Transport Properties of Water and Pentane in Langmuir–Blodgett Films

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The transport of water and pentane vapor in Langmuir–Blodgett (LB) films of arachidic acid is investigated. A quartz crystal microbalance is used to monitor the mass increases of the films upon exposure to the vapor as a function of the pressure. By examining films of different thicknesses, it is shown that it is possible to measure both surface adsorption and solubility. Diffusivity is calculated from the rate of uptake. Water and pentane have Fickian diffusion coefficients of 4×10^{-12} cm²·s⁻¹ and 1×10^{-12} cm²·s⁻¹, respectively. The effect of both aging and annealing of the LB films on the vapor uptake is studied and it is shown that the uptake is sensitive to the state of the film.

Introduction

Langmuir–Blodgett (LB) deposition provides a means of controlling at the molecular level the fabrication of ultrathin organic films (Blodgett, 1935). The technique entails transferring a monolayer of amphiphiles from a water surface onto a solid support and building up the film incrementally by repeated depositions. Film thickness is specified by the number of layers deposited, while the architecture of the film can be governed by varying the composition of the water-supported monolayers. This ability to construct films on a microscopic level has stimulated much research into the potential use of LB films as optical devices, electronic components, and membrane materials (Roberts, 1990).

The study of LB films as membrane constituents is motivated by the possibility of modifying the transport of mass through a film by controlling the structure of the film (Conner et al., 1993; Okahata et al., 1986). While the thinness of an LB film would allow very high throughput of material, it would also require that the film be physically supported to withstand pressure differences. Thus composites made of a permeable polymer coated with an LB film could serve as practical membranes. The polymer would provide the mechanical support while the LB film would be used to control selectivity and allow high permeation rates (Gaines and Ward, 1977; Rose and Quinn, 1968; Conner et al., 1993; Albrecht et al., 1984; Bruinsma and Stroeve, 1994; Kim et al., 1989; Osiander et al., 1988).

Similarily, the viability of engineering materials with nanoscale dimensions has stimulated many investigations of LB films as components of electronic devices (Roberts, 1990). For example, an LB film could serve as an ultrathin dielectric material within a high-performance capacitor; more generally, semiconductor surface properties could be modified by coating with LB films. The measurement of the electrical properties of LB films, such as conductance (Roberts, 1990) and capacitance (Srinivasan et al., 1988), are important because of the possible use of the films in electronic devices. It has been found, for example, that conductivity depends on the humidity of the ambient environment (Tredgold and Winter, 1981; Barraud et al., 1977), a result that is probably due to the presence of moisture in the films.

In this work, we examine the transport properties of both water and pentane into LB films. We focused our studies on well-characterized LB films, in particular those composed of arachidic acid $(C_{20}H_{40}O_2)$ multilayers. Our interest in water is motivated by its inherent presence in LB fabrication as well as its importance in governing the film's electrical properties (Barraud et al., 1977). The dual hydrophobic/hydrophilic nature of LB films stimulated our investigation of the nonpolar molecule pentane as a complement to water. We are able to study transport in these extremely thin films by utilizing an extremely sensitive mass detector known as the quartz crystal microbalance (QCM).

The QCM is one of a family of acoustic wave devices that are all based on the piezoelectric effect (Ward and Buttry,

1990). The QCM consists of an oscillating quartz crystal whose resonant frequency of vibration changes as mass is added to its surface. Measurement of the resulting frequency change allows the QCM to be used as a very sensitive mass balance (Deakin and Buttry, 1989; Lu and Czanderna, 1984; Ward and Buttry, 1990). In fact, the QCM is commonly used as a thickness monitor in commercial metal evaporators. Over the past decade, the great sensitivity of the QCM has been exploited in a variety of research applications that involve mass and rheological changes at solid–fluid interfaces (Ward and Buttry, 1990; Buttry and Ward, 1992; Ricco et al., 1989; Bruckenstein and Shay, 1985; Yang et al., 1993; Johannsmann et al., 1992).

One such application, particularly relevant to this work, has been investigating vapor transport in polymers (Laatikainen and Lindström, 1986; Moylan et al., 1991; Yang and Tong, 1985; Tong and Saenger, 1988; Ognjanovic et al., 1990; Topart and Josowicz, 1992). In these experiments, the polymer of interest is coated onto the surface of the QCM and exposed to a vapor. The QCM is used to monitor the mass change resulting from vapor penetrating into the polymer. The rate of mass increase is related to the diffusivity, and the final mass change is related to the solubility (Crank, 1956). This method of measuring both diffusion and solubility of permeants into a material is known as the sorption method.

It is important to realize that the final mass change resulting from vapor exposure arises from mass both absorbed within, and adsorbed onto, the polymer. The solubility of the vapor is strictly the mass absorbed divided by the initial film mass. With thick polymer films, it is reasonable to neglect surface adsorption, and hence attribute the final mass change to absorption. The mass of the vapor-free polymer needed to calculate solubility can be readily measured using the QCM. While the sorption method can be applied to LB films, their thin nature makes it necessary to account for surface adsorption to get an accurate measurement of solubility. In this work, we demonstrate how this can be accomplished.

We employ the QCM to examine both the transport in LB films as well as their fabrication. With regard to the latter, we use the QCM to measure the mass of the vapor-free LB film, and to monitor the deposition of the individual layers during film formation. The incremental frequency change resulting from each layer deposited can be recorded to confirm the transfer of the layer from the water surface onto the QCM (Hanley et al., 1994; Okahata and Ariga, 1987; Okahata et al., 1992; McCaffrey et al., 1986; Roberts et al., 1988, Facci et al., 1993; King, 1971). Recently, we have also shown that the QCM can be used to estimate certain average molecular properties of the resultant films such as molecular area and degree of ionization (Hanley et al., 1994).

