Adsorption of Mixed Surfactants at the Oil−Water Interface

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The adsorption of the mixed nonionic/anionic surfactants of hexaethylene glycol monododecyl ether ($C_{12}E_6$) and sodium dodecyl sulfate (SDS) at the hexadecane/water interface has been measured. Small-angle neutron scattering (SANS) in combination with hydrogen/deuterium isotopic substitution, has been used to obtain the structure and composition of the adsorbed mixed surfactant layer at the hexadecane/water interface of a hexadecane in water emulsion, and of the mixed micelles in equilibrium with the emulsion. Measurements of the adsorption of SDS alone have established the experimental approach, and the analysis procedures used. The adsorption isotherm obtained for the SDS from the SANS data is in good agreement with that obtained from surfactant electrode measurements. The SANS data show clearly the point at which, with increasing surfactant concentration, free micelles are formed in equilibrium with emulsion droplets. The variation of the composition of the adsorbed layer for the $C_{12}E_6$/SDS mixture at the hexadecane/water interface is not consistent with that previously obtained at the air−water interface, or in mixed micelles. Furthermore, it is not consistent with the straightforward application of theories, such as regular solution theory. The evolution of composition with concentration can be explained if it is assumed that there is partitioning of the $C_{12}E_6$ into the oil phase, and that some solubilization of hexadecane into the mixed micelles takes place. Analysis of the scattering data for the micelles in equilibrium with the emulsion confirms the latter of these two assumptions. On the basis of the data obtained, we have also been able to estimate directly the monomer concentrations of the surfactants in both the oil and water phases.

Introduction

The widespread industrial, technological, and domestic applications of surfactants usually involve mixtures. This is often because the materials used in commercial applications are impure, but more importantly because different surfactants are often mixed to provide enhanced performance.[1]

There is a rich background of information available on surfactant mixing, as a result of classical measurements, such as surface tension,[2] and the extensive thermodynamic descriptions, such as regular solution theory,[3] and related theoretical approaches.[4] In recent years the development of new experimental techniques, such as neutron reflectivity,[5] second harmonic generation,[6] sum frequency,[7] and atomic force microscopy (AFM),[8] have provided a fresh impetus to the study of the adsorption of mixed surfactants at interfaces.

We have demonstrated that neutron reflectivity, in combination with isotopic substitution, is particularly powerful for the study of mixed surfactants at the air−water and liquid−solid interfaces. The H/D isotopic labeling provides the sensitivity and selectivity for the study of mixtures. A strong feature is that the adsorbed amounts and structural information can be obtained over a wide concentration range (from below the cmc to ≫cmc), and we have illustrated this with studies of different systems at both the air−liquid[9] and liquid−solid[10] interfaces. Furthermore, we have used the complementary approach of small-angle neutron scattering (SANS) to determine the structure and composition of mixed surfactant micelles.[11]

In marked contrast the adsorption of mixed surfactants at the oil−water interface has received much less attention. This is largely due to a lack of suitable experimental techniques. Neutron reflectivity is, in principle, a promising technique for the study of the oil−water interface. In practice there have, however, been few neutron reflection measurements at the oil−water interface, apart from the pioneering work of Richardson et al.[12] This is mainly associated with the experimental difficulties arising from the need to establish a thin (∼a few micrometers) layer of either the oil or aqueous phase for sufficient penetration of the neutron beam at grazing incidence. Furthermore, for the mixtures of interest to us, the ability of one or more of the surfactant components to partition into both phases presents an added complication.

We report in this paper the development of an experimental approach using SANS which is based on and is an extension of the method used by us to study surfactant mixing in micelles.[11] A key aspect of this work is the production of stable and reproducible hexadecane in water emulsions (diameter ∼0.2 μm). A wide range of surfactant concentrations and compositions can be adsorbed to the emulsion droplet surface without any loss of integrity, size, or stability. By H/D isotopic labeling of the oil, water, and surfactant, the contrast between the different components can be manipulated such that the SANS arises only from the adsorbed surfactant layer at the oil−water interface of the emulsion.

We have used SANS in this way to measure sodium dodecyl sulfate (SDS) adsorption at the hexadecane−water emulsion interface from partial to complete coverage, and at concentrations where the emulsion is in equilibrium with SDS micelles in the aqueous phase. For this system we have also used

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Surfactant Adsorption at the Oil−Water Interface

J. Phys. Chem. B, Vol. 104, No. 3, 2000 **607**

surfactant electrode measurements[13] to provide an independent and additional estimate of the adsorption isotherm. Similar SANS measurements have been made to determine the adsorption of the surfactant mixture of SDS/$C_{12}E_6$ ($C_{12}E_6$ = hexaethylene glycol monododecyl ether) at the hexadecane−water emulsion interface. In this case the analysis of the mixed surfactant micelles in equilibrium with the emulsion provides an estimate of the amount of hexadecane solubilized into the micelles.

Experimental Details

Small-Angle Neutron Scattering. The SANS meaurements were made on the LOQ diffractometer at the ISIS pulsed neutron facility, Rutherford Appleton Laboratory, U.K.,[14] and the D22 diffractometer at the Institut Laue Langevin, Grenoble, France.[15] On LOQ the data were obtained using the white beam time-of-flight method, using wavelengths from 2.0 to 12.0 Å, and a scattered flight path of 4.3 m, to cover the Q range of 0.007−0.2 Å^{-1}. The data were normalized to the incident beam spectral distribution and converted to the absolute scattering cross-section using standard procedures.[16] On D22 two different instrument configurations were used, a wavelength of 4.6 Å and a sample to detector distance of 2.5 m, and 9.0 Å and 10.0 m, to cover Q ranges of 0.0037−0.046 and 0.028−0.35 Å^{-1}. Data are normalized and converted to an absolute scale by reference to the scattering from H_2O. All samples were measured in 2 mm Hellma quartz spectrophotometer cells (for the D22 data H_2O calibration measurements were made in 1 mm cells). The SANS measurements were all made at 25 °C.

Surfactant Electrode. The SDS surfactant-sensitive membrane electrodes used in this work were fabricated according to previously published procedures,[17] with the slight variation that the inner reference electrode was composed of silver chloride to permit operation in a chloride environment. All solutions were prepared containing 0.01 M NaCl (see later in this section), and this allows measurements to be performed relative to a chloride solid-state ion selective electrode (Orion 94-17JRI). The electromotive force measurements (EMF) were made at 25 °C. The variation of the measured EMF with SDS concentration was corrected for changes in E_o, the sum of the fixed potentials in the Nernst equation, following normal practice.[18] Measurements were made to show that the exposure to the emulsion does not harm the membrane response. The EMF gradients prior to the onset of micellization were 56 ± 3 mV/decade, which is within the established parameters for such membranes.[18] Hence, this enables the free monomer activity of the SDS to be evaluated in the presence of the emulsion, from which it is possible to obtain the binding isotherm of the SDS.

