

**Studies in the Coagulation of Colloids. Part VIII.**  
**The Viscosity Changes in Colloid Arsenious Sulphide when Coagulated by Binary Mixtures of Potassium Halides in the Slow Region.**

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The earliest observations of the effect of electrolytes on the viscosity of colloidal solutions were made by Gokun (*Z. Chem. Ind. Kolloide*, 1908, 3, 84), who showed that the rate of increase of the viscosity with time of pure gelatine solutions is diminished by the addition of ammonium nitrate. Schorr (*Biochem. Z.*, 1908, 13, 173), Pauli and Handovsky (*ibid.*, 1909, 18, 340), and Woudstra (*Z. Chem. Ind. Kolloide*, 1911, 8, 73) studied  $\eta$ , the viscosity of colloidal solutions as a function of  $c$ , the concentration of the added electrolyte. The chief result of these investigations is that the  $\eta$ - $c$  relation is not a simple one, a *minimum* being usually observed in the early part of the curve. Dhar and co-workers (*J. Phys. Chem.*, 1926, 30, 1646; *Kolloid Z.*, 1928, 44, 225 ; 1929, 48, 43) have confirmed this in the case of a number of colloidal solutions.

It would appear, however, that despite the investigations of Kawamura (*J. Coll. Sci. Imp. Univ. Tokyo*, 1908, 25, No. 8), Freundlich and Ishizaka (*Trans. Faraday Soc.*, 1913, 9, 66), Wo. Ostwald (*ibid.*, p. 34), Pauli (*ibid.*, p. 64), Smoluchowski (*Kolloid Z.*, 1916, 18, 190), and especially Gann (*Koll. Chem. Beih.*, 1916, 8, 65), detailed information is not available on the time variation of the viscosity of a colloid of the *lyophobic* type when treated with an electrolyte solution.

Work carried out in these laboratories (Joshi and Viswanath, *J. Indian Chem. Soc.*, 1933, 10, 329; Joshi and Menon, *ibid.*, 1933, 10, 599; Joshi and Nanjappa, *ibid.*, 1934, 11, 133) has shown that in the *slow* region, the coagulation is not a time-continuous process unless viscosity change is not always an index of the corresponding

coagulation. It has been observed that the  $\eta$ -time curve is discontinuous and that a diminution of  $\eta$ , soon after the start of coagulation is usually produced. In view of the obvious bearing of these facts on our views on the kinetics of coagulation it was of interest to examine the above phenomena under conditions different from those used previously, (*loc. cit.*). In the present work mixtures of KF, KCl, KBr and KI in different proportions have been used as the coagulating agents. It might also be added that practically no information is available in the literature on the viscosity variations produced in colloids when coagulated by electrolyte mixtures. Observations with the fluoride have been made in some detail in view of the marked paucity in the literature of coagulation data made with this coagulant.

#### EXPERIMENTAL.

The arsenious sulphide sol used in these experiments was prepared by adding intermittently small quantities of a triturated solution of arsenious oxide to a saturated solution of hydrogen sulphide in water. The excess of  $H_2S$  was removed by passing a current of hydrogen. The colloid content of the sol, thus prepared, was estimated by coagulating a known volume of the sol with a suitable electrolyte and after washing the coagulum free of the electrolyte, drying it at  $200^\circ$  and weighing. Thus determined, the colloid content was 10.7 g. per litre. The viscosity of the colloid mixed with an equal volume of a solution of any one or more of the alkali halides in suitable proportions was determined by the Scarpa's method with appropriate modifications as described by Joshi and Menon (*loc. cit.*). The results are expressed relative to the viscosity of water taken as unity. The temperature of the thermostat was kept constant at  $35^\circ \pm 0.1$  in all the experiments. The suction applied was regulated within 0.2 mm. at 26 cms. of water. The condition of the apparatus to give reproducible results was repeatedly examined by measuring the viscosity of water at different times during the course of these experiments. The accuracy of measurements with water was never found to be less than 0.15. Changes exceeding by at least three times the last quantity only have been reported. The viscometer was well illuminated by a light behind the thermostat. During every observation the colloid in the viscometer and that in the outside jar containing the viscometer was very carefully exa-

mined for the slightest appearance of flocculation, *i.e.*, of fine particles of the coagulum produced either in the liquid, or left on the walls of the viscometer. When this was observed  $\eta$ -measurements were discontinued.

In curves 1—45 (Figs. 1—4) abscissa stands for the time axis and ordinates for  $\eta$ . In order to prevent overlapping of curves in a given series and especially to economise space, a number of curves have been drawn with separate time and  $\eta$ -axis. The scale units chosen are indicated in the figure with reference to the curve or curves to which they correspond. The composition of the coagulating mixture corresponding to the  $\eta$ -time curves in a vertical row is shown in a tabular form preceding the diagrams (*cf.* Table II).

