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Molecular-Orientation Change in Langmuir Films of Stearic Acid and Cadmium Stearate upon Surface Compression, as Studied by Infrared External-Reflection Spectroscopy

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For interpretating the various phases appearing in a two-dimensional system, we have recorded in situ polarized FT-IR external reflection spectra of Langmuir films of stearic acid and cadmium stearate on the water surface at various surface areas, and evaluated the molecular orientation angles quantitatively. In the stearic acid monolayer, the orientation angle of the hydrocarbon chain from the surface normal decreased from 20° to almost 0° upon monolayer compression. In the cadmium stearate monolayer, on the other hand, the orientation angle (near 0°) did not change upon monolayer compression, though it was widely scattered at large surface areas, because of the formation of a rigid crystalline island. These results correspond well to the π–A isotherms.

Recently, Langmuir (L) films at the air–water interface are of technological concern as a precursor of Langmuir–Blodgett films.[1,2] They also show interesting scientific phenomena in themselves; for example, they exhibit various phase transitions in a two-dimensional system.[3]

Many investigations of L films have been performed by various methods. Grazing-incidence X-ray diffraction has been most frequently used in studying the microscopic molecular structure of L films, such as the in-plane positional ordering, lattice structure, and molecular orientation in monolayers of fatty acid,[4,5] fatty alcohol,[6] and so on. In addition, there are some other techniques for this study; optical second-harmonic generation,[7] sum-frequency vibrational spectroscopy,[8] Raman spectroscopy,[9] and infrared spectroscopy.[10—24]

Infrared spectroscopy has the advantage of being easy to use, nondestructive against samples, and sensitive to changes in the molecular conformation. However, the accumulation of studies of L films by infrared spectroscopy is not so sufficient that the method can yet be said to be established. More recently, several studies have dealt with the molecular orientation in monolayers using infrared spectroscopy. Fina et al.[13,14] presented expressions for an anisotropic film, and simultaneously estimated the molecular orientation and surface density in soluble monolayers of sodium dodecylsulfonate by using p- and s-polarized beams. Gericke et al.[16] derived expressions for a film that includes an integration of the depth gradient in the optical constants, and showed good accordance between the theoretical and experimental intensities in L films of hexadecane-1-ol in the liquid-condensed state. Buontempo et al.[18,19] derived equations of the dichroic ratio, which facilitates an intuitive interpretation, and clarified that the molecular orientation depends on the molecular area and temperature in relaxed L films of heneicosanol. Ren et al.[24] determined the transition moments and extinction coefficients by minimizing the sum of the differences between the calculated and measured absorbances at various angles of incidence, and estimated the molecular orientation in the L films of fatty and fluorinated alcohols in a well-packed state.

In the present work, we measured the polarized Fourier-transform infrared external-reflection spectra (FT-IR/ERS) of L films of stearic acid (C_{18}) and cadmium stearate at various molecular areas, and evaluated the molecular tilt angles quantitatively based on the following motivations. Although there have been many fundamental studies of L films of stearic acid because of the structural simplicity, no accurate data about molecular orientation angles have been gained. Moreover, few studies have been carried out about the molecular orientation in L films by infrared spectroscopy, especially on the condition that the surface area changes. That is why we took up the well-known stearic acid. There is an obvious difference between the π–A isotherms of stearic acid and cadmium stearate, and it has been clarified that there is a different tendency concerning the conformational change of the hydrocarbon chain during surface compression.[9,15] The purpose of this work was to clarify the orientational change quantitatively. For calculating the orientation angles, we used formulae that Hasegawa et al. had derived.[25] This formula, which is strict, but easy to use, is suitable for studying L films, because one can calculate the molecular-orientation angles from only the p-polarized beam measurement. Of course, the method[13,14,18,19] used to measure both the p- and s-polarized measurements is excellent, if the L-film structure is stable with time. However, since the state of L films sometimes changes with time,[26] the present method becomes more superior in such cases. We also paid serious attention to the amount of infrared radiation due to concern that it may perturb the structure of L films.[27] As a result, we could quantitatively explain the different tendency of orientational change between the L films of stearic acid and cadmium stearate.

