Structural Change in Some Solutions Having Structural Viscosity

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The amount of liquid flowing out in unit time, Q, from a capillary tube of a in radius and l in length, is proportional to the pressure difference, P, between both ends of the tube. According to Poiseuille, the viscosity of the liquid, η_0, is obtained by:

$$\eta_0 = \alpha P/Q \tag{1}$$

where,

$$\alpha = \frac{\pi a^4}{8l} \tag{2}$$

For some colloidal solutions, however, the viscosity obtained from this equation shows abnormally large value for smaller pressure difference. For such abnormal viscosity, Freundlich and Schalek[1] gave an explanation of "elasticity of flow". Wo. Ostwald[2], on the other hand, named it "structural viscosity", considering that a net-work structure as in jellies has been formed in such solutions. It was assumed that the structure was readily destroyed by pressure, thus exhibiting the usual viscosity for higher pressure.

In the present report, the structural viscosity of vanadium pentoxide (V_2O_5) sol and mercury sulfosalicylate (Hg-SS) sol are measured. Then, the structural changes of these sols by shaking and by the irradiation of ultrasonic wave are observed under the electron microscope, and the structural viscosity is explained by it.

Experimental

V_2O_5 sol was prepared from ammonium vanadate by hydrolysis. 5 g. of ammonium vanadate was put in a mortar and smeared, adding drop by drop 25 cc. of dilute nitric acid (1 volume of $d=1.4$ nitric acid was diluted by 5 volume of water). Then, it was filtered by suction, washed with distilled water repeatedly, till the filtrate showed distinct red color. The precipitate on the

1) H. Freundlich and E. Schalek, *Z. physik. Chem.*, **108**, 153 (1924).
2) Wo. Ostwald, *Z. physik. Chem.*, **111**, 62 (1924).

filter paper was then put in 100 cc. of distilled water and stirred vigorously. The sol was aged about one month.

Hg-SS (mercury sulfosalicylate) was prepared by boiling 4 cc. of sulfosalicylic acid solution (containing 4 g. of solute) with 2 g. of yellow mercury oxide, stirring continuously. After the powders had been completely dissolved by the reaction, the solution was heated to dryness, and the powder obtained was ground. 0.3 g. of powder was dissolved in 200 cc. of water.

The structural viscosity was measured by Ostwald's overflow viscometer, shown in Fig. 1.

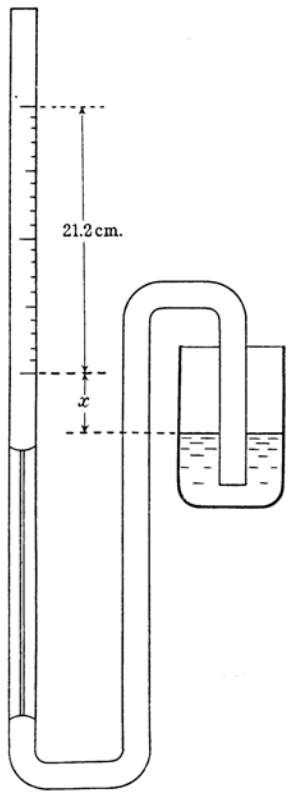

Fig. 1. Overflow viscometer.

A capillary tube of 21.2 cm. in length and 0.67 mm. in inner diameter was connected with a mess-pipette of 2 cc. in capacity. The grade of the pipette from 0.0 to 2.0 corresponded to the height of 21.2 cm. The height indicated by x in Fig. 1 was measured every time. It was usually 3.0—4.5 cm. The time, which 0.4 or 0.2 cc. of liquid required to flow down, was measured by stop watch, to calculate the mean amount of flow, Q. The pressure difference, P, was obtained from the mean difference of liquid levels.

The Electron microscope used was the Hitachi HU-4 type, operated under the direct enlargement of 10,000—5,000 ×. Plates were enlarged, 3—6 times, photographically. If necessary, a shadow was cast by Cr metal.

The ultrasonic apparatus was Shimazu P-200 type, used under the condition of 2 kV., 0.2 A. in input, and output current was also 0.2 A. The frequency was 610 kC.

