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# Surface Aggregate Phase Transition

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A surface aggregate phase transition is described. Atomic force microscopy has been used to image the equilibrium association of sodium dodecyl sulfate (SDS) and 1-dodecanol molecules at the interface between graphite and aqueous solutions. In pure SDS solutions, the molecules associate into long, parallel hemicylindrical surface aggregates over a concentration range from about one-third to at least 10 times the critical micelle concentration (cmc). Above the cmc, dodecanol has little influence on the surface aggregate structure, probably because dodecanol is partitioned into the bulk micelles. Below the cmc, dodecanol causes a transition from hemicylindrical aggregates to a two-phase mixture in which flat sheets coexist with swollen hemicylindrical aggregates. In this mixture, the hemicylindrical aggregates are preferentially located at and parallel to steps on the underlying graphite substrate. Under conditions where hemicylinders and flat sheets coexist, an increase in bulk dodecanol concentration results in an increase in surface coverage by flat sheets. No bulk solution changes were detected by NMR in the region where the surface phase transition was observed.

## Introduction

In aqueous solution, surfactants self-assemble into a variety of aggregate shapes including spherical and rod like micelles and planar bilayers. Reasonable predictions of aggregate shape can be made on the basis of the forces acting on the surfactant monomer, and phase transitions can be understood in terms of changes in these forces. For example, an increase in electrolyte concentration in ionic surfactant solutions reduces the electrostatic repulsion between headgroups and lowers the curvature of the aggregate. For certain ionic surfactants, this is manifest as a sphere-to-rod transition.<sup>1</sup> Addition of a long-chain alcohol to surfactant solutions swells the hydrocarbon component of the aggregate and results in a lower curvature aggregate.<sup>2</sup> For example, several *n*-alcohols induce the sphere-to-rod transition of sodium dodecyl sulfate (SDS) in NaCl solutions.<sup>1</sup> The forces on the monomer are sometimes summarized in terms of a packing parameter,<sup>3</sup> which is the ratio of the hydrocarbon volume to the product of the area occupied by the headgroup and the length of the hydrocarbon chain. The packing parameter is higher for surfactants which form lower curvature aggregates.

When surfactants are present in solution, they often also spontaneously aggregate at solid–liquid interfaces and these surface aggregates can be studied directly with the atomic force microscope (AFM), after the method of Manne *et al.*<sup>4</sup> Previously the equilibrium surface aggregation of cationic,<sup>4,5</sup> anionic,<sup>6–9</sup> and zwitterionic<sup>8,10</sup>

surfactants in aqueous solution has been investigated using this method. These studies have emphasized that the surface aggregate morphology is frequently different from the bulk solution aggregate shape, with the substrate playing a dominant role in determining the surface aggregate structure. To date, different surface aggregate structures have been observed on different substrates<sup>10</sup> and for different surfactants on the same substrate.<sup>8</sup> The zwitterionic surfactant, (dodecyltrimethylammonio)propanesulfonate, forms spherical micelles on mica whereas the cationic surfactant, dodecyltrimethylammonium bromide, forms cylindrical micelles. Mixtures of the two surfactants form structures of intermediate length, so a transition from one structure to another is observed. A surface phase transition for a single adsorbate on a single substrate has not yet been observed.

In this work we describe a phase transition for a surfactant–cosurfactant system. AFM is used to show the effect of 1-dodecanol on the aggregation of dodecyl sulfate at the graphite–solution interface. The surface aggregation of dodecyl sulfate on graphite in the absence of dodecanol has been thoroughly characterized:<sup>6</sup> above 2.8 mM dodecyl sulfate assembles in an organized periodic structure consisting of long parallel aggregates. The aggregates appear as stripes in the AFM images and are observed when the tip and the solid substrate are slightly separated. These aggregates are believed to be hemicylindrical structures and can be characterized by their period and the thickness of the adsorbed layer.<sup>7</sup> The hemicylindrical structure is retained even when the surfactant concentration and electrolyte concentration are varied significantly.<sup>6,7</sup> Although the addition of electrolyte to SDS solutions induces a sphere-to-rod transition in bulk, there is no clear evidence for a salt-induced transition at the graphite–solution interface. Since *n*-alcohols are known to be more effective than electrolyte in inducing bulk phase changes,<sup>1,11</sup> we have investigated the influence of an *n*-alcohol on surface aggregation.

