Chapter 1

Introduction.

The objective of this thesis was primarily to determine the morphology of surfactant and mixed surfactant adsorbed films at solid / solution interfaces and to understand the factors influencing these morphologies. This thesis is divided into 7 chapters. In chapter 1, the experimental techniques used for studying these systems are summarised. Surfactant self-assembly at both hydrophobic and hydrophilic solid surfaces is then reviewed, with emphasis placed on morphologies deduced using atomic force microscopy (AFM) or other direct visualisation techniques. The packing parameter is introduced and related to self-assembled adsorbed structures. Following this, structures formed when surfactants are mixed are then summarised.

In Chapter 2, the first results on surfactant structure are presented. The morphologies formed by single chained and double chained quaternary ammonium surfactants on mica at a variety of concentrations are studied. When these two types of surfactants are mixed and their ratios varied systematically, a novel mesh structure is observed and this is explained in detail in Chapter 3. Other systems in which a mesh is observed are also described in this section including some material obtained in collaboration with Dr Mari Kadi and Professor Mats Almgren from Upsala University, Sweden. This structure is characterised using AFM on both mica and quartz and neutron reflectometry.
In Chapter 4, this mesh structure is observed again in nonionic surfactants adsorbed to silica as the AFM cell temperature is increased to the cloud point. This is discussed with respect to mechanisms describing clouding in the bulk, particularly a recently proposed theory involving network entropy and mesh formation in the bulk\(^1\). The AFM results on silica are compared with adsorption onto graphite.

In Chapters 5 and 6, the effect of grafting nonionic surfactants into adsorbed quaternary ammonium surfactant films of different adsorbed morphologies is examined. Grafting polyoxyethylene nonionic surfactants into an adsorbed cylindrical or globular film modified this underlying structure whereas grafting a nonionic diblock copolymer into an adsorbed bilayer film did not. This is explored using AFM, adsorption depletion measurements and surface force apparatus (SFA). The SFA work was performed in collaboration with Drs Phillippe Richetti and Carlos Drummond from the Centre de Recherche Paul Pascale, Bordeaux. Finally, the major results are summarised in Chapter 7.

The chapters in this thesis are written in the format of paper publications with a small introductory section, experimental section and results and discussion. This is preceded by a thorough literature review of experimental techniques and adsorbed surfactant morphologies.

1.1 Techniques for studying surface structure.

1.1.1 Atomic Force Microscopy (AFM).

In atomic force microscopy, a sharp tip mounted on a cantilever is used to probe lateral morphology on a substrate. The substrate is mounted on top of a piezoelectric element, which is then raster scanned beneath the tip. A laser focused onto the back of the cantilever and reflected into a position sensitive detector
measures the vertical deflection in the tip as the sample moves laterally beneath it (Figure 1.1a). The deflection at each position is then used to construct the surface image.

In order to probe the nanostructure of adsorbed surfactant films, the method of soft contact imaging is utilised. This is achieved by setting the imaging pressure to a value within the repulsive part (region ii) of the force curve, before film rupture. This method works well when concentrations are above the critical surface aggregation concentration (csac) or when the surfactant is arranged such that headgroups are facing the aqueous solution and a strong repulsion is present. Contrast is obtained from variation in the force between the tip and adsorbed material and is usually maximised when the applied force is close to rupture (see arrow on the force curve shown in Figure 1.1).

Using this method of imaging generates a force map of the adsorbed layer without the tip physically contacting the sample. The tip is held above the film by colloidal stabilisation forces (often through adsorption of surfactant onto both the tip and the substrate) such as electrostatic repulsion between the surfaces. Film stability and colloidal interaction forces are measured by raising the substrate towards the tip and measuring the deflection of the cantilever as a function of separation. A force curve such as the one shown in Figure 1.1b is typical of an adsorbed surfactant film at concentrations above the cmc and shows a long range exponential repulsion, followed by a steeper, steric repulsion at smaller separations. Further increase in force ruptures the surfactant film, pushing the tip in contact with the underlying substrate.
Figure 1.1: (a) Schematic of AFM imaging in which the tip is skimmed over the surface of an adsorbed film. A force curve (b) is captured in which the scanner is held constant in all directions except z and variation in cantilever deflection with separation between the tip and substrate is measured. The region in (i) is where the tip is sampling the long-range electrostatic forces which extend to distances up to 100 nm from the plane of contact, (ii) the tip is in the region immediately prior to film rupture, where resolution is maximised and (iii) the tip has ruptured the surfactant film and is in contact with the underlying substrate.

Using sharpened tips maximises lateral resolution. The tips typically have a radius of about 10 nm, which is still greater than the radius of curvature of most adsorbed micelles. This means that the actual shape and size of highly curved adsorbed micelles can not be accurately mapped. However, the periodicity and lateral arrangement of adsorbed micelles can be determined by AFM with excellent accuracy and from their arrangement, the shape inferred.

An AFM was used to deduce adsorbed layer structures in all of the following chapters. Imaging was performed on a Digital Instruments NanoScope IIIa Multimode in contact mode with solutions held in a standard fluid cell. Cantilevers used were standard Si$_3$N$_4$ with sharpened tips (Digital Instruments, CA) which were irradiated with ultraviolet light for 30 minutes prior to use. The solution was held in a fluid cell and sealed by a silicone O-ring. Both were cleaned by sonication for 10 minutes in the surfactant solution to be studied, rinsed copiously in ethanol and deionised water and dried using filtered nitrogen. In a typical experiment, scan rates
were varied between 8Hz and 15Hz with integral gains between 0.8-1. Variation in frequency, scan angle and gains had no effect on the observed morphology and all images are unmodified except for flattening along scan lines. Images displayed as part of a figure have the same z-scales, which are usually between 0.8-1 nm.

