33. *Morphology of Barium Sulfate Precipitate by Electron Microscope.*

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Various studies have hitherto been made concerning the relation between the condition of precipitation and the particle size of the precipitate. Various theories have also been proposed regarding the mechanism of the growth of crystal. Especially it is of interest to observe the change from gel to crystalline state. Recently the size and the shape of the precipitate of colloidal dimension have become measurable by electron microscope, and some studies on barium sulfate have been reported¹⁾²⁾. An attempt was made in our investigation to employ the electron microscope for the observation of barium sulfate precipitates, both fresh and aged, and to look for direct indication of the mechanism of formation and also the precipitation theory. About five hundred electron micrographs were taken for these purposes. The morphology of the colloidal precipitate of barium sulfate is mainly reported in this paper.

Experimental Procedure.

Barium hydroxide and sulfuric acid were used as the reagents for preparation of barium sulfate precipitate. But at the concentrations higher than 0.2 mol/l barium acetate and manganous sulfate were also used because of their solubilities. For each precipitation equal volumes of these reagents, which were of the same concentration, were simultaneously mixed under stirring in a large test tube at 18°C. A drop of the reaction product was placed on the specimen holder for electron microscope and dried. The samples were photographed, directly or after metallic shadowing, by means of electron microscope (SM-T4).

Experimental Results.

Fifteen kinds of precipitates were prepared varying the range of total concentrations of barium sulfate, 1.0~0.0001 mol/l. Several samples for electron microscopy were prepared from each precipitate; and several electron micrographs were taken for each

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

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

of the samples. The size and the shape of barium sulfate precipitates formed in different total concentration (C_0) are shown collectively in table 1.

Table 1

The relation of the shape and the size to the total concentration of barium sulfate precipitate

Group	No.	Total concentration C_0 (mol/l)	Particle size* L ($m\mu$)	$C_0 \times L$	Particle shape***	Note
A	1	1.00	13	13.0	amorphous	gel changes to crystal by aging
	2	0.50	25	12.5	"	"
	3	0.25	51	12.7	sphere	
B	4	0.10	251	25.1	spindle	no change takes place by aging
	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	no change takes place by aging
	10	0.03	270	8.1	"	"
	11	0.02	466	9.3	"	"
D	12	0.01	1650	16.5	diamond (rugged)	no change takes place by aging
E	13	0.001	2030**	20.3	diamond (round)	
F	14	0.0003	850	0.255	rectangle	
	15	0.0001	110	0.011	"	

* Average length of ca. 200 particles of the precipitate.

** It contained large and small particles. The size is for the larger one.

*** The shape of the fresh precipitate.

1. The Shape of Barium Sulfate Precipitate.

Generally, barium sulfate is orthorhombic crystal, but several kinds of different shapes are formed by changing its total concentration.

The freshly precipitated barium sulfate, which formed in high concentrations (1.0~0.5 mol/l), was gel. Their electron micrographs are shown in photo. 1. And they seem to be in an amorphous state according to the resolving power of the electron microscopes used to-day. At the total concentration of 0.25 mol/l the precipitate was crystalline and each particle was sphere as in photo. 2.

In the range of total concentrations, 0.10~0.05 mol/l (B group

in table 1), the shape of the precipitate was spindle, which had rugged edges as shown in photo. 3. The ratio of major axis to minor axis was almost constant, namely, 10:5.5. The number of projection was eight or ten, and the direction of the projection was about 70° to the major axis.

In the range of total concentrations, 0.04~0.02 mol/l (C group in table 1), many cross spindle shaped particles were found besides simple spindle shaped ones as shown in photo. 4. In this case the length of both spindles were the same and these spindles crossed with about 70° and the projection decreased in number.

In the total concentration of 0.01 mol/l (D group in table 1) the shape of the precipitate was diamond having rugged edges as shown in photo. 5 and 6. They were flat and the ratio of thickness to length was 1/10. This shape was of the same type as the large crystals of barium sulfate having two axes crossed with about 70°, which were prepared according to the usual method, as shown in photo. 12. It would seem probable from this, that the projections of the microcrystals also indicated the direction of branched crystal growth.

