Electronic Supplementary Information

Ionic liquids and non-ionic surfactants: a new combination for aqueous segregation

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Materials and methods

The non-ionic surfactants belonging to the polyoxyethylene t-octylphenol family Triton X-100 and Triton X-102 were purchased from Sigma-Aldrich, and used as received without further purification. Triton X-102 possesses a Critical Micellar Concentration (CMC) of 267 ppm and a Hydrophilic Lipophilic Balance (HLB) of 14.4. In relation to Triton X-100, its CMC and HLB are 189 ppm and 13.4, respectively. The ionic liquid $C_2MIMC_2SO_4$ was purchased from IoLiTec, and $C_2MIMC_4SO_4$ and $C_2MIMC_6SO_4$ were supplied by Merck (purities higher than 98%). All of them were subjected to vacuum ($2{\cdot}10^{-1}$ Pa) and moderate temperature (50 ºC) for several days to remove possible traces of solvents and moisture, always prior to their use. The water content was determined using a Mettler-Toledo coulometric KF titrator model C20, showing that the mass fraction of water was less than $6{\cdot}10^{-4}$. The ionic liquids were kept in bottles under inert atmosphere until use.

The immiscibility region was determined by calculating the solubility curves. The solubility curves experimental data were obtained by the cloud point method, as reported elsewhere, by adding water to binary mixtures of surfactant and ionic liquid with known composition, until a slight turbidity in samples was observed. Then, more water was added up to a monophasic region was again detected. The data obtained for the systems {Triton-X 100 (1) + $C_2MIMC_2SO_4$ (2) + H_2O (3)} and {Triton-X 102 (1) + $C_2MIMC_2SO_4$ (2) + H_2O (3)} are listed in Tables 1 and 2, respectively.

Tie-line data determination was performed in a jacketed glass vessel containing a magnetic stirrer connected to a temperature controlled circulating bath (controlled to ± 0.01 K). The temperature in the cell was measured with a F200 ASL digital thermometer with an uncertainty of ± 0.01 K. The measurements of the tie-line started with the addition of 30 mL of immiscibility ternary components of known composition to the vessel, the temperature was adjusted and the mixture was stirred vigorously during 1 h and left to settle for 24 h. Samples were taken by a syringe from the upper and lower phases. The binodal curves were carried out by two techniques: the experimental determination of the tie-lines that shows the composition of each layer and the characterization of the immiscible gap. Density and refractive index calibration curves of the coexisting phases were made with known composition samples of the ternary mixture to determine the mass fraction from (25 to 60) ºC.

Table S1

Binodal data for {Triton-X 100 (1) + $C_2MIMC_2SO_4$ (2) + + H_2O (3)} at several temperatures

25ºC		40ºC		50ºC		60ºC	
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
61.66	33.49	76.72	18.96	80.50	14.98	85.16	9.45
59.12	32.11	73.00	18.04	76.17	14.17	81.22	9.02
56.65	37.67	72.63	24.05	72.65	24.25	81.84	14.61
53.54	35.60	67.15	22.24	65.38	21.82	75.66	13.50
52.47	42.80	62.41	33.51	58.19	38.97	73.11	24.20
49.22	38.52	55.68	29.89	48.99	32.81	64.35	21.30
47.18	47.18	58.29	38.98	52.79	44.09	63.39	33.96
43.21	43.21	50.44	33.73	43.77	36.56	52.01	27.86
37.66	56.28	51.87	42.45	48.15	48.42	58.28	39.24
33.89	50.64	46.00	37.64	39.27	39.49	46.85	31.54
33.12	61.29	47.09	47.65	38.39	57.14	52.61	44.52
28.96	53.59	40.53	41.01	30.43	45.29	41.28	34.93
24.13	69.81	38.01	57.36	33.57	63.00	48.28	48.74
20.71	60.00	31.34	47.28	26.05	48.83	36.71	37.06
18.65	73.91	30.98	64.38	28.91	66.83	38.04	58.63
16.18	64.13	25.17	52.31	22.00	50.86	27.89	42.99
9.09	82.14	28.48	66.52	23.57	71.58	33.86	62.60
7.84	70.82	22.87	53.41	17.75	53.90	24.16	44.67
4.19	87.13	23.26	71.46	9.42	83.18	28.98	67.52
3.65	75.86	18.63	57.24	7.59	67.03	20.26	47.20
		9.66	85.41	4.51	87.09	23.92	72.05
		7.17	63.40	3.49	67.47	16.91	50.94
		4.67	86.52			14.93	79.69
		3.78	69.98			11.03	58.89
						9.12	81.87
						7.00	62.86
						4.24	82.69
						3.87	75.45

