

# KINETICS OF SOL-GEL TRANSFORMATION

## Part V. The Influence of Different Coagulating Electrolytes on the Setting of Ferric Phosphate Gel

BY HIRA LAL DUBE, M.Sc., D.Phil.

(Chemical Laboratory, Meerut College, Meerut)

AND

SATYA PRAKASH, D.Sc., F.A.Sc.

(Chemical Laboratory, University of Allahabad)

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IN previous publications of this series,<sup>1</sup> the authors have studied the expression  $\log S = \log R + p \log C$ , where  $S$  is the inverse setting time of the jelly when coagulation has been affected with an electrolyte of concentration  $C$ .  $R$  and  $p$  are constants, the significance of which has been mentioned in previous papers. We have shown that the expression is valid for almost all the jellies obtained by slow gelation of sols in presence of varying concentrations of electrolytes. The influence of dilution, temperature and purity of sols on the setting of these jellies has been investigated already. In the present communication, we have studied the influence of various coagulating ions on the setting of ferric phosphate jellies.

The quantitative expression for the coagulating power of electrolytes, especially with reference to the valency of coagulating ions, was given by Whetham.<sup>2</sup> According to him, if discharge requires the presence of ions of opposite charge in the vicinity of the particle, there must be present simultaneously 2 trivalent, 3 divalent or 6 monovalent ions. Since the probabilities for simultaneous presence are proportional to the corresponding powers of the concentrations, Whetham arrived at the following formula for the flocculating concentrations of monovalent, divalent and trivalent ions,  $c_1$ ,  $c_2$  and  $c_3$ :

$$1/c_1 : 1/c_2 : 1/c_3 = 1 : x : x^2.$$

Chakravarti, Ghosh and Dhar<sup>3</sup> have modified the Whetham's equation slightly. According to them, if  $N_1, N_2, N_3, \dots, N_x$  be the precipitating concentrations of uni-, bi-, tri-,... $x$ -valent ions, then

$$N_1 : N_2 : N_3 : \dots : N_x = 1 : \frac{1}{2} \alpha : \frac{1}{3} \alpha^2 : \dots : \frac{1}{x} \alpha^{x-1},$$

where  $\alpha = e^{-\frac{qe/Dr}{KT}}$ .

These expressions are only valid when the coagulation process does not involve any complication and is guided by the mere electric attraction between the colloidal particle and the ion. The possible complications in the case of an ordinary coagulation are the adsorption of similarly charged ion, the marked adsorbability of the precipitating ion and the large differences in the ionic velocity of the coagulating ions. When applied to the coagulation processes leading to the formation of a jelly, all these expressions are bound to fail. The process of jelly formation starts with the charge neutralisation and the formation of secondary or tertiary aggregates from the primary ones, and then continues through the regular imbibition of water molecules round the completely or partially discharged colloidal aggregates, and finally ends into the formation of a jelly-mesh which entangles the whole of the dispersing phase. Most of these stages directly or indirectly depend on the valency of coagulating ions. It is difficult to find out the exact conditions of aggregation and still more difficult would be to assign quantitative relationships to the surficial and structural hydration. According to Rice,<sup>4</sup> colloidal particles do not aggregate if  $\frac{4\pi\sigma^2r}{D} > r_0^\infty$ , where  $\sigma$  is the surface density of electric charge,  $r$  the thickness of the double layer,  $D$  the dielectric constant of the medium and  $r_0^\infty$  is the non-electrical surface tension of the colloid particle. Rice has also shown that aggregation will become very rapid when a definite  $\sigma$  is reached. The surface density of electric charge,  $\sigma$ , is bound to be effected by the adsorbed solvent layers round the partially discharged colloidal particle. The non-electrical surface tension of the colloidal particle in such cases would tend to merge into the surface tension of the solvent medium.

### *Experimental*

We have carried experiments with different coagulating electrolytes, such as potassium chloride, potassium sulphate, potassium citrate, calcium chloride and barium chloride. The ferric phosphate sols were prepared by the usual Holmes method by adding potassium dihydrogen phosphate solution to a solution of ferric chloride in concentrations short of precipitation and dialysing the sol. The values of  $P$  and  $\log R$  have been calculated from the observations given below.

Concentration of the sol = 62.92 g. ferric phosphate per litre. Purity of the sol  $\text{Fe/Cl} = 0.3873/0.0765 = 5.06$ . Amount of sol taken = 3 c.c. and the total volume = 5 c.c.

