Physicochemical Properties of the Surface of Aqueous Solutions. III. Mechanical Behavior of Surface of Micellar and Macromolecular Solution*

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Introduction

Recently the methods and concepts of modern rheology have been applied to the investigations on the mechanical properties of the surface of aqueous saponin solution.(1), (2) The present authors have also studied the surface viscosity of aqueous solutions foaming when shaken.(3) The surface viscometer thereby employed was, however, unfortunately unsuitable for the quantitative measurements of surface rigidity and surface viscosity coefficient. So the present authors have attempted further experiments to obtain more detailed results by means of a torsion ring method. The present paper describes the mechanical behaviour of the surfaces of solutions thus measured.

Experimental

The essential part of the apparatus used is shown in Fig. 1. In this figure, A is a platinum ring of 4 cm. in diameter suspended by a phosphorbronze torsion wire, B, of 0·04 mm. in diameter and 30 cm. in length, the torsion constant of which being 0.494 dyne/cm. A shallow glass vessel C of 6 cm. in diameter and 1.3 cm. in depth, contains a solution for measurement. D is a glass cylinder of 1 cm. in diameter and 1.3 cm. in height, and M is a small mirror for the measurement of an angle of deflexion of the platinum ring. C and D are placed concentrically with each other. The apparatus shown in Fig. 1 is set in a closed vessel to keep it free from occasional contamination.

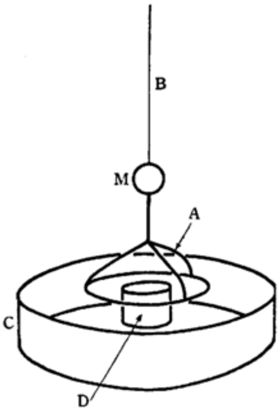

Fig. 1.

To carry out an experiment, the platinum ring is allowed to come in contact with the surface of the solution concentrically both to C and D. After the desired time of aging of the surface, the top of the torsion wire is rotated by a definite angle, and each successive position of the platinum ring expressed by an angle of rotation, θ, is measured with time by means of a lamp and scale method. As the surface film is distorted with the ring, θ is considered to be a strain of the surface.

In case of pure elastic deformation, the relation between a strain, θ, and a stress applied to the surface, $\kappa(\theta_0-\theta)$, κ being a torsion constant of the suspension wire and θ_0, a rotated angle initially given to the top of torsion wire, is expressed by the equation:

$$\theta=\frac{\kappa}{E}(\theta_0-\theta), \qquad (1)$$

where E is a constant proportional to the surface rigidity, G, as shown by the following relationship:

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* This work was reported at the meeting for general discussion of colloid chemistry held in Kyoto, on Nov. 19, 1950, under the auspices of the Chemical Society of Japan.

(1) J. R. van Wazer, *J. Coll. Sci.*, **2**, 223 (1947).

(2) A. A. Trapeznikov, *Kolloid Zhur.*, **12**, 67 (1950).

(3) H. Kimizuka and T. Sasaki, This Bulletin, **24**, 230 (1951).

$$G=\frac{E}{4\pi}\,\frac{\left(\frac{1}{r_1^2}-\frac{1}{r_2^2}\right)\left(\frac{1}{r_2^2}-\frac{1}{r_3^2}\right)}{\left(\frac{1}{r_1^2}-\frac{1}{r_3^2}\right)}\equiv KE \qquad (2)$$

where r_1, r_2 and r_3 are the radii of the shallow glass vessel, wire ring and inner glass cylinder respectively. The value of K was 0.0315 cm.$^{-2}$ in the present case.

In the case of pure viscous flow, the rate of deformation is given by the equation;

$$\frac{d\theta}{dt}=\frac{\kappa}{R}(\theta_0-\theta), \qquad (3)$$

and the constant R is related with surface viscosity coefficient as shown by the following relationship,

$$\eta=KR. \qquad (4)$$

As will be described later, the surface of solutions investigated generally exhibited the mechanical behaviour in which the elastic and viscous deformations were superposed.

