

## STUDIES ON THE GELATION OF SILICIC ACID SOLS. PART IV. ON THE DEVELOPMENT OF YIELD VALUE AND STRUCTURE OF SILICIC ACID SOLS

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The rate of change of turbidity with time of silicic acid sols increases, becomes maximum approximately at or near the time of gelation and then gradually decreases. The time of gelation can be determined graphically from turbidity measurements. The viscosity of freshly prepared silicic acid sols is very low. As ageing continues it increases at first very slowly, then with appreciable speed and finally, a little before gelation, it shoots up to a very high value. A gradual increase in the extent of aggregation of silicic acid in the sol state is noticeable from the viscosity data of different systems by the application of Staundinger's viscosity relation. Yield value develops roughly at about 75%, 80% and 86% of the time of gelation in the cases of sols prepared by using HCl, H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub> respectively at room temperatures. Shaking prevents the formation of 'macro-structures' but does not hinder the formation of 'micro-structures' in silicic acid sols. Ultrafiltration of silicic acid sols in HCl system indicates that appreciable aggregation of silicic acid sols does not take place before 82% of the time of gelation at room temperatures.

The gelation of silicic acid accompanies changes in optical, viscous and polymerisation properties of the sol. Physical properties, such as turbidity and viscosity of the sol which are amenable to more accurate measurements, have been determined for the purpose of obtaining a more exact and reproducible value of the time of gelation. Since such measurements are easy to make, it has been possible to study the rate of gelation, starting from the freshly prepared sol, and thereby to gain an insight into the kinetics of the process. Furthermore, viscosity measurements enable calculation of the sizes of the particles. In this way it has been possible to get an idea of the state of aggregation of silicic acid molecules at various stages of gelation. Gelation is usually accompanied by the development of a certain kind of plasticity and the formation of structures. Viscosity measurements have also indicated at what stages of gelation plasticity develops. An attempt has also been made to ascertain whether physical factors like shaking have any effect on gelation. Ultrafiltration of a silicic acid sol has indicated the stage of gelation at which appreciable structure formation of silicic acid takes place.

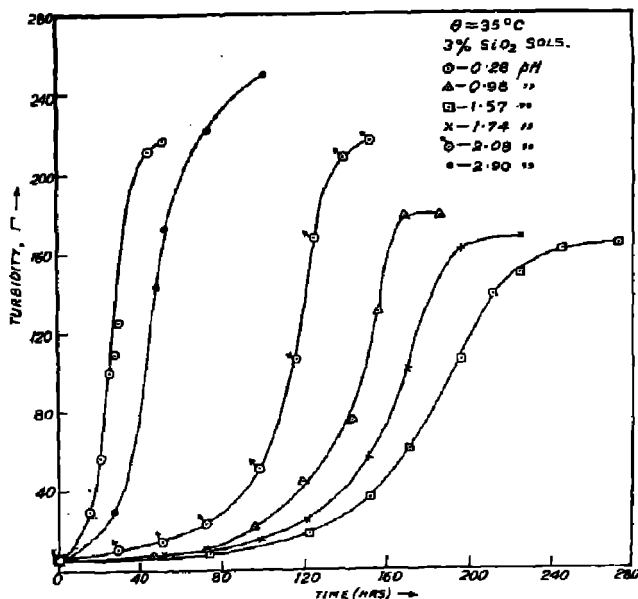
### EXPERIMENTAL

#### *Turbidity*

A freshly prepared silicic acid sol, irrespective of the acid used in its preparation, is transparent, almost like water, and the turbidity,  $I'$ , is very low. With ageing turbidity

increased at first slowly, then with appreciable speed, then rapidly as the time of gelation was approached, after which it increased rather slowly and finally approached or tended to approach a limiting value.

FIG 1



is nearly equal to the time of gelation,  $t$ . The two from Fig. 2 are compared in Table I.

TABLE I

Temperature =  $35^{\circ}$ .

