Adsorption behavior of hexadecyltrimethylammonium bromide (CTAB) to mica substrates as observed by atomic force microscopy

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Abstract Atomic force microscopy is employed to study the adsorption behavior of CTAB to mica surfaces. Results show that conformational transitions from globular micelles→cylindrical micelles→flat films are observed in the process of the adsorption of CTAB to mica at twice the bulk critical concentration. However, in 0.5 cmc CTAB solution, the adsorbed CTAB molecules to mica form the layered film structures, and apparent conformational transitions do not appear. Meanwhile, the phenomena of the adsorption of CTAB to mica and the dissociation of mica surfaces are periodically observed.

Keywords: atomic force microscopy (AFM), micelle, behavior of adsorption, the dissociation of mica surfaces.

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The study of the adsorption behavior of surfactants to interfaces is very important in colloid and interface science[1] owing to the important applications such as floating, wetting and release of drugs, etc. The adsorption characteristics of surfactants at interfaces have been described by many classic theories[2]. Among them, adsorption isotherms are one of the most popular theoretical modes. Later, many experimental methods have been employed to study the adsorption behavior at interfaces, such as NMR[3], calorimetry[4] and surface force measurements[5]. In the past, direct morphological observation of surfactants adsorbed at interfaces has been lacking owing to the limitation of experimental conditions. Recently, the advent of AFM gives a powerful support to the visualization of the adsorbed surfactant on solid substrates. AFM was first used to image surfactant surface-aggregates by Manne et al.[6], and promote the development of this filed[7−10], which makes people further study the adsorption mechanism at the molecular level.

In situ AFM measurements of adsorbed surfactants on solid/liquid interfaces have been demonstrated in many reports[11−13]. The main advantage of using *in situ* AFM is that it eliminates any possible changes in the structure of the adsorbed layers as a result of the drying process that is integral to AFM in air. Therefore, the images of the adsorbed layers are more representative of the natural adsorption conditions in the presence of the bulk solution[14]. On the other hand, during the imaging process the AFM tip is in contact with the layers, so that the perturbation by the scanning tip inevitably affects the adsorption process on solid substrates[15]. Compared to *in situ* AFM measurements, *ex situ* AFM can preclude this influence and possibly reflect the true adsorption behavior in the solution as long as the experimental conditions are strictly controlled[16,17].

One of the most widely studied systems is cationic surfactant hexadecyltrimethylammonium bromide. Pashley[18] systemically studied the adsorption behavior of CTAB on mica, quartz or glass surfaces, and postulated that CTAB adsorption on mica surfaces results in bilayer formation. Later the morphology of surfactant CTAB aggregates on mica surfaces has been visualized by Sharma[10] and Ducker [7]. The adsorption process of CTAB to mica is a dynamical process. The morphology of CTAB aggregates on solid substrates will show different characteristics at different time. However, the systemically experimental investigations are still lacking so far. In this study, the dynamical adsorption behavior of CTAB on mica was investigated by AFM. We focused on the conformational changes of the adsorbed CTAB on mica with the adsorbed time, and the formation mechanism was illustrated.

1 Experimental

Hexadecyltrimethylammonium bromide (CTAB) was of the analytical reagent grade (Beijing Xi Zhong Chemical Factory) and purified by extraction with diethylether followed by three rounds of recrystallizations from anhydrous ethanol. After the recrystallization no minimum was observed in a plot of surface tension vs concentration. AFM (Digital Instrument, Co) was adopted. All water used was double distilled.

Freshly cleaved mica was dipped into CTAB solution for various time, then taken out and dried with a stream of nitrogen; afterward it was visualized by AFM in the tapping mode using silicon ultralecers. All the images are in the height mode. They were smoothed, without any other treatment.

2 Results and discussion

2.1 Study of adsorption from 2cmc CTAB solution

Fig. 1 shows AFM images of CTAB absorbed to mica from 2 cmc CTAB solution at various absorbed time. Fig. 1(a) clearly shows that the CTAB molecules absorbed on mica surfaces appear in the form of cylinder aggregates after 2 min, and the average height is about 6 nm. At 5 min, the morphological transitions of CTAB molecule aggregates from cylinder aggregates to flat layered films occur, and the height is 9 nm. At 8 min, the morphology of CTAB aggregates on mica remains unchanged while only the fractional coverage increases. However, the image of fig. 1(d), observed at 10 min, clearly shows that the height of the layered films decreases to 6 nm. After 30 min, the CTAB aggregates still show the layered film structures while the height of films again increases to 10 nm.

