A Bilayer Formed by Soluble Amphiphiles with Single Chain at the Mica–Solution Interface

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We investigated the aggregate morphologies of tetradecyldimethylamine oxide hemihydrochloride (C14DAO·1/2HCl) on mica surface in the surfactant solutions by Atomic Force Microscopy (AFM). C14DAO·1/2HCl forms a flat bilayer on mica. This morphology is different from spheres or cylinders which have been reported for other cationic surfactants with a single tetradecyl tail. The reason for this lower curvature of the C14DAO·1/2HCl aggregate on mica is discussed in terms of the hydrogen bond between the headgroups.

At solid–liquid interfaces, surfactants spontaneously aggregate to form a variety of microstructures. The Atomic Force Microscopy (AFM) has been recently applied to the surface aggregates of quaternary ammonium surfactants on mica in solution.[1] The AFM images of the aggregates showed a variety of morphologies on mica : spheres, cylinders and a flat bilayer.[2–4] The aggregate morphologies have been found to be closely related to the surfactant packing parameter[5] as it does in bulk solutions.

Alkyldimethylamine oxide(CnDAO) solutions are mixtures of the nonionic $[C_nH_{2n+1}(CH_3)_2N\rightarrow O]$ and the protonated cationic species $[C_nH_{2n+1}(CH_3)_2N^+–OH]$. The composition (the degree of ionization α) is determined by pH under a given ionic strength. On dodecyldimethylamine oxide (C12DAO) at $\alpha = 0.5$, the characteristic properties have been found with respect to the micelle size and the micelle stability(the critical micelle concentration, cmc).[6] These characteristic behaviors at $\alpha = 0.5$ have been interpreted in terms of a hydrogen bond between the headgroups on the micelle surface, the nonionic–cationic pairs $(–N^+–OH\cdots O\leftarrow N–)$. The hydrogen bond is expected to affect the morphology of adsorbed aggregates of CnDAO on mica surface because the formation of nonionic–cationic complex is expected to increase the packing parameter of the surfactant. In this paper, we report the aggregate morphology of tetradecyldimethylamine oxide hemihydrochloride (C14DAO·1/2HCl) (i.e., $\alpha = 0.5$) on mica in the surfactant solution at pH 5 by AFM.

Water was twice distilled from a glass still and then filtered through a Millipore filter (0.2 μm). Tetradecyldimethylamine oxide (GERBU Co.) and cethyltrimethylammonium bromide (C16TABr) (NACALAI TESQUE Co.) were recrystallized three times from hot acetone. AFM images were captured with SPA 400 (Seiko Instruments, JAPAN) at 25 ± 1 °C, using silicon nitride tips (OLYMPUS Co., JAPAN) with a nominal spring constant of 0.09 Nm^{-1}. The mica was freshly cleaved just before use. The surfactant was adsorbed on the surface of a freshly cleaved mica by immersing the mica in the surfactant solution for at least 12 h. Imaging force was adjusted to as small value as possible, typically between 100 and 800 pN under a repulsive force. No filtering of images was performed other than that inherent in the feed back loop.

The surface acid dissociation exponent of mica and the surface isoelectric point of the Si_3N_4 AFM tip have been reported to be 5.6 ± 0.2 [7] and 6.2 ± 0.2 [8], respectively. According to these results, the surface charges for the mica and the AFM tip in water at pH 5 have opposite signs (i.e., negative charge for the mica and positive charge for the AFM tip). As might be expected, we observed the electrical double layer attraction between bare mica and the tip in water at pH 5 (not shown). In the C14DAO·1/2HCl solutions of 10^{-3} M without added salt, on the other hand, the exponential long-range repulsion force appears at moderate separations (Figure 1A). The exponential decay length becomes smaller in the presence of 0.1 M NaCl. This indicates that the longer repulsive force originates from the electrical double layer repulsion between the AFM tip and the sample. Since the AFM tip has positive charges, the cationic

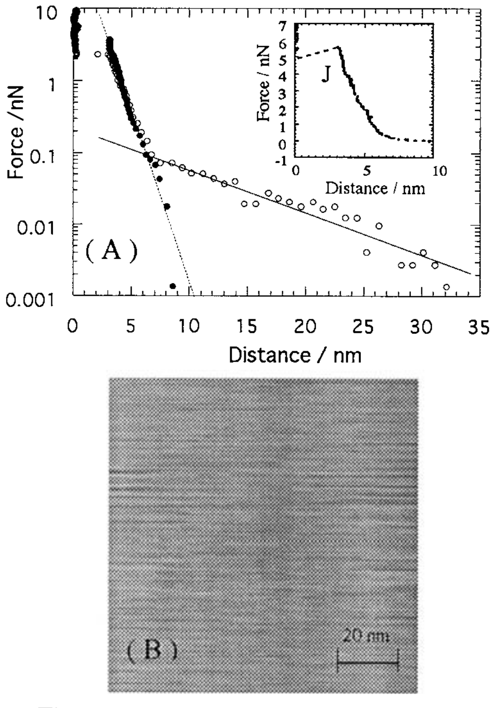

Figure 1. (a) Force curves for C14DAO·1/2HCl surfactans adsorbed on mica in the surfactant solutions at pH 5. The insert shows the force curve for 1 mM C14DAO·1/2HCl in the presence of 0.1 M NaCl. ○ : 1 mM C14DAO·1/2HCl. ● : 1 mM C14DAO·1/2HCl + 0.1 M NaCl. (b) The AFM image of C14DAO·1/2HCl aggregates at the mica - the surfactant solution of 1 mM interface at pH 5 without added salt.

