Physicochemical Properties of the Surface of Aqueous Solutions VI. Breaking of the Solid Surface

By Hideo KIMIZUKA

(Received May 14, 1953)

In one of our preceding papers, the study on the mechanical properties of the surface of a solution[1] was carried out in relation to the foam stability and a further investigation was continued on the mechanical behavior of the surface[2]. As to the foam stability, however, it may be pointed out that the formation of the coherent adsorbed layer though closely related is not an exact explanation for the stabilizing action of the foam, because the mechanical behaviors thereby investigated was that of the surface film suffering no destruction. On the other hand, some complicated phenomena such as an irreproducibility in the surface tension value[3], and the membrane effect were observed when the surface tension was measured with a solution forming a solid film. So a further study on the mechanical property of the film near the yield point, where so-called time dependent phenomena[4,5] were frequently observed, was attempted to obtain a more plausible explanation for these phenomena.

Experimental and Result

In the present study, the solutions used were chosen so that the liquid might form a solid film[2]. In the first place, a distribution of the life-time of the aqueous film was observed under a constant tension using du Noüy's tensiometer. A platinum ring of the tensiometer, 1.5 cm. in diameter, was just touched to a fresh surface of 1% saponin solution contained in a shallow glass vessel, 6 cm. in diameter and 1.3 cm. in depth. A constant tension was applied to the ring and the breaking time, t, elapsed before the detouchment of the ring from the surface was measured. The experiments were carried out at 28±1°C. The results showed that N, the number of breakings which occurred after a time t, was empirically approximated by the equation,

$$N=N_0\, e^{-mt} \tag{1}$$

where N_0 and m are constants excepting the case in the region of the smaller time. The results of similar experiments under diffrent tensions were shown in Fig. 1. For water, ethyl alcohol and its aqueous solution, m was either zero or infinity.

A measurement of the breaking time as a function of stress was carried out by means of the torsion ring method. The apparatus[2]

---

[1] H. Kimizuka and T. Sasaki, This Bulletin, **24**, 230 (1951).

[2] H. Kimizuka and T. Sasaki, This Bulletin, **25**, 318 (1952); H. Kimizuka, ibid, **26**, 30, (1953).

[3] du Noüy, "Surface Equilibria of Biological and Organic Colloids" *J. Am. Chem. Soc.*, Monograph Series No. 27, Chemical Catalog Comp. Inc., New York (1926).

[4] W. F. Busse, E. T. Lessig, D. L. Loughborough and L. Larric, *J. App. Phys.*, **13**, 715 (1942).

[5] H. Kubota, *Oyo Butsuri* (*J. App. Phys.*), **17**, 286 (1948).

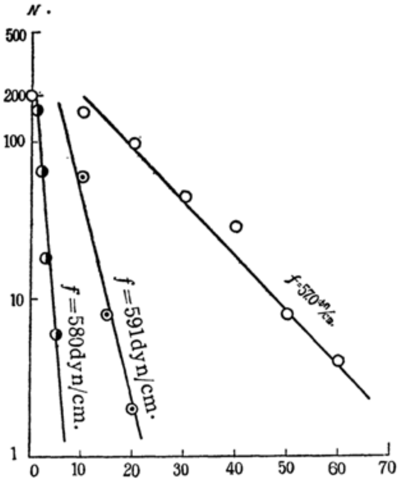

Fig. 1. Distribution of breaking time with constant tension. Saponin solution (10g./l.).

used was essentially the same as described already, but in this case a suspension wire with a torsion constant, κ, of 5.35 dyn. cm. and a platinum ring with diameter of 2.0 cm. was used and the inner cylinder was removed. The breaking time, τ, elapsed before the sudden increase in a strain of the surface, $d\theta$ was measured under a constant torsional force, f $(=\kappa\theta_0$, θ_0 being a torsion angle) for 1 g./l. saponin solution aged for one hour. The temperature of this and all of the following experiments was 10±1°C. One of the results is shown in Fig. 2. The following relation can then be found to hold as shown in Fig. 3 a,

$$log\tau=a-bf \qquad (2)$$

where a and b are constants.

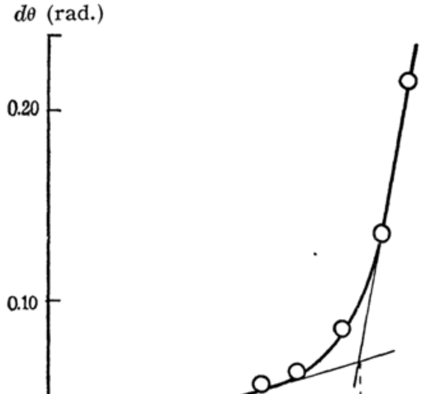

Fig. 2. Strain∼time curve near rupture of absorbed layer of saponin solution (1g./l.) aged for 1 hr. $f=\kappa\theta_0=22.8$ dyn. cm.

