Formation and Aging of Precipitates. IX*. Formation of Monodisperse Particles (2) Barium Sulfate Precipitate by EDTA Method

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Sparingly soluble salts were suitable in the study of the physicochemical properties of precipitates and the precipitation reaction in analytical chemistry. Barium sulfate has been widely used for these purposes. The author previously reported the size and shape of barium sulfate particles precipitated by the direct mixing of ions[1]. In this paper the monodisperse particles of barium sulfate precipitated from a homogeneous solution, are reported. A few methods, e.g. the dimethyl sulfate method[2], and the sulfamic acid method[3] have been investigated to precipitate barium sulfate from a homogeneous solution, but the particles produced by these procedures were almost all polydisperse. The author has produced the monodisperse particles by means of the decomposition of the complex of barium and ethylenediaminetetra-acetate (EDTA) with hydrogen peroxide in the presence of sulfate. The EDTA method was used to precipitate ferric hydroxide by McNevin and Dunton[4] and the present author improved the method of precipitating barium sulfate.

Experimental

Formation of the Precipitate.—Equivalent quantities of barium chloride and EDTA solutions were mixed and an ammonium chloride-ammonia buffer was added to bring the pH of the solution to 10. After addition of ammonium sulfate which was equivalent to barium chloride, the mixed solution was warmed at 80°C and hydrogen peroxide was added to decompose EDTA. The reaction mixture was kept at 80°C during the course of reaction.

Measurement of the Particle Size.—Barium sulfate precipitates produced were observed with

* The eighth paper of this series, This Bulletin, **31**, 944 (1958).

1) E. Suito and K. Takiyama, This Bulletin, **27**, 121, 123 (1954); **28**, 305 (1955).

2) P. J. Elving and R. E. van Atta, *Anal. Chem.*, **22**, 1375 (1950).

3) W. F. Wagner and J. A. Wuellner, ibid., **24**, 1031 (1952).

4) W. M. McNevin and M. L. Dunton, ibid., **26**, 1246 (1954).

TABLE I

PARTICLE SIZES OF BARIUM SULFATE PRECIPITATES

Concn. C (M)	Size of particle					Number of particle N (per ml.)
	Length of long axis a (mμ)	Standard deviation σ_a (mμ)*	Length of short axis b (mμ)	Standard deviation σ_b (mμ)*	Mole number of particle M (mole)	
0.0022	993	34	298	21	8.89×10^{-16}	2.47×10^{9}
0.0033	1022	63	346	37	1.23×10^{-15}	2.68×10^{9}
0.0044	1066	68	420	44	1.87×10^{-15}	2.35×10^{9}
0.0066	1237	67	473	32	2.79×10^{-15}	2.37×10^{9}
0.0088	1400	58	535	41	4.04×10^{-15}	2.20×10^{9}

Reaction mixture:

$BaCl_2$	original solution (0.022, 0.22 M)	same volume (3～10 ml.)
EDTA	original solution (0.022, 0.22 M)	same volume (3～10 ml.)
$(NH_4)_2SO_4$	original solution (0.022, 0.22 M)	same volume (3～10 ml.)
Buffer solution	5 ml.	
H_2O_2 (30%)	20 ml.	
Total volume	100 ml.	

* σ_a and σ_b are the standard deviation of a and b respectively.

an electron microscope. All particles were spindle-shaped, and the mean lengths of long and short axes and their standard deviation were determined. Then, the mole number of one particle, M (mole), was calculated according to the following equation:

$$M=(4/3)\pi(a/2)(b/2)^2\rho/W \quad (1)$$

where a and b are the mean length of long and short axes, ρ and W are the density and the molecular weight of barium sulfate.

Measurement of the Reaction Rate.—The quantity of EDTA present at any given time was determined by titration. At various times during the course of the reaction, 10 ml. samples of the reaction mixture were poured into beakers, which were kept in ice water, and were titrated with 0.010 M zinc sulfate using Eriochrome Black T as indicator in the presence of a large excess of ammonium sulfate.

The growth of the particles was determined by electron microscopy as follows. At various intervals one drop of the reaction mixture was taken onto a tiny Formvar film floating on the surface of cold water. About ten minutes, the product was allowed for the diffusion of mother liquid ions from the drop into the water below. The film was then scooped up with a sample grid for electron microscopy.

Exprimental Results

Relation between the Particle Size and the Concentration of Reagents.—Barium sulfate particles precipitated at various concentrations of the reagents* are shown in Fig. 1 and the sizes of particles determined are listed in Table I. Particles are spindle-shaped and monodisperse over a range of 0.0022 to 0.0088 M

* The concentraton of reagents means the initial concentration of barium ion which is equivalent to that of EDTA or sulfate, and is expressed by mole per liter.

