KINETICS OF SOL-GEL TRANSFORMATION

Part III. The Influence of Temperature on the Setting of Some Inorganic Jellies

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Introduction

In two of the previous publications,[1] the authors have made a systematic study of the formation of inorganic gels from sols by bringing out coagulation of the latter. The coagulation velocities of sols giving out lyophobic coagulum have been hitherto studied by authors like Paine and others, but very little attention has been paid to the gelation velocities of lyophilic inorganic sols. It must be mentioned here that no rigid distinction appears to be existing between a lyophobic and a lyophilic sol, especially when one has to deal with inorganic substances. An inorganic sol giving out a jelly is both lyophilic and lyophobic. It is lyophilic so far as its water binding capacity is concerned. It is lyophobic because it is not generally heat-reversible, nor its aged or dehydrated particles show that amount of swelling which one experiences in the case of gelatin, agar agar and other lyophilic organic substances. But the authors have experienced that suitably prepared sols of iron, chromium and aluminium salts or hydroxides exhibit these properties also to some extent.

In his experiments on copper sol, Paine[2] observed that on addition of an electrolyte, there is an initial period in which the sol remains quite clear; when coagulation commences at the end of this period, the speed at which it occurs, diminishes in a continuous manner. For colloidal solutions of different concentrations, the rate of coagulation is proportional to the square of the initial concentration. This, according to Paine, is in agreement to the mass action law and indicates that coagulation is brought about by the mutual attraction of the particles. Paine has also studied the rate of coagulation with respect to the variation of the electrolyte concentration. He finds that the rate of coagulation in case of copper sol is proportional to some power of the concentration of the anion, that is, $R \propto C^p$. Within the limits

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of the experimental errors, the value of the index p is the same as the index n in the adsorption formula $y = a\,C^{1/n}$. Paine also found that p has the same value for coagulation with ions of different valencies, this agreeing with the Freundlich's view of the mode of action of the ions. When equivalent quantity of ions have been adsorbed, the colloidal particles behave quite similarly in reference to the process of coagulation.

In the present series of papers, the authors have made an attempt to see how far the Paine's expression can be applied to the gelation processes. In the first paper, they have shown that in the case of the jellies of ferric arsenate, ceric hydroxide, zirconium hydroxide and chromium arsenate (positively and negatively charged both), the following expression gives the relation between the setting time of the jelly (θ) and the concentration of the electrolyte (C) :

$$S = 1/\theta = RC^p$$

or

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

In this expression, S denotes the velocity of jelly formation and is equal to the inverse of the setting time of the jelly. The mechanism of jelly formation is more complicated than the mechanism of coagulation and as such, it will be interesting to see that the index p very much differs from the index n of the Freundlich's adsorption formula.

Experimental

We have applied this expression to some more sols as aluminium hydroxide and ferric phosphate, and have found that it is invariably applicable. We shall give here our results with four different samples of ferric phosphate sols prepared separately and having different concentrations.

Ferric phosphate sol I.—Concentration of the sol = 42·64 g. of ferric phosphate per litre. The sol was prepared by the Holmes[3] method by adding potassium dihydrogen phosphate to an excess of ferric chloride solution and then dialysing the sol thus formed. To three c.c.'s of the sol. were added different amounts of N-potassium chloride solution, making total volume in each case 5 c.c. The setting time of the jellies was measured in seconds. The values of p and log R were calculated out from the two observed values, and then applied to determine the values of log S in other cases. From the two values S_1 and S_2, corresponding to the concentrations of electrolyte, C_1 and C_2,

$$p = \frac{\log S_1 - \log S_2}{\log C_1 - \log C_2}$$

From the value of p, log R is easily determined.

TABLE I

$$p = 3 \cdot 366 \, ; \log R = -0 \cdot 044$$

Conc. of KCl (C)	log C	Time of setting, θ (secs.)	log S = $-\log \theta$ found	log S calculated
0·20 N	− 0·6990	252	− 2·4014	− 2·3968
0·18	− 0·7447	345	− 2·5378	− 2·5506
0·16	− 0·7959	510	− 2·7076	− 2·7230
0·14	− 0·8539	965	− 2·9845	− 2·9182
0·12	− 0·9208	1380	− 3·1399	− 3·1434
0·10	− 1·0000	2580	− 3·4116	− 3·4100
0·08	− 1·0969	5940	− 3·7738	− 3·7362

Sol. II.—Concentration of the sol = 53·64 g. ferric phosphate per litre. 1·5 N KCl was used as coagulating electrolyte and the total volume was kept to be 5 c.c.

