

MEASUREMENT OF OPACITY DURING THE COAGULATION OF THE CONCENTRATED SOLS OF ZIRCONIUM AND STANNIC HYDROXIDES AND THE GELATION OF STANNIC PHOSPHATE AND ZIRCONIUM HYDROXIDE GEL-FORMING MIXTURES

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SINCE the classical researches of Powis¹ and the mathematical treatment of the process of coagulation by Smoluchowsky² various methods have been employed from time to time to study the phenomenon of coagulation. More extensively used of these are the methods depending upon the measurement of changes in viscosity and optical properties. Amongst the latter methods those involving the measurement of transparency, turbidity and refractive index have been commonly used. The spectroscopic method of Mukherjee and Papa Constantinou³ and the tyndallmeter method of Ghosh⁴ form some of the attempts in this direction. The refractive index method has been used extensively by Joshi and co-workers⁵ during their study of the phenomenon of slow coagulation.

Krishnamurti⁶ measured the scattering of light by agar sols and gels by a photometric arrangement and concluded that the micelles in gels are much bigger than those in sols. Arsiz⁷ also studied the intensity of light scattered by glycerol sol of gelatin by means of photographic method.

The transparency method was first employed by Mukherjee and Majumdar⁸ in the study of sols undergoing coagulation. A beam of light of constant intensity was allowed to fall on a transparent cell containing the coagulating mixture and the intensity of the transmitted light was measured by means of a thermopile connected to a galvanometer. Changes in the deflection of the galvanometer were taken to represent directly the changes

¹ *Zeit. physikal Chem.*, 1915, **89**, 186; *J.C.S.*, 1916, **109**, 1734.

² *Zeit. Physik.*, 1916, **17**, 557; *Zeit. Physikal Chem.*, 1917, **92**, 123.

³ *J.C.S.*, 1920, **17**, 156.

⁴ *J. Indian Chem. Soc.*, 1933, **10**, 509.

⁵ *Ibid.*, 1936, **13**, 141, 309; 311.

⁶ *Proc. Roy. Soc.*, 1928, **25**, 377.

⁷ *Koll. Chem. Beih.*, 1915, **7**, 19.

⁸ *J. Indian Chem. Soc.*, 1924, **125**, 785.

taking place in the sol. This method was employed later for the study of the kinetics of coagulation of sols and of setting of gels.⁹

Desai and co-workers¹⁰ modified this method by employing a photocell instead of the thermopile. They obtained an important result that the coagulation velocity curves of thorium hydroxide sol could be smooth or 'S'-shaped according as the sol is highly or slightly dialysed.

In the present investigation the photocell method of Desai and co-workers has been improved as described below and has been employed to study the course of (i) coagulation of concentrated sols of zirconium and stannic hydroxides and (ii) gelation of stannic phosphate and zirconium hydroxide gel-forming mixtures.

Experimental

Description of the Apparatus.—

Light from a cinema projector lamp 120 watts, 230 volts, working at a constant current was allowed to fall on an optical cell containing the coagulating or the gelating mixture under investigation. The incident light was rendered parallel by passing through a condensing lens and the heat rays were cut off by passing the light through a cell in which water was kept circulating.

Light transmitted through the optical cell was allowed to fall on an Osram Cæsium Photo Cell enclosed in a wooden box which was covered with black paper and in which no stray light was allowed to enter. The current generated in the photocell was magnified by a single stage amplification unit and was measured by means of a galvanometer connected in the circuit. Differences in galvanometer deflections noted at different intervals of time after the coagulation or gelation has commenced, are taken as proportional to the opacity of the coagulating or the gelating mixture. The amplifying arrangement was used particularly with a view to magnify even the smallest changes which may be taking place in a sol or a gel during coagulation or gelation. Constancy of the initial reading of the galvanometer with initial dark current and also with the light falling directly on the photocell was checked from time to time during the period of observation. The reproducibility of the results was ascertained before the apparatus was employed for final readings. The whole apparatus was enclosed in a thermostat kept constant within $\pm 0.02^\circ$.

⁹ Cf. Prasad and Nabar, *J. Indian Chem. Soc.*, 1933, 10, 53; Mehta and (Miss) Joseph, *ibid.*, 1933, 10, 177; Prasad and Hattiangadi, *ibid.*, 1929, 6, 653; Joshi and Rao, *ibid.*, 1936, 13, 311.

¹⁰ *Trans. Farad. Soc.*, 1928, 18, 24.

