Rheology of Surface Films. II. A Surface Rheometer for Measuring the Film Creep under Constant Shear Stress[1]

By Kiyoshi INOKUCHI

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Introduction

In a previous paper[2], it has been proved that the rheological study of monomolecular films is a valuable tool for gaining more insight into the structure of materials. Before further development of this study is attempted, it is first necessary to establish the standard procedure of the measurement. The most simple and convenient method of this study would be to determine the creep as a function of time after applying the constant stress to the film materials. The apparatus[2]

1) Presented at the Symposium of Colloid Chemistry of the Chemical Society of Japan, Nov. 1952, Fukuoka.

2) K. Inokuchi, This Bulletin, **26**, 500 (1953).

used in the previous paper, although it involves the determination of creep against time, was not satisfactory in achieving the quantitative analysis of the creep curve, since the stress was not kept constant during the test, but decayed with the creep. In fact, quantitative analysis of the data obtained with the previous apparatus becomes rather involved and often impractical, when the experiment is carried out with films, the rheological properties of which are more or less complicated. The desirable condition is that the stress remains constant throughout the creep test. In this paper, an apparatus useful under such condition is described.

Construction of Apparatus

The essential elements of the apparatus consist of a ring and a suspending wire similar to those used in the previous case. The torque applied to the ring is supplied from the distorsion of the wire. In order to realize the condition of constant stress, it is only necessary to maintain the twisted angle of the torsion wire, which is given at the beginning of the measurement, to be constant during the experiment. In the present apparatus, such mechanism is automatically conducted by a phototube relay system. The essential part is divided into the following two systems: (1) optical system, and (2) driving system.

(1) Optical System Fig. 1 illustrates the

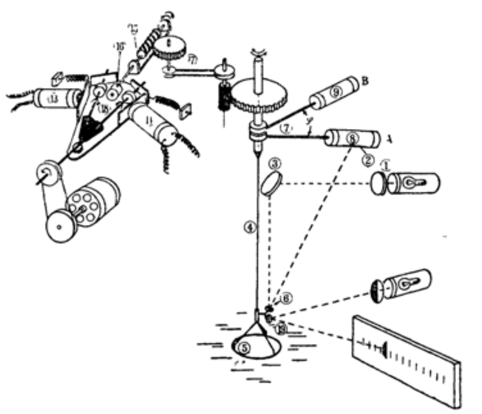

Fig. 1. Schematic view of the apparatus

schematic view of the apparatus. A beam of parallel light, passed through a condensing lens (1), is projected to the first mirror (3) which is fixed closely near the torsion wire with oblique inclination so that the light beam is made parallel to the torsion wire (4). The ring (5) provides a small concave mirror (6) of about 4 mm. in diameter which moves with the rotation of the ring. This second mirror (6) reflects a part of the parallel light from the first mirror (3) to form an intense light spot at a certain point within the plane determined by the wire (4) and the center of the mirror (6). Such a design of the optical system would enable the angular displacement of the light spot to be equal to that of the ring, because the projecting light is made parallel to the rotating axis of the mirror (6). Thus, if the driving of the torsion head is so conducted that it always moves together with the light spot, the condition of constant stress would be satisfied. The conduction mechanism of the torsion head is as follows.

The torsion head provides two rods (7) of about 15 cm. long, extending outwards at right angles to it, at each end of which phototube housings (8, 9) are attached respectively. These rods can be turned around the torsion head and be fixed at any position desired. Each of the housings encases two RCA–921 phototubes (A, B) respectively with each photosurface downwards. Each housing provides a narrow and long slit (2) of 2×40 mm. along the median line of its ventral side respectively, so that the photosurface can receive the light beam through the slit, when the position of the rod is properly adjusted.

(2) Driving System The driving of the torsion head is wholly conducted by a phototube relay system. The principal manner is as follows: as soon as a photosurface receives light, the driving system of the torsion head is so actuated that the head rotates toward one direction, whereas once the photosurface becomes dark, it is inversely actuated so that the head rotates toward the opposite direction. Such mechanism would render the torsion head a reciprocating motion about the light spot if the motion of the light spot is sufficiently slow compared with that of the torsion head. Such a function is quite similarly given to both phototubes (A) and (B), and the alternative use of these tubes, either (A) or (B), is achieved by the switch (10) (see Fig. 3).

