

Transport and Ion Exchange in Langmuir-Blodgett Films: Water Transport and Film Microstructure by Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy

Tracy L. Marshbanks,[†] Dong June Ahn, and Elias I. Franses*

School of Chemical Engineering, Purdue University, West Lafayette, Indiana 47907-1283

Received July 16, 1993. In Final Form: October 1, 1993*

Langmuir-Blodgett (LB) films of calcium stearate were studied by FTIR before, during, and after contact with water and aqueous solutions of hydrochloric acid. The films retain from 1.5 to 3 wt % water of hydration, and they absorb at least 8 wt % (possibly up to 16 wt %) water, probably in voids, when contacted with bulk liquid water. The effective diffusivity of water in the films was estimated from the data to be in the range from about 10^{-13} to 10^{-10} $\text{cm}^2\text{-s}^{-1}$, but water transport was probably neither purely diffusive nor one-dimensional. The effects of ion exchange and thermal annealing at 100–140 °C on the film microstructure was monitored by detailed analysis of polarized ATR spectra. Conversion of calcium stearate to stearic acid caused film dehydration, recrystallization, and an increase in trans conformations. Certain implications on the barrier, transport, and ion exchange properties of LB films are discussed.

1. Introduction

LB films have been studied extensively in the past 15 years for their potential importance as materials for thin barriers, membranes, and optical applications.¹⁻³ Because the film quality is important for these applications, many workers have reported on the use of various microscopic and spectroscopic techniques for probing pinholes, defects, grain boundaries, etc.¹⁻⁴ Little is known, however, on how these defects affect the overall transport properties of LB films.

Calcium stearate has been chosen for study, because it readily forms stable, crystalline, and well-characterized LB films.^{5,6} This paper focuses on measuring the transport rate of water, because it is important for barrier or membrane applications, and also because it may provide an overall measure of the film microstructure and quality. The film microstructure is also probed by attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy before and after ion exchange of Ca^{2+} by H^+ . The ion exchange dynamics results for the same systems have been obtained and will be reported later.

2. Experimental Section

2.1. Materials. Stearic acid (puriss grade, 99%), calcium chloride dihydrate (purum grade, > 99%), and hydrochloric acid were purchased from Fluka Chemical Co. The sulfuric and acetic acids were of reagent grade and were obtained from Fisher Scientific. All water used was purified using a Mili-Q four-bowl system, from Millipore Corp., and had an initial resistivity of 18

$\text{M}\Omega/\text{cm}$. The germanium internal reflection plates were purchased from Harrick Scientific and Wilmad Glass Co.; they were $50 \times 10 \times 2$ mm trapezoids with 45° angle faces.

2.2. Apparatus and Procedures. The Langmuir trough was a MiniTrough-4 purchased from Joyce-Loebl of Gateshead, England. The trough used a Wilhelmy paper plate for measuring surface tension and a continuous constant-perimeter Teflon barrier for film containment. The trough was housed in a clean room equipped with a laminar flow hood.

The subphase calcium ion concentration (CaCl_2) was 1×10^{-4} M, and NH_4OH was added to control the subphase pH to 8. The surface was cleaned by pipette suction until there was no detectable surface pressure upon maximum area compression. Sufficient stearic acid was spread from droplets of a 1 mg/mL hexane solution, to provide an initial area of 40 \AA^2 per molecule. The film compression was started 15 min after the surfactant spreading to allow for the hexane to evaporate completely. All depositions were conducted at a surface pressure of 25 mN/m. The film was held at this pressure for 10 min prior to the start of the deposition. This allowed for the film to stabilize prior to the film transfer procedure. The transfer ratio ranged from 0.95 to 1.0.

The ATR plates were cleaned by first washing with a detergent solution, followed by rinsing in deionized water, ethyl alcohol, and water again. The crystal was then cleaned in a Harrick Scientific PDC-3XG cleaner/sterilizer, first in an oxygen plasma for 5 min and then for 5 min in an argon plasma. The final step in the cleaning procedure was a Millipore water rinse. This cleaning procedure produced substrates which consistently yielded uniform film disposition, if they were still coated by a water film. Deposition onto dried crystals resulted in poor quality films which had lateral striations.

Infrared spectra were collected with a Nicolet System 800 FTIR spectrometer. The optical bench was equipped with a DTGS room temperature detector and a narrow band MCT-A cryogenic detector. The removal beamsplitter was constructed of Ge and KBr. The instrument was continually purged with dry air from a Balston air purifier. The bench was equipped with an internal, computer-controlled, wire-grid, polarizer. The ATR optics for the System 800 spectrometer were custom-built by Connecticut Instruments, Inc. This accessory held the crystal face at a horizontal position and was capable of angles of incidence from 30° to 60° .

A sample chamber which fit on the ATR top crystal surface was constructed (Figure 1). This chamber allowed liquid to contact the LB film covering the top side of the ATR element. The LB film on the bottom side of the ATR crystal was removed, to enhance the sensitivity of the experiment to the transport and reaction occurring on the upper surface and to simplify the

* Author to whom correspondence should be addressed, telephone (317) 494-4078.

[†] Present address: Amoco Oil, Amoco Research Center, P.O. Box 3011, Naperville, IL 60566-7011.

* Abstract published in *Advance ACS Abstracts*, November 15, 1993.

(1) Stroeve, P.; Franses, E. I., Eds. *Molecular Engineering of Ultrathin Polymeric Films*; Elsevier: London, 1987, also *Thin Solid Films* 1987, 152 (1, 2).

(2) Petty, M. C. In *Langmuir-Blodgett Films*; Roberts, G. G., Ed.; Plenum Press: New York, 1990; p 133.

(3) Ulman, A. *An Introduction to Ultrathin Organic Films. From Langmuir-Blodgett to Self-Assembly*; Academic Press: New York, 1991.

(4) Lesieur, P.; Barraud, A.; Vandevyver, M. *Thin Solid Films* 1987, 152, 155.

(5) Takenaka, T.; Nogami, K.; Gotoh, H.; Gotoh, R. *J. Colloid Interface Sci.* 1971, 35, 395.

(6) Kimura, F.; Umemura, J.; Takenaka, T. *Langmuir* 1986, 2, 96.