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Structural studies of non-ionic dodecanol ethoxylates at the oil-water interface: the effect of increasing head group size

Journal:	<i>Langmuir</i>
Manuscript ID:	Draft
Manuscript Type:	Article
Date Submitted by the Author:	n/a
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3 **Structural studies of non-ionic dodecanol ethoxylates at the oil-water interface:**
4 **the effect of increasing head group size**
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28 **Abstract**
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30 The conformation of charged surfactants at the oil-water interface was recently reported. With the
31 aim to assess the role of the head group size on the conformation of the adsorbed layer, we have
32 extended these studies to a series of non-ionic dodecanol ethoxylate surfactants ($C_{12}E_n$, ethylene
33 oxide units n from 6 to 12). The study was performed using neutron reflectometry to enable
34 maximum sensitivity to buried interfaces. Similarly to charged surfactants, the interface was found
35 to be broader and rougher compared to the air-water interface. Irrespectively of the head group size,
36 the tail group region was found to assume a staggered conformation. The conformations of the
37 head group were found to be significantly different compared to the air-water interface, moving
38 from a globular to an almost fully extended conformation at the oil-water interface. The stretching
39 of the head groups is attributed to the presence of some hexadecane oil molecules, which may
40 penetrate all the way to this region. It is proposed here that the presence of the oil, which can
41 efficiently solvate the surfactant tail groups, plays a key role in the conformation of the adsorbed
42 layer and is responsible for the broadening of the interface.
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Introduction

The conformation of surfactants at the oil-water interface is generally very different from the air-water interface. At the air-water interface, when a surfactant molecule in the aqueous phase reaches the water surface it partially interacts with the air phase. The only favourable interactions left available for the hydrophobic part of the surfactant are Van der Waals interactions between different tail groups. For this reason, the hydrophobic part of the adsorbed layer tends to be confined to a specific region in contact with the air phase where it assumes a relatively tightly packed conformation, i.e. a well-ordered monolayer [1,2]

At the oil-water interface, on the other hand, oil molecules can efficiently solvate surfactant tail groups. When a surfactant molecule in water reaches the interface, its tail group can establish Van der Waals interactions both with other surfactant tail groups and with oil molecules. As a result, the tail group region can assume a more relaxed and energetically favourable conformation and the whole adsorbed layer results in a broader structure. The effect of the presence of charges in the surfactant head group on the structure of the adsorbed layer was recently investigated both for cationic and zwitterionic surfactants [3-5]. The results obtained suggested a multilayer structure, where a staggered conformation was observed.

With this study we aimed to extend the knowledge of surfactants adsorption at the oil-water interface to non-ionic surfactants. Particularly, the effect of an increasing size of the head group on the structure of the adsorbed layer was investigated. A series of non-ionic dodecanol ethoxylate surfactants ($C_{12}E_n$) was chosen for this study. By increasing the number of ethylene oxide units, n , from 6 to 12, the size of the head group can be steadily increased. Alkyl ethoxylates are extensively used in detergency, shampoo, fabric softening, cosmetics and pharmacy. Their interfacial adsorption and aggregation in solution have a key role in their use in many product formulations. Much is known about bulk properties of dodecanol ethoxylates such as cloud point as a function of increasing n [6], or properties of mixed micelles containing $C_{12}E_n$ [7,8]. The addition of $C_{12}E_n$ to SDS solutions efficiently reduces the solubilisation of zein proteins, thus reducing the extent to which the detergent formulations will provoke adverse skin reactions [9]. Interfacial behaviour at the solid-water interface has been reported at a number of different substrates such as graphite [10], silicon [11] and cellulose [12].

Besides their extensive use, there were two reasons for choosing dodecanol ethoxylates for this study:

1. The structural conformation of dodecanol ethoxylates at the air-water interface was fully characterised in the 90s. In a series of a neutron reflectivity experiments the size of the ethoxylate head group was gradually increased from $n = 1$ to 12. The interface was investigated for a series of concentrations above and below the CMC and the effects of the increasing head group on the structural conformation was studied [13-17]. Extensive knowledge of the system at the air-water interface is essential to understand how the head group affects the surfactant conformation at the oil-water interface.
2. As the number of ethylene glycol units increases from $n = 1$ to $n = 12$, the thickness of the tail group region at the air-water interface, as determined by neutron reflectivity, varies very little. The thickness varies between 11 and 13 Å, suggesting a tilted conformation of the tail groups ($\theta \sim 40^\circ$). Hence, it is the size of the head group that plays a key role on the conformation at the air-water interface. One would expect a similar behaviour on the final conformation at the oil-water interface.

Neutron Reflectivity (NR) has been extensively used in the past few years for the investigation of surfactant adsorption at the oil-water [3-5]. The short wavelength of neutrons allow the structural resolution normal to the interface on the length scale of few Å. NR also having the important advantage to employ isotopic substitution to achieve large and tunable contrast between chemically discrete entities and allows precise structural determination. This paper concentrates on detailed aspects of the structure of non-ionic surfactants at the oil-water interface.

Materials

Dodecanol ethoxylate surfactants ($C_{12}E_n$) with progressively increasing head group size ($n = 6, 8$ and 12) were used in this study. Surfactants were synthesised by Dr R. K. Thomas and co-workers from University of Oxford and were available as fully hydrogenous. Hydrogenous hexadecane was purchased from Aldrich and was purified by passing it seven times through an alumina column prior to use. Hexadecane- d_{34} was obtained from Cambridge Isotope Laboratories (> 98% D) and was used with no further purification. D_2O was obtained from Fluorochem (> 99.9% D). All solutions and isotopic mixtures were prepared by mass. Contrast-matched silicon hexadecane contains approximately 35% d-hexadecane mixed with h-hexadecane (CMSi oil).

