Physicochemical Studies of Stearic Acid Monolayer-Aluminum Ion Interaction. II. The Surface Viscoelasticity

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In the preceding paper(1) we investigated the interaction of the stearic acid monolayer with aluminum ion in underlying solutions by means of surface pressure measurement and concluded that the interacted monolayer had an analogous structure to the polymeric aluminum distearate monolayer adsorbed by aluminum ion. In order to confirm and further to develop this conclusion, it is most desirable to measure the surface rheological property of the monolayer, because a two-dimensional polymeric structure is most clearly revealed by surface viscoelasticity. Qualitative investigations have alcready been performed(2,3), but no quantitative study has been done with this system. Many investigators have tried to shed light on the rheological behavior of the monolayers of synthetic high polymers and proteins by making use of the aperiodic torsion pendulum(4-7) or the oscillating torsion pendulum(8,9), and it has been shown that these methods indeed give useful information about the structure of the monolayer. However, since the methods used by

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1) K. Motomura and R. Matuura, This Bulletin, **35**, 285 (1962).

2) R. Matuura, ibid., **24**, 278 (1951).

3) H. Kimizuka, ibid., **29**, 123 (1956).

4) K. Inokuchi, ibid., **28**, 453 (1955).

5) K. Inokuchi, ibid., **26**, 500 (1953).

6) T. Tachibana and K. Inokuchi, *J. Colloid Sci.*, **8**, 341 (1953).

7) T. Tachibana. K. Inokuchi and T. Inokuchi, *Kolloid-Z.*, **167**, 141 (1959).

8) C. W. N. Cumper and A. E. Alexander, *Trans. Faraday Soc.*, **46**, 235 (1950).

9) N. W. Tschoegl and A. E. Alexander, *J. Colloid Sci.*, **15**, 168 (1960).

these authors are either instrumentally unsatisfactory or mathematically only approximate in analysis, a new and more exact treatment seems to be required in order to obtain more detailed information about the molecular structure of the monolayer. Here we employed a ring torsion pendulum method similar to that used by Kimizuka[3] and performed an exact mathematical analysis based on Oka and Sato's equation[10]. The object of this paper is to show, from the results of rheological measurements, the structure and constitution of the stearic acid monolayer formed on the substrate solution containing aluminum ion.

Theoretical

The viscoelasticity of a monolayer is usefully expressed by a mechanical model made up of various combinations of springs indicating elasticity and dashpots indicating viscosity. Two examples of models are shown in Fig. 2. In order to evaluate the viscoelasticity, it is necessary to obtain the deformation-time curve of the monolayer under surface shearing stress and to analyze it through a given mechanical model.

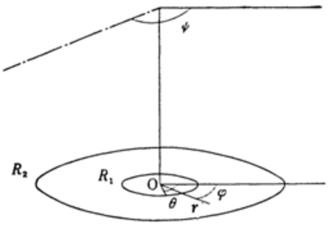

Fig. 1. Schematic diagram of the apparatus.

Let us now imagine a system in which the monolayer is spread between the ring of radius R_1, suspended with a very fine wire of phosphorus bronze just so its lower edge touches the underlying solution, and that of radius R_2, as shown in Fig. 1. When the head of the suspending wire is twisted at a given angle ψ, the ring R_1 will turn round by θ after the time t, and at the same time the monolayer being distant r from the origin O will also be displaced at an angle φ. Suppose, moreover, that the monolayer gets surface shear strain γ under the surface shearing stress S, which is brought about by the restoring torque of the suspending wire. If the monolayer is expressed by a certain mechanical model, we can obtain

$$L\gamma=MS \tag{1}$$

in which L and M are the operators characteristic of the mechanical model. The shear strain γ is subject to the relation

$$\gamma=-r\frac{\partial\varphi}{\partial r} \tag{2}$$

And then the shearing stress is expressed by

$$\sigma\frac{\partial^2\varphi}{\partial t^2}=-\frac{1}{r^3}\frac{\partial}{\partial r}(Sr^2) \tag{3}$$

