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Note

Monodisperse Sols of Barium Sulfate. III. Electron-Microscopic Study of Internal Structure of Particles

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The internal structure of monodisperse barium sulfate particles precipitated from homogeneous solution was studied. The elliptically shaped particles were examined by a sufficiently penetrating electron beam (acceleration voltage 80 kV) and by the ultramicrotomic technique. The particles did not appear compact but had a sponge-like structure with an average pore size of 30 Å. The present results are supporting the assumption of barium sulfate particles being possibly formed by an aggregation mechanism predominantly over the direct diffusion growth of primary particles.

In previous papers[1,2] we reported on our results in preparing monodisperse particles of barium sulfate by the methods of homogeneous precipitation of Takiyama[3] and Andreasen[4]. Some morphological features of barium sulfate systems, prepared under different experimental conditions, such as the variation of concentration of reactants, temperature, and addition of foreign substances, were also described. As the study of macromorphological characteristics of barium sulfate particles allowed certain conclusions concerning the mechanism of nucleation and particle growth, by indicating a possible particle formation by aggregation processes[2], it was of interest to study the internal or micromorphological structure of barium sulfate particles.

Several authors have investigated the nature of the internal structure of barium sulfate precipitates by means of the methods of X-ray diffraction[5,6], electron microdiffraction[7–9] and electron microscopy[10,11]. Two papers[9,11] report on precipitates prepared by the method of homogeneous precipitation, while all other work was devoted to precipitates obtained by direct mixing of reagents or by diffusion mixing of ions.

In the present work we used the conventional method of transmission electron microscopy, but an attempt was also made to apply the technique of ultrathin sections in studying the internal structure of barium sulfate particles. This technique, customary in studying biological material and very useful in giving information on the microstructure of particles and cellular material, has rarely been used in investigations on the morphological properties of inorganic precipitates. As far as we know, only two papers have been published on the studies of ultrathin sections of β-ferric oxide monohydrate[12] and noncrystalline calcium phosphate[13].

Fresh monodisperse sols of barium sulfate (systems S-45 and S-58) were prepared as described in the first paper of this series[1]. A stable sol (system S-30) was obtained by dispersion of precipitated barium sulfate particles in an aqueous medium containing 0.05% of Triton X-100. The details of the whole experimental procedure were given previously[1]. In the moment of the performance of the present experiments this sol was about two years and six months old.

The electron microscope observations were made using a Siemens Elmiskop I, at magnification of 20,000 : 1 and 40,000 : 1. A high voltage electron beam (acceleration voltage 80 kV) allowed the barium sulfate particles to be penetrated sufficiently to show their internal structure.

The specimens of fresh sols of barium sulfate were prepared as described by Takiyama[3], while the ultrathin sections of barium sulfate particles were obtained in the following way: The original sol was centrifuged and the sediment was mixed with a small amount of a 1.5—2% aqueous solution of agar. Small pieces of the jelly mass were dehydrated by successive changes of acetone. The material treated in such a way was embedded into an Araldite mixture by the method described by Parsons[14]. The ultrathin sections of particles were prepared by a LKB ultramicrotome (Model Ultrotome LKB, 4801 A). A glass knife was used for cutting ultrathin sections 30 to 50 mμ thick.

The measurements of particle size were made directly from electron micrographs as before[1].

Figs. 1 and 2 show the barium sulfate particles precipitated by Takiyama's method[1]. The particles are of an approximately ellipsoidal shape and are remarkably monodisperse.

System S-45, shown in Figs. 1a and 1b, was taken for electron micrography ten minutes after the starting of the reaction. The arithmetic mean lengths of the long and short axes (Fig. 1a) are $\overline{D}_c = (270 \pm 12)$ mμ and $\overline{D}_b = (123 \pm 6)$ mμ, respectively. The present micrograph is direct evidence that barium sulfate particles have not a compact but a sponge-like internal structure. This is more evident from the detail in Fig. 1a where two particles are photographed at greater magnification. The average size of pores was (28 ± 4) Å. This value is fairly close to that reported by Dawson and Mc Gaffney[10] who, investigating stable films of colloidal barium sulfate, found a mean pore diameter of about 35 Å.

Fig. 1b shows particles of the same system, but the micrograph was taken after several seconds of intensive irradiation by the electron beam. During the irradiation it was possible to observe evaporation effects and partial deterioration of particle structure on the edges of the particle. The evaporation effect was presumably a result of the presence of mother liquor included in the particle pores. This sensitivity of barium sulfate particles to structure changes suggests that great care has to be taken when electron microscopic methods are used for studying precipitates.