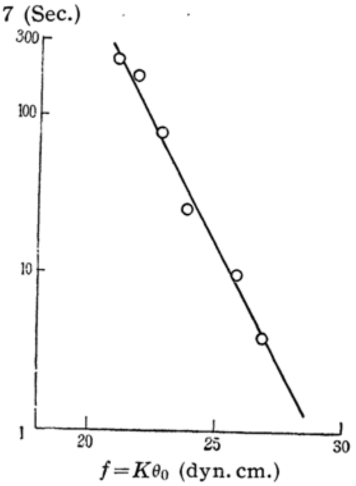

Fig. 3 a. Breaking time as a function of stress. Saponin solution (1g./l.).

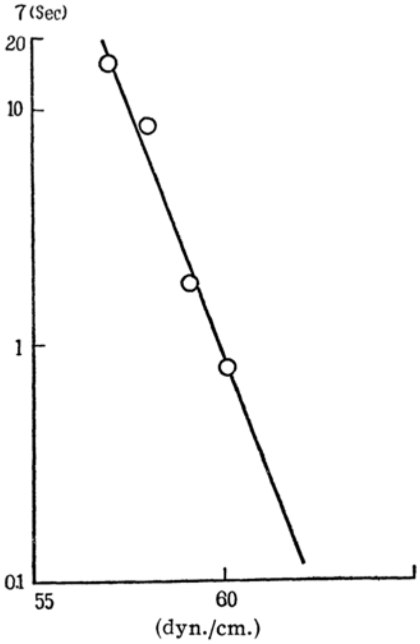

Fig. 3 b. Breaking time as function of stress. Saponin solution (10g./l.).

The torsion ring method was also applied for the measurement of yield value. Immediately after a breaking of the surface by rotating the top of torsion wire with the angle of θ_r under the condition of $\tau \doteqdot 0$, the top was returned to the initial position and θ_a, an angle at which the motion of the ring was stopped, was measured. Thus we obtained the values $\kappa\theta_r$ and $\kappa\theta_a$ which were considered to correspond to the yield value of breaking and solidifying respectively. The membrane effect[1], M, was measured by the capillarimeter with a radius of 0.0284 cm. Now it can easily be seen that $\kappa\theta_r$ and $\kappa\theta_a$ should correspond to M_r and M_a respectively, where M_r and M_a represent the membrane effect acting on the receding and advancing meniscii in the capillary tube. Here the true surface tension is assumed to be situated between the two apparent surface tensions and $M=M_r+M_a$. Both the measurements of the yield value and the membrane effect were carried out for the surfaces of solutions containing various substances aged for one hour. The result is shown in Fig. 4, in which the ordinate represents M; the abscissa, $F_0=\kappa(\theta_r+\theta_a)$.

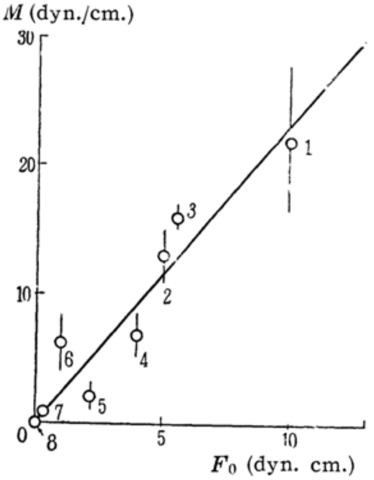

Fig. 4. Membrane effect versus yield value of adsorbed layer diagram for solutions. 1, 0.25 g./l. saponin solution; 2, 0.10g./l. saponin solution; 3, 1g./l. egg albumin solution; 4, 10g./l. peptone solution; 5, 5g./l. polyvinyl alcohol solution; 6, 5×10^{-3} M./l. night blue solution; 7, 5g./l. gum arabic solution; 8, water.

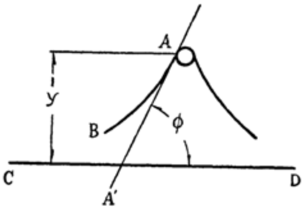

Fig. 5.