headgroups of the aggregate on mica should face the bulk solution. This is expected if a bilayer is formed on the mica. A steep repulsion (i.e., a force barrier) is observed at a separation of about 2.5–3 nm in the presence of 0.1 M NaCl(J in the insert of Figure 1A), which has been assigned to the adsorbed layer thickness.[4] From this force barrier, we infer that the thickness of the C14DAO•1/2HCl film on mica is about 2.5–3 nm. This thickness is close to the thickness of the compressed bilayer of C16TABr adsorbed on mica (3.1–3.5 nm) by the surface force measurements.[9] Figure 1B shows the AFM image of the C14DAO•1/2HCl aggregates in the surfactant solution of 10^{-3} M without added salt. The featureless of the AFM image indicates a flat surface of the aggregate on mica. The above results on the C14DAO•1/2HCl aggregates : (1) the positively charged flat surface and (2) the bilayer thickness of the surfactant film on mica, they strongly suggest that the C14DAO•1/2HCl forms a flat bilayer on mica in the surfactant solution.

In the aqueous surfactant solutions of 10^{-6} M and 10^{-5} M, the AFM images on mica showed patches of different sizes which may be surfactant aggregates (not shown). The surface coverage of the surfactant aggregates increased with the concentration up to 10^{-4} M, and then the featureless of the AFM images were observed in the concentration range between 5×10^{-4} M and 10^{-2} M (cmc ~ 1.5×10^{-3} M at pH 5 without added salt). This suggests that the flat bilayer on mica above 5×10^{-4} M reaches the saturated adsorption.

We have measured the force curves of the C14DAO•1/2HCl and the C16TABr without added salt in this study. These force curves were obtained with the same tip in this study, so the relative magnitude is comparable. It is found that the force barrier of the C14DAO•1/2HCl is larger than that of C16TABr which has been reported to form a flat bilayer on mica (i.e., 4–6 nN for the C14DAO•1/2HCl at 10^{-3} M, 1.5–2 nN for the C16TABr at 2×10^{-3} M). The greater force barrier of C14DAO•1/2HCl suggests that the surfactant film on mica is mechanically more stable than that of C16TABr. Some additional cohesive force should exist in the C14DAO•1/2HCl aggregates on mica.

It is instructive to consider why the C14DAO•1/2HCl forms a flat bilayer on mica, but not other cationic surfactant with a single tetradecyl chain (e.g., cylinders for tetradecyltrimethylammonium chloride)[4], in spite of similar headgroup structures each other. Flat bilayers on mica have been reported for quaternary ammonium surfactants with two dodecyl chains (e.g., didodecyldimethylammonium and the symmetric gemini surfactant with quaternary ammonium headgroups)[2] and C16TABr [3]. The flat bilayer of the C14DAO•1/2HCl suggests the higher packing parameter character of the C14DAO•1/2HCl, compared with quaternary ammonium surfactants of the same hydrocarbon chain. It may be interpreted that the higher packing parameter character arises from the complex formed by a hydrogen bond between the nonionic and the cationic headgroup on the aggregate surface ($-N^+-OH\cdots O\leftarrow N-$). Due to the hydrogen bond, the area per headgroup decreases. The complex is expected to behave as the surfactant with double chains, leading to the higher packing parameter character. Recently, we found that the OH stretching band assigned to the hydrated OH group appeared around 2700 cm^{-1} for the cationic C12DAO•HCl (i.e., $\alpha = 1$) in the lyotropic hexagonal phase, while this band disappeared for the C14DAO•1/2HCl in the lyotropic hexagonal phase.[10] This strongly suggests that the OH group of the C12DAO•1/2HCl forms the hydrogen bond to the neighboring headgroup on the micelle surface but not to water molecules. It is thus likely that the C14DAO•1/2HCl forms the hydrogen bond in the flat bilayer on mica. It is interesting to compare C14DAO•1/2HCl with nonionic C14DAO since the proposed hydrogen bond cannot be formed for nonionic C14DAO. We have found that the nonionic C14DAO at 10^{-3} M (cmc: 2.7×10^{-4} M)[11] does not form a flat bilayer, but it forms many stripe structures of about 5 nm scale on mica, as shown in the AFM image (Figure 2). The latter structure is consistent with that of the other cationic surfactants with a C14 chain.

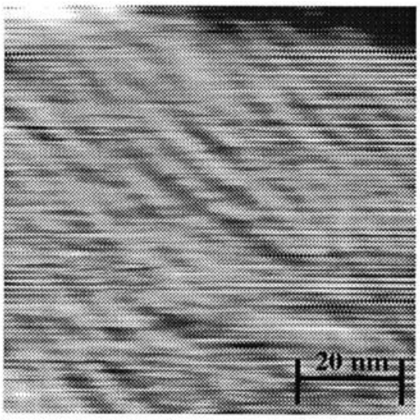

Figure 2. AFM image of nonionic C14DAO at the mica - the surfactnat solution interface at pH 8 ; 1mM nonionic C14DAO + 10 mM tris(hydroxymethy) aminomethane buffer solution.

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