

# Structure and growth of stearate monolayers on calcite: first results of an *in situ* x-ray reflectivity study

P. Fenter and N.C. Sturchio

Environmental Research Division, Argonne National Laboratory, Argonne, IL 60439 USA

## Introduction

The role of organic ligands in natural waters has gained attention in studies of mineral-fluid interactions during recent years. Interactions between mineral surfaces and organic ligands are critically important, but as yet are less understood than purely inorganic interactions. Direct knowledge of the molecular-level properties of organic thin films at the mineral-fluid interface, particularly through *in situ* measurements, is presently limited. In many cases, even the most basic features of the organic thin-film structure (monolayer or multilayer, ordered vs. disordered) have not been probed, and much of what we know of these systems is typically derived from *ex situ* measurements. Here we describe our first efforts to understand the *in situ* structure and growth of stearate thin films on a calcite surface [1].

## Methods and Materials

A well-defined (104) surface is obtained by cleaving an optical quality spar calcite crystal. The freshly cleaved sample is immediately transferred to the sample cell and allowed to equilibrate with deionized water for a period of hours to "heal" the surface [2]. We chose methanol as the solvent because the high solubility of stearic acid facilitates control of its concentration over a broad range and obviates concern about microbial degradation [3]. The adsorption of a stearate monolayer is controlled through the concentration of stearic acid in a methanolic solution that is reacted with the calcite surface after pre-equilibration with water.

The x-ray reflectivity technique has been described previously [4, 5]. X-ray reflectivity is defined as the ratio of the reflected to incident x-ray fluxes. The reflected intensity is directly proportional to the magnitude of the Fourier transform of the electron density profile,  $\rho(x)$ , through the relation  $R \sim |\int \rho(z) \exp(iQz) dz|^2$ , where  $Q$  is related to the scattering angle,  $2\theta$ . The calcite reflectivity is  $\sim 1$  at the Bragg peaks but is typically  $< 10^{-7}$  between Bragg peaks.

## Results and Discussion

In Figure 1, we show the x-ray reflectivity of the calcite-methanol interface with a 5 mM stearic acid solution in methanol. In addition to the variation in the reflected intensity associated with the calcite surface (known as a crystal truncation rod) that peaks near  $0 \text{ \AA}^{-1}$  and  $2 \text{ \AA}^{-1}$ , the reflectivity data clearly exhibit a periodic modulation in which the reflectivity varies by nearly two orders of magnitude. The period of the oscillations,  $\Delta Q \sim 0.24 \text{ \AA}^{-1}$ , corresponds to a spacing of  $L = 2\pi/\Delta Q = 26 \text{ \AA}$ , which corresponds closely to the  $\sim 24 \text{ \AA}$  length of the stearate molecule.

By comparing the data to representative atomistic models of the stearate-calcite interface structure, we can learn about the detailed structure of this film, the stearate coverage, and its structural relationship to the substrate lattice. In Figure 1, the solid line corresponds to the best-fit structure and explains nearly all the features in the experimental data. The best-fit structure (shown

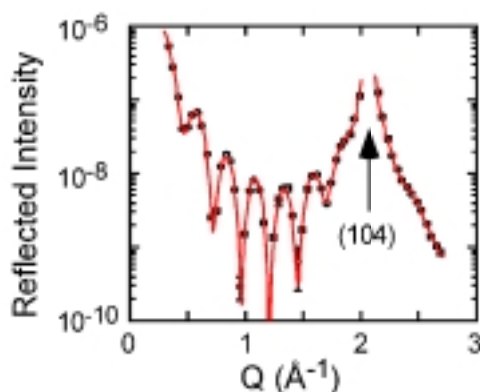


Figure 1: X-ray reflectivity of the calcite-methanol interface with a 5 mM stearic acid solution in methanol.

schematically in Figure 2) includes a stearate coverage of  $1.02 \pm 0.05 \text{ ML}$  (where  $1 \text{ ML} = 4.95 \times 10^{14}/\text{cm}^2$ , the density of Ca sites on the calcite surface). The tilt of the hydrocarbon chain is determined to be  $9.5 \pm 4^\circ$  with respect to the surface normal. These results confirm that the stearate molecules "stand up" to form a dense monolayer at the calcite-fluid interface surface.

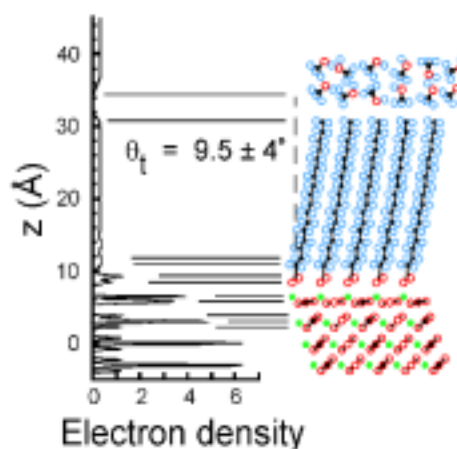


Figure 2: Schematic of best-fit structure.

Additional measurements reveal that the monolayer coverage is a strong function of the solution concentration. This observation suggests that the observed structure is a result of a dynamic equilibrium between adsorption and desorption processes.

## Conclusion

Through direct *in situ* measurements, x-ray reflectivity provides detailed information on the structure and adsorption mechanism of simple organic ligands adsorbed on mineral surfaces. A broad understanding of the processes and interactions associated with organic-mineral interfaces can be directly probed through similar

measurements of a range of mineral surfaces, organic ligands, and solution environments.

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