

Molecular Organization of Surfactants at Solid-Liquid Interfaces

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Interactions between surfactant solutions and solid surfaces play a key role in technologically important processes such as colloidal stabilization, ore flotation, and soil removal; however, the interfacial aggregation of surfactant molecules is not yet well understood. Direct images of surfactant aggregates at solid surfaces in aqueous solutions were obtained with atomic force microscopy. The resulting structures for quaternary ammonium surfactants (above the critical micelle concentration) are consistent with half-cylinders on crystalline hydrophobic substrates, full cylinders on mica, and spheres on amorphous silica. These structures—surprisingly different from earlier models—appear to result from a compromise between the natural free curvature as defined by intermolecular interactions and the constraints imposed by specific surfactant-surface interactions. Such interfacial aggregates can potentially be used to pattern surfaces at nanometer-length scales.

The self-assembly of amphiphilic molecules into spheres, cylinders, bilayers, and bicontinuous phases in free solution is fairly well understood (1–3), but it is not clear how these aggregates are affected by the presence of a solid boundary surface. Pioneering research into interfacial aggregation with adsorption isotherms (4) and the surface force apparatus (SFA) (5) has provided quantitative measures of adsorption but little information on aggregate structure. Recent efforts to probe this structure have used fluorescence decay (6) and neutron reflection (7). Here we report direct images of surfactant aggregates at a variety of hydrophilic and hydrophobic substrates with the use of atomic force microscopy (AFM) (8). We restrict this study to (i) atomically flat substrates, where surface corrugation is less than the surfactant dimensions; (ii) cationic surfactants with quaternary ammonium headgroups [typically tetradecyl trimethylammonium bromide ($C_{14}TAB$)], whose aggregation properties have been characterized (9); and (iii) surfactant concentrations above (typically twice) the critical micelle concentration (CMC). In general, the AFM images show interfacial aggregates with a high degree of curvature and periodic structure, in contrast to previously assumed models of flat monolayers and bilayers (see below).

AFM imaging of surface aggregates was performed not in the usual contact mode but by means of precontact repulsive forces as described (10, 11). The imaging tip and sample surface were immersed in surfactant solution in the AFM fluid cell and conse-

quently became charged through adsorption of the cationic surfactant ion. Force curves showed repulsion between the tip and sample, due to electric double-layer forces at long range and probably additional steric forces at short range. The adsorbate layer was imaged by setting the force setpoint in the precontact region, thus “flying” the tip at a few nanometers above the plane of hard contact while scanning (12, 13).

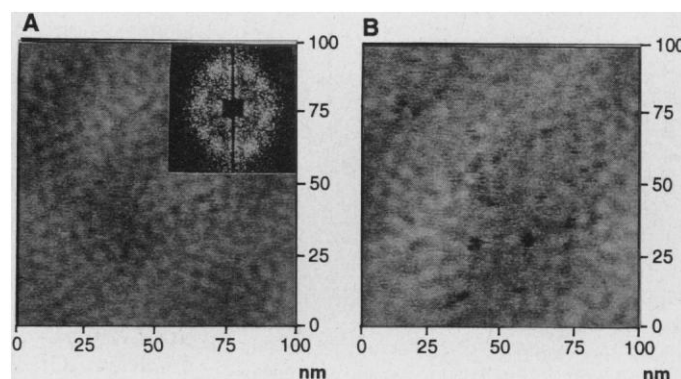
For quaternary ammonium surfactants (above the CMC) on silica, a variety of aggregate structures have been proposed, ranging from uniform bilayers (14–16) to patchy bilayers (7, 17) to spherical aggregates resembling bulk micelles (18). AFM images of the adsorbate layer (Fig. 1, A and B) revealed roughly symmetrical dots consistent with previously proposed spherical aggregates (18). Fourier transforms (Fig. 1A, inset) typically showed a bright ring, indicating a well-defined nearest neighbor distance between aggregates but little orientation on a large scale (resembling a glassy or random close-packed structure). Neighboring micelles often appeared to be connected by a thin neck, giving rise to

two-dimensional networks similar to bicontinuous surfactant phases in bulk solution (3). The observed nearest neighbor distance varied inversely with solution pH (compare Fig. 1A with 1B), ranging from 5.6 ± 0.6 nm at pH 9.9 to 9.0 ± 1.2 nm at pH 2.6 (19). This result is in agreement with previous studies (14, 16, 20) showing that the adsorbate density decreases with decreasing solution pH, because of a reduction in the surface charge by protonation of SiO^- groups.