Acoustic wave devices have been used previously to examine the solubility of vapors into ultrathin organic films. Holcraft and Roberts (1988), Furuki and Sun Pu (1992), and Rapp et al. (1991, 1992) probed the response of LB multilayers to gases. However, their objective was to evaluate the potential of the LB film as a gas-sensing material for pollutant detection, and thus diffusion and surface adsorption were not examined. Okahata and Ebato (1991a,b) and Okahata and Shimizu (1987) employed a QCM to study the response to certain vapors of surfactant films deposited by casting; again, there was no measurement of surface adsorption.

More recently, Ariga and Okahata (1994a) used a QCM to examine the transfer process of LB deposition. They show that during deposition, LB films entrain a substantial amount of water in the outermost bilayer. By examining the rate at which this water subsequently evaporates, they estimate a diffusion constant for water in the outer layer. In this work, we show that the water still resides in the LB film after this evaporation process. We also show that when the LB films are subsequently exposed to water vapor, the water actually penetrates deep in to the LB layer. By measuring the kinetics of the water uptake, we not only estimate a diffusion coefficient but show that it is Fickian and varies with water concentration. We also estimate the extent of surface adsorption by examining the water pickup in films of different thicknesses. As a complement to the water data, we have also investigated the transport of pentane into the LB films.

LB films are usually not in equilibrium. Their properties are, for example, noticeably affected by aging and annealing (Tredgold and Winter, 1981; Bourdieu et al., 1993; Leuthe and Riegler, 1992; Holley, 1938). Submerging the films in water has also been shown to change their structure. Schwartz et al. (1992) have used atomic force microscopy to show that molecules can overturn upon submersion, while Ariga and Okahata (Okahata and Ariga, 1989; Ariga and Okahata, 1994b) used the QCM to show that the films take up substantial amounts of water, resulting in the swelling of the submerged film. Since "solubility" implies an equilibrium phenomenon, we prefer to use the general term "uptake" instead of "solubility" to highlight the nonequilibrium nature of LB films. In this article, we examine the metastable behavior of LB films by investigating how aging and annealing affect vapor uptake.

Many of the previous investigations addressing transport across LB films—most notably those of Rose and Quinn (1968), Gaines and Ward (1977), and more recently Albrecht et al. (1984)—have relied on the permeation method. A pressure gradient is applied across the film and the resulting flux through the film is measured. This type of rate measurement is, however, greatly affected by the presence of any small holes in the film; and indeed it was observed (Rose and Quinn, 1968; Gaines and Ward, 1977; Albrecht et al., 1984) that the measured permeability of LB films depended on the thickness, that is, number of layers. In contrast, the sorption method, which we use in this work, requires no pressure differential across the film, and thus has the advantage that measurements are relatively insensitive to the presence of pin holes (Crank and Park, 1968). Applying the sorption method to extremely thin layers such as LB films requires great sensitivity in mass detection, however, and it is the remarkable sensitivity of the QCM that makes this study feasible.

This article is divided as follows. First we describe how surface adsorption and uptake can be individually determined by examining films of different thicknesses. Then we report on a set of experiments that form an important prerequisite for the rest of our studies: namely, we confirm that the LB films are stable under vacuum and that they release the same amount of water upon exposure to vacuum or to desiccant. The remainder of the article describes the measured response of LB films upon exposure to both water and pentane vapors over a range of pressures. Finally, we investigate the effect of both aging and annealing of the LB films

on the vapor uptake and show that uptake is sensitive to the state of the film.

Uptake Measurements in LB Films: Subtleties of the QCM Method

Mass adsorbed to the surface of the QCM is manifested by a decrease in the crystal's resonant frequency. The mass of the material can be determined by use of the Sauerbrey equation (Sauerbrey, 1959; Ricco et al., 1989; Ward and Buttry, 1990), which assumes that the adsorbed material is rigid and of negligible thickness in comparison to the crystal:

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

Here, Δf is the frequency change observed resulting from material being adsorbed on both sides of the crystal; $\Delta M/A$ is the change in mass per unit area; ρ_q is the density of quartz (2648 kg·m^3); μ_q is the shear modulus of the quartz (2.947 $\times$ 10^{10} kg·m^{-1}·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 per square centimeter.

It should be noted that the mass of material per unit area is equivalent to the product of density and thickness of material. As the thickness of material increases, viscoelastic effects, which are not accounted for in the Sauerbrey equation, may become significant. However, we have used LB films with thicknesses less than 3000 Å, and for such thin films, viscoelasticity can be generally neglected. This can be confirmed (as we do; see Figure 2B) by demonstrating that, as is predicted by the Sauerbrey equation, frequency changes scale linearly with thickness (Orata and Buttry, 1987; Hanley et al., 1994).

Evaluating a film's uptake by basing it on the total frequency change upon vapor exposure can lead to errors. This is because a portion of the response is due to surface adsorption. Uptake and surface adsorption can be distinguished by measuring the response of films of different thicknesses. For a homogeneous film, the response should scale linearly with thickness; the slope reflects the mass of vapor absorbed per layer; uptake is then calculated by dividing the mass of vapor absorbed per layer by the mass of the layer. The intercept at zero thickness can be attributed to surface adsorption.

