OPACITY CHANGES DURING THE COAGULATION OF SOLS BY ELECTROLYTES

By Mata Prasad, S. Guruswamy* and N. A. Padwal

(*From the Chemical Laboratories, Royal Institute of Science, Bombay*)

THE opacity method of following the coagulation of a sol was first developed by Mukherjee and Mujumdar[1] by allowing the light transmitted through the coagulating system to fall on a thermopile connected to a galvanometer. Desai[2] modified this method by using a photo-cell in place of thermopile. Prasad and Modak[3] modified Desai's method by amplifying the current from the photo-cell. Recently, Prasad and Gogate[4] have designed an apparatus for the measurement of opacity of gel-forming systems and they find that results of fairly high repetibility can be obtained by the use of this apparatus. This was therefore used to study the kinetics of coagulation of sols by electrolytes, and the effects of temperature and the addition of non-electrolytes on the coagulation were also examined. The sols employed were those of thorium, stannic, and zirconium hydroxides; the coagulation of some of these has been studied previously by some workers. The results obtained are discussed in the following pages.

1. Results and Discussion

(*a*) *Thorium hydroxide sol.*—The sol was prepared by the method adopted by Desai (*loc. cit.*), and was dialysed for 7 days. The concentration of the sol was found to be 4·1 g. of ThO_2 per litre.

Equal volumes of the sol and electrolytes (K_2SO_4, KCl, KNO_3, $BaCl_2$, NaCl) of different concentrations were mixed and the opacity of the coagulating mixture was measured at different intervals of time commencing from the time of mixing. The time-deflection curves obtained during the coagulation of the sol by the highest and lowest concentrations employed are shown graphically in Figs. 1 and 2. The concentrations of the electrolytes mentioned refer to the amounts of electrolytes present in the total volume (9 c.c.) of the coagulating mixture.

* Springer Research Scholar of the Bombay University.