Emulsion Preparation. An aqueous emulsion (oil in water emulsion) with minimal polydispersity that is stable to both creaming and coalescence and that is reproducible is a prerequisite for such measurements. The presence of a small amount of an ionic surfactant (SDS in this case) adsorbed at the emulsion interface provides the required electrostatic barrier to coalescence, while particles <0.2 μm in diameter are stable to creaming and yet provide adequate scattering in the "Porod" regime,[19] when only the adsorbed layer ("shell" contrast) is visible at a phase volume of ∼5% (phase volume of hexadecane). Hexadecane emulsions, at a phase volume of 10%, were prepared in the presence of SDS (and 0.01 M NaCl) using an ultrasonic probe. The number-averaged particle size was monitored using photon correlation spectroscopy (PCS) as a function of SDS concentration and sonication time. It was found that an emulsion diameter of 1900 ± 50 Å was obtained over a wide range of SDS concentrations, and for sonication times of 120−150 s, provided the SDS concentration was >2.0 mM for a 10% emulsion. The surface dilation associated with the "ultrasonic" droplet formation is such that surfactant transport is not significant and hence the hexadecane−water interfacial tension is the pertinent parameter. Any droplets formed remain stable if sufficient surfactant can diffuse to the surface to provide the required charge stabilization before droplet−droplet approach occurs. The PCS measurements were made at extreme dilution of the "stock" emulsion, and no evidence for instability with dilution was observed.

The emulsion used in the SANS measurements was prepared using partially deuterated (93.7 vol %) hexadecane in D_2O with 1.85 mM h-SDS and 0.01 M NaCl. The hexadecane scattering length density was thus matched to that of D_2O, ensuring that any small-angle scattering would arise from the adsorbed layer of hydrogenous surfactant. An initial estimate of the emulsion diameter and surface area was obtained from PCS, and verified by SANS measurements of the emulsion in different H_2O/D_2O mixtures (see later). Individual sample preparations involved the dilution of the concentrated stock emulsion to a 6.4% phase volume with the appropriate surfactant, electrolyte, and solvent (at particular isotopic combinations for both the surfactant and solvent).

Sample Details. SANS measurements were made for a 6.4 vol % hexadecane in D_2O emulsion with h-SDS in the concentration range 1.25−20.0 mM. For the SDS/$C_{12}E_6$ mixture at a solution composition of 70:30 mole ratio, at the same emulsion concentration, for h-SDS/h-$C_{12}E_6$ and h-SDS/d-$C_{12}E_6$, in the concentration range 1.8−14.3 mM. All measurements were made in the presence of 0.01 M NaCl. Separate SANS measurements were made in 1.83 mM h-SDS and different H_2O/D_2O ratios (15, 24, and 38%) to provide an independent evaluation of the surface area and diameter of the emulsion. The surfactant electrode measurements for the SDS/emulsion mixture were made under the same conditions as the SANS measurements.

Chemicals. The protonated surfactants were obtained from Nikkol (h-$C_{12}E_6$) and BDH (h-SDS), and the d- and h-hexadecane from Aldrich. The deuterium-labeled $C_{12}E_6$, d-C_{12}-hE_6, was synthesized, purified, and characterized at the Physical and Theoretical Chemistry Laboratory, Oxford, by R. K. Thomas's group, using methods described previously.[20] The chemical purity of all the surfactants was assessed by surface tension methods and TLC. D_2O was supplied by Flourochem, and high-purity water (Elga Ultrapure) was used throughout. All glassware and sample cells were cleaned using alkali detergent (Decon 90), followed by copious washing in high-purity water.

Scattering Theory

The scattering cross-section for colloidal particles in solution can be written as[21]

$$d\sigma/d\Omega = N|\int_v (\rho_p(r) - \rho_s) \exp iQ \cdot r \, d^3r|^2 \qquad (1)$$

where ρ_p and ρ_s are the particle and solvent scattering length densities, and N is the number of particles per unit volume.

For spheroidal monodisperse particles (such as micelles) in solution[22]

$$d\sigma/d\Omega \approx NP(Q) \, S(Q) \qquad (2)$$

where N is now the particle or micelle number density, $P(Q)$

the particle form factor (where $P(Q) = 3((\sin(QR) - QR\cos(QR))/(QR)^3)$ for spherical particles of uniform density), R the particle radius, and $S(Q)$ the interparticle structure factor arising from the interparticle or intermicellar interactions in solution.

Model-Independent Micelle Composition Determination. One estimate of the micellar composition and the composition of the adsorbed surfactant layer at the emulsion−water interface can be obtained from the simple approximation described previously.[11] For a dilute solution of particles or micelles, in the limit of small Q, where $P(Q) \approx S(Q) \approx 1.0$, the scattered intensity can be written as

$$I(Q) \approx \sum_i N_i V_i^2 (\rho_{ip} - \rho_s)^2 \qquad (3)$$

where N is the micelle number density, V the micelle "dry" volume, and ρ_p the micelle scattering length density, and the summation is over all the micelle or layer compositions (in the case when the scattering arises only from the adsorbed layer) for the binary mixture.

By making two different measurements, one with both surfactants hydrogenated and the other with one surfactant deuterated, the ratio of the two measured intensities, extrapolated to $Q = 0$, gives directly an estimate of the composition of the micelle or adsorbed layer. For the case of h-SDS/h-C$_{12}$E$_6$ and h-SDS/d-C$_{12}$E$_6$ in D$_2$O where the monomer scatter is negligible, the volume and mole fractions of C$_{12}$E$_6$ are given by

$$V_f = \frac{(\sqrt{R} - 1)(\rho_{h-SDS} - \rho_{D_2O})}{(\rho_{h-C_{12}E_6} - \rho_{h-SDS}) - \sqrt{R}(\rho_{d-C_{12}E_6} - \rho_{h-SDS})} \qquad (4)$$

$$M_f = \frac{V_f/V_{C_{12}E_6}}{V_f/V_{C_{12}E_6} + (1 - V_f)/V_{SDS}} \qquad (5)$$

where V_f, and M_f are the volume and mole fractions of C$_{12}$E$_6$, R is the intensity ratio $I_{h-SDS/h-C_{12}E_6}/I_{h-SDS/d-C_{12}E_6}$ (at $Q = 0$), ρ_i is the scattering length density of component i, I_i is the scattered intensity for system i (at $Q = 0$), and V_i is the molecular volume of component i.

For such SANS measurements, instrument-related systematic variations, such as detector response and calibration uncertainties, introduce errors in the determination of the absolute scattering cross-sections which are typically ∼10%. However, in determining the micellar or surface layer composition from the intensity ratio in eq 4, many of these errors effectively cancel, resulting in a typical error in composition of ∼1%. Equation 4 assumes also that both $P(Q)$ and $S(Q) \approx 1.0$, and that the system is dilute; however, for finite concentrations, provided $S(Q)$ does not vary with isotopic content, the contribution from $S(Q)$ in the ratio of intensities cancels, and we have recently shown this in mixed micelles.[11] Furthermore, we have shown in this work, for the coexistence of the emulsion and free micelles, that provided the scattering from the two components is sufficiently separated in Q, the composition of the adsorbed layer and the micelles in equilibrium with the adsorbed layer can both be obtained.

