Probing the Three-Dimensional Structure of Soft Organized Surfactants at the Solid-Liquid Interface via Atomic Force Microscopy

Application Note

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Introduction

Atomic force microscopy (AFM) provides a unique direct-visualization tool to study the three-dimensional structure of adsorbed surfactants on solid surfaces. In the limited body of reported topography data, however, the heights of observed surfactant aggregates were significantly lower than expected values.

The reduced corrugation on an AFM topography image is usually due to the fact that the surface adsorbates are soft compared to the spring constant of the cantilever and the applied force is too high. The technique commonly used to image weakly adsorbed surfactant aggregates in contact mode AFM is to maintain a force within the pre-contact double-layer electrostatic interaction range (1, 2). Generally, the force is on the order of 10^1 to 10^2 pN. The difficulty encountered in obtaining uncompressed topography images on adsorbed surfactant aggregates seemed to suggest that such small forces were still too high for the soft surfactants.

Alternatively, MAC Mode from Agilent Technologies enables precision control of the oscillation of a magnetically coated AFM cantilever and makes it possible to image with an average force well below 1 pN. This lower force minimizes the distortion of soft molecules. In our work, topography structures of cationic surfactant aggregates, dodecyltrimethylammonium bromide (DTAB), adsorbed on a negatively charged hydrophilic mica surface above the critical micelle concentration (cmc) have been studied under different imaging conditions.

In contact mode, using double-layer electrostatic interaction, the measured heights of the organized aggregate images varied depending on the applied force. They were nevertheless all significantly lower than the estimated length of the DTAB molecule. In MAC Mode, however, corrugations near half of the proposed DTAB aggregate cylinders on mica have been obtained. This result, to the best of our knowledge, represents the most realistic three-dimensional topography structure directly observed on surfactant aggregates at the solid-liquid interface.

Experiment

Water was pre-filtered with a reverse osmosis system and then passed through a Milli-Q system, resulting in 18 Mø·cm-1 final conductivity. DTAB was purchased from Sigma-Aldrich, 99% pure, and then diluted to 40 mM solution, about three times the cmc (3), in Milli-Q water before use. All containers and sample-contacting AFM parts, including the liquid cell and cantilever holder, were sonicated in detergent and then sonicated and rinsed with Milli-Q water. Mica was cleaved immediately before the solution was applied.

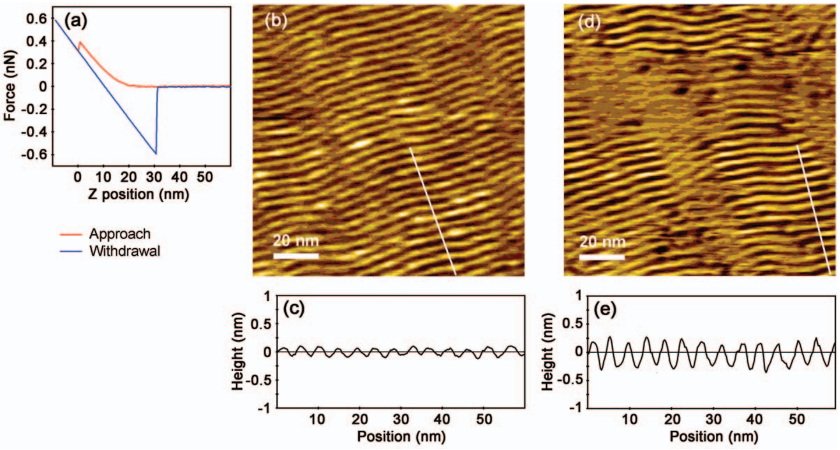
All data were acquired using an Agilent 5500 atomic force microscope with a 10mm multipurpose scanner. In contact mode, standard silicon nitride cantilevers with a nominal spring constant of 0.03 nN/nm were used. In MAC Mode, cantilevers of the same type coated with a magnetic film were used. All images presented are topography images acquired at scan rates from 1.5 to 4 lines/sec. The scanner's z dimension was carefully calibrated using both a 100nm height-calibration standard and the height of atomic steps on Au (111) surface. Before imaging, about 400 ml surfactant solution was applied to a large AFM liquid cell and equilibrated for 20 minutes. The large amount of solution allowed stable scanning for many hours without evaporation-related problems.

Results and discussion

Figure 1 summarizes the results of DTAB surfactant aggregates adsorbed on mica in contact mode using the double-layer electrostatic interaction. Figure 1(a) is a typical force versus distance curve. Both approach (red) and withdrawal (blue) have been plotted. During approach, the tip experienced a double-layer electrostatic interaction force before jumped into contact. The interaction range was around 0.3 nN.

Organized DTAB aggregate images were obtained when the force was set inside the electrostatic range before the tip jumped into contact. Figure 1(b) shows a typical example. The force was set near the middle of the range, about 200 pN from Figure 1(a). The measured period of the parallel DTAB aggregate cylinders was 4.6 ± 0.2 nm, consistent with previous observations (4). The height of the cylinders, measured from a number of images acquired under similar conditions, was only 1.8 ± 0.2 Å, as shown in the cross-section plot, Figure 1(c), along the line in Figure 1(b). Based on different measurements and calculations (3, 4, 5), the height of the proposed DTAB aggregate cylinders on mica was estimated in the range of 4–5 nm.

