# Electrical Properties of Langmuir Films of Fatty Acid Salts and Carotenoic Acid

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(Received May 26, 1978)

Electric conductivities have been studied for Langmuir molecular layers of barium salt of fatty acids and for the layers of barium arachidate mixed with *all-trans-β-apo*-8′-carotenoic acid. These results have been interpreted based on an electron tunneling model taking account of the mirror image force. The conduction levels of the layers have thereby been estimated to be 1.00 eV for barium stearate, 1.31 eV for barium arachidate and 1.45 eV for barium behenate below vacuum level. The conduction level of the carotenoic acid has been derived to be 1.9 eV from these results. The structure of these layers has been discussed from the above mentioned experimental results, together with those on surface pressure, absorption spectrum and electric capacitance.

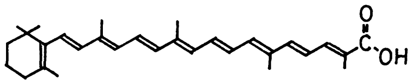
Recently, the physicochemical properties of Langmuir films were extensively investigated by Kuhn *et al.*[1,2] They showed from electric conductivity measurements of fatty acid layers that electron tunneling predominantly contributes to the conductivity through the monomolecular layers. They estimated the conduction levels of these fatty acid salts from a theoretical equation for the tunneling current and their experimental results.[3,4]

We have investigated electrical and spectroscopic properties of molecular layers of fatty acid mixed with *all-trans-β*-carotene.[5] It has been shown that, contrary to our expectation, β-carotene molecules lie parallel to the plane of the molecular layer and are aggregated.

*All-trans-β-apo*-8′-carotenoic acid is expected to form a stable mixed monolayer with fatty acids in which the molecules are perpendicular to the layer because of its hydrophobic chain and the hydrophilic end group. It is of interest to investigate the electrical properties of the surfaces, where long π-conjugated chain molecules are perpendicularly aligned, in connection with the action of carotenoids in biological electron transport. We have studied the surface pressure, the absorption spectrum and the electric conductivity of the monolayers of fatty acid salts with and without the carotenoic acid in order to clarify the structure of these layers and the mechanism of their electric conduction.

## Experimental

The method for the preparation of aluminum/Langmuiir film/aluminum junctions was described in detail in a previous paper.[5] The surface pressure of monolayer spread at an air–water interface was kept constant at 30 dynes/cm during transferring the monolayer onto a substrate by use of a compression barrier automatically driven by a servomotor combined with a Wilhelmy balance.



carotenoic acid

*All-trans-β-apo*-8′-carotenoic acid (carotenoic acid) ethyl ester was obtained from F. Hoffmann-La Roche and Co.† Carotenoic acid was prepared by hydrolysis of the ester, followed by recrystallization from a benzene solution according to Isler *et al.*[6] Absorption spectrum of the purified carotenoic acid in hexane was confirmed to agree with that reported in benzene solution.[7] No band ascribable to the cis-isomer was found in the spectrum.[8] Arachidic acid from P-L Biochemicals, Inc. was purified by recrystallization twice from an ethanol solution. Other materials were prepared and purified in the same procedures as described previously.[5]

The dc conductivity was measured with a Keithley 414S picoammeter and a Shimadzu VM101 voltmeter. The dc voltage was applied by coupling a potentiometer and a dry cell. Capacitance measurement was made with a Yokogawa-Hewlett-Packard 4265B bridge at 1 kHz, 20 mV peak-to-peak. The visible-UV absorption spectra of the films were measured with an ultra sensitive spectrophotometer constructed in our laboratry.[9]

All measurements and preparation of the mixed layers of the carotenoic acid were performed in an atmosphere of nitrogen under red light.

## Results and Discussion

*Structure of the Mixed Layers.* Figure 1 shows the surface pressure (π) *versus* the area per molecule (*A*) of the monolayers of carotenoic acid mixed with arachidic acid in various molar fractions at the air–water interface. The π-*A* curves consist of two components: the slow rising part below 10—20 dyn/cm and the steep part in the higher pressure region. The limiting areas per molecule, $A_0$, were derived by extrapolating the steep part in the curves at zero-pressure. The value of $A_0$ was obtained to be 28 Å$^2$ for the pure carotenoic acid monolayer, which was between the polyene chain cross section (about 20 Å$^2$) and the β-ionone ring cross section (about 50 Å$^2$). This result strongly suggests that carotenoic acid molecules are standing perpendicularly at the water surface. A linear relationship between the $A_0$ value and the molar fraction was found for the mixed monolayers, also implying that carotenoic acid molecules are perpendicularly standing in the mixed monolayers.

