

Supplementary Information

Combining ionic liquids and polyethylene glycols to boost the hydrophobic-hydrophilic range of aqueous biphasic systems

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Materials and Experimental Procedure

Chloranilic Acid (CA, > 99 wt% pure) was purchased from Merck, while Indigo Carmine (IC, \geq 98 wt% pure) and Indigo Blue (IB, > 95 wt% pure) were acquired from Sigma-Aldrich. All the ILs were commercially acquired from Iolitec with purities > 98 wt %. All samples were dried for 24 h under vacuum and at a moderate temperature (323 K) before use. PEG of average molecular weight 1500 g.mol⁻¹ (PEG 1500) was supplied by Fluka and used as received. The water used was ultrapure water, double distilled and passed by a reverse osmosis system before finally treated with a Milli-Q plus 185 purification device.

The ABS combining PEG 1500 and four different ILs, namely [C₂mim]Cl, [C₄mim]Cl, [C₄mpyr]Cl and [C₄mpip]Cl, were determined by the turbidimetric titration method. A mixture point into the biphasic region, approximately 38 wt% of PEG, 52 wt% of IL and 10 wt% of water, was selected and used to evaluate the partitioning of three different dyes, Chloranilic acid (CA), Indigo Carmine (IC) and Indigo Blue (IB). In each system, a small amount of dye, \approx 0.30 mg, was added to glass tubes containing the ternary compositions with a total mass of 5 g. The ABS were then allowed to equilibrate at 323 K and atmospheric pressure conditions during 3 h. After that period, the top and bottom phases were carefully separated, and the partition coefficients of each dye were evaluated. The partition coefficient is defined as the concentration of the dye in the IL-rich phase to that in the PEG-rich one. The quantification of each dye in both phases was carried out by UV-Vis spectroscopy.

Experimental Results

Table S1. Binodal weight fraction data for the systems composed of PEG 1500 (1) + IL (2) + H₂O (3) at 323 K.

[C ₂ mim]Cl		[C ₄ mim]Cl		[C ₄ mpip]Cl		[C ₄ mpyrr]Cl	
100 w ₁	100 w ₂	100 w ₁	100 w ₂	100 w ₁	100 w ₂	100 w ₁	100 w ₂
9.1583	58.7473	14.9858	55.6914	10.60	56.20	5.23	67.60
13.4287	48.6955	15.3017	54.5986	14.96	50.76	13.96	48.78
21.9476	41.9476	24.7752	44.0133	15.30	48.46	25.28	39.77
23.4840	40.6187	36.6849	35.2397	22.49	41.13	35.44	34.93
29.5908	35.0914	39.5797	33.6221	27.62	35.76	47.89	24.07
34.4612	34.7182	49.4692	27.3325	43.56	26.53	62.66	18.64
36.7184	32.3570	52.7198	26.4656	51.19	21.29	62.66	18.64
42.5423	26.9599			51.42	21.50		
42.9489	26.6317			66.03	12.86		
44.9723	27.1613						
52.3509	21.1144						
58.9322	16.9953						

Table S2. Weight fraction compositions, partition coefficients (K) of neutral and charged Chloranilic Acid (CA), and pH of the respective top- and bottom-rich phases, for the ABS composed of PEG 1500 + IL, PEG 1500 + Na₂SO₄ and PEG 4000 + Dextran 40000 at 323 K and atmospheric pressure. The results represent the average of three independent experiments \pm associated standard deviation.

