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Thermal Stability of Metal Stearate LB Films Studied by Infrared Reflection-Absorption Spectroscopy

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Infrared reflection-absorption spectra of LB films of Cd, Ca, Ba, and Al stearates were measured at elevated temperatures, and thermal stability of the films was semiquantitatively examined. The conformational disorder suddenly increased at 110 °C for Cd salt, at 125 °C for Ca salt, and above 150 °C for Ba and Al salts. The spectral changes for the LB films subjected to cyclic thermal treatments were also studied.

It has been known that infrared reflection-absorption (RA) spectroscopy[1)] is governed by the preferential selection rule of the electric field perpendicular to the metal surface, and therefore provides useful information about the molecular orientation and conformation in thin organic films.[2-7)] Swalen et al.[8)] have first applied this technique to study thermal order-disorder transitions of the hydrocarbon chains in Langmuir-Blodgett (LB) films of Cd arachidate. Kobayashi et al.[9)] have also performed a similar study on LB films of arachidic acid and its Cd salt. In the present study, we used the same technique for the semiquantitative comparison of thermal stabilities of LB films of divalent-metal (Cd, Ca, and Ba) stearates. We also examined LB films of trivalent Al stearate, regarding it as a typical example of extremely hard monolayers.

Stearic acid used here was the same as that reported previously.[10)] Spread monolayers of Cd, Ca, Ba, and Al stearates were prepared by a dropwise addition of benzene solution of stearic acid (1mg/ml) on doubly distilled water with 3×10^{-4}M $CdCl_2$ and 3×10^{-4}M $NaHCO_3$ (pH 6.2), 1×10^{-4}M $CaCl_2$, 1.5×10^{-4}M KH_2PO_4 and 1×10^{-4}M Na_2HPO_4 (pH 9.5 adjusted by NaOH), 3×10^{-4}M $BaCl_2$ and 2×10^{-4}M Na_2HPO_4 (pH 9.4 adjusted by NaOH), and 1×10^{-4}M $AlCl_3$ and 4.5×10^{-4}M $NaHCO_3$ (pH 6.1), respectively. The monolayers were compressed to the surface pressure of 20 mN/m (13 mN/m for Al salt), and transferred to the silver-evaporated glass slides by the LB method with the dipping speed of 10 mm/min at room temperature. The transfer ratios were almost unity throughout the experiments.

Infrared RA spectra were recorded on a Nicolet 6000C FTIR spectrophotometer equipped with an MCT detector and a Harrick model RMA reflection attachment. The p-polarized radiation was incident upon the LB films at an angle of 85° from the surface normal. The resolution was 4 cm^{-1} and the number of interferogram accumulations was 3000.

In order to raise the temperature of LB films, a flat Al plate incorporating a Nichrome wire was clamped to the glass substrate on which the LB films had been deposited. A copper-constantan thermocouple was pressed on the substrate. A temperature in the range from 20 to 150 °C could be maintained to within ±1 °C. After reaching each scheduled temperature, the sample stood for 10min prior to infrared measurements to establish the thermal equilibrium.

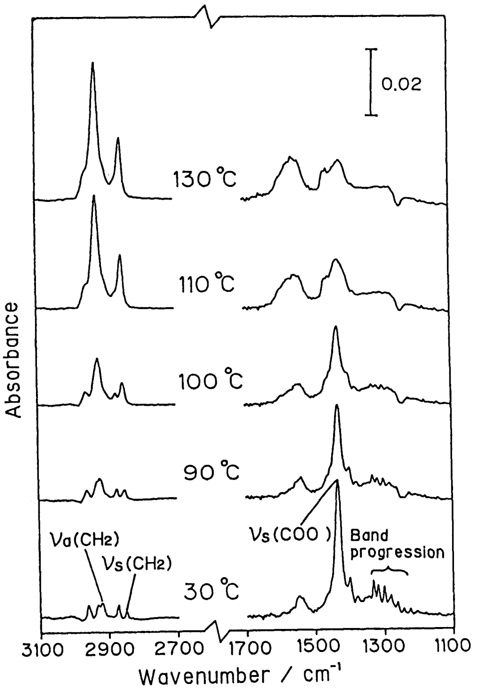

Fig.1. Infrared RA spectra of 9-layer LB film of Cd stearate at elevated temperatures.

