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Studies of Built-up Films by Means of the Polarized Infrared ATR Spectrum. III. Elaidic Acid Films[1]

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Attenuated total reflection studies with polarized infrared radiation have been made of multilayers of elaidic acid built up on a germanium plate by the Blodgett technique. It is concluded that the built-up films prepared from the tap-water substrate are made of calcium elaidate monohydrate. From the intensity changes in the regularly-spaced peaks (progression bands) in the region from 1350 to 1180 cm^{-1}, the planarity of the chain segment between the carboxylate group and the double bond is found to be dependent upon the surface pressure applied in the process of monolayer transfer onto the germanium plate. Studies of the anisotropy of the absorption index in the films show that the molecules assume a uniaxial orientation with respect to the axis normal to the germanium-sample interface (the z-axis), with an angle from 30° to 33° (in average) between the z-axis and the molecular axes. Furthermore, from the changes in the reflectivity with the number of layers, the film thickness per layer is estimated to be *ca.* 21.9 Å, a value which is in good agreement with the half-value of the long spacing, 44.16 Å, of the films as determined by X-ray diffraction studies. This apparently indicates that the films appear as the Y type.

In previous papers[2,3] of this series, attenuated total reflection (ATR) studies[4-6] have been made of multilayers of stearic acid and mixed multilayers of stearic acid and barium stearate built up on a germanium plate by the Blodgett technique.[7] It has been found that they are made of microcrystallites in the monoclinic or triclinic form, and that the hydrocarbon chains of stearic acid assume a uniaxial orientation on the axis normal to the germanium-sample interface, whereas the hydrocarbon chains of barium stearate give rise to a specific orientation in the interface with respect to the polishing direction of the germanium plate in its cleaning procedure. The film thickness per layer has been estimated to be 23.8 Å for the stearic acid films and 24.3 Å for the mixed films of stearic aicd and barium stearate; both values are in good agreement with the value previously reported.[7,8]

Since elaidic acid has the double bond in the *trans* form at the center of the C_{18} hydrocarbon chain, it is worth studying the multilayers of elaidic acid by the same method and discussing the effect of the double bond on the structure of the films as well as on their molecular orientation. Thus, in the present work, the polarized infrared ATR method was extended to studies of the multilayers of elaidic acid built up on the germanium plate by the Blodgett technique.[7] Unfortunately, attempts to compare the results of this study with those of oleic acid, which is the *cis* isomer, were unsuccessful, for the transfer of the oleic acid monolayer onto the germanium plate was incomplete and reproducible results could not be obtained, although Alexander[9] has prepared "excellent" multilayers of oleic acid (much less readily than the *trans* form) from the Cambridge tap-water substrate.

Theoretical

A full discussion of the theory used in this study has been given in the previous paper,[2] and so it will not be repeated here.

Experimental

The elaidic acid was a material of the highest purity (99%); it was purchased from the Sigma Chemical Co., and was used without further purification. It melted at 44.0°C, the melting point being in good agreement with the value in the literature.[10]

The multilayers of elaidic acid were formed by transferring the monolayer spread on a substrate (from a 0.04% solution in benzene) onto a germanium trapezoidal ATR plate, 50 mm long, 18 mm high, and 2 mm thick, by the Blodgett technique.[7] As Alexander[9] has pointed out, the best substrate was found to be ordinary tap water, filtered before use. Its pH was *ca.* 7.7, and it contained approximately 5×10^{-5} mol of calcium bicarbonate per liter of water. A synthetic substrate of the same pH and calcium concentration was comparatively poor for multilayer building, but the reason for this marked difference has not been investigated. The plate was slowly dipped in the water and then withdrawn, with its large faces (50 mm long × 18 mm high) vertical through the monolayer, at the fixed rate of 5 mm/min maintained with the use of a motor and reduction gear. Rapeseed oil (spreading pressure: 10.5 dyn/cm) or triolein (15 dyn/cm) was employed as the piston oil, with reference to the surface pressure-area isotherm of the elaidic acid monolayer reported by Marsden and Rideal.[10]

The germanium plate was cleaned by the same procedure as that reported in the previous paper.[2] The main step was the repolishing of the plate on a plane ground pitch plate covered with a silk cloth by the use of a polishing material (Linde) and a detergent solution. The plate was then thoroughly rinsed with water. This was followed by ultrasonic cleaning in alcohol and in chloroform.

