

Infrared Study of the Molecular Orientation in Ultrathin Films of Behenic Acid Methyl Ester: Comparison between Single Langmuir–Blodgett Monolayers and Spin-Coated Multilayers

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Single Langmuir–Blodgett (LB) monolayers of behenic acid methyl ester (BAME) were studied by infrared spectroscopy. Anisotropic optical constants of this system were calculated from a perpendicular-polarized attenuated total reflectance spectrum and a parallel-polarized reflection–absorption spectrum and were compared to those obtained, in a previous article, for spin-coated multilayers (Pelletier, I.; Bourque, H.; Buffeteau, T.; Blaudez, D.; Desbat, B.; Pérolet, M. *J. Phys. Chem. B* **2002**, *106*, 1968). These optical constants were used to calculate the tilt angle of the alkyl chains in both types of films deposited on solid substrates and to simulate polarization modulation reflection–absorption spectra of the Langmuir film at the air/water interface. The results indicate that the molecular tilt angle is near 30° for spin-coated multilayers, while single LB monolayers have a tilt angle of $11 \pm 2^\circ$. A similar orientation of the alkyl chains is obtained on single monolayers deposited onto solid substrates or spread at the air/water interface (Langmuir films), showing that no change of molecular orientation results from the Langmuir–Blodgett transfer. The presence in the infrared spectra of several bands due to the methylene wagging and twisting modes and of the splitting of the band due to the methylene bending mode at 1463 and 1473 cm^{-1} indicates that in all types of films BAME alkyl chains are in the all-trans conformation and packed in an orthorhombic subcell. However, under certain circumstances, the splitting of the methylene bending mode band was not observed. This phenomenon is associated with the roughness of the solid substrates supporting the LB film leading to the formation of gauche defects in the film and thus to a molecular disordering of the monolayer.

Introduction

In recent years, the study of molecular orientation in ultrathin films has become of major interest to establish the relationship between the film structure and surface functionality. Different techniques such as X-ray diffraction,^{2,3} neutron diffraction,³ Brewster angle microscopy,⁴ and infrared spectroscopy have been developed to study these films. Infrared spectroscopy is particularly useful for studying ultrathin films because it gives information about the molecular orientation in films at the air/water interface or deposited on solid substrates.⁵ Infrared reflection–absorption spectroscopy with or without polarization modulation (PM-IRRAS^{6–8} and IRRAS^{9–17}) is particularly well suited to study molecular conformation

and orientation of films at the air/water interface.¹⁴ PM-IRRAS spectroscopy provides spectra in which the sign of the different bands with respect to the baseline depends directly on the molecular orientation. In the case of thin films deposited on metallic substrates, IRRAS spectroscopy is quite effective since the only bands present in the spectra are those having some component of their transition moment normal to the surface of the film. On the other hand, attenuated total reflection (ATR) spectroscopy is a very efficient tool to investigate structure and orientation of the molecules in films deposited on non-metallic solid substrates.^{18,19} It is a powerful tool to study single monolayers, since the multiple internal reflections in the ATR crystal result in spectra with very high signal-to-noise ratios in a relatively short time.

Several approaches have been developed to calculate molecular orientation from infrared spectra. These meth-

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ods used ATR spectra,^{20–23} IRRAS spectra,²⁴ transmittance and IRRAS spectra,^{25,26} or transmittance and ATR spectra.^{27–29} Recently, another method has been developed to calculate molecular orientation; this method is based on the determination of the anisotropic optical constants of the film^{30–33} and has successfully been used for multilayers of bacteriorhodopsin,³⁰ cadmium arachidate (CdAr),³¹ dimyristoylphosphatidic acid (DMPA),³⁴ poly(γ -benzyl-L-glutamate),^{32,33} and behenic acid methyl ester (BAME).¹

Ultrathin films can be prepared by different methods such as spin-coating and the Langmuir–Blodgett technique. Spin-coating films are prepared by depositing a small quantity of a dilute solution of the sample on a solid substrate that is rotated at high speed. The solvent evaporates readily, leaving a thin homogeneous film on the substrate. Although spin-coated films are usually disordered, some compounds like amphiphilic molecules such as phospholipids can form highly ordered films. In these cases, spin-coating becomes a very quick and reproducible way to prepare ultrathin films. The Langmuir–Blodgett (LB) technique has also been widely used to prepare monolayers and multilayers. With this technique, monolayers are transferred from the air/water interface onto solid substrates by plunging and withdrawing a solid substrate from a water subphase supporting the Langmuir film. With the LB technique, it is possible to control several important parameters, such as temperature, molecular area, and surface pressure of the film and the withdrawing rate of the substrate. However, the influence of the transfer on the structure, conformation, and molecular orientation of the films is neither precisely known nor predictable since the transfer can change the molecular order and the organization of the films. For example, it has been observed that the LB transfer induces in-plane reorientation of the α -helices in multilayers of the polypeptide poly(γ -benzyl-L-glutamate).^{32,33} Steitz et al. have shown that behenic acid monolayers undergo some changes in the packing of the alkyl chains during the LB transfer.³⁵ Kamata et al. have observed that LB transfer causes a molecular reorganization of stearic acid films while, on the other hand, it does not influence the structure of cadmium stearate films.³⁶

