576. *Silica Sols. Part I. The Titration of Silica Sols.*

By K. C. Bryant.

The effect of particle size and electrolyte concentration on the titration curve of alkaline silica sols has been investigated, the pH being depressed by an increase in electrolyte concentration and by a decrease in particle size. The results obtained are compared with those obtained with polymeric acids by other workers. The qualitative difference is explained by the dissolution of the silica particles at high pH, and the effects observed are interpreted as a consequence of the preferential adsorption of cations.

Despite the numerous investigations of the titration of silica sols (see Mukherjee and Chatterjee, *Nature*, 1945, **155**, 85, for references) the influence of particle size and electrolyte content on the titration curve appears not to have been studied. Evidence is presented here to show that these factors exert a considerable effect, and the results have been examined in the light of recent theories of the titration of polymeric electrolytes.

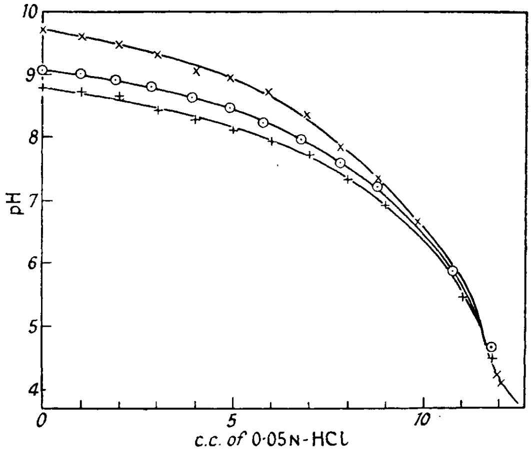
Experimental

(a) *Preparation of Silica Sols.*—These were of three types, A, B, and C, differentiated chiefly by their particle size, which was governed by the method of preparation. The A type sol was produced by acidifying sodium silicate solution with hydrochloric acid until the pH had fallen to a low value, and allowing the reaction mixture to gel. After ageing, and removal of electrolyte by washing of the gel with water, the product was treated with dilute sodium hydroxide and dispersed by autoclaving. Lumps of undispersed gel were removed by centrifugation. The final product was a white mobile liquid, resembling diluted milk. It contained about 15% of silica (w/w), with a $SiO_2 : Na_2O$ ratio of about 250, and pH *ca.* 10. When an A sol was required with low $SiO_2 : Na_2O$ ratio, the sol as prepared above was made up to the required value with sodium hydroxide solution. Type B sols were made by percolation of a 2·5% (w/w) sodium silicate solution through a column of cation-exchange resin, Nalcite, until the pH of the bulk effluent had risen to about 7. On concentration to 15% by evaporation at 100°, the pH rose to a final value of about 10. The product with 15% of silica was a slightly turbid liquid, with a $SiO_2 : Na_2O$ ratio about 70. If a B sol was required with a higher $SiO_2 : Na_2O$ ratio the 15% sol was passed through the cation-exchange resin to remove all the sodium, and was then made up to the required $SiO_2 : Na_2O$ ratio with sodium hydroxide solution. Type C sols were prepared by percolating a 2% sodium silicate solution through the cation-exchange resin, to remove all the sodium, and making it up to the required $SiO_2 : Na_2O$ ratio with sodium hydroxide solution. The sol was then evaporated to a 4% silica content. These sols were only very slightly turbid.

(b) *Particle-size Measurement.*—The average molecular weights of the particles in the A and the B sols were determined by Debye's light-scattering technique. The molecular weights found were 250×10^6 for 15% A sols, and 3×10^6 for 15% B sols as prepared above. The C sols were of much smaller molecular weight, and this would be a function of the $SiO_2 : Na_2O$ ratio. It would probably be of the order of 10^4—10^3.

(c) *Titration Technique.*—Since the sols, as prepared, were alkaline, they were generally titrated with acid, instead of removing the sodium and titrating with alkali, but both methods should yield the same result.

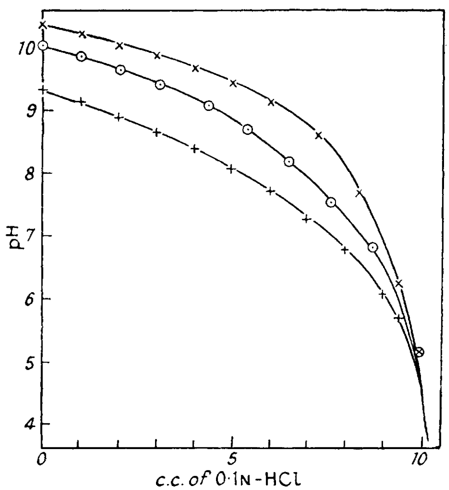
FIG. 1. *Effect of electrolyte on titration curve.*



100 *C.c. of* 0·8% *sol titrated with* 0·05N-HCl.

×, No added electrolyte.
⊙, [NaCl] = 0·2N.
+, [NaCl] = 0·4N.

FIG. 2. *Effect of particle size on titration curve.*



50 *C.c. of* 4% *sol titrated with* 0·1N-HCl.