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[1] Presented at the 24th Symposium of Colloid and Surface Chemistry, Gifu, October, 1971.

[2] T. Takenaka, K. Nogami, H. Gotoh, and R. Gotoh, *J. Colloid Interfac. Sci.*, **35**, 395 (1971).

[3] T. Takenaka, K. Nogami, and H. Gotoh, *ibid.*, **39**, (1972) in press.

[4] N. J. Harrick, *J. Phys. Chem.*, **64**, 1110 (1960).

[5] J. Fahrenfort, *Spectrochim. Acta*, **17**, 698 (1961).

[6] N. J. Harrick, "Internal Reflection Spectroscopy," Interscience publishers, New York (1967).

[7] K. B. Blodgett, *J. Amer. Chem. Soc.*, **57**, 1007 (1935).

[8] A. Müller, *Proc. Roy. Soc., Ser. A*, **114**, 542 (1927).

[9] A. E. Alexander, *J. Chem. Soc.*, **1939**, 777.

[10] J. Marsden and E. K. Rideal, *ibid.*, **1938**, 1163.

The polarized infrared ATR spectra of the multilayers were recorded by a Perkin-Elmer model 521 grating spectrophotometer equipped with a multiple ATR attachment as well as a wire grid polarizer.[2] The ATR attachment has been designed so that the radiation can be reflected between the germanium-plate faces 25 times at the average angle of incidence of 45°. The semiangle of the radiation cone incident upon the ATR plate is *ca.* 3°. The error due to this beam convergence was estimated to be relatively small and was ignored in this study. The X-ray diffraction patterns of the multilayers were obtained with the aid of a Rigaku Denki X-ray diffractometer through the reflection method using the copper-K_α line.

All the experiments were carried out in a room of a constant temperature (20±0.2°C) and a constant humidity (45±2%).

Results and Discussion

The Polarized ATR and Transmission Spectra. In Fig.1 the infrared absorption specturm of elaidic acid obtained by the KBr pellet technique is reproduced for reference. Figures 2A and 2B represent the polarized ATR spectra of the 3-layer and 31-layer films, respectively, of elaidic acid prepared by the use of rapeseed oil as the piston oil. The solid line refers to the orientation of the electric vector parallel to the plane of incidence ($R_{\parallel}$), while the broken line refers to the electric vector perpendicular to it ($R_{\perp}$). Unfortunately, the latter line could not be recorded in the region lower than *ca.* 850 cm^{-1}, since the intensity of this particular polarized radiation was largely reduced in this region by various causes, such as the polarization characteristics of the grating in the monochromator and the absorption by the germanium plate. The transmission spectrum of the 31-layer films is also given (by the dotted line) in Fig. 2B. Apparently, the peaks are much stronger in the ATR spectra than in the transmission specturm.

It should be noticed that the C=O stretching band observed at 1710 cm^{-1} in the specturm of elaidic acid itself (Fig. 1) disappears in Fig. 2A and 2B, and that a pair of new peaks appears at 1550 and 1522 cm^{-1} in the spectra of the 3-layer film (Fig. 2A). With an increase in the number of layers, another pair of peaks appears at 1573 and 1537 cm^{-1}; these peaks are enhanced, while the intensities of the 1550 and 1522 cm^{-1} peaks are kept unchanged (Fig. 2B). Since the pair of bands at 1572 and 1536 cm^{-1} observed in the spectra of calcium salts (monohydrates) of long-chain fatty acids has been assigned to the antisymmetrical stretching vibration of the carboxlyate group,[11-13] the pair of peaks at 1573 and 1537 cm^{-1} observed in this