In this article, we have studied by infrared spectroscopy the molecular orientation of single monolayers of behenic

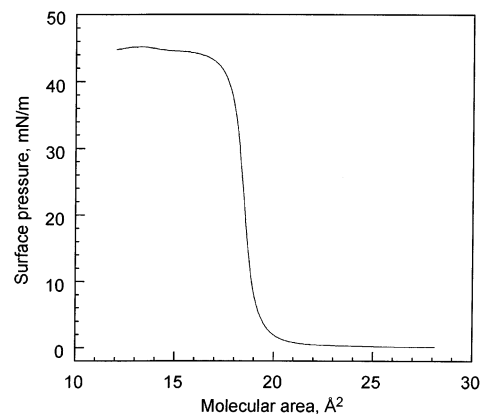


Figure 1. Surface pressure/molecular area isotherm of a BAME monolayer at 17 °C.

acid methyl ester deposited either on solid substrates or directly at the air–water interface. The results have been compared with those obtained on multilayered films spin-coated on various substrates to investigate the influence of the deposition technique on the molecular orientation of BAME.

Materials and Methods

Langmuir–Blodgett Film Deposition. BAME ($\text{CH}_3\text{-(CH}_2\text{)}_{20}\text{-COO-CH}_3$) and HPLC grade chloroform were purchased from Sigma-Aldrich and used without any further purification. Monolayers of BAME were formed by spreading 80 μL of a 1.5 mg/mL solution in chloroform on a Millipore quality water subphase at 20 °C temperature, in a 500 \times 150 \times 5 mm KSV 3000 trough (KSV, Helsinki, Finland). After an equilibrating period of 15 min allowing solvent evaporation, the Langmuir films were compressed at a rate of 1.2 \AA^2 molecule⁻¹ min⁻¹. The surface pressure/molecular area (Π/A) isotherm measured is shown in Figure 1. This isotherm is typical of a fatty acid ester that forms compact, low compressibility monolayers. Indeed, it is very steep, and the intercept of its extrapolation to zero surface pressure is near 19 \AA^2 /molecule, like in the isotherm of stearic acid ethyl ester.³⁷ Films were transferred on solid substrates by the Langmuir–Blodgett technique at a surface pressure of 20 mN/m that corresponds to the solidlike part of the isotherm. Monolayers were deposited on CaF_2 windows, gold mirrors, and ATR germanium crystals that were withdrawn from the water subphase at a rate of 2 mm/min. The ATR crystals were parallelograms (angle of incidence, 45°) of 50 \times 20 \times 2 mm, allowing 24 internal reflections. Before deposition, the substrates were cleaned with chloroform and methanol, immersed in chloroform in a Branson 1510 ultrasonic bath (Branson Ultrasonics Corp., Danbury, CT) for 5 min (except for gold mirrors), and put in a plasma cleaner (Harrick Scientific, Ossining, NY) for 30 s to 2 min depending on the nature of the substrate. Finally, dust was removed with a nitrogen gas flow.

Fourier Transform Infrared (FTIR) Measurements. Transmittance at normal incidence, reflection–absorption, and attenuated total reflectance spectra were recorded using a Magna 760 Fourier transform infrared spectrometer (Thermo-Nicolet, Madison, WI) equipped with a MCT detector. A motorized rotating ZnSe wire-grid polarizer (Specac, Orpington, U.K.) was positioned in front of the sample to obtain parallel (p)- and perpendicular (s)-polarized spectra without breaking the purge of the spectrometer. To obtain ATR spectra, the germanium crystals were placed in a vertical ATR accessory (Harrick Scientific). A total of 250 scans was sufficient to achieve a high signal-to-noise ratio. Polarized transmittance spectra at normal incidence and p-polarized IRRAS spectra at an incidence angle of 75° were recorded by coadding 1000 scans. All spectra were obtained at a resolution of 4 cm^{-1} with two levels of zero filling.

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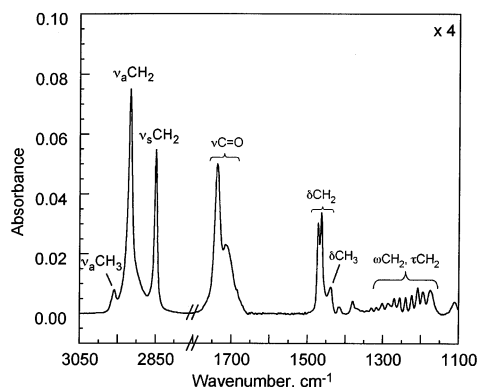


Figure 2. The p-polarized ATR spectrum of a BAME monolayer on germanium.

