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# Organization of Sodium Dodecyl Sulfate at the Graphite–Solution Interface

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The aggregated structure of sodium dodecyl sulfate (SDS) adsorbed to the graphite–solution interface has been determined. Atomic force microscopy reveals that SDS adsorbs in periodic structures when the solution concentration is in the range 2.8–81 mM. Using previously obtained adsorption isotherms, we deduce that these structures are hemicylindrical, but we are not able to determine their length. The long axes of the hemicylinders lie parallel in grains which typically extend over  $(500\text{ nm})^2$  to  $(1000\text{ nm})^2$ , but the grain size can be reduced by adsorption of other species from solution. Two basic types of grain boundaries have been identified: broad boundaries, where the periodicity of both grains continue into the boundary for several periods, and narrow boundaries, where one or both of the hemicylindrical arrays terminate within a short distance. The period within each grain decreases when the concentration of SDS or the concentration of added NaCl is increased and approaches the diameter of bulk micelles at high concentration. In NaCl solutions, the period is proportional to the solution Debye length. We propose that this is a result of a decrease in interaggregate spacing rather than a decrease in aggregate size. Using a simple geometric argument, we suggest that the curvature of surfactant aggregates on hydrophobic surfaces will usually be lower than that of aggregates in bulk solution with which they are in equilibrium.

## Introduction

Surfactant adsorption at interfaces has been widely studied because of its importance in a number of processes: for example, detergency, froth flotation, lubrication, and colloid stabilization. Of fundamental importance is the determination of the amount adsorbed (the adsorption isotherm) and its relation to the properties of the surfactant, the native surface, and the altered surface. Isotherms have been widely investigated and used to infer aggregation at surfaces,<sup>1</sup> but the lack of suitable tools has prevented direct investigation of the *structure* of adsorbed surfactant aggregates. Recently, Manne *et al.*<sup>2</sup> have demonstrated that an atomic force microscope (AFM) can be used to image surfactant aggregates at surfaces. The key to this approach is to use a delicate force which is insufficient to displace the surfactant but has sufficient gradient, stability, and proximity to discriminate surface structures. This set of conditions is often met by surfaces coated in surfactant<sup>3</sup> because of the presence of double-layer and hydration forces and the energy of adsorption of the surfactant. Manne *et al.*<sup>2</sup> used this technique to provide the first microscopic evidence of surfactant aggregation at a surface in the study of hexadecyltrimethylammonium bromide on graphite. In a subsequent study by Manne and Gaub,<sup>4</sup> the aggregation of quaternary ammonium surfactants on both hydrophobic and hydrophilic substrates was investigated. The observed structures are attributed to a compromise between the geometrical considerations used for bulk assembly of surfactants and specific surfactant–surface interactions. A double-chain surfactant was found to form a homogeneous layer at a surface, while the analogous single-chain surfactant formed a periodic structure.

The adsorption of sodium dodecyl sulfate (SDS) to a graphitic substance (heat-treated carbon black or “graphon”) has been extensively studied.<sup>5,6</sup> Greenwood *et al.*<sup>5</sup> showed that adsorption was first measurable at about 1 mM SDS, reached a plateau at approximately half maximum density from about 2 to 4 mM, and then reached a maximum at about 7 mM SDS. Similar

results were obtained by Zettlemoyer.<sup>6</sup> Greenwood *et al.* attributed the lower and higher density regions to SDS lying parallel and perpendicular to the graphon, respectively, and Zettlemoyer attributed the increase in density between the plateaus to a progressive decrease in the proportion of hydrocarbon tail lying parallel to the surface.

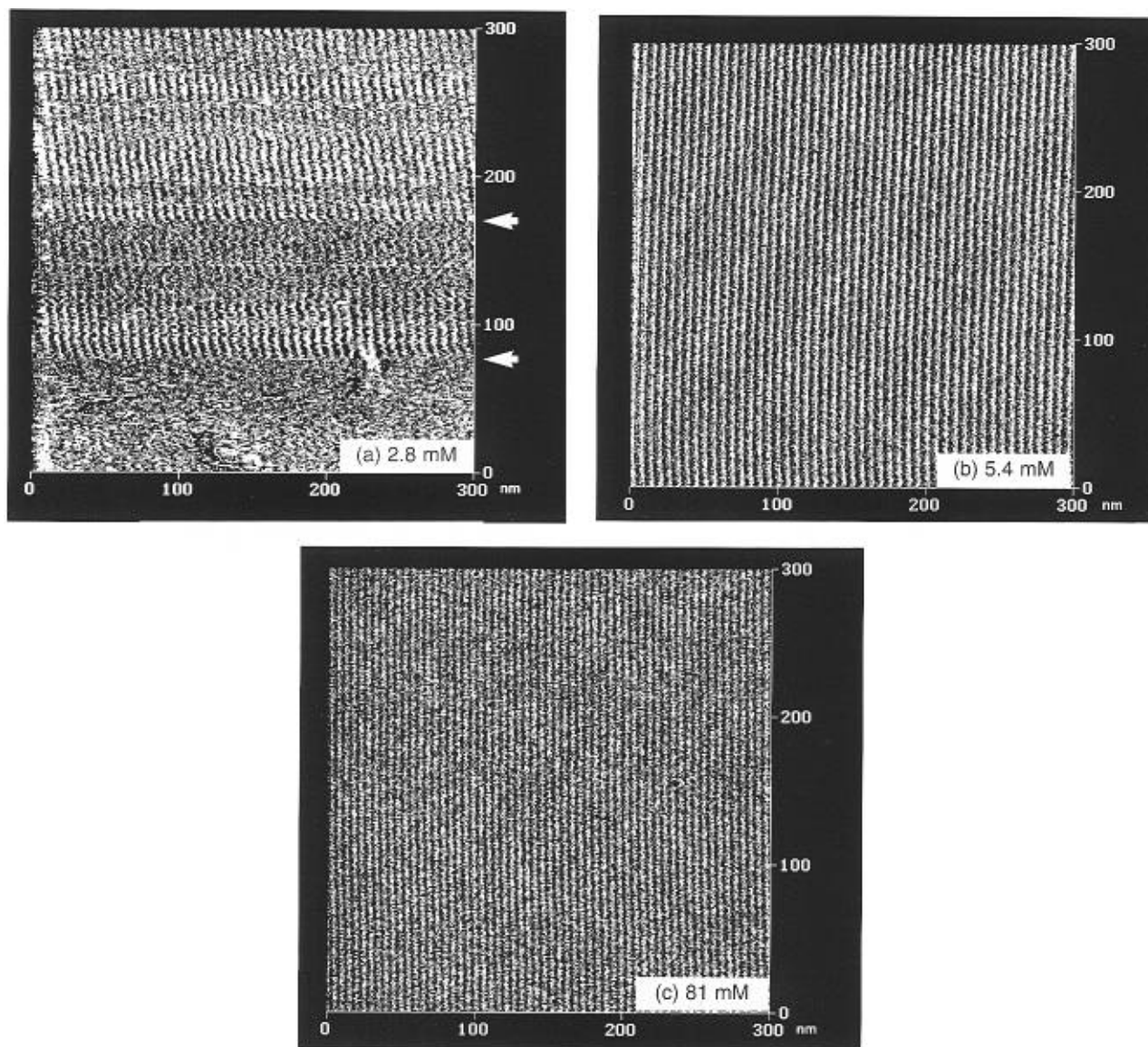
In this work we have measured the structure of adsorbed SDS on graphite near the critical micelle concentration, cmc (8.1 mM).<sup>7</sup> We do not observe any structures in the dilute plateau region. At higher concentrations we observe aligned hemicylinders of undetermined length. We find that, in the region of increasing SDS surface density, the morphology remains apparently unchanged, but the distance between neighboring aggregates decreases.