Figure 1 shows a series of the RA spectra of 9-layer LB film of Cd stearate obtained at various temperatures from 30 to 130 °C. The spectrum at 30 °C is identical with that reported previously.[6] The antisymmetric and symmetric CH_2 stretching ($\nu_a(CH_2)$ and $\nu_s(CH_2)$) bands at 2920 and 2850 cm^{-1}, respectively, and the antisymmetric COO stretching ($\nu_a(COO)$)band at 1543 cm^{-1} are very weak, but the symmetric COO stretching ($\nu_s(COO)$) band at 1433 cm^{-1} strongly appears. Further, the band progression which is due to coupling of the CH_2 wagging vibrations of the trans-zigzag alkyl chain is clearly seen in the range from 1380 to 1180 cm^{-1}. These spectral features indicate that the alkyl chains of Cd stearate are oriented nearly perpendicular to the film surface (the angle of inclination with respect to the surface normal is 7°±2°).[6] Upon heating the films, the $\nu_a(CH_2)$ and $\nu_s(CH_2)$ bands begin to enhance their intensities while the $\nu_s(COO)$ band and the band progression weaken. Above 110 °C, significant spectral changes happen ; the $\nu_a(CH_2)$ and $\nu_s(CH_2)$ bands largely increase in intensity, the $\nu_a(COO)$ and $\nu_s(COO)$ bands broaden and come to have almost the same intensities, and the band progression disappears. These observations are nearly the same as those reported by Swalen et al.,[8] who have interpreted these facts as due to the introduction of disordered conformation into the alkyl chains and a breakup of the Cd lattice. This is supported by our present result that the frequency of the $\nu_a(CH_2)$ band increased from 2920 to 2927 cm^{-1} when the film was heated from 30 to 130 °C.[5]

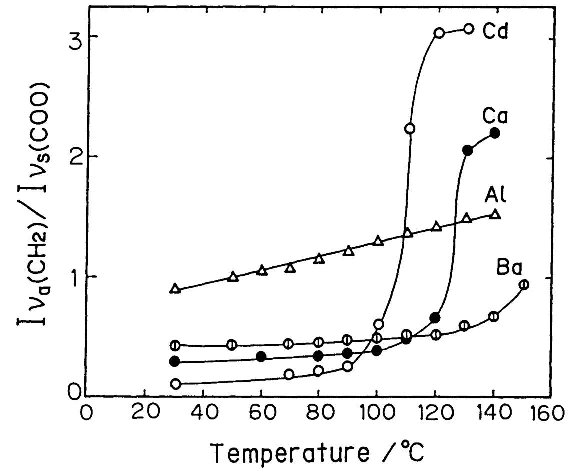

Fig.2. $I\nu_a(CH_2)/I\nu_s(COO)$ vs. temperature for metal stearate LB films.

The similar spectral changes were also observed for LB films of other divalent-metal stearates, except for an initial change for the Ca stearate film. Below 50 °C, the $\nu_s(COO)$ band of Ca stearate consists of the main peak at 1477 cm^{-1} and the subpeak at 1424 cm^{-1}

which have been ascribed to the monohydrate.[11] At 60 °C, the band suddenly changes to a singlet at 1438 cm^{-1} attributed to the anhydride. On further heating, it broadens and weakens as described above.

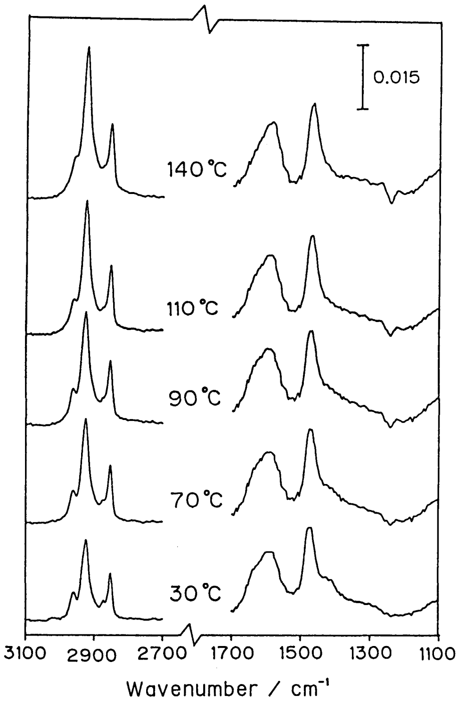

Fig.3. Infrared RA spectra of 9-layer LB film of Al stearate at elevated temperatures.

In Fig.2, the intensity ratios of the $\nu_a(CH_2)$ band to the $\nu_s(COO)$ band are plotted as a function of temperature for the three divalent-metal salts. Since, at 30 °C, the three salts apparently show the band progression, the intensity ratio reflects the overall orientation of the metal salts with the trans-zigzag alkyl chains. The fact that the ratio is the smallest for Cd salt and the largest for Ba salt reveals that the tilting angle of the molecules increases in order of Cd < Ca < Ba salts at room temperature. Upon heating, after slight increases in lower temperature range, the ratios sharply increase at 110 °C for Cd salt, at 125 °C for Ca salt, and above 150 °C for Ba salt. These findings suggest that a great conformational disorder happens at these higher temperatures owing to the marked increase in the number of the gauche conformers. Interestedly, the above temperatures for Cd and Ca salts coincide with the transition temperatures from the orthorhombic to hexagonal subcells of the corresponding bulk samples (110 and 125 °C) determined by X-ray analysis.[12] Further, it is apparent from Fig. 2 that the more perpendicularly oriented salt at room temperature has the lower transition temperature.