Structural viscosity

Some of the results obtained for distilled water, V_2O_5 sol (about 0.6%), and Hg-SS sol (about 0.04%) are shown in Fig. 2. P/Q is proportional to the

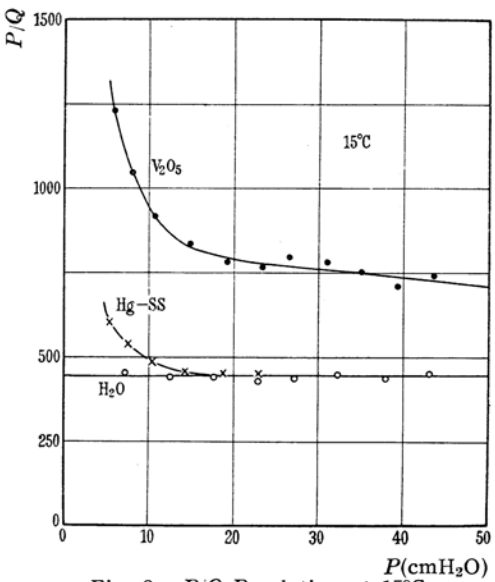

Fig. 2. P/Q-P relation at 15°C.

viscosity, as shown in Eq. (1). Curves for V_2O_5 and Hg-SS, therefore, show structural viscosity, as already known[1,2,3]. As for water, a typical Newtonian liquid, P/Q is constant regardless of pressure P. The mean value of $P/Q=446$ for water gives the α value, using the viscosity of water at 15°C[4], $\eta_0=11.45\times10^{-3}$ dyne. sec./cm.^{2}, $\alpha_{(obs)}=\eta_0/(P/Q)=2.57\times10^{-5}$ (dyne. cm./cmH_2O) (3) where cmH_2O means the pressure expressed by the height of the water column. On the other hand, using the size of capillary tube cited above,

$$\alpha_{(calc)}=\frac{\pi a^4}{8l}g=2.3\times10^{-5}\ \text{(dyne. cm./cm}H_2O\text{)} \quad (4)$$

where the constant of gravity, g, is used to recalculate the pressure to water pressure in *cm.* Values of Eq. 3 and 4 are in good agreement.

The ratio of P/Q for a specimen and for water is equal to the relative viscosity η/η_w. As shown in Fig. 3 and 5, the relative viscosity is linear to $1/Q$:

$$\eta/\eta_w=a+(b/Q) \quad (5)$$

at least in the measured range of pressure. This relation is explained as follows. In the pressure P applied to the liquid, P_0 is used to destroy the net-work structure, and the residue is effective to flow:

$$P_{eff}=P-P_0 \quad (6)$$

P_0 corresponds to the yield value. It is, then, assumed that the flow of broken net-work is Newtonian:

3) Wo. Ostwald and M. Mertens, *Kolloid-Beih.*, **23**, 242 (1927); S. Berkman and H. Zocher, *Kolloid-Z.*, **42** 322 (1927).
4) "International Critical Tables," Vol. 5 (1929), p. 10.

$$Q=\alpha P_{eff}/\eta_N, \tag{7}$$

η_N is the viscosity of this Newtonian flow. The apparent viscosity, η, is

$$\eta=\alpha P/Q=\eta_N+\alpha P_0/Q. \tag{8}$$

Then, the coefficients, a and b, in the empirical equation (5) are

$$\left.\begin{aligned} a&=\eta_N/\eta_w \\ b&=\alpha P_0/\eta_w=P_0/446. \end{aligned}\right\} \tag{9}$$

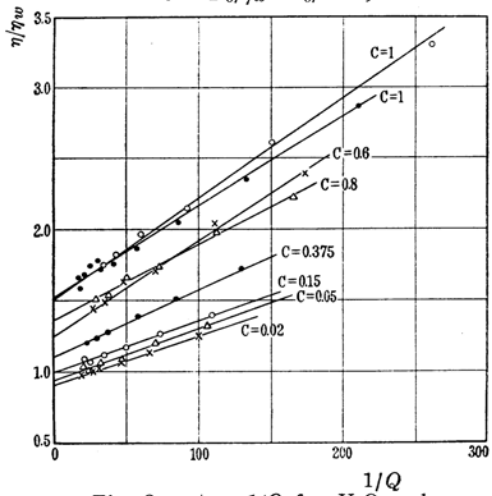

Fig. 3. $\eta/\eta_w-1/Q$ for V_2O_5 sol.

