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ORIGINAL CONTRIBUTION

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Effects of nonionic surfactant and sodium dodecyl sulfate layers on electroacoustics of hexadecane/water emulsions

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Abstract Hexadecane-in-water emulsion droplets were formed in a homogeniser in the presence of a mixture of an anionic surfactant (sodium dodecyl sulfate, SDS) and nonionic surfactants of various chain lengths [nonylphenol ethoxylate ($C_9\phi E_N$, $N = 100$, 40 and 30) or an alcohol ethoxylate (Brij35)]. The dynamic mobility of the oil droplets was then measured using a flow-through version of an AcoustoSizer. Large changes were observed in the dynamic mobility of the particles formed with the mixed surfactants compared to particles formed with SDS alone. O'Brien's "gel layer" model was employed to interpret the data. The characteristics of the adsorbed layer appeared to be similar whether the nonionic surfactant was adsorbed concurrently with the SDS as the emulsion formed or was merely added afterwards to the emulsion established. The particle size, the charge and the molar fraction of SDS had virtually no effect. The layers formed with the nonionic surfactants decreased in thickness with decreasing molecular weight as expected. Passage through the homogeniser itself had no effect on the properties of the largest nonionic surfactant and, hence, on the adsorption layer formed with it.

Key words Polymer layer · Emulsion · Electroacoustics · Sodium dodecyl sulfate · Nonionic surfactant

Introduction

Industrial emulsions are often composed of mixtures of ionic and nonionic surfactants. The presence of different components is known to strongly affect the physical properties of the interfaces: stability, shape, surface tension and viscoelastic behaviour. In general, the mechanism of stabilisation of emulsion droplets by a macromolecular surfactant is of the steric type, whilst the stabilisation by an anionic surfactant is of the electrostatic repulsion type. Emulsions stabilised by mixtures present both types of stabilisation. In particular, with particulate dispersions, one segment (the anchor fraction) of the macromolecular surfactant may be strongly adsorbed at the interface, preventing desorption, whilst the second segment type (the solvophilic part) will extend into the solvent, providing an effective steric barrier to aggregation.

The effect of the adsorbed macromolecular stabiliser on the colloidal stability of the disperse system is determined largely by the amount adsorbed and by the hydrodynamic thickness, both of which are influenced strongly by the molecular structure, molar mass and adsorption energy of the surfactant. For good steric stabilisation of dispersions or emulsions the following requirements are necessary: a high amount adsorbed, firm attachment of the adsorbed layer to the surface and good solvency conditions for the stabilising moiety [1].

In another work [2] we examined a system in which the hexadecane-in-water emulsion was first formed in the presence of an anionic stabiliser (sodium dodecyl sulfate, SDS) and then the effects of the nonionic surfactant (nonylphenol ethoxylate ($C_9\phi E_N$, $N=100$) were studied at various levels of solution concentration. It was shown that the nonionic surfactant produced significant changes in the electroacoustic signals of oil drops. Application of O'Brien's "gel layer" model [3] enabled us to interpret those changes in terms of the properties of the adsorbed surfactant layer. This model requires two parameters, the apparent outer thickness of the adsorbed layer, *d*, and the extent to which the adsorbed polymer was able to displace the shear plane out from the surface of the particle by forming a dense inner layer, Δ. To enable comparison with direct current (d.c.) (static) electrophoresis and other measurements, an effective static mobility thickness, Δ_s, can also be calculated from the low-frequency limit of the model.

In this article we examine what differences, if any, appear if the nonionic surfactants are added at the same time as the SDS, prior to passage of the crude emulsion through the homogeniser. We also examine the effect of the nonionic chain length ($N=100$, 40 and 30) and an alternate anchoring group (Brij35 with a fatty alcohol anchor) on the electroacoustics [4, 5] of these oil-in-water emulsions.

Experimental

Instruments and chemicals

All the instruments and chemicals were as described previously [2] except for the following. Brij35 was obtained from Ajax Chemicals (minimum purity 97%). $C_9\phi E_N$ were obtained from ICI Australia Operations Pty., with *N* values of 30, 40 and 100. These are denoted N30, N40 and N100, respectively.

Methods

The required quantity of pure water was weighed into a conical flask. Then SDS and nonionic surfactant were added separately to keep their bulk concentrations as required. The remaining processes were as described previously [2].

Dynamic mobility measurement and calculation procedure

After passing the samples through the homogeniser, the dynamic mobility spectra were measured. The calculation of the zeta potential and the size from the measured dynamic mobility is comparatively straightforward for a dilute uncoated system (6%). The relevant relationship is given by O'Brien et al. [5] and is built into the instrument software.

After the dynamic mobility values had been obtained from the electrokinetic sonic amplitude measurement, the ratio μ_d(coated)/μ_d(uncoated) was calculated, where "coated" refers to the mixed surfactant system and "uncoated" to the emulsion with SDS alone. The outer "gel layer" thickness, *d*, can then be obtained from the best fit between the experimental values and the theoretical ones for the argument difference. After *d* had been determined, the average value of $\exp(-\kappa\Delta)$ and, hence, Δ can be obtained at the frequencies selected. The total adsorbed layer thickness is the sum of *d* and Δ, and finally Δ_s is calculated [3].

Evaluation of structure parameters for nonionic surfactants

The structure parameters of the nonionic surfactants were determined following the molecular-structure method used previously [2] and the results are shown in Table 1.

Results

Homogeniser effect on the molecular properties of the nonionic surfactant

Before the series of experiments was conducted in which the nonionic surfactant was added before the emulsification, it was necessary to determine whether the homogenising process has any effect on the molecular structure, i.e., whether the nonionic surfactant chain is broken during the passage through the homogeniser. A solution of N100 (2.5 mM) was passed ten times through the homogeniser at 25 °C. The calculated volume of this N100 solution was then added to two sets of emulsions in which the bulk SDS concentration was 1 mM and 3 mM, respectively. The final bulk N100 concentrations were 0.10, 0.15, 0.20 and 0.40 mM. About 1 hour later, the dynamic mobility of each sample was measured using an AcoustoSizer. The layer thickness was estimated from the dynamic mobility ratio. Comparing the results with those obtained with N100 solutions (2.5 mM) which had not been first passed through the homogeniser revealed that there was no detectable difference. Since the lower-molecular-weight surfactants are less likely to be degraded, it seems that the homogeniser has no effect on the molecular structure of the nonionic surfactants.