Core + Shell Model. The scattering arising from the adsorbed layer of surfactant at the emulsion−water interface is modeled as a uniform layer and the form factor for a "core + shell" configuration[23]

$$F(Q) = V_1(\rho_1 - \rho_2) F_0(QR_1) + V_2(\rho_2 - \rho_s) F_0(QR_2) \qquad (6)$$

where, $V_1 = 4/3\pi R_1^3$, $F_0(QR) = 3j_i(QR)/(QR)$, $\rho_1 = \rho_s$, the scattering length density of the hexadecane (emulsion droplet), and D$_2$O solvent, ρ_2 is the scattering length density of the adsorbed surfactant layer, R_1 and R_2 are the radii of the inner core and outer shell, and the thickness of the adsorbed layer, d, is $R_2 - R_1$.

For the emulsions studied here $R_1 \approx 0.2$ μm and $d \approx 10-20$ Å, such that at low Q the scattered intensity follows a Q^{-2} behavior, and the contribution due to the thickness of the adsorbed layer is seen in the deviation from Q^{-2} at higher Q. There is no evidence within the Q range measured for interparticle interactions from the emulsion, and it is not included in the modeling of the adsorbed layer.

Micelles. For the modeling of the scattering data from the mixed micelles, and the mixed micelles in equilibrium with the emulsion, we have used the now well-established model for micelles.[23] In this case, for a solution of globular polydisperse interacting particles, the coherent scattering cross-section can be written within the "decoupling approximation" (which assumes that there are no correlations among position, orientation, and size)[23] as

$$d\sigma/d\Omega = N_p[S(Q)\langle|F(Q)|^2\rangle + |\langle F(Q)\rangle|^2 - \langle|F(Q)|^2\rangle] \quad (7)$$

where the averages denoted by the angular brackets are averages over particle size and orientation, N_p is the particle number density, $S(Q)$ is the structure factor, and $F(Q)$ is the particle form factor.

The micelles are modeled as a core + shell, using the form factor described in eq 6, and the following constraints. The inner core, made up of alkyl chains only, is constrained to space fill a volume determined by a radius R_1, defined as the fully extended chain length of the surfactant, and contains a fraction, alf, of the alkyl chains. Any remaining chain (1 − alf), headgroups, and corresponding hydration then define the outer radius R_2. Polydispersity is included using a Schultz size distribution of micelle sizes,[24] which is a convenient distribution, whose form is closely associated with the accepted theoretical forms of micelle polydispersity. Interparticle interactions are included using the rescaled mean spherical approximation, (RMSA) calculation[25] for a repulsive Yukawa potential. For the micelle data the adjustable model parameters are the aggregation number, agg, the surface charge, z, and the polydispersity, poly. The micelle composition is fixed from values obtained using eqs 4 and 5.

Adsorbed Layer Determination. In the evaluation of the adsorbed layer using the form factor in eq 6, the adjustable parameters are the thickness of the adsorbed layer, d, ($R_2 - R_1$), and the scattering length density, ρ_2. The radius of the emulsion, R_1, is kept fixed and was measured using PCS and SANS measurements with core contrast (with sufficient SDS adsorbed to stabilize the emulsion, and contrast matched to the H/D hexadecane) using 15, 24, and 39 vol % H$_2$O/D$_2$O solvent contrasts.

The amount of surfactant adsorbed is evaluated from[26]

$$\Gamma = \frac{d(\rho_s - \rho_2)}{N_a V(\rho_s - \rho_a)} \qquad (8)$$

where N_a is Avogadro's number, V is the surfactant molecular volume, ρ_s and ρ_a are the scattering length densities of the solvent (emulsion) and surfactant, and ρ_2 is the fitted scattering length density of the adsorbed layer. For the SDS/C$_{12}$E$_6$ mixtures, measurements with h-SDS/h-C$_{12}$E$_6$ provide an estimate of the total surfactant adsorption, whereas those with the h-SDS/d-C$_{12}$E$_6$ combination provide the SDS adsorption (it is assumed

Surfactant Adsorption at the Oil−Water Interface

J. Phys. Chem. B, Vol. 104, No. 3, 2000 **609**

that the scattering length density of d-$C_{12}E_6$ is sufficiently close to that of D_2O to provide a negligible contribution).

Monomer concentrations are inferred from the difference between the total surfactant and that modeled as being associated with the adsorbed layer. The SDS is assumed to be absent from the hexadecane, while a partition coefficient of 25:1 (mole ratio hexadecane/water) is assumed for the $C_{12}E_6$[27] at 25 °C.

Background Subtraction. The scattering for the adsorbed layer at the emulsion−water interface is weak at high Q, and the scatter from the oil component of the emulsion is relatively strong and Q dependent. Very accurate background subtractions are therefore essential. We have adopted an approach based on the work of Geissler[28] for the subtraction of incoherent scattering as follows:

$$I_s' = I_s - \frac{I_d}{t_d}\phi_d\frac{(1-t_s)}{(1-t_d)} - I_c\frac{(t_s-t_d)}{(1-t_d)} - I_0\phi_0\frac{(1-t_0)}{(1-t_d)} \quad (9)$$

where ϕ_d and ϕ_0 are the solvent (D_2O) and hexadecane (emulsion) phase volumes (0.936 and 0.064), t_s, t_d, and t_0 the sample, D_2O, and hexadecane transmissions, and I_s, I_c, I_d, and I_0 the sample, cell, D_2O, and hexadecane scattering intensities. Minor adjustments of t_s are required to provide a reliable and consistent background subtraction, and will be discussed later.

In the evaluation of the data for the adsorbed layer at the emulsion−water interface, the "free" micelles, and the micelles in equilibrium with the emulsion, the model is convolved with the known instrument resolution, and compared with the data on an absolute scattering cross-section scale on a least-squares basis. Acceptable model fits require not only that the shape of the scattering is reproduced, but also that the absolute value of the scattering cross-section is in agreement to within 10%.

Results and Discussion

Emulsion Surface Area. For an accurate estimation of the adsorption of the surfactant at the oil−water interface, it is necessary to know the emulsion size and surface area. PCS was used to monitor the emulsion droplet size during formation and its subsequent stability and integrity upon dilution and with the addition of surfactant. This provided an initial estimate of the droplet radius (∼1000 ± 100 Å). As extreme dilution ($\phi \approx$ 0.01%) was required for the PCS measurements, an independent measurement of the droplet size was made. SANS measurements of the SDS stabilized hexadecane emulsion were made in three different solvent contrasts, or H_2O/D_2O combinations, and where a mixture of h- and d-SDS was used to index match the stabilizing surfactant layer to the oil (see Figure 1). A simultaneous fit to all three profiles (using eq 2 and assuming negligible interactions) provided a reliable estimate of the droplet radius of 1300 ± 50 Å. Subsequent analysis of the scattering data does, however, indicate that the calculation of the adsorbed amount is not strongly dependent upon the droplet radius (proportional to $R^{1/2}$). The value obtained above was used throughout the subsequent analysis (see later discussion).