Long-chain alcohols are sparingly soluble in water. This solubility is increased in aqueous surfactant solutions, with a particularly large increase above the critical micelle concentration (cmc) where the alcohol is partitioned into the micelles.<sup>2</sup> The surfactant cmc is also lowered in the presence of *n*-alcohols.<sup>12,13</sup> This decrease is the result of an increase in the entropy of mixing and a decrease in the

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**Table 1.**  $^1\text{H}$  NMR Data

[SDS] (mM)	[dodecanol] (mM)	$\delta$ ( $\text{O}_3\text{SO}-\text{CH}_2$ ) (ppm)	$\delta$ ( $-\text{CH}_3$ ) (ppm)
4	0	4.0005	0.7980
4	0.02	4.0010	0.7995
4	0.2	4.0010	0.7990
4	0.5	4.0015	0.8000
16	0	3.9820	0.8185
16	0.5	3.9815	0.8200
16	2.5	3.9795	0.8200

charge–charge interactions when the alcohol groups are located between the charged headgroups. At greater concentrations of alcohol, binary phase systems are formed such as the mixed micellar/lamellar phase in the magnesium dodecyl sulfate/decanol/water system.<sup>14</sup>

### 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  $\mu\text{m}$  filter. The purified 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  $^\circ\text{C}$ . Sodium dodecyl sulfate, SDS (BDH, 99%), was recrystallized from ethanol. 1-Dodecanol (Sigma, 99%) was used as received. Adhesive tape was used to cleave a fresh sample of graphite for each experiment from a pyrolytic graphite monochromator (grade ZYH, Union Carbide).

All solutions were prepared at least 24 h before use. The solutions were sonicated, then clarified at about 40  $^\circ\text{C}$ , and left to equilibrate at the temperature of the experiment for several hours.

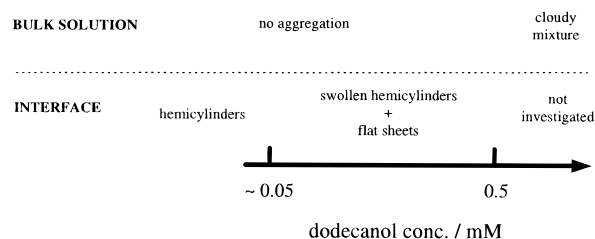
**Microscopy.** Images were captured using a Nanoscope III AFM<sup>15</sup> (Digital Instruments, CA, USA) at  $27 \pm 1$   $^\circ\text{C}$  (the melting point of dodecanol is 26  $^\circ\text{C}$ ),<sup>16</sup> using silicon ultralevers (Park Scientific, CA, USA) with nominal spring constants of 0.07 N  $\text{m}^{-1}$ . The ultralevers were irradiated for 40 min ( $\sim 9$   $\text{mW cm}^{-2}$  at 253.7 nm) in a laminar flow cabinet before use. 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 lateral dimensions were calibrated by imaging a standard grid (2160 lines/mm), and distances normal to the surface were calibrated by measuring etch pits (180 nm deep).

Before the images were captured, the graphite substrate was left to equilibrate in the solution of interest for at least 30 min. Solutions were changed by flushing the AFM cell with about 20 times its volume of new solution over 5 min. Imaging was performed at a force which was insufficient to observe the graphite lattice<sup>4</sup> but with sufficient gradient to obtain high resolution of the adsorbed surfactant aggregates.

**NMR Spectroscopy.** Changes in the environment of SDS molecules in  $\text{D}_2\text{O}$  solution were detected from the change in chemical shift in  $^1\text{H}$  NMR spectra recorded on a 200 MHz spectrometer (Gemini, Varian, Palo Alto, CA, USA).<sup>17</sup> Chemical shifts were measured relative to an external reference of dioxane, taken as 3.7 ppm. The error in determining the chemical shift was  $\pm 0.001$  ppm.

### Results and Analysis

The effect of dodecanol on the surface aggregation of dodecyl sulfate in aqueous solution on graphite was investigated both above (16 mM) and below (4 mM) the cmc of pure SDS (8.1 mM).<sup>18</sup> A range of dodecanol



**Figure 1.** Bulk and surface aggregate structures for SDS in 4 mM SDS with added dodecanol.

concentrations between zero and the phase boundary was studied for both SDS concentrations.

**The Bulk Solution.** In 4 mM SDS, transparent, single-phase solutions can be prepared with up to 0.5 mM dodecanol. Above this concentration of dodecanol, the mixture is cloudy. In 16 mM SDS, the transition from clear to cloudy occurs at 3.7 mM dodecanol. The greater solubility of dodecanol at 16 mM can be attributed to solubilization within the micelles. A summary of  $^1\text{H}$  NMR measurements of the solution state is shown in Table 1. In the absence of dodecanol, there is a 0.02 ppm change in chemical shift from 4 to 16 mM consistent with some molecule residence in micelles at the higher concentration. The change in chemical shift on addition of dodecanol to 4 mM SDS is not significant (error =  $\pm 0.001$  ppm), suggesting that no SDS micellization occurs in bulk solution. The  $^1\text{H}$  NMR signal from dodecanol is too weak to quantify, but we find that the solubility of dodecanol is increased by at least a factor of 10 in the presence of 4 mM SDS suggesting that there is some interaction between the dodecanol and SDS.