## Experimental Section

**Sample Preparation.** Water was prepared by distillation and then passage through a Milli-Q RG system consisting of charcoal filters, ion-exchange media, and a  $0.2\text{ }\mu\text{m}$  filter. The resulting water has a conductivity of  $18\text{ M}\Omega\text{ cm}^{-1}$  and a surface tension of  $72.4\text{ mJ m}^{-2}$  at  $22.0\text{ }^\circ\text{C}$ . Sodium dodecyl sulfate (SDS) was obtained from BDH Chemicals (Poole, U.K.), 98% pure, a mixture of primary sulfates, chiefly C12. It was recrystallized from water. The result of this recrystallization was to increase the concentration at which adsorption to graphite occurred. Analytical grade sodium chloride, obtained from Ajax Chemicals, was roasted at  $500\text{ }^\circ\text{C}$  for 12 h to remove organic material. Adhesive tape was used to cleave a fresh sample of graphite for each experiment from a pyrolytic graphite monochromator grade ZYH manufactured by Union Carbide. The advancing and receding contact angles of water on the freshly cleaved graphite were  $86 \pm 5^\circ$  and  $78 \pm 5^\circ$ , respectively.

**Microscopy.** Images were captured using a Nanoscope III AFM (Digital Instruments, CA) using silicon ultralevers (Park Scientific, CA) with nominal spring constants of  $0.07\text{ N m}^{-1}$ . The ultralevers were irradiated for 40 min ( $\sim 9\text{ mW/cm}^2$  @  $253.7\text{ nm}$ ) in a laminar flow cabinet before use. The ultralevers were generally used for several experiments, but multiple

<sup>®</sup> Abstract published in *Advance ACS Abstracts*, January 1, 1996.



**Figure 1.** AFM images showing the one-dimensional periodicity of adsorbed SDS on graphite in aqueous SDS solutions. At 2.8 mM SDS, the range of force over which the structures were observed was very small ( $\sim 0.1$  nN). The arrows indicate points where it was necessary to change the setpoint during imaging in order to achieve a force for which the structures were resolved. Changes were made because the drift in the absolute value of zero force moved our applied force out of the appropriate range. At higher concentrations (e.g. 5.4 and 81 mM), it was not necessary to alter the setpoint during an image since the structures were visible over a larger range of force.

radiation treatments gave less satisfactory results than singly irradiated ultralevers. All images presented are deflection images (showing the error in the feedback signal) with integral and proportional gains of between 1 and 2 and scan rates of 10 Hz. No filtering of images was performed other than that inherent in the feedback loop. Distances in the lateral dimensions were calibrated by imaging a  $1\ \mu\text{m}$  standard grid. All measurements were performed in the range  $25 \pm 2\ ^\circ\text{C}$ , which is above the Krafft temperature of our SDS solutions.

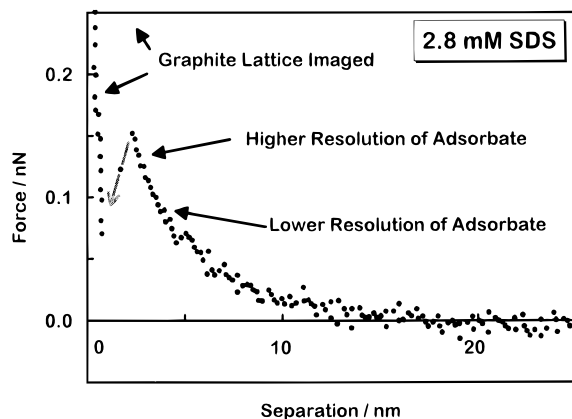
Before the images were captured the sample was left to equilibrate in solution for at least 30 min, and then the force was measured as a function of separation between the probe and sample. Imaging was then performed at a force which was insufficient to observe the graphite lattice but still had sufficient gradient to obtain high resolution of the adsorbed surfactant aggregates.<sup>2</sup>

Most images were collected after waiting between 1 and 2 h after changing solutions. In the intervening period, the orientation of grains depended on the direction of slow scan direction ("up" vs "down" images). Consistency of grain direction was obtained over the whole sample after this period, indicating that it was not a function of pre-scanning a particular region.

