# *Estimation of Specific Surface Area of Particles in Colloidal Silica Sols From the Rate of Dissolution*

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The performance of colloidal silica in many of its applications largely depends on particle size or specific surface area. However, the application of currently available methods[1-7] for the determination of this property encounters difficulty in many cases, and a more rapid and simple method is urgently needed. An attempt has been made in the present investigation to determine the specific surface area of colloidal silica from the rate of dissolution of particles in a solution containing sodium fluoride and hydrochloric acid.

## Experimental

**Materials.**—*Colloidal silica.*—Sols of colloidal silica were prepared by allowing to stand the mixture of the solution of sodium metasilicate and the solution of silicic acid prepared from sodium metasilicate by ion exchange. Colloidal silica having a small specific surface area was prepared by aging at higher temperatures.

*Aluminum chloride solution.*—Two hundred and seventy g. of aluminum chloride hexahydrate was dissolved in distilled water and made up to 1 l. One mililitre of this solution contains about 30 mg. of aluminum ions.

*Ammonium molybdate solution.* — Ten % (w/v) aqueous solution.

*Concentrated hydrochloric acid solution*

All reagents were of purest grade commercial products and used without further purification.

**Apparatus.**—A photoelectric colorimeter equipped with a glass prism and a barrier layer cell was employed for the colorimetric determination of molecularly-dispersed form of silica. The dissolution reaction was conducted in polyethylene

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1) G. B. Alexander, *J. Am. Chem. Soc.*, **75**, 2887 (1953).
2) G. B. Alexander, ibid., **76**, 2094 (1954).
3) G. B. Alexander and R. K. Iler, *J. Phys. Chem.*, **57**, 932 (1953).
4) P. V. Nauman and P. Debye, *J. Phys. & Colloid Chem.*, **55**, 1 (1951).
5) M. F. Bechtold, *J. Phys. Chem.*, **59**, 532 (1955).
6) R. K. Iler, "The Colloid Chemistry of Silica and Silicates," Cornell Univ. Press, New York (1955), p. 100.
7) G. W. Sears, Jr., *Anal. Chem.*, **28**, 1981 (1956).

bottles to avoid contamination from glass vessels.

**Measurements of dissolution rate.**—Colloidal silica is dissolved in a medium prepared fulfilling the conditions given in Table I. Ten mililitre portions of the solution in which the colloidal silica sample is being dissolved are taken at definite intervals in beakers containing 0.5 ml. of aluminum chloride solution, the dissolution reaction being stopped by this procedure. To each beaker 0.5 ml. of ammonium molybdate solution is then added and the absorbancy is measured after 6 or 8 min. at wave-length of 430 m$\mu$. The amount of conecntration of a molecularly-dispersed form of silica is calculated from the color intensity and is plotted against the time of sampling. Since, as is discussed later, the plot was a straight line over a wide range of time, the dissolution rate, which is expressed by the ratio of the initial rate of increase in the concentration of molecularly-dispersed silica (mg./l./min.) to the initial concentration of colloidal silica (mg./l.), could be easily obtained from the slope.

TABLE I

CONDITIONS EMPLOYED FOR THE DISSOLUTION REACTION

| | |
|---|---|
| Concentration of sodium fluoride | 300 mg./l. with respect to $F^-$ |
| Concentration of hydrochloric acid | 0.12 N |
| Temperature | 25.0±0.1°C |
| Concentration of colloidal silica sample | around 20 mg./l. with respect to $SiO_2$ |

## Results

Fig. 1 shows the dissolution rate as a function of the specific surface area as determined by the titration procedure developed by Sears[7]. Correction was made, in the titration, for molecularly-dispersed silica which exists in equilibrium with colloidal silica and also reacts with the titrant. For sols of higher degrees of secondary aggregation, the dissolution rate is generally higher than is expected from the titration. This may be due to the gelation taking place during the titration of such sols, giving rise to difficulty in reaching equilibrium between the silica particles and the titrant.

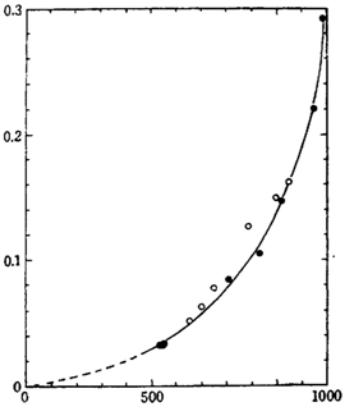

Fig. 1. Correlation of dissolution rate with specific surface area. ● indicates that gelation did not take place during titration.

