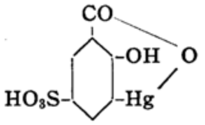
Rheological Properties of Gels. Viscoelasticity of Mercury Sulfosalicylate Solution

By Takaaki DANNO

(Received February 18, 1959)

The study on the visco-elastic properties of agar-agar gel was reported previously[1]. The agar gel shows interesting flow properties superposed on the elastic ones, especially in its softening and melting region. These are interesting from the view point of the relation between the rheological properties and the change of internal structure in the course of the melting of gel. More detailed experiments, however, could not be carried out by reason of the structural limit of our instruments.

On the other hand, mercury sulfosalicylate solution has interesting elasto-viscous properties, as shown by T. Nakagawa[2] who attributed the "Spinnbarkeit" of the solution to its elastic property. The solution is very elastic and also has viscous flow properties. It has been assumed[3] that the structural formula of mercury sulfosalicylate is



It is interesting to seek the origin of strong elasticity of the solution of such a simple substance.

The author measured the visco-elastic parameters of them and studied their dependence on frequency, amplitude, concentration, temperature change, and other factors, by using the coaxial dynamical rheometer.

Experimental

As the experimental procedure for studying the visco-elastic properties of mercury sulfosalicylate solution, the author adopted the method of coaxial type rheometer, which was designed by T. Nakagawa[4].

In this dynamic method for measuring visco-elastic constants, a sinusoidal oscillation is applied at the top of a torsion wire, from which the inner cylinder is suspended, and whose torsion constant is k dyn./cm. Then, the displacement of the top of the torsion wire is given by

$$\Theta = \Theta_0 \sin \omega t \qquad (1)$$

and the equation of motion of the inner cylinder is

$$I\ddot{\theta}+R\dot{\theta}+E\theta = k(\Theta-\theta) \qquad (2)$$

---

[1] T. Danno, *Bull. Tokyo Gakugei Univ.*, **6**, 103 (1955).

[2] T. Nakagawa, This Bulletin, **25**, 93 (1952).

[3] Wo. Ostwald and M. Mertens, *Kolloid-Beih.*, **23**, 242 (1926).

[4] T. Nakagawa and M. Seno, This Bulletin, **29**, 471 (1956).

where I is the moment of inertia of the inner cylinder, and R and E are the viscous and elastic resistance respectively of the solution between the two cylinders. The stationary solution of this equation is

$$\left.\begin{aligned} \theta &= \frac{k\Theta_0}{\sqrt{\{(E+k)-I\omega^2\}^2+R^2\omega^2}} \sin(\omega t-\phi) \\ &\equiv A\sin(\omega t-\phi) \\ \tan\phi &= \frac{R\omega}{(E+k)-I\omega^2} \end{aligned}\right\} \quad (3)$$

where A is the amplitude of motion of the inner cylinder induced by the sinusoidal torque of the suspension wire, and ϕ is the angle of phase difference between the motion at the top of the suspension wire and the forced oscillation of the inner cylinder. The amplitude ratio m is given by

$$m \equiv \frac{A}{\Theta_0} = \frac{k}{\sqrt{(E+k-I\omega^2)^2+R^2\omega^2}} \quad (4)$$

from Eq. 3, R and E are calculated as

$$\left.\begin{aligned} R &= \frac{kT\sin\phi}{2\pi m} \\ E &= k\left(\frac{\cos\phi}{m}-1\right)+\frac{4\pi^2 I}{T^2} \end{aligned}\right\} \quad (5)$$

where T is the period of oscillation ($\omega=2\pi\nu=2\pi/T$).

When two simple harmonic motions, i. e., the motion at the top of the suspension wire and the forced oscillation of the inner cylinder, whose directions of oscillation are at right angles to each other, are composed, the resulting Lissajous' figure is an ellipse as long as they are of the equal period. Let the area of an ellipse be S_e and that of the rectangle tangent to the ellipse be S_r. Then the next relation is known to hold.

$$\sin\phi = \frac{4}{\pi}\cdot\frac{S_e}{S_r} \quad (6)$$

The scheme of obtaining m and ϕ is realized by a mechanical and optical system. The dynamic viscosity η and the dynamic rigidity G are calculated from the observed R and E by the conventional formulae

$$\left.\begin{aligned} \eta &= \frac{R}{4\pi h}\left(\frac{1}{r_1^2}-\frac{1}{r_2^2}\right) \\ G &= \frac{E}{4\pi h}\left(\frac{1}{r_1^2}-\frac{1}{r_2^2}\right) \end{aligned}\right\} \quad (7)$$

where h, r_1 and r_2 are the length of the immersed portion of the internal cylinder, the radii of the internal and external cylinder, respectively.