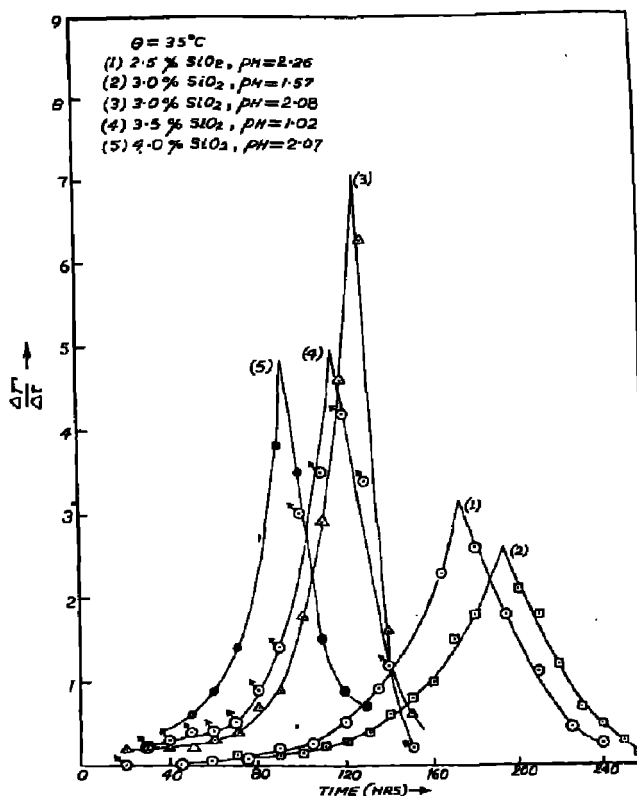
Curve No.	1	2	3	4	5
$t'$ (hrs.)	274	193	128	116	92
$t$ (hrs.)	196	211	139	115	94

The time required for attaining the maximum rate of increase in turbidity may therefore be taken as a measure of the time of gelation, *i.e.*, the time of gelation of silicic acid sols can be determined graphically from turbidity measurements.

If the rate of change of turbidity is considered as a measure of the rate of gelation, the maximum rate of change of turbidity would correspond to the maximum rate of gelation. It suggests that the gelation process involves a chain mechanism, and the maximum rate of increase in turbidity corresponds to the completion of a definite fraction of the reaction. Theoretically therefore the maximum rate of increase in turbidity seems to

be a more accurate method of determining the time of gelation than the direct ones, e.g., the falling ball method.

FIG 2



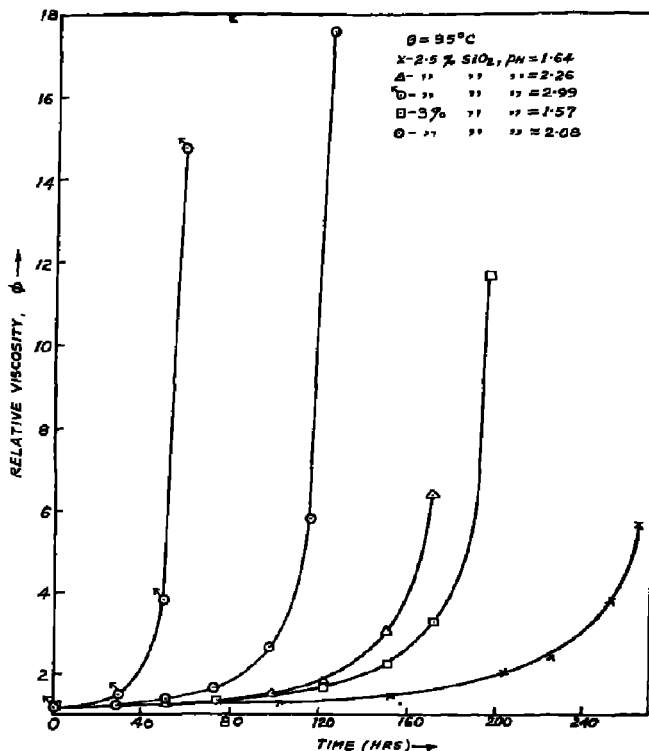
The limiting turbidity appears to be greater, the higher the temperature at which gelation occurs (studied only in the case of sols prepared by using HCl).