Effects of surfactant concentration

Total surfactant concentration constant

The dynamic mobility spectra (both magnitude and argument) for the SDS/N100 system are shown in Fig. 1. The total surfactant was kept at 1 mM and the ratio between the surfactants was changed. It can be seen that with increasing N100 concentration, the magnitude decreases, as does the absolute value of the argument (becomes much less negative). Although

Table 1 Structure parameters for nonionic surfactants

	N100	N40	N30	Brij35
M	4620	1980	1540	1198
l (nm)	35.88	14.88	11.38	9.60
d_c (nm)	5.10	3.34	2.94	2.60
s (nm)	0.27	0.27	0.27	0.047
α/η (nm^{-2})	0.038	0.068	0.081	0.019

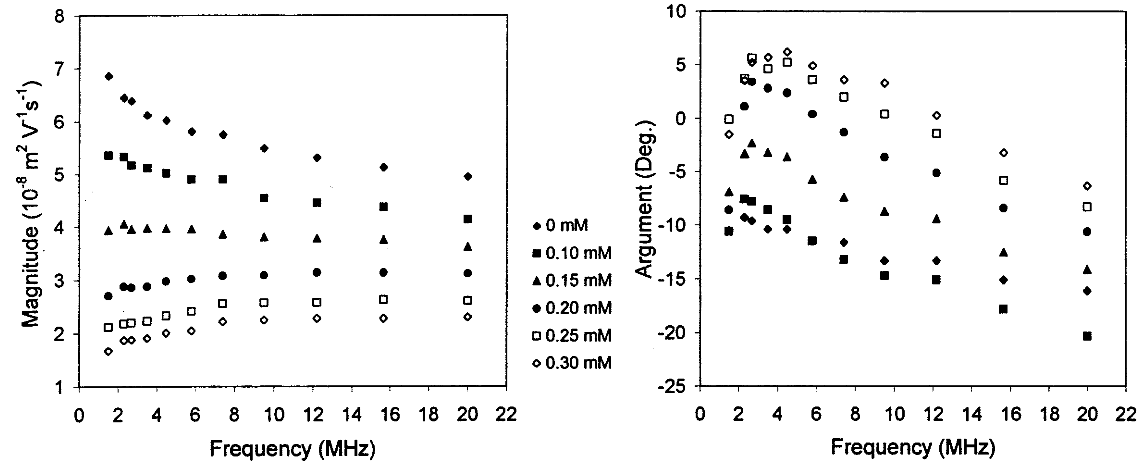
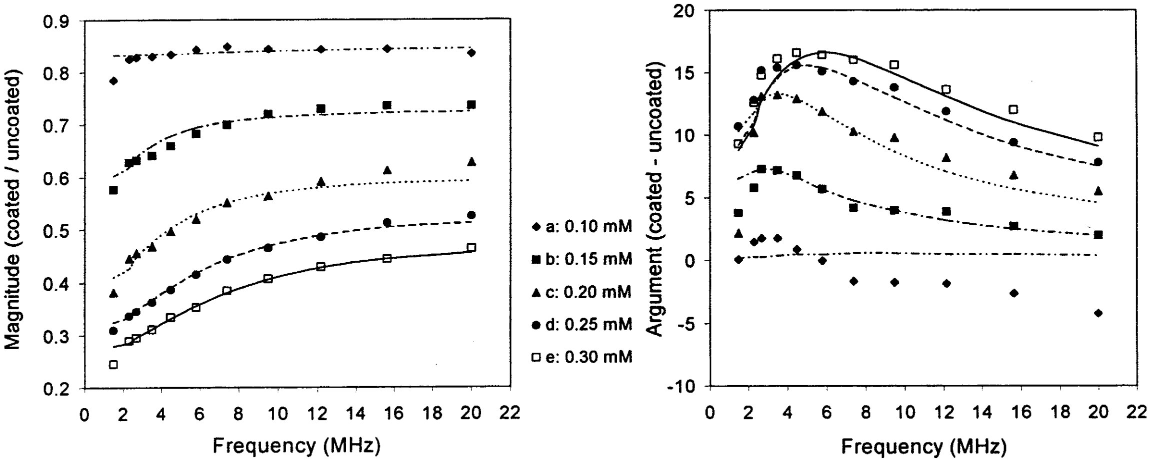


Fig. 1 Variation of dynamic mobility with frequency and N100 concentration, total surfactant 1 mM, five passes

the magnitude decreases regularly with increasing nonionic surfactant concentration at any given frequency, the effect is more pronounced at lower frequencies, with the result that, at a given concentration, the magnitude decreases with frequency at lower levels of polymer addition and increases with frequency at higher levels. The shape of the phase-angle spectrum changes as well. In the absence of the nonionic surfactant, it shows the normal increase in phase lag with increase in frequency, which is due to the inertia effect of the particles, which becomes more important at higher frequencies. However addition of the nonionic surfactant produces a maximum at low frequency, which becomes more pronounced as the polymer concentration increases. A comparison between the experimental data and O'Brien's theory for the dynamic mobility ratio μ_d(coated)/ μ_d(uncoated) at five different N100 concentrations is given in Fig. 2.

At the lowest concentration (0.10 mM) of N100 the magnitude of the mobility ratio was independent of frequency, with a value of about 0.85, showing not much deviation from the mobility of the uncoated particles. As the concentration was increased, the magnitude decreased and showed an increasingly strong dependence on the applied frequency in such a way that at the highest concentration (0.30 mM) there was about a 60% increase in the magnitudes from the lowest (0.28) to the highest frequency (0.46). The arguments of the mobility ratio were also affected by the increasing concentration of N100. At 0.10 mM, the phase angles remained mostly within 2° of those of the uncoated particles, again indicating no significant difference from the uncoated particles. As the concentration was increased, a well-defined trend with frequency developed, consisting of a