**Surface Aggregation above the cmc.** The effect of dodecanol on the surface aggregation in 16 mM SDS was investigated in the range 0–3.7 mM dodecanol. In pure 16 mM SDS, a hemicylindrical surface–aggregate structure with a period of 5.3 nm was observed as reported by us previously.<sup>6</sup> We observed no change in surface–aggregate morphology on addition of dodecanol up to the limit of 3.7 mM where the solution became too cloudy for AFM measurements. However, there was a small decrease in period to 5.0 nm at the maximum dodecanol concentration. The lack of structural change on addition of dodecanol is consistent with the partitioning of dodecanol into the bulk solution micelles rather than to the graphite–solution surface. It is well-known that dodecanol reduces the *air*–solution interfacial energy of SDS solutions below the cmc, but not above the cmc.<sup>13</sup> There is thus a similarity of behavior at the *air*–solution and graphite–solution interfaces in the SDS/dodecanol system.

The rest of the results deal exclusively with measurements below the cmc (at 4 mM SDS).

**Surface Aggregation below the cmc.** The effect of dodecanol on the surface aggregation in 4 mM SDS in the range 0–0.5 mM dodecanol is summarized in Figure 1. Figure 2 shows AFM images of the structure at 0 mM dodecanol and the predominant structure at 0.26 mM dodecanol, demonstrating a transition from hemicylindrical structures to a laterally homogeneous layer. Four millimoles per liter SDS is below the cmc but above the surface aggregation concentration (sc) on graphite,<sup>6</sup> so hemicylindrical surface aggregates exist in equilibrium with monomers in solution. The measured period of  $6.4 \pm 0.3$  nm agrees with our previously published measurements.<sup>6</sup> In the presence of more than about 0.05 mM dodecanol, there are two structures; hemicylinders coexist with the laterally homogeneous layer which we will refer to as the flat sheet structure. The coexistence of the two phases is shown in Figure 3. Only hemicylindrical

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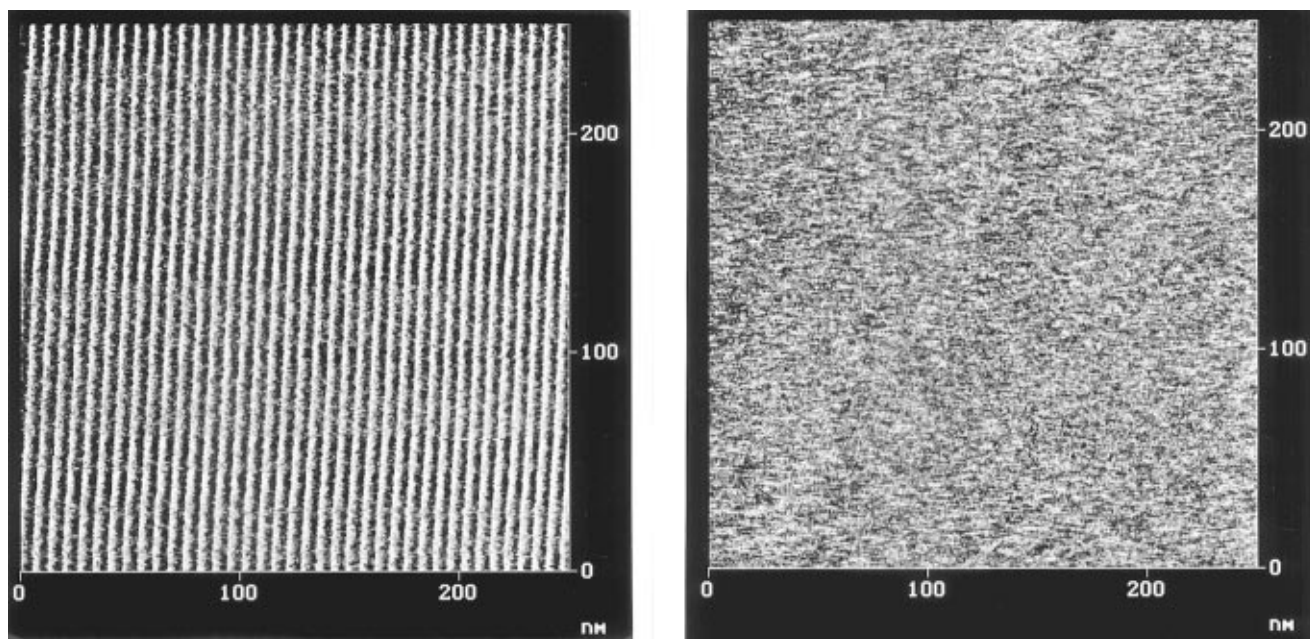
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**Figure 2.** AFM images illustrating the effect of dodecanol on the aggregation of dodecyl sulfate in 4 mM SDS: (a, left) In SDS only, a hemicylindrical surface aggregate structure is resolved; (b, right) In SDS plus 0.26 mM dodecanol, a laterally homogeneous adsorbed layer covers most of the surface.

