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Characterization of Langmuir–Blodgett Multilayers Using a Quartz Crystal Microbalance: Estimation of Molecular Area and Ionization

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This paper describes how the quartz crystal microbalance can be used to estimate both the molecular area and percent ionization of Langmuir–Blodgett multilayers composed of fatty acids. This is done by doing a series of depositions of a variety of fatty acids (palmitic, stearic, arachidic, and behenic acid) onto the quartz crystal. The added mass decreases the vibrational frequency of the crystal. Relating the frequency change for each layer to the molecular weight of the fatty acid allows one to estimate the molecular area and the mass of any other inclusions in the multilayers. The method assumes that the different fatty acids have similar structure under the same deposition conditions. The assumption that the multilayers do not contain water allows the mass of the inclusions to be related to the mass of metal ions and thus to the percentage ionization of the fatty acid. The estimates of the molecular area and percent ionization, as determined using this procedure, are compared to data in the literature obtained by other techniques.

Introduction

Developed over 70 years ago, the Langmuir–Blodgett (LB) deposition technique remains today one of the most versatile and promising methods of fabricating solid-supported ultrathin films. This process involves the transfer of insoluble monolayers residing at the air–water interface onto a substrate as it is passed vertically through the interface; this strategy allows films to be fabricated incrementally, layer by layer. The most studied films to date are those composed of simple fatty acids. It is known[1,2] that the stability of these films is enhanced if divalent ions (e.g., Cd^{2+}, Ba^{2+}, Ca^{2+}) are present in the water. The amount of cations incorporated into the multilayers depends on the ionization of the acid, which in turn is determined by the pH and ion content of the water subphase.[3]

LB films have been characterized by a variety of techniques.[4] In particular, molecular areas and crystal structure have been elicited most often by diffraction techniques and, more recently, by atomic force microscopy. The incorporation of metal ions into films has been studied by infrared spectroscopy (IR),[3,5,6] neutron activation analysis,[7] X-ray photoelectron spectroscopy,[6] and radioactive tracer studies.[8] Many of these aforementioned techniques require sophisticated or costly instrumentation. In this paper, we demonstrate that both molecular area and metal content of films can be determined accurately using a simple device: the quartz crystal microbalance (QCM).

The QCM is one of a variety of acoustic wave devices which are all based on the piezoelectric effect.[9-11] The QCM is composed of a quartz crystal set into vibration by application of an oscillating electric field. The frequency of vibration changes as mass is added to surface of the crystal. As a tool to characterize LB films, the QCM has been employed to confirm that the amount of film lifted off the water surface is indeed transferred onto the substrate.[12,13]

The mass of material adsorbed to the surface of the QCM, which is manifested as a decrease in the crystal's resonant frequency, can be estimated from the Sauerbrey equation[14] (which assumes that the adsorbed material is rigid and of negligible thickness in comparison to the crystal)

$$\Delta \mathrm{f} = -4\,\frac{\Delta M}{A}\,\frac{f^2}{(\rho_q \mu_q)^{0.5}} \tag{1}$$

Here, Δf is the frequency change, $\Delta M/A$ is the change in mass per unit area, ρ_q is the density of quartz (2648 $\mathrm{kg \cdot m^{-3}}$), μ_q is the shear modulus of the quartz (2.947×10^{10} $\mathrm{kg \cdot m^{-1} \cdot s^{-2}}$), and f is the fundamental frequency of the crystal (we use 10-MHz crystals in our studies). To appreciate the sensitivity of the QCM, we note that a 1-Hz frequency change—which is easily detectable—corresponds to 2.21 ng of adsorbed material/cm^2.

It is convenient to cast eq 1 in terms of appropriate variables for LB films. The mass per unit area for each deposited layer can be approximated as

$$\frac{\Delta M}{A} = \frac{\mathrm{MW}_{\mathrm{acid}} + \phi}{\mathcal{A}} \tag{2}$$

Here $\mathcal{A}$ is the molecular area of the acid, $\mathrm{MW}_{\mathrm{acid}}$ its molecular weight, and ϕ is the apparent molecular weight of all other species incorporated into the film, such as the

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divalent ions and water. The frequency change per layer, $\overline{\Delta f}$, is then given by

$$\overline{\Delta f}\,[\mathrm{Hz}] = -7.5\,\frac{\mathrm{MW}_{\mathrm{acid}} + \phi}{\mathcal{A}\,[\text{Å}^2]} \qquad (3)$$

In this paper, we show that it is possible to determine both ϕ and $\mathcal{A}$ by a judicious experimental design. This is in contrast to previous studies[12,13] using the QCM to determine the mass of layers transferred, where values for ϕ and $\mathcal{A}$ were estimated from other techniques. Our method is based on measuring $\overline{\Delta f}$ for a variety of films differing only by the chain length of the fatty acid. Our analysis is based on the assumption that, under similar conditions of deposition, ϕ and $\mathcal{A}$ do not vary among these films. As is readily noted from eq 3, a plot $\overline{\Delta f}$ versus $\mathrm{MW}_{\mathrm{acid}}$ is linear, with slope and intercept related directly to $\mathcal{A}$ and ϕ.

