	55.1993	27.1740	67.1663	15.3696	38.5105	47.1826
18.9670	60.8661	63.1755	19.1051	61.4805	20.9516	18.1705	74.2477
		32.5180	52.3198	51.2120	32.0353	18.6854	73.9177
		52.4930	30.4357	43.4019	40.6228	76.4035	9.6909
		65.5732	16.5931	38.3056	46.9542		
		25.5616	61.5299				
		21.5581	67.2910				
		66.7575	15.2761				
		60.9145	20.7588				
		51.0135	31.8230				
		43.1310	40.3689				

Table S5. Weight fraction data for the ternary system composed of $[C_4NH_3][But]$ (1) + PEG-2000 (2) + H_2O (3) at 323, 333 and 343 K.

323 K		333 K		343 K	
100 w_1	**100 w_2**	**100 w_1**	**100 w_2**	**100 w_1**	**100 w_2**
18.3657	73.3218	12.1640	82.2192	18.6854	73.9177
27.2236	61.0389	19.1258	71.5494	26.8549	63.1006
34.9885	51.8855	26.5212	62.0305	35.8336	52.4777
58.0527	25.5716	45.2480	40.8825	43.6680	43.2358
76.7577	8.6059	50.8088	34.2322	52.0391	34.5412
43.4334	42.7715	58.8314	25.5709	58.8183	28.5255
52.3220	32.9693	68.0163	16.4728	68.7164	17.3123
65.3617	18.3658	74.1672	10.0502		
66.4165	18.1190				

Table S6. Weight fraction data for the ternary system composed of $[C_4NH_3][Pro]$ (1) + PEG-2000 (2) + H_2O (3) at 323, 333 and 343 K.

323 K		333 K		343 K	
100 w_1	**100 w_2**	**100 w_1**	**100 w_2**	**100 w_1**	**100 w_2**
75.9140	8.5207	9.3658	85.7627	11.1712	82.8446
58.5871	25.6276	21.0623	70.6054	18.1282	74.0322
52.7205	32.2800	26.8341	62.5634	30.8424	58.2475
43.5107	42.7820	34.8845	52.3098	36.8617	51.6602
36.1269	51.0039	43.0496	43.3885	44.0703	43.2475
28.6189	60.6282	50.6802	33.5565	60.0536	24.9837
18.3139	73.9166	60.5089	23.4414	66.9564	17.4618
69.4079	14.7306	66.6412	16.5842	75.7718	8.9395
		74.9542	8.8914		

Table S7. Weight fraction data for the ternary system composed of $[C_3NH_3][But]$ (1) + PEG-2000 (2) + H_2O (3) at 323, 333 and 343 K.

323 K		333 K		343 K	
100 w_1	**100 w_2**	**100 w_1**	**100 w_2**	**100 w_1**	**100 w_2**
59.3252	25.8385	26.8537	63.6596	23.0142	69.1179
19.6495	71.1870	35.6653	52.5161	27.6222	63.1106
33.9115	53.7087	44.3632	43.2081	36.2112	52.6200
36.9585	50.3080	53.5070	32.9179	44.8068	43.1020
50.1825	36.1902	60.5645	25.0826	52.1530	34.3266
				60.5045	25.7346

Table S8. Weight fraction data for the ternary system composed of $[C_8NH_3][OAc]$, $[C_6NH_3][But]$, $[C_8NH_3][But]$ and $[C_4NH_3][Hex]$ (1) + PEG-2000 (2) + H_2O (3) at 323 K.

$[C_8NH_3][OAc]$		$[C_6NH_3][But]$		$[C_8NH_3][But]$		$[C_4NH_3][Hex]$	
100 w_1	**100 w_2**	**100 w_1**	**100 w_2**	**100 w_1**	**100 w_2**	**100 w_1**	**100 w_2**
23.9853	54.3066	35.9266	36.1627	15.4517	54.7840	9.3899	81.9170
27.6235	48.1338	42.6797	27.8771	21.1941	48.3347	19.0195	67.2323
37.0421	36.9329	49.3903	21.4054	38.5815	33.1897	24.9684	57.5769
39.8662	33.7663	53.9641	16.7127	59.9768	14.8823	31.8814	45.3892
55.2775	18.5752	26.9716	46.7228	20.7737	50.3444	37.3136	37.1814
58.7654	15.5066	37.2980	33.6823	52.0304	20.5489	44.5446	29.0263
25.2152	53.4454	47.2916	22.7760	31.2887	38.8243	53.1422	20.9456
31.3087	44.7039			39.3675	31.6984	58.9000	15.0533
29.0481	47.3945					71.4009	7.3504
53.8383	20.4216						
21.1202	59.8030						
62.5798	12.5417						

Table S9. pH values in the monophasic region and minimum concentration point (*MC*) of each PIL-based ABS. The pH values were determined at 323 K as the average of, at least, three independent mixtures.

System	pH	*MC*		
	323 K	**323 K**	**333 K**	**343 K**
[NH_4][OAc]	7.77 ± 0.13	24.02	21.66	13.13
[C_3NH_3][OAc]	7.37 ± 0.21	44.74	38.90	34.93
[C_4NH_3][OAc]	7.26 ± 0.03	51.22	43.64	43.03
[C_6NH_3][OAc]	7.57 ± 0.43	43.03	43.03	49.00
[C_4NH_3][Pro]	7.98 ± 0.18	50.01	47.61	51.84
[C_4NH_3][But]	8.14 ± 0.07	49.42	49.48	64.14
[C_3NH_3][But]	8.31 ± 0.04	63.25	64.62	66.65
[C_6NH_3][But]	7.90 ± 0.15	21.29	-	-
[C_8NH_3][But]	8.00 ± 0.16	23.38	-	-
[C_4NH_3][Hex]	8.07 ± 0.18	22.71	-	-
[C_8NH_3][OAc]	7.85 ± 0.19	25.44	-	-