Nanoscale Aggregate Structures of Trisiloxane Surfactants at the Solid–Liquid Interface

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The self-associating structures at the solid–liquid interface of three nonionic trisiloxane surfactants [(CH₃)₃SiO₂Si(CH₃)(CH₂)₃(OCH₂CH₂)₉OH (n = 6, 8, and 12), or BEₙ], are studied as a function of substrate properties by atomic force microscopy (AFM) imaging and force measurement. These trisiloxane surfactants are known as superwetters, which promote rapid spreading of dilute aqueous solutions on low-energy surfaces. This study also attempts to relate the BEₙ surface aggregate structures at the solid–liquid interface to their superwetting behavior. Four substrates are used in the study: muscovite mica, highly oriented pyrolytic graphite, and oxidized silicon wafer with and without a full monolayer of self-assembled n-octadecytrichlorosilane (OTS). The concentration of BE₉ is fixed at 2 times the critical aggregation concentration (CAC). The BEₙ surfactants are only weakly attracted to hydrophilic surfaces, more on oxidized silicon than on mica. All three form ordinary planar monolayers on HOPG and OTS-covered oxidized silicon. The significance of surfactant adsorption on the AFM tip is investigated by comparing the force curves obtained by tips with and without thiol modification. The surface aggregate structures of the BEₙ surfactants correlate with their bulk structures and do not exhibit anomalous adsorption behavior. The adsorption behavior of the BE₉ superwetters is similar to that of the C₁₂E₅ surfactants. Thus, our results confirm previous work showing that superwetting shares its main features with other classes of surfactants.

Introduction

Siloxane surfactants are amphiphilic materials containing a methylated siloxane hydrophobe coupled to one or more polyoxyethylene (EO) polar groups. Their surface and phase properties have been extensively researched because of their use in antifoaming, in enhanced wetting, in bactericides, and in skin, hair, and fabric conditioning.۱ Certain trisiloxane polyoxyethylene glycol surfactants (Me₂SiO)₂Me(OCH₂CH₂)₉OH (n = 5, 6, 8, and 12), or BEₙ, have been shown to promote rapid spreading of dilute aqueous solutions on low-energy surfaces.۲,۳ Recent research on the superwetters has been reviewed by Hill.۴,۵ Surfactants that form turbid dispersions are found to enhance wetting. Other work has specifically linked the presence of dispersed bilayer particles (vesicles) to enhanced wetting.۶–۸ Vesicle-containing solutions (BE₆ or BE₉) spread faster than a micelle-containing solution (BE₁₂).۹,۱۰ Other studies link the enhanced spreading rate to the formation of a bilayer at the spreading edge.۱۱,۱۲ A maximum spreading rate at intermediate substrate surface energy has been found for both nonionic and ionic surfactants,۱۳ though only the trisiloxane surfactants are able to wet extremely hydrophobic surfaces. The link between particles in solution and wetting, which is an interfacial phenomenon, is not obvious and demands deeper investigation. The work reported here is inspired by this enigma and explores the relationship between the surfactant aggregate structures in solution and those at interfaces.

The Soft-Contact atomic force microscopy (AFM) technique images surfactant surface aggregates such as cetyltrimethylammonium bromide (CTAB), sodium dodecyl sulfate (SDS), and poly(oxyethylene)₉-dodecyl ether (C₁₂E₉) by maintaining an image force as small as 10⁻¹² N.۱۴–۱۶ Using this technique, we have found a surface phase transition for C₁₂E₅ near its cloud point temperature on mica.۱۷ BE₁₂ has been found to exhibit aggregate structural changes at the solid–liquid interface that resemble its
bulk phase sequence. BE12 changes its surface aggregate structure with increasing surface hydrophobicity, from spherical micelles, to elongated micelles, to defected monolayer, and to continuous monolayer. Direct force measurements have been conducted in polymerized silicone- and hydrocarbon-based surfactant solutions in order to determine the adsorption behavior of the surfactants as a function of molecular chain structure and solvent quality. The film thickness of the polymeric sample has been found to be proportional to (number of oxyethylene units)\(^n\). Here the adsorption behavior of the trisiloxane surfactants at the solid--liquid interface is studied by combining the Soft-Contact imaging and direct force measurement. We report the equilibrium aggregate structures of BE6, BE8, and BE12 on mica, graphite, hydrophilic silica, and hydrophobic silica. We compare the adsorption behavior of the trisiloxane surfactants to that of hydrocarbon poly(oxyethylene) \(\text{C}_m\text{E}_n\) surfactants.

