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Static Viscoelastic Characteristics-Aggregation Structure Relationships of Monolayers at Air-Water Interface

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The melting temperature, T_m of fatty acid monolayers on the water surface was evaluated from the relationships between the subphase temperature dependence of static viscoelasticities and the aggregation structure of those monolayers. T_ms of myristic, palmitic, and stearic acids in a monolayer state are ca. 278 K, 301 K, and 317 K, respectively. These values are 26-50 K lower than those in respective three-dimensional crystalline states. With an increase of subphase temperature, the aggregation state of those monolayers on the water surface varied from an oriented crystalline state, an unoriented crystalline one, an amorphous one and finally, a dissoluble unstable state.

It has been generally accepted that phase transitions of gas, liquid, liquid condensed, and solid phases occur upon compressing fatty acid molecules on the water surface. However, it was recently proposed that two-dimensional domains were grown at the surface pressure of 0 $mN\cdot m^{-1}$ right after spreading a solution of fatty acid on the water surface.$^{1,2)}$ The aggregation state of monolayer strongly depends on the value of spreading temperature, T_{sp}, in relative to the melting temperature, T_m, of the monolayer on the water surface. In this study, the temperature dependence of static viscoelastic properties of monolayers was investigated in conjunction with morphological observation and electron diffraction study of monolayers. The crystalline relaxation behavior and the melting behavior of monolayers on the water surface were also investigated.

Benzene solutions of myristic (C_{14}), palmitic (C_{16}) and stearic (C_{18}) acids were prepared at the concentrations of 3.7×10^{-3}, 2.8×10^{-3}, and 2.2×10^{-3} $mol\cdot l^{-1}$, respectively. Surface pressure-area (Π-A) isotherms were measured at various T_{sp} with a Micro Proseccer Film Balance System (Sanesu Keisoku Co.Ltd.). The static elasticity, K_S of monolayer on the water surface was evaluated from the Π-A isotherm by using the following equation.

$$K_S = -A(d\Pi/dA)$$

Figure 1 shows the Π-A (solid line) and the $\log K_S$-A (broken line) isotherms for the stearic acid monolayer at T_{sp} of 293 K. The regions of a-b, b-c, c-d in the $\log K_S$-A isotherm correspond to the phases which are generally called a liquid expanded, a liquid condensed, and a solid phase, respectively. The maximum of $\log K_S$, $\log K_{S(max)}$ was observed around the collapsing point (d), where molecules in the monolayer were packed most closely, although locally collapsed domains overlapped the monolayer.[1)] In this paper, the temperature dependence of $\log K_{S(max)}$ was adopted to determine T_m of the monolayer as well as the characteristic viscoelastic behaviors of the monolayer. The monolayer was transferred onto collodion-covered copper grids at various T_{sp} by a vertical dipping method with the speed of 40 $mm \cdot min^{-1}$, at the surface pressures where each monolayer was morphologically homogeneous.[1)] Bright field electron micrographs and electron diffraction (ED) patterns were taken with a Hitachi H-500 electron microscope. Pt-carbon was vapor-deposited onto the monolayer samples with the shadowing angle of 25° for the bright field electron microscopic observation.

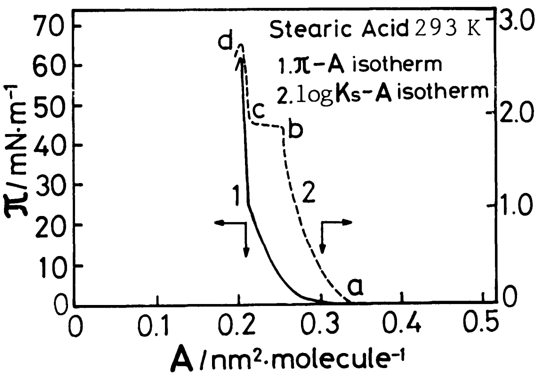

Fig. 1. Π-A and $\log K_S$-A isotherms of stearic acid monolayer.

Figure 2 shows the T_{sp} dependence of $\log K_{S(max)}$ for the stearic acid monolayer on the water surface and the ED patterns of the monolayer transferred at the surface pressure of 20 $mN \cdot m^{-1}$. The slope of the $\log K_{S(max)}$ vs. T_{sp} curve fairly changed at ca. 298 K. In a T_{sp} region lower than 298 K, the ED pattern was a very sharp hexagonal spot, which indicated a regularly packed crystalline state. On the other hand, at a higher T_{sp} region, the electron diffraction spot tended to be arc along an azimuthal direction with an increase of T_{sp}, resulting in the Debye ring. This indicates that molecular and/or crystalline orientations become broader or less regular with an increase of T_{sp} above ca. 298 K. The value of $\log K_{S(max)}$ decreased abruptly at ca. 317 K and the ED pattern at 318 K showed an amorphous halo. This indicates that T_m of stearic acid monolayer on the water surface is ca. 317 K.