The data given in Table I were deduced from curves in Figs. 1—4. The normalities in the coagulating mixture of each one of the four electrolytes used are indicated in the second column, the third gives the total halide content in the mixture. The fourth and fifth columns represent  $\eta_i$ , the initial and  $\eta_m$ , the first minimum viscosity. The difference between these quantities has been expressed as a percentage of the initial viscosity and results shown under  $\eta_a$ , in the sixth column. To give an idea of the discontinuities of the  $\eta$ -time curves,  $\eta_a$  the lowest viscosity observed in 2 hours (except in cases when coagulation with deposition of particles occurred earlier as in coagulations represented by curves 2, 4 in Fig. 1; 15, 18 in Fig. 2; 25, 27, 44 in Fig. 3 and 32 in Fig. 4) is shown in column 8, *e.g.*,  $a = 1.005$  in curve 14, Fig. 2,  $\eta_b$ , the highest viscosity reached in the same period is given in column 9, *e.g.*,  $b = 1.027$ , in the same curve. The difference between these two, *viz.*, 0.022 is expressed as a percentage, *viz.*, 2.13 of  $\eta_i$ , the initial viscosity, 1.033, and the results quoted in column 10, under R.  $T_{\eta_m}$  indicates the time in minutes corresponding to  $\eta_m$ , the first minimum on the  $\eta$ -time curve.

TABLE I.

Curve No.	1	2	3	4	5	6	7	8	9	10		
	KCl.	KBr.	KI,	KF.	Total halide normality.	$\eta_{11}$	$\eta_{12}$	$\eta_{13}$	$\eta_{14}$	$\eta_{15}$		
1	0.03125 + Nil	+	Nil	+	Nil	1.034	1.015	1.84	19	1.015	1.020	0.48
2	0.05000 + "	+	"	+	"	1.047	1.041	—	9	1.041	—	—
3	Nil + 0.03125	+	"	+	"	1.030	1.008	2.14	32	1.007	1.013	0.60
4	" + 0.05000	+	"	+	"	1.026	—	—	—	—	—	—
5	" + "	+	0.03125	+	"	1.033	1.016	1.65	32	1.012	1.019	0.68
6	" + "	+	0.05000	+	"	1.040	1.015	2.40	43	1.015	1.022	0.67
7	" + "	+	Nil	+	0.03125	1.029	1.004	2.43	24	1.003	1.014	1.07
8	" + "	+	"	+	0.05000	1.030	1.007	2.23	25	1.002	1.009	0.58
9	" + "	+	"	+	0.06250	1.021	1.002	1.86	33	1.002	1.007	0.49
10	" + "	+	"	+	0.07500	1.013	1.000	1.28	18	1.000	1.007	0.69
11	" + "	+	"	+	0.08750	1.006	0.9880	1.80	34	0.9879	0.9936	0.57
12	" + "	+	"	+	0.12500	0.9995	0.9788	2.07	23	0.9777	0.9847	0.70
13	" + 0.02500	+	0.00625	+	Nil	1.028	1.004	2.34	24	1.002	1.009	0.68
14	" + 0.00625	+	0.02500	+	"	1.033	1.005	2.71	36	1.005	1.027	2.13
15	" + 0.02500	+	0.02500	+	"	1.035	1.019	1.55	17	1.019	—	—

16	0.02500	+	0.00625	+	Nil	+	0.03125	1.028	1.009	1.85	42	1.007	1.013	0.58
17	0.00625	+	0.02500	+	"	+	0.03125	1.019	1.006	1.28	24	1.005	1.010	0.50
18	0.02500	+	0.02500	+	"	+	0.05000	1.047	—	—	—	—	—	—
19	0.02500	+	Nil	+	0.00625	+	0.03125	1.006	0.9951	1.0	17	0.9951	1.004	0.89
20	0.00625	+	"	+	0.02500	+	0.03125	1.035	1.015	1.93	40	1.015	1.019	—
21	0.02500	+	"	+	0.02500	+	0.05000	1.024	1.000	1.86	32	1.000	1.012	1.17
22	0.00625	+	"	+	Nil	+	0.03125	1.006	0.9752	3.06	17	0.9752	0.9897	1.44
23	0.02500	+	"	+	"	+	0.03125	0.9974	0.9716	2.59	17	0.9716	0.9783	0.67
24	0.02500	+	"	+	"	+	0.05000	0.9845	0.9670	1.78	16	0.9627	0.9721	0.96
25	0.03750	+	"	+	"	+	0.07500	0.9991	0.9897	0.84	9	0.9897	—	—
26	0.02500	+	"	+	"	+	0.10000	0.9940	0.9743	1.98	17	0.9743	0.9954	2.12
27	0.02500	+	"	+	"	+	0.12500	0.9974	—	—	—	—	—	—
28	0.01250	+	"	+	"	+	0.06250	0.9886	0.9714	1.74	24	0.9872	0.9849	1.79
29	Nil	+	"	+	0.00625	+	0.03125	0.9902	0.9727	1.77	17	0.9709	0.9769	0.55
30	"	+	"	+	0.02500	+	0.03125	0.9995	0.9747	2.50	17	0.9712	0.9772	0.60
31	"	+	"	+	0.02500	+	0.05000	0.9959	0.9656	3.04	27	0.9656	0.9721	0.65
32	"	+	"	+	0.03750	+	0.07500	0.9974	0.9779	1.95	17	0.9779	—	—
33	"	+	"	+	0.02500	+	0.07500	0.9970	0.9665	2.08	33	0.9645	0.9727	0.83
34	"	+	"	+	0.02500	+	0.10000	0.9951	0.9766	1.65	32	0.9766	0.9835	0.69
35	"	+	"	+	0.02500	+	0.12500	0.9954	0.9822	1.33	17	0.9822	0.9991	1.70