×, A sol. ⊙, B sol. +, C sol.

Results.—1. *Effect of electrolyte concentration on titration curves.* The effect of electrolyte (sodium chloride) concentration on the titration curve of an A sol is shown in Fig. 1. The inflection point corresponds to the equivalence of sodium and mineral acid anions. Within experimental error the titration curves of hydrochloric, nitric, and sulphuric acids were identical, indicating that anion adsorption does not play any significant part, which is consistent with the negative charge on the particles. The change in pH caused by a given electrolyte concentration falls off as the $SiO_2 : Na_2O$ ratio of the sol decreases, and becomes negligible at a ratio of about 10.

At relatively high electrolyte concentrations the clear C sols and translucent B sols became cloudy, and it was apparent that their average particle size had increased. This is believed to be a normal preliminary to the gelation of silica sols at high pH.

2. *Effect of particle size on titration curve.* Arising from the observation that the particle size increased during the addition of electrolyte and acid, it was of importance to observe whether the titration curves for sols of the same silica content and $SiO_2 : Na_2O$ ratio depended on the initial particle size. The average particle sizes quoted refer to the initial sols from which those used for the titration were obtained by dilution and adjustment of the $SiO_2 : Na_2O$ ratio. The particle-size distribution in the initial and the final sol need not be the same, but since the qualitative difference in appearance between A, B, and C sols was retained in the final sols, the average particle sizes almost certainly lie in the same order.

It was observed that, the larger the particle size, the higher the pH at a given $SiO_2 : Na_2O$ ratio, electrolyte content, and silica concentration (Fig. 2). Again, the differences between the curves for sols derived from the A, B, and C types were least marked at low $SiO_2 : Na_2O$ ratios, again being insignificant at a $SiO_2 : Na_2O$ ratio of 10.

3. *Effect of* $SiO_2 : Na_2O$ *ratio on particle size.* In sodium silicates of $SiO_2 : Na_2O$ ratio greater than 1 : 1, the silicate ions consist of condensed silicic acid residues, the size and charge depending on the pH. This was indicated by Harman's work (*J. Phys. Chem.*, 1927, **31**, 616) on sodium silicates of varying $SiO_2 : Na_2O$ ratios, and confirmed by that of Naumann and Debye (*J. Phys. Colloid Chem.*, 1951, **55**, 1), who studied the molecular weight of sodium silicates of varying $SiO_2 : Na_2O$ ratio by the light-scattering method. Harman showed that this aggregation was reversible by preparing Na_2SiO_3 from sodium silicates of higher $SiO_2 : Na_2O$ ratio and conversely. The breakdown of large particles is a rate process which takes time, and it has been shown here in two ways.

First, the change in conductivity with time was observed on addition of a known amount of a silica sol to a sodium hydroxide solution at pH *ca.* 12. For equal volumes of two sols of the same silica content, the initial rate of change of conductivity varied inversely with the initial particle size.

Secondly, a 15% A sol was made up to various $SiO_2 : Na_2O$ ratios, at the same silica content, and the particle size measured after several weeks. The results are shown in the following table, from which it follows that, while the particle size of an A sol varied with the $Na_2O : SiO_2$ ratio, the rate of change may be quite slow and the particle size will be sensibly constant over a period of minutes or even hours.

$SiO_2 : Na_2O$ ratio	250	80	50
Average M	250×10^6	220×10^6	150×10^6

DISCUSSION

The physical structure of the particle is regarded as similar to that of a sponge, in which the total surface area is much greater than that of a sphere of the same diameter. Such a structure could be heavily hydrated and would also enclose much water, which would lead to the low particle density indicated by light-scattering measurements (see below). It would seem therefore that the equations derived for the titrations of polymeric acids, *e.g.*, by Katchalsky and Gillis (*Rec. Trav. chim.*, 1949, **68**, 879) and Overbeek and Arnold (*ibid.*, 1950, **69**, 192) would be applicable in this case. Both these derivations lead to an equation of the same form, namely,

$$pH = pK_a + n \log \alpha/(1 - \alpha)$$

where α is the degree of dissociation of the acid and n a constant. A similar expression has been derived and applied successfully to soluble proteins by Cannan, Palmer, and Kibrick (*Ann. N.Y. Acad. Sci.*, 1941, **41**, 243). To calculate α one needs to know the total number of acid groups present. In the case of the polymers of unsaturated carboxylic acids this is known from the amount of monomer taken, and for proteins it is derived from the length of the " steps " on the titration curves. However, comparison of the curves obtained from polymethacrylic acid (Katchalsky and Spitnik, *J. Polymer Sci.*, 1947, **2**, 432) with Fig. 1 reveals a qualitative difference, since on addition of alkali to acidified silica sols $\Delta pH/\Delta(\text{alkali})$ decreases steadily, with no indication of an inflection, even for A sols titrated to a point where the $Na_2O : SiO_2$ ratio is greater than 3. K_a being taken to be about 10^{-9}, as earlier work indicates (see Treadwell, *Trans. Faraday Soc.*, 1935, **31**, 297), the pH at equivalence will be about 11. In the case of a polymeric acid of the same K_a the pH will be higher still. The explanation of the absence of an increase in $\Delta pH/\Delta(\text{alkali})$ as the equivalence point is approached is believed to lie in the sensitivity of silica particles to alkali at high pH, which causes a lowering of the average particle size and an increase in the total number of ionised and un-ionised $\vdots Si{\cdot}OH$ groups, both of which will result in the pH being lower than that which would be observed in their absence. As the pH increases, so the rate of dissolution rises and the equivalence point is never reached. The impossibility of determining the total number of acid groups present in the sol thus prevents the use of the above-mentioned theories.