SDS Adsorption. Figure 2 shows the scattering data for a 6.4 vol % hexadecane in D_2O emulsion with the addition of h-SDS in the concentration range 1.25−20.0 mM. The change in the form of the scattering for SDS concentrations of 12 mM and below is consistent with the scattering arising from a thin adsorbed layer of surfactant whose coverage increases with increasing surfactant concentration. Between 12.0 and 14.0 mM the form of the scattering changes markedly and is now consistent with the scattering from the adsorbed surfactant layer at the emulsion−water interface and the additional contribution
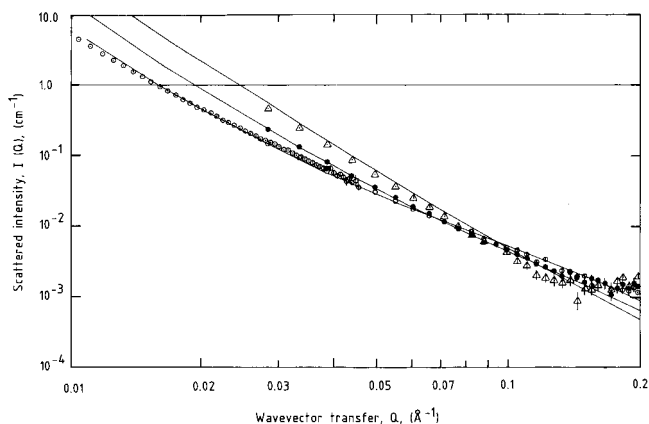

Figure 1. Scattering intensity, $I(Q)$ (cm^{-1}), from a 6.4 vol % d/h-hexadecane in water emulsion for (○) 14.76 vol % H_2O/D_2O, (●) 24.3 vol % H_2O/D_2O, and (△) 37.9 vol % H_2O/D_2O. The solid lines are a model fit for a droplet radius of 1300 Å.
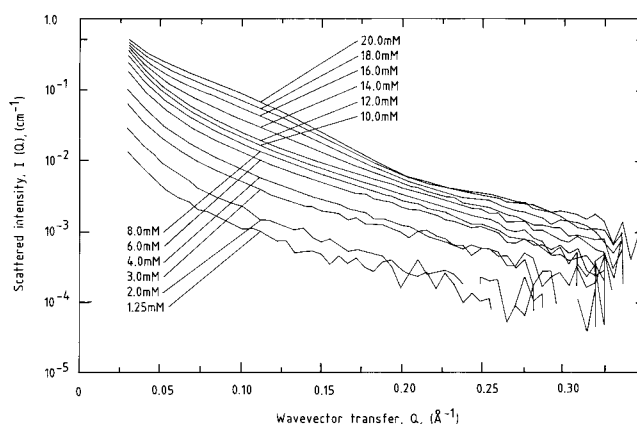

Figure 2. Scattered intensity, $I(Q)$ (cm^{-1}), for a 6.4 vol % d/h-hexadecane in D_2O emulsion with h-SDS in the concentration range 1.25−20.0 mM.
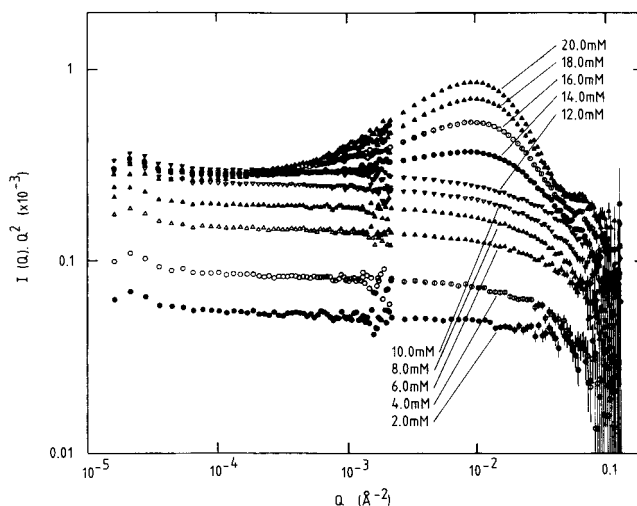

Figure 3. $I(Q)Q^2$ vs Q^2 for the data in Figure 2.

from free micelles in equilibrium with the emulsion droplets. Analysis yields a monomer concentration at this transition of 5.6 mM consistent with that expected for SDS in 0.01 M NaCl. The transition is illustrated more clearly in Figure 3, where the same data are now plotted as $I(Q)Q^2$ vs Q^2. At low concentrations the data is essentially invariant with Q^{-2} as the scattering is dominated by the adsorbed surfactant layer, whereas at higher concentrations the contribution from free interacting SDS micelles (in a marked deviation from Q^{-2} behavior) is clearly
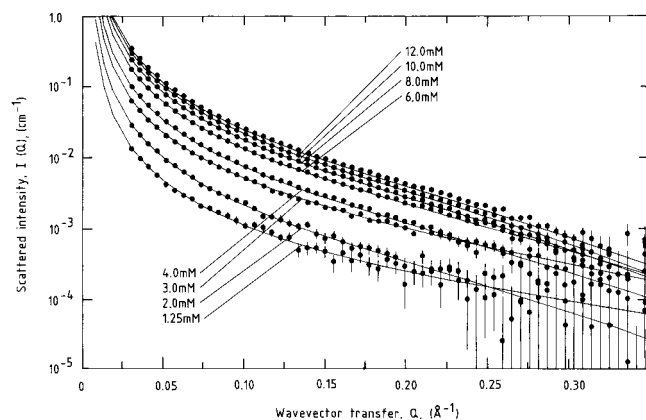
Figure 4. Same as Figure 2 except for SDS concentrations from 1.25 to 12.0 mM. The solid lines are model fits to a uniform layer of SDS at the interface for the parameters summarized in Table 1.

TABLE 1: Fitted Model Parameters for the SDS Adsorbed Layer at the Hexadecane−Water Emulsion Interface (6.4 vol % Emulsion)

SDS concn (mM)	d (Å)	ρ_2 (x 10^{-5} Å^{-2})	$\Gamma(\times 10^{-10}$ mol cm$^{-2})$
1.25	6.0	0.45	0.74
2.0	12.7	0.51	1.07
3.0	8.8	0.38	1.51
4.0	12.4	0.40	1.96
6.0	11.9	0.32	2.53
8.0	13.0	0.29	3.01
10.0	13.1	0.20	3.30
12.0	12.7	0.22	3.55

seen. Furthermore, at low surfactant concentrations and at low Q, there is no evidence of interactions between the emulsion droplets, and this is not included in the subsequent modeling of the adsorbed surfactant layer.

For lower surfactant concentrations, and at high Q where the data are most sensitive to the form of the adsorbed layer, the scattering is extremely weak and comparable to the background scattering (see Figure 2). Accurate background subtractions are hence essential, and the Geissler approach described earlier is used (see eq 9). However, minor adjustments to the sample transmission (<0.5%) are required to obtain a consistent background subtraction.