V_2O_5 sol of about 0.6% is diluted to various concentrations, left alone for 2 hrs., and the structural viscosity is measured. The results are shown in Fig. 3. The linear relation of Eq. (5) are verified. The concentration, C, is the relative one, assigning that of original solution (about 0.6%) as 1. Fig. 4 shows (η_N/η_w) and P_0 obtained from the data of Fig. 3, as a function of C. Fig. 4a shows that η_N/η_w increases linearly with the increase of C. Assuming the concentration of the original solution as 0.6%, and the density of V_2O_5 as 3.5[5], the relation.

$$\eta_N/\eta_w=0.91+128\phi \tag{10}$$

is obtained, where ϕ is the volume fraction of dispersed particles. The coefficient 128 is about 51 times larger than Einstein's 2.5. Comparing the fluctuation of plots in Fig. 4a and b, it is concluded that the yield value, P_0, sensitively depends on the structure, or the history of the specimen, while the Newtonian viscosity, or the viscosity after the structure has been broken, depends a little on its history.

As shown in Eq. (10), the relative viscosity becomes smaller than that of the solvent itself at smaller concentration. This is more clearly shown for Hg-SS in Fig. 5. This may be attributed to the slip of liquid on the surface of a capillary tube. The elasticity of flow will usually accompany the slip. Then, the amount of flow, Q, is assumed as the sum of the flow amount by Newtonian flow, Q_η, and the flow amount by slip, Q_s, on the surface of the tube (in this case, liquid is pushed out as a whole). Assuming that the slipping velocity at the tube surface, v_s, is

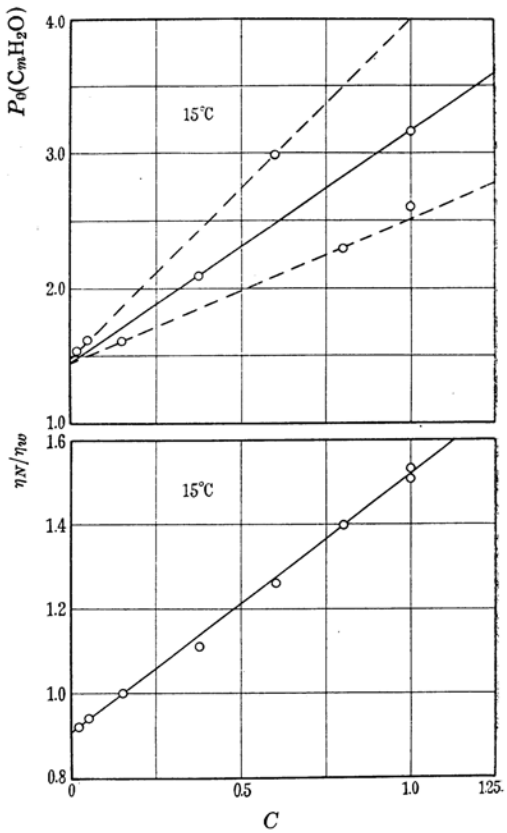

Fig. 4. η_N/η_w and P_0 for V_2O_5 sol.

proportional to the pressure P,

$$v_s=kP \tag{11}$$

Q_s becomes

$$Q_s=\pi a^2kP \tag{12}$$

On the other hand, Q_η is, using Eq. (6) and (7),

$$Q_\eta=\alpha(P-P_0{}^0)/\eta_N^0 \tag{13}$$

Then, the apparent viscosity η is obtained in the same form as Eq. (8)

$$\eta=\alpha P/Q=\eta_N+\alpha P_0/Q \tag{14}$$

But in this case, the apparent Newtonian viscosity η_N and the apparent yield value P_0 are related to their real values, $\eta_N{}^0$ and $P_0{}^0$, by the equation:

$$\left.\begin{aligned} P_0&=P_0{}^0/(1+\beta) \\ \eta_N&=\eta_N^0/(1+\beta) \\ \beta&=\pi a^2k\eta_N{}^0/\alpha \end{aligned}\right\} \tag{15}$$

Owing to this correction factor $(1+\beta)$, the apparent Newtonian viscosity η_N may become smaller than that of water. For example, at the infinite dilution of V_2O_5 sol,

$$\eta_N/\eta_w=\eta_N^0/\{\eta_w(1+\beta)\}=0.91 \tag{16}$$

is obtained from Eq. (10). Then, $\beta\simeq0.10$. If $P_0{}^0\ll P$ at infinite dilution,

$$Q_s/Q_\eta\simeq0.1. \tag{17}$$

For more concentrated sol, the slip may be more important by its greater elasticity, but no method to estimate it is found.