Normality of electrolytes in the system

Total  
halide  
normality

Curve No.

	KCl	KBr	KI	KF	$\eta_i$	$\eta_m$	$\eta_s$	$T\eta_m$	$\eta_a$	$\eta_b$	R
36	+	"	+ 0.01250	+ 0.05000	0.9854	0.9757	0.98	25	0.9738	0.9772	—
37	+	0.00625	+	0.02500	0.9837	0.9607	2.40	17	0.9561	0.9632	0.72
38	+	0.02500	+	"	0.9919	0.9605	3.17	17	0.9592	0.9665	0.74
39	+	0.02500	+	"	0.9595	0.9612	2.86	16	0.9596	0.9642	—
40	+	0.03750	+	"	0.9833	0.9642	1.94	26	0.9642	0.9863	2.25
41	+	0.02500	+	"	0.9900	0.9610	2.93	16	0.9598	0.9658	0.61
42	+	0.02500	+	"	0.9902	0.9672	2.32	16	0.9672	—	—
43	+	0.02500	+	"	0.9763	0.9736	0.28	32	0.9736	0.9874	1.41
44	+	0.05000	+	"	1.005	0.9917	1.32	8	0.9917	—	—
45	+	0.01250	+	"	0.9900	0.9645	2.58	24	0.9601	0.9661	0.61



(Fig. 4)

Curve	20 c.c. sol + 1.00 c.c. N-KF + 0.25 c.c. N-KI + 18.75 c.c. water	Curve	20 c.c. sol + 2.00 c.c. N-KF + 0.50 c.c. N-KI + 17.50 c.c. water
29	+0.25	36	+1.00
30	+1.00	39	+1.50
31	+1.50	40	+2.00
32	+2.00	41	+3.00
33	+3.00	42	+4.00
34	+4.00	43	+2.00
35	+18.75	45	+18.00

TABLE III.

*Influence on  $\eta_m$  by 20% change of composition.*

Total halide conc. = 0.03125N

Cl	Br	I	F
1.84	1.85	1.08	2.59
Br	Cl	I	F
2.14	1.28	2.34	3.17
I	Cl	Br	F
1.65	1.93	2.71	2.50
F	Cl	Br	I
2.43	1.85	2.40	1.77

TABLE IV.

*Influence on  $\eta_m$  by 50% change of composition.*

Total halide conc. = 0.05N.

Cl	Br	I	F
0.57	—	1.86	1.78
Br	Cl	I	F
—	—	1.55	2.86
I	Cl	Br	F
2.40	1.86	1.55	3.04
F	Cl	Br	I
2.23	1.78	2.86	3.04



FIG. 1.

Sol + KCl ; KI ; KF.