Ternary System	PEG 1500 / (wt%)	IL/salt/dextran / (wt%)	K	pH_{Top-phase}	pH_{Bottom-phase}
Acidic pH – neutral CA					
Na ₂ SO ₄	16.40 \pm 0.05	22.97 \pm 0.20	0.01 \pm 0.00	3.85 \pm 0.54	3.24 \pm 0.74
Dextran	10.03 \pm 0.07	9.98 \pm 0.01	0.72 \pm 0.08	2.80 \pm 0.22	3.00 \pm 0.80
[C ₂ mim]Cl	39.29 \pm 1.41	51.91 \pm 0.12	0.43 \pm 0.10	3.80 \pm 0.01	3.70 \pm 0.21
[C ₄ mim]Cl	38.54 \pm 0.54	51.65 \pm 0.39	0.82 \pm 0.12	3.23 \pm 0.82	3.09 \pm 0.74
[C ₄ mpip]Cl	38.42 \pm 0.10	51.82 \pm 0.10	1.85 \pm 0.02	3.64 \pm 0.31	4.04 \pm 0.34
[C ₄ mpyrr]Cl	38.54 \pm 0.18	51.88 \pm 0.08	2.15 \pm 0.16	3.53 \pm 0.25	4.17 \pm 0.12
Neutral pH – charged CA					
[C ₂ mim]Cl	40.07 \pm 0.31	49.74 \pm 0.19	1.75 \pm 0.11	5.56 \pm 0.21	5.60 \pm 0.08
[C ₄ mim]Cl	38.50 \pm 0.31	51.80 \pm 0.48	2.58 \pm 0.26	6.21 \pm 0.59	6.25 \pm 0.47
[C ₄ mpip]Cl	38.78 \pm 0.73	51.43 \pm 0.90	3.47 \pm 0.75	5.92 \pm 0.03	5.95 \pm 0.18
[C ₄ mpyrr]Cl	37.26 \pm 1.60	52.98 \pm 1.51	6.19 \pm 1.36	5.70 \pm 0.07	5.66 \pm 0.06

Table S3. Weight fraction compositions, partition coefficients (K) of Indigo Blue and Indigo Carmine, and pH of the respective Top- and Bottom-rich phases, for the ABS composed of PEG 1500 + IL and PEG 1500 + Na₂SO₄ at 323 K and atmospheric pressure. The results represent the average of three independent experiments \pm associated standard deviation.

Ternary System	PEG 1500 / (wt%)	IL/Salt / (wt%)	K	pH_{Top-phase}	pH_{Bottom-phase}
Indigo Carmine					
Na ₂ SO ₄	15.94±0.16	22.45±0.23	0.02±0.03	7.02±0.21	6.51±0.04
[C ₄ mim]Cl	38.08±0.50	52.18±0.83	6.03±4.20	5.50±0.06	5.53±0.11
[C ₄ mpip]Cl	37.83±0.86	53.34±0.68	53.74±15.41	5.90±0.10	5.82±0.13
[C ₄ mpyrr]Cl	38.27±0.14	52.01±0.28	9.87±0.98	7.56±0.24	7.13±0.58
Indigo Blue					
Na ₂ SO ₄	15.89±0.10	22.60±0.21	0.03±0.01	7.42±0.10	6.96±0.02
[C ₄ mim]Cl	37.63±0.13	52.89±0.44	0.21±0.09	6.72±0.39	6.75±0.45
[C ₄ mpip]Cl	37.74±0.22	52.79±0.15	3.76±0.98	6.44±0.76	6.46±0.90
[C ₄ mpyrr]Cl	38.04±0.35	52.18±0.60	0.73±0.19	7.68±0.18	7.65±0.19

