

VISCOSITY MEASUREMENTS DURING THE COAGULATION AND GELATION OF CONCENTRATED SOLS OF ZIRCONIUM AND STANNIC HYDROXIDES

BY MATA PRASAD AND K. V. MODAK

(*Chemical Laboratories, Royal Institute of Science, Bombay*)

Received September 11, 1941

MOST of the early studies in gels were confined to gels of organic substances. This was probably because they can be easily prepared in a transparent or translucent state and many of them are heat reversible. During recent years a large number of gels of inorganic substances have been prepared in as transparent a condition as the organic gels¹ and some of them have been shown to exhibit the phenomena of reversible isothermal sol-gel transformation and thixotropic behaviour. These inorganic gels have been prepared by either of the three following methods:—

- (1) by metathetical reactions,
- (2) by the addition of electrolytes to a suitably dialysed sol,
- (3) by diluting a true solution of the gel-forming substance in a suitable solvent.

It appears from the above that the first requisite for the formation of gels is that the gel-forming substance should be obtained in a sol condition. This takes place in the first method, in some cases, by the condensation of the molecules of the substance and, in others, by the peptisation of its precipitate by ionic adsorption and mechanical action. In the third method the gel-forming substance being less soluble in the diluted medium, goes over to the sol condition due to the condensation of molecules.

The second necessary condition seems to be that the density of charge on the particles of the sol should be low and that the sol should undergo coagulation in some way. These necessities are evidenced by the facts that (i) gels have been prepared by the second method mentioned above and (ii) they are sometimes observed to form in the dialysing bag when a suitable sol is extremely dialysed.

The third and rather important condition for the formation of gels is that the concentration of the gel-forming substance should be reasonably large. The necessity of this condition has been pointed out by Weiser and

Bradford² who conclude that the supersaturation of the gel-forming substance should be very high. Von Wiemarn³ has found that a gel is formed only when the value of N , the form coefficient of the precipitate, given by the relation

$$N = V \frac{P}{L}$$

(where V is a function of the viscosity of the reaction system, P the excess of the concentration of the substance to be precipitated and L its solubility), is very great. Further, various investigators⁴ have experimentally shown that no gel is formed by the first method if the concentrations of the gel-forming solutions are not suitably chosen. Also no gel will be formed by the second method if the sol is not fairly concentrated. These conclusions are also supported by the theory suggested by Bogue⁵ and accepted in principle by McBain and co-workers,⁶ Barrat,⁷ and Krishnamurti.⁸ According to this theory a gel is formed only when a large number of fibrils of which it is composed and which are in a highly hydrated state, cohere in a small volume.

The discussion set forth above leads to the conclusion that gelation consists in (i) the coagulation of the concentrated sols of the gel-forming substance, the particles of which do not carry a high density of charge and (ii) the subsequent formation of specific structures. The process of gelation should, therefore, be akin to the coagulation of concentrated sols. De Jong⁹ concludes from his experiments that the gelation of agar sol has all the characteristics of flocculation.

In the present investigation an attempt has been made to examine the relationship between the processes of coagulation and gelation of systems which contain the same coagulating and gelating substance. For this purpose sols and gels of zirconium hydroxides were first studied and later, experiments were performed with sols of stannic hydroxide since they, under not very different conditions, were found to give rise to true coagulation and gelation.

Processes of coagulation and gelation have been studied by several workers by various methods, such as those involving the measurements of viscosity, the optical properties (refractive index, extinction coefficient, scattering of light, transparency or opacity) and others. For the purpose of this investigation the viscosity method was employed and the results obtained are given in the following pages.

Experimental

Experimental method employed in the study of viscosity has been described by Prasad and Modak.¹⁰ The length and the diameter of the capillary

of the viscometer were 6.40 cm. and 0.062 cm. respectively. The constant of the apparatus determined by using 60 per cent. solution of sucrose was found to be 0.00218.

(a) *Coagulation of zirconium hydroxide sol.*—Zirconium hydroxide sol was prepared in the same manner as described by Prasad and Modak¹¹ and its concentration was also the same, *i.e.*, 0.06042 moles of zirconium oxide per litre.

3 c.c. of the sol were drawn out with a clean pipette into a clean dry test tube and a known volume of the solution of the electrolyte was taken into another clean dry test-tube. To each of these test tubes sufficient amount of twice-distilled water was added to make up the volume in each of the test tubes to 5 c.c. These were then corked and kept in the thermostat for 35 minutes during which period they attained the temperature of the thermostat. The maximum error in the adjustment of the thermostat never exceeded $\pm 0.02^\circ$. The two solutions were then mixed by pouring the contents of one test tube into the other; this was repeated four times. To make this process of mixing as uniform as possible the test tube containing the mixture was just resting on the other while pouring, and the actual pouring was done fairly slowly.

Viscosity readings were continued until particles were visible in the coagulating system. As a rule, this happened suddenly and immediately the separation of the liquid and solid portions into two layers could be detected in the viscometer. When this condition was reached, the readings were either very low or could not be taken at all since the particles formed obstructed the capillary.

