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## COMMUNICATION

## Direct observation of surfactant aggregate behavior on a mica surface using high-speed atomic force microscopy

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The processes of dynamic aggregate transformations of micelles at a mica surface were observed using high-speed atomic force microscopy. We showed that salt concentration affects not only the equilibrium state adsorbed structure but also the time required to reach the equilibrium state on the mica surface.

Surfactant molecules containing long hydrophobic alkyl chains and hydrophilic groups can organize into various self-assemblies, both in bulk solution and at a solid interface. Atomic force microscopy (AFM) has been employed to demonstrate a strong correlation between the bulk self-assembly structure and the morphology of adsorbed surfactant layers.<sup>1</sup> Adsorbed layers comprised of globular and cylindrical aggregates on hydrophilic substrates, of which mica is the most widely studied, have been well-characterized.<sup>1c-e</sup> Micellar structures of common cationic surfactants, such as hexadecyltrimethylammonium bromide (CTAB) and hexadecyltrimethylammonium chloride (CTAC), adsorbed at the mica/liquid interface have been directly observed by AFM.<sup>1c-e</sup> These ordered interfacial aggregates have well-defined sizes and shapes that can be controlled by the addition of metal halide salts.<sup>1</sup> When a higher concentration of competing cations is introduced, the density of available lattice anions on the mica surface is reduced, so that the spacings between surfactant headgroups increase. In other words, the influence of the mica interface is reduced by the introduction of the salt, and hence the surface aggregated structure becomes more similar to the micellar structure found in bulk solution.

Lamont and Ducker have shown that CsCl tends to increase the curvature of CTAC aggregates on a mica surface due to the transformation from cylinders to globules with variation of the salt concentration.<sup>1c</sup> However, these measurements were performed at equilibrium conditions and no information was gained regarding the initial aggregation dynamics, due to the lack of available techniques for observing the dynamic behavior of surfactant aggregates. Rapid acquisition of successive highresolution images of surfactant aggregates is required. The scanning speeds of commercially-available AFMs are usually

several minutes per frame, and are therefore too slow to monitor many physicochemical processes in liquids that occur at much faster rates. Recently, this limitation has been challenged by the use of high-speed AFM,<sup>2</sup> which can capture images at a frame rate of more than 30 frames  $s^{-1}$ . Various imaging studies have attempted to capture biological processes on video at high imaging rates.<sup>2</sup> In this study, high-speed AFM was used to observe the initial aggregate behavior of CTAC at the mica-water interface, and provide new insights regarding surfactant aggregation dynamics at a mica surface.

The muscovite mica used in this study was cleaved immediately prior to use. Water was prepared using a Milli-Q system and the resulting water had a conductivity of 18 M  $\Omega$  cm<sup>-1</sup>. CTAC (>95%, TCI, Tokyo, Japan) was recrystallized three times from ethanol. Analytical grade CsCl (99.9%, Wako, Tokyo, Japan) was used as received. Observations of the CTAC aggregates were performed in soft tapping mode using a laboratory-built high-speed AFM. The cantilever (Olympus, Tokyo, Japan) is 6-7 µm long, 2 µm wide, and 90 nm thick with a spring constant of 0.1-0.2 N m<sup>-1</sup>. Its resonant frequency in an aqueous solution is  $\sim 1$  MHz. To achieve a small tip-sample loading force, the free-oscillation peak-topeak amplitude of the cantilever  $(A_0)$  was set to ~1 nm and the amplitude set point was set at more than 0.9  $A_0$ . The probe tip was grown on the tip of a cantilever by electron beam deposition and was further sharpened by argon plasma etching. The tapping force estimated was less than 30 pN. All observations were performed at room temperature (25 °C) and at a surfactant concentration equal to twice the critical micelle concentration (CMC) in the absence of salt. The scan area was 200  $\times$  200 nm<sup>2</sup> with 200  $\times$  200 pixels. The imaging rate was 1-2 frames s<sup>-1</sup>. The high-speed AFM used in this study can be used to observe at a video rate of ca. 15-30 frames  $s^{-1}$  for a scan range of *ca*. 250 nm under feedback operation that is capable of preventing weak interactions from being disturbed by the scanning tip. However, high-resolution observations were necessary in this study, so we measured at 1-2 frames s<sup>-1</sup>. High-speed AFM measurements were recorded immediately after injection of CsCl solutions including the CTAC. The diameters of the observed globular or cylindrical micelles are approximately 9-11 nm. Taking the tip radius into account, the true sizes of the micelles are actually smaller than the observed diameters.<sup>3</sup> Their heights are in fact approximately 5-6 nm.

