Reversible Light-Induced Critical Separation - Electronic Supplementary Information

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Experimental details: The critical phase separation is achieved in a water-in-decane microemulsion with an AOT concentration of 88 mmol dm^{-3}, AZOT-S4 concentration of 1.5 mmol dm^{-3}, and *w* value of 67 (w.r.t. total surfactant concentration).

UV-vis light was produced by a 100 W broad-spectrum mercury lamp (Oriel) through a grating monochromator (Nortech Laboratories) set to 350 nm or 450 nm. Drop shape analysis (DSA) tensiometry was performed using a Krüss DSA10 Mk.2. Drops of aqueous surfactant solution were created using a syringe with a micro-dispensing screw-plunger into a 1 cm path-length quartz cuvette containing decane. Interfacial tensions were determined from drop profiles by the algorithm contained in the software which fits the photographed drop profile using the Young-Laplace equation.[1]

Neutron scattering experiments were carried out on the D22 small-angle diffractometer at the Institut Laue-Langevin, Grenoble, France. A neutron wavelength of λ = 10 Å with a spread of 9% and two sample-detector positions of 1.4 and 14 m were used with a detector offset to provide a Q range of 0.003 - 0.387 Å^{-1}. Absolute intensities for I(Q) (cm^{-1}) were determined to within 5% by measuring the incoherent scattering from 1 mm of H_2O. Samples were prepared as core contrast D_2O, H-surfactants, H-decane) in Hellma quartz cells with a path-length of 1 mm. Spectra were normalized by subtracting the scattering of the empty cell and a solvent background (H-decane). Model fits for neutron data were generated using the FISH program.[2] In the model fitting, floated parameters were the droplet radius, R^{av}, polydispersity, σ/R^{av}, the Schultz scale and interaction parameters, κ and ζ. The scattering profiles were fitted as hard spheres with added Schultz polydispersity and Ornstein-Zernike structure factor[3] (as appropriate). The Schultz distribution function is described by a root mean square deviation:[4]

$$\sigma = \frac{R^{av}}{(Z+1)^{1/2}} \tag{1}$$

where R^{av} is the average droplet radius, and Z is a width parameter. The Ornstein-Zernicke structure factor takes the form:

$$S(Q) = 1 + \frac{\kappa}{1 + \zeta^2 Q^2} \tag{2}$$

where the coefficient κ relates to the osmotic isothermal compressibility, κ_T as:

$$\kappa = N k_b T \kappa_T \tag{3}$$

Typical values and uncertainties for the pre-separation sample are shown in Table 1.

Table 1: Floated SANS parameters and the absolute uncertainties in their fitted values.

Parameter	Value	Uncertainty
R^{av}/nm	6.07	0.08
σ/R^{av}	0.318	0.007
κ	1.78	0.05
ζ/nm	11.0	0.5

Synthesis of 4-Butyl-4-hydroxy azobenzene precursor: 4-butylaniline (12 g, 80 mmol) was dissolved in of a 1:1 mixture of acetone and water (200 ml), and concentrated HCl (20 ml) and the solution was stirred for 20 minutes in an ice bath. In a separate beaker, $NaNO_2$ (5.6 g, 80 mmol) was dissolved in distilled water (100 ml) and placed in a freezer to cool to 1-3°C. Additionally, phenol (7.6 g, 80 mmol), NaOH (3.2 g, 80 mmol) and Na_2CO_3 (14 g, 80 mmol) were dissolved in distilled water (200 ml) by stirring for 5 minutes, and placed in a freezer to cool to 1-3°C. Once the original solution had cooled to 2°C, the $NaNO_2$ solution was added slowly, and this mixture was left for 20 minutes to stir in the ice bath. The resultant diazonium salt solution was placed in the freezer while the phenol solution was placed in the ice bath and stirred. The diazonium salt solution was then added drop-wise to the phenol solution, ensuring that the reaction temperature did not exceed 8°C at any time. The yellow/brown precipitate was filtered off and dried over night in a vacuum oven. The crude product was re-crystallized from ethanol, yield 12.3 g (69%).

^{1}H NMR: (270 MHz, $CDCl_3$, 25°C, TMS): δ=0.93 (t, ^{3}J(H,H)=6.75 Hz, 3H, CH_3), 1.30-1.43 (m, 2H, CH_2), 1.57-1.68 (m, 2H, CH2), 2.67 (t, ^{3}J(H,H)=8.1 Hz, 2H,CH_2), 5.17 (s, 1H, OH), 6.92 (d, ^{3}J(H,H)=10.9, 2H, 2 CH), 7.29 (d, ^{3}J(H,H)=10.9 Hz, 2H, 2 CH), 7.78 (d, ^{3}J(H,H)=8.1 Hz, 2H, 2 CH), 7.84 (d, ^{3}J(H,H)=8.1 Hz, 2H, 2 CH). 13CNMR: (300 MHz, $CDCl_3$, 25°C, TMS): δ=14.05, 22.04, 33.54, 35.65, 116.0, 122.6, 124.9, 129.2, 146.2, 147.1, 151.0, 158.4. Mass Spec (EI): 254 (M), 161 ($C_{10}H_{13}N_2$), 133 ($C_{10}H_{13}$), 121 ($C_6H_5N_2$), 93 (C_6H_5O), 65 (C_5H_5).