Results obtained are shown graphically in which the viscosity (expressed in millipoises) has been plotted against the average time (expressed in minutes) after the mixing of the sol and the electrolyte solution, at which the viscosity readings were taken. Fig. 1 gives the changes in viscosity during the coagulation of the sol on the addition of various volumes of 2.5 N-KCl solution at 33°.

(b) *Gelation of zirconium hydroxide gels.*—Gels of zirconium hydroxide were prepared by the method of Prakash.¹² Solutions of sodium acetate and zirconium nitrate of the same concentrations as employed by Prasad and Modak (*loc. cit.*) were used. The gels prepared as above presented considerable difficulty in the measurement of viscosity. In the first instance these gels became very stiff during the course of setting and secondly some bubbles appeared in the capillary tube during the rise and fall of the gel-forming mixture. The result obtained with a mixture containing

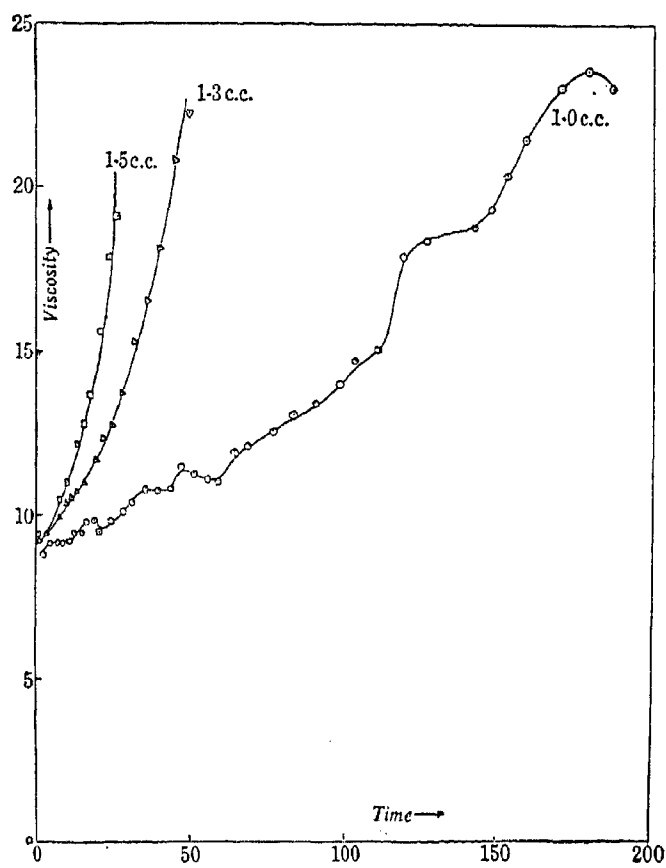


FIG. 1

Zirconium hydroxide sol
Coagulator KCl (2.5 N)
Temperature 33°

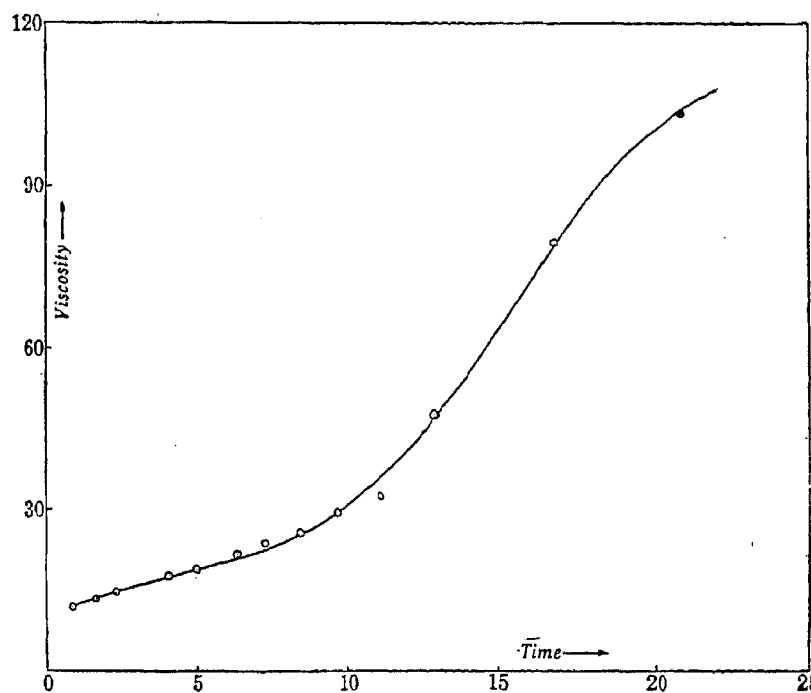


FIG. 2

Zirconium hydroxide gel
Temperature 33°

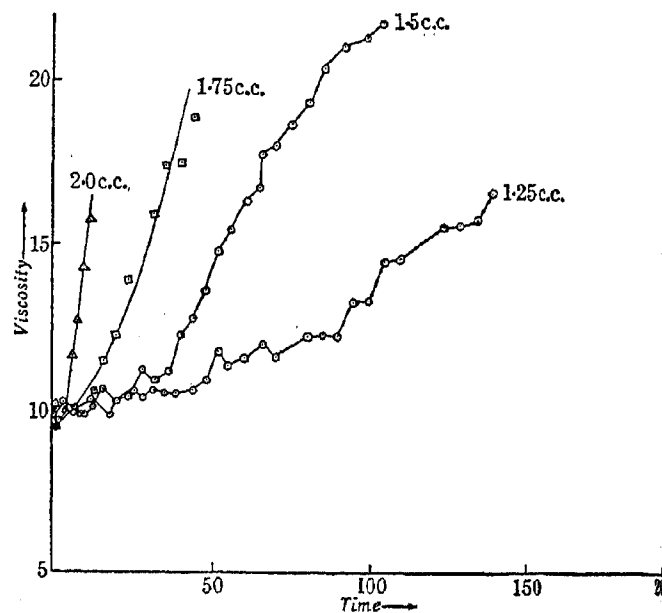


FIG. 3

Coagulator KCl (2.5 N)
(Stannic hydroxide undialysed sol)

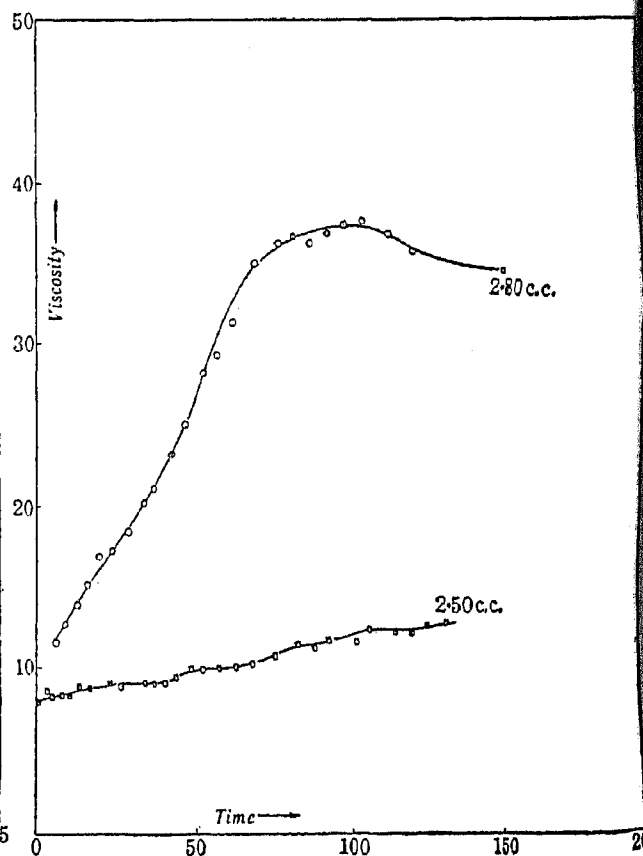


FIG. 4

Stannic hydroxide sol (undialysed)
Coagulator HgCl₂ (0.037 N)
Temperature 33°

4.86 c.c. of zirconium nitrate solution (10%) diluted to 5 c.c. and 1.62 c.c. of sodium acetate solution (3.84 N) also diluted to 5.0 c.c. is shown in Fig. 2.

