OPACITY CHANGES IN GEL-FORMING MIXTURES DURING SETTING

Part II. Thorium Phosphate, Cerium Phosphate, Thorium Arsenate and Stannic Phosphate Gels

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In a previous communication Prasad and Gogate[1] have reported the results of the measurement of the opacity changes during the formation of thorium molybdate, stannic arsenate, and silicic acid gels with the help of a newly devised apparatus which involves the use of a compensated photocell circuit. The description of the apparatus is given in the author's paper (*loc. cit.*).

In the present investigation the study of the opacity changes has been continued by the same apparatus during the setting of thorium phosphate, cerium phosphate, thorium arsenate and stannic phosphate gels.

Experimental Procedure

The experimental procedure adopted was practically the same as employed by Prasad and Gogate. Varying amounts of the solutions of the two constituents of the gel-forming mixture were taken in two test-tubes and certain amount of distilled water was added so that the total volume of the gelating mixture was 8 c.c. in the case of stannic phosphate and thorium arsenate gels and 9 c.c. in the case of thorium phosphate and cerium phosphate gels. The two test-tubes were corked and kept in the thermostat for about 15 minutes. Then the contents of the test-tubes were mixed and the opacity readings were taken.

The results obtained with each of these gels are given below.

1. Thorium Phosphate Gels

They were prepared by the method of Prasad, Mehta and Parmar.[2] It was found that if a mixture of potassium phosphate and phosphoric acid is employed instead of phosphoric acid alone, the whole system is initially opaque and there is a change in transparency during gelation and the mixture sets into a very transparent gel in a short time. This method of preparing thorium phosphate gel was used and the following solutions were employed:

(A) 6% solution of thorium nitrate (Kahlbaum).

(B) 12% solution of potassium phosphate (Merck).

(C) 1·6 N phosphoric acid.

(D) 0·2 N HCl.

The results obtained during the gelation of thorium phosphate gels are shown by means of curves obtained by plotting the opacity in terms of observed deflections in cm. against time in minutes. The effects of the addition of different amounts of (A), (B) and (C) (D) and of methyl and ethyl alcohols on the opacity changes during the course of gel-formation were investigated.

The effect of thorium nitrate was studied by adding 4 to 6 c.c. of (A) to a mixture containing 0·5 c.c. of (B) and 0·3 c.c. of (C). The effect of phosphoric acid was studied by adding 0·1 to 0·5 c.c. of (C) to 0·5 c.c. of (B) before it was added to 4·5 c.c. of (A). The effect of HCl was studied by adding 0·2 to 0·8 c.c. of (D) to a mixture containing 0·5 c.c. of (B) and

