Physicochemical Properties of the Surface of Aqueous Solutions. II. Foam Stability and Mechanical Properties of Surface

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Introduction

It has been generally accepted that the viscoelastic properties of the surface of a solution has an intimate relation to the various phenomena occurring in them such as the foam or the emulsion formation.(1) In these relations, we have already studied the foam of saponin solution, especially in connection with the surface tension, the membrane effect and the semiquantitative measurement of the surface viscosity of the aqueous solution.(2), (3) In the present paper the results of further experiments on these lines are described.

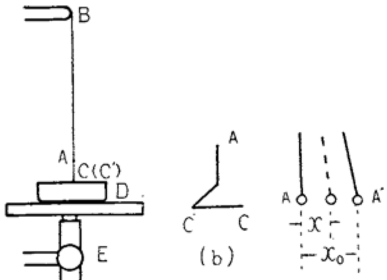

Fig. 1.—Surface viscometer.

Apparatus and Method

Up to the present, various methods have been employed for the measurement of the surface viscosity.(1), (4) In the present study, however, a new and simple apparatus was employed as shown in Fig. 1a. In this figure AB shows a fine thread of glass with the diameter of 0.02 cm. and the length of 30 cm., of which one end (B) is fused to a firm glass rod support, while a platinum wire with horizontal part CC′ of 1 cm. in length as shown in Fig. 1b is fixed to the other end (A). Again in Fig. 1a, D is a shallow glass vessel with the diameter of 6 cm. and the depth of 1.5 cm., in which a solution for measurement is introduced. E is a table, carrying the vessel on it and is able to move vertically by means of a screw.

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(1) R. E. Wilson and E. D. Ries, "*Colloid Symposium Monograph*," **1**, 145 (1923); D. Talmud, S. Suchowolskaja and L. Lubman, *Z. Physik. Chem.*, A **151**, 401 (1930); etc.

(2) T. Sasaki, This Bulletin, **15**, 449 (1940); T. Sasaki and S. Mitui, *ibid.*, **18**, 259 (1943).

(3) H. Kimizuka and T. Sasaki, *Mem. Fac. Sci., Kyûsyû University, Ser. C*, **1**, 197 (1950); T. Sasaki, unpublished.

(4) L. Fourt and W. D. Harkins, *J. Phys. Chem.*, **42**, 897 (1938); E. R. Washburn and H. R. R. Wakeham, *J. Am. Chem. Soc.*, **60**, 1294 (1938); L. Fourt, *J. Phys. Chem.*, **43**, 887 (1939).

The measurement of the surface viscosity is carried out as follows. Platinum wire CC′ is first forced to shift from the rest position A (in the air), fixed by a suitable device to a certain position A′ as shown in Fig. 1c, and the distance between A and A′ is measured. Then the surface of solution is carefully forced up untill it just touches the platinum wire at A′. After a desired time of aging of the surface, the platinum wire is set free and allowed to return from A′ to A under the action of force chiefly exerted by the elasticity of glass thread. Now the successive measurements of the position of platinum wire and accordingly the distance X from A is measured with the time t. When we plot $\ln X$ against t is plotted, and a linear relation can be obtained, as follows;

$$\ln X = \ln X_0 - kt. \tag{1}$$

Differentiating Eq. (1) with respect to time, an equation of the form can be gained:

$$l\frac{dx}{dt} + mx = 0,$$

where

$$k = m/l. \tag{2}$$

Eq. (2) means that the motion of platinum wire is governed by two forces: namely a restoring force mx, proportional to the deflection of glass thread, and a viscous resistance $l\ dx/dt$, proportional to the velocity of platinum wire, mainly exerted by the surface of a solution. Consequently, m is a constant relating to the elasticity of glass thread, and l is a measure of surface viscosity. Since m is known ($m=2.16\times10^{-3}$ dynes/cm.), the relative surface viscosity coefficient l can be calculated according to Eq. (2). It can be noted here, that a lack of a constant term in Eq. (2) is an indication of the absence of surface elasticity. For carrying out the experiment, the initial displacement given to the platinum wire, x_0, is kept constant to 0.2 cm., and x is measured by means of a comparator to the accuracy of 10^{-3} mm. Whole apparatus is set in a large glass vessel to keep it free from the occasional contamination such as dust.