### 1.1.2 Reflectance Techniques

Whilst AFM can be used to accurately deduce film structure, it cannot be used to determine adsorbed quantities. This information, however, can be determined using reflectometry. Thin films can be probed using the angular dependence of the reflectance of an incident beam from a surface in equilibrium with an adsorbed layer. Differences in refractive index of the adsorbed film allow probing using light, x-rays are sensitive to electron density differences (atomic number) and neutron contrast is determined by the nuclear structure. Neutron reflectometry was used in Chapter 3 to complement the AFM images and determine film composition in a mixed surfactant system.

#### 1.1.2.1 Neutron Reflectometry

Neutron reflectometry is capable of high spatial resolution employing the reflection of a collimated neutron beam from a flat surface. It probes the structure normal to an interface and gives information on a molecular scale of the adsorbed film. The maximum achievable resolution depends on wavelength, so the shorter wavelengths of neutrons allow much greater spatial resolution than optical techniques. The reflection of the beam from the solid/film and film/solution interfaces, generate an interference fringe that can be characterised by thickness and scattering length density.
A powerful feature of neutron reflection is that the scattering length density can be altered by isotopic substitution, offering the capability of probing parts of the adsorbed film selectively.

Classically, the conventional interpretation of neutron reflectometry experiments was that the film was a laterally featureless film. This was despite the observation that adsorbed layers virtually never form a uniform film with 100% surface coverage. From this, an interpretation of patchy bilayers at the interface has been derived which is at odds with the vast bulk of AFM studies showing discrete aggregates. Recently, a model based on adsorbed cylindrical or spherical micelles has been developed which correctly predicts the reduction in surface coverage as film morphology reduces in curvature from a bilayer at 100%, cylinders at 79% and spheres at 61% fractional coverage.\(^3\)

In a neutron reflection experiment, the layer of interest is on top of a known, uniform substrate. The incident beam is specularly reflected and transmitted and this specular reflectivity is measured as a function of the momentum transfer vector, \(Q\). \(Q\) is defined as:

\[
Q = \frac{4\pi \sin \theta}{\lambda}
\]

(1.1)

where \(\theta\) is the angle of incidence and \(\lambda\) is the wavelength of the radiation.

Different \(Q\) values are obtained by varying the angle of incidence or the wavelength of the incident beam. Experiments performed in this thesis were done at two neutron sources, HIFAR in Australia and at the Rutherford Appleton Laboratories in the United Kingdom (ISIS). The HIFAR reflectometer (X172) operates in a monochromatic, angular dispersive mode and collects reflectivity data as a function of angle.\(^4\) The experimentally accessible \(Q\) range generally was from 0.005 to 0.15Å.
At ISIS, because the neutron source is pulsed, the SURF reflectometer uses the “white” time of flight method and has the possible Q range was from 0.005 to 0.4Å. In the experimental setup, the liquid was deuterium oxide (D₂O), or water, or a mixture of the two, contrast matched to the quartz substrate (q-cmw). The substrate was a solid quartz block. The neutron beam entered the solid at the grazing angle of incidence $\theta$, was reflected from the interface and left at $\theta$.

### 1.1.2.2. Optical Reflectometry and Ellipsometry

Both optical reflectometry and ellipsometry examine variation in reflectivity of an interface with adsorption through changes in the refractive index profile of the substrate as species adsorb from solution. Linearly polarised light is reflected from a surface and the characteristics of the reflected light monitored. Optical reflectometry records the amplitudes of the perpendicularly polarised components of the reflected beam. The change in beam polarisation is split into its parallel and perpendicular components using a polarising beamsplitter and this ratio is altered by an adsorbed film. The change in interfacial refractive index as a result of surfactant adsorption is measured. When the interface is illuminated by a parallel polarised laser beam at an angle of incidence close to the Brewster angle, there is a change in the reflectivity of the interface. A reflectivity profile is generated by scanning over a range of angles around the Brewster angle and the surface excess of the adsorbed surfactant calculated. For a homogeneous adsorbed layer model, reflectivity is determined by the optical average thickness ($d$) and refractive index ($n$) of the film and surface concentration is then calculated from de Feijter equation:

$$\Gamma = \frac{d(n - n_0)}{dn / dc}$$

(1.2)
where \( n_0 \) is the refractive index of the bulk solution, and \( \text{dn/dc} \) is the refractive index increment of the adsorbed species. Silica is the primary substrate used for these studies. Adsorbed structure cannot directly be deduced so this technique must be used in conjunction with a technique such as AFM.

Ellipsometry is an optical technique in which the changes of polarisation state of a light beam before and after reflection are measured. Examining surfactant adsorption employs null ellipsometry, in which an elliptically polarised beam is linearly polarised after reflection. This proceeds by monitoring the variation in two ellipsometric angles, \( \psi \) and \( \Delta \) with wavelength, \( \lambda \). \( \psi \) measures the change in amplitude of the polarised beam after reflection from the surface while \( \Delta \) measures the change in phase. Ellipsicity (\( \rho \)) can be related to both the ratio of overall reflection coefficients (\( R_\rho \) and \( R_s \)) and \( \psi \) and \( \Delta \) by

\[
\rho = \frac{R_\rho}{R_s} = \tan \varphi e^{j\Delta}
\]

(1.3)

Using the optical matrix method to fit refractive index profiles to \( \psi \) and \( \Delta \), the thickness and surface excess of the adsorbed film can be obtained. This technique is very sensitive to adsorbed amounts but it is difficult to unambiguously determine adsorbed layer structure.

