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Electrical and Spectroscopic Investigations of Molecular Layers of Fatty Acids Including Carotene

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Spectroscopic and electrical studies have been made for the mono- and multi-molecular layers of barium stearate mixed with carotene. The results of the electronic spectra have indicated that the carotene molecules lie parallel to the monolayer plane and are aggregated. The capacitances measured are expressed well as those of parallel plate capacitors. From these results, the structure of the layers containing carotene has been deduced.

Kuhn and his colaborators have extensively investigated the physicochemical phenomena occurring at interfaces of Langmuir films made of some organic molecules such as fatty acid salts and organic dyes.[1,2]

We have investigated the electrical and spectroscopic properties of sandwitch-type assemblies of fatty acid salt layers mixed with *all-trans-β*-carotene in order to clarify the structure of these layers and its relation with the electrical properties.

Experimental

Aluminum/Langmuir film/aluminum junctions were prepared as follows. Aluminum film was evaporated on a slide glass using 99.999% aluminum at a pressure of 10^{-5} Torr. Monolayers or multilayers were deposited on such films by means of the Langmuir-Blodgett technique.[3] Finally, aluminum was evaporated in an array of stripes on the layers as shown in Fig. 1. The effective electrode area of each of the junctions formed was about 0.1 cm^2. The monolayers were spread on an aqueous subphase containing 3×10^{-5} M barium chloride and 4×10^{-4} M potassium bicarbonate by introducing a small amount of a benzene solution of a fatty acid or a mixture of fatty acid and β-carotene. The water used as the subphase was prepared by distilling deionized water twice. Oleic acid was used as a piston oil having a surface pressure of 29.5 dyn/cm. Stearic acid from Sigma Chemical Co., 99% pure arachidic acid and 99% pure behenic acid both from Nakarai Chem. Co. were purified by recrystallization twice from distilled ethanol solutions. *All-trans-β*-carotene, 97% pure, from Merk & Co. was used without further purification. Capacitance measurements were made with a Yokogawa-Hewlett-Packard 4265B bridge at 1 kHz, 20 mV peak-to-peak. Absorption spectra were measured by use of a Cary 15 spectrophotometer.

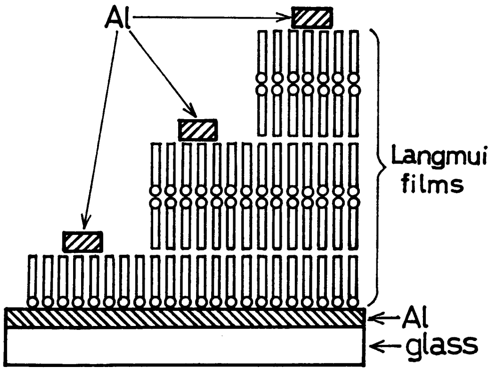

Fig. 1. The structure of Al/monolayers/Al assemblies.

Results and Discussion

Electronic Absorption Spectra. Figure 2 shows the electronic absorption spectra, measured at normal incidence, of various molecular layers of barium stearate mixed with β-carotene. The benzene solution of carotene is well known to have a strong absorption due to the $^1\text{B}\leftarrow{}^1\text{A}$ transition with fine structures in the region from 500 to 350 nm. The absorption spectra of the layers are somewhat different from that in solution. The peak positions of the layers, 513, 474, and 447 nm are essentially the same as those of a β-carotene film formed on glass by solvent evaporation from a benzene solution containing carotene and stearic acid at the same molar ratio, and are at slightly shorter wavelengths than those reported for a solid state carotene film by Rosenberg *et al.*[4] When the number of the superposed monolayers increased, the absorption intensity increased proportionally, but no change in the spectral shape was found.

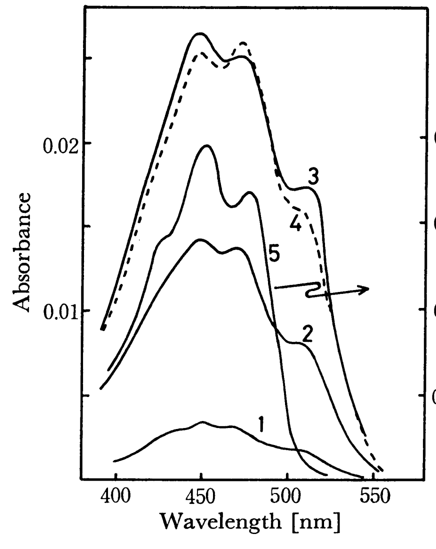

Fig. 2. Absorption spectra of Langumuir films containing *all-trans-β*-carotene taken at normal incidence: (1) monomolecular layer. (2) 3 molecular layers. (3) 5 molecular layers. (4) 5 molecular layers at an angle of incidence of 45°. (5) The hexane solution of β-carotene. All films are made of a mixture of β-carotene and barium stearate in a molar ratio of 1: 12.3.

The $^1\text{B}\leftarrow{}^1\text{A}$ transition moment of carotene lies in the molecular plane and directs along the polyene chain. Therefore, if the carotene molecules are assumed to lie perpendicularly on the glass plane, no absorption should be observed with light of normal incidence. On the other hand, if the carotene molecules are assumed to be randomly oriented, the absorption intensity should change with the angle of incidence, θ, being proportional to $1/\cos\theta$. Finally, if the molecules are assumed to lie parallel to the glass, the absorption intensity is expected to be proportional to $(1+\cos^2\theta)/(2\cos\theta)$, so that the ratio of the absorption intensity measured at $\theta=45°$ to that at $\theta=0°$ is calculated to be 1.06. In the present work, the absorption spectrum obtained at an angle of incidence of 45° showed no significant difference in shape and intensity from that obtained at normal incidence (Fig. 2). This result suggests that the carotene molecules lie parallel to the glass plate. The large difference between the absorption spectrum of carotene in the layers and that in solution can be explained by taking account of the aggregation of the molecules in the former. Based on these results, a plausible model for the structure of the mixed monolayers is shown schematically in Fig. 3.[5] It is reasonable to assume that the carotene molecules are stacked face to face on the glass plane in view of the π-π type molecular interaction giving a large amount of stabilization.