(A) *Preparation of Sols.*—

(i) *Zirconium hydroxide.*—A concentrated sol of zirconium hydroxide was prepared by the method of Sharma and Dhar.¹¹ 52 g. of pure zirconium nitrate were dissolved in twice distilled water and the solution was made to 500 c.c. After 15 days of continuous dialysis of this solution a fairly concentrated sol was obtained. A portion of this sol was taken out and stored in a Jena glass flask and was used for the investigation. The zirconium contents of the sol were found to be 0.06042 moles of zirconium oxide per litre.

(ii) *Stannic hydroxide.*—Dhar and Varadanam's method¹² was followed for the preparation of a concentrated sol of stannic hydroxide. About 55 g. of Merck's pure stannic chloride were dissolved in 100 c.c. of distilled water and Merck's extra pure liquor ammonia was added to the solution drop by drop with constant stirring, the solution being kept cool throughout. The precipitate formed was washed free from the electrolytes and about 600 c.c. of distilled water were added to it. The stannic hydroxide was brought in colloidal form by the addition of Merck's pure ammonium hydroxide to the suspension kept continuously stirred by a glass stirrer. On standing overnight a clear sol was formed. A portion of this sol was taken out and stored for the experimental investigation. The SnO₂ contents of the sol were found to be 0.4725 moles per litre.

Experimental Procedure.—

The coagulating mixtures were prepared by mixing 1.5 c.c. of the sol diluted to 2.5 c.c. by the addition of distilled water, with a known volume of the coagulator solution, also diluted to 2.5 c.c. Test-tubes containing the two solutions were kept at constant temperature for sufficient time to acquire the temperature of the thermostat and the contents were then mixed in a definite manner. The method of mixing was maintained constant throughout. Readings were recorded at definite intervals. Unless otherwise stated white light was used as the source.

(B) *Preparation of Gels.*—

(i) *Stannic phosphate gels.*—Gels of stannic phosphate were prepared in the same manner as described by Prasad and Modak.¹³ The concentrations of the solutions employed were also the same, *i.e.*, the solution of stannic chloride was 0.4725 N with respect to SnO₂ content and that of phosphoric acid was 0.2 N. The gel-forming mixtures were prepared from different volumes of these two solutions in the same manner as described in the case of zirconium hydroxide gels.

¹¹ *J. Indian Chem. Soc.*, 1932, 9, 455.

¹² *Ibid.*, 1936, 13, 602.

¹³ *Proc. Ind. Acad. Sci.*, 1940, 11, 282.

(ii) *Zirconium hydroxide gels*.—Gels of zirconium hydroxide have been prepared by Sharma and Dhar¹⁴ and also by Prakash.¹⁵ The latter method which was followed in the present investigation, consists in mixing solutions of sodium acetate and zirconium nitrate of suitable concentrations in proper proportions. A ten per cent. solution of zirconium nitrate was made in distilled water and was stored in a Jena glass flask and used throughout the investigation. Solution of sodium acetate used was 3.84 N.

A known volume (x) of zirconium nitrate solution was taken in a test-tube and distilled water was added to it to make the volume to 5.0 c.c. In another test-tube a suitable volume of sodium acetate solution (y) was taken and it was also diluted to 5.0 c.c. The contents of the two tubes were mixed and the readings were taken in the same manner as described above.

Results obtained are shown graphically in which the ordinate represents the deflection differences ($di - df$) where di is the initial deflection and df the deflection at time t (expressed in minutes), in centimeters.

Fig. 1 shows the opacity changes during the coagulation of zirconium hydroxide sol with different amounts of 2.5 N solution of KCl.

