Monodisperse Sols of Barium Sulfate. II. Morphological Characteristics, Aging and Dissolution of Particles

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A morphological study is made of barium sulfate particles precipitated from a homogeneous solution at 25^0 and 50^0 C in the presence of various foreign substances and without them. As foreign substances several types of compounds were chosen: a nonionic detergent *(Triton X-100)*, an anionic detergent *(Aerosol MA)*, and complexing agents (citrate and EDTA). The particles were studied by electron microscopy. In all cases anisotropic particles were formed with more or less defined structures, and most of the systems were monodisperse. The appearance of twins, grown together in different profile planes, was observed. The aging of particles in mother liquor was studied, as well as the dissolution of particles in water. On the basis of particle size data, the morphological characteristics of particles, and their aging and dissolution, the mechanisms of particle formation were discussed. The influence of foreign substances is discussed in terms of their chemical properties. It is suggested that particles of barium sulfate are predominantly formed by aggregation of primary particles, whilst pure diffusion growth is encountered only under restricted conditions.

INTRODUCTION

In the first paper of this series[1] we reported on the preparation of stable monodisperse sols of barium sulfate by the method of precipitation from a homogeneous solution. Although homogeneous precipitation was often applied to the precipitation of barium sulfate[2-7], there are few systematic investigations on the morphology and properties of the particles formed.

Extensive morphological studies of the homogeneously precipitated barium sulfate are those of Suito and Takiyama.[6,8-10]. They studied the formation, aging and dissolution of particles by the methods of electron microscopy and electron diffraction. However, these experiments were performed at equal initial concentrations of both barium and sulfate ions, and without addition of foreign substances, except those present as reactants.

Since the general knowledge of the morphology and the mechanism of formation of barium sulfate particles by homogeneous precipitation appears to be incomplete, we believe that a more elaborated study of particles prepared under different conditions (variation of concentration, temperature, and ad-

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dition of foreign substances), as well as a study of aging and dissolution of particles, is desirable.

The particles described in this paper are prepared exclusively by using a less known reaction of the generation of sulfate ions by oxidation of thio-sulfate ions by hydrogen peroxide:

$$2\,S_2O_3^{2-} + 4\,H_2O_2 \rightarrow SO_4^{2-} + S_3O_6^{2-} + 4\,H_2O.$$

This is the reaction applied by Andreasen[2] for studying the precipitation of barium sulfate. This reaction appeared to be very suitable for our type of work. Previous experience[1,8] has shown that barium sulfate tends to form mono-dispersed precipitates pronouncedly in the concentration region from 10^{-2} to 10^{-3} M. In that concentration region and at room temperature the Andreasen reaction is fast enough to produce almost completely formed barium sulfate particles after a few minutes, as proved by preliminary experiments, allowing experimentation without errors from the irregular mixing of solutions.

The size and shape of particles was determined by electron microscopic techniques (direct observation of samples and the technique of shadow-casting).

<div align="center">EXPERIMENTAL</div>

Materials

Standard solutions of barium chloride, sodium thiosulfate, hydrogen peroxide and sodium ethylenediaminetetraacetate (EDTA) were prepared as described earlier[1]. In order to prevent some possible effects observed with freshly prepared barium chloride solutions[11,12], only aged solutions were used.

Solutions of the nonionic detergent *Triton X-100* (octylphenoxyethanol, obtained by courtesy of Rohm & Haas Co., Philadelphia, Pa., U. S. A.) and of the anionic detergent *Aerosol MA* (sodium dihexylsulfosuccinate, obtained by courtesy of American Cyanamid Co., Wayne, New Jersey, U. S. A.) were prepared from original samples by dilution with redistilled water and kept in dark at room temperature.

Electron Microscopy

The shape and size of barium sulfate particles were observed by a Trüb, Täuber & Co. electron microscope (Model KM-4). Some samples having very small particles were observed by a Siemens electron microscope (Model Elmiskop I) having a higher resolution.

