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Molecular Aggregation Structure of Barium Stearate Monolayer Based on Electron Microscopy

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Synopsis. Aggregation structure of barium stearate monolayers prepared from a benzene solution at various surface pressures was investigated by using a transmission electron microscope. Two-dimensional crystallites of the monolayer were formed even at the surface pressure of 0 mN·m^{-1}. The monolayer crystallites on the water surface became a continuous phase at 25 mN·m^{-1} and collapsed at 40 mN·m^{-1}. The surface pressure-area isotherm represents an aggregating process of the small two-dimensional crystallites on the water surface, instead of a generally accepted concept on phase transitions among gas, liquid, and solid phases.

It has been generally accepted on the basis of π–A isotherm behavior that monolayer on the water surface is homogeneous at every surface pressure and also that the gaseous monolayer state at very low surface pressure converts into the liquid expanded one, liquid condensed one and finally the solid monolayer state with increasing surface pressure on the water surface. To ascertain this concept, morphology for monolayers prepared from various amphiphiles has been studied.[1–6] However, there has been no morphological observation with diffraction experiment for phase assignment of monolayers at various surface pressures.

In this study, the aggregation structure of barium stearate monolayer transferred onto a substrate at various surface pressures was investigated on the basis of electron microscopic observations, a bright field electron micrograph and an electron diffraction, ED pattern.

Experimental

Benzene solution of stearic acid was prepared at the concentration of 3.5×10^{-3} mol·l^{-1}. The monolayer was spread on the water subphase containing 3×10^{-5} mol·l^{-1} of $BaCl_2$ and 4×10^{-4} mol·l^{-1} of $KHCO_3$ and then, compressed to a given surface pressure at the barrier speed of 48 mm·min^{-1}. The subphase temperature, T_{sp} was maintained at 290±0.5 K. The monolayer was transferred onto a substrate by a horizontal lifting method at the surface pressure of 0 mN·m^{-1} or by a vertical lifting method at 10, 25 and 40 mN·m^{-1}. The transfer rate was 10 mm·min^{-1}. The prepared substrate was Formvar-covered electron microscope grids (200-mesh).[2] It was confirmed by an electron micrograph and an ED pattern that the substrate surface was smooth and the substrate itself was in an amorphous state. Therefore, this substrate was suitable for observation of the monolayer structure by using an electron microscope. Transmission electron micrographs were taken with a Hitachi H-500 electron microscope, operated at 75 kV and a beam current of 2.5 μA. Pt-carbon was vapor-deposited onto the monolayer samples with shadowing angle of 23°.

Results and Discussion

Figure 1 shows the surface pressure-area (π–A) isotherm for barium stearate monolayers spread on the buffered water at T_{sp} of 290 K. This temperature was much lower than the melting temperature, T_m of the monolayer which was estimated from the T_{sp} dependence of the maximum area modulus of the monolayer.[7] This isotherm showed a rapid rise of surface pressure with decreasing surface area. On the basis of a generally accepted concept, this π–A behavior is interpreted as that a gas state monolayer at very low surface pressure converts into a solid state monolayer at higher surface pressure without appearance of a liquid expanded state monolayer. The limiting area for the monolayer was 0.21 nm^2·molecule^{-1}. The value was close to the area of 0.20 nm^2·molecule^{-1} which corresponded to the occupied cross-sectional area of closely packed hydrocarbon chains.

Figure 2 shows the bright field electron micrographs and the ED patterns of barium stearate monolayers which were spread from a benzene solution on the water surface and also, were transferred at the surface pressures of (a) 0, (b) 10, (c) 25, and (d) 40 mN·m^{-1}. The transfer ratios at 10, 25, and 40 mN·m^{-1} were 0.9, 1.0, and 1.7, respectively. The direction of Pt–C shadowing is shown by an arrow. At 0 mN·m^{-1} (a), many isolated domains were observed in the bright field image. At 10 mN·m^{-1} (b), these domains covered almost all region of the water surface. The bright field image of the monolayer at 25 mN·m^{-1} (c) exhibited the fairly uniform, smooth, and continuous monolayer. The bright field image at 40 mN·m^{-1} (d) showed heterogeneous aggregation which was composed of