TABLE II

$$p = 2 \cdot 24 \, ; \log R = -1 \cdot 7156$$

Conc. of KCl (C)	log C	Time of setting, θ (secs.)	log S found	log S calculated
0·36 N	− 0·4437	512	− 2·7093	− 2·7095
0·33	− 0·4815	640	− 2·8062	− 2·7942
0·30	− 0·5229	780	− 2·8921	− 2·8869
0·24	− 0·6198	1138	− 3·0562	− 3·1039
0·21	− 0·6778	1612	− 3·2073	− 3·2339
0·15	− 0·8239	3240	− 3·5105	− 3·5611
0·12	− 0·9208	6000	− 3·7782	− 3·7782

Sol. III.—Concentration of the sol = 62·92 g. ferric phosphate per litre. 3 c.c. of the sol were set with different amounts of 1·5 N KCl, and the total volume was 5 c.c.

TABLE III

$$p = 3 \cdot 259 \,;\, \log R = -1 \cdot 8935$$

Conc. of KCl (C)	log C	Time of setting, θ (secs.)	log S found	log S calculated
0·54 N	− 0·2676	523	− 2·7185	− 2·7656
0·51	− 0·2924	702	− 2·8463	− 2·8465
0·45	− 0·3468	1020	− 3·0086	− 3·0237
0·42	− 0·3768	1380	− 3·1399	− 3·1215
0·39	− 0·4089	1680	− 3·2253	− 3·2261
0·36	−· 0·4437	2100	− 3·3222	− 3·3395
0·33	− 0·4815	2880	− 3·4594	− 3·4627
0·30	− 0·5229	3960	− 3·5977	− 3·5976
0·27	−· 0·5686	5580	− 3·7466	− 3·7466

Sol IV.—Concentration of the sol = 93·82 g. ferric phosphate per litre. 3 c.c. of the sol were set with different amounts of N KCl, and the total volume was 5 c.c.

TABLE IV

$$p = 4 \cdot 290 \,;\, \log R = 0 \cdot 593$$

Conc. of KCl (C)	log C	Time of setting, θ (secs.)	log S found	log S calculated
0·20 N	− 0·6990	255	− 2·4065	− 2·4060
0·18	− 0·7447	360	− 2·5563	− 2·6017
0·16	− 0·7959	660	− 2·8195	− 2·8214
0·14	− 0·8539	1140	− 3·0569	− 3·0702
0·12	− 0·9208	2280	−3·3579	− 3·3572
0·10	− 1·0000	6180	− 3·7910	− 3·6970

Thus it will be seen from all these tables that the calculated values of log S are in fair agreement with the observed values. So long as the sol is capable of setting to a jelly, the relation between the concentration of electrolyte and the time of setting of the jelly is given by the proposed expression.

In one paper, we have already discussed how the constant p and log R vary with respect to the concentration of the sol, and there we have observed that though these jelly-forming sols may behave normally towards the dilution effect when coagulation is studied, yet their behaviour is abnormal as regards jelly formation. To set a dilute sol in a particular time, more electrolyte is necessary than to set a concentrated sol. In this paper, we shall make an attempt to see how the constants p and log R vary with reference to the temperature effect.

In one of the papers, Dhar and Prakash[4] have shown that the sols of ferric hydroxide, stannic hydroxide, zirconium hydroxide, aluminium hydroxide and chromium hydroxide require smaller quantities of electrolytes when coagulated at higher temperature. On the other hand, sols of gamboge, gum dammar and mastic become more stable towards coagulation at higher temperatures. The stability of the latter sols is due to the hydrolysis at higher temperatures. In another publication, Prakash[5] has observed that almost all the inorganic jellies like zirconium hydroxide, zirconium molybdate, zirconium borate, thorium phosphate, chromium arsenate, stannic arsenate, stannic phosphate and stannic tungstate set more readily at higher temperatures, whereas, the jellies of thorium arsenate, vanadium pentoxide and mercuri-sulphosalicylic acid are exceptions and they do not set above 60°. The temperature effect on jelly formation has an importance, because it is with regards to this, that the inorganic and organic jellies differ so much. In this paper, we shall communicate our results with ferric phosphate, ferric arsenate, aluminium hydroxide and zirconium hydroxide sols.

