

STUDIES IN THORIUM PHOSPHATE GELS.

BY M. U. PARMAR, S. M. MEHTA

AND

MATA PRASAD.

(From the Department of Inorganic and Physical Chemistry,
Royal Institute of Science, Bombay.)

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THORIUM phosphate gels were first prepared by Satya Prakash¹ by directly mixing solutions of thorium nitrate and potassium phosphate. A precipitate which is first obtained disappears on shaking and gives rise to a more or less opaque solution. This when kept for some time becomes clear and sets to a firm transparent gel. According to him the precipitated thorium phosphate is peptised by the hydrogen and thorium ions present in the gel-forming mixtures and this process is greatly accelerated by shaking. Later on, the colloidal solution of thorium phosphate coagulates and the particles get hydrated and in course of time the whole mixture sets to a solid looking mass imbibing within itself all the liquid present in the mixture, provided suitable concentrations of solutions of thorium nitrate and potassium phosphate are employed.

It has been found by the authors that thorium phosphate gels can be easily prepared if a solution of phosphoric acid instead of that of potassium phosphate is used. Only a slight precipitate is obtained when solutions of thorium nitrate and phosphoric acid are mixed and it quickly disappears on shaking. The resulting solution is quite transparent and sets to a firm transparent gel.

In the following an attempt has been made to investigate systematically the factors that affect the time of setting of these gels. Consequently the behaviour of thorium and hydrogen ions and the effect of temperature and of the addition of extra amounts of electrolytes and non-electrolytes to the gel-forming mixtures has been investigated.

Experimental

Kahlbaum's purest thorium nitrate and phosphoric acid whose purity was tested, were used. A number of trials indicated that 6 per cent. solution of thorium nitrate and 2N solution of phosphoric acid gave very good

¹ *J. Indian Chem. Soc.*, 1929, 6, 587.

gels when different volumes of these solutions were mixed. Hence these solutions were used throughout the investigation.

A known amount of thorium nitrate solution was taken in one test tube and in another a known amount of the solution of phosphoric acid together with some distilled water so that when the two solutions were mixed the total volume of the mixture was 10 c.c. The mixture was then slightly shaken for about 15 seconds and was then poured into a tube which was gently inverted twice and set aside. This method of mixing was followed throughout the investigation.

The time required by the gel-forming mixture to reach a state when it did not flow out of the tube and showed a firm meniscus on inverting it was taken to be the time of setting of the gel. The accuracy of these measurements was increased by repeating the observations several times and each time disturbing the mixture as few times as possible during setting. This enabled the determination of the time of setting fairly accurately. The results obtained are given in Tables I and II in which

Q = grams of thorium nitrate in 10 c.c. of mixture ;
 X = equivalent of phosphoric acid in the mixture ; and
 T = time of setting in minutes.

TABLE I.

Q	0.48	0.42	0.36	0.39
X	T	T	T	T
0.24 N	8	ppt. settles down ; no gel.	ppt.	ppt.
0.22 N	15	7.5	ppt.	ppt.
0.20 N	32	20	6	ppt.
0.18 N	105	49	23	2
0.16 N	233	162	88	18
0.14 N	about 24 hrs.	about 12 hrs.	185	42.5
0.12 N	does not set : a clear sol.	a clear viscous sol : does not set.	about 14 hrs.	91

TABLE II.

X	0.18	0.16	0.14	0.12
Q	T	T	T	T
0.48	105	233	about 24 hrs.	Clear viscous sol: no gel.
0.42	49	162	about 12 hrs.	"
0.36	23	88	185	about 14 hrs.
0.30	2	18	42.5	91
0.24	no gel: ppt.	no gel: ppt.	6.5	22.5
0.18	"	"	ppt.	2
0.12	"	"	"	ppt.
0.06	"	"	"	"

All the gels mentioned in the tables were absolutely transparent throughout the entire process of gelation and the gel-forming mixtures were acidic.