Methods

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3 Although most ionic surfactants are practically insoluble in oil, this is not always the case for non-
4 ionic surfactants, mainly because of the absence of charges in the head group. It has already been
5 reported that $C_{12}E_n$ surfactants present a higher solubility in hydrocarbons than in water [17]. As a
6 result, partition processes between oil and water occur, thus lowering the aqueous concentration of
7 the surfactant. When neutron reflectivity is used to probe the buried liquid-liquid interface the
8 volume of the hydrophobic phase is much smaller than that of the aqueous phase (with the deployed
9 setting $\sim 15 \mu\text{l}$ of hexadecane, $\sim 25 \text{ ml}$ of aqueous phase). Therefore, partition processes only cause
10 a minor decrease of surfactant aqueous concentration.
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13 Neutron reflectometry is a technique sensitive to neutron refractive index profile normal to an
14 interface, $Nb(z)$, averaged for the whole sample region [18]. In absence of strong neutron absorbers
15 such as cadmium or boron, the neutron refractive index can be written as:
16

$$n(\lambda) \approx 1 - \frac{\lambda^2}{2\pi} Nb \quad (1)$$

17
18 N is the atomic number density and b the coherent scattering length. The multiple Nb , referred to as
19 the scattering length density, varies linearly with the volume fraction composition:
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$$Nb \approx \sum_j \Phi_j Nb_j \quad (2)$$

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22 where Φ_j is the volume fraction and $(Nb)_j$ the scattering length density of component j , respectively.
23 Possibly the main advantage of neutron reflectivity is that the scattering length b varies in a random
24 fashion within different elements in the periodic table; particularly b varies within different
25 isotopes. Above all, b is substantially different between hydrogen ($b_H = -3.74 \text{ fm}$) and deuterium
26 ($b_D = 6.67 \text{ fm}$). This difference is at the basis of the methodology called contrast variation. By
27 changing the isotopic ratio, the Nb of the molecule can be adjusted to match that of other
28 components in the system or to maximise the difference in refractive index.
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31 The methodology developed by Zarbakhsh et al. [3] was used for these experiments. To avoid
32 drastic attenuation of the neutron beam upon trespassing the oil phase, a thin layer of hexadecane
33 was deposited by spin-coating onto a silicon block which had been rendered hydrophobic by
34 coupling of trimethylchlorosilane. The film was frozen in place, and the sample cell assembled with
35 the oil still frozen. The aqueous surfactant solution was slowly injected in the sample cell,
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sandwiching the oil film between the silicon substrate and the aqueous phase. Once the cell was deemed to be bubble free, the hexadecane film was allowed to melt. A circulating water bath was used to cool the cell at ~ 278 K while assembling the sample cell and maintain a thermostated temperature of 298 ± 1 K throughout the whole neutron reflectivity measurement.

The thick film approximation gives the reflectivity R for a sufficiently thick oil film [19]:

$$R = R_1 + \frac{AR_2(1 - R_1)^2}{1 - AR_1R_2} \quad (3)$$

R_1 is the reflectivity from the silicon-hexadecane interface (generally minimised by using CMSi oil), and R_2 the reflectivity from the hexadecane-aqueous solution interface. The attenuation factor A takes into account the loss of intensity upon the beam crossing the oil film twice:

$$A = \exp\left(\frac{-2\chi d_{oil}}{\sin\theta_{oil}}\right) \quad (4)$$

The attenuation coefficient χ was experimentally determined prior to the experiment, d_{oil} is the thickness of the oil film and θ_{oil} is the incidence angle of the neutron beam in the oil phase [3].

Since a large number of measurements was required to fully characterise three surfactants at different concentrations, a series of neutron reflectivity investigations were planned and three different reflectometers were used for this study. $C_{12}E_6$ was analysed using FIGARO, at ILL, Grenoble, France [20], $C_{12}E_8$ was analysed using INTER, at ISIS, Didcot, UK [21] and $C_{12}E_{12}$ was analysed using SURF, also at ISIS [22]. The three instruments are time-of-flight reflectometers and the available wavelength range changes significantly between them. The incident angle was therefore varied to cover a most suitable Q range. The incident angle was 3.82° for $C_{12}E_6$, 2.3° for $C_{12}E_8$ and 1.5° for $C_{12}E_{12}$. In all measurements D_2O was chosen as the aqueous subphase to exploit the contrast with the fully hydrogenous surfactant and maximise the sensitivity to the adsorbed layer. CMSi oil was used to minimise the R_1 part of the reflectivity.

Results

A series of reflectivity profiles were measured for all surfactants for a series of concentrations above and below the recorded CMC at the air-water interface. CMC values for the three surfactants at the air-water interface are given in Table 1. Reflectivity profiles for all concentrations are shown in Figure 1 for $C_{12}E_6$, Figure 2 for $C_{12}E_8$ and Figure 3 for $C_{12}E_{12}$. Because the attenuation of the neutron beam upon traversing the oil phase is wavelength-dependent, the data analysis must be

carried out in wavelength (λ). The data are, however, conventionally presented in Q ($Q = (4\pi\sin\theta)/\lambda$) for clarity.

Table 1. CMC values at the air-water interface for the surfactants used.