The samples were prepared by dropping the suspension onto a copper grid with a *Mowital* membrane, and immediately removing the liquid phase from the grid by filter paper. This simple procedure proved satisfactory, except in some cases of high concentrations of the detergent and EDTA ($> 1^0/0$ *Triton X-100*, > 0.1 M EDTA). In these cases a 10-minute dialysis through the *Mowital* membrane against water was successful.

Shadow-casting was performed by vacuum evaporation of palladium at an angle of 30^0.

The particle size was measured as before[1]. The approximate particle height was determined from shadowed samples by measuring the shadow length[13].

Preparation of Barium Sulfate Systems

The barium sulfate systems were prepared by mixing solutions A and B containing reagents of an appropriate concentration. Solution A consisted of barium chloride, sodium thiosulfate, and a foreign substance (if added) dissolved in redistilled water. Solution B contained hydrogen peroxide diluted with redistilled water. Both solutions were kept before mixing in a water bath at constant temperature ($\pm 0.1^0$) for at least ten minutes. The mixing was performed by pouring solution B into solution A and a subsequent thorough mixing of the whole system for 20—25 seconds.

No special precautions were taken to clean solutions from dust and mechanical impurities, except when the effect of filtration on the particle size was investigated. In that case all solutions and glassware were cleaned as described previously[1].

Aging and Dissolution of Particles

The systems were aged by keeping at room temperature in a place isolated from greater temperature oscillations.

Dissolution in water was performed by immerging the grids with previously dried samples into freshly redistilled water for a given period. Normally only samples previously not taken for observation in the electron microscope were used, except when the irradiation effects of the electron beam were studied.

RESULTS

The size of barium sulfate particles can conveniently be characterized by three mutually perpendicular axes a, b, and c. These axes should not be mistaken for crystallographic axes of the orthorhombic system that barium sulfate belongs to. In our notation axis c is always the longest one, axis b normally lies in the plane of the micrograph, and axis a is, as a rule, not accessible to direct observation and measurement, lying in most cases perpendicularly to the plane of the micrograph. The lengths of these axes are given by symbols D_c, D_b, and D_a, respectively. D_a can be estimated from shadowed samples. In some cases, the *Mowital* membrane cracked under the weight of the particle or under the influence of the electron beam, and we could observe and even take a photograph of particles in their other profile. If the particle was turned by 90^0, D_a could be estimated with satisfactory precision. Particles sometimes happened to be situated in such a way as to have their c-a-profile or b-a-profile parallel to the micrograph plane.

Formation of Barium Sulfate Particles

In all systems the concentration of sodium thiosulfate (4.4×10^{-3} M) and hydrogen peroxide ($4.8^0/\text{o}$) was kept constant. It follows from the reaction equation that the final concentration of sulfate ions amounts to 2.2×10^{-3} M. The solubilities of barium thiosulfate and polythionates are a great deal larger than the solubility of barium sulfate[14], thus no or only a very slight interaction of these ions during particle formation can be expected. The concentration of hydrogen peroxide was chosen as the most suitable one, knowing from experience that the reaction rate, reflected in the particle size, does not change appreciably in a concentration range from 1.2 to $4.8^0/\text{o}$.

a) Precipitates Formed Without the Presence of Foreign Substances

Fig. 1 shows typical shapes of the particles of these »pure« systems obtained at 25.0^0 C by changing the concentration of barium chloride. Particles of the system *A1* are of the familiar rectangular shape often observed at concentrations $(1 — 5) \times 10^{-4}$ M of barium ions[15,16]. These particles are spindle--shaped in profile (see Fig. 4a). System *A3* has nearly elliptical particles. Their c-a-profile can be seen on Fig. 1b, detail II. Actually, this profile corresponds to the same particles shown in detail I of the same figure, photographed immediately before the cracking of the membrane. Two types of twins could be observed in this preparation. Twin 1 is formed by the particles grown together in their c-b-planes, whereas Twin 2 is formed by the particles grown together in their c-a-planes. Detail II is a direct evidence of Twin 1 being a grown-in structure and not a picture of two overlapped particles. The arrow indicates

TABLE I

Number Density of Barium Sulfate Particles, N, Precipitated Without the Presence of Foreign Substances

Final concentration of sulfate ions: 2.2×10^{-3} M; temperature: 25.0° C; age: 10 minutes. $\overline{D}_c$, $\overline{D}_b$ — arithmetic mean lengths of axes c and b, respectively; D_a — length of axis a; $s_r(D_c)$, $s_r(D_b)$ — relative standard deviations of axes c and b, respectively.