## Results and Analysis

**General Features of Aggregation and Imaging.** SDS adsorbed to graphite forms periodic structures above a bulk SDS concentration of 2.8 mM ( $0.35 \times \text{cmc}$ ). We will use the term surface aggregation concentration (sac) to describe the concentration above which periodic structures were observed by AFM. These structures appear as long parallel stripes as shown in Figure 1. The structures are stable for long periods of time (at least 3 days) and form in less than 15 min. The structure is a function of concentration, but is independent of the previous surfactant concentration. When older surfactant solutions are used ( $>2$  weeks), on initial adsorption the periodicity is greater than that for fresh solutions, but decreases with time. This may result from contamination by the hydrolysis product, 1-dodecanol.

In AFM the contrast occurs because of variations in force between the tip and sample, so it is necessary to understand this force in order to interpret images. Figure 2 shows an example of the measured force on a silicon tip approaching graphite in a 2.8 mM SDS solution. Zero separation is defined to be where there was a very high gradient in force and where



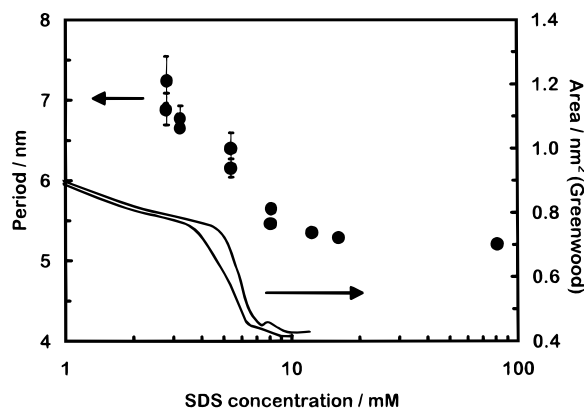
**Figure 2.** Normal force as a function of separation between a silicon ultralever and a freshly cleaved graphite surface in 2.8 mM SDS. As the tip approaches the surface, the resolution of adsorbed species increases. At about 1.8 nm separation, there is a discontinuity due to mechanical instability in the cantilever spring (shown by the light arrow) beyond which the graphite surface is resolved.

the graphite lattice could be imaged. As the tip approaches the surface, the force increases exponentially, consistent with a double-layer force, and then reaches a maximum several nanometers from zero separation. Near the maximum, there may also be contribution from steric, hydration, and protrusion forces<sup>8</sup> and the energy to desorb the surfactant. When the tip is pushed toward the sample from this position, it moves rapidly toward the graphite and then a high-gradient repulsion is experienced. The periodic structures shown in Figure 1 were observed when the tip was positioned at a slightly greater separation than where the maximum force occurred. The greatest contrast was obtained closest to the maximum in force, i.e. where the force gradient was greatest in magnitude and the tip was closer to the graphite, and presumably very close to the surfactant structures.

At higher concentrations, the double-layer force decayed more quickly, and the maximum in force before touching the graphite occurred at a higher force and was less obvious. Frequently, the structures were also visible at forces above which the surfactant is displaced when the tip moves normal to the graphite surface. This implies that the lateral motion stabilizes the surfactant between the graphite and the tip.<sup>9</sup> The contrast improved with concentration, probably because a shorter solution Debye length and an increased energy for surfactant desorption allowed imaging at higher force gradients.

The measured period of adsorbed structures was found to be a strong function of scan angle: the period increased as the fast scan direction was made more parallel to the long axis of the structures. This was observed independent of the absolute orientation of the adsorbed structures. To obtain self-consistent results, all measurements of period were made on images obtained while scanning perpendicular to the long axes. Using this criterion, structures in grains of all absolute orientations gave the same period for a given solution condition.

**Structure of Adsorbed SDS Aggregates.** The images in Figure 1 show that the period of adsorbed structures decreases as the SDS concentration increases. This is shown more clearly in Figure 3 for a range of SDS concentrations. The observed equilibrium spacing is independent of whether the previous solution concentration was more or less dilute, but the process of increasing the spacing (by diluting the solution) was slower, typically requiring several hours. The error bars indicate the full range of measured values and are greater for the lower surfactant concentrations because the aggregates were more difficult to image. Figure 3 also shows the adsorption



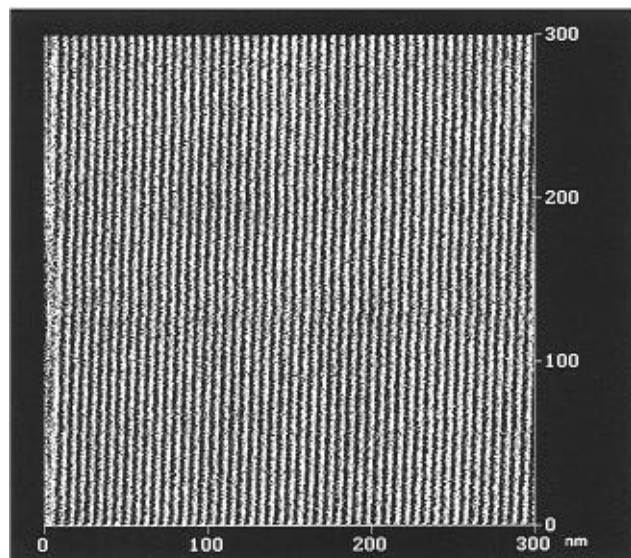
**Figure 3.** Effect of SDS concentration on adsorbate periodicity. The filled circles show data from AFM measurements, and the lines show the area per molecule determined by Greenwood *et al.*<sup>5</sup> For the AFM measurements, each point is the average of at least three measurements on each of at least three different areas of graphite, and the error range indicates the difference between the maximum and minimum values obtained. (The range is not shown when it falls within the symbol size.) No periodic structures were observed at or below 1.6 mM.

isotherm for SDS on graphon measured by Greenwood *et al.*<sup>5</sup> Graphon is a graphitic material made by heat treatment of carbon black. The AFM measurements show a decrease in aggregate period over the same concentration range as the increase in adsorption density.