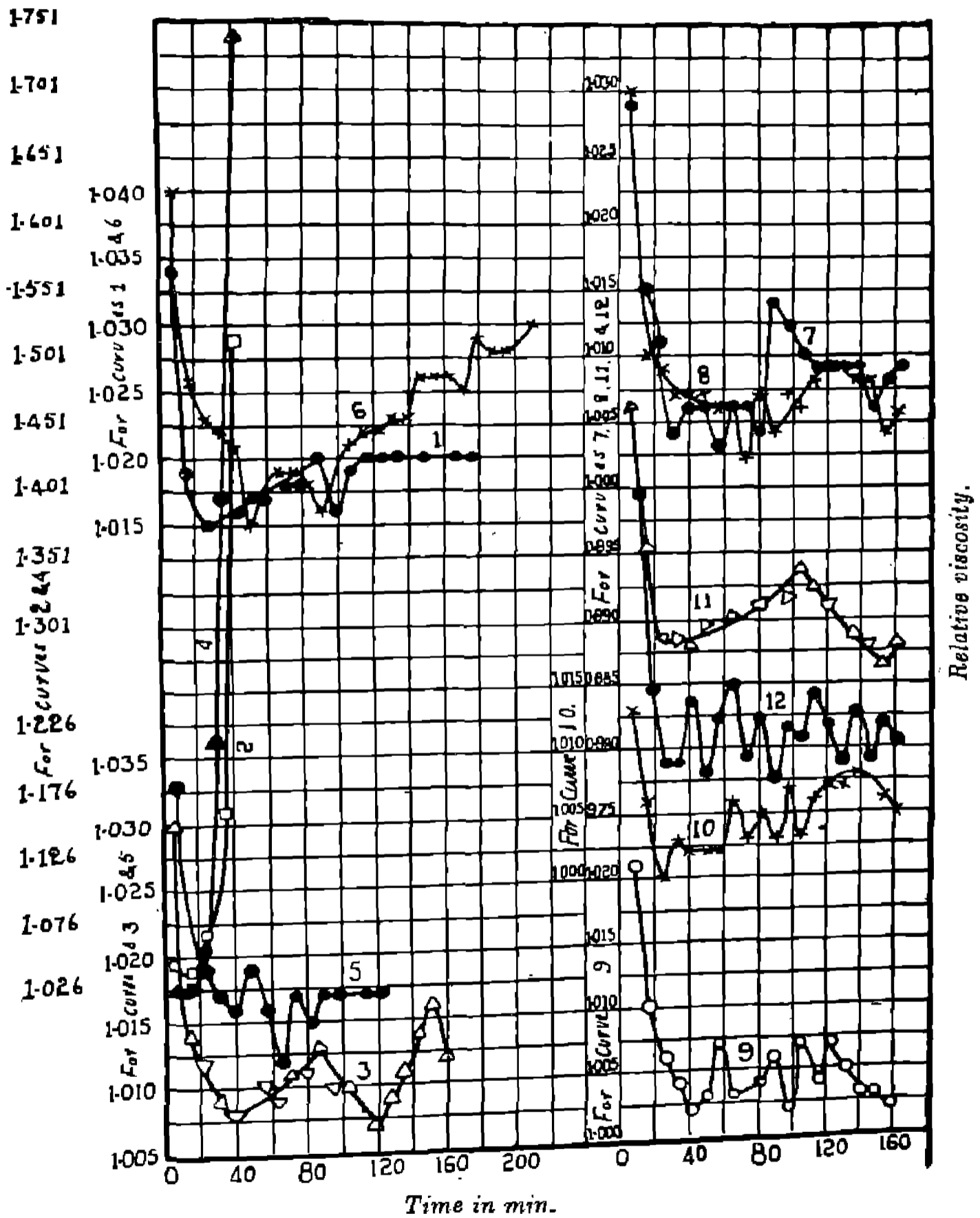


FIG. 2.