Experimental

The pure stearic acid (melting point: 70.0 °C) used in this study was the same as that reported previously.[28] All other reagents were either highly pure (>98%) or spectroscopic grade. Distilled water was made by a modified Mitamura Riken Model PLS-DFR automatic lab still consisting of a reverse-osmosis module, an ion-exchange column, and a double distiller.

The L films of stearic acid and its cadmium salt were prepared by spreading 10 μl of 8.12×10^{-4} M (1 M = 1 mol dm^{-3}) benzene solution of acid on pure water at pH 6.2 and on the aqueous solution of 3×10^{-4} M $CdCl_2$, buffered with 4×10^{-4} M $NaHCO_3$ to pH 6.6, respectively. We used a trough with a 80×22 mm^2 effective surface area attached to a Specac 19650 monolayer/grazing angle accessory that was modified as follows. The water level of the trough was kept constant during the experiment by using an external Teflon® reservoir connected by a siphon. We used a bandpath (3500—2000 cm^{-1}) filter to remove any thermal agitation of the water surface due to the infrared beam. A S. T. Japan Model STJ-100 wire-grid polarizer with 1300 line/mm Al wires on KRS-5 was settled just above the water surface to optimize the polarization.[29] FT-IR/ERS of L films were recorded on a Nicolet 6000C FT-IR spectrophotometer equipped with an InSb detector with a resolution of 8 cm^{-1}. The angle of incidence was 38°. The measurements were performed with only a *p*-polarized beam. First, the background spectrum was collected with 500 scans for the water surface, and then the solution was spread. After waiting for 10 min to allow the solvent to be fully evaporated, the L film was compressed to various surface areas, and FT-IR/ERS were recorded with 500 scans.

The transmission spectra of isotropic KBr pellet of stearic acid (0.371 mg/200 mg KBr)with resolution of 4 cm^{-1} and 8 cm^{-1} were recorded on the same FT-IR spectrophotometer with 300 scans, using an MCT detector.

The π–A isotherms were measured with a Wilhelmy balance attached to a Kyowa Interface Science Model HBM-AP Langmuir trough. All experiments were performed at 23 °C.

Results and Discussion

π–A Isotherms. Figure 1 shows π–A isotherms of stearic acid and cadmium stearate at 23 °C. In the stearic acid monolayer, we have observed liquid-condensed (L_2) and super-liquid (LS) phases, while there is only the LS phase in its cadmium salt. In a previous paper[15] we described how the conformation of the hydrocarbon chain changed during monolayer compression. In stearic acid, the wavenumber of the antisymmetric CH_2 stretching band decreased from 2919 to 2917 cm^{-1} upon monolayer compression. The value of 2917 cm^{-1} is typical for the all-*trans* conformer of the alkyl chain, and higher wavenumbers are indicative of an inclusion of the *gauche* conformer. Thus, the observed shift in wavenumber of stearic acid indicates a conformational change from *gauche* to *trans* isomers upon monolayer compression. In the case of cadmium stearate, on the other hand, there was no wavenumber shift (2917 cm^{-1}) on the monolayer compression, indicating that only the all-*trans* conformer appears.

