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Aggregation in a high internal phase emulsion observed by SANS and USANS

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Abstract

As part of a wider study into high internal phase emulsions, we have prepared and studied by SANS and USANS the structure of an unstable emulsion consisting of 90% by volume saturated ammonium nitrate dispersed as micron-scale droplets in hexadecane, stabilised by the surfactant Pluronic L92. Similar emulsions produced using polyisobutylene-based surfactants, reported earlier, are highly stabilised by a significant number of surfactant rich reverse micelles a few nanometres in diameter in the oil phase. The aqueous-oil droplet interfaces are coated with a monolayer of surfactant, while a very small amount of surfactant is aggregated into micron-scale surfactant-rich objects. In contrast, the Pluronic emulsion contains an insignificant number of reverse micelles and a complex multilayered interface between oil and aqueous phases. Now, the great majority of added surfactant is in the form of micron scale, fractally linked, blocks of lamellar phase at the aqueous-oil droplet interfaces. The lamellar phase can be characterised by the Bragg peaks observed in three different isotopic contrasts by SANS. We attribute the shear instability of the Pluronic emulsion to the more hydrophilic nature of the surfactant which causes both depletion of reverse micelles in the oil phase, and aggregation into the blocks of lamellar phase.
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1. Introduction

High internal phase emulsions, where the dispersed phase may be much higher than 74% in volume fraction, have been little studied by neutron scattering [1–6]. We have studied such emulsions stabilised by PIBSA-based surfactants. We find the majority of surfactant in the form of reverse micelles in the oil phase, and dissolved in the oil phase. Rather less occurs as a monolayer at the aqueous droplet oil interface, with a very small amount in the form of micron scale surfactant aggregates. We present here a neutron scattering study of an emulsion, stabilised by Pluronic L92, whose structure is very different.

2. Experimental

Attempts were made to produce emulsions from four Pluronic surfactants (L31, L64, L92, L121).[1] These were chosen to span available ranges of hydrophobe molecular weight and hydrophile/hydrophobe ratio while remaining in the lipophilic region. The emulsions were prepared by dispersion of a 90% aqueous internal volume fraction of almost saturated ammonium nitrate solution into a hexadecane/surfactant mixture by use of a shearing propeller [3]. At the concentration tried, only L92 formed an emulsion. This was stable to phase separation when not subject to shear, but shearing caused rapid breakdown. However stability was sufficient to load the emulsion into

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[1]The identification of any commercial product or trade name does not imply endorsement or recommendation by the NIST.

Table 1
Compositions of the isotopically varying samples

	Pluronic L92	$C_{16}H_{34}$	$C_{16}D_{34}$	Ammonium nitrate	D_2O	H_2O
E1	0.075	0.717		6.33	5.50	
E2	0.075	0.220	0.625	6.32	5.50	
E3	0.076	0.227	0.628	6.32		4.95
M1	0.038	0.362		0.02	0.02	
M2	0.037		0.410	0.02	0.02	
M3	0.035		0.414	0.02		0.02
M4	0.018			1.58	1.38	

the SANS/USANS cells without decomposition. In addition to the emulsion (E1–E3) we also prepared solutions of L92 in hexadecane (M1–M3), which were allowed to equilibrate with a small amount of aqueous ammonium nitrate as a second phase, and also L92 was dispersed in saturated ammonium nitrate (M4). The compositions of the various isotopically varying samples are given in Table 1.

The USANS experiments were performed using the BT5 thermal neutron double-crystal instrument at NIST, NCNR in Gaithersburg, MD, USA [7]. The samples E2 and E3 were run for 6–8 h each in 1 mm sample thickness in quartz cells at a neutron wavelength of 2.4 Å. A background from an empty beam run was subtracted from all the data, and the subtracted data processed to an absolute scale by use of the straight through beam intensities. The Q (wavevector component in the horizontal plane) range corresponds to probing length scales from 1500 to 200,000 Å. We perform a vertical line-focus convolution on our model intensity and fit it to the observed, line-focus, intensity from E2 versus Q. The Q-dependent scattered beam intensity was less than 10% of the incident intensity. With these low values multiple scattering can and has been neglected.

All SANS and USANS fits were performed by the use of interactive IGOR procedures [8].