A method for the measurement of the surface tension was devised as follows. A platinum ring of the du Noüy's tensiometer was just touched to the surface of a solution, which was pulled upward by the applied force, and a rise of liquid meniscus was measured. Under such a condition, the principal section of the free liquid surface is represented as shown by a curve AB in Fig. 5. In this figure, A shows a cross section of the platinum ring and AA′ is a tangent to the curve AB at the point of contact A, and makes an angle ϕ with the horizontal surface of liquid. Then a rise of meniscus y is given by the equation[6],

$$\rho g y^2 = 2\sigma(1-\cos\phi), \qquad (3)$$

where ρ is the density of liquid; g, the gravity constant and σ, the surface tension. Now if f is a force exerted by the ring per unit length,

$$f=\sigma \sin\phi. \qquad (4)$$

A simple calculation* using Eqs. (3) and (4) leads to the expression,

$$\lim_{y\to0}\frac{df}{dy}=(\rho g\sigma)^{\frac{1}{2}}$$

or

$$\sigma=\frac{1}{\rho g}\left(\lim_{y\to0}\frac{df}{dy}\right)^2 \qquad (5)$$

This relation holds fairly well for ethyl alcohol solutions with varying concentrations as shown in Fig. 6, where σ is measured by the usual method. In the case of the surface exhibiting the nature of a solid film, σ in Eq. (5) should be replaced by σ' of the following equation,

$$\sigma'=\sigma+Ed\zeta, \qquad (6)$$

where E is the elastic constant and $d\zeta$, an increase in surface area with relation to y. Since the condition of $y\to0$ corresponds to that of $d\zeta\to0$, σ' is equal to σ in such a case and again the Eq. (5) is valid, namely the equation gives a true surface tension even when the surface film becomes somewhat

---

6) F. C. Chapman and N. Davy, "Properties of matter". Blackie & Son Ltd., London and Glasgow, (1936) p 104.

* If we assume further the condition of $f=\sigma$ and therefore $\phi=\pi\ 2$ in this calculation, $\sigma=\frac{1}{2}\rho g y^2_0$ results, where y_0 is y when $\phi=\frac{\pi}{2}$, a maximum rise of the meniscus. This equation was confirmed by the experiment using ethyl alcohol solution with varying concentration. The result is shown in Fig. 8.

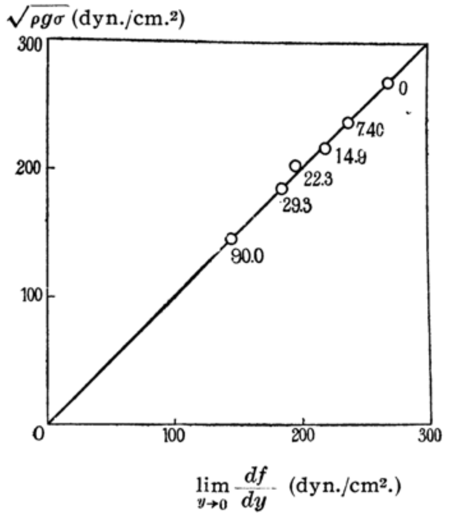

Fig. 6. Relation between $\lim_{y\to o}\frac{df}{dy}$ observed and $\sqrt{\rho g\sigma}$ calculated. Number listed at each point represents the concentration (%) of aqueous ethyl alcohol solution.

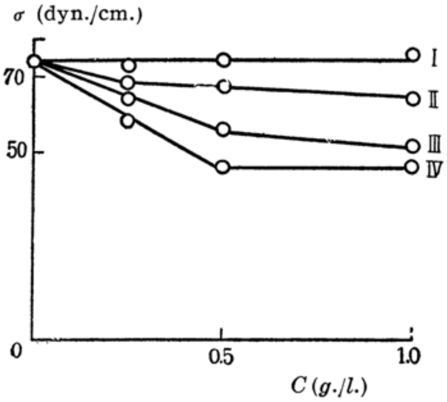

Fig. 7. Surface tensions of saponin solution. Each curve shows the values of surface tension measured by the ring method (II), present method (III) and capillary method (I and IV which correspond to receding and advancing meniscii respectively.).

solid in nature. Thus the present method was adopted for the measurement of surface tension of the saponin solution aged for one hour. The values obtained for various concentrations were plotted in Fig. 7, together with those of apparent surface tension obtained by the capillary rise method with receding and advancing conditions, and the ring method.

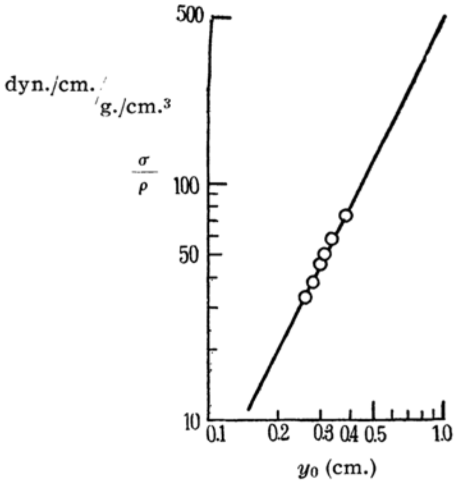

Fig. 8. Ethyl alcohol solution.