Surfactant	CMC / mM
$C_{12}E_6$ [14]	0.080
$C_{12}E_8$ [15]	0.091
$C_{12}E_{12}$ [17]	0.125

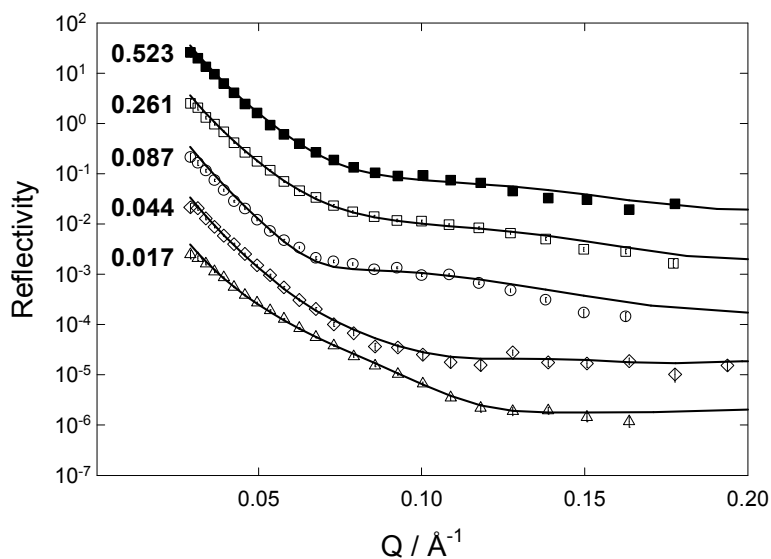


Figure 1. Reflectivity profiles for a series of h- $C_{12}E_6$ at the CMSi oil- D_2O interface, solid lines correspond to the fit to the data. The concentration is shown in mM units. Profiles are shifted by a factor of $\times 10$ for the purpose of clarity.

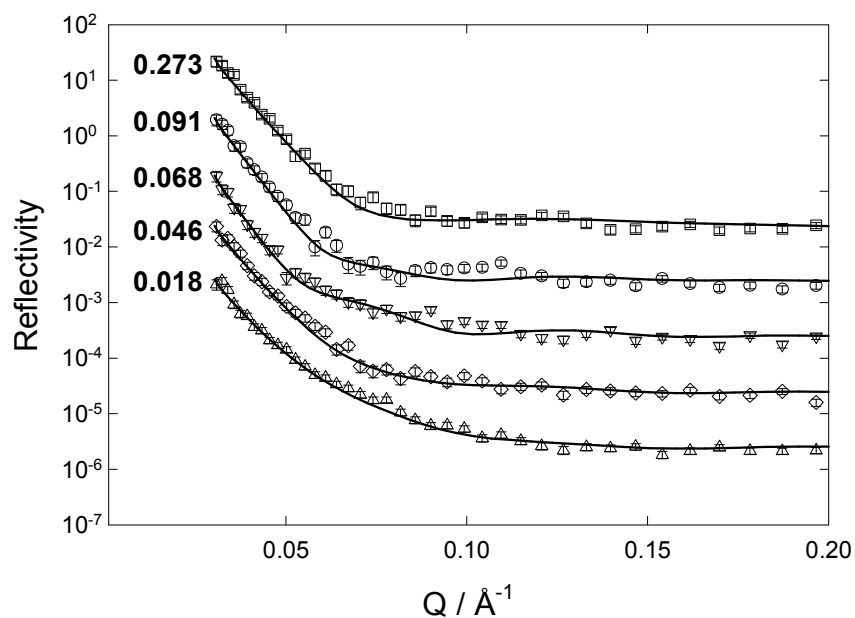


Figure 2. Reflectivity profiles for a series of $h\text{-C}_{12}\text{E}_8$ at the CMSi oil- D_2O interface, solid lines correspond to the fit to the data. The concentration is shown in mM units. Profiles are shifted by a factor of $\times 10$ for the purpose of clarity.

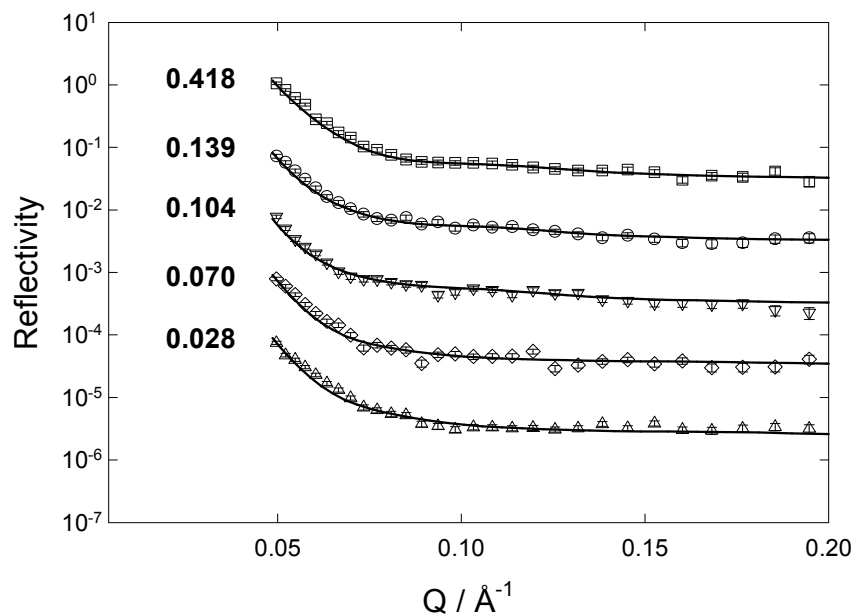


Figure 3. Reflectivity profiles for a series of $h\text{-C}_{12}\text{E}_{12}$ at the CMSi oil- D_2O interface, solid lines correspond to the fit to the data. The concentration is shown in mM units. Profiles are shifted by a factor of $\times 10$ for the purpose of clarity.

