Vapor Sorption into Pure and Mixed Fatty Acid Multilayers

Kevin P. Girard, John A. Quinn, and T. Kyle Vanderlick*,†

Department of Chemical Engineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104, and Department of Chemical Engineering, Princeton University, Princeton, New Jersey 08540

Received February 7, 2002. In Final Form: May 13, 2002

The sorption of polar and nonpolar vapors into Langmuir−Blodgett multilayers of pure arachidic acid (C_{20}) was compared to that in films formed of a 1:1 mixture of behenic acid (C_{22}) and stearic acid (C_{18}). The mass of vapor sorbed was quantified using a quartz crystal microbalance. Film swelling was determined using multiple beam interferometry as implemented in the surface forces apparatus. We find that the solubility of water in the pure and the mixed films is the same. Moreover, the absorption of water is ideal in the sense that the film swelling observed is consistent with the incorporation of water at its bulk molar volume. In contrast, the solubilities of pentane, decane, and pentanol were higher in the mixed fatty acid films than in the pure film. The additional free volume available in the mixed films (due to alkane chain mismatch) also results in nonideal absorption of these organic vapors. Vapor sorption kinetic data support the hypothesis that the transport rate is governed primarily by large "pitlike" defects spanning multiple layers within the film structure.

Introduction

Effective separations using membrane technology rely on materials which display high selectivity while also allowing high throughput. The two characteristics, however, are generally at odds with one another, such that steps made to improve one aspect usually degrade the other.

The permeability of a membrane, P, controls the resultant throughput (flux) associated with a given driving force for mass transport. Inversely proportional to membrane thickness, L, the permeability of a sorbent is regulated by its diffusivity, D, and solubility, S, in this elusively simple way:

$$P = DS/L$$

An obvious possibility for increasing membrane permeability is to make the membrane thinner. This, however, can have detrimental consequences on mechanical stability and general robustness of the membrane. Hence, an attractive strategy for maximizing permeability is to create composite membranes: a thin selective layer supported on a mechanically stable but less discriminating layer. Easier said than done, one must still find or create materials which display high selectivity toward permeants of interest. From the equation above, this must originate from a comparatively high diffusivity and/or high solubility.

One class of materials which has been proposed as thin selective layers is Langmuir−Blodgett (LB) films.[1−8] These films, which are built one molecular layer at a time, can be produced as thin as a few nanometers and as thick as several thousand. The extremely small thickness, coupled with the ability to systematically vary it, might be exploited in membrane applications to generate large, controllable fluxes. The real challenge, then, is to create LB films which exhibit interesting and valuable selectivity characteristics. Such characteristics could be useful in sensor applications as well as in membrane technology.

Even simple fatty acids, which formed the first and perhaps the most well studied LB multilayers, are capable of imparting selectivity. These films are highly anisotropic with distinct hydrophilic, polar "head" group regions and lipophilic, nonpolar "tail" regions. We have previously shown that this dual nature gives rise to contrasting sorption characteristics for polar and nonpolar sorbents;[9] a similar phenomenon has been explored in detail for micellar systems[10] which share some of the same anisotropic structural features as LB multilayers.

As a class of molecules, fatty acids are ideal constituents of LB films. They pack well into planar structures, and individual lamellae are readily and strongly "glued" together with divalent cations to form well-ordered, stable, multilayered films. Although only hydrocarbon chain length distinguishes one fatty acid from another, the flexibility of the LB film fabrication process affords many opportunities to vary film structure and properties without necessarily appealing to new, or less cooperative, film ingredients. As one rather dramatic example, the inventive Blodgett[11] proposed long ago that fatty acid LB films could undergo a "skeletonization" process in which un-ionized fatty acids were pruned out of the film by immersing it

---

* To whom correspondence should be addressed. Tel: 609-258-4891. Fax: 609-258-0211. E-mail: vandertk@princeton.edu.

† Princeton University.

[1] Rose, G. D.; Quinn, J. A. *Science* **1968**, *159*, 636−637.

[2] Rose, G. D.; Quinn, J. A. *J. Colloid Interface Sci.* **1968**, *27*, 193−207.