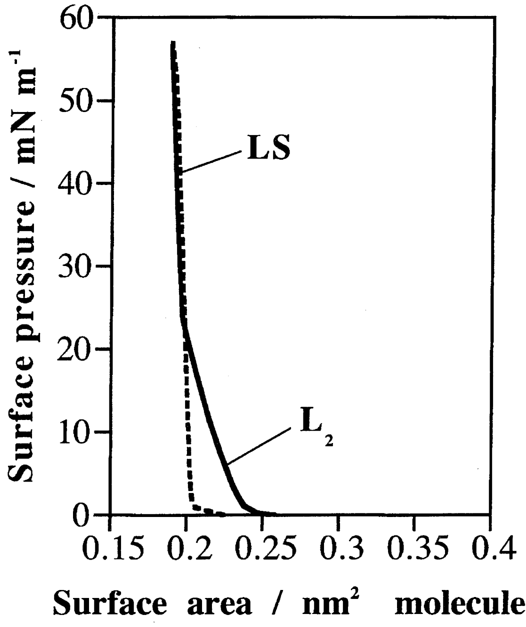

Fig. 1. The π–A isotherms of stearic acid (solid line) and cadmium stearate (broken line) on the water surface at 23°C.

Polarized Infrared External Reflection Spectra (FT-IR/ERS). Figures 2 and 3 show the ERS of L films of stearic acid and cadmium stearate at various surface areas. In this frequency region we can observe the antisymmetric and symmetric CH_2 stretching bands (ν_aCH_2 and ν_sCH_2) at ca. 2918 and 2850 cm^{-1}, respectively. At an angle of incidence of 38°, these bands show negative-reflection absorbances.

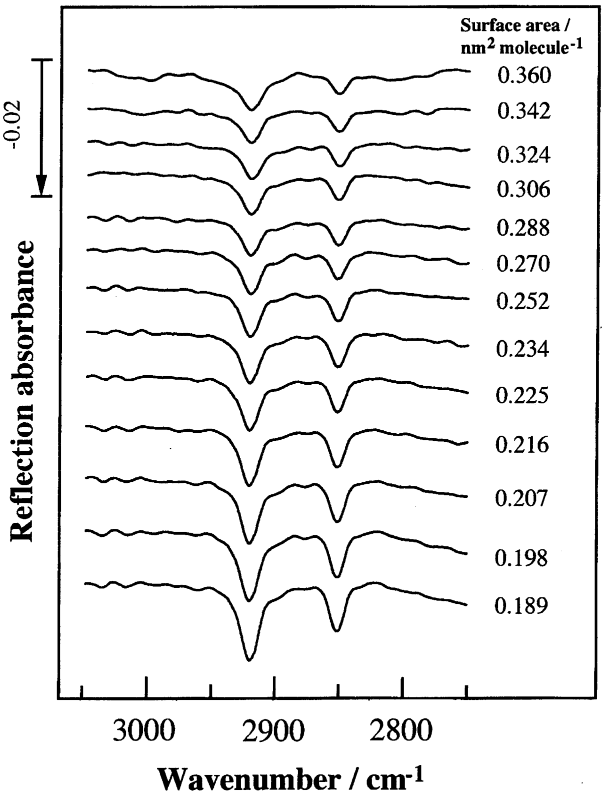

Fig. 2. FT-IR/ERS of L films of stearic acid measured by *p*-polarized beam at various surface areas.