(c) *Coagulation of stannic hydroxide sol.*—The sol was prepared in the same manner as described by Prasad and Modak (*loc. cit.*) and the concentration of the sol was also the same (SnO_2 content = 0.4725 moles, per litre). The viscosity measurements were made with undialysed sol and the sol dialysed for 12 days. Water outside the dialysing bag was changed twice and sometimes thrice a day and was always maintained at the same level as that of the sol in the bag.

4.0 c.c. of the sol were taken out in a clean test tube and 1.0 c.c. of distilled water was added to it. In another test tube a known volume of the electrolyte solution was taken and it was suitably diluted to make up the volume to 5.0 c.c. The rest of the procedure was the same as described before.

Figs. 3 and 4 give the various changes with time on the addition of different volumes of 2.5 N-KCl and 0.037 N-HgCl₂ solutions, respectively, at 33°, to the undialysed sol.

Figs. 5 and 6 give the results obtained with sol dialysed for 12 days, under the same conditions as given above. The coagulating mixture was observed to become very viscous when 0.60 c.c. and 0.80 c.c. of the HgCl₂ solution were added to the sol, and on standing for a long time the coagulum separated out but the mixture never set to a gel.

(d) *Gelation of stannic hydroxide sol.*—It has been found by Dhar and Varadanam¹³ that the stannic hydroxide sol prepared as described above sets to a jelly on continued dialysis. A transparent jelly of stannic hydroxide is also formed when its concentrated sol is treated with a solution of hydrochloric acid or of potassium and barium chloride. The gels obtained by them showed thixotropic behaviour.