One of the aims of this work was to determine the shape of adsorbed SDS aggregates. Using AFM, we have found that the force above a graphite surface undulates in a periodic fashion in a direction parallel to the graphite–solution interface. Determination of the shape of the aggregates also requires measurement of the height of these undulations. Variation in measured height across an aggregate during imaging was typically about 0.1–0.2 nm, but this is not very informative because the values of the height were a function not only of the feedback parameters and scanning velocity (as expected) but also of the imaging force. This is because imaging was not performed in a region of constant normal-force gradient; that is, traces of different but constant force do not show the same contrast. Not imaging in hard-contact mode has the advantage of allowing discrimination on the basis of chemistry, but does not produce a single value for the size (height) of observed features. In addition (for all AFM images) resolution in vertical height is dependent on the ability of the tip to access the low points between objects. We do not know the shape of our tip on the nanometer scale, but we would expect that features are actually more curved than indicated by the microscope.

An alternate procedure for determining the height of the adsorbed structure is to measure the displacement of the tip when the force is increased from a value where the periodic structures are observed to where the graphite lattice is observed. For 2.8 mM SDS this displacement was in the range  $1.7 \pm 0.5$  nm (e.g. 1.8 nm in Figure 2). Accurate interpretation of this value is made more difficult because the magnitude of the displacement is dependent on both the total force and force gradient between the tip and sample, but the height of the aggregate is only one contribution to this force.

To determine the shape of the adsorbed structure, it is also useful to quantitatively compare the data presented here to the adsorption isotherm of SDS on graphon measured by Greenwood *et al.*<sup>5</sup> To convert their values of area density to our periodicity requires an estimate of the width of a hydrocarbon chain. The *minimum* width is the van der Waals radius of a hydrocarbon chain, approximately 0.6 nm. If we consider the highest concentration in Figure 3, the period is 5.2 nm, so that



**Figure 4.** Structure of adsorbed surfactant in 2.8 mM SDS and 20 mM NaCl. The SDS concentration is the same as that in Figure 1a, but the adsorbates are much more clearly resolved and the period is smaller.

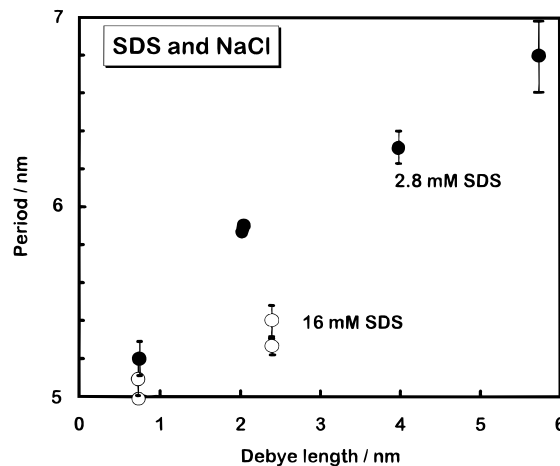
a section of aggregate one chain wide covers an area of about  $3 \text{ nm}^2$ . Greenwood *et al.*'s data at the same concentration indicates that the surfactant occupies  $0.42 \text{ nm}^2/\text{molecule}$ . Thus, there are *at least* seven molecules in the cross section. This is not consistent with the hydrocarbon chains of all the surfactant molecules lying parallel to the surface in a two-dimensional array.

To summarize, four pieces of data have been obtained: the force above the surface oscillates in a periodic fashion parallel to the graphite surface; the adsorbed structures are about 1.7 nm high; there are about seven molecules per period in a cross section; there is a repulsive exponential force normal to the adsorbate surface. The structure which best fits these data is an array of hemicylindrical adsorbates coated in surfactant head groups. (Our value of 5.2 nm for the periodicity of aggregates in 81 mM SDS is similar to the micellar diameter, 5.06 nm (100 mM), measured by small angle neutron scattering.<sup>10</sup>)

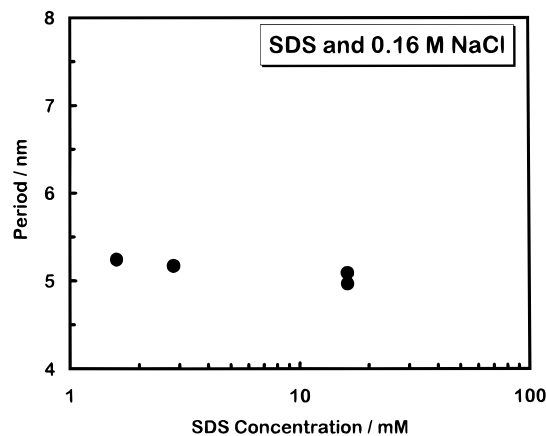
It should be noted that a single value for the number of SDS molecules per cross section cannot be used to transform all of the adsorption isotherms to fit the AFM data. As the concentration of SDS decreases it is necessary to invoke a greater width per chain and/or a smaller number of molecules in the aggregate cross section. For example, if we assume that the width of the chain is the same at 81 and 2.8 mM, then the number of molecules in the cross-section decreases from about 7 to about 5 over the same concentration range. This is consistent with a greater degree of repulsion between the charged head groups and the smaller aggregation numbers and micelle sizes observed in bulk.<sup>10</sup>

One question remaining is whether the observed decrease in periodicity is due to a decrease in aggregate size or to a decrease in interaggregate spacing. As the SDS concentration is increased, there is increased shielding of head group charges, so it is expected that the curvature of the aggregate would *decrease*, leading to an *increase* in aggregate period. This strongly suggests that on increasing the surfactant concentration, the aggregates are moving closer together rather than decreasing in diameter.

