

Chemistry. — "*Lyophilic Colloids and POISEUILLE'S Law*". By Prof. H. R. KRUYT and CONMAR ROBINSON, A.I.C., A.R.C.Sc.I.

(Communicated at the meeting of October 25, 1924).

1. In recent years there has been much controversy as to whether lyophilic sols have a real viscosity in accordance with POISEUILLE'S law or whether they possess elastic properties similar to solids. HATSCHER¹⁾ is inclined to ascribe elastic properties to these sols; ROTHLIN²⁾ who carried out viscosity measurements after the manner of HESS, divides colloids into two groups, those which show elastic properties and those which do not. FREUNDLICH and SCHALEK³⁾ find that some sols exhibit elasticity while others do not. Wo. OSTWALD⁴⁾ some years ago expressed a similar opinion when dealing with the hysteresis phenomena which these sols often exhibit.

H. G. BUNGENBERG DE JONG⁵⁾ has criticised much of this work on the grounds that the measurements were carried out on sols in which gelation had already commenced. Agar solutions below 40° C. and gelatin solutions below about 30° C. show gelation phenomena even at low concentrations which will not set to solid gels. The experiments of BACHMANN⁶⁾ have plainly shown that even in these dilute solutions gelation coagula are present and it is obvious that these may be accompanied by elastic properties. DE JONG showed that a $\frac{1}{7}$ % agar sol followed POISEUILLE'S law exactly at 40° C., while on the other hand ROTHLIN has shown that at 27° C. a $\frac{1}{8}$ % sol possessed elasticity. FREUNDLICH has recently confirmed DE JONG'S result.

2. In the paper of FREUNDLICH and SCHALEK already referred to, it is once more stated that a number of sols show deviations from POISEUILLE'S law. They again investigated the viscosity of a gelatin sol, using a $\frac{1}{8}$ % solution at 23° C. We contend that this deviation

¹⁾ Koll. Zeit. **8**, 34 (1911); **12**, 238 and **13**, 88 (1913).

²⁾ Biochem. Zeit. **98**, 34 (1919).

³⁾ Z. physik. Chem. **108**, 153 (1924).

⁴⁾ Trans. Faraday Soc. **9** (1913), Koll. Zeit. **12**, 213 (1913).

⁵⁾ Rec. Trav. Chim. **42**, 1 (1923).

⁶⁾ Z. anorg. Chem. **73**, 125 (1911); **79**, 202 (1912).

can be altogether accounted for by the fact that gelation had already set in, since DE JONG¹⁾ has established the fact that with gelatin at 40° C., POISSEUILLE'S law is followed exactly.

FREUNDLICH and SCHALEK and also SZEGVARI²⁾ maintain that these investigations should not be carried out with the OSTWALD viscometer, but with either the COUETTE or the HESS viscometer. Whether this contention is correct or not, we shall see in the following paragraph; but so that there should be no doubt we have used the HESS apparatus for investigating gelatin sols at temperatures above and below the temperature where gelation commences. For this purpose certain modifications of the HESS apparatus had to be introduced.

Firstly it had to be possible to bring the apparatus conveniently to temperatures higher than that of the room and to maintain such temperatures for long periods. The two capillaries were therefore placed in a long narrow trough through which water from a thermostat could be circulated.

Further, the liquid whose viscosity is to be measured must be introduced into the apparatus without being allowed to cool below the temperature of the experiment. For this purpose a *T*-piece was attached to the end of the tube leading to the capillary. The lower end of this *T*-piece was made to pass through the bottom of the trough and was fitted with a ground glass stopper. (See fig. 1).

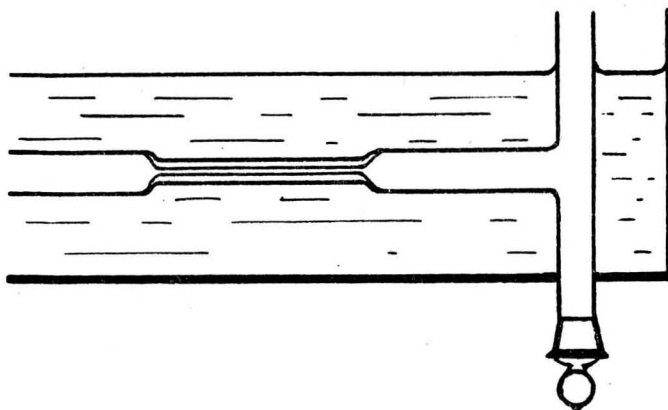


Fig. 1.

