Formation and Aging of Precipitates. III. Electron Microscopic Studies on Barium Sulfate Precipitates in Aqueous Alcohol

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Introduction

It is interesting to examine the precipitates that are formed not only in water but also in other media. Many investigations have been made about precipitates which are produced in more soluble media than water to study their analytical conditions, and those which are produced in less soluble media to prepare the colloidal solutions. The authors reported about the morphology and aging of barium sulfate precipitates in water previously[1], and also examined the change of the shape and size of the precipitates produced by changing the solubility of barium sulfate. This paper is a report on barium sulfate precipitates produced in aqueous alcohol in the relations of the shape and size, the total concentration, the concentration of alcohol and the solubility of barium sulfate.

Solubility of Barium Sulfate in Aqueous Alcohol

As there have been practically no investigations reported about the solubilities of barium sulfate in aqueous alcohol, the authors have measured them by the electric conductivity method, which will be explained by an example as follows.

The electric conductivity was measured by the method of the Wheatstone bridge. The specific conductivity of distilled water was 2.23×10^{-6} mho and that of the saturated aqueous barium sulfate was 5.1×10^{-6} mho. Then the solubility of barium sulfate in water was calculated as 1.2×10^{-5} M. The specific conductivity of 45% alcohol was 5.3×10^{-6} mho and that of the saturated barium sulfate solution in 45% alcohol was 6.6×10^{-6} mho. Then to 15 ml. of 45% alcohol the saturated aqueous barium sulfate was added drop by drop from a micro-burette and the conductivities of these mixed solutions were measured. After 0.11 ml. of the saturated aqueous barium sulfate was added to the aqueous alcohol, the specific conductivity became 6.6×10^{-6} mho. From these results the solubility of barium sulfate in 45% alcohol was calculated as follows:

$$\frac{1.2\times10^{-5}\times0.11}{15.11}=8\times10^{-8}\ (\mathrm{M})$$

The solubilities of barium sulfate in alcohol of various concentrations were measured by the same method and the results are shown in Table I and Fig. 1. As the concentration of the alcohol in

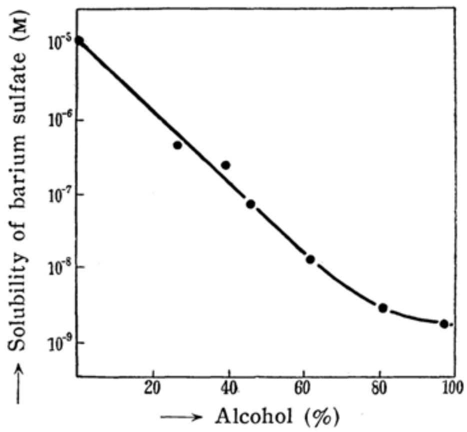

Fig. 1. The solubility of barium sulfate in aqueous alcohol.

which barium sulfate was saturated was somewhat different from that of the alcohol to which the saturated aqueous barium sulfate was added, the percentage of alcohol shown in Table I contains some errors, but they are negligible.

TABLE I

SOLUBILITIES OF BARIUM SULFATE IN AQUEOUS ALCOHOL

Concentration of Alcohol %	Solubility of Barium Sulfate M
0	1.2×10^{-5}
30	3×10^{-6}
39	4×10^{-7}
45	8×10^{-8}
62	2×10^{-8}
80	4×10^{-9}
99	2×10^{-9}

Morphology of Barium Sulfate Precipitates in Aqueous Alcohol

The barium sulfate precipitates in aqueous alcohol were prepared as follows. To 10 ml. of alcohol of a certain concentration were added simultaneously 5 ml. of barium hydroxide solution and sulfuric acid which were of the same concentration. The reaction temperature was 18°C. The precipitates produced were observed by an electron microscope.

The conditions of the precipitation and the properties of the precipitated particles are collectively

1) E. Suito and K. Takiyama, This Bulletin, 27, 121, 123 (1954).

shown in Table II. A, B and C groups in Table II are the cases in which the total concentrations of barium sulfate were kept constant and the concentrations of alcohol were changed. In these groups the precipitates produced in water, that is 0 % alcohol, are to be compared with the condition of the precipitation reported previously[1]. In D group the concentration of alcohol was kept definite; that is to say, the solubility of barium sulfate was definite, and the total concentration of barium sulfate was changed.