The sol of stannic hydroxide prepared for the coagulation experiments was allowed to dialyse till practically no electrolytes passed out during dialysis. This sol was stored in a Jena glass flask and was used for all the experiments. On the addition of electrolytes to this sample, no coagulation was observed and the whole mixture set to a clear thixotropic gel after sometime.

5 c.c. of the sol were taken in one test tube and different volumes of solutions of electrolytes were made up to 5 c.c. in the other test tube and the two were mixed in the usual manner after they had attained the temperature of the thermostat. The viscosity readings of the gel-forming system were

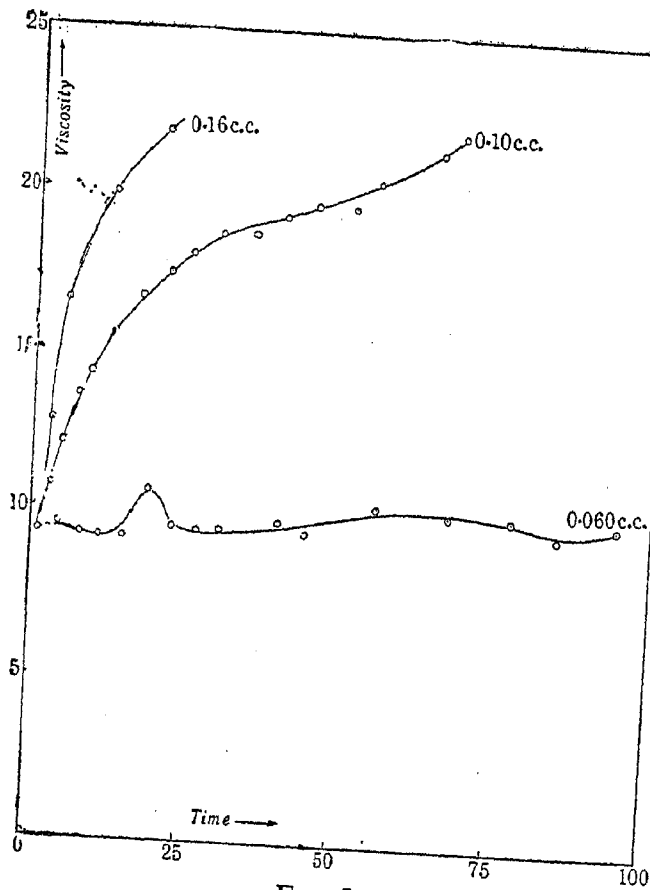


FIG. 5
Coagulator KCl (2.5 N)
Temperature 33°
(12 days dialysed sol)
Sn (OH)₄ sol

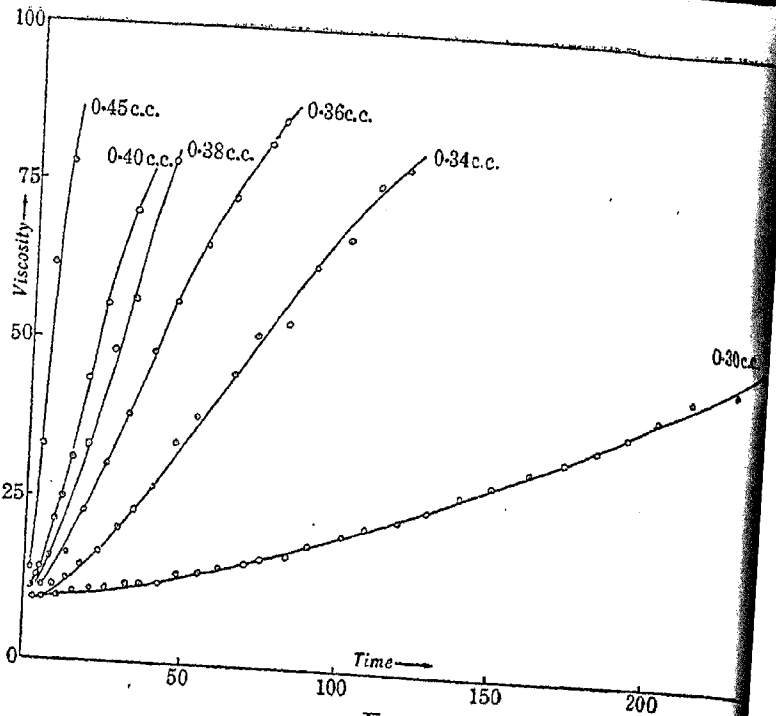


FIG. 7
Extremely dialysed sol
Coagulator KCl (0.5 N)
Temperature 33°
Sn (OH)₄ sol

