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Electron Microscopic Studies of Crystalline and Amorphous Monolayers of Fatty Acids

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A crystalline monolayer was observed at the subphase temperature T_{sp} below the melting point T_m of monolayers, while an amorphous monolayer was observed at T_{sp} above T_m of the monolayer, irrespective of the magnitude of surface pressure. A Π-A isotherm depends on the phase of a monolayer; a plateau on the Π-A isotherm (coexistence of solid and liquid phases) was observed for an amorphous monolayer and also, no plateau on the Π-A isotherm (coexistence of solid and gas phases) for a crystalline monolayer. The phase transition from an amorphous to a crystalline state was not detected during compressing a monolayer.

It has been generally considered that the gaseous monolayer state at very low surface pressure converts into the liquid expanded one, the liquid condensed one and finally the solid monolayer state during the compressing the monolayer on the water surface. However, several authors recently proposed that the amphiphiles with a large intermolecular aggregation force formed the crystalline monolayer domains on the water surface even at very low surface pressure as well as zero surface pressure and also, that these crystalline domains aggregate with increasing the surface pressure.[1,2] It is, therefore, indispensable for a general understanding on the aggregation structure of a monolayer on the water surface to investigate the structure of the monolayers prepared from amphiphiles with different intermolecular aggregation forces at various surface pressures. In this study, the aggregation structure of fatty acid monolayers was investigated on the basis of transmission electron microscopic studies: the bright field electron micrograph and the electron diffraction (ED) pattern. Also, the surface structure of the monolayers was investigated by a gold decoration method.

Benzene solutions of behenic and myristic acids were prepared at the concentrations of 3.0×10^{-3} and 4.4×10^{-3} $\mathrm{mol\cdot l^{-1}}$, respectively, as spreading solutions. In this study, the subphase temperature (spreading temperature) T_{sp} was 293 K. Table 1 shows T_m

Table 1. Melting points of fatty acids with different length of alkyl chains

Fatty acid(C_n)	Melting point T_m/K monolayer (area modulus)	 bulk (DSC)
myristic acid(C_{14})	278	327.5
palmitic acid(C_{16})	301	335.6
stearic acid (C_{18})	317	342.6
behenic acid (C_{22})	(ca.340)	352.4

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of various fatty acids for a bulk state (by a DSC measurement) and also, for a monolayer state (from the T_{sp} dependence of the maximum area modulus of the monolayer$^{3)}$). It was difficult to evaluate the accurate T_m of a behenic acid monolayer because of the equipmental limitation for raising T_{sp}. T_m of a behenic acid monolayer must be higher than T_m (318 K) of a stearic acid monolayer. The monolayers were transferred onto carbon-covered electron microscope grids by a horizontal lifting method at various surface pressures. The transmission electron micrographs and ED patterns were taken with a Hitachi H-500 electron microscope. Pt-carbon was vapor-deposited onto the monolayer samples with shadowing angle of 23°. To investigate the surface structure of the monolayers, decorating gold was evaporated onto the monolayer samples.

Figure 1 shows the Π-A isotherm for the behenic acid monolayer spread on the water surface at T_{sp} below T_m of the monolayer, and the bright field images and the ED patterns of the monolayers at the surface pressures of 0, 20 and 35 $mN\cdot m^{-1}$. The Π-A isotherm indicates a gas-solid coexisting system without appearance of a liquid expanded state. At 0 $mN\cdot m^{-1}$, the bright field image and ED pattern of the monolayer showed an island structure with high contrast and a hexagonal diffraction spot, respectively. These indicate that the two-dimensional crystallites grow right after spreading a solution on the water surface and also, that all crystallites in the fairly wide area (the diameter of an electron beam was several μm) orient in the crystallographically same direction. With increasing the surface pressure, the bright field images represented the aggregating process of the two-dimensional crystallites, whereas the ED pattern showed the hexagonal spot at every surface pressure. The reason why crystallites arrange their crystallographic orientation approximately in the same direction on the water surface, is unknown at present. However, it is speculated that the sintering behavior caused from fusion or recrystallization at the boundary surfaces proceeds owing to the higher surface pressure of 25 $mN\cdot m^{-1}$, resulting in the formation of a large homogeneous two-dimensional single crystal (monolayer) with a small fraction of crystalline defect. This molecular aggregation type was designated the crystalline monolayer.