As we could not detect any perceptible amount of bulk viscosity, the viscoelasticity observed solely came from the surface itself, just as in the case of the preceding paper.(3) Of samples used, saponin was purified by electrodialysis(4) and crystal violet, by salting out.(5) The horse serum albumin was a highly purified specimen, kindly supplied by Mr. Ômura, of Takeda Pharm. Ind. Ltd. and purified polyvinyl alcohol in degree of polymerization of 1200, kindly supplied by Mr. Kai, of Dep. Applied Chem., Fac. Tech., Kyûsyû University, Both of these were used without further purification. The time of aging was kept to one hour throughout this experiment. The time scale was taken in a range from 60 to 300 sec. The experiments were carried out at room temperature, 17 ± 2°C.

After each meaurement, $\theta\sim t$ curve and $d\theta/dt\sim\theta$ curve were drawn, the corresponding mechanical model was constructed and the related constants were calculated.

Viscous deformation.—The surface of 0.100 g./l. saponin solution exhibited pure viscous deformation. The result was shown in Fig. 2.

Maxwell model.—The surface of 0.002 g./l. polyvinyl alcohol solution behaved according to Maxwell model. The equation of motion, except for $t=0$, is

$$\frac{d\theta}{dt}=\frac{E\kappa}{R(E+\kappa)}(\theta_0-\theta). \qquad (5)$$

The value of E and therefore G can be calculated according to equations (1) and (2) from the measurement of instantaneous elastic deformation. Then the value of R and therefore η can be calculated from the observed data using equations (4) and (5). The result was shown in Fig. 3.

Non-Newtonian flow.—The surface of 10^{-3} mole/l. crystal violet solution exhibited this behaviour. In this case, the empirical relationship* between the rate of deformation and the strain could be expressed by the equation;

$$\log\frac{d\theta}{dt}=A-B\theta, \qquad (6)$$

where A and B are constants. The result was shown in Fig. 4.

Maxwell model with non-Newtonian flow.—The surface of 0.500 g./l. horse serum albumin solution exhibited this behaviour. The empirical equation, except for $t=0$, was similar to the equation (6). The result was shown in Fig. 5.

Voigt model.—The surface of 0.250 g./l. saponin solution exhibited this behaviour the result was shown in Fig. 6. The equation of motion is

$$\frac{d\theta}{dt}=-\frac{E+\kappa}{R}\theta+\frac{\kappa}{R}\theta_0. \qquad (7)$$

E can be calculated by the equation;

$$E=\frac{\kappa(\theta_0-\theta_r)}{\theta_r} \qquad (8)$$

in which θ_r is θ when $d\theta/dt=0$. R and η can be calculated according to the equations (4) and (7).

Three parameter model.—The surface of 0.100 g./l. polyvinyl alcohol solution exhibited this behaviour. The result was shown in Fig. 7. The equation of motion, except $t=0$, is

$$\frac{d\theta}{dt}=-\frac{EE'+\kappa(E+E)}{R(E'+\kappa)}\theta+\frac{\kappa(E+E')}{R(E'+\kappa)}\theta_0. \qquad (9)$$

The term of retarded elasticity, E, can be calculated by the equation

$$E=\frac{E'E^*}{(E'-E^*)} \qquad (10)$$

where E' is instantaneous elasticity and E^* is given by the relationship;

$$E^*=\frac{\kappa(\theta_0-\theta_r)}{\theta_r} \qquad (11)$$

in which θ_r is the value of θ when $d\theta/dt=0$. R can be calculated according to the equation (9).