For both optical reflectometry and ellipsometry the quality of the reflecting surface and particularly its roughness is important. For this reason many studies have been performed on silicon onto which a silica layer is either thermally grown or deposited.
1.1.2.3. **Fluorescence probes**

The use of fluorescent probes to study micellar aggregation numbers has long been an established tool for studying bulk solution behaviour and involves observing the quenching of emission of a micelle-bound fluorophore by an added quencher. The extension of this technique to the study of adsorbed surfactants at a solid interface by Levitz and others provided some of the first direct evidence for surface micelles. This technique divides aggregates into four categories: micelles with quencher and fluorophore, micelles with fluorophore or quencher only, and micelles with neither fluorophore nor quencher. Only micelles containing fluorophore can be probed.

To obtain aggregation numbers, \( N \), fluorescence decay curves are recorded in the presence and absence of quencher using:

\[
N = \frac{[S]_{\text{surface}}}{[Q]_{\text{surface}}} \ln \left( \frac{I(0)}{I(Q)} \right)
\]

(1.4)

where \([S]\) and \([Q]\) are the concentrations of surfactant and quencher on the surface.

This technique relies on several key assumptions; the fluorophore and quencher must not exchange between adsorbed aggregates on the timescale of the fluorescent decay and solubilisation is assumed not to alter the aggregate structure; the concentration of surfactant within the aggregate must be known (which on the surface can be measured using depletion experiments).

This technique has been shown to fail for long, cylindrical aggregates which is the preferred adsorbed layer structure for many conventional quaternary ammonium surfactants on mica. It also has limitations in the bulk when concentrations are high as intermicellar exchange of fluorophores and quencher can occur, falsely increasing
the apparent aggregation number\textsuperscript{14}. This applies to adsorbed films at high coverage and is independent of aggregate morphology resulting in conflicting determinations of structure from that determined by AFM. Above the cmc, this technique probes both bulk and surface micelles and can not be used on its own to infer adsorbed film structure. However, at concentrations below the cmc where AFM imaging can be difficult, fluorescence quenching is a very powerful technique for studying aggregation.

1.1.3. Force Measurement Techniques

The nature of a particular adsorbed layer morphology at the solid/liquid interface can be probed by measuring surface forces. These may be forces derived from van der Waals\textsuperscript{15}, electrostatics\textsuperscript{16}, solvation effects\textsuperscript{17}, steric\textsuperscript{18}, hydration\textsuperscript{19}, hydrophobic\textsuperscript{20} and many more interactions\textsuperscript{21}. The two major techniques used to study these forces are the surface force apparatus (SFA) and AFM where sensitivity is enhanced by an attached colloid probe. In this thesis, force measurements were primarily taken using the AFM without a colloid probe attached. Derived parameters were therefore only compared when experiments were performed on the one tip. In Chapter 6, both normal force and sliding force measurements are presented from SFA experiments.

1.1.3.1. Surface Force Apparatus (SFA).

The SFA measures forces between two curved mica sheets mounted in a crossed cylinder configuration. The separation between these surfaces is measured independently to a precision of 0.1 nm using multiple beam interferometry. The surfaces are attached to a piezoelectric crystal tube and capable of highly linear and
precise movement. Force is determined by moving one of the surfaces a known amount and measuring optically the actual distance travelled and multiplying by a spring constant according to Hooke’s Law. Comparison with theory relies on an assumed lateral structure of the film which cannot be directly determined by force measurements alone. Previously, cationic surfactants have been assumed to form flat bilayers on mica at concentrations above the cmc and this has been the basis for many theoretical calculations\textsuperscript{22-24}.

This technique has been extended to allow the study of lateral (friction) forces. One of the surfaces is attached to a strain gauge and the other is moved laterally using a micrometer. If the attached mica surface experiences a transverse friction force due to its contact with the moving surface this will be measured by the strain gauge. The movement of the surface can be varied from 0.01 – 100µm/s as can the applied normal force, all whilst the shear force between the two surfaces is simultaneously measured.

1.1.3.2. Colloid Probe / AFM Friction and forces

An unmodified AFM is capable of producing force data for any system (Figure 1.1b) and is useful for examining the relative change in film thickness or strength with change in a particular parameter. However, for quantitative force measurements it is less practical largely because the separation between tip and the surface cannot be measured independently and the shape of the imaging tip is ill-defined. The question of tip shape was answered with the advent of the colloid probe technique,\textsuperscript{25,26} in which a colloidal particle of known radius and composition is glued to the end of an AFM cantilever. The problem of independent tip-sample separation has yet to be resolved with separations calculated relative to a hard wall contact.
This technique enables the examination of interactions between many different surfaces and substances such as titanium dioxide\textsuperscript{27}, zinc sulphide\textsuperscript{28}, silica\textsuperscript{29} and latex particles,\textsuperscript{30} all of which have been used as colloid probes.

The use of AFM for studying friction is possible as the position sensitive photodiodes are divided into four elements. Torsion of the cantilever as it is moved across the surface from regions of low to high friction result in horizontal deflection of the reflected laser beam on the detector and a map of surface friction can be generated in the same way as a conventional (vertical) deflection image. This can be useful for probing the film properties and for identification of the film structure. For friction analysis, the AFM can present the data from the trace and retrace of the sample under the tip in an oscilloscope format. The separation between the trace and retrace lines provide an indication of the amount of friction between the two surfaces with, for example, no friction resulting in an overlay of both trace and retrace scans. Such lateral force microscopy (LFM) has been used for the study of both bare surfaces\textsuperscript{31} and model lubricated systems\textsuperscript{32}.