Strictly speaking, the inertia effect of the sample which was discussed by S. Oka[5] can not be neglected. But in our present experiments, in which very low frequencies (long period of oscillation) were applied, the rigorous treatment taking into account the inertia of the sample is not necessary.

The experimental condition was as follows: Three hardened steel wires, whose diameter ranged from 0.29 mm. to 0.90 mm. in accordance with the concentration of the sample solution, were used. Coaxial glass vessels of the outer diameter 9.386 cm., and inner one 5.905 cm., were used.

Mercury sulfosalicylate was prepared as follows[6]: An equivalent mass of yellowish mercuric oxide was mixed into the solution of commercial sulfosalicylic acid. When this mixture is heated in a water bath, flesh-colored mercury sulfosalicylate is obtained. The sample thus prepared, mixed with water, is boiled in a flask with reflux condenser for about an hour. After having been dissolved completely in water, it is poured into the space between the two cylinders, cooled and settled for two days in room temperature for conditioning.

The concentration of the solution was determined by evaporation, and was represented in weight per cent. The temperature of the sample to be tested was controlled at 20~65°C, by a water bath thermostat.

Results

Aging of the Solution.—As is usual in all colloidal solutions[7], the marked effect of aging in the physico-chemical properties is observed in our case. The solution of mercury sulfosalicylate, when it is newly prepared, appears as a transparent solution, but gradually loses its transparency and becomes a visco-elastic fluid. Fig. 1 shows the increase of the viscosity and modulus of the rigidity as a function of time.

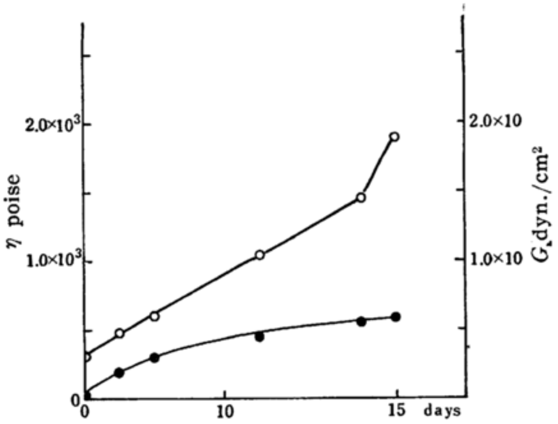


Fig. 1. Viscosity and rigidity of 3.16% mercury sulfosalicylate aq. solution vs. aging time. ○ indicates viscosity and ● rigidity.

---

[5] S. Oka et al., *Bull. Kobayashi Inst. Phys. Res.*, **3**, 9, 17 (1953).

[6] For instance, J. Samejima, "Koshitsugaku (Colloid Science)", Shokabo, Tokyo (1949), p. 537.

[7] For instance, C. Dittmar et al., *J. Poly. Sci.*, **18**, 275 (1955).

In our case of mercury sulfosalicylate solution, the viscosity increases rapidly in a few days, while the rigidity increases slowly. In the course of 10 or 15 days, rigidity seems to reach a saturation value, but viscosity continues to increase to a very large value.

Dependence on Frequency. — As is usually observed in the ordinary polymeric solutions, the dynamic viscosity and elasticity of the present system change with frequency.

Fig. 2 shows the viscosity and rigidity of 2.2% mercury sulfosalicylate solution, plotted against the period of oscillation (reciprocal frequency) from 8 sec. to 1286 sec. (about 22 min.). From this figure we see that, in a range of a short period, the viscosity decreases rapidly as the period of oscillation becomes shorter. But, when the period of oscillation is very long, it reaches a constant value.