We use this procedure to determine the mean molecular area and the barium ion content of fatty acid films, ranging from palmitic ($C_{16}H_{32}O_2$) to behenic ($C_{22}H_{44}O_2$) acids. We presume that these films are void of water and are composed of nothing more than acid and divalent ions. In this case, the ratio of ions to acid molecules in the film is given by ($\phi/\mathrm{MW}_{\mathrm{ion}}$). Metal contents and molecular areas were determined at two different pHs, and the results were compared to those obtained via other techniques.[3,7,15] We attempted to test the hypothesis of negligible water content by exposing an arachidic acid film of 106 layers to a desiccant and measuring the attendant mass loss.

Experimental Procedure

We purchased 10-MHz quartz crystals, polished to less than 1 μm, from International Crystal Manufacturing Co. Before fabricating the electrodes, we first cleaned the crystals using the RCA method.[16] We then deposited by thermal evaporation an adhesive underlayer of 100 Å Cr followed by 1000 Å Au onto the quartz disk using a mask purchased from Fotofabrication Corp., yielding an electrode area of 20.5 mm^2. The resulting disk has a surface composed both of gold and quartz. Unlike the quartz surface which is hydrophilic, the gold surface is difficult to keep clean and hydrophilic when exposed to air.[17,18] A good substrate for LB deposition should be hydrophilic or hydrophobic so that either the head or tail groups of the fatty acid have an enhanced affinity for adhering to the surface. We therefore made the entire disk hydrophobic, by coating it with a chemisorbed organic layer. To do this, we first placed the crystals in a 1 mM ethanol solution of octadecyl mercaptan for 12 h to coat the gold surface[19] and then in octadecyltrichorosilane (OTS) solution to coat the quartz surface.[20]

The quartz crystal was resonated at its natural frequency using a home-made oscillator. Frequency measurements were made using a HP5334B frequency counter and the frequency changes due to deposition of layers were recorded in relation to the initial frequencies of the crystals.

Multilayers of fatty acids were deposited onto the quartz crystals using a KSV 5000 trough (KSV Instruments Ltd., Helsinki, Finland), which was housed in a class 10000 clean room to reduce the risk of dust contamination. Milli-Q water having a resistivity of 18 MΩ cm was used to prepare the subphases. The pH values of samples of the subphases were measured using pH indicator sticks. The subphases used were either 10^{-4} M $BaCl_2$, 10^{-4} M $KHCO_3$, 10^{-7} M $CuCl_2$, pH 6.5[21] or 10^{-4} M $BaCl_2$, 10^{-5} M $KHCO_3$, 10^{-7} M $CuCl_2$, pH 5.5. The fatty acids (palmitic, stearic, arachidic, behenic) were purchased from Sigma and used without further purification.

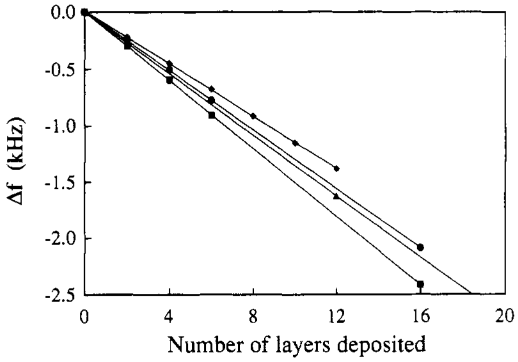

Figure 1. Frequency change measured versus number of layers of palmitic (◆), stearic (●), arachidic (▲), and behenic acid (■) deposited from a barium-containing subphase at pH 6.5. The data are fit with a least-squares regression.

Deposition of the fatty acids onto the QCM was carried out as follows. First the fatty acid was spread as a 1 mg/mL chloroform solution onto the water surface. Next the monolayer was compressed to a surface pressure of 30 mN/m, which was maintained throughout the entire deposition. The first layer is deposited on the downstroke as the QCM is submerged into the subphase. On the upstroke, the second layer is transferred onto the QCM, yielding a bilayer structure. Subsequent strokes result in a multilayered "Y-type" [4] film. In all work here, we used a dipping speed of 10 mm/min, and the subphase temperature was 20 °C. A 5-min delay was allowed after each upstroke to promote drying of the film.[22] The frequency of the crystal was measured before and at intervals during the deposition.