[1] *J. C. S.*, 1924, 125, 785.
[2] *Trans. Farad. Soc.*, 1928, 24, 181.
[3] *Proc. Ind. Acad. Sci.*, 1940, 12, 235.
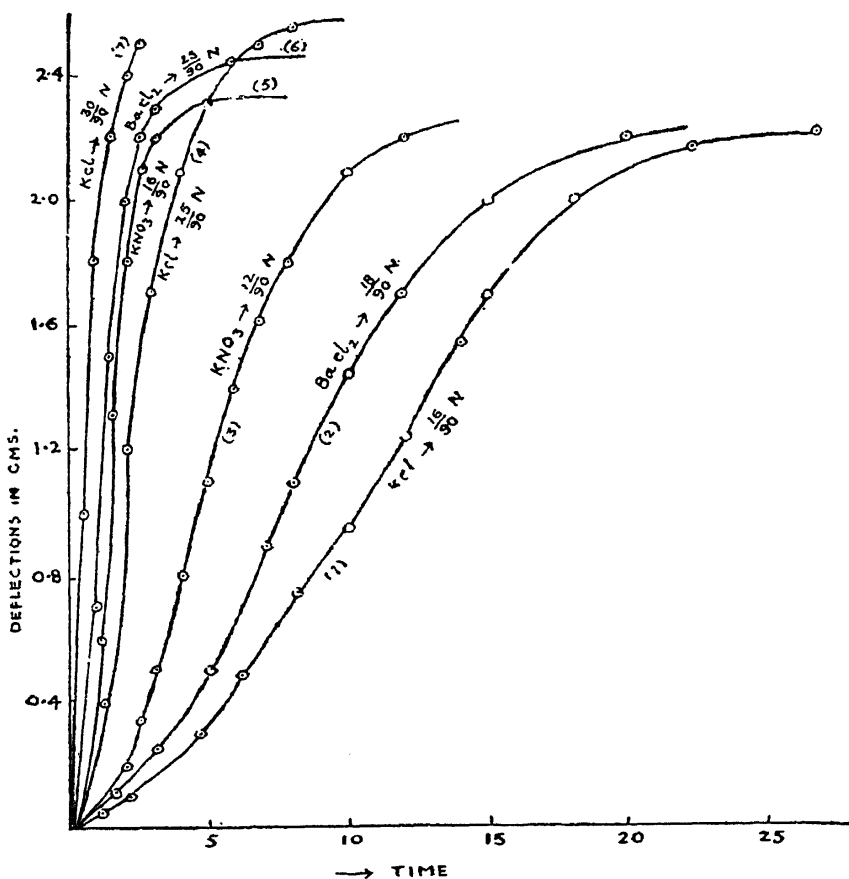[4] *Ibid.*, 1943, 17, 163.
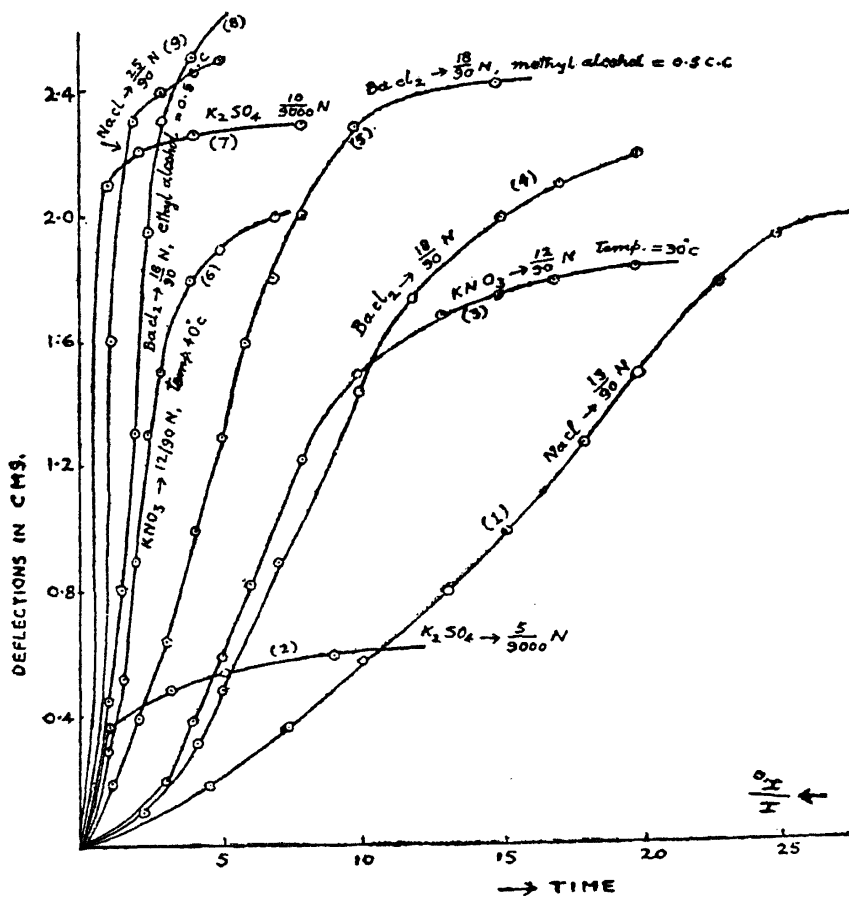
FIG. 1. Coagulation of Thorium Hydroxide Sol.

FIG. 2. Coagulation of Thorium Hydroxide Sol.

All the curves in Figs. 1 and 2 are continuous showing thereby that coagulation is a continuous phenomenon. Potassium sulphate is a good coagulator (*cf.* curves 2 and 7, Fig. 2) since its concentration required for coagulation is relatively smaller than those of other electrolytes. This may be due to the bivalent nature of the coagulating ion. Moreover, the coagulation in the presence of potassium sulphate is rapid, it being nearly completed in about 2 minutes in the presence of 1/900 N K_2SO_4; if its concentration is less than this only partial coagulation takes place.

The behaviour of the other electrolytes is very similar to each other but different from that of potassium sulphate. The coagulation of the sol by barium chloride in the presence of ethyl and methyl alcohols shows that the rate of coagulation is greatly increased by such an addition (*cf.* curves 4, 5 and 8, Fig. 2), the increase being greater in the presence of ethyl than methyl alcohol.

Temperature has a great effect on the coagulation velocity (*cf.* curves 3 and 6, Fig. 2). The rate of coagulation is accelerated by the increase in temperature, but the nature of the curves remains the same.