At the total concentration of 0.05 M (A group) the particles precipitated in water were spindle-shaped, as shown in Photo 1, but in aqueous alcohol the shapes of the particles were thin hexagonal plates, and their size became smaller with the increase of the concentration of alcohol as shown in Photos 2, 3 and 4. The hexagonal particles of barium sulfate were found only under these conditions and were not found in the precipitates formed in water nor at the other total concentrations in aqueous alcohol. As the particles of the specimen of No. 4 were very small, namely, the size was below 10 mμ, the shape was not clear.

At the other total concentrations the particles precipitated in the aqueous alcohol were practically diamond-shaped and their size became smaller with the increasing percentage of alcohol in the aqueous alcohol as shown in Table II.

change at the definite solubility was similar to the change of the size of the precipitated particles produced in water medium[1].

At the total concentrations higher than 0.05 M the size of the precipitated particles became extremely small with the addition of alcohol. None of the precipitated particles produced in the aqueous alcohol have changed their shape and size for 2 years on standing in the media.

In these precipitates the similar shaped particles were formed after the same induced period. Namely, the precipitates of diamond shape began to deposit immediately after mixing the reagents and completed their crystallization after 10 to 20 seconds. The precipitates of spindle shape were completly formed directly after mixing the reagents. Such phenomena have been observed both in cases of water and aqueous alcohol media. It seems that the mechanism of the growth of the crystals was similar, when the induced period of the formation of the crystals was identical.

Identification of Crystals by the Electron Micro-Diffraction Method

The electron micro-diffraction method by means of the three stage electron microscope, SM-C3, was applied to analyze the crystal structure of the precipitated particles mentioned above. A few examples of the electron diffraction patterns obtained are shown in Photos 9 (a), (b) and (c).

TABLE II

THE PROPERTIES OF BARIUM SULFATE PRECIPITATES IN AQUEOUS ALCOHOL

Group	No.	Total concentration C_0 (M)	Alcohol concentration (%)	Solubility S (M)	Particle size (mean) (mμ)	Particle shape
A	1	5×10^{-2}	0	1×10^{-5}	470	Spindle
"	2	"	2.5	9×10^{-6}	90	Thin hexagonal plate
"	3	"	10	5×10^{-6}	70	"
"	4	"	50	7×10^{-8}	<10	——
B	5	5×10^{-3}	0	1×10^{-5}	3200	Diamond (rugged)
"	6	"	2.5	9×10^{-6}	3000	"
"	7	"	5	8×10^{-6}	2500	"
"	8	"	7.5	7×10^{-6}	2000	"
"	9	"	10	5×10^{-6}	1100	Diamond (smooth)
"	10	"	15	3×10^{-6}	400	"
"	11	"	50	7×10^{-8}	<10	——
C	12	5×10^{-4}	0	1×10^{-5}	3500	Ellipse
"	13	"	2.5	9×10^{-6}	3100	Diamond (rugged)
"	14	"	10	5×10^{-6}	3000	Diamond (smooth)
"	15	"	25	6×10^{-7}	2000	Spindle (thin rugged)
"	16	"	35	3×10^{-7}	70	Sphere (rugged)
"	17	"	50	7×10^{-8}	<10	——
D	18	5×10^{-2}	10	5×10^{-6}	70	Hexagon
"	19	4×10^{-2}	"	"	710	Diamond (rugged)
"	20	3×10^{-2}	"	"	820	"
"	21	1×10^{-2}	"	"	830	"
"	22	5×10^{-3}	"	"	1600	"
"	23	5×10^{-4}	"	"	3000	Diamond (smooth)

In D group the precipitated particles became larger with the decreasing total concentration of m sulfate as shown in Photos 5~8. This

Photo 9 (a) obtained from the diamond-shaped particles shown in Photo 7 (No. 21) is of coarse Debye-Scherrer rings, because there are not

Electron micrographs of various barium sulfate precipitates

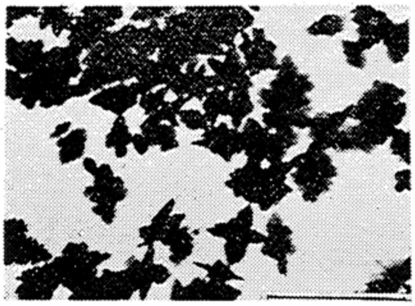

Photo. 1. No. 1. $C_0=5\times10^{-2}$ M, $S=1\times10^{-5}$ M ($\times$20,000)