All reflectivity profiles were fitted to a three layer model. The thickness of the first layer, in contact with the oil phase, was found to be constant ($22 \pm 2 \text{ \AA}$) regardless of the increasing size of the head group. On the other hand, the thickness of the second, intermediate layer increased with increasing head group size. A small decrease in thickness of the second layer was observed for $C_{12}E_{12}$ when the concentration decreases to low values ($[C_{12}E_{12}] < 0.104 \text{ mM}$). A third layer, with Nb close to that of D_2O , was required to model the reflectivity data. The thickness of this layer increased from $C_{12}E_6$ to $C_{12}E_8$ and no further changes were observed upon increasing the head group to 12 ethylene oxide units. The thickness of this layer decreased for $C_{12}E_6$ with decreasing concentration ($[C_{12}E_6] < 0.261 \text{ mM}$).

Changes in interlayer roughness between the oil phase and the first layer, between the first and the second layer, and between the third layer and the D_2O , affect very little the reflectivity profiles. Conversely, small variations in the roughness between the second and the third layer significantly affect the quality of the fitting. Roughness between the second and the third layer increases considerably between $C_{12}E_6$ and $C_{12}E_8$ and a further increase is observed between $C_{12}E_8$ and $C_{12}E_{12}$. Roughness between the second and the third layer is particularly relevant in the fitting procedure and will henceforth be referred to as σ_3 .

All the fitting parameters are shown in Table 2, 3 and 4, for $C_{12}E_6$, $C_{12}E_8$ and $C_{12}E_{12}$ respectively. The corresponding Nb profiles are shown in Figure 4, Figure 5 and Figure 6 for $C_{12}E_6$, $C_{12}E_8$ and $C_{12}E_{12}$.

Table 2. Fitting parameters for $C_{12}E_6$ at the contrast-matched silicon hexadecane- D_2O interface.

High concentration			
Concentration / mM	0.523	0.261	
Layer thickness $\text{\AA} (\pm 2)$	$Nb \times 10^{-6} / \text{\AA}^{-2}$		Roughness / \AA
Hexadecane	2.07		-
22	2.77	2.78	2
25	3.10	2.88	2
35	5.93	5.94	5
D_2O	6.35		2

Low concentration

Concentration / mM	0.087	0.044	0.017	
Layer thickness $\text{\AA} (\pm 2 \text{\AA})$	$Nb \times 10^{-6} / \text{\AA}^{-2}$			Roughness / \AA
Hexadecane	2.07			-
22	3.20	3.43	3.88	2
25	3.32	4.98	5.89	2
24	5.96	6.03	6.13	5
D ₂ O	6.35			2

Table 3. Fitting parameters for C₁₂E₈ at the contrast-matched silicon hexadecane-D₂O interface.

Concentration / mM	0.273	0.091	0.068	0.046	0.018	
Layer thickness Å (± 2)	$Nb \times 10^{-6} / \text{Å}^{-2}$					Roughness Å
Hexadecane	2.07					-
22	2.46	2.87	3.24	3.36	3.66	2
30	3.29	3.95	4.33	4.59	5.08	2
42	5.70	5.76	5.77	6.09	6.15	11
D ₂ O	6.35					2

Table 4. Fitting parameters for C₁₂E₁₂ at the contrast-matched silicon hexadecane-D₂O interface.

High concentration

Concentration / mM	0.418	0.139	0.104	
Layer thickness Å (± 2)	$Nb \times 10^{-6} / \text{Å}^{-2}$			Roughness / Å
Hexadecane	2.07			-
22	2.33	2.47	2.54	2
42	2.57	2.86	2.98	2
42	5.64	5.73	5.77	13
D ₂ O	6.35			2

Low concentration

Concentration / mM	0.070	0.028	
Layer thickness Å (± 2)	$Nb \times 10^{-6} / \text{Å}^{-2}$		Roughness / Å
Hexadecane	2.07		-
22	2.87	2.96	2
35	4.44	4.49	2
42	6.13	6.13	13
D ₂ O	6.35		2

