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Effect of the Skeletonization Process on Vapor Sorption into Langmuir−Blodgett Multilayers

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One of simplest Langmuir−Blodgett films is a stack of fatty acid layers bridged together by divalent cations. A certain fraction of fatty acids remain protonated, an amount dictated by aqueous subphase conditions during film deposition; these films are thus comprised of two components with different solubilities in organic solvents. We investigated the so-called skeletonization process that occurs when behenic acid multilayers are immersed in benzene. In particular, we used a quartz crystal microbalance to measure the loss of film mass and found that it agrees well with the amount of protonated acid in the original film. We also used the quartz crystal microbalance to investigate the equilibrium vapor sorption properties of unmodified films and compared them to those of skeletonized films. Both types of films take in nearly the same amount of water but absorb distinctly different amounts of selected organic vapors.

Introduction

Long before the recent enthrallment with nanotechnology—over 65 years ago, in fact—Katherine Blodgett and Irving Langmuir at the General Electric Research Lab in Schenectady, New York, were manipulating molecules to fabricate novel nanomaterials.[1,2] These so-called Langmuir−Blodgett (LB) films are stacks of molecular layers, constructed one at a time by way of an ingenious deposition process in which molecules are transferred from an air−water interface onto a solid-supported substrate. LB films have continued to capture and sustain the interest of researchers ever since their discovery.[3]

Blodgett's initial research with these films focused on their potential applications in optics and interferometry. Not long after perfecting the building process, she discovered an interesting film modification method that she termed "skeletonization".[4,5] The method makes use of the fact that fatty acids are much more soluble in organic solvents than are their corresponding fatty acid salts. LB films that contain both acid and salt molecules can easily be constructed by including divalent cations in the aqueous subphase and controlling the pH to a value where the fatty acid is partially ionized. The basic film architecture is shown schematically in Figure 1. Blodgett immersed such films into benzene and proposed to create a resultant film that is pruned of the acid molecules, leaving behind a "skeleton" of the original film comprised only of fatty acid salts.[4,5] She demonstrated a drastic reduction in film refractive index as a result of the skeletonization process and also showed that this effect could be reversed by allowing oily materials such as tetradecane to penetrate the film. On this basis, she suggested the use of skeletonized LB films as refractive index modifiers to extinguish light reflection (glare) from glass surfaces.[6]

Our interest in LB films is rooted in their potential applications in membrane-based separation processes. Such processes rely on materials that exhibit high transport selectivity while sustaining high throughput. One can take advantage of the thinness of LB films to ensure high permeability (which is inversely proportion to thickness). The open question is the degree of selectivity that might be displayed by these films and how this might be controlled by judicious choice of film constituents.

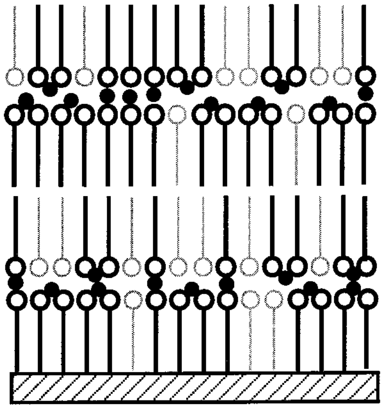

Figure 1. Schematic of unmodified LB film. Un-ionized fatty acids (shown in gray) are removed during the skeletonization process, presumably leaving intact a skeleton of fatty acid salts (shown in black).

One might intuitively expect that even the simplest LB films, such as those composed of fatty acids, might exhibit significant selectivity to absorbates on the basis of polarity and size. Indeed, this work, which builds on our previous investigations,[7] demonstrates this phenomenon. The vapor sorption characteristics of these simple films (made from behenic acid in our case) are easily rationalized in terms of their well-known structure. We can then compare this behavior to that of films taken through the skeletonization process. As will be shown, these films exhibit distinctly different sorption characteristics. Although of interest in their own right, our results lend support to the film structure imagined by Blodgett.