Figure 2 shows the electronic absorption spectra of carotenoic acid dissolved in hexane and those incorporated in cadmium arachidate monolayers at various molar ratios deposited on slide glass. The absorption spectra of the carotenoic acid in the mixed layers are somewhat broader than that of the solution. The

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† The authors wish to express their gratitude to F. Hoffmann-La Roche and Co. for the kind donation of *all-trans-β-apo-8′*-carotenoic acid ester.

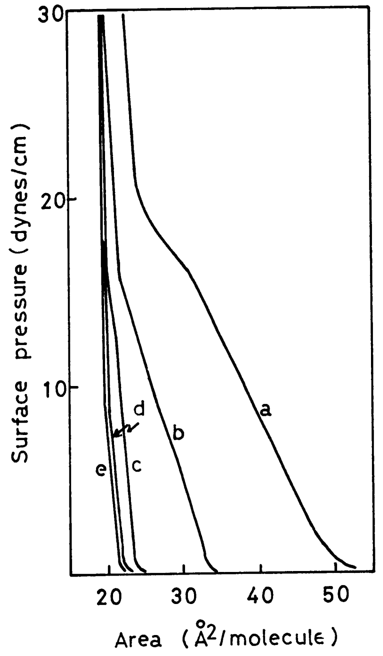

Fig. 1. The surface pressure-area curves for mixed layers of carotenoic acid and arachidic acid on the surface of solution containing $3\times10^{-5}$ mol/l barium chloride and $4\times10^{-4}$ mol/l potassium bicarbonate. The molar fractions of carotenoic acid were 1.0 for a, 0.464 for b, 0.0709 for c, 0.017 for d, and 0 for e, respectively.

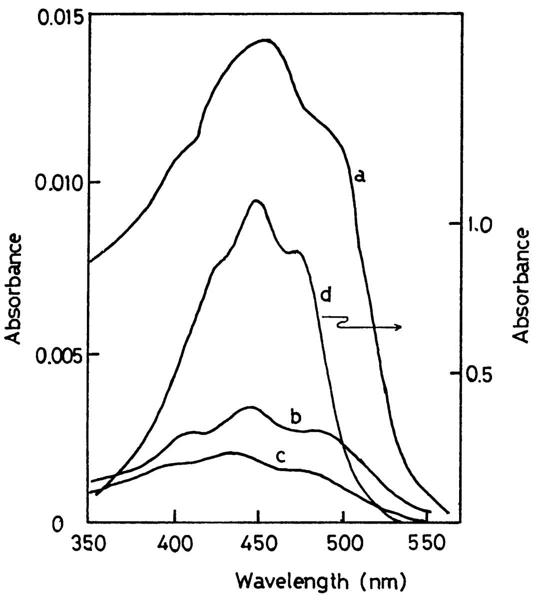

Fig. 2. Absorption spectra of the mixed monolayers of carotenoic acid and cadmium arachidate at normal incidence. The molar fractions of carotenoic acid are 1.0 for curve a, 0.194 for curve b, and 0.0973 for curve c. Curve d is for the $10^{-5}$ mol/l hexane solution of carotenoic acid.

spectra of the films show a slight blue-shift with decreasing molar fraction of carotenoic acid.

The "molar" extinction coefficient of carotenoic acid in the layers at the absorption peak may be defined by $\varepsilon_m = A/\Gamma$ mol$^{-1}$ cm$^2$ where $A$ is the absorbance of the monolayer and $\Gamma$ is the number of moles of carotenoic acid per 1 cm$^2$ of the film. Taking $A$ to be 0.014 from the maximum of curve a in Fig. 2 and $\Gamma$ to be $5.9\times10^{-10}$ mol cm$^{-1}$, corresponding to the value of 28 Å$^2$/molecule obtained for pure carotenoic acid layer, we obtain $\varepsilon_m = 2.4\times10^7$ mol$^{-1}$ cm$^2$. If the carotenoic acid molecules were to lie randomly in the pure carotenoic acid monolayer, $\varepsilon_m$ would take the value of *ca.* $1.1\times10^8$ mol$^{-1}$ cm$^2$, corresponding to the maximum molar extinction coefficient measured in the hexane solution. The experimental $\varepsilon$ value obtained is 5 times as small as the latter. As the direction of the transition moment for the absorption band is thought to be parallel to the polyene chain, no absorption band should be observed in the wavelength region measured if the molecules are aligned in an exactly perpendicular array in the film. Simple calculation by use of our result leads to the conclusion that the carotenoic acid molecules in the pure film on an average make an angle of 20° with the line normal to the film plane. Curves b and c in Fig. 2 also indicate that the molecules are similarly oriented in the mixed films as well.