Figure 2 shows the Π-A isotherm for the myristic acid monolayer spread

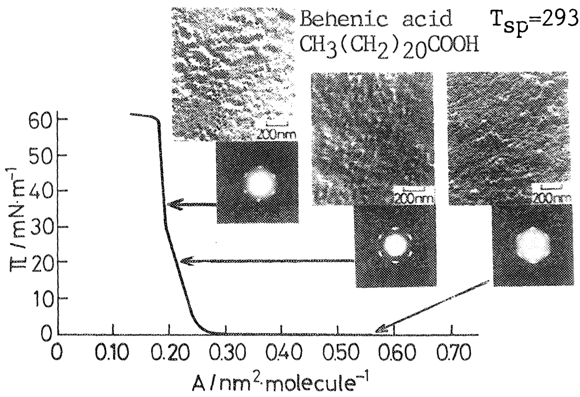


Fig.1. Electron micrographs and ED patterns of behenic acid monolayer at 293 K.

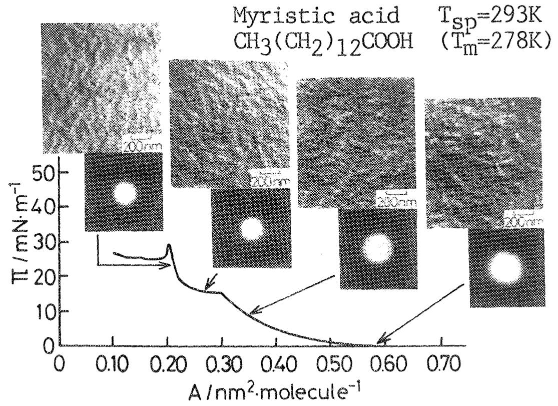


Fig.2. Electron micrographs and ED patterns of myristic acid monolayer at 293 K.

on the water surface at T_{sp} above T_m of the monolayer, and the bright field images and ED patterns of the monolayers at 0, 10, 15, and 23 mN·m^{-1}. A plateau region on the Π-A isotherm was observed, which indicated a solid-liquid coexisting system. The bright field image and ED pattern of the monolayer even at 0 mN·m^{-1} showed an island structure with low contrast and an amorphous halo, respectively. These indicate that isolated domains in an amorphous state grow right after spreading a solution on the water surface. With increasing the surface pressure, the bright field images exhibited the aggregating process of the amorphous domains, while the ED pattern at every surface pressure showed the amorphous halo. Therefore, it should be noted that the phase transition of a monolayer from an amorphous to a crystalline state does not occur by compressing the monolayer up to the collapse pressure at T_{sp} above T_m. Figure 3 shows the schematic representation of the aggregation structure of fatty acid monolayers at different surface pressures. Figure 3(a) shows the aggregating process of a crystalline monolayer at T_{sp} below T_m. There is no plateau region on the Π-A isotherm. As mentioned above, two-dimensional crystallites are formed right after spreading a solution on the water surface. During compressing the water surface, these crystalline domains aggregate and finally form the homogeneous monolayer. On the other hand, the aggregating process of a monolayer at T_{sp} above T_m of the monolayer is shown in Fig. 3(b). A plateau region on the Π-A isotherm is apparently recognized. The monolayer forms the island structure consisting of amorphous domains in which the molecules aggregate randomly on the water surface. With an increase of surface pressure, the amorphous domains aggregate, the molecules start to stand on the plateau region. Finally, all molecules are considerably well arranged in spite of an amorphous state, on the water surface at higher surface pressure. These results indicate that the aggregation structure of a fatty acid monolayer is mainly determined by the magnitude of T_{sp} and T_m of the monolayer.