**Experimental Section.** The BE\(n\) (\(n = 6, 8, \text{and} 12\)) surfactants are used as received from Dow Corning Corp. with 95% purity, n-Octadecytrichlorosilane (OTS) is purchased from United Chemical Technologies and distilled just before use. Hexadecane (99%) and carbon tetrachloride (99.9%) are purchased from Sigma and used as received. Reagent grade ammonium hydroxide, 30% hydrogen peroxide, and reagent grade concentrated nitric acid are purchased from Fisher Scientific and used as received. Water is deionized to 18 M\(\Omega\) cm resistivity (Nanopure System, Barnstead). Grade 2, muscovite mica is purchased from Mica New York and hand-cleaned just before use. \(\text{SiO}_2\) grade highly oriented pyrolytic graphite (HOPG) (12 \(\times\) 12 \(\times\) 2 mm\(^3\)) is purchased from Advanced Ceramics and hand-cleaned with an adhesive tape until a smooth surface is obtained. Polished N type silicon (111) wafers are purchased from Wafer World with resistivity between 50 and 75 \(\Omega\) cm. The silicon substrate is cleaned following the "RCA clean" procedures of 0.2 nN), the maximum value of the force barrier, and subsequent data captured in a 3-h period. An E scanner with a maximum scan area of 16 \(\times\) 16 \(\mu\)m\(^2\) is used. Silicon nitride integral tips (NP type) are used with factory-specified nominal tip radii of curvature between 20 and 40 nm. All AFM images are deflection images unless specified. The integral and proportional gains are kept at a minimum of approximately 0.1. The force curves shown here are obtained from the same AFM tip so that the force magnitude can be compared. The spring constant of the cantilever is calibrated using the deflection method against a reference cantilever. Some measurements are deflection images unless specified. The integral and proportional gains are kept at a minimum of approximately 0.1. The force curves shown here are obtained from the same AFM tip so that the force magnitude can be compared.

The contact angle values of BE\(n\) surfactants at 2 times the critical aggregation concentration (CAC) and pure water on the various substrates are listed in Table 1. The contact angle is measured by an NRL contact angle goniometer (model 100, Rame-Hart) in the laboratory atmosphere. A droplet of 20 \(\mu\)L is placed on the substrate, and contact angles are read on both sides of the droplet. Five droplets are placed at various spots near the center of the substrate, and contact angles are averaged with an error of ±3°. Contact angles less than 10° cannot be measured accurately, and 0° is assigned in such cases. When the solution does not wet the substrate completely, as in the cases of graphite and the OTS monolayer, air bubbles can be appended at the surface, which gives rise to unusual images and force curves. It is possible to eliminate the bubbles by slowly purging the liquid cell with the solution.

**AFM Characterization.** A Multimode Nanospectro IIIa AFM (Digital Instruments) is used. The substrate is mounted onto a stainless steel disk and scanned in the aqueous solution of the surfactant. The solution is injected through silicone rubber tubing into a fluid cell (Digital Instruments), sealed by an O-ring. All measurements are performed at 22 ± 1°C. The AFM data reflect the equilibrium structure of the surfactant surface aggregates because no changes are observed between the first image or force curve collected, approximately 5 min after the solution injection, and subsequent data captured in a 3-h period. An E scanner with a maximum scan area of 16 \(\times\) 16 \(\mu\)m\(^2\) is used. Silicon nitride integral tips (NP type) are used with factory-specified nominal tip radii of curvature between 20 and 40 nm. All AFM images are deflection images unless specified. The integral and proportional gains are kept at a minimum of approximately 0.1. The force curves shown here are obtained from the same AFM tip so that the force magnitude can be compared. The spring constant of the cantilever is calibrated using the deflection method against a reference cantilever. Some measurements are deflection images unless specified. The integral and proportional gains are kept at a minimum of approximately 0.1. The force curves shown here are obtained from the same AFM tip so that the force magnitude can be compared.

**Results and Discussion.**

The surface aggregate structures of the three surfactants adsorbed on four substrates are studied by simultaneously imaging surface topography and measuring the surface force (F) versus the surface separation distance (D) profile, or F(D). All force curves are taken in Contact Mode unless specified. The force curves are quantified by the force onset distance (at an arbitrarily defined value of 0.2 nN), the maximum value of the force barrier, and the jump-in distance. The values in three surfactant solutions on four different substrates are listed in Table 2. The CACs for BE6, BE8, and BE12 are 9.6 \(\times\) 10\(^{-4}\), 1.09 \(\times\) 10\(^{-4}\), and 2.7 \(\times\) 10\(^{-4}\) mol/L, respectively. All surfactant concentrations are maintained at 2 \(\times\) CAC. At this concentration, BE6 and BE12 form clear solutions while BE8 forms a slightly cloudy solution.