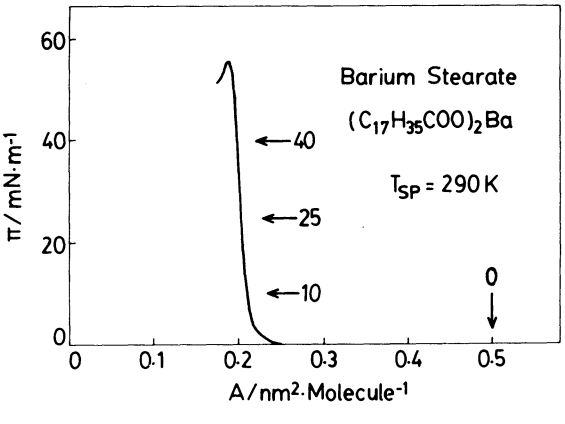

Fig. 1. π–A isotherm of barium stearate monolayer.

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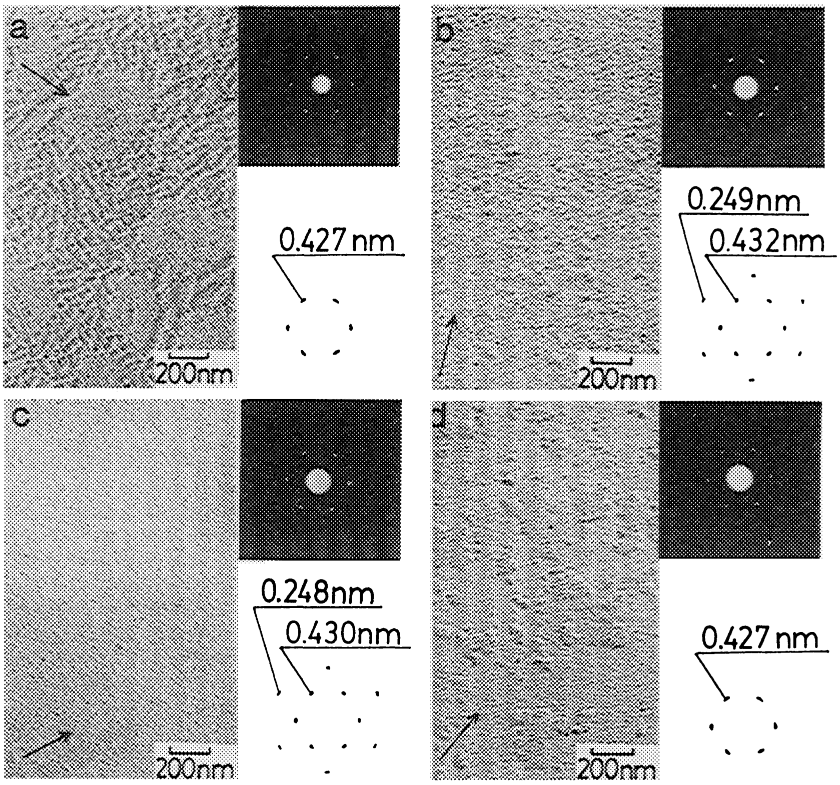

Fig. 2. Electron micrographs and electron diffraction patterns of barium stearate monolayers transferred at (a) $0\,\mathrm{mN\cdot m^{-1}}$, (b) $10\,\mathrm{mN\cdot m^{-1}}$, (c) $25\,\mathrm{mN\cdot m^{-1}}$, and (d) $40\,\mathrm{mN\cdot m^{-1}}$.

partially overlapped domains due to collapse of the monolayer. Figure 2(d) indicates that the monolayer starts to collapse at a lower surface pressure than the generally defined collapse pressure as the peak of the π–A isotherm. This partial collapse of monolayer cause the excess transfer of monolayer with the transfer ratio of 1.7 more than 1. The height of these overlapped domains was evaluated to be 5 nm from the shadowed length of Pt–C. Since the value of 5 nm corresponds to the thickness of a double layer of barium stearate, the monolayer collapses in a similar mechanism proposed by Ries.[8]

