Chapter 3

Direct Visualisation of Mesh Structures at Solid/Solution Interfaces.

3.1 Introduction

Over the past few years “soft-contact” AFM imaging has been employed to demonstrate a strong correlation between bulk self-assembly structure and the morphology of surfactant adsorbed layers.\(^2,36\) On hydrophilic substrates, of which mica is the most widely studied, adsorbed layers comprised of globular and cylindrical aggregates as well as bilayers have been well-documented, reflecting the three most common geometries for the constituents of bulk micellar solutions and lyotropic liquid crystals.

The concept of a surfactant packing parameter, \(\nu/a_0\ell_c\),\(^52\) widely used in understanding trends in bulk self-assembly, can readily be translated to the solid-solution interface if the properties of the substrate are properly accounted for. In general, systematic variation in surfactant structural parameters such as head-group charge and structure,\(^54,50\) alkyl chain length,\(^2,58\) structure\(^96\) and number,\(^36,54\) and electrolyte concentration\(^50,66-11\) all follow the same, predictable trends as bulk surfactant aggregation patterns. However the effect of added salt on aggregate structure on the surface of mica and other clays may be complicated by cation exchange.\(^58,51,57\)
The surface aggregate structures so far reported (and summarised in Chapter 1) only represent a fraction of the rich diversity of aggregate morphologies known to form in bulk phases. These include branched micelles,\textsuperscript{130} bicontinuous cubic phases,\textsuperscript{131} sponge phases,\textsuperscript{132} and intermediate structures such as ribbon phases and perforated bilayers or meshes.\textsuperscript{133,134,135} In the bulk phase diagram such structures occur near planar bilayers, often between hexagonal and lamellar phases. The most common ordered phase in this region is the bicontinuous cubic phase, but a wide variety of intermediate phases containing structures that satisfy the packing constraints between cylinders and bilayers have been reported.\textsuperscript{133,134,136,137}

Intermediate structures found between the hexagonal and lamellar phases can be divided into three broad structural categories.\textsuperscript{138} The first are a distortion of the more usual hexagonal phase and are known as ribbon phases.\textsuperscript{139} The second include mesh structures that are essentially lamellae pierced by water-filled defects. Experimental evidence exists for mesh phases in which lamellae are pierced by water-filled holes and correlated mesh structures with either tetragonal\textsuperscript{134} or rhombohedral symmetry. The last category is a distortion of one of the bicontinuous cubic phases into an anisotropic structure.

It is possible for both ribbon and mesh phases to simply align at an interface, whereas triply-connected structures like bicontinuous cubic phases cannot do so. However Fogden \textit{et al.} have recently shown that the three-branched cubic phases can be distorted to give a hexagonal mesh.\textsuperscript{140} This may contribute to making mesh phases more prevalent at the solid-liquid interface under the correct curvature conditions.

In terms of surfactant packing or aggregate curvature, mesh structures are stable in the range $1/2 < v/a_0l_c < 2/3$.\textsuperscript{141} Described here are AFM results for a variety

\* \textit{refer Section 1.3.1}
of surfactant systems in which the aggregate curvature is systematically varied between rods and bilayers, so that they exhibit mesh structures at a solid-solution interface. The systems described in section 3.6 were performed in collaboration with Dr. Mari Kadi and Professor Mats Almgren from Upsala University, Sweden. The experiments described in sections 3.7 and 3.8 were performed by Dr. Franck Duval and Dr. Laszlo Kovacs. However, interpretation of these results remained ambiguous until the work performed in sections 3.3 and 3.4 was completed. This was work done solely by the author.

3.2 Materials and Methods

Dodecyltrimethylammonium bromide (DTAB, Aldrich) and didodecyldimethylammonium bromide (di-C_{12}DAB, Fluka) were used as received. Tetradecyltriethylammonium bromide (TTeAB) was synthesised as described previously.\textsuperscript{142} The solid substrate used in all AFM experiments was muscovite mica (Brown Co., Sydney). The mica substrate was cleaved using adhesive tape immediately before use. Experiments were performed at room temperature (approx. 23°C) in Millipore water with a conductivity of 18 MΩcm\textsuperscript{-1}.

Adsorbed layer structures at the solid/solution interface were examined using soft contact imaging as described in Section 1.1.