1.1.4. Surface composition

Surfactant adsorption is often measured using solution depletion methods. The interfacial adsorption of surfactants is determined by measuring the decrease in surfactant concentration in free solution with exposure to a solid of known surface area\textsuperscript{33}. The surface excess is calculated according to

$$\Gamma = \frac{(C_{\text{tot}} - C_{eq}) V}{mA}$$

(1.5)

where $C_{\text{tot}}$ and $C_{eq}$ are the initial total and equilibrium concentrations of surfactant, respectively, $V$ is the solution volume, $m$ is the mass of adsorbent and $A$ is the specific
surface area of the adsorbent. Typically this is measured as a function of initial surfactant concentration from which an adsorption isotherm is constructed. These isotherms generally show a gradual increase in adsorption density at low concentrations then a rapid increase towards the cmc, followed by a plateau. The surface structure at this plateau was traditionally inferred as a vertical monolayer for hydrophobic substrates and a bilayer for hydrophilic substrates. Some evidence in support of surface micelles at surface saturation, however, has been shown when adsorption isotherms have been compared between systems. For example the saturation adsorption density on silica of tetradecylpyridinium was found to increase six fold when the counterion was changed from chloride (weakly binding) to salicylate (strongly binding). This is inconsistent with a bilayer film but very consistent with interfacial aggregate growth with a more strongly binding counterion since similar increases in aggregation number are observed in solution.

1.2 Surfactants on hydrophobic surfaces

1.2.1 Anisotropic hydrophobic surfaces.

The first AFM examination on self-assembly was the adsorbed morphology of surfactants on the cleavage plane of graphite. The basal plane of graphite consists of sheets of hexagonal rings of carbon atoms with a threefold rotational axis of symmetry and is useful for AFM imaging because it is atomically smooth. The cationic surfactant cetyltrimethylammonium bromide (CTAB – Table 1.1), which forms spherical micelles in solution, was the first surfactant studied by AFM and was found to adsorb to the surface as hemicylinders. Further examination with other cationic, anionic, zwitterionic and non-ionic surfactants similarly revealed an adsorbed structure of very straight, parallel hemicylinders (Figure 1.2a). The axis
of each adsorbed hemi-cylinder is aligned perpendicular to one of the graphite lattice axes.

<table>
<thead>
<tr>
<th>Charge / type</th>
<th>Example</th>
<th>Structure</th>
</tr>
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</table>
| Cationic      | Dodecyltrimethylammonium bromide (DTAB), tetradeccyltrimethylammonium bromide (TTAB), cetyltrimethylammonium bromide (CTAB). | ![Structure of DTAB](image)
|               | Dodecylpyridinium bromide (DPC) | ![Structure of DPC](image) |
|               | Didodecyldimethylammonium bromide (DDAB) | ![Structure of DDAB](image) |
| Anionic       | Sodium dodecyl sulfate (SDS) | ![Structure of SDS](image) |
| Zwitterionic  | (Dodecyl(dimethylammonio)propyl)anesulfonate (DDAPS) | ![Structure of DDAPS](image) |
| Nonionic      | Dodecylpentaethylene glycol ($C_{12}E_5$) | $CH_3(CH_2)_{11}O(CH_2)O(CH_2)O(CH_2)O(CH_2)O(CH_2)OH$

Table 1.1: Representative examples of types of surfactants discussed in this thesis.

The graphite crystal lattice and resulting anisotropy of its interactions with linear alkyl chains was found to be the sole defining feature in aggregate morphology for a large variety of surfactants with a range of molecular geometries. The interaction between the substrate and alkyl chain via hydrophobic and van der Waals interactions orient the alkyl chain on a zigzag line connecting nearest-neighbour carbon atoms on graphite. Scanning tunnelling microscopy (STM) images of deposited alkanes and alcohols and cationic surfactants show the
commensurability between the molecular adsorbate and substrate lattice with these molecules organising into lamellae with alkyl chains oriented parallel to a lattice axis of the graphite basal plane. The alkyl chain adsorbs in an all trans configuration with two methylene units fitting within one hexagonal ring of the lattice. This head to head and tail to tail arrangement templates the subsequent surfactant layer into very straight hemicylinders. Surfactants with 12 or more carbon atoms in the tail group, all form hemicylindrical aggregates on graphite regardless of headgroup chemistry.

![Figure 1.2](image)

**Figure 1.2:** 200x200 nm deflection images showing two morphologies observed on graphite, (a) 0.02 mM (2 cmc) C\textsubscript{14}E\textsubscript{6} adsorbed film of straight, parallel hemicylinders. The inset shows a 2 x 2 nm filtered contact mode friction image of the underlying graphite crystal lattice. (b) C\textsubscript{12}E\textsubscript{3} forms vertical bilayers.

Similar structures have also been reported for the hydrophobic cleavage plane of MoS\textsubscript{2} despite the marked difference in lattice symmetry, spacing and surface chemistry from graphite.

Surfactants that do not assemble into hemicylindrical aggregates on graphite are either double chained surfactants or those only forming a lamellar mesophase in solution, surfactants with 10 or fewer carbon atoms in the tailgroup, and those
surfactants with very large headgroups. Double chained surfactants such as didodecyldimethylammonium bromide (di-C12DAB)\(^{44}\) and surfactants such as dodecyltriethylene glycol (C12E3)\(^ {39}\) which form only lamellar mesophases in solution aggregate into periodic stripes with a larger spacing than the hemicylinders described above (Figure 1.2b). These are described as vertical bilayers oriented normal to the graphite surface.