For quaternary ammonium surfactants on mica, the generally held view is that surfactant molecules above the CMC adsorb in the form of a uniform bilayer (5). Such systems have been used as model bilayers in the investigation of double-layer forces (21), bilayer fusion (22), and micellar depletion forces (23). Surprisingly, AFM images showed an adsorbate structure consisting of meandering stripes (Fig. 2, A and B), which were separated by 5.3 ± 0.3 nm and showed no consistent orientation relative to the underlying lattice. Considering these images together with previous SFA measurements (5) of the adsorbate layer thickness (roughly twice the molecular length), we propose interfacial aggregates in the form of full cylinders (Fig. 2C) (24). The stripe spacing on mica did not vary with solution pH (in the pH range from 2.6 to 11.4) and was always less than or equal to the interaggregate spacing on silica, probably reflecting a difference in the adsorption mechanism between the two substrates (see below).

Aggregate curvature in free solution can be altered markedly by changing the geometry of the surfactant ion (1). Specifically, low curvature can be attained by increasing the tail-group cross-sectional area. Accordingly, the double-chained surfactant didodecyl dimethylammonium bromide [$(C_{12})_2DAB$] gave rise to uniform and featureless images (Fig. 2D) indicative of a flat bilayer on mica, in agreement with previous interpretations (22) of double-chained adsorbates.

Fig. 1. Aggregation of the cationic surfactant $C_{14}TAB$ on silica from 7 mM aqueous solution (twice the CMC). **(A)** A 100 nm by 100 nm AFM image of surfactant aggregates on silica at pH 6.3. The observed dots suggest roughly spherical micelles. The Fourier transform of a larger image (**inset**) shows a ring with a few bright spots, indicating a well-defined nearest neighbor distance



between aggregates (5.7 $\pm$ 0.7 nm in real space) but little crystalline symmetry. **(B)** A 100 nm by 100 nm image of the same sample at pH 2.9. The micelles are now spaced farther apart, at 7.0 ± 0.9 nm.

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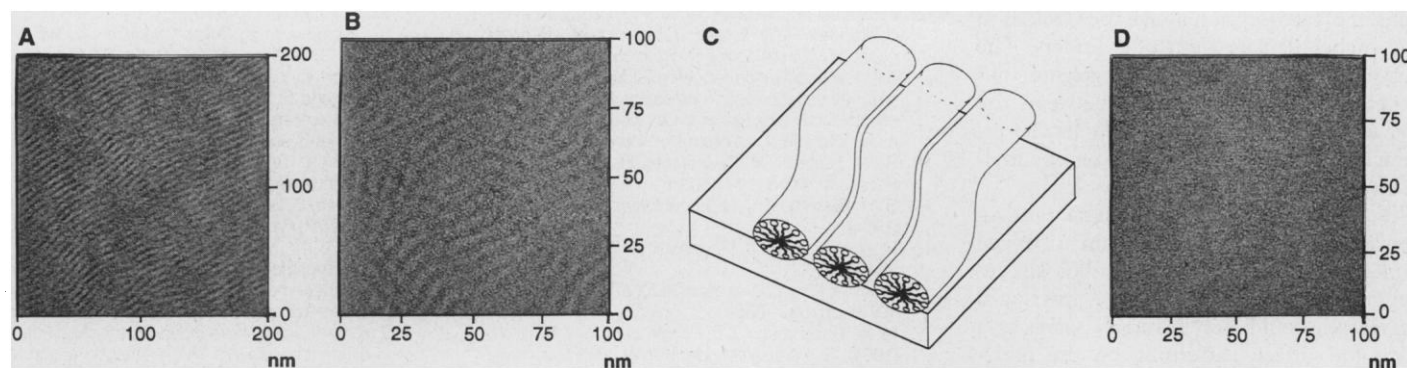


Fig. 2. Cationic surfactant aggregates on mica. **(A)** A 200 nm by 200 nm AFM image of C_{14} TAB aggregates from 7.0 mM solution, showing mean-dering stripes spaced 5.3 ± 0.3 nm apart. **(B)** A 100 nm by 100 nm image of C_{14} TAB aggregates, showing that the stripes have variable orientations over the sample surface. **(C)** Proposed schematic of cylindrical surfactant aggregates, consistent with AFM images and previous SFA data (5). (Cyl-

inders may be flattened at the bottom to allow greater contact area between headgroups and surface.) **(D)** A 100 nm by 100 nm image of the double-chained $(C_{12})_2$ DAB adsorbate layer from 0.30 mM solution (twice the CMC). Although force curves indicate electrical double-layer forces as for C_{14} TAB, the images of the double-chained adsorbate are featureless and indicate a flat bilayer.