Results and Discussion

Figure 1 shows the frequency change observed versus the number of layers deposited for four LB films each composed of a different fatty acid (palmitic ($C_{16}H_{32}O_2$), stearic ($C_{18}H_{36}O_2$), arachidic ($C_{20}H_{40}O_2$), behenic ($C_{22}H_{44}O_2$)). They were deposited onto the quartz crystal from the surface of a barium-containing subphase at a pH of 6.5. The sensitivity of the QCM is beautifully demonstrated by Figure 1: as the chain length of the fatty acid is increased by two carbon units, we observe a systematic increase in the frequency change per layer. The frequency change per layer, $\overline{\Delta f}$, for each film is found from the slope of a linear fit to the data.

By use of the procedure previously discussed, $\overline{\Delta f}$ is plotted versus the molecular weight of the fatty acid, $\mathrm{MW}_{\mathrm{acid}}$, as shown in Figure 2. The linearity of the data, as predicted by eq 3, supports the premise that $\mathcal{A}$ and ϕ do not vary among these films as long as the deposition conditions (e.g., pH) are the same. By use of a least-squares analysis, the slope and intercept of the linear fit through the data are determined; these quantities can then be directly related to $\mathcal{A}$ and ϕ. This procedure was repeated for the same series of films deposited at a pH of 5.5. The results are summarized in Table 1.

The estimate of the molecular area, $\mathcal{A}$, of these films is 18.2 ± 1.7 Å^2 at pH 5.5 and 19.2 ± 2.7 Å^2 at pH 6.5; these are the same within the calculated error.[23] Our estimate of $\mathcal{A}$ compares favorably with that determined by Bourdieu et al. using atomic force microscopy:[15] 19 ± 0.2 Å^2 for

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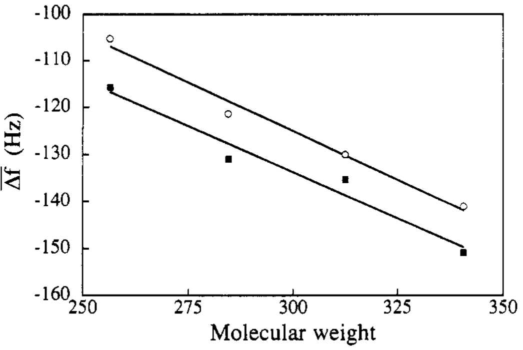

Figure 2. Frequency change per layer, $\overline{\Delta f}$, versus the molecular weight of the fatty acid for multilayers deposited from a barium-containing subphase at pH 5.5 (○) and pH 6.5 (■). The data are fit with a least-squares regression.

Table 1. Parameters Estimated from Figure 2

	pH 5.5	pH 6.5
slope	−0.41 ± 0.038	−0.39 ± 0.055
intercept	−1.2 ± 11.27	−16.41 ± 16.65
$\mathcal{A}$ [Å^2]	18.2 ± 1.7	19.2 ± 2.7
ϕ	2.91 ± 27.04	41.94 ± 36.65
$\phi/\mathrm{MW}_{\mathrm{ion}}$	0.02 ± 0.2	0.305 ± 0.27
ionization (%)	4 ± 40	61 ± 54

an annealed stearic acid film deposited from a barium-containing subphase at a pH of 6.5. Similar values of $\mathcal{A}$ at these two pHs are expected since the fatty acid monolayers exhibit nearly identical isotherms (i.e., surface pressure vs molecular area) on various salt solutions in this pH range.[2,24-26] Furthermore, the similarity of these isotherms for the different fatty acids corroborates the assumption of constant $\mathcal{A}$,[27] as discussed above.

Our estimate of molecular area has ignored the effect of surface roughness. This effect can be accounted for by way of a simple correction factor relating the geometric surface area of the gold to the true surface area. Lando and co-workers[28] found this correction factor to be only 1.1 ± 0.2 for quartz disks polished to better than 0.15 μm, a tolerance higher than ours. However, Krim[29] has shown that the uniformity of the quartz substrate has little influence on the surface homogeneity of the gold electrode film. Since our estimates of molecular area agree well with those determined from other techniques, and we do not expect the surface roughness correction factor to be significantly different from Lando's, we have neglected roughness effects in our analysis.

The estimate of ϕ in Table 1 was calculated from the division of the intercept by the slope. The large error in ϕ arises from the large error estimated for the intercept, a manifestation of extrapolation to zero $\mathrm{MW}_{\mathrm{acid}}$. This error can be reduced by including more data points in the least-squares analysis; additional data could be obtained by repeating the depositions and/or extending the series of fatty acids examined. In spite of the limited number of data points used in this analysis, it is apparent from Figure 2 that the variation in ϕ associated with a change in pH can be detected with the QCM.