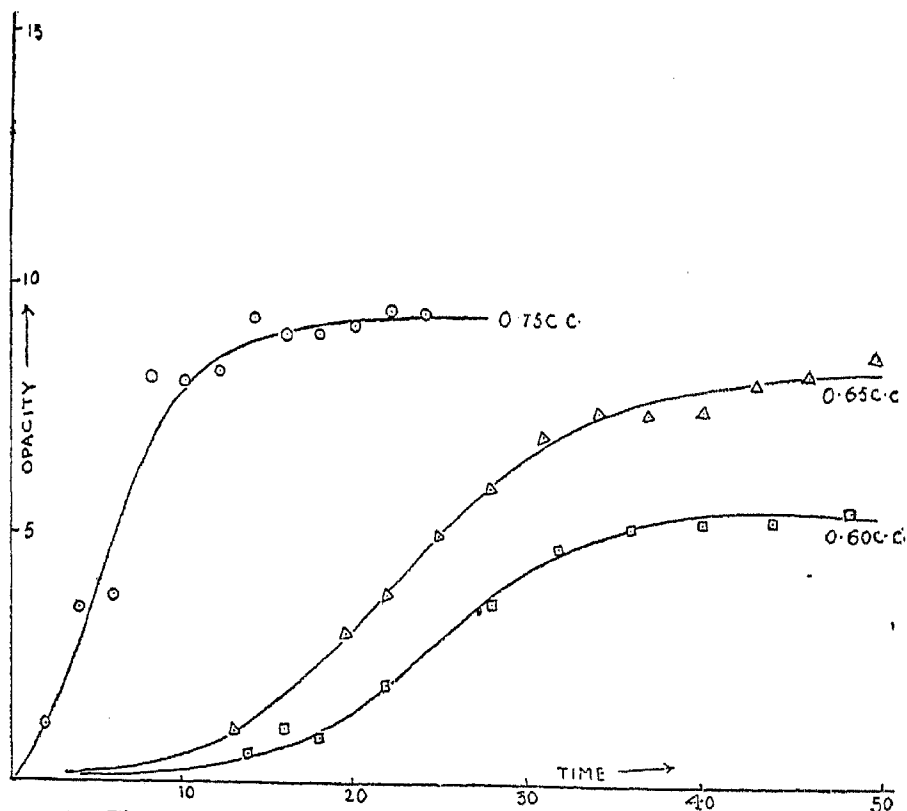


FIG. 1. Zirconium Hydroxide Sol. Coagulator KCl (2.5 N). Temperature 33°.

Fig. 2 shows the opacity changes during the coagulation of stannic hydroxide sol with different amounts of 2.15 N solution of KCl and Fig. 3 with different amounts of 0.037 N solution of HgCl_2 .

¹⁴ *Loc. cit.*

¹⁵ *J. Indian Chem. Soc.*, 1932, 9, 193.

Coagulation of Concentrated Sols of Zirconium & Stannic Hydroxides

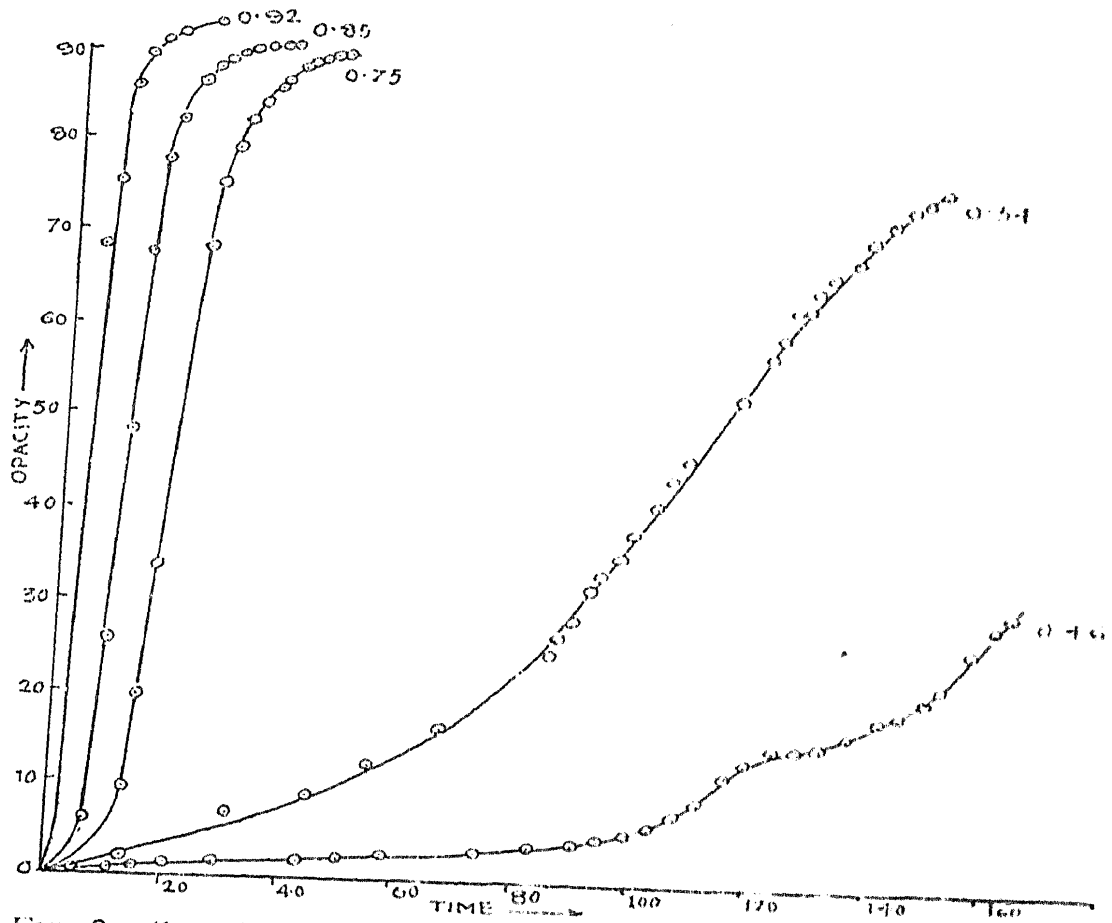


FIG. 2. Stannic Hydroxide Sol. Coagulator $KClO_4$ (1% N). Temperature 33°.