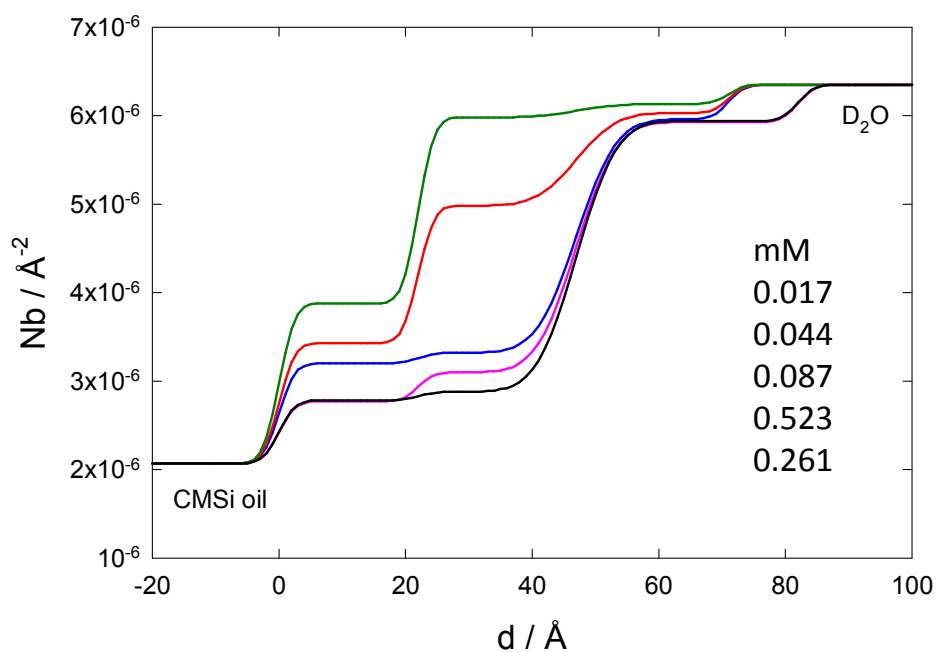


Figure 4. Nb profiles for a series of $C_{12}E_6$ at the CMSi hexadecane- D_2O interface.

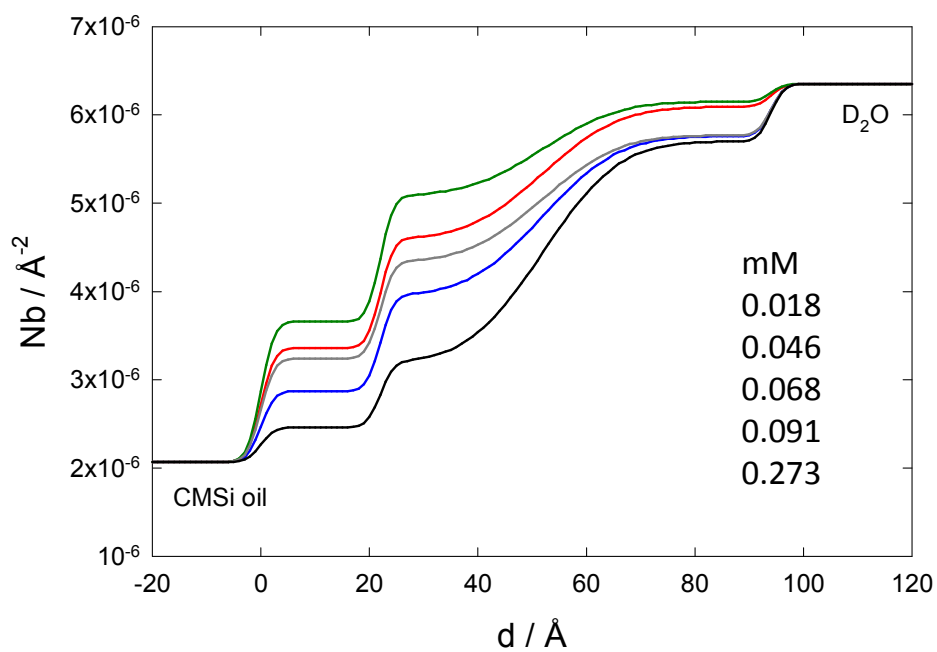


Figure 5. Nb profiles for a series of $C_{12}E_8$ at the CMSi hexadecane- D_2O interface.

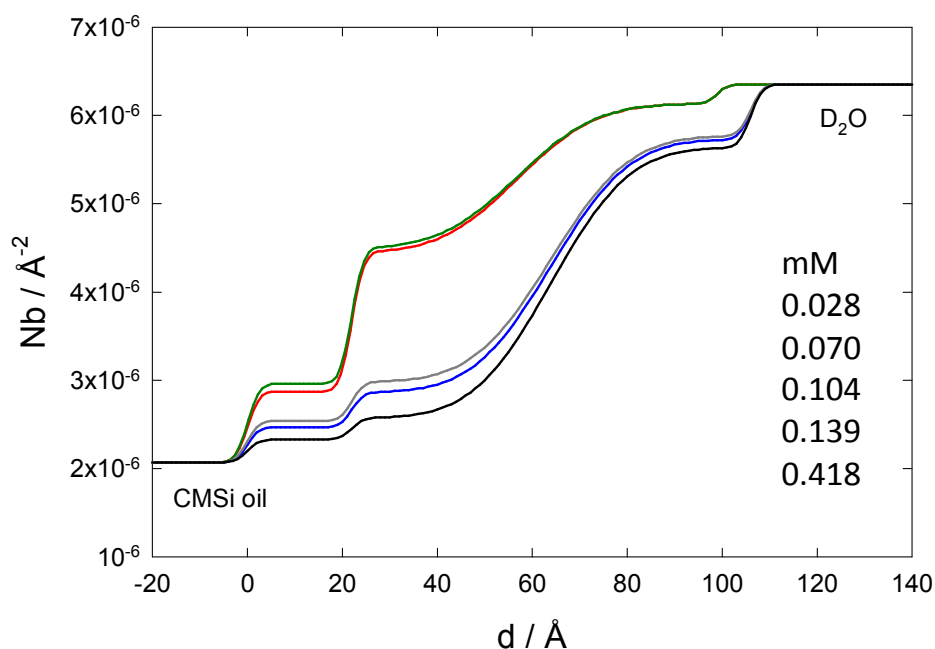


Figure 6. Nb profiles for a series of $C_{12}E_{12}$ at the CMSi hexadecane- D_2O interface.