Surfactants with fewer than 10 carbons in their alkyl chain form flat, laterally unstructured monolayers on graphite.\(^ {45}\) An exception to this are fluorinated surfactants with hemicylinders observed on graphite at chain lengths of 8 CF\(_2\) units\(^ {46}\) however this is consistent with the higher rigidity and hydrophobicity of fluorinated chains.

Polydispersity within the alkyl chain length of non-ionic surfactants was found not to inhibit the formation of hemicylinders, however chain branching and / or the presence of a phenyl ring hindered strong registry with the graphite lattice, again resulting in a featureless monolayer\(^ {47}\).

1.2.2 **Isotropic hydrophobic surfaces.**

Isotropic, non-crystalline hydrophobic surfaces behave very differently to graphite or MoS\(_2\) as substrates for surfactant adsorption. One of the earliest studies involved the preparation of an isotropic hydrophobic surface through the reaction of hydrophilic silica with diethyloctylchlorosilane (DEOS)\(^ {45}\). A range of non-ionic surfactants with headgroup sizes from 5 to 8 ethylene oxide units and alkyl chain lengths between 10 to 16 carbons all displayed a featureless structure consistent with formation of a simple monolayer. This was rationalised as the result of minimisation
of contact with the aqueous environment on the hydrophobic substrate inducing an adsorbed structure which maximised aqueous contact with the surfactant headgroups.

A more recent study examined the structure of non-ionic surfactants adsorbed to a gold surface coated with self-assembled monolayers of hexadecanethiol and \( \omega \)-hydroxyhexadecanethiol. The systematic variation in hydrophobicity of the surface allowed an examination into the effect on surface structure\(^{48} \). At the completely hydrophilic surface and when 25\% and 50\% coated in CH\(_3\) terminal thiol, the non-ionic surfactant C\(_{12}\)E\(_8\) formed spherical aggregates. When 100\% coated, the layer was again featureless and interpreted to be a monolayer.

The possibility of the surfactant alkyl chain inserting into the fluid or “hairy” hydrophobic layer has been raised and a study examining the adsorbed morphology on trimethylchlorosilane - modified silica surfaces undertaken.\(^{49} \) The resulting surface was hydrophobic yet rigid, preventing insertion of the alkyl chain and single chained non-ionic, anionic and cationic surfactants all formed globular aggregates at the surface, while double - chained (lamellar forming) surfactants adsorbed as a monolayer.

A wide range of adsorbed nanostructures arise on hydrophobic surfaces. However, the precise structural features of hydrophobic surfaces that determine adsorbed layer morphology have yet to be fully resolved.

### 1.3 Surfactants on hydrophilic surfaces

There are a very large number of hydrophilic surfaces suitable for surfactant adsorption. Provided the roughness of the underlying substrate is not prohibitive to imaging, surfaces that are not atomically smooth can, and have been studied by AFM. The most common surfaces studied have been clays such as mica, and mineral oxide
surfaces such as silica and quartz. Figure 1.3 displays AFM deflection images of a bare quartz surface (Figure 1.3a), silica surface (Figure 1.3b) and mica surface (Figure 1.3c) for comparison.

![AFM deflection images](image)

**Figure 1.3:** AFM deflection images (5µm x 5µm) of (a) a bare quartz surface, (b) bare silica surface and (c) bare mica surface.

### 1.3.1 Mica

Most clay minerals possess a layered structure of parallel alumino-silicate sheets of primarily Si, Al, O, OH, Fe and Mg. Within each layer, atoms are arranged in a hexagonal symmetry and are often not electrically neutral due to isomorphous replacement of atoms. For example in muscovite mica replacement of Si by Al produces a negatively charged layer counterbalanced by positive potassium ions occupying positions between the layers. In aqueous solution, the area per charge on the surface is 0.48 nm², which in the bulk mineral is neutralised by potassium ions. The main advantage of using mica as a substrate for AFM imaging is the ease of preparing large molecularly smooth areas and the majority of adsorbed layer images have been carried out on muscovite mica. However, it has been shown that results on muscovite mica cannot be generalised even to other clays, with different morphologies observed on kaolinite, synthetic micas and mineral oxides under the same solution conditions.
In their pioneering study of soft-contact imaging, Manne and Gaub\textsuperscript{36} found that tetradecyltrimethylammonium bromide (TTAB) adsorbed to mica as full cylinders whereas didodecyldimethylammonium bromide (di-C\textsubscript{12}DAB) forms a featureless bilayer. Aspects of cationic surfactants adsorption to mica have been studied including the effect of alkyl chain length and type, counterion type, headgroup structure and salt concentration. The influence of these factors on aggregate morphology at the interface have been related to behaviour in the bulk via the surfactant packing parameter, a geometric model developed by Israelachvili et al and others to describe bulk micellar structures\textsuperscript{52}.

The packing parameter\textsuperscript{52} describes the average shape of a surfactant molecule in an aggregate (eg. a micelle or vesicle) as a ratio of the volume of the hydrophobic chain ($v$), the length of the hydrophobic chain ($l_c$) and the optimal area of the headgroup ($a_0$).

$$g = \frac{v}{a_0 l_c}$$

(1.6)

This approach predicts that surfactants with a packing parameter less than 1/3 will yield spherical aggregates, between 1/3 and 1/2 rodlike micelles and above 1/2 bilayers.

The length and volume of a hydrophobic saturated alkyl chain can be calculated using\textsuperscript{53}:

$$l_c = 1.54 + 1.265 n_c$$

(1.7)

$$v = 27.5 + 26.9 n_c$$

(1.8)
where \( n_c \) is the number of carbons in the alkyl chain.

The optimal headgroup area is the only parameter influenced by most solution conditions, as it is determined from a balance of attractive and repulsive interfacial forces. Steric and electrostatic repulsion between the headgroups is countered by the hydrophobic attraction amongst the alkyl chains.

