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Temperature dependence of the thickness of Langmuir multilayer assembly films

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The thickness of Langmuir films was examined for temperatures ranging from -193 up to 80 °C by using x-ray diffraction. Up to around -40 °C, the thickness remains almost constant or the thermal expansion coefficient $\alpha \sim 1 \times 10^{-5}$ deg^{-1}. Beyond -20 °C, the thickness tends to decrease; $\alpha < 0$ and $|\alpha|$ increases with temperature.

Fatty acids and their metal salts, in the crystalline state, are known to have the linear thermal expansion coefficients $\alpha \sim 1 \times 10^{-4}$ deg^{-1} over a wider temperature range.[1] However, the Langmuir multilayer assembly films built up with those salts may be different in the temperature behavior from the corresponding bulk materials. Mann and Kuhn have found that the Langmuir films of Cd salts show negative thermal expansion coefficient or decrease in thickness with temperature around room temperature.[2]

We have examined the thickness variation of the Cd salt films for temperatures ranging from liquid-nitrogen temperature up to 80 °C by using x-ray diffraction. X-ray diffraction measurements were performed using a Rigaku-Denki 2035 (Cu $K\alpha$) diffractometer with a cryostat. The results are given in this report.

The samples prepared were *Y*-type films of Cd salts of arachidic, stearic, and palmitic acids [$CH_3-(CH_2)_{n-2}-COOH$, $n = 20$, 18, and 16], as shown in Fig. 1, each deposited on a slide glass by employing the Langmuir-Blodgett technique.[3] The number N of monolayers deposited was 11, 21, 31, or 41. As seen in the figure, *Y*-type films are characterized with the one-dimensional bilayer unit cell with a Cd–Cd spacing corresponding to twice the monolayer thickness.

Figure 2(a) shows an example of the variation of the Cd–Cd spacing of a Cd arachidate 11-layer assembly film. The spacing increases with temperature for a range from liquid-nitrogen temperature up to around -40 °C. The expansion coefficient α is therefore positive in this range. Near liquid-nitrogen temperature, α is actually comparable with those of the bulk fatty acids and their salts, $\alpha \sim 1 \times 10^{-4}$ deg^{-1}, and then decreases remarkably in magnitude. In the range of $-160 \sim -40$ °C, $\alpha \sim 1 \times 10^{-5}$ deg^{-1}, which is rather comparable with those of solid metals (e.g., for Pt, $\alpha = 0.8 \times 10^{-5}$ deg^{-1} in the same range). Around -40 °C, the spacing tends to decrease; that is, $\alpha < 0$. The results from the multilayer films with N up to 41 were quantitatively the same as those for 11-layer films.

Figures 2(b) and 2(c) are the examples of the thickness variation for the stearate and the palmitate, respectively. Each lacks the region of $\alpha \sim 1 \times 10^{-4}$ deg^{-1} which is observed in the arachidate near the liquid-nitrogen temperature, while other two regions, $\alpha \sim 1 \times 10^{-5}$ deg^{-1} and $\alpha < 0$ are seen in a similar manner as in the case of the arachidate.

In the region of negative expansion coefficient, $|\alpha|$ increases with temperature and $\alpha \sim -1 \times 10^{-4}$ deg^{-1} at $50 \sim 60$ °C for all three cases 2(a), 2(b), and

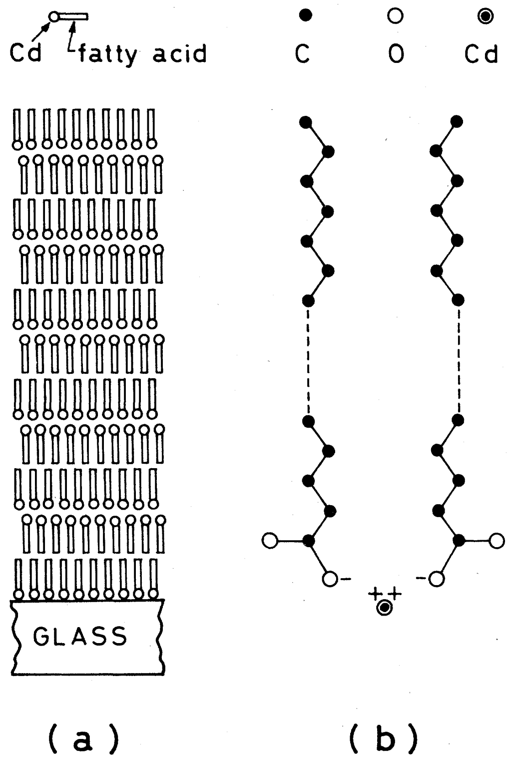

FIG. 1. Schematic representation of the Langmuir assembly structure. (a) Cross section of a *Y*-type 11-layer film. (b) The straightened conformation of the constituent molecular chains. The largest spacing is attained with the planar conformation of the hydrocarbon chains.

