CHEMISTRY LETTERS, pp. 1231-1234, 1988.

Structure Study of Langmuir-Blodgett Films of Stearic Acid and Cadmium Stearate Deposited by Different Techniques

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Structure of LB films of stearic acid and cadmium stearate was studied by X-ray diffraction and infrared ATR methods. Stearic acid LB films prepared by the horizontal lifting method were mixtures of the A- and C-crystal forms, but those prepared by the vertical dipping method mainly consisted of the C-form. Cadmium stearate LB films gave X-ray diffraction peaks indicating the long spacing of 5.03 nm, irrespective of the deposition method.

There are two techniques for transferring amphiphilic monolayers from water surface onto solid substrates. One is the conventional Langmuir-Blodgett (LB)1) or vertical dipping (VD) method,2) and the other the horizontal lifting (HL) method.2-5) The former has been commonly used since the pioneer work of Blodgett,1) while the latter has been known to be widely applicable to various amphiphiles even at lower surface pressures. Fukuda et al.2) pointed out from thickness measurements of LB films of anthraquinone derivatives that by the VD method the molecular packing was loosened during the transferring process, but by the HL method the molecular packing in the LB films was the same as that on water surface. These results suggest that, in general, there can be some structural difference between LB films deposited by the two different techniques. In the present work, structure of LB films of stearic acid and cadmium stearate prepared by the VD and HL techniques was studied by means of X-ray diffraction and infrared ATR methods.

Stearic acid used in this study was the highest purity material donated from Nippon Yusi Co. Ltd., and recrystallized from an ethanol solution. The sample thus obtained melted at 69.5-70 °C. No impurity peak was detected by a GC analysis.6) The stearic acid monolayer spread from a benzene solution on doubly distilled water was compressed to the surface pressure of 20 mN/m at 20°C and built-up on a slide glass by the HL method as well as the VD method. The cadmium stearate monolayer was prepared on water with 3×10^{-4}M $CdCl_2$ buffered with $NaHCO_3$ to pH 5.8 and deposited on a slide glass at the surface pressure of 30 mN/m by the same methods. As the glass surface is hydrophilic, the first monolayer was transferred by the VD method to have the hydrophobic surface, and the following monolayers were deposited by the respective methods. In the case of the HL deposition, two modifications were adopted. (i) After one large face of the glass plate was touched to the spread monolayer, a Teflon frame with an inside measure

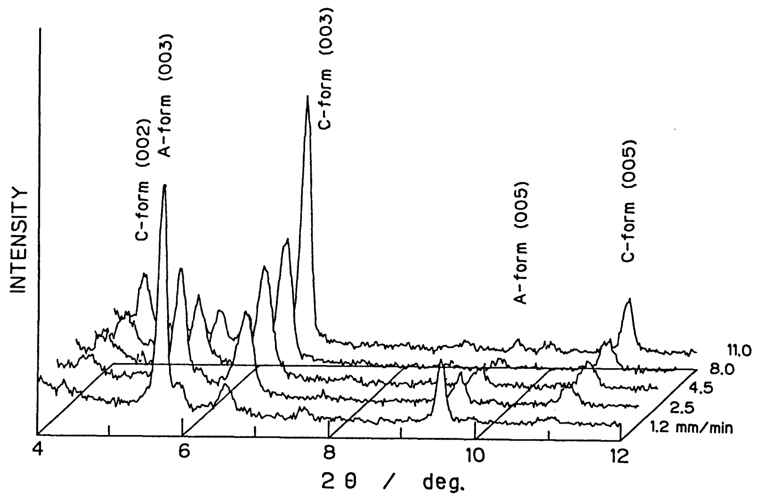

Fig.1. X-Ray diffraction patterns of 21-monolayer films of stearic acid deposited by the HL method without a Teflon frame at various moving speed of the glass substrates.