The essential elements of the arrangement employed in the driving system are indicated in the functional block diagram of Fig. 2. The

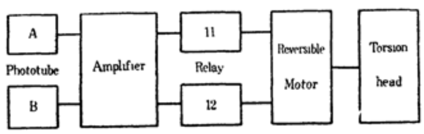

Fig. 2. Block diagram of driving mechanism using phototube relay.

two-step amplifier is ordinarily designed as illustrated in Fig. 3. The amplified photocurrent actuates the relays (11, 12) which transfer the photosignal to the reversible motor, which in turn drives the torsion head toward the alternative directions. Each of the relays (11, 12) is separately actuated by the phototubes (A) and (B), respectively, and the alternative use of them is also accomplished by the reversible switch (10). Each relay provides two contacts respectively, which intermit the rectified current for the reversible motor according to the following mechanism. Even when the relay is

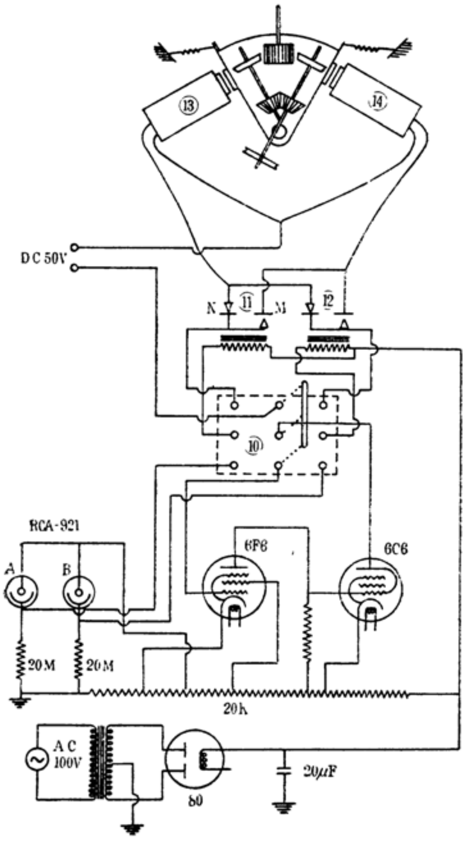

Fig. 3. Schematic circuit of phototube amdlifier

at rest, one of these contacts (for example, M) is closed by means of a spring, while another contact (N) is opened. Once the relay is actuated, however, the situation is inverted, that is, the contact (M) is opened, and (N) is closed. Since each contact is connected to the magnets (13, 14) of the reversible motor respectively, the reciprocating motion of the motor takes place according to whether or not the relay is actuated.

The construction of the reversible motor will be apparent when referred to Fig. 1 and 3. The gear shaft (15) with a friction rotor (16) is connected to the torsion head through the gear system (17). The reciprocating motion of the rotor is transmitted through the friction gear clutch assembly (18) which alternatively works by actuation of the magnet, either (13) or (14).

Principle of Operation

Suppose that the ring is allowed to touch the surface of the water covered with the film materials, being suspended by untwisted torsion wire, and the position of the phototube (A) is so adjusted that the photosurface just receives the light beam from the mirror (6) of the ring. If the switch (10) is so turned that the phototube (A) becomes active, and the phototube (B) is at rest, the torsion head would, according to the mechanism mentioned above, be driven toward one direction until the light spot is left outside of the slit of the phototube housing and accordingly the photosurface becomes dark, whereas once the surface becomes dark, the torsion head begins to return to the position where the light spot again enters into the slit. Here the situation becomes the same as at the beginning, and such to and fro motion further continues. In other words, the torsion head exercises a reciprocating motion about the light spot.

It must be mentioned here that the ring on the film, although suspended by a reciprocally twisted torsion wire, caused hardly perceptible reciprocating motion, but took a static position, so long as the amplitude as well as the period of the reciprocating motion of the torsion head was sufficiently small. Accordingly the film does not suffer any alternative shear in spite of the reciprocating motion of the torsion head. In the present apparatus, the frequency of the reciprocating motion was about 2–3 times per second and the amplitude of the motion was not more than 0.5 degree when the system was well adjusted.