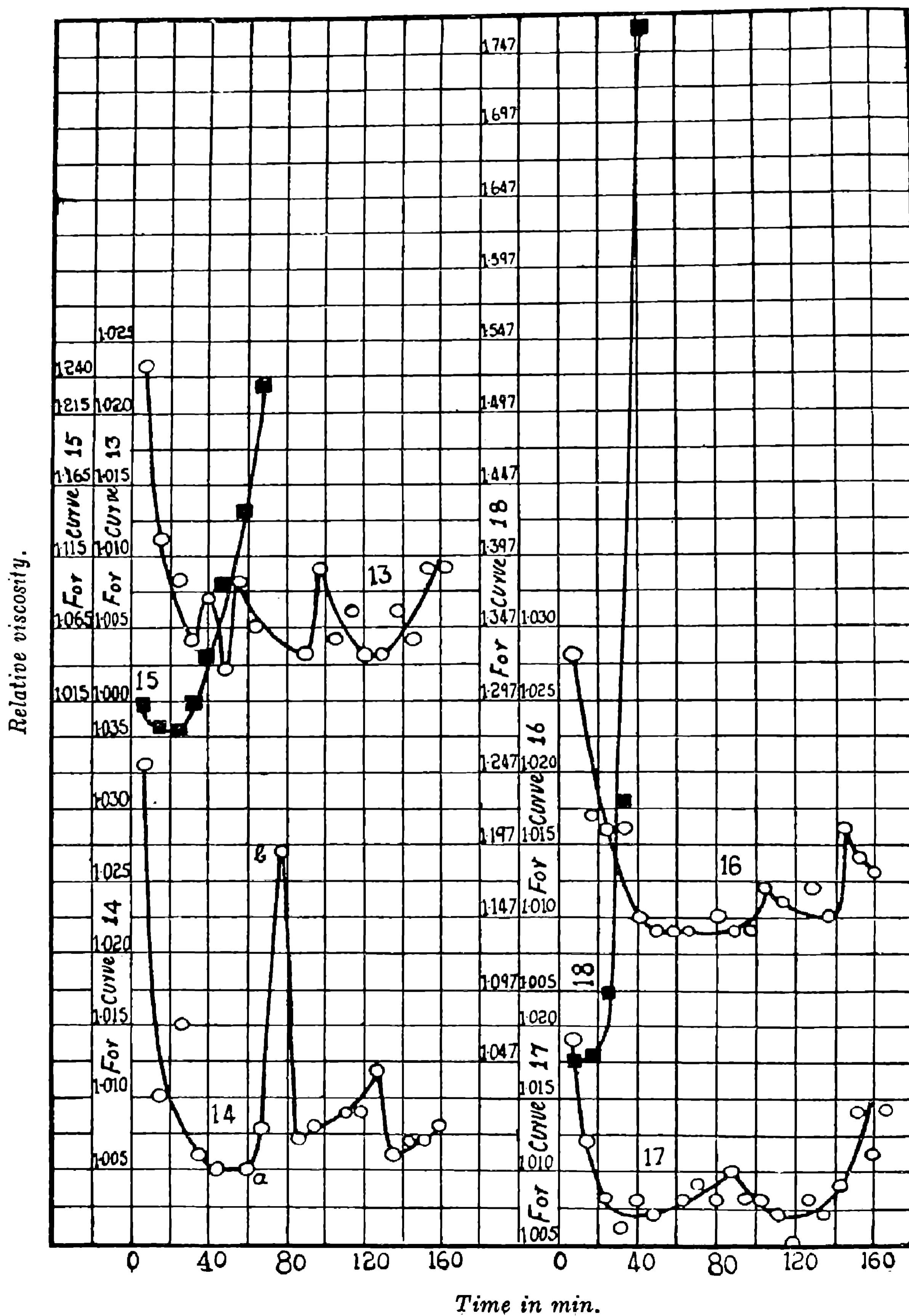
*Sol + KBr ; Sol + KCl + KBr.*

FIG. 3.