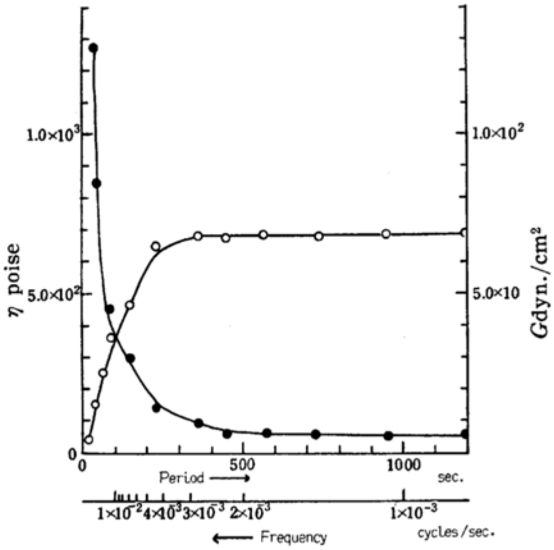


Fig. 2. Frequency dependence of viscosity η and rigidity G of 2.2% mercury sulfosalicylate aq. solution at 24°C. ○ indicates viscosity and ● rigidity.

On the other hand, the rigidity falls steeply in a range of short period. As the viscosity reaches to a certain constant value in a range of a long period, the rigidity also becomes constant. In other words, in a high frequency range, viscosity increases rapidly and rigidity decreases also steeply as the frequency becomes lower. And then, when the frequency is below 2.5×10^{-3} cycl./sec., viz., the period of oscillation is above 400 sec., both viscosity and rigidity are almost constant.

Dependence on Amplitude. — The amplitude effect is shown in Fig. 3, in which $\theta_{\max\, r=r_1}$ is the amplitude of the shear strain at the wall of the internal cylinder, as given by the following equation,

$$\theta_{\max\, r=r_1}=\left[\frac{2Ar_1^2r_2^2}{(r_2^2-r_1^2)r^2}\right]_{r=r_1}=\frac{2Ar_2^2}{r_2^2-r_1^2}$$

where A is the amplitude of the oscillation of the internal cylinder and r_1 or r_2 is the radius of the internal and external cylinder, respectively. In the present case, $\theta_{\max\, r=r}=3.316\ A$ ($r_1=2.953$ cm., $r_2=4.693$ cm.). The concentration of the sample is 1.58 wt. %, and the frequency of oscillation is kept constant. (In the present case, it is 1.29×10^{-1} cycl./sec.).

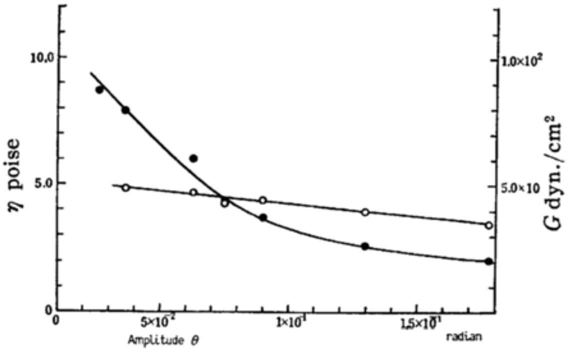


Fig. 3. Amplitude dependence of viscosity η and rigidity G of 1.58% mercury sulfosalicylate aq. solution. ○ indicates viscosity and ● rigidity.

It seems that the viscosity increases as amplitude decreases. But its gradient is fairly slight. As to the rigidity, on the other hand, the situation is somewhat different. It is large in the region of small amplitude, but decreases rapidly as the amplitude increases, and finally tends to a constant value. This is a noticeable experimental result. An explanation of this effect may be given by assuming a sort of structural breakdown by shear strain. An elastic structure breaks into a viscous flow process by a large deformation.

Effect of Concentration of Solution.—So long as we are concerned with dilute solutions, the rigidity seems to be proportional to the third power of concentration as is shown in Fig. 4. This result is in accord with that of agar-agar sol formerly reported[8].

---

[8] T. Danno, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **72**, 1061 (1951).

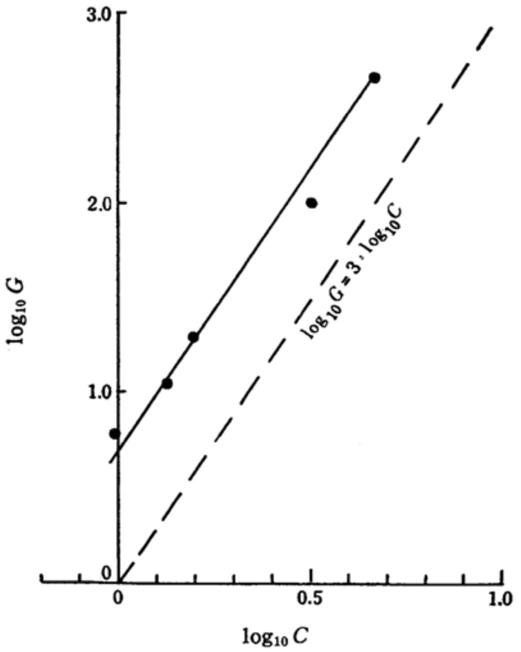


Fig. 4. Effect of concentration of mercury sulfosalicylate aq. solution.

