578. *Silica Sols. Part III.* Accelerated Gelation, and Particle Size.*

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The resistance of various types of silica sol to an accelerated gelation test has been investigated. By using, in most cases, mixtures of sodium chloride and alcohol the conditions for gelation in 1 hour have been determined over a wide range of salt and alcohol concentrations. The addition of acid increased the resistance of the sol to the accelerated gelation test. Also for a given $SiO_2 : Na_2O$ ratio the resistance to accelerated gelation decreased as the particle size increased. If these different particle size sols are brought to the same stability then the titratable sodium is shown to decrease with increase in particle size. The experimental results presented are qualitatively explained on the theory developed in Parts I and II.*

Silica sols of high pH are very stable, and since the viscosity increases continuously but slowly over a period of weeks or months, it is difficult to attach a quantitative value to the gelation time. A direct correlation of stability with such variables as pH, silica content, and electrolyte content would be lacking in precision, and would require an impracticably long time for the accumulation of experimental data. An attempt was therefore made to compare the stabilities of different sols by determining the amount of alcohol required to bring about gelation in a short time. In this connection, an investigation was undertaken into the relation between the electrolyte content of a sol and the amount of alcohol which caused gelation in 1 hour.

Experimental

Sols.—The sols used were all of the type A and B (see Part I, *J.*, 1952, 3017). The silica content was about 15% (w/w), and the T_0 values varied from 0·14N to 0·02N.

From methods of preparation, the sols contained small amounts of sodium chloride and sodium sulphate, respectively, which had to be included in the total electrolyte content. These were found conductometrically or potentiometrically to be about 0·001—0·01N.

Gelation Technique.—The normal practice in gelation measurements is to fix the conditions and to measure the gelation time. In this instance, however, it was more convenient to reverse this procedure and to determine the conditions of electrolyte content and dielectric constant

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* Part II, preceding paper.

which produced gelation in a fixed time of 1 hour. Unless the silica content of the gelling mixture was being deliberately varied, 10 ml. of 15% sol were always used, being added rapidly to 10 ml. of the mixed electrolyte solution, the non-electrolyte, and water. Gelation was assumed to have taken place when the sol no longer flowed on inversion of the tube after 1 hour at 30°. The results obtained were consistent and reproducible to 0·1 ml. of non-electrolyte.

It was observed that, if an excess of alcohol was added, no sharp onset of gelation was observed, though the viscosity increased immediately, followed later by syneresis.

Unless otherwise specified the subsequent results refer to experiments carried out with sodium chloride as the electrolyte and ethyl alcohol as the non-electrolyte.

Results.—1. *Effect of alcohol.* Since, in any theoretical approach to the stability of colloids, the dielectric constant of the medium will play an important rôle, the non-electrolyte concentration was represented by the dielectric constant of the medium which, for different non-electrolyte concentrations, was calculated from Akerlof's data (*J. Amer. Chem. Soc.*, 1932, **54**, 4125), with neglect of the water chemically bound to the silica particles and any absorbed non-electrolyte. The dielectric constants were measured at a frequency of 2 Mc/sec., so these approximate to the static values.

On using sodium chloride and alcohol it was found that a plot of log (electrolyte concentration) against the dielectric constant of the medium for sols which gelled in 1 hour gave a straight line over a wide range of electrolyte content (Fig. 1). Both A and B sols became white and opaque during gelation, and the gels obtained were thixotropic. Different sols gave lines which were parallel within the experimental error, but were by no means coincident. It was soon established that this was not due to minor variations in silica content, and the position of the line was defined arbitrarily by the value of the dielectric constant corresponding to 0·1N-sodium chloride, which will be referred to as the alcohol constant.

FIG. 1. *Log (electrolyte content)–dielectric constant plots for typical A sols.*

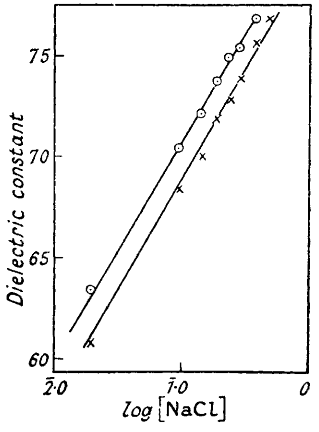
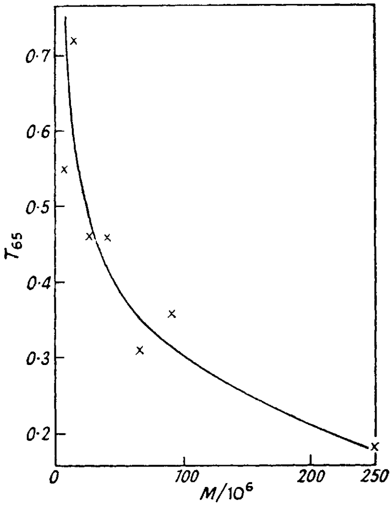


FIG. 2. *Variation of T_{65} with molecular weight.*



It was later found that with other non-electrolytes such as higher alcohols and dioxan a linear relationship was not obtained, and the dielectric constant corresponding to a given electrolyte content varied with the nature of the non-electrolyte.

2. *Effect of variation of electrolyte.* It was found that with a series of the potassium salts of various strong acids, such as the chloride, bromide, nitrate, sulphate, ferricyanide, and ferrocyanide, the behaviour was almost independent of the nature and valency of the anion.