There are a number of CTAB micelles in the 2 cmc CTAB solution. Upon the mica sheet is dipped CTAB solution, CTAB micelles are absorbed to the negatively charged mica surfaces because of electrostatic attraction interactions. There exists certain spacing between CTAB micelle aggregates owing to the electrostatic repulsions between the polar headgroups, as shown in fig. 1(a). The formation mechanism of CTAB globular micelles is a compromise between electrostatic repulsion and attraction due to exposure of the hydrophobic interior. The headgroup area for a CTAB micelle is about 0.64 nm^2[8], the surface of mica has one negative site per 0.48 nm^2[8], so when the surfactant adsorbs, the density of potential surfactant counterions is greater on mica than in the micelle. It is reasonable to expect that this increase in counterions density on the mica surface will lead to the screening of the repulsive electrostatic forces between the $CTA+$ headgroups and thus to a lower curvature aggregate such as a cylinder or flat sheet[8], as shown in fig. 1(a)—(e). In the 2 cmc CTAB solution, the morphology of CTAB aggregates on mica is altered in the sequence globular micelles→cylindrical micelles→layered films, which is illustrated in fig. 2.

Fig. 3 is a plot of the height of absorbed CTAB aggregates versus the absorbed time. It clearly shows that the height is a dynamical process with the increased absorbed time. The absorbed height was found to increase at the initial 8 min, and to decrease at 10 min, then to increase again at 30 min. For the periodical changes of the height of CTAB aggregates, possible reasons are shown as follows: mica is a layered aluminosilicate mineral, chemical interactions between SiO_4 and K^+ are weak, so that two neighboring mica surfaces are easy to dissociate. When K^+ ions exchange