System	c BaCl$_2$ (moles/l.)	$\overline{D}_c$ (mμ)	$s_r(D_c)$ (%)	$\overline{D}_b$ (mμ)	$s_r(D_b)$ (%)	D_a (mμ)	s	v (μ)³	G (g./ml.)	N (ml⁻¹) $\times 10^{-6}$
A1	1×10^{-4}	1430	12.0	1160	14.7	480	47	0.625	2.33×10^{-5}	8.3
A3	1×10^{-3}	3860	4.9	2480	8.1	1000	150	5.01	2.33×10^{-4}	10.3
A4	2×10^{-3}	6500—11000	—	4500—7000	—	2100—3500	210	32—141	4.67×10^{-4}	3.2—0.74
A7	4.4×10^{-3}	4060	3.4	2590	4.2	1630	310	8.98	5.12×10^{-4}	12.6
A8	6×10^{-3}	4860	4.5	2940	5.4	1950	360	14.6	5.12×10^{-4}	7.8

a part of the second branch of Twin 1. Particles of the system $A4$ are big and of a rather irregular shape. This is a property of precipitates formed at equimolar concentrations of barium and sulfate ions (2.2×10^{-3} M). The particles are polydisperse, but not plates, as shown in Fig. 2, where Particle 2 in Fig. 2b is a profile picture of the same particle in Fig. 2a. Fig. 2c shows a typical twin found among the particles of that system. The particles are grown together with mixed axes (c-b-plane with c-a-plane). Particles of the systems $A7$ and $A8$ are again of uniform size. The arrow in Fig. 1e indicates a particle seen in the c-a-profile, and there are two twins (1 and 2) of the mixed-axes type. And finally, particles of $A9$ show a very complicated and irregular shape, being heterodisperse, rather thin, but not fully plate-like. These structures are very brittle, and we frequently observed small chips of particles in the samples.

Taking samples of these systems 5, 10 and 60 minutes after the mixing, we could see no significant difference in their size and shape.

From the particle size data we can estimate the number density of particles, N. In Table I data on D_c, D_b, and D_a are given. These data show that, excepting system $A4$, D_c and D_b values are reliable and that the relative standard deviations indicate a rather high degree of monodispersity. Since system $A4$ is polydispered, only ranges of values are indicated. Values of D_a are estimated from c-a-profiles and are affected by a greater experimental error than D_c and D_b. Here s is the supersaturation ratio, and G is the mass of the precipitated particles per unit volume calculated from c_{BaCl_2}, assuming in the first approximation that practically all of the barium sulfate is precipitated (this produces an error of the order of 10% for $A1$, and of the order of 1% for other systems).

The volume v of a single particle of system $A1$ was calculated by $\dfrac{\pi}{4}D_cD_bD_a$, assuming that particles are elliptic cylinders. Particles of other systems were assumed to be triaxial ellipsoids with a volume $\dfrac{\pi}{6}D_cD_bD_a$. The number density is then obtained from

$$N = G/v \, \varrho,$$

where ϱ is the particle density. Taking $\varrho = 4.5$ g. cm^{-3}. for the approximate density of barium sulfate[17] and the solubility of barium sulfate[14] at 25° C 2.23×10^{-3} g. per liter of saturated solution, data on s and N are obtained.

The error of N is rather big, owing to the approximations made, especially concerning the particle shape. However, from the particle size data the error can be estimated to amount to about 12% for $A7$ and $A8$, to about 18% for $A3$, and to about 33% for $A1$. These figures show that N can be ranged into two distinct groups: system $A4$ having $N \sim 10^6$ ml^{-1} and other systems having $N \sim 10^7$ ml^{-1}.