The above results have been summarised in Table II which show that the values of  $p$  and  $\log R$  are not exactly the same and thus it is evident that ferric phosphate does not adsorb chloride, bromide and nitrate ions to the same extent, or these ions have some other more complicated preferential influence. The influence of different coagulating ions has been shown in Fig. 1.

TABLE I  
With uni-univalent electrolytes

Conc. of electrolyte used (C)	log C	Setting time, $\theta$ (secs.)	log S (-log $\theta$ )	The values of $p$ and log R calculated
<i>With 1.5 N-KCl</i>				
(1) 0.51 N	-0.2924	702	-2.8463	From (1) and (2)— $p=3.24$ ; log R = -1.90
(2) 0.33	-0.4815	2880	-3.4594	From (1) and (3)— $p=3.26$ ; log R = -1.89
(3) 0.27	-0.5686	5580	-3.7466	Mean value— $p=3.25$ ; log R = -1.90
<i>With N-KNO<sub>3</sub></i>				
(1) 0.40 N	-0.3979	4080	-3.6107	From (1) and (3)— $p=3.36$ ; log R = -2.27
(2) 0.38	-0.4202	4860	-3.6866	From (2) and (3)— $p=3.35$ ; log R = -2.28
(3) 0.33	-0.4815	7800	-3.8921	Mean value— $p=3.35$ ; log R = -2.28
<i>With 1.5 N-KBr</i>				
(1) 0.60 N	-0.2218	3960	-3.5977	From (1) and (3)— $p=2.75$ ; log R = -2.99
(2) 0.57	-0.2441	4560	-3.6590	From (2) and (3)— $p=2.75$ ; log R = -2.99
(3) 0.48	-0.3188	7320	-3.8645	Mean value— $p=2.75$ ; log R = -2.99

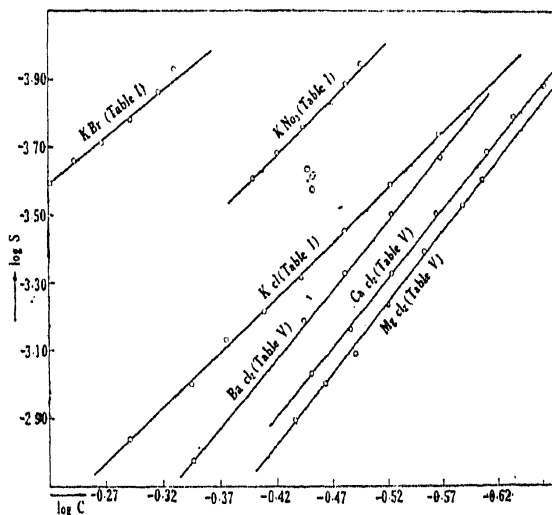


FIG. 1. Influence of different coagulating ions

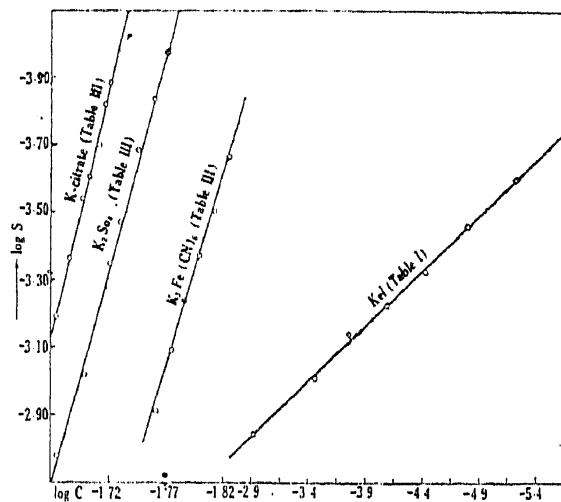


FIG. 2. Influence of uni-polyvalent electrolytes

TABLE II

Electrolyte	$p$	log R
1.5 N-KCl	3.25	-1.90
N-KNO <sub>3</sub>	3.35	-2.28
1.5 N-KBr	2.75	-2.99