aggregates were observed when the dodecanol concentration was  $<0.02$  mM, and at 0.5 mM dodecanol, hemicylindrical aggregates were only observed in one of five experiments (and on that occasion, covered only a very small portion of the area examined). At intermediate concentrations, the proportion of surface occupied by flat sheets increased with the dodecanol concentration. The structure that we observed did not depend on previous exposure of the graphite to more dilute dodecanol solutions. However, when we replaced a solution with a solution less concentrated in dodecanol, a much longer time was required to reach the equilibrium structure.

In the two-phase regime ( $\sim 0.05$ – $0.5$  mM dodecanol), the hemicylindrical aggregates were preferentially located along steps in the underlying graphite substrate. This is shown in Figure 3b. Thus a variation in the density of substrate steps leads to a variation in the ratio of the two phases observed.

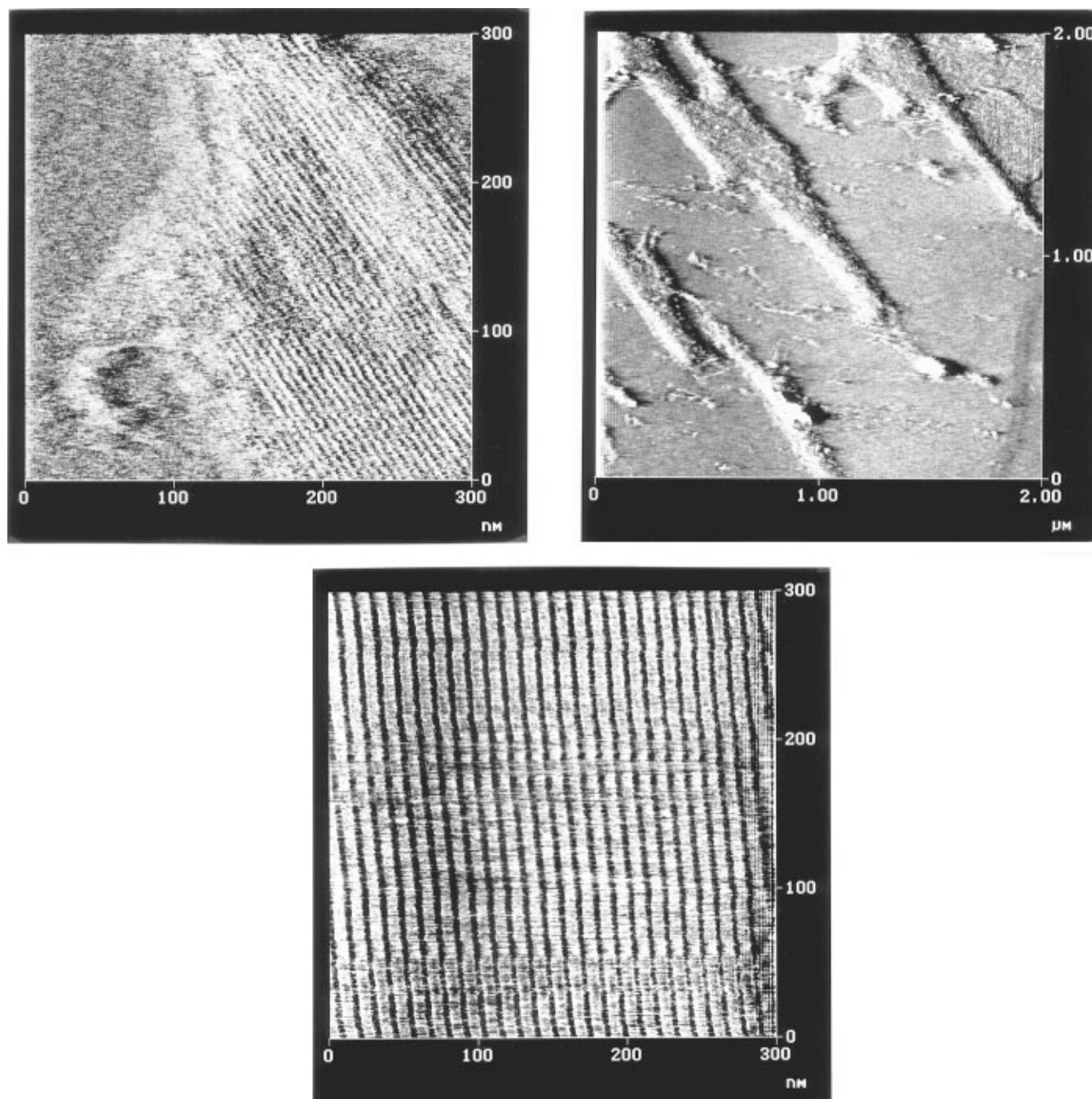
We interpret the period of the observed hemicylindrical structures as the sum of the aggregate diameter and the interaggregate separation.<sup>7</sup> For solutions when only hemicylinders were present, the period of the hemicylinders was constant at  $6.4 \pm 0.3$  nm, but in the coexistence region the period was variable but larger than that in the pure hemicylinder regime. Figure 3c shows a region in 0.19 mM dodecanol with a swollen period of 12 nm. We were not able to gather enough accurate data to give a meaningful period distribution as a function of concentration in the coexistence regime. (One reason for this was the pressure sensitive resolution described below.)