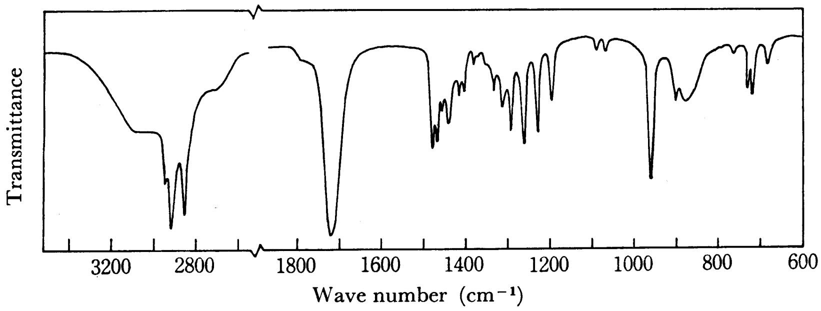

Fig. 1. Infrared absorption spectrum of elaidic acid obtained by the KBr pellet technique.

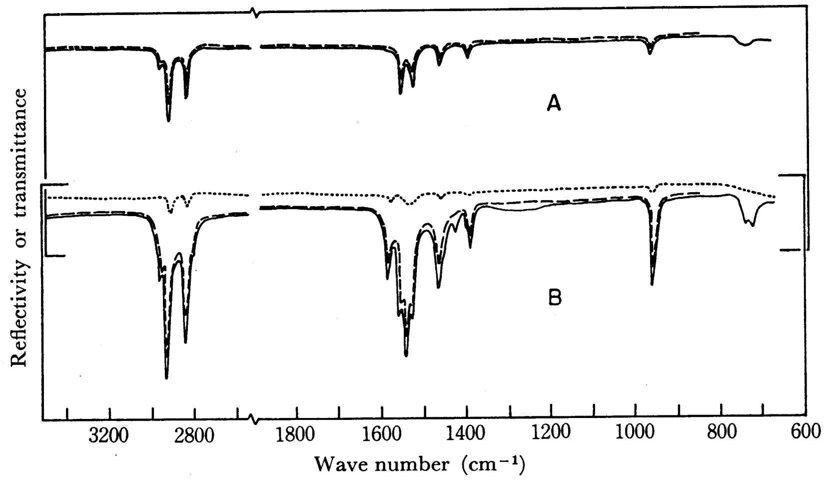

Fig. 2. Polarized infrared ATR and transmission spectra of the 3-layer (A) and 31-layer films (B) of elaidic acid (piston oil; rapeseed oil):

——: $R_{\parallel}$ — —: $R_{\perp}$ } ATR spectra, -----: transmission spectrum.

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11) B. Ellis and H. Pyszora, *Nature*, **181**, 181 (1958).

12) M. Kawano, *Nippon Kagaku Zasshi*, **81**, 1805 (1960).

13) Y. Koga and R. Matuura, *Memo. Fac. Sci., Kyushu Univ.*, Ser. C, **4**, 1 (1961).

study (Fig. 2B) can confidently be attributed to the same vibration of calcium elaidate monohydrate. In other words, the multilayers of elaidic acid are prepared in the form of calcium salt (monohydrate) from the tap-water substrate. The disappearance of the peaks of elaidic acid itself at *ca.* 3100 cm^{-1} (the OH stretching vibration) and at 870 cm^{-1} (the OH out-of-plane deformation vibration) in Fig. 2B can also be interpreted in the same way. The first pair, at 1550 and 1522 cm^{-1}, observed in the spectra of the very thin-layer films (Fig. 2A) may be ascribed to calcium salts interacting with the germanium surface. Corresponding to the pair of peaks assigned to the antisymmetrical stretching vibration of the carboxlate group, the two peaks at 1432 and 1398 cm^{-1} can be attributed to the symmetrical strecthing vibration of the same group in calcium elaidate monohydrate.

Another marked difference in the spectra between the elaidic acid crystal and films is seen in the region from 1350 to 1180 cm^{-1}. In the spectrum of the elaidic acid crystal (Fig.1), regularly-spaced peaks of a medium intensity are found in this region, but only traces are observed in the spectra of the elaidic acid films (Fig. 2B). This is different from the cases of the multilayers of stearic acid[2] and of barium stearate,[3] for which the progression bands have been observed in the ATR spectra as in the spectra of their crystals. According to Susi,[14] the bond progression of the elaidic acid crystal is to be ascribed to the coupled wagging and/or twisting vibrations of the methylene groups in the chain segment between the carboxyl group and the double bond,[15] and it appears only when the segment is in the planar *trans*-zigzag configuration. The above-mentioned finding, therefore, suggests that the first chain segment of elaidic acid is scarcely in the planar configuration in the films prepared with rapeseed oil (spreading pressure: 10.5 dyn/cm).

