VISCOSITY OF STANNIC PHOSPHATE GELS DURING SETTING

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THE viscosity of several gel-forming mixtures during the process of setting has been studied by Prasad and co-workers.[1,2,3] In studies[1,2] it has been found that the viscosity of the gel-forming mixtures increases with time and the viscosity-time curves are continuous. This observation has led these workers to the conclusion that the various processes involved in the setting of gels, such as the formation of colloidal particles, their coagulation and subsequent hydration and the formation of specific structures, are continuous functions of time. However, in the case of thorium molybdate gels[3] it has been found that the viscosity-time curves are discontinuous or zonal. These gels exhibit the phenomenon of thixotropy and it is possible that their peculiar behaviour is due to their thixotropic nature.

Several mathematical expressions have been found to represent the viscosity changes taking place in a gel-forming mixture at different intervals of time. The simplest of them is by Mardles[4] who found that the relation

$$\eta - \eta_0 = ae^{kt}$$

holds good for the viscosity changes during the gelation of a sol of cellulose acetate in benzyl alcohol. Mehta, Prasad and Parmar[2] found that the relation between the viscosity changes in thorium phosphate gel-forming mixtures and time is given by

$$\eta - \eta_0 = at^b.$$

No systematic attempt has been made so far to study the effect of temperature on the viscosity-time relation during the formation of a gel, although the effect of temperature on the time of setting of gels has been observed by several workers. The only reference to a systematic work on the subject is by Mardles (*loc. cit.*) who found that the value of ' k ' in the equation given above increases at first slowly and then rapidly as the temperature is decreased. Prasad, Mehta and (Miss) Rathnamma[3] found that in general the viscosity-time curves are lowered as the temperature is raised.

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It has been found that the addition of non-electrolytes to the gel-forming mixtures alters the viscosity changes with time. Prasad, Mehta and Desai[1] found that the addition of increasing quantities of alcohols to silicic acid gel-forming mixtures increases the rate of change of viscosity of the alkaline mixtures and retards that of the acidic ones. Mehta, Prasad and Parmar[2] found that the rate of change of viscosity of thorium phosphate gel-forming mixtures decreases with an increase in the amount of non-electrolytes in the gel-forming mixtures. They also found that the addition of mineral acids and sodium chloride increases the rate of change of viscosity with time.

In the present investigation the viscosity changes in the stannic phosphate gel-forming mixtures have been studied with time and the effects of temperature and of the addition of non-electrolytes to these mixtures have also been examined.

Gels of stannic phosphates were first prepared by Prakash and Dhar by mixing 1 c.c.–3·0 c.c. of a 22 per cent. solution of potassium phosphate to 3·0 c.c. of N/1·099 solution of stannic chloride and making the volume to 6 c.c. However Prasad and Desai[5] found that if phosphoric acid is used, instead of potassium phosphate, the gels obtained are fairly transparent.

Experimental

Scarpa's method[6] modified by Farrow[7] and subsequently improved by Prasad, Mehta and Desai[1] was used in this investigation.

The constant of the apparatus was determined by using sucrose solution of known absolute viscosity and was found to be 0·00218.

Preparation of Solutions :

(a) *Stannic Chloride.*—About 175 g. of Merck's commercial stannic chloride were dissolved in distilled water and a few c.c. of concentrated hydrochloric acid were added to it. The solution was boiled and after cooling was made up to 1,000 c.c. This solution was stocked in a Jena glass flask and was used in all the experiments. A slightly yellowish colour which developed in the beginning was found to disappear on standing for some time. The stannic oxide (SnO_2) content of the solution was found to be 0·4725 M. per litre of the solution.

(b) *Phosphoric Acid.*—An approximately 0·2 N solution was made by dissolving the requisite amount of Merck's extra pure phosphoric acid in a known volume of twice distilled water and its exact strength was determined. It was then suitably diluted to give exactly 0·2 N solution which was stocked in Jena glass flask and was used throughout the investigation.

