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Surface Pressure Dependence of A-T Isobars and Two-Dimensional Thermal Expansion coefficient of Insoluble Monolayers of Tristearin at the Air/Water Interface[1)]

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Pressure dependence of A-T isobars of insoluble monolayers of tristearin(TS) was measured with the instrument developed in our laboratory. The isobars look like a group of straight lines in the temperature span measured(5-45 ℃). Pressure dependence of the two-dimensional thermal expansion coefficient of the monolayers was calculated by the numerical differentiation of the A-T isobar data with respect to temperature using a simple regression analysis.

Isobaric thermal expansion coefficient is one of the most important physical properties of materials and is obtained by differentiation of isobars with respect to temperature. But two-dimensional isobaric thermal expansion coefficients(α^S) of monolayers at the air/water interface have never been reported, because of the difficulty of measurement of precise A-T isobars. Albrecht and his coworkers have reported A-T isobars of monolayers of some amphiphilic materials.[2,3)] Accuracy of their measurements, however, was not adequate to calculate thermal expansion coefficients of monolayers.

We have developed a microcomputer-controlled instrument for measuring precise A-T isobars of insoluble monolayers, and have reported thermally stimulated area relaxations of monolayers using this instrument.[4,5)] α^S can be calculated by numerical differentiation of the A-T isobar data with respect to temperature using a simple regression analysis which corresponds to the method of least square. The object of this paper is to reports surface pressure dependence of α^S of insoluble monolayerrs of tristearin on the water surface and to compare this with the values calculated from the three-dimensional thermal expansion coefficients of some triglycerides.

Tristearin was purchased from Sigma Chemicals(Sigma grade, 99%, mp, obs. 74.0-74.5 ℃, ref. 71.5 ℃(β-type crystal)) and was used without further purification. Spectro-grade benzene(Dojin Chemicals) was used as a spreading solvent. A Cloehn microsyringe of a gas-tight type was used to spread monolayers of TS. Reproducibility of the spreading technique was less than ±1% in molecular area axis of A-T isobars. Dissolution and/or leak of film material give a serious error to measurement of A-T isobars. If the two isobars measured at temperature rising and at temperature lowering coincide well with each other, one can confirm that there was no dissolution and/or leak of the film material during the measurement. Structural or area relaxation of monolayers also introduces serious errors especially to values of α^S and should be avoided. Thermal treatment of monolayers up to a certain high temperature under a constant surface pressure can eliminate the effect of the area relaxation on α^{S}.4)

Figure 1 shows surface pressure dependence of A-T isobars of TS monolayers on the pure water, measured following the procedures cited above. TS monolayers exhibit no phase transition in the temperature span measured and A-T isobars look like a group of straight lines. At higher pressures, monolayers exhibit partial collapsing at high temperatures pointed by the small upward arrow in the figure, and A-T isobars begin to bend downward. Molecular area depends slightly on surface pressure and only less than 6% of molecular area reduction was observed by changing surface pressure from 10 to 40 mN/m. This is because TS monolayers are in a solid state in these temperature and pressure ranges, and surface compressibilities of the monolayers are very small(0.0015 m/mN at 6 ℃).

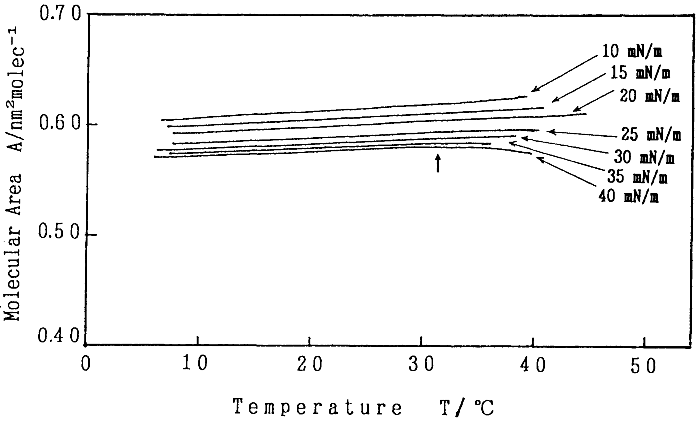

Fig.1. Surface pressure-dependence of A-T isobars of TS.

Figure 2 shows surface pressure dependence of α^{S}, calculated using A-T isobar data in Fig.1. Correlation factors obtained from the simple regression analysis using whole data of the straight parts of the A-T isobars are also shown in the figure. Error-bars mean scatter of α^{S}'s obtaind by the simple regression analysis using about one severalth of A-T isobar data. Filled circles in the left part of Fig. 2 show two-dimensional thermal expansion coefficients of some triglycerides which were estimated from the data of bulk thermal expansion coefficients of them at one atomospheric pressure, assuming that two-dimensional thermal expansion coefficient may be equivalent to two thirds of the three-dimensional one.6) Correspondence of them are quite well. This means that water molecules included in the monolayer are squeezed out above about 10 mN/m. There is a tendency that α^{S} becomes small with increasing pressure but tend to be constant at higher pressures, as shown in Fig.2. This may be a reflection of the character and pressure-dependence of the unharmonicity of averaged intermolecular potential in two-dimensional molecular crystals of tristearin.

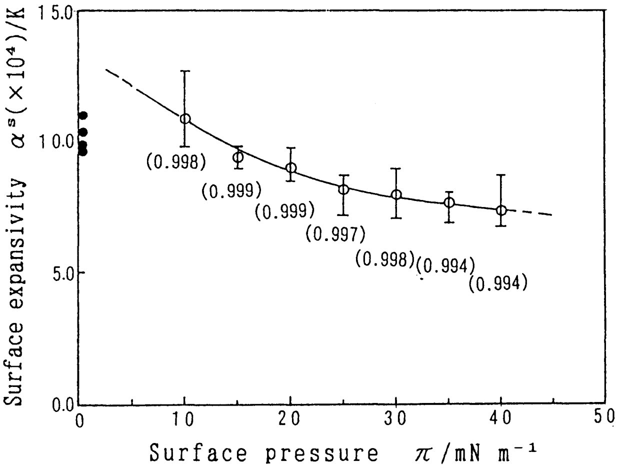

Fig.2. Surface pressure-dependence of α^{S} of TS.

References
1)This paper is part III of the series of papers entitled "Studies on A-T isobars of insoluble monolayers". The part 2 is Ref.5.
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