**Effect of Ionic Strength on Aggregate Spacing.** To better isolate the influence of ionic strength, we have measured the period of the adsorbed structure in 2.8 mM SDS as a function of NaCl concentration. Figure 4 shows an example of these structures (in 20 mM NaCl), and Figure 5 is a plot of the period



**Figure 5.** Effect of NaCl on adsorbate periodicity. The filled circles show the change in period for 2.8 mM SDS solutions. There is an approximately linear relationship between period and Debye length (and also with  $\log[\text{concentration}]$ ). Some data for 16 mM SDS (open circles) are shown on the same figure.



**Figure 6.** Effect of SDS concentration on interaggregate spacing at constant high ionic strength, 0.16 M NaCl. The period is smaller than for pure surfactant solutions (Figure 3) at the same concentration, and the aggregates are visible at a lower surfactant concentration.

as a function of solution Debye length. The period decreases approximately linearly with Debye length for the conditions examined. This provides strong evidence that, for this system, the period is controlled by charge–charge interactions between aggregates rather than by changes in size of the aggregates. As stated above, one would expect that the aggregates would become more curved at lower ionic strength, so the diameter would decrease. A plot of interaggregate spacing as a function of Debye length would thus have a slightly increased slope compared to Figure 5.

**Effect of Ionic Strength on Surface Aggregation Concentration.** Figure 6 shows the measured adsorbate period as a function of SDS concentration in 0.16 M NaCl. Compared to the data in Figure 3 for surfactant-only solutions, the period is smaller and decreases only marginally with SDS concentration. In 0.16 M NaCl, the structures are imaged at lower surfactant concentration (1.6 mM SDS). It is well-known that the cmc of charged surfactants is reduced in the presence of salt,<sup>11</sup> and in particular it is known that the cmc of SDS is reduced to about 1 mM in 0.16 M NaCl.<sup>7</sup> This is because the salt reduces the repulsive interactions between the negatively charged head groups which oppose aggregation. We have now observed that the surface aggregation concentration (sac) decreases in the presence of salt. Screening of charge–charge interactions *within* an aggregate should be a major reason for this. The data in Figure 5 show that charge screening has a major effect on the

period of aggregates, so screening of the repulsive interactions *between* surface aggregates should also lower the sac. The spacing between aggregates on the surface is much less than between bulk aggregates at the cmc, so repulsive aggregate–aggregate interactions will have a larger effect on the sac than on the cmc.

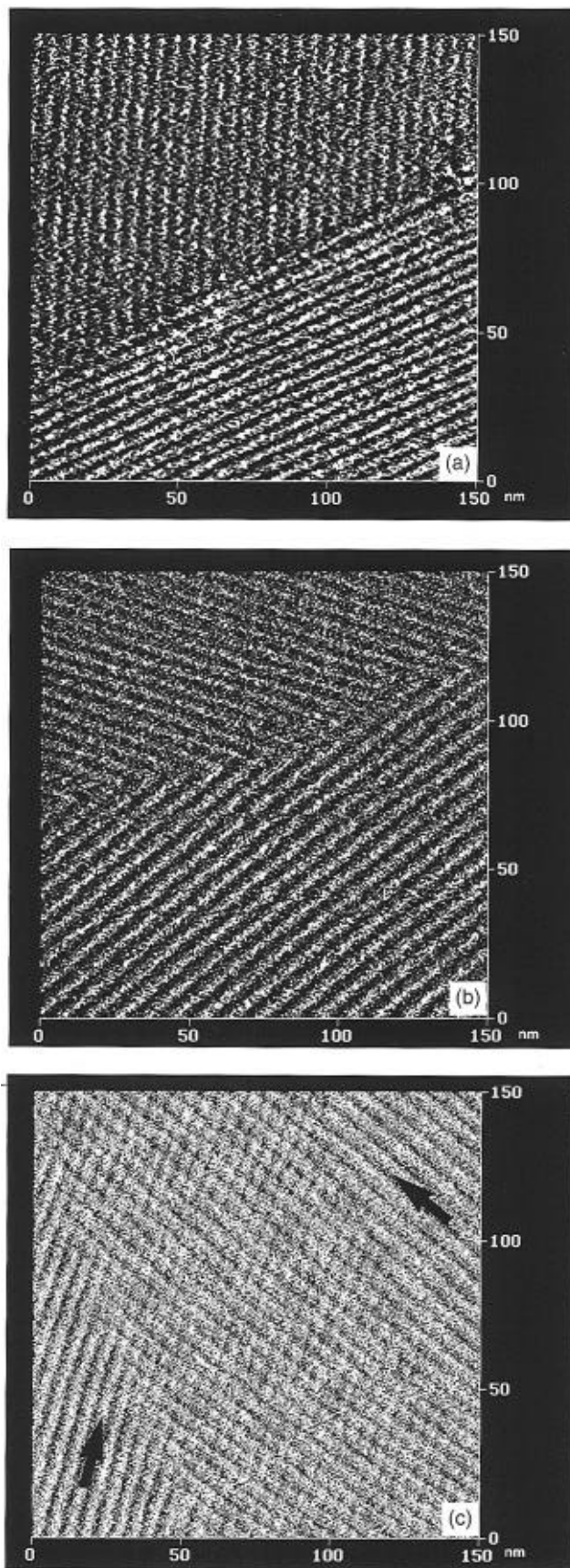
The aggregate period decreases only a small amount from 5.2 nm for the SDS concentrations measured. Since the cmc at this salt concentration is 1 mM, all the measurements at high salt (Figure 6) are above the cmc. For SDS-only solutions, the spacing also decreased only a small amount above the cmc (Figure 3), but at this stage we do not have enough data to determine whether there is a general relationship between the CMC and the period of adsorbed surfactant structures. We do observe that the presence of NaCl facilitated observation of structures at any surfactant concentration.