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Different known volumes of the gel-forming constituents were taken and diluted each to 5·0 c.c. with distilled water. On allowing them to attain constant temperature in a thermostat, they were mixed at a known time and poured in the viscometer bottle. The method of mixing was maintained constant as far as possible. Viscosity readings were taken after known intervals of time from the starting time and the results obtained (viscosity expressed in milli poises) are presented graphically.

Effects of the Concentration of the Constituents of the Gel-forming Mixtures :

The viscosity changes in the gel-forming mixtures containing the same amount of stannic chloride and different quantities of phosphoric acid are shown in Figs. 1 and 2, in which ' B ' indicates the c.c. of stannic chloride
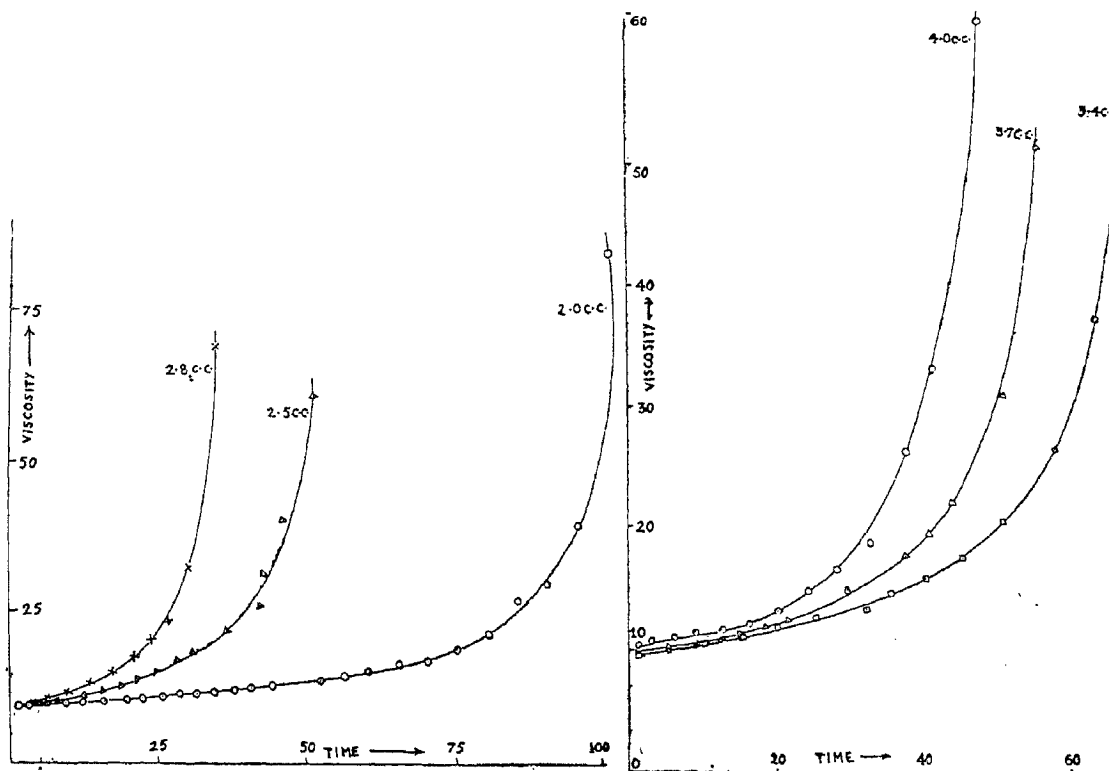

FIG. 1.

B = 3·0 c.c. Stannic chloride

Temperature = 35°

FIG. 2.

