

577. *Silica Sols. Part II.* Conditions of Stability.*

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The effect of electrolyte concentration and titratable sodium on the stability of small-particle silica sols has been determined. At low electrolyte concentrations a minimum in the stability- T_R curve was found, but at higher concentrations the stability increased progressively with decrease in T_R . As the initial titratable sodium, T_0 , of a silica sol increases from zero, the stability passes through a maximum and then through a minimum. A qualitative explanation of these observations is given in terms of Verwey and Overbeek's theory.

IN earlier work (see Hurd, *Chem. Reviews*, 1938, **22**, 403) the behaviour of silica sols has been related to their pH and silica content, with neglect of electrolyte concentration and particle size. The results already presented (Part I *) show that the pH of a sol is affected by particle size and electrolyte concentration, and in the work described here, the initial and residual titratable sodium are used to describe the silica sols investigated. The extension of this work to include the influence of particle size was prevented by circumstances, though an effect has been observed. The experimental results, together with those of other workers, can readily be explained qualitatively on a theory based on current concepts of colloid stability.

EXPERIMENTAL

Sols.—Unless otherwise stated all the sols used were of the type C described in Part I.

Gelation Measurements.—A known amount of dilute hydrochloric acid was added to the sol in a boiling-tube to bring the pH or, more strictly, the value of T_R (see Part I), to the required value. Sodium chloride solution was added until the concentration in the sol was as required (allowance being made for sodium chloride formed from the acid), and the corked tube was placed, after being shaken, in a thermostat at 30°. Gelation was assumed to have taken place when the sol no longer flowed on tilting the tube, the time being measured from the moment of mixing. (The term stability is used synonymously with gelation time in the description and discussion below.)

This method probably lacks the precision of Hurd's "tilted rod" technique (*J. Phys. Chem.*, 1932, **36**, 2194), and the silica content in a given series of measurements varies by $\pm 3\%$ (*i.e.*, $3.8 \pm 0.1\%$) over extreme values of T_R . However, the errors introduced were found to be negligible, and the results reproducible to $\pm 5\%$.

Results.—The results given in Part I show that the pH of a silica sol is a function of both the particle size and the electrolyte content, and also that it may vary with time. It was therefore considered desirable to replace the pH scale by that of the titratable sodium content, which is independent of particle size and electrolyte content. Fig. 1 shows stability- T_R curves for various electrolyte concentrations, and it is seen that at low electrolyte concentrations there is a minimum in the curve whereas at the higher electrolyte concentrations the stability rises continuously as T_R decreases. These effects were observed for A, B, and C type sols.

The behaviour of a series of C sols of 0.4N-sodium chloride and different T_0 is shown in Fig. 2. The stability passes through a maximum at low values of T_0 and a minimum at higher values. The shape of this curve is of fundamental importance for an understanding of the factors affecting the stability of silica sols. It was found that, as T_0 was decreased, so T_R at the minimum of stability, expressed as a fraction of T_0 , increased.

DISCUSSION

A. Mechanism of Gelation of Silica Sols.—It has already been pointed out by Hurd, Pomatti, Spittle, and Alois (*J. Amer. Chem. Soc.*, 1944, **66**, 388) that sols formed above pH 8 are soft, thixotropic, and opaque, while below pH 8 they are hard, elastic, and only slightly turbid. It has been found here that A-type sols always give soft gels while B sols give hard gels below about pH 8.

It therefore appears that there are two mechanisms of gelation, operative at different

* Part I, preceding paper.

pH's. The differences between the two types of gel, and the fact that they are related to sols of different particle size, are explicable on this basis, one mechanism involving the chemical reaction of Si-OH groups to form Si-O-Si linkages, the other being a physical coagulation. The chemical mechanism is considered first; this will be favoured by high concentrations of Si-OH groups (*i.e.*, high silica content, high T_0 , and low T_R), high collision number (small particle size), and a low activation energy (absence of steric hindrance). Since chemical bonds join the particles, the gel may be expected to be hard, elastic, and irreversible. Thus C type sols may be expected to form hard gels at low pH's, while it is reasonable that A sols give soft gels at all pH's owing to the low value of the collision number and the steric hindrance in the case of large particles.