Unlike silica and mica, hydrophobic substrates interact primarily with surfactant tailgroups through hydrophobic and van der Waals interactions. Adsorption isotherms

for ionic surfactants on graphite have indicated a coverage roughly consistent with a vertical monolayer above the CMC (25), although hemispherical aggregates have also been suggested (26). However, AFM images (Fig. 3, A and B) of C_{14} TAB aggregates on graphite and MoS_2 , revealed straight, parallel stripes, separated by roughly twice the length of the surfactant molecule and oriented perpendicular to a substrate symmetry axis. These results are consistent with half-cylindrical aggregates (Fig. 3C) (11), in which the tailgroups adjacent to the surface lie parallel to a line connecting nearest neighbor surface atoms.

It has been suggested that epitaxy is responsible for surfactant tailgroups and alkane chains adsorbing parallel to a graphite symmetry axis (11, 27), because the positions of carbon atoms in an alkane chain closely match those of the graphite surface (27). Yet we observed similar surfactant aggregates at the same relative orientation on the cleavage plane of MoS_2 , which consists of sulfur atoms in a symmetry and periodicity different from that of graphite. The common mechanism might be a crystalline anisotropy in van der Waals interactions (analogous to bulk anisotropy in polarizability, refractive index, and so forth)

rather than a specific correspondence between adsorbate and substrate atoms. Although the effect of such an anisotropy may be insignificant on small symmetrical adsorbates, the linearity of the surfactant molecule should enhance the direction sensitivity of its adsorption.

Comparison of observed adsorption morphologies (28) for the above four substrates provides some general insight into surfactant aggregation at interfaces. Single-chain quaternary ammonium surfactants do not adsorb in uniform layers—neither uniform monolayers on hydrophobic substrates nor uniform bilayers on hydrophilic ones—evidently because of a spontaneous curvature that results from interheadgroup repulsion (1). The same geometric packing considerations that determine aggregate shapes in bulk solution also affect aggregate shapes at interfaces. A double-chained surfactant, which is capable of forming bilayers in solution, is capable of doing so at interfaces as well.

Although surfactant geometry is important, the substrate also plays a role in determining the adsorbate structure. Hydrophobic surfaces interact primarily with tailgroups, causing them to orient along directions of crystalline symmetry; the resulting molecular strips or ribbons adjacent to the surface serve as a foundation for half-cylindrical aggregates above the CMC. In contrast, oppositely charged hydrophilic substrates interact primarily with surfactant headgroups, giving rise to aggregate structures that depend on the density of the electrostatically bound headgroups. On silica, the solution pH can be used to vary the surface charge, thus varying the nearest neighbor spacing of the roughly spherical aggregates. On mica, where ion exchange between the surface K^+ ions and headgroups can give rise to a greater density of electrostatically bound surfactants indepen-

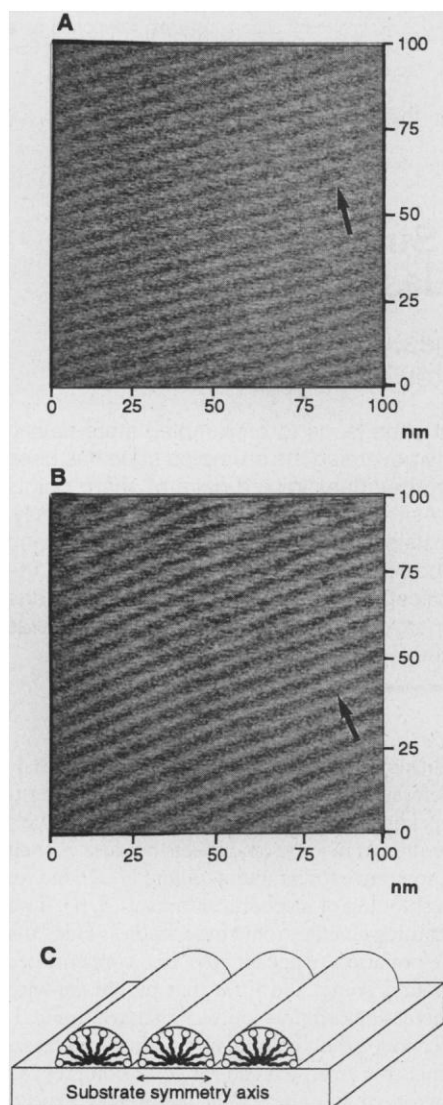


Fig. 3. Aggregates of C_{14} TAB from 7.0 mM solution on hydrophobic substrates. **(A)** A 100 nm by 100 nm image on graphite, showing parallel stripes spaced at 4.7 ± 0.3 nm. The arrow indicates a symmetry direction of the underlying lattice as determined by lattice scans. **(B)** A 100 nm by 100 nm image on MoS_2 , showing parallel stripes spaced at 5.1 ± 0.4 nm. Arrow indicates a symmetry direction of the underlying lattice. **(C)** Proposed model of half-cylindrical aggregates, consistent with AFM images and with adsorption isotherms (25) indicating coverage roughly equivalent to a monolayer. The bottom plane of molecules is oriented with tails parallel to a substrate symmetry axis.

dent of pH, adsorption above the CMC is in the higher density form of cylinders. The curvature of the interfacial aggregate thus appears to be a compromise between the free curvature defined by intermolecular interactions and constraints imposed by molecule-surface interactions.