Synthesis of 1-(4-(4-bromobutoxy)phenyl)-2-(4-butylphenyl)diazene precursor: 4-butyl-4-hydroxy azobenzene (2.5 g, 8.64 mmol) was dissolved in acetone (100 ml), and to this solution was added 1,4-dibromobutane (13.0 g, 51.9 mmol), anhydrous potassium carbonate (excess - 4 g, 29 mmol) and a catalytic amount of potassium iodide. The reaction mixture was refluxed at 65°C and stirred for 20 hours. The solution was allowed to cool to room temperature after which the solvent was removed by rotary evaporation. The solid was dissolved in hexane and washed with water until the washings remained clear. The hexane was then removed by rotary evaporation and the solid product was re-crystallized from ethyl acetate and dried under vacuum overnight, yield 2.7 g (71%).

^{1}H NMR: (400 MHz, $CDCl_3$, 25°C, TMS): δ = 0.94 (t, ^{3}J(H,H)=6.0 Hz, 3H, CH_3), 1.33-1.42 (m, 2H, CH_2), 1.60-1.67 (m, 2H, CH_2), 1.95-2.01 (m, 2H, CH_2), 2.06-2.13 (m, 2H, CH_2), 2.67 (t, ^{3}J(H,H)=8.0 Hz, 2H, CH_2), 3.50 (t, ^{3}J(H,H)=6.0 Hz, 3H, CH_3), 4.07 (t, ^{3}J(H,H)=6.0 Hz, 3H, CH_3), 6.98 (d, ^{3}J(H,H)=12.0 Hz, 2H, 2 CH), 7.30 (d, ^{3}J(H,H)=8.0 Hz, 2H, 2 CH), 7.80 (d, ^{3}J(H,H)=8.0 Hz, 2H, 2 CH), 7.89 (d, ^{3}J(H,H)=8.0 Hz, 2H, 2 CH).

Synthesis of AZOT-S4: (*E*)-1-(4-(4-bromobutoxy)phenyl)-2-(4-butylphenyl)diazene (3g, 7.27 mmol) was dissolved in hot ethanol (100 ml) and to this was added sodium sulfite (3.3 g, 29.1 mmol) dissolved in hot water (100 ml). The mixture was refluxed at 95°C for 48 hours, after which the solution was allowed to cool and the solvent was removed by rotary evaporation. The crude solid was purified by dispersing in toluene and centrifuging it for 20 min, retaining the solid and discarding the supernatant (which contained any unreacted bromide). This was repeated until the toluene wash was no longer coloured. The solid was then dried and re-crystallised from water. The purified solid was dried under vacuum overnight, yield 1.97 g (62%).

^{1}H NMR: (300 MHz, D6-DMSO, 25°C, TMS): δ = 0.91 (t, ^{3}J(H,H)=7.5 Hz, 3H, CH_3), 1.27-1.39 (m, 2H, CH_2), 1.55-1.65 (m, 2H, CH_2), 1.71-1.84 (m, 4H, 2 CH_2), 2.67 (t, ^{3}J(H,H)=7.5 Hz, 2H, CH_2), 3.33-3.38 (m, 2H, CH_2), 4.07 (t, ^{3}J(H,H)=6.0 Hz, 3H, CH_3), 7.12 (d, ^{3}J=9.0 Hz, 2H, 2 CH), 7.38 (d, ^{3}J=9.0 Hz, 2H, 2 CH), 7.77 (d, ^{3}J=6.0 Hz, 2H, 2 CH), 7.85 (d, ^{3}J=9.0 Hz, 2H, 2 CH). Mass spec (-ESI): m/z: 389.15 (M-Na)

References

[1] Krüss GmbH, *Krüss DSA10 User Manual*, 2001.

[2] R. K. Heenan, *Fish Data Analysis Program, Rutherford Appleton Laboratory Report, RAL-89-129*, 1989.

[3] M. Kotlarchyk, S.-H. Chen, and J. S. Huang, *Physical Review A*, 1983, **28**, 508.

[4] M. Kotlarchyk, S.-H. Chen, J. S. Huang, and M. W. Kim, *Phys. Rev. A*, 1984, **29**, 2054.