The experimental setup for infrared reflection-absorption with polarization modulation measurements at the air/water interface has been described elsewhere.^{6–8,38} Langmuir films were formed by spreading 20 μL of a 1.5 mg/mL solution of BAME in chloroform on a Millipore quality water subphase in a $290 \times 10 \times 5$ mm Teflon Langmuir trough (Nima, Coventry, U.K.). The monolayer was compressed and maintained at a pressure of 20 mN/m for 15 min prior to the spectrum acquisition. PM-IRRAS spectra of the film, $S(d)$, and of the water surface, $S(0)$, were recorded at an angle of 75° by coadding 300 scans at a resolution of 4 cm^{-1} . Spectra were obtained by setting the photoelastic modulator at a frequency of 1450 cm^{-1} , with the entrance polarizer perpendicular to the plane of incidence. Normalized PM-IRRAS spectra ($S(d) - S(0)/S(0)$) are presented in this paper.

Determination of Optical Constants. The anisotropic optical constants of the film (i.e., the real part (n) and the imaginary part (k) of the complex refractive index in the three directions of the space coordinate system) were evaluated using an iterative procedure, based on the inversion of spectral simulation programs. Details related to this procedure are given elsewhere.^{31,32,34} In the following, the term “extinction coefficient” has been used to describe the imaginary part (k) of the complex refractive index.

Results

Determination of the Optical Constants of BAME Monolayers. Figure 2 shows a p-polarized ATR spectrum of a BAME monolayer deposited on germanium and the assignment of the major bands. On this figure, the $2000\text{--}1000 \text{ cm}^{-1}$ spectral region has been magnified by a factor of 4. The complete assignment of the different bands observed has already been given elsewhere.^{1,17} The spectrum of the monolayer is quite similar to that obtained for the multilayer system. The presence of the band progression in the $1200\text{--}1360 \text{ cm}^{-1}$ region due to the methylene wagging and twisting modes and the low-frequency position of the methylene symmetric, $\nu_s\text{CH}_2$, and antisymmetric, $\nu_a\text{CH}_2$, stretching modes at 2850 and 2915 cm^{-1} , respectively, indicate that the alkyl chains are in the all-trans conformation. The splitting of the methylene bending mode (δCH_2) at 1463 and 1473 cm^{-1} indicates that the alkyl chains are packed in either an orthorhombic or a monoclinic structure with an orthorhombic subcell containing two mutually orthogonal molecules. Since bands in the spectral region below 1800 cm^{-1} are very weak in spectra of the single monolayer, it is difficult to determine accurately their intensity. The optical constants were thus determined only for the spectral region between 3200 and 2600 cm^{-1} .

To calculate the in-plane optical constants (n_x , k_x and n_y , k_y), a transmittance spectrum at normal incidence of

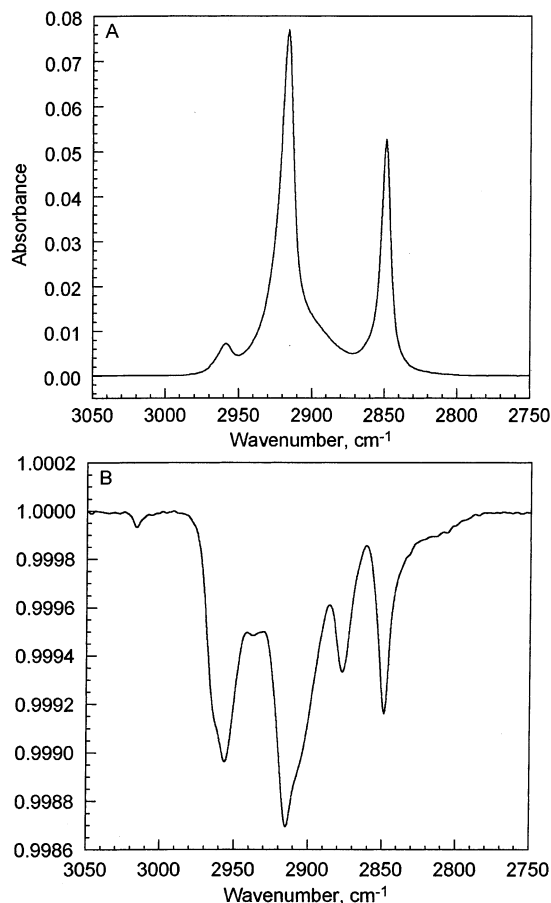


Figure 3. (A) The s-polarized ATR spectrum of a LB monolayer of BAME on germanium and (B) the p-polarized IRRAS spectrum of a LB monolayer of BAME on a gold surface.

the film on a transparent substrate is generally used. However, in the case of a single monolayer, it is difficult to obtain transmittance spectra with high enough signal-to-noise ratios and reliable baselines. For these reasons, an s-polarized ATR spectrum of a BAME monolayer deposited on each side of a germanium crystal has been used to calculate the optical constants in the plane of the film. Indeed, for s-polarized ATR spectra, the electric field of the incident radiation is totally in the y -direction, allowing the determination of the optical constants in that direction. Since transmission measurements have shown that there is no anisotropy of orientation in the plane of the film, the same optical constants were used for the x -direction. To calculate the out-of-plane optical constants (n_z and k_z), a p-polarized IRRAS spectrum of a monolayer deposited on a gold mirror was used. In this case, the electric vector is quasi-perpendicular to the surface and interacts only with the normal component (z) of the transition moment in the thin film.