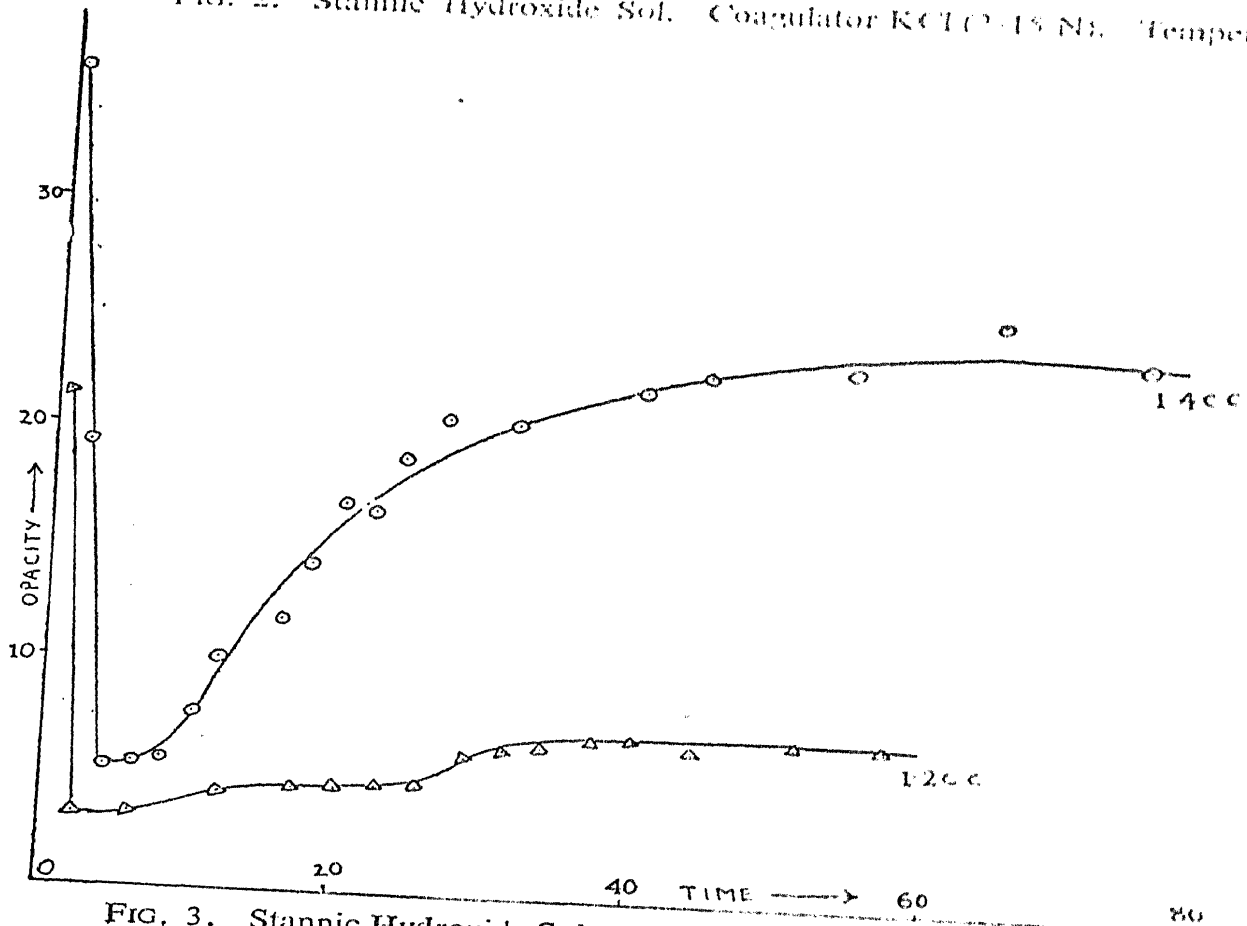


FIG. 3. Stannic Hydroxide Sol. Coagulator $HgCl_2$ (0.037 N). Temperature 33°.