Further study of interfacial surfactant aggregation may lead not only to an enhanced understanding of self-assembly but also to applications in materials science. Interfacial aggregates could, for example, serve as a basis for surface patterning on the nanometer scale, complementing recent patterning strategies on the submicrometer scale (29). "Fixing" the liquid-crystalline aggregates could be accomplished by ultraviolet polymerization of modified tailgroups, electroless metal deposition (30), or polymerization of certain inorganic counterions (31) such as silicates.

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- We used a commercial atomic force microscope (Digital Instruments, Santa Barbara, CA) and cantilevers (Ultralevers; Park Scientific Instruments, Sunnyvale, CA) cleaned by exposure to ultraviolet light for 15 to 60 min. Typical imaging times were 30 to 60 s, and imaging forces were ~ 1 nN. Samples were immersed in surfactant solution long enough to minimize thermal drift of the cantilever (15 to 120 min); mica immersed for several days showed no difference in the aggregate structure, indicating that the adsorbate reaches equilibrium configuration within a few minutes. Surfactants were purchased from Fluka (Buchs, Switzerland) ($>98\%$ pure), and solutions were prepared in Millipore water. Highly oriented pyrolytic graphite (Digital Instruments), mica, and the MoS_2 crystal were exposed to surfactant solution within 3 min of cleavage. Silica samples [thermally grown oxide on a Si (100) wafer (Wacker, Burghausen, Germany)] were cleaned and stored as described (13) and were mounted and exposed to surfactant solution within 20 min of removal from the storage oven. All images shown are unfiltered except for slope removal along scan lines. Typical force versus distance curves in 7 mM C_{14}TAB solution showed a long-range repulsion that varied exponentially (32) with a measured decay length of 2.8 ± 0.3 nm, comparing favorably to a theoretical double-layer decay length of 2.9 nm [calculated from (21), assuming that micelles are composed of ~ 70 molecules of which 25% are dissociated]. The short-range repulsion (at separations $< \sim 6$ nm) was usually steeper, indicating steric or entropic effects such as hydration forces, counterion confinement, and adsorbate protrusion forces.
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- Previous SFA measurements (21) with quaternary ammonium surfactants have found that aggregate layers on mica have dissociation constants (20 to 25%) similar to those of spherical micelles. Given that any aggregate curvature should be a function of the dissociation constant (because the degree of charge neutralization affects the interheadgroup spacing), the above measurement is more consistent with curved surface aggregates (such as the proposed cylinders) than with flat bilayers.
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- Control experiments were performed to ensure that the adsorbate morphology was not an imaging artifact: (i) The adsorbate layer on each substrate was imaged in at least three independent experiments with different cantilevers. (ii) The imaged adsorbate morphology was confirmed to be repeatable and independent of scan size, speed, and direction. (iii) In many cases, a single cantilever was used to image two or more different aggregate structures (such as stripes and spheres) on different substrates.
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Scaling Properties of Stretching Ridges in a Crumpled Elastic Sheet

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Strong deformation of a sheet of solid material often leads to a crumpled state having sharp points of high curvature. A scaling property governing the crumpled state has been numerically demonstrated by an examination of the ridges joining pairs of sharp points in a range of simple geometries of variable size. As the linear size X increases sufficiently, the deformation energy grows as $X^{1/3}$ and consists of similar amounts of bending and stretching energy. The deformation energy becomes concentrated in a fraction of the sheet that decreases as $X^{-1/3}$. Despite this concentration, the local strain in the ridge decreases as $X^{-2/3}$. Nearly all the deformation energy in thin, crumpled elastic sheets was found to be concentrated in ridges that obey these scaling laws.

Buckled sheets such as a crumpled piece of paper, a collapsed storage tank, or a shriveled raisin represent a ubiquitous form of material deformation. These objects may be considered

as thin, elastic sheets that have been strongly deformed by some external force. Such "post-buckling" phenomena have been extensively studied in macroscopic sheets because of their importance for structural failure (1, 2) and for cushioning of mechanical impact (3, 4). Two features emerge from these studies. First, the deformation appears to be concentrated around points and lines that proliferate with increasing compression, as illustrated in Fig. 1. Second, the compressive force increases smoothly over a broad range of compression factors (3, 5). These same features are expected

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