357c Studying Surfactant Aggregates on Metals by Atomic Force Microscopy

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Structural in-situ investigations of adsorbed surfactant at the solid-liquid interface by Atomic Force Microscopy (AFM) have received a lot of interest within the past decade. It has been demonstrated that surfactants form micellar aggregates that depend on the properties of both the solution (e.g. surfactant type and concentration, ionic strength, pH value, etc.) and the substrate. In most cases, graphite, mica or silica surfaces have been investigated. On hydrophobic substrates, the structures are generally interpreted as hemi-cylinders or hemi-spheres, whereas the structures on hydrophilic surfaces are usually considered as cylinders or spheres. Metallic substrates, however, have only received very little attention. We have studied the aggregates of Sodium dodecyl sulfate (SDS) on atomically flat gold as a function of the surfactant concentration in the range from 0.1mM to 100mM. At concentrations around the critical micelle concentration (cmc) of SDS (8mM), we find linear structures that resemble the cylindrical/hemicylindrical structures which are found on mica or graphite (see image below). However, we find that the periodicity of these structures can be as low as 3.7nm which is far below the values reported for SDS on graphite (5.2–7.0nm). Images acquired at 1mM, far below the cmc, show isolated patches of adsorbed surfactant with linear structure. These laterally confined aggregates allow us to measure the actual height of the adsorbed structures. For non-metallic surfaces, total coverage is usually found, which doesn't allow for such direct height measurements by means of AFM. Surprisingly, our measurements yield height values around 0.5nm which is very close to the diameter rather than the length of a single surfactant molecule. This suggests that the surfactant molecules form a flat layer rather than cylinders or hemi-cylinders on metallic surfaces at low concentrations. Our findings indicate that the adsorption scheme and the structure of the adsorbed aggregates on metals are different from what is reported for non-metallic surfaces.