Discussion

In the deformation of viscous flow and the Maxwell model, θ increases with time, finally reaching θ_0, an angle initially given to the top of torsion wire, and this behaviour permits no

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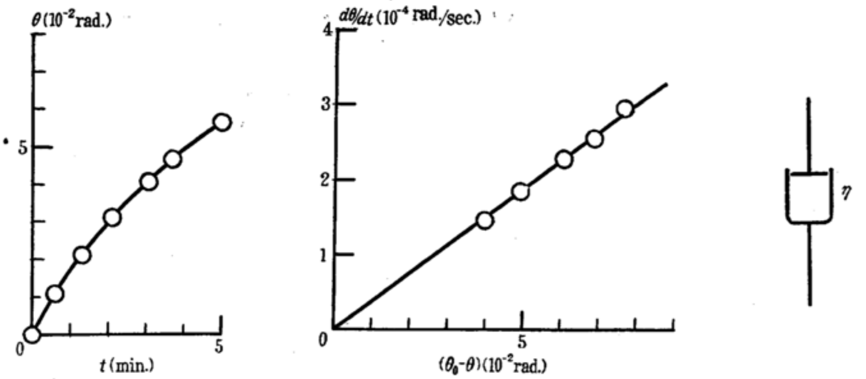
(4) G. Klein, "Handbuch der Pflanzen Analyse" 1932, III, 1109.

(5) C. Robinson and H. A. T. Mills, *Proc. Roy. Soc., A* **131**, 576 (1931).

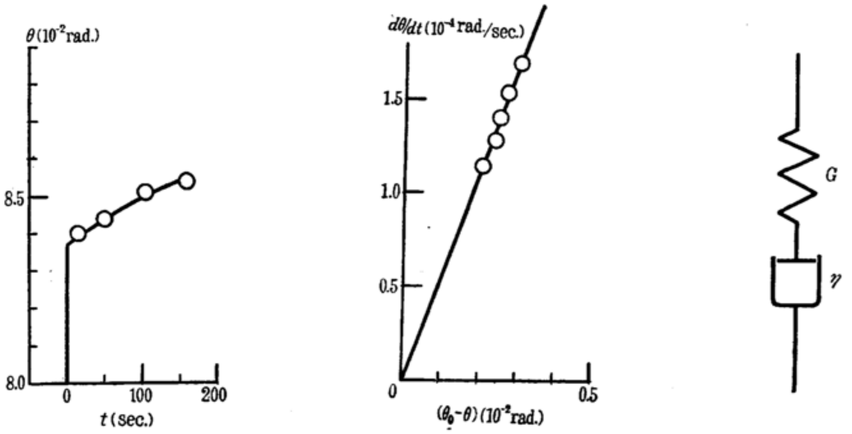


(a) $\theta \sim t$ curve
$\theta_0 = 0.0872$ rad.

(b) $d\theta/dt \sim (\theta_0 - \theta)$ curve

(c) Model
$\eta = 3.89$ g./sec.

Fig. 2.—Saponin solution (0.100 g./l.).

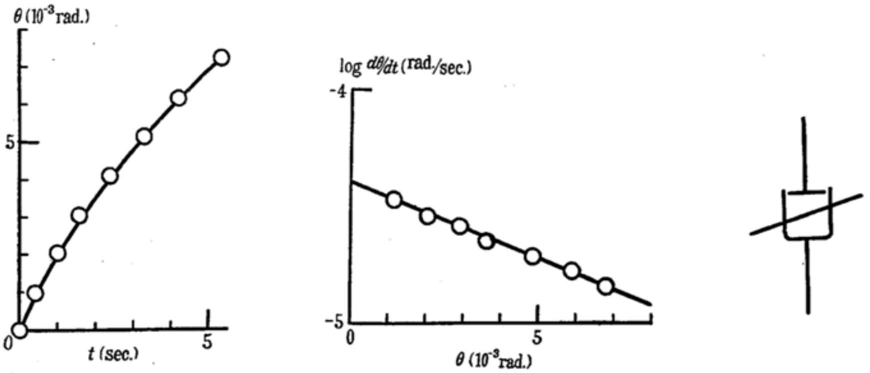


(a) $\theta \sim t$ curve
$\theta_0 = 0.0872$ rad.

(b) $d\theta/dt \sim (\theta_0 - \theta)$ curve

(c) Model
$G = 7.34 \times 10^{-4}$ dyne/cm.
$\eta = 1.15 \times 10^{-2}$ g./sec.

Fig. 3.—Polyvinyl alcohol solution (0.002 g./l.).