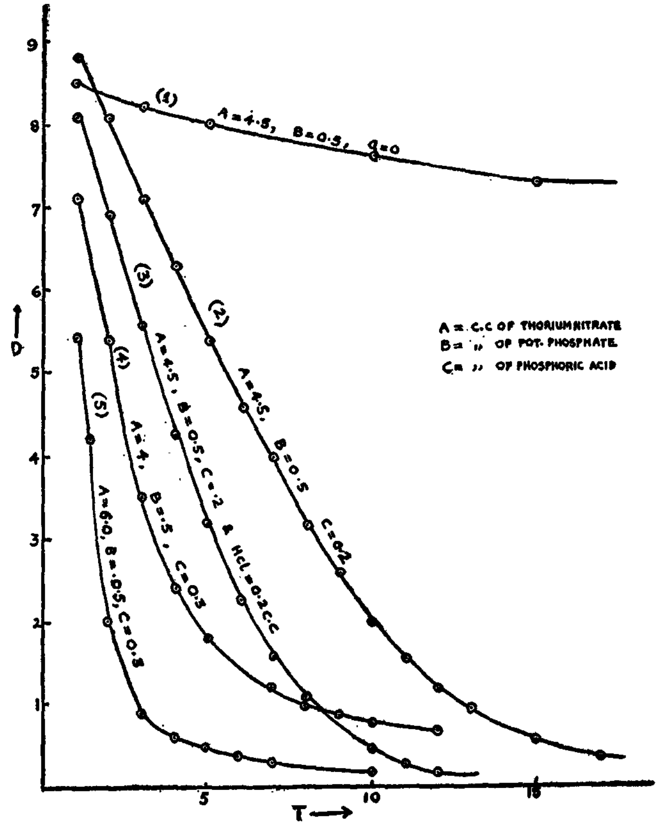

FIG. 1

0·2 c.c. of (C) before it was added to 4·5 c.c. of (A). The effect of ethyl alcohol was studied by adding 0·5 to 1·0 c.c. of ethyl alcohol to a mixture containing 0·5 c.c. of (B) and 0·3 c.c. of (C) before it was added to 4·5 c.c. of (A). The effect of methyl alcohol was studied by adding 0·5 c.c. to 1·5 c.c. of methyl alcohol to a mixture containing 0·5 c.c. of (B) and 0·4 c.c. of (C) before it was added to 4·5 c.c. of (A).

Some results indicating these effects are given in Figs. 1 and 2.

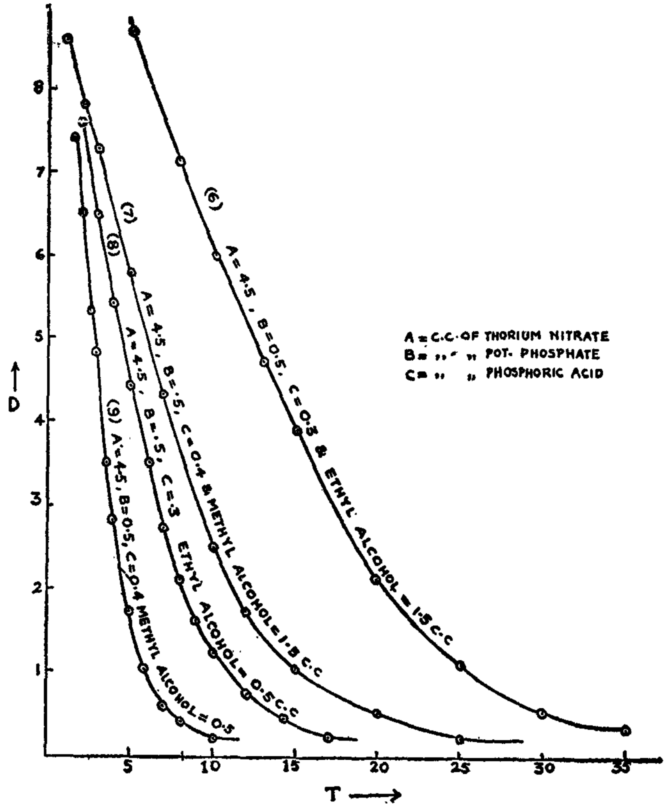

FIG. 2

2. *Cerium Phosphate Gels*

These gels were prepared by the method of Prasad and Desai.[3] The following solutions were used:

(A) 10% cerium nitrate.

(B) 12% potassium phosphate.

(C) 0·2 N HCl.

The effect of cerium nitrate was studied by addding 4·5 to 7·0 c.c. of (A) to 1·0 c.c. of (B). The effect of potassium phosphate was studied by adding

1·0 to 1·5 c.c. of (B) to 4·5 c.c. of (A). The effect of the addition of HCl was studied by adding 0·5 to 1·0 c.c. of (C) to 1·0 c.c. of (B) before it was added to 4·5 c.c. of (A). The effect of ethyl alcohol was studied by adding 1·0 to 2·0 c.c. of the same to 1·0 c.c. of (B) before it was added to 4·5 c.c. of (A).

Some results indicating these effects are given in Fig. 3.

