

In-situ study of organic monolayer adsorption on calcite using X-ray scattering techniques

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The presence of dissolved organic compounds is known to have a profound impact upon the dissolution and growth of minerals[1], and the controlled nucleation of minerals at organic membrane surfaces is suspected to be an important feature of the formation of the exoskeletons of many invertebrate species[2]. Consequently, a fundamental understanding of the organic-mineral interface is of wide interest to many fields. Yet there are relatively few experimental tools which are capable of following the *in situ* formation and growth of organic films at the mineral-fluid interface. Here we describe some recent results obtained using X-ray scattering techniques to measure a well-defined model system: the adsorption of stearic acid monolayers at a calcite surface.

Experimental

A more detailed description of the X-ray reflectivity technique is given elsewhere in this volume[3], although here we make note of a few details that are specific to these studies. The sample is held in a cylindrical cell which is shown schematically in the inset to Fig. 1. The cell is constructed of Kel-F and contains ~2cc of solution. By using a photon energy of 19.5 keV (corresponding to a wavelength $\lambda = 0.635 \text{ \AA}$), the attenuation of the X-ray flux through the solution is only ~50%. The advantage of this type of cell is that the relatively small sample surface area to solution volume ratio limits the extent to which the solution composition may be influenced by surface reactions. Furthermore, the cell construction allows for real-time control over the solution composition during measurements so that kinetic processes can be directly studied.

A well-defined (104) surface is obtained by cleaving an optical quality spar calcite crystal. The adsorption of the stearic acid monolayer is controlled through the concentration of stearic acid in a

methanolic solution. All data shown here were taken after the sample was allowed to fully equilibrate and therefore should not be influenced by adsorption/dissolution kinetics.

For the X-ray reflectivity measurements, the presence of an organic monolayer has a strong impact upon the observed specular reflectivity. Small angle reflectivity of a clean surface is described by the Fresnel reflectivity and has the functional dependence $R_F \sim 1/Q^4$, where Q is the momentum transfer and is related to the incident angle, θ , through the relation: $Q = (4\pi/\lambda)\sin(\theta)$. Upon formation of a monolayer with thickness L , X-rays which scatter from the monolayer-substrate interface interfere with those scattered from the monolayer-fluid interface resulting in an oscillatory variation of the reflected intensity which is analogous to the optical interference fringes observed in thin soap bubbles. For a monolayer with uniform density, the magnitude of the oscillations provides a direct measure of the monolayer density, while its period provides a direct measure of the monolayer thickness. More generally, the reflectivity is proportional to the Fourier transform of the laterally averaged electron density profile, $\rho(z)$. [4]

Results

The X-ray specular reflectivity of the calcite/methanol interface is shown in Fig. 1 as a function of the stearic acid concentration, and the data are plotted as a function of the momentum transfer, Q . As might be expected, while the data taken with $C = 0\text{mM}$ exhibit a monotonic decrease in intensity characteristic of a clean calcite surface, as the concentration is increased significant oscillations in the scattering intensity are observed. These oscillations are indicative of the presence of a monolayer of stearic acid. From the periodicity of the oscillations, we can estimate that the film thickness is ~25 Å (a

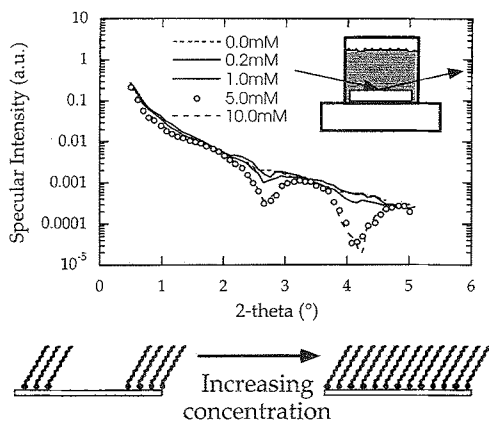


FIG. 1. Specular reflectivity as a function of stearic acid concentration. Scattering geometry shown in inset.

more detailed quantitative determination of the film thickness and structure is in progress). When compared with the length of a stearic acid molecule of 24 Å, these data clearly suggest that the molecules are standing upright on the calcite surface. This provides direct support for previous suggestions that carboxylic acid molecules bond to the calcite surface through the carboxylate group[5], and suggest that the mechanism for inhibiting growth and dissolution by carboxylic acids is through the formation of a dense diffusional barrier.

A second interesting aspect of these data is that while the magnitude of the oscillations is observed to vary strongly with solution concentration, C , the periodicity of the oscillations is independent of C . This suggests that the local structure of the monolayer is fixed as a function of the surface coverage, while the fraction of the surface which is covered by the monolayer is driven by the solution concentration, C .

As most techniques are not capable of studying the structure of an organic monolayer *in-situ*, it is useful to determine the degree to which the monolayer structure is influenced by its environment. Our data (not shown) demonstrate that while the *in situ* data are characterized by rather regular oscillations of the reflectivity over a broad range of momentum transfer, the *ex-situ* data are clearly different and are characterized by a more complex functional form. This immediately shows that the stearic acid monolayer structure relaxes in the process of extracting the surface from the solution.

We have also applied the technique of X-ray standing waves (XSW) [6] to probe the internal

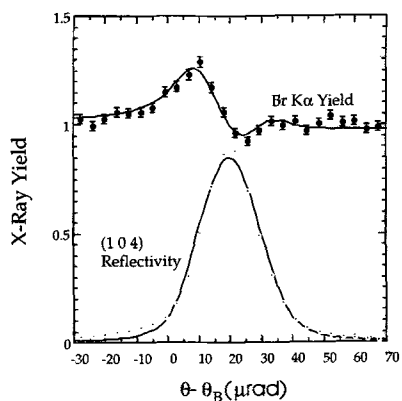


FIG. 2. X-ray standing wave data showing Bromine fluorescence and calcite reflectivity near the calcite (104) Bragg peak.

uniformity of the stearic acid monolayer structure using *ex-situ* measurements. To do this, we formed a monolayer of 9(10) bromostearic acid through procedures similar to those described above. XSW provides precise structural information concerning the location of a particular species (in this case Br) by measuring the modulation of the X-ray induced fluorescence of that species as the sample is rotated through a strong reflection condition (in this case, the (104) Bragg reflection). Since the phase of the X-ray standing wave changes in a well-defined way through a substrate Bragg reflection, its influence upon the fluorescence yield provides a simple and direct probe of the Br location. The results of the XSW measurement are shown in Fig. 2, and consist of the bromine $K\alpha$ fluorescent yield and the calcite (104) reflectivity as a function of the incident angle. From these experimental data, we determine that the bromine location is characterized by a width of only $\sigma = 0.47$ Å (given the assumption that the bromine position is defined by a Gaussian distribution with a width, σ), and a distance from the calcite substrate which is consistent with the Br position on the molecule. A more detailed analysis of these data are in progress.

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