3.3 Didodecyldimethylammonium bromide (di-C_{12}DAB) + Dodecyltrimethylammonium bromide (DTAB)

The adsorbed layer structure of di-C_{12}DAB on both mica and quartz has been documented to be a laterally unstructured bilayer.\textsuperscript{36, 68} DTAB forms cylindrical
aggregates on mica\textsuperscript{143} whereas TTeAB forms globular structures\textsuperscript{50}. di-C\textsubscript{12}DAB and DTAB have been shown to mix approximately ideally in bulk solution,\textsuperscript{144} and mixtures of di-C\textsubscript{12}DAB and TTeAB are expected to do likewise (Section 3.4). As the composition of mixtures of these compounds is varied, the expected sequence of “Euclidean Solids” aggregate morphologies is

\begin{equation*}
\text{bilayer (di-C}_{12}\text{DAB)} \rightarrow \text{cylinders (DTAB)}\text{,}
\end{equation*}

\begin{equation*}
\text{bilayer (di-C}_{12}\text{DAB)} \rightarrow \text{cylinders} \rightarrow \text{globules (TTeAB)}.
\end{equation*}

Figure 3.1 shows AFM images of a sequence of mixed di-C\textsubscript{12}DAB:DTAB adsorbed layers at various bulk compositions, together with their Fourier transforms as insets. di-C\textsubscript{12}DAB (Figure 3.1(a)) exhibits no lateral structure, and likewise no periodicity is evident in the Fourier transform. DTAB-rich compositions (Figures 3.1(c) and (d)) display stripes characteristic of adsorbed cylinders, and the anisotropic pattern is reflected in the Fourier transform. The periodicities of these cylinders are approximately 5.3 nm which is comparable to a pure DTAB film\textsuperscript{50} This is similar to the results reported previously for the adsorption of pure DTAB on mica.\textsuperscript{50} However at intermediate compositions an adsorbed layer with a periodic but isotropic structure in the plane was observed. This is evident in the increased roughness and texture in the direct image (Figure 3.1(b)), and also appears as a faint but distinct isotropic ring in the Fourier transform. This isotropic structure is interpreted as a mesh or perforated bilayer.
Figure 3.1. AFM deflection images of mixed adsorbed layers of di-C\textsubscript{12}DAB and DTAB on mica at bulk compositions (a) di-C\textsubscript{12}DAB 0.1 mM; (b) di-C\textsubscript{12}DAB 0.043 mM, DTAB 15.0 mM; (c) di-C\textsubscript{12}DAB 0.041 mM, DTAB 15.3 mM; (d) di-C\textsubscript{12}DAB 0.025 mM, DTAB 19.5 mM.

3.4 Didodecyldimethylammonium bromide (di-C\textsubscript{12}DAB) + Tetradecyltri-ethylammonium bromide (TTeAB)

The same progression in morphology is also apparent in Figure 3.2, which shows AFM images of mixed adsorbed films with various compositions of di-C\textsubscript{12}DAB and TTeAB. Pure di-C\textsubscript{12}DAB is shown again for reference (Figure 3.2(a)), and TTeAB forms globular micelles (Figure 3.2(f)). Intermediate compositions show the same progression as Figure 3.1, yielding overall

bilayer $\rightarrow$ mesh $\rightarrow$ cylinders $\rightarrow$ globules
In both Figures 3.1(b) and 3.2(b), the Fourier transforms of the isotropic mesh differs from those of globular aggregates (e.g. Figure 3.2(f)) in two ways. The correlation length is larger (smaller ring radius) in the mesh, and the isotropic ring is "filled in" in the mesh, indicating a structure with longer range correlations.

![AFM deflection images of mixed adsorbed layers of di-C12DAB and TTeAB on mica at bulk compositions](image)

**Figure 3.2.** AFM deflection images of mixed adsorbed layers of di-C12DAB and TTeAB on mica at bulk compositions (a) di-C12DAB 0.1 mM; (b) di-C12DAB 0.035 mM TTeAB 4.10 mM; (c) di-C12DAB 0.033 mM TTeAB 4.26 mM; (d) di-C12DAB 0.023 mM TTeAB 4.89 mM; (e) di-C12DAB 0.02 mM, TTeAB 5.04 mM, (f) TTeAB 6.3 mM.

### 3.5 Discussion

The curvature or packing parameter of the surfactant adsorbed layer has been varied in these systems by mixing the surfactants (di-C12DAB \((v/a_{0}l_{C} \approx 0.62)\) with DTAB\(^{145}\) or TTeAB \((v/a_{0}l_{C} \approx 0.33)\). As the packing parameter of the surfactant
mixture is varied between $\frac{1}{2}$ and 1, the transition between cylinders and homogeneous bilayers is interrupted by the appearance of an intermediate curvature structure – a perforated bilayer or mesh, or equivalently a two-dimensional layer of densely branched micelles.

While the conditions for the formation of these structures are rarely met in bulk surfactant phases, the surface can facilitate their formation in two ways. As previously noted, the surfactant “concentration” in the adsorbed layer is high, and the lateral structure is close to that of bulk liquid crystals. (The adsorbed layer can even be used to nucleate multilayer growth of liquid crystals on the surface.)