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Fig. 1 Continuous high-speed AFM images of CTAC aggregates at the interface between the mica surface. 0.0027 mol  $L^{-1}$  CTAC. Images are 200 × 200 nm<sup>2</sup>. (a) At 10 s worm-like micelle shapes are evident, while at (b) 20 s and at (c) 30 s cylindrical micelle shapes are observed, and (d) at 300 s a flat bilayer is observed.

Fig. 1 shows continuous high-speed AFM images of the CTAC aggregate structure at the mica surface. Interestingly, for CTAC at twice the CMC, worm-like and cylindrical structures were observed at 10 to 30 s, which then transformed into a flat layer after approximately 300 s. It is known that CTAC forms a bilayer at a mica surface.<sup>1c</sup> However, this dynamic behavior shows that CTAC is not instantaneously stabilized by binding to the mica surface, but gradually changes into a bilayer over a few minutes. Mica has exchangeable surface cations, and the density of charges on the mica substrate (1 negative lattice charge per  $0.48 \text{ nm}^2$ )<sup>4</sup> is such that surfactants are adsorbed to the surface with their head-groups closer together than that for equilibrium bulk separation (the head-group area for CTAC in a micelle is 0.64 nm<sup>2</sup>).<sup>5</sup> It is considered that this dynamic behavior leads to adsorbed aggregates with a lower degree of curvature, such as a flat bilayer, than the corresponding micelles in solution.

Fig. 2 and 3 show the structure of CTAC aggregates at the mica surface for different CsCl concentrations and with a constant CTAC concentration of  $0.0027 \text{ mol } L^{-1}$ . When CTAC was coexistent with a relatively low concentration of CsCl  $(0.034 \text{ mol } \text{L}^{-1})$ , a transformation from globular to cylindrical micelles was observed after approximately 20 s, and an equilibrium state with stable cylindrical structures was reached after about 30 s (Fig. 2). When CTAC was coexistent with a high concentration (0.1 mol  $L^{-1}$ ) of CsCl, the adsorbed structure formed globular micelles and no further transformation was observed, that is, an equilibrium state was reached after 10 s (Fig. 3). These equilibrium states of CTAC aggregate shapes on a mica surface with addition of CsCl have been reported,<sup>1c</sup> and reported shapes are very similar to our results at 300 s. Fig. 4 shows a schematic representation of the CTAC aggregation states on the mica surface for different exposure



Fig. 2 Continuous high-speed AFM images of CTAC aggregates at the interface between the mica surface. 0.0027 mol  $L^{-1}$  CTAC/ 0.034 mol  $L^{-1}$  CSCl. Images are 200 × 200 nm<sup>2</sup>. (a) At 10 s globular micelle shapes are evident, (b) at 20 s and (c) 30 s globular to cylindrical micelle shapes are observed, and (d) at 300 s cylindrical micelle shapes are evident.