The surface tension was measured by means of du Noüy's tensiometer and a capillarimeter. The membrane effect was also measured which was expressed by the difference between the apparent surface tension calculated from the capillary rise under the condition of receding and advancing menisci.(3)

For the measurement of the foam formation, 10 cc. of solution is introduced in a well stoppered test tube of 1.5 cm. in diameter and 17 cm. in length, and is shaken fifty times for ten seconds with an amplitude of 12 cm. After shaking, the height of the foam zone (h) produced just after the stop of shaking and the time (τ) required for the foam to breakdown into half of its initial volume were measured.

Samples used were the commercial one and were not purified further. Water used for the preparation of the solution is freshly distilled. The experiments were carried out at room temperature.

Results of Experiments

In order to visualize the surface viscosity of a certain solution, a series of experiments was carried out which is shown in Table 1. Accuracy of the value l is ±0.01 g./sec.

Table 1

Sample	Experimental condition	Time of aging, hr.	Surface viscosity l, g./sec.
Water	Pt wire touching a surface	0	0.00
	〃	5	0.00
	Pt wire dipping in water	5	0.00
Saponin solution (0.030 g./l.)	Pt wire touching a surface	5	0.60
	Pt wire dipping in solution	5	0.00

The results of measurements of the surface tension σ, surface viscosity l, foam height h and life of foam τ are shown in Fig. 2 where l and σ are the values referred to a solution surface aged for one hour. In Fig. 2 the ordinate represents the substances under investigation where the numbers in brackets indicate the concentration (in percentage) of solutions employed, and the abscissa, τ, h, σ and l.

The measurements of the surface viscosity, surface tension, height of foam, life of foam and membrane effect were also carried out with the saponin∼ethyl alcohol∼water system containing a fixed amount of saponin (0.030 g./l.) and varying amount of ethyl alcohol. These values were plotted against the logarithm of concentration in mol./l. of ethyl alcohol as shown in Fig. 3, where the values of the surface viscosity and surface tension are those

Table 2

Effect of Electrolyte on the Life and Height of Foam of Saponin Solution (0.030 g./l.)

Electrolyte	Concentration, N	pH	Surface viscosity l, g./sec.	Life of foam τ, hr.	Height of foam h, cm.
—	0	5.9	0.10	0.5	1.2
HCl	1×10^{-2}	2.0	0.10	0.5	1.2
KCl	5×10^{-1}	5.9	15.0	4.0	1.2
$BaCl_2$	5×10^{-4}	5.9	145.	25	1.2
$AlCl_3$	3×10^{-5}	3.0	280.	26	1.2
$Th(NO_3)_4$	5×10^{-6}	2.0	350.	28	1.2