![Table 1. Contact Angles (deg) of Pure Water and BE\(n\) Solutions at 2 \(\times\) CAC on Various Substrates](image1)

<table>
<thead>
<tr>
<th>Substrate</th>
<th>BE6 at 2 (\times) CAC</th>
<th>BE8 at 2 (\times) CAC</th>
<th>BE12 at 2 (\times) CAC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mica</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Silica</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>OTS</td>
<td>108</td>
<td>10</td>
<td>19</td>
</tr>
</tbody>
</table>

a Data taken from ref 32.

![Table 2. Summary of Data Extracted from the Force--Distance Measurement Curves](image2)

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Data Type</th>
<th>BE6</th>
<th>BE8</th>
<th>BE12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mica</td>
<td>Force Onset at 0.2 nN (nm)</td>
<td>5.0</td>
<td>4.3</td>
<td>4.8</td>
</tr>
<tr>
<td>Silica</td>
<td>Force Onset at 0.2 nN (nm)</td>
<td>6.0</td>
<td>13.0</td>
<td>12.0</td>
</tr>
<tr>
<td>Graphite</td>
<td>Force Onset at 0.2 nN (nm)</td>
<td>6.4</td>
<td>7.5</td>
<td>8.5</td>
</tr>
<tr>
<td>OTS</td>
<td>Force Onset at 0.2 nN (nm)</td>
<td>8.1</td>
<td>10.8</td>
<td>11.0</td>
</tr>
</tbody>
</table>

(24) Prater, C. B.; Maivald, P. G.; Kjoller, K. J.; Heaton, M. G. Probing Nanoscale Forces with the Atomic Force Microscope; Application Note No. 8; Digital Instruments: Santa Barbara, CA, 1995; see also references therein.
On Mica. The AFM images are featureless on mica for all three trisiloxane surfactants. Figure 1 is the $F(D)$ curve in BE6 solution on mica. A purely attractive force is observed at 5 nm, and it decreases in magnitude to $-0.4$ nN at contact. The $F(D)$ curves measured in BE8 and BE12 solutions on mica are similar to Figure 1 with slight variations in the jump-in point. The jump-in point, as marked in Figure 1, is defined as the start of the unstable region in the force measurement when the cantilever tip snaps suddenly onto the substrate. The jump-in occurs frequently during the cantilever-based force measurements due to the force gradient exceeding the spring constant. There exists a subtle difference between Figure 1 and the $F(D)$ curve obtained in pure water. $F(D)$ measured in pure water displays a weak long-range repulsion before the attraction sets in. The absence of the electrostatic repulsion in the surfactant solution suggests some modification to the surface charge due to surfactant adsorption, perhaps in the form of adsorbed isolated molecules or molecular patches. However, such sporadic adsorption does not present the necessary steric repulsion for the Soft-Contact imaging. We can conclude that on mica, the BE$_n$ surfactants behave similarly to the C$_m$E$_n$ surfactants.

On Hydrophilic Silica. Figures 2 and 3 summarize the AFM imaging and force measurement results of the trisiloxane surfactants. All the images presented here are obtained at a minimum image force. However, the reader should bear in mind that the imaged features are still affected by the contact force. The films consist of particles...
whose center-to-center distance varies with EO number, 40–50 nm for BE6 (Figure 2a,b), 12–20 nm for BE8 (Figure 2c), and 6–9 nm for BE12 (Figure 2d). All the force curves show the steric repulsion due to the dehydration of the EO headgroups, compression, and removal of the surfactant molecules from the contact zone. The maximum force is measured to be 1.8 nN at 4.3 nm for BE6 (Figure 3a), 1.0 nN at 3.9 nm for BE8 (Figure 3c), and 1.3 nN at 3.9 nm for BE12 (Figure 3d). The force maximum is followed by the jump-in process, which corresponds to the removal of surfactant from the contact zone. After the jump-in process, the repulsion rises rapidly. The unperturbed film thickness is estimated (from the onset force distance taken at $F = 0.2$ nN) to be 6.0 nm for BE6, 13.0 nm for BE8, and 12.0 nm for BE12. The fully stretched chain length is calculated to be 2.8 nm for BE6, 3.5 nm for BE8, and 4.8 nm for BE12. The bilayer thickness is 3.4 nm in BE6 vesicles and 4.0 nm in the BE8 lamellar phase, in which the polyoxyethylene chain is believed to be in a coiled structure. BE12 forms micelles in solution with a diameter of 7.0 nm. The higher film thickness compared to the respective bulk structure is present in a number of AFM force measurement studies of the nonionic surfactant system. However, the absolute thickness value taken from the AFM force curves should be treated with caution due to the uncertainty in surfactant adsorption on the tip and interpretation of the force curves. In a later part, we compare the F(D) curves obtained by unmodified tips and by tips that are coated with a thiol monolayer in order to determine whether the BE$_n$ surfactants adsorb on the AFM tip.