Previously we observed that surface structures in equilibrium with aged SDS solutions ( $>2$  weeks) had a larger period than those in equilibrium with fresh SDS solutions.<sup>6</sup> At the time, we attributed this phenomenon to the swelling of the surface aggregates due to incorporation of dodecanol produced by hydrolysis of SDS. The current work shows that the effect of adding dodecanol is different to that observed in our experiments on aged SDS solutions.

It is interesting to consider why dodecanol would change the surface structure below the cmc, but not above the cmc. From the great increase in solubility of dodecanol in the presence of micelles, we know that dodecanol finds

a low energy state in an SDS aggregate. The free energy of the system is lower when the alkyl chain is inside a micelle instead of next to water (the hydrophobic effect). As a first approximation, we will for now assume that the free energy change is the same for transferring a dodecanol molecule from a water environment into an aggregate in bulk or into an aggregate on the surface. In the graphite–SDS system below the cmc, the only aggregates available are at the surface, so it is reasonable to expect that the dodecanol is at a much higher mole fraction at the surface than on average throughout the solution. Above the cmc, there are many low-energy compartments for dodecanol throughout the system, so once the cmc is exceeded, the mole fraction of dodecanol at the surface should drop drastically. Hence, above the cmc we observe a much smaller effect of dodecanol at the surface. (In our system at 4 mM, about 1 in  $10^4$  SDS molecules are aggregated (mainly at the surface), whereas at 16 mM, about half the SDS molecules are aggregated so the mole fraction of dodecanol at the surface would drop by a factor of about  $10^4$  above the cmc.)

*Forces between the Tip and Sample.* The measured force of interaction between the tip and sample is shown in Figure 4 for 4 mM SDS with and without dodecanol. The force in the dodecanol solution was measured on a region entirely covered by a flat sheet. (In the coexistence regime we were never able to measure a force curve, which we were sure was completely determined by hemicylindrical adsorbates.) The change in force can be used as a diagnostic both to study the surface properties and to interpret the image. In the presence of dodecanol, there was no significant change in the instability distance (marked J on Figure 4), which has previously been assigned to the adsorbed layer thickness.<sup>7</sup> The most notable difference between these two force profiles is the increase in the height of the repulsive barrier on the addition of dodecanol. At intermediate dodecanol concentrations, this barrier was of intermediate height. The change in the barrier height tells us that adding dodecanol in bulk solution changes the nature of the surface and, in particular, that the adsorbed layer is more difficult to displace by normal motion of the tip. Previous work on adsorbed cylindrical surfactant layers<sup>8</sup> indicated that



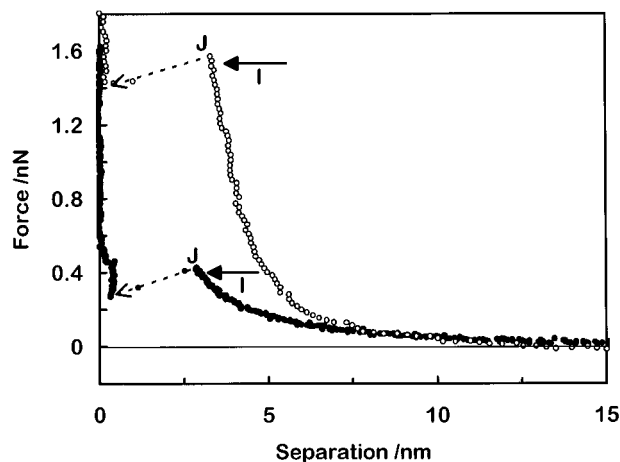
**Figure 3.** AFM images showing the coexistence of hemicylinders with flat sheets. (a, top left) Clearly resolved hemicylinders adjacent to a flat sheet (4 mM SDS and 0.26 mM dodecanol). This image is adjacent to the region shown in Figure 2b. (b, top right) Large scale image showing patches of hemicylindrical surface aggregates. The hemicylinders are preferentially located along steps, one of which is visible as a dark line in the top right hand corner. The flat sheet structure has been displaced by the tip in this image (4 mM SDS and 0.26 mM dodecanol). (c, bottom) Swollen hemicylinders in the coexistence regime (4 mM SDS and 0.19 mM dodecanol).

when the tip moves normal to the surface, the cylindrical aggregates are displaced laterally (across the surface) not into solution. This mode of displacement is not available to a continuous sheet and may be responsible for the increase in displacement force when dodecanol is in the film. In contrast, the hemicylinders were more difficult to displace than the flat sheets when subject to lateral shear during imaging. (E.g., in Figure 3b the flat sheet has been displaced, but not the hemicylinders.)