At the microscopic level, LB films can be inhomogeneous. Variations in thickness across the film have been detected with the atomic-force microscope (Garnaes et al., 1993; Bourdieu et al., 1993), and the presence of domains and grain boundaries have been observed using both atomic-force microscopy (Garnaes et al., 1993; Bourdieu et al., 1993) and polarized-reflection microscopy (Leuthe and Riegler, 1992). However, the frequency change of the QCM results from mass adsorbed over the total electrode area (Buttry and Ward, 1992), and thus only the average response of the film is measured.

The frequency of the crystal can also be affected by changes in the medium within which it is oscillating. These influences on the resonant frequency are important when operating the QCM in a liquid (Kanazawa and Gordon, 1985). However, the corrections due to changes in the gas pressure and gas viscoelasticity are small (Watts et al., 1990; Lando and Slutsky, 1970a,b; Stockbridge, 1966), and we have neglected them in this article.

Experimental Procedure

The procedure for depositing LB films onto the QCM was similar to that described previously (Hanley et al., 1994). We purchased 10-MHz quartz crystals polished to less than one micron from International Crystal Manufacturing Co., OK. Before fabricating the electrodes, we first cleaned the crystals using the RCA method (Kern and Puotinen, 1970). 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., IL, yielding an electrode area of 20.5 mm^2. The resulting disk has a surface composed of both gold and quartz. Unlike the hydrophilic quartz surface, the gold surface is difficult to keep clean and hydrophilic when exposed to air (Smith, 1980; Peterson et al., 1986).

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 placed the crystals in a 1-mM ethanol solution of octadecyl mercaptan for 12 hours to coat the gold surface (Whiteside and Laibinis, 1990), and then in octadecyltrichlorosilane (OTS) solution to coat the quartz surface (Sajiv, 1980).

Multilayers of arachidic acid were deposited onto the quartz crystals using a KSV 5000 trough (KSV Instruments Ltd., Helsinki, Finland), which was housed in a class 10,000 clean room to reduce the risk of dust contamination. Milli-Q water having a resistivity of 18 MΩcm was used to prepare the subphase. The pH of samples of the subphase were measured using pH indicator sticks. The subphase used was 10^{-4} M BaCl$_2$, 10^{-4} M KHCO$_3$, 10^{-7} M CuCl$_2$, pH 6.5 (Batemand and Covington, 1961). Previous investigators (Blodgett, 1935; Bateman and Covington, 1961) have found that this subphase is excellent for building up a large number of layers. Arachidic acid was purchased from Sigma and used without further purification.

Deposition of the arachidic acid onto the QCM was carried out as follows. First the arachidic 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 to the QCM, yielding a bilayer structure on both sides of the crystal. Subsequent strokes result in a multilayered "Y-type" film (Roberts, 1990). 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 (Srinivisan et al., 1988).

The quartz crystal was resonated at its natural frequency using a homemade oscillator. Frequency measurements were made using a HP5334B frequency counter. The frequency of the crystal was measured before and at intervals during the

deposition. Frequency changes due to the deposition of layers were recorded in relation to the initial frequencies of the crystals. The frequency changes measured can then be used with the Sauerbrey equation to verify the transfer of the monolayer from the water surface onto the QCM. The Sauerbrey equation can be used to predict the frequency change expected for perfect transfer if we know the molecular area of the fatty acid and the ion content of the film. Previously we have shown that with careful experimental design the QCM can be used to estimate both these quantities (Hanley et al., 1994). A film deposited using the conditions described earlier has a barium content of about 30% on a mole basis and a molecular area of 19 $Å^2$ (Hanley et al., 1994). Knowing these parameters of the film, we can use the Sauerbrey equation to predict the expected mass of a monolayer. The average ratio of the measured mass of the monolayer transferred onto the QCM to the expected mass was 0.9 to 1.

After depositing the LB film onto the QCM, we exposed it to either water or pentane vapor. The QCM is loaded into an apparatus similar in design to that used for investigating vapor transport in polymers (Laatikainen and Lindström, 1986; Moylan et al., 1991). The apparatus is housed in a room with temperature constant at $25 \pm 1°C$. The films are initially evacuated to less than 50 mtorr, and a baseline frequency is recorded by a computer. The pressure is monitored by two MKS Baratron capacitance manometers (with a measuring range of 0 to 10 torr and 10 to 1000 torr, respectively). The water or pentane sample is initially freeze-cycled twice and the vapor pressure is checked for purity before dosing. Vapor is then dosed into the apparatus; the corresponding pressure increase is measured, and the resulting frequency change in relation to the initial baseline frequency is recorded by a computer.

Results

LB films in vacuum: water loss and film stability

The study of transport in LB films by the sorption method requires putting the films under vacuum before exposing them to a vapor. Roberts and Gaines (1962) observed that monolayers of stearic acid desorb under high vacuum. Hence, a prerequisite of our experiments is to verify the stability of the multilayers under our vacuum conditions (about 50 mtorr). Since we are investigating the transport of water, it is also important to quantify the water content of the film after deposition. We examined both the stability of the film under vacuum and the water content of the film by monitoring the mass change of an LB film upon exposure to both a desiccant and low vacuum.