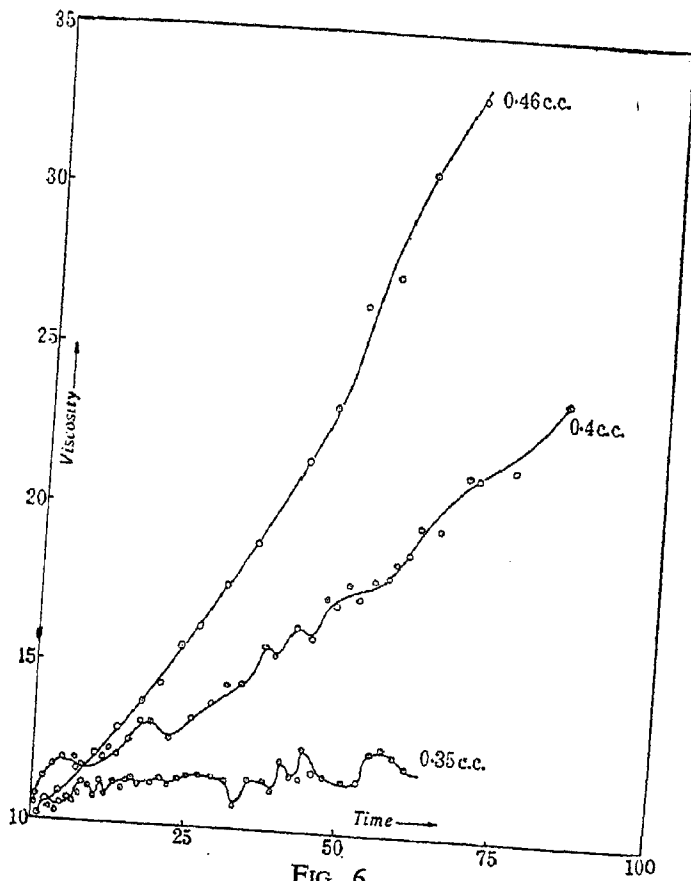


FIG. 6
Coagulator HgCl₂ (0.037 N)
Temperature 33°
(12 days dialysed sol)
Sn (OH)₄ sol.

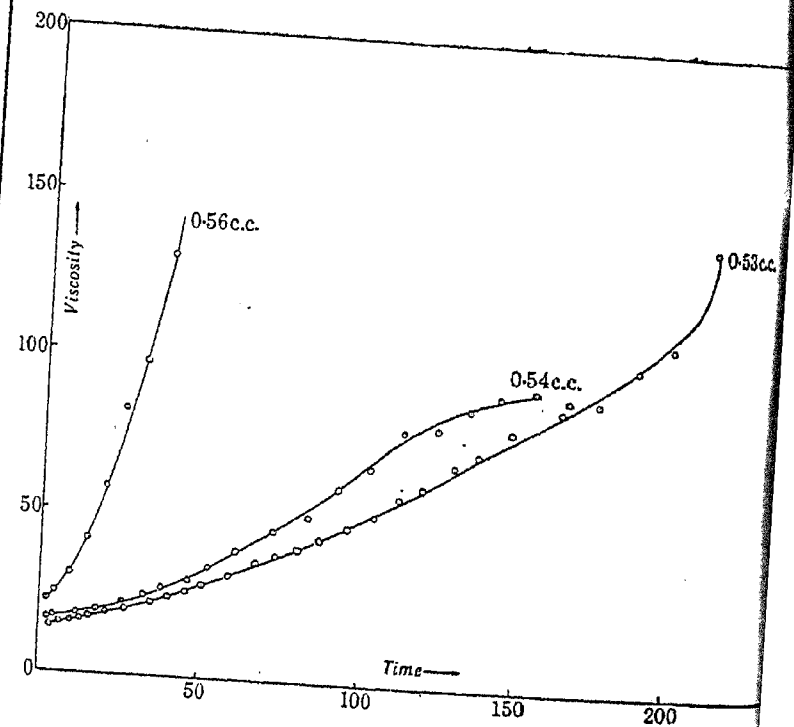


FIG. 8
Coagulator BaCl₂ (0.031 N)
Temperature 33°
Highly dialysed Sn (OH)₄ sol

taken in the manner described above and they were continued till the viscosity increased so high that the time of rise and fall of the mixture in the viscometer was sufficiently long.

Figs. 7, 8 and 9 give the results obtained on the addition of different volumes of 0.5 N-KCl, 0.031 N-BaCl₂ and 0.018 N-HgCl₂, respectively, at 33°.

Discussion and Results

The addition of electrolytes to the zirconium hydroxide sol and the sol of stannic hydroxide undialysed or dialysed for 12 days produces coagulation. A gel is formed, on the other hand, by the addition of coagulators, to the extremely dialysed stannic hydroxide sol.

It would be observed that the curves in Figs. 1 and 3 show a common behaviour in the sense that whereas some curves rise continuously and smoothly, a few represent an 'S' shape comprised of zones¹⁴. This is markedly observed in the case of the curves for 1.0 c.c. in Fig. 1 and of those for 1.25 c.c. and 1.50 c.c. in Fig. 3. Generally an increase in the concentration of the coagulator appears to remove the zones (*cf.* curves for 1.25 c.c., 1.65 c.c. and 2.0 c.c. in Fig. 3; 1.0 c.c., 1.3 c.c. and 1.5 c.c. in Fig. 1). Joshi and Nanjappa noticed larger changes in the viscosity values during the coagulation of ferric hydroxide sol than those shown in Figs. 1 and 3. The smaller changes in the present case may be due to the fact that fairly concentrated sols have been used and this may have caused increased autocatalytic effect of coagulation under these conditions. An interesting point in the curve for 2.0 c.c. in Fig. 3, is the initial decrease in viscosity before it tends to rise rapidly in a smooth manner, a fact observed by Joshi and co-workers in several cases of slow coagulation.