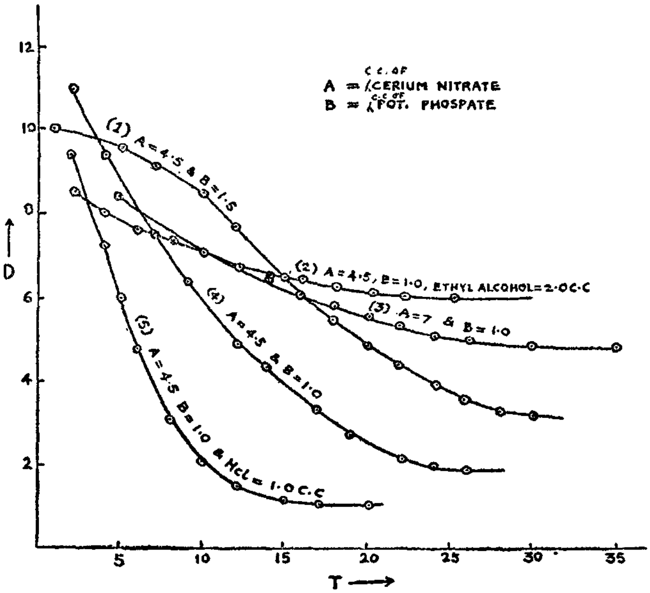

FIG. 3

3. *Thorium Arsenate Gels*

These gels were prepared by the method of Prasad and Desai (*loc. cit.*). The following solutions were used:

(A) 6% thorium nitrate (Kahlbaum).

(B) 10% solution of pyro-arsenic acid (extra pure Merck).

(C) 2 N HCl.

The effect of thorium nitrate was studied by adding 4 to 6 c.c. of (A) to 0·54 c.c. of (B). The effect of pyro-arsenic acid was studied by adding 0·48 to 0·72 c.c. of (B) to 4 c.c. of (A). The effects of HCl, ethyl alcohol, methyl alcohol and glycerine were studied by adding 0·06 to 0·2 c.c. of (C), 0·2 to 0·4 c.c. of ethyl alcohol, 0·1 to 0·3 c.c. of methyl alcohol and 0·06 to 0·1 c.c. of glycerine to 0·54 c.c. of (B) before it was added to 4·0 c.c. of (A).

Some results indicating these effects are given in Fig. 4.

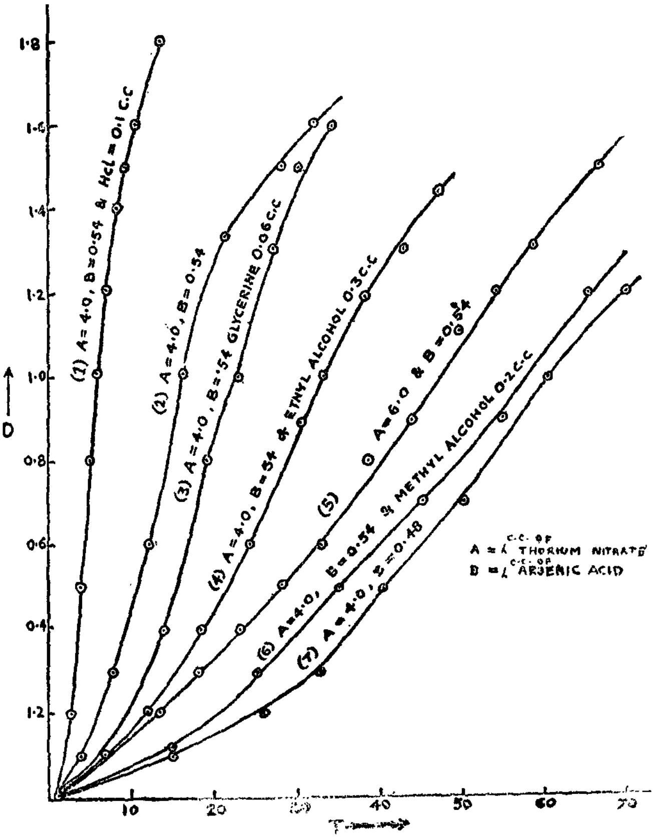

FIG. 4

4. *Stannic Phosphate Gels*

These gels were prepared by the method of Prasad and Desai (*loc. cit.*). The following solutions were used:

(A) 43·82 g. of stannic chloride dissolved in 250 c.c. of distilled water in the presence of 1·0 c.c. of nitric acid to prevent hydrolysis.

(B) 0·2 N phosphoric acid.