As previously discussed, ϕ represents the apparent molecular weight of all species other than the fatty acid incorporated into the film. We assume that the films are composed of only fatty acid, divalent ions, and possibly water. Regarding the extent of the latter, we deposited 106 layers of arachidic acid from a barium-containing subphase at pH 6.5 and then exposed this film to the desiccant P_2O_5. Using the QCM to monitor mass loss, we found a decrease of less than 1% of the total mass of the film over 130 h, as shown in Figure 3. Although this drying process is not guaranteed to remove all water from the film, it is in accord with the assumption that our films contain negligible water. Further support for this premise is given by Srinivasan[22] who used, a capacitance technique to determine water entrainment as a function of drying time. As per their findings, we waited 5 min between each bilayer transferred to minimize the final water content. Hence, we neglect the water content of the films and relate ϕ directly to the metal content.

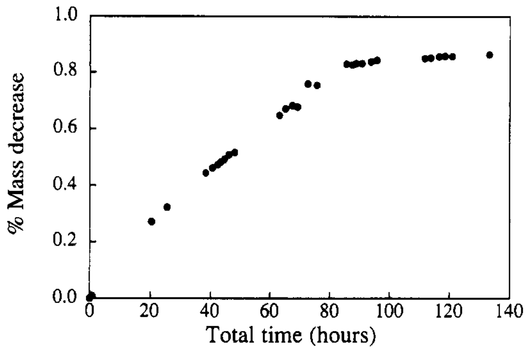

Figure 3. Mass loss (as percent of original mass of film) versus time for a 106 layer arachidic acid film exposed to the desiccant P_2O_5. The film was deposited from a barium-containing subphase at pH 6.5.

The ionization of the fatty acid can be related to ϕ. The amount of metal ions included in LB films is based on the degree of ionization of the fatty acid at the air/water interface.[30-34] Since fatty acids of different lengths have similar acid strengths in the bulk,[35] it is reasonable to presume that their pK_a's on the water surface are not significantly different. Although this assumption is not supported by desorption kinetic experiments,[36] it is in agreement with surface potential[32,33,37] and interfacial tension measurements.[38] Hence, we shall assume that ionization (and consequently metal content) will be the same for each of the fatty acids deposited from a subphase of a given pH and ion content.[30,39]

To calculate percent ionization we assume that, for neutralization, two ionized acids are associated with each divalent barium ion.[7] The ratio of ions to acid molecules is simply $\phi/\mathrm{MW}_{\mathrm{ion}}$, and so the ionization is $2\phi/\mathrm{MW}_{\mathrm{ion}}$. (This neglects the mass loss of deprotonation which changes $\mathrm{MW}_{\mathrm{acid}}$ insignificantly.) The results for the two different pHs examined are shown in Table 1. At pH 5.5

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the percent ionization is 4 ± 40% and at pH 6.5 it is 61 ± 54%. Given the large errors inherent to these estimates, we can only conclude that the degree of ionization does indeed depend on pH, with films deposited at the larger pH having a higher degree of ionization. This phenomenon is consistent with the studies made using IR[3] and neutron activation analysis.[7] For similar films, these studies determined that the percent ionization was 20% at a pH of 5.5 and 57% at a pH of 6.5.

Finally, we demonstrate the self-consistency of the above results. We deposited 106 layers of arachidic acid and measured the corresponding frequency change, as shown in Figure 4. (Note that the frequency response remains linear, as predicted by the Sauerbrey equation, even for a film 106 layers thick.) The consistency is nicely demonstrated by comparing the data to the predicted frequency changes using the estimates of $\mathcal{A}$ and ϕ from Table 1.

Conclusions

We have developed a procedure which uses the quartz crystal microbalance as a tool to determine the molecular area and degree of ionization of fatty acid Langmuir–Blodgett films. While there is a large error (due to extrapolation) associated with an absolute determination of the degree of ionization, this error could be reduced through repeated measurements. Results obtained by using this procedure agree well with values obtained by using other experimental techniques.

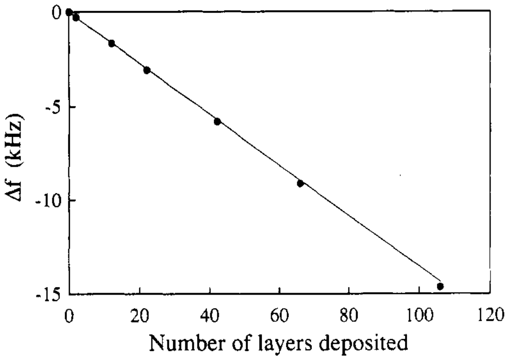

Figure 4. Frequency change measured versus number of layers for arachidic acid deposited from a barium-containing subphase at a pH 6.5: (——) predicted frequency change using eq 3 with the estimated parameters evaluated from the procedure; (●) observed frequency change.

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