Figs. 4 and 5 give the opacity changes in stannic phosphate gels containing different amounts of solutions of phosphoric acid (A) and stannic

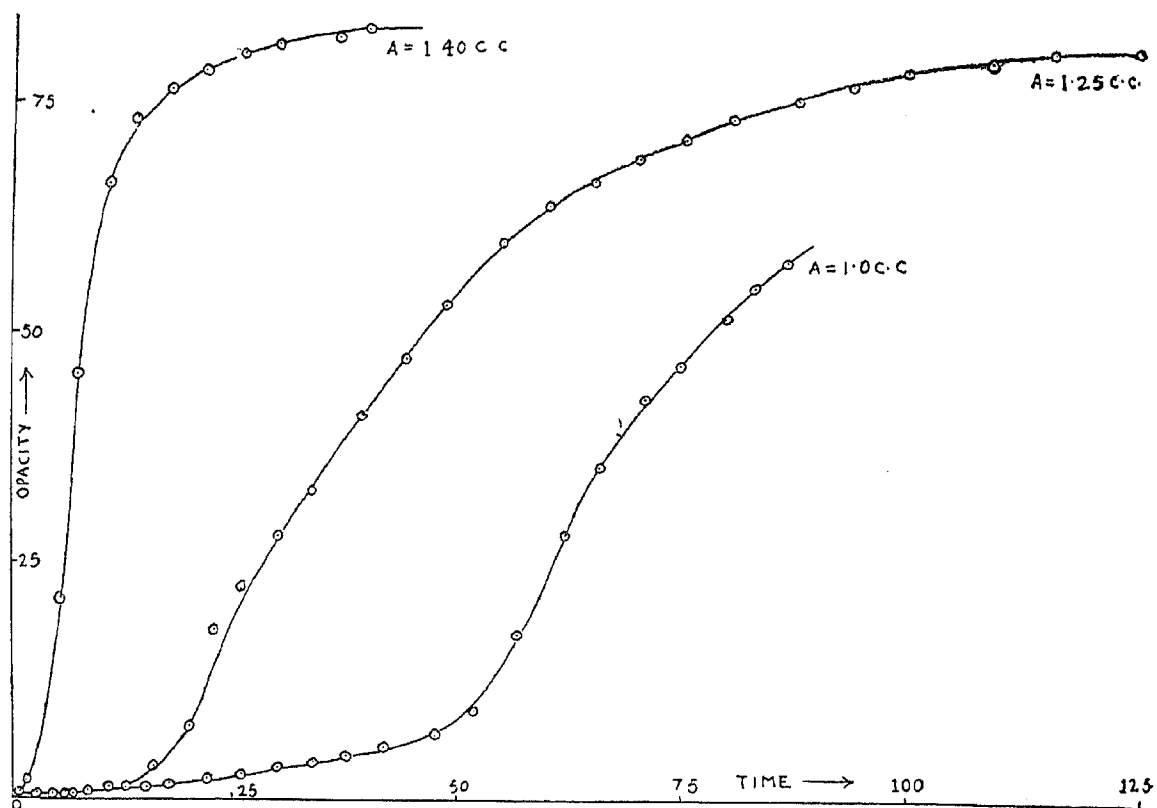


FIG. 4. Stannic Phosphate Gels. Temperature 35°. B = 1.5 c.c.