The sols of ferric arsenate and phosphate were prepared as usual by Holmes method, by adding potassium arsenate and phosphate to an excess of ferric chloride solution and then dialysing. Zirconium hydroxide was prepared by dialysing 10% solution of zirconium nitrate and aluminium hydroxide sol was obtained by peptising well washed aluminium hydroxide with minimum amount of acetic acid and then subjecting to dialysis. The jellies were set at different temperatures in thermostats, and their setting time noted for the various concentrations of electrolytes added. On the basis of these observations, the values of p and log R have been calculated. We shall feel satisfied in giving three observation readings out of many in each case which would suffice to give the values of the above constants.

Ferric phosphate jelly.—Concentration of the sol = 93·82 g. ferric phosphate per litre. 3·5 c.c. of the sol were mixed with different concentrations of N-KCl and the total volume was made 5 c.c. in each case.

TABLE V

Conc. of KCl (C)	log C	Time of setting, θ (secs.)	log S	Values of p and log R calculated
Temperature 35°				
(1) 0·14 N	− 0·8539	360	− 2·5563	From (1) and (2)— $p = 4·458$; log R = 1·2506
(2) 0·09	− 1·0458	2580	− 3·4116	From (1) and (3)— $p = 4·444$; log R = 1·2391
(3) 0·08	− 1·0969	4320	− 3·6355	Mean— $p = 4·451$; log R = 1·2448
Temperature 45°				
(1) 0·10 N	− 1·0000	365	− 2·5623	From (1) and (2)— $p = 4·543$; log R = 1·9807
(2) 0·09	− 1·0458	590	− 2·7709	From (1) and (3)— $p = 4·329$; log R = 1·7667
(3) 0·08	− 1·0969	960	− 2·9823	Mean— $p = 4·436$; log R = 1·8737
Temperature 55°				
(1) 0·08 N	− 1·0969	220	− 2·3424	From (1) and (3)— $p = 4·216$; log R = 2·2821
(2) 0·07	− 1·1549	360	− 2·5563	From (2) and (3) $p = 4·341$; log R = 2·4571
(3) 0·04	− 1·3979	4080	− 3·6107	Mean— $p = 4·278$; log R = 2·3696

The results of this table may be summarised as below :

TABLE VI

Temperature	log R	p
35°	1·2448	4·451
45°	1·8737	4·436
55°	2·3696	4·278

These results show that the value of log R increases and that of p slightly decreases with the rise of temperature.

Ferric arsenate jelly.—Concentration of the sol = 84·56 g. ferric arsenate per litre. 3 c.c. of the sol were mixed with different amounts of N/2 KCl and the total volume was made 5 c.c.

<div align="center">TABLE VII</div>

Conc. of KCl (C)	log C	Time of setting, θ (secs.)	log S	Values of p and log R calculated
		Temperature 35°		
(1) 0·17 N	− 0·7696	677	− 2·8306	From (1) and (3)— $p = 4·769$; log R = 0·8350
(2) 0·16	− 0·7959	920	− 2·9638	From (2) and (3)— $p = 4·736$; log R = 0·8046
(3) 0·12	− 0·9208	3600	− 3·5563	Mean— $p = 4·752$; log R = 0·8198
		Temperature 45°		
(1) 0·13 N	− 0·8861	505	− 2·7033	From (1) and (3)— $p = 4·025$; log R = 0·8631
(2) 0·12	− 0·9208	690	− 2·8388	From (2) and (3)— $p = 4·049$; log R = 0·8895
(3) 0·075	− 1·1249	4620	− 3·6646	Mean— $p = 4·037$; log R = 0·8763
		Temperature 55°		
(1) 0·09 N	− 1·0458	402	− 2·6042	From (1) and (3)— $p = 3·758$; log R = 1·3259
(2) 0·045	− 1·3468	5520	− 3·7419	From (1) and (2)— $p = 3·780$; log R = 1·3489
3) 0·040	− 1·3979	8460	− 3·9274	Mean— $p = 3·769$; log R = 1·3374

These results have been summarised in the following table :

<div align="center">TABLE VIII</div>

Temperature	log R	p
35°	0·8198	4·752
45°	0·8763	4·037
55°	1·3374	3·769

Aluminium hydroxide jelly.—Concentration of the sol = 20·00 g. Al_2O_3 per litre. 4 c.c. of the sol were taken and mixed with different amounts of N/2 KCl. The total volume was made 5 c.c.