The capacitance measurements for the mixed films with various number of monolayers revealed that a good linear relationship between the reciprocal of capacitance and the number of the monolayers was observed. The value of thickness of the mixed monolayer divided by its relative permittivity was obtained to be 11.2 Å from the slope. Assuming that the electric polarization of the film is a simple sum of those due to the fatty acid and the carotenoic acid and taking the relative permittivities for the fatty acid and carotenoic acid to be 2.41[5] and 3.6[10] respectively, the thickness of carotenoic acid array was estimated to be 28 Å, corresponding to the length of the molecule, by the same methods as employed for the layers of fatty acid salt mixed with $\beta$-carotene.[5] This result also confirms that the carotenoic acid molecules are perpendicularly standing in the mixed monolayers deposited on the solid substrate. The conclusion on the molecular orientation of carotenoic acid in the layers agrees with that reported by Reich[11] and Engelsen.[7]

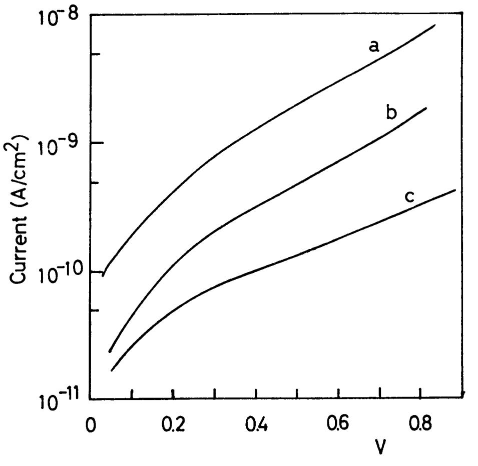

Fig. 3. The current-voltage curves for the monolayers of fatty acid salts: (a) barium stearate, (b) barium arachidate, and (c) barium behenate.

*Conductivity Measurements.* The current-voltage ($j$-$V$) curves obtained for the fatty acid salt monolayers at room temperature are shown in Fig. 3. The magnitude of current decreased with increasing fatty acid chain length, *i.e.*, in the order of barium stearate, barium arachidate and barium behenate. Each of the currents was proportional to the applied voltage in the low voltage region ($V<0.1$ V), but increased exponentially above 0.3 V. The currents obtained were about 100 times as small as those measured for Al/fatty acid salt/metal junctions by Kuhn *et al.*,[3,4] though the shapes of our $j$-$V$ curves were very similar to theirs. The currents for 3-, 5-, 7-, and 9-layer films were much smaller than that for the monolayer, and proportional to the voltage up to about 0.8 V. The dc conductivity, $\sigma_0$, calculated from this ohmic behavior of the multi-layer films was $2.3\times10^{-16}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ for barium stearate, $1.1\times10^{-16}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ for barium arachidate and $4.8\times10^{-17}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ for barium behenate. The $\sigma_0$ values fall into the range of conductivities of paraffin in the solid state.[12] This fact indicates that the fatty acid multi-layer films prepared have no substantial pinholes.

Table 1. Tunneling conductivity, potential barrier height and conduction level of fatty acid salt monolayers and carotenoic acid array in the mixed monolayer

| Material | $\sigma_t$ ($\Omega^{-1}$ cm$^{-1}$) | $\bar{\phi}$(eV) | $V_0$(eV) | $d$(Å) |
|---|---|---|---|---|
| Barium stearate | $2.7\times10^{-16}$ | 2.53 | 1.00 | 25.8[a] |
| Barium arachidate | $8.7\times10^{-17}$ | 2.26 | 1.31 | 28.0[a] |
| Barium behenate | $1.96\times10^{-17}$ | 2.05 | 1.45 | 30.2[a] |
| Carotenoic acid | $1.95\times10^{-14}$ | 1.7 | 1.9 | 28 |

a) Taken from Ref. 4.

The $j$-$V$ curves obtained for the monolayers are reasonably explained by the electron tunneling model given for thin oxide films by Simmons.[13] The tunneling conductivity, $\sigma_t$, for the fatty acid salt monolayers was derived by subtracting $\sigma_0$ from the conductivity obtained for the monolayers at low voltage region and listed in Table 1. According to a Simmons' equation for a rectangular potential barrier in the low voltage region,[13] the tunneling current, $j_t$, can be expressed as a function of potential barrier height, $\bar{\phi}$, as follows:

$$j_t=[(2m\bar{\phi})^{1/2}/d](e/h)^2\cdot V\cdot\exp[-4\pi d/h\cdot(2m\bar{\phi})^{1/2}], \quad (1)$$

