AFM Study of Trisiloxane Surfactant Aggregate Structures at the Solid/Liquid Interface

J. Dong¹, G. Mao¹*, and R. M. Hill²

¹Department of Chemical Engineering and Materials Science, Wayne State University, Detroit, MI 48202
²Dow Corning Corporation, Midland, MI 48686

The aggregate structure of a nonionic trisiloxane surfactant at the liquid/solid interface was studied by Atomic Force Microscopy (AFM) as a function of substrate surface energy. The hydrophobicity of oxidized silicon wafer was gradually increased by increasing the amount of n-octadecyltrichlorosilane (OTS) monolayer coverage. AFM soft-contact imaging and force measurements captured the variation in surfactant aggregate structures from spherical micelles to elongated micelles, defected monolayer, and continuous monolayer with increasing surface hydrophobicity. The aggregate structural evolution at the solid/liquid interface resembles the microstructural sequence of the surfactant in bulk solution at room temperature. It is speculated that the hydrophobic attraction between the surfactant and the solid surface induces two-dimensional analogues of the surfactant bulk microstructures. The hydrophobic attraction affects the geometric packing parameter in a similar fashion as the increase in surfactant concentration.
Introduction

The wetting, surface activity, and phase behavior of silicone surfactants have been studied extensively because of their wide use in anti-foaming, enhanced wetting, corrosion protection, bactericides, and cosmetic formulations (1). Specifically a group of trisiloxane surfactants have excited much research interests because they promote rapid spreading of aqueous solution on hydrophobic surfaces. Various causes were said to contribute to the superspreading capability of the trisiloxane surfactants, which include the molecular structure, solution turbidity, and formation of lamellar- or bicontinuous-like structure near the interfaces (2).

Surfactant phase behavior and microstructure in bulk solution are well understood (3,4). However only recently significant progress has been made in the understanding of the aggregate structure at the solid/liquid interface. It is possible to visualize the surfactant aggregate structure directly at the solid/liquid interface by soft-contact AFM (5). Soft-contact AFM is performed by floating the AFM tip above the adsorbed surfactant layer with the image force set below the breakthrough force to the underlying substrate. Soft-contact imaging together with direct force-versus-distance measurements make it possible to define the aggregate morphology at the nanometer scale. Nonionic oligo(oxyethylene) n-alkyl ethers, i.e. CE₅ surfactants, were found to form an epitaxial layer of hemicylindrical hemimicelles on highly oriented pyrolytic graphite (HOPG) (6). In the absence of epitaxy, the aggregate structure of CE₅ surfactants was found to depend on temperature (7) and surface chemistry (8,9,10,11). Combined with data from other techniques such as ellipsometry, fluorescence, and neutron reflection, the adsorption behavior of CE₅ surfactants on hydrophilic surfaces versus on hydrophobic surfaces is summarized as following (12): 1) on hydrophilic surfaces, CE₅ surfactants form surface micelles or flat bilayers depending on the geometric packing parameter; and 2) on hydrophobic surfaces, CE₅ surfactants form flat monolayers similar to those at the air/water interface. In one study where the substrate hydrophobicity was gradually changed by the mixed monolayers of thiols, no intermediate structures between micelles/bilayers and monolayers were observed (10). Here we search for additional surfactant aggregate structures by studying a surfactant with unusually rich phase behavior - nonionic trisiloxane surfactant ((CH₃)₃SiO)₂Si(CH₂)₃(CH₂)₃(OCH₂)₁₂OH or in short M(D’E₁₂OH)M (13,14). The AFM images and force curves presented here will show that new types of aggregate structures were formed by M(D’E₁₂OH)M at the solid/liquid interface. The AFM study was carried out in a fixed concentration of M(D’E₁₂OH)M, 2 × Critical Aggregation Concentration (CAC), on surfaces with gradual variation of
hydrophobicity. The surface hydrophobicity was gradually increased by increasing the surface coverage of n-octadecyltrichlorosilane (OTS) monolayer on oxidized silicon. The surface hydrophobicity was characterized by its contact angle with water. We present a possible link between the surfactant surface aggregate structural evolution and its bulk microstructural sequence.