The observations for the same sol taken at 30° with 12/90 N potassium nitrate given in Fig. 2 (curve 3) differ from those given in Fig. 1 (curve 3); the former were taken about a month after the latter. The observed differences are apparently due to the ageing of the sol during this period.

An examination of the various curves in Figs. 1 and 2 shows that the final value of opacity in the presence of different amounts of the same electrolyte is not the same. Usually it increases, though slightly, when increasing amounts of the electrolytes are added. This increase is also noticeable when the sol is coagulated at different temperatures and in the presence of ethyl and methyl alcohols. These changes are predominant in the coagulation of the sol by potassium sulphate. A comparison of the curves obtained with a freshly prepared sol and the one which has aged for a month shows that the final value of opacity in the case of the aged sol is less than that in the fresh one. The above-mentioned differences may have been caused by a number of factors which come into play during and immediately after the process of coagulation.

The coagulating power of an electrolyte is the reciprocal of the minimum concentration of the electrolyte required to effect a definite stage of coalescence (from the first appearance of turbidity to complete separation of the coagulum) in a given time. The results obtained in this investigation can be used to compare accurately the coagulating powers of the electrolytes employed for the coagulation of the sol since the measurements of

opacity give fairly high reproducible and accurate results. For this purpose curves were drawn between the time required for the coagulating mixture to attain a certain value of opacity (deflection of 1 cm.) against concentrations of several electrolytes used for coagulation. It is found from these curves that the concentrations of the different electrolytes necessary to cause coagulation in a given time follow the following descending order $KNO_3 >$ $NaCl > KCl > BaCl_2$. Hence the descending order of coagulating power of these electrolytes is $KNO_3 > NaCl > KCl > BaCl_2$. For a time equal to 2 minutes the coagulating powers are $KNO_3 : NaCl : KCl : BaCl_2 =$ $1 \cdot 76 : 1 \cdot 17 : 1 \cdot 07 : 1 \cdot 00$.

(b) *Stannic hydroxide sol.*—This sol was prepared by the same method as adopted by Dhar and Vardhanam.[5] Three samples of the sol were employed for coagulation experiments: (A) undialysed sol, (B) sol dialysed for 8 days and (C) sol dialysed for 15 days. The colloidal contents of the three samples of the sol were $33 \cdot 1$, $17 \cdot 4$ and $13 \cdot 9$ g. of SnO_2 per litre.

The experimental procedure followed was exactly the same as that adopted in the case of thorium hydroxide sol.

Some of the results obtained are graphically shown in Figs. 3 and 4. It will be seen in this case also that all the curves are continuous thereby showing that coagulation is a continuous phenomenon. Most of the curves are 'S' shaped while some of them are steep rising ones.

The coagulating power of the electrolytes employed for coagulation of this sol was compared by the same method as used in the case of thorium hydroxide sol and it was found that the coagulating power of potassium sulphate is greater than that of potassium chloride for all the three samples. This may be due to the bivalent nature of the coagulating ion in potassium sulphate. Moreover it appears from the large differences in opacity that the coagulation in the presence of potassium sulphate is more complete than that by potassium chloride. Further, it will be observed that the rate of change and the final values of opacity increase as the amount of the coagulating electrolyte increases. The coagulating powers of the two electrolytes for deflection equal to 2 cm. and time 10 minutes is $K_2SO_4 : KCl =$ $1 \cdot 88 : 1 \cdot 00$.

The coagulation by potassium chloride of the three samples of the sol in the presence of ethyl and methyl alcohols has been investigated. A comparison of the curves 1 and 4, 1 and 2, Fig. 3, for undialysed sample shows that the rate of coagulation is accelerated by the presence of alcohols