For the scattering data for SDS concentrations of 12.0 mM and less, the analysis has been made by assuming that the adsorbed surfactant layer is a uniform layer containing SDS and solvent (see eq 6), and the amount of SDS in the layer is evaluated using eq 8 (see Figure 4).

The values of the thickness of the adsorbed layer, d, the scattering length density of the layer, ρ_2, and the adsorbed amount are summarized in Table 1 (evaluated from the data in the Q range 0.028−0.35 Å^{-1}).

Analysis over that extended Q range (to the lower Q of 0.0037 Å^{-1}) provides the same fitted parameters as reported in Table 1. The thickness of the adsorbed SDS layer varies from 6.0 to 13.0 Å. The thickness of the adsorbed layer is always less than the fully extended chain length of the surfactant, and at saturation coverage is still only 70% of the fully extended chain length. The analysis is not particularly sensitive to the droplet size: in the analysis a 10% variation in the droplet radius has little or no effect on the derived thickness and changes the adsorbed amount obtained by ∼5%. Figure 5 shows the adsorption isotherm for the SDS at the emulsion−water interface, and the values obtained from the surfactant electrode measurements are also plotted: the two estimates of adsorption with surfactant concentration are in reasonable agreement. The
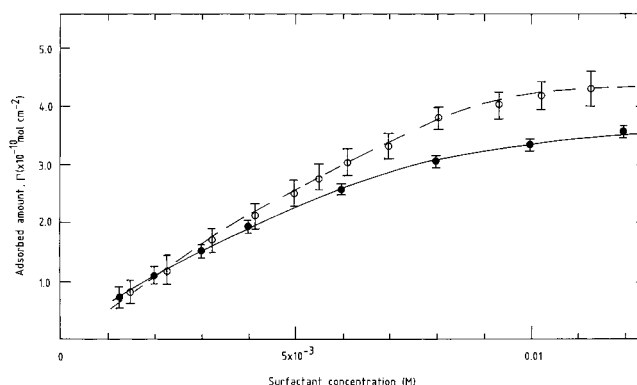

Figure 5. SDS adsorption isotherm at the hexadecane emulsion−water interface (●) from SANS measurements and (○) from surfactant electrode data. The lines are a guide to the eye only.
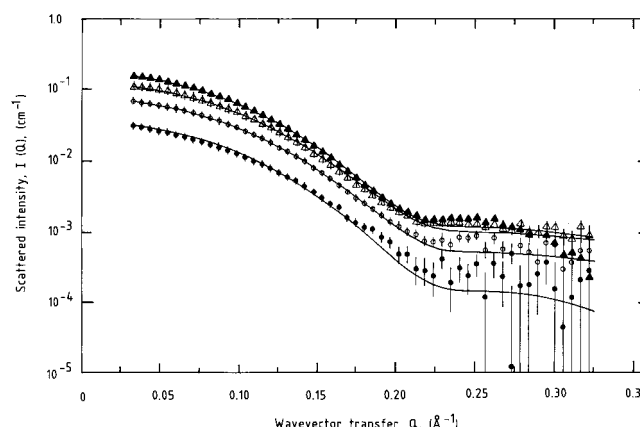

Figure 6. Scattered intensity, $I(Q)$ (cm^{-1}), for SDS micelles in equilibrium with a hexadecane in D$_2$O emulsion: (●) 14−12 mM, (○) 16−12 mM, (△) 18−12 mM, (▲) 20−12 mM. The solid lines are model fits described in the text for parameters summarized in Table 2.

agreement is within error at the lower concentrations (<5 × 10^{-3} M), and deviates progressively at higher concentrations. This discrepancy arises from difficulties in making surfactant electrode measurements. The continued exposure of the electrode to the emulsion resulted in a cumulative error, arising from the unavoidable drift in E_0.

From the SANS measurements the adsorbed amount at saturation is ∼3.6 × 10^{-10} mol cm^{-2}, and corresponds to a mean area per molecule of ∼48 Å^2. The saturation coverage at an area/surfactant molecule ∼48 Å^2 is similar to that obtained at the air−water interface.[29]

The abrupt change in the scattering between 12.0 and 14.0 mM SDS suggests, provided there are no significant correlations between the emulsion droplets and the free SDS micelles that are in equilibrium with the emulsion for SDS concentrations >12.0 mM, that subtracting the 12.0 mM data from the higher concentration data will give a reliable measure of the micelle scattering at these higher concentrations. In Figure 6 we show the data for 14, 16, 18, and 20 mM SDS, from which the 12 mM data have been subtracted.

Normalizing these data sets to the unbound SDS concentration gives an excellent overlap of the four sets of data. This suggests that the subtraction method is a valid procedure, and that, as expected in this concentration range, the size and aggregation number of the micelles are independent of concentration.[23] To confirm this, we have analyzed these four sets of data using the core + shell model for spherical micelles described earlier,[23] and used extensively for a range of different small spherical

Surfactant Adsorption at the Oil−Water Interface

J. Phys. Chem. B, Vol. 104, No. 3, 2000 **611**

TABLE 2: Fitted Model Parameters for SDS Micelles in Equilibrium with a 6.4 vol % Hexadecane in Water Emulsion

SDS concn (mM)	agg	R_1 (Å)	R_2 (Å)	Z^a	poly^a
14.0	83	16.7	20.0	1.0	0.15
16.0	78	16.7	19.5	1.0	0.15
18.0	78	16.7	19.5	1.0	0.15
20.0	82	16.7	20.0	1.0	0.15

^{a} For definitions, see the Scattering Theory, Micelles subsection.
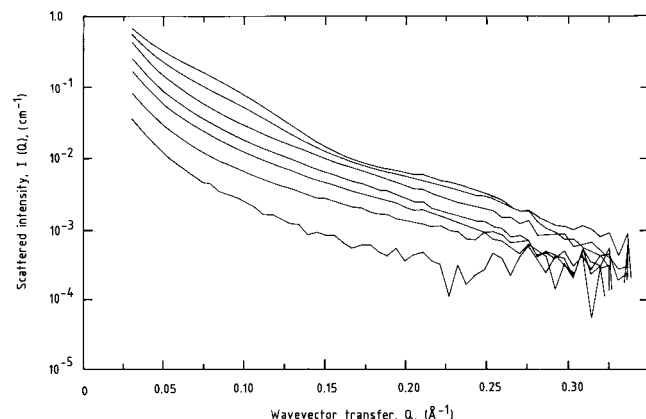
Figure 7. Scattered intensity, $I(Q)$ (cm^{-1}), for a 6.4 vol % d/h-hexadecane in D$_2$O emulsion with SDS/C$_{12}$E$_6$ in the concentration range 1.8−14.3 mM, h-SDS/h-C$_{12}$E$_6$.

micelles. The model fits are also shown in Figure 6, and the model parameters are sumarized in Table 2.