A more strongly bound counterion reduces the effective headgroup area and therefore increases the packing parameter and induces a change in solution aggregate morphology from spheres to rods. This trend is also evident in adsorbed DTAC and DTAB films, spheres and rods, respectively\(^{50}\). Addition of salicylate ions results in the formation of long, entangled wormlike micelles in solution and is observed to induce cylinders on the surface even for sphere forming surfactants with large headgroups.\(^{50}\)

The effect of physical headgroup size has been studied through substitution of trimethylammonium headgroups with larger moieties such as triethyl and tripropyl. In all cases this was found to increase film curvature as predicted by the packing parameter.\(^{50}\) The use of gemini surfactants (two single chained surfactants whose headgroups are joined covalently by a spacer of variable length) to systematically control monomer geometry similarly revealed a dependence of film structure with bulk behaviour. Asymmetric monomers with large headgroups formed globular aggregates arranged in a hexagonal pattern, symmetric geminis with spacer groups between 4 and 6 units formed cylinders and those with short spacers of 2 units formed bilayers\(^{54}\). Representative AFM images of aggregated films of spherical, cylindrical and bilayer morphologies on mica are shown in Figure 1.4.
Figure 1.4: AFM deflection images of a (a) featureless bilayer formed by the double chained surfactant di-C$_{12}$DAB, (b) parallel rods by the single chained DTAB and (c) hexagonally arranged globules formed by TTeAB on a mica surface. Insets show the Fourier transforms of the images showing repeat spacings and spatial arrangements of cylindrical and globular aggregates.

In solution, addition of salt to ionic surfactants reduces aggregate curvature by reducing coulombic repulsion between the charged headgroups$^{55,56}$. This reduces the effective headgroup size allowing it to pack into a less curved structure. On a surface, this is observed when a counterion that has a greater affinity for the surfactant cation is used, for example addition of a bromide salt to a quaternary ammonium chloride surfactant.

However, the effect of rival cations for the mica surface can be important and has been observed to reverse the curvature sequence to that in solution. For example, a CTAB bilayer can be increased in curvature to rods and then globules with addition of Li$^+$, K$^+$ or Cs$^+$. Further, the efficiency with which the film increased in curvature was influenced by the softness of the cation, with Cs$^+$ imparting the greatest effect.$^{57}$ The influence of rival cations, H$^+$, K$^+$ and N(CH$_2$CH$_3$)$_4$$^+$ on the aggregate structure of a CTAB film has also been studied. Cations with higher binding affinities for the mica surface were found to more effectively increase film curvature$^{58}$. Both of these studies highlight the influence of the substrate on adsorbed morphologies.
Aromatic molecules and counterions have a strong influence on bulk and adsorbed quaternary ammonium surfactant morphology \(^{59}\). Solubilisation of uncharged aromatic solutes lowers film curvature from globules to rods by preferentially adsorbing in the palisade layer of the aggregate.

In the packing parameter model, increasing alkyl chain length increases both \(v\) and \(l_c\). In the bulk this results in a net increase in the packing parameter and a reduction in aggregate curvature. This is also observed on mica when adsorbed spherical aggregates of dodecyltrimethylammonium chloride (DTAC) are compared with the cylinders produced by tetradecyltrimethylammonium chloride (TTAC)\(^{50}\). Likewise, surfactants with two alkyl chains eg. di-C\(_{12}\)DAB tend to form lamellar structures in solution and are observed to form flat bilayers at the surface.

**1.3.1.1 Slow kinetics of long alkyl chained surfactants.**

For surfactants with alkyl chains C\(_{16}\) and longer the time required for equilibrium adsorbed structures to fully form can exceed 24 hours, and this is largely due to slow ion exchange kinetics on the mica surface. For CTAB at concentrations above its cmc this results in the formation first of cylinders and then a bilayer after 24 hours.\(^{58}\) Surfactants with C\(_{18}\) and C\(_{20}\) alkyl chains also possess slow ion exchange kinetics and form a bilayer at equilibrium without forming cylinders as an intermediate. Instead the mechanism of growth is via the nucleation and expansion of bilayer patches over time\(^{60-62}\).

AFM studies performed on dried di-C\(_{16}\)DAB\(^{63}\) and C\(_{18}\)TAB\(^{64,62}\) films on mica, at temperatures below the gel transition and Krafft temperature respectively showed patches of monolayer of differing heights interpreted to be two types of monolayers with different packing densities. The higher region was the result of alkyl chains
oriented vertically surrounded by areas in less densely-packed monolayer in which the alkyl chains were randomly oriented.

### 1.3.2. Quartz and Silica.

The charge on most surfaces is governed by potential determining ions that chemically alter the total charge per unit area of surface. For mineral oxides such as quartz, this is caused by protonation and deprotonation of surface hydroxyl groups as shown below:

\[
\begin{align*}
\text{SiOH} + H^+ & \iff \text{SiOH}_2^+ \\
\text{SiOH} + OH^- & \iff \text{SiO}^- + H_2O
\end{align*}
\]

As silica is the most abundant material on earth its surface chemistry has been well characterised. The amphoteric hydroxyl sites are weak acids and bases therefore any one particular site may be positive, negative or neutral at a particular pH. The total surface charge is therefore determined by the relative population of each charged species at the surface. Two main silica surfaces have been used for both AFM and reflectance studies; quartz and amorphous silica. Quartz is a crystalline surface and amorphous silica is a piece of silicon which has been oxidised to form a silica layer and then hydrolysed by soaking in either water or basic solution.