Dependence on Temperature.—Both viscosity and rigidity decrease with the increase of temperature. Fig. 5 shows the results, where viscosity is plotted against the reciprocal of absolute temperature. The author has used the Andrade formula[9]

$$\eta = Ae^{\Delta E/RT}$$

to express the temperature sensitivity of viscosity η; A and ΔE were determined by the method of least square with regard to various periods of oscillation. Results are given in Table I. The apparent heat of activation in relation to the viscous flow process is about 4 kcal./mol. This value makes one assume the existence of the cross-linking due to the weak secondary bonding like a hydrogen bond.

TABLE I. CONSTANTS OF THE ANDRADE FORMULA

Period, sec.	$-\log A$	E, kcal.
8.1	−0.649	4.11
41.7	−0.210	3.96
89.2	−0.0147	4.10
452.9	−0.147	4.79

(For 4.53 wt. % solution).

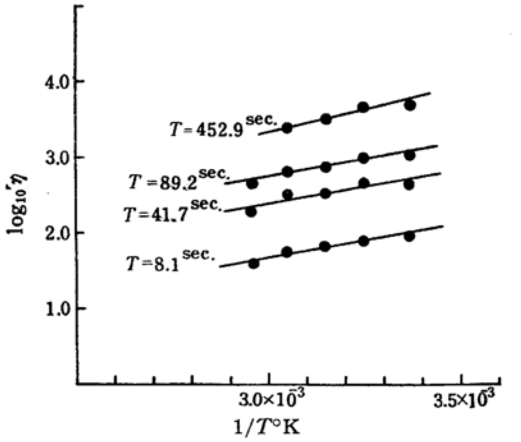


Fig. 5. Temperature dependence of viscosity.

Discussion

From the results of frequency dependence, it is assumed that this solution has two mechanisms of relaxation. A mechanism which relaxes easily finishes its relaxation during the small period. When the period increases to a certain value, both viscosity and rigidity do not change with frequency due to the nearly complete relaxation of the first mechanism (Fig. 2). We have already seen that viscosity increases, while rigidity does not suffer a remarkable change in the course of aging (Fig. 1). An elastic scaffolding structure is formed in the first stage of gelation, and afterwards the gradual growth of suspending particles in a cavity follows. This is shown in the electron-micrograph

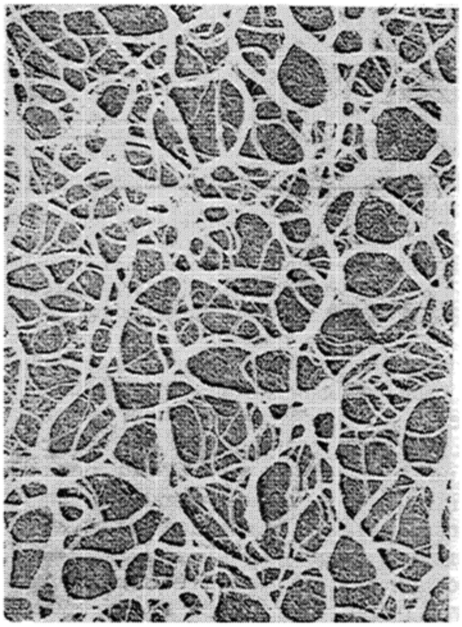


Photo. 1. Electron-micrograph of the aq. solution of mercury sulfosalicylate (×10,000).

---

[9] E. N. da C. Andrade, *Phil. Mag.*, **17**, 497, 698 (1934).

(see Photo. 1). This means that the solution of mercury sulfosalicylate has a network structure of two phases.

As to the nature of cross-linking between these submicroscopic network structures, weak secondary bonding, for example, by hydrogenbond, is assumed, because the apparent activation energy of viscosity is calculated to be about 4 kcal./mol.

The author wishes to express his gratitude to Professor H. Akamatsu and Dr. T. Nakagawa both of the University of Tokyo for their leadership and encourgement throughout this investigation. It is also a pleasure to acknowledge the help of the members of Electron-microscope Laboratory of the University of Tokyo.

Department of Chemistry
Tokyo Gakugei University
Setagaya-ku, Tokyo