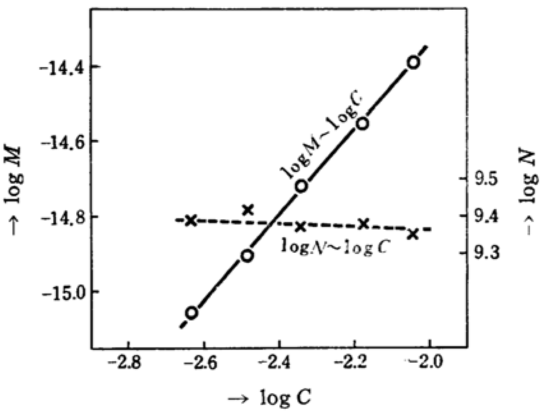


Fig. 2. Relation of the particle size to the concentration of reagents.

of the reagents. The size of particles increased with the increase of concentration of reagents. The logarithm of the mole number of particle, $\log M$, is linear with the logarithm of the concentration, $\log C$, as shown in Fig. 2. Then the relation between M and C is expressed by the following equation:

$$MC^{\alpha}=K \quad (2)$$

where α and K are constants, being -1.2 and 1.15×10^{-12} respectively. As the number of particles per ml., N, is given as $C/M \times10^{-3}$, $\log N$ is also linear with $\log C$ as shown in Fig. 2. The number of particles per ml. remained almost constant over the range of cocentration listed in Table I.

Growth Process of Particle.—*Reaction rate determined by titration.*—The rate of decomposition of EDTA in two series of experiments, in which the concentrations of reagents were 0.0022 and 0.0044 M, was expressed by curve (EDTA) in Fig. 3. The decomposition of EDTA was of the first order with respect to EDTA concentration. Barium ion liberated with decomposition of EDTA was expressed by curve (Ba^{2+}) in Fig. 3.

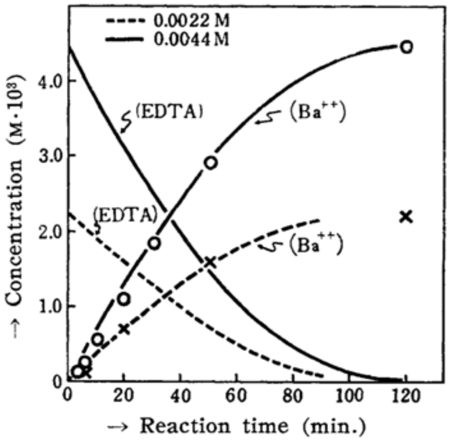


Fig. 3. Rate of formation of barium sulfate precipitate.
(EDTA): Concentration of EDTA in the reaction mixture
(Ba^{2+}): Rate of liberation of barium ion calculated from (EDTA)
○, ×: Quantity of barium sulfate precipitate determined by electron microscopy

Growth rate of particle observed by electron microscopy.—The particles during the course of reaction are shown in Fig. 4. The particles were monodisperse from the initial stage of the reaction. The value obtained by multiplication of the mole number of one particle, x(mole), obtained by electron microscopy at the time listed by the number of particles per liter of suspension, $N\times10^3$, calculated after completion of the reaction is equal to the quantity of barium sulfate precipitated. The values obtained as described above are shown by ○ and × in Fig. 3. It was proved from Fig. 3 that the rate of formation of barium sulfate determined by electron microscopy was almost the same as that of liberation of the barium ion obtained by titration.

Discussion

Barium sulfate precipitates formed at the concentration of reagents over a range from 0.0022 to 0.0088 M by EDTA method contained monodisperse particles. According as the concentration of the barium ion generated by the decomposition of EDTA increased, the ion product (Ba^{2+}) $\times$ (SO_4^{2-}) increased. It seemed that, when the ion product exceeded a certain critical value, corresponding to the limiting degree of supersaturation reported by LaMer and Dinegar[5], crystal nuclei were formed rapidly and after the nucleation the particles grew according to the liberation of barium ion as discussed later. If the concentration of reagents was too high, the rate of the generation of barium ion was rapid and the new particles were formed even after the nucleation. If the concentration of reagents was too low, the rate of formation of nuclei was slow and the growth of the nuclei previously formed proceeded faster than those formed later. Then in these cases the particles produced were polydisperse.

The relation of the particle size to the concentration of reagents was expressed by equation 2. The value of α in the equation was negative and the size of particles increased with the increase of concentration. The number of particles per unit volume of the suspension formed at various concentrations was almost constant as shown in Fig. 2. Thus a definite number of nuclei was formed over the range of concentration described above. O'Rourke and Johnson[6,7] reported that the number of particles per unit volume of barium sulfate suspension formed by direct mixing of ions over a range of initial concentration of 10^{-3} to 10^{-4} M was almost independent of concentration and the size of particles increased with the increase of initial concentration. These relations were also confirmed by the EDTA method over the range of concentration slightly above that proved by the direct mixing method.