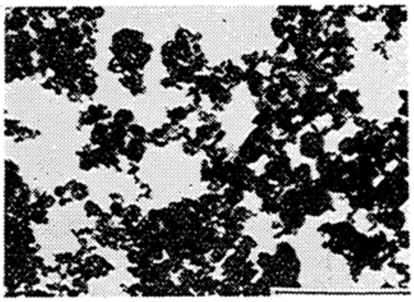

Photo. 2. No. 2. $C_0=5\times10^{-2}$ M, $S=9\times10^{-6}$ M ($\times$20,000)

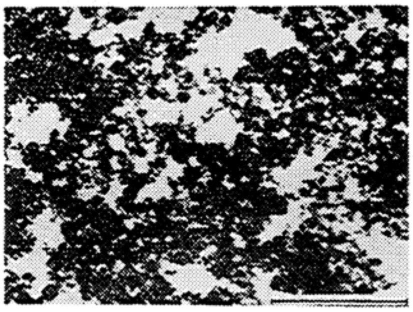

Photo. 3. No. 3. $C_0=5\times10^{-2}$ M, $S=5\times10^{-6}$ M ($\times$20,000)

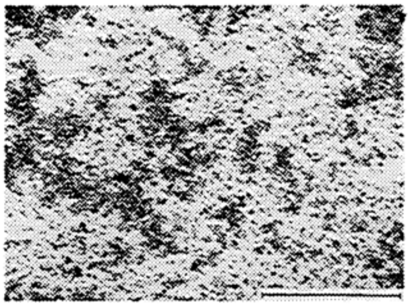

Photo. 4. No. 4. $C_0=5\times10^{-2}$ M, $S=7\times10^{-8}$ M ($\times$20,000)

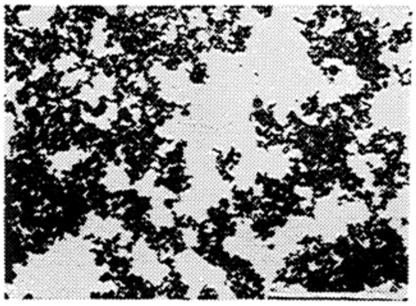

Photo. 5. No. 18. $C_0=5\times10^{-2}$ M, $S=5\times10^{-6}$ M ($\times$20,000)

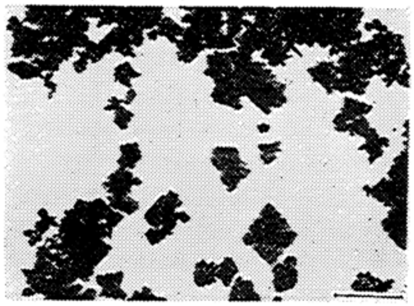

Photo. 6. No. 20. $C_0=3\times10^{-2}$ M, $S=5\times10^{-6}$ M ($\times$10,000)

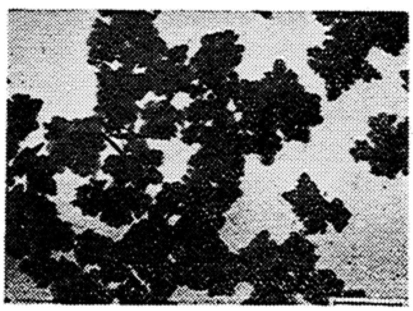

Photo. 7. No. 21. $C_0=1\times10^{-2}$ M, $S=5\times10^{-6}$ M ($\times$10,000)

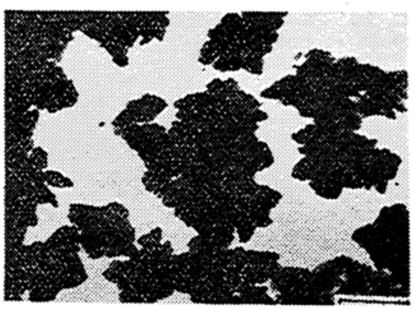

Photo. 8. No. 22. $C_0=5\times10^{-4}$ M, $S=5\times10^{-6}$ M ($\times$10,000)

(a)

(b)

(c)