5 *J. Indian Chem. Soc.,* 1936, 13, 602.
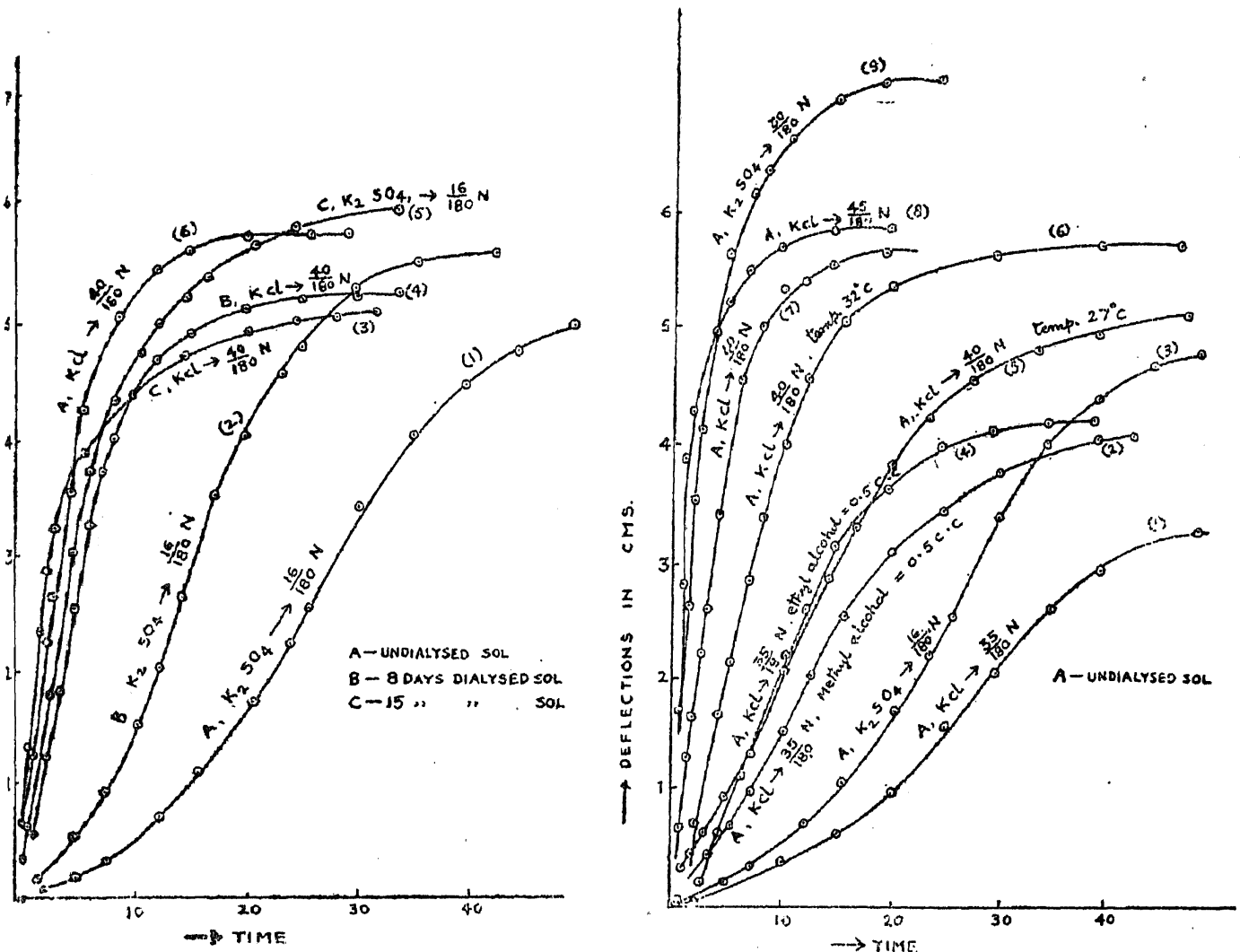
FIGS. 3 and 4. Coagulation of Stannic Hydroxide Sol.

and that the effect of ethyl (curves 1 and 4) is greater than that of methyl (curves 1 and 2) alcohol. The effect of these alcohols on the other two samples is also of the same nature as on the undialysed sol.

Temperature increases the rate of coagulation (curves 5 and 6, Fig. 3). This observation is similar to that for thorium hydroxide sol (curves 3 and 6, Fig. 2).