With various chlorides it was found that the gelling efficacy varied with the valency of the cation, and slightly within a given valency. Thus at the same non-electrolyte concentration bivalent ions such as calcium and barium produced gelation in 1 hour at a normality only about one-quarter of that required by a univalent electrolyte. This ratio was much less than that found by Freundlich and Cohn (*Kolloid Z.*, 1926, **39**, 28) though here the conditions were not strictly comparable.

This sensitivity to cations, and insensitivity to anions, is in agreement with the negative charge on the particles, shown by electrophoretic measurements.

3. *Effect of addition of mineral acids.* It was found, however, that on lowering the pH by adding dilute hydrochloric, nitric, or sulphuric acid to the test mixtures more alcohol was required for a given electrolyte concentration, *i.e.*, the stability to the 1-hour gelation test had increased. The slope of the log (electrolyte content)–D.C. plot was unaltered, but the line was displaced to a lower alcohol constant. The displacement was independent of the acid, for equivalent additions.

It has already been shown that the pH of a silica sol varies with the electrolyte content (Part I, *loc. cit.*), and it was also found that the pH was raised by the addition of alcohol. It therefore follows that it is possible to prepare a series of sols of different electrolyte and alcohol content with the same stability but different pH. This is another example of the weakness inherent in the use of pH in discussions of silica sols. As before, this difficulty can be surmounted by the use of the residual titratable sodium, T_R, for while the pH varies in these sols, they will all have the same T_R if made from the same initial sol.

Since the alcohol constant of a sol can be lowered to almost any required value by the addition of acid, a series of sols of different initial alcohol constants can be brought to the same level of stability by the addition of a suitable amount of acid. In this work the stability selected was that corresponding to an alcohol constant of 65, and the value of T_R at that level is designated T_{65}.

This property, T_{65}, appears to be independent of the value of T_0 for sols of the same particle size, though this could only be shown for those sols with large particles and low T_0, in which the particle size only changed slowly with T_0.

4. *Effect of particle size on stability.* When a B sol was heated in an autoclave at a high temperature, it became progressively more turbid, and finally resembled an A sol. It was confirmed by light-scattering measurements that the particle size had increased, and thus it was possible to study the effect of particle size on stability in the 1-hour test.

It was found that as the particle size increased the alcohol constant increased, indicating that the sol was less stable. Similarly, T_{65} had decreased, and T_{65} was plotted against the particle size of the sol. It was therefore possible to obtain a semi-quantitative value for the average particle size without recourse to light-scattering measurements.

The scatter in the points in Fig. 2 is probably due to a variation of the shape of the particle-size distribution curve with T_0, for the molecular weights measured are weight-averages, and do not imply identical distributions of particle size.

DISCUSSION

In the gelation experiments described here the gel formed is always of the same type, white and thixotropic, irrespective of the pH. It is thus considered that the physical mechanism of gelation, as developed by Verwey and Overbeek ("Theory of the Stability of Lyophobic Colloids," Elsevier, Amsterdam, 1948), is predominant at all pH's considered, for at high values the concentration of ⋮Si·OH groups will be low, while even at low values the collision number will be low and the energy barrier to condensation probably high for steric reasons. Verwey and Overbeek's theory indicates that a lowering of the dielectric constant will cause a decrease in stability, but does not explain the linear log (electrolyte content)–D.C. relation found with alcohol and sodium chloride. However, in addition to lowering the dielectric constant, specific absorption effects with different non-electrolytes will doubtless affect the stability of the sols.

The increase in turbidity on mixing the components of the gelation mixture indicates that the particle size is increasing, leading to increased cationic adsorption. As with sols containing a high concentration of electrolyte, the addition of acid leads to neutralisation of the ⋮SiO⁻ groups, with a consequent reduction in cationic adsorption and hence increase of stability. By analogy with gelation experiments at high and low electrolyte concentrations, it might have been expected that at low salt contents the stability would decrease as the pH fell, but this is offset by the effect of the alcohol. On the present theory, the effect of lowering the pH is to reduce the concentration of ⋮SiO⁻ groups, and hence the amount of adsorption of cations decreases. This leads to a less rapid decay of potential with distance and so, a constant particle-potential being assumed, to increased stability. It would be expected that the stability in the 1-hour gelation test would pass through a maximum and eventually decrease, but in the present series of experiments it was not possible to explore this region owing to limitations on the amount of acid and alcohol possible in the experimental scheme used.

The increase of particle size when a B sol was autoclaved is to be accounted for as the progressive attainment of an equilibrium. The rate at which condensation takes place between the ⋮Si·OH groups of different particles may be virtually zero at room temperature, or even at 100°, but if the activation energy is high these condensations may take place much more rapidly at higher temperatures. (If the temperature is too high, then gelation takes place, which is probably to be understood as a result of the rapid condensation to form a loose network of particles throughout the system instead of a comparatively slow growth to form large particles.) This equilibrium is approached from the opposite direction in the production of A sols by the dispersion of an elastic gel by autoclaving it with sodium hydroxide. As the particle size increases at a constant T_0 value, then (Part I) the charge concentration of adsorbed ions within the particle increases also. A constant particle potential being again assumed, then the fall off of potential with distance will become more rapid as the particle size increases, giving rise to less stable conditions, *i.e.*, the alcohol constant increases with particle size at a constant T_0. Clearly, then, the T_{65} value will decrease as particle size increases, a result shown experimentally in Fig. 2.

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