The perpendicular tube of the *T*-piece was filled with the solution, the necessary quantity of liquid drawn through the capillary and the remainder allowed to run out by removing the glass stopper.

¹⁾ Rec. Trav. Chim. **43**, 35 (1924).

²⁾ Z. f. physik. Chem. **108**, 175 (1924).

The reading of the graduated tubes was facilitated by placing a mirror scale under the tubes, and a capillary was chosen of such dimensions as to give with the pressures used in the experiments an error of less than 0.1 % as shown by GRÜNEISEN'S¹⁾ formula.

In the following table are the results of our experiments with 0.25 % Gelatin sol.

Temperature	Pressures (mm. of Hg)	Ts/Tw
40°	60	1.13 ⁰
	30	1.13 ²
	10	1.13 ¹
30°	60	1.15 ⁴
	30	1.15 ⁸
	10	1.15 ⁶
23°	60	1.47 ⁶
	40	1.49 ¹
	20	1.50 ²
	10	1.51 ¹

Here we see that the Gelatin sol follows POISEUILLE'S law exactly at 40° C. and 30° C., while at 23° C. the expected deviations appear.

3. HESS, FREUNDLICH and SCHALEK, and SZEGVARI have condemned the use of the OSTWALD viscometer for the viscosity measurements of these systems. Here, however, we think one should first consider with what purpose the experiment is to be carried out.

When elastic properties are exhibited as for example in the case of old V_2O_5 -sols, then one obtains a relationship between viscosity and pressure as shown in fig. 2. Further SZEGVARI has shown theoretically that the following general formula holds when elastic properties are present:

$$w = \frac{\vartheta}{G} + \eta$$

where w is a quantity proportional to the amount of liquid which

¹⁾ Wiss. Abh. Phys. Techn. Reichsanst. 4, 151 (1905).

flows through in unit time, \mathcal{P} the liquid elasticity, G the fall of velocity and η the actual viscosity. This equation is that of an hyperbola with the ordinate as an asymptote.

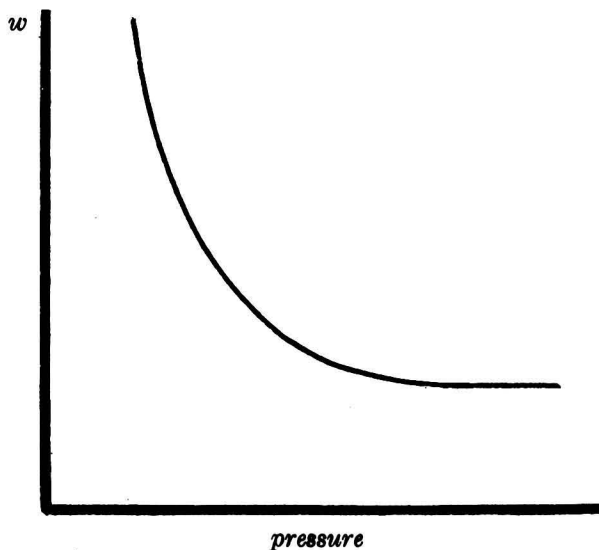


Fig. 2.

From this one sees that the term $\frac{\mathcal{P}}{G}$ plays a smaller and smaller rôle the greater the fall in velocity, that is to say the greater the pressure employed. An apparatus in which the measurements are carried out at high velocities of flow, that is to say, at high pressures will thus give results which approximate very closely to the actual viscosity of the liquid. But the question whether elasticity is present or not is best answered by working at very low velocities and pressures corresponding to the steep part of the curve where the deviations will be most easily detected.