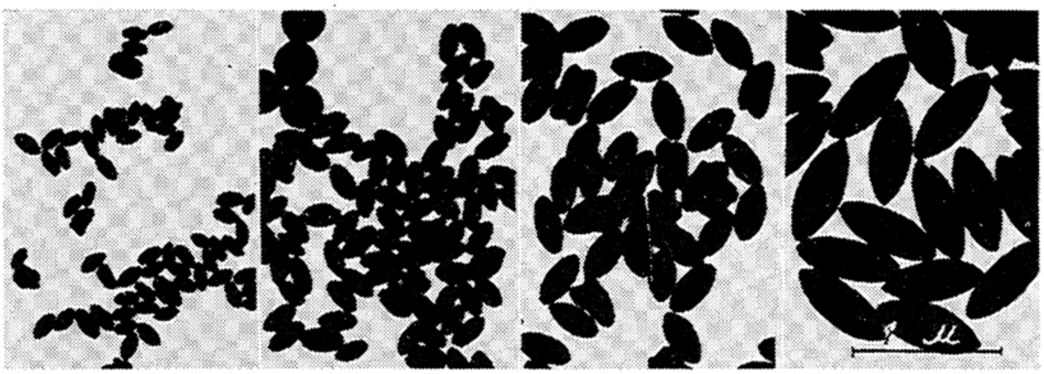
The author previously reported the shape and size of particles of barium sulfate precipitated by direct mixing of ions[1]. Taking the data from that report, the logarithm of the mole number of one particle, $\log M$, and the logarithm of the initial concentration of barium sulfate, $\log C$, were calculated. The relation of $\log M$ to $\log C$ was shown in Fig. 5, and M and C were expressed by equation 2. The value of α was 2.7 and -1.4 at the concentration above and below about

5) V. K. LaMer and R. H. Dinegar, *J. Am. Chem. Soc.*, **73**, 380 (1951).
6) R. A. Johnson and J. D. O'Rourke, ibid., **76**, 2124 (1954).
7) J. D. O'Rourke and R. A. Johnson, *Anal. Chem.*, **27**, 1699 (1955).

a b c d

(×15,000)

Fig. 1. Electron micrographs of barium sulfate particles produced at various concentrations.
a: 0.0022 M, b: 0.0044 M, c: 0.0066 M, d: 0.0088 M



a b c d

(×20,000)

Fig. 4. Electron micrographs of barium sulfate particles during the growth process.
(C = 0.0044 M) a: 3 min., b: 5 min., c: 10 min. d: 40 min.
(Spherical particles shown in b are polystyrene latex used as the calibration standard to measure the particle size.)

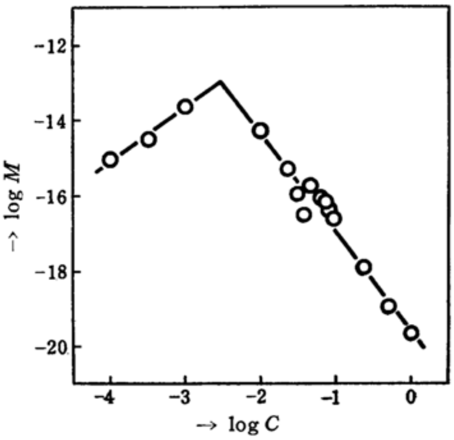


Fig. 5. Relation of the particle size to the initial concentration of barium sulfate formed by direct mixing of ions.

0.002 M respectively. The value of K was always constant and was 2.2×10^{-20}. The number of particles per ml. suspension, which was calculated from the initial concentration and the mean size of particles, increased rapidly with the increase of concentration above about 0.002 M, but was nearly constant at the concentration below about 0.002 M. The induction period of the precipitation appeared over the range of the initial concentration below about 0.002 M, that is, over the range of α being negative. The precipitation by EDTA method was made above 0.0022 M and the concentration was such that the induction period in the direct mixing did not appear. As EDTA method was one of the homogeneous solution methods, the induction period was, of course, found before the precipitation. It seems that when the induction period appears in the case of the precipitation, the size of particles increases with the increase of concentration of reagents.

Generally speaking, it would be plausible that when the nucleation plays a predominant role in the precipitation, the particle size decreases with the increase of initial concentration (Weimarn theory), and that when the growth of particles plays a predominant role, the particle size increases with the increase of initial concentration.

The rate of liberation of the barium ion calculated from the titration of EDTA agreed with that of the formation of barium sulfate precipitate obtained by electron microscopy. Thus the number of particles per unit volume of suspension was kept constant and no new particles were formed during the growth period of particles. Furthermore, the barium sulfate were deposited on each particle immediately after the liberation of barium ion, and the growth of particles was balanced with the liberation of barium ion.

Summary

Monodisperse spindle-shaped particles of barium sulfate were formed by means of the decomposion of barium-EDTA complex with hydrogen peroxide in the presence of sulfate. The logarithm of the size of the particle produced was linear with the logarithm of the concentration of reagents. The particles grew at the same rate of liberation of barium ion from the complex. The number of particles per unit volume of the reaction mixture was kept constant during the growth process of particles.

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