in which σ is the surface density of the monolayer which is often neglected because of its small value. Using Eqs. 1, 2 and 3, φ can be given in the form of the function of r and t. From this φ and Eqs. 1 and 2, the relation between S and θ becomes

$$2\pi R_1{}^2MS=CL\theta \tag{4}$$

by making use of the expression

$$\theta(t)=\varphi(R_1,\ t) \tag{5}$$

In Eq. 4 C is given by

$$C=4\pi\Big/\left(\frac{1}{R_1{}^2}-\frac{1}{R_2{}^2}\right) \tag{6}$$

On the other hand, if I is the moment of inertia of the ring R_1 and κ the torsion constant of the suspending wire, the equation of motion with regard to the ring R_1 is given by

$$I\frac{\mathrm{d}^2\theta}{\mathrm{d}t^2}=\kappa(\psi-\theta)-2\pi R_1{}^2S \tag{7}$$

By substituting from 4 into 7, this becomes

$$IM\frac{\mathrm{d}^2\theta}{\mathrm{d}t^2}=\kappa M(\psi-\theta)-CL\theta\text{[10]} \tag{8}$$

When the monolayer is very rigid, then $\mathrm{d}^2\theta/\mathrm{d}t^2$ becomes negligibly small. Hence, Eq. 8 reduces to a simple form

$$\kappa M(\psi-\theta)-CL\theta=0 \tag{9}$$

with sufficient accuracy. The approximate formula 9 is to be used throughout this paper, since the monolayer studied in the present experiment is so rigid that the condition for Eq. 9 is almost completely fulfilled. The general equation 8 will be used in another paper

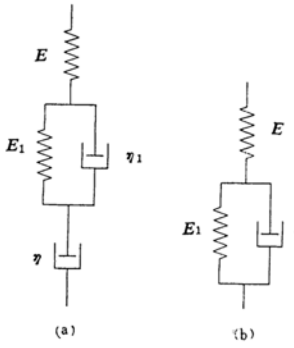

Fig. 2. Mechanical models: (a) four-parameter model; (b) three-parameter model (elasticity+Voigt element).

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[10] S. Oka and Y. Sato, *Bull. Kobayashi Inst. Phys. Res.*, 5, 96 (1955).

for the study of the rheological behavior of high polymer monolayers (which are not so rigid as in the present case).

In the first place let us consider the general mechanical model, i. e., the four-parameter model illustrated by a in Fig. 2. The relation between γ and S for the model is given by

$$\eta_1 \frac{\mathrm{d}^2\gamma}{\mathrm{d}t^2} + E_1 \frac{\mathrm{d}\gamma}{\mathrm{d}t} = \frac{\eta_1}{E} \frac{\mathrm{d}^2 S}{\mathrm{d}t^2} + \left(1 + \frac{E_1}{E} + \frac{\eta_1}{\eta}\right) \frac{\mathrm{d}S}{\mathrm{d}t} + \frac{E_1}{\eta} S \tag{10}$$

It follows thus that the operators $\boldsymbol{L}$ and $\boldsymbol{M}$ are expressed dy

$$\boldsymbol{L} = \eta_1 \frac{\mathrm{d}^2}{\mathrm{d}t^2} + E_1 \frac{\mathrm{d}}{\mathrm{d}t} \tag{11}$$

and

$$\boldsymbol{M} = \frac{\eta_1}{E} \frac{\mathrm{d}^2}{\mathrm{d}t^2} + \left(1 + \frac{E_1}{E} + \frac{\eta_1}{\eta}\right) \frac{\mathrm{d}}{\mathrm{d}t} + \frac{E_1}{\eta} \tag{12}$$

when Eq. 10 is compared with Eq. 1. Inserting the operators into Eq. 9 and arranging, we can obtain a differential equation

$$\frac{\mathrm{d}^2\theta}{\mathrm{d}t^2} + b \frac{\mathrm{d}\theta}{\mathrm{d}t} + \mathrm{d}\theta = \mathrm{d}\psi \tag{13}$$