There is excellent agreement between the model and data for each SDS concentration out to a Q of 0.3 Å^{-1}, and the model fitting confirms that the aggregation number is constant with concentration at ∼80 ± 2, consistent with previous measurements on SDS micelles.[23]

SDS/C$_{12}$E$_6$ Adsorption. Figure 7 shows the variation in scattered intensity for a 6.4 vol % hexadecane in D$_2$O emulsion and 70:30 mole ratio SDS/C$_{12}$E$_6$ for the contrast h-SDS/h-C$_{12}$E$_6$ in the surfactant concentration range 1.8−14.3 mM. Similar data (not shown here) have been obtained for h-SDS/d-C$_{12}$E$_6$. For surfactant concentrations of 8.6 mM and less, the data are consistent with an adsorbed layer at the emulsion−water interface, as previously described for SDS. The data in Figure 7 for h-SDS/h-C$_{12}$E$_6$ provide an estimate of the total amount adsorbed at the interface, whereas the data for h-SDS/d-C$_{12}$E$_6$ provide an estimate of the SDS adsorption (as discussed earlier), using eq 8.

For concentrations >8.6 mM the form of the scattering changes markedly due to the onset of mixed micelle formation in equilibrium with the emulsion (similar to that described previously for SDS alone).

From the ratio of the intensities for h-SDS/h-C$_{12}$E$_6$ and h-SDS/d-C$_{12}$E$_6$ (see eqs 3 and 4), the composition of the adsorbed layer and, for concentrations >8.6 mM, the composition of the mixed micelles in equilibrium with the emulsion can be estimated (see Table 3).

The data for concentrations <8.6 mM have been modeled in the same way as the SDS data, and the data and model fits are shown in Figure 8, and the model parameters for both SDS/C$_{12}$E$_6$ isotopic combinations are summarized in Table 4.

The thickness of the adsorbed layer varies from 8.0 to 15.0 Å, slightly thicker than that obtained for SDS alone. The total adsorption is evaluated from the h-SDS/h-C$_{12}$E$_6$ data, and the amount of SDS from the h-SDS/d-C$_{12}$E$_6$ data, using eq 8. From

TABLE 3: Adsorbed Layer and Micelle Compositions for 70:30 SDS/C$_{12}$E$_6$ at a 6.4 vol % Hexadecane in Water Emulsion, Estimated from Intensity Ratios, R, for h-SDS/h-C$_{12}$E$_6$ and h-SDS/d-C$_{12}$E$_6$ Using Eqs 4 and 5^a

surfactant concn (mM)	surface layer			micelles		
	R	V_f	M_f	R	V_f	M_f
1.8	1.69	0.60	0.73			
2.9	1.75	0.58	0.72			
4.3	1.75	0.58	0.72			
5.7	1.83	0.55	0.69			
8.6	2.03	0.49	0.63			
11.4	2.00	0.50	0.64	2.0	0.50	0.64
14.3	2.00	0.50	0.64	2.0	0.50	0.64

^{a} V_f and M_f are the volume and molar fractions of SDS.
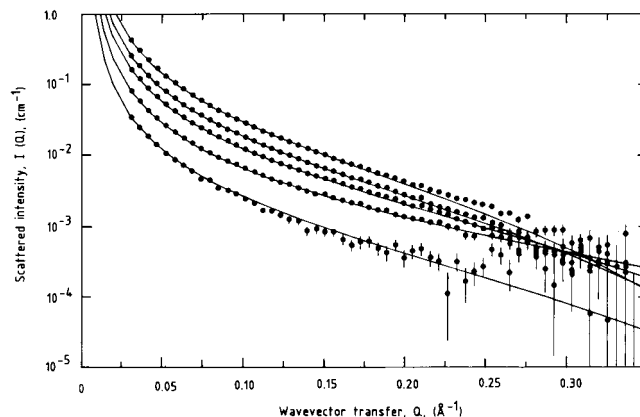
Figure 8. Same as Figure 9, except for SDS/C$_{12}$E$_6$ concentrations of 1.8−8.6 mM. The solid lines are model fits to a uniform layer of the surface at the interface for parameters summarized in Table 4.

these adsorbed amounts an alternative estimation of the composition of the adsorbed layer can be made. The composition of the adsorbed layer estimated from the h-SDS/h-C$_{12}$E$_6$ and h-SDS/d-C$_{12}$E$_6$ intensity ratios and from the detailed modeling of the adsorbed layer provides a consistent estimate of the variation of composition with surfactant concentration (see Tables 3 and 4). The total adsorbed amount corresponds to a mean area per molecule of ∼42 Å^2 (59 Å^2 for SDS and 160 Å^2 for C$_{12}$E$_6$): this compares to a mean area per molecule of ∼40 Å^2 for SDS/C$_{12}$E$_6$ at the air−water interface.

Micelle Structure. We have previously measured the composition of the SDS/C$_{12}$E$_6$ mixtures at the air−water interface and in mixed micelles,[11,28] but in 0.1 M NaCl. However, to make a more direct comparison with those data, we have also measured the composition of the mixed SDS/C$_{12}$E$_6$ micelles in 0.01 M NaCl at surfactant concentrations of 3.58, 7.15, and 14.3 mM, for the mixtures h-SDS/h-C$_{12}$E$_6$ and h-SDS/d-C$_{12}$E$_6$. The composition is estimated from the h-SDS/h-C$_{12}$E$_6$ and h-SDS/d-C$_{12}$E$_6$ intensity ratios using eqs 4 and 5 (see Table 5). A detailed analysis of the structure of the micelles using the model described earlier is summarized in Table 6, and the data and model fits for 14.3 mM are shown in Figure 9 and are typical of the fits obtained for the other surfactant concentrations. A mean aggregation number of 63 ± 4 and a micellar radius of 23 Å are in good agreement with other measurements.

In Table 7 we compare the surfactant composition at the oil−water interface with that measured at the air−water interface (in 0.1 M NaCl), in mixed micelles (in 0.01 and 0.1 M NaCl), and in mixed micelles in equilibrium with the emulsion.

From regular solution theory (RST)[3] and more general thermodynamic arguments, we expect the micelle (and surface) to be rich in the most surface-active component (C$_{12}$E$_6$ in this

TABLE 4: Fitted Model Parameters for a SDS/C$_{12}$E$_6$ Adsorbed Layer at the Hexadecane−Water Emulsion Interface (6.4 vol % Emulsion)

surfactant concn (mM)	h-SDS/h-C$_{12}$E$_6$			h-SDS/d-C$_{12}$E$_6$			composition (mol % SDS)
	d (Å)	ρ_2 (Å^{-2} × 10^{-5})	Γ (×10^{-10} mol cm^{-2})	d (Å)	ρ_2 (Å^{-2} × 10^{-5})	Γ (×10^{-5}) mol cm^{-2}	
1.8	12.7	0.50	1.15	8.6	0.45	0.70	0.78
2.9	8.2	0.32	1.74	14.2	0.50	1.34	0.77
3.4	12.1	0.32	2.57	13.5	0.43	1.87	0.73
5.7	14.0	0.31	3.07	14.0	0.39	2.31	0.75
8.6	14.9	0.35	3.88	14.6	0.35	2.8	0.72