Fig. 3 Continuous high-speed AFM images of CTAC aggregates at the interface between the mica surface. 0.0027 mol  $L^{-1}$  CTAC/0.1 mol  $L^{-1}$  CsCl. Images are 200 × 200 nm<sup>2</sup>. (a) At 10 s globular micelle shapes are evident, while at (b) 20, (c) 30, and (d) 300 s, no further transformation was observed.

times. It is known that CTAC forms cylindrical aggregates at a mica surface at equilibrium state with the addition of 0.034 mol  $L^{-1}$  CsCl;<sup>1c</sup> however, there have been no previous reports of the change in shape from globular to cylindrical aggregates. The initial globular structure is induced by the adsorption of Cs<sup>+</sup> to negative sites of the mica lattice, which decreases



**Fig. 4** Schematic representation of CTAC aggregation states at the interface between the mica surface for different exposure times. (a)  $0.0027 \text{ mol } \text{L}^{-1}$  CTAC, (b)  $0.0027 \text{ mol } \text{L}^{-1}$  CTAC/0.034 mol  $\text{L}^{-1}$  CSCl, and (c)  $0.0027 \text{ mol } \text{L}^{-1}$  CTAC/0.1 mol  $\text{L}^{-1}$  CSCl.

the number of adsorption sites available for CTAC, and it is considered that the structural change of the aggregate shape is caused by the slow exchange of CTA ions for potassium ions in the mica lattice. These transformations occur in the opposite order to that observed in bulk solution, indicating a different mechanism for surfactant aggregation at a mica interface.

We conclude that salt concentration affects not only the equilibrium state adsorbed structure but also the time required to reach the equilibrium state on the mica surface, which is a new result that was previously unknown. In this study, we directly observed the initial dynamics using a high-speed AFM until an equilibrium state was reached. We observed the gradual transformation of the adsorbed structures until an equilibrium state was reached and clarified for the first time that the addition of CsCl affects the time required to reach an equilibrium state. Thus, we believe that it is important to determine the time required for the adsorbed structure to reach an equilibrium state in order to understand the nature of various phenomena that take place at the interface.

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## Notes and references

- (a) S. Manne, J. P. Cleveland, H. E. Gaub, G. D. Stucky and P. K. Hansma, Langmuir, 1994, 10, 4409; (b) S. H. Manne and H. E. Gaub, Science, 1995, 270, 1480; (c) R. E. Lamont and W. A. Ducker, J. Am. Chem. Soc., 1998, 120, 7602; (d) H. N. Patrick, G. G. Warr, S. Manne and I. A. Aksay, Langmuir, 1999, 15, 1685; (e) W. A. Ducker and E. J. Wanless, Langmuir, 1999, 15, 160; (f) G. G. Warr, Curr. Opin. Colloid Interface Sci., 2000, 5, 88; (g) S. B. Velegol, B. D. Fleming, S. Biggs, E. J. Wanless and R. D. Tilton, Langmuir, 2000, 16, 2548; (h) S. Xu, M. Chen, E. Cholewa, G. Szymanski and J. Lipkowski, Langmuir, 2007, 23, 6937; (i) U. Retter, Langmuir, 2000, 16, 7752; (j) U. Retter and A. Avranas, Langmuir, 2001, 17, 5039.
- 2 (a) M. B. Viani, L. I. Pietrasanta, J. B. Thompson, A. Chand, I. C. Gebeshuber, J. H. Kindt, M. Richter, H. G. Hansma and P. K. Hansma, *Nat. Struct. Biol.*, 2000, **7**, 644; (b) T. Ando, N. Kodera, E. Takai, D. Maruyama, K. Saito and A. Toda, *Proc. Natl. Acad. Sci. U. S. A.*, 2001, **98**, 12468; (c) A. D. L. Humphris, M. J. Miles and J. K. Hobbs, *Appl. Phys. Lett.*, 2005, **86**, 034106.
- 3 J. Vesenka, S. Manne, R. Giberson, T. Marsh and E. Henderson, Biophys. J., 1993, 65, 992.
- 4 G. Mao, Y. Tsao, M. H. Tirrel and H. T. Davis, *Langmuir*, 1993, 9, 3461.
- 5 (a) H. N. Patrick, G. G. Warr, S. Manne and I. A. Aksay, Langmuir, 1997, 13, 4349; (b) Y. Asai, Chem. Phys. Lipids, 2003, 124, 103; (c) J. Israelachvili, Intermolecular and Surface Forces, Part III, Academic Press, London, 2nd edn, 1992.