[3] Albrecht, O.; Laschewsky, A.; Ringsdorf, H. *Macromolecules* **1984**, *17*, 937−940.

[4] Kim, K. J.; Fane, A. G.; Fell, C. J. D. *J. Membr. Sci.* **1989**, *43*, 187−204.

[5] Maximychev, A. V.; Matyukhin, V. D.; Stepina, N. D.; Yanusova, L. G. *Thin Solid Films* **1996**, *285*, 866−869.

[6] Bruinsma, P. J.; Stroeve, P. *Thin Solid Films* **1994**, *244*, 958−961.

[7] Conner, M.; Janout, V.; Regen, S. L. *J. Am. Chem. Soc.* **1993**, *1993*, 1178−1180.

[8] Hanley, C. M.; Quinn, J. A.; Vanderlick, T. K. *Langmuir* **1994**, *10*, 1524−1527.

[9] Girard, K. P.; Vanderlick, T. K.; Quinn, J. A. *Ind. Eng. Chem. Res.* **2001**, *40*, 4283−4287.

[10] Klevens, H. B. *Chem. Rev.* **1950**, *47*, 1−74.

[11] Blodgett, K. B.; Langmuir, I. *Phys. Rev.* **1937**, *51*, 964−982.

10.1021/la0201366 CCC: $22.00

in benzene. We recently investigated this process using the extremely sensitive mass detection capabilities afforded by the quartz crystal microbalance sensor, and we compared the permeation properties of skeletonized films to the precursor simple fatty acid films.[9]

In this paper, we pursue the more versatile and well-controlled strategy of modulating film permeation properties by creating LB films from a fatty acid mixture composed of molecules with different chain lengths. The motivation is that films made of mixtures with disparate chain lengths may show selectivity toward organic constituents of a particular size. In other words, one can imagine that mixed fatty acid films might harbor nanoscopic regions of disorder, or “pockets”, with corresponding high and/or selective absorption affinities. As before, we take advantage of extremely sensitive tools for mass detection (quartz crystal microbalance, QCM) and film thickness measurement (multiple beam interferometry, MBI, as employed in the surface forces apparatus, SFA). The use of these tools in tandem is especially interesting in this case; the correlation between mass pickup and degree of film swelling indeed reveals the presence of free volume within the film very deliberately created by using a fatty acid mixture.

Experimental Section

Stearic, arachidic, and behenic fatty acids were of the highest grade available, purchased from Sigma (St. Louis, MO) and used as received. Films were fabricated using a commercial deposition system (KSV, Finland). In all cases, the aqueous subphase contained 10^{-4} M $BaCl_2$, 2×10^{-4} M $KHCO_3$, and 4×10^{-7} M $CuCl_2$ and was held constant at 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.[12,13]

Two types of films were fabricated: pure arachidic acid films and 1:1 stearic/behenic acid mixtures. Spreading solutions for each were formulated by dissolving the single fatty acid or the mixture of the two fatty acids in chloroform to yield a total concentration of about 1 mg/mL. The spread chloroform solutions were allowed to evaporate for at least 10 min before compressing the monolayer to 30 mN/m. Once this pressure was reached, the films were allowed 15 min to stabilize before conventional dipping began at a speed of 10 mm/min. At least 5 min elapsed between each upstroke and the following downstroke to allow entrained subphase to evaporate.

Films were created on either gold-plated quartz substrates (for microbalance experiments) or on molecularly smooth mica sheets (for swelling experiments in the surface forces apparatus). In both cases, the substrates were made hydrophobic prior to LB film formation. The microbalance crystals were coated with a self-assembled monolayer of octadecyl mercaptan;[14] mica substrates were coated with an LB monolayer of DPPE as previously described.[15]

Details on the construction and operation of our home-built microbalance have been previously described.[16] Similarly, details on the use of the surface forces apparatus for measuring film thicknesses and associated swelling have been fully described in a previous publication.[17] We note that both techniques in our laboratory are configured similarly to allow vapor evacuation and dosing to controlled pressures. Films used in this study were exposed to a variety of carefully chosen vapors of interest, each at a relative saturation of 0.6 (i.e., $P/P_{sat} = 0.6$) and at ambient temperature.