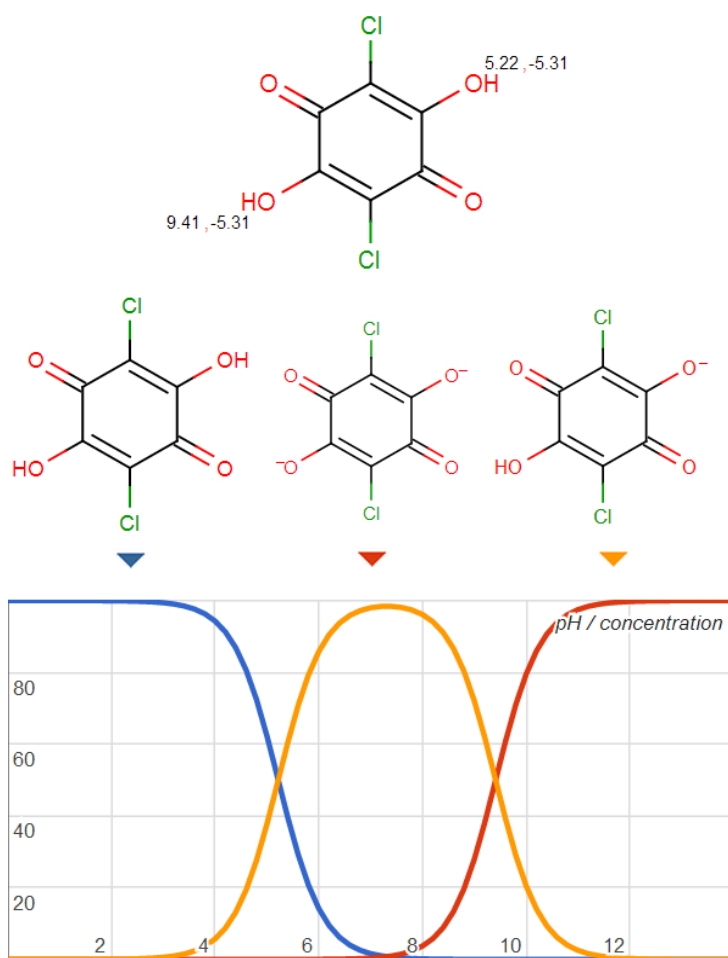


Fig. S1. Speciation curve of Chloranilic Acid as a function of pH. This content was adapted from the Chemspider chemical database.¹

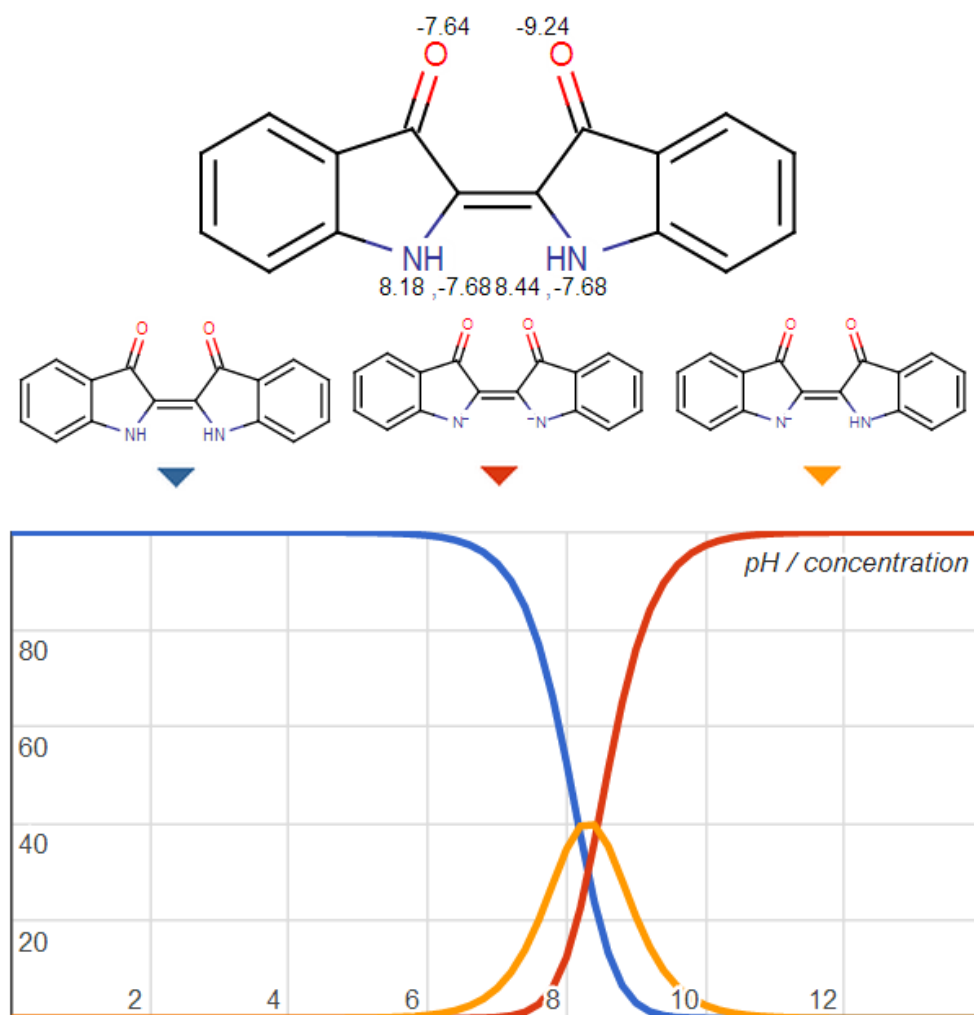


Fig. S2. Speciation curve of Indigo Blue as a function of pH. This content was adapted from the Chemspider chemical database.¹