Fig. 2 shows typical shapes of monodisperse barium sulfate particles (system S-58) 45 minutes after the starting of the reaction. Their average size was: $\overline{D}_c = (488 \pm 25)$ mμ and $\overline{D}_b = (192 \pm 15)$ mμ. The internal structure of these particles was also sponge-like and similar to the one presented in Fig. 1a. However, the particles were thicker, so that the sponge-like structure was clearly visible only on the tapered ends (detail I in Fig. 2 which shows one particle at magnification 100,000 : 1). The average size of pores was (30 ± 5) Å, which is close to the value observed for system S-45.

Many examples of so-called X- and Y-shaped twins (Fig. 2, solid and clear arrow, respectively) and sometimes of star-shaped particles (picture not

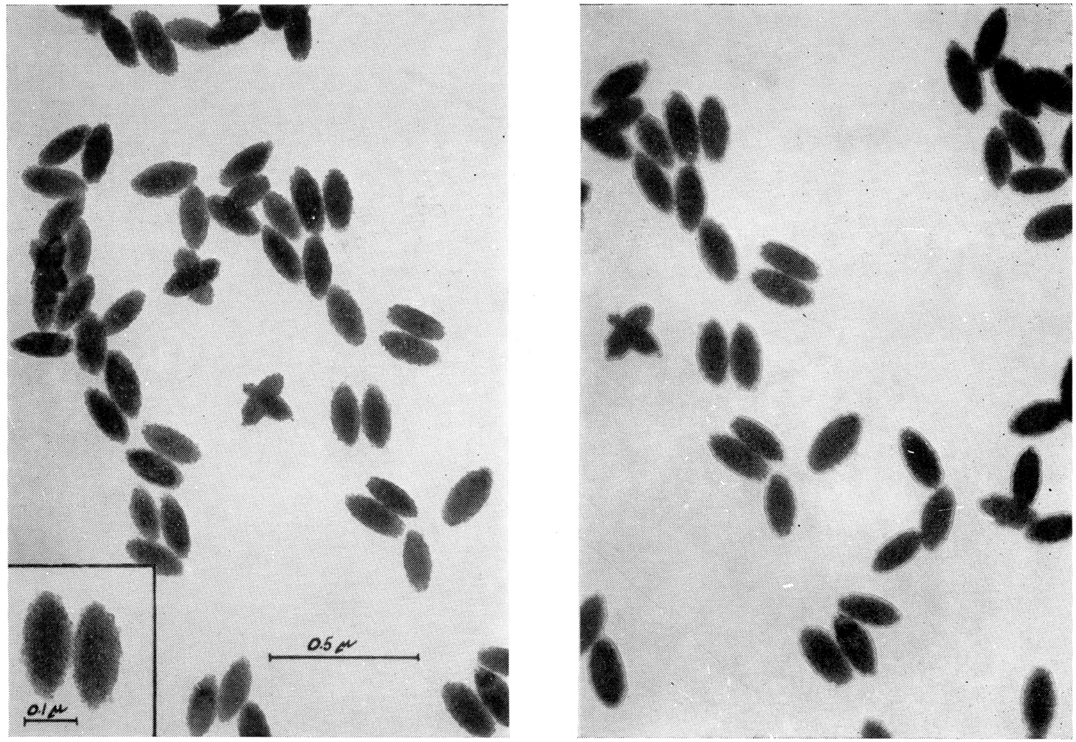

Fig. 1.

(a) Electron micrograph of unsectioned barium sulfate particles (System S-45) formed 10 minutes after the starting of the reaction. Magnification: 60,000 : 1. Detail shows particles at magnification 100,000 : 1;

(b) the same sample after several seconds of intensive irradiation by the electron beam.