Figure 1 shows the comparison of the mass change observed for 106 layers of arachidic acid LB film. The frequency changes shown (and the corresponding mass ratio) are in relation to the baseline frequency in vacuum. After we deposited the film, we exposed it to the desiccant P_2O_5 at atmosphere pressure (point A). This resulted in a mass loss from the film of about 0.9%. Subsequent exposure of the film to a saturated atmosphere (point B) caused a 1.2% mass gain in the film. The film was then removed from the saturated environment and was reexposed to the ambient environment (point C) with a corresponding mass loss of about 0.3%. At this point in the experiment the weight of the film was in
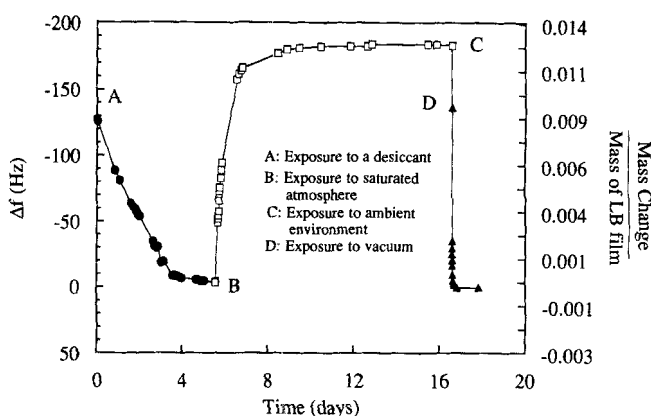
Figure 1. Measured frequency change for 106-layer arachidic acid film resulting from exposing the film first to the desiccant P_2O_5 (point A), a saturated atmosphere (point B), and then the ambient environment (point C), and finally vacuum (point D).

The frequency change is in relation to the final frequency in vacuum.

good agreement to that initially at point A. The film was then put under vacuum with an immediate mass loss of about 0.9%. After this initial loss, the baseline frequency in vacuum was stable on a time frame of days. This baseline frequency in vacuum could be generally reobtained, even after reexposing the LB films to the ambient environment for a few days.

The equivalency of the mass loss observed upon exposing the film to a desiccant and putting it under vacuum suggests that the mass loss upon pulling a vacuum is, only loss of water. This conclusion agrees with the results of Jones and Webby (1987). They observed that the mass loss of LB films upon pulling a vacuum depended on the humidity of the atmosphere evacuated. The estimation of the water content of about 0.9 wt. % after deposition is in good agreement with that observed by Marshbanks et al. (1994). They used attenuated total reflectance Fourier transform infrared spectroscopy to determine the water of hydration of calcium stearate to be from 1.5 to 3 wt. %. We have also shown that the water content depends on the humidity. This conclusion corroborates the observation of Barraud et al. (1977) that the conductivity of LB films depends on humidity.

Response of LB films to water vapor

After confirming the stability of the LB films under vacuum, we investigated the transport of water in the films. We obtained a baseline frequency of the crystals under vacuum and then exposed the LB films to water vapor. The vapor was dosed incrementally to successively higher pressures, and the corresponding final frequency for each pressure was recorded. By final frequency we mean the steady frequency ultimately observed after changing the pressure. After dosing to the highest pressure, we then evacuated incrementally to successively lower pressures, again recording the final frequency at each pressure. After evacuating to baseline vacuum, we reobtained the original baseline frequency.

Films of various thicknesses were examined, and Figure 2A shows the final frequency change from the baseline fre-
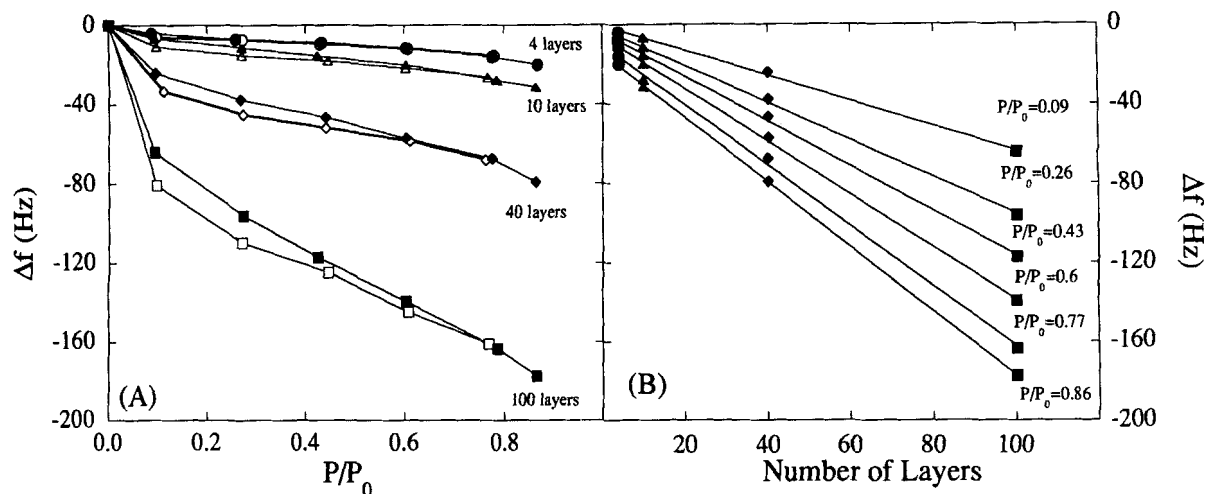
Figure 2. (A) Frequency change measured for exposing water vapor at various pressures to arachidic acid films of different thicknesses; (B) data for dosing arachidic acid films with water vapor to various pressures with respect to the number of layers of the film.