(C) 2 N HCl.

The effect of stannic chloride was studied by adding 2·2 to 3·0 c.c. of (A) to 2·4 c.c. of (B). The effect of phosphoric acid was studied by adding 2·4 to 3·0 c.c. of (B) to 3·0 c.c. of (A). The effect of HCl was studied by adding 0·1 to 0·2 c.c. of (C) to 2·4 c.c. of (B), before it was added to 3·0 c.c. of stannic chloride. The effects of methyl, ethyl, propyl alcohols were studied by adding 1·0 to 2·0 c.c. of methyl alcohol, 1·0 to 2·0 c.c. of ethy alcohol and 1·0 to 3·0 c.c. of propyl alcohol, respectively to 2·4 c.c. of (B) before it was added to 2·4 c.c. of (A).

Some results indicating these results are given in Fig. 5.

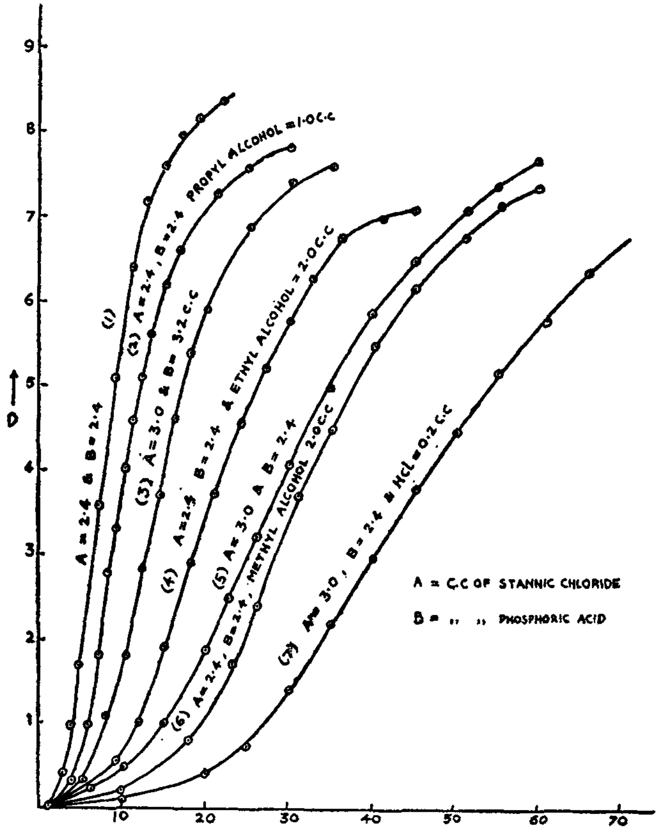

FIG. 5

5. *Discussion of Results*

All the results given above are reproducible and the experimental error is within ± 2 per cent. These results are therefore important as they represent accurately the changes in opacity taking place during the setting of the gels studied in this investigation. The time-deflection curves in all these cases are continuous and thereby indicate that gelation is a continuous phenomenon.

The results obtained in the case of each gel are discussed separately in the following.

1. Thorium Phosphate Gels—

The time-deflection curves (Figs. 1 and 2) show that the gels are opaque in the beginning. The opacity decreases during gel-formation and it reaches a constant value.

It will be noticed from the various curves in Fig. 1 that increasing amounts of thorium nitrate (curves 4 and 5), phosphoric acid (curves 1 and 2) and HCl (curves 2 and 3) in the gel-forming mixture increase the rate of change of opacity and make the gel more and more transparent. It is interesting to note that a small quantity of phosphoric acid is able to make the gel very transparent.

Non-electrolytes exercise a great influence on the course of gel-formation. Increasing amounts of methyl alcohol (curves 6 and 8) and ethyl alcohol (curves 7 and 9, Fig. 2) in the gel-forming mixture decrease the rate of change of opacity. In these cases there are no great changes in the final value of opacity.

In the case of these gels the plot of log d against t (d being the deflection at the time t), was found to be a straight line, showing thereby that $d = ae^{-kt}$.

2. Cerium Phosphate Gels—

These gels, like thorium phosphate gels, are opaque in the beginning and become transparent during setting (Fig. 3).