Every ED pattern of the monolayers transferred at the surface pressures of 0, 10, 25, and $40\,\mathrm{mN\cdot m^{-1}}$ exhibited sharp crystalline spots with the spacing of 0.43 nm as shown in Fig. 2. At 10 and $25\,\mathrm{mN\cdot m^{-1}}$, the crystalline spots with the spacing of 0.25 nm which is $1/\sqrt{3}$ of the spacing of 0.43 nm, were also observed in the ED patterns. These results indicate that the ED patterns are analyzed as a hexagonal structure and that the spacings of 0.43 and 0.25 nm are assigned to $(10\bar{1}0)$ and $(11\bar{2}0)$ reflections, respectively. When one molecule is assigned to the unit cell, the surface area occupied is estimated to be $0.21\,\mathrm{nm^2\cdot molecule^{-1}}$ which agrees with that found from the extrapolation of the π–A isotherm. It should be noted that the domains observed in the bright field image are in a crystalline state even at $0\,\mathrm{mN\cdot m^{-1}}$ and also, that monolayer crystallites in a fairly wide area (corresponding to an electron beam diameter of several μm) aggregate with the crystallographically same orientation. Therefore, it is reasonable to consider that small two-dimensional crystallites grow right after spreading a solution on the water surface. The reason why crystallites arrange along their crystallographic direction on the water surface, is unknown at present. However, it is expected that crystallographic sintering at the boundary surfaces was caused from fusion or recrystallization at a higher surface pressure of 25 or $40\,\mathrm{mN\cdot m^{-1}}$, resulting in formation of a large homogeneous two-dimensional single crystal (monolayer). For obtaining a larger single crystalline monolayer, it is necessary to anneal the monolayer on the water surface after compressing it to the surface pressure where the monolayer is morphological homogeneous.

The aggregation state of monolayer domains during compression is schematically shown in Fig. 3 in the case of T_{sp} lower than T_m. Barium stearate molecules form two-dimensional crystallites right after spreading a solution (at π_0) as mentioned above. The schematic crystallites are represented by the hatched domains in Fig. 3. The free area (white space) presented among crystallites is reduced with decreasing the surface area from A_0 to A_1. Contact between crystallites gives rise to an increase in surface pressure (at π_1). Monolayer crystallites in surface pressure range between π_1 and π_2 gather closer, resulting in the formation of a large-area monolayer at π_2. At a higher surface pressure than π_2,

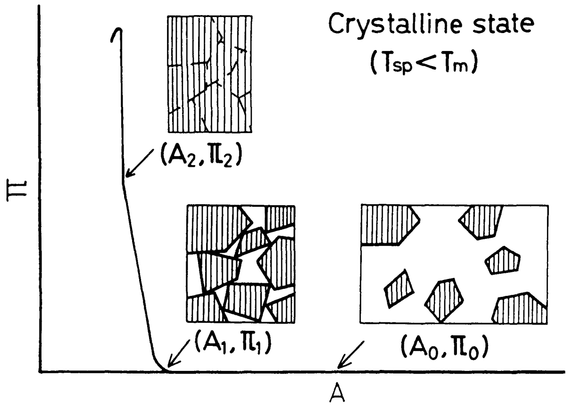

Fig. 3. Schematic representation of aggregation structure of monolayer during compression.

the monolayer starts to collapse locally, even though the surface pressure is lower than the generally defined collapse pressure as the peak of the π–A isotherm. Thus, in the case of barium stearate, a compression process on the water surface corresponds to an aggregation one of monolayer crystallites formed right after spreading a solution. The similar concept was also proposed by other researchers, on the basis of microscopic observations for a polydiacetylene monolayer,$^{9)}$ dialkylammonium monolayer$^{10)}$ and fatty acids or these salts.$^{11)}$

Conclusion

It became apparent that a molecular aggregation state in the barium stearate monolayer is quite different from the generally accepted concept based on the π–A isotherm. Barium stearate molecules aggregate in a crystalline state even at zero surface pressure when the subphase temperature is lower than the melting temperature of the monolayer. Therefore, the π–A isotherm represents an aggregating process of small two-dimensional crystallites on the water surface.

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