A higher height of the organized DTAB aggregate cylinders was observed when the imaging force was decreased to the minimum right before the tip broke off from the surface. Figure 1(d) was such an example. The organized DTAB aggregates at different locations, even on a single scan line, appeared to have different heights. The cross-section along a row of high DTAB aggregates, as shown in Figure 1(e), clearly demonstrated a noticeable height increase compared to Figure 1(c). The average height of those highly corrugated surfactant aggregates measured from a number of similar images was 5.6 ± 0.5 Å. It is still significantly lower than the estimated height of the DTAB aggregate. Imaging with such a low force, or even negative (attractive) force, required a more stabilized condition than scanning with a normal double-layer repulsive force. No



Caption: Figure 1. (a) Typical force versus distance curve of a silicon nitride cantilever on mica in 40 mM DTAB aqueous solution. During approach, the tip experience double-layer electrostatic repulsive force before it jumped onto the surface. (b) Typical topography image of DTAB surfactants adsorbed on mica obtained in contact mode when the force was set near the middle of the double-layer electrostatic repulsive range. (c) Cross-section along the line in (b) showing corrugation around 1.8 Å. (d) Image of DTAB surfactants on mica when the force was decreased to the minimum right before the tip broke off from the surface. (e) Cross-section along the line in (d) showing corrugation around 5.6 Å.

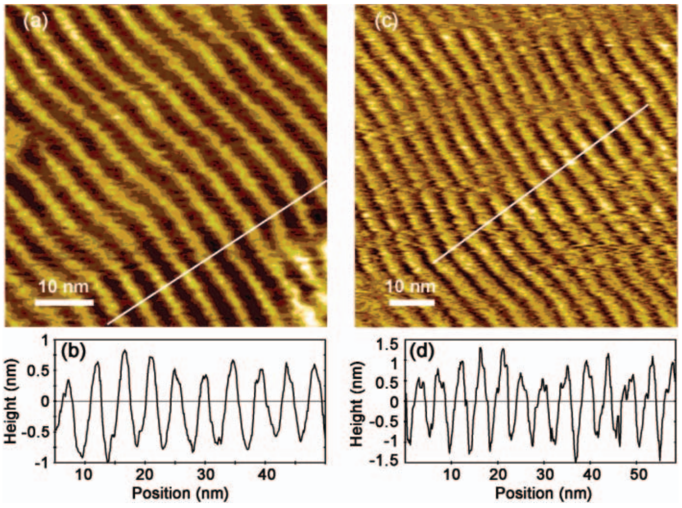
height above 8 Å on the DTAB aggregate cylinders has been observed using any of the contact-mode operations.

Figure 2 shows a couple of topography images of organized DTAB aggregate cylinders on mica obtained in MAC Mode. The period was measured to be consistent with that obtained in contact mode. A cross-section along the line in each image was plotted to display the heights of the cylinders. While each image showed a slightly different height, and even the same image had different corrugations at different locations, the overall height of the DTAB cylinders was significantly higher than that obtained in contact mode, as shown in Figure 1. Some of the cylinders were measured clearly above 2 nm, as shown in Figure 2(d), which is about half of the estimated height of the proposed DTAB aggregate cylinders on mica surface. Figure 2(c) was captured 1 hour 43 minutes after Figure 2(a) on the same sample. The similar topography feature in both images indicated a stable condition for scanning as well as the structure.

The full height in the range of 4–5 nm of the adsorbed DTAB aggregate cylinders on mica was not observed. One possible reason was that the operation condition used in MAC Mode still caused a certain amount of compression on the soft surfactants scanned. Another possibility was that the tip might not have been able to reach the lower half of the DTAB cylinders because the soft, flexible cylinders were closely packed. In that case, the observed three-dimensional images of DTAB aggregates would be the actual adsorbed surfactant topography that could be detected by AFM. Unlike deflection, undisturbed three-dimensional surface topography can be used as direct evidence of the adsorption mechanism of the surfactant aggregates at the solid-liquid interface.

Conclusion

The three-dimensional topography structure of organized DTAB surfactants on mica in aqueous solution above the cmc has been studied using AFM under different operation conditions. In contact mode, using pre-contact electrostatic interaction, the observed height of the DTAB aggregates was 1.8 ± 0.2 Å when a force near the middle of the electrostatic repulsive range was used; the observed height was 5.6 ± 0.5 Å when the force was reduced to the minimum. In MAC Mode, more than 2-nm-high DTAB aggregates were clearly observed, which is about half of the estimated height of the proposed DTAB aggregate cylinders on mica surface. This highly sensitive, three-dimensional topography imaging capability will undoubtedly help to further resolve and understand adsorption mechanisms of a variety of self-assemblies at the solid-liquid interface.



Caption: Figure 2. Topography images (a and c) of DTAB surfactants adsorbed on mica in 40 mM aqueous solution obtained in MAC Mode. Graphs (b) and (d) present cross-section plots along the lines in (a) and (c), respectively, showing corrugation of DTAB aggregates around 2 nm.

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