<center>TABLE IX</center>

Conc. of KCl (C)	log C	Time of setting, θ (secs.)	log S	Values of p and log R calculated
Temperature 35°				
(1) 0·06 N	— 1·2218	420	— 2·6232	From (1) and (2) — $p = 3·97$; log R = 2·2273
(2) 0·045	— 1·3468	1320	— 3·1206	From (1) and (3)— $p = 3·58$; log R = 1·7508
(3) 0·04	— 1·3979	1800	— 3·2553	From (1) and (4)— $p = 3·42$; log R = 1·5553
(4) 0·030	— 1·5229	4500	— 3·6532	Mean— $p = 3·65$; log R = 1·8444
Temperature 45°				
(1) 0·05 N	— 1·3010	240	— 2·3802	From (1) and (3)— $p = 3·585$; log R = 2·2839
(2) 0·045	— 1·3468	330	— 2·5185	From (2) and (3)— $p = 3·690$; log R = 2·4523
(3) 0·025	— 1·6021	2880	— 3·4594	Mean— $p = 3·637$; log R = 2·3681
Temperature 55°				
(1) 0·035 N	— 1·4559	230	— 2·3617	From (1) and (2)— $p = 3·675$; log R = 2·9884
(2) 0·020	— 1·6990	1800	— 3·2553	From (1) and (3)— $p = 3·723$; log R = 3·0582
(3) 0·015	— 1·8239	5400	— 3·7324	Mean— $p = 3·699$; log R = 3·0233

These results on aluminium hydroxide sol have been summarised in the following table :

<center>TABLE X</center>

Temperature	log R	p
35°	1·8444	3·656
45°	2·3681	3·637
55°	3·0233	3·699

These values show that as the temperature increases, the values of log R increase, whereas p appears to be independent of the temperature.

Zirconium hydroxide jelly.—Concentration of the sol = 30·84 g. ZrO_2 per litre. 4 c.c. of the sol were mixed with different amounts of N-KCl and the total volume was made 6 c.c.
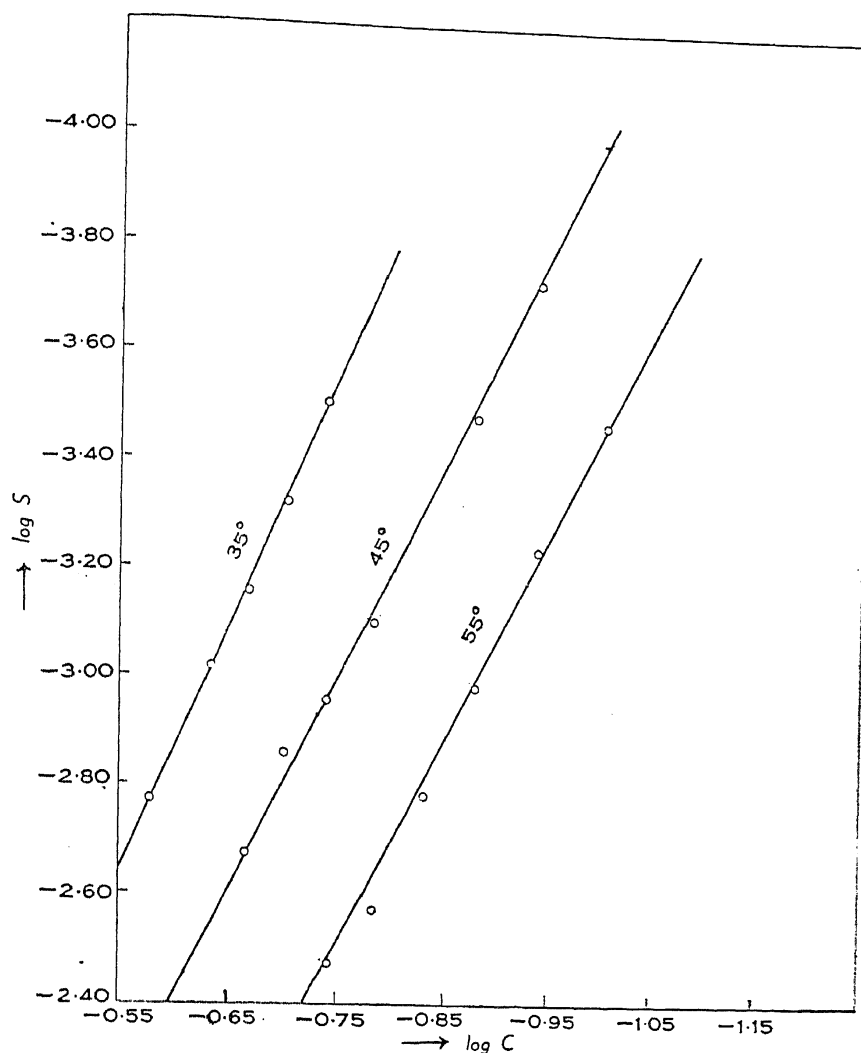
TABLE XI