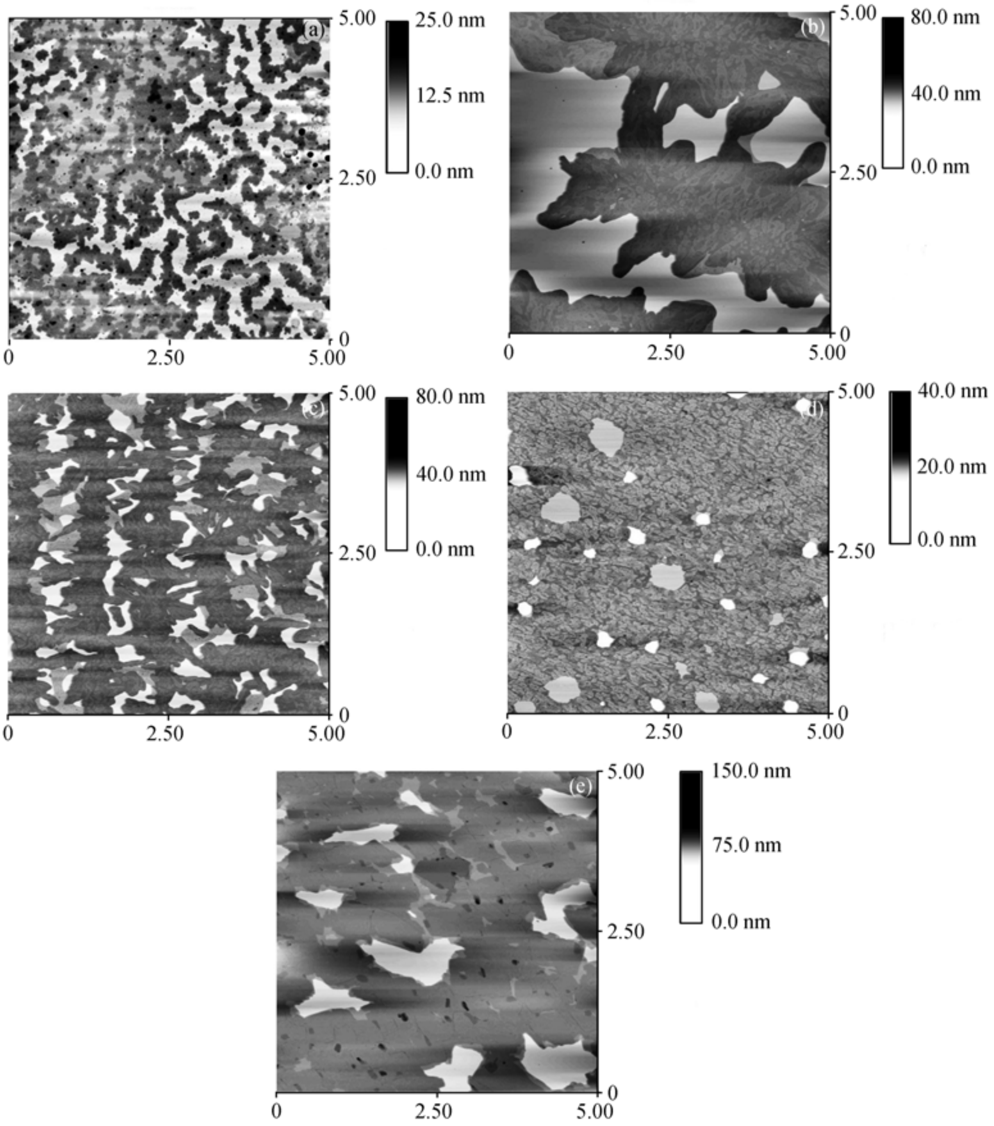

Fig. 1. Representative AFM images of the adsorbed CTAB to mica from the 2 cmc CTAB solution at various times. (a) 1 min; (b) 5 min; (c) 8 min; (d) 10 min; (e) 30 min.

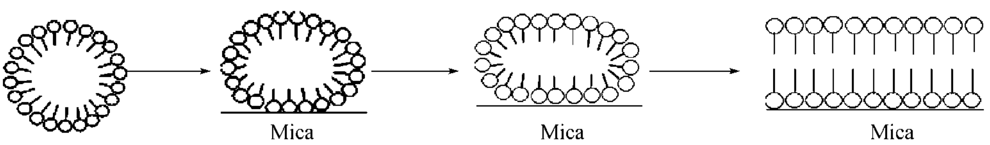

Fig. 2. Schematic pictures of the conformational changes of CTAB micelles on mica in the 2 cmc CTAB solution.

CTA$^+$ ions, the water molecules are extruded from the mica crystals since the hydrated interactions of CTA$^+$ with water molecules are weaker than that of K$^+$, which decreases the interactions between mica layers, so that mica surfaces dissociate to some extent, resulting in the decrease of the height of CTAB aggregates on mica. Then CTAB molecules are absorbed to the next mica surface, which results in the increase of the height of CTAB aggregates again. The similar experimental results can be found in refs. [19, 20].

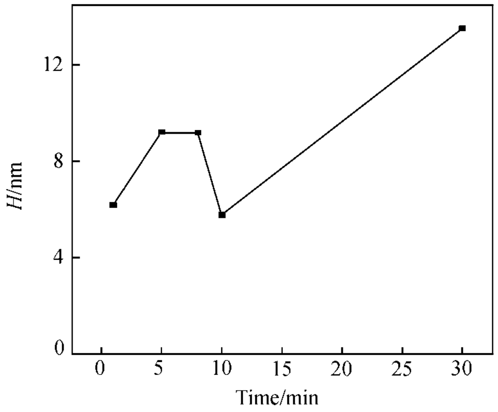

Fig. 3. A plot of the height of the adsorbed layer versus the adsorbed time in the 2 cmc CTAB solution.

2.2 Study of adsorption from 0.5 cmc CTAB solution

Fig. 4 shows AFM images of CTAB absorbed to mica from 0.5 cmc CTAB solution at various absorbed times. The images of fig. 4 clearly show that CTAB molecules are adsorbed to mica surfaces in terms of the layered films. No conformational transitions were observed in the experiments. Theoretically, CTAB molecules disperse in the solution as monomers in the 0.5 cmc solution. The process of adsorption occurs