Capacitance Measurements. Figure 4 shows the reciprocal of capacitance per unit area measured for barium stearate layers with and without β-carotene versus the number of superposed monolayers between aluminum electrodes. The capacitance, C, of these layers, being regarded as parallel type capacitors, is expressed as a function of the number of the monolayers, n, as follows:

$$1/C = 1/C_{\mathrm{ox}} + (d/\varepsilon_0\varepsilon)n, \tag{1}$$

where C_{ox} is the capacitance due to the oxide layer presumably formed on the aluminum electrode surface, ε_0 is the dielectric constant of vacuum, ε is the relative permittivity of the organic layers, and d is the thickness of the monolayer. As is seen from Fig. 4, a good linear relationship is obtained between $1/C$ and n for all cases.

By taking the relative permittivity of aluminum oxide to be 8,[6] the oxide thickness is calculated to be 35 Å for the stearate layer assemblies and 42 Å for the mixed layer assemblies from the $1/C$ values extrapolated to $n=0$. Similar plots were made for other fatty acid salts and the d/ε values derived from the slopes are listed in Table 1. Using the d values obtained by Kuhn *et al.*,[7] the ε values were derived for the fatty acid salts as seen in Table 1, being in good agreement with those obtained by Kuhn *et al.*[8] and Reynolds *et al.*[9]

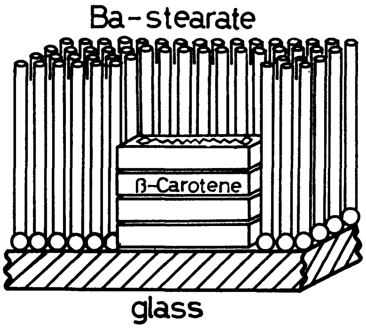

Fig. 3. Schematic representation of the mixed layer of *all-trans-β*-carotene and a fatty acid salt.

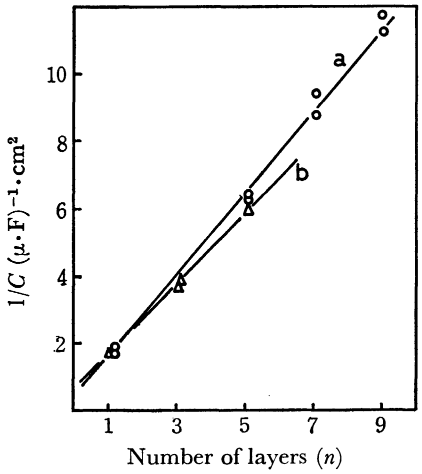

Fig. 4. Reciprocal of capacitance, $1/C$, *vs.* predicted number of layers, n; (a) for the monolayers of barium stearate and (b) for those mixed with β-carotene in a mole ratio of 1: 12.3.

TABLE 1. THE d/ε AND ε OF FATTY ACID SALTS OBTAINED FROM THE CAPACITANCE MEASUREMENTS

Material	d/ε (Å)	d[a] (Å)	ε
Barium stearate	10.5	25.8	2.46
Barium arachidate	11.6	28.0	2.41
Barium behenate	13.0	30.2	2.32
Barium stearate–β-carotene	9.7		

a) Taken from Ref. 8.

Somewhat smaller d/ε values were obtained for the mixed layers than those for the pure barium stearate layers. Assuming that the electric polarization of the mixed layer is a simple sum of those by the fatty acid salt array and the carotene array indicated in Fig. 3, the capacitance of the layer can be calculated only if the stacking number of β-carotene molecules in each of the monolayer is assumed. Using the d/ε values obtained both for the fatty acid salt layers and for the mixed layers, the molecular cross-section of barium stearate of 20 Å², the molecular plane area of carotene of 230 Å², the thickness of the carotene plane of 4 Å, and ε of carotene assumed to be 2.5 or 3.0,[10] the number derived is 3.58 or 4.09, respectively. The relative actual thickness of the carotene layers is such as illustrated in Fig. 3. In the above discussion, it was assumed that there are no interstices between the molecular layers.

Surface pressure-area (π-A) curve measured for β-carotene at the air–water interface has been measured. It is in good agreement with that obtained by Leblanc and Orger.[11] The limiting area of 18.0 Å² per molecule was derived by extrapolating the steep part of the π-A curve. This corresponds to the cross sectional area of β-carotene calculated from the molecular structural model, indicating that the β-carotene molecules are standing perpendicularly on the surface. The π-A curves for samples containing both carotene and fatty acid in various molar ratios have also indicated the perpendicular standing of β-carotene. Therefore, the structure proposed in Fig. 3 for the mixed Langumuir film of β-carotene with the fatty acid salt seems to be formed when the layer was transferred from the air–water interface onto the glass surface.

References

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5) In this figure, β-carotene molecules are shown to exist as a single molecular column surrounded by the fatty acid. Naturally, it is possible that they form larger islands consisting of two or more columns in the fatty acid.

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10) The values of the permittivity are 2.44 for benzene and 2.85 for napthalene in solid state, respectively. It is presumed that β-carotene has a value in permittivity near those of unsaturated hydrocarbons such as benzene and naphthalene.

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