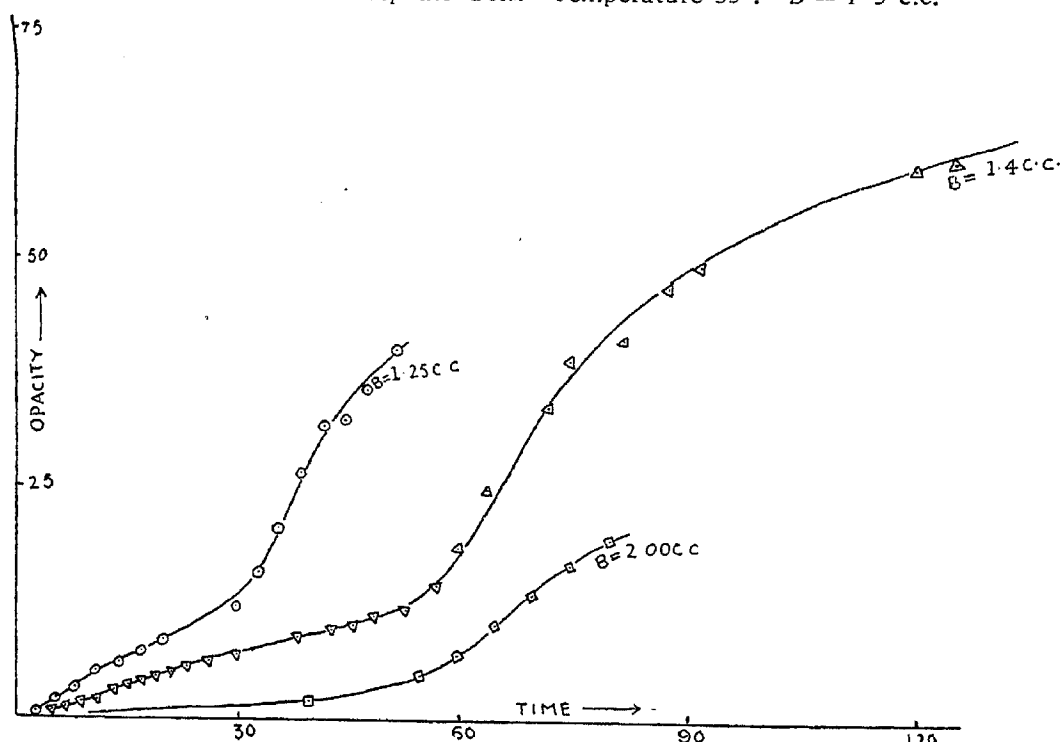


FIG. 5. Stannic Phosphate Gels. Temperature 35°. A = 10 c.c.

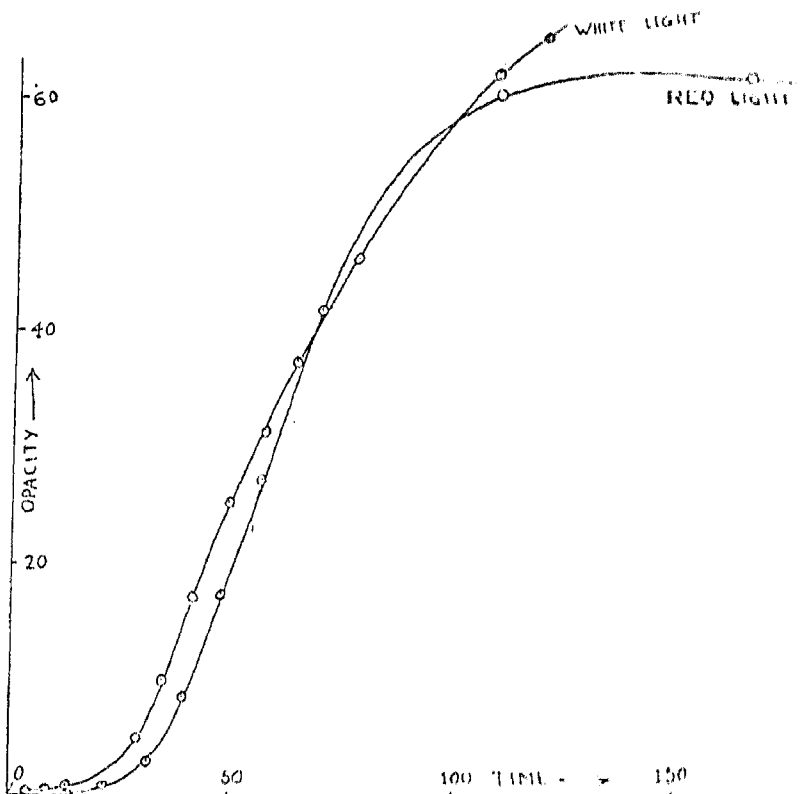


FIG. 6. Effect of Nature of Light. Temperature 35°. A = 1.20 c.c.; B = 1.75 c.c.