*Sol + KCl + KI ; Sol + KF + KBr.*

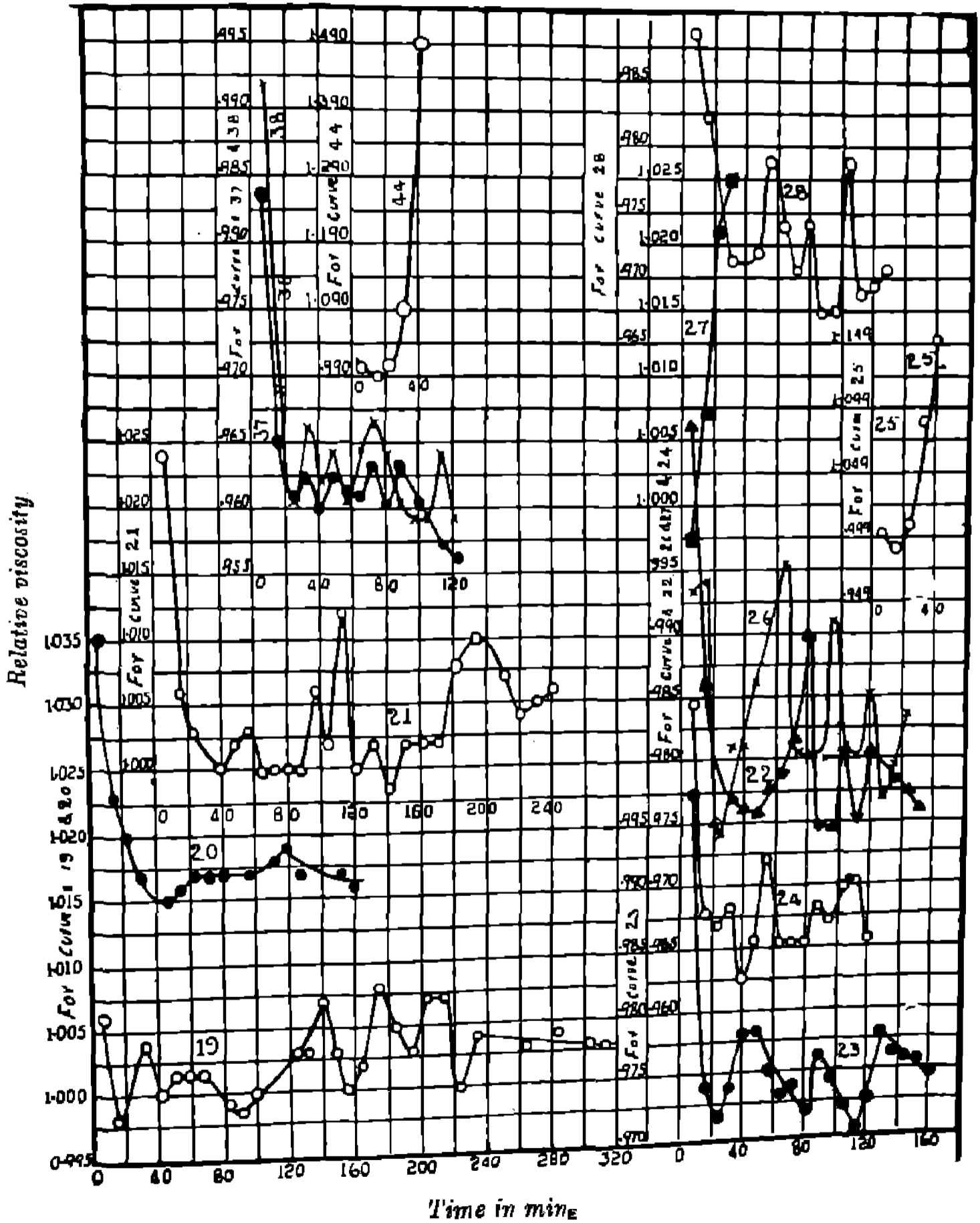
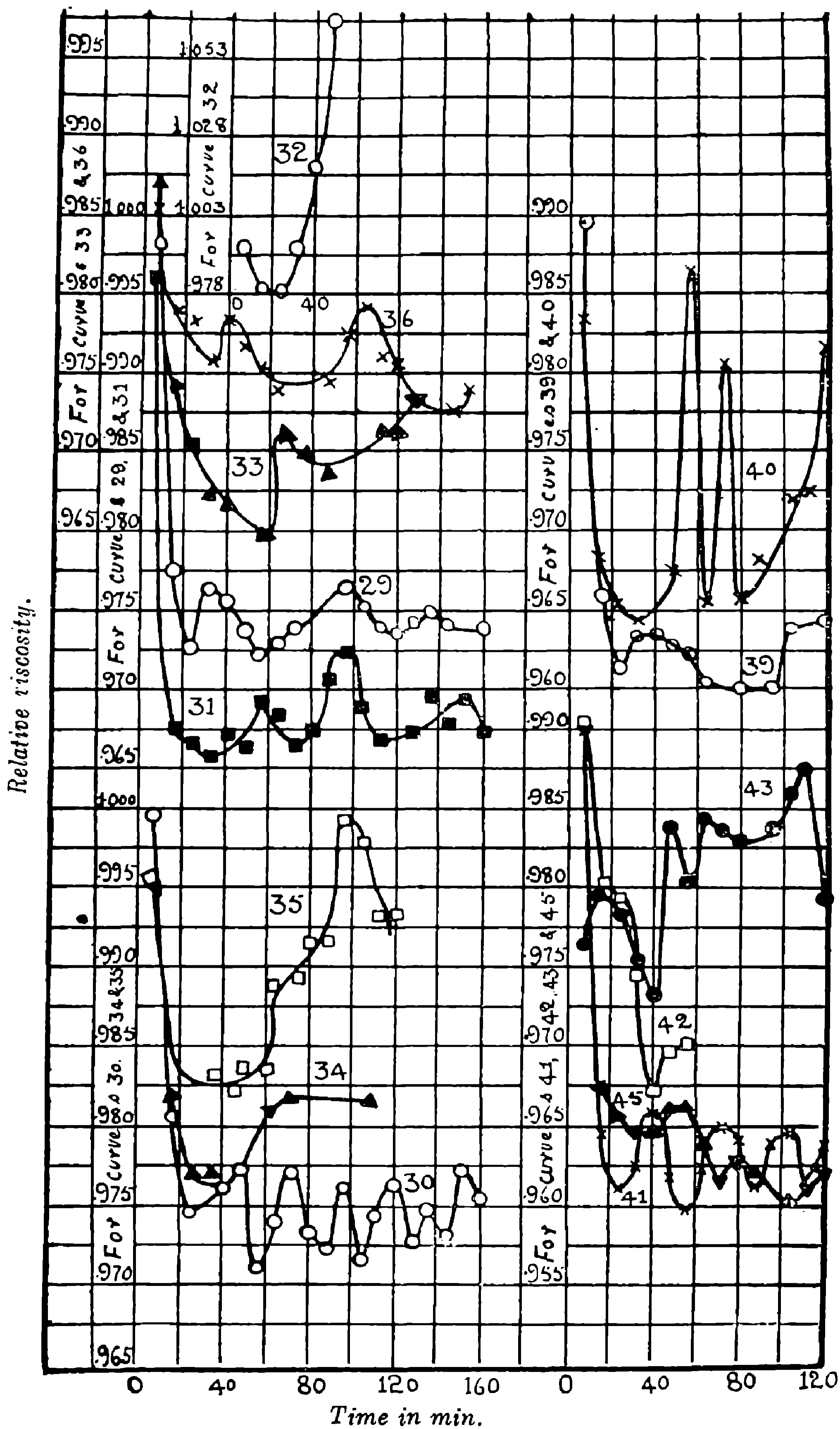


FIG. 4

$Sol + KF + KI$  ;  $Sol + KF + KBr$ .