Discussion

The interface was divided into three layers which represent three distinct regions of the interfacial area. The first layer, with a thickness of $22 \pm 2 \text{\AA}$ for all contrasts, represents the region where the tail group inserts into the oil phase. The thickness is broader compared to the fully extended dodecyl chain length ($\sim 16.3 \text{\AA}$), indicating a relatively staggered conformation. This is not surprising given the rougher nature of the oil-water interface. The chain solvation by the hexadecane molecules prevents the perfect alignment of the tail groups, playing a key role in maintaining the staggered conformation in this region of the interface. Such broadening of the tail group region at the oil-water interface was also observed for the zwitterionic $C_{16}PC$ molecules [4], indicating that solvation of the tail group occurs regardless of the presence or absence of charges in the head group. The Nb of the first layer is in all cases higher than that of the oil and the surfactant, indicating the presence of water (D_2O) in the region. The Nb of the first layer decreases as a function of increasing head group size, therefore the presence (volume fraction) of D_2O in this region must also decrease. The phenomenon might be related to surface activity: the surfactant with the smaller head group ($C_{12}E_6$) is more surface active and leads to better intermixing between oil and water. The increase in head group size leads to a decrease in the surface activity of the

compound; hence the progressively worse intermixing between oil and water and the reduced presence of water (D_2O) in the layer.

The second layer contains mostly surfactant head groups. The thickness of this layer increases as a function of increasing head group size, which is to be expected as the head group gets bulkier. The thickness of the region is comparable to the length of the fully extended head group for all surfactants. It must be stated, however, that a reduction in layer thickness was observed for $C_{12}E_{12}$ at low concentrations and as a result the thickness deviates from the fully extended length of the ethoxylated fragment.

Figure 7 shows the thickness of the head group region both at the air-water (\bullet) and at the oil-water (\circ) interface. At the air-water interface the increase in thickness above $n = 4$ was limited because of globular shape assumed by the ethoxylated region upon folding.

As a staggered conformation was already observed for the tail group region, it is not realistic to expect a perfectly aligned orientation for the head groups either. However, the staggered conformation alone cannot account for the significant increase in thickness compared to the air-water interface. A possible explanation for such an increase in thickness compared to the air-water interface is that at the oil-water interface the head group assumes a comparably less globular and more extended conformation, with no appreciable folding of the head group region.

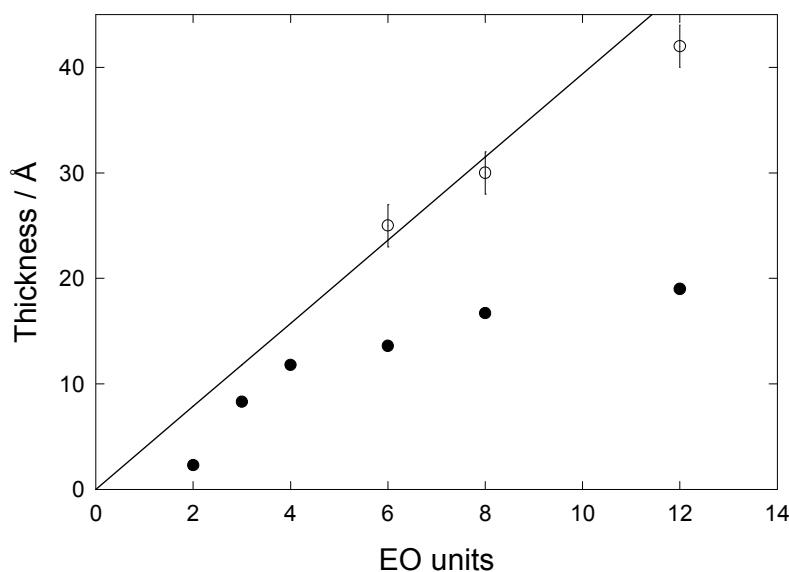


Figure 7. Thickness of the head group region as a function of head group size at the air-water (\bullet) and the oil-water interface (\circ). The straight line indicates the length of the fully extended head group.