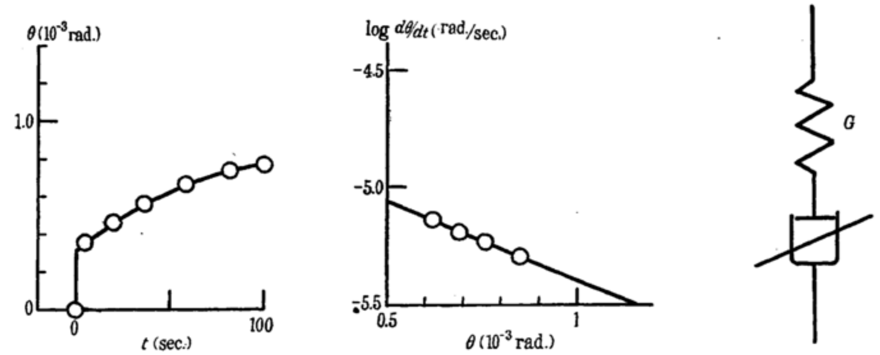


(a) $\theta \sim t$ curve
$\theta_0 = 0.0872$ rad.

(b) $\log \frac{d\theta}{dt} \sim \theta$ curve

(c) Model

Fig. 4.—Crystal violet solution (10^{-3} mole./l.).

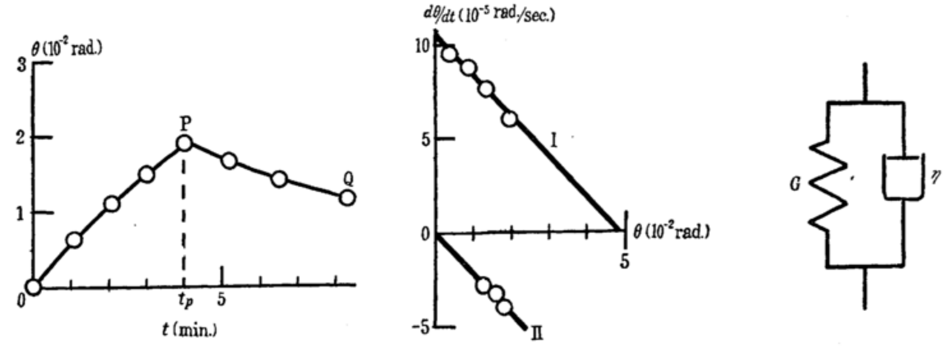


(a) $\theta \sim t$ curve
$\theta_0 = 0.872$ rad.

(b) $\log \frac{d\theta}{dt} \sim \theta$ curve

(c) Model
$G = 4.32$ dyne/cm.

Fig. 5.—Horse serum albumin solution (0.500 g./l.).

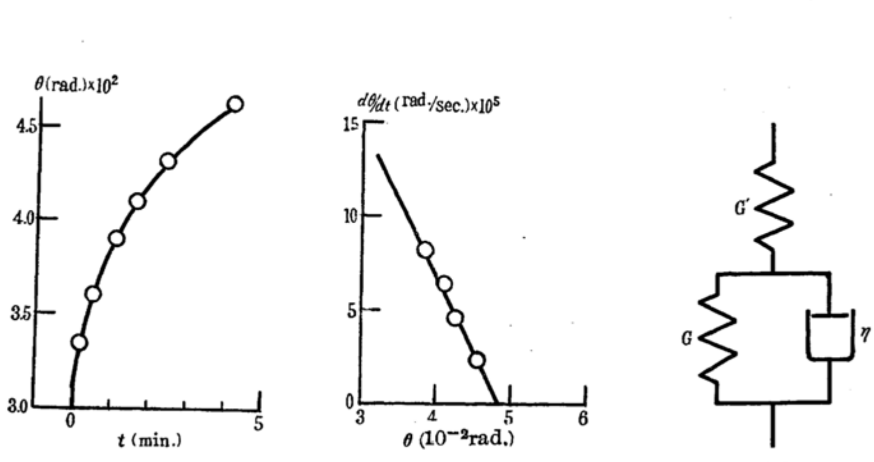


(a) $\theta \sim t$ curve
$\theta_0 = 0.0872$ rad.