Fig. 2 Comparison of gel layer theory (*lines*) with experimental data (*symbols*) for the dynamic mobility ratio, μ_D(coated)/μ_D(uncoated), for N100, total surfactant 1 mM, five passes. (*a*) $\kappa=0.253$ nm^{-1} $\omega_0=0.5$ s^{-1}, $d=2.0$ nm, $\Delta=0.65$ nm, $\Delta_s=0.73$ nm; (*b*) $\kappa=0.251$ nm^{-1}, $\omega_0=1.0$ s^{-1}, $d=5.5$ nm, $\Delta=1.26$ nm, $\Delta_s=2.29$ nm; (*c*) $\kappa=0.250$ nm^{-1}, $\omega_0=2.0$ s^{-1}, $d=7.3$ nm, $\Delta=2.04$ nm, $\Delta_s=3.91$ nm; (*d*) $\kappa=0.249$ nm^{-1}, $\omega_0=3.3$ s^{-1}, $d=7.9$ nm, $\Delta=2.54$ nm, $\Delta_s=4.73$ nm; (*e*) $\kappa=0.248$ nm^{-1}, $\omega_0=4.0$ s^{-1}, $d=8.2$ nm, $\Delta=2.98$ nm, $\Delta_s=5.34$ nm



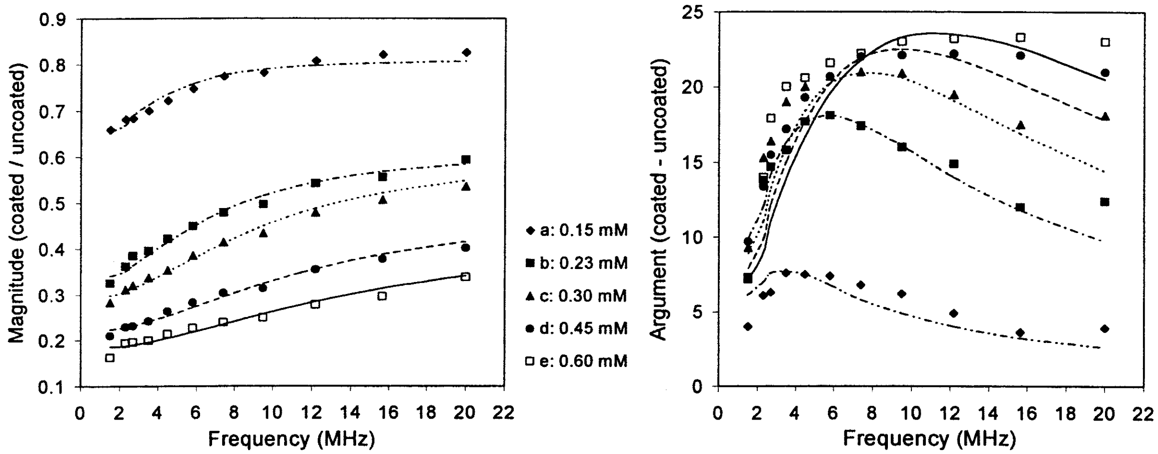


Fig. 3 Comparison of gel layer theory (*lines*) with experimental data (*symbols*) for the dynamic mobility ratio for N100, total surfactant 3 mM, five passes. (*a*) $\kappa = 0.291$ nm^{-1}, $\omega_0 = 1.2$ s^{-1}, $d = 5.4$ nm, $\Delta = 0.71$ nm, $\Delta_s = 1.64$ nm; (*b*) $\kappa = 0.290$ nm^{-1}, $\omega_0 = 4.0$ s^{-1}, $d =$ 8.2 nm, $\Delta = 1.69$ nm, $\Delta_s = 3.90$ nm; (*c*) $\kappa = 0.289$ nm^{-1}, $\omega_0 = 6.2$ s^{-1}, $d = 8.9$ nm, $\Delta = 1.73$ nm, $\Delta_s = 4.30$ nm; (*d*) $\kappa = 0.286$ nm^{-1}, $\omega_0 = 8.2$ s^{-1}, $d = 9.3$ nm, $\Delta = 2.54$ nm, $\Delta_s = 5.34$ nm; (*e*) $\kappa = 0.283$ nm^{-1}, $\omega_0 = 10.2$ s^{-1}, $d = 9.6$ nm, $\Delta = 3.06$ nm, $\Delta_s = 6.04$ nm

phase lead which increased progressively with concentration with a peak at around 3–5 MHz. At 0.30 mM N100, the phase lead was almost 17° at the peak with respect to the particles covered with only SDS.

The results for the system with a total surfactant concentration of 3 mM are shown in Fig. 3. They are very similar to the results for the 1 mM system described earlier. The adsorbed layer thicknesses were again very similar to those observed previously; the total layer thickness is shown in Fig. 4. It is clear that with increasing N100 concentration, the adsorbed layer thickness increases as well and is essentially the same at both 1 and 3 mM total surfactant concentration. It must be mentioned here that with the increase in SDS concentration from 1 to 3 mM, the particle size decreased from 0.56 to 0.36 μm (zeta potentials remained at -105 ± 5 mV) in the absence of nonionic surfactant as calculated using the AcoustoSizer software. So, for the higher SDS system, smaller particles were obtained and consequently a larger droplet surface was provided. This may account for the very slight difference between the two results.

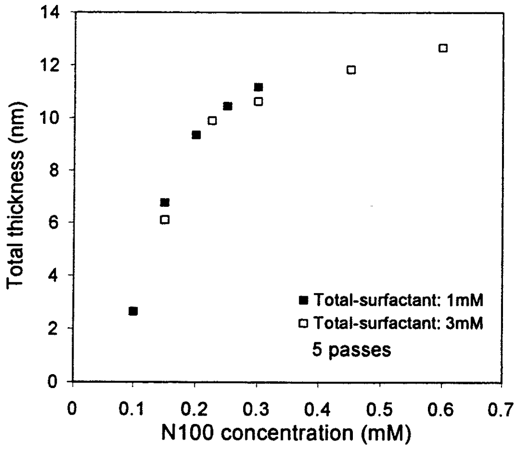


Fig. 4 Variation of total layer thickness with N100 and total surfactant concentration

SDS concentration constant

In order to eliminate any influence of the charge on the dynamic mobility, in another series of measurements the anionic surfactant (SDS) concentration was kept at 1 mM. The magnitude of the mobility ratio and the phase difference caused by increasing levels of the nonionic surfactant can be seen clearly in Fig. 5. The dynamic mobility spectra for different levels of added nonionic surfactant are very similar to those shown in Fig. 1.