The second mechanism is physical and is explained on Verwey and Overbeek's theory of colloidal stability ("Theory of the Stability of Hydrophobic Colloids," Elsevier, 1948). This theory predicts that under certain conditions colloidal particles will be attracted to one another, leading to coalescence and precipitation.

The distance of approach of the centres of two colloidal silica particles is limited by their size and steric factors, but if they can approach close enough they will experience a weak

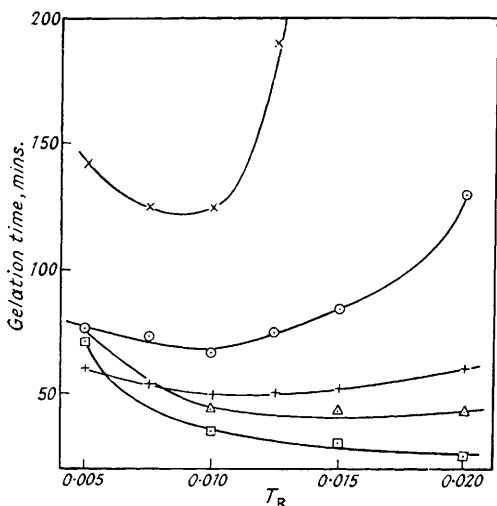


FIG. 1. Effect of electrolyte concentration on shape of T_R -stability curve.

Normality of NaCl:

x, 0.2; o, 0.3; +, 0.4; Δ, 0.5; □, 0.6.

attraction. This, repeated throughout the volume of the sol, will produce in time a "brushwood heap" type of structure with contact between particles. This will be a rate process with an activation energy, but this is reduced by increasing the electrolyte concentration, and hence the velocity will be increased. Furthermore, if the separation of the particles requires only a small energy expenditure, then the linkages will readily be broken by agitation; *i.e.*, the gel will be thixotropic.

It can be shown that as the potential of the particles increases the repulsive force similarly increases, leading to a higher potential barrier to coalescence, and so to increased stability. However, as the potential increases, adsorption of oppositely charged ions will take place, and a limiting potential will be reached. It has already been shown (Part I) that sol particles will adsorb cations to reduce their surface potential, which will increase the ionic strength both within and around the highly porous particle. The concentration of cations within the particle is thus higher than that which would exist in the double layer round a solid particle of the same size and of the same potential as that to which the silica particle is finally brought. Hence the concentration gradient at a given distance from the surface in the liquid round the silica particle is greater than at the same point in the double layer round the solid particle. For a given net surface potential and overall ionic strength, therefore, the greater the adsorption the more rapidly will the potential decay in the vicinity of the particles. The variation with interparticle distance of the repulsive forces between charged particles depends, among other things, on the rate of

decay of potential with distance from each particle. Increasing this rate of decay leads to a more rapid change of repulsive force with distance for a given surface potential, and hence to a lower stability.

These two mechanisms are in no way mutually exclusive. The physical mechanism will always be operative, but under suitable conditions it will be reinforced by the chemical combinations.

B. *Experimental Results.*—In view of Debye and Naumann's results (*J. Phys. Colloid Chem.*, 1951, **55**, 1), together with results given in Part I, there seems no doubt that the average particle size of a silica sol at equilibrium is a function of the $\text{SiO}_2 : \text{Na}_2\text{O}$ ratio, the molecular weight falling as T_0 increases. The experimental results are most conveniently discussed in terms of Fig. 2, the curve being considered in three sections, *AB*, *BC*, and *CD*. At this point the use of titratable sodium becomes important as a scale of reference instead of pH, since it influences the cationic adsorption. At *A*, corresponding to a pure silica sol, free from sodium ($T_0 = 0$), the surface potential of a small particle is much less than $\frac{3}{2}kT$ and there is no adsorption of cations. As T_0 is increased by the addition of sodium hydroxide, the potential increases, and as it approaches a certain maximum value, V_m at *B*, cationic adsorption commences. This adsorption leads to a decrease of the repulsive