It will be seen that for the same thorium nitrate content of the mixture the time of setting decreases as the concentration of phosphoric acid in the mixture is increased while for the same concentrations of phosphoric acid it increases with an increase in the amount of thorium nitrate in the mixture.

It may be pointed out that gels can be obtained only within the range of concentrations of thorium nitrate and phosphoric acid given in the above tables. If the amount of phosphoric acid in the mixture is increased or decreased beyond these limits a curd (or a gelatinous precipitate) or a perfectly transparent solution which never sets to a stiff gel, is obtained. The reverse happens in the case of thorium nitrate. A more or less viscous and transparent loose mass is obtained when the amount of thorium nitrate in the mixture is more and a curd when it is less than the amounts given in the above tables.

Effect of Temperature

Prakash² has found that the time of setting of thorium phosphate gels decreases as the setting takes place at a higher temperature. Table III gives

² *J. Indian Chem. Soc.*, 1932, 9, 192.

the results obtained with gels prepared in the manner mentioned above. These results are in agreement with the conclusions of Prakash.

TABLE III.

$$X = 0.16 N$$

Temp.	Q	0.30	0.36	0.42	0.48
50°C.	T	6	17	61	170
40°C.	T	10	38	130	192
28°C.	T	18	88	182	233

It was noticed that gels prepared at higher temperatures were cloudy and the cloudiness disappeared gradually after some time. They were also stiffer than those prepared at lower temperatures. These observations indicate that the gels prepared at higher temperature consist of bigger aggregates which are not highly hydrated.

Effect of Electrolytes

Electrolytes are known to cause the coagulation of a sol. In a gel-forming mixture this is brought about by the electrolytes formed due to the metathetical reaction. If extra amounts of electrolytes are added to this mixture, the coagulation process may be hastened. Thus Prasad and Hattiangadi³ found that the time of setting of the silicic acid gel-forming mixtures is decreased as a larger quantity of electrolytes is added to them. In the following the effect of the addition of some salts, acids and sodium hydroxide on the setting of thorium phosphate gels has been described. For this purpose different quantities of the solutions of the electrolytes were added to fixed amounts of phosphoric acid solutions and the requisite amount of distilled water was added to make up the total volume of the gel-forming mixture to 10 c.c. In the following tables A represents the normality of the electrolytes in the gel-forming mixtures.

(a) *Effect of salts.*—The salts used were chlorides of sodium and barium and sodium sulphate.

³ *J. Indian Chem. Soc.*, 1930, 7, 341.

TABLE IV.

NaCl

 $Q = 0.36$

X	A	0	0.2 N	0.4 N	0.6 N	0.8 N	1.0 N
0.12 N	T (hrs.)	14	10	6.5	5	3.5	1.5
0.14 N	T (min.)	200	155	117	84	58	36
0.16 N	T (min.)	88	57	37	32	28	17

TABLE V.

 $Q = 0.36$. $X = 0.16$ N

BaCl ₂			Na ₂ SO ₄		
A	T	Remarks	A	T	Remarks
0	88	transparent gel	0	88	transparent gel
0.005 N	63	translucent gel	0.02 N	60	„
0.010 N	56	„	0.04 N	16	translucent gel
0.015 N	50	„	0.06 N	4	opaque
0.020 N	41	completely opaque gel	0.08 N	—	disjointed hydrates

It is clear that the time of set decreases as the amount of salts in the forming mixtures is increased.

The gels obtained in the presence of sodium chloride were quite transparent from the beginning of gelation till they set, but slight turbidity developed when the amount of sodium chloride was fairly large. No transparent gels were obtained in the presence of BaCl₂ and Na₂SO₄ when concentrations equivalent to NaCl were used but only a gelatinous precipitate was obtained. However, with very small amounts of these electrolytes translucent and opaque gels were obtained.

(b) *Effect of sodium hydroxide.*—1 N sodium hydroxide solution was used.