Our investigations take advantage of the simplicity and exquisite sensitivity of the quartz crystal micro-

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balance (QCM) as a tool for mass pickup measurements. We use the tool not only to track vapor uptake into films deposited on the crystal, but also to investigate the mass loss phenomenon associated with Blodgett's skeletonization process.

Experimental Section

Behenic acid, subphase salts ($BaCl_2$, $KHCO_3$, and $CuCl_2$), octadecyl mercaptan, and octadecyltrichlorosilane (OTS) were of the highest grade available, purchased from Sigma (St. Louis, MO) and used as received. HPLC chloroform for spreading solutions was purchased from Fisher (Pittsburgh, PA). Water used as a subphase in the depositions was produced by a Milli-Q unit and had a resistivity of 18 MΩ cm. The fatty acid LB multilayers used in this study were prepared on quartz microbalance crystals supplied by Classic Frequency Control (Oklahoma City, OK) using a Langmuir trough and automated dipping device built by KSV Instruments of Finland.

The QCM consisted of a homemade oscillator circuit,[8] a removable quartz crystal, and an HP5334B frequency counter (Hewlett-Packard, Rockville, MD). Electrodeless 10-MHz crystals with $\sim$0.3-μm average roughness were chemically cleaned by the RCA method[9] before being made hydrophobic with OTS.[10] Gold electrodes were then evaporated onto the quartz and made hydrophobic by forming an octadecyl mercaptan self-assembled monolayer. The baseline frequency in air (stable to $\pm$0.5 Hz) was noted before LB layers were deposited on the crystal as described below.

The fatty acid multilayers in this study were deposited from an aqueous subphase that was 1×10^{-4} M $BaCl_2$, 2×10^{-4} M $KHCO_3$, and 4×10^{-7} M $CuCl_2$ and held at a constant temperature of 20 °C. Previous investigators have found that this subphase, buffered to pH 6.5 by the $KHCO_3$, is excellent for building up a large number of layers.[2,11]

Monolayer films were spread from a $\sim$1 mg/mL solution of fatty acid in chloroform. The chloroform used to spread the acid was allowed to evaporate for 10 min before the monolayer was compressed to 30 mN/m. Once this pressure was achieved, the films were allowed to stabilize for 15 min before conventional dipping on the hydrophobic QCM commenced at a speed of 10 mm/min. At least 5 min elapsed between the upstroke and the downstroke to allow entrained subphase to evaporate and to enhance further transfer. The crystal frequency following deposition was again noted so that the dry film weight (i.e., before vapor pickup) could be established. Transfer ratios were always 0.95−1.02 as measured by both barrier movement and measured film mass.

QCM measurements of vapor sorption into the films were performed in a vacuum system similar to that used by others to study vapor transport in polymers.[12] The apparatus was housed in a constant temperature room at 25.0 ± 0.1 °C. The chamber was initially evacuated to less than 30 mTorr as measured by two capacitance manometers (with measuring ranges of 0−10 Torr and 10−1000 Torr), and the baseline frequency was recorded by a computer. The liquid sample was initially freeze-cycled twice, and the vapor pressure was checked for purity before dosing. A controlled amount of the degassed vapor was introduced into the chamber while the frequency change, and thus the mass pickup, was recorded with a computer as time progressed. The vapor was subsequently evacuated, and the baseline frequency was generally re-obtained.

In all cases, the Saurbrey equation was used to derive mass per unit area from raw frequency measurements.[13,14] In this case, the increase in resonant frequency is directly proportional to the decrease in mass per unit area. The applicability of this approach for these systems has been previously verified.[7,8,15]

Results and Discussion

Our work is divided into two parts. The first concerns direct observations of film mass loss associated with the skeletonization process as measured with the quartz crystal microbalance. We compare our results to those of others who have examined the process using other techniques. We then proceed to report on the equilibrium vapor sorption characteristics of both whole (unmodified) and skeletonized fatty acid multilayers.