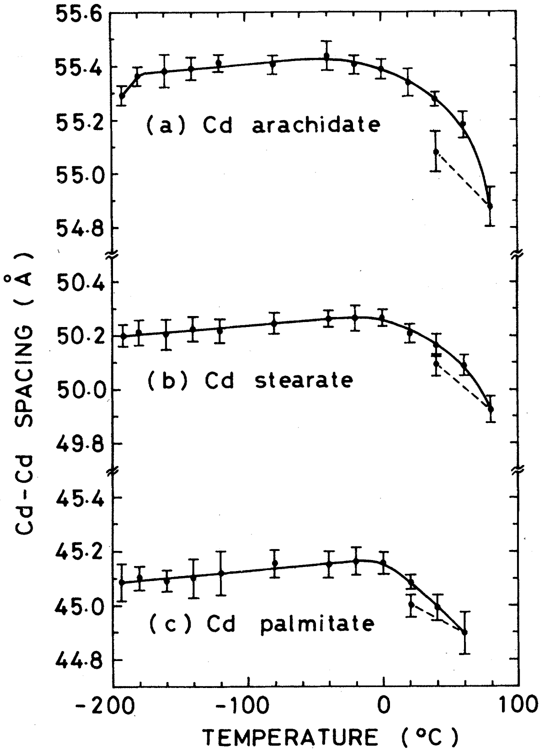

FIG. 2. (a)–(c) Cd – Cd spacing of Langmuir films as a function of temperature taken from 11-layer films.

2(c). The dotted lines in Figs. 2(a), 2(b), and 2(c) indicate that each film is subjected to a creep in the temperature region above 60 °C. Upon cooling, the Cd – Cd spacing increases again, but does not recover the initial value. The higher the temperature experienced, the larger the residual contraction. It should be noted that the thickness relaxation involves actually slow components with time constants considerably longer than 30 min. Such components, although small in magnitude, were traceable above 60 °C as a drift of the spacing towards smaller values during the measurement. They may contribute to the residual contraction observed actually.

The intensity of the diffracted x ray varies with temperature in a similar manner as the Cd – Cd spacing; it holds almost constant as long as $\alpha > 0$ and then decreases with temperature. Referring to the film structure shown in Fig. 1, the regions, $\alpha > 0$ and $\alpha < 0$ are interpreted as follows. The Cd – Cd spacing is governed by the chain length of constituent acid radicals which are hexagonally arranged in a straightened conformation.[4] Upon increasing the temperature, various modes of thermal vibration[5] are activated to cause the change in the spacing. The stretching and the scissoring modes of C – C bonds will contribute to increase the spacing as usually seen in the bulk solids, while the freedom of rotation around C – C axis, although it is more or less hindered in a solid, will lead to a rubberlike elasticity, and the spacing will be decreased. These two contributions compete against each other, resulting in the smaller thermal expansion coefficient $\alpha \sim 1 \times 10^{-5}$ deg^{-1} observed for the wide temperature range.

The region of $\alpha \sim 1 \times 10^{-4}$ deg^{-1} seen in the arachidate indicates that the freedom of rotation is frozen near the liquid-nitrogen temperature, suggesting that the arachidate monolayer is tighter in the chain arrangement than the others.

The constant intensity of the diffracted x ray in the $\alpha > 0$ region indicates that the dynamic or thermal disturbance in the film structure does not exceed the spatial disturbance frozen in the monolayers, which is inevitably introduced through the deposition procedure at room temperature.

When the temperature is further enhanced, the rotation around the C – C axis or the rubberlike elasticity predominates over others, resulting in the negative expansion coefficient and the decrease in the diffracted x ray intensity as well.

It is finally noted that no reasonable assumption of the Poisson's ratio of the film explains the observed behavior of the film thickness; the glass substrate used for the present experiment has a thermal expansion coefficient $\alpha \sim 1 \times 10^{-5}$ deg^{-1}, which is also about a decade smaller than that of the ordinary organic bulk solids.

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