Conc. of KCl (C)	log C	Time of setting, θ (secs.)	log S	Values of p and log R calculated
		Temperature 35°		
(1) 0·233 N	− 0·6326	1050	− 3·0212	From (1) and (2)— $p = 4·560$; log R = − 0·1366
(2) 0·200	− 0·6990	2100	− 3·3222	From (1) and (3)— $p = 4·625$; log R = − 0·0954
(3) 0·183	− 0·7375	3180	− 3·5024	Mean— $p = 4·592$; log R = − 0·1160
		Temperature 45°		
(1) 0·216 N	− 0·6655	480	− 2·6812	From (1) and (3)— $p = 3·874$; log R = − 0·1034
(2) 0·183	− 0·7375	900	− 2·9542	From (2) and (3)— $p = 3·904$; log R = − 0·0753
(3) 0·116	− 0·9355	5340	− 3·7275	Mean— $p = 3·889$; log R = − 0·0893
		Temperature 55°		
(1) 0·183 N	− 0·7375	300	− 2·4771	From (1) and (2)— $p = 3·633$; log R = 0·2022
(2) 0·133	− 0·8761	960	− 2·9823	From (1) and (3)— $p = 3·734$; log R = 0·2746
(3) 0·100	− 1·0000	2880	− 3·4594	Mean— $p = 3·683$; log R = 0·2384

These results (see Graph) have been summarised in the following table :

TABLE XII

Temperature	log R	p
35°	− 0·1160	4·592
45°	− 0·0893	3·889
55°	+ 0·2384	3·683

Influence of temperature on the setting of zirconium hydroxide jelly (Table XI).

It will be seen from Table XII, that the value of log R increases and the value of p decreases as the temperature increases.

Discussion

From the results recorded in the previous tables, it will be seen that in the case of ferric phosphate, ferric arsenate and zirconium hydroxide, the values of log R are increasing with the rise of temperature and so is the case with aluminium hydroxide jellies also. In the first three cases, the values of p are slightly decreasing with respect to temperature, whilst in the case of aluminium hydroxide, p appears to be independent of it.

The authors have assumed that the process of jelly formation is very much similar to the process of coagulation, and therefore, two definite stages in the course of gelation ought to be conceived. By the addition of an

electrolyte, the ζ-potential should fall to a critical value before the process of gelation starts.   The initiation of the gelation process includes the beginning of the charge neutralisation and subsequent development of surficial hydration.   When once started the gelation then proceeds continuously with the time.   This stage corresponds to the stage of slow coagulation, and we shall call it the stage of " continuous gelation ".   Prakash[6] has shown that during this stage, the viscosity of the sol increases according to the following Prakash's equation :

$$\eta_t = \eta_0 e^{ht},$$

where η_0 is the viscosity at any initial time η_t and η_0 the viscosity after the time t, h is the hydration constant depending upon the thickness of the hydrated layer.   It has been shown by the author that in the case of all jellies obtained by slow coagulation, this expression is always followed within a particular range of jelly formation.   We are not concerned here with the exact mechanism of hydration.   In the present series of investigations, we are investigating the rate at which this hydration is developed. From our results, we can definitely say, that this speed of hydration is related in some way to the concentration of the coagulating electrolyte.

Within the region of " continuous gelation ", the speed with which hydration develops appears to be associated with the concentration of the coagulating ion in the following way :

$$H = R \cdot C^p$$

where H is the speed of hydration, R the proportionality constant and p the index of concentration C of the coagulating ion.   This equation, though of the same form as the Freundlich's adsorption equation, is yet not identical with it, because the course of hydration depends on many other factors, besides adsorption of the oppositely charged ion.