We have used a model to fit the E2 USANS data which consists of spheres, which are fractally linked together into an aggregate. Following Teixeira [9] we approximate

$$I(Q) = \left(\frac{4\pi}{3r_0^3}\right)\Delta\rho^2 N_0 S(Q) P(Q), \qquad (1)$$

where $I(Q)$ is the observed intensity, r_0 the rough sphere radius, $\Delta\rho^2$ the SLD difference between the sphere and external medium, N_0 the sphere number density, $S(Q)$ the fractal structure factor and $P(Q)$ the sphere structure factor.

We can define $P(Q)$ and $S(Q)$ as

$$P(Q) = \left(1 + \frac{2^{1/2}}{3}Q^2 r_0^2\right)^{((D_s-6)/2)},$$

$$S(Q) = 1 + (Qr_0)^{(-D_m)} D_m$$
$$\times \Gamma(D_m - 1)\frac{\sin((D_m - 1)\tan^{-1}(Q\xi))}{(1 + Q^{-2}\xi^{-2})^{((D_m-1)/2)}},$$

where D_s is the surface fractal dimension of the sphere, which we will fix at 2; D_m the mass fractal dimension of the aggregates of spheres; ξ is a cut-off distance defining the aggregate size, which we will set to be infinite, and $\Gamma(x)$ is the gamma function of argument x.

SANS experiments were performed on the LOQ instrument at the Rutherford Appleton Laboratory, United Kingdom [10], data correction and reduction were as previously described [3,4].

We have modelled the observed SANS scattering as a two slab aqueous-oil interface with a flat background. This was convoluted with the experimental resolution function.

3. Results and discussion

The USANS data shows structures visible in both contrasts. In E2, the oil and aqueous phases have the same scattering length density, thus we are observing surfactant structure. We see from Fig. 1 that the scattering is well fitted by a system of fractally linked smooth-surfaced blocks. The fit shows the blocks are linked in an almost three-dimensional array, with a linking dimension of 2.97(1), and a block radius of 960(20) Å. This dimensionality of block linking indicates very dense almost solid packing of fractal blocks, which are assumed to be spheres. The amount of Pluronic L92 found in the blocks in total depends on the composition of the blocks. If we assume pure material then 92(4)% of the added surfactant is in the blocks. As we shall see later there is SANS evidence for the presence of a lamellar surfactant phase containing ~70% surfactant. This can be identified as the aggregate if we acknowledge that the fractal fitting is not completely quantitative.

The USANS from E3 would be expected to show scattering from all three interfaces between oil, aqueous and lamellar phases, since none are matched in contrast. Optical microscopy shows an emulsion with aqueous droplets of a few microns diameter. Further optical studies on the geometry of the droplets are in progress, however
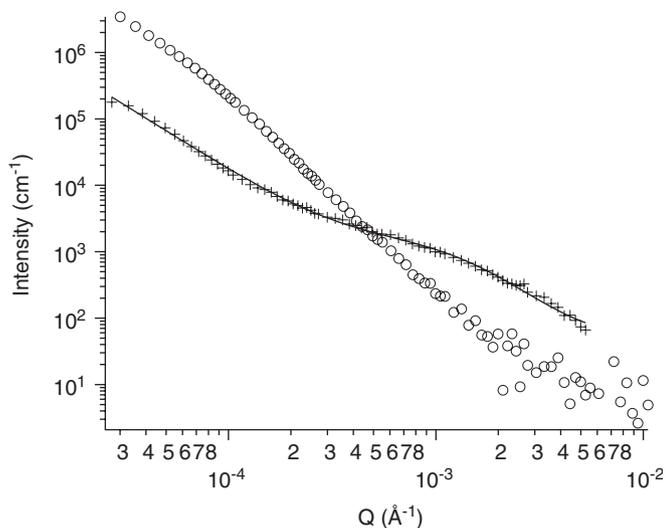
Fig. 1. Experimental USANS results from Pluronic L92 emulsions with a fit to one set of data [+ contrast matched emulsion (E2); O contrast unmatched emulsion (E3)].
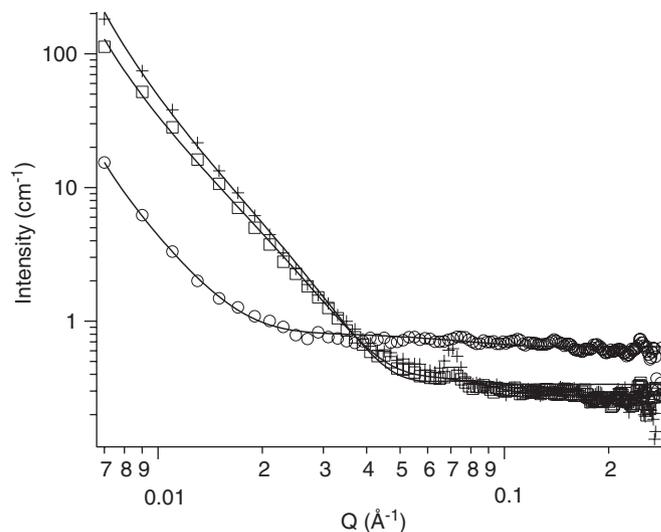
Fig. 2. Experimental SANS results and model fits from Pluronic L92 emulsions [+ contrast matched emulsion; O and □ differently contrast unmatched emulsions].