Furthermore, we investigated the surface structures of crystalline and amorphous monolayers by using a gold decoration technique.[4)] The size of gold colloidal particles on a material surface depends on the surface roughness of the material; the gold particles aggregate to be larger as the material surface is flatter. Figure 4(a) shows the gold decoration patterns of crystalline monolayers at different surface pressures and the schematic representation of the molecular aggregation state, including the average dimension of monolayer domain evaluated from the number of gold particle in a unit area. The gold decoration pattern of the carbon-covered substrate is also shown in this figure. The gold-decorated pattern at low surface pressure showed the two regions, the substrate and the two-dimensional crystallites of which the average colloidal particle size was smaller than that on the carbon-covered

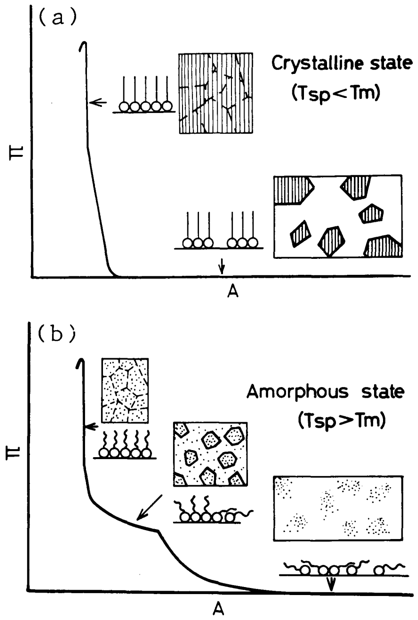
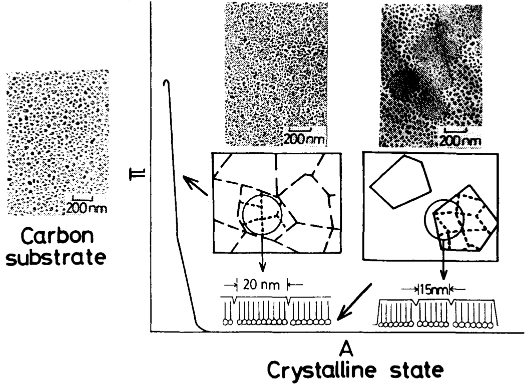


Fig.3. Molecular aggregating process of (a)crystalline monolayer; (b)amorphous monolayer.

substrate, and of which surface was rougher than the substrate surface. At higher surface pressure, the inter-crystallite boundary was not observed on the gold-decorated micrograph. The surface flatness size of the homogeneous monolayer (20 nm) at higher surface pressure was rather larger than that of the crystalline domain (15 nm) at lower surface pressure, indicating that at higher surface pressure the sintering at the boundary surface of crystallites possibly occur. Fig.4(b) shows the gold-decorated patterns of amorphous monolayers at different surface pressures and the schematic representation of the molecular aggregation state. The fairly flat isolated aggregates correspond to amorphous domains in a gel state. At a plateau region on the Π-A isotherm, there are two kinds of amorphous aggregates whose surfaces are rougher and flatter than the substrate surface. The rough surface region may consist of amorphous domains where molecules straightforwardly stand on the water surface. At still higher surface pressure, all molecules stand and the monolayer surface was rougher than that at lower surface pressure, as schematically shown by the molecular aggregation model of Fig.4(b). It is expected that a large two-dimensional single crystal with a small number of defect can be prepared by cooling the amorphous monolayer down to the temperature region below T_m of the monolayer and by further crystallizing the monolayer for a long time. We will report how to prepare a defect-free two-dimensional single crystal elsewhere.$^{5)}$


(a) Bright field image after gold decoration

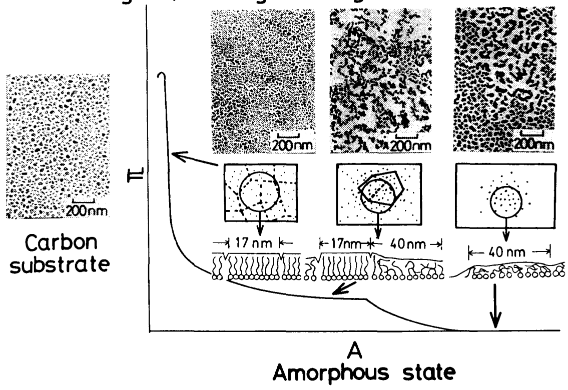

(b) Bright field image after gold decoration

Fig.4. Gold decoration patterns of (a)crystalline monolayer; (b)amorphous monolayer.

In conclusion, the Π-A isotherm for a monolayer represents the aggregating process of isolated domains grown right after spreading a solution on the water surface. Formation of crystalline or amorphous monolayers of fatty acids mainly depends on the magnitude of T_{sp} and T_m of the monolayer. The transition from a amorphous phase (gas or liquid state) to a crystalline one (solid state) was not observed upon compressing a amorphous monolayer on the water surface.

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