where

$$b = \frac{\kappa}{\kappa + CE} \left(\frac{E}{\eta_1} + \frac{E_1}{\eta_1} + \frac{E}{\eta} + \frac{C}{\kappa} \frac{EE_1}{\eta_1} \right) \tag{14}$$

and

$$d = \frac{\kappa}{\kappa + CE} \frac{EE_1}{\eta \eta_1} \tag{15}$$

It can easily be found that the solution of Eq. 13 is

$$\theta = \psi - A\mathrm{e}^{-\alpha t} - B\mathrm{e}^{-\beta t} \tag{16}$$

in which A and B are arbitrary constants, and α and β are expressed by

$$\alpha = \frac{b - \sqrt{b^2 - 4d}}{2} \tag{17}$$

and

$$\beta = \frac{b + \sqrt{b^2 - 4d}}{2} \tag{18}$$

When α is much smaller than unity, Eq. 16 can be written in the form of

$$\theta = \psi - A + A\alpha t - B\mathrm{e}^{-\beta t} \tag{19}$$

for small values of t. If the θ-t curve obtained experimentally of a certain monolayer coincides with the expression 16 or 19, it is thought natural that the rheological behavior of this monolayer can be analyzed by the four-parameter model. It is possible, therefore, to estimate the values of A, B, α and β, and, further, of b and d by making use of

$$b = \alpha + \beta \quad \text{and} \quad d = \alpha\beta \tag{20}$$

Thus using the values of A, B, b and d, we can evaluate the viscoelasticity by means of equations

$$E = \frac{\kappa}{C} \cdot \frac{A + B}{\psi - A - B} \tag{21}$$

$$E_1 = 1 \Big/ \left(\frac{C}{\kappa} \frac{\psi - A}{A} - \frac{1}{E} \right) \tag{22}$$

$$\eta_1 = \frac{\kappa}{\kappa + CE} \cdot \frac{E + E_1 + (C/\kappa) EE_1}{b} \tag{23}$$

and

$$\eta = \frac{\kappa}{\kappa + CE} \cdot \frac{EE_1}{d\eta_1} \tag{24}$$

Let us next consider the three-parameter model, the elasticity being accompanied by the Voigt model, as shown by b in Fig. 2. In a way similar as to that of the four-parameter model, it is readily found that for the three-parameter model

$$\boldsymbol{L} = \eta_1 \frac{\mathrm{d}}{\mathrm{d}t} + E_1 \tag{25}$$

and

$$\boldsymbol{M} = \frac{\eta_1}{E} \frac{\mathrm{d}}{\mathrm{d}t} + \left(1 + \frac{E_1}{E}\right) \tag{26}$$

By substituting the operators into Eq. 9, the expression for this model corresponding to Eq. 13 for the four-parameter model is given by

$$\frac{\mathrm{d}\theta}{\mathrm{d}t} + b\theta = d\psi \tag{27}$$

in which

$$b = \frac{\kappa}{\kappa + CE} \left(\frac{E}{\eta_1} + \frac{E_1}{\eta_1} + \frac{C}{\kappa} \frac{EE_1}{\eta_1} \right) \tag{28}$$

and

$$d = \frac{\kappa}{\kappa + CE} \left(\frac{E}{\eta_1} + \frac{E_1}{\eta_1} \right) \tag{29}$$

Then we, by solving Eq. 27, obtain

$$\theta = \frac{d}{b} \psi - A\mathrm{e}^{-bt} \tag{30}$$

A being an arbitrary constant. In the same way as the four-parameter model, from a comparison of the θ-t curve obtained experimentally with the expression 30 the evaluation of A, b and d is made easily. And hence the viscoelasticity can be evaluated by relations

$$E = \frac{\kappa}{C} \cdot \frac{(1 - d/b)\psi + A}{(d/b)\psi - A} \tag{31}$$

$$E_1 = (b - d) E \Big/ \left(\frac{\kappa + CE}{\kappa} d - b \right) \tag{32}$$

and

$$\eta_1=\frac{\kappa}{\kappa+CE}\cdot\frac{E+E_1}{d} \tag{33}$$

This treatment for the three-parameter model leads to the same result as that which has been used to investigate the rheological properties of adsorbed films by Sasaki and Kimizuka[11].