Finally, we note that the integral nature of LB films, built one layer at a time, allows an experimental design that is quite conducive for probing intensive properties. In particular, by investigating films of varying thickness (i.e., numbers of layers) one can readily determine a signal or response on a per layer basis (e.g., from the slope of the obtained data). In the case of vapor solubility measurements, this approach also allows one to distinguish between mass absorbed within the film and mass adsorbed to its boundaries (surface adsorption).[8,18]

Results and Discussion

LB films composed of a single fatty acid with a 20-carbon aliphatic chain (arachidic acid) are compared to those composed of an equimolar mixture of 18-carbon (stearic) and 22-carbon (behenic) fatty acids. We first address an open and interesting question regarding the microstructure of the multicomponent films. Namely, it is well-known that certain fatty acid mixtures can display nonideal behavior, including phase separation. For example, using infrared spectroscopy Widayati and co-workers[19] saw evidence of microdomains consisting of 80−100 molecules when the chain length disparity was 6 carbons; their AFM measurements, however, did not reveal any discernible phase separation. Ekelund and co-workers[20] also reported domain formation (about 200 nm in size) observed in a lignoceric (24-carbon)/palmitic (16-carbon) mixture.

Our mixture is composed of fatty acids differing by only four carbons, as present in equimolar amounts. Previous investigators[21−23] working with such systems have suggested a homogeneous, if not idealized, microstructure wherein the short-chained acids in one layer are matched to the long-chained acids in an adjacent layer, in essence creating a mock pure-component film. This picture was supported, for example, by X-ray diffraction measurements which showed the intrinsic repeat spacing of the mixed films to be identical to that for a pure film formed solely of the intermediate acid.[23]

Film thickness measurements using the surface forces apparatus can be obtained with angstrom level resolution. An experimental design based on using films of differing numbers of layers (as described above) allows even more precise measurements of the repeat spacing (i.e., layer thickness). As reported previously,[24] such measurements made on pure arachidic acid films yielded a thickness of 28.0 ± 0.3 Å per layer. Thicknesses of the 1:1 stearic/behenic acid films are shown in Figure 1. The slope of the data yields a repeat spacing of 26.8 ± 0.3 Å per layer. Our results suggest that a fortuitous matching of short and long chains is incorrect (a result further substantiated by the vapor sorption measurements). Rather, chain mismatch does indeed create some disorder which leads to a small decrease in film thickness. The optical measurements carried out in the surface forces apparatus can also yield the thin film refractive index. We find that pure arachidic acid layers have an index of 1.4951 ± 0.007, agreeing reasonably well with ellipsometric determina-

---

(12) Tsionsky, V.; Gileadi, E. *Langmuir* **1994**, *10*, 2830−2835.

(13) Bateman, J. B.; Covington, E. J. *J. Colloid Interface Sci.* **1961**, *16*, 531−548.

(14) Sagiv, J. *J. Am. Chem. Soc.* **1980**, *102*, 92−98.

(15) Marra, J. *J. Colloid Interface Sci.* **1985**, *107*, 446−458.

(16) Hanley, C. M. Ph.D. Thesis, University of Pennsylvania, Philadelphia, PA, 1995.

(17) Girard, K. P.; Quinn, J. A.; Vanderlick, T. K. *J. Colloid Interface Sci.* **1999**, *217*, 146−153.

(18) Hanley, C. M.; Quinn, J. A.; Vanderlick, T. K. *AICHE J.* **1996**, *42*, 1234−1243.

(19) Widayati, S.; Dluhy, R. A. *Mikrochim. Acta* **1997**, *14* (Suppl.), 683−685.

(20) Ekelund, K.; Sparr, E.; Engblom, J.; Wennerström, S. *Langmuir* **1999**, *15*, 6946−6949.

(21) Ganguly, P.; Paranjape, D. V.; Chaudhari, S. K. *J. Phys. Chem.* **1993**, *97*, 11965−11968.

(22) Caruso, F.; Serizawa, T.; Furlong, D. N.; Okahata, Y. *Langmuir* **1995**, *11*, 1546−1552.