In addition to the primary jump-in point, a second jump-in point at a longer separation is observed at 13.0 nm for BE6 (Figure 3b) and at 7.0 nm for BE8 (Figure 3c). In the case of BE6, we find that when the tip is on top of a bump, two jump-in points are obtained, and when the tip is between the bumps, only one jump-in is recorded in the F(D) curves. Therefore the bumps represent an additional discrete bilayer with a thickness of 7.0 nm. In the case of BE8, the coverage of the second bilayer must be higher because most of the force curves measured in the BE8 solution contained two jump-in points. Both BE6 and BE8 are known to form vesicles in solution. It is possible that after the formation of the anchoring bilayer by the fast molecular diffusion, the adsorption and rupture of their vesicles contribute to the second bilayer patches.

The adsorption of BE$_n$ on silica agrees largely with what is known about C$_m$E$_n$ surfactants: (1) hydrogen bonding is necessary for adsorption; (2) both surface micelle and bilayer structures are possible; and (3) the aggregate size depends on the molecular packing constraints. For example, surfactants with large headgroups such as BE12 favor the formation of small, discrete micellar structure. A second discrete bilayer in the case of BE6 and BE8 is consistent with the presence of dispersed bilayer structures, such as vesicles, in the bulk phase.

**On Graphite.** The images captured in all three surfactant solutions showed smooth surfaces. We do not observe the stripelike structure as reported elsewhere. However, the strip pattern for BE8 is only observed after waiting for many hours in the previous study, while all our measurements are completed within 2–3 h after solution is injected. The stripe pattern is induced by one-dimensional epitaxy between all-trans hydrocarbon chains and the graphite lattice. It is difficult to envision such a match in the case of trisiloxane surfactants. The F(D) curves in the three surfactant solutions on HOPG are shown in Figure 4. All three curves exhibit repulsive forces consistent with the steric repulsion followed by the jump into contact. The unperturbed film thickness for BE6, BE8, and BE12 is determined at $F = 0.2$ nN to be 6.4, 7.5, and 8.5 nm, respectively. The steric barrier height and jump-in point are determined to be 2.8 nN and 5.1 nm for BE6, 3.2 nN and 4.9 nm for BE8, and 6.6 nN and 3.9 nm for BE12.
Both the steric barrier thickness and the height increase with increasing EO number. The increase in the film thickness with chain length is consistent with the end-on molecular adsorption configuration. Despite the thickness being longer than the calculated fully stretched chain length, an ordinary planar monolayer structure remains the most likely structure. Bilayer formation is energetically prohibited because of the hydrophobic nature of graphite, while the formation of 3 or more layers can be ruled out by the presence of only one jump-in in the F(D) curves. Unlike the C\textsubscript{m}E\textsubscript{n} surfactants that self-assemble into hemicylindrical hemimicelles, the BE\textsubscript{n} surfactants form a planar monolayer structure with vertically oriented molecules on graphite. The vertical monolayer structure is further supported by the lack of a 0.4 nm steric barrier close to the substrate as observed in the case of C\textsubscript{m}E\textsubscript{n} due to the flat-lying template layer.

**On Hydrophobic Silica.** On the silica that is hydrophobized by an OTS monolayer, a smooth surface is obtained in all three surfactant solutions as represented by Figure 5a. Figure 5b shows the F(D) curves for BE\textsubscript{6}, BE\textsubscript{8}, and BE\textsubscript{12} at 2 \times CAC on OTS. The steric barrier thickness values measured at 0.2 nN are 8.1, 10.8, and 11.0 nm for BE\textsubscript{6}, BE\textsubscript{8}, and BE\textsubscript{12}, respectively. The barrier height and jump-in distance are 8.6 nN and 4.4 nm for BE\textsubscript{6}, 10.0 nN and 3.0 nm for BE\textsubscript{8}, and 20.6 nN and 3.4 nm for BE\textsubscript{12}, respectively. The monotonic increase in the steric force followed by a single jump-in indicates a monolayer structure formed on the hydrophobic silica by all three surfactants. Similar to the graphite case, both the steric barrier thickness and height increase with increasing EO number. The magnitude of the steric barrier gives a qualitative measurement of the adsorbed amount since it is proportional to the surface pressure exerted by the surfactant film. The wider and shorter trisiloxane hydrophobe is able to accommodate a larger hydrophilic group before the onset of lateral repulsion between neighboring headgroups, which tends to reduce packing density. The large flexibility of the trisiloxane group may also contribute to closer packing. The BE\textsubscript{n} surfactants adsorb more strongly on OTS than on graphite with roughly 200% increase in the barrier height and 30% increase in the film thickness. The increase in the film thickness suggests decreasing tilt in the surfactant orientation with respect to the substrate as a result of closer packing on OTS. The adsorption energy is expected to be larger on the more hydrophobic OTS substrate because of higher water/substrate and lower surfactant/substrate interfacial energy terms.