The effect of ultrasonic wave on the structural viscosity of Hg-SS is shown in Fig. 5. The time recorded in this Fig. show that elapsed after the

5) R. Abegg, "Handb anorg. Chem.," Vol. 3, p. 738 (1927).

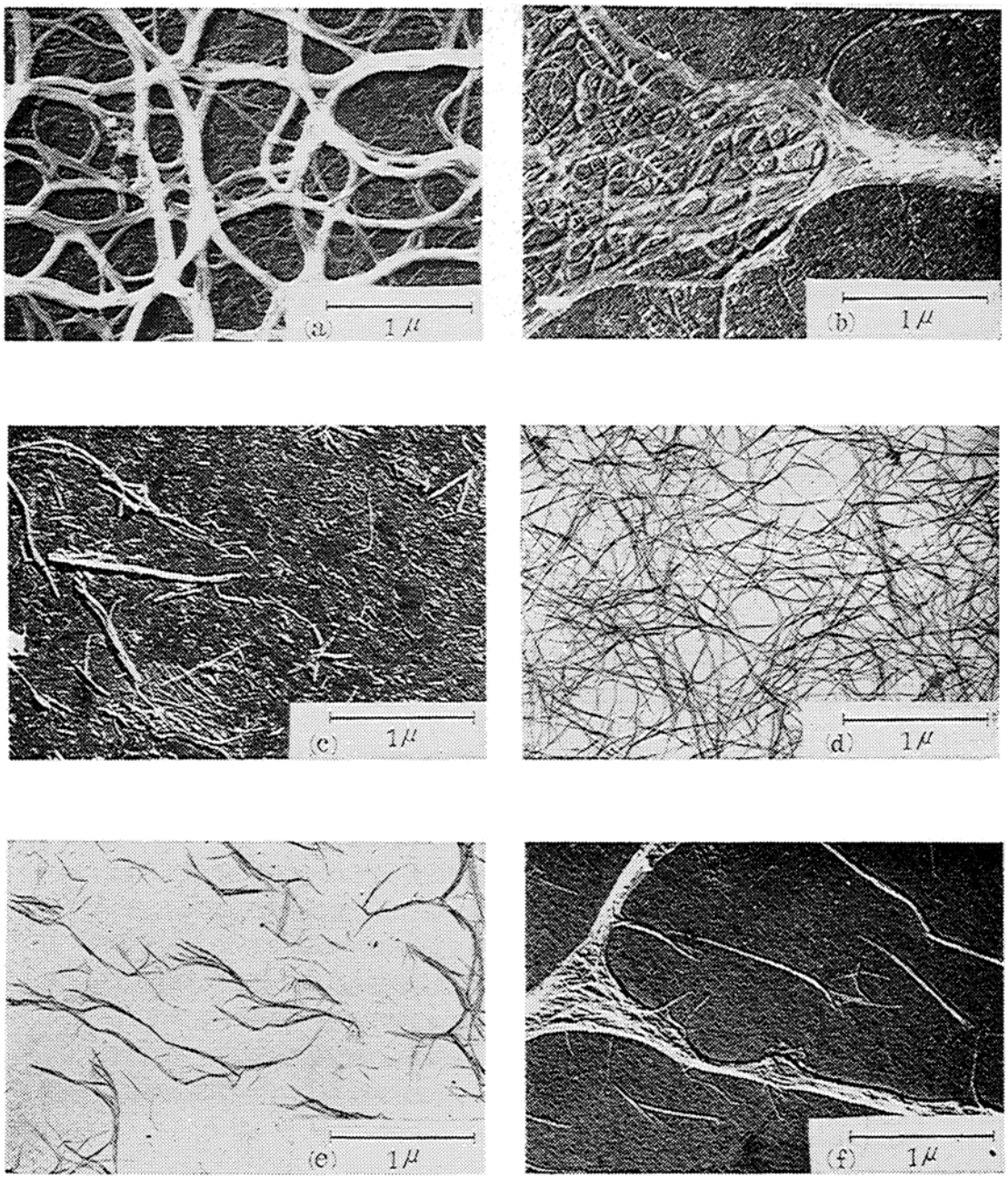

Fig. 6 Electron micrographs for Hg-SS:
(a) No treatment (b) Left alone for 3 min. after shaking
(c) Ultrasonic irradiation
and for V_2O_5:
(d) No treatment (e) Just after shaking (f) Just after shaking