Now let the second tube (B) be set by φ angles with respect of the first tube (A) and the switch (10) be so turned that the second tube (B) becomes active, leaving the first (A) at rest. Since, in this instance, the photosurface of the tube (B), which becomes newly active, remains still dark, the torsion head will be so driven until the second tube (B) catches the light spot. Here, the wire is twisted by φ. If the ring thereafter causes rotation owing to the stress imposed on it, the torsion head would also moves together with the moving light spot making a fine reciprocating motion about it, and the constant distortion of the wire will be maintained during the experiment.

At a later time, if the switch is returned to the original position so that the first tube (A) becomes active while the second (B) is at rest, the torsion head would inversely be driven so that the torsion of the wire is always set to the original state (zero). Such a condition would provide the curve of the after-effect of the testing film upon removal of the stress.

In the present study, where the motion of the ring in question was sufficiently slow compared with the rate of motion of the torsion head, there was no appreciable time lag of the head for pursuing the light spot, and the relative situation between the ring and the torsion head is considered to be constant throughout the experiment.

Performance

Briefly, the operation of the present apparatus is as follows. The ring is allowed to touch the clean surface of water. The phototubes are so set that the light spot from the mirror (6) just fits at the photosurface of the first tube (A) through the slit, and the second (B) is laid by φ angles with respect of the first (A). The testing film is now spread on the water surface. The position of the ring at respective time is measured by means of a lamp and scale system using the mirror (19) attached to the ring. The switch (10) is so turned that only the tube (A) is active, being the tube (B) at rest, and the original position of the ring is marked on the scale. Then, in order to impose the stress on the ring, the switch (10) is changed so that only the tube (B) is active, leaving the tube (A) at rest, and the deflection of the ring is recorded with time. If a study of the after-effect upon removal of the stress is intended, it is enough to return the switch (10) to the original position.

The equations to calculate the surface shear modulus of rigidity (G) and surface viscosity coefficient (η) may be expressed as follows

$$G=\frac{k}{4\pi}\left(\frac{1}{r_1^2}-\frac{1}{r_2^2}\right)\frac{\varphi}{\theta} \tag{1}$$

$$\eta=\frac{k}{4\pi}\left(\frac{1}{r_1^2}-\frac{1}{r_2^2}\right)\frac{\varphi}{\dot{\theta}} \tag{2}$$

where r_1, r_2 are the radii of the ring and of the circular film coaxial to the ring, respectively, θ, the angular displacement of the ring, and k, the torsion constant.

Test and Results

The measured extent of coincidence between the rotating angles of the ring and the corresponding angles of the light spot was shown in Fig. 4. Fairly good coincidence

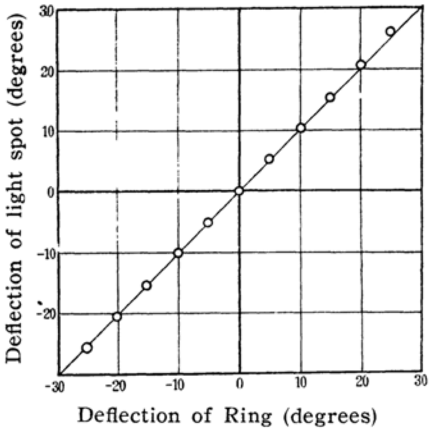

Fig. 4. Relation between rotating angles of the ring and the corresponding deflection angles of light spot.

was seen over the range of about 50 degrees within the error of a few per cent.

Fig. 5 shows the deformation-time curve (θ—t curve) of serum albumin monolayer determined with the present apparatus. Here, it was intended that the present ap-

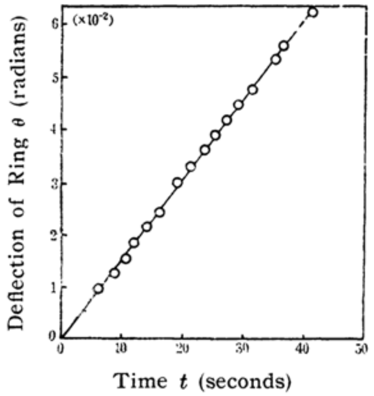

Fig. 5. $\theta-t$ plot of serum albumin monolayer determined by the present apparatus on 5 % ammonium sulfate aqueous solution, surface area, 1.03 sq. m. per mg., temperature, 16°C.

paratus was tested by being referred to the data obtained with the apparatus presented in a previous paper. Fig. 6 gives the $\theta-t$