An alternative approach to the problem regards the particle as behaving as if surrounded by a membrane permeable to all ions except the ionised particles. The Donnan theory, however, cannot be applied because the net charge on the particle is known to vary with the pH (Hazel, *J. Phys. Chem.*, 1938, **42**, 409). As would be expected, the equation derived on the basis that the particle is uncharged does not represent the experimental data. Further, differences due to particle size could not be accounted for on the Donnan theory.

It is, however, possible to explain the results qualitatively by a consideration of the electrical potential of the particle. As for any weak acid partly neutralised, to a first approximation, $[\mathrm{Na}^+] = [{:}\mathrm{SiO}^-]$, *i.e.*, the sum of the negative charges on all the particles due to $:\mathrm{SiO}^-$ groups numerically equals the total charge on all the sodium ions. The sodium concentration in a sol as prepared here is referred to as the initial titratable sodium T_0, since it can be determined by titration with hydrochloric acid. On addition of this acid to a sol the above equation must be modified to $T_0 = [{:}\mathrm{SiO}^-] + [\mathrm{Cl}^-]$; and hence $T_0 - [\mathrm{Cl}^-] = [{:}\mathrm{SiO}^-]$, the left-hand side of this being referred to as the residual titratable sodium, T_R. Thus at any point during the titration of an alkaline sol with hydrochloric acid, or during the addition of sodium hydroxide to a pure sol, the total charge, due to silicate ions, on all the particles can be calculated. Hence, if the particle radius is known, the electrical potential can be estimated. The particle radius, r, is given by

$$r^3 = \frac{M_s(d_s - 1)}{(d - 1)} \times \frac{3k}{4\pi}$$

where M_s is the molecular weight of the silica skeleton, k is the mass of the hydrogen atom, and d_s and d are the density of silica and of the hydrated particles respectively. Taking d as 1·5 (obtained from light-scattering measurements) and $d_s = 2{\cdot}4$, we have

$$r = M_s^{1/3} \times 7{\cdot}8 \times 10^{-9} \text{ cm.}$$

The charge per particle for a 15% sol is given by

$$q = T_\mathrm{R} \times M_s \times 1{\cdot}09 \times 10^{-21} \text{ coulombs}$$

The particle potential is therefore

$$V = T_\mathrm{R} \times M_s^{2/3} \times 1{\cdot}6 \times 10^{-3} \text{ volts}$$

T_R being assumed to be 0·02N, V varies from about 70 mv at $M_s = 10^5$ to about 30 v at $M_s = 10^9$. Such high potentials would attract cations (*i.e.*, H^+ and Na^+) until the net potential of the particle was of the order of 40 mv. This is in agreement with the results of Kargin and Rabinovitch (*Trans. Faraday Soc.*, 1935, **31**, 284), who found that the adsorption of barium ions increased as the pH rose, *i.e.*, as T_0 increased.

If it is asumed that the net potential to which the particle is reduced does not vary much with the electrolyte content, then the effect of adding electrolytes will be to alter the relative proportions of adsorbed sodium and hydrogen ions. Thus, on addition of a sodium salt, hydrogen ions will be displaced from the particle into the inter-particle liquid, and so the pH of the solution will fall, as observed. It was noted by Kargin and Rabinovitch (*loc. cit.*) that the number of H^+ ions displaced is about one-hundredth of the amount of Ba^{++} ions adsorbed.

The effect of particle size can also be deduced from the above theory, if it is assumed that the adsorption reduces the potential to a value V_0 (a few kT) which is sensibly constant.

The charge, q_a, which has to be adsorbed, per particle, to accomplish this is given by

$$q_a = (T_0 \times M_s^{2/3} \times 1{\cdot}6 \times 10^{-3} - V_0) \times 80r$$

and the charge adsorbed per c.c., Q_a, is given by

$$Q_a = (T_0 M_s^{2/3} \times 1{\cdot}6 \times 10^{-3} - V_0) \times 80r \times N$$

where N is the number of particles per c.c.

Now $r = \text{constant} \times N^{-1/3}$ and so

$$Q_a = GT_0 - HN^{2/3}$$

where G and H are constants for a given silica content.

In these circumstances $N \propto M_s^{-1}$, and so as M increases, Q increases, *i.e.*, more adsorption takes place. Hence the pH rises, as observed (Fig. 2).

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