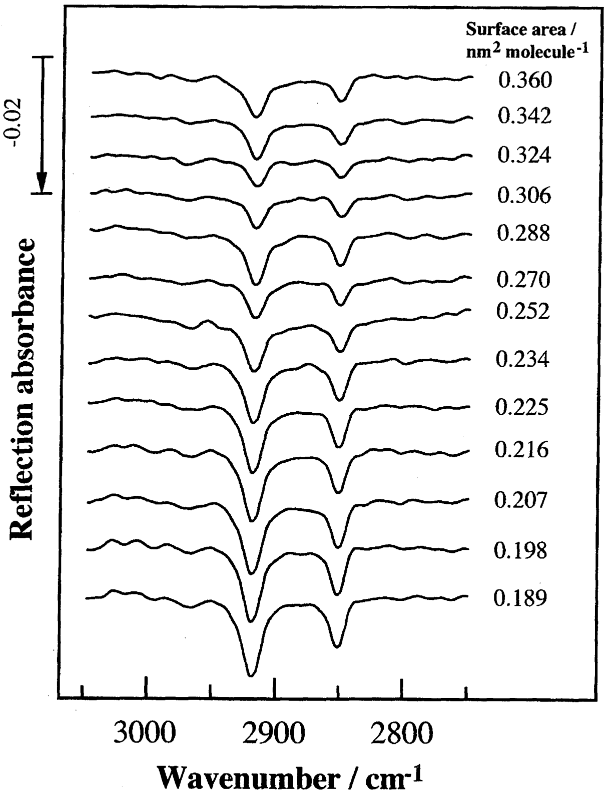

Fig. 3. FT-IR/ERS of L films of cadmium stearate measured by p-polarized beam at various surface areas.

In external-reflection measurements of L films on the water, there appear positive or negative reflection absorbances, depending on the direction of the transition moment, the angle of incidence, and the polarization of the incident beam.[11)]

In Figs. 4 and 5, the peak intensities of $\nu_a CH_2$ and $\nu_s CH_2$ for the acid and the cadmium salt films observed in Figs. 2 and 3 are plotted against the surface area. These data were calibrated based on the difference in the surface density to the point at the smallest surface area (0.189 nm^2/molecule), because the peak intensity is contributed by both the surface density and the molecular orientation. After a calibration, only information about the molecular orientation can be extracted explicitly. In the stearic acid monolayer, although the peak intensities of both bands are invariant at large surface areas, upon monolayer compression the absolute peak intensities increase at surface areas smaller than 0.23 nm^2/molecule. In the cadmium stearate monolayer, however, the peak intensities do not change upon monolayer compression, though they are widely scattered at large surface areas. This indicates the presence of a highly crystalline island due to the strong aggregation property of the cadmium salt.[15)]

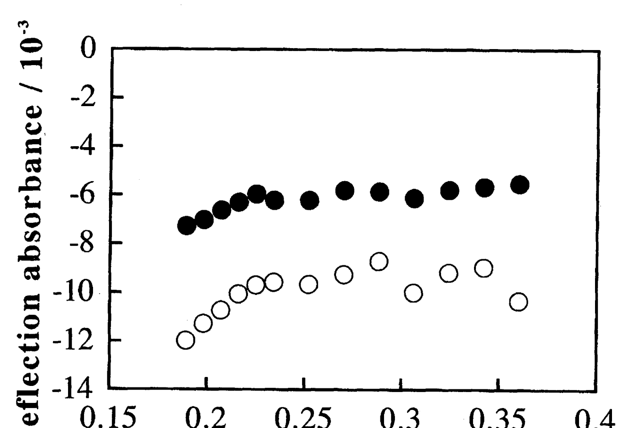

Fig. 4. Peak intensities of $\nu_a CH_2$ (○) and $\nu_s CH_2$ (●) in L films of stearic acid vs. surface area.

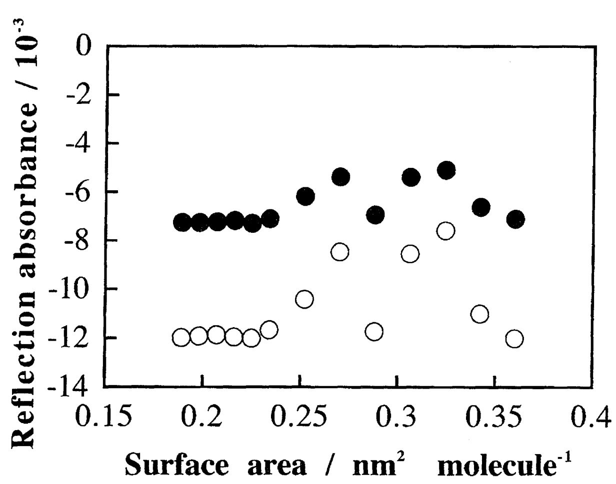

Fig. 5. Peak intensities of $\nu_a CH_2$ (○) and $\nu_s CH_2$ (●) in L films of cadmium stearate vs. surface area.