The major differences between silica or quartz and mica surfaces are the difference in charge density and smoothness of the surface. A charge density of one per 20 nm² at pH 7 is expected for a silica surface whereas for mica there is one ionisable site per 0.48 nm². This influences the ability of the surfactant molecules to pack closely together, and for cationic surfactants results in less curved aggregates on mica than on silica. Non-ionic surfactants do not adsorb onto mica but can adsorb
onto silica through hydrogen bonding between the ethylene oxide headgroups and surface silanol groups\textsuperscript{65}.

A major advantage in the use of a silica substrate is the ability to use reflection techniques for examining the surface. This allows information such as adsorbed amounts and film thickness to be determined, and for the examination of adsorption kinetics.

Compared to the wealth of AFM studies performed on mica, there have been few on silica or quartz. However, as with mica, the factors that influence aggregation in solution affect structures at the silica – water interface.

Single chained quaternary ammonium surfactants form spherical\textsuperscript{66} or short rod aggregates\textsuperscript{67} up to an alkyl chain length of C\textsubscript{18}. At this chain length and above the film forms a featureless bilayer after initially forming globular aggregates\textsuperscript{60}.

The effect of counterion binding affinity has also been studied for silica surfaces both above and below the cmc (Figure 1.5). Here the binding of cations to the silica substrate is insignificant and the situation much simpler than with clays. Above the cmc, cylinders were observed by AFM for CTAB and spheres for CTAC with a correspondingly higher surface excess at the interface for the bromide surfactant measured by optical reflectometry and paralleling bulk solution behaviour\textsuperscript{67}. As bromide was a more strongly binding counterion than chloride, the effective headgroup area of the surfactant reduced and film curvature decreased from spheres to cylinders, as predicted by the packing parameter model. Below the cmc, the influence of the counterion was found to be markedly less\textsuperscript{67}. The addition of KBr or KCl increased the surface excess for both counterions at concentrations above the cmc (Figure 1.5).\textsuperscript{67} Highly polarisable anions such as S\textsubscript{2}O\textsubscript{3}\textsuperscript{2−} were found to effect a sphere to cylinder transformation on silica as the enhanced partitioning of the soft
anion to the micelle surface screens electrostatic repulsion between neighbouring headgroups (Figure 1.5c).  

**Figure 1.5**: 300 nm x 300 nm AFM deflection images showing the adsorbed film structure of (a) 10 cmc CTAC and (b) CTAB structures on the hydrophilic silica surface. The greater binding of the Br- counterion shields headgroup repulsion and reduces the film curvature as predicted by the packing parameter model. 7c shows the transformation from a globular morphology of CTAAc to cylinders after addition of 5 mM Na$_2$S$_2$O$_3$.

The adsorption of quaternary ammonium surfactants to the quartz surface is similarly influenced by solution conditions. Spherical aggregates are observed for single chained surfactants and a featureless bilayer for double chained surfactants. AFM shows that TTAB forms globular aggregates on quartz which, on addition of NaBr, transform to cylindrical aggregates while di-C$_{12}$DAB, as expected, forms a featureless bilayer. Neutron reflectometry on these films have traditionally been modelled assuming a planar bilayer structure with patches invoked when coverage is less than unity. Recently, a new model has been developed taking into account the surface aggregate structure of the adsorbed film. Complementary AFM and neutron reflectometry has revealed an increase in fractional surface coverage with reduction in film curvature and a reduction in thickness of the film from spheres to a bilayer.
The adsorbed layer structure of adsorbed spherical TTAB and CTAB micelles on quartz are influenced by surface charge density and hence by pH. At pH 3, where the zeta potential of the surface is less than -20mV, the aggregates are further apart than at pH 11 when the zeta potential of the surface is more negative than -100mV. However despite the film containing densely packed spherical aggregates, the increased charge density was insufficient for promotion of cylindrical aggregates as observed on mica\textsuperscript{71}.

Poly(oxyethylene) non-ionic surfactants adsorb to the silica interface by hydrogen bonding between the surface silanol groups and the headgroup ether oxygens\textsuperscript{65}. Interfacial curvature is determined by the size of the headgroup radius of gyration and alkyl chain length and volume with headgroup sizes in excess of 5 ethoxy units yielding a film of adsorbed globules\textsuperscript{45}.

### 1.3.3. Other Mineral Oxide Surfaces

Other mineral oxide surfaces such as sapphire (Al\textsubscript{2}O\textsubscript{3}) and rutile (TiO\textsubscript{2}) also have hydrolysable surface sites, however their points of zero charge lie at higher pH than SiO\textsubscript{2} (p\textsubscript{H2})\textsuperscript{72}; 5-6 for rutile\textsuperscript{27} and 8 for sapphire\textsuperscript{73}. This allows facile comparison between adsorbed layer nanostructures formed by cationic and anionic surfactants. Both SDS and TTAB have been shown to form spherical micelles on the rutile surface. The spacing between aggregates depends on surface charge density (and hence pH)\textsuperscript{71} as observed on quartz. Globular aggregates of both TTAB and SDS\textsuperscript{74} and a planar bilayer for di-C\textsubscript{12}DAB were similarly observed on a sapphire crystal surface. Addition of salicylate resulted in a reduction in film curvature from spheres to cylinders as expected from solution behaviour. Neutron reflectivity showed a fractional surface coverage much less than 100% for TTAB and SDS and a
significantly higher coverage was observed for the di-C\textsubscript{12}DAB bilayer, as consistent with the AFM images\textsuperscript{74}.

Surface aggregates of TTAB on Al\textsubscript{2}O\textsubscript{3} below the cmc were also inferred from pyrene fluorescence quenching\textsuperscript{75}, which revealed a corresponding increase in aggregation number of the adsorbed micelles within this region.