When, however, the multilayers of elaidic acid are formed with triolein (spreading pressure: 15 dyn/cm), the weak progression bands appear as shown in Fig. 3. The positions of the bands are identical with those of the progression bands in the crystal spectrum (Fig. 1). The high parallel polarization of the progression bands can be interpreted in terms of an orientation of the planar chain segment toward the *z*-axis (Fig. 4), because the transition moments of the wagging and/or twisting modes of the methylene groups lie along the chain axes.[2,3] The other parts of the spectra are the same as those in Fig. 2B. It is apparent from these facts that the planarity of the chain segment is largely dependent upon the surface pressure applied in the process of monolayer transfer onto the germainum plate. The presumption that the multilayers prepared at higher surface pressures will give rise to stronger progression bands could not be ascertained, because of the collapse of the monolayer at such a surface pressure. The poor planarity of the chain segment of elaidic acid in the films may arise from the expanded structure of its monolayer which is seen in the surface pressure–area isotherm.[10]

The intense peak at 963 cm^{-1} is assigned to the CH out-of-plane deformation vibration of the *trans*-vinylene group, and the peak at *ca.* 720 cm^{-1}, to the rocking vibration of the methylene groups.[16] The other major peaks will be dicussed below.

The Molecular Orientation. The orientation of the elaidic acid molecules in the films was discussed by calculating three components of their absorption indices[5,17] (κ_x, κ_y, and κ_z) from Eqs. [5] and [8] in Ref. 2. Three axes, *x*, *y*, and *z*, of the germanium plate are shown in Fig. 4. The plane of incidence is the *yz*-plane. The dipping direction of the plate during the course of the film transfer and the polishing direction of the plate in its cleaning procedure are parallel to the *x*- and *y*-axes, respectively. The reflectivities ($R_{\parallel}$ and $R_{\perp}$) were obtained from the polarized ATR spectra. Some typical results are shown in Fig. 2 for the 3-layer and 31-layer films. The coefficients, *A*, *B*, and *C*, of Eq. [5] in the previous paper[2] were evaluated from Eq. [6] as $A=18.0$, $B=15.2$, and $C=20.7$ using the above-mentioned number of reflections (q=25) and the angle of incidence ($\theta_1=45°$), on the assumption that the refractive indices of the germanium plate (n_1) and the elaidic acid films (n_2) were 4.00 and 1.46,[18] respectively, at room temperature.

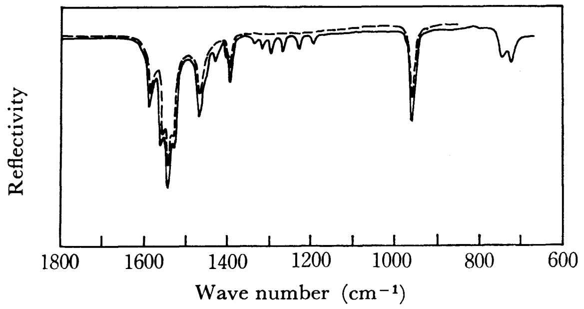

Fig. 3. Polarized infrared ATR spectra of the 31-layer film of elaidic acid (piston oil; triolein):
——: $R_{\parallel}$, – –: $R_{\perp}$.

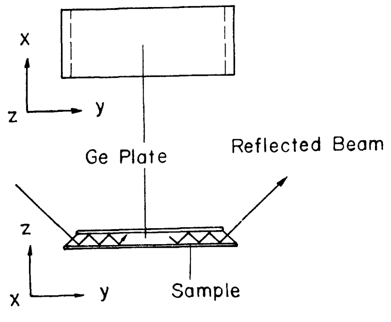

Fig. 4. Three axes of the germanium ATR plate.

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14) H. Susi, *Anal. Chem.*, **31**, 910 (1959).