Standard uncertainties for w and T are 0.0002 and 0.01 K, respectively

Table S2

Binodal data for {Triton-X 102 (1) + $C_2MIMC_2SO_4$ (2) + H_2O (3)} at several temperatures

25ºC		40ºC		50ºC		60ºC	
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
56.30	37.78	71.75	24.03	79.75	16.02	80.95	14.93
54.32	36.45	67.79	22.70	76.96	15.46	76.95	14.19
52.02	42.49	63.13	33.56	72.46	24.61	73.50	23.99
49.03	40.05	57.13	30.37	66.33	22.53	65.61	21.42
47.35	47.07	58.02	38.87	56.79	40.17	62.50	34.78
44.52	44.26	52.02	34.85	49.07	34.71	53.47	29.76
37.48	56.59	52.42	43.14	52.57	43.10	58.51	39.10
34.36	51.87	46.86	38.57	45.60	37.60	49.18	32.86
32.71	60.39	49.36	47.26	49.03	48.29	53.65	43.94
29.59	54.63	43.18	41.34	41.38	40.76	44.31	36.30
23.05	70.07	38.39	57.41	38.22	57.73	48.81	48.69
20.75	63.08	32.97	49.31	31.97	48.29	40.03	39.94
9.01	82.59	33.42	62.12	33.68	62.73	38.56	58.15
8.05	73.79	28.42	52.82	27.48	51.20	31.19	47.03
4.62	85.77	28.76	66.58	29.67	66.23	33.42	62.38
4.22	78.19	24.31	56.29	24.63	53.31	28.94	53.75
		23.63	71.12	24.15	71.56	28.97	67.40
		19.94	60.03	19.45	57.64	22.55	52.45
		9.37	84.27	9.24	84.61	24.01	71.68
		7.73	69.51	7.70	70.56	19.37	57.83
		4.56	86.76	4.44	86.94	14.14	80.64
		3.93	74.67	3.80	74.34	11.26	64.21
						9.56	84.69
						7.71	68.26
						4.79	86.86
						4.09	74.09

Standard uncertainties for w and T are 0.0002 and 0.01 K, respectively

Table S3

Experimental tie–lines in mass percentage for {Surfactant (1) + $C_2MIMC_2SO_4$ (2) + H_2O (3)} at several temperatures

Surfactant-rich phase		Ionic liquid-rich phase		Feed	
$100\,w_1^{I}$	$100\,w_2^{I}$	$100\,w_1^{II}$	$100\,w_2^{II}$	$100w_1$	$100w_2$
Triton X-100 (1) + $C_2MIMC_2SO_4$ (2) + H_2O (3) T = 25ºC					
58.19	33.06	1.87	79.35	25.74	59.43
59.79	35.01	3.18	84.98	27.59	63.66
55.86	34.14	3.43	75.30	25.36	58.16
59.50	33.64	2.34	84.53	27.22	62.56
Triton X-102 (1) + $C_2MIMC_2SO_4$ (2) + H_2O (3) T = 25ºC					
54.74	40.37	3.44	85.97	27.55	64.22
53.83	39.24	2.66	84.11	27.18	62.92
51.97	38.14	2.18	82.34	26.17	61.27
Triton X-100 (1) + $C_2MIMC_2SO_4$ (2) + H_2O (3) T = 40ºC					
75.86	20.25	3.64	84.39	22.34	68.05
72.89	20.05	3.76	82.48	21.766	66.05
69.90	21.12	2.22	79.64	21.36	63.72
65.80	23.30	2.18	76.41	19.99	61.87
59.66	27.11	1.90	73.89	19.89	59.66
Triton X-102 (1) + $C_2MIMC_2SO_4$ (2) + H_2O (3) T = 40 ºC					
69.82	26.19	3.18	86.28	27.59	64.36
69.54	25.10	2.38	83.79	26.71	62.64
65.65	25.47	2.05	81.95	26.20	61.15
62.55	27.45	1.93	79.17	25.36	59.42
58.66	29.93	1.99	78.00	24.94	58.09
Triton X-100 (1) + $C_2MIMC_2SO_4$ (2) + H_2O (3) T = 50 ºC					
79.29	16.81	4.15	83.94	27.21	63.64
78.63	15.29	2.59	81.64	26.38	61.22
76.79	15.16	2.24	77.82	25.45	58.96
74.92	15.81	2.56	73.08	23.93	56.28
Triton X-102 (1) + $C_2MIMC_2SO_4$ (2) + H_2O (3) T = 50 ºC					

