

Probing the Dynamics of Template-Directed Calcite Crystallization with in Situ FTIR

Dong June Ahn,[†] Amir Berman, and Deborah Charych*

Center for Advanced Materials, Lawrence Berkeley National Laboratory, Berkeley, California 94720

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Organic template-directed mineralization of calcite crystals has been probed in situ by external reflection–absorption FTIR spectroscopy in an effort to understand the dynamics of the organic–inorganic interface during crystal growth. The main focus is to elucidate structural changes that may occur in the organic template as crystal growth progresses. The nucleation face types of calcite were visually identified according to known crystal morphologies and by the corresponding carbonate stretching and deformation vibrational bands. Structural reorganization occurring in the organic template could be observed by intensity variations and frequency shifts in the methylene stretching bands of octadecanoic acid, octadecyl sulfate, and acidic polydiacetylenic lipid film. These organic templates nucleated calcite at the (010), (001), and (012) planes, respectively. The surfactant thin films uniquely adapt themselves in order to optimize the geometrical and stereochemical fit to the growing calcite crystals.

Introduction

The oriented growth of crystalline solids in biological systems¹ has inspired numerous studies of template-directed crystallization at condensed surfactant thin films.² Thin membrane-like films at the air–solution interface (Langmuir monolayers) provide an ideally flat organic surface with controllable chemical composition and molecular density.³ These surfaces have been used as templates to direct the crystal nucleation and growth of amino acids,⁴ ice,^{5,6} proteins,⁷ semiconductor particles,⁸ organic salts,⁹ and a variety of minerals including sodium chloride,¹⁰ calcium carbonate,¹¹ and barium sulfate.¹² In most cases, the crystals are extensively characterized by diffraction and microscopic methods. However, interpretation of the lattice match between the organic template and the nucleation face may rely upon template structures determined in the *absence* of mineralizing conditions. Recently, the structures of different surfactant monolayers were accurately determined using grazing incidence X-ray diffraction (GIXD).^{13,14} Given that the structure of monolayer films can be highly dependent on subtle variations of experimental conditions,¹⁵ it is reasonable to suggest that the monolayer film on mineralizing subphases would restructure. Dynamic molecular reorientations and rearrangements are expected as nucleation and growth occurs. For example, using GIXD, Majewski et al.,¹⁶ were able to probe changes in hydrocarbon chain tilt angle of an alcohol monolayer on water during cooling that subsequently lead to hexagonal ice nucleation. The experimental techniques that are capable of probing such subtle changes are often highly specialized and require instrumentation not found in most laboratories (eg. synchrotron source). Given the potential wealth of information obtainable by probing the monolayer film during crystal formation, we desired a relatively simple, low cost method for at least *partial* accounting of monolayer surface restructuring.

Vibrational spectroscopy is a powerful tool for probing the structure and dynamics of organic monolayer films. Most FTIR studies have focused on Langmuir–Blodgett (LB) films on solid supports: for example, grazing angle reflection–absorption^{17,18} and attenuated total reflection (ATR)^{19–21} infrared spectroscopy

have been extensively used to probe LB films on metallic and single-crystal substrates. FTIR spectroscopic studies of phospholipids at the air–water interface have focused on probing two-dimensional phase transitions.^{22–25} Recently, binding of dissolved cations to fatty acid and phospholipid monolayers has been investigated by infrared external reflection spectroscopy at the air–water interface.^{26,27}

In this report, we focus on the in situ analysis of nucleation and growth of calcite under surfactant films of monomers and polymers at the air–solution interface. The nucleation of a particular crystal face under the film induces structural adaptations in the film as probed by in situ FTIR. Vibrational bands from the hydrophilic headgroup region, C–H stretching bands from the hydrophobic alkyl chains and the carbonate from the forming crystals are readily obtained by detecting a reflected signal at near-normal incidence angle of the IR beam. Calcite crystals were nucleated from different planes (hence, grew to different morphologies) depending on the interfacial chemistry of the template film. Assuming that the crystal surface is a rigid termination of the bulk structure²⁸ (i.e., no crystal surface restructuring), it is possible to relate the observed changes in the FTIR spectra to restructuring of the organic film that optimize the match with the known crystal face structure. In principle, a wide variety of molecular recognition interactions at functionalized surfactant thin films can be studied using this technique.

Experimental Section

Materials. Stearic acid (octadecanoic acid) and octadecyl-sulfate sodium salt were purchased from Aldrich. Monomeric 10,12-pentacosadiynoic acid (m-PDA) was from Farchan Laboratories. Distilled water was purified with a Millipore water purifier and the resistivity was 18.2 M Ω . Spreading solvents used were chloroform of spectral grade (Fisher) for stearic acid and m-PDA, and methanol/chloroform mixture (40:60 v/v, reagent grade) for octadecyl sulfate. The solutions of surface-active materials were prepared in the concentration range of 1.0–2.5 mM and were kept at a temperature of 4 °C in the dark. The solutions were allowed to equilibrate at room temperature before use in the experiments.

Preparation of Supersaturated CaCO₃ Solution. The solutions were prepared according to the procedures of Kitano²⁹

* To whom correspondence should be addressed.

[†] Present address: Department of Chemical Engineering, Korea University, Seoul 136-701, Korea.

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