15) The terminal chain segment (from the double bond to the methyl group) does not give rise to regularly spaced, medium intensity bands, and may cause some weak, irregular bands occuring among the main progression bands.[14]

16) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen, London (1958).

17) P. A. Flournoy and W. J. Schaffers, *Spectrochim. Acta*, **22**, 5, 15 (1966).

18) "Yushi Kagaku Binran," ed. by Nippon Yukagaku Kyokai Maruzen, Tokyo (1958), Chap. 3.

TABLE 1. MOLECULAR ORIENTATION IN THE ELAIDIC ACID FILMS

	Wave number (cm^{-1})	$\kappa_x(=\kappa_y)$	κ_z	D_{xz}	F	α
31 layers	2920	0.071	0.022	3.26	−0.301	31°
	2850	0.044	0.012	3.83	−0.327	29°
163 layers	2920	0.123	0.041	3.01	−0.286	32°
	2850	0.080	0.028	2.89	−0.279	33°

The polarized transmission measurements were also carried out for the thicker films with more than 31 layers, because they are sufficient for the detection of the absorption bands in the 2900-cm^{-1} region. For all the films examined, no difference was found between the transmission spectra obtained by the use of polarized radiations with the electric vectors parallel to the x- and y-axes, as in the case of the stearic acid films.[2] This apparently indicates that $\kappa_x=\kappa_y$, suggesting that the molecules in the films give rise to a random orientation on the z-axis, in other words, to a uniaxial orientation with respect to the z-axis, irrespective either of the dipping direction or of the polishing direction during the film preparation. From these discussions, we obtain, for example, the values of $\kappa_x(=\kappa_y)$ and κ_z shown in Table 1 for the peaks at 2920 and 2850 cm^{-1} (the antisymmetrical and symmetrical stretching vibrations of the methylene groups, respectively) of the 31-layer and 163-layer films.

In the case of the uniaxial orientation, the orientation of the molecules is evaluated by the orientation function, F,[19] calculated from:

$$F=\frac{1-D_{xz}}{1+2D_{xz}} \tag{1}$$

with:

$$D_{xz}=\kappa_x/\kappa_z. \tag{2}$$

Here, F defines the degree of the orientation of the transition moments with respect to the z-axis, as has been described in the previous paper.[2] The values of D_{xz} and F are given in Table 1 for 31-layer and 163-layer films. As a model of uniaxial orientation, if we assume that the molecular axis is uniformly oriented with an angle of α around the z-axis and that, further, the transition moment of the peak is uniformly oriented with an angle of β around the molecular axis, F can be expressed by the following equation:[13]

$$F=\frac{1}{2}(3\,\overline{\cos^2\alpha}-1)\cdot\frac{1}{2}(3\cos^2\beta-1), \tag{3}$$

where $\overline{\cos^2\alpha}$ denotes the average value of $\cos^2\alpha$. Since it is well known that the antisymmetrical and symmetrical stretching modes of the methylene guoups do not mix with the other modes, and that both their transition moments are perpendicular to the molecular axis ($\beta=90°$), while they are normal to each other, the values of α can be obtained for the 31-layer and 163-layer films as is shown in the last column of Table 1. The results are in agreement with the corresponding values of stearic acid,[2] suggesting that the inclination of the molecular axes in the elaidic acid films is nearly the same, on the average, as that in the stearic acid films.[2] In other words, the effect of the double bond in the *trans* form on the molecular orientation can virtually be ignored.

Film Thickness per Layer. In Fig.5, the reflectivity, $R_\perp$, is plotted against the number of layers, m, for five major peaks at 2920, 2850, 1537, 1465, and 1398 cm^{-1}. In the process of calculating the reflectivity, the effect of the absorption of radiation by the sample films on both sides of the germanium trapezoidal plate upon the polarized ATR spectra was corrected by the method described in the previous paper.[2] For each peak, $R_\perp$ decreases first with the increase of m and attains a constant value at a certain number of layers, m_c (indicated by an arrow in Fig. 5), which is characteristic of the peak. The larger $R_\perp$ values for the 1537 cm^{-1} peak at the small m values are interpreted as resulting from the peak shift in the very thin films as a result of the interaction between the carboxylate group and the germanium surface described previously.