LB multilayers of behenic acid were fabricated directly on the quartz crystal microbalance as described in the previous section. We note that, for simplicity, we refer to our films as behenic acid films even though they are ultimately composed of undissociated (acid) and dissociated (salt) molecules, as dictated by aqueous subphase ionic conditions during deposition. We have previously used the QCM to estimate the relative fractions of each in our films;[15] we found them to contain approximately 40% acid at the fabrication pH (6.5−7.0), in good agreement with the findings of others.[16]

The skeletonization process was investigated by monitoring the mass of film as a function of solvent immersion time. Previous researchers have determined that the process is equivalent, whether undertaken continuously or in intervals (i.e., continuous immersion for 1 h is equivalent to 6 10-min intervals or 12 5-min intervals).[17] As our quartz crystal microbalance is not configured to operate in solution, we took the latter approach. We immersed each multilayer film into benzene for a series of intervals. After each interval, the crystal was removed from solution, and excess benzene was removed by gently touching the edge of the crystal to a piece of tissue (we note that the entire periphery of the crystal surface is not implicated in the frequency response). After a wait of a few minutes for evaporation of benzene (as reflected by a stabilized frequency), the mass removed was recorded, and the crystal was then immersed back into the solution. This process was continued until the crystal resonant frequency no longer increased (i.e., until the mass no longer decreased).

We examined 10 individually prepared behenic acid films ranging from 10 to 100 layers thick (more specifically, five samples at 100 layers and one each at 8, 40, 60, and 80 layers). The average mass loss was 40 ± 13%, consistent with the amount of fatty acid estimated to be present in the original film. We note the value of testing films of different thickness, namely, to show that the process leads to a consistent fractional mass loss.

The kinetics of the skeletonization process, as measured for a 100-layer film, is shown in Figure 2. Assuming the applicability of a one-dimensional Fick's law for this system, the diffusion coefficient of the acid from the film can be estimated from the initial slope of a plot of mass verses $t^{1/2}$.[18] Such analysis yields a value of 9.7×10^{-14} cm^2/s, in excellent agreement with the value of 8.0×10^{-14} cm^2/s measured by Honig using ellipsometry.[17] As is readily seen in Figure 2, two time scales

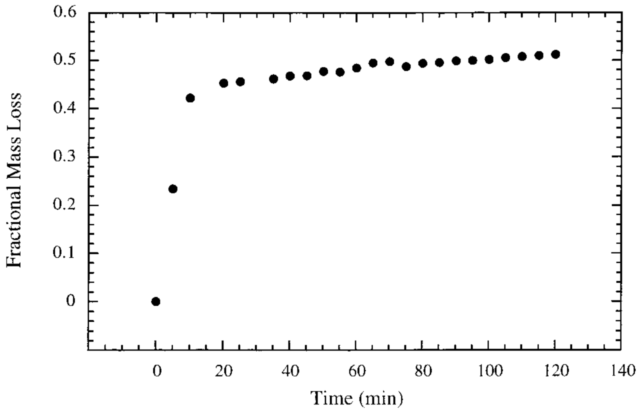

Figure 2. Fractional mass loss experienced by a 100-layer behenic acid film immersed in benzene. Skeletonization proceeds rapidly to about 40% removal, which corresponds to the amount of fatty acid originally in the film.

characterize the behavior of our film, a result that is also in agreement with previous observations put forth by Honig and de Koning.[17] They attributed the slow changes in film thickness and optical constants to the dissolution of the remaining insoluble salt molecules. Our QCM data support this conclusion as well, as the mass loss continues, at a much slower rate, beyond the 40% that is expected based on estimated ionization of the film.

The ellipsometric studies of previous investigators[17,19] also provide indirect information on the structure of the resultant film. Both studies report a marked decrease in refractive index, but no change in film thickness, when films were skeletonized for short amounts of time (several seconds to a few minutes). More direct information on the structure of skeleton films has recently been obtained using atomic force microscopy. Kurnaz and Schwartz[20] found the surface of post-skeletonized films to consist of mostly labyrinth-shaped domains, one or two monolayers deep. The atomic force microscope, however, can only probe the surface morphology, and so the question remains whether the specific surface structure observed persists in the underlayers.