TABLE 5: Micelle Compositions for 70:30 SDS/C$_{12}$E$_6$ in 0.01 M NaCl

surfactant concn (mM)	R	V_f	M_f
3.58 × 10^{-3}	2.3	0.41	0.56
7.15 × 10^{-3}	2.1	0.47	0.61
14.3 × 10^{-3}	1.8	0.56	0.70

TABLE 6: Fitted Model Parameters for Mixed SDS/C$_{12}$E$_6$ Micelles in 0.01 M NaCl and at a Solution Composition of 70:30 Mole Ratio

surfactant concn (M)	isotopic combination	agg	R_1	R_2	z	poly
3.58 × 10^{-3}	hh	67	16.7	23.7	5.0	0.15
	hd	59	16.7	21.7	5.0	0.15
7.15 × 10^{-3}	hh	63	16.7	23.4	5.0	0.15
	hd	59		22.5		
14.3 × 10^{-3}	hh	66	16.7	23.4	5.0	0.15
	hd	63		23.1		
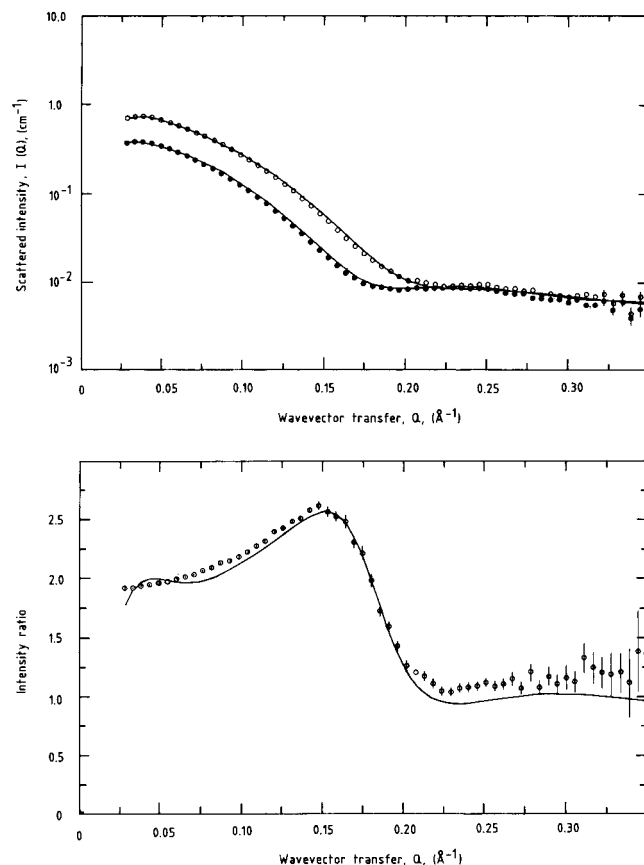
Figure 9. (a, top) Scattered intensity, $I(Q)$ (cm^{-1}), for 14.3 mM SDS/C$_{12}$E$_6$ in 0.01 M NaCl/D$_2$O: (○) h-SDS/h-C$_{12}$E$_6$, (●) h-SDS/d-C$_{12}$E$_6$. (b) Intensity ratio (h-SDS/h-C$_{12}$E$_6$)/(h-SDS/d-C$_{12}$E$_6$). The solid lines are model fits for the parameters in Table 6.

case) at concentrations close to the cmc, and that the composition will then evolve toward the solution composition with increasing surfactant concentration. This trend, in reasonable quantitative agreement with RST, has been reported by us[11,30] for the SDS/
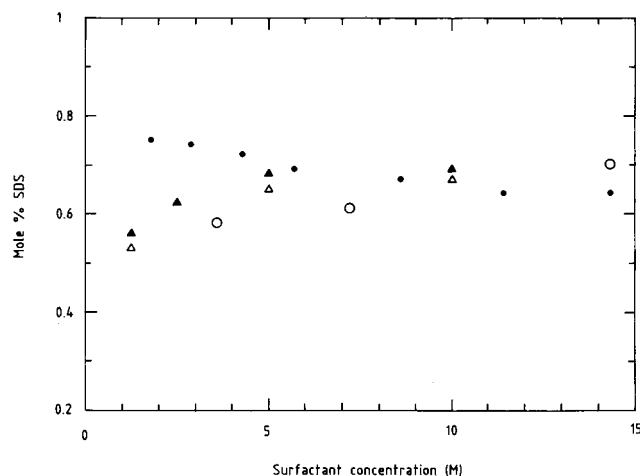
Figure 10. Comparison of oil−water and air−water interfaces and micelle compositions (mol % SDS) with surfactant concentration for a 70:30 solution composition of C$_{12}$E$_6$/SDS: (●) oil−water interface, (○) micelles (0.01 M NaCl), (▲) air−water interface and (△) micelles (both in 0.1 M NaCl).

C$_{12}$E$_6$ mixture in micelles and at the air−water interface, but in 0.1 M NaCl. The limited values obtained here for mixed micelles in 0.01 M NaCl gave different compositions compared to those for 0.1 M NaCl, but are entirely consistent with a change in electrolyte concentration. The values obtained for the oil−water interface and the micelles in equilibrium with the emulsion show a somewhat different behavior, where now the composition becomes more rich in C$_{12}$E$_6$ with increasing concentration. This is inconsistent with the predictions of theories such as RST Figure 10 shows the oil−water, air−water, and micelle compositions along with the calculated values from RST.

The form of the composition data can be explained if it is assumed that there is significant partitioning of the C$_{12}$E$_6$ into the hexadecane, and if there is some solubilization of hexadecane into the mixed SDS/C$_{12}$E$_6$ micelles. In the evaluation of the monomer concentrations, we have assumed, consistent with other work,[27] a partition coefficient for C$_{12}$E$_6$ into the hexadecane phase of 25:1, and that there is no partitioning of SDS into the hexadecane. It might be expected from electrostatic arguments[31] that the ionic surfactants would favor the highly curved mixed micelle surface rather than the flatter emulsion drop interface. This is not observed, and is consistent with our previous comparison of the composition of mixed ionic−nonionic micelles and mixed monolayers at the air−water interface.[11,30]

We have analyzed the structure of the mixed micelles (SDS/C$_{12}$E$_6$) in equilibrium with the emulsion, and this provides some direct evidence of the solubilization of hexadecane into the core of the mixed micelles. The onset of the formation of free mixed micelles in equilibrium with the emulsion occurs at a surfactant concentration between 8.6 and 11.3 mM, as discussed earlier. However, as we do not have a sample at the exact concentration above which free micelles form, we have no means of

Surfactant Adsorption at the Oil−Water Interface

J. Phys. Chem. B, Vol. 104, No. 3, 2000 **613**

TABLE 7: Comparison of Surfactant Composition (mol % SDS) for 70:30 SDS/C$_{12}$E$_6$ at the Air−Water Interface, in Mixed Micelles and at the Oil−Water Interface[a]

surfactant concn (×10⁻³ M)	air/water interface (0.1 M NaCl)	micelles (0.1 M NaCl) (in absence of oil)	micelles (0.01 M NaCl)	micelles in equilibrium with the emulsion	oil−water interface of the emulsion
0.313	0.32	0.4			
0.625	0.41	0.5			
1.0		0.53			
1.25	0.53	0.61			
1.8					0.72 (0.78)
2.0					
2.5	0.62	0.62			
2.9					0.72 (0.77)
3.6			0.58	0.56	
4.3					0.72 (0.73)
5.0	0.65	0.68			
5.7					0.69(0.75)
7.15			0.61	0.61	
8.6					0.63(0.72)
10.0	0.67	0.69			
11.4				0.64	0.64
14.3			0.70	0.64	0.64