The spectra used for the optical constant calculations are shown in Figure 3A,B for the $2750\text{--}3050 \text{ cm}^{-1}$ range. The IRRAS spectrum shown in Figure 3B has a completely different shape from that of Figure 3A. Indeed, the bands due to the C–H stretching modes of the methyl group of the alkyl chain at 2959 and 2877 cm^{-1} are almost as intense as the bands due to the methylene C–H stretching modes at 2915 and 2848 cm^{-1} , even though there is only one terminal methyl group for 20 methylene groups in each alkyl chain. This shows clearly that the transition moments associated with the $\nu_a\text{CH}_2$ and $\nu_s\text{CH}_2$ modes are almost totally in the plane of the film and that the alkyl chains are almost perpendicular to the gold substrate.

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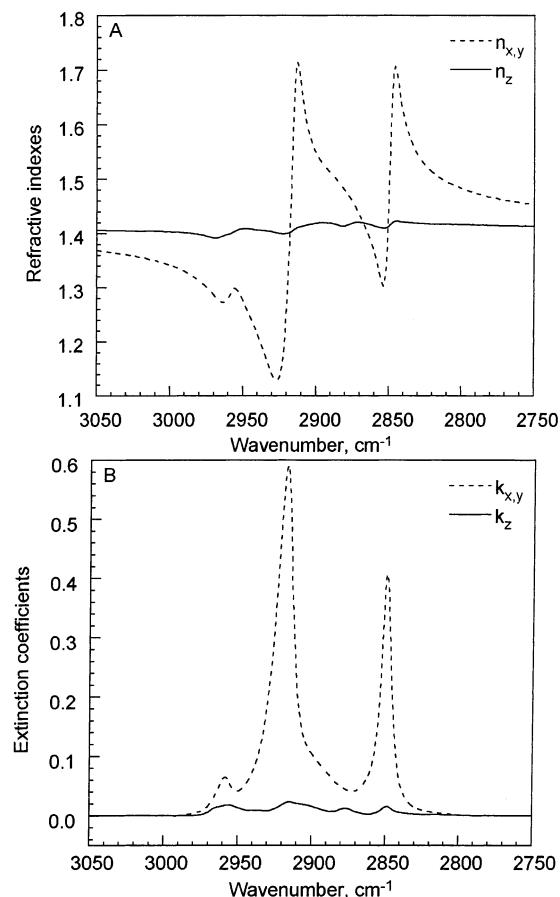


Figure 4. (A) Refractive indexes and (B) extinction coefficients of a LB monolayer of BAME calculated from the spectra shown in Figure 3.

The calculations of the optical constants were performed using an n_{∞} value (refraction index in the visible) of 1.41.¹⁷ A first set of optical constants was calculated using a film thickness equal to the theoretical length of the BAME molecule in the all-trans conformation (30.6 Å).¹⁷ Then, the molecular tilt angle found with these optical constants was used to calculate the real thickness of the films (30.0 Å). A final set of optical constants was then calculated with this new value for the film thickness. It is important to emphasize the fact that both sets of optical constants give the same molecular tilt angle since the film thickness affects only the absolute values of $k_{x,y}$ and k_z but not their relative value. The calculated optical constants are shown in Figure 4A,B. These optical constants were used to simulate p- and s-polarized ATR spectra of a BAME monolayer on germanium. The experimental and simulated spectra are compared in Figure 5. The simulated spectra reproduce very well those obtained experimentally for both polarizations, thus showing that the molecular orientation is the same on germanium and gold substrates.

Splitting of the Band Due to the Methylene Bending Mode. During the course of this study, it was observed that the band due to the methylene bending mode could either be split into two components at 1473 and 1463 cm^{-1} or appear as a single feature at 1467 cm^{-1} . This splitting is characteristic of the presence of an orthorhombic subcell for the packing of the alkyl chains in the film.^{39,40} We have observed that the spectra obtained did not always exhibit the same frequency difference between the two components of the band. This phenomenon

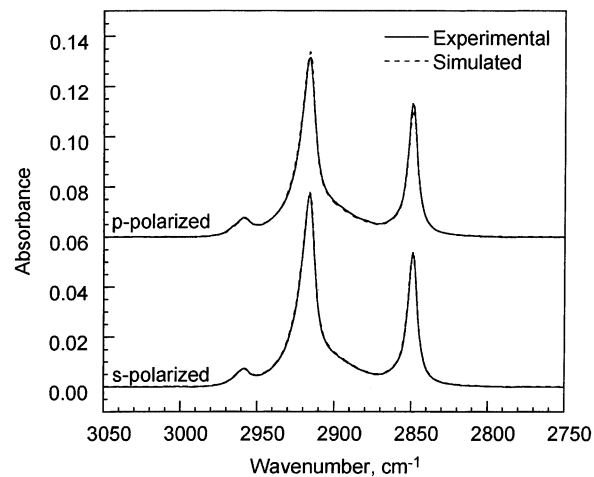


Figure 5. Experimental and simulated p- and s-polarized ATR spectra of a BAME monolayer on a germanium ATR substrate. The p-polarized spectra were shifted for clarity.