TABLE VI.

$$Q = 0.36$$

X	0.16 N		0.18 N		0.20 N	
A	T	Remarks	T	Remarks	T	Remarks
0	88	transparent gel	20	transparent gel	6	transparent gel
0.02 N	102	"	26	turbid mixture	7	turbid mixture
0.05 N	108	} gel-forming mixture turbid	35	"	—	—
0.10 N	360		105	"	14	translucent gel ; ppt. separates and settles down
0.20 N	—	no gel ; ppt. slowly settles down	—	no gel ; ppt. sepa- rates and settles down	—	—

TABLE VII.

$$X = 0.18 N$$

Q	0.30		0.36		0.42	
A	T	Remarks	T	Remarks	T	Remarks
0	1	transparent gel	20	transparent gel	72	transparent gel.
0.02 N	3	gel-forming mix- ture turbid	26	turbid mixture	90	"
0.05 N	5	"	35	"	120	"
0.10 N	7	"	105	"	about 6 hrs.	"
0.15 N	15	translucent gel	140	"	—	—
0.20 N	—	ppt. separates and settles down	—	No gel ; ppt. sepa- rates and settles down	—	transparent viscous mass ; ppt. separat- es and settles down

While preparing the gels it was noticed that they were turbid and the turbidity persisted in some gels till the setting point and disappeared in others just when they were about to set. Also the opacity of these mixtures increased with an increase in the concentration of NaOH. Thus in the presence of limited amounts of NaOH both transparent and opaque gels were obtained. Some of the set opaque gels became clear on keeping for some time while others did not undergo any change in their opacity. The

gels obtained by Satya Prakash⁴ by using potassium phosphate were similar to those obtained by us in the presence of NaOH. These gels, however, do not look quite homogeneous.

It will be seen that the time of set increases as the amount of NaOH in the gel is increased. On testing the various gel-forming mixtures by various indicators it was found that they were fairly acidic. The pH of the mixture with no amount of NaOH was nearly 1.2 and this increased to nearly 2.5 as different amounts of NaOH were added to them. If larger amounts of NaOH were added, no gel but an amorphous precipitate was formed.

(c) *Effect of acids.*—4 N nitric and hydrochloric acids and 0.5 N sulphuric acid were used for the purpose. As the behaviour of nitric acid was found to be similar to that of hydrochloric acid, only the results with the latter acids are given.

TABLE VIII.
Effect of Hydrochloric Acid
X = 0.14 N

A	Q = 0.30		A	Q = 0.36	
	T	Remarks		T	Remarks
0	42.5	transparent gel	0	185	transparent gel
0.2 N	29	"	0.08 N	70	"
0.4 N	40	"	0.20 N	30	"
0.6 N	about 12 hrs.	"	0.40 N	22	"
0.8 N	20	opaque	0.60 N	50	"
1.0 N	17	"	0.72 N	21	slightly opalescent
1.2 N	12	transparent	1.0 N	7	opaque gel
			1.2 N	—	hydrated flakes

It is clear that with increasing amounts of hydrochloric acid the time of setting at first diminishes, reaches a minimum, then suddenly increases and again diminishes till a second minimum is reached. With the addition of sulphuric acid, however, the time of setting at first increases and then begins to decrease and the first minimum found with hydrochloric acid is

⁴ *Loc. cit.*

TABLE IX.
Effect of Sulphuric Acid.
 $Q = 0.36$

A	X = 0.14 N		X = 0.16 N	
	T	Remarks	T	Remarks
0	185	transparent gel	88	transparent gel
0.01 N	255	loose and translucent gel	110	loose and translucent gel
0.02 N	310	"	90	"
0.03 N	220	"	58	"
0.04 N	71	"	18	"
0.05 N	35	"	8	"
0.06 N	14	"	4	"
0.07 N	6	"	1.5	"
0.08 N	3	"	< 1	"
0.09 N	1	"	—	no gel; the ppt. separates and settles down slowly
0.10 N	< 1	"	—	—

not observed. It may correspond to some concentration of the acid lower than 0.01 N which has not been used in the investigation. With further increase in the amount of the acid, *i.e.*, more than that corresponding to the minimum, at first hydrated flakes are formed and then a clear solution is obtained which shows no turbidity nor any increase in viscosity on keeping.