Calculation of Molecular Orientation. For calculating the molecular orientation, we used a formulae derived by Hasegawa et al.[25)] These are formulae that were developed for a uniaxially oriented film by anisotropically expanding Hansen's isotropic optical theory for a multilayered system.[30)] The formulae roughly consist of two parts: One is a part representing the reflection absorbance as a function of the macroscopic optical constants (from Eq. 1 to Eq. 11 below); the other part relates the macroscopic constants to the microscopic model of the molecular level, from which information about the molecular orientation can be extracted (from Eq. 12 to Eq. 15).

In this study, we deal with the three layers that comprise air/film/water. We assumed that the film was uniaxial, and that the air and water were isotropic. We used only a p-polarized beam. The equations that we transformed for this study are as follows:

$$A = -\log \frac{R}{R_0} \tag{1}$$

$$R = |\tilde{r}_p|^2 \tag{2}$$

$$\tilde{r}_p = \frac{(\tilde{m}_{11} + \tilde{m}_{12}\tilde{q}_3)q_1 - (\tilde{m}_{21} + \tilde{m}_{22}\tilde{q}_3)}{(\tilde{m}_{11} + \tilde{m}_{12}\tilde{q}_3)q_1 + (\tilde{m}_{21} + \tilde{m}_{22}\tilde{q}_3)} \tag{3}$$

$$\tilde{M}_2 = \begin{bmatrix} \tilde{m}_{11} & \tilde{m}_{12} \\ \tilde{m}_{21} & \tilde{m}_{22} \end{bmatrix} = \begin{bmatrix} \cos \tilde{\beta}_2 & -\frac{i}{\tilde{q}_2} \sin \tilde{\beta}_2 \\ -i\tilde{q}_2 \sin \tilde{\beta}_2 & \cos \tilde{\beta}_2 \end{bmatrix} \tag{4}$$

$$q_1 = \frac{\cos \theta_1}{n_1} \tag{5}$$

$$\tilde{q}_2 = \frac{(\tilde{n}_{2e}^2 - n_1^2 \sin^2 \theta_1)^{1/2}}{\tilde{n}_{2o}\tilde{n}_{2e}} \tag{6}$$

$$\tilde{q}_3 = \frac{(\tilde{n}_3^2 - n_1^2 \sin^2 \theta_1)^{1/2}}{\tilde{n}_3^2} \tag{7}$$

$$\tilde{\beta}_2 = \frac{2\pi}{\lambda} h_2 \frac{\tilde{n}_{2o}}{\tilde{n}_{2e}} (\tilde{n}_{2e}^2 - n_1^2 \sin^2 \theta_1)^{1/2} \tag{8}$$

$$\tilde{n}_{2e} = n_{2e} + ik_{2e} \tag{9}$$

$$\tilde{n}_{2o} = n_{2o} + ik_{2o} \tag{10}$$

$$\tilde{n}_3 = n_3 + ik_3 \tag{11}$$

Here A is the reflection absorbance, R and R_0 are the reflectances of the absorbing and non-absorbing three-layer system, respectively, r_p is the reflection coefficient for p-polarization, M_2 the characteristic matrix of the film, θ_1 the angle of incidence, λ the wavelength in vacuum, h_2 the film thickness, n the index of refraction, and k the extinction coefficient. A tilde (˜) is attached to the complex value. The subscripts (1, 2, 3, e, and o) refer to the first medium (air), second medium (film), third medium (water), extraordinary (out of plane), and ordinary (in plane), respectively.