The coagulation by the same concentration of KCl and K_2SO_4 of sols (A), (B) and (C) is graphically shown in Fig. 4. The effect of dialysis on the coagulation of the sol by the same concentration of electrolytes cannot be well compared because the amount of colloidal matter in the three samples is not the same; it has been found to decrease as dialysis is continued. The curves in Fig. 4 show that the rate of change of opacity and the final values of opacity increase on dialysis when the sol is coagulated by potassium sulphate (curves 1, 2 and 5) and decrease when potassium choride (curves 6, 4 and 3) is used as the coagulator; they thus point out the specific nature of the action of the coagulating electrolyte.

(c) *Zirconium hydroxide sol.*—The method employed for the prepara-
tion of this sol was the same as that used by Sharma and Dhar.[6] Two
samples of the sol were employed for coagulation experiments: sol dialysed
for 20 days (A) and 30 days (B). The concentrations of the two samples
were 6·5 and 5·0 g. ZrO_2 per litre, respectively.

The results obtained are shown graphically in Fig. 5. The continuous
nature of the curves points to the continuous nature of the coagulating
process. It will be seen from the various curves in Fig. 5, that the rate of
coagulation, as indicated by the rate of change of opacity, and the final values
of opacity increase as larger amounts of electrolytes are used for coagula-
tion.

The effect of dialysis on the coagulation of this sol also cannot be well
compared as the concentrations of the differently dialysed sol are not the same.
However, it can be said that the amount of electrolyte necessary for co-
agulation decreases as the sol is further dialysed (*cf.* curves 1 and 6, Fig. 5).

The effect of temperature is brought out by curves 3 and 5, Fig. 5.
Temperature accelerates coagulation. The effect of alcohols on coagula-
tion by electrolytes of this sol is the same as that for other sols investigated,
namely, it increases the rate of coagulation (*cf.* curves 4 and 8, Fig. 5).

2. *Explanation of the Observed Results on Smoluchowski's Theory*

Smoluchowski has developed a theory of rapid coagulation velocity on
the assumptions that (1) round each discharged particle there exists a sphere
of attraction of radius r and (2) if two particles approach during molecular
motion so closely that the centre of one enters the sphere of attraction of
the other they would remain adherent. According to this theory the total
number of particles Σv at any time t is given by $v_0 (1 + t/\theta)$, where v_0 is the
number of single particles originally present in the sol and $\theta = Kv_0$, the
specific coagulation time, is a constant. The number of single, double, tri-
ple, etc., particles at any time is given by the following relations:

$$v_1 = \frac{v_0}{\left(1 + \frac{t}{\theta}\right)^2} \;;\quad v_2 = \frac{v_0 \cdot \frac{t}{\theta}}{\left(1 + \frac{t}{\theta}\right)^3} \;;\quad v_3 = \frac{v_0 \left(\frac{t}{\theta}\right)^2}{\left(1 + \frac{t}{\theta}\right)^4} \;..$$