Experimental Section

Materials

M(D’E₁₂OH)₃ was used as received from Dow Corning Corp. with 95% purity. n-Octadecyltrichlorosilane (C₁₈H₃₇SiCl₃) or OTS was purchased from United Technologies and distilled just before use. Water was deionized to 18 MΩ·cm resistivity (Nanopure system, Barnstead). One-sided polished N type silicon (111) wafer was purchased from Wafer World with resistivity of 50 to 75 Ω·cm. The silicon substrate was oxidized following the “RCA” procedures used in the integrated circuit manufacturing (15). The freshly oxidized substrate was completely wettable by water with a contact angle close to 0°.

Substrate Surface Modification

Vapor phase deposition of OTS on oxidized silicon was carried out in a desiccator. The substrate was placed 2 to 3 cm above OTS liquid droplets. Vacuum was pulled until the OTS liquid started to boil at approximately 1.3 kPa. The deposition time was changed from 15 to 90 min in order to obtain substrates with water contact angles between 20° and 107°. Subsequently the substrate was annealed at 150 °C for 2 hr. Only freshly prepared substrates were used in the experiments. All substrates were imaged by AFM prior to injection of the surfactant solution. All substrates showed flat and featureless surfaces with mean surface roughness between 3 and 8 Å over a scan area of 500 × 500 nm². No domain structure was imaged on any OTS-modified substrates.

Characterization Methods

The contact angle was measured by an NRL contact angle goniometer (Model 100, Rame-Hart) in the laboratory atmosphere. A water droplet of 20 µl
was placed on the substrate and contact angles were read on both sides of the droplet. Five droplets were placed at various spots near the center of the substrate, and contact angles were averaged with an error of ± 3°.

AFM imaging and force measurements were conducted in a liquid cell using Nanoscope IIIa AFM (Digital Instruments). An E-scanner with maximum scan area of 16 × 16 µm² was used. The z scale of the scanner was calibrated with Ultra-Sharp Calibration TGZ02 set (step height 100 nm, Silicon-MDT). Silicon nitride (Si₃N₄) integral tips (NP type) were used with a nominal tip radius of 20 to 40 nm. In order to compare our results, we present data that were obtained by the same cantilever tip. The spring constant of the cantilever was calibrated using the deflection method against a reference cantilever (Park Scientific Instruments) of known spring constant (0.157 N/m) (16). The calibrated value 0.17 ± 0.05 N/m was used in all force plots. The force calibration curve was converted to the force-versus-separation plot following a standard procedure (7). AFM images of the surfactant layer were obtained in the soft-contact mode. The scan rate was between 3 and 12 Hz. Height images were captured with feedback gains between 3 and 5. Deflection images were captured with feedback gains less than 1. Height images were flattened in order to remove background slopes. No other filtering procedures were performed on these images. The tip to substrate velocity was fixed at 0.1 µm/s in force calibration. We found that the force curves became independent of approach speed below 0.5 µm/s for the nonionic surfactant systems. The temperature was maintained at 22 ± 1 °C.

Results

The concentration of M(D’E12OH)M was fixed at 2 × CAC (5.4 × 10⁻⁴ mol/l). Deflection images obtained by contact mode and amplitude images obtained by tapping mode are shown here unless specified. All oxidized silicon substrates with or without OTS coverage appeared to be smooth and featureless under AFM at the nanometer scale. A typical surface roughness Ra was measured to be 5 Å over a scan size of 500 × 500 nm². There is no evidence for domain formation by OTS at any surface coverage according to the AFM results.