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5 The third layer, the one in contact with D₂O, represents a diffuse underlying structure. The *Nb* of
6 the layer is very close to D₂O in all cases, indicating that little surfactant is adsorbed in this region.
7 It must be stressed that since the ΔNb between the diffuse layer and D₂O is very small, the
8 sensitivity of neutron reflectivity to this interfacial region is rather limited and the discussion
9 regarding the structure of this layer is bound to be highly speculative. For all surfactants, as the
10 concentration decreases below the CMC, the amount of surfactant in the underlying structure
11 decreases (the *Nb* of the underlying structure increases to almost that of D₂O). C₁₂E_n surfactants
12 form Gibbs monolayers where molecules from the bulk keep exchanging with those adsorbed at the
13 interface. The underlying structure, adjacent to the adsorbed primary monolayer, represents the
14 interfacial region where the exchange between the bulk phase and the monolayer takes place. This
15 region could be interpreted as a surfactant-enriched area of the bulk phase in the vicinity of the
16 interface; a necessary pathway for surfactant molecules to reach the interface. This hypothesis is
17 also suggested by the observation that the *Nb* of the third layer consistently decreases as the size of
18 the head group increases. In fact, surfactants with larger head groups present higher CMC, so that
19 the concentration of free monomers in solution increases steadily with increasing head group size,
20 hence increasing the concentration in the surfactant-enriched layer and slightly diminishing its *Nb*.
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35 Interlayer roughness plays an important role in the data fitting for C₁₂E_n surfactants. No interlayer
36 roughness was required between the oil phase and layer 1, between layer 1 and layer 2 and between
37 layer 3 and D₂O. A roughness of 2 Å was used solely to smooth the steps in the *Nb* profiles in
38 Figure 4, Figure 5 and Figure 6 and to improve the visual representation. Conversely, the roughness
39 between the second layer and the diffuse layer (σ_3) increases significantly from 5 to 11 Å when
40 moving from 6 to 8 ethylene oxide units in the head group. A further small increase was observed
41 for $n = 12$ ($\sigma_3 = 13$ Å). The increased roughness indicates that the interdigitation between the
42 primary monolayer and the diffuse region increases. The increased intermixing between the two
43 regions could be caused by a combination of two factors:
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- 51 1. Increased disorder in the head group region of the primary monolayer with increasing head
52 group size. This is not unlikely as it has already been observed at the air-water interface
53 [17].
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- 56 2. As the size of the head group increases, the CMC increases, and so does the concentration
57 of free monomers in the aqueous phase. The surfactant molecules become more hydrophilic
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3 and progressively less surface active, consequently the interaction between the surfactant
4 molecules and the interface becomes less favourable. The turnover between the primary
5 monolayer and the diffuse region becomes much faster with increasing head group size,
6 therefore it becomes progressively more difficult using neutron reflectivity to discern neatly
7 between the two regions. An increase in roughness is then required to represent the
8 imperfectly neat separation between the two regions.
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14 The structure of the primary monolayer in direct contact with the oil phase significantly differs from
15 that at the air-water interface. At the air-water interface the tail region was constant and thinner than
16 the fully extended length of the alkyl region, so that the tail groups were assuming a tilted
17 conformation. At the oil-water interface the thickness of the tail group region also remains constant
18 as a function of increasing head group size, but the thickness is now larger than the fully extended
19 alkyl chain length. This effect is caused by the presence of hexadecane, which is now solvating the
20 alkyl chains so that tail-tail interactions are reduced. This results in a staggered conformation of the
21 surfactant molecules where steric repulsion between the tail groups is much reduced. A similar
22 increase in layer thickness for the tail group region when moving from the air-water to the oil-water
23 interface was already observed for C₁₆PC surfactants and it was associated with a significant
24 reduction in tilt angle [4].
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33 Penfold et al., suggested a possible increase of water presence in the tail group region with
34 increasing head group size at the air-water interface [22]. The opposite seems to happen at the oil-
35 water interface: the *Nb* of the tail group region decreases with increasing head group size, clearly
36 indicating that the presence of D₂O in the layer decreases as the head group gets bulkier.
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41 Of particular interest is the increase of layer thickness for the head group region as a function of
42 increasing head group size. It was shown earlier that the thickness of the head group region at the
43 air-water interface increases linearly up to $n = 4$; after that, the increase is not as pronounced
44 because of globular conformation assumed by the head group. At the oil-water interface, on the
45 other hand, the thickness of the head group region seems to increase linearly with increasing size
46 (Figure 7). The much faster increase observed at the oil-water interface can be caused by the head
47 group assuming an almost fully extended conformation. One possible explanation for the extended
48 conformation could be as follows. If some hexadecane molecules were to be present in this region,
49 they could form van der Waals interactions with the hydrocarbon part of the head group preventing
50 it from folding and assuming a globular conformation. This is clearly highly speculative and more
51 detailed contrast schemes would be required to prove it. However, some support for the validity of
52 this theory comes from the presence of the diffuse underlying structure. The hydrocarbon tail
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3 groups of the surfactants in the underlying structure require a partially hydrophobic anchoring
4 surface in order to adsorb onto the primary monolayer. As the diffuse region was not observed at
5 the air-water interface, the surfactant head group alone is clearly not able to provide a suitable
6 partially hydrophobic surface. At the oil-water interface, the presence of hexadecane molecules
7 intermixed with the head groups could provide a higher degree of hydrophobicity to the head group
8 region, hence the presence of the underlying structure.
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14 The overall conformation of the primary monolayer is much more extended at the oil-water
15 interface than it is at the air-water interface. The possible presence of hydrophobic hexadecane
16 molecules would provide solvation of the surfactant tail groups and the hydrophilic head groups
17 would also have some hexadecane molecules associated. Such solvation would also justify the far
18 more stretched conformation of the adsorbed monolayer observed compared to the air-water
19 interface. The presences of the oil layer seems to efficiently solvate the surfactant tail groups and
20 pull the adsorbed surfactant molecules towards the more hydrophobic phase. This effect could
21 clearly not be observed at the air-water interface as no solvation can be provided by air. To some
22 extent, air can be considered as a “passive” hydrophobic medium. At the air-water interface, air
23 behaves as a hydrophobic medium but it is clearly not capable of establishing any interactions with
24 the substrates present at the interface. When a surfactant molecule in the aqueous phase reaches the
25 interface it cannot interact with the air phase and the only favourable interactions left available for
26 the hydrophobic part of the surfactant are van der Waals interactions between different tail groups.
27 For this reason, the hydrophobic part of the adsorbed layer tends to be confined to a specific region
28 in contact with the air phase where it is forced to form a relatively well ordered structure. At the oil-
29 water interface, on the other hand, oil molecules can efficiently solvate surfactant molecules. When
30 a surfactant molecule in water reaches the interface, its tail group can establish van der Waals
31 interactions both with other surfactant tail groups and with oil molecules. As a result, the tail group
32 region can assume a more relaxed and energetically favourable conformation and the whole
33 adsorbed layer results in a broader structure. For this reason, the oil surface can be considered as an
34 “active” hydrophobic medium.
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49 **Conclusion**