## DISCUSSION.

It is now well known that Smoluchowski's theory (*Z. physikal. Chem.*, 1917, 92, 129) for the kinetics of coagulation breaks down for *slow* coagulations. The mechanism of the coagulation process as contemplated in this theory is that, coagulation is but a *continued* coalescence of the original colloid particles to form bigger aggregates. The change is, therefore, considered as progressing continuously during the coagulation-time. On this basis, therefore, it is to be anticipated that a colloid-sensitive property like viscosity, would vary continuously during the coagulation. The  $\eta$ -time curves in Figs. 1—4 show, however, that distinctly the contrary is the case at any rate in the *slow* region. It is seen from column 10 in Table I that the breaks in these curves vary in the range 0.5 to 2% of the initial viscosity. It is considered that this is appreciably greater than the probable experimental error. Now it is probable for instance starting with a certain number of primaries (by which is meant simply the original particles of the sol) when mixed with the coagulator, the formation of agglomerates through successive coalescence might obtain as the main process during a certain period, and that during this period the viscosity might vary in a certain sense, *e.g.*, increase. After this period depending upon the stage of the coalescence, the agglomerate might suffer a break down due (i) either to instability induced as a result of the change on the size and the nature of the structure of the sol particles reached, or (ii) by the action of the ions carrying the same charge as the sol. This will produce a viscosity change in a direction opposite to what happened previously. When examined over a prolonged time, the operation of the two sets of factors mentioned above will produce breaks on the  $\eta$ -time curve, as observed. A considerable amount of evidence has now been accumulated in these laboratories on the existence of these breaks by using other properties besides viscosity to measure coagulation, which will be published shortly.

It is not unlikely that the occurrence of the initial viscosity fall observed in a very large number of coagulations reported already (*loc. cit.*) is distinctive of some early stage in the process of coagulation. In the present work this quantity varies in the range 0.5 to 4% of the initial viscosity (column). It is significant that  $T\eta_m$ , the time corresponding to the attainment of  $\eta_m$ , the minimum viscosity varies in the range 16 to 40 minutes in 40 out of 45 coagulations examined, when both the nature and the concentration of the coagulator were varied over a markedly wide range. It is known that but small

changes in  $c$ , the electrolyte concentration produce very marked changes in  $T$ , the time corresponding to the attainment of a given stage of coagulation as is for example illustrated by Paine's well known exponential relation for  $c$  and  $T$  (*Koll. Chem. Beih.*, 1912, 16, 430). It is to be noted that  $T_{\eta_m}$  the time required for attaining the first minimum viscosity is not influenced markedly by alterations in  $c$ . Presently therefore, it corresponds to some change which is of a different nature from that represented by  $T$ .

It is instructive to examine the magnitude of the initial fall in  $\eta$  and the discontinuousness of the  $\eta$ -time curves in relation to the composition of the coagulating mixture. The amount of colloid was constant; except when potassium flouride was used, (curves 7-12, Fig. 1; 22-28, Fig. 3 and 29-45, Fig. 4) that of any of the other halides, or of the binary mixture was generally increased up to 2 c.c.  $N$ . With this maximum amount of the coagulating substance, the  $\eta$ -time curves show a *continuous* rapid rise (*cf.* curves 2, 4, 15, 18, 25, 27, 32, 42 and 44). The initial fall occurs in 6 out of these 9 coagulations and varies in the range 0.8 to 2%; its absence in the remaining three coagulations (curves 4, 18 and 27) might be due to the viscosity rising rapidly to large values from the very start of the coagulation, and thus marking the comparatively smaller changes in the initial stages. Precisely similar results under above conditions have been reported in previous publications (*loc. cit.*).

$\eta$ -time curves for coagulations with the flouride show a comparatively large initial fall and subsequent discontinuities, although its amount in the coagulating mixture was increased to 5 c.c.  $N$  (curves 7-12, Fig. 1). For less than half this normality, curves for KCl and KBr rise rapidly and continuously (*cf.* curves 2 and 4, Fig. 1). The influence of KI appears to be intermediate between KF on the one hand and KCl and KBr on the other. Thus for example, for 2 c.c. of  $N$ -KI, the  $\eta$ -time curve (No. 6, Fig. 1) has a greater initial fall, is slower rising, and more discontinuous than those when the same normality of KCl and KBr was added (curves 2 and 4, Fig. 1). A rapid rising and continuous curve is obtained only when 0.5 c.c. of  $N$ -KCl is added to 2 c.c. of  $N$ -KI (No. 44, Fig. 3). An interesting comparison of the relative influences of these halides is obtained by examining the following curves :

Curve 12, Fig. 1 refers to coagulation by 5 c.c. of  $N$ -KF only; it shows first a large fall of viscosity, *viz.*, 2.07% in the

initial stage; then, on the whole, the viscosity tends to diminish during coagulation, and that markedly *discontinuously*. When the above amount of KF is replaced partly by KI, that is, when the coagulant is 4 c.c. N-KF + 1 c.c. of N-KI, the  $\eta$ -time curve (No. 35, Fig. 4) shows a smaller initial fall, *viz.*, 1.33% and the viscosity increases almost up to the initial value; as in the previous case the curves consist of a number of breaks. Now, with 4 c.c. of N-KF and 1 c.c. N-KBr (curve 43, Fig. 4) there is no initial fall, but the viscosity rises comparatively rapidly though discontinuously. When 1 c.c. N-KCl is substituted for KBr that is with 4 c.c. N-KF + 1 c.c. N-KBr, the curve has no initial fall and is markedly steep and continuous (No. 27, Fig. 3). An examination of curves 7-12, Fig. 1 shows that although the amount of KF is increased five fold, the  $\eta$ -time curve shows an appreciable initial fall, is discontinuous and the viscosity does not rise beyond the initial value.