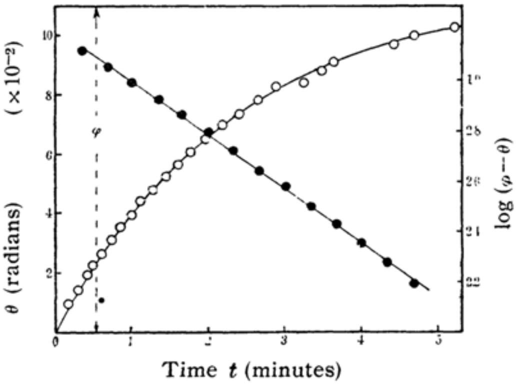

Fig. 6. $\theta-t$ curve (open circles) and $\log(\varphi-\theta)-t$ curve (full circles) of serum albumin monolayer, determined by the previous apparatus.

curve together with the $\log(\varphi-\theta)-t$ plot when the previous apparatus was applied to the same film. From the linearity of $\log(\varphi-\theta)-t$ plot[3], it was found that this film behaves as a simple viscous matter of Newtonian nature. This fact predicts that the present apparatus would give a straight line to the $\theta-t$ plot if only the stress is kept constant during the test, in contrast with the droop curve in case of the previous apparatus. This prediction was verified in Fig. 5 in which good linearity was yielded in the $\theta-t$ plot. The basic requirement of this apparatus—constant stress—was found to be fulfilled within experimental error.

As an example of a less simple creep curve, a monolayer of ovalbumin film was subjected to our test. The deformation-time

3) V. E. Hatschek and R. S. Jane, *Koloid-z.* **39**, 300 (1926).

curve determined by the present apparatus was given in Fig. 7, where the experimental

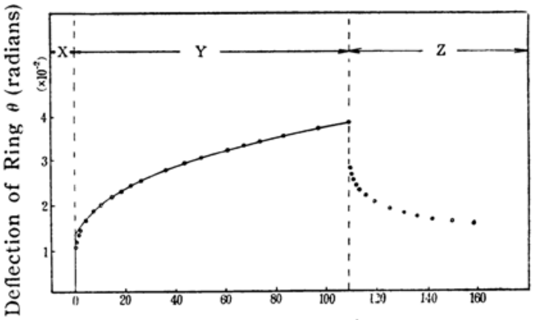

Fig. 7. $\theta-t$ curve for ovalbumin monolayer on 5% ammonium sulfate solution, surface area, 0.904 sq. m. per mg., temperature, 19°C. Full circles indicate the observed values, and solid line, the calculated curve. (X) represents the dead time, (Y), the time in which the stress was imposed, and (Z), the time, after the stress was removed.

conditions are indicated in the legend. From inspection of the shape of the curve, it will be apparent that the curve is characterized by instantaneous elastic response, retarded elastic response and irreversible flow. The solid curve represents the trace which was drawn according to the following well-known equation, putting the proper numerical values into the respective variables

$$\theta=\theta_0+A(1-e^{-t/\tau})+\lambda t \qquad (3)$$

where θ represents the angular displacement of the ring at time t, θ_0, an initial displacement of the ring due to an instantaneous elasticity, λ, the constant motion rate of the ring in viscous flow region, A, the final and maximum response due to a retarded elasticity, and τ, the retardation time. It was noted here that, except for the initial transcient creep region, the observed values were well expressible by such a simple equation. Putting θ_0, A, and λ into the equation (1) and (2), an instantaneous surface shear modulus of rigidity (G_1), a retarded surface shear modulus of rigidity (G_2), and surface viscosity coefficient (η) of the constant rate flow were calculated as follows: $G_1=2.7$ dynes/cm. $G_2=3.2$ dynes/cm., $\eta=2.1\times10^4$ dynes/cm./sec., and $\tau=21.7$ minutes.

Summary

A surface rheometer was presented which enables the creep of surface films to be measured under constant shear stress. The main construction consists of a ring and a suspending torsion wire. Automatic adjustment of the torsion head driving, which made distorsion of the wire to be constant throughout the creep test, was accomplished by means of a phototube relay mechanism. The creep curve and its analysis data of ovalbumin monolayer were also presented.

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Department of Chemistry,
Faculty of Science,
Ochanomizu University, Tokyo