In the total concentration of 0.001 mol/l (E group in table 1) the precipitate consisted of large diamond shaped particles having smooth edges and small spindle shaped ones as shown in photo. 7.

In the range of total concentrations below 0.0003 mol/l (F group in table 1) the flat and rectangular particles were formed as shown in photo. 8. Their sizes were not uniform.

2. The Particle Size of Barium Sulfate Precipitate.

The size of particles of freshly precipitated barium sulfate generally increased with the decrease in the total concentration as shown in table 1. In A, B and C groups, which have the same shape, the relation of total concentration (C_0) to the size of precipitated particle (L) is hyperbolic, namely, $C_0 \times L = \text{constant}$, as shown in fig. 1. Accordingly, so long as the crystalline shapes remain the

Fig. 1. The relation between the total concentration and the particle size.

same, the precipitation law advocated by P.P. von Weimarn can be established.

3. *Aging of Barium Sulfate Precipitates.*

Barium sulfate precipitates were kept in mother liquor and they were sampled out for electron microscopy at various intervals of time.

In the range of total concentrations, $1.0 \sim 0.5$ mol/l, the fresh precipitates were like gel, but after several days they settled down and changed to crystalline state and each particle was observed in the micrographs like photo. 2. Further studies are carried on concerning this noteworthy change from amorphous state to that of crystalline with electron micro-diffraction. In the range of total concentrations, $0.1 \sim 0.01$ mol/l, no change of size and shape was observed during aging. In the total concentration of 0.001 mol/l the fresh precipitate composed of two sizes as we have mentioned above; but the smaller one disappeared after several minutes. This phenomenon is probably due to the solubility of the small particles being greater than that of the large ones. In the range of total concentrations below 0.0003 mol/l the fresh precipitates contained particles of every size, but after several minutes they became uniform in size.

4. *Precipitates formed by Other Mixing Processes.*

10 ml of barium hydroxide and sulfuric acid (both 0.0021 mol/l) were added at the same time by pipets into 10 ml of water. After few seconds precipitate appeared. The fresh precipitate contained both large flat elliptical shaped particles and small rectangular and spindle shaped particles as shown in photo. 9. But after several minutes only large elliptical particles were found as shown in photo. 10.

5 ml of barium hydroxide and sulfuric acid (both 0.0021 mol/l) were added simultaneously by pipets into 20 ml of water. Precipitate appeared about one minute later. The crystals were rectangular, having small straight and long curved edges as shown in photo. 11. The ratio of the lengths of the two edges was almost constant, namely, 2:1. From the shadow they were flat and have a semi-circular face. Occasionally twin crystals appeared besides these rectangular single crystals. As marked in photo. 11 two twins were observed from different directions by shadowing. The angle of these crossed crystals was 70° .

Summary.

The shape and the size of barium sulfate precipitates prepared in the range of total concentrations, $1.0 \sim 0.0001$ mol/l, were observed by electron microscope. Shapes were spherical, spindle, diamond and rectangular forms. So long as these shapes remained the same, the precipitation law advocated by P. P. von Weimarn was established. The crystals became perfect by aging without changing their shapes.

Electron Micrographs of Barium Sulfate Precipitates (1~6)

Photo. 1. $C_0=1.0$ M
($\times 20,000$)

Photo. 2. $C_0=0.25$ M
Chromium shadowing ($\times 20,000$)

Photo. 3. $C_0=0.05$ M
Chromium shadowing ($\times 15,000$)

Photo. 4. $C_0=0.03$ M
Chromium shadowing ($\times 15,000$)

Photo. 5. $C_0=0.01$ M
($\times 10,000$)

Photo. 6. $C_0=0.01$ M
Chromium shadowing ($\times 10,000$)

Electron Micrographs of Barium Sulfate Precipitates (7~11)

Photo. 7. $C_0=0.001$ M
($\times 10,000$)

Photo. 8. $C_0=0.0003$ M
Chromium shadowing ($\times 10,000$)

Photo. 9. (H_2O 10 ml)
Before aging ($\times 6,000$)

Photo. 10. (H_2O 10 ml)
After aging ($\times 6,000$)

Photo. 11. (H_2O 20 ml)
Chromium shadowing ($\times 10,000$)

Photo. 12. Optical
Micrograph ($\times 400$)