Figure 3 shows the T_{sp} dependence of $(10\bar{1}0)$ spacing evaluated from ED

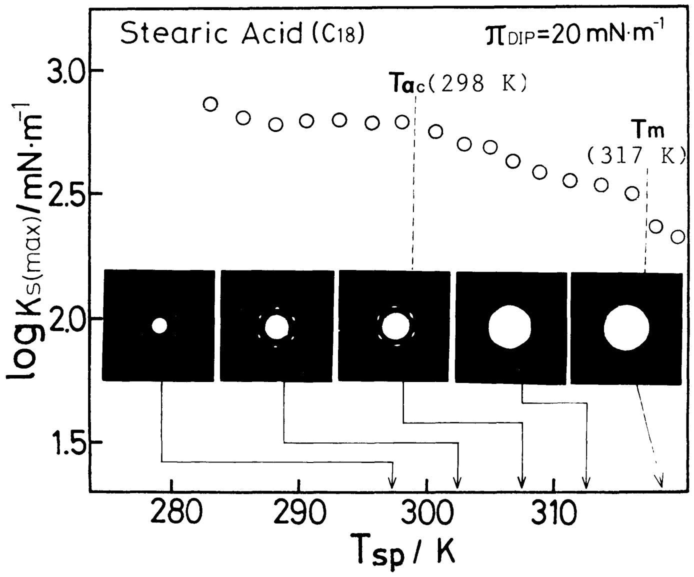

Fig. 2. T_{sp} dependence of $\log K_{S(max)}$ and ED patterns of stearic acid monolayers transferred at a surface pressure of 20 $mN \cdot m^{-1}$.

patterns for stearic acid monolayers of which crystal system was considered to be hexagonal. The $(10\bar{1}0)$ spacing vs. T_{sp} curve exhibited a distinct break at ca. 298 K; the thermal expansion coefficient of crystal lattice became greater above this temperature. In general, the thermal expansion of the lattice spacing starts to deviate from an approximate linear relationship with measuring temperature when abrupt changes of physical or viscoelastic properties in the crystalline region cause an increase in contribution from the anharmonic term for the intermolecular potential energy.$^{3)}$ Therefore, Figs.2 and 3 indicate that the thermal molecular motion in the stearic acid crystalline region must be in close relation to the viscoelastic crystalline relaxation process; this will be accompanied by the remarkable break of the thermal expansion of the $(10\bar{1}0)$ spacing.

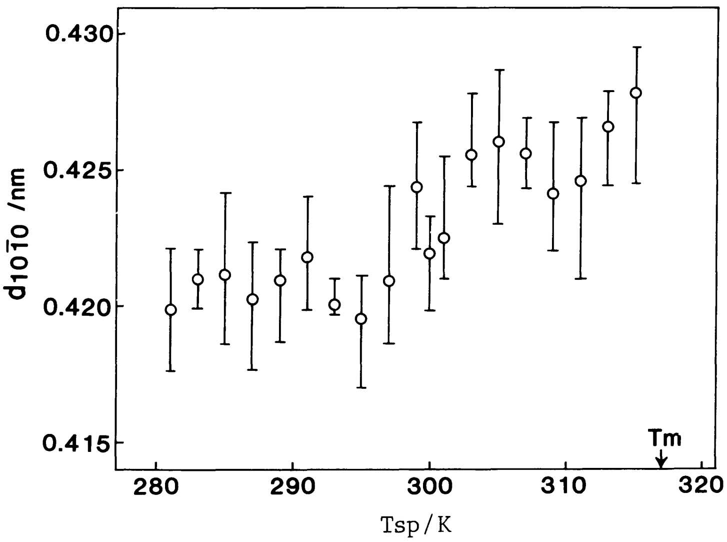

Fig. 3. T_{sp} dependence of $(10\bar{1}0)$ spacing of stearic acid monolayers transferred at a surface pressure of 20 mN·m^{-1}.