Bicontinuous cubic phases are frequently observed in bulk surfactant systems between hexagonal and lamellar phases, and the most common of these is the $Ia3d$ interpenetrating three-fold branched gyroid structure. As noted above, Fogden et al. have demonstrated that this structure can easily be rearranged into an intermediate mesh phase. The presence of a planar macroscopic interface may thus facilitate this rearrangement, which accommodates the aggregate curvature but reduces the periodicity to two dimensions in the plane of the surface.

It should be noted that some of the isotropic intermediate lateral structure reported here can be difficult to distinguish from adsorbed globular or spherical aggregates. Taken individually, some of these images do look like adsorbed globular micelles. However when a direct comparison between globules and meshes is possible, the difference between the structures is often clear from the images (e.g. Figures 3.2(b) and 3.2(f)). In the absence of a direct comparison, it is only the curvature or packing parameter progression with composition and bulk solution properties that necessitates a lower curvature structure.
Nearest-neighbour spacings highlight the differences between interconnected meshes and globules. TTeAB globules have nearest neighbour distances of 5.7±0.5 nm (Figure 3.2(f)), consistent with previous observations. The mesh shown in Figure 3.2(b) has a noticeably larger repeat spacing (smaller ring in the Fourier transform) of 7.3 ± 0.3 nm.

Conversely, we would expect mixed globular micelles of di-C_{12}DAB and TTeAB to have a nearest neighbour spacing no greater than that of TTeAB alone, due to the shorter chain of di-C_{12}DAB. Dodecyltriethylammonium bromide on mica forms globular adsorbed structures with a nearest neighbour spacing of 5.0 nm. Note also that the spacing decreases as the surface morphology changes from globules into cylinders (Figures 3.2(f) → 3.2(c)), and then abruptly increases when the mesh is formed. A smaller nearest-neighbour distance for cylinders is routinely reported for comparable surfactants under similar conditions.

To elucidate the features observed in the AFM images, we have generated various surface patterns to simulate possible adsorbed layer structures. These are shown in Figure 3.3 together with their Fourier transforms. All of the patterns are based on a random hard disk tiling. By varying the nearest-neighbour connectivity, Z, patterns of disks (Z=0), representing globular adsorbed micelles, flexible stripes representing adsorbed cylinders (Z=2), or a mesh (Z=3) are produced.

* The hard disk tilings were generated using the DOCPIC program kindly provided by Thomas Zemb. This was developed to create two-dimensional representations of discrete and bicontinuous microemulsions according to the disordered open connected (DOC) model of microemulsion structure.
This simple, coarse-grained depiction of the adsorbed layer reproduces the essential features of the direct images and their Fourier transforms. The hard disk system exhibits a sharp, isotropic correlation ring. $Z = 2$ shows an anisotropic pattern with arcs whose length depends on the flexibility of the cylinders. The $Z = 3$ mesh system shows an isotropic Fourier transform, as expected, but also reproduces the distinctive "filled-in" feature of many of the experimental meshes due to the existence of correlations between adsorbed material over extended distances. (This is not expected to be very sensitive to the exact coordination number, which can be as high as 6 or 7 in the simulation.) Similar features have also been reported in the small-angle scattering from bicontinuous microemulsions well-described by the DOC model in three dimensions.37 Here also, the scattered intensity at low angles increases with increasing connectivity ($Z$) as this tends to diminish the order arising from hard core repulsions. Note that we have not attempted to draw any conclusions about the correlation lengths (ring size) from the model, as this will be sensitive to the amount of adsorbed material, and has not been measured.

Finally, we consider a possible alternative explanation for the observed sequence of images, which is
bilayer → hemispheres → cylinders → globules.

That is, hemispheres may form on top of a hydrophobic “head-groups down” monolayer. This structure has been suggested elsewhere on theoretical grounds, and adsorbed hemispheres have been observed by AFM on hydrophobically-modified silica. While such a structure is feasible, where di-C\textsubscript{12}DAB may adsorb to form a hydrophobic monolayer on which DTAB or TTeAB forms hemispheres or hemi-globules, we rule it out on several grounds.

First, we did not observe any effect of the order of addition of components on the adsorbed layer structures. Our attempts to pre-cast a di-C\textsubscript{12}DAB film followed by addition of DTAB or a di-C\textsubscript{12}DAB /DTAB mixture always led to the same final morphology, and particularly to the formation of cylinders at high DTAB concentrations.

Second, such a structure would necessitate demixing between the single and double tailed components, which is at odds with their behaviour in bulk. Third, we return to the discussion of repeat spacings above.

The similarity in the adsorbed layer morphologies and their progressions lead us to eliminate interpretations based around globular aggregates in favour of perforated bilayers or meshes. The mesh emerges as the preferred adsorbed layer morphology for systems with aggregate curvatures between cylinders and spheres. It is also clear from these studies that whenever adsorbed bilayers form, they do so with approximately 100% surface coverage.