In the third place, let us consider the monolayer having elasticity only. The operators as a matter of course are given by

$$\boldsymbol{L}=1 \tag{34}$$

and

$$\boldsymbol{M}=1/E \tag{35}$$

Therefore, we directly obtain the expression

$$E=\frac{\kappa}{C}\cdot\frac{\psi-\theta}{\theta} \tag{36}$$

from Eq. 9, where θ is independent of t.

Experimental

The measurement of surface viscoelasticity was carried out with the aid of the ring torsion pendulum apparatus used by Kimizuka[2] as shown schematically in Fig. 1. The ring R_1 was a platinum ring 2 cm. in diameter suspended with a phosphorus bronze wire, the torsion constant of which was 1.23 dyn. cm. As for the ring R_2, it was assumed that the radius was replaced by the distance from the origin 0 to the brim of the trough, i. e., 7.5 cm., with sufficient accuracy. The deflection angle θ of the ring R_1 was read by means of the lamp scale method and expressed by the moving distance on the scale.

The experiment was made on the stearic acid monolayer on a 10^{-4} mol./l. aluminum chloride solution and the aluminum distearate monolayer on both water and a 10^{-4} mol./l. aluminum chloride solution as described in the preceding paper[1]. All experimental conditions were entirely the same as in the preceding paper, except that the pH of the underlying solutions was kept constant at 5.5, which is in the region of maximum expansion of the monolayers.

After being spread on the substrate solutions, the monolayers were left to stand for 60 min. before the ring R_1 was deposited and then allowed to stand for another 30 min. because it was found that the values of viscoelasticity depended on the time of film aging.

Results and Discussion

It was found that the monolayer of aluminum distearate shows remarkable viscoelastic behavior even at considerably large areas. Fig. 3 illustrates an example of the θ-t relation obtained at 81.8 Å²/molec. of the aluminum distearate monolayer on water. This relation is well expressed by the equation

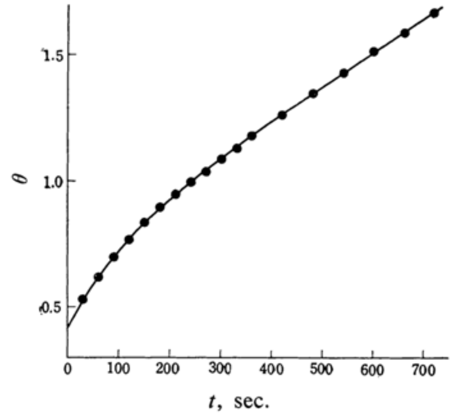

Fig. 3. θ-t curve of the aluminum distearate monolayer on water. Area 81.8 Å²/molec.; Temperature 25°C.

$$\theta=0.714+0.00133\,t-0.297\,\mathrm{e}^{-0.00882t} \tag{37}$$

which is shown as a full line in Fig. 3. Eq. 37 is in the same form as Eq. 19. We can say, therefore, that the surface rheological behavior of aluminum distearate can be explained in terms of the four-parameter model. From this result the values of viscoelasticity can be easily evaluated by applying Eqs. 21, 22, 23 and 24 in the manner described previously. We thus obtain 18.1 dyn./cm., 25.3 dyn./cm., 2.87×10^3 dyn. sec./cm. and 5.65×10^3 dyn. sec./cm. for E, E_1, η_1 and η respectively. These values are large enough to be compared with those of nylon 6 film at an area smaller than the limiting area as studied by Inokuchi[5]. Therefore, it is evident that the aluminum distearate spread on water holds the polymeric structure in the monolayer as well as in bulk and that its surface rheological behavior is due to a two-dimensional network brought about by its linear polymeric structure. Another proof comes from the studies on the aluminum distearate monolayer spread on sodium fluoride solution[12]. The viscoelasticity decreases with increase in the concentration of sodium fluoride, and at 10^{-3} mol./l. no rheological behavior is found anywhere over the area by means of this method. This may be explained by the destruction of the polymer chain through the bonding of fluorine with the aluminum atom in the chain, as stated in the preceding paper. The measured θ-t curves of the aluminum distearate monolayer on water at other areas than 81.8 Å²/molec. are in shape quite similar to that illustrated in Fig. 3. By the same procedure as above, the values