Effect of Non-electrolytes

The rôle of non-electrolytes in their action towards colloidal solutions is not yet clearly understood. Several examples are known in which they act either as coagulating or inhibiting agents. Billitzer⁵ found that a

⁵ *Zeit. Phys. Chem.*, 1903, 45, 312.

negatively charged platinum sol could be sensitized, discharged or even changed into a positive sol by the addition of suitable amounts of alcohol. Prasad and Hattiangadi⁶ found that the addition of alcohols decreases the time of setting of the alkaline silicic acid gels and increases that of the acidic ones. In the following the effect of the addition of methyl, ethyl and propyl alcohols and glycerine on the time of setting of thorium phosphate gels has been described. The addition of the non-electrolytes was done in the same manner as that of electrolytes.

TABLE X.
Q = 0.36. X = 0.16 N

Amount of non-electrolyte.	Methyl alcohol	Ethyl alcohol	Propyl alcohol	Glycerine
	T	T	T	T
0	88	88	88	88
1.0 c.c.	104	115	97	4.5 hrs.
2.0 c.c.	125	175	178	7 "
3.0 c.c.	230	213	about 5 hrs.	about 24 hrs.

It will be seen that the setting of gels is retarded by the presence of the non-electrolytes and this effect is enhanced as the amount of the non-electrolytes is increased.

Gels prepared with larger amounts of alcohols were turbid in the beginning, but after some time the turbidity slowly disappeared and transparent gels were obtained. Glycerine seems to have a considerable retarding influence. All gels obtained in the presence of glycerine were perfectly transparent from the beginning to the end of gelation but the structure of these gels was extremely loose.

Discussion of Results

The observations described above can be used to define the conditions which govern the formation of thorium phosphate gels. When solutions of thorium nitrate and phosphoric acid are mixed, they react and thorium phosphate and nitric acid are formed; all the gel-forming mixtures, therefore, show an acid reaction. A slight precipitate is obtained because thorium phosphate dissolves only in concentrated solution of acids and is insoluble

⁶ *J. Indian Chem. Soc.*, 1929, 6, 991.

in dilute ones. The insolubility and the appearance of the precipitate are necessary, for when this precipitate goes over to the colloidal state on shaking, it supersaturates the solution with the gelling substance and in accordance with the views of von Weimarn creates circumstances favourable for the formation of a gel. The gel formation is, of course, determined by the hydration tendency of thorium phosphate and the agglomeration tendency of the micelles.

An increase in temperature (i) decreases the hydration tendency and increases the agglomeration tendency of the micelles and (ii) may also decrease the peptising capacity of the peptising ions. Both these effects cause the gel to set early with larger aggregates at a higher temperature. If the temperature is, however, further increased, no gel but only a precipitate should be obtained. This is probable as it was observed that in mixture, containing 0.30 g. of thorium nitrate and 0.18 N phosphoric acid, the precipitate obtained remained suspended for a long time before a homogeneous mass was formed.

The addition of extra amounts of salts also increases the agglomeration tendency of the gelling substance and decreases the hydration tendency since such an addition hastens the coagulation of the micelles more so if ions of higher valency are employed. Thus the gels set early and are turbid.

H⁺-ions seem to be very effective in peptising thorium phosphate. The first decrease in the time of setting observed in Table VIII is an evidence of this effect since with an increase in the H⁺-ion concentration in the mixture the rate of peptisation of the precipitate is also increased. Reverse happens when the H⁺-ion concentration is decreased by the addition of sodium hydroxide (*cf.* Tables VI and VII). This effect of the H⁺-ions is supported by the observation that the precipitate in mixtures containing the amount of the acid corresponding to the first minimum gets peptised without shaking.