(23) Matsuda, A.; Sugi, M.; Fukui, T.; Iizima, S.; Miyahara, M.; Otsubo, Y. *J. Appl. Phys.* **1977**, *48*, 771−774.

(24) Girard, K. P.; Quinn, J. A.; Vanderlick, T. K. *Thin Solid Films* **2000**, *371*, 242−248.

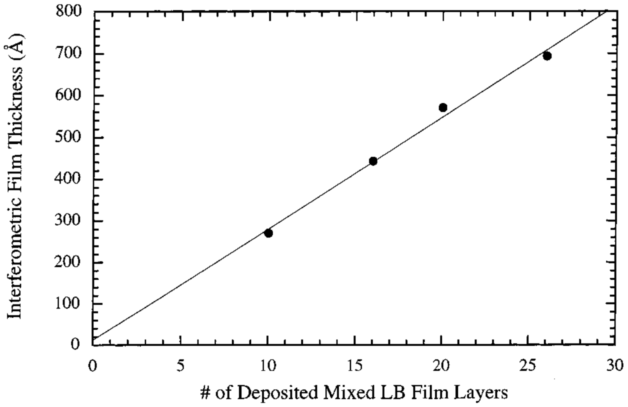

Figure 1. Interferometric thickness of mixed fatty acid multilayers as a function of film thickness. The slope of the best fit line gives a layer thickness equal to 26.8 Å.

tions by Honig et al.[25] (1.511), Petrov et al.[26] (1.51), and Knobloch et al.[27] (1.514). Similar measurements on our mixed films yield a refractive index of 1.4875 ± 0.007. The slightly lower value compared to the pure film is again indicative of disorder and extra free volume.

We turn now to the main result of this work, namely, a comparison of equilibrium vapor sorption characteristics of the mixed and pure films. Four different vapors, chosen to probe effects of size and polarity, were selected for study: water, pentane, decane, and pentanol. We used the QCM to measure vapor pickup into films of differing thicknesses ranging from 4 to 100 layers (six separate pure LB films, seven separate mixed LB films). Vapor pressures were set to 60% of the saturation value at ambient temperature ($P/P_{\mathrm{sat}} = 0.60$). For the most part, linear regression analysis of the data was undertaken to yield the vapor solubility (moles of vapor sorbed per moles of fatty acid in a layer). The exceptions concerned the sorption experiments of decane and pentanol in the pure fatty acid films; since the solubility of these vapors is extremely small, the numbers reported below represent the average solubility as measured for two different films each comprising 100 layers.

We first consider the case of water adsorption. Shown in Figure 2 are water pickup measurements for pure and mixed films. Clearly, the solubilities of water in the films, given by the slopes of the lines (in the pure film, 0.19 ± 0.05 mol water per mol of LB film; in the mixed film, 0.18 ± 0.04 mol/mol), are not significantly different for the two types of films considered. It is also evident that they share the same intercept, which gives an estimate of the amount of surface adsorption: 3.3×10^{-9} mol/cm^2 (ca. 1 monolayer). Our results support our earlier findings that water sorption is completely controlled by headgroup hydration, irrespective of structural differences between the fatty acid films.[9]

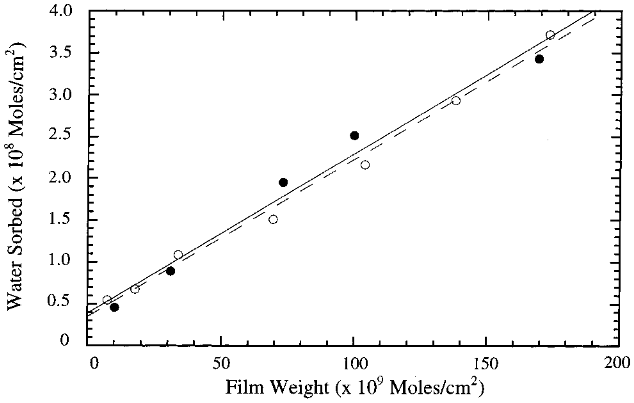

Figure 2. Equilibrium uptake of water in unmodified (closed circles, solid line) and mixed (open circles, dashed line) films as a function of film mass. The solubility is given by the slope of the best fit line.