We now turn to the vapor sorption characteristics of unmodified and skeletonized LB films. We have previously shown that vapor uptake into LB films scales with film thickness (i.e., number of layers), thus establishing a veritable vapor solubility in these materials that we typically report as moles of vapor absorbed per mole of fatty acid making up the film. This solubility is, as expected, a function of the imposed vapor pressure.[7] For the sake of the studies here, we fix the relative saturation pressure for each vapor to 60%, and we report the final equilibrium uptake of vapors studied. Our previous investigations concerned only the uptake of water vapor and pentane into behenic acid films. We found solubilities of 0.20 mol/mol and 0.03 mol/mol for water and pentane, respectively.

In this work, we extend these measurements to two other vapors: decane and pentanol. As we have previously confirmed our original results for water sorption,[21] we also take this opportunity to generate additional data for pentane. The following solubilities were obtained (using 100-layer films): pentane, 0.02 mol/mol; decane, 0.0024 mol/mol; and pentanol, 0.0020 mol/mol. For all vapors considered, we found that the results were reproducible from one film to the next to within 10%.

These results clearly demonstrate that these simple LB films exhibit absorption selectivity on the basis of size and polarity. In particular, the solubility of pentane is about eight times greater than that of decane, a molecule only twice its size. Meanwhile pentanol, about the same size as pentane but with an additional polar group, is as sparingly soluble as decane, indicating the lack of a favorable region for its sorption. Clearly, our measurements cannot confirm the whereabouts of absorbed species (e.g., whether alkanes are interdigitated between the fatty acid chains). Our current work is focused on correlating mass uptake measurements with direct film swelling measurements (as provided by interferometry) to shed light on this issue.

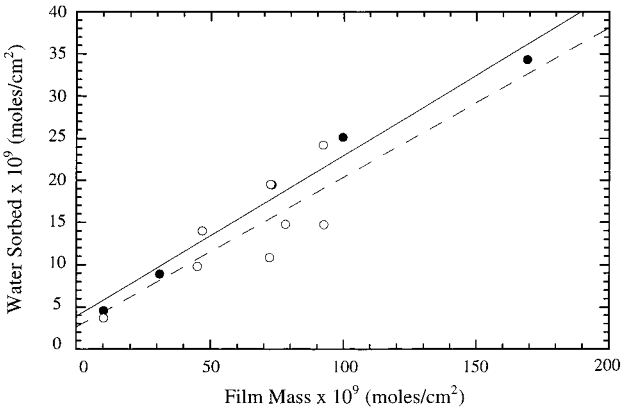

Figure 3. Uptake of water in unmodified (solid circles, solid line) and skeletonized LB films (open circles, dashed line) as function of film mass. The solubility is given by the slope of the best-fit line.

We turn now to the solubility of vapors into skeletonized films. First, we consider water sorption. Figure 3 graphically shows the sorption of water in both unmodified and skeletonized behenic acid multilayers as a function of film mass. It is clear from the data that the solubilities of water in the two types of film, given by the slopes of the lines in Figure 3, are nearly equivalent (0.19 mol/mol for the unmodified film, 0.18 mol/mol for the skeletonized film). The observation that the measured uptake consistently scales with film mass, whether the films are modified or not, suggests that water sorption in fatty acid films is a headgroup hydration phenomenon.

In contrast to their water sorption properties, unmodified and skeleton films behave very differently from each other with respect to organic-based vapor sorption. All such vapors are more soluble in the skeletonized films; more interestingly, the skeletonization process has a significant impact on selectivity, as shown in Figure 4. We also note that the solubility of each vapor in the skeletonized films (nine tested) was reproducible from one film to the next to within only 50%, a far greater variation than the random relative error for the more well-defined unmodified LB films. The large variation in sorption is perhaps an indication of the irreproducible nature of the skeletonization process itself, as well as a reflection of the inhomogeneous spatial distribution of ionized fatty acids from one film to another.