The frequency change is in relation to the baseline frequency in vacuum. The data are for both dosing (filled symbols) and evacuating (open symbols) the water vapor. For films of 4 layers (●), 10 layers (▲), 40 layers (◆), and 100 layers (■). P_0 is the saturated vapor pressure of water. The data are fit with a least-squares regression for each different vapor pressure of water.

quency in vacuum for both dosing and evacuating as a function of the relative vapor pressure. Data for both dosing (closed symbols) and subsequent evacuation (open symbols) are shown in Figure 2. The relative vapor pressure is the ratio of the vapor pressure to the saturated vapor pressure.

As explained previously, the investigation of these ultrathin films requires that we distinguish between surface adsorption and uptake in these films. To make this distinction, we replotted the final frequency change as a function of the number of layers of the LB film. This is shown for the dosing data in Figure 2B; and, as is seen, the data at each pressure are linear and are fit with a least squares regression. The data for the evacuation of the vapor are similarly replotted but are not shown. Excellent linear correlation is obtained for both sets of data, clearly demonstrating that the vapor response is a bulk-like phenomenon. We determine the frequency change per layer and the surface adsorption from the slope and the intercept (zero layers), respectively.

Figure 3 shows the calculated uptake of water vapor into arachidic acid multilayers. It is plotted in terms of a mass ratio and a mole ratio. The error in terms of mass ratio is estimated from the linear regression of the data in Figure 2B (Bevington, 1969). There is hysteresis in the data for dosing and evacuation that becomes more appreciable at lower pressures. Hysteresis is often observed in water sorption by polymers (Crank and Park, 1968), and the phenomenon is generally explained by localized sorption or capillary condensation of the water (Crank and Park, 1968; Chatterjee, 1985). Close to the saturation pressure the uptake is about 0.23 on a mole ratio basis. This seems to be in reasonable agreement with studies of water solubility into liquid stearic acid $C_{18}H_{36}O_2$, in which a water content of 0.15 on a mole ratio basis was determined (Hanahan, 1986; Hoerr et al., 1942).

The surface adsorption of water is determined from the intercept of the data in Figure 2B. As shown in Figure 4, the data are converted to both an average thickness (using the bulk density of water) and a number of adsorbed water

monolayers (using an average molecular area of water of 12.5 $\mathring{A}^2$ (McClellan and Harnsberger, 1967)). The error shown for the data is in terms of the thickness of the water adsorbed and is estimated from the linear regression of the data in Figure 2B (Bevington, 1969). As the saturation pressure is approached, the adsorbed layer increases in thickness, probably indicating that condensation is occurring. At a relative vapor pressure of 0.8, the thickness of the adsorbed water layer is about 3 $\mathring{A}$. This agrees favorably with the findings of Tadros et al. (1974). They used ellipsometry to measure the thickness of adsorbed water on a monolayer of stearic acid; at a similar vapor pressure, they determined this to be about 4 $\mathring{A}$.

We then examined the time dependence of the uptake of the LB films. Two films of 40 and 100 layers were placed initially in vacuum; water vapor was dosed to a relative vapor pressure of 0.6; and the frequency response with time was
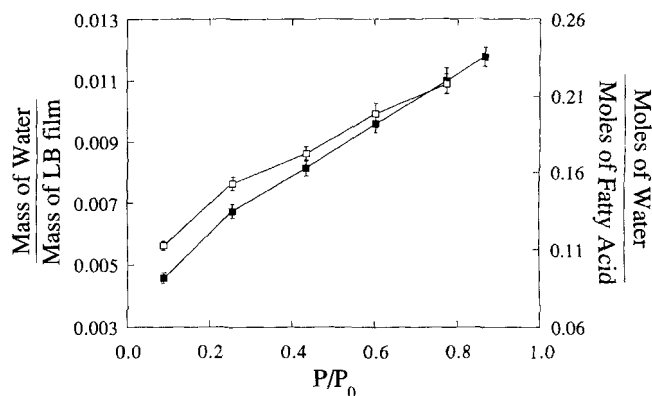
Figure 3. Uptake of water vapor into arachidic acid multilayers as a function of vapor pressure.
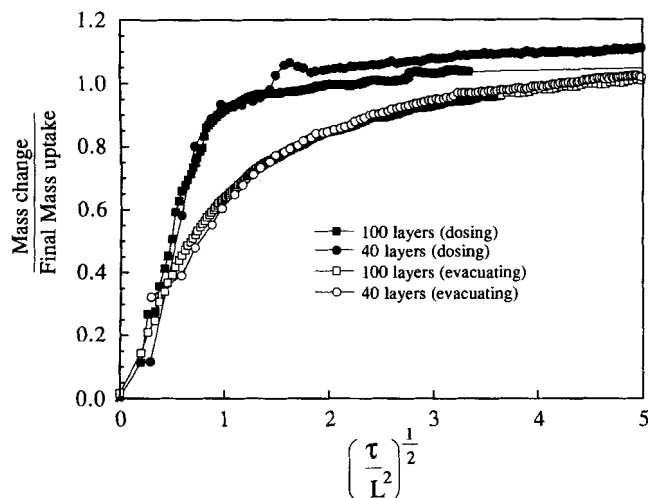
The data are for both dosing (filled symbols) and evacuating (open symbols) the water vapor. P_0 is the saturated vapor pressure of water.
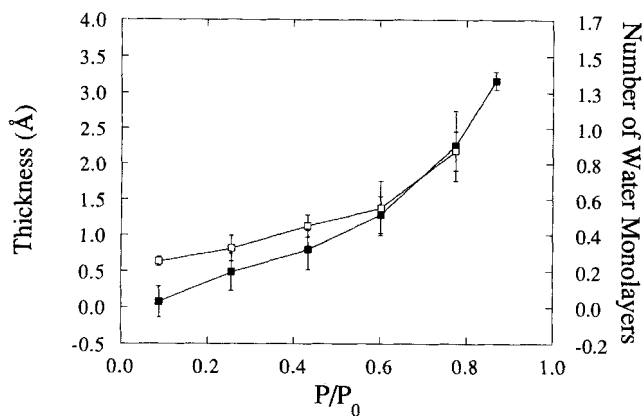
Figure 4. Surface adsorption of water vapor on arachidic acid multilayers as a function of vapor pressure.