B = 4·0 c.c. Stannic chloride

Temperature = 33°

solution. The effect on the viscosity changes on the addition of increasing amounts of stannic chloride is shown in Fig. 3, in which ' A ' represents the c.c. of the phosphoric acid solution.
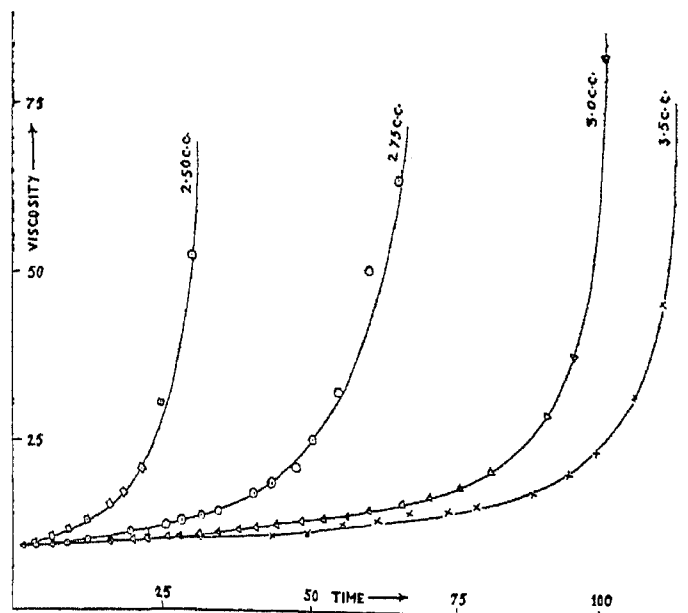
FIG. 3.

A = 2·0 c.c. Phosphoric acid.   Temperature = 35°

Effect of Temperature :

The effect of temperature on the viscosity changes with time on the gel-forming mixtures containing the same quantities of ' A ' and ' B ' is shown in Fig. 4.
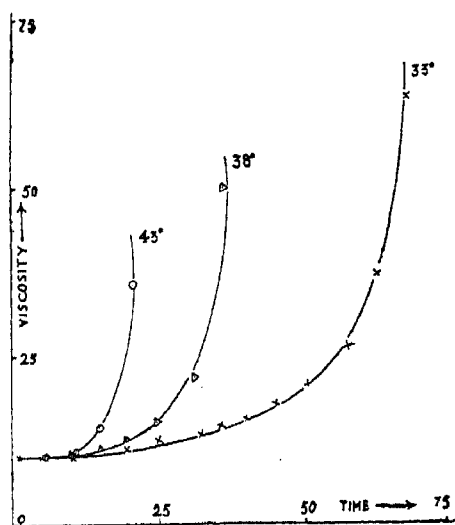

FIG. 4.

A = 3·4 c.c.   B = 4·0 c.c.   Effect of Temperature

Effect of Non-electrolytes :

The effect of the addition of various amounts of ethyl alcohol on the gel-forming mixtures containing the same quantities of ' A ' and ' B ' was examined. The results obtained are shown in Fig. 5.
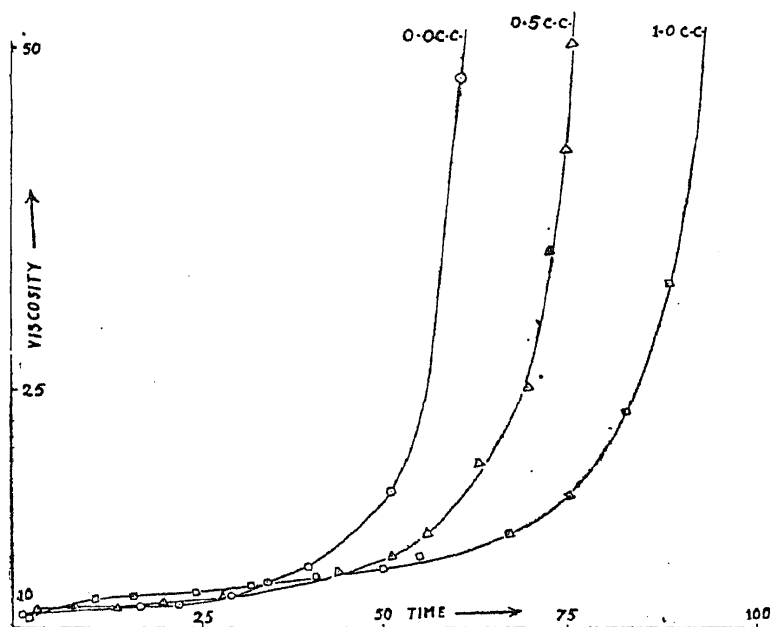
FIG. 5.