The lowest SDS concentration that assures emulsion stability is 2.7 mM [6] and at this concentration the surface of the oil droplets should be covered completely by the SDS molecules. We therefore increased the SDS concentration to 3 mM, and again the experimental results at different levels of nonionic surfactant were like those in Fig. 1. The results derived by comparing those spectra with the spectrum for SDS alone are shown in Fig. 6. They give very similar results for the layer thicknesses to those for the 1 mM SDS (Fig. 7) although the layer is slightly thinner at the higher SDS level.

Effects of particle size

We have already described briefly the influence of SDS concentration on particle size. There is another way to change size whilst maintaining the surfactant concentration constant and that is by varying the number of

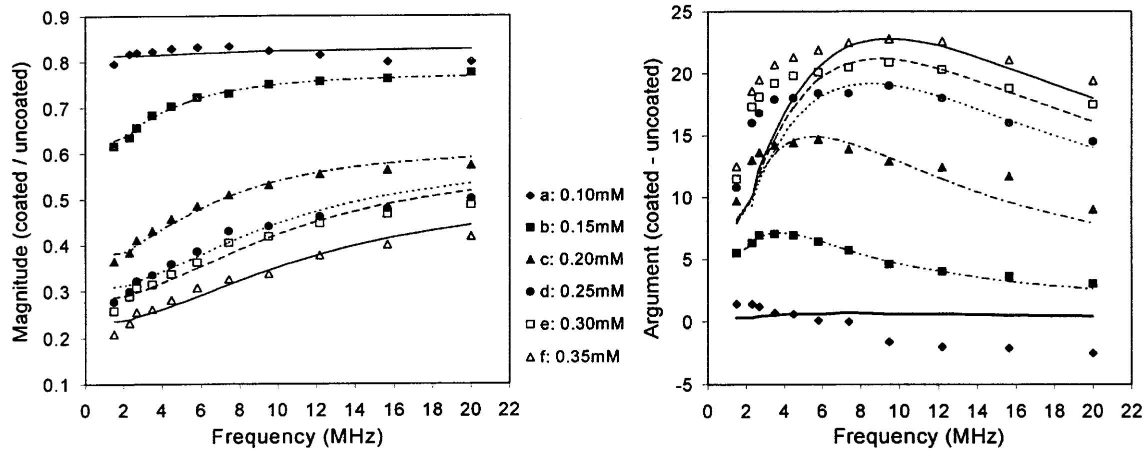


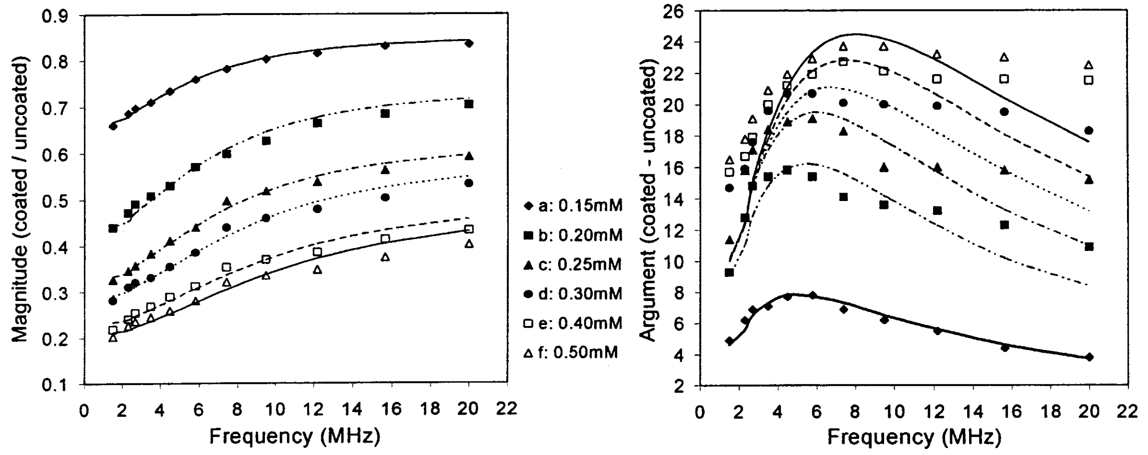
Fig. 5 Comparison of gel layer theory (*lines*) with experimental data (*symbols*) for the dynamic mobility ratio for N100, SDS 1 mM, 5 passes, $\kappa = 0.255\ \mathrm{nm}^{-1}$. (*a*) $\omega_0 = 0.5\ \mathrm{s}^{-1}$, $d = 2.1$ nm, $\Delta = 0.73$ nm, $\Delta_s = 0.82$ nm; (*b*) $\omega_0 = 1.3\ \mathrm{s}^{-1}$, $d = 5.4$ nm, $\Delta = 1.00$ nm, $\Delta_s = 1.98$ nm; (*c*) $\omega_0 = 3.5\ \mathrm{s}^{-1}$, $d = 7.7$ nm, $\Delta = 1.91$ nm, $\Delta_s = 3.97$ nm; (*d*) $\omega_0 = 6.5\ \mathrm{s}^{-1}$, $d = 8.8$ nm, $\Delta = 2.04$ nm, $\Delta_s = 4.71$ nm; (*e*) $\omega_0 = 7.5\ \mathrm{s}^{-1}$, $d = 9.3$ nm, $\Delta = 2.06$ nm, $\Delta_s = 5.01$ nm; (*f*) $\omega_0 = 8.5\ \mathrm{s}^{-1}$, $d = 9.7$ nm, $\Delta = 2.59$ nm, $\Delta_s = 5.78$ nm

passages through the homogeniser. At 1 mM SDS, the particle size decreased from 0.56 to 0.43 μm as the passage number increased from 5 to 20, whilst the zeta potential remained at −105 ± 5 mV. At 3 mM SDS, the particle size changed from 0.36 to 0.23 μm during the same passage change, and the absolute value of the zeta potential was about 10 mV less because of the small particle size obtained. This influence of the passage number, or we can say the influence of the particle size, on the dynamic mobility and its ratio are again indistinguishable in general terms from the earlier results. The change in adsorbed layer thickness for the different passage numbers can be seen from Fig. 7. The higher passage number, and hence the smaller particle size, leads, as would be expected, to a somewhat thinner adsorbed layer. We examined this passage number effect in some detail in earlier work [7].