**Grain Boundaries.** Periodic surfactant structures were found to cover the entire surface of the graphite, but the direction of the long axis of the “hemicylinders” varied from region to region across the surface. The long axis was often parallel to a step in the graphite, so the area over which the axis pointed in the same direction, “a grain”, was dependent on the step density. A typical grain size for our experiments was  $(500\text{ nm})^2$ – $(1000\text{ nm})^2$ . A majority of boundaries were associated with steps in the graphite surface, but not every step contained a grain boundary, and not every boundary was located at a step. (Since all the graphite steps are not parallel, some grain boundaries must occur away from steps.) Further, we could not find a strong correlation between the angle at which a grain met a step and the probability of the grain continuing across the step.

Some examples of grain boundaries are shown in Figure 7, and they can be divided into two classes: those in which the boundaries occupy roughly one period and those in which the boundary extends over several periods. Figure 7a,b shows thin boundaries. For the boundary shown in Figure 7a, structures from one grain terminate at the boundary, while in Figure 7b structures from both grains either terminate or merge at the boundary. Figure 7c shows a broad boundary in which the periodicity of both neighboring grains is continued for several periods. The result is a two-dimensionally ordered array of hemimicelle-like structures. Similar structures have been observed for hexadecyltrimethylammonium bromide on graphite.<sup>2</sup>

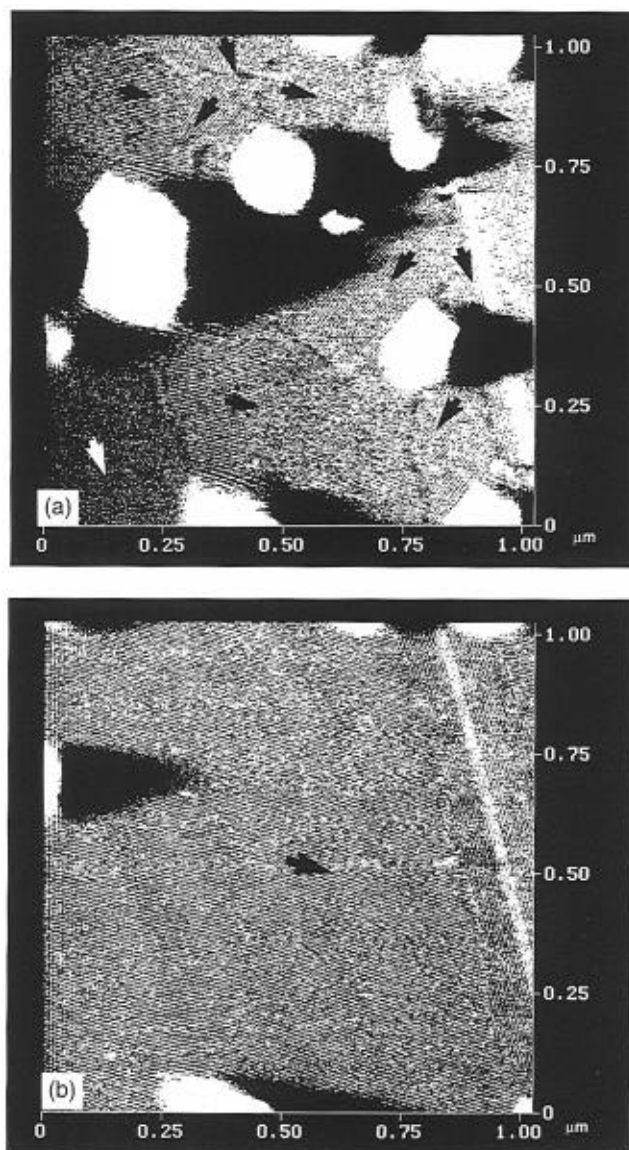
When the surfactant was desorbed by imaging at high applied force, it usually reformed as a grain in the same orientation as observed originally. However, some small grains could be converted to the orientation of a neighboring grain by desorption at high force followed by self-assembly. This indicates that grain formation is influenced by nucleation kinetics.

**Density of Grain Boundaries.** The density of grain boundaries was dependent on further adsorption from solution. Figure 8 shows an image of the graphite–solution interface in 3.2 mM SDS 4 days after an experiment was started. The large, high, soft structures shown in Figure 8a adsorbed overnight, and we do not know their origin. Their importance lies in the fact that their adsorption is correlated with a much higher density of grain boundaries. Figure 8a shows that after adsorption the grain size is quite small. When the large structures were imaged at high force (2 nN), they desorbed from the surface, and the original low density of grain boundaries returned (Figure 8b). This shows that the presence of grain boundaries is strongly influenced by adsorption from solution. It is interesting to note that *the orientation of the hemicylinders can be changed at distances up to 200 nm or 30 periods away from the new adsorbate*. It is also interesting to note that all the grains in Figure 8a are aligned in one of three directions. Manne *et al.*<sup>2</sup>



**Figure 7.** The structure of grain boundaries where there is no obvious feature in the underlying graphite. (a) Structures from only one grain terminate at the boundary (2.8 mM SDS + 160 mM NaCl). (b) Structures from both grains terminate at the boundary. (3.2 mM SDS). (c) A broad boundary (100 nm) where the periodicity from both grains propagates into the boundary region. The arrows show the orientation of the grains. Both dimensions of the aggregates are similar in size within the boundary region (16.2 mM SDS).