These equations relate the reflection absorbance of a band to macroscopic optical parameters. For a theoretical calculation of the reflection absorbance, we need the optical constants of the media (n_1, n_{2o}, n_{2e}, k_{2o}, k_{2e}, n_3, k_3), the angle of incidence (θ_1), the film thickness (h_2), and the wavelength of the band (λ). Among these parameters, k_{2o}, k_{2e}, and h_2 are thought to depend on the molecular orientation. We assumed that the other parameters did not depend on the molecular orientation. The values which we used were as follows: n_1=1.0, n_{2o}=1.48, n_{2e}=1.56,[31] n_3=1.4146 (2918 cm^{-1}), 1.398 (2850 cm^{-1}), k_3=0.01606 (2918 cm^{-1}), 0.00941 (2850 cm^{-1}).[32]

An ellipsoid of the extinction coefficient was considered because of the optical anisotropy of the uniaxial crystal. This ellipsoid can be represented by the following equations:

$$k_{2o} = k_x = k_y = \frac{3}{2} k_{\text{bulk}} \sin^2 \phi, \tag{12}$$

$$k_{2e} = k_z = 3k_{\text{bulk}} \cos^2 \phi, \tag{13}$$

where ϕ is the orientation angle of the transition moment from the surface normal, and k_{bulk} is the extinction coefficient of the isotropic bulk medium. By comparing the theoretical value (A) with the observed value (A_{obs}), the most appropriate orientation values were determined. The extinction coefficients of the $\nu_a CH_2$ and $\nu_s CH_2$ band of octadecanethiolate in bulk at a resolution of 4 cm^{-1} are known to be 0.3 and 0.2 at room temperature, respectively.[33] These values have given good results in a study of LB films.[25] The coefficients of stearic acid at a resolution of 8 cm^{-1} could be determined by comparing the transmission intensities of a KBr pellet at a resolution of 4 and 8 cm^{-1}, and taking the number of methylene groups into consideration.

In this manner, we calculated the orientation angles of the transition moment, $\nu_a CH_2$ and $\nu_s CH_2$. From the values of the orientation angles, α and β of the transition moment of $\nu_a CH_2$ and $\nu_s CH_2$, the tilt angle (γ) of the hydrocarbon chain axis from the surface normal could be calculated, since these three directions are mutually orthogonal (Fig. 6):

$$\cos^2 \alpha + \cos^2 \beta + \cos^2 \gamma = 1. \tag{14}$$

The film thickness (h_2) changes depending on the molecular orientation. We assumed the following relationship between h_2 and γ:

$$h_2 = -0.1313\gamma + 25, \tag{15}$$

where the unit is in Å. This linear equation was derived from the length of the stearic acid molecule (25 Å) and the long spacing (39.9 Å) of the *C* form bulk crystal of stearic acid, whose crystal angle is 38.46°. Around the angle which we dealt with, it is essentially the same as the simple equation h_2=25cos γ. We first calculated γ using a hypothetical h_2 and Eq. 1 to Eq. 14, and then we changed h_2 to satisfy Eq. 15 as much as possible.

Figures 7 and 8 show the orientation angles of the transition moments, $\nu_a CH_2$ and $\nu_s CH_2$, of stearic acid and cadmium stearate in L films against the surface area. In the stearic acid monolayer, the angles of the transition moments of two bands are between 70° and 80° from the surface normal at large surface areas, where the surface pressure is ca. 0 mN m^{-1}; however, upon monolayer compression, the angles start to increase in the L$_2$-phase region, and reach almost 90° in the LS-phase region, corresponding to the π–A isotherms. A great difference in the orientation angle is not seen between $\nu_a CH_2$ and $\nu_s CH_2$, though the $\nu_s CH_2$ band might be slightly larger than $\nu_a CH_2$. This indicates that there is no preferred orientation around the molecular axis (free rotation) or if any the plane of all-*trans* hydrocarbon chain has a slight trend to face to the direction of the surface normal during compression. On the other hand, in the cadmium stearate monolayer, the angles of the transition moments do not change upon monolayer compression, but are very widely scattered at large surface areas because of the presence of a rigid crystalline island; that is to say, these values do not present their intrinsic ones at these areas. In fact, repeated experiments