depends on several factors, the most important being the nature and the roughness of the substrates used for the LB deposition and the drying of the film. To investigate this phenomenon more deeply, two experiments were performed, using either a new germanium ATR crystal or a crystal already used for some time. After the deposition of the film, the samples were kept in an atmosphere saturated with water vapor to prevent drying of the films until they were placed in the dry atmosphere of the sample compartment of the spectrometer. Then, p- and s-polarized ATR spectra were recorded as a function of the drying time. The results obtained show that if the substrate is smooth, as for the new substrate, the drying of the film has very little effect on the frequency difference between the two components of the δCH_2 band. On the other hand, if the substrate used is slightly scratched, as for the old substrate, the drying of the film caused a diminution of the observed splitting. Figure 6 shows the variation with the drying time of the p-polarized spectra and of the magnitude of the splitting for an old substrate. This figure reveals that the frequency difference varies almost linearly with time from approximately 10 cm^{-1} at 0 min to 6 cm^{-1} after 60 min drying time. Noteworthy, films deposited on calcium fluoride substrates rarely showed any splitting of the δCH_2 band. The relation between the magnitude of the frequency difference and the molecular orientation will be examined in the discussion section. All spectra used for the calculation of the molecular orientation were recorded using new substrates and had a splitting of 8 cm^{-1} or more.

Discussion

Oscillator Strength of the Methylene Stretching Modes. The anisotropic values of the extinction coefficient ($k_{x,y}$ and k_z) shown in Figure 4B allow calculation of the maximum extinction coefficient, k_{max} , for each wavenumber by using the following equation:³¹

$$k_{\text{max}} = 2k_{x,y} + k_z \quad (1)$$

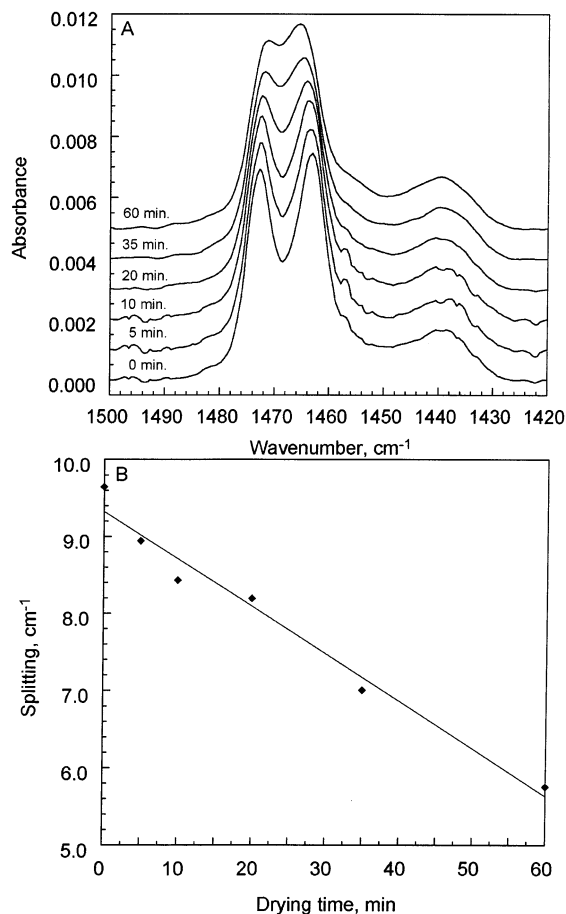
The value of k_{max} for each band depends on the strength and number of oscillators probed and thus on the molecular density of the film. Table 1 shows the values of $k_{x,y}$, k_z , and k_{max} determined for BAME LB monolayers for the $\nu_a\text{CH}_2$ and $\nu_s\text{CH}_2$ bands along with those determined for spin-coated multilayers in a previous article.¹ The maximum extinction coefficients (k_{max}) determined for the BAME

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Table 1. In-Plane ($k_{x,y}$), Out-of-Plane (k_z), and Maximum (k_{\max}) Extinction Coefficients, Tilt Angle of the Transition Moment (γ), and Molecular Tilt Angle (θ) Values of BAME Deposited on Solid Substrates by the LB Technique and by Spin-Coating

film preparation	band (cm ⁻¹)	$k_{x,y}$	k_z	k_{\max}	γ (deg)	θ (deg)
LB	2915	0.592 ± 0.027	0.024 ± 0.006	1.207 ± 0.060	82 ± 1	11 ± 2
	2850	0.405 ± 0.018	0.016 ± 0.004	0.827 ± 0.040	82 ± 1	11 ± 2
spin-coating ^a	2915	0.553 ± 0.030	0.128 ± 0.004	1.234 ± 0.064	71 ± 1	27 ± 1
	2850	0.372 ± 0.020	0.128 ± 0.004	0.872 ± 0.044	68 ± 1	32 ± 1

^a From ref 1.**Figure 6.** (A) The p-polarized ATR spectra in the methylene bending region of a BAME monolayer on an old germanium substrate and (B) splitting observed in the ATR spectra as a function of the drying time of the film. Spectra at drying times between 5 and 60 min were shifted for clarity.