**Figure 8.** Effect of further adsorption on the density of grain boundaries. (a) An area of the graphite–solution interface showing the adsorption of large structures from solution. Adsorption is accompanied by the fracturing of a single grain of surfactant aggregates into many grains. The arrows indicate the orientation of each grain. (b) The same region of graphite (note step on right-hand side) after imaging at 2 nN (high force). Removal of the aggregates was accompanied by conversion of the periodic structures to a single grain. It is interesting that adsorption from solution can cause changes in structure which propagate over distances of 200 nm.

have proposed that the orientation of hexadecyltrimethylammonium bromide grains on graphite is determined by the underlying hexagonal structure of the graphite. Alternately, the orientation may be due to growth from steps on the graphite, and the step orientation is determined by crystallography.

**Large-Period Structures.** Occasionally, regular structures similar to those shown in Figure 1, but with periods of up to 20 nm, were observed in SDS solutions on graphite. These features were detected only when the scan size was large; they were not visible at scan sizes of 200 nm or less. The lack of reproducibility prevented us from determining whether these were real structures or an artifact of scanning.

## Discussion

**Determining the Structure of Adsorbates.** The AFM has been shown to be valuable for determining the existence of organized surfactant adsorbates and for measuring the change in structure in response to solution conditions. The salient

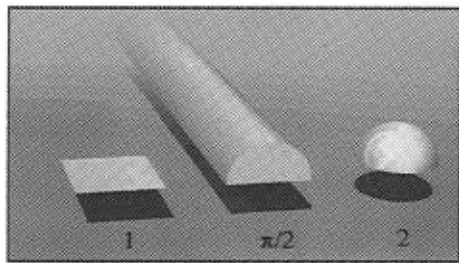
advantages are that (1) measurement can be made in solution, thus reducing the chance of preparation artifacts, and (2) resolution is sufficient to identify individual structures, obviating the need for model dependent measurements such as enthalpy of adsorption. The high lateral resolution also allows determination of structure as a function of position across a surface, allowing studies of grain boundaries and correlations with surface features.

Insofar as our goal has been to determine the shape of adsorbed aggregates, we have found that atomic force microscopy *alone* is inadequate. Atomic force microscopy is very useful for determining the periodicity of adsorbates, but owing to the problems in height measurement, it is difficult to determine whether the surfactant adsorbs as hemicylinders or as a monolayer of parallel stripes of two tail-to-tail molecules. A better estimate of the height of the aggregates is obtained from force measurements, but the most reliable method to determine the final shape is in conjunction with an adsorption isotherm.

**Why Hemicylinders?** The relationship between the properties of an individual surfactant monomer and the structure of an aggregate in bulk are well understood. The structure can be calculated by considering the various interactions between all the molecules and surrounding solution. A very useful concept is the critical packing parameter, or shape factor,<sup>12,13</sup> which is a recognition that the unfavorable interaction between the surfactant hydrocarbon and water drives the hydrocarbon to the interior of the aggregate. The shape of the aggregate is then determined by the ratio between the volume of hydrocarbon which must be encapsulated by hydrophilic head groups and the product of the head group area and the length of the hydrocarbon chain. Repulsive interactions between (e.g. charged) head groups increase the effective headgroup area. A critical packing parameter of 1/3 results in micellar structures, and SDS in solution has a value of 0.37, so slightly nonspherical micelles are predicted.<sup>13</sup>

The interaction between surfactant molecules is altered by the presence of a phase boundary. A difference in dielectric constant will change electrostatic interactions (counterion binding, head group–head group interactions and aggregate–aggregate interactions), the constraint of the surface will change the entropy, the morphology of the surface may influence interactions, and specific interactions between the surface and solvent/solutes must be considered. A complete understanding of surface aggregation must consider all these influences.

In this section we will consider only one factor which is important for SDS adsorption to graphite, namely, that the hydrophobic graphite surface provides a driving force to minimize the contact area between the hydrophobic graphite and water. We are thus interested to know for which shape of adsorbate is the maximum graphite surface covered for a given total headgroup area? Figure 9 shows schematic drawings of various structures, together with the ratio of the headgroup area to the area covered when they adsorb to a surface. The ratio is 1 for a flat layer of infinite extent,  $\pi/2$  for infinite hemicylinders, and 2 for hemispheres. If the only factor affecting the structure of adsorbed aggregates were for the headgroup to cover the maximum area of hydrophobic *solid* interface, we would expect that adsorbing surfactants would form flat sheets, the structure of minimum curvature. This suggests that a rough guide to adsorbate structure on hydrophobic surfaces can be obtained by calculating or measuring the structure in solution and then choosing a hemistructure of lower curvature. (The surface aggregate will be less curved for bulk critical packing parameters *greater* or less than 1; that is, the hydrophobic surface packing parameter is closer to 1 than the bulk packing parameter.) For



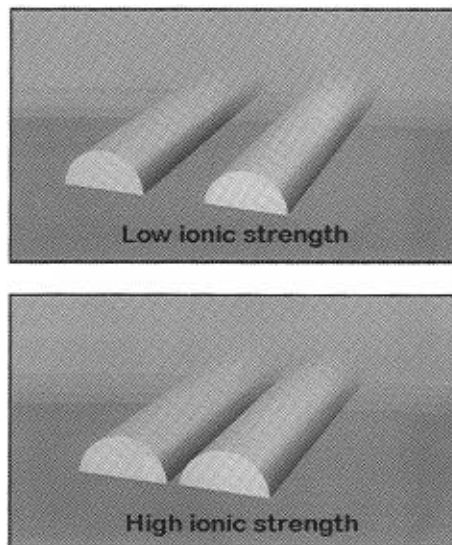
**Figure 9.** Ratio of aggregate–solution interface generated to solid–solution interface lost when an aggregate forms on a surface. The more highly curved aggregate covers less hydrophobic solid–solution interface for a given headgroup area. Prediction of the final surface–aggregate shape requires a full calculation of all interactions in the system, but a hydrophobic surface favors surface aggregates of lower curvature than for the same surfactant in bulk solution.