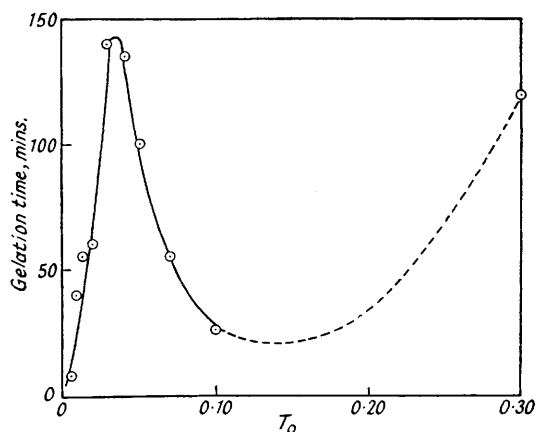


FIG. 2. Effect of T_0 on stability of sols of constant silica content (3.8%) and electrolyte content 0.4N-NaCl.

forces between particles, and hence as V_m is approached there are two opposing effects, namely, the increase of stability due to increasing potential, and the decrease due to the more rapid decay of this potential with distance. At *B*, the second factor takes control, and though T_0 increases, the particle potential is kept constant by cationic adsorption, while the stability is progressively lowered by the increased adsorption. As T_0 increases further, the particle size is diminishing, and although the potential of the fragments will be approximately the same as before, the total amount of adsorption by the sol will be less than before. This means that the density of adsorbed charges within the particle and its double layer decreases as the particle size decreases. Thus a stabilising effect comes into operation, and as T_0 increases further a minimum of stability appears at *C*. After that the colloidal properties of the sol diminish steadily as the particle size falls.

The effect of adding acid to sodium silicate can be explained similarly.

The effect of electrolyte content on the shape of the stability- T_R curve is to be interpreted as due to a decrease in the repulsive force between particles, and hence the formation of larger particles by coalescence, though this need not be followed by gelation until much later. It has been shown (Part I) that on addition of electrolyte to a sol the pH falls, but the titrations were carried out immediately, to avoid gelation. It has been observed repeatedly that the pH of a sol increases on storage, and this is attributed to increase of particle size. The effect of electrolyte in increasing the particle size is shown by the increased opacity immediately upon addition of high electrolyte concentrations, leading to greater cation adsorption, and consequently reduced stability. On addition of hydro-

chloric acid the number of :SiO^- groups is reduced, and the cation adsorption decreases. This effect overshadows that due to the increased number of $\text{:Si}\cdot\text{OH}$ groups and the stability increases. Similarly, if alkali is added to a sol containing sufficient electrolyte, then at some value of T_0 gelation will take place immediately.

It has also been observed that as T_0 is lowered the value of T_R at the minimum of stability approaches T_0 . This can also be explained, for the rate of dissolution of silica particles will be very small at low pH, and since the pH is a function of the $\text{SiO}_2 : \text{Na}_2\text{O}$ ratio, the above argument indicates that T_R tends towards T_0 as T_0 decreases.

It has been stated by several authors that there is a range of pH values between which the stability of silica sols has a minimum value. Values given include 9.5—11 (Freundlich and Cohn, *Kolloid-Z.*, 1926, **39**, 28), 8.3 (Hurd *et al.*, *J. Amer. Chem. Soc.*, 1944, **66**, 388), 6—8 (Ray and Ganguly, *J. Phys. Chem.*, 1930, **34**, 352), 6.5—7.5 (Batchelor, *ibid.*, 1938, **42**, 575), 5.8 (Treadwell, *Trans. Faraday Soc.*, 1935, **31**, 297), and —0.5 to 0.5 (Hurd and Barclay (*J. Phys. Chem.*, 1940, **44**, 847)). In the light of the facts and theory presented here, the experimental conditions under which these various values were obtained have been examined in detail. It is considered that there is no real discrepancy between these widely differing pH values, since they refer to different silica concentrations and several methods of varying the stability.

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