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Shape of tetradecyltrimethylammonium chloride aggregates at liquid/solid interfaces in mixtures of water and formamide

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Here we report the visualization by AFM of the adsorbed layer structures of the cationic surfactant tetradecyltrimethylammonium chloride (TTAC) on graphite and mica in solutions of formamide and formamide/water mixtures.

Surfactant self assembly in polar solvents other than water has been an area of active interest since the 1970's.[1] Early work identified the importance of a hydrogen bonding network in driving aggregation by the apolar tails of the surfactant,[1–3] and most work has focused on H-bond network forming liquids like formamide, ethylene glycol, and glycerol. Despite important progress in understanding certain aspects such as the key role of the counterion, a great deal remains to be understood about the shape and size of micelles as well as process of micelle formation.[4,5] The state of this field was most recently reviewed in 1997, where it was suggested that research in this area had stalled somewhat.[6,7]

By contrast, the related phenomenon of surfactant adsorption from formamide and other like solvents onto solid substrates has received virtually no attention. Atomic force microscopy (AFM) has been instrumental in showing the close relationship between surfactant adsorption onto solid surfaces and bulk self-assembly in aqueous solutions.[8,9] AFM has permitted the direct *in situ* visualization of adsorbed layer structure. On hydrophilic surfaces in aqueous solution surfactants have been shown to form micelle-like globular or cylindrical surface aggregates more often than laterally unstructured bilayers. Changes in shape of the surface aggregates may been induced using similar approaches as in bulk, for example by addition of salt.[10,11]

Tetradecyltrimethylammonium chloride (TTAC) and formamide, both from Aldrich, were used as received. Unlike the corresponding bromide salt, TTAC is soluble in formamide at room temperature up to at least 1 M. Water solutions were prepared using Milli-Q water with resistivity > 18 MΩ cm^{-1}. Critical micelle concentrations (cmc) were measured by conductivity, and AFM images were recorded in 'soft contact' mode as described previously.†

In aqueous solutions it is well known that adsorption onto both hydrophobic and hydrophilic surfaces plateaus at the cmc. This corresponds to a fully-developed or saturated adsorbed layer whose structure is relatively insensitive to further change in concentration.[12] In mixtures below 40% formamide adsorbed layers were imaged above the cmc, as determined by conductivity. However in formamide-rich solutions the critical micelle concentration has been well-documented to be difficult to determine,[13] so the existence of an adsorbed layer was inferred from the force curves.

As the surfactant concentration is increased, the force *versus* separation curves between the AFM tip and substrate first show an increasing attraction and between substrate and tip, indicating the formation of a hydrophobic layer on the substrate and/or the tip. When the surface is retracted, this attraction is manifested as a strong adhesion or 'pull-off' force. At higher concentrations the adhesion decreases, coinciding with the development of a soft repulsion in the force curve on approach between the tip and substrate, indicating that the adsorbed layers are no longer hydrophobic, but repel one another through electrostatic or steric interactions. Fig. 1 shows representative force curves between the AFM tip and mica in formamide. In 10 mM TTAC solution the approach and retraction curves are virtually identical with no indication of an adsorbed layer. However in 600 mM solution the force curve on approach shows a soft repulsion extending into solution over a few nanometers before a discontinuous jump into contact as the tip is pushed through the adsorbed layer into 'constant compliance' contact with the substrate. (Constant compliance refers to the motion of the AFM tip in contact with the substrate, and is conventionally used as the reference of zero separation as the AFM has no absolute measure of separation.) On retraction, the negative deflection in the 600 mM TTAC solution represents an adhesion between the tip and the mica substrate, and the maximum is referred to as the pull-off force. The pull-off deflection reaches a maximum at approximately 200 mM TTAC. Here the deflection and separation range of the jump into contact on approach and jump out on retraction exceed the scale of Fig. 1.

