*Formation and Aging of Precipitates. I. Electron Microscopic Studies of the Formation of Barium Sulfate Precipitate**

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Introduction

The relations between the formation of the precipitates and their physical and chemical properties have been studied by a number of investigators. Especially the precipitation of barium sulfate has been investigated as a fundamental case. Fischer[1] and Okada[2] employed the electron microscope to study the precipitates of barium sulfate. The authors also used an electron microscope to study the formation, the aging and the growth mechanism of the crystals of barium sulfate. In this paper the relation between the concentration of the reagents and the shape and size of the precipitated particles is described.

Experimental Procedure

Barium sulfate precipitates were formed on mixing barium hydroxide with sulfuric acid to keep out the disturbance of other ions. But at concentrations higher than 0.2 M barium acetate and manganous sulfate were used because of their solubilities. These reagents were all guaranteed. The reagents of equal volumes and of the same concentrations were mixed rapidly by pouring into a large test tube at 18°C. Directly after mixing, a drop of the reaction products was placed on a specimen holder for the electron microscope and was dried. The specimens were observed directly or after chromium shadowing by the electron microscope SM—T4.

Experimental Results

Fifteen kinds of precipitates were prepared, varying the total concentration of barium sulfate from 1.0000 to 0.0001 M (i.e. the concentration of the reagents from 2.0000 to 0.0002 M). Several specimens for electron microscopy were prepared from each precipitate, and several electron micrographs were taken for each of the specimens. The shape and the size of the particles of each precipitate were observed, then the length of the longest part of the particles was measured. From about 200 particles the size distribution curves of each precipitate were obtained as shown in Fig. 1, in which the relative frequency is plotted against the length of the particle. These distribution curves are for the samples ranging from 0.25 to 0.02 M in the total concentration. From these distribution curves the arithmetic mean sizes of the particles were calculated. The shape and the size of barium sulfate precipitates formed in different total concentrations are shown collectively in Table 1.

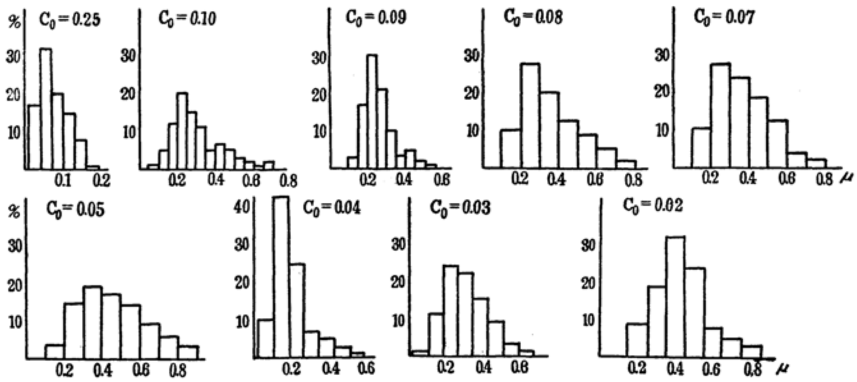

Fig. 1. Frequency histogram of particle size.
abscissa: size of particles (μ).
ordinate: relative frequency (% of particles).

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* Some parts of this experiment were published in *Proc. Japan Acad.*, **28**, 133 (1952) as a preliminary report.

1) R. B. Fischer, *Anal. Chem.*, **23**, 1667 (1951).

2) S. Okada, M. Kawane and S. Magari, *Mem. Faculty Eng. Kyoto Univ.*, **13**, 198 (1951).

TABLE I

THE RELATION OF THE SHAPE AND SIZE TO THE TOTAL CONCENTRATION OF BARIUM SULFATE PRECIPITATES

Group	No.	Total concentration C_0(M)	Particle size (mean) L(mμ)	$C_0 \times L$	Particle shape
A	1	1.00	13	13.0	Amorphous
"	2	0.50	25	12.5	"
"	3	0.25	51	12.7	Sphere
B	4	0.10	251	25.1	Spindle
"	5	0.09	266	23.9	"
"	6	0.08	307	24.5	"
"	7	0.07	317	22.2	"
"	8	0.05	470	23.5	"
C	9	0.04	182	7.3	Cross spindle
"	10	0.03	270	8.1	"
"	11	0.02	466	9.3	"
D	12	0.01	1650	16.5	Diamond (rugged)
E	13	0.001	2030	20.3	Diamond (round)
F	14	0.0003	850	0.255	Rectangle
"	15	0.0001	110	0.011	

I. The Shape of Barium Sulfate Precipitates.

The natural habit of barium sulfate is orthorhombic. But several kinds of different shapes were formed by changing the total concentrations as shown in Table I. The degree of perfection of the crystals was excellent at lower concentration.