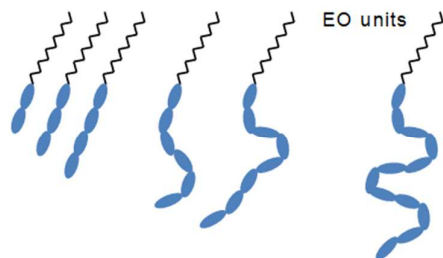
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52 The conformation of $C_{12}E_n$ surfactants at the hexadecane-water interface was studied as a function
53 of increasing head group size using neutron reflectivity. It was found that the interface can be
54 divided into two main regions: a rough, staggered monolayer in contact with the oil phase and a
55 diffuse region, extending towards the aqueous phase. The conformation of the head group
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3 significantly changes compared to the air-water interface, moving from a globular to an almost fully
4 extended conformation at the oil-water interface. We believe that an important role in the stretching
5 of the head groups could be attributed to the presence of hexadecane molecules in this region. The
6 presence of oil molecules in the head group region also could be responsible for the existence of a
7 diffuse underlying structure, which was not observed at the air-water interface. It was believed that
8 the interfacial roughening observed at the oil-water interface for ionic and zwitterionic surfactants
9 was mainly caused by the necessity to accommodate the charges in the head groups [3, 4, 5]. In this
10 paper we have shown that a broader and rougher adsorbed layer is also observed for non-ionic
11 $C_{12}E_n$ surfactants at the oil-water interface. Since these surfactants do not carry any charges in the
12 head group, the broadening of the interface must be attributed to the presence of the oil phase,
13 which efficiently solvates the adsorbed layer.
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References:

1. Penfold J., Thomas R. K.; *J. Phys.: Condens. Matter*, **1990**, 2, 1369.
2. Denton A.R., Gray C.G., Sullivan D.E.; *Chem. Phys. Lett*, **1994**, 219, 310.
3. Zorbakhsh A., Querol A., Bowers J., Webster J. R. P.; *Faraday Discuss.*, **2005**, 129, 155.
4. Zorbakhsh A., Querol A., Bowers J., Yaseen M., Lu J. R., Webster J. R. P.; *Langmuir*, **2005**, 21, 11704.
5. Zorbakhsh A., Webster J. R. P., Eames J.; *Langmuir*, **2009**, 25, 3953.
6. Sharma K. S., Patil S. P., Rakshit A. K.; *Colloid Surface A*, **2003**, 219, 67.
7. Wang Z. N., Li G. Z., Mu J. H., Zhang W. X.; *J. Surfactants Deterg.*, **2002**, 5, 39
8. Zhang H., Li Y., Dubin P., Kato T.; *J. Colloid Interf. Sci.*, **1996**, 183, 546.
9. Moore P. N., Puvvada S., Blankschtein D.; *Langmuir*, **2003**, 19, 1009.
10. Patrick H. N., Warr G. G., Manne S., Aksay I. A.; *Langmuir*, **1997**, 13, 4349.
11. Desbene P. L., Portet F., Treiner C.; *J. Colloid Interf. Sci.*, **1997**, 190, 350.
12. Singh S. K., Notley S. N.; *J. Phys. Chem. B*, **2010**, 114, 14977.
13. Lu J. R., Lee E. M., Thomas R. K., Penfold J., Flitsch S. L.; *Langmuir*, **1993**, 9, 1352.
14. Lu J. R., Li X. Z., Thomas R. K., Staples E. J., Tucker I., Penfold J.; *J. Phys. Chem.*, **1993**, 97, 8012;.
15. Lu J. R., Li Z. X., Thomas R. K., Staples E. J., Thompson L., Tucker I., Penfold J.; *J. Phys. Chem.*, **1994**, 98, 6559.
16. Lu J. R., Hromadova M., Thomas R. K., Penfold J.; *Langmuir*, **1993**, 9, 2417.
17. Lu J. R., Su T. J., Li Z. X., Thomas R. K., Staples E. J., Tucker I., Penfold J.; *J. Phys. Chem. B*, **1997**, 101, 10332.
18. Lu J. R., Li Z. X., Thomas R. K., Penfold J.; *J. Chem. Soc., Faraday Trans.*, **1996**, 92, 403.
19. Dickinson E., Horne D. S., Phipps J. S., Richardson R. M.; *Langmuir*, **1993**, 9, 242.
20. Campbell R. A., Wacklin H. P., Sutton I., Cubitt R., Fragneto G.; *Eur. Phys. J. Plus*, **2011**, 126, 107.
21. Webster J. R. P., Langridge S., Dalgliesh R. M., Charlton T. R.; *Eur. Phys. J. Plus*, **2011**, 126, 112.
22. Penfold J., Richardson R. M., Zorbakhsh A., Webster J. R. P., Bucknall D. G., Rennie A. R., Jones R. A. L., Cosgrove T., Thomas R. K., Higgins J. S., Fletcher P. D. I., Dickinson E., Roser S. J., McLure I. A., Hillman A. R., Richards R. W., Staples E. J., Burgess A. N., Simister E. A., White J. W.; *J. Chem. Soc., Faraday Trans.*, **1997**, 93, 3899.
23. Penfold J., Thomas R. K.; *Phys. Chem. Chem. Phys.*, **2002**, 4, 2648.

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