79.55	17.49	2.79	85.19	27.32	63.59
78.01	16.55	1.87	82.57	26.57	61.82
75.98	16.63	2.21	79.52	26.62	59.14
70.22	20.18	3.20	75.96	25.00	58.29
Triton X-100 (1) + $C_2MIMC_2SO_4$ (2) + H_2O (3) T = 60 ºC					
83.48	11.69	2.49	86.32	27.54	63.71
82.96	10.73	3.26	81.34	26.09	61.00
78.36	10.38	2.15	76.67	24.74	57.87
73.66	15.68	1.93	74.21	23.68	56.49
69.02	22.12	2.99	69.20	23.08	53.73
Triton X-102 (1) + $C_2MIMC_2SO_4$ (2) + H_2O (3) T = 60 ºC					
81.14	21.56	4.27	85.89	28.36	64.25
78.70	16.31	3.74	83.53	27.44	62.47
76.23	16.87	3.29	80.28	27.22	60.51
73.98	17.15	2.86	79.00	26.17	59.09

Table S4

Parameters of Othmer-Tobias equation and correlation coefficient for {Surfactant (1) + [C_2MIM][C_2SO_4] (2) + H_2O (3)} at several temperatures

	a	*b*	R^2
T = 25ºC			
Triton X-100 (1) + $C_2MIMC_2SO_4$ (2) + H_2O (3)	0.2421	1.0199	0.946
Triton X-102 (1) + $C_2MIMC_2SO_4$ (2) + H_2O (3)	0.4036	1.7065	0.945
T = 40ºC			
Triton X-100 (1) + $C_2MIMC_2SO_4$ (2) + H_2O (3)	1.1164	2.0472	0.972
Triton X-102 (1) + $C_2MIMC_2SO_4$ (2) + H_2O (3)	0.8725	1.9941	0.901
T = 50ºC			
Triton X-100 (1) + $C_2MIMC_2SO_4$ (2) + H_2O (3)	0.3909	0.4935	0.993
Triton X-102 (1) + $C_2MIMC_2SO_4$ (2) + H_2O (3)	0.8472	1.0745	0.928
T = 60ºC			
Triton X-100 (1) + $C_2MIMC_2SO_4$ (2) + H_2O (3)	0.9166	0.9057	0.918
Triton X-102 (1) + $C_2MIMC_2SO_4$ (2) + H_2O (3)	0.8189	1.0169	0.980

Table S5
Literature data about temperature effect on different types of aqueous biphasic systems.

Compounds		Temperature (K)	Effect	Ref.
Polymer-based ABS				
PEG 20000	$CuSO_4$	290.15, 299.15, 308.15 317.15	Proportional	[1]
PEG 10000	$MgSO_4$	295.15, 301.15, 305.15 311.15	Proportional	[2]
PEG 400	$MgSO_4$, Na_2SO_4	298.15, 318.15	No variation	[3]
PEG 6000	$MgSO_4$, Na_2SO_4, Li_2SO_4, $ZnSO_4$	283.15, 298.15, 313.15	No variation	[4]
PEG (600,1000,1450,3350,8000)	$Na_3C_6H_5O_7$	295.15, 310.15, 323.15	Proportional	[5]
PEG 8000	$MgSO_4$, Na_2SO_4	298.15, 323.15	No variation	[6]
PEG 4000	K_3PO_4	283.15, 288.15, 293.15, 303.15	Proportional	[7]
PEG 4000	Na_2-Tartrato	298.15, 308.15, 318.15	Proportional	[8]
PEG 6000	$(NH_4)_3C_6H_5O_7$	298.15, 303.15, 313.15 318.15	Proportional	[9]
PEG 6000	$Na_2WO_4.2H_2O$	298.15, 303.15, 308.15 313.15	Proportional	[10]
PEG 4000	$(NH_4)_3C_6H_5O_7$	298.15, 308.15, 318.15	Proportional	[11]
Ionic liquid-based ABS				
[EPy]Br	NaH_2PO_4	298.15, 308.15, 318.15 328.15	Inverse	[12]
[EMIM]BF_4	NaH_2PO_4, Na_2HPO_4	298.15, 303.15, 308.15	Inverse	[13]
[BMIM]BF_4	$MnSO_4$	288.15, 293.15, 303.15 308.15	Inverse	[14]
[BPy]BF_4	$Na_2C_4H_4O_6$	298.15, 308.15, 328.15	Inverse	[15]
Surfactant-based ABS				
$POELE_{10}$	K_3PO_4, K_2CO_3, KOH	288.15, 293.15, 303.15 308.15	Proportional	[16]
Organic solvent-based ABS				
Acetone	$MgSO_4$, $(NH_4)_2SO_4$, Li_2SO_4, $ZnSO_4$	288.15, 298.15, 308.15	Proportional	[17]

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