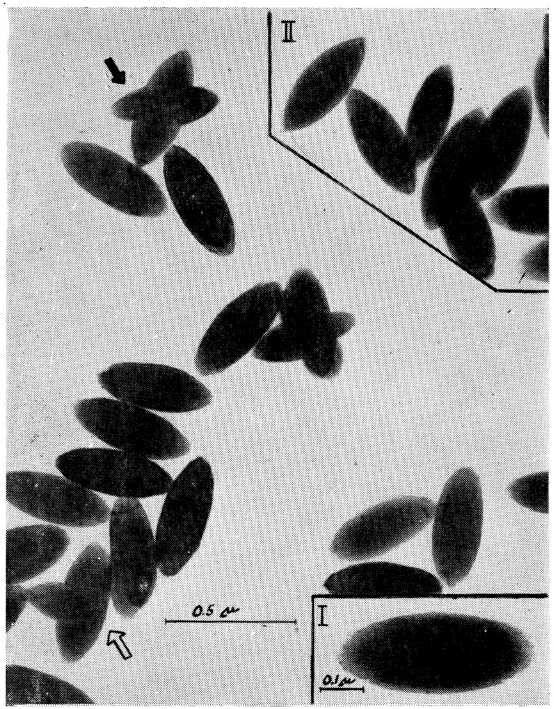

Fig. 2. Electron micrograph of unsectioned barium sulfate particles (System S-58) formed 45 minutes after the starting of the reaction. Magnification: 60,000 : 1. Detail I shows a particle at magnification 100,000 :1. Detail II shows three overlapped particles

Fig. 3. Electron micrograph of typical sections of barium sulfate particles (System S-30) at magnification 160,000 : 1.

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shown) could be observed in this system. In detail II, Fig. 2, three overlapped particles can be observed showing the capability of the high-voltage electron microscopy in differentiating overlapping from true twinning. By measuring the twinning angle from the micrographs it was possible to distinguish two groups of angles: the first group ranging from 65° to 73° and the second group from 80° to 88°. The experimental error of these data is rather high, as seen from the appreciable range of angles. However, it is difficult to obtain more accurate data owing to differences in orientation of the twins with respect to the plane of the specimen membrane. The differences in twinning angles are possibly the result of the particles growing together in different profiles, as discussed previously[2]. The values of twinning angles around 70° were normally observed with particles grown together in the same planes (c—b-plane with c—b-plane, or c—a-plane with c—a-plane), whereas twinning angles of about 85° seemed to be afflicted with twins grown together with mixed planes (c—b-plane with c—a-plane).

Fig. 3 shows a typical example of ultrathin sections of barium sulfate particles. In this particular case, the particles belonged to system S-30, being more than two years old at the moment of sectioning. The particles were cut in all possible profiles, with the mean lengths of axes $\overline{D}_c = (200 \pm 10)$ mμ and $\overline{D}_b = (97 \pm 8)$ mμ. Two years ago[1] the values were $\overline{D}_c = (195 \pm 11)$ mμ and $\overline{D}_b = (95 \pm 7)$ mμ, showing a remarkable stability of particles over a long period. The sponge-like structure is very clearly observable. The average pore size was (31 ± 4) Å, which is similar to the values observed for systems S-45 and S-58. Consequently, the average pore size does not vary essentially with the particle size. The sections illustrate the internal particle structure with no indication of some preferential orientiation of structural elements within the particles. This finding is different from the one relating to structures encountered in other systems, such as the colloidal β-ferric oxide monohydrate system[12].

From the results of previous precipitation experiments[2] it was assumed that barium sulfate particles were possibly formed by aggregation and that this mechanism predominated over the direct diffusion growth of primary particles. The present results seem to support this assumption, but final conclusions may be possible only after collecting additional experimental data on X-ray and electron diffraction examinations, as well as using other methods which directly or indirectly give information on the microstructure of particles.

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IZVOD

Monodisperzni solovi barium-sulfata. III. Elektronsko-mikroskopska studija unutarnje strukture čestica

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Pomoću elektronskoga mikroskopa istraživana je unutarnja ili mikromorfološka struktura monodisperznih čestica barium-sulfata priređenih metodom homogene precipitacije. Čestice su bile približno elipsoidnog oblika veličine od 200 do 490 mμ za dužu os, odnosno od 97 do 190 mμ za kraću os. Upotrebom dovoljno probojnog elektronskog snopa (napetost ubrzanja 80 kV) i primjenom ultramikrotomske tehnike bilo je moguće promatrati unutarnju strukturu čestica. Utvrđeno je da čestice nisu kompaktne, već imaju poroznu unutarnju strukturu. Prosječna veličina pora iznosi oko 30 Å i ne varira bitno s veličinom čestica. Na temelju iznesenih rezultata može se pretpostaviti, u skladu sa prethodnim nalazima, da čestice barium-sulfata pretežno imaju strukturu nastalu agregacijom primarnih čestica.

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