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Infrared External Reflection Spectra of Langmuir Films of Stearic Acid and Cadmium Stearate

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In situ FT-IR external reflection spectra of spread monolayers (Langmuir films) of stearic acid and Cd stearate on the water surface were recorded at various surface areas. In the stearic acid monolayer, the trans-gauche conformational change upon monolayer compression was observed, while only the all-trans conformer was observed in the Cd stearate monolayer. Even in largely expanded monolayers of Cd stearate, present is the rigid crsytalline island instead of the rather flexible island in the acid monolayer.

Recently, morphology and molecular structure of the Langmuir (L) film on the water surface have attracted much interest as the precursor of the Langmuir-Blodgett (LB) film. In a previous paper,1) we have succeeded in recording the non-resonance Raman spectra of L films of stearic acid-d_{35} and Cd stearate-d_{35} at various surface areas by using a low-noise detector. From the line-width analysis of the symmetric CD_2 stretching band, we could discuss the change in the lateral packing and

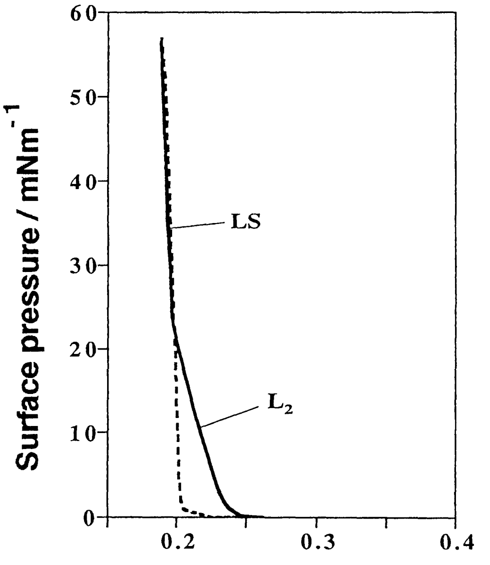

Fig. 1. The π-A isotherms of stearic acid (——) and Cd stearate (----) on the water surface at 23 °C.

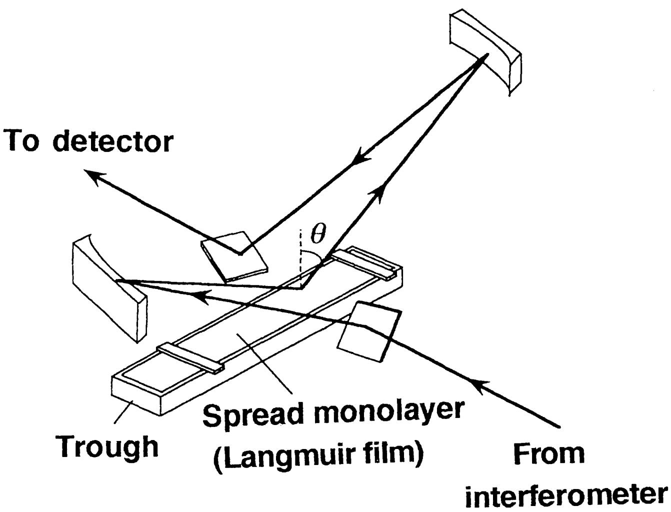

Fig. 2. Schematic of ERS accessory.

conformational order of the hydrocarbon chain during the monolayer compression. In the surface pressure (π)-area (A) isotherm of stearic acid monolayer, we have the liquid-condensed (L_2) and super-liquid (LS) phases,[2] while there is only the LS phase in its Cd salt (Fig. 1). In the case of the stearic acid-d_{35} monolayer, the conformational order of the hydrocarbon chain was improved by the monolayer compression and attained the highly crystalline state in the LS phase.[1] For the Cd stearate monolayer, however, the molecules are in the highly crystalline state at all surface areas examined, suggesting the presence of the crystalline island even in largely expanded monolayers. In the present paper, we have investigated the L films of the corresponding non-deuterated substances, by recording their Fourier transform infrared (FT-IR) external reflection spectra (ERS), to confirm the previous results.