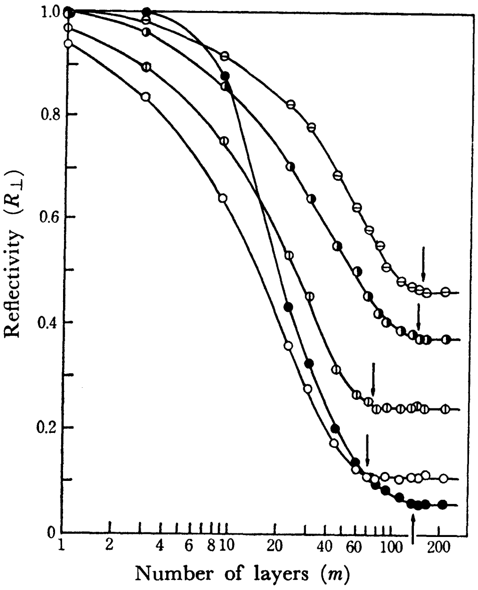

Fig. 5. Reflectivity $R_\perp$ as a function of the number of layers m:
—○—: 2920 cm^{-1}, —⦶—: 2850 cm^{-1}, —●—: 1537 cm^{-1}, —◑—: 1465 cm^{-1}, —⊖—: 1398 cm^{-1}.

Since, from the discussions in the previous paper,[2] m_c is thought to be the number of layers which gives the penetration depth,[4] d, of the radiation (into the sample films) expressed by Eq. [1] of the previous paper,[2] we can obtain the film thickness per layer, d_0, by dividing d by m_c. The results are summarized

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[19] R. Zbinden, "Infrared Spectroscopy of High Polymers," Academic Press, New York (1964), Chap. V.

Table 2. Film thickness per layer of the elaidic acid films

Wave number (cm^{-1})	Assignment	d (Å)	m_c	d_0 (Å)
2920	CH_2 antisym. stretching	1560	70	22.3
2850	CH_2 sym. stretching	1600	75	21.3
1537	COO^- antisym. stretching	2960	135	21.9
1465	CH_2 scissoring	3110	140	22.2
1398	COO^- sym. stretching	3260	150	21.7
			Mean	21.9 Å

in Table 2 for all the peaks examined, together with their assignments.

The X-ray diffraction pattern of the 163-layer films is shown in Fig.6. An analysis of the main peaks in Fig.6 gives the value of 44.16 Å as the long spacing of the films. The fact that half of this value, 22.08 Å, is in good agreement with the mean value of d_0, 21.9 Å, suggests that the elaidic acid films appear as the Y type,⁷⁾ as Alexander⁹⁾ has pointed out.

In the case of stearic acid, the long spacing of the film has been found to be equal to that of the crystal.³⁾ In the case of elaidic acid, however, the above-mentioned value of the long spacing of the film is apparently shorter than that of the crystal, 48.9 Å.²⁰⁾ This may correspond to the finding that the chain segment of elaidic acid is not in a clear planar configuration in the films.

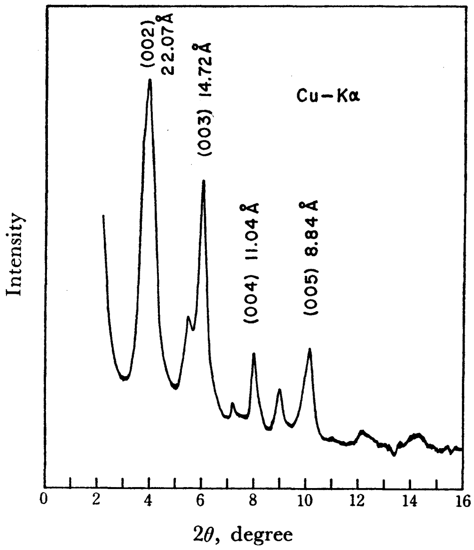

Fig. 6. X-Ray diffraction pattern of the 163-layer film of elaidic acid.

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20) J. H. Benedict and B. F. Daubert, *J. Amer. Chem. Soc.*, **71**, 4113 (1949).

21) Present address: Tohoku Women's University, Hirosaki, Aomori.