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[11] T. Sasaki and H. Kimizuka, This Bulletin, **25**, 318 (1952).

[12] K. Motomura and R. Matuura, to be published soon.

of viscoelasticity were calculated for various areas of the monolayer. The results are shown in Fig. 4, where these values are plotted against the area per aluminum distearate molecule. It is seen that the viscoelasticity increases first gradually and then a little steeply as the area decreases.

If we accept the view that aluminum distearate is formed in the monolayer when the stearic acid monolayer was spread on aluminum ion, as discussed in the preceding paper, the interacted monolayer will show a rheological behavior. It was really found that the viscoelasticity of the stearic acid monolayer was so large as to be measured by the apparatus described here. Fig. 5 illustrates a typical θ-t curve for the monolayer of stearic acid on aluminum ion of 10^{-4} mol./l. at the area 38.9 Å^2/molec. The curve is essentially similar to that of the aluminum distearate monolayer on water. Furthermore, the curve is represented by

$$\theta=0.552+0.00302\,t-0.143\,\mathrm{e}^{-0.0103t} \qquad (38)$$

bearing a resemblance to Eq. 37. Hence, this monolayer can also be analyzed in terms of the four-parameter model. We, in a like manner, obtained the similar θ-t curves at various areas. In Fig. 6, the values of E, E_1, η_1 and η evaluated from these curves are plotted against the area. It will be seen from Fig. 6

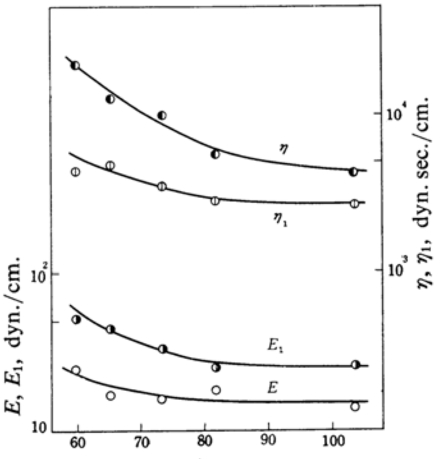

Fig. 4. Viscoelasticity-area curve of the aluminum distearate monolayer on water at 25°C.

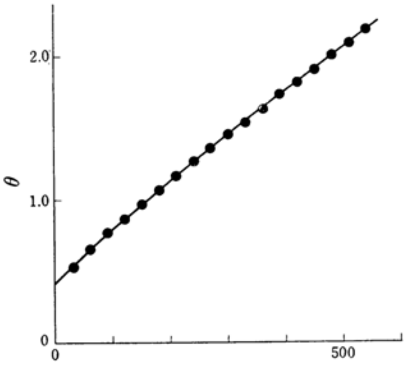

Fig. 5. θ-t curve of the stearic acid monolayer on 10^{-4} mol./l. aluminum chloride solution. Area 38.9 Å^2/molec.; Temperature 25°C.