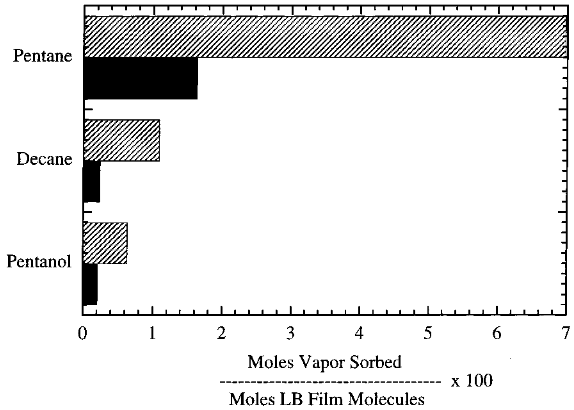

Figure 3. Equilibrium solubilities of nonpolar and semipolar vapors in pure (solid bar) and mixed (crosshatched bar) LB films. Each vapor was presented at the same relative saturation of 60%.

Differences in structure between the pure and mixed films are, however, intuitively expected to regulate the sorption characteristics of lipophilic vapors, and indeed they do. The solubilities of pentane, decane, and pentanol in the pure and mixed films are shown in Figure 3. For the pure arachidic acid films, these solubilities are 0.016 ± 0.012, 0.002 ± 0.0002, and 0.002 ± 0.0008 mol/mol, respectively. Note that the film is selective based on the size of the organic vapor: the solubility of pentane is about 8 times greater than that of decane. Meanwhile, the polarity of the sorbent also critically limits its solubility: pentanol is as sparingly soluble as decane. Data for the mixed multilayers are strikingly different. Most notably, the solubility of all three organic vapors is significantly increased: 0.069 ± 0.032 mol/mol for pentane, 0.011 ± 0.0025 mol/mol for decane, and 0.006 ± 0.004 mol/mol for pentanol. In comparison to the pure film, the solubility of pentane is 4 times larger, for decane it is 5 times larger, and for pentanol it is 3 times larger. The mixed film continues to display selectivity based on size (pentane vs decane), though it is slightly less discriminating. Meanwhile, the amphiphilic pentanol continues to be the least soluble.

The solubility data support the notion that films formed of fatty acids with disparate chain lengths will harbor regions, if not pockets, of disorder located where the mismatched hydrocarbon tails of one molecular layer meet those of an adjacent layer. Such regions would be expected to be very lipophilic, a result supported by our data (e.g., pentane vs pentanol). Furthermore, one expects that such disorder in the mixed film is accompanied by an excess free volume relative to that of the pure film. In other words, small organic sorbents may "fill the molecular gaps" without inducing much or any expansion of the film. To confirm this, we turn to swelling information obtained in the surface forces apparatus.

For these more difficult experiments, we were not successful in fabricating very thick films on the curved

---

(25) Honig, E. P.; Hengst, J. H. T.; den Engelsen, D. *J. Colloid Interface Sci.* **1973**, *45*, 92−102.

(26) Petrov, J. G.; Pfohl, T.; Möhwald, H. *J. Phys. Chem. B* **1999**, *103*, 3417−3424.

(27) Knobloch, H.; Peñacorada, F.; Brehmer, L. *Thin Solid Films* **1997**, *295*, 210−213.

Table 1. Comparison of the Actual and Predicted Amounts of Swelling Due to Absorption of Water in Pure and Mixed LB Multilayers[a]

film type	measured swelling, SFA	predicted swelling, QCM
pure	0.22 ± 0.12	0.30 ± 0.02
1:1 mixed	0.23 ± 0.15	0.29 ± 0.02

[a] Predicted swellings are derived assuming the molar volume of the sorbent is equivalent to its bulk molar volume ($\rho = 1$ g/cm^3). Swelling units are Å/layer.