The data are for both dosing (filled symbols) and evacuating (open symbols) the water vapor. P_0 is the saturated vapor pressure of water.

recorded. After reaching a final uptake the films were evacuated and the corresponding frequency changes were recorded. The time dependence of the mass changes are shown in Figure 5. The mass changes for both films have been put in dimensionless form by dividing by the final mass change due to uptake. The time axis has been reduced by dividing by the square of the thickness of the film (Bourdieu et al., 1993) and then taking the square root (Crank, 1956). As shown in Figure 5 the data for both thicknesses collapse on each other; this, as well as the linearity of the data at short times, indicate Fickian diffusion (Crank, 1956). Previous studies using the permeation method to determine the transport properties of LB films found that the permeability of LB films varied with the number of layers (Gaines and Ward, 1977; Albrecht et al., 1984; Rose and Quinn, 1968; Bruinsma and

Stroeve, 1994). As explained previously, this is probably due to the sensitivity of the permeation method to pin hole defects in the films.

The mass change for dosing is faster than that for evacuation, which is indicative of a diffusion coefficient that increases with concentration (Crank, 1956). A varying diffusion coefficient, which leads to hysteresis in the rates of dosing and evacuation, often denotes localized sorption of the vapor in the film. In polymers, this hysteresis for water is most apparent with polar crystalline polymers (Crank and Park, 1968). An average diffusion coefficient can be determined from the slope of the data at short times (Crank, 1956) and is about 4×10^{-12} cm$^2 \cdot$s^{-1}, estimated from the initial dosing data of the 100 layers. This is in favorable agreement with the diffusion coefficient of bulk water in calcium stearate that was estimated by Marshbanks et al. (1994) using attenuated total reflectance Fourier transform infrared spectroscopy to be in the range of 1×10^{-10} to 1×10^{-13} cm$^2 \cdot$s^{-1}. Ariga and Okahata (1994a,b) used the evaporation rates of entrained water during the deposition of fatty acids of different chain lengths to estimate the diffusion coefficient of water in the outermost alkyl chains to be 9.7×10^{-12} cm$^2 \cdot$s^{-1}. The diffusion coefficient of water in the polymer polyvinylalcohol is also determined to be 1.7×10^{-11} or 2.8×10^{-12} cm$^2 \cdot$s^{-1} (Long and Thompson, 1955; Crank and Park, 1968).

Response of LB films to pentane vapor

As a complement to the measurements of water transport in LB films, we also investigated the transport of pentane. The uptake of pentane into arachidic acid multilayers is shown in Figure 6. The uptake is determined with the same procedure as that described for water. The final frequency changes recorded for pentane exposure are replotted as a function of the number of layers of the LB film. The errors shown are again in terms of the mass ratio and are estimated from the linear regression of the data. The magnitude of the surface adsorption is not very different from that of water, but since the errors in the linear regression were large at the higher pressures, we do not show the pentane surface adsorption data. Although the uptake for pentane is similar in magnitude to that of water on a mass ratio basis, on a mole

Figure 5. Rate of mass change for 40 (●) and 100 (■) layer arachidic acid film upon exposure to water vapor at a relative vapor pressure of 0.6.
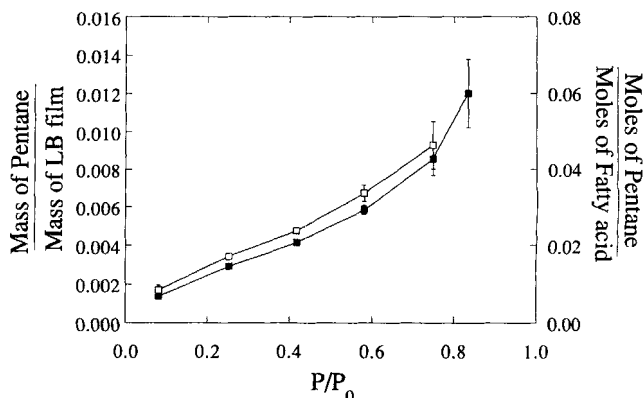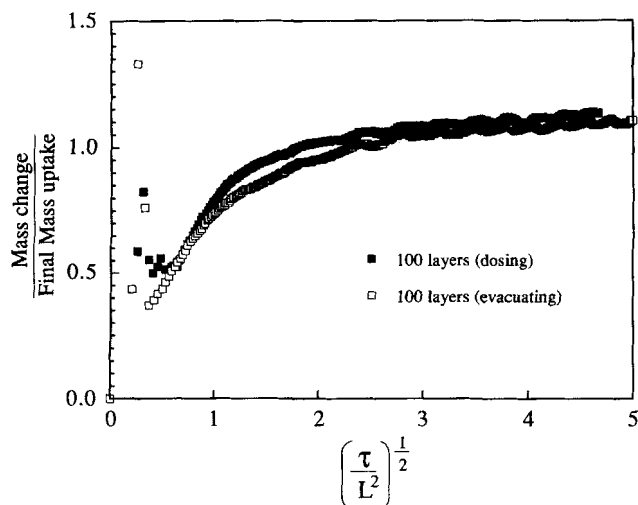
The data are for both dosing (filled symbols) and evacuating (open symbols) the water vapor. τ is time (s) $\times 10^{-15}$ and L is the thickness (m) of the film.

