Atomic Force Microscopy has revolutionised our understanding of coatings consisting of adsorbed surface-active molecules or colloidal particles at the solid-liquid interface. These delicate structures may be present wherever the solution contacts a solid material.

Imaging Delicate Coatings under Water using Atomic Force Microscopy

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**Introduction to Atomic Force Microscopy**

The atomic force microscope (AFM) was invented by Binnig, Quate & Gerber (1986) following closely after the invention by Binnig & Rohrer of the scanning tunneling microscope (STM) in 1981. Both techniques were developed at the Zurich IBM laboratories and were made possible by new piezoelectric ceramic materials which exhibited very linear expansion and contraction on a subnanometre scale under an applied voltage. These materials formed the basis of the high resolution raster scanning of the sample inherent in these new scanning probe microscopes. A great increase in resolution was suddenly possible with 0.1 nm lateral and 0.01 nm in the vertical direction, now typical. In both microscopes, a sharp tip is traced across the sample surface like a record player (for those who remember what that was!). The image is then constructed from either the tunnelling current between the tip and sample (in STM), or the tip deflection (in AFM). While STM is perfect for conducting or semiconducting surfaces, AFM can readily be used to image the surface of insulating materials and most importantly for this review, it can readily be operated on samples immersed in water.

The basis of AFM imaging is the deflection of a weak spring or cantilever with a sharp tip at the end.

The AFM has proven invaluable for clarifying the morphology of surfactant aggregates adsorbed at the solid-aqueous solution interface. The traditional view of monolayers and bilayers has been replaced with a richer family of periodic nanostructures since topography or as a force map. Importantly in the latter case, an atomically flat but heterogeneous surface can still yield a useful and interesting image. It is this inherent force measurement which can be translated into an image that has made AFM such a valuable tool for surface and colloid science, with its fundamental basis in understanding the intermolecular forces between materials.

**Imaging Adsorbed Surfactant Micelles**

One of the most fascinating classes of molecules from a surface chemistry point of view is surfactants. You may know of these molecules under a different name based upon their application; perhaps as detergents, emulsifiers or collectors? In all cases, the role of the surfactant is to lower the energy of a phase boundary through adsorption at that interface. Another behaviour exhibited by surfactants in solution is that they spontaneously assemble into aggregates of various shapes including spherical or cylindrical micelles, vesicles or bilayers. For example, lipids (biological surfactants) self-assemble into cellular membranes. The driving force behind this assembly is also to lower the system free energy by minimising the contact between the hydrophobic hydrocarbon section of the molecule and the solvent, which in this case is water. The result is a compartmentalisation of the solution into aqueous zones and hydrophobic zones. This coexistence of regions of very different polarity can be readily harnessed to, for example, solubilise a hydrophobic drug, dye or fragrance. Small self-assembled aggregates such as spherical micelles can thus be used to solubilise and then transport hydrophobic molecules through aqueous media in all manner of applications from medicine to materials science and engineering.

AFM has proven invaluable for clarifying the morphology of surfactant aggregates adsorbed at the solid-aqueous solution interface. The traditional view of monolayers and bilayers has been replaced with a richer family of periodic nanostructures since in the hard-contact region and no features would be visible on this scale. Thus careful control of the imaging force is required to resolve these delicate structures which are in equilibrium and molecular exchange with the adjacent solution.

In this deflection image, the parallel lines are the surfactant hemimicelles. Another example is shown in Figure 2 in which the parallel lines can be seen at two orientations at 60° to one another. Grain boundaries can be seen where hemicylinders of two different orientations meet. The very straight parallel nature of the aggregates is evidence of the...
templatting influence of the hexagonally-symmetric substrate (as shown in the schematic in Figure 1).