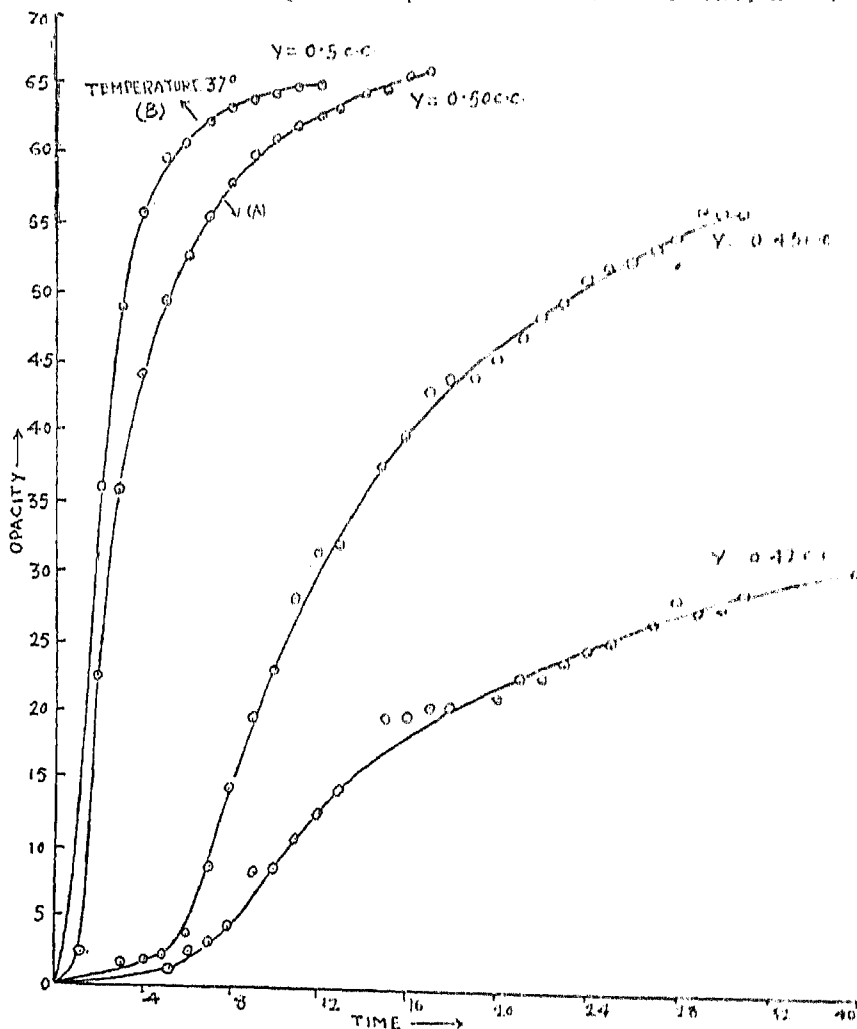


FIG. 7. Zirconium Hydroxide Gels. Temperature 33°. X = 3.0 c.c.

chloride (B). Fig. 6 shows the effect of change in the nature of incident light on the time-opacity relation with a mixture containing 1.2 c.c. of stannic chloride and 1.75 c.c. of phosphoric acid solution. The red light was obtained by introducing a red gelatin filter (610–715 $\mu\mu$) obtained from the Kodak Company.

Fig. 7 gives the opacity-time curves during the setting of zirconium hydroxide gels containing X = 3 c.c. of zirconium nitrate solution and different amounts of sodium acetate solution (Y). In this figure curve B is obtained at 37° and depicts the effect of temperature on the opacity-time relation of a gel containing 3.0 c.c. of zirconium nitrate solution and 0.50 c.c. of sodium acetate solution. Curves 1, 2 and 3 correspond to 33°.

Discussion of Results

The striking feature of all the opacity curves during coagulation shown in Figs. 1 and 2 is that they are S-shaped. In the case of both the zirconium and stannic hydroxide sols coagulated by potassium chloride, the opacity rises at first slowly, then rapidly and again slows down in the later stages. Higher concentrations (0.75 c.c.) of the coagulator seem to produce a sudden rise in the early stages of the coagulation of zirconium hydroxide sol (Fig. 1) and the S-shape of the curve is also not so perfect as in the presence of 0.60 c.c. and 0.65 c.c. of the coagulator. In the case of stannic hydroxide sol the opacity curves in the presence of larger amounts of the coagulator are very regular and steep rising but in the presence of smaller amounts they are not so smooth.

The opacity-time curves obtained during the coagulation of stannic hydroxide sol by HgCl_2 solution (Fig. 3) are very peculiar and very different from those shown in Figs. 1 and 2. In this case the opacity produced is very great in the beginning and decreases equally rapidly so that in about two or three minutes it comes down to a very low value. It then rises in the usual manner in the presence of 1.4 c.c. and the curve obtained is an S-shaped one while in the presence of 1.2 c.c. of HgCl_2 solution the opacity developed is not as much and the curve is also definitely irregular or zonal.