$$v_n = \frac{v_0 \left(\frac{t}{\theta}\right)^{n-1}}{\left(1 + \frac{t}{\theta}\right)^{n+1}}$$
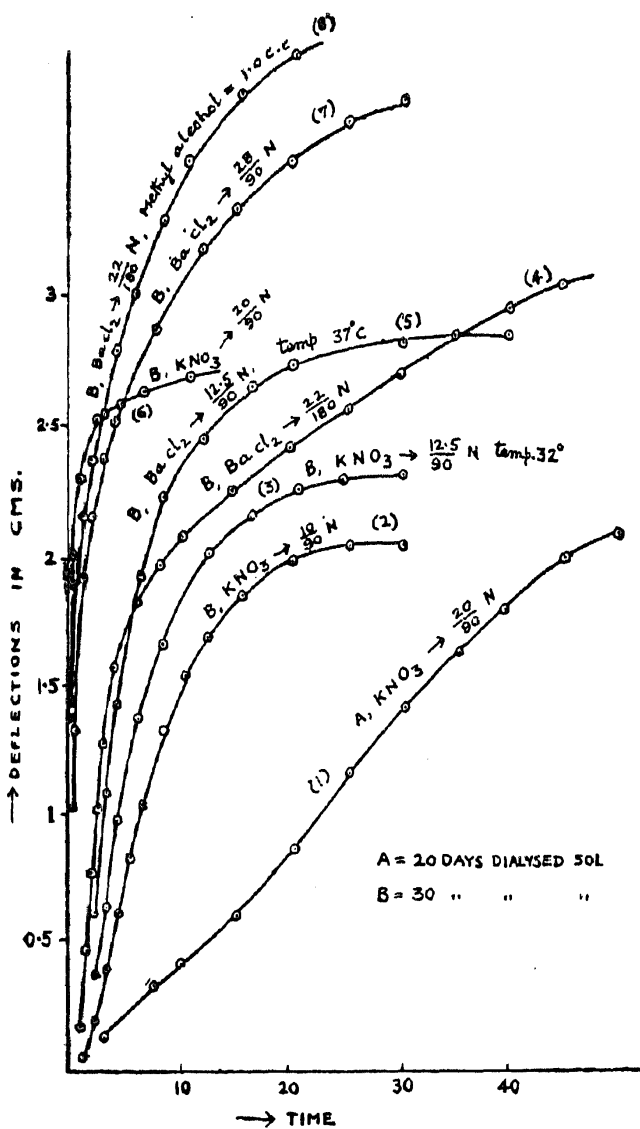
6 *Ibid.*, 1932, **9**, 455.
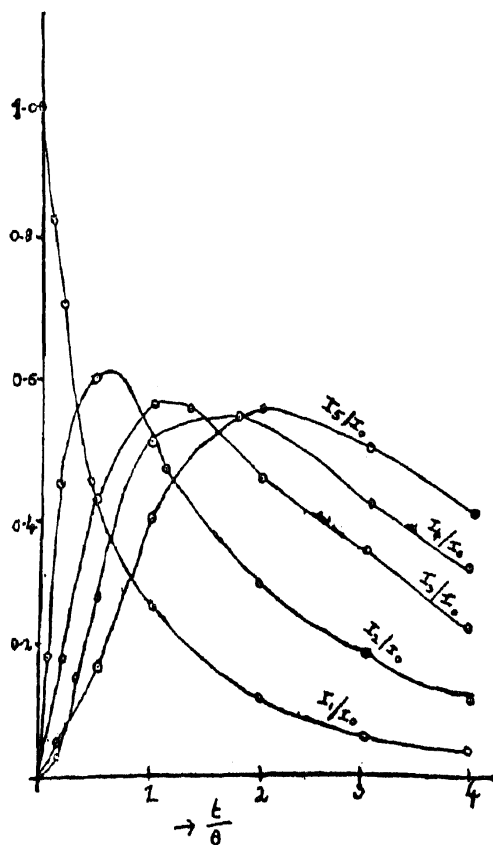
FIG. 5. Coagulation of Zirconium Hydroxide Sol

FIG. 6

The intensity of light scattered transversely by a colloidal system consisting of N particles of size V is proportional to NV^2 provided the diameter of the particles is less than the wavelength of light. The diameter of the colloidal particles varies from 1-$100\,\mu\mu$; taking the upper limit for the particle size, it is apparent that the law (Rayleigh) will hold true for the coalescence of a large number of particles. The intensity of light transversely scattered (I_1, I_2, I_3, etc.) by single, double, triple, etc., particles of twice, thrice, etc., the volume of the single particles, will be given by the following relations:

$$I_1 = \frac{I_0}{\left(1 + \frac{t}{\theta}\right)^2} \;\; ; \;\; I_2 = \frac{4\,I_0\,\frac{t}{\theta}}{\left(1 + \frac{t}{\theta}\right)^3} \;\; ; \;\; I_3 = \frac{9\,I_0\left(\frac{t}{\theta}\right)^2}{\left(1 + \frac{t}{\theta}\right)^4}$$

and so on

where $I_0 = kv_0 V^2$, V being the volume of the single particles.