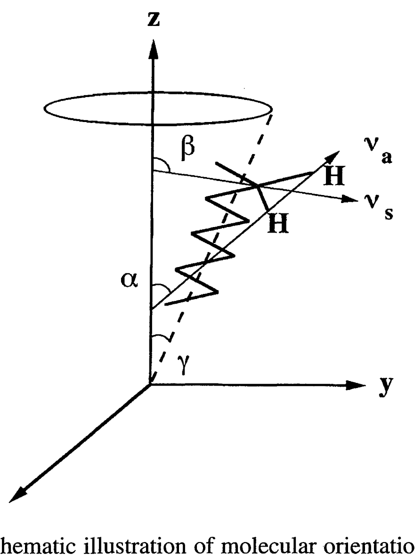

Fig. 6. Schematic illustration of molecular orientation in L film of stearic acid.

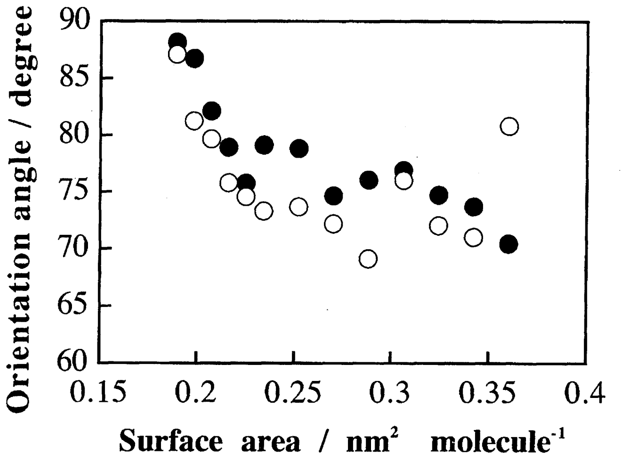

Fig. 7. The orientation angles of transition moment ν_aCH_2 (○) and ν_sCH_2 (●) in L films of stearic acid vs. surface area.

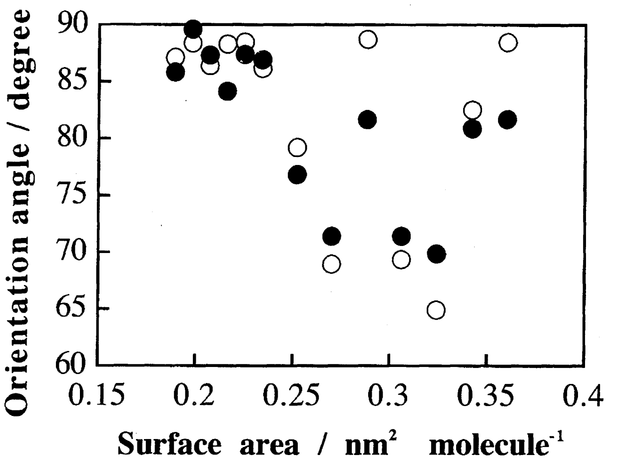

Fig. 8. The orientation angles of transition moment ν_aCH_2 (○) and ν_sCH_2 (●) in L films of cadmium stearate vs. surface area.

showed much dispersion at these areas; however, at small areas and at any area in stearic acid, the values were almost the same within the experimental error.

Figure 9 shows the orientation angles of the hydrocarbon chain axes of stearic acid and cadmium stearate in L films against the surface area. In the stearic acid monolayer, the orientation angle is more than 20° from the surface normal at large surface areas; however, upon monolayer compression, the angle decreases down to almost 0° in the LS-phase region. This tendency coincides well with the results of X-ray diffraction in L films of arachidic acid (from 33° to 0°)[4] and behenic acid (from 29° to 0°).[5] Moreover, molecular-dynamics simulations also support this result.[34] Here, a question appears. In a previous paper[15] we reported the *trans–gauche* conformational change upon monolayer compression. A molecule that contains a *gauche* conformer can not be regarded as a plane. In this case, since Eq. 14 holds for each methylene segment, the angle becomes the average of the segment. However, since the number of *gauche* conformers is few, as revealed by the wavenumber of ν_aCH_2 (2919 cm^{-1}), we could almost regard the molecule as being planar. In the cadmium stearate monolayer, however, the