Other systems that form meshes have been studied by others and are discussed below.
3.6  *Glycerol monooleate (GMO) + Alkyltrimethylammonium chloride (DTAC, TTAC and CTAC) + 100 mM NaCl*

GMO does not adsorb onto mica by itself, but can form mixed adsorbed layers on mica with TTAC or DTAC at various compositions. TTAC in 100 mM NaCl was found to form cylinders on mica, while DTAC in 100 mM NaCl formed globules (not shown).

Figure 3.4 shows the AFM images of the adsorbed layers formed by mixtures of GMO and TTAC. TTAC-rich samples showed adsorbed cylinders (Figure 3.4(c)). Samples with relatively low TTAC concentrations showed adsorbed bilayers (Figure 3.4(a)), and at intermediate compositions we observed an isotropic structure that we again interpreted as a mesh (Figure 3.4(b)).

![AFM deflection images](image)

**Figure 3.4.** AFM deflection images of mixed adsorbed layers of GMO and TTAC on mica at bulk compositions (a) GMO 0.5 mM, TTAC 2.5 mM (b) GMO 0.25 mM, TTAC 2.75 mM (c) GMO 0.15 mM, TTAC 2.85 mM. All solutions contained 100 mM NaCl

The adsorbed layer structures formed by mixtures of GMO and DTAC in 100 mM NaCl on mica are shown in Figure 3.5. With increasing DTAC content, the observed sequence of aggregates was

bilayer $\rightarrow$ mesh $\rightarrow$ globules
Cylindrical aggregates may form over a narrow composition range between the observed isotropic morphologies, but were not observed.

The difference between the mesh and globular aggregates are evident in Figures 3.5(b) and (c). The texture of the direct images are quite different, with Figure 3.5(c) displaying higher contrast and order, and a smaller nearest-neighbour distance (although on its own Figure 3.5(b) might just be regarded as a poorer quality image). The Fourier transforms clearly show once again that the periodicity in the mesh (8.9 nm) is greater than that in the globular aggregates (6.5 nm).

**Figure 3.5.** 200x200 nm² AFM deflection images of mixed adsorbed layers of GMO and DTAC on mica at the following bulk compositions (a) GMO 1.6 mM, DTAC 12.8 mM (b) GMO 0.55 mM, DTAC 13.85 mM (c) GMO 0.30 mM, DTAC 14.1 mM. All solutions contained 100 mM NaCl.

Mixtures of GMO with CTAC (cetyltrimethylammonium chloride) were also investigated. This mixture was found to form a laterally unstructured bilayer on mica at all compositions examined, as was also found for pure CTAC in 100 mM NaCl.

### 3.7 12-2-12 or 12-3-12 + CsCl on mica

Adsorbed layer structures of cationic gemini surfactants on mica have been partially characterised by Manne *et al.* They showed that increasing spacer length (s
in 12-s-12) leads to differences in adsorbed layer morphologies; bilayer for $s = 2$ and cylinders for $s = 4$. As Lamont and Ducker have shown for monomeric cationic surfactants,\textsuperscript{57} caesium ion competes more effectively with surfactant cations than potassium, tending to raise the curvature of CTAB aggregates from cylinders to globules. A similar effect is observed in cationic gemini surfactants.\textsuperscript{100}

Figure 3.6 shows AFM images of the adsorbed layers formed by 12-2-12 and 12-3-12 in aqueous CsCl solutions. Both surfactants form laterally unstructured bilayers in aqueous solution (e.g. 12-2-12, Figure 3.6(a)). 12-2-12 only forms spherical micelles in bulk aqueous solution very near its cmc. These rapidly transform into cylinders and grow into worm-like micelles with increasing concentration. 12-3-12 follows the same aggregation pattern, but spherical micelles are stable to somewhat higher concentrations.\textsuperscript{147,148}
Adding CsCl is expected to increase the curvature of the adsorbed aggregate by decreasing the number of available adsorption sites on the mica. 12-3-12, with its longer spacer, should more readily transform to rods (and to spheres if this is possible on the surface). Where 12-3-12 does indeed form adsorbed cylinders in 25 mM CsCl (Figure 3.6(d)), the adsorbed layer structure of 12-2-12 again transforms from a bilayer (Figure 3.6(a)) into an isotropic lateral structure from 25 mM up to 0.10M added CsCl (Figure 3.6(b) and (c)). Again we conclude this to be a mesh of densely-branched micelles that in this case never makes the next transition into cylinders. The
emergence of the periodic lateral structure in the 12-2-12 adsorbed layer with increasing CsCl concentration is clear from the Fourier transforms of Figures 3.6(b) and 3.6(c), which again show the distinctive "filled-in" isotropic ring. Similar results are obtained in the presence of added CsBr, so we can rule out an effect primarily due to counterion-exchange with the surfactant.