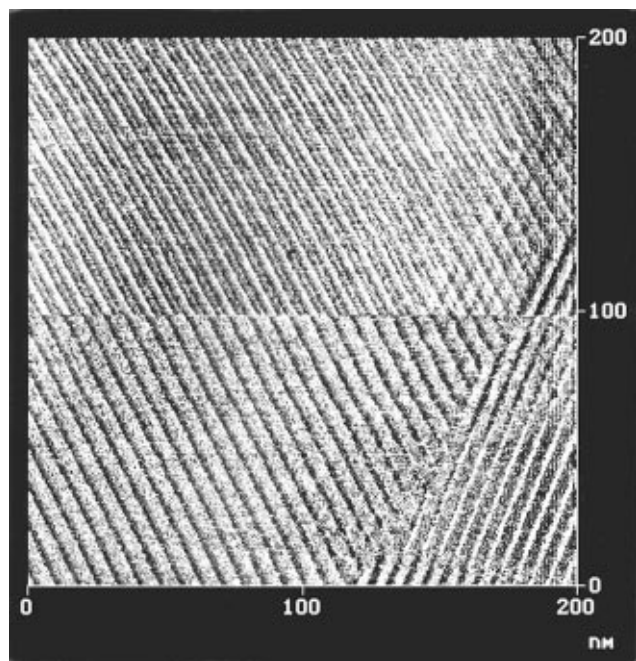
**Pressure Sensitive Structure/Resolution.** In the SDS/dodecanol mixtures with at least 0.006 mM dodecanol, a notable feature of the hemicylindrical aggregate structure was the frequent period splitting. For example, in 0.006 mM dodecanol a period of 6.4 nm (i.e., similar to pure SDS) was observed at low force, but at a slightly higher

force, the periodic features were split into two parts. This splitting was also observed for the swollen hemicylinders at higher dodecanol concentrations. This effect is shown in Figure 5 where the upper half of the image was recorded at 0.1 nN more force than that recorded in the lower half. The larger period single stripes were only observed at the lowest force at which aggregates were observed, while the split structure was visible over a range of forces up to that at which the adsorbed layer was displaced. We do not have an explanation for this phenomenon; it is not clear whether a change in structure or a change in resolution occurs when the force is changed. This phenomenon was never observed in pure SDS solutions.

When the imaging was performed at a much greater force than that at which the hemicylindrical aggregates

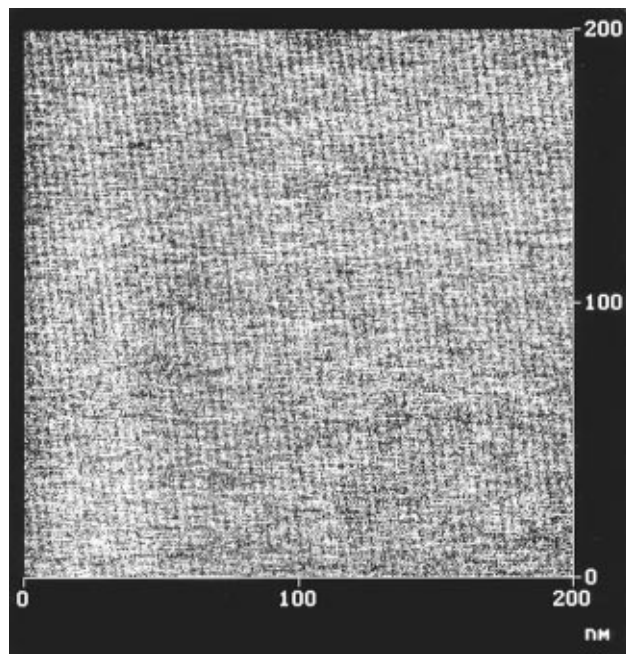


**Figure 4.** Normal force as a function of separation as a silicon ultralever approaches a freshly cleaved graphite surface in aqueous solution for both pure 4 mM SDS (closed circles) and 4 mM SDS plus 0.5 mM dodecanol (open circles). The labeled arrows indicate the following: I shows the force at which aggregates were imaged, J is the point of mechanical instability where the tip jumps into the graphite surface. For the pure-SDS force curve, the tip apparently sits about 0.2 nm away from the surface for a short time after the jump (as observed previously).<sup>7</sup> This feature was not present in every measured curve, and when present, there was variation in the force over which it was measured. This may be an artifact caused by the tip sticking and slipping on the graphite surface or the displacement of an adsorbed layer. The thickness is somewhat smaller than the width of a hydrocarbon chain (0.36 nm) but similar to the width of a water molecule (0.25).<sup>19</sup>