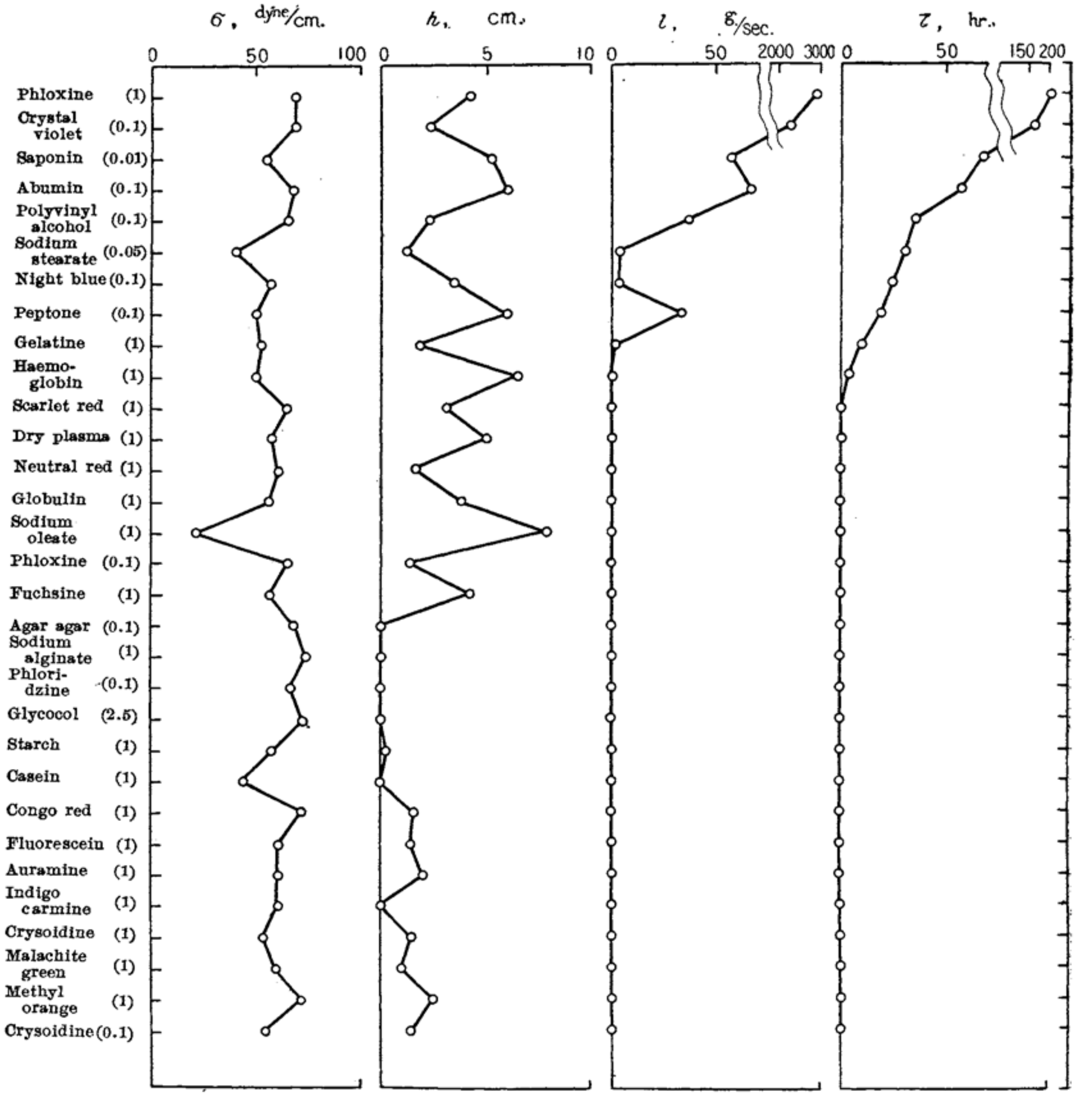

Fig. 2.—Surface tension σ, height of foam h, surface viscosity l and life of foam τ of solutions.

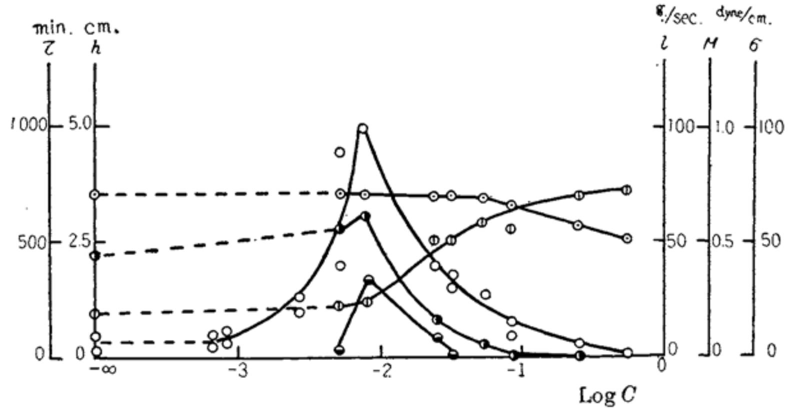

Fig. 3.—Saponin∼ethyl alcohol∼water system: C; concentration of ethyl alcohol in mol./l.; ○ life of foam, τ; ⦶ height of foam, h; ◒ surface viscosity, l; ⊙ surface tension, σ; ◑ membrane effect, M.

of the solution surface aged for one hour. The similar measurements were also carried out for the saponin$\sim$electrolyte$\sim$water systems containing the fixed amount of saponin (0.030 g./l.) and varying amount of electrolyte. The results are tabulated in Table 2. Here *p*H was controlled by hydrochloric acid.

Discussion

As shown in Table 1, no appreciable amount of viscosity was susceptible by the present device in the surface and interior of distilled water, and also in the interior of many solutions. Consequently, it must be emphasized that the apparent viscosity frequently observed in the surface of aqueous solution is considered to be due to the surface only.

Many investigators have studied the formation of the coherent adsorbed layer in the surface of the aqueous solution. Wilson and Ries(1) showed qualitatively that the surface plasticity is parallel with the foam stability. Rehbinder(5) also reported a similar result. It can be seen in Fig. 2 that a close correlation can be found only between the surface viscosity and the life of foam, while no correlation between any other pairs of properties can be found. Wo. Ostwald(6) pointed out that the solutions of saponin, sodium stearate, night blue, gelatine, albumin and peptone which showed a remarkable membrane effect were capable of producing the extremely stable foam. These circumstances are just the same as in present experiment.