TABLE III  
With uni-polyvalent electrolytes

Conc. of electrolyte used (C)	log C	Setting time, $\theta$ (secs.)	log S ( $-\log \theta$ )	The values of $p$ and log R calculated
<i>With N/10-K<sub>2</sub>SO<sub>4</sub></i>				
(1) 0.021 N	-1.6778	608	-2.7839	From (1) and (2)— $p=12.98$ ; log R=18.99
(2) 0.0186	-1.7305	2940	-3.4683	From (1) and (3)— $p=12.90$ ; log R=18.86
(3) 0.017	-1.7696	9300	-3.9685	Mean value— $p=12.94$ ; log R=18.93
<i>With 0.0529 N-Potassium citrate</i>				
(1) 0.02116 N	-1.6745	1560	-3.1931	From (1) and (3)— $p=14.67$ ; log R=21.37
(2) 0.02063	-1.6855	2280	-3.3579	From (2) and (4)— $p=14.66$ ; log R=21.35
(3) 0.01957	-1.7085	4920	-3.6920	Mean value— $p=14.66$ ; log R=21.36
(4) 0.01904	-1.7203	7380	-3.8681	
<i>With 0.0455 N-K<sub>3</sub>Fe (CN)<sub>6</sub></i>				
(1) 0.01683 N	-1.7739	1252	-3.0976	From (1) and (2)— $p=11.27$ ; log R=16.89
(2) 0.01592	-1.7980	2340	-3.3692	From (1) and (3)— $p=11.29$ ; log R=16.93
(3) 0.01501	-1.8236	4560	-3.6590	Mean value— $p=11.28$ ; log R=16.91

The influence of uni-polyvalent electrolytes has been summarised in Table IV. In Fig. 2 are given the graphs showing the influence.

TABLE IV

Electrolyte	$p$	log R
1.5 N-KCl .. ..	3.25	- 1.90
N/10-K <sub>2</sub> SO <sub>4</sub> .. ..	12.94	18.93
0.0529 N-K-citrate .. ..	14.66	21.36
0.0455 N-K <sub>3</sub> Fe (CN) <sub>6</sub> .. ..	11.28	16.91

It is clear from these figures that the values of  $p$  and log R markedly increase if the jelly is formed by the uni-bivalent ion. The difference between uni-bivalent and uni-trivalent is not so marked as between uni-monovalent and uni-bivalent. The ferrocyanide ion does not fall into the series, probably due to the chemical reactivity with the iron sol.

TABLE V  
With poly-univalent electrolytes

Conc. of electrolyte used (C)	log C	Setting time, $\theta$ (secs.)	log S ( $-\log \theta$ )	The values of $p$ and log R calculated
<i>With 1.36 N-CaCl<sub>2</sub></i>				
(1) 0.3536 N	-0.4515	1104	-3.0429	From (1) and (3)— $p=4.06$ ; log R = -1.21
(2) 0.2992	-0.5240	2160	-3.3345	From (2) and (3)— $p=4.09$ ; log R = -1.19
(3) 0.2448	-0.6112	4920	-3.6920	Mean value— $p=4.07$ ; log R = -1.20
<i>With 1.5 N-BaCl<sub>2</sub></i>				
(1) 0.45 N	-0.3468	608	-2.7839	From (1) and (2)— $p=4.12$ ; log R = -1.35
(2) 0.30	-0.5229	3240	-3.5105	From (1) and (3)— $p=4.02$ ; log R = -1.39
(3) 0.27	-0.5686	4740	-3.6758	Mean value— $p=4.07$ ; log R = -1.37
<i>With 1.075 N-MgCl<sub>2</sub></i>				
(1) 0.3655 N	-0.4371	798	-2.9020	From (1) and (3)— $p=4.21$ ; log R = -1.06
(2) 0.3440	-0.4634	1020	-3.0086	From (2) and (3)— $p=4.23$ ; log R = -1.05
(3) 0.2472	-0.6069	4140	-3.6170	Mean value— $p=4.22$ ; log R = -1.05

The influence of poly-univalent electrolytes has been summarised in the following table:

TABLE VI

Electrolyte	$p$	log R
1.5 N-KCl .. ..	3.25	-1.90
1.36 N-CaCl <sub>2</sub> .. ..	4.07	-1.20
1.5 N-BaCl <sub>2</sub> .. ..	4.07	-1.37
1.075 N-MgCl <sub>2</sub> .. ..	4.22	-1.05

As is expected, the values of  $p$  and log R do not much change with the valency of the positively charged ions as the sol itself is positively charged.