Traditionally these adsorbed layers on hydrophobic substrates were viewed as monolayers (Zettlemoyer, 1968) yet here is evidence of a periodic structure that could not be resolved using any other technique. This finding opened the door to a flurry of investigations to catalogue and characterise interfacial surfactant aggregates, and thus understand their relationship to substrate character. Much of this early research has been reviewed by Warr (2000). On hydrophobic substrates, the surfactant hydrocarbon tails are in contact with the substrate as illustrated in Figure 1 and hemimicelles predominate. On hydrophilic substrates, surfactant headgroups face both the substrate and the solution, so full micellar aggregates are generally formed. Occasional systems do form traditional monolayers or bilayers.

Much effort has also gone into understanding the relationship between interfacial aggregates and the geometry of self-assembly of surfactants in solution as exemplified by the critical packing parameter of Israelachvili et al. (1976). Wanless & Ducker (1996) lead the way by demonstrating that the addition of salt reduced the interheadgroup repulsion and thus the periodicity of hemimicellar aggregates.

**Interfacial aggregates represent a balance between surfactant molecular geometry and substrate influences such as crystallinity and polarity.**

The diblock copolymer PDMA-b-PDEA adsorbed to mica from a solution of spherical micelles above the polymer pK_a. Upon reduction in the overlying solution pH, the surface micelles swell with solvent and form a close-packed micellar coating.

**Imaging Adsorbed Polymeric Micelles**

Diblock copolymer micelles may also be adsorbed at the solid-solution interface and characterised using AFM imaging. High glass transition temperature copolymer micelles with their glassy cores have long-lifetimes and can be robust to post-drying imaging (e.g. Potemkin et al. 1999). However, adsorbed low-glass transition temperature copolymer micelles are best characterised at equilibrium in solution using direct soft-contact imaging methods as used for the small molecule surfactants discussed above. One family of such polymers that we have studied in detail are tertiary amine based methacrylates such as poly(2-(dimethylamino)ethyl methacrylate)-b-poly(2-(diethylamino)ethyl methacrylate), PDMA-b-PDEA. This polymer forms micelles in aqueous solution above pH 8 owing to poor solubility of the PDEA block which forms the micelle core. The PDMA block is slightly less hydrophobic and forms the micelle corona. The polymeric micelles adsorb on substrates like mica and silica and form a self-organised adsorbed layer of micelles not dissimilar to the surfactant surface micelles shown in Figure 3. Figure 4 shows one polymer from this family adsorbed onto mica and imaged using soft-contact mode AFM (Webber et al. 2002). What is most remarkable about this image is that we now know that the adsorbed layer is predominantly water (>
80% as determined by quartz crystal microbalance) with the remainder consisting of the polymer (Sakai et al. (2006)). Thus, once more the unique capability of soft-contact AFM imaging is proven.

Now this copolymer has a characteristic response to pH variation that consists of the micelles reversibly forming above the pKa ~ pH 8 and disintegrating below this pH owing to protonation and hence greater solubility. We were thus interested as to what would happen to surface micelles exposed to pH variation. The result is shown in the right hand image of Figure 4. The surface micelles have swollen to be completely space-filling in the plane of the surface and this is attributed to their protonation and solvent uptake (as is also evident in the AFM force curves). This is in marked contrast to what would happen to analogous surfactant micelles which would simply wash off the surface. So the copolymer micelle coating is far more robust than the surfactant micelle coatings discussed earlier.

A slightly different polymer from the same family with a shorter PDMA block was subsequently shown by Webber et al. (2004) to form a similar adsorbed layer at pH 9, but a laterally featureless adsorbed layer at pH 4 quite unlike the fish-scale morphology of Figure 4. This anchored polymer brush layer is uninteresting in terms of the AFM image which is therefore not shown, however, the structure is confirmed by the force curve and other physical measurements. Importantly, this structure was able to be switched back into surface micelles like those shown in the lefthand side of Figure 4 simply by raising the pH again. This reversible switch in adsorbed layer structure was then harnessed to reversibly capture the fluorescent hydrophobic molecule pyrene into the surface micelle cores and then release it back into solution as shown in Figure 5 for the adsorbed layer on silica particles. A particulate substrate was used in this case to illustrate the potential use of these active coatings for capture and release of small target molecules.