Fig. 3. Experimental SANS results in the region of the lamellar Bragg peaks [+ contrast matched emulsion; O and □ differently contrast unmatched emulsions].

the lack of flattening out of the scattering at low Q indicates a simple array of spherical droplets of maximum size 10–20 μm is not occurring here. This contrasts to PIBSA-based emulsions where this is so. Fitting of the mid-Q intensities to Porod scattering from an aqueous-oil interface gives an interfacial area of $0.13\,m^2\,mL^{-1}$ of emulsion. This is incompatible with the optical results, which clearly indicate much larger areas. In the Pluronic case, unlike PIBSA, we must invoke a more complex interface than a simple surfactant monolayer. If we assume a smooth aqueous–Pluronic interface, and a very rough Pluronic-oil interface we obtain an aqueous–Pluronic interface of ca. $4\,m^2\,mL^{-1}$ once the additional area due to the Gaussian roughness is taken into account. This is compatible with the optical results. Hence we have indications that the lamellar aggregate decorates the surface of the aqueous droplets.

There is no evidence in the SANS fits from E1–E3 of reverse micelles of surfactant in the oil phase. In addition, none of the solutions M1–M4 show any scattering above the expected background. Thus in contrast to PIBSA-based systems, reverse micelles in the oil phase are negligible in number.

All three curves may be fitted with a single model [11] (Fig. 2). The aqueous phase is coated with a layer of surfactant and oil about 110 Å thick. This is topped by a ~110 Å thick aqueous layer, which in turn is topped by a lamellar layer of large thickness. The first layer, for physical reasons, would be presumed to be a surfactant–oil–surfactant trilayer, but we are unable to resolve this detail, which would have a less strong effect on the SANS than the other factors. This again contrasts with PIBSA-based emulsions where we observe a simple, thin, monolayer of surfactant at this interface. Thus, complementing the USANS we have at the aqueous interface a lamellar structure. Such layer structures have been previously
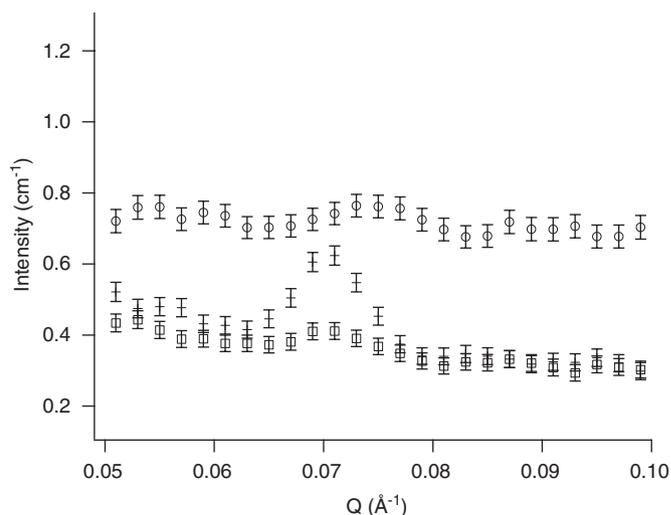
observed at a silicon surface in related emulsions by reflectometry [12].

We have modelled this complex interface as a sum of large lamellar blocks stuck to the interface with a thinner layer between blocks. This is probably an approximation to a more disordered thickness distribution.

Lastly, we note as shown in Fig. 3 that there are peaks in the SANS at $Q \sim 0.07\,\text{Å}^{-1}$. This is characteristic of a lamellar phase. Using the Bragg peak position and the two intensity ratios between the peak intensities we obtain a 90 Å period lamellar phase composed of alternating ~15 Å thick oil or aqueous layers sandwiched between ~30 Å thick surfactant layers. This is a typical lamellar crystal structure.

Acknowledgements

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