[a] The numbers in parentheses are from Table 4, from modeling of the adsorbed layer. All other values are derived from *hh/hd* intensity ratios using Eqs 4 and 5.
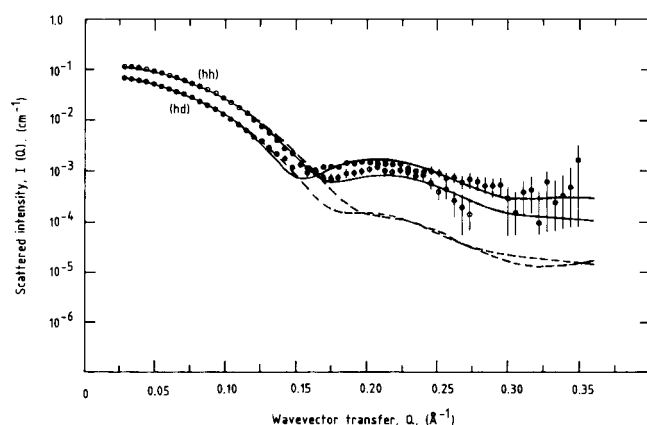

Figure 11. Scattered intensity, $I(Q)$ (cm⁻¹), for SDS/C$_{12}$E$_6$ mixed micelles in equilibrium with a 6.4 vol % hexadecane in water emulsion, 17.4−14.3 mM data: (○) *h*-SDS/*h*-C$_{12}$E$_6$, (●) *h*-SDS/*d*-C$_{12}$E$_6$. The solid lines are model calculations using the parameters summarized in Table 8. The dashed lines are for a model without hexadecane solubilization into the micelle core.

Figure 12. Monomer concentrations for (○) SDS and (●) C$_{12}$E$_6$ as a function of surfactant concentration for 70:30 SDS/C$_{12}$E$_6$ and a 6.4 vol % hexadecane in water emulsion.

TABLE 8: Fitted Model Parameters for SDS/C$_{12}$E$_6$ Mixed Micelles in Equilibrium with a 6.4 vol % Hexadecane in Water Emulsion (14.3−11.4 mM Data)

contrast	agg	R_1	R_2	z	poly	number of hexadecane molecules/surfactant molecules
hh	67	16.7	24.4	5.0	0.12	0.4
hd	70	16.7	24.8	5.0	0.12	0.4

subtracting the scattering contribution from the emulsion, and thereby extracting the scattering from the micelles. However, if changes in the composition of the adsorbed layer are small, subtracting the 14.3 mM data from the data for 17.4 mM provides a reliable estimate of the additional scattering from the mixed micelles between 14.3 and 17.4 mM. These data, for the two isotopic combinations *h*-SDS/*h*-C$_{12}$E$_6$ and *h*-SDS/*d*-C$_{12}$E$_6$, are shown in Figure 11.

The dashed lines in Figure 11 are the model fits using the conventional micelle model described previously for mixed SDS/C$_{12}$E$_6$ micelles in the absence of hexadecane. At low Q the scatterings from the two isotopic combinations are very similar, confirming that the micelle compositions are similar. However, for values of $Q > 0.15$ Å⁻¹ the data and model deviate significantly. The solid lines in Figure 11 are for the same basic model, but modified to include some hexadecane in the core of the mixed micelles. The model parameters are summarized in Table 8, and the aggregation number of ∼64 ± 3 is consistent with previous mixed SDS/C$_{12}$E$_6$ micelles at this concentration. The additional model parameter is the number of hexadecane/surfactant molecules, and this is found to be ∼0.4 for the data in Figure 11 and Table 8. In this model we have made the
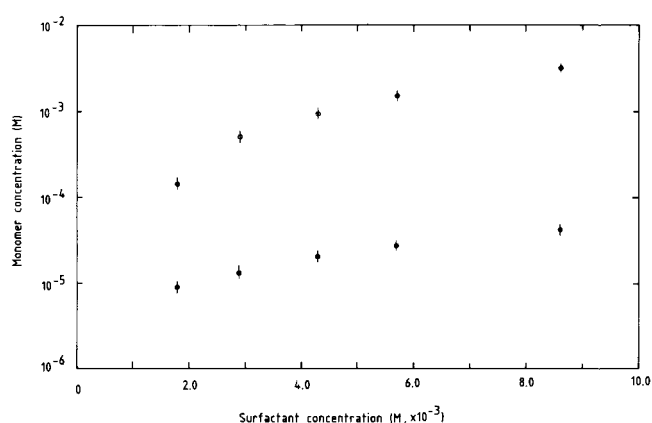
simplest assumption that the hexadecane is adsorbed in the hydrophobic core, and that the core dimension is still constrained to be the extended length of the surfactant alkyl chain. Relaxing that constraint on the core dimension does not substantially alter the parameters obtained. The figure of 0.4 hexadecane/surfactant molecule in the mixed SDS/C$_{12}$E$_6$ micelles compares favorably with the compositions obtained for mixed dodecane/surfactant monolayers at the air−water interface, 0.45 for dodecane/C$_{16}$-TAB (C$_{12}$TAB)[32] and 1.0 for dodecane/C$_{12}$E$_5$.[33]

Monomer Concentrations. From the mixed surfactant data (as discussed earlier) we can estimate the monomer concentrations of both the SDS and C$_{12}$E$_6$ as a function of surfactant concentration (see Figure 12).

This additional information of the free monomer concentration, in equilibrium with the emulsion, is difficult to obtain using any other experimental method, and further demonstrates the sensitivity of this experimental approach.

Summary

We have demonstrated the use of small-angle neutron scattering, in combination with H/D isotopic substitution, to obtain the structure and composition of the adsorbed mixed surfactant layer of SDS/$C_{12}E_6$ at the hexadecane/water interface of a hexadecane in water emulsion, and at the mixed micelles in equilibrium with the emulsion.

The methodology was first established by measurements of the adsorption of SDS, and the adsorption isotherm obtained for SDS is in good agreement with other measurements.

The results obtained for the SDS/$C_{12}E_6$ mixture are not in agreement with the straightforward application of theories such as RST, and this is to be expected in that a third, non-surface-active, component in the micelle is now involved. The evolution of composition with surfactant concentration at the oil−water interface can be rationalized if it is assumed that there is partitioning of $C_{12}E_6$ into the oil phase, and that some hexadecane is soublized into the mixed micelles. Evidence from the solubilization of hexadecane into the micellar phase is presented, and future experiments will be designed to evaluate the partitioning of $C_{12}E_6$ into the oil phase.

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