Building on our success of characterising adsorbed layers of the diblock copolymer micelles, we recently demonstrated that by taking great care it is even possible to image each layer of an electrostatically assembled micelle-micelle multilayer of these low transition temperature diblock copolymers (Smith et al. (2007)). Others had previously imaged micellar multilayers with rigid cores (Cho et al. 2006) but, as shown in Figure 6, we were able to do this with the highly hydrated low glass transition temperature soft core micelles of PDMA-b-PDEA as the cationic layer and a related anionic copolymer. The figure shows the successful construction of a four layer micelle stack, with micelles confirmed to be present in each layer. This is despite the fact that simply mixing the two polymers in solution would result in overall complexation and precipitation. By imaging the fourth layer at slightly greater force we were even able to scrape away the top layer and show micelles present in the bottom of the 12 nm deep hole created, providing solid proof of the integrity of the multilayer. Such complex coatings are increasingly being touted for controlled release applications.

**Imaging Adsorbed Polymeric Microgel Latexes**

The final example that illustrates what careful AFM imaging can yield, consists of objects an order of magnitude larger than the copolymer micelles. These lightly cross-linked polymer latex particles or microgels swell in good solvents and return to their latex form in poor solvents. They can be thought of as permanent micelles for the purpose of this discussion: adsorbing for the same reason (electrostatic attraction). We have demonstrated that the swollen and deswollen states can be imaged directly with AFM as shown in Figure 7 (FitzGerald, 007)). Note that the polymer used in this case is poly(2-vinylpyridine) which has a glass transition temperature far in excess of room temperature. The most obvious manifestation of this is that the adsorbed latex particles in (a) appear to flatten very little upon adsorption. In solution when the solvent is made more acidic than the polymer pKa, each monomer is protonated and the solvent swells the particle volume by a factor of 39. It is clear from (b) that when present at the interface, the latex-to-microgel transition is hindered. However, the particles clearly swell within the constraints of their nearest neighbours and in fact displace about 75% of the initially adsorbed particles. Subsequently the particles can be deswollen (c) and remain fixed in position. The number of adsorbed particles remains constant with further changes to the overlying solution pH.

For imaging the microgel latexes, we found that soft-contact was not the optimal AFM imaging mode as even these gentle forces were sufficient to...
imaging is illustrated to be a valuable AFM imaging mode that is not widely used. For certain delicate samples requiring in situ imaging it offers the best possible resolution as it does on understanding and controlling the surface forces in the system. In this way, soft-contact imaging has resulted in new models for the adsorption of surface active molecules based upon discrete surfactant micelles that had previously only been dreamt about. Importantly these surface micelles can be exchanging molecules with solution micelles during imaging. While the focus of this review has been on AFM imaging, the conclusions relating to many of the examples draw upon other complementary physical measurements leading to system understanding that is greater than microscopy alone could provide.

Conclusion

Through the examples presented, soft-contact imaging is illustrated to be a valuable AFM imaging mode that is not widely used. For certain delicate samples requiring in situ imaging it offers the best possible resolution as it does on understanding and controlling the surface forces in the system. In this way, soft-contact imaging has resulted in new models for the adsorption of surface active molecules based upon discrete surfactant micelles that had previously only been dreamt about. Importantly these surface micelles can be exchanging molecules with solution micelles during imaging. While the focus of this review has been on AFM imaging, the conclusions relating to many of the examples draw upon other complementary physical measurements leading to system understanding that is greater than microscopy alone could provide.

References


Wanless, E.J. & Ducker, W.A. (1996) “The organisation of monolayer films of stimulus responsive diblock copolymers. This research has been a very fruitful collaboration with Steven Armes at the University of Sheffield.

The underlying theme of Erica’s research is the understanding of solid-liquid interfacial structure on the nanoscale. This theme commenced at Otago where her pioneering work used AFM to reveal detail of the lateral structure of adsorbed surfactant layers on the molecular scale. At Newcastle she has applied these methods and others to the detailed investigation of the adsorption of water-soluble pH-responsive diblock copolymers. This research has been a very fruitful collaboration with Steven Armes at the University of Sheffield.