**Figure 5.** AFM image showing hemicylinder period splitting in a 4 mM SDS and 0.006 mM dodecanol solution. The bottom half of the image was recorded at about 0.05 nN force and shows a period of 6.5 nm. The top half of the image was recorded at about 0.15 nN and shows a period of about 3.2 nm. There is a step in the graphite in the lower right hand corner of the image and a change in aggregate orientation along this line.

and flat sheet were seen (about 2–6 nN), a different surface-adsorbed structure was observed as shown in Figure 6. These indistinct parallel stripes of period  $3.6 \pm 0.1$  nm were generally stable over a much greater range of forces (up to 1.5 nN) than the clear hemicylindrical aggregates of Figure 2a. They occurred at small separations (0–0.2 nm) and were not correlated with any feature



**Figure 6.** AFM image at high force ( $\sim 4$  nN). At high force, indistinct parallel stripes are visible over a range of force up to 1.5 nN (4 mM SDS and 0.095 mM dodecanol).

on the tip–sample force curve. Under a very high force it was occasionally possible to observe period splitting of these structures, so that the period was 1.8 nm.

We have no conclusive evidence to identify the thin stripes, but the size and properties are consistent with a layer of fully extended dodecanol molecules lying parallel to the surface. A molecular model<sup>19</sup> of dodecanol has an extended length of 1.8 nm. The period of 3.6 nm is thus consistent with rows of two dodecanol molecules lying head-to-head and tail-to-tail. The half-period structure resolved at higher force may be resolution of rows of individual molecules. These small period features were never observed in pure SDS solutions.

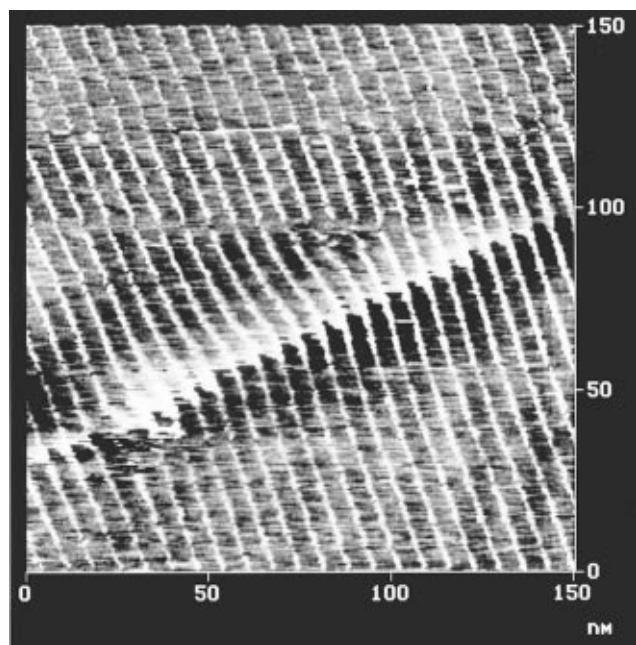
**Defects.** The hemicylinders observed on graphite in pure SDS solutions are very long and straight and adjacent aggregates terminate along a line, or grain boundary.<sup>6,7</sup> In SDS/dodecanol mixtures isolated termini are also found on rare occasions. Figure 7 shows the terminus of a single aggregate located near a step on the graphite substrate. In the previous image, this terminus was located at the step, and thus it is a mobile feature. The existence of an extra aggregate in the top portion of the image is a one-dimensional defect in the otherwise ordered array and causes bending of the neighboring aggregates. For a hemicylinder to continue across a step requires a departure from the curvature found on flat surfaces and a concomitant increase in energy. The formation of an aggregate terminus plus bending of the neighboring aggregates is an alternative means of lowering the energy of the adsorbed material. Similar isolated termini have been observed in the surface aggregates of lithium perfluorooctanesulfonate on graphite,<sup>9</sup> but it is unclear why defects occur in either of these systems.

## Discussion

The shape of surfactant aggregates in bulk solution is determined by the minimization of the energy of the solvent molecules and the hydrophilic and hydrophobic portions of the individual surfactant molecules. The result of this minimization is that the hydrocarbon segments

(19) CPK Atomic Models, Harvard Apparatus, Massachusetts.