Figure 4 shows the T_{sp} dependence of $\log K_{S(max)}$ with the electron micrographs and ED patterns for the myristic acid monolayer transferred at 15·mN m^{-1}. The value of $\log K_{S(max)}$ decreased abruptly at ca. 278 and 294 K. The ED patterns at 274 K and 288 K showed a crystalline ring and an amorphous halo, respectively. Therefore, T_m of myristic acid monolayer at the air-water interface is ca. 278 K. The ED pattern and the bright field electron micrograph of the monolayer at 303 K showed an amorphous halo and a extremely uniform structure, respectively. In a T_{sp} region higher than 294 K, the limiting area of the Π-A isotherm became smaller

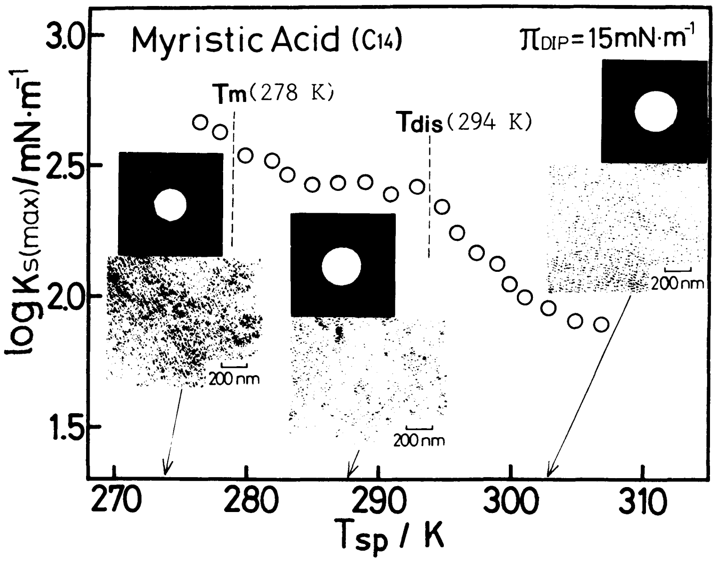

Fig. 4. T_{sp} dependence of $\log K_{S(max)}$, electron micrographs, and ED patterns of myristic acid monolayers transferred at a surface pressure of 15 mN·m^{-1}.

with an increase of T_{sp} or a standing time on the water surface after spreading a solution. This indicates a decrease in the number of myristic acid molecules on the water surface, probably owing to their dissolution into the water phase. Also, in the case of palmitic acid monolayer, the crystalline relaxation temperature, $T_{\alpha c}$ (291 K), T_m (301 K) and T_{dis} (308 K) were evaluated on the basis of $\log K_{S(max)}$-T_{sp} behavior.

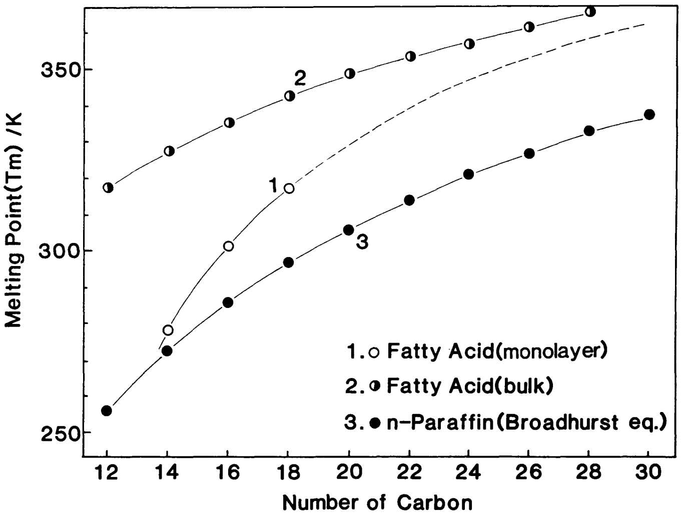

Fig. 5. Variation of T_m with alkyl chain length for (1) fatty acids in a monolayer state; (2) fatty acids in a three-dimensional crystalline state; and (3) n-paraffine in a three-dimensional crystalline state.

Figure 5 shows the variations of T_m with alkyl chain length for fatty acids in a monolayer state, and a three-dimensional crystalline one based on the DSC measurement together with those of n-paraffin in a three-dimensional crystalline one. T_m of n-paraffin was evaluated from the Broadhurst's equation.$^{4)}$ T_ms of myristic, palmitic, and stearic acids in a monolayer state were ca. 278 K, 301 K, and 317 K, respectively. It is difficult to evaluate the accurate T_m of fatty acids with alkyl chain longer than C_{18} in a monolayer state due to equipmental limitation on increasing T_{sp}. T_ms of fatty acids in a monolayer state are much lower than those in a three-dimensional crystalline one as shown in Fig.5. However, the difference between T_ms in these two states decreased with an increase of alkyl chain length; this indicates the formation of more stable monolayer due to an increase of intermolecular aggregation force with increasing alkyl chain length.

In conclusion, the T_{sp} dependence of $\log K_{S(max)}$ was strongly related to the phase transitions of monolayer or thermal motion of amphiphilic molecules. $T_{\alpha c}$ and T_m of monolayer can be evaluated from the temperature dependence of Π-A isotherm and morphological or structural informations at different T_{sp}. It became clear that T_m of a monolayer at air-water interface was much lower than that in a three-dimensional crystalline state.

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