The result of measurements with the saponin$\sim$ethyl alcohol$\sim$water system is shown in Fig. 3, in which a distinct correlation between the membrane effect, the surface viscosity and the life of the foam can be found, *i. e.*, all these quantities exhibit sharp maxima at the same concentration of alcohol. The surface tension and the foam height, however, do not show a simple correlation to these quantities. Wo. Ostwald(6) made the measurements of the membrane effect and the foam height, and concluded that no direct correlation could be found between them. As discussed in the preceding paper,(3) however, the membrane effect can be interpreted as the measure of mechanical strength of surface layer, so it might well be considered to relate rather to the foam stability than to the foaminess or foam height as in the present experiment. The formation of such a stable coherent adsorbed layer by the addition of ethyl alcohol is considered to be due to its action of dehydration towards saponin with a subsequent promotion of the saponin adsorption to the surface. At a high concentration of alcohol, however, the life of foam again becomes almost zero resulting perhaps from the preferential adsorption of alcohol in the surface layer with the exclusion of saponin. This may also offer an explanation for the fact that the surface tension and the life of foam decrease rapidly at the same region of the concentration of alcohol.

In Table 2, the effect of electrolytes upon some properties of the aqueous saponin solution is shown. There we can see a marked valency effect of added cation even in high dilution upon the surface viscosity and the life of foam of the saponin solution. Cataphoretic behavior indicates that saponin is a negative colloid,(7) so that these effects may be explained as the coagulation of the adsorbed layer of saponin by electrolytes, which will be compared with the case of the stabilization of the gelatine foam by the added electrolytes studied by one of the present authors(8) and also with some other cases of the protein foam.(9),(10) In Table 2, it is also confirmed that the surface viscosity and the foam life are closely related to each other, while the height of foam shows no simple relation to both of them.

Further, the assumption in the preceding paper(3) that the membrane effect is not a phenomenon of the hysteresis of wetting, but is the indication of the formation of the coherent adsorbed layer and is therefore a measure of strength of surface film, is in good agreement with the experimental facts shown in Fig. 3. Recently Nakagaki(11) accounted for the foam formation of aqueous solutions of alcohols and several electrolytes assuming that the foam stability is closely related to the energy required to remove the unit area of adsorbed layer from the surface of the solution, thereby using the Gibbs' adsorption equation. But the systems studied in our experiment are those in which the surface tension changes irregularly with time, and frequently even an irreversible surface gelation takes place. Therefore Gibbs' adsorption equilibrium cannot be considered to hold in such a case. We should seek for some other factors to arrive at a more

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(5) P. A. Rehbinder and A. A. Trapeznikov, *Comptes rends* (*Doklady*) *de l'Academie des Sciences d l' U. S. S. R.*, **18**, No. 7, 423 (1938); *ibid*, 427 (1938).

(6) Wo. Ostwald and A. Steiner, *Kolloid-Z.*, **36**, 342 (1925); Wo. Ostwald and M. Meiszner, *Kolloidchem.-Beih.*, **26**, 1 (1926).

(7) R. Ruyssen and R. Loos, *J. Colloid Sci.*, **2**, 429 (1947). Present authors also confirmed this.

(8) T. Sasaki, unpublished.

(9) J. M. Perri and F. Hazel, *J. Phys. Colloid Chem.*, **51**, 661 (1947).

(10) W. C. Tolman, A. G. Brown and J. W. McBain, *J. Am. Chem. Soc.*, **71**, 3129 (1948).

plausible explanation. Burcik⁽¹²⁾ and Matalon⁽¹³⁾ explained the foam formation upon somewhat different viewpoint. Burcik emphasized the importance of the change with the time of the surface tension, and regarded the surface viscosity to be required only in the case of a remarkable foam formation. Our systems are considered to belong rather to the latter case, but a more precise explanation of the mechanism should be made in future.

Summary

1. The surface viscometer, the main part of which consisted of a fine vertical thread of glass, carrying a horizontal platinum wire at its lower end, was devised for the measurement of the surface viscosity of solutions.

2. The measurements of the surface viscosity as well as some other surface properties of solutions of a number of dyes and saponin were carried out. The effect of coexisting alcohol and inorganic electrolyte for the saponin solution were also examined. The results showed a close correlation between the surface viscosity, the life of foam and so called membrane effect.

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(11) M. Nakagaki, This Bulletin, **23**, 127 (1950).
(12) E. J. Burcik, *J. Colloid Sci.*, **5**, 421 (1950).
(13) R. Matalon, *Compt. rend.*, **227**, 634 (1948).