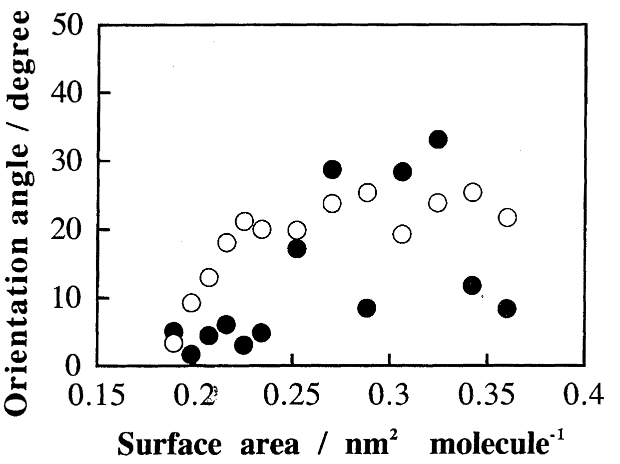

Fig. 9. Molecular orientation in L film of stearic acid (○) and cadmium stearate (●) vs. surface area.

orientation angle (near 0°) does not change upon monolayer compression, though it is widely scattered at large surface areas because of the crystalline island. The angle is literal at small surface areas of less than 0.23 nm^2/molecule, but is virtual at larger surface areas, only indicating the existence of an island. In studies of LB films of cadmium stearate,[25,35] the molecular-orientation angle was reported to be 7° or 14°. The angle in L film is slightly smaller than those in LB films. This might mean that the LB method introduces a structure change during preparation.

These results seem to correspond to the π–A isotherms. In the L_2-phase region of stearic acid, the molecular angle changed and the surface pressure increased. Probably, after the molecular chain almost became vertical, the surface pressure increased steeply in the LS region. In cadmium stearate, the chain was vertical, even at a low surface pressure, because of the presence of a highly crystalline island due to the strong aggregation property of cadmium salt. That is why there is no L_2 phase in the cadmium stearate monolayer.

Finally, we must consider the error. One of the main factors for the error is due to an irregular dispersion of the molecules because of the formation of the island. In the cadmium stearate monolayer at surface areas larger than 0.23 nm^2/molecule, the angle is widely scattered, because we have observed the number of molecules that deviate much from the average. Some repeated measurements have shown different peak intensities. However, at surface areas smaller than 0.23 nm^2/molecule, the intensities were almost the same within the experimental error, because there was no irregular dispersion of the molecule at these areas. In the stearic acid monolayer, on the other hand, since repeated measurements showed almost the same intensities within the experimental error, we could calculate the angles at any area.

The other contribution to the error was due to a calculation. At small angles, especially below 10°, the error becomes large upon calculation, because the theoretical absorbance changes only slightly with the orientation around there. Although there may be some uncertainty about the numerical precision of the angles, it is certain that the chain tends to become vertical upon compression in the stearic acid monolayer, but continues to be vertical upon compression in the cadmium stearate monolayer.

Conclusion

In situ polarized FT-IR external reflection spectra of L films of stearic acid and cadmium stearate on the water surface were recorded at various surface areas, and the molecular orientation angles were quantitatively evaluated. In the stearic acid monolayer, the orientation angle decreased from 20° to almost 0° upon monolayer compression. On the other hand, in the cadmium stearate monolayer, the orientation angle (near 0°) did not change upon monolayer compression, though it was widely scattered at large surface areas because of the presence of a rigid crystalline island. These results correspond well to the π–A isotherms.

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