SHORT COMMUNICATIONS

State of Aggregation of Primary Particles in Colloidal Silica

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It has been shown in our previous reports[1,2] that the rate of polymerization of silicic acid increases with pH, and larger particles of colloidal silica are formed at higher pH values.

On the other hand, measurements carried out by many investigators of gelation time have shown that silicic acid gels most rapidly in a slightly acidic medium[3]. The fact seems to be an indication of the most rapid polymerization in a slightly acidic medium.

The present investigation was undertaken to reconcile the above two contrasting results, as well as to show that, as has already been suggested by Goto[4], different types of colloidal silica are formed at different pH values.

For these purposes, measurements were made of the relative viscosity and the dissolution time (i. e., the time required for the complete dissolution of colloidal silica particles in a proper medium) at various aging times.

Experimental

Preparation of Silicic Acid.—Silicic acid solutions containing 8 g./l. of SiO_2 were prepared from sodium metasilicate by ion exchange, and the pH was adjusted by adding appropriate amounts of sodium metasilicate solution. The aging of silicic acid solutions were carried out at room temperature.

Measurement of Dissolution Time (τ).—The method used for the determination of dissolution time was similar to that reported in the previous papers[1,2] with the following exceptions:

a) Instead of a solution of sodium carbonate, a solution containing sodium fluoride (300 mg. F^-/l.) and hydrochloric acid (0.1 N) was used for the dissolution of colloidal silica.

b) Aluminum chloride was employed to stop the dissolution reaction and to reduce the interference of the fluoride ion in the colorimetric determination of molecularly dispersed silica. The temperature was kept constant at 25°C during the measurement of dissolution time. Full descriptions of the method of measurement will be reported later.

Measurement of Relative Viscosity.—The viscosity was measured with the usual Ostwald viscosimeter.

Results and Discussion

The results are summarised in Table 1. The volume, V, immobilized by 1 g. of SiO_2 in water was estimated on the basis of the well known Einstein's formula, by using the equation

$$V=\frac{\eta_{rel}-1}{0.0025\,C}$$

where η_{rel} is the relative viscosity, C, the concentration of silica in g./l., and V is expressed in cc. The effect of the charge was ignored in the calculation. The results were also shown in Table I.

It is clearly shown in this Table that at pH values slightly below 7, V increases

TABLE I

CHANGES IN τ, η_{rel}, AND V WITH AGING TIME

Initial pH		Aging time (Day)			
		1	4	14	63
	τ(min.)	<1	<1	1	2.0
2.4	η_{rel}	1.009	1.010	1.018	1.070
	V(cc.)	0.45	0.50	0.90	3.5
	τ(min.)	<1	1.4	2.1	3.7
3.7	η_{rel}	1.009	1.035	1.062	1.140
	V(cc.)	0.45	1.8	3.1	7.0
	τ(min.)	3.2	6.8	12.8	29.6
5.2	η_{rel}	1.095	1.125	1.150	1.135
	V(cc.)	4.8	6.3	7.5	6.8
	τ(min.)	10.3	17.3	29.3	40.0
6.6	η_{rel}	1.060	1.060	1.060	1.070
	V(cc.)	3.0	3.0	3.0	3.5
	τ(min.)	14.2	24.7	38.5	50.0
8.2	η_{rel}	1.012	1.020	1.012	1.010
	V(cc.)	0.6	1.0	0.6	0.5

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1) K. Goto, *J. Chem. Soc. Japan, Pure Chem. Sec.*, (*Nippon Kagaku Zassi*) **77**, 958 (1956).

2) K. Goto, *J. Phys. Chem.*, **60**, 1007 (1956).

3) R. C. Merrill and R. W. Spencer, *J. Phys. & Coll. Chem.*, **54**, 806 (1950); I. A. Heald, K. B. Coates and J. E. Edwards, *J. Appl. Chem.*, **5**, 425 (1955); M. F. Bechtold, *J. Phys. Chem.*, **59**, 532 (1955); Also see R. K. Iler, "The Colloid Chemistry of Silica and Silicates," Cornell Univ. Press (1955), p. 45.

4) K. Goto, *J. Chem. Soc. Japan, Purs Chem. Sec.*, (*Nippon Kagaku Zassi*) **76**, 729 (1955).

considerably with aging time, while the dissolution time remains very small. At higher pH values, V remains very low, even when the dissolution time has acquired a very high value.

There are two possible forms of colloidal silica, as has been suggested by Iler⁵⁾:

a) particles of colloidal silica which are aggregates of many smaller primary particles as schematically shown in Fig. 1 a.

b) dense, descrete particles as shown in Fig. 1 b.

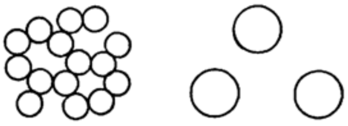
a b

Fig. 1

Since dissolution time, which is theoretically proportional to the radius of particles, may be influenced mainly by the size of primary particles, it may be reasonable, to take the dissolution time as a measure of the size of primary particles. On the other hand, the viscosity and the value of V may be a measure of the looseness with which primary particles are associated together, or the packing density of primary particles.

It is thus suggested from the above results that the aging in slightly acidic media leads to the formation of aggregates of very fine primary particles, while a tendency towards the formation of larger, descrete particles becomes marked as the pH increases.

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5) R. K. Iler, "The Colloid Chemistry of Silica and Silicates," Cornell Univ. Press (1955), p. 96.