At the total concentration of 1.0 M the colorless and transparent jelly was formed immediately after mixing the reagents. This jelly turned white in a few minutes. The precipitates prepared over the range 1.0 to 0.5 M in the total concentrations were jelly or gel. One of the electron micrographs is shown in Photo 1. It seems to be in an amorphous state according to the resolving power of the electron microscope used today. At the total concentration of 0.25 M the precipitate was crystalline, each particle being an irregular sphere as shown in Photo 3.

It seemed that the precipitates prepared in this range (A group in Table I) were affected by acetate and manganous ions. When barium hydroxide saturated in boiling water reacted with 6 N sulfuric acid, beautiful spherical particles, 80 mμ in diameter, were formed.

In the range of the total concentrations, 0.10～0.05 M (B group), the powdery precipitates appeared directly after mixing the reagents and the shape of the precipitated particles was like a spindle with rugged edges as shown in Photo 4. The ratio of major axis to minor axis was almost constant, namely, 10 : 5.5. The number of projections was eight or ten, and the crystal seemed to have grown in the direction of the projections.

In the range of the total concentrations, 0.04～0.02 M (C group), many cross spindle shaped particles were found besides simple spindle shaped ones as shown in Photo 5. The both lengths of the cross spindles were the same and the projections decreased in number.

At the total concentration of 0.01 M (D group) the precipitate appeared a few seconds after mixing the reagents, and it was diamond shaped having rugged edges as shown in Photo 7. The particles were flat and the ratio of thickness to length was 1 : 10.

At the total concentration of 0.001 M (E group) the precipitate formed about ten seconds after mixing the reagents and consisted of large diamond shaped particles having smooth edges and small spindle shaped ones, which were about 1/10 in size of the large ones, as shown in Photo 8.

In the range of the total concentrations below 0.0003 M (F group) the precipitates appeared about one or two minutes after mixing the reagents. The particles sampled before the completion of the crystals were flat and rectangular, consisting of irregular sizes as shown in Photo 10.

II. The Particle Size of Barium Sulfate Precipitates.

The size of particles of freshly precipitated barium sulfate generally increased with the decrease of the total concentration as shown in Table I. In the A, B and C groups, each of which has the same shape, the relation of the total concentration C_0 (M) to the size

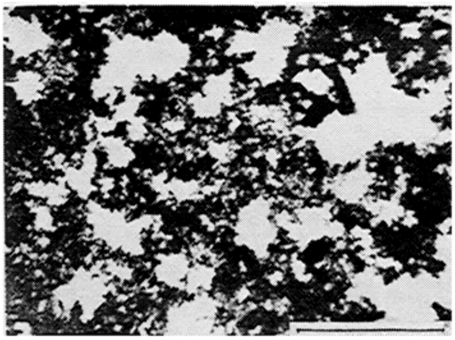

Photo. 1. $C_0=1.0$ M
(×20,000)

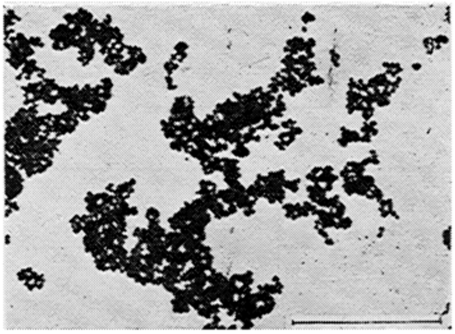

Photo. 2. $C_0=1.0$ M
After 3 months (×20,000)

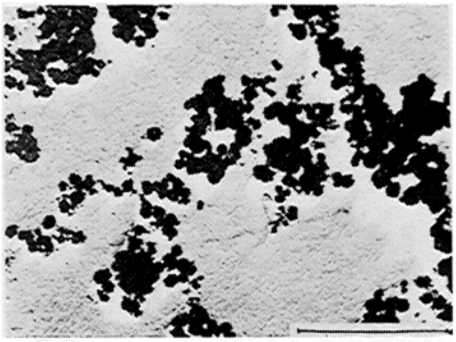

Photo. 3. $C_0=0.25$ M
(Cr-shadowing, ×20,000)

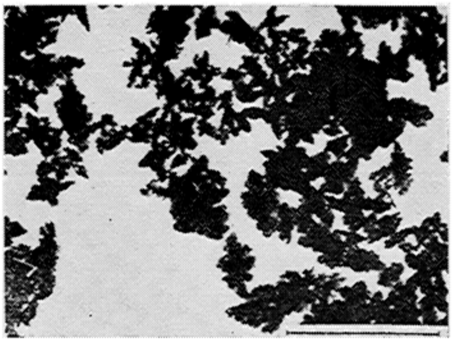

Photo. 4. $C_0=0.10$ M
(×20,000)