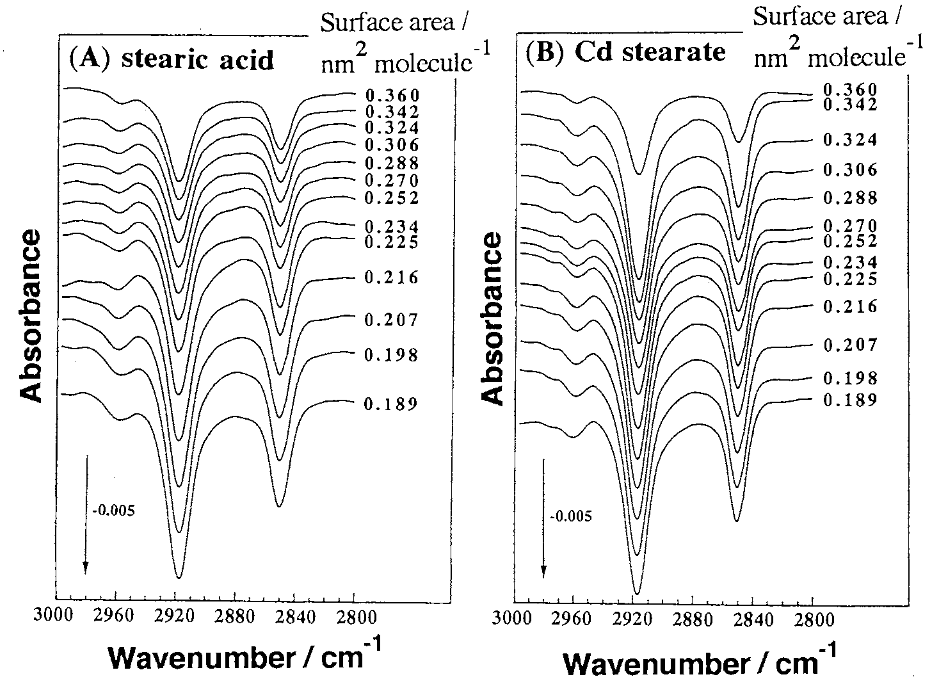

Fig. 3. FT-IR/ERS of L films of (A) stearic acid and (B) Cd stearate at various surface areas at 23 °C.

The L films of stearic acid and its Cd salt were prepared by spreading 10 μl of 8.12×10^{-4} M benzene solution of acid on the pure water at pH 6.2 and on the aqueous solution of 3×10^{-4} M $CdCl_2$, buffered with 4×10^{-4} M $NaHCO_3$ to pH 6.6, respectively. We used a trough with a 80×22 mm^2 effective surface area attached to a Specac 19650 monolayer/grazing angle accessory (Fig. 2). The water level of the trough was kept constant during the experiment by using an external teflon reservoir connected by a siphone. FT-IR/ERS of L films at various surface areas were recorded on a Nicolet 6000C FT-IR spectrophotometer equipped with an InSb detector with a resolution of 8 cm^{-1}. We used a bandpath (3400-2100 cm^{-1}) filter to remove the thermal agitation of the water surface by the infrared source. The angle of incidence was 38° and the number of interferogram accumulation was 500. Since the experimental data fluctuates owing to the island formation in the L film, we performed six independent experiments in each amphiphile of acid and salt, and recorded the maximum, minimum, and average of the band frequency and intensity.

Figure 3 represents FT-IR/ERS of L films of stearic acid and Cd stearate at various surface areas. In this frequency region, we can observe the asymmetric CH_3 stretching band (ν_aCH_3), antisymmetric and symmetric CH_2 stretching bands (ν_aCH_2 and ν_sCH_2) at ca. 2955, 2917, and 2850 cm^{-1}, respectively, with an appreciably good S/N. At the angle of incidence of 38°, which is smaller than the Brewster angle $\theta_B=\tan^{-1}(n_3/n_1)=54.7°$ at the air ($n_1=1$) / water ($n_3=1.41$ at 2900 cm^{-1}) interface, these bands show negative absorbances, in accord with the theoretical expectations for the non-polarized beam.[3,4] In Fig. 4, frequencies of ν_aCH_2 for the acid and Cd salt films observed in Fig. 3 are plotted against surface area. Hereafter, in the graphical representations, the mean value of six separate measurements are expressed by circle, and maximum and minimum values are expressed by limits of an error bar. On monolayer compression of stearic acid, the frequency stays constant at ca. 2919 cm^{-1} above 0.25 nm^2/molecule, but it decreases down to 2917 cm^{-1} in the L_2 phase region in Fig. 1. The value of 2917 cm^{-1} is typical for the all-trans conformer of the alkyl chain, and higher frequencies are indicative of the inclusion of the gauche conformer.[5] Thus, the observed shift in frequency of stearic acid indicates the conformational change from gauche to trans isomers upon monolayer compression. Now, the question arises why the acid molecule is subjected to such conformational change, in spite of the fact that the aggregated island formation has been observed by recently developed techniques of Brewster angle microscopy[6] or pahse contrast microscopy.[7] Referring to the results of a molecular dynamics simulation of amphiphilic monolayers,[8] it is quite plausible that molecules in the border of an island are responsible for the observed conformational change.