The coagulation of the same sol (undialysed stannic hydroxide sol) by mercuric chloride, Fig. 4, does not show the same characteristics as observed during its coagulation by KCl (*cf.* Fig. 3). The viscosity curve in the presence of 2.5 c.c. is a very slow rising one and the zones are not very significant. On increasing the amount of the electrolyte to 2.8 c.c. the curve becomes a rapidly rising one. It appears that the changes in viscosity at any given interval of time are not commensurate with the amount of the electrolyte added.

The dialysis of the stannic hydroxide sol for 12 days changes its condition to a very great extent. This effect can be seen best by comparing the coagulation curves for the dialysed sol by KCl and HgCl₂, Figs. 5 and 6, respectively, with those for the undialysed sol in Figs. 3 and 4. The curve with 0.35 c.c. in Fig. 6 is a zonal one and does not show large total changes in viscosities.

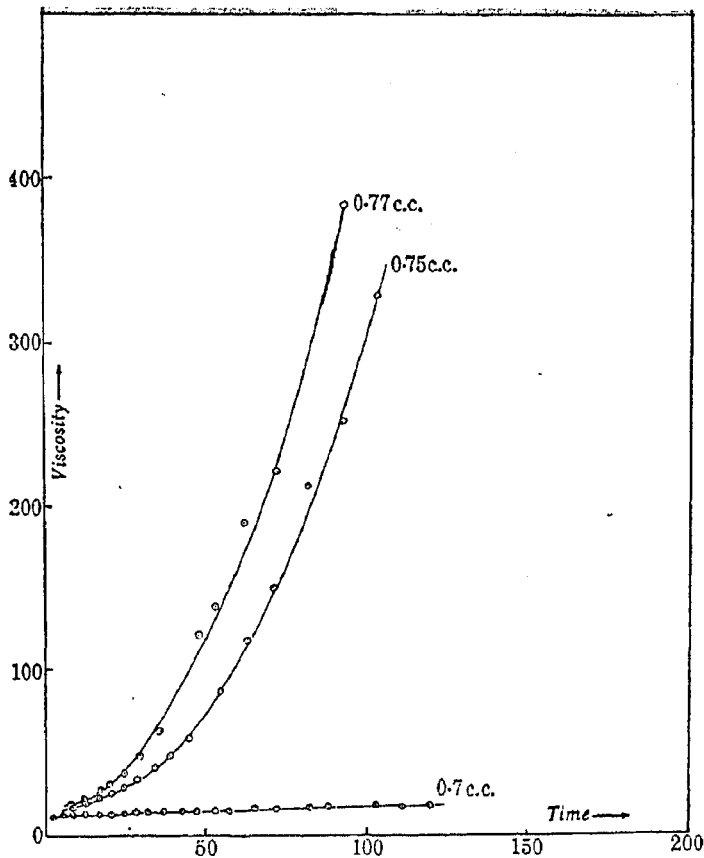


FIG. 9

Coagulator HgCl_2 (0.018 N)
 Temperature 33°
 Highly dialysed $\text{Sn}(\text{OH})_4$ sol