monolayer are quite close to those obtained for the spin-coated film for both bands. Indeed, values of 0.827 and 0.872 are found for the $\nu_s\text{CH}_2$ band and values of 1.207 and 1.234 are found for the $\nu_a\text{CH}_2$ band for LB and spin-coated films, respectively. This indicates that LB films are slightly less dense than the spin-coated ones. This can be due to the presence of holes in the monolayer. Previous studies have shown by using Brewster angle microscopy that BAME molecules at the air/water interface form crystalline domains at low surface pressure and that compression induces the coalescence of these domains.^{1,4} At 20 mN/m, the monolayers may still show some holes that eventually disappear at higher surface pressure. We can thus conclude that LB monolayers deposited at 20 mN/m have more holes or defects than spin-coated films. Even though the k_{\max} values are quite close for the spin-coated and LB films, the relative value of k_z and $k_{x,y}$ is much smaller for LB films compared to spin-coated films. This behavior is related to the molecular orientation in the film and will be discussed in the next section. Flach

et al. found a k_{\max} equal to 1.07 for the 2915 cm⁻¹ band of a Langmuir film at a surface pressure of 14 mN/m.¹⁷ That value is about 15% smaller than that found here and is most likely due to the lower surface pressure used for the transfer resulting in a less dense film.

Orientation of the Alkyl Chains Calculated from the Optical Constants. The $k_{x,y}$ and k_z values allow the quantitative determination of the orientation of the alkyl chains, assuming a conformational and orientational molecular model. For alkyl chains in the all-trans conformation and considering both a uniaxial orientation of the molecules and a cylindrical symmetry around the molecular axis, Fraser and MacRae derived the following equations for the relationship between the anisotropic extinction coefficients ($k_{x,y}$ and k_z) with k_{\max} and the tilt angle of the alkyl chains with respect to the normal of the surface (θ):⁴¹

$$k_{x,y} = \left[\frac{f \sin^2 \alpha}{2} + \frac{(1-f)}{3} \right] k_{\max} \quad (2)$$

$$k_z = \left[f \cos^2 \alpha + \frac{(1-f)}{3} \right] k_{\max} \quad (3)$$

where $f = (3\langle \cos^2 \theta \rangle - 1)/2$ is the second moment of the orientation function of the molecular axis and α is the angle between the transition moment of the considered infrared mode and the alkyl chain axis. For bands with a transition moment perpendicular to the chain axis ($\alpha = 90^\circ$), like the stretching modes of the methylene considered here, and assuming an infinitely narrow distribution of orientation,⁴² eqs 2 and 3 can be rearranged to calculate θ :

$$\theta_{\alpha=90} = \arccos \sqrt{\frac{2k_{x,y} - k_z}{2k_{x,y} + k_z}} \quad (4)$$

It is also possible to calculate the tilt angle of the transition moments (γ) using the relation

$$\gamma = \arctan \sqrt{\frac{2k_{x,y}}{k_z}} \quad (5)$$

Table 1 shows the transition moment tilt angle (γ) and the molecular tilt angle (θ) calculated for the 2915 and 2850 cm⁻¹ bands using eqs 4 and 5 for LB and spin-coated films of BAME. For the monolayer, the tilt angles calculated are 11° for each band, while the molecular tilt angles calculated for the spin-coated films are 27° and 32° for the $\nu_a\text{CH}_2$ and $\nu_s\text{CH}_2$ bands, respectively. These results show that the BAME molecules are much less tilted in LB films than in spin-coated films.

Other molecules similar to behenic acid methyl ester, such as fatty acids and fatty acid esters, have been

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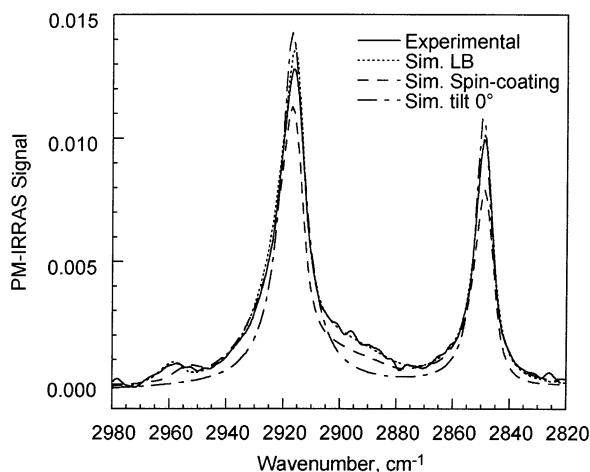


Figure 7. Experimental and simulated PM-IRRAS spectra of BAME at the air/water interface. Spectra were simulated with the optical constants obtained for a LB monolayer, for a spin-coated multilayer, and for BAME molecules having a tilt angle equal to 0° .