Table 2. Comparison of the Actual and Predicted Amounts of Swelling Due to Absorption of Pentane in Pure and Mixed LB Multilayers[a]

film type	measured swelling, SFA	predicted swelling, QCM
pure	0.16 ± 0.09	0.16 ± 0.04
1:1 mixed	0.34 ± 0.09	0.69 ± 0.13

[a] Predicted swellings are derived assuming the molar volume of the sorbent is equivalent to its bulk molar volume ($\rho = 0.62$ g/cm^3). Swelling units are Å/layer.

supports used in the apparatus, and so the studied films range only from 4 to 26 layers thick. We also limited our studies to pentane and water as the solubility of the other vapors is too small to yield a measurable signal. Each result represents the average and standard deviation of at least four different films built on separate days.

Table 1 shows the amount of swelling, in units of Å/layer, associated with water sorption for both the pure and mixed films. (These values are derived from the total film thickness changes observed minus a constant offset to account for surface adsorption at the mica/DPPE interfaces, which we previously measured to be approximately 3−5 Å.) As is readily seen, both pure and mixed films swell and do so equivalently to within experimental error (ca. 0.22 Å per layer). The latter suggests that the structure of the headgroup region (where water is expected to reside) is similar in both types of film. We can also compare the swelling data to predictions which assume that (i) the films in the SFA have intrinsic vapor solubilities as determined using the QCM and (ii) the molar volume of any given sorbent is equal to its bulk molar volume as in ideal adsorption. As shown in Table 1, the data agree reasonably well with these predictions.

Table 2 shows the swelling results and associated predictions for pentane absorption. In the case of the pure film, the swelling amounts agree well with the ideal absorption predictions outlined above. It is likely that the absorbed pentane resides between adjacent monolayer leaflets (where tail groups meet tail groups), a conjecture supported by the X-ray studies of McIntosh and co-workers who examined the swelling of phospholipid bilayers upon exposure to short-chain (C_6–C_{10}) alkanes.[28] The swelling data for the mixed films are striking in comparison. First, although the solubility of pentane is 4 times greater in the mixed film than in the pure film, the amount of swelling is increased by only a factor of 2. In other words, the partial molar volume of absorbed pentane is but half its bulk value. This result confirms the presence of some free volume in the mixed multilayers which pentane can occupy without causing the film to expand. This volume is most likely in the form of molecular size voids which are present in the alkane tail region and arise from the chain length mismatch of the fatty acids.

Clearly, the use of mixed fatty acids changes the equilibrium solubility characteristics of the films relative to those of pure films. Both the QCM and the SFA, however, also allow one to explore the kinetics of vapor uptake into these materials. We have previously shown that due to geometrical considerations, the QCM primarily measures transport normal to the deposited layers, while the SFA primarily measures transport laterally or parallel to the layers.[17] It was found that for pure fatty acid LB films, the lateral diffusion rate of water was at least 100 times faster than the normal diffusion rate.[17] In this work, we focus on the differences in transport rates between the pure and mixed films.

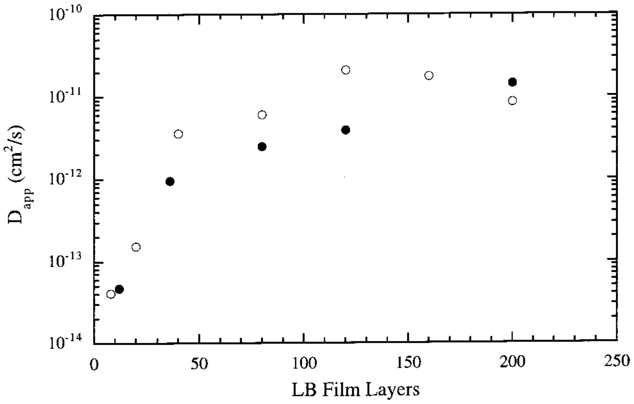

Figure 4. Variation of apparent diffusivity of water in pure (closed circles) and mixed (open circles) LB films of varying thickness. Data for pentane (not shown) is similar.

The time rate of mass pickup directly measured with the QCM allows one to estimate an apparent diffusion coefficient from the slope, m, of a plot of fractional uptake versus the square root of time:

$$D = 4\pi m l^2$$

where l is the thickness of the film.