Figure 1a and 1b are the soft-contact AFM image and force-versus-separation curve between an AFM tip and oxidized silicon in the M(D’E12OH)M solution. The oxidized silicon was completely wettable by a water droplet. On oxidized silicon, M(D’E12OH)M molecules aggregated into small globular particles with unit size between 6 to 9 nm. The diameter was determined manually in the AFM sectional analysis by measuring the center-to-center distance between neighboring particles. The particle size is identical to the size of M(D’E12OH)M micelles in solution below 10 %w/w, which is 7.0 nm (13). The force curve showed a repulsion starting at 9.1 nm. The repulsion reached a local
maximum of 0.9 nN at 3.9 nm. Force decreased and then increased rapidly upon further approach. The force curve lacked a clear gap or jump-in event. The jump-in event is associated with a sudden removal of surfactant layer from the interacting zone. The absence of this abrupt event implies continuous compression and/or removal of surfactant layer. Previous AFM studies of CE$_i$ surfactants on silica have associated the continuous type of force curves with surface micelles and the discontinuous type with bilayers (9,7). The wide spatial distribution of surfactant molecules in micelles interacting with substrate functional groups may cause the surfactant molecules to be removed at various compression distances. It was concluded that M(D’E$_{12}$OH)M formed spherical micelles on oxidized silicon.

The structure of M(D’E$_{12}$OH)M on OTS-modified oxidized silicon substrate with 20° water contact angle is represented by Figure 2a and 2b. Bundles of elongated rod-like features were observed with width between 6 and 10 nm and length between 30 and 80 nm. The force curve identified as Force Curve 1 showed a continuous repulsion that started at 4.5 nm. No jump-in was observed. The range of the repulsion was in between monolayer thickness and micelle diameter (13). However, the measured force curves varied widely on this surface because of the surface heterogeneity. Force Curve 1 represented those that gave longer range of repulsions with the tip contacting mostly micelle-covered area. Force Curve 2 represented those that were positioned in between micelles. All the force curves should be treated as averages between the rods and that of the background. On a substrate with 40° water contact angle, rod-like features with lower aspect ratio (between 8 and 15 nm in width and between 25 and 35 nm in length) but higher coverage (roughly 8 and 4 rods per 100 nm$^2$ on 40° and 20° surface respectively) were observed as shown in Figure 3a. The corresponding force curve is shown in Figure 3b. The individual rods co-existed with bigger aggregates of 40 to 80 nm in size. The force curve showed a continuous repulsion starting at 9.5 nm. OTS did not form anisotropic domains on silica and therefore cannot account for the rod formation. The rods cannot be induced by AFM scanning because they appeared at random angles, at the lowest allowable set point force, and only on relatively hydrophilic surfaces. However, the rods gradually rotated to be perpendicular to the fast scan direction with repeated scanning. Therefore the alignment of rods was likely an artifact of the AFM scanning. The elongated features on 20° and 40° surfaces suggest that M(D’E$_{12}$OH)M formed cylindrical (or less likely hemicylindrical) micelles on the relatively hydrophilic surfaces.

The structure of M(D’E$_{12}$OH)M aggregates on an OTS-modified substrate with 80° water contact angle is represented by Figure 4. Figure 4a shows a smooth film with randomly distributed defects as indicated by the arrows. The height image (Figure 4b) indicates that the defects were holes. The depth of the holes was less than 1.5 nm as determined in the AFM sectional height profile of
Figure 4c. The defects were unchanged during repeated scanning and with different set point forces. This is in contrary to the case where holes were generated by the AFM tip (7). The holes are an inherent feature of the surfactant film. Figure 4d shows a repulsive force with an onset at 14.9 nm and a force maximum of 6.5 nN at 5.4 nm. The jump-in event was clearly present. From the jump-in distance and the fact that only one jump-in event was observed, it was concluded that M(D’E$_{2}$OH)M formed an imperfect monolayer on a substrate with 80° water contact angle. We would like to point out that almost identical force curves were obtained in the same surfactant solution on graphite surface with contact angle between 75° and 78° (17). Figure 5a and 5b are the AFM image and force curve obtained on oxidized silicon with a fully covered OTS monolayer. Its water contact angle was 107°. The image remained smooth with no holes up to the highest allowable set point force. The repulsion started at 11.5 nm and reached a maximum of 20.2 nN at 3.8 nm. It should be pointed out that AFM-measured film thickness of nonionic polyoxyethylene surfactants often is larger than the thickness measured by other methods, probably due to surfactant adsorption on the AFM tip (6, 18). The jump-in event was also observed here indicating an instantaneous push-out of the monolayer segment from the interacting zone. Comparison between Figure 4 and Figure 5 suggests that M(D’E$_{2}$OH)M monolayer packing density increased with increasing surface hydrophobicity.