(b) $d\theta/dt \sim \theta$ curve
Lines I and II correspond to
OP and QP in (a) respectively.

(c) Model
$G = 1.27 \times 10^{-2}$ dyne/cm.
$\eta = 13.3$ g./sec.

Fig. 6.—Saponin solution (0.250 g./l.).



(a) $\theta \sim t$ curve
$\theta_0 = 0.174$ rad.

(b) $d\theta/dt \sim \theta$ curve

(c) Model
$G' = 6.90 \times 10^{-2}$ dyne/cm.
$G = 9.30 \times 10^{-2}$ dyne/cm.
$\eta = 53.2$ g./sec.

Fig. 7.—Polyvinyl alcohol solution (0.100 g./l.).

other interpretation than these mechanical models. On the other hand, the Voigt and three parameter model may be replaced by somewhat different interpretation under the conditions of the present experiment, viz., the Voigt model may possibly be replaced by purely plastic flow and the three parameter model, by the Maxwell model with yield point. In this connection, Fig. 6 might offer the means for the correct interpretation of the mechanical behaviour. In Fig. 6a, the change in effective torque from $\kappa(\theta_0-\theta)$ to $-\kappa\theta$ at time t_p caused the deformation of the film to reduce from θ to zero as shown by the portion PQ. The corresponding $d\theta/dt\sim\theta$ curve was shown as II in Fig. 6b. If the behaviour can be described according to the Voigt model, the following equation must hold

$$\frac{d\theta}{dt}=-\frac{(E+\kappa)\theta}{R}. \tag{12}$$

In the case of plastic flow, the residual deformation should remain after the torque was changed to-$\kappa\theta$. The result showed an absence of yield value in the surface and the correctness of the Voigt model in this case. For the three parameter model, the similar result can be obtained.

The non-Newtonian flow observed may be interpreted to be either of Eyring's non-Newtonian flow or quasi-viscous flow, which cannot be decided clearly at least in the present experiment.

In the present experiment, the value of θ could be measured down to 10^{-4} radian and the angle of torsion, θ_0, initially given to the top of torsion wire was ranged between 0.1 and 1 radian, so that the rigidity could be measured in the region from 1.5×10^{-5} to 150 dynes/cm., according to equations (1) and (2). The lower limit of viscosity measurement proved to be 1.5×10^{-3} g./sec. by a similar calculation. As was mentioned above, the measurement of low rigidity and viscosity requires a suspension wire of low torsion constant. Since the surface of solution may be of a low yield value if any,(1) it is advisable to use the suspension wire of torsion constant as low as possible for the measurements of mechanical properties of surface without disturbing an adsorbed layer.

It should be noticed that the above viscoelastic constants were obtained referring to the time scale of the present experiment, while the complete description of the mechanical behaviour requires the information of a complete viscoelastic spectrum of the material.(6) For the mechanical model of the surface of saponin solution, Wazer(1) presented the Voigt model, while Trapeznikov,(2) the four parameter model consisting of a series combination of a spring, a Voigt model and a dashpot. Difference between these results is probably due to the difference in the experimental conditions.

Summary

1. A torsion ring method using a suspension wire of low torsion constant was employed for the measurement of a surface viscosity and rigidity of aqueous solutions.

2. The mechanical behaviours of the surfaces of the solutions of saponin, polyvinyl alcohol, crystal violet and horse serum albumin aged for one hour were analysed and expressed using mechanical models. The corresponding rigidity and viscosity were estimated.

3. The mechanical models observed were the Newtonian flow, non-Newtonian flow, Maxwell model with Newtonian or non-Newtonian flow, Voigt model, and three parameter model consisting of a series combination of a spring and a Voigt element.

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(6) T. Alfrey, Jr., "Mechanical Behavior of High Polymers," Interscience Publishers, Inc., New York, 1948, pp 116-175.