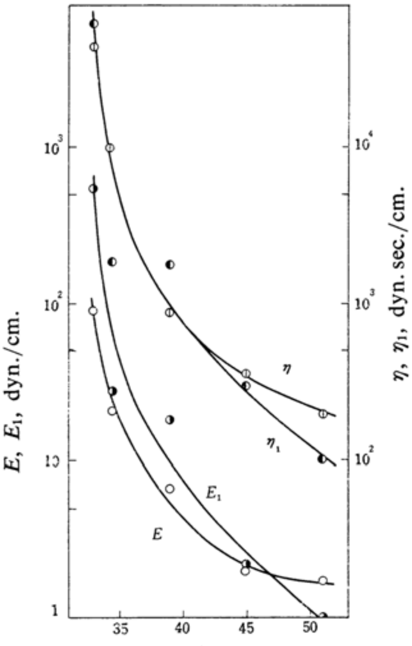

Fig. 6. Viscoelasticity-area curve of the stearic acid monolayer on 10^{-4} mol./l. aluminum chloride solution at 25°C.

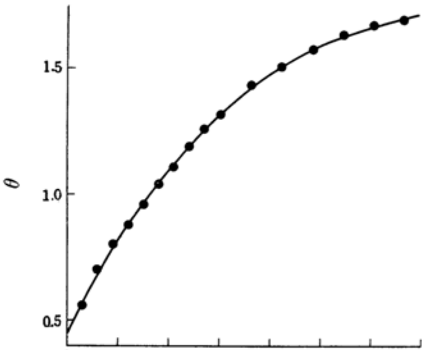

Fig. 7. θ-t curve of the aluminum distearate monolayer on 10^{-4} mol./l. aluminum chloride solution. Area 98.9 Å^2/molec.; Temperature 25°C.

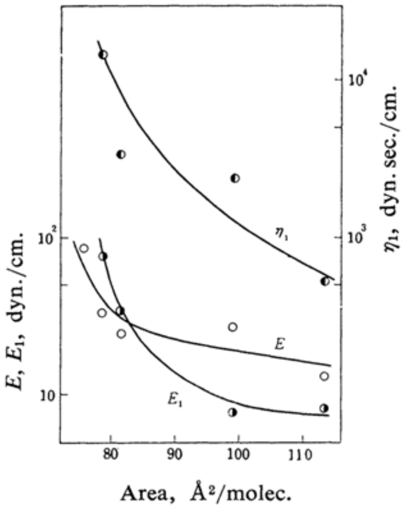

Fig. 8. Viscoelasticity-area curve of the aluminum distearate monolayer on 10^{-4} mol./l. aluminum chloride solution at 25°C.

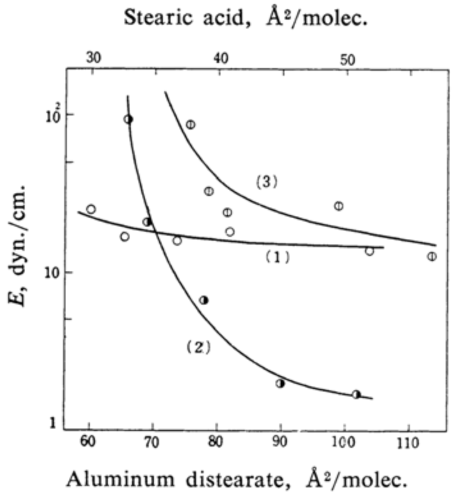

Fig. 9. Comparison among E-area curves of the monolayers of stearic acid and aluminum distearate on underlying solutions at 25°C:
(1) Aluminum distearate on water (○);
(2) Stearic acid on aluminum ion (◑);
(3) Aluminum distearate on aluminum ion (⦶).

that the curves, in contrast with those of aluminum distearate monolayer, rise steeply with a decrease in the area. In addition, it is to be noticed, when Fig. 6 is compared with Fig. 4, that the curves are lower than the latter at larger areas whereas higher at smaller areas. This fact may be more clearly revealed by the comparison between curves 1 and 2 in Fig. 9, which are the E-area curves for the aluminum distearate monolayer on water and the stearic acid monlayer on aluminum ion respectively. This difference leads us to the conclusion that, although the polymeric soaps are probably formed on water between stearic acid and aluminum ion, the structure of the monolayer thus formed is not just the same as that of aluminum distearate.