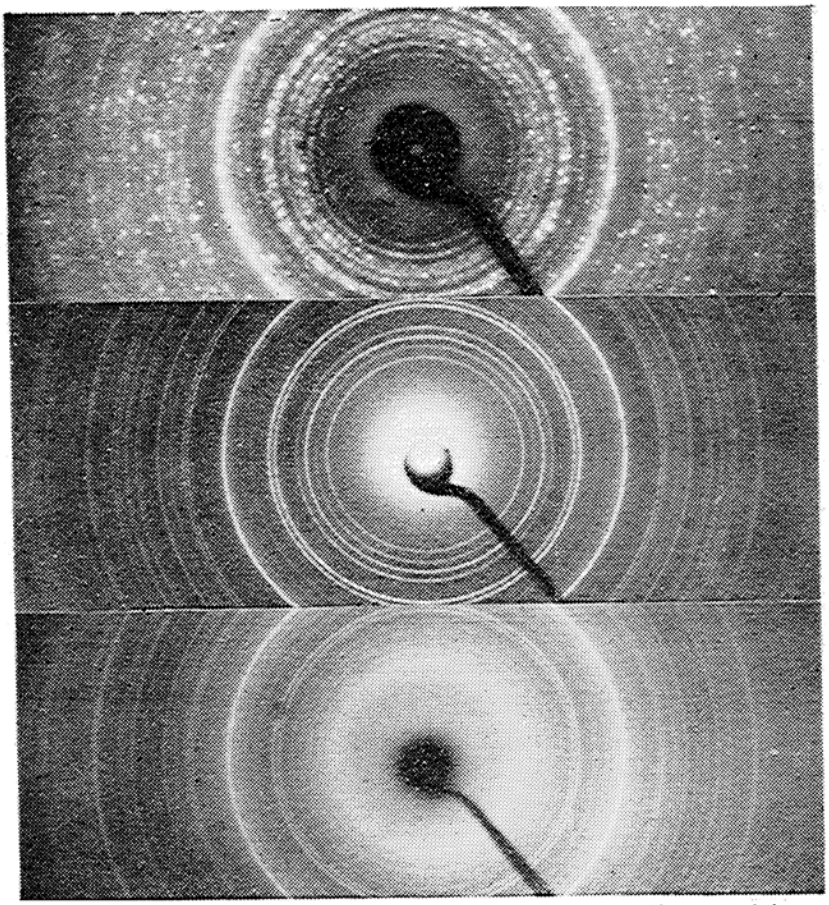

Photo. 9. Electron diffraction patterns of various barium sulfate precipitates.
(a) diamond type (No. 21)
(b) hexagonal type (No. 3)
(c) small particle (No. 4)

many crystalline particles in the selected area (5 μ) of the electron microscope. The patterns obtained from the particles of the hexagonal plates and the small particles shown in Photo 3 (No. 3) and Photo 4 (No. 4) were obtained by the ordinary electron diffraction technique for many crystalline particles, and are very fine as shown in Photos 9 (b) and (c). It is interesting that the pattern obtained from the small particles which are observed as "amorphous" by the electron microscope (<10 mμ) is very sharp, and the particles are obviously crystalline.

The arrangements of the rings of every diffraction pattern are the same as observed with barium sulfate crystals obtained by X-ray diffraction as shown in Fig. 2.

Differences in the intensity of each line in the electron and X-ray diffraction diagrams intimate the orientation of the flat particles on the film of the specimen holder of the electron microscope, though the difference in technique between the electron and X-ray diffractions have to be taken into consideration.

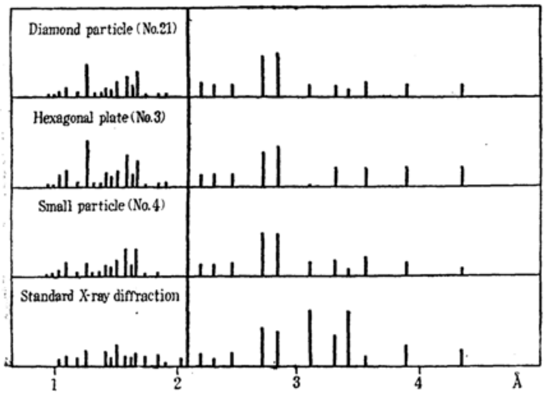

Fig. 2. Electron diffraction diagrams of various barium sulfate precipitates.

Summary

1. The solubilities of barium sulfate in aqueous alcohol were measured.

2. The barium sulfate particles precipitated in aqueous alcohol became smaller with the increasing concentration of alcohol; namely, with the decreasing solubility of barium sulfate.

3. In the case of the aqueous alcohol of the certain percentage (for a definite solubility of barium sulfate) the precipitated particles became larger with the decreasing total concentration of barium sulfate.

4. The barium sulfate precipitates prepared in the aqueous alcohol were practically diamond shaped; and spindle, hexagonal and sphere particles were also found. The shape of the precipitated particles seemed to depend on the induced period of the precipitation.

5. The electron micro-diffraction method was applied to analyze the crystal structure and, of course, the patterns obtained from various types of crystals agreed with those of barium sulfate.

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