### Viscosity

The relative viscosity of a large number of silicic acid sols was determined by the Ostwald viscometer at a constant temperature in the thermostat at different stages of ageing. Some of these data are illustrated in Fig. 3. The viscosity of the freshly prepared silicic acid sol was very low, irrespective of the acid used in its preparation. As ageing continued, it increased at first very slowly, then with appreciable speed and finally, a little while before gelation, it shot up to a very high value such that it became very difficult to take measurements with the viscometer. In the case of sols, prepared by using HCl or  $\text{H}_2\text{SO}_4$ , the initial viscosity was almost equal to that of water. It is possible in these cases to predict the approximate time of gelation from the viscosity-time curves. Thus, the relative viscosities,  $\eta$ , of sols obtained with HCl and  $\text{H}_2\text{SO}_4$  attain values

equal to 2.0 and 3.0 at 55° at approximately 71% and 80% and at approximately 66% and 78% of the time of gelation respectively. The initial viscosities of sols obtained with other acids, although low, can vary within wide limits due to the presence of variable quantities of free acids, and so the approximate proportionality of viscosity to the time of gelation does not hold good. This is, however, applicable in a limited sense to the case of sols of a particular system, initial viscosities of which are almost identical.

FIG. 3



From the rate of change of viscosity with time it has been possible to visualise the degree of aggregation of silicic acid in the sol state by the application of Staundinger's viscosity relation,

$$\tau_{sp} = \frac{\eta - \eta_0}{\eta_0} = K.C.M. \quad \dots \quad (1)$$

where  $\tau_{sp}$  is the specific viscosity and  $\eta_0$ , the viscosity coefficient of the medium,  $K$  is a constant for the polymer,  $C$  is its concentration and  $M$ , the molecular weight.

The molecular weight of silicic acid in a number of sols at different stages of ageing has been calculated from equation (1) in terms of  $M_0$ , the assumed molecular weight in a freshly prepared sol. A gradual increase in the extent of aggregation of silicic acid

in the sol state is noticeable from the viscosity data of different systems. Results of two such sols in HCl system are illustrated in Table II.

TABLE II

Molecular weight ( $M$ ) from specific viscosity.

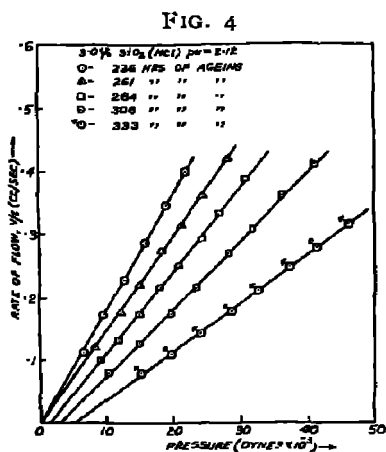
Temp. = 35°.

(i) SiO <sub>2</sub> conc. = 3.0%. $\rho_{sp} = 1.57$ .			(ii) SiO <sub>2</sub> conc. = 3.0%. $\rho_{sp} = 2.58$ .		
$t$ .	$\eta_{sp}$ .	$M$ .	$t$ .	$\eta_{sp}$ .	$M$ .
0 hr.	0.12	1.00 $M_0$	0 hr.	0.16	1.00 $M_0$
74	0.29	2.42	20	0.21	1.31
122	0.63	5.25	51	0.36	2.25
152	1.20	10.00	73	0.65	3.94
171	2.25	18.75	98	1.63	10.19
195	10.61	88.42	116	4.76	29.75
			124	16.58	103.60

### Yield Value

The development of yield value by the silicic acid sols has been studied with the Bingham viscometer. Viscosity measurements of standard cane sugar solutions by this apparatus are found to be reproducible. If a freshly prepared silicic acid sol is forced through a capillary tube, the rate of flow is directly proportional to the applied pressure and the plot of the rate of the flow against the pressure gives a straight line passing through the origin.