From an examination of the results in Table I for  $\eta_m$  (which denotes the percentage diminution of viscosity in the initial stage) the results in Tables III and IV would appear to be deducible. For the same halide normality, the initial fall is greater with potassium fluoride than with potassium chloride, the influence of the bromide and the iodide being intermediate. This is clear from the data for the initial fall quoted in the first vertical column of Tables III and IV in which the normality of any *one* of the halides used, *viz.*, KCl, KBr, KI and KF was 0.03125 and 0.050 respectively. The data in the other vertical columns show the influence of substituting for the halide in the first vertical column by that mentioned in the subsequent columns.

Thus for example considering the first horizontal row in Table III,  $\eta_m$  due to 0.03125N-KCl *only* is 1.84%. It is 1.85 when the coagulation is due to 0.02500N-KCl mixed with 0.00625 KBr (*cf.* curve 16). This result shows, therefore, the influence of substituting KCl by 25% KBr. In precisely the same way, by comparing the results for a mixture of KCl and KF (*cf.* curve 23) with that obtained when only KCl was used, the influence on  $\eta_m$  of substituting 25% of KCl by KF is obtained. The data in the second horizontal row show the influence on  $\eta_m$  of substituting 25% KBr by KCl, KI and KF. Table IV records similar results when the total halide concentration was higher, *viz.*, 0.05N. These results show that  $\eta_m$  increases by introducing KF in the halide mixture used as a coagulant. Conversely it is seen that  $\eta_m$  diminishes when KF is partly or wholly displaced by any of the other halides.

In an attempt to correlate the above differences in the influence of the halides with some of their characteristic properties, the viscosity of their aqueous solutions would appear to be the first to suggest itself. For the order of the concentrations of the halides used in the present experiments, *viz.*,  $N/8$  to  $N/20$ , the viscosities of solutions appear to be practically the same as that of water (*cf.* Landolt-Bornstein, 1923, Erster Band, pp. 160-61). At higher concentrations, however, the order is  $KI < KBr < KCl < KF$ , the effect of  $KF$  in increasing  $\eta$  being very markedly greater than that of any of the other three halides. The second factor to be considered is the concentration of the ions derived from the dissociation of each of the above halides. This is sufficiently indicated by their equivalent conductivities (corrected for the viscosity). The order deduced from known data for the above quantity for the concentrations used here (*loc. cit.*, Zweiter Band, p. 1079) is  $KF < KCl < KI < KBr$ . The conductivity of the last three is approximately the same, while that of  $KF$  is markedly lower. The failure to get a rapid rising  $\eta$ -time curve with  $KF$  using concentrations more than twice that of any other halide might, therefore, be ascribed in part to its lower ionisation. One more factor to be considered in this connection and which very probably involves the two other mentioned above, is the coagulative power. This is largely determined by the adsorbability of coagulator by the colloid, and therefore depends upon the nature of the latter. In the absence of relevant data, however, the case of colloid ferric oxide might be considered. The order is  $KI < KBr < KCl$  (*cf.* Freundlich, "Colloid and Capillary Chemistry," 1926, p. 421). The colloid power for the iodide being markedly less than those of the other two which are similar. This is in agreement with their influence on the viscosity change during coagulation as discussed already.

It would appear to be almost a tacit assumption with colloid chemists that viscosity increases as a result of coagulation. Work now in progress in these laboratories shows, however, that this assumption is not warranted (Joshi and Nanjappa, *J. Indian Chem. Soc.*, 1934, 11, 133). This is also seen from the  $\eta$ -time curves in Figs. 1—4. In at least 30 out of the 45 coagulations examined, the viscosity does not rise beyond the initial value during quite an appreciable time. This together with the finding of discontinuities on the  $\eta$ -time curves would appear to invalidate the use of viscosity as a measure of coagulation at any rate in the *slow* region.



## SUMMARY.

1. The progress of coagulation in the *slow* region of the arsenious sulphide sol by solutions of KCl, KBr, KI and KF, and also of their mixtures in different proportions have been examined by measurement of  $\eta$ , the viscosity by Scarpa's method.

2. It has been found that (a) the coagulation does not progress continuously with time, but occurs in a number of discontinuous stages marked by breaks on the  $\eta$ -time curves, and (b) that usually the first stage of the change is marked by a diminution of viscosity in the range 0.5 to 4% of the initial value. Both these features disappear in rapid coagulations. The initial viscosity diminution and the discontinuousness of the  $\eta$ -time curve have been found to increase by increasing the proportion of KF in the mixture of potassium halides used as a coagulant.

3. It has been also observed in a number of coagulatives that during quite an appreciable period of time, *viz.*, about two hours after the start of the coagulation the viscosity of the mixture does not increase beyond the initial value.

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