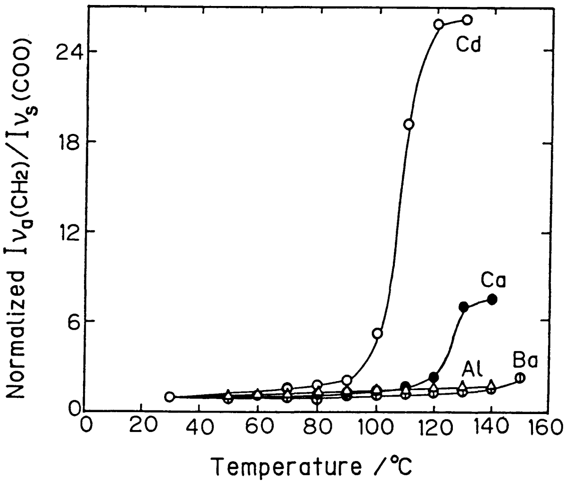

Fig.4. Normalized $I\nu a(CH_2)/I\nu s(COO)$ vs. temperature for metal stearate LB films.

In the case of the LB film of Al stearate shown in Fig.3, intensities of the $\nu_a(CH_2)$ and $\nu_s(CH_2)$ bands at 30 °C are much stronger as compared with those of the divalent-metal salts. In addition, the $\nu_a(COO)$ and $\nu_s(COO)$ bands have comparable intensities with each other, and the band progression disappears. Therefore, Al stearate is in a considerably disordered state even at room temperature. Upon heating, the $\nu_a(CH_2)$ and $\nu_s(CH_2)$ bands show a gradual increase in intensity until 140 °C, but $\nu_a(COO)$ and $\nu_s(COO)$ bands show almost constant intensities. As seen in Fig. 2, the intensity ratio $I\nu_a(CH_2)/I\nu_s(COO)$ for Al stearate has larger value at 30 °C, and slightly increases with increasing temperature. In order to emphasize the difference in the conformational change which happened on heating the all salts examined, the intensity ratio in Fig. 2 is normalized in such a way that the respective values at 30 °C equal to unity as shown in Fig.4. The conformational change is remarkable at 110°C for Cd salt, and fairly small at 125 °C for Ca salt. For both Ba and Al salts, however, the changes are trivial up to 150 °C.

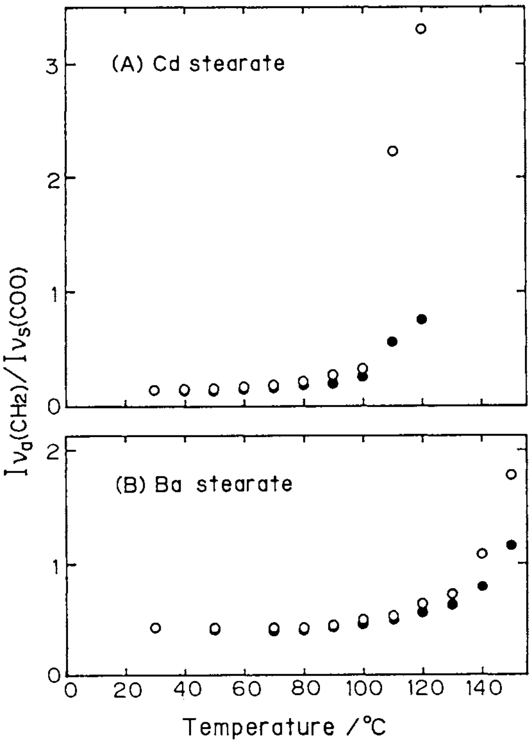

Fig.5. Changes in $I\nu a(CH_2)/I\nu s(COO)$ for LB films of (A) Cd and (B) Ba stearates subjected to cyclic thermal treatments. For details, see text.

Finally, we studied the spectral change for the LB films subjected to cyclic thermal treatments. The results for the 9-layer LB films of Ca and Ba salts are shown in Fig.5. The sample was once heated to an elevated temperature, its RA spectrum was recorded (the intensity ratio is shown by the open circle at that temperature in Fig.5), then cooled to 30 °C and a subsequent RA spectrum obtained (the intensity ratio is shown by the solid circle at the elevated temperature in Fig.5). This heating and cooling cycle and the accompanied RA measurements were repeated with raising the elevated temperature. When the Cd stearate LB film is cooled even from 110 or 120 °C to 30 °C, the ratio returns to a certain extent toward its original value. In the case of the Ba salt LB film, however, the recovery of the ratio is not so good as that for the Cd salt LB film, in spite of the above-mentioned fact that the former is more stable to simple heating. The Ca salt film shows an intermediate tendency between the Cd and Ba salt films.

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