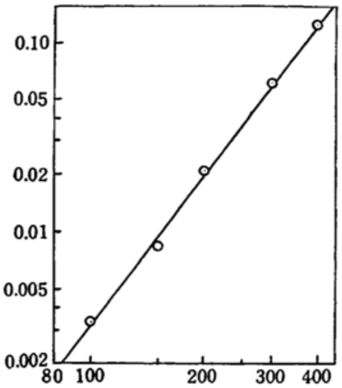

Fig. 2. Fffect of fluoride ion concentration on the dissolution rate.

The effect of fluoride ion concentration on the dissolution rate is shown on logarithmic scale in Fig. 2, from which it is apparent that the dissolution rate is roughly proportional to the 2.6th power of fluoride concentration.

The concentration of hydrochloric acid in the range 0.09 to 0.14 N has little effect on the dissolution rate, as is shown in Table II.

TABLE II

EFFECT OF THE CONCENTRATION OF HYDROCHLORIC ACID ON THE DISSOLUTION RATE

| Normality of HCl | Dissolution rate |
|---|---|
| 0.03 | 0.050 |
| 0.06 | 0.039 |
| 0.09 | 0.0314 |
| 0.12 | 0.0320 |
| 0.14 | 0.0315 |

The fact that, as is shown in Table III, the aluminum ion greatly reduces the dissolution rate at high concentrations permits the use of aluminum salt to stop the dissolution reaction. Although 600 mg./l. of the aluminum ion is sufficient for this purpose, an aluminum-ion concentration of about 1500 mg./l. was used in the present investigation. It is shown in Table

TABLE III

EFFECT OF ALUMINUM ION (a)

| Concentration of Al (mg./l.) | Dissolution rate |
|---|---|
| 0 | 0.0675 |
| 150 | 0.0025 |
| 300 | ca. $8\times10^{-5}$ |
| 600 | ca. $2\times10^{-5}$ |
| 0, in the absence of fluoride | ca. $1\times10^{-5}$ |

TABLE IV

EFFECT OF ALUMINUM ION (b)

| Concentration of Al (mg./l.) | Dissolution rate |
|---|---|
| 0 | 0.0300 |
| 0.2 | 0.0315 |
| 0.4 | 0.0280 |
| 0.6 | 0.0278 |
| 0.8 | 0.0264 |

TABLE V

EFFECT OF THE CONCENTRATION OF COLLOIDAL SILICA SAMPLE

| Concentration (mg. $SiO_2$/l.) | Dissolution rate |
|---|---|
| 10.8 | 0.068 |
| 20.0 | 0.065 |
| 32.0 | 0.062 |
| 40.5 | 0.053 |

IV, however, that small amounts of aluminum, which is the most common among the impurities in colloidal silica, have little effect on the dissolution rate.

The concentration of a colloidal silica sample in a dissolution medium also affects the dissolution rate as shown in Table V. It is essential, therefore, to measure the dissolution rate at about a constant concentration of colloidal silica.

## Discussion

The foregoing results indicate a possibility of estimating the specific surface area of colloidal silica particles from the measurement of dissolution rate in an acid solution of sodium fluoride under carefully controlled conditions.

It is very interesting to note in Fig. 1 that the surface of a smaller particle is more reactive than that of a larger one: the dissolution rate per unit surface area increases with decreasing particle size. Since, therefore, the decrease in surface area during dissolution is compensated by the increasing rate of dissolution per unit surface area, the concentration of molecularly-dispersed silica increases linearly with time over an unexpectedly wide range, permitting an easy graphical determination of the initial rate of dissolution.

The dissolution reaction may be of first order with respect to colloidal silica, since the dissolution rate given in Table V is about the same for varying silica concentrations. It is interesting to note that the dissolution reaction is of the order between 2 and 3 with respect to the fluoride concentration and that it is more rapid at lower acidities. Further discussion of the reaction mechanism, however, is not described here since it is beyond the scope of this paper.