Now it is necessary to know the action of aluminum ion in the underlying solutions on the aluminum distearate monolayer. As an example of the viscoelastic behavior of the aluminum distearate monolayer on aluminum ion of 10^{-4} mol./l. over larger areas, the θ-t curve at the area 98.9 Å²/molec. is given in Fig. 7. It will be at once recognized that the curve behaves unlike those of Figs. 3 and 5. Since the curve can be represented in the form of the equation

$$\theta = 1.89 - 1.47\,\mathrm{e}^{-0.00320t} \qquad (39)$$

which has just the same form as Eq. 30, the behavior of the monolayer must be expressed with the three-parameter model, the values E, E_1 and η_1 of which are calculated according to Eqs. 31, 32 and 33. In a smaller area, e. g., 75.6 Å²/molec., on the other hand, it was found that the value of θ kept constant throughout the measuring time within experimental errors. This means pure elasticity. Hence, the value is evaluated by use of Eq. 36. The values of elasticity at much smaller areas were too large to be measured by making use of this apparatus. In Fig. 8, the values of viscoelasticity in this system are plotted against the area. In comparing the curves in Fig. 8 with the corresponding curves in Fig. 4, it will be found that the former curves are incomparably higher than the latter at small areas, while equal to or rather a little less than the latter at large areas. It may be possible to say, therefore, that the aluminum ion in underlying solutions acts on the aluminum distearate monolayer through changing the four-parameter model into the three-parameter model, or pure elasticity, and making its values extremely large at smaller areas. In other words, we may be able to conclude that the aluminum ion is adsorbed on the monolayer of polymeric aluminum distearate, probably in a form of basic ion, and strengthens its two-dimensional network structure.

In the preceding paper, in which the interaction of stearic acid monolayer with aluminum ion was discussed from the viewpoint of surface pressure, it was suggested that the interacted monolayer might have the structure of the polymeric aluminum distearate adsorbing aluminum ion. According to this theory, the rheological behavior of both the stearic acid and aluminum distearate monolayers on aluminum ion can be expected to agree. An appreciable difference exists, however, between them, e. g., curves 2 and 3 in Fig. 9, although aluminum distearate seems undoubtedly to be formed in the stearic acid monolayer. In Fig. 9 it is clear that the *E* of film 2 gets greater than that of film 1 and approaches to that of film 3 as the area decreases, while the former is lower than the latter two at large areas. It is quite possible that at much smaller areas the viscoelastic behavior of stearic acid monolayer on aluminum ion finally turns into the elastic one and that films 2 and 3 perfectly agree with each other. Therefore, this difference may be ascribed to the fact that the polymeric aluminum distearate formed in the interacted stearic acid monolayer is of a chain length shorter than that prepared in bulk. As elucidated by Singer's[13] or our[14] equation of state for high polymer, the effect of the chain length on surface pressure is very little when the high polymer has a fairly long one. The above result is not thought, therefore, to conflict with the well agreed results of surface pressure measurement between them. It thus may be concluded that the interacted monolayer of stearic acid with aluminum ion in underlying solution is constructed from the monolayer of polymeric aluminum distearate of a short chain length adsorbing basic aluminum ion.

Summary

By using the ring torsion pendulum method and applying the correct mathematical analysis, surface viscoelasticity measurements were carried out on the monolayers of (1) stearic acid on a 10^{-4} mol./l. aluminum chloride solution, (2) aluminum distearate on distilled water, and (3) aluminum distearate on a 10^{-4} mol./l. aluminum chloride solution. It was found that the rheological behavior of 1 and 2 could be analyzed in terms of the four-parameter model and of 3 by the three-parameter model or elasticity. Also, with regard to the values of viscoelasticity, it was shown that at large areas 1 was smaller than both 2 and 3, and at small areas 1 approaches to 3. From the viewpoint of these results, it was concluded that the interacted monolyer of stearic acid with aluminum ion in an underlying solution might be analogous to the monolayer of aluminum distearate with a short chain length adsorbing basic aluminum ion.

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[13] S. J. Singer, *J. Chem. Phys.*, **16**, 872 (1948).
[14] K. Motomura and R. Matuura, to be published.