The last stage of jelly formation corresponds to the stage of rapid coagulation, and we call it the period of " rapid or structural gelation ", corresponding to the rapid or sudden structural increase in the viscosity.   Similar to the rapid coagulation, this period is also independent of the concentration of the coagulating ion.   If we assume, that irrespective of the concentration of electrolyte, the jellies develop the same texture in all cases by the time they set, this last stage can be eliminated in studying the relation of the setting time with the concentration of the electrolyte.   This assumption is not true with very high concentrations of electrolytes where the jellies are formed almost instantaneously and exhibit marked syneresis. Such rapidly formed jellies have an altogether different texture.

The total setting time of a jelly is equal to the time of continuous hydration plus the time of rapid gelation. The rate of jelly formation, S, may be taken to be an inverse of the setting time. Thus we can write

$$S = 1/\theta = R \cdot C^p + a,$$

where a is a constant for rapid gelation

or,
$$S = R \cdot C^p \left[1 + \frac{a}{RC^p} \right].$$

Thus, $\log S = \log R + p \log C + \log \left[1 + \frac{a}{RC^p} \right]$

$$= \log R + p \log C + \frac{a}{RC^p} \text{ (neglecting the higher terms}$$

of the expansion).

The period of the rapid gelation is very small, and therefore, the third term on the right-hand side may be neglected, and therefore, the expression for the slowly formed jellies is:

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

We shall say, that in this expression, R is the speed constant and p is the " jelly-characteristic". So long as the characteristic nature of the jelly is not changed, the value of p would remain the same. It appears that in ideal cases, the temperature will have no influence on the texture of the jelly, and then the values of p would remain constant. The higher the temperature, the greater would be the rate of coagulation and consequently the greater will be the speed of gelation too, and therefore, the values of log R will continuously increase.

The present authors have, however, also shown that a jelly obtained at higher temperatures is not exactly similar to the jelly obtained at the lower temperature. The higher temperature jelly is more opalescent, and sometimes more loose in texture. Prakash[7] has shown that the jellies exhibit more syneresis at higher temperatures. This would explain why the " jelly-characteristic " p slightly decreases in some cases at the higher temperature.

It is difficult to work out quantitatively how the values of R ought to vary with respect to temperature. It all depends how the temperature influences the following factors: the velocity of coagulation, the surface activity of the particle, the hydration tendency, the network development, and the hydrolysis of the substances concerned. It will be seen that the substances like ferric arsenate or ferric phosphate undergo marked hydrolysis at higher temperatures.

Summary

In continuation with the previous work, the authors have studied the kinetics of sol-gel transformation with reference to the concentration of the coagulating electrolyte. Differently prepared samples of ferric phosphate show that in every case where a jelly is formed, the equation $\log S = \log R + p \log C$ is applicable during the period of slow gelation, where S is the rate of jelly formation, C the concentration of electrolyte, p the jelly-characteristic, and R the rate constant. The authors have studied the influence of temperature on the rate of setting of ferric arsenate, ferric phosphate, aluminium hydroxide and zirconium hydroxide jellies, and they have found that the value of R increases as the temperature is increased, whereas, the value of p shows only a very slight decrease. It is expected that so long as the jelly is not characteristically changed in texture, the value of p ought to remain constant, but in most cases, the texture also undergoes some variation as the temperature is increased (the jelly becomes opalescent and more synerising), the constant p slightly decreases.

REFERENCES

1.	Prakash and Dube	.. *Zeit. anorg. Chem.*, 1932, **208**, 163.
	Dube	.. *Ibid.*, 1934, **217**, 284.
2.	Paine	.. *Kolloidchem. Beih.*, 1912, **4**, 24; *Proc. Camb. Phil. Soc.*, 1912, **16**, 430.
3.	Holmes and Arnold	.. *J. Amer. Chem. Soc.*, 1918, **40**, 1014.
	—— and Rindfusz	.. *Ibid.*, 1916, **38**, 1970.
4.	Dhar and Prakash	.. *J. Phys. Chem.*, 1930, **34**, 954.
5.	Prakash	.. *J. Indian Chem. Soc.*, 1932, **9**, 139.
6.	——————	.. *Kolloid-Z.*, 1932, **60**, 184.
7.	—— and Dhar	.. *J. Indian Chem. Soc.*, 1930, **7**, 417.