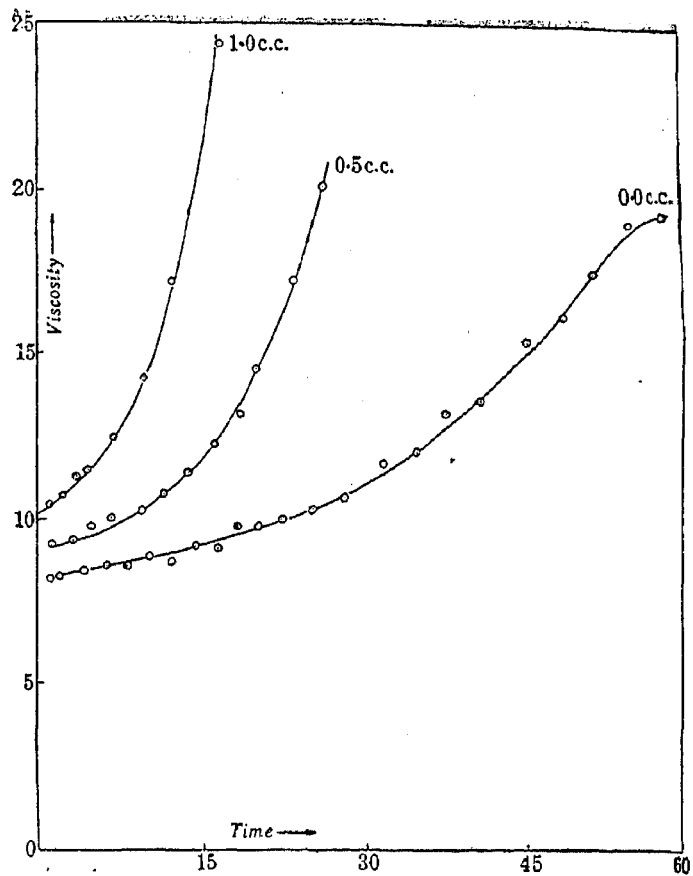


FIG. 11

Effect of alcohol
 Temperature 43°

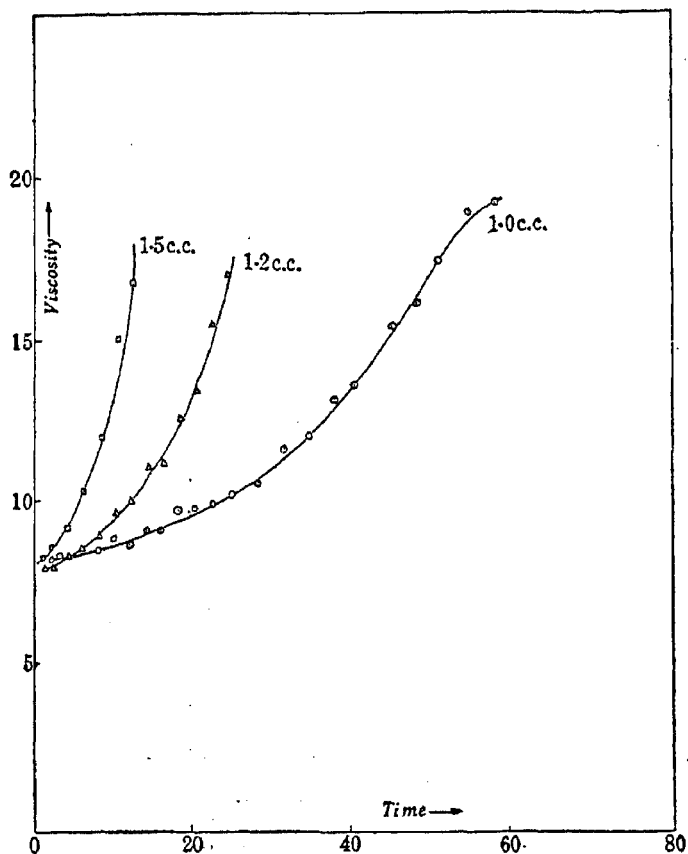


FIG. 10

Zirconium hydroxide sol
 Coagulator KCl
 Temperature 43°

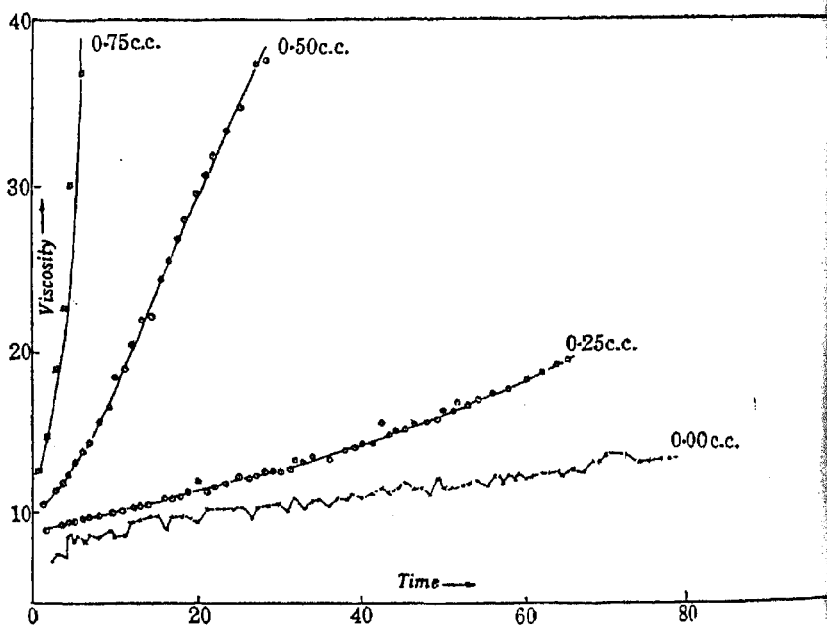


FIG. 12

Effect of alcohol on gelation by HgCl_2
 Temperature 43°
 (28 c.c. of 0.037 N)
 Highly dialysed $\text{Sn}(\text{OH})_4$ sol

It appears necessary to make a distinction between two types of viscosity-time curves indicative of rapid coagulation. The type of curve indicated by 0.46 c.c. of HgCl_2 solution in Fig. 6 seems to be obtained if the rate of coagulation indicated by the viscosity-time curves is comparatively slow. Curves of this type have previously been obtained by various workers using the viscosity and the transparency methods.¹⁵ If, however, the coagulation is very rapid, the curve is of the type obtained with 0.16 c.c. of KCl shown in Fig. 5. Such curves too have been obtained by a number of workers by using the above-mentioned methods.¹⁶ These types of curves could probably have been obtained with the sol dialysed for 12 days by using concentrations of HgCl_2 higher than 0.60 c.c. or 0.80 c.c. Attempts made in this direction showed that no curves could be obtained easily for these amounts of the coagulator but an observation was made that the whole mixture sets very rapidly.