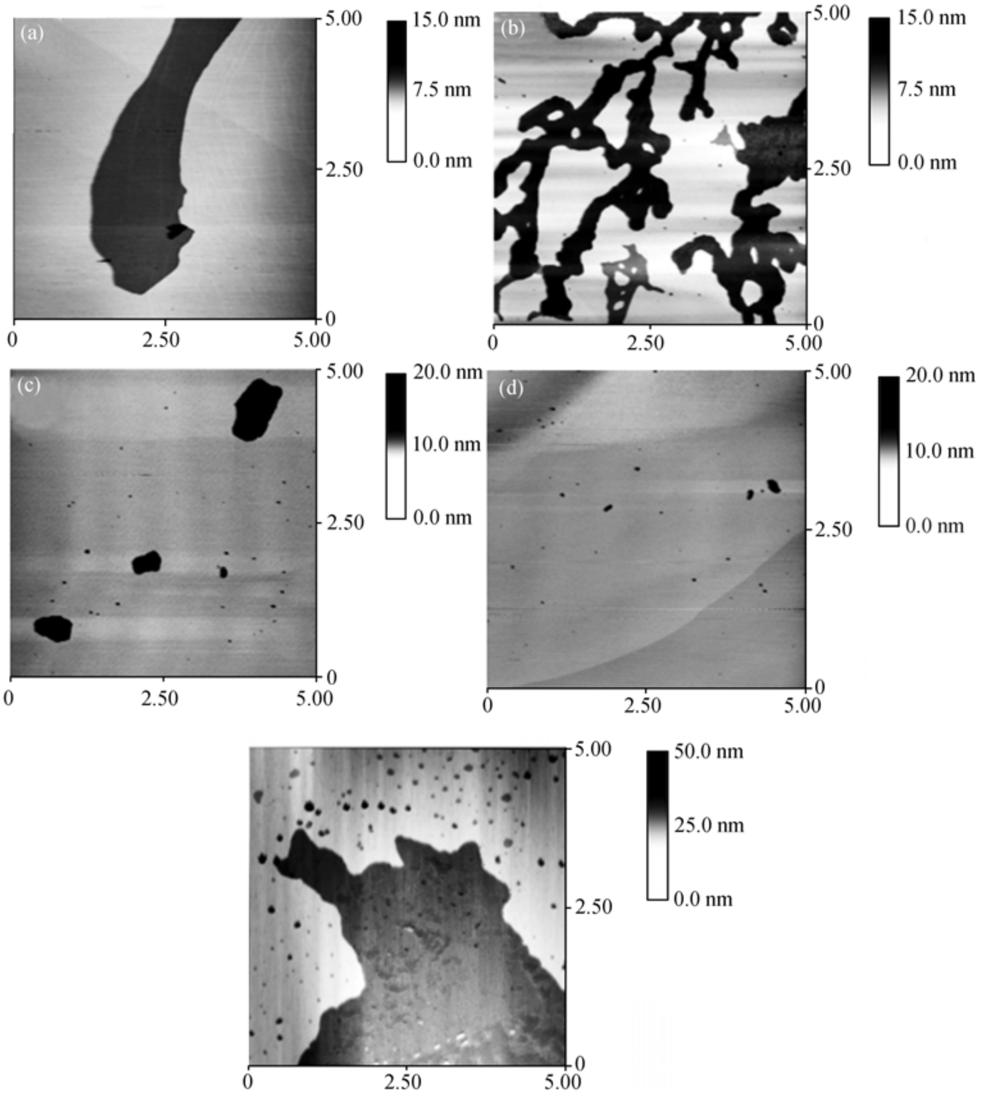

Fig. 4. Representative AFM images of the adsorbed CTAB to mica from the 0.5 cmc CTAB solution at various times. (a) 1 min; (b) 5 min; (c) 8 min; (d) 10 min; (e) 30 min.

when the mica sheet is dipped into the solution. The layered film structure is formed with increased immersion time, which is demonstrated in fig. 5.

The height of the film is 2 nm in fig. 4(a) and 6 nm in fig. 1(a), so that the adsorbed layered film on mica is about monolayer in the 0.5 cmc CTAB solution and two bilayers in the 2 cmc CTAB solution since the length of CTAB molecules is about 1.5 nm. In the 0.5 cmc CTAB solution, the height of adsorbed CTAB molecules on mica is similar to that in fig. 3, and the process of periodical changes from adsorption→dissociation→adsorption were also observed. The variation of the height of adsorbed layer versus the immersion time for C_{18}TAB/mica system reported by Mellott[21] is very different from ours. The reason may be any disturbing effect inevitably introduced in the preparation of samples. The similar discrepancy has been observed elsewhere[15,22].