3.8 Tetradecyltrimethylammonium chloride (TTAC) + sodium benzoate on mica

Aromatic counterions and neutral molecules have been shown to strongly affect the curvature of surfactant aggregates in bulk and at an interface. It has recently been shown that the adsolubilization of aromatic molecules (naphthalene and 1- and 2- naphthol) can cause an abrupt cylinder to bilayer transition in TTAB adsorbed on mica. However in the presence of a competing cation, the balance between the effect of cation exchange (raising curvature) and aromatic additive (lowering curvature) may stabilise branched and mesh structures that occur between cylinders and bilayers. An example is shown in Figure 3.7 for a TTAC adsorbed layer in various concentrations of sodium benzoate. As the sodium benzoate concentration increases, branches are introduced into the adsorbed TTAC cylinders so that they gradually transform into a dense mesh. The Fourier transforms similarly become increasingly isotropic as the benzoate concentration increases, exhibiting the distinctive filled ring in 3.7(d). This system does not transform to a bilayer.
3.9 Didodecyldimethylammonium bromide and dodecyltrimethylammonium bromide mixtures on quartz: AFM and Neutron Reflectometry.

3.9.1 Introduction

In order to better characterise this new structure, di-C_{12}DAB and DTAB on quartz were also examined by AFM and adsorbed amounts measured by neutron reflectometry. Experiments were performed at two different neutron sources, the Australian HIFAR reflectometer (X172) and the SURF reflectometer at the Rutherford Appleton Laboratories in the UK (Section 1.1.2.1).
Recent calculations for different surface aggregates have highlighted the importance of including aggregate geometry in modelling neutron reflectivity\textsuperscript{68,70}. This model uses an iterative method to calculate the reflectivity from an adsorbed surfactant layer comprised of head and tail regions and calculates the reflectivity curves for an adsorbed film composed of cylinders, of close-packed spheres as well as for bilayer structures. Closely packed spheres cover at most 60% of the surface; cylinders cover at most 80% of the surface, and a bilayer 100% of the surface. In this study, the structure of a mixed di-C\textsubscript{12}DAB /DTAB film on quartz was determined using AFM and the composition determined using neutron reflectometry.

\textbf{3.9.2 Materials and methods.}

The surfactants used in this study were di-C\textsubscript{12}DAB and DTAB, and the substrate was a quartz crystal (40 x 80 x 15mm\textsuperscript{3}). Table 3.1 summarises the molecular volumes, scattering lengths and scattering length densities of the materials used. The solvent used in these neutron reflectometry experiments was either D\textsubscript{2}O or an isotropic solvent mixture contrast matched to the quartz substrate (68\% v/v D\textsubscript{2}O). The reflectivity cell clamped the quartz crystal against a trough machined into a stainless steel backing and sealed with a Teflon O-ring. All the cell parts were cleaned by scrubbing with detergent solution and copious rinsing with Milli Q water and distilled ethanol. The quartz crystal was soaked in Aqua Regia for 10 minutes, followed by H\textsubscript{2}O\textsubscript{2} / H\textsubscript{2}SO\textsubscript{4} solution for 15 minutes and copious rinsing in Milli Q water. After the cell was assembled, solution was introduced into the cell through filling ports at the top of the sample cell using pipettes. Following assembly, the cell was not dismantled unless necessary. Subsequent solutions were flushed through the cell three times before being measured.
<table>
<thead>
<tr>
<th>Material</th>
<th>Scattering length (10^{-5}\ \text{Å})</th>
<th>Scattering length density (\beta) (10^{-6}\ \text{Å}^{-2})</th>
<th>Volume (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz (SiO₂)</td>
<td>15.71</td>
<td>4.16</td>
<td>38</td>
</tr>
<tr>
<td>D₂O</td>
<td>19.15</td>
<td>6.36</td>
<td>30</td>
</tr>
<tr>
<td>di-C₁₂DAB</td>
<td>-20.4</td>
<td>-0.26</td>
<td>795</td>
</tr>
<tr>
<td>h-DTAB</td>
<td>-11.23</td>
<td>-0.23</td>
<td>483</td>
</tr>
<tr>
<td>d-DTAB</td>
<td>249.0</td>
<td>5.16</td>
<td>483</td>
</tr>
</tbody>
</table>

Table 3.1 Volumes, scattering lengths and scattering length densities of the chemicals used in this section.

3.9.3 Modelling reflectivity curves.

Background reflectivity data was collected for the three data sets obtained from the reflectometer at ANSTO but not from the SURF reflectometer. Background was collected by introducing an offset into the detector angle so that an angle dependent, off-specular reflectivity profile could be obtained (Figure 3.8). A new background curve was collected for each solvent used. Raw reflectivity data was processed using reflect_reduceMONBKG (Andrew Nelson, ANSTO) and the background subtracted from each curve. A constant background of \(5 \times 10^{-7}\) was used to fit the data obtained from the SURF reflectometer.
Figure 3.8: Background reflectivity curve from a 0.1 mM di-C\textsubscript{12}DAB film adsorbed onto quartz in D\textsubscript{2}O.