Discussion

It has frequently been pointed out for the measurement of surface tension of such a solution as saponin solution that the reproducible results could hardly be obtained even when the experimental conditions such as temperature, concentration and time of ageing were carefully controlled[3]. Among the other factors which are responsible for such a fluctuation, the breaking of the solid film hereby formed can be considered most important. In fact, if the measurement is carried out by means of du Noüy's tensiometer, the measured "surface tension" may actually be the force required for the breaking of the surface film. Results obtained as shown in Fig. 1 evidently show this fact. Kubota[5] obtained a similar result for the breaking of glass which he accounted for by introducing the probability of breaking, m, which was independent of time. Now it was confirmed that in the case of common liquids, m sharply changed from zero to infinity as the external force increased, whereas in the case of saponin solution m changed gradually from zero to infinity.

We should like further to refer to the equations (1) and (2). The phenomena expressed by these equations are liable to conflict with each other. As shown in Fig. 1, however, the deviation from the constancy of the value of m was observed in the region of shorter time, and in fact a frequency of occurrence of breaking showed a maximum in this range of time. A time, τ, at which the maximum frequency was observed was again related with the corresponding stress, f, by the equation (2). This was shown in Fig. 3b.

This relation was further confirmed by the measurement of the thin film withdrawn from the surfaces of 1% solutions of saponin and egg albumin, which was not given here. A possibility may further be considered that the surface tension effect would also be the cause of this phenomenon, but the result of the torsion ring method may exclude such a possibility, since here the surface area is kept constant and the motion of the ring is free from the action of surface tension. Thus the coincidence of the results of both techniques gives us the confirmation that they can be explained by the same mechanism, the breaking of a solid film. A similar relation was also observed for the breaking of high polymer[4] and was also treated theoretically[7]. These fact together with our former result[2] lead us to the opinion that the rupture of an aqueous saponin film rather resembles the breaking of a solid body such as glass or high polymer, and should not be treated as the rupture of the ordinary liquid film. Thus the breaking of the surface film, proved to occur in some range of stress, may result in the irreproducibility of apparent surface tension, if we do not specify the time required for the rupture of film, for instance, to be sufficiently small. A number of explanations[8] for the foam stability have already been presented, but they all neglected to take into account of this fact.

As shown in Fig. 4, the membrane effect was proportional to the yield value of the solid film, which was valid for the several solutions. This will be a confirmation of the view presented in a preceding paper[9] that the membrane effect is a measure of the strength of the surface.

As pointed out before, the irregularity of surface tension is due to the rupture of solid film, so a method free from such an influence is required for a measurement of true surface tension. The technique devised proved to be applicable for common liquids as shown in Fig. 6, which showed a good agreement with the result obtained by the usual method for ordinary solutions. On the other hand, the apparent surface tension of saponin solution measured by the usual method was somewhat higher than that by the present method as shown in Fig. 7. This probably means that the usual method involves an inevitable rupture of surface film. Fig. 7 also showed that the true surface tension is situated between two apparent surface tensions measured previously by a capillarimeter[9].

Summary

(1) The rupture of aqueous saponin film was studied by measuring the variation of the frequency of the breaking with tension as well as by measuring the breaking time as a function of stress. The results showed that the irreproducibility of the observed data upon surface tension was due to the breaking of the solid film and this mechanism was also responsible for the nature of the stability of such a foam as that produced by saponin, which was also considered to consist of solid film.

(2) A new method for the measurement of surface tension, applicable to the solution forming a solid adsorbed layer, was presented.

(3) It was shown that the membrane effect is a breaking stress of the adsorbed layer.

In conclusion, the author expresses his hearty thanks to Prof. T. Sasaki for his kind guidance and encouragement throughout this study and he is also indebted to Dr. T. Tanaka of this University for his kind suggestion and criticism. A part of the cost of this research has been defrayed from the Scientific Research Expenditure of the Ministry of Education given to Professor Sasaki.

Department of Chemistry, Faculty of
Science, Kyushu University,
Fukuoka

---

[7] A. Tobolsky and H. Eyring, *J. Chem. Phys.*, **11**, 125 (1943).

[8] T. Sasaki, *Kagaku no Ryoiki*, **5**, 16 (1951).

[9] H. Kimizuka and T. Sasaki, *Memoirs of the Faculty of Science, Kyushu University, Ser. C*, **1**, 197 (1950).