Discussion

The AFM study revealed an evolution of M(D’E$_{2}$OH)M aggregate structures on substrates with increasing substrate surface hydrophobicity. The AFM results of the trisiloxane surfactant agreed for the most part with previous studies of C$_{i}$E$_{j}$ surfactants (12): 1) M(D’E$_{2}$OH)M formed surface micelles on silica surface with the oxyethylene head groups anchored at the hydroxyl surface and also exposed toward the aqueous solution; 2) M(D’E$_{2}$OH)M formed a monolayer on fully covered OTS surface with the trisiloxane hydrophobe anchored at the methylated surface and the oxyethylene head group exposed toward the aqueous solution; and 3) monolayer packing density increased with increasing surface hydrophobicity. M(D’E$_{2}$OH)M also displayed intriguing intermediate structures that are worth further discussion: 1) cylindrical-shaped aggregates at relatively hydrophilic surfaces between 20° and 40° contact angle; and 2) imperfect monolayer structure with holes at 80° contact angle. Though the various intermediate microstructures in C$_{i}$E$_{j}$ surfactant bulk solution were never previously identified on surface, it was known that surface coverage is
influenced by the surfactant chemical structure, i.e. the geometric packing parameter. Surfactants with geometric packing parameter that favors flat bilayers tend to have the highest adsorption plateau.

The molecular packing parameter $S$ is defined as $S = V/(AL)$, where $V$ and $L$ are the volume and length of the hydrophobic chain respectively, and $A$ is the head group area. $S$ less than 0.33 favors spherical micelles, $S$ between 0.33 and 0.5 favors rod-like micelles, and $S$ larger than 0.5 favors disk-like micelles and vesicles (3). Increase in concentration or temperature of $\text{CE}_3$ surfactant solutions causes an increase in $S$ value (3).

At room temperature, $\text{M(D'E}_1\text{E}_2\text{OH)}M$ forms a single isotropic phase at all concentrations in water, but its microstructure evolves with increasing concentration as determined by small angle neutron scattering, small angle x-ray scattering, cryo-transmission electron microscopy, pulse-gradient spin-echo NMR, and rheology measurement (13): 1) spherical micelles below 10 %w/w, 2) elongated micelles between 10 and 35 %w/w by speculation, 3) entangled long worm-like micelles between 35 and 45 %w/w, 4) multi-connected tubular network between 50 and 70 %w/w, 5) bilayer network between 70 and 80 %w/w, and 6) disordered and fluctuating bilayers above 80 %w/w. It was calculated that if the head group area is below 153 Å$^2$ ($S = 0.33$), $\text{M(D'E}_1\text{E}_2\text{OH)}M$ forms sphere-shaped micelles; if the head group area is below 102 Å$^2$ ($S = 0.5$), $\text{M(D'E}_1\text{E}_2\text{OH)}M$ forms rod-shaped micelles; and if the head group area is below 51 Å$^2$ ($S = 1$), $\text{M(D'E}_1\text{E}_2\text{OH)}M$ forms disk-shaped micelles or infinite bilayer structure (14). One cannot help but notice the strong resemblance between the sequence of $\text{M(D'E}_1\text{E}_2\text{OH)}M$ bulk microstructure and that observed on solid surface by soft-contact AFM. We speculate that surface interactions give rise to $S$ value changes in $\text{M(D'E}_1\text{E}_2\text{OH)}M$ surface aggregates in a similar fashion as those caused by concentration increase in solution. The intermediate surface aggregate structures must correspond to the microstructures at intermediate concentrations with comparable $S$ values. In other words, the effective head group area of $\text{M(D'E}_1\text{E}_2\text{OH)}M$ reduces from no smaller than 153 Å$^2$ on a silica substrate to less than 102 Å$^2$ when surface is covered by OTS. The decrease in head group area can be induced by the hydrophobic attraction between surfactant and solid surface, which dehydrates the head group and reduces the repulsion between head groups. It was argued that the hydrophobic attraction is the main driving force for nonionic $\text{CE}_3$ surfactant adsorption on both hydrophobic and hydrophilic surfaces (10). The hydrophobic attraction becomes stronger with increasing OTS coverage, which causes gradual increase in $\text{M(D'E}_1\text{E}_2\text{OH)}M$ $S$ values from those favoring spherical micelles to those favoring rod-like micelles and planar structures.
Conclusions