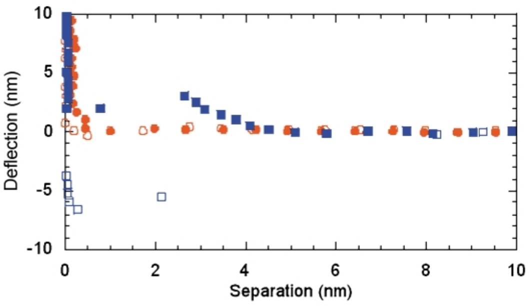

Fig. 1 Force *vs.* tip-mica substrate apparent separation for TTAC solutions in formamide. Full symbols show forces measured on substrate extension towards the tip, and empty symbols show retraction; ●,○ 10 mM TTAC; ■,□ 600 mM TTAC. Force is shown as deflection of the AFM tip.

A fully-developed adsorbed layer was thus deemed to have formed when the force curve for the approach of the substrate surface towards the tip yielded a soft repulsion followed by a jump into contact, as reported previously for imaging adsorbed layers in aqueous solutions.[8–11]

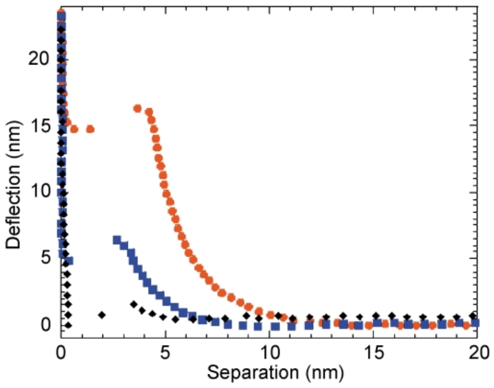

Fig. 2 Force (approaching) *vs.* tip-graphite substrate apparent separation for TTAC solutions in a range of formamide/water mixtures; ● 0% v/v (pure water); ■ 40% v/v; ◆ 100% v/v (pure formamide). Force is shown as deflection of the AFM tip.

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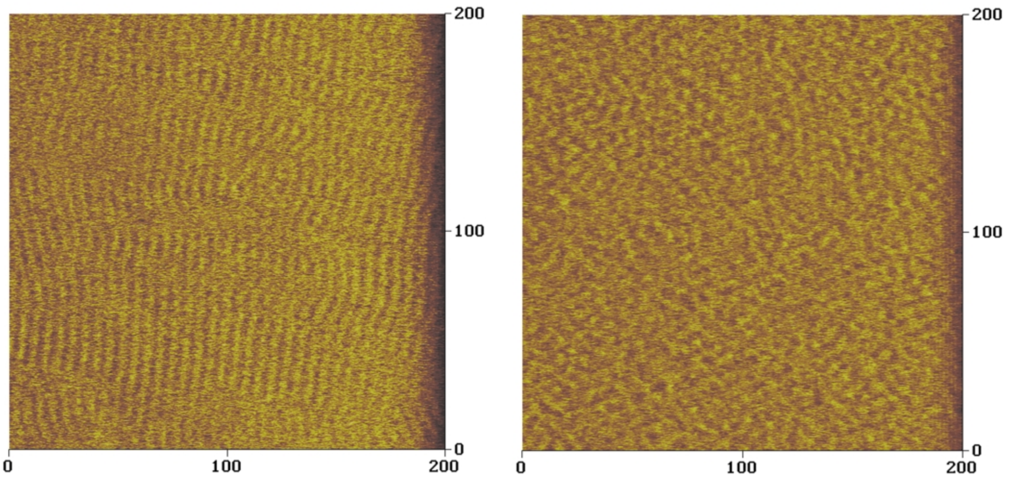

Fig. 3 AFM deflection images of TTAC aggregates at the mica/solution interface in 10% ([TTAC] = 18.0 mM, left) and 20% ([TTAC] = 20.5 mM, right) formamide in water. Only 200×200 nm images are shown, but similar results were observed in 300×300 nm and 100×100 nm scans.