So if we use a viscometer with small hydrostatic pressures and so arranged that one can work at different pressures, we have a very sensitive instrument to test whether POISEUILLE'S law holds or not. Such a viscometer is the modification of the OSTWALD viscometer described by H. G. BUNGENBERG DE JONG (l.c.)¹⁾. With such viscometers he investigated sols of agar, starch, iso-electric gelatin and acid gelatin, all at 40° C.

These all appeared to follow the law of POISEUILLE exactly. Miss VAN DER MADE²⁾ investigated in the same way CeO₂ sols, and

¹⁾ Rec. Trav. chim. **42**, 1 (1923). Further **43**, 35 and 189 (1924).

²⁾ Diss. Utrecht 1922.

found very good agreement. LIER¹⁾ obtained the same result with acid and alkaline casein sols, TENDELOO²⁾ with gum arabic and POSTMA³⁾ with the sol of SiO_2 . Since the fact that all these sols agree with POISEUILLE's law has been shown for the range of pressures where any deviation would be most easily detected, we can say with certainty that the sols mentioned would exhibit a viscosity uncomplicated by elasticity in other apparatuses under the same conditions and within the same limits of accuracy.

4. We come to the conclusion that sols consisting of only primary particles always follow POISEUILLE's law, but that deviations first appear when the primary particles have united to form greater aggregates either due to temperature gelation or due to slow or rapid electrolytic coagulation.

Fresh V_2O_5 -sol follows POISEUILLE's law, but the investigations of FREUNDLICH and SCHALEK and of Wo. OSTWALD⁴⁾ (which we have been able to confirm with the HESS apparatus at 23° and 40°) show that old V_2O_5 sols showed marked deviations. In these sols which show double refraction (as is also the case with sodium stearate) long needle shaped particles are present.

We are thus able to establish the fact that the deviations from POISEUILLE's law first appear after the formation of *complex* particles. Several theories may be put forward to explain this. DE JONG⁵⁾ considers the reason to be that particles are broken up at greater rates of flow but coalesce again when the rate of flow becomes less. It may also be that the phenomenon depends on the particles not being spherical; this deviation being very slight in the case of the primary, but often very large for the secondary and higher particles. The CeO_2 sol follows POISEUILLE's law even when the gelation has proceeded quite far, as Miss VAN DER MADE found. Since with this sol there was disagreement between her results and those of FREUNDLICH and SCHALEK (who found that CeO_2 sol did not follow POISEUILLE's law in the HESS apparatus), we repeated this experiment with the result that we got good agreement also in the HESS apparatus as will be seen from the following table:

¹⁾ Diss. Utrecht, 1924.

²⁾ As yet unplublished.

³⁾ Diss. Leiden, 1924.

⁴⁾ Z. physik. Chem. 111, 62 (1924).

⁵⁾ Rec. Trav. Chim. 42, 1 (1923).

Temperature	Pressures (mm. of Hg)	T _s /T _w
20°	60	1.56 ⁶
	40	1.56 ¹
	20	1.56 ²
	10	1.56 ¹

The fact that an ordinary sol with primary particles follows POISEUILLE'S law is of great importance in the interpretation of viscosity measurements. In fact if this were not the case, simple relations like that of EINSTEIN would not be applicable for these systems¹⁾. The interpretation of viscosity measurements for lyophile sols would hence be very much more difficult.

The controversy over these phenomena became singularly subjective on account of the theoretical interpretations which the various workers attached to their results. Thus W. O. OSTWALD²⁾ has no hesitation in understanding by viscosity the combined effects of the internal friction of the liquid and the elasticity, since he is satisfied with the phenomenology of the matter. Whoever takes up the real standpoint of the physical chemist and tries to obtain a mechanical picture from the results of his viscosity measurements wishes to obtain from his measurements something capable of mechanical-kinetic interpretation.

Without for a moment wishing to minimise the importance of the elasticity phenomena, we, however, consider the uncomplicated viscosity a more repaying subject for physico-chemical research since it is more easily interpretable and will lead us sooner to a knowledge of the internal constitution of lyophilic systems.

Utrecht, Oct. 1924.

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¹⁾ Comp. KRUYT and DE JONG, Z. physik. Chem. **100**, 250 (1922).

²⁾ Z. physik. Chem. **111**, 62 (1924).