Effects of different nonionic surfactants

The other three surfactants were selected to study their effects on the adsorbed layer thickness, and the results are shown in Table 2. During each experiment the total surfactant was kept at 3 mM with five passes at 25 °C. The fit of the theory to the experimental results for dynamic mobility ratios for N40, N30, and Brij35 at different concentrations can be seen from Figs. 8, 9 and 10. The phase lead for N40 at 0.60 mM at higher frequencies is about 10°, whilst for N30 the phase lead is only 6° at higher frequencies even though the concentration was increased to 0.90 mM. The phase lead for Brij35 was not very obvious; when its concentration was increased to 1.5 mM, the maximum phase lead observed was about 3°. At 0.60 mM nonionic surfactant, the total

Fig. 6 Comparison of gel layer theory (*lines*) with experimental data (symbols) for the dynamic mobility ratio for N100, sodium dodecyl sulfate (*SDS*) 3 mM, five passes, $\kappa = 0.294\ \mathrm{nm}^{-1}$. (*a*) $\omega_0 = 1.8\ \mathrm{s}^{-1}$, $d = 5.4$ nm, $\Delta = 0.53$ nm, $\Delta_s = 1.46$ nm; (b) $\omega_0 = 3.5\ \mathrm{s}^{-1}$, $d = 7.7$ nm, $\Delta = 1.00$ nm, $\Delta_s = 2.94$ nm; (*c*) $\omega_0 = 4.5\ \mathrm{s}^{-1}$, $d = 8.5$ nm, $\Delta = 1.57$ nm, $\Delta_s = 3.91$ nm; (*d*) $\omega_0 = 5.5\ \mathrm{s}^{-1}$, $d = 8.9$ nm, $\Delta = 1.77$ nm, $\Delta_s = 4.32$ nm; (*e*) $\omega_0 = 6.5\ \mathrm{s}^{-1}$, $d = 9.3$ nm, $\Delta = 2.31$ nm, $\Delta_s = 5.08$ nm; (*f*) $\omega_0 = 7.5\ \mathrm{s}^{-1}$, $d = 9.7$ nm, $\Delta = 2.43$ nm, $\Delta_s = 5.41$ nm



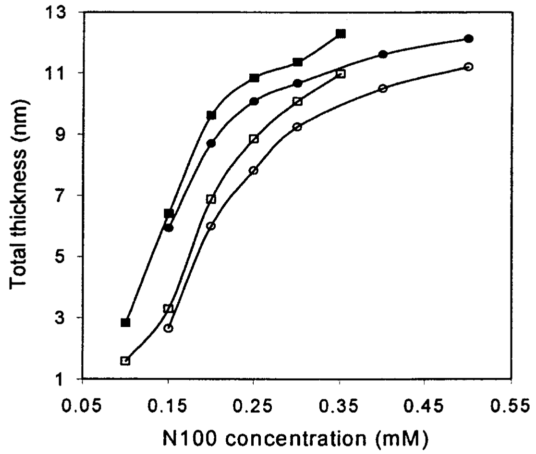


Fig. 7 Variation of total layer thickness with N100 concentration: SDS 1 mM, five passes (■), SDS 1 mM, 20 passes (□), SDS 3 mM, five passes (●), SDS 3 mM, 20 passes (○)

adsorbed layer thickness formed by N100 can reach 12.7 nm, whilst it is 7.0 and 4.9 nm for N40 and N30, respectively, at the same concentration. The thickness formed by Brij35 is slightly lower than with N30.

Comparison of the results of N100 addition before and after emulsification

The total layer thickness is compared between the N100 addition before the emulsification and after in Fig. 11. No matter what the SDS concentrationwas, the adsorbed layer thickness was slightly larger (roughly 10%) for the system with the N100 addition after the emulsification than before. In addition, the overall layer became slightly thicker with time. It can be seen from Figs. 12 and 13 that the inner layer thickness, Δ, and the outer layer thickness, *d*, changed to some extent for the N100 addition before and after the emulsification, with the change in Δ being more obvious.

Discussion

Passage of a polymeric material through the homogeniser might well be expected to lead to some degradation since the molecule will be subjected to both simple shear and extensional flow. Evidently in this case the molecular weight, even of the largest nonionic surfactant (N100), was too small for it to be affected by the shearing regime in the homogeniser.

The model for adsorption of SDS and the nonionic surfactant was discussed in detail previously [2] and the results in this work require no adjustments to that picture. The results shown in Fig. 4 imply that even at 1 mM total surfactant concentration, the combination of SDS and N100 is able to provide a stable emulsion. Even the addition of sufficient SDS to saturate the droplet surface makes very little difference to the overall adsorption of the nonionic surfactant. We showed previously how the presence of SDS can be accommodated and how little room is required for the adsorption of the nonionic anchors compared to the very large area or volume occupied by the hydrophilic moiety in the nonionic surfactant. Adding the nonionic surfactant before the homogenisation step also appears to have little effect on the overall thickness of the polymer layer, which is again around 12 nm as we found previously. There is, however, some discernible difference, which is discussed in the following.

Effect of particle size

The effect revealed in Fig. 7 is most likely due to a change in particle size as we either increase the total

Table 2 Adsorbed layer thickness (nm) for different surfactants

N100	*c* (mM)	0.15	0.23	0.3	0.45	0.6
	d	5.4	8.2	8.9	9.3	9.6
	Δ	0.71	1.69	1.73	2.54	3.06
	Δ_s	1.64	3.90	4.30	5.34	6.04
N40	*c* (mM)	0.23	0.3	0.45	0.6	
	d	2.3	3.7	4.6	5.0	
	Δ	0.03	0.46	1.20	1.97	
	Δ_s	0.23	1.09	2.23	3.21	
N30	*c* (mM)	0.3	0.45	0.6	0.9	
	d	2.6	2.9	3.4	3.9	
	Δ	0.02	0.62	1.45	2.18	
	Δ_s	0.33	1.03	2.05	3.01	
Brij35	*c* (mM)	0.3	0.9	1.5		
	d	3.1	4.1	4.6		
	Δ	0.00	0.76	2.23		
	Δ_s	0.13	1.03	2.60		