Fig. 2 shows representative force (deflection) *versus* separation between the tip and the graphite substrate for TTAC solutions in various water/formamide mixtures, showing the soft repulsion on approach due to the presence of adsorbed surfactant, similar to those shown in Fig. 1 for mica. The maximum deflection decreases as formamide is added, consistent with a decrease in the hydrophobic interactions responsible for formation of the adsorbed layer relative to water, however the force curve clearly shows the existence of an adsorbed layer even in 100% formamide.

Imaging of the adsorbed layer is only possible when the feedback force can be reliably set on the adsorbed layer repulsion. This is increasingly difficult as the formamide content increases, and the quality of the images obtained also decreases. Straight, parallel stripes, normally interpreted as hemi-cylindrical micelles,[9] were observed in all formamide/water mixtures. In pure formamide only a noisy image was obtained at 1 M TTAC, but this also showed straight, parallel stripes.

These structures arise due to strongly anisotropic interactions between surfactant alkyl chains and graphite that form a “stripe phase” aligned normal to the crystallographic axes of the graphite cleavage plane.[8] This observation suggests that the interactions between the alkyl chains and graphite responsible for templating the hemicylinders are still strong enough to do so up to high formamide contents. This is somewhat surprising, as previous work on nonionic surfactants with shorter alkyl chains in water has shown that weakening these interactions leads to the disappearance of regular structures.[14]

AFM images of the TTAC adsorbed layer on mica above the cmc in 0, 5, and 10% formamide showed meandering stripes interpreted following previous work to be cylindrical micelles.[8] In 20, 40 and 60% formamide, globular micelles were observed in the fully-developed adsorbed layer. Fig. 3 shows typical results for the two different aggregate morphologies in 10% and 20% formamide above their respective cmcs. Adsorbed aggregate curvature increases with the proportion of formamide. This is consistent with expectations based on previous observations of bulk micelle formation in formamide, which are smaller and more highly charged than in water.[4,15]

Adsorbed layer structure of TTAC in pure formamide solution was examined over concentrations from 10 mM to 1 M. At concentrations up to 200 mM no aggregates were visible on mica. At and above 400 mM, a stable but weak soft repulsion yielded images of globular aggregates similar to those shown in Fig. 3. A cmc in the range of 200–400 mM is what we would expect for TTAC in formamide, based on studies of alkyl pyridinium compounds.[4]

This study has shown that the adsorbed layer formed by TTAC on mica and graphite in water/formamide mixtures or pure formamide consists of micelle-like aggregates similar to those formed in pure water. Even though there is no clear signature of a cmc from bulk conductivity above about 20% formamide, the lateral structure that has been used as a signature for self-assembly is visible in AFM images at all solvent compositions. Cylindrical aggregates on mica are transformed into globular aggregates between 10 and 20% v/v formamide, whereas hemi-cylindrical aggregates on graphite are unchanged up to 100% formamide.

Notes and references

† Atomic force microscopy was performed using a multimode Nanoscope III (Digital Instruments) in contact mode with an E-scanner. The imaging method was to use the double-layer (or steric) repulsion between the tip and the surface layer and fly the tip over the adsorbed film, following the procedure described previously.[8,10] Mica (Probing and Structure) and graphite (XYH monochromator, Advanced Ceramics) substrates were freshly cleaved before use with adhesive tape. Silicon nitride N-P cantilevers (Digital Instruments) were cleaned by UV irradiation prior to use. The solution was injected into the cell, sealed with an o-ring, and thermally equilibrated for 15 min to 2 h before imaging. Scan rate, integral gain and *z*-deflection range were varied between 8 to 15 Hz, 0.4 to 0.6, and 0.4 to 0.6 nm, respectively (all other gains were set at 0). All experiments were performed at room temperature (23 ± 2 °C). All images shown are raw deflection images that have been flattened along the scan lines to remove any tilt from the sample, and with no other image processing.

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