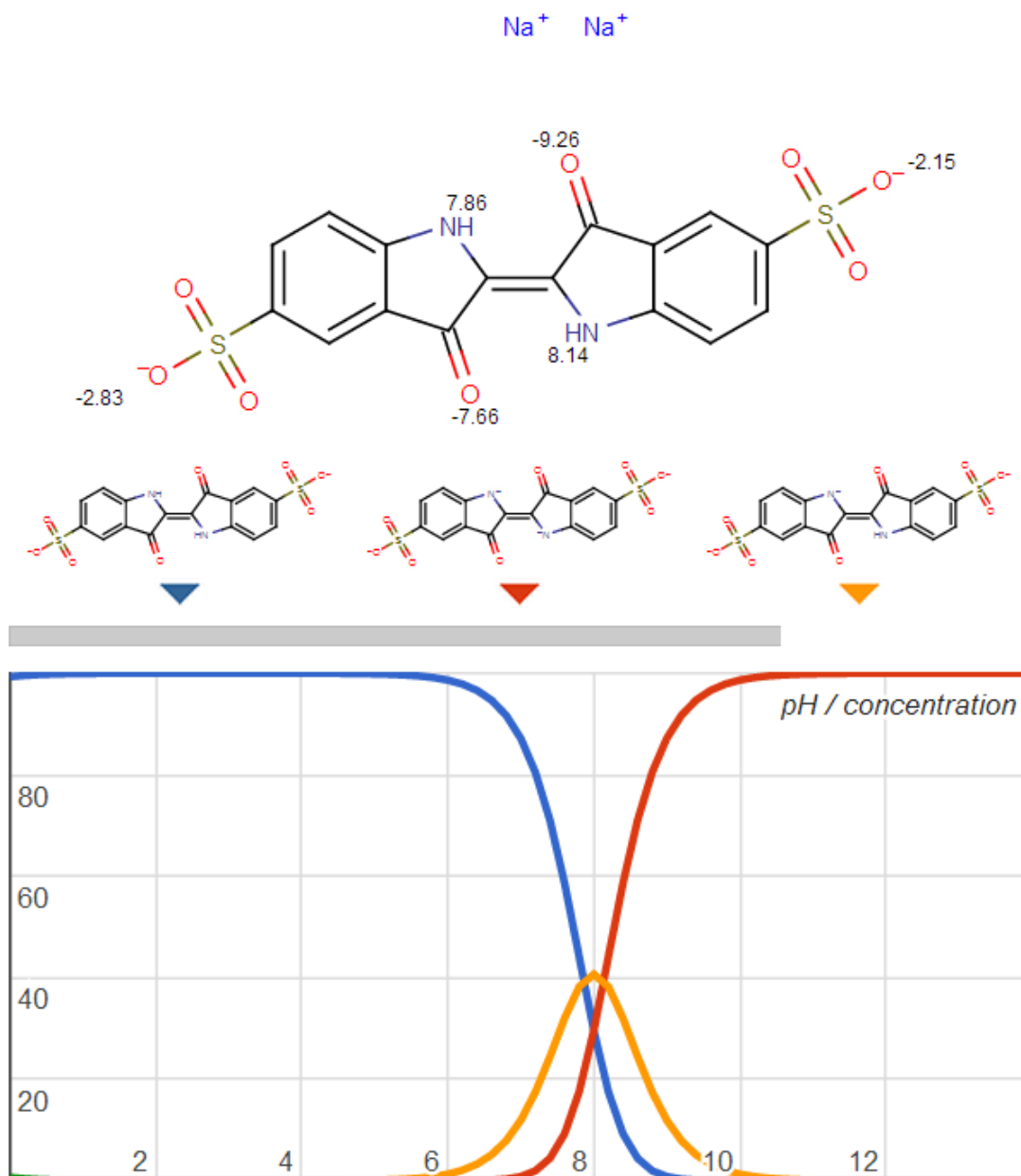


Fig. S3. Speciation curve of Indigo Carmine as a function of pH. This content was adapted from the Chemspider chemical database.¹

References

1. Chemspider, The free chemical database, <http://www.chemspider.com/>. Accessed at 06-05-2013.