extensively studied. In the solid state, most even-numbered saturated fatty acids^{43–46} and fatty acid esters^{40,47,48} generally adopt a monoclinic structure in which the alkyl chains are tilted. Fatty acids with 10, 12, and 18 carbons exhibit tilt angles of 41° , 34° , and 24° , respectively,^{43,44} while methyl and ethyl stearate (18 carbons) display tilt angles of 26° and 28° , respectively.^{47,48} For ultrathin films, it has been shown that behenic acid molecules (22 carbons) in multilayers have their molecular axis more or less tilted depending on the thickness of the film. Multilayers composed of 1, 2, and 5 Langmuir–Blodgett layers exhibit tilt angles of 0° , 14° , and 15° , respectively, while films composed of 7 layers or more have tilt angles around 20 – 25° .^{49–51} A very similar behavior has been observed for films of manganese arachidate.² Clearly, bulk samples and thick multilayers (more than 5 layers) tend to have their alkyl chains tilted at an angle near 30° while monolayers and films having fewer than 5 layers have their chains more perpendicular to the plane of the film. The BAME films studied here seem to display the same behavior. Indeed, the tilt angle is 11° for monolayers while it is close to 30° for spin-coated multilayers (6–8 layers). The difference between the tilt angles measured for single monolayers and spin-coated multilayers is really due to a change of orientation and not to the presence of conformational disorder. Indeed, the frequency of the bands due to the methylene C–H stretching modes shows clearly that the alkyl chains are very well-ordered in both systems.

Orientation at the Air/Water Interface. To determine the orientation of the BAME molecules at the air/water interface, a PM-IRRAS spectrum of a Langmuir monolayer was recorded and compared to spectra simulated from the optical constants determined from both LB and spin-coated films. Figure 7 shows the experimental spectrum recorded at a surface pressure of 20 mN/m with

a modulation frequency of 1450 cm^{-1} , along with three different simulated spectra. The first one has been calculated using the optical constants determined in this paper for a LB film having a thickness of 30.0 \AA . The second spectrum has been calculated with the optical constant of spin-coated films with a thickness of 28.9 \AA (tilt angle of 30°). The last spectrum has been simulated using the theoretical optical constants of the two bands located at 2918 and 2850 cm^{-1} , with a Lorentzian band shape and full width at half-height of 11 and 7 cm^{-1} , respectively. The optical constants used have been calculated with eqs 2 and 3 considering α equal to 90° , θ equal to 0° , and the k_{max} values equal to those found in Table 1. The film thickness for this case was 30.6 \AA . The three simulated PM-IRRAS spectra are quite different in intensity. The k_{max} for each band and film thickness being almost equal, this difference arises almost uniquely from the difference of molecular orientation, the alkyl chains being tilted at 11° (LB film), 30° (spin-coated film), or 0° for the three simulated spectra.

It is clear from Figure 7 that the experimental spectrum is not well reproduced by the spectrum arising from the optical constants calculated for spin-coated films while it is very well reproduced by the optical constants arising from the LB films. This shows clearly that the alkyl chains of the molecules adopt almost the same orientation in LB films and at the air/water interface, the alkyl chains having a tilt angle near 11° in both cases. These results thus show that the LB transfer has a negligible influence on the orientation of the alkyl chains of BAME. On the other hand, Figure 7 shows that the intensities of the PM-IRRAS spectra of BAME molecules having tilt angles of 0° and 11° are quite close to each other. It is thus difficult to conclude unambiguously that alkyl chains have a tilt angle of 11° rather than 0° at the air/water interface, the difference being close to the experimental error. This result is in agreement with the tilt angle of 0° proposed by Flach et al. for a Langmuir film of BAME at the air/water interface at 14 mN/m .¹⁷

Correlation between the Splitting of the Band Due to the Methylene Bending Mode and the Conformational Order of the Alkyl Chains. For hydrocarbon chains, the band due to the bending mode of the methylene of the alkyl chain (δCH_2) is very sensitive to the packing of the chains. As discussed above, this band appears as a doublet if the packing on the alkyl chains of the film is orthorhombic (with the alkyl chains normal to the plane of the film) or monoclinic (with the chains tilted with respect to the normal of the film). It is very difficult to distinguish these two structures on the basis of infrared spectra alone since they have the same crystalline unit cell (with two mutually orthogonal molecules per unit cell), the only difference being the molecular tilt angle. The absence of splitting of the δCH_2 band indicates that the film is amorphous or has a hexagonal or triclinic packing of the alkyl chains. This feature has been used for many purposes, for example, to distinguish the packing of the alkyl chains between monolayers and multilayers,⁵² to monitor a phase transition in phospholipids,⁵³ and to monitor the aggregation of alkyl chains and the size of the domains formed in phosphatidylcholine mixtures and in fatty acid homogeneous ceramide 2.^{54,55} As mentioned in