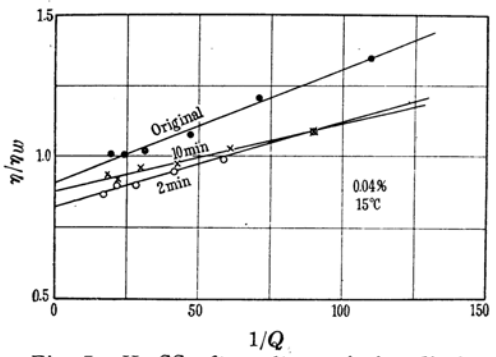

Fig. 5. Hg-SS after ultrasonic irradiation.

end of ultrasonic irradiation. It is shown that the Newtonian viscosity begins to recover after about 10 min., while the yield value does not recover yet. The net-work structure of Hg-SS seems to be destroyed by ultrasonic wave, but broken pieces soon join together to form fibers. Some time is spent, however, before these fibers form rigid knots to complete a net-work. This idea will be supported by electron micrographs shown later. The slip on the wall, however, is so great that a confident conclusion cannot be obtained.

Electron micrograph

Hg-SS has a typical net-work structure as shown in Fig. 6a. The net-work is built of yarns of about 0.1 μ in width, and the latter is a bundle of fibers of about 200 Å in its thickness. After shaking the solution in a test tube for 1 min., the net-work is destroyed and dispersed to single yarn or to single fiber, or on the other hand, they aggregate to a rope of 0.3—1 μ in thickness. Letting the solution stand for about 3 min., (Fig. 6b), the rope again disperses to reproduce a net-work. After 10 min., almost complete net-work structure has been reconstructed. By the irradiation of ultrasonic, (Fig. 6c), the net-work of Hg-SS is torn to pieces of 0.1—1 μ in length. When it is left alone for 3—10 min., broken pieces join together to form fibers, or further coagulaie to yarns and ropes. After 2.5 hrs. they reconstruct a complete net-work structure.

A similar change of structure is observed also for V_2O_5 sol. Original sol (Fig. 6d) has a net-work structure, constructed from fibers of about 100 Å in thickness. By vigorous shaking, the net-work is destroyed and torn to pieces as shown in Fig. 6e, or coagulates to thick ropes of~0.1 μ

The structural changes observed above are favourable to explain their rheological behavior. Destruction of net-work structure may correspond to the lowering of viscosity under higher pressure. The recovery of the net-work structure may explain the recovery of its viscosity and elasticity of flow after keeping the sol standing, and the in thickness as shown in Fig. 6f. After being left alone for 2.5 hrs. or so, they recover a net-work structure again. The recovery of the net-work seems to take more time for V_2O_5 than for Hg-SS. Irradiation of ultrasonic brings nearly the same effects as that by shaking.
dependence of yield value on the history of teh specimen.

Summary

The structural viscosity of V_2O_5 sol is measured by Ostwald's overflow viscometer. A linear relation is found between the relative viscosity (η/η_w) and the reciprocal of flow amount ($1/Q$). Viscosity of Newtonian flow η_N and yield value P_o are calculated from it. η_N and P_0 is nearly linearly varied with concentration. A decisive conclusion however, cannot be obtained owing to the slip of liquid on the capillary wall.

Hg-SS (Hg-sulfosalicylate) sol also showed a linear relation between η/η_w and $1/Q$. By the irradiation of ultrasonic wave, η_N and P_0 decreases. η_N again increases after about 10 min., but the recovery of P_0 took more time. A clear conclusion cannot be obtained due to the slip.

Electron micrographs showed that Hg-SS has a net-work structure, which is broken by shaking or by the irradiation of ultrasonic wave. When it is kept standing, the net-work is again constructed. V_2O_5 sol showed analogous structural changes.

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