Reflectivity curves were modelled using ReflectJCS\textsuperscript{70}, which uses physical properties of the surfactant molecules as inputs. The surfactant surface layer was considered to be composed of unit cells as shown in Figure 3.9. A bilayer filled the unit cell, whereas cylinders and spheres only partially filled the cell. This unit cell is divided into a number of consecutive layers and the scattering length density of each layer is a weighted contribution of the surfactant and solution. The reflectivity was then calculated using Parratt’s recurrence formula\textsuperscript{149} and best fit to the experimental data determined by the method of least squares.
**Figure 3.9:** Diagram of the unit cell used to calculate reflectivity for surfactant aggregates. The cell is divided into layers and a scattering length density profile generated.

### 3.9.4. Results and discussion.

AFM deflection images of di-C₁₂DAB / DTAB mixtures on quartz are displayed in Figure 3.10. DTAB was found to form globules and di-C₁₂DAB a bilayer, as observed previously⁶⁸. Addition of DTAB to di-C₁₂DAB transformed the bilayer film to a mesh like structure (Figure 3.10b). This structure was observed only over a very narrow composition range and looks distinctly different to the mesh morphologies observed on mica (Figures 3.1 and 3.2). The roughness of the quartz surface also masks the characteristic filled in ring in the Fourier transform observed on mica in Figures 3.1 and 3.2. Further addition of DTAB was expected to transform the film to rods; but it was not possible to obtain a clear image of this structure due to the roughness of the surface (Figure 3.10c). However, the Fourier transform in Figure 3.10c displays an anisotropic pattern indicative of a rod-like morphology and a faint texturing can be distinguished from the background noise in the image.
Figure 3.10: 200 nm AFM deflection images of (a) 0.1 mM di-C_{12}DAB, (b) 0.07 mM di-C_{12}DAB and 8.1 mM DTAB, (c) 0.06 mM di-C_{12}DAB and 9.8 mM DTAB and (d) 26 mM DTAB showing the change in curvature of the film from a bilayer to mesh, rods and globules on quartz.

In order to clarify the morphologies of these images and to deduce film compositions, neutron reflectometry experiments on each of the four different structures were performed at Australia’s HIFAR research reactor (X172) and the SURF reflectometer at the ISIS Rutherford Appleton Pulsed neutron laboratories (SURF). Four different sets of experiments were performed, three on X172 and one on SURF. For each of the four morphologies, two different solution contrasts; D_{2}O and an H_{2}O/D_{2}O solvent contrast matched to the quartz substrate (q-cmw), and two
different film contrasts, hydrogenated-DTAB (h-DTAB) and deuterated-DTAB (d-DTAB) were studied mixed with hydrogenous di-C$_{12}$DAB. Through hydrogen/deuterium isotopic substitution, the scattering length density and hence reflectivity of DTAB within the mixed film could be selectively varied without altering the chemical composition of the film.

Shown in Figure 3.11 are reflectivity profiles of the pure di-C$_{12}$DAB and DTAB films for both D$_2$O (Figure 3.11a) and quartz contrast matched solvent (Figure 3.11b). An offset of 10 has been introduced into the reflectivity from the DTAB film in both solvents for clarity. Fitted to these experimental curves are theoretical bilayer and sphere models for the di-C$_{12}$DAB and DTAB film, respectively. The fitted parameters are displayed in Table 3.4.

**Figure 3.11:** Reflectivity profiles for (a) a bare quartz/D$_2$O interface, pure di-C$_{12}$DAB bilayer and pure DTAB spheres in D$_2$O and (b) pure di-C$_{12}$DAB bilayer and pure DTAB spheres in quartz contrast matched water. In both graphs, the DTAB data has been offset by a factor of 10 for clarity. Fitted to these experimental curves are a bilayer model for the bilayer and a spherical model for the globules.$^{70}$

The composition of the mixed films was first estimated by modelling both the mesh and cylinders as a bilayer structure to determine the scattering length density of
the mixed film for each contrast studied. Assuming a single homogenous layer, the reflectivity fitting program, Parratt32 Version 1.5.2 (Hahn Meitner Institute, Berlin) was used to calculate the film scattering length density. Film composition at each contrast should be the same and can be represented by:

$$\beta_{\text{film}} = \beta_{\text{DTAB}} \phi_{\text{DTAB}} + \beta_{\text{di-C12DAB}} \phi_{\text{di-C12DAB}} + \beta_{\text{SOLVENT}} \phi_{\text{SOLVENT}}$$  \hfill (3.1)

where $\beta$ is scattering length density and $\phi$ the volume fraction of each component within the film. Solving this equation simultaneously for three contrasts gave an approximate mixed film composition for the mesh and rod structures. This is presented in Table 3.2 and is compared with the more rigorous analysis of film compositions described below.