#### Discussion

From the above tables we see that in case of uni-univalent electrolytes such as potassium chloride, potassium nitrate and potassium bromide, the values of  $p$  and log R do show only a slight variation. The small differences are due to the specific nature of different ions which are not adsorbed by ferric phosphate to the same extent. The uni-polyvalent electrolytes as potassium chloride, potassium sulphate and potassium citrate show a marked change

in the values of  $p$  and  $\log R$ , while in the case of potassium ferricyanide, the values of these constants lie between those for potassium chloride and potassium sulphate. It seems that this is due to the chemical reaction taking place between the sol and the electrolyte as it is evident from the change of colour exhibited during gelation. The gelation of ferric phosphate sol qualitatively obeys the Schulze-Hardy law. The behaviour of poly-univalent electrolytes as calcium chloride, barium chloride and magnesium chloride is practically the same and the values of  $p$  and  $\log R$  do not show much change. The constants in the case of poly-univalent electrolytes are a little higher than in the case of uni-univalent electrolytes.

The jelly formation of ferric phosphate sol in this respect closely resembles the coagulation of positively charged ferric hydroxide sol. It is interesting to note that the results obtained by Freundlich, Weiser and Dhar on positively charged ferric hydroxide sol are in fair agreement with ours. From Freundlich's observations,<sup>5</sup> the order of precipitating power of the anions is dichromate > sulphate > hydroxide > benzoate > chloride > nitrate > bromide > iodide. Dhar<sup>6</sup> has obtained from this sol the following series:

Ferricyanide > citrate > oxalate > sulphate > hydroxide > nitrate > chloride.

No work has been done in this line on the coagulation of ferric phosphate and arsenate sols, but it is expected that these sols would also behave similarly. We have shown that gelation is also essentially a coagulation process and therefore, similar results are expected in gelation too. From the results recorded in the previous tables, the values of  $\log R$  are in the following order:

With anions: citrate > sulphate > ferricyanide\* > chloride > nitrate > bromide.

With cations: magnesium > calcium > barium > potassium. The values of  $p$  are in the following order for the ferric phosphate sol.

K-citrate >  $K_2SO_4$  >  $K_3Fe(CN)_6$  >  $MgCl_2$  >  $BaCl_2$  >  $CaCl_2$  >  $KNO_3$  >  $KCl$  >  $KBr$ . The difference in the value of  $p$  is very much marked only when we proceed from  $KCl$  to  $K_2SO_4$  or to K-citrate, while in other cases the values are almost the same.

By coagulating or flocculating power is usually meant the concentration of electrolyte (expressed in moles or millimoles per litre) necessary to precipitate the sol completely in a stated time. The gelation power of an electrolyte can also be similarly defined in terms of the concentration of electrolyte necessary to set the sol to a gel in a stated time. In order to set a sol in

\* Anomalous due to chemical reaction.

time  $S$ , let the concentration of the monovalent electrolyte be  $C_1$ , so that

$$S = \log R + p \log C_1.$$

The sol with the same characteristics,  $p$  and  $R$ , would require the concentration  $C_2$  to set the sol to a jelly in the same time  $S$  with the polyvalent electrolyte. If the two concentrations are related according to Whetham or some other general law so that  $C_1 = a C_2^r$ , where  $r$  denotes some power depending upon the valency of the ion, the gelation time  $S$  would be given by:

$$S = \log R + p \log (a C_2^r)$$

or 
$$S = \log R + p \log a + r \cdot p \log C_2.$$

Thus the constant  $\log R$  is replaced by another constant  $\log R + p \log a$  and the constant  $p$  is replaced by another constant  $r \cdot p$ . The variations observed in the values of  $\log R$  and  $p$  when gelation is affected with different ions as recorded in the previous tables qualitatively agree with these assumptions. The quantitative differences are due to the influence of the similarly charged ions, different adsorbabilities and other factors which do not make the results exactly comparative.

### Summary

In continuation with the previous work, the authors have studied the influence of different coagulating ions on the setting of ferric phosphate jellies. The values of  $p$ , the jelly characteristic and  $R$  the rate constant in the equation  $\log S = \log R + p \log C$  do not change much with uni-univalent electrolytes. The slight variations with chloride, bromide and nitrate ions are due to the different adsorbabilities of these ions by ferric phosphate. When the jelly formation is affected with uni-polyvalent ions the marked variations are observed consistent with Whetham's law, or any other generalized expression. With poly-univalent electrolytes, the values of  $p$  and  $\log R$  do not markedly change as the sol itself is positively charged.

In the end, the authors are grateful to Prof. N. R. Dhar for his interest throughout the work.

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