At present, it is impossible to determine when the adsorption process on mica reaches a maximum density and when CTAB molecules start to adsorb after the dissociation of mica surfaces since the process of adsorption is very fast. Fig. 6 lists a series of representative AFM images at 5, 10, 12 and 60 s and a plot of the height of the absorbed layer versus the adsorbed time, which demonstrates that the changes from adsorption→dissociation→adsorption occur in a short period of 1 min.

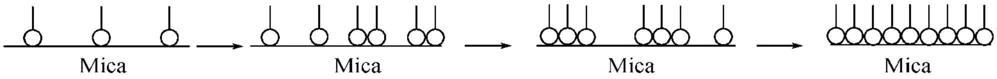

Fig. 5. Schematic pictures of the conformational changes of CTAB molecules on mica in the 0.5 cmc CTAB solution.

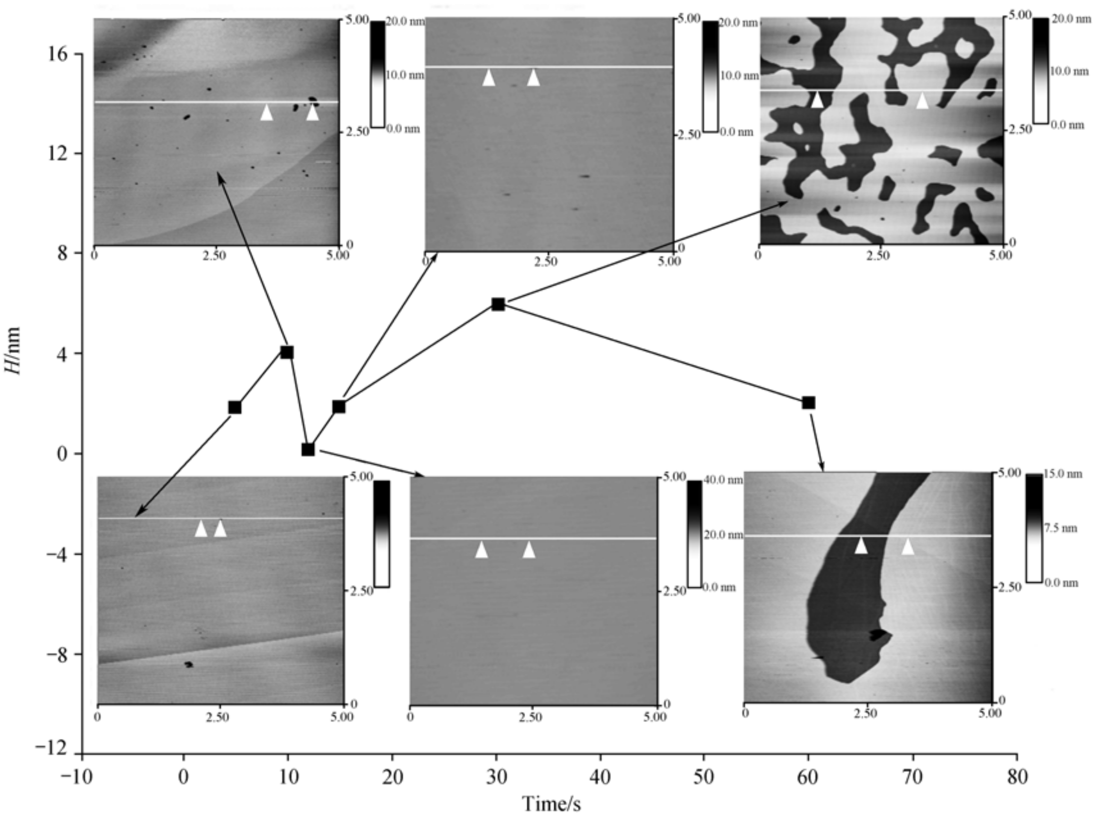

Fig. 6. A plot of the height of CTAB adsorbed to mica from the 0.5 cmc CTAB solution within 1 min and the corresponding AFM images (inset).

3 Conclusion

In the 2 cmc CTAB solution, the morphology of the adsorption behavior of CTAB to mica is altered in the sequence globular micelles→cylinder aggregates→layered films. In the 0.5 cmc CTAB solution, CTAB molecules adsorbed to mica form the layered film structure without the occurrence of conformational transitions. Meanwhile, the adsorption behaviour of CTAB to mica is a dynamical process from adsorption→dissociation→adsorption.

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