<table>
<thead>
<tr>
<th>Film composition</th>
<th>JCSReflect</th>
<th>$\text{Equation 3.1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\text{Bilayer}$</td>
<td>$\text{Mesh}$</td>
</tr>
<tr>
<td>$\text{Vol}_{\text{DTAB}}$</td>
<td>0%</td>
<td>$1.8 \pm 1.5%$</td>
</tr>
<tr>
<td>$\text{Vol}_{\text{di-C12DAB}}$</td>
<td>$94 \pm 4%$</td>
<td>$90.8 \pm 3.5%$</td>
</tr>
<tr>
<td>$\text{Vol}_{\text{Sol}}$</td>
<td>$6 \pm 4%$</td>
<td>$7.4 \pm 3%$</td>
</tr>
</tbody>
</table>

Table 3.2: The film compositions determined using ReflectJCS for the bilayer, mesh, rod and globular structures. Film compositions determined using equation 3.1 are included for comparison.

A more accurate method for determining film composition was performed using ReflectJCS$^{70}$. As described above, this fitting protocol can model the film as either spherical, cylindrical or bilayer aggregates$^{70}$. As the mesh structure can be thought of as either densely branched rods or perforated bilayers, both cylindrical and bilayer models were initially used. However, a bilayer rather than cylindrical model was found to best describe the mesh as the cylindrical model allowed neighbouring rods to overlap. Not only is this scenario physically unreasonable, the degree to
which the model allowed neighbouring rods to overlap proved to be arbitrary. A cylindrical model in which the unit cell was divided into 10 layers was found best able to describe the rod-like structure and provide best agreement between fitted parameters and those deduced from the AFM.

Firstly, the solvent composition for the mixed film mesh and rods structure was determined by systematically varying the fitted film composition for the h-DTAB systems (both D$_2$O and q-cmw). The surfactant fractional surface coverage was allowed to vary freely for both structures and $\chi^2$ monitored. Only fits with parameters that agreed with the AFM data previously collected were considered and the solvent composition with the smallest $\chi^2$ was found. Presented in Figure 3.12 are reflectivity profiles from the mesh and rod structure in D$_2$O (Figure 3.12a) and in q-cmw (Figure 3.12b). In both figures, the reflectivity profile from the rod structure has been multiplied by 10 for clarity. Fitted to these curves are model bilayer fits to the mesh structures and cylindrical fits to the rods.
Figure 3.12: Reflectivity profiles for (a) mesh (0.07 mM di-C$_{12}$DAB and 8.1 mM DTAB) and rod structures (0.06 mM di-C$_{12}$DAB and 9.8 mM DTAB) in D$_2$O and (b) mesh and rod structures in quartz contrast matched water. In both graphs, the rods data has been offset by a factor of 10 for clarity. Fitted to these experimental curves are a bilayer model for the mesh and a cylindrical model for the rods.

Using the determined solvent composition for both mixed films, the mesh and rod structures were re-modelled using ReflectJCS for the deuterated-DTAB systems (both D$_2$O and quartz-cmw). This time the model could be constrained to the determined solvent compositions and the best fit to the experimental data determined. Again, only fits with parameters agreeing with the AFM data were considered. Figure 3.13 shows the reflectivity profiles for the deuterated DTAB mixed mesh and rods films for both D$_2$O and q-cmw. The profile from the rods film is again offset by a factor of 10 for clarity.
Figure 3.13: Reflectivity profiles for (a) mesh (0.07 mM di-C\textsubscript{12}DAB and 8.1 mM deuterated-DTAB) and rod structures (0.06 mM di-C\textsubscript{12}DAB and 9.8 mM deuterated DTAB) in D\textsubscript{2}O and (b) mesh and rod structures in quartz contrast matched water. In both graphs, the rods data has been offset by a factor of 10 for clarity. Fitted to these experimental curves are a bilayer model for the mesh and a cylindrical model for the rods.

The film compositions for the bilayer, mesh, rods and globules deduced from ReflectJCS are presented in Table 3.2 and compared with those obtained using equation 3.1.

Considering the mesh was modelled in both cases as a bilayer, it was expected there would be reasonable agreement in derived compositions between the two modelling methods. For the rods however, the film composition is significantly different, compare 90% di-C\textsubscript{12}DAB using equation 3.1, with 69.3% using ReflectJCS. Considering the different film structures assumed in each model, this variation is expected. A fractional surface coverage of 91.5% deduced assuming a homogenous bilayer over-estimates the total adsorbed amount at the surface and is physically unreasonable. The maximum surface coverage a cylindrical structure can possess before overlap between neighbouring rods is 79%.
A feature of these film compositions is the enrichment of di-C12DAB on the surface despite there being far less than 1 mole % di-C12DAB in the bulk. Table 3.3 summarises the composition of di-C12DAB in the bulk, the calculated di-C12DAB mole fraction in the micelle using group contribution theory$^{98,99}$ and both the di-C12DAB fractional surface coverage and di-C12DAB mole fraction in the film. For both mixed films, there is a dramatic enhancement of di-C12DAB in the mixed film compared with the bulk.