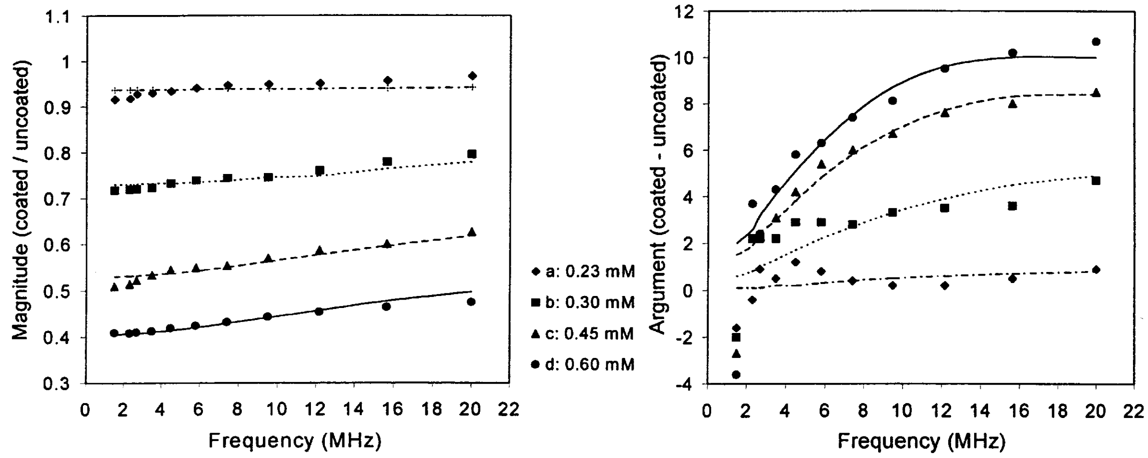
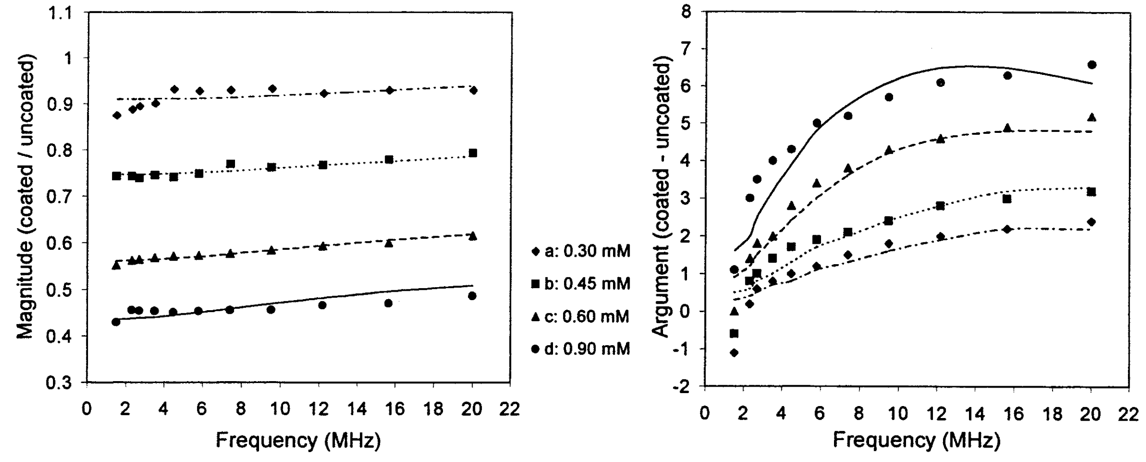


Fig. 8 Comparison of gel layer theory (*lines*) with experimental data (*symbols*) for the dynamic mobility ratio for N40, total surfactant 3 mM, five passes, $\omega_0 = 8.0\ \mathrm{s}^{-1}$. (*a*) $\kappa = 0.290\ \mathrm{nm}^{-1}$, $d = 2.3$ nm, $\Delta = 0.03$ nm, $\Delta_s = 0.23$ nm; (*b*) $\kappa = 0.289\ \mathrm{nm}^{-1}$, $d = 3.7$ nm, $\Delta = 0.46$ nm, $\Delta_s = 1.09$ nm; (*c*) $\kappa = 0.286\ \mathrm{nm}^{-1}$, $d = 4.6$ nm, $\Delta = 1.20$ nm, $\Delta_s = 2.23$ nm; (*d*) $\kappa = 0.283\ \mathrm{nm}^{-1}$, $d = 5.0$ nm, $\Delta = 1.97$ nm, $\Delta_s = 3.21$ nm

surfactant concentration or increase the number of passes through the homogeniser. When only SDS is present, both these changes lead to a smaller particle size as would be expected. That increases the available area per litre of emulsion by a factor proportional to the reciprocal of the droplet radius. If that effect were solely responsible for the thickness change one might expect to be able to normalise the results and to reduce them all to a common curve by multiplying each set by the reciprocal of the radius. Unfortunately that is not easy to do because it requires an independent determination of the radius; the AcoustoSizer cannot determine the radius of the polymer-covered particles and it may well be different from that obtained when the nonionic surfactant is added after formation of the emulsion. Using the radii determined for the emulsions made with SDS alone certainly overcompensates for the area effect, which suggests that the differences in the particle size are smaller when the emulsions are made with both surfactants added together compared to when the nonionic surfactant is added after emulsion formation.

The thickness of the nonionic surfactant layer observed in these experiments may be compared with that described by Barnes and Prestidge [8] for the adsorbed layer on the emulsion drop surface when poly(ethylene oxide) (PEO)–poly(propylene oxide) (PPO)–PEO block copolymers with molar masses from 4200 to 12000 are used as stabilisers. The copolymer blocks have different molecular features to the $C_9\phi E_N$, but the incorporation of the polymer with the oil phase is similar. The former has an anchor (PPO) in the middle and two tails extend into the water phase. For the lower value of the molar mass, which is near that of N100, the

Fig. 9 Comparison of gel layer theory (*lines*) with experimental data (*symbols*) for the dynamic mobility ratio for N30, total surfactant 3 mM, five passes, $\omega_0 = 5.0\ \mathrm{s}^{-1}$. (*a*) $\kappa = 0.289\ \mathrm{nm}^{-1}$, $d = 2.6$ nm, $\Delta = 0.02$ nm, $\Delta_s = 0.33$ nm; (*b*) $\kappa = 0.286\ \mathrm{nm}^{-1}$, $d = 2.9$ nm, $\Delta = 0.62$ nm, $\Delta_s = 1.03$ nm; (*c*) $\kappa = 0.283\ \mathrm{nm}^{-1}$, $d = 3.4$ nm, $\Delta = 1.45$ nm, $\Delta_s = 2.05$ nm; (*d*) $\kappa = 0.277\ \mathrm{nm}^{-1}$, $d = 3.9$ nm, $\Delta = 2.18$ nm, $\Delta_s = 3.01$ nm



