

Supporting material - Photo-stabilised microemulsions

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Sample preparation

Since *E*-SGP was insoluble in heptane, and its Krafft temperature in water T_K was $\sim 45^\circ\text{C}$, the samples were prepared as follows: surfactants and D_2O were weighed in a 5 mL volumetric flask, heptane was added, the mixtures were then sonicated at $\sim 50^\circ\text{C}$ for ~ 15 minutes. Additional heptane was added to 5 mL and the samples were equilibrated at 50°C for at least 2 hours prior to irradiation/measurement. In this way, two sets of samples were prepared, one set for irradiation and another for SANS experiments.

Irradiation and characterization of photo-products

Samples were irradiated for 30 minutes, thermostated at 50°C and stirred with a magnetic flea, in quartz cuvettes (2 cm path length) with a 100 W High pressure Hg lamp (LPS-220/250 power supply from PTI; lamp housing from HI-TECH Scientific and Mercury short arc photo optic lamp HBO[®] 103 W/2), which was polychromatic to maximize the photon flux. The photographs in Figure 1 were taken at room temperature, with a maximum time delay of 15 seconds after irradiation at the higher temperature. The identity and composition of photoproducts was analyzed by ^1H NMR (Jeol Delta 270), using a post-irradiated sample $X_{\text{SGP}} = 7.5\%$ and $w_0 = 30$, the heptane was removed by rotary evaporation and replaced by 1 mL of methanol- d_4 (Cambridge Isotopes Laboratories, 99.8%). Spectral assignments were made as documented elsewhere [1].

SANS experiments were carried out at the D22 diffractometer at ILL (Grenoble, France) using a neutron wavelength of $\lambda = 10 \text{ \AA}$ at two different detector distances to cover a Q range of $0.0024 \rightarrow 0.37 \text{ \AA}^{-1}$, and also at the time-of-flight LOQ instrument at ISIS, UK where incident wavelengths are $2.2 \leq \lambda \leq 10 \text{ \AA}$, resulting in an effective Q range of $0.009 \rightarrow 0.249 \text{ \AA}^{-1}$ [2]. Absolute intensities for $I(Q)$ (cm^{-1}) were determined to within $\pm 5\%$ by measuring the incoherent scattering from 1 mm of H_2O at ILL, whereas at ISIS a partially deuterated polymer standard was employed [2]. Two neutron contrasts were prepared: “shell”, comprising D_2O :H-SGP + H-DDAB:*d*-heptane “shell” (Figure 1, Table 1), and “core” contrast with D_2O :H-SGP + H-DDAB:*h*-heptane (Table A). The neutron beam was scattered from the upper transparent microemulsion phase, missing the denser separated part in the case of pre-irradiated samples. Experiments were carried out at 50°C , using 2 mm (shell contrast), or 1 mm (core contrast) path-length quartz cells.

SANS analysis model

For polydisperse, homogeneous spherical particles the SANS intensity $I(Q)$ / (cm^{-1}) is given by,

$$I(Q) = N_P [P(Q,R) p(R)] S(Q) + B_{inc} \quad (\text{A1})$$

where $I(Q)$ is the absolute scattering intensity, N_P is the particle number density, $P(Q)$ is the single particle form factor, $p(R)$ is a normalised distribution function, $S(Q)$ is the inter-particle structure factor, which accounts for interactions. In these dilute w/o systems, away from attractive phase boundaries (absence of low Q critical scattering), inter-particle interactions may be approximated to a hard-sphere structure factor $S_{HS}(Q)$, based on the known surfactant + water volume fraction and estimated droplet radius [3 - 5]. The level B_{inc} represents a sample-dependent isotropic incoherent background, which is determined by measuring an appropriate solvent. For the core-shell spherical particles in “shell” contrast $P(Q,R)$ is given by [3]

$$P(Q,R) = \frac{16\pi^2}{9} \left[(\rho_{shell} - \rho_{oil}) 3R_D^3 \left(\frac{\sin QR_D - QR_D \cos QR_D}{(QR_D)^3} \right) - 3R_C^3 \left(\frac{\sin QR_C - QR_C \cos QR_C}{(QR_C)^3} \right) \right]^2 + (\rho_{core} - \rho_{oil}) 3R_C^3 \left(\frac{\sin QR_C - QR_C \cos QR_C}{(QR_C)^3} \right)^2 \quad (\text{A2})$$

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where R_D the droplet radius, R_C the core radius (also called R_{D2O}), Q is the momentum transfer ($\{4\pi/\lambda\}\sin(\theta/2)$, θ scattering angle) and ρ_{oil} , ρ_{shell} , ρ_{core} represent the coherent scattering length density of the oil medium, shell, core respectively. The interfacial adsorbed layer thickness t_{surf} is $R_D - R_C$. For “shell” contrast $\rho_{shell} \approx \rho_{oil}$ which reduces Eq. A2 to the better-known form factor for homogeneous spheres. Because $P(Q,R)$ is size and shape sensitive, a polydispersity term $p(R)$ is included in Eq. A1. This polydispersity was a Schultz distribution function $p(R)$, [4] defined by an average radius \bar{R} and a root mean square (RMS) deviation σ given by

$$\sigma = \left[\overline{(R - \bar{R})^2} \right]^{1/2} = (\overline{R^2} - \bar{R}^2)^{1/2} = \bar{R} / (Z + 1)^{1/2} \quad (A3)$$

where Z is a width parameter. The polydispersity reported in Table 1 is σ / R_{D2O} . The SANS data were fitted using the interactive FISH program [5], which is a flexible multimodel package comprising a variety of different form factors $P(Q)$, structure factors $S(Q)$, and polydispersity functions. After extensive trials the most appropriate model was found to be for Schultz polydisperse two shell hard spheres.

References – supporting material

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Table A. Changes in volume fraction of D₂O (ϕ_{D_2O}) and water core radius R_{D_2O} incorporated

into the microemulsion phase as a function of X_{SGP} and w_0 , before and after irradiation, as

obtained from SANS analysis of “core” contrast data with D₂O:SGP + DDAB:*n*-heptane. T =

50 °C, [SGP + DDAB] = 0.10 mol dm⁻³. Uncertainties: $\phi_{D_2O} \pm 10\%$, $R_{D_2O} \pm 2 \text{ \AA}$.

$X_{SGP}(\%)$	w_0	before UV ϕ_{D_2O}	after UV ϕ_{D_2O}	$\Delta(\phi_{D_2O})$	% solubilised D ₂ O change	before UV $R_{D_2O} / \text{ \AA}$	after UV $R_{D_2O} / \text{ \AA}$
0	25	0.045	0.045	-	-	44.1	45.5
2.5	25	0.023	0.040	0.017	174	23.1	40.1
	30	0.034	0.050	0.016	148	33.9	50.5
4.0	25	0.033	0.041	0.008	123	33.1	40.8
	30	0.040	0.053	0.013	132	40.1	53.0
7.5	25	0.033	0.044	0.011	134	33.2	44.2
	30	0.041	0.055	0.014	134	41.2	55.0