When this surface was annealed at 1600\textdegree C resulting in an atomically smooth surface with a faceted terrace and step morphology, the surface behaved atypically. Over a pH range of 2 to 11, TTAB adsorbed as short cylinders which reduced in length with decrease in pH. This highlights the influence and importance of surface preparation on adsorbed structure for mineral oxide surfaces.

From AFM imaging results, it has become clear that self-assembled morphologies at the solid interface show similarities to solution self-assembled structures. A number of studies have highlighted this through systematic variation in monomer geometry. In particular variation in headgroup size and alkyl chain length within a quaternary ammonium surfactant homologous series on mica\textsuperscript{50} and the systematic control of monomer geometry via the use of gemini surfactants\textsuperscript{54}.

1.4 Mixed surfactants

Mixed surfactant systems are of both fundamental and industrial interest because of the enhanced behaviour of some mixtures compared to that of the individual components and because it is relatively easy to tune the surface film nanostructures. This synergistic behaviour is evidence of non-ideal interactions and whilst mixtures are widely used in many applications the basic processes are relatively poorly understood. Much of the theoretical effort in studying these systems, has been generated from ideal\textsuperscript{76} and regular solution theories\textsuperscript{77,78} where the departure
from ideality is quantified by an interaction parameter. More recently, molecular and thermodynamic theories\textsuperscript{79-81} have been developed which provide the potential to predict the cmc, micellar composition and aggregation number. Experimental techniques used to study mixed surfactant micellisation include static and dynamic light scattering\textsuperscript{82}, neutron scattering\textsuperscript{83-85}, NMR\textsuperscript{86}, fluorescence quenching and other techniques\textsuperscript{87}.

At the solid-solution interface mixed surfactants have traditionally been studied using solution depletion techniques. From measurements of the relative adsorption densities of both adsorbing species, surface composition and an understanding of the interaction between the surfactants and between the surfactants and the substrate has been gained\textsuperscript{88,89}. Using microcalorimetry and spectroscopy the thermodynamics of mixed surfactant adsorption have been examined and reviewed\textsuperscript{90}. More recently, the technique of neutron reflectometry has been applied to the study of mixed surfactant systems\textsuperscript{91,92} using the approach of contrast matching one of the surfactant species. This is a very powerful means of probing the adsorbed quantities of each surfactant independently.

The structure of mixed surfactant adsorbed films, however, has been less well studied. As AFM is the only technique able to provide nanoscale information about the lateral structure of the film it is an obvious choice for such studies, yet only a handful have so far been performed. One of the early AFM studies examining the effect of mixing on film curvature involved two adsorbing surfactants on mica; the zwitterionic surfactant dodecyldimethylammoniopropanesulfonate (DDAPS) preferring a spherical morphology and the cylinder forming DTAB\textsuperscript{93}. As the composition ratio was varied, film morphology transformed from long cylinders
through to short rods to globules with enrichment of the more highly curved surfactant.

The properties of di-C\textsubscript{12}DAB and DTAB mixtures on mica have also been examined using the surface force apparatus (SFA)\textsuperscript{94}. As expected, the bilayer structure of di-C\textsubscript{12}DAB at the surface displayed superior lubrication properties compared to the cylindrical morphology of DTAB. The authors found that addition of DTAB reduced the load-carrying ability of the film, which was attributed to the destabilizing effect the decrease in film packing parameter had on lubrication.

Finally, the effect of partial miscibility of the hydrophobic tail on adsorbed layer morphologies has been examined using hydrocarbon and fluorocarbon surfactant mixtures\textsuperscript{95-97}. Hydrocarbon alkylpyridinium surfactants dodecyl-, tetradecyl- and hexadecylpyridinium chloride (See Table 1.1) and tetradecyltriethylammonium chloride (TEC\textsubscript{14}Cl) were mixed with the fluorocarbon surfactant heptadecafluorodecyl-pyridinium chloride (HFD\textsubscript{e}PC) and examined using AFM and solution depletion. Surface compositions deviated substantially from that predicted by group contribution theory\textsuperscript{98,99} in the bulk. Mixing hydrocarbon surfactants produced a continuous transformation between globules and cylinders on the surface. However, addition of fluorocarbon surfactants produced a striking discontinuity in which the hydrocarbon component was excluded from the surface almost completely\textsuperscript{97}.

\textbf{1.4.1. Tethered polymers}

Diblock polyoxyethylene copolymers with hydrophobic octadecyl or polystyrene chains have recently been attached or “tethered” to DTAB\textsuperscript{100} and trimeric surfactant 12-3-12-3-12\textsuperscript{101} adsorbed films of different morphologies on mica. The
hydrophobic block is adsolubilised into the surfactant film, leaving the polyoxyethylene headgroup free in solution.

Adsorbed cylinders of DTAB were observed by AFM to gradually shorten along one axis with increasing amount of added copolymer with 50, 100 or 1300 ethoxy units, ultimately yielding globules\textsuperscript{100}. A greater mole fraction was required to completely effect the cylinder to globule transformation for a smaller number of ethylene oxide units. The surface force apparatus confirmed the inclusion of block copolymer as the force curve transformed from a purely electrostatic repulsion in the DTAB film into a steric component visible when the surfaces were separated by less than the Flory radius of gyration of the polymer headgroup\textsuperscript{100}.

The trimeric surfactant 12-3-12-3-12 forms a laterally unstructured adsorbed bilayer on mica under normal solution conditions. Incorporation of the diblock copolymer facilitated hemifusion, allowing the frictional properties of the film to be mapped\textsuperscript{101}.