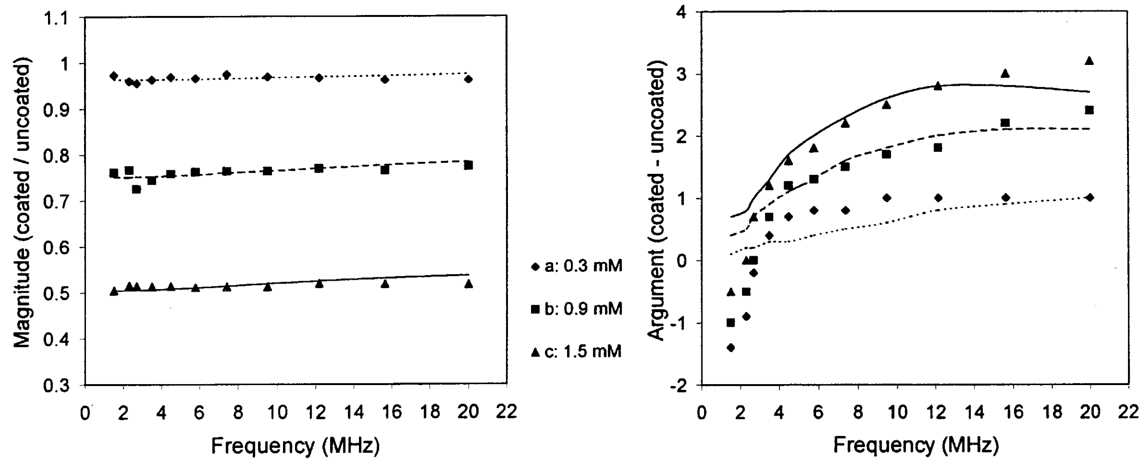


Fig. 10 Comparison of gel layer theory (*lines*) with experimental data (*symbols*) for the dynamic mobility ratio for Brij35, total surfactant 3 mM, five passes, $\omega_0 = 2.0\ s^{-1}$. (*a*) $\kappa = 0.289\ nm^{-1}$, $d = 3.1$ nm, $\Delta = 0.00$ nm, $\Delta_s = 0.13$ nm; (*b*) $\kappa = 0.277\ nm^{-1}$, $d = 4.1$ nm, $\Delta = 0.76$ nm, $\Delta_s = 1.03$ nm; (*c*) $\kappa = 0.265\ nm^{-1}$, $d = 4.6$ nm, $\Delta = 2.23$ nm, $\Delta_s = 2.60$ nm

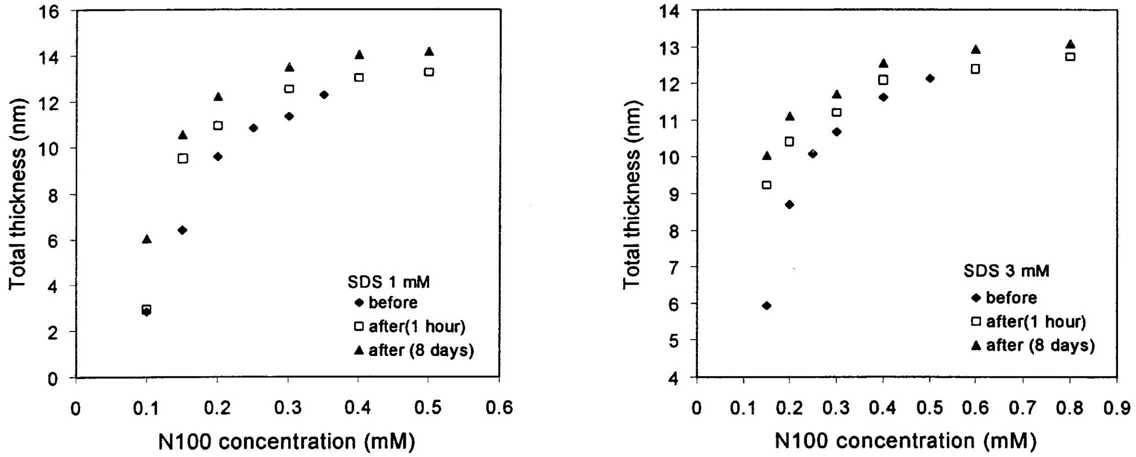
adsorbed layer at the emulsion drop surface obtained by zeta-potential measurement [8] varies from 5.7 to 7.1 nm. This value should be compared with the value of $\Delta_s = 6$ nm shown in Table 2 since it is derived from a d.c. measurement.

Washington et al. [9] used similar block copolymers adsorbed to perfluorocarbon emulsions. In the case of Poloxamer 188 (M_{PEO}: 6700, M_{PPO}: 1800) the adsorbed layer extends almost 5 nm from the surface, whilst that of Poloxamer 407 (M_{PEO}: 8600, M_{PPO}: 4000) extends 3 times as far, according to small-angle neutron scattering observations. Such measurements would be expected to detect not only the effective thickness of the compact layer (as the zeta-potential measurements do) but also the more extended coil, here recorded as the total thickness of the nonionic surfactant layer. Again the results are comparable.

Effect of molecular weight of the nonionic surfactant

The results in Table 2 call for little further comment. As the molar mass of the nonionic surfactant decreases, the thickness of the hydrophilic polymer layer decreases and so too does the thickness of the denser polymer layer near the surface (Δ). Both effects are to be expected. It should be noted in interpreting these results that there will in most cases be a significant amount of nonionic surfactant left in the aqueous phase, even when the emulsion droplet surface appears to be coming to a saturation level. The individual molecules of the surfactant at these concentrations can easily be accommodated in the aqueous solution, with their anchors shielded to some extent from the water. The critical micelle concentrations of N100, N40, N30 and Brij35 are 1.0, 0.28, 0.20 and 0.065 mM, respectively [10], and it was observed they dissolved in the water phase easily. It is

Fig. 11 Variation of total layer thickness with N100 and SDS concentration, and comparison between N100 addition before and after the emulsification, five passes