A = 3·5 c.c.　　　　B = 5·0 c.c.　　　　Effect of Alcohol.　　　　Temperature = 45°

It would be noted, in the first instance, that the general nature of all the curves (Figs. 1–5) for the setting process of the stannic phosphate gel-forming mixtures is essentially the same. The viscosity increases at first slowly, then slightly, rapidly and in the later stages of gelation, it tends to be very high, the curves practically running parallel to the axis of viscosity. No breaks can be observed in any of the curves mentioned above. This indicates that the several stages in the process of gelation pointed out by Prakash and Dhar[8] fail to show their distinct different existence. It might be that all these intermediate stages of gelation, though actually distinct from each other, run simultaneously and lend to the whole process of gelation an aspect of continuity. The results obtained in this investigation are in conformity with those of Prasad, Mehta and Desai (loc. cit.). On plotting the value of log $(\eta - \eta_0)$ against log t, no straight lines are obtained as is the case with thorium phosphate gels. But when the values of log $(\eta - \eta_0)$ are plotted against t straight lines are obtained in several cases. Mardles (loc. cit.) finds a similar behaviour.

A change in the amounts of the constituents of the gel-forming mixtures considerably alters the rise of viscosity in a given interval of time. With an increase in the amount of phosphoric acid the rate of change of viscosity rises considerably while an increase in the stannic ions decreases this rate both in the earlier as well as in the latter stages of gelation. Increase in the stannic ions probably peptises the gelling substance to a greater degree, thereby increasing the degree of dispersity of the micelles and the density

of charge on them. The increase in the rate of gelation consequent upon an increase in the amount of phosphoric acid may be due to (1) decrease in the density of charge on the micelles, since more of the peptising stannic ion is removed to form stannic phosphate micelles, and consequent increase in the degree of their hydration; (2) an increase in the rate of coagulation since nearly the same amount of coagulating ion effects the coagulation of a sol containing greater number of micelles having a lower density of charge.

Effect of temperature on the gel-formation appears to show that an increase in temperature causes a small decrease in viscosity in early stages (not noticeable in the graph) but after a certain stage of gelation is reached, the rate of change of viscosity increases with temperature. The rise in temperature increases the coagulating power of the coagulating ions and this causes an appreciable increase in the rate of change in viscosity.

The effect of the addition of ethyl alcohol to the gel-forming mixture is to retard the rate of increase of viscosity with time; the extent of the retardation increases as the quantity of the non-electrolyte in the mixture is increased. Parmar, Mehta and Desai (*loc. cit.*) observe a similar effect. The addition of the non-electrolyte probably decreases the dielectric constant of the dispersion medium and thereby increases the density of charge on the micelles[9] and thus behaves in the same manner as the addition of increased quantities of stannic ions. This view is in agreement with the investigation of Prasad and Hattiangadi.[10] It is, however, probable that the addition of ethyl alcohol may favour the adsorption of stannic ions by the micelles and cause the observed decrease in the rate of increase in viscosity.

Summary

Viscosities of gel-forming mixtures containing various quantities of stannic chloride and phosphoric acid have been measured during the formation of gels at constant temperature. Effects of change of temperature and of the addition of non-electrolytes on the changes in viscosities have also been examined. It has been found that the rate of increase in viscosity with time increases with (*a*) an increase in (i) the quantity of phosphoric acid and (ii) temperature and (*b*) a decrease in the quantity of (i) stannic chloride and (ii) non-electrolytes.

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