To determine whether BE\textsubscript{n} absorbs on the silicon nitride tip, we compare the F(D) curves obtained in two configurations: methylated tip/surfactant solution/methylated substrate and bare silicon nitride tip/surfactant solution/methylated substrate. A silicon nitride tip is hydrophobic.

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bized by first sputter coating it with a thin film of gold (5 nm chromium + 7 nm gold) and subsequently depositing a monolayer of 1-hexadecanethiol (> 99%, Aldrich). The tip is placed in 10 mM thiol ethanolic solution for 2 h. Figure 6 shows the F(D) curve measured in the BE₈ solution on the OTS surface with the thiol-coated tip, which shows two jump-in points, one at 6.1 nm and the other at 4.7 nm. The same measurement with the uncoated tip shows only one jump-in point at 3.0 nm. Two jump-in events indicate that two layers are being pushed out at different force magnitudes. In the case of the bare tip, only one layer is pushed out. However, we cannot rule out the possibility of a thin yet strongly bound layer on the tip because such a layer cannot be distinguished from the hard substrate. The force values of the two configurations cannot be directly compared because the coated tip is a different tip with a different tip geometry.

In summary, the adsorption behavior of the trisiloxane surfactants at the solid–liquid interface, as summarized schematically in Figure 7, bears remarkable similarity to that of the CₙEₙ surfactants on both hydrophobic and hydrophilic surfaces. Thus our results confirm the previous conclusion¹³ that superwetting, albeit enigmatic, shares its main features with other types of surfactants. We do not find anomalous adsorption behavior for the trisiloxanes.

**Conclusion**

The self-associating aggregate structures of three trisiloxane surfactants BE₆, BE₈, and BE₁₂ are studied by Soft-Contact AFM imaging and direct force measurements at the solid–liquid interface. There are many similarities between the BEₙ and CₙEₙ surfactants that can be summarized below.

1. Surface micelles or bilayers form on hydrophilic surfaces. The aggregate size is connected to the molecular packing parameter as in the bulk phase.
2. The nonionic surfactant only adsorbs on hydrophilic surfaces with hydrogen bonding sites.
4. Surfactant adsorption, measured by both the steric barrier thickness and height, increases with increasing EO numbers and surface hydrophobicity.
5. The adsorbed amount of the BEₙ surfactant is comparable with that of an equivalent CₙEₙ surfactant. According to the literature, BE₆ closely resembles C₁₂E₄ in phase behavior, BE₈ is similar to C₁₂E₅, and BE₁₂ is similar to C₁₂E₆.¹⁰ We obtain similar steric force magnitude numbers for the pairs. For example, the steric barrier height for C₁₂E₅ on OTS at 2 × CMC is 9.5 nN while for BE₈ it is 10.8 nN at 2 × CAC when the same AFM tip is used.

The different structure formed by the BEₙ surfactants on graphite can be attributed to the lack of a dimensional match between the trisiloxane hydrophobe and the graphite lattice. The double bilayer structure found on silica by the BE₆ and BE₈ surfactants can be linked to the dispersed bilayer structure in the bulk phase.

In conclusion, we find the surface aggregate structures of the BEₙ surfactants essentially paralleling those of the CₙEₙ surfactants, with differences reflecting the size, shape, and chemical nature of the trisiloxane hydrophobe. The surface aggregate structures resemble bulk structures. Therefore, despite the enigmatic nature of the superwetting phenomenon, we do not find anomalous adsorption behavior for the trisiloxane superwetters. This study agrees with previous conclusions by Stoebe et al. that the superwetters display bulk and interfacial features similar to those of other surfactants, especially the CₙEₙ surfactant series. The surface aggregate structures of surfactants are not only important for the understanding of various colloidal phenomena but may also offer insight into the “bottom-up” approach to nanotechnology by the self-assembly of hierarchical structures.

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