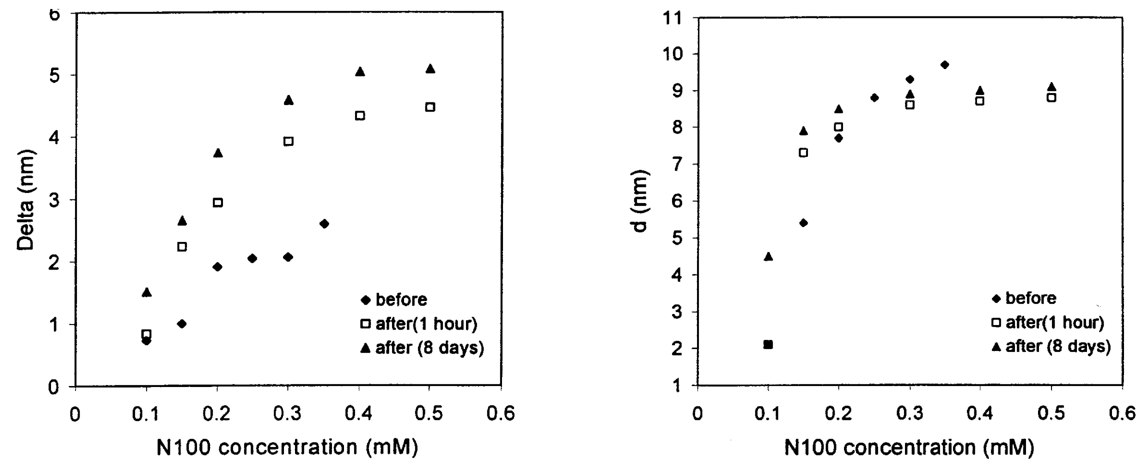


Fig. 12 Variation of Δ and d thickness with N100 concentration, and comparison between N100 addition before and after the emulsification, SDS 1 mM, five passes

usually necessary to add an excess of the surfactant to the system to force the formation of the stabilising monolayer. That point is supported by the results in Fig. 11, which show that adding the nonionic surfactant after emulsion formation gives rise to a plateau adsorption after 1 hour but further adsorption after 8 days.

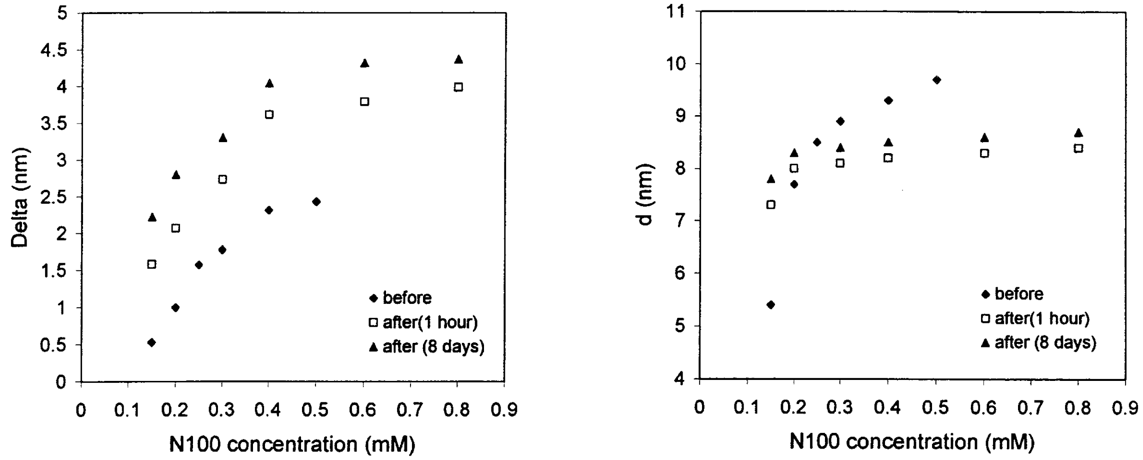
Tadros [11] investigated the molecular weight influence on the adsorbed layer. $C_9\phi(PPO)_{13}(PEO)_N$ was adsorbed on paraffin oil/water emulsions. As N increased from 27 to 174, the molecular weight increased from 2180 to 8650 accordingly. As a result, the hydrodynamic thickness measured doubled from 5.8 to 11.6 nm. These values can be compared with the values of Δ_s shown in Table 2.

Figures 11 and 12 show that there are significant differences in the disposition of the nonionic surfactant layer depending on whether it is added with SDS before homogenisation or after formation of the SDS-stabilised emulsion. Although the total thickness of the surface layer is not greatly affected (Fig. 11) the thickness of the dense layer near the droplet surface is very much smaller when the nonionic surfactant is added before homogenisation. This result is unlikely to be an artefact of the uncertainty in the size of the droplets created by the mixed emulsion system (referred to earlier). The thickness parameter, Δ, is determined essentially by the fall in the magnitude of the mobility and, hence, in the zeta potential. That is not greatly affected by the size, especially at lower frequencies. The effect is quite reproducible (cf. Fig. 13) and is again essentially independent of the degree of saturation of the droplet surface with the SDS molecules.

Conclusions

Several factors were found to influence the thickness of the layer of nonionic surfactant adsorbed at the interface of oil droplets in water but none of the effects were very large. The most important factor was the molecular

Fig. 13 Variation of Δ and d thickness with N100 concentration, and comparison between N100 addition before and after the emulsification, SDS 3 mM, five passes



structure of the surfactant. Longer chains, with bigger coil diameter and chain radius, were strongly adsorbed and produced a thicker layer. An inner compact polymer layer could be distinguished from the outer more open layer. Both the inner and the outer layer thicknesses became larger with an increase in the surfactant concentration and molar mass. The adsorbed layer tended to a plateau as the surfactant concentration increased. Reducing the size of the emulsion drops (by increasing the SDS concentration or by passing the system more often through the homogeniser) produced a detectable but very small change in the layer thickness. On the other hand, the charge on the oil surface had hardly any effect on the adsorbed layer thickness.

The overall adsorbed layer thickness ($\Delta + d$) was slightly larger for the system in which nonionic surfactant was added after the emulsification compared to when it was mixed with SDS before homogenisation. The effective static mobility thickness was calculated for each adsorption measurement. It was roughly twice the dense inner layer thickness, Δ. Passage through the homogeniser itself had no effect on the molecular features of the nonionic surfactant and, hence, on the adsorption layer formed.

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