It was observed that the zones observed with zirconium hydroxide sol in the presence of 1.0 c.c. of the coagulator at 33°, disappear when the temperature is raised to 43°. The viscosity-time curves for other mixtures of the coagulator and the zirconium hydroxide sols also undergo a change in magnitude but not in their characteristics. This effect has been brought out in curves shown in Fig. 10. The effect of temperature on the coagulation of zirconium hydroxide sol would thus appear to hasten the process of coagulation, carrying it from the slow region to the rapid one. A rise in temperature by 10° reduces the total time of coagulation to nearly $\frac{1}{3}$ of that at the lower temperature and the curve for 1.3 c.c. of sol at 33° corresponds fairly well to that for 1.0 c.c. at 43°.

Similar effect is observed when methyl or ethyl alcohol is added to the coagulating sol. The addition of 0.5 c.c. and 1.00 c.c. of ethyl alcohol to the zirconium hydroxide sol coagulated by 1.5 c.c. of KCl at 33° and 43° and the addition of the same amounts of methyl and ethyl alcohols to the stannic hydroxide sol (dialysed for 12 days) coagulated by 0.43 c.c. of 0.037 N- HgCl_2 showed a shortening of the coagulation period and the removal of any irregularities. The 'S' shape nature of the curves changes to that corresponding to rapidly rising ones and the reduction in the period of coagulation is fairly proportional to the original coagulation time. Two such curves representative of this effect are shown in Fig. 11. The effect of the higher alcohol seems to be greater than that of the lower ones.

Viscosity-time curves obtained with the extremely dialysed sol in the presence of potassium, barium and mercuric chlorides are shown in Figs. 7, 8 and 9. In the presence of potassium chloride in smaller concentrations these

curves are 'S' shaped but become rapidly rising ones when larger amounts are used. The addition of BaCl_2 yields the same type of results. Mercuric chloride shows a different behaviour. The curves obtained in the presence of 0.77 c.c. and 0.75 c.c. are rapidly rising ones and they change over to an almost flat curve showing practically no viscosity changes, when 0.70 c.c. of HgCl_2 are used. Similar behaviour of HgCl_2 is seen from curves in Fig. 4. The curves for viscosity changes during the gelation of stannic hydroxide sol show no indications of any zonal effect during gelation. On the whole, the curves for gelation correspond to the first type of rapid coagulation referred to above.

As has been already stated in the beginning highly dialysed sol of stannic hydroxide produced gels on the addition of electrolytes. However, the addition of a little NH_4OH produced no gelation but effected a very slow coagulation. Since the stannic hydroxide sol is negatively charged, it is shown from the above that the tendency of stannic hydroxide sol to give rise to coagulation or gelation depends on the concentration of the hydroxyl ions adsorbed by the micelles.

The viscosity-time curve obtained from another sample of extremely dialysed stannic hydroxide sol prepared in a similar manner as described above and coagulated by 0.28 c.c. of 0.037 N- HgCl_2 is shown in Fig. 12. The effect of the addition of different amounts of ethyl alcohol on the same gelating mixture is also shown in this figure. These curves show that under the conditions stated above the course of gelation of stannic hydroxide gels is zonal and these zones disappear on the addition of alcohol.

The curve for the viscosity changes in zirconium hydroxide gel obtained at temperature 33° is shown in Fig. 2. The curve is precisely 'S' shaped and is similar to the ones obtained during the coagulation of a sol. This nature of the curves was also observed with other mixtures which could not be studied upto the gelation point due to reasons stated before. It shows the usual characteristics of a slow increase in the first and a rapid one in the latter stages. The method of preparation of this gel is evidently different from that of the stannic hydroxide sol.

It would appear from the foregoing conclusions that the curves for the coagulation and the gelation of the same sol show similar characteristics. Though coagulation is the first step in the complex process of gelation, the main characteristics of coagulation seem to dominate the total changes brought about during the gelation process leading upto the formation of a definite structure. While it cannot be visualised that the processes latter to the coagulation of the gelating substances are not different from the former, it is certain

that the viscosity as a property fails to show the changes occurring at this stage. Opacity measurements carried out by Prasad and Modak (*loc. cit.*) have also yielded results which indicate a similarity in the coagulation and gelation processes. Thus it appears that both viscosity and opacity measurements have also their limitations in the study of colloids and their behaviour. It is possible that some property of colloids other than those employed so far may reveal the inner characteristics of the gelation process taking place subsequent to coagulation stage.

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