Such calculations for water sorption into the various film types are plotted in Figure 4 as a function of the number of film layers. Although apparent diffusion coefficients for pentane sorption are not shown for the sake of clarity, we note that for a given film, the diffusivities are almost always the same as those of water to within a factor of 2 or better. Figure 4 displays a peculiar trend: the apparent diffusion coefficient varies with film thickness. We return to this point later but concentrate first on the differences in transport measured between the pure and mixed films.

As is readily seen, in comparison to the pure arachidic acid films, transport rates are systematically higher in the mixed fatty acid films. As stated above, the QCM experiments probe transport normal to the film strata. In the surface forces apparatus, where films are confined by solids, penetration of vapors into the film is regulated primarily by lateral transport. Apparent diffusivities estimated from the kinetics of swelling are shown in Table 3. Again, these transport coefficients are higher for the mixed films than for the pure films. Hence, the increased free volume within the mixed multilayers clearly reduces the resistance to mass transport in both the normal and lateral directions and enhances the permeation rate through these films.

Last, we speculate on the origin of the unexpected result that the effective diffusivity as obtained in QCM measurements showed a dependence on film thickness, a result not consistent with one-dimensional Fickian kinetics. Our best explanation for this behavior is that diffusion in these

---

(28) McIntosh, T. J.; Simon, S. A.; MacDonald, R. C. *Biochim. Biophys. Acta* **1980**, *597*, 445−463.

Table 3. Average Lateral Diffusion Coefficients Estimated from Film Thickness Measurements (Swelling) Using Multiple Beam Interferometry for Pure and Mixed LB Multilayers[a]

film type	water diffusivity (cm^2/s)	pentane diffusivity (cm^2/s)
pure	2.83×10^{-10}	1.38×10^{-10}
1:1 mixed	1.20×10^{-9}	1.16×10^{-9}

[a] Diffusivities are derived from fitting first-order Fickian kinetics to the swelling data (not shown) (ref 17).

films is not purely one-dimensional[17,29] as prescribed by the experimental geometry of the QCM. Conceivably, various film imperfections could serve to enhance the amount of lateral diffusion relative to the amount of normal diffusion, especially for films consisting of only a few layers. There appear to be three different kinds of imperfections in LB films, each with a different length scale. Molecular-sized defects occur at regularly spaced intervals in the crystal lattice to aid in packing.[30] These packing defects serve to reduce the molecular area, bringing alkane tails closer together, and thus it is unlikely that they enhance the permeation rate. Grain boundaries, where two "domains" with different crystallographic orientations meet, have also been observed.[31−33] The domains, about 2 μm in size, typically intersect at very specific angles, and molecular order is maintained close to the boundary. Because of this fact, it has been suggested that grain boundaries are not routes of enhanced diffusion.[32] The largest of the imperfections in LB films are pits, hundreds of nanometers across, which have been shown to extend as deep as a bilayer.[32−37] With their expansive areas and penetration several layers deep, these holes are the most likely of the LB film imperfections to provide significant enhancement of lateral diffusion.

To estimate the significance of such holes in regulating transport, we consider a simple, idealized case in which pits span the entire thickness of the film, that is, from the outermost molecular layer to the substrate surface. This extreme situation would generate the greatest amount of lateral diffusion relative to the amount of normal diffusion. The distance between pits is the characteristic length scale for the lateral diffusion, while the thickness of the film is the characteristic dimension for normal diffusion. For the time scales of both modes to be competitive, the distance between holes would be proportional to ($D^{1/2}_{\mathrm{Normal}}L/D^{1/2}_{\mathrm{Lateral}}$). As film thicknesses are of order 100 Å, this distance scales as $(10^{-10}/10^{-14})^{1/2} \times 100$ Å, or about 1000 nm. This value appears to coincide well with the spacing between holes observed using atomic force microscopy.[32−37] Perhaps coincidentally, this is also roughly the same as the size of grains typically found in these layers.