When plasticity develops, the plot of the flow against pressure, although a straight line, makes an intercept on the pressure axis, which is called the yield value. It has been found that the yield value develops roughly at about 75%, 80% and 86% of the time of gelation in the case of sols prepared by using hydrochloric, sulphuric and phosphoric acids at the room temperatures. The development of yield value in a particular sol, prepared with hydrochloric acid, is illustrated in Fig 4.



prepared with hydrochloric acid, is illustrated in Fig 4.

### Effect of Shaking

An attempt has also been made in the following way to gain information regarding the stage where structure formation preceding the gelation of silicic acid takes place. The

silicic acid sol, prepared with HCl, was divided into two parts. One was kept static, while the other was kept stirred continuously, except during measurements. The turbidity and viscosity (by Ostwald viscometer) of the two samples were determined at regular intervals. The turbidity of the sol in the shaker was always slightly greater than that of the sol at rest. It was also found that initially at any stage of ageing, the viscosities of the sol at rest were identical with those in the shaker. Sometime before gelation the viscosity of the sol in the shaker became slightly greater than that of the sol at rest: The sol in the shaker, however, never set to a gel; when the sol at rest set to a gel the sample in the shaker was a very thick sol of high turbidity. If, however, a part of the thick sol in the shaker is allowed to remain at rest, gelation takes place within a few hours. This gel is generally weak and highly turbid.

The viscosity-time curves indicate that the viscosity of the sol in the shaker becomes slightly greater than that of the sol at rest at about 72% of the time of gelation. Comparing this observation with that noticed previously, it appears that the development of greater viscosity of the sol in the shaker roughly corresponds to the development of yield value of silicic acid sols. It is likely that shaking does not prevent the formation of micro-structures but perhaps hinders the development of macro-structures in silicic acid sols.

#### Ultrafiltration

Some information regarding the structure formation may possibly be obtained from a study of the ultrafiltrate of a silicic acid sol. A silicic acid sol (3.0% SiO<sub>2</sub>), prepared with HCl, was allowed to age at the room temperature. A small fraction of the sol was filtered through cellophane paper at regular intervals and the silica concentration of the ultrafiltrate was determined. If structure formation of silicic acid takes place gradually the concentration of silica in the ultrafiltrate would diminish in a similar manner and becomes zero when the sol sets to a strong gel. The results obtained are recorded in Table III. The sol, when just prepared, completely passed through the cellophane. As ageing proceeded, the concentration of silica in the ultrafiltrate very slightly diminished and then remained practically constant up to about 82% of the time of gelation. A little before gelation the sol could not be filtered through the cellophane at all. An attempt to separate the dispersion medium of the sol by means of centrifugal forces, ten times as strong as the suction pressure used for ultrafiltration, failed. Again, when the sol had set to a strong gel but no syneresis had taken place, it was neither possible to filter nor to separate the dispersion medium by means of centrifuging (3200 r.p.m.).

TABLE III

3.0% SiO<sub>2</sub> sol (HCl). Time of gelation = 264 hours.  $\eta_{sp} = 2.30$ .

Time (hrs.)	0	25	168	192	216	240	264	288	336
SiO <sub>2</sub> conc. in the ultrafiltrate	3.016	2.944	2.894	2.884	2.850	Could not be filtered.		1.064	0.889

Some time after gelation when syneresis took place, the gel could be separated from its dispersion medium with the help of a centrifuge. The complete separation was,

however, effected by ultrafiltration. The silica content of the ultrafiltrate was then determined. It is found that in this ultrafiltrate silicic acid is present only in relatively small amount.

Assuming that the difficulty in the ultrafiltration or in the separation of the dispersion medium is associated with the formation of macro-structures, it appears that the latter takes place in an appreciable extent not earlier than 82% of the time of gelation.

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