The vapor solubility characteristics of the skeletonized films can be used to make inferences about their structure as well as the mechanisms for sorption. The increase in organic solubility, as compared to that of the unmodified film, is consistent with an increase in free volume created by removal of the fatty acid molecules. Such free volume is conducive to absorption of alkanes

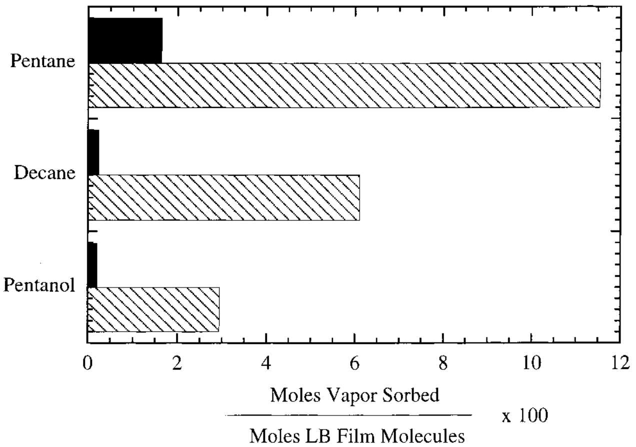

Figure 4. Sorption of nonpolar and semipolar vapors in unmodified (solid bar) and skeletonized (crosshatched bar) LB films. Each vapor is present at the same relative saturation of 60%.

that can interact favorably with the alkane chains of the resident fatty acid salts. Although our measurements cannot discern the exact size and distribution of the free volume, the available space is sufficiently large that sorption selectivity based on size is reduced. This selectivity is, in fact, lost in the case of pentane and decane, which absorb nearly equally on a mass basis. The sorption characteristics of the voids are still dominated by hydrophobic interactions, as pentanol shows reduced uptake compared to that of the alkanes. In addition, the added free volume seems not to affect the water sorption at all.

In summary, the sorption characteristics lend support, albeit indirect, to Blodgett's view of the structure of skeletonized films. If so, it is intriguing to think of a soft material being able to sustain its intricate structure with half of the original mass removed. Moreover, although the skeletonization process dons these materials with less desirable selectivity properties (from the point of view of separations applications), the process offers opportunities to create new materials by "filling the holes" with other ingredients that might not otherwise be incorporated into conventionally fabricated LB films.

Conclusions

Fatty acid multilayers prepared by Langmuir−Blodgett deposition exhibit a repeating bilayer substructure. One can imagine the basic unit as a bilayer having a smectic hydrocarbon interior that is bounded by the acid headgroups; divalent cations serve as the "glue" needed to create multilayer structures from these subunits. This internally stratified structure of fatty acid multilayers endows these LB films with sorption selectivity on the basis of size and polarity, as was demonstrated herein for the case of four different vapors. We find that these films are readily hydrated (1 molecule of water for 5 molecules of acid) in comparison to their ability to take in hydrocarbons. The amphiphilic vapor pentane was the least soluble of all.

The main goal of this work, however, was to examine the intriguing process of skeltonization and its impact on vapor sorption properties. We used the quartz crystal microbalance to measure directly the mass lost upon immersing the film in benzene. The amount of mass lost was consistent with the amount of protonated acid estimated to be in the original film. A much slower, longer-time mass loss was also observed, probably associated with dissolution of the remaining salt molecules. Interestingly, the resultant skeletonized films absorb nearly the same amount of water as the unmodified film, indicating that water sorption is controlled by salt hydration. On the other hand, the skeletonized films are less effective barriers to organic permeation; in addition, these more porous films exhibit diminished selectivity.

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J.A.Q. wishes to acknowledge his 40-some year friendship with Jimmy Wei, including his unsuspecting role as "catalyst" in launching Dean Wei's academic career.[22] Our first acquaintance dates back to 1960 when Wei was gaining wide recognition for his early work at Mobil with Dwight Prater on the modeling of catalytic cracking. Over the intervening years, I have served with Jimmy on a variety of committees and professional activities and have witnessed the major impact he has had on our profession as teacher, mentor, researcher, administrator, and national spokesman for chemical engineering. From these numerous activities, he has emerged as a senior statesman for our profession. I know of no one better qualified to serve in this role than Jimmy Wei, and may he continue to do so for many years.

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