The self-associating aggregate structure of a nonionic trisiloxane surfactant \( \text{M(D'E}_2\text{OH)M} \) was studied by AFM soft-contact imaging and force measurements. The hydrophobicity of the oxidized silicon wafer substrate was gradually increased by increasing the amount of OTS monolayer coverage from vapor phase deposition. In the absence of OTS, spherical micelles were observed. On relatively hydrophilic surfaces with 20° and 40° water contact angles, rod-like micelles and their clusters were observed. On hydrophobic surfaces with 80° and 107° water contact angles, defected and perfect monolayers were observed. These surface aggregate structures are speculated to be two-dimensional analogues of the surfactant microstructures in bulk solution. The surface aggregate structural evolution bears close resemblance to that in bulk from spherical micelles, to worm-like micelles, tubular network, planar layer network, and ordinary planar layer with increasing concentration at room temperature. The surface structural evolution is attributed to the continuous increase in hydrophobic attraction between surfactant and solid surface with increasing surface hydrophobicity. The hydrophobic attraction dehydrates the head group, reduces the head group area, and increases the geometric packing parameter \( S \). It will be interesting to find out if surfactants with equally rich bulk phase microstructures as \( \text{M(D'E}_2\text{OH)M} \) will exhibit similar trend. The surfactant aggregate structures are not only interesting for fundamental study but also may serve as templates for novel nanostructures and applications.

References

17. Unpublished results.
**Figure Captions**

**Figure 1.** AFM image and force-versus-distance curve on oxidized silicon wafer in \(M(D'E_{12}OH)M\) solution. (a) AFM image showing globular particles. The contact angle is written at the upper right corner. (b) Force-versus-distance curve with the approximate set point force marked as SP.

**Figure 2.** AFM image and force-versus-distance curve on OTS modified silicon wafer with 20° contact angle in \(M(D'E_{12}OH)M\) solution. (a) AFM image showing elongated rods and rod clusters. (b) Force-versus-distance curve.

**Figure 3.** AFM image and force-versus-distance curve on OTS modified silicon wafer with 40° contact angle in \(M(D'E_{12}OH)M\) solution. (a) AFM image showing elongated rods and rod clusters. Circle a and b highlight a region with individual rods and a region with clusters of rods respectively. (b) Force-versus-distance curve.

**Figure 4.** AFM images and force-versus-distance curve on OTS modified silicon wafer with 80° contact angle in \(M(D'E_{12}OH)M\) solution. (a) AFM image showing holes in otherwise smooth surface. The holes are pointed out by the arrows. (b) The corresponding AFM height image. The arrows point out the holes. The dashed line in the image is where the sectional profile was taken. (c) The AFM sectional height profile along the dashed line in (b) showing the holes approximately 1.5 nm in depth. (d) Force-versus-distance curve. The jump-in is marked by the arrow.

**Figure 5.** AFM image and force-versus-distance curve on OTS modified silicon wafer with 107° contact angle in \(M(D'E_{12}OH)M\) solution. (a) AFM image showing smooth surface. (b) Force-versus-distance curve. The jump-in is marked by the arrow.
Figures

Figure 1a
Figure 1b
Figure 2b
Figure 3a
Figure 4d
Figure 5a

107°

500 nm
Figure 5b