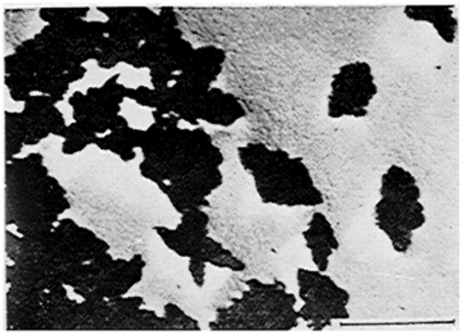

Photo. 5. $C_0=0.02$ M
(Cr-shadowing, ×15,000)

Photo. 6. $C_0=0.02$ M
After 2 years (Cr-shadowing, ×15,000)

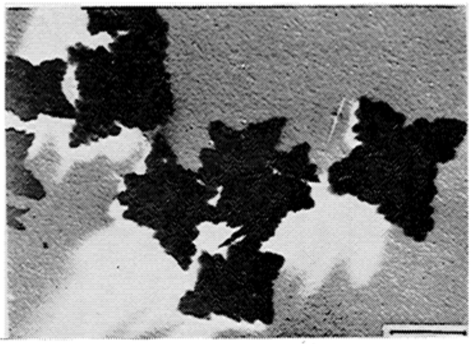

Photo. 7. $C_0=0.01$ M
(Cr-shadowing, ×10,000)

Photo. 8. $C_0=0.001$ M
(×10,000)

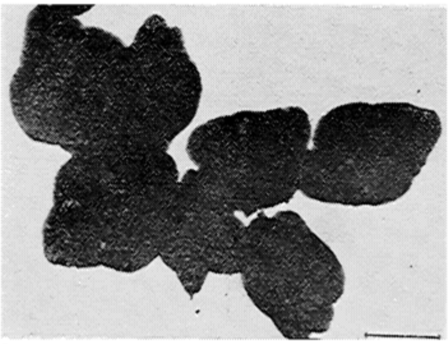

Photo. 9. C_0=0.001 M
After 5 hours (×10,000)

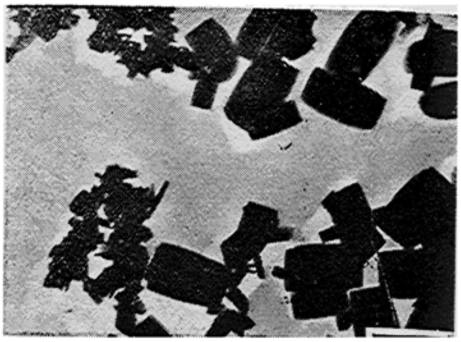

Photo. 10. C_0=0.0003 M
(Cr-shadowing, ×10,000)

Photo. 11. C_0=0.0003 M
After 5 hours (Cr-shadowing, ×10,000)

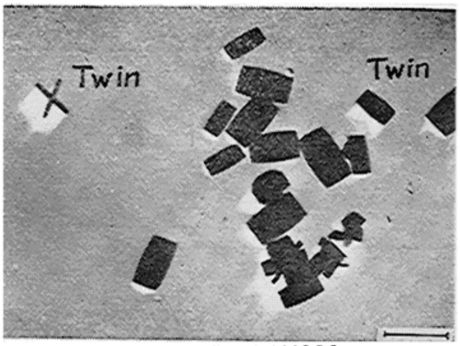

Photo. 12. C_0=0.0003 M
(Cr-shadowing, ×8,000)

Photo. 13.
Precipitation condition
(Cr-shadowing, ×5,000)

Photo. 14.
Crystalline nuclei
(Cr-shadowing, ×5,000)

Photo. 15.
Produced crystals
(Cr-shadowing, ×5,000)

of the precipitated particles L (mμ) is hyperbolic, i.e. $C_0 \times L$=constant, as indicated in Fig. 2. Accordingly, so long as the particles

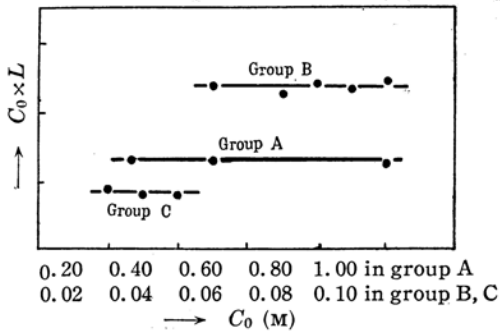

Fig. 2. The relation between the total concentration and the particle size.

of the same shape were concerned, the precipitation law advocated by von Weimarn accorded well with this experiment.

Summary

The shape and the size of barium sulfate precipitate prepared within the range of the total concentrations from 1.0000 to 0.0001 M were observed by an electron microscope. The particles were observed to precipitate in various forms (spherical, spindle, diamond and rectangular) in response to the total concentration of barium sulfate. It was confirmed that the precipitation law advocated by von Weimarn was still substantiated so far as the particles of the same shape were concerned.

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