The variation of I_1/I_0, I_2/I_0, I_3/I_0, etc., with different intervals of t/θ is shown in Fig. 6. It will be seen that the scattering due to single particles steadily decreases whereas that due to double and multiple particles at first increases, reaches a maximum value, and then falls off. At any instant, the total scattering will be the sum of I_1/I_0, I_2/I_0, I_3/I_0, etc. The variation of $\Sigma\,I/I_0$
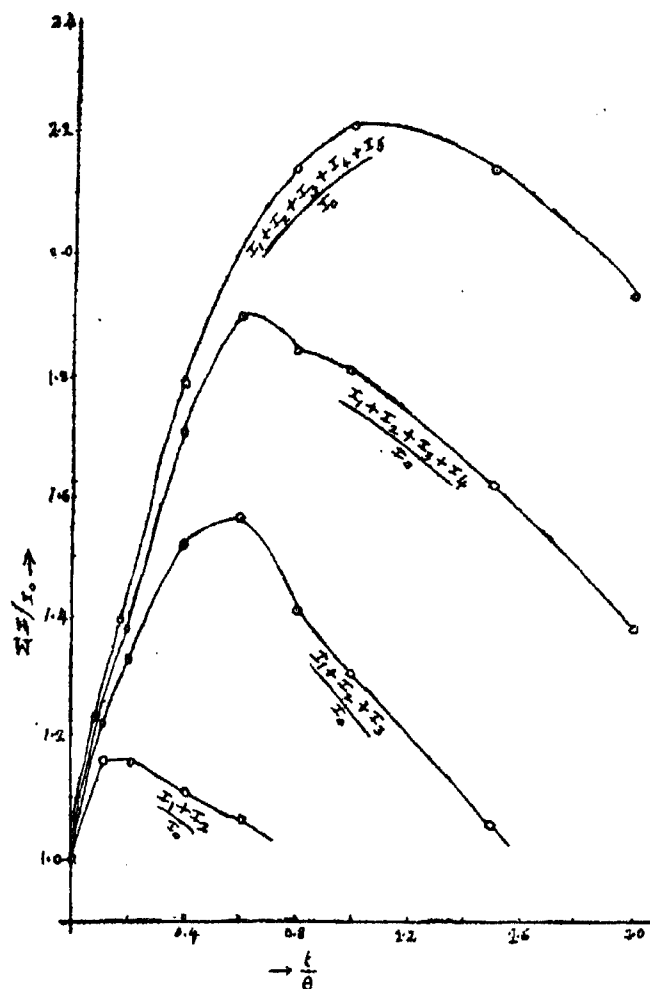
FIG. 7.

with t/θ is given in Fig. 7. It will be seen that $\Sigma\,I/I_0$ increases with time, reaches a maximum value and then begins to decrease. The time taken to reach the maximum value increases as the particles of greater multiplicity are formed when the intensity of scattered light also increases more rapidly with time.

According to Smoluchowski the kinetics of slow coagulation is the same as that for rapid; only in the case of slow coagulation the " adherence factor " is less than one. Hence $\Sigma I/I_0$-t curves for slow coagulation must be the same as that for rapid.

The opacity-time curves during the coagulation of sols represent roughly the variation of the intensity of scattered light with time. The similarity of the curves in Fig. 7 with those rapidly rising curves in Figs. 1 to 5 explains the results in this investigation. The "S" shaped opacity-time curves obtained for slow coagulation show that the assumption of Smoluchowski, namely, that the kinetics of slow coagulation is the same as that for rapid coagulation may not be true.

3. Verification of Smoluchowski's Equation from Opacity Data

The opacity data obtained can be employed to examine the applicability of Smoluchowski's equation to the coagulation of the sols studied in this investigation.

According to Smoluchowski Σv, the total number of particles (single, double, triple, etc.) at a time t is given by $v_0/(1 + t/\theta)$ as stated before and the stages of coalescence are independent of the external conditions which can change only the rapidity of succession of these stages. According to Mukherjee and Papaconstantinou[7] any property that varies continuously with the progress of coalescence without having a maxima or minima can be utilised to characterise the stages of coalescence, for each value of this property is characteristic of the time that has elapsed since the mixing of the electrolyte and the sol. Hence the coagulation velocity curves with the same electrolyte of different concentrations must be related to each other; that is, the values of the ratios of T_1/T, T_2/T, T_3/T, etc., must be the same for all concentrations of the same electrolyte (T, T_1, T_2, T_3, etc., being the respective times taken to reach the same stage of coalescence with an electrolyte of concentrations C, C_1, C_2, etc.).