The variation of the rate of dissolution per unit surface area with particle size, however, prevents the accurate determination of a specific surface area of colloidal silica in polydisperse systems. It is also a serious question associated with this method whether the dissolution rate is the same or not for sols prepared under different conditions. However, since the sols used in the present investigation were prepared under alkaline conditions, where silica particles of uniform size can be formed[8], the method may be applicable at least to alkaline sols, including the active silica used in water purification.[9]

Sears' titration procedure[7] is applicable only to sols containing more than 10 g./l. of silica since it deals with 150 ml. of sols containing 1.5 g of silica. On the other hand, only a few mg. of silica is sufficient for the present method, which may therefore be applicable also to extremely dilute sols. This may well offset the disadvantage discussed above.

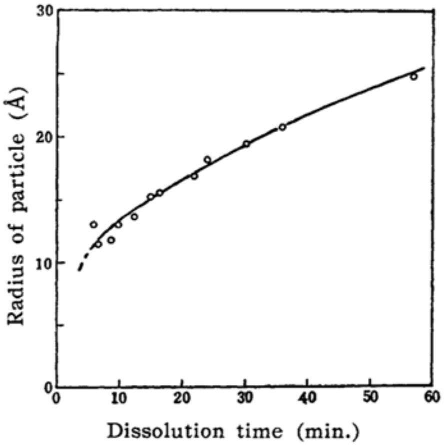

Fig. 3. Relation between particle size and dissolution time.

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[8] R. K. Iler and R. L. Dalton, *J. Phys. Chem.*, **60**, 955 (1956).

[9] Ref. 6 p. 119

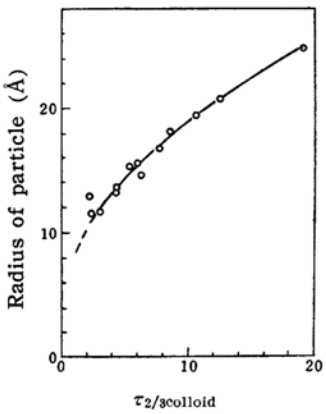

Fig. 4. Relation between the particle size and the time required for the dissolution of two thirds of colloidal silica.

It is essential, in determining a specific surface area from Fig. 1, to observe as strictly as possible the conditions given in Table I, since the reduction in the concentration of available fluoride during the dissolution reaction was not taken into account in the present investigation.

Molecularly-dispersed silica, when present in large amounts, may interfere with the method by reducing the concentration of available fluoride. This, however, may be removed by passing through a column containing a mixture of cation- and anion-exchange (strongly basic type) resins.

In our earlier report[10], dissolution time was used as a measure of particle size. It is the time required for the complete dissolution of particles and was determined by plotting the cube root of the concentration of colloidal silica versus time and extrapolating the plot to the abscissa, based on the assumption that the rate of dissolution per unit surface area remains constant during the process of dissolution. Though such an assumption has been proved to be incorrect, the dissolution time may still be a rough measure of the particle size, and is shown in Fig. 3 as a function of the particle size calculated from the result of titration on the assumption that the particles are spheres with a specific gravity of 2.2[11].

The reactivity toward alkaline solutions was also used in earlier works[12,13] as a measure of particle size. The reaction with alkali, however, is greatly retarded by traces of aluminum[14] and thus may be applicable only to sols prepared with special precautions.

It is also desirable to use the time, $\tau_{2/3\mathrm{colloi}}{}^{\mathrm{d}}$, required for particles to lose two thirds of their initial masses under conditions given in Table I. As the concentration of remaining colloidal silica decreases linearly with time at least up to this point, the $\tau_{2/3\mathrm{colloid}}$ can be easily determined graphically. In Fig. 4 is shown the relation between $\tau_{2/3\mathrm{colloid}}$ and particle size.

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[10] T. Okura, K. Goto and T. Komatsu, This Bulletin, **31**, 139 (1958).

[11] Ref. 6 p. 135.

[12] K. Goto, *J. Phys. Chem.*, **60**, 1007 (1956).

[13] K. Goto, *J. Chem. Soc. Japan, Pure Chem. Sec.*, (*Nippon Kagaku Zassi*), **77**, 957 (1956).

[14] G. Okamoto, T. Okura, and K. Goto, *Geochim. et Cosmochim. Acta*, **12**, 123 (1957).