Increasing amounts of cerium nitrate (curves 3 and 4) and potassium phosphate (curves 1 and 4) decrease the rate of change of opacity and make the gel more and more opaque. However, increasing amounts of HCl increase the rate of opacity and make the gel more and more transparent (curves 4 and 5).

The effect of ethyl alcohol is the same as that of cerium nitrate; the rate of change of opacity is decreased and the gel becomes more and more opaque as the amount of alcohol in the gel increases (curves 2 and 4).

In the case of this gel also, log d plotted against t, was found to be a straight line, so that $d = ae^{-kt}$.

3. Thorium Arsenate Gels—

These gels are clear in the beginning and become opaque during setting as shown by the deflection-time curves (Fig. 4).

Increasing amounts of thorium nitrate (curves 2 and 5) decrease the rate of change of opacity, whereas increasing amounts of pyro-arsenic acid (curves 2 and 7) increase the rate. Increasing amounts of HCl increase the rate of change of opacity (curves 1 and 2). Non-electrolytes employed are ethyl and methyl alcohols, and glycerine. Curves 2 and 4, 2 and 6, 2 and 3, respectively, show their effects. It will be seen that non-electrolytes decrease the rate of change of opacity.

4. Stannic Phosphate Gels—

The deflection-time curves in Fig. 5 show that the stannic phosphate gels are clear in the beginning and they increase in opacity during gel-formation and reach a constant value.

The rate of change of opacity is decreased by the addition of increasing amounts of stannic chloride to the gel-forming mixture (curves 1 and 5), whereas increasing amounts of phosphoric acid increase the rate of change of opacity (curves 3 and 5).

Increasing amounts of HCl decrease the rate of change of opacity (curves 5 and 7). Curves 1 and 6, 1 and 4, and 1 and 2 represent the effects of the addition of increasing amounts of methyl, ethyl and propyl alcohols to the gel-forming mixture. It will be seen that their addition causes the decrease in the rate of change of opacity of the gel-forming mixture.

One of the factors that causes the change of opacity is the change in the intensity of the scattered light by the gel-forming mixture with time. The intensity of light scattered by a colloid system is given by Lord Rayleigh's equation,[4] which under standard and fixed conditions can be written as

$$I = kV^2 N,$$

where N is the number and V, the volume of the scattering particles. The observed changes in the opacity during gel-formation may be due to changes in these two factors during the setting of the gels.

Changes in the intensity of scattered light which cause changes in opacity may also be brought about by changes in the anisotropy, arrangement and distribution of the micelles in a gel as pointed out by Prasad and Gogate. It is quite probable that changes in the anisotropy, distribution and arrangement of the micelles in the gel taking place with the changes in the amounts of the constituents of the gel-forming mixtures may be responsible, to a great extent, for the rate of change of opacity and also for the final value reached at the completion of the gelation process.

Further work on the changes in the intensity and depolarisation factors of the light scattered by gels during and after gelation is in progress. From the total scattering observed an attempt is being made to separate the scattering due to size, number and anisotropy and to study their changes during gelation.

The authors feel grateful to Dr. Mata Prasad, D.SC., F.I.C., for suggesting the problem and for the guidance throughout the progress of this work.

6. *Summary*

The opacity changes during the formation of gels of thorium phosphate, cerium phosphate, thorium arsenate and stannic phosphate have been investigated. Opacity-time curves, in the case of thorium and cerium phosphate gels, are exponential in character.

The changes in the opacity with time of the gels formed from different amounts of the constituents of the gel-forming mixture and the effects of HCl and non-electrolytes on the course of gel-formation have been investigated. In general non-electrolytes decrease the rate of change of opacity, while HCl increases the same.

The final values of opacity are not the same in all these cases but they vary with the concentration of the constituents of the gel-forming mixture. It has been suggested that the changes in the rate of changes of opacity and the final value of opacity may be due to the changes in the number, size, anisotropy, distribution and arrangement of the micelles taking place under the different conditions of the gel-formation.

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4. *Phil. Mag.*, 1899, **47**, 375.