<table>
<thead>
<tr>
<th>Morphology</th>
<th>$\alpha_{\text{DDAB}}$</th>
<th>$X_{\text{DDAB}}$ (Group Contribution Theory)</th>
<th>$\Phi_{\text{DDAB}}$ (in film)</th>
<th>$X_{\text{DDAB}}$ (in the film)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bilayer</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Mesh</td>
<td>0.008</td>
<td>0.6</td>
<td>0.91</td>
<td>0.98</td>
</tr>
<tr>
<td>Rods</td>
<td>0.006</td>
<td>0.5</td>
<td>0.69</td>
<td>0.95</td>
</tr>
<tr>
<td>Spheres</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 3.3: di-C12DAB mole fraction in the bulk ($\alpha$), in mixed micelles calculated using group contribution theory, surface fraction of di-C12DAB in the film ($\Phi$) and mole fraction of di-C12DAB (X) in the mixed film.

Also derived from ReflectJCS for each structure are film properties such as thickness, periodicities and surface excesses. These are presented in Table 3.4 and compared with AFM film thickness and periodicity data.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Thickness (Å)</th>
<th>Fractional surface coverage (θ)</th>
<th>Inter-aggregate spacing (Å)</th>
<th>Periodicity (Å)</th>
<th>Surface excess (μmol m$^{-2}$)</th>
<th>Periodicity from AFM (Å)</th>
<th>Separation at breakthrough (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bilayer</td>
<td>25 ± 0.1</td>
<td>94 ± 4</td>
<td>-</td>
<td>-</td>
<td>4.8 ± 0.3</td>
<td>23 ± 3</td>
<td></td>
</tr>
<tr>
<td>Mesh</td>
<td>25 ± 0.5</td>
<td>91 ± 2</td>
<td>-</td>
<td>-</td>
<td>4.8 ± 0.3</td>
<td>41 ± 6</td>
<td>33 ± 3</td>
</tr>
<tr>
<td>Rods</td>
<td>31 ± 3</td>
<td>73 ± 1.9</td>
<td>2.4 ± 0.7</td>
<td>33 ± 3</td>
<td>4.7 ± 0.5</td>
<td>49 ± 10</td>
<td>34 ± 1</td>
</tr>
<tr>
<td>Globules</td>
<td>36 ± 0.1</td>
<td>50 ± 0.1</td>
<td>3.7 ± 0.2</td>
<td>40 ± 0.1</td>
<td>5.9 ± 0.1</td>
<td>58 ± 2</td>
<td>44 ± 4</td>
</tr>
</tbody>
</table>

Table 3.4: Fitted parameters of adsorbed surfactant aggregates
Reasonable agreement is obtained between fitted parameters for the pure di-
C\textsubscript{12}DAB and DTAB films with studies previously examining these surfactants on a 
quartz substrate\textsuperscript{68}. Fitted film thicknesses similarly agree reasonably well with 
separation at breakthrough distances measured from the force-distance curves from 
the AFM, however, fitted nearest-neighbour spacings were slightly smaller than 
measured from the AFM images.

### 3.9.5. Conclusions

Using a variety of strategies surfactant adsorbed layers with aggregate 
curvatures intermediate between cylinders and bilayers were designed, and 
demonstrate the existence of a laterally periodic and isotropic adsorbed layer 
structure. This structure is consistent with a mesh of branched micelles, or 
equivalently a perforated bilayer. The lateral period is similar to that observed in 
other adsorbed surfactant films, as it is governed by the characteristic length scale of 
the surfactant, but differs somewhat from adsorbed globular micelles.

Mixtures of di-C\textsubscript{12}DAB and DTAB on quartz also revealed the same 
morphological sequence and this was further characterised using neutron 
reflectometry. The composition of the mixed film was determined and shown to be 
enriched in di-C\textsubscript{12}DAB despite there being only trace amounts of this surfactant in the 
bulk. The fitted parameters of film thickness, aggregate periodicity and surface 
excess were found to agree well with AFM data.

These results suggest that the range of adsorbed layer morphologies formed by 
surfactants is substantially richer than has previously been reported, or anticipated, 
and is strongly correlated to bulk lyotropic phases. It is concluded that the mesh may
be more commonly observed at the solid-solution interface as it is the surface morphology that corresponds to the bulk gyroid, as well as arising when a mesh structure is present in bulk.