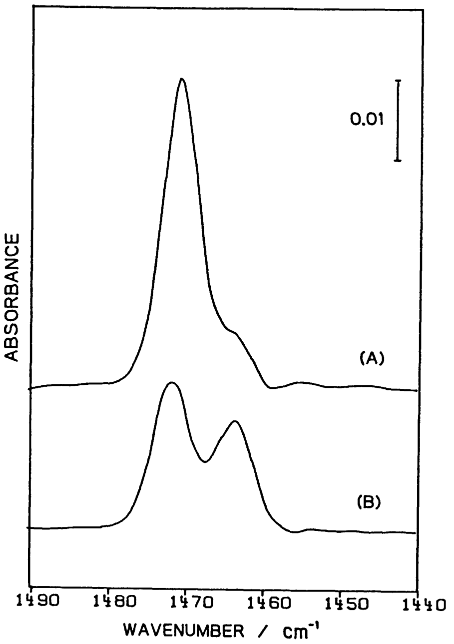

Fig.2. Infrared ATR spectra of 21-monolayer films of stearic acid deposited by the HL method at the moving speeds of (A) 1.2 and (B) 11.0 mm/min.

slightly larger than the face of the glass plate was floated on water surface to keep the residual monolayer away from the plate. Then the plate was lifted up from the water surface inside the Teflon frame. (ii) The same manipulation of the glass plate was made without the Teflon frame. In any cases, the moving speed of the glass plate was varied from 1.2 to 11.0 mm/min and the 21-monolayer films were deposited.

X-Ray diffraction patterns were obtained by a Rigaku Denki model RAD-2B diffractometer with the use of Cu-Kα radiation, indicating that all the LB films examined had the Y-type structure. Infrared spectra were recorded on a Nicolet model 6000C FT-IR spectrophotometer equipped with an MCT detector. A Perkin-Elmer multiple internal reflection attachment with a KRS-5 prism was used for ATR measurements. The angle of incidence was 45° and the number of internal reflections was 6. Interferograms were accumulated 2000 times.

Figure 1 shows X-ray diffraction patterns of the 21-monolayer films of stearic acid deposited by the HL method without a Teflon frame at various moving speeds of the glass substrate (transfer ratios : 2). There are two series of diffraction peaks. Those at $2\theta=4.41°$, $6.58°$, and $11.0°$ are due to the (002), (003), and (005) reflections, respectively, of the C-crystal form with the long spacing of 3.99 nm, in which the hydrocarbon chains are in the orthorhombic subcell packing.7) The peaks at $2\theta=5.70°$ and $9.53°$, on the other hand, are ascribed to the (003) and (005) reflections, respectively, of the A-crystal form with the long spacing of 4.64 nm,8) in which the hydrocarbon chains are in the triclinic subcell packing.

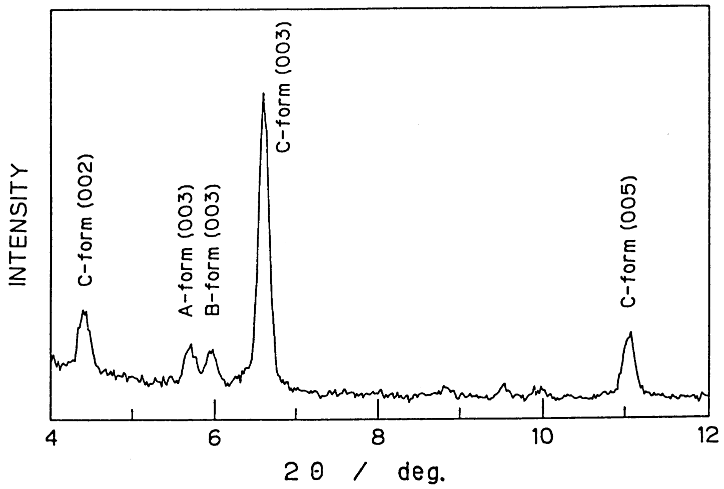

Fig.3. An X-ray diffraction pattern of a 21-monolayer film of stearic acid deposited by the VD method. Results are independent of the moving speed of the substrate.

Interestingly, the former series of peaks increase their intensities with the increase in the moving speed of the substrate, while the latter series decreases. At the highest moving speed of 11.0 mm/min, the diffraction pattern becomes that of almost pure C-form. The same trend was obtained by the HL method with a Teflon frame (transfer ratios were considered to be unity).