where $m$ and $e$ are the electron mass and charge, respectively, $h$ is Planck's constant and $d$ the thidkness of monolayer. The $\bar{\phi}$ values calculated from the $\sigma_t$ values using Eq. 1 are listed in Table 1. Assuming that $\bar{\phi}$ is simply represented by the difference between the work function of the metal electrode and the electron conduction level of the monolayer, $V_0$, the $V_0$ values of 1.7—2.1 eV were calculated for these fatty acid salts taking 4.2 eV as the work function of aluminum.[14] On the other hand, if one takes account of a mirror image force due to the metal electrodes, the $V_0$ values as listed in Table 1 were obtained with the aid of Simmons' method (Eqs. 48 and 49 in Ref. 13).

Figure 4 shows $j$-$V$ curves measured for mono- and multi-layer films of barium arachidate with and without carotenoic acid at room temperature. The current measured for the mixed monolayer was much higher than that for the barium arachidate monolayer. The electric conductivity of the mixed monolayers is considered to be a sum of those by the barium arachidate array and the carotenoic acid array, so that the current in the mixed monolayer is caused mainly by electron flowing through the carotenoic acid array. The $\sigma_0$ and $V_0$ values were roughly estimated to be $1.1\times10^{-13}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ and 1.73 eV for the mixed monolayer, respectively.[15]

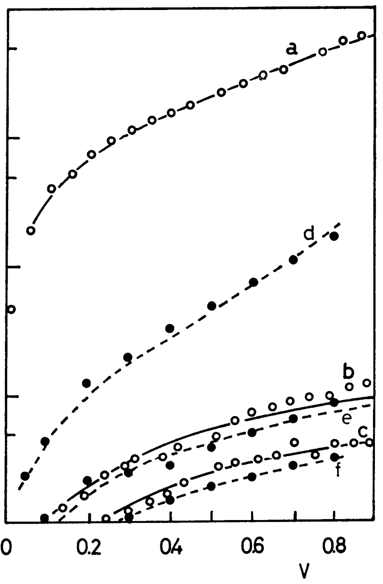

Fig. 4. The current-voltage curves for mono- and multi-layer films of arachidic acid salt with and without carotenoic acid. Curves a, b, and c; for 1-, 5-, and 7-layer films of arachidic acid salt mixed with carotenoic acid, respectively (○). Curves d, e, and f; for 1-, 5-, and 7-layer films of arachidic acid salt, respectively (●). Solid and dotted lines are calculated curves (Ref. 15). Molar fraction of carotenoic acid in the mixed layers is 0.0709.

In the case of multi-layer films, the increase in the current due to the addition of carotenoic acid was small. The conductivity of the multi-layer films of barium arachidate mixed with carotenoic acid was obtained to be $1.3\times10^{-16}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ from the $j$-$V$ curves shown in Fig. 3.

The conduction band level of a dry electron has been estimated to be almost zero for alkanes,[16,17] and the depth of electron trap in alkane matrices and benzene matrices have been obtained to be 0.26 eV[17—19] and 0.5 eV,[19] respectively. Our $V_0$ values are somewhat larger than either of these values.

The Simmons' equations have been derived for the tunneling current at 0 K.[13] At higher temperatures, the metal electrons should be populated in the higher electronic states of the electrode metal according to the Fermi distribution. It is, therefore, expected that part of the metal electrons are allowed to have kinetic energies much more than the average thermal energy ($kT\approx0.03$ eV) at room temperature. Though the number of electrons in such highly excited states are relatively few according to the Fermi distribution, they can contribute largely in the tunnel current by the exponential dependence of the effective barrier height. Consequently, it becomes likely that our room temperature experiment brings about the larger $V_0$ value.

Inelastic electron tunneling process coupled with vibrational excitation and polarization of molecules has been investigated at low temperature.[20] It has been pointed out that an inelastic process for a monolayer of simple organic molecules adsorbed on metal oxide surface changes the conductance by *ca.* 1%,[21] and that the inelastic tunneling channels increase with applied voltage. In the inelastic processes, the electrons either lose or gain energy by interactions with the film material. In the first case, electrons should have excess energy to compensate the energy loss due to the inelastic processes in order to reach another electrode. In the second case, the film material should be in a higher lattice vibration-rotation states. Therefore, in either case, the probability of the inetastic tunneling is increased at higher temperature. It is, therefore, suggested that such an inelastic process, giving more important contributions at higher temperature, makes the experimental $V_0$ values larger than those corresponding to the conduction band levels for the alkane matrices obtained by other experimental methods.

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