Assuming that the opacity measurements correctly represent the different stages of coalescence, the values of T, T_1, T_2, T_3, etc., were read from the opacity-time curves obtained with different electrolytes of several concentrations in the case of sols studied in this investigation and the results obtained are given in Tables I to III, in which the different stages of coalescence are represented by opacity (d) of the coagulating mixture.

It will be seen from the results that the values of T_n/T are fairly constant at higher concentrations and as the concentrations of the electrolytes are reduced, there are variations in the value of T_n/T, which shows definitely that the equation is applicable only upto a certain stage of coagulating

[7] *Phil. Mag.*, 1922, **44**, 305.

Mata Prasad and others

TABLE I

Thorium hydroxide sol

Values of T_n/T for various electrolytes

(a) Barium chloride

d.	25/90 N	22/90 N	20/90 N	18/90 N
cm.				
0·7	1	2·5	3·3	6·0
1·5	1	2·5	4·0	7·2
2·0	1	2·5	4·3	7·5
2·2	1	2·5	4·0	8·0

(b) Potassium chloride

d.	30/90 N	25/90 N	22/90 N	20/90 N	18/90 N	16/90 N
cm.						
1·0	1	3·5	4·2	8·0	16·0	20·8
1·8	1	3·3	4·6	7·0	11·8	16·0
2·2	1	3·1	4·6	6·6	10·0	13·3

(c) Potassium nitrate

d.	16/90 N	15/90N	14/90 N	13/90 N	12/90 N
cm.					
0·6	1	1·2	1·7	2·3	3·4
1·3	1	1·1	1·8	3·0	3·6
1·8	1	1·2	2·0	3·2	4·0
2·1	1	1·6	2·4	3·6	4·0

(d) Sodium chloride

d.	25/90 N	20/90 N	17/90 N	15/90 N	13/90 N
cm.					
1·6	1	4·3	9·0	10·3	21·0
1·9	1	4·4	8·8	11·2	19·2
2·1	1	4·3	8·7	11·3	..

TABLE II

Stannic hydroxide sol

Values of T_n/T for different electrolytes

(a) Potassium chloride

d.	45/180 N	40/180 N	37·5/180 N	35/180 N
cm.				
1·7	1	2·7	10·0	34·8
2·8	1	3·0	10·0	37·0
3·5	1	2·9	9·5	..

(b) Potassium sulphate

d.	30/180 N	26/180 N	20/180 N	16/180 N
cm.				
1·6	1	4·0	10·5	18·5
3·5	1	3·3	9·5	15·5
4·6	1	3·0	9·0	14·3
5·2	1	2·6	8·0	..

TABLE III

Zirconium hydroxide sol

(a) Barium chloride

d.	28/180 N	25/180 N	22/180 N
cm.			
1·3	1	2·0	3·0
1·9	1	2·0	4·0
2·1	1	2·0	5·0
2·5	1	1·5	6·2
3·0	1	1·1	4·0

(b) Potassium nitrate

d.	40/180 N	30/180 N	20/180 N
cm.			
1·6	1	3·0	20·0
2·1	1	3·3	33·0

concentrations. This conclusion is in good agreement with those obtained by previous workers.

Summary

The changes in opacity during the coagulation of (*a*) thorium hydroxide, (*b*) stannic hydroxide and (*c*) zirconium hydroxide sols have been investigated. The results have been used to compare the coagulating power of electrolytes and also to study the applicability of Smoluchowski's equation to the coagulation of these sols. It has been found that Smoluchowski's equation is applicable upto a certain stage of coagulator concentrations only (corresponding to rapid coagulation). The effect of temperature and the influence of alcohols have also been studied. Both these factors accelerate the rate of coagulation in the case of all the sols investigated.

Basing on the theory of Smoluchowski for rapid coagulation an attempt has been made to follow theoretically the changes in the intensity of light scattered transversely (I) by a system undergoing coagulation. The opacity-time curves obtained during the coagulation of sols have been compared with I–T curves obtained theoretically. The curves experimentally obtained for rapid coagulation are similar to those theoretically deduced. However the I–*t* curves for slow coagulation are " S " shaped and it has been inferred that Smoluchowski's equation is not applicable in the region of slow coagulation. This conclusion is the same as that obtained from the direct verification of Smoluchowski's equation from the opacity data.