SDS, the surfactant forms micelles in bulk (perhaps not spherical) but cylinders on a hydrophobic surface, the result of two opposing trends: minimizing curvature so as to cover the maximum surface area of graphite and packing an appropriate amount of hydrocarbon within the surface area of the head groups. At high surfactant concentration, when much of the hydrophobic surface is covered, the latter effect may dominate, leading to more curved structures. However, at these high concentrations, other factors such as screening of head group interactions and interaggregate interactions on the surface may prevent this from occurring. To this end it is worth noting that close-packed identical hemispheres cover only about 90% of a surface, whereas hemicylinders cover nearly all of a surface, and a flat layer covers the entire surface.

**Curvature Change or Separation Change?** We observe that the period of the adsorbed structure decreases as a function of both surfactant concentration and salt concentration. There are at least two structural changes consistent with this observation: (1) an increase in aggregate curvature and (2) a decrease in aggregate separation. We strongly favor the latter possibility. Adsorption and aggregation are a function of two opposing effects: association to reduce hydrophobic interactions and repulsion due to Coulombic interactions between headgroups. An increase in electrolyte concentration is expected to screen the interactions between charged head groups, thus decreasing the effective head group area and *decreasing* the curvature of adsorbed structures. This decrease in curvature is observed for SDS aggregates in *bulk* solution when the concentration of SDS solution is increased<sup>10</sup> or on addition of salt (including the sphere to rod transition).<sup>7</sup> At the surface, the screening of repulsive interactions between surfactant aggregates will allow a more dense surface coverage with less hydrophobic graphite exposed to solution. Figure 10 shows a schematic figure of the structural change consistent with the data in Figure 5 and a crude model which we use to justify the comparison between measured period and the magnitude of the repulsive interaction is described in the Appendix.

**The Length of Hemicylinders.** It is much easier to observe a periodic structure than a single defect, and our failure to observe the ends of the hemicylinders must be considered in this context. The ends of hemicylinders could be identified at grain boundaries where their positions were ordered, so we do have the ability to observe ordered termini. We can thus have some confidence that the positions of the termini of the hemicylinders within a grain were not correlated. Thus, our measurements do not rule out the possibility of the aggregates forming a two-dimensional nematic phase, but are evidence against a smectic phase.

**Changing the Structure by Coadsorption.** Figure 8 shows that adsorption from solution can change the organization of a



**Figure 10.** Schematic illustration of the change in adsorbate structure on addition of NaCl. At low ionic strength (top), the surface aggregates are more widely separated than at high ionic strength (bottom).

self-assembled structure up to 200 nm from the site of adsorption. In this case adsorption resulted in a change in orientation of the self-assembled structure and in an increase in the amount of differently ordered boundary region. The fact that this occurs when the original structure was partly determined by interactions with the graphite surface suggests that the effect will be even stronger for free-standing, self-assembled structures such as biological membranes. This may have implications for the mechanism by which transmembrane transport is mediated in cells.

## Conclusions

Sodium dodecyl sulfate adsorbs to graphite in an organized structure when the solution concentration exceeds 2.8 mM. The AFM images show an adsorbed structure that is ordered in one dimension. This is consistent with two models: (a) hemicylinders and (b) a monolayer of surfactant molecules lying tail-to-tail with aligned headgroups. The latter structure can be excluded on the basis of the adsorption isotherm. Alignment of the long axis of the aggregates is explicable in terms of electrostatic double-layer repulsions between the aggregates.

At or below a concentration of 1.6 mM, no structure is observed, so the surface aggregation concentration (sac) lies between 1.6 and 2.8 mM, at about one-fourth of the cmc. The sac occurs at a lower SDS concentration in the presence of NaCl. When the SDS concentration or the NaCl concentration is increased above the sac, the shape of the adsorbed aggregate does not change greatly; instead the aggregates move closer together. For SDS solutions, the spacing decreases until an approximately constant minimum separation occurs at about twice the cmc. When NaCl is added, the aggregate period is roughly proportional to the Debye length.

The ends of the hemicylinders were not observed, except at grain boundaries. From this we conclude that either the position of neighboring ends is not correlated or the aggregates are very long.

The shape of the surface aggregates can be altered by the presence of surfactant–aggregate grain boundaries. At the boundary of two angled grains, the aggregates sometimes maintain the periodicity of both grains, resulting in a two-dimensionally ordered surface of hemimicelles.

The highly ordered structure of the adsorbed aggregates can be altered by further adsorption from solution. Adsorption of



large (100–200 nm) soft particles causes a proliferation of grains (and grain boundaries) in the pre-existing structure. These particles are able to propagate the formation of grain boundaries over a distance of 200 nm. This mechanism for the reorganization of assembled structures may have implications for biological membrane processes.

A major advantage of the AFM technique for studying adsorption is that the structure of adsorbates can be measured on a nanoscopic scale. This allows determination of typical aggregate structure as well as the variation in adsorption and aggregation across a morphologically and chemically inhomogeneous surface.

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## Appendix

**Electrostatic Forces between Aggregates.** A very crude estimate of the repulsion between aggregates on the surface can be made by assuming that the only two forces between aggregates are repulsive double-layer interactions and the graphite interfacial energy pulling the cylinders together (thus ignoring, for example, van der Waals forces):

$$\begin{aligned} E_D &= (\gamma_{\text{HG}} - \gamma_{\text{WG}})S \\ &= (\gamma_{\text{HG}} - \gamma_{\text{WG}})(P - S_0) \end{aligned}$$

where  $E_D$  is the double-layer energy per unit length of

hemicylinder,  $\gamma_{\text{HG}}$  is the hemicylinder–graphite interfacial energy,  $\gamma_{\text{WG}}$  is the water–graphite interfacial energy,  $S$  is the separation between aggregates,  $P$  is the measured period, and  $S_0$  is the diameter of the hemicylinder. If we further assume a roughly constant hemicylinder diameter

$$E_D \propto P + \text{constant}$$

and thus the period can be used as an estimate of the double-layer interaction between adsorbed hemicylinders.

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