Opacity-time curves obtained during the gelation of stannic phosphate gel-forming mixtures are also S-shaped and appear to show the autocatalytic nature of the gelation process. These curves are either flat or rising S-shaped, depending upon the amounts of phosphoric acid and stannic chloride contained in the gel-forming mixtures. Increase in the amount of phosphoric acid increases the rate of rise in opacity; the curves in the presence of 1.00 c.c. and 1.25 c.c. of phosphoric acid are S-shaped while the one corresponding to 1.4 c.c. (Fig. 4) is practically a rapidly rising one. If coagulation precedes

the actual formation of specific structures, which is a characteristic of gel state alone, it would appear that the curves with lower phosphoric acid content indicate slow coagulation of the sol of the gelling substance and those containing larger amounts indicate rapid coagulation. These observations point out that at any time after mixing the gel-forming constituents the density of charge on the micelles in the gel-forming mixture containing 1.0 c.c. of phosphoric acid is comparatively greater and their number and their degree of hydration smaller than in mixtures which contain 1.25 c.c. and 1.40 c.c. of phosphoric acid. Same conclusions have been drawn from the measurements of viscosity made during the gelation of stannic phosphate gel-forming mixtures, containing different amounts of phosphoric acid.¹⁶

The rate of rise of opacity decreases with an increase in the amount of stannic chloride in the gel-forming mixtures. Assuming that the amount of stannic phosphate formed in the gel does not greatly increase, the slowing down of the gelation process on increasing the quantity of stannic chloride appears to be due to the increase in the degree of dispersity and the density of charge on the micelles and this may have been brought about by the increased preferential adsorption of the stannic ions by the colloidal particles. These results further indicate that the slowing down of gelation (possibly the coagulation which precedes it) process can be achieved by increasing the concentration of the peptising ions which increase the degree of dispersity and the density of charge on the micelles.

The increase of opacity with time may be assigned to an increase in the number and size of the micelles. When the opacity changes become minimum or the opacity reaches a constant value, the changes in the above-named factors also become minimum or come to a stop. Prasad and Hattiangadi¹⁷ have considered this condition to be the criterion of setting of gels and have employed this method for determining the time of setting of silicic acid gels. The opacity-time curves shown in Figs. 4 to 5 can be employed also to determine the time of setting of stannic phosphate gels. The importance of such a method for determining the time of setting of a gel has been pointed out by Prasad and Parmar.¹⁸

The increase of the opacity of the gel-forming mixtures, at any time after the formation of gels has commenced, on increasing the phosphoric acid contents of the mixtures may have been caused also on account of all the three factors mentioned above. However, the decrease in opacity observed

¹⁶ Cf., Prasad and Modak., *loc. cit.*

¹⁷ *J. Indian Chem. Soc.*, 1929, 6, 653.

¹⁸ *Curr. Sci.*, 1935, 4, 310.

with an increase in the stannic chloride content is mostly due to the increase in the size of the micelles, since the amount of stannic phosphate in colloidal condition cannot increase with decrease in the quantity of stannic chloride in the gel-forming mixture.

The opacity-time curves obtained with different sources of incident light (Fig. 6) are very nearly the same; the red filter having no particular advantage on the sensitivity of the method as compared to white light.

Zirconium hydroxide gel-forming mixtures appear to behave similarly to those which give rise to stannic phosphate gels. The opacity-time curves are definitely S-shaped in the presence of small amounts of sodium acetate and become rapidly rising ones (Fig. 7) when sodium acetate content of the mixture is increased. The curves with 0.42 c.c. and 0.45 c.c. appear to correspond to slow and the third one to the rapid coagulation. The increase in the opacity produced by the addition of increasing quantities of sodium acetate at any time after mixing the constituents is due to the increase in the number and the size of zirconium hydroxide micelles. These results are similar to those obtained with the stannic phosphate gel-forming mixtures to which increasing quantities of phosphoric acid are added.

It should, however, be noted that there is a distinct difference in the modes of the formation of zirconium hydroxide and stannic phosphate gels. Stannic phosphate is formed by the direct interaction of the constituents while this does not happen in the formation of zirconium hydroxide.

The opacity-time curves for the mixtures containing 3 c.c. of zirconium nitrate and 0.50 c.c. of sodium acetate solution obtained at 33° and 37° (Curves A and B, Fig. 7) are similar to each other but the curve at 33° lies lower than the curve at 37°. This may have been caused by (i) an increase in the number of micelles in the mixture due to increased hydrolysis with rise in temperature or (ii) an increase in the size of micelles, probably due to increased rate of coagulation at higher temperature or (iii) both.

In conclusion it may be mentioned that the optical results on the whole fail to show any distinct differences between the processes of coagulation and gelation. The distinct stages of gelation, often stated as three independent processes, fail to show their individual existence and as a whole the gelation process appears to be smooth. The fact that coagulation is the first step in the complex process of gelation may be responsible for the evidently similar curves for coagulation and gelation, the latter two steps failing to produce a marked effect on the opacity.