**Figure 7.** An isolated defect in the hemicylindrical aggregate structure located near a step in the underlying graphite substrate. The step is marked by the bright region running diagonally across the image. Above the step in the middle of the image, three aggregates enter a region and only two continue on the other side. In the previous scan, the defect was located at the step (4 mM SDS and 0.002 mM dodecanol).

aggregate inside a shell of headgroups to avoid the weak interactions with water (the hydrophobic effect). Since the headgroups are confined to the surface of the aggregate, interactions between the headgroups make an important contribution to the energy. The combination of interactions which determine the aggregate shape can be summarized by the critical packing parameter.<sup>3</sup> The charge–charge interactions between  $\text{DS}^-$  ions lead to a lower density of headgroups for SDS than for dodecanol and a packing parameter for SDS of about  $1/3$ , which is consistent with the formation of spherical micelles in solution. Dodecanol molecules are uncharged, so dodecanol should have a packing parameter  $>1/3$  (although dodecanol does not form micelles in water). When dodecanol is added to an SDS micelle, the hydrocarbon volume increases commensurate with the addition of the new chain. At the same time the change in total headgroup area is small because the alcohol group is small and because the alcohol can occupy the gaps between the dodecyl sulfate headgroups and screen the repulsive interactions between them. Thus in bulk solution, alcohols cause ionic surfactant micelles to have lower curvature.<sup>11</sup>

When dodecanol is titrated into the graphite–solution system, we can also rationalize the observed morphological changes in terms of the packing parameter, but with the added complication of the surface interactions. In the absence of dodecanol, SDS forms hemicylindrical aggregates on graphite over a wide range of bulk concentrations. There are at least two possible reasons for the lower curvature compared to bulk solution: (i) a specific interaction between the surfactant hydrocarbon tail and the graphite<sup>4</sup> and (ii) a hemicylindrical aggregate covers more hydrophobic graphite per molecule than a hemisphere at all surface concentrations and can pack more closely on a surface, thus reducing the area of the unfavorable contact between a hydrophobic substrate and water.<sup>6</sup>

When dodecanol is added into the SDS/water/graphite system, packing parameter arguments suggest that if it

is present at the interface, it will cause a drop in surface–aggregate curvature. At 16 mM (above the cmc) no change in surface–aggregate shape was observed suggesting that nearly all the dodecanol is in the micellar phase. Below the cmc (at 4 mM) there is no micellar phase, so the dodecanol cannot be segregated away from the interface. Instead it causes two changes at the graphite–solution interface: the cylindrical aggregates swell and parts of the surface undergo a hemicylinder to flat sheet transition. Both changes represent a decrease in curvature. As in bulk solution, this can be explained by the smaller effective headgroup area of the alcohol compared to the  $\text{DS}^-$  molecule. When either dodecanol or  $\text{DS}^-$  is added to a surface aggregate, the same volume of hydrocarbon is added, but dodecanol makes a smaller contribution to the surface area because of the smaller van der Waals radius and the fact that it does not increase repulsive electrostatic forces. These two factors force a lower aggregate curvature. The observed structures of swollen hemicylinders and flat sheets satisfy this requirement. We have observed that the fraction of the interface covered by flat sheets increases with the mole fraction of dodecanol in solution. Since the flat sheet has a lower curvature than the hemicylinder, this suggests that the flat sheet is a dodecanol rich phase and the swollen hemicylinders are *relatively* SDS rich. It is not clear why a two-phase coexistence occurs, since a gradual and continuous swelling of the hemimicelles (although not observed) is also consistent with the expected packing parameters. The preferential location of hemicylinders at, and parallel to, step sites provides a clue which may be used to explain this phenomenon in the future.

It is interesting to compare the effect of dodecanol and  $\text{Mn}^{2+}$ . One might expect that  $\text{Mn}^{2+}$  would also decrease the curvature of SDS micelles by screening electrostatic headgroup interactions, but previous work has shown that this does not in fact occur.<sup>7</sup>

## Conclusions

When there are no micelles in bulk solution, dodecanol causes a change in the morphology of SDS aggregates adsorbed to graphite. The lack of electrostatic repulsion between dodecanol headgroups suggests that when dodecanol molecules are added into charged SDS surface aggregates, they will lower the aggregate curvature. AFM images show that on addition of dodecanol, the surface is covered by two types of lower-curvature adsorbate structures: swollen hemicylinders and flat sheets. The fraction of surface covered by the less-curved structure (flat sheets) increases with the bulk concentration of dodecanol. Thus the average curvature of the surface structures decreases with dodecanol concentration. Using the packing parameter model, the average curvature decreases as the average packing parameter of the surfactant mixture increases. Imperfections in the graphite substrate as steps also alter the ratio of hemicylinders to flat sheets in favor of hemicylinders. The entire transition occurs in the absence of a corresponding transition in bulk.

When micelles are present in bulk solution, the surface structure is almost independent of the dodecanol concentration, most likely because the dodecanol partitions into the micelles and so is dilute at the surface.

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