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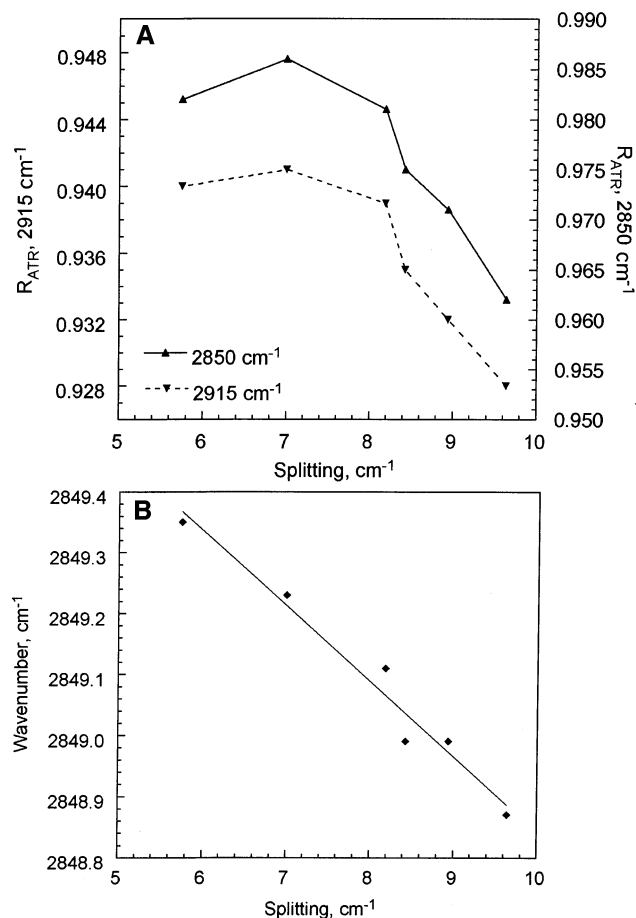


Figure 8. (A) Dichroic ratios calculated from polarized ATR spectra for the 2915 and 2850 cm^{-1} bands and (B) the frequency of the methylene symmetric stretching band as a function of the splitting observed on the methylene bending mode.

the results section, the magnitude of the splitting of the δCH_2 band in the spectrum of BAME depends on the sample preparation. On rough germanium substrates, the splitting decreases when the film is allowed to dry. The effect of aging on molecular orientation and structure of LB monolayers has already been studied for stearic acid,⁵⁶ octadecyldimethylamine oxide and dioctadecyldimethylammonium chloride,⁵⁷ and 2-dodecyl-, 2-pentadecyl-, and 2-octadecyl-7,7,8,8-tetracyanoquinodimethane.⁵⁸ It was found that molecules could become more or less ordered depending on their nature and on the nature of the substrate. To investigate the orientational changes that occur in the film while the splitting disappears, the p- and s-polarized ATR spectra were used to calculate the dichroic ratios of the 2915 and 2850 cm^{-1} bands. As seen in Figure 8A, the values obtained show that the dichroic ratios tend to increase when the splitting decreases. Since a higher dichroic ratio indicates that the mean tilt angle of the molecules increases,³⁴ this result could mean that the film becomes more disordered (broader distribution of orientation) on drying. Figure 8B also shows that the position of the $\nu_s\text{CH}_2$ band increases as the splitting decreases. Since the frequency of this band increases with the number of gauche defects present in the hydrocarbon chains, we can conclude that the disappearance of the splitting is due to a greater disorder in the film and not to a change in the

packing of the alkyl chains toward hexagonal or triclinic packing. It is likely that the small cavities present on the rough substrate are filled with water during the LB deposition, thus allowing the film to be on a smooth surface and to adopt an ordered state. The evaporation of the water filling the cavities during the drying process most likely results in the partial loss of crystalline packing and the appearance of gauche conformers in order to be able to cover the holes on the substrate.

We have also observed that spectra of single LB monolayers of BAME deposited on CaF_2 windows usually show a doublet with a small frequency difference or no doublet at all. This could be due to an intrinsic roughness of the calcium fluoride windows or, most probably, to specific interactions between the methyl ester headgroup and the calcium fluoride windows as observed by Blaudez et al. for monolayers of cadmium arachidate deposited on various substrates.⁵² Jang and Miller have also observed that calcium fluoride interacts with fatty acids through the hydroxyl or carbonyl groups causing the acids to be chemisorbed to the substrate.^{59,60}

Conclusions

The in-plane and out-of-plane optical constants of a BAME monolayer were calculated from an s-polarized ATR spectrum on germanium and an IRRAS spectrum on a gold mirror, respectively. These optical constants were used to calculate the molecular orientation of the films and to simulate spectra in different experimental conditions. This is the first time that this method of calculation was applied to single monolayers. The optical constants calculated from LB monolayers were compared to those calculated in a previous article for spin-coated BAME multilayers. While the maximum extinction coefficients are similar for both films, the molecular orientation calculated is quite different. The molecular tilt angle is near 30° for the spin-coated film, while it is 11° in the case of Langmuir–Blodgett monolayers. The molecular orientation of BAME alkyl chains at the air/water interface was determined to be similar to that in single Langmuir–Blodgett monolayers, thus proving that the LB transfer has little influence on the structure of the film. The splitting of the methylene bending mode and the presence of band progression due to the methylene wagging and twisting modes in all the infrared spectra indicate that the alkyl chains of the BAME molecules at the air/water interface, in Langmuir–Blodgett monolayers and in spin-coated multilayers, are in the all-trans conformation and packed in an orthorhombic or monoclinic structure. However, under certain conditions, the splitting of the band due to the methylene bending mode may be absent. This phenomenon was associated with a greater disorder in the film and with the loss of the crystalline structure due, in particular, to the roughness of the substrate and to the drying of the film.

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