In the case of Cd stearate, however, there is no frequency change upon monolayer compression, indicating the presence of the highly crystalline island even at large surface areas, due to the strong aggregation property of the Cd salt. These observations fully support the previous Raman results.[1]

In Fig. 5, the peak intensities of ν_aCH_2 in six independent experiments are plotted against surface area. On casual inspection, it is found that the dispersion of experimental data is much wider in the Cd stearate film than in the stearic acid film. This is due to the presence of rigid crystalline islands in Cd salt, and data points even in a single experimental step scattered widely. In the stearic acid film, however, the presence of more flexible conformers

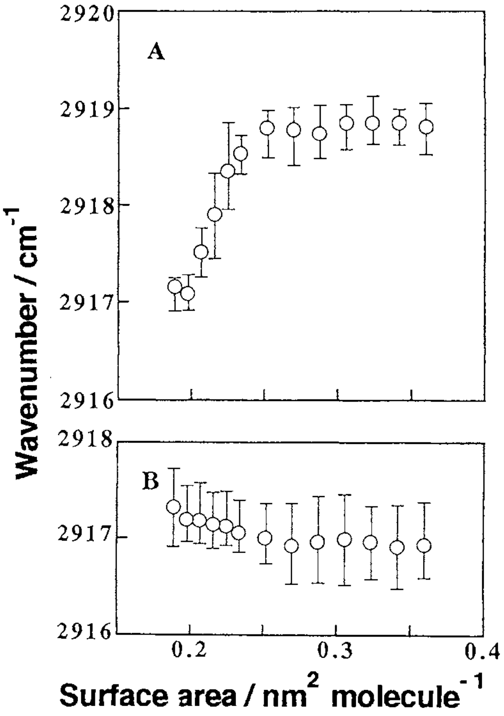

Fig. 4. Frequencies of ν_aCH_2 in L films of (A) stearic acid and (B) Cd stearate vs. surface area.

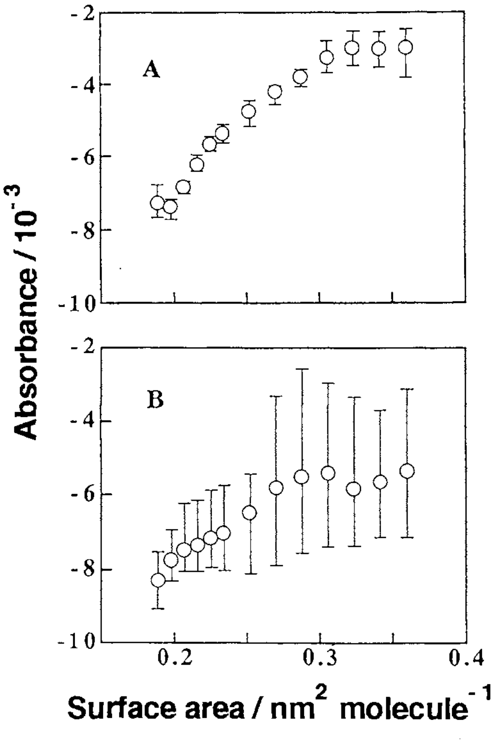

Fig. 5. Peak intensities of ν_aCH_2 in L films of (A) stearic acid and (B) Cd stearate vs. surface area.

around the island, and perhaps among islands, could help to average out the space among islands. The degree of data scattering is reduced at small surface areas in both acid and Cd salt. The increase in absolute peak intensity on monolayer compression is contributed by both the surface density increase and the molecular orientation. The data in Fig. 5 are calibrated by the difference in surface density to the point at smallest surface area. The results are shown in Fig. 6. In the acid film, the absolute peak intensity slightly increases, partly due to the stronger peak intensity of the trans conformer than the gauche conformer, and partly due to the change in molecular orientation by the conformational transformation. This result seems to be consistant with the tilt angle decrease in the L_2 phase of the behenic acid L films detected by the synchrotron X-ray reflection technique.9) In the Cd salt film, on the other hand, there seems no appreciable change in calibrated peak intensity. However, these points concerning molecular orientation awaits further clarification by polarization measurements which is now in progress, since the data points scatter too widely in Fig. 6.

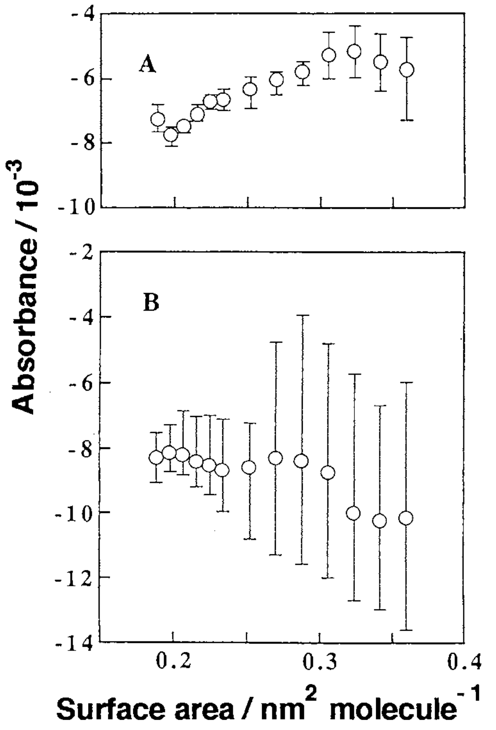

Fig. 6. Peak intensities of ν_aCH_2 in L films of (A) stearic acid and (B) Cd stearate after calibration of surface density vs. surface area.

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