Finally, we note that while film imperfections of various kinds are indeed likely to exist, we believe the equilibrium sorption properties of LB films as measured in our experiments are not dominated by these. Rather, the mass pickup measurements reported here represent intrinsic solubilities of vapors with the film proper. Evidence to support this includes the near-perfect linear scaling of mass adsorbed with the number of molecular layers constituting the film; it is hard to imagine generating defects or imperfections with such regularity. Moreover, it is difficult to imagine how any of the imperfections described above could display characteristics leading to the vapor selectivity characteristics observed.

Conclusions

By using two fatty acids with disparate chain lengths, we have created Langmuir−Blodgett films with equilibrium vapor sorption characteristics different from those of a pure fatty acid film. In particular, the solubility of hydrocarbons in the mixed films is significantly larger, while the solubility of water is not changed. Although only a few representative vapors were examined, the pure and mixed films appear to exhibit selectivity based on the sizes of the sorbents as well as their hydrophobicity. The unique sorption characteristics of the mixed films are derived from free volume "built in" to the material by the choice of these molecular constituents. Swelling measurements with angstrom level resolution confirm that the uptake of pentane in the mixed film leads to minimal film expansion; in contrast, pentane adsorbed into the pure fatty acid films increases their thickness by the added bulk volume of pentane.

Clearly, a wide spectrum of materials can be formed by mixing together various film-forming molecules in various proportions. In this sense, the LB fabrication method is extremely versatile. In addition to these "prefabrication" strategies for creating different materials, LB films can also be modified after they are formed. For example, films with voids and associated excess free volume can be fabricated by film skeletonization. As we have previously shown, these films absorb even more lipophilic vapors than do the mixed films; however, the size selectivity between pentane and decane is lost.

Although this work shows that permeability properties of LB films can be tuned by various strategies, the selectivities displayed for all films we considered (pure, mixed, and skeletonized fatty acid films) are significantly lower than those typically realized in many industrially useful membranes. It is perhaps more realistic to think about the use of films in the role of water permeation barriers. Recall that the permeability is proportional to the diffusivity and the solubility of water in the film. Both the pure and the modified films were found to have extremely slow water diffusion rates. These rates are comparable to the rate of water diffusion through cuticular waxes, which are nature's efficient barriers for keeping water inside plant leaves.[38−40] The water solubility in a fatty multilayer, however, is a factor of 10 lower than that found in the cuticular waxes, making them even better barriers to water penetration than their natural counterparts.

Acknowledgment. We gratefully acknowledge support for this work from the National Science Foundation (CTS-9615868).

LA0201366

---

(29) Marshbanks, T. L.; Ahn, D. J.; Franses, E. I. *Langmuir* **1994**, *10*, 276−285.

(30) Schwartz, D. K.; Viswanathan, R.; Garnaes, J.; Zasadzinski, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 7374−7380.

(31) Garnaes, J.; Schwartz, D. K.; Viswanathan, R.; Zasadzinski, J. A. N. *Nature* **1992**, *357*, 54−57.

(32) Garnaes, J.; Schwartz, D. K.; Viswanathan, R.; Zasadzinski, J. A. N. *Synth. Met.* **1993**, *55−57*, 3795−3800.

(33) Leuthe, A.; Chi, L.; Riegler, H. *Thin Solid Films* **1994**, *243*, 351−357.

(34) Viswanathan, R.; Schwartz, D. K.; Garnaes, J.; Zasadzinski, J. A. N. *Langmuir* **1992**, *8*, 1603−1607.

(35) Bourgoin, J. P.; Palacin, S.; Vandevyver, M.; Barraud, A. *Thin Solid Films* **1989**, *178*, 499−503.

(36) Chi, L. F.; Eng, M.; Graf, K.; Fuchs, H. *Langmuir* **1992**, *8*, 2255−2261.

(37) Kato, T.; Ohshima, K. *Jpn. J. Appl. Phys.* **1990**, *29*, 2102−2104.

(38) Becker, M.; Kerstiens, G.; Schonherr, J. *Trees* **1986**, *1*, 54−60.

(39) Kirsch, T.; Kaffarnik, F.; Riederer, M.; Schreiber, L. *J. Exp. Bot.* **1997**, *48*, 1035−1045.

(40) Baur, P. *Plant, Cell, Environ.* **1997**, *20*, 167−177.