Figure 6. Uptake of pentane vapor into arachidic acid multilayers as a function of vapor pressure.

The data are for both dosing (filled symbols) and evacuating (open symbols) the pentane vapor. P_0 is the saturated vapor pressure of pentane.

Figure 7. Rate of mass change for 100-layer film upon exposure to pentane vapor at a relative vapor pressure of 0.6.

The data are for both dosing (filled symbols) and evacuating (open symbols) the pentane vapor. τ is time (s) $\times 10^{-15}$ and L is the thickness (m) of the film.

ratio basis there is dramatically less pentane taken up by the multilayers. Another contrasting feature in the uptake data to that of water is the minimal hysteresis observed in the dosing and desorbing data.

Figure 7 shows the time dependence of the mass change of a 100-layer LB film for both dosing pentane to a relative vapor pressure of 0.6 and then subsequent evacuation to vacuum. The initial jump in the response of the crystal is due to the disturbance of dosing and evacuating the vapor. The most contrasting feature in the time dependence of pentane uptake to that of water is the minimal hysteresis between the dosing and evacuation data. An average diffusion coefficient can be determined from the slope of the data at short times (Crank, 1956) and is found to be about 1×10^{-12} cm$^2 \cdot$s^{-1}.

The differences in the transport properties observed between these two vapors, the difference in their chemical character and the amphiphilic nature of LB films, all suggest that water and pentane are absorbed at different sites in the films. Most likely, water is absorbed at or near the carboxylic acid head groups, and pentane within the alkane chains. The assumption of water associating with the headgroups is also corroborated by the observation of Höhne and Möhwald (1994). They observed, using X-ray studies, that the bilayer spacing of manganese stearate decreases with decreasing humidity, which could be explained by water being absorbed between the headgroups. This localized sorption would be consistent with the hysteresis observed for the water uptake (Crank and Park, 1968). It is difficult to conjecture where and how the pentane is absorbed within the alkane chains. However, we note that LB films after deposition are well known to have domains of ordered close-packed alkane chains as well as defective regions (Bourdieu et al., 1993; Schwartz et al., 1993; Garnaes et al., 1993; Leuthe and Riegler, 1992; Barraud et al., 1985; Gaines and Ward, 1977; Peterson and Russell, 1985). Although unproved, we expect that the pentane is more likely absorbed at the defective regions than the well-ordered, closely packed alkane chains.

Effect of aging and annealing

LB films are affected by both heat and age. Bourdieu et al. (1993) have used atomic-force microscopy to observe that upon heating, the films can rearrange into a different crystal structure and also exhibit height modulations. Leuthe and Riegler (1992) used polarized reflection microscopy to show domain growth in LB films after heating. Changes in film properties after aging have been observed in conductivity measurements; Tredgold and Winter (1981) have noticed that the conduction of a stearic acid monolayer becomes less as the age of the film increases. Because the transport properties of the film may be sensitive to structure changes within the film (Osiander et al., 1988; Vanderveen and Barnes, 1985; Okahata et al., 1986), we examined the effect of film aging and annealing on the uptake of vapor in the film.

The final frequency changes measured for exposing different 100-layer LB films to water vapor at a relative vapor pressure of 0.8 are shown in Figure 8. The data for the different films, all prepared independently, show some scatter. However, when a particular film is reexposed to water vapor, the frequency change measured was found, remarkably, to decrease with increasing age of the film. The film was probably restructuring with time.

The water uptake of the LB film seems to decrease with the increasing age of the film. However, Schwartz et al. (1992) have observed with atomic-force microscopy that when LB films are submerged in water for long periods of time, the films can rearrange with molecules overturning. The question arises whether the water vapor exposure itself is affecting our uptake measurements. To answer this, we note from Figure 8 that we observe minimal changes in uptake if the uptake is remeasured on the same day. Hence any structural changes in the LB films induced by vapor exposure are either reversible, or too small to measure in comparison to those that occur when the films are left alone to age.

To study aging further, we measured the uptake of 40 and
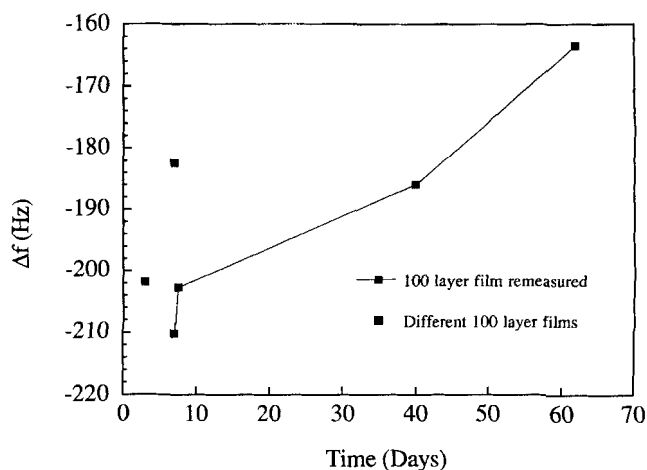
Figure 8. Frequency change measured for dosing different 100-layer arachidic acid films with water vapor to a relative vapor pressure of 0.8.