The above facts were also confirmed by infrared ATR measurements of the stearic acid LB films. Figures 2A and B are the results obtained in the CH_2 scissoring vibration region of the 21-monolayer films prepared by the HL method at the moving speeds of 1.2 and 11.0 mm/min, respectively. Figure 2A shows a singlet at 1471 cm^{-1} with a weak shoulder at 1465 cm^{-1}, but Fig.2B represents a clear doublet at 1472 and 1465 cm^{-1}. It has been established that the splitting of the CH_2 scissoring vibration is caused by the crystal field and is characteristic of the hydrocarbon chains which crystallize with the orthorhombic subcell packing where the chains are packed alternately.[9)] On the other hand, the frequency (1471 cm^{-1}) of the singlet band observed in Fig.2A suggests that the hydrocarbon chains are in the triclinic subcell packing where the chains are packed in parallel each other.[10)] The weak shoulder at 1465 cm^{-1} in Fig.2A is due to the presence of a small amount of the C-form.

These facts suggest that when a large stress due to rapid surface flow of water is applied to the monolayer, stearic acid tends to crystallize as the stable C-form during the process of LB film formation. However, a small stress gives rise to the less-stable A-form. Since the A-form has a denser structure than the C-form,[11)] this result reveals that stearic acid in the compressed monolayer on water surface is in a more condensed but less-stable state. Under a small stress, this state may be retained without perceptive change during the transferring process, but under a large stress, it may suffer a considerable change and consequently the molecular packing in the LB films is loosened as in the C-form.

Stearic acid LB films prepared by the VD method gave an X-ray diffraction pattern shown in Fig.3, irrespective of the moving speed of the substrate. Three strong and medium peaks at 2θ=4.41°, 6.60°, and 11.0° belong to a series ascribable to the C-form as described above. Two weak peaks at 2θ=5.70° and 5.96° are due to the (003) reflections of the A- and B-forms (the orthorhombic chain packing,

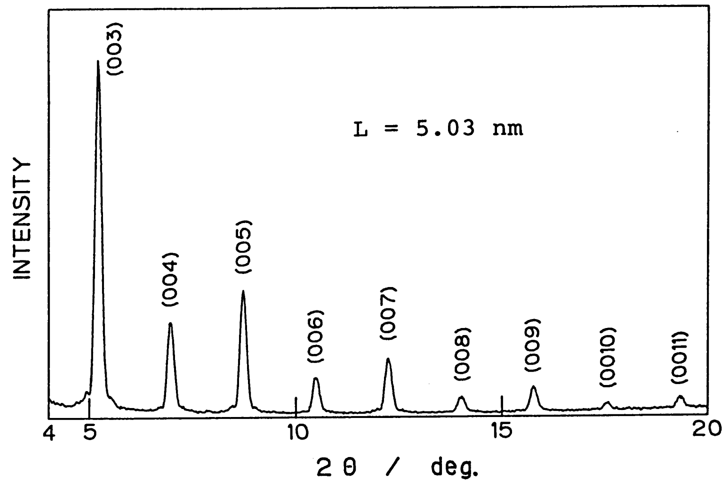

Fig.4. An X-ray diffraction pattern of a 21-monolayer film of cadmium stearate. Results depend neither on the deposition method nor on the moving speed of the substrate.

long spacing : 4.43 nm),[11] respectively. It is apparent therefore that stearic acid LB films deposited by the VD method mainly consist of the C-form including a small amount of the A- and B-forms. This means that the VD method causes larger stress than the HL method does at lower moving speeds of the substrate. Considering the above-mentioned discussions on difference in the molecular packing between LB films deposited under small and large streesses, this result is consistent with that for LB films of anthraquinone derivatives obtained by Fukuda et al.[2]

Figure 4 shows an X-ray diffraction pattern of the 21-monolayer LB films of cadmium stearate. A series of peaks can be assigned to the (003) to (0011) reflections of crystallites with the long spacing of 5.03 nm, this value being in a good aqreement with those reported by Sugi et al.[13] The diffraction patterns depend neither on the deposition method nor on the moving speed of the substrate. This result is mainly due to the fact that the Y-type structure of cadmium stearate LB films is highly stable.

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(Received April 19, 1988)