With an increase in the concentration of the acid beyond that corresponding to the first minimum the increased peptising action of the H⁺-ions increases the degree of dispersity of the micelles and delays the setting. After a certain concentration of the acid which imparts the maximum charge to the micelles any further addition increases the concentration of the coagulating ion and decreases the time of set; at some concentration the coagulation becomes very rapid and a precipitate is formed. The gels corresponding to the range between the maximum and the second minimum are opalescent and this supports the view that further addition of acids increases the agglomeration tendency. The coagulating effect of the anions is also apparent from the fact that gels of greater opalescence are obtained as the concentration of sulphuric acid beyond that corresponding to the maximum is

increased. Further, due to the increased coagulating effect of the divalent sulphate ion the concentrations of sulphuric acid employed are ten times smaller than those of hydrochloric acid.

Prasad and Hattiangadi⁷ have also observed that with concentrated acids a second minimum time of set is obtained in the gelation of silicic acid. Holmes⁸ has also made a similar observation in the gelation of silicic acid by sulphuric and hydrochloric acids. He has pointed out that the second minimum is caused by the dehydrating influence of the concentrated acids, but Prasad and Hattiangadi have shown that it is the coagulating effect of the anion which comes more into play after the density of charge on the colloidal particles of the gelling substance has attained its maximum value.

Thorium phosphate is peptised to a fairly large extent by thorium ions as well. This is seen from the fact that all mixtures in Tables I and II contain thorium nitrate in excess of that required for the complete precipitation of thorium phosphate. Consequently if the amount of thorium nitrate in mixtures containing the same concentration of phosphoric acid is increased, the degree of dispersity of the colloidal particles increases and they take longer time to form bigger aggregates in order to set to a stiff gel. If the amount of thorium nitrate in the mixtures is increased or decreased beyond the limits indicated in the tables, the amount of the peptising ion in the mixture is either too great or too small and hence, as observed, either a viscous mass or a curd, respectively, is obtained.

If the concentration of phosphoric acid is increased beyond the limit given in the tables, the amount of thorium phosphate formed is increased and the concentration of thorium ions falls. Thus the gelling substance does not reach a sufficiently high degree of dispersity and supersaturation and a curd are obtained. If the concentration of phosphoric acid is lower than that indicated in the tables no gel but a viscous mass is formed for (i) the dispersity of the precipitate is very high as there are a large number of thorium ions to peptise a small amount of the precipitate and (ii) the amount of the precipitate (number of micelles) is insufficient to enmesh the whole of the liquid.

These observations, therefore, support the suggestion of I'ernau and Pauli⁹ that for the formation of a gel it is necessary that the concentration of the micelles must be high. Their second suggestion that the micelles

⁷ *Loc. cit.*

⁸ *J. Phys. Chem.*, 1918, 22, 510.

⁹ *Biochem. Zeit.*, 1915, 70, 426; *Kolloid Zeit.*, 1917, 20, 20.

should be hydrophillic in nature and should remain so upon coagulation is satisfied by the chemical nature of thorium phosphate which has a great tendency for hydration.

The action of alcohols and glycerine is similar to that observed by Prasad and Hattiangadi¹⁰ for the acidic silicic acid gel-forming mixtures as these gels also take a longer time to set in the presence of alcohols. These authors concluded from their observation that alcohols exert a protective influence on the positively charged sols by causing an increase in the density of charge on the particles. In the present case an increase in the density of charge and thereby in the degree of dispersity of thorium phosphate is caused by alcohols probably by effecting an increase in the adsorption of H⁺-ions by the micelles. The first appearance of the turbidity in the presence of alcohols caused by the insolubility of thorium phosphate in alcohol-water mixtures and its disappearance after a certain time leads one to believe that the above assumption is justifiable. In the presence of glycerine thorium phosphate gets dispersed to such a high degree that aggregates big enough to give a rigid structure are not formed.

¹⁰ *Loc. cit.*