The frequency change is in relation to the baseline frequency in vacuum. The time frame refers to the number of days after deposition of the film. The data that are connected refer to a particular film that was remeasured over time.
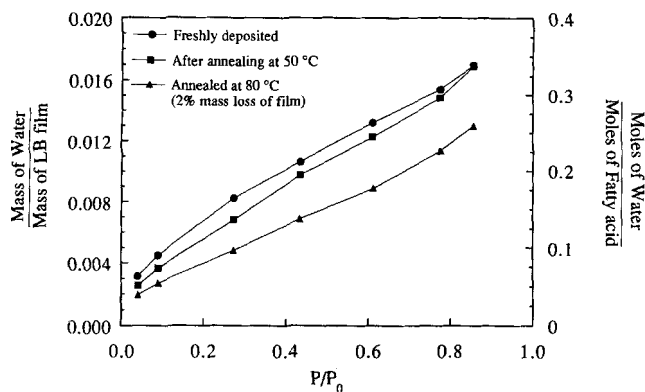
Figure 9. Uptake of water vapor into arachidic acid multilayers as a function of vapor pressure.

P_0 is the saturated vapor pressure of water. The data are for dosing the water vapor to the multilayers before annealing (●), after annealing at 50°C for 2 h (■), and after annealing at 80°C for 2 h (▲).

Figure 10. Uptake of pentane vapor into arachidic acid multilayers as a function of vapor pressure.

P_0 is the saturated vapor pressure of pentane. The data are for dosing the pentane vapor to the multilayers before annealing (●), after annealing at 50°C for 2 h (■), and after annealing at 80°C for 2 h (▲).
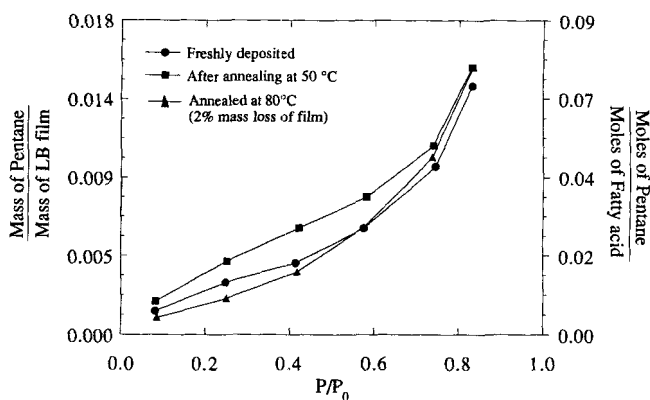
100 layers of arachidic acid before and after annealing. The annealing process should enhance any slow restructuring of the film due to aging. The annealing entailed heating the multilayers to 50°C for 2 hours. The melting point for arachidic acid is 75°C (Bourdieu et al., 1993) so no macroscopic changes of the film would be expected to occur. This was verified since the baseline frequency in vacuum was re-obtained, and also no change in the thickness was detected using ellipsometry. Although no macroscopic changes in the films were observed, the water uptake as shown in Figure 9 was found to be reduced from that of the freshly deposited multilayers. Subsequent annealing at 80°C for 2 hours caused the film structure to change dramatically. There was a mass loss of the films of about 2% as determined by the change in the baseline frequency in vacuum. Additionally, the films did not appear to be homogeneous—they seemed to have formed small droplets. This phenomenon of dewetting was previously observed by Bourdieu et al. (1993). The water uptake was found to be reduced dramatically after this annealing step. We see, then, that annealing and aging cause the same trend of decreasing water uptake.

The uptake of pentane into the 40 and 100 layers was also measured before and after annealing, as shown in Figure 10. After annealing at 50°C, the uptake surprisingly increased. After annealing at 80°C, there was not much change in the uptake, but there was a dramatic increase in surface adsorption. This was probably due to the increase in surface area because of the droplet formation.

Bourdieu et al. (1993) used atomic-force microscopy to study the structural changes of arachidic acid multilayers induced by annealing. They observed that the ordered regions restructure into a slightly more condensed phase, and large defective regions of bulk-like fatty acid are formed by dewetting. It is perhaps this formation of these defective regions that actually cause the pentane uptake to increase after annealing.

Conclusion

The QCM has been used to show that LB films are stable in low vacuum and that any initial mass loss upon evacuation is most probably loss of water from the films. We have described how the QCM can be applied to examine the transport properties of vapors in extremely thin films and how it is possible to measure both the surface adsorption and uptake by examining films of different thicknesses. The response of LB films to water and pentane vapors have been shown to scale linearly with the thickness of the film. We have been able to measure both the surface adsorption and uptake as a function of the vapor pressure. The diffusion of these penetrants into these LB films is shown to be Fickian with a diffusion coefficient of water and pentane of 4×10^{-12} cm²·s⁻¹ and 1×10^{-12} cm²·s⁻¹, respectively. Contrasting behavior is observed in the transport properties of water and pentane, which is no doubt due to the amphiphilic nature of the films. Greater understanding of the transport of vapors through LB multilayers is needed before their application as a membrane material is realized. We show that the uptake of vapors into LB films are affected by aging and annealing of the films. The effect of deposition conditions, aging, annealing, as well as the fabrication of pin-hole free layers (Gaines and Ward, 1977; Rose and Quinn, 1968; Albrecht et al., 1984) all need to be investigated further.

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