Experiments at elevated temperature (50.0° C) show more complicated aggregated structures. As an example we can take a particle, shown in Fig 2d, corresponding in concentration to system $A4$. These particles are very thin, but not plate-like, as seen in the detail of Fig. 2d showing the particle in profile.

b) *Precipitates Formed in the Presence of Foreign Substances*

Addition of a nonionic detergent (*Triton X-100*) to the precipitation system causes changes in the particle size. It was generally found that the increasing

concentration of *Triton X-100* from 0.001% ($\sim 1.6 \times 10^{-5}$ *M*) to 1% ($\sim 8 \times 10^{-3}$ *M*) causes a decrease in the particle size. Fig. 3 shows some characteristic micrographs of these systems (series *B*). The particles are remarkably monodisperse and are predominantly elliptically shaped. A detailed examination has shown that only the *c-b*-profile is elliptical (Fig. 3c, Particle 1), the *c-a*-profile having the shape of a spindle (Particle 2). The same is evident by observing shadowed particles having a different shadow length (details of Fig. 3c). At higher concentrations of *Triton X-100* the particle size does not decrease any more, but new, small particles are formed (Fig. 3c).

TABLE II

The Size of Barium Sulfate Particles (in mµ) *Precipitated in the Presence of Triton X-100*

Final concentration of sulfate ions: 2.2×10^{-3} *M*; temperature: 25.0⁰ C; age: 10 minutes. Sign (') denotes filtered systems. $\overline{D}_c$; $\overline{D}_b$ — arithmetic mean lengths of axes *c* and *b*, respectively; $s_r(D_c)$, $s_r(D_b)$ — corresponding relative standard deviations.

System	$c_{BaCl_2} \times 10^3$ (moles/l.)	c_{Triton} (%)	$\overline{D}_c$ (mµ)	$s_r(D_c)$ (%)	$\overline{D}_b$ (mµ)	$s_r(D_b)$ (%)
B17	2.0	0.01	1500	10.0	900	8.9
B17'			2840	7.1	1950	7.2
B18	3.0	0.01	2920	6.2	1850	5.4
B18'			4230	2.4	3130	4.2
B19	4.0	0.01	3400	4.7	2090	5.8
B19'			5080	4.5	3500	4.6
B20	2.0	0.05	1610	7.4	900	8.9
B20'			3010	5.0	2040	8.8
B21	3.0	0.05	1590	10.0	890	10.1
B21'			2730	9.2	1810	7.7
B22	4.0	0.05	1560	6.4	860	10.5

The effect of filtration on the particle size and distribution can be seen from the results summarized in Table II. It is obvious that filtration produces significatantly coarser particles. The results also show that the particle size depends strongly on the concentration of barium ions at the 0.01% *Triton X-100* concentration but becomes rather insensitive to concentration changes if the concentration of *Triton X-100* is increased (0.05%).

Anionic detergents *(Aerosol MA)* play a somewhat different role during the precipitation of barium sulfate, since they strongly interact with barium ions, owing to the negative charge of their surface-active part. In the concentration range of barium ions we studied there is only a limited interval where no visible opalescence was observable. This interval was between 1×10^{-4} *M* and 1×10^{-3} *M* of barium chloride with *Aerosol MA* concentrations 0.05% and 0.1% (1.3×10^{-3} *M* and 2.6×10^{-3} *M*, respectively), if the systems were kept at 25.0⁰ C and observed after 10 minutes. If left overnight, even these systems showed a faint opalescence. For this reason only a few systems of barium sulfate precipitated in the presence of *Aerosol MA* were prepared. Fig. 4 show typical particles obtained at 25.0⁰ C (series C). If compared with »pure« systems, particles are bigger, with characteristically jagged edges.

TABLE III

The Size of Barium Sulfate Particles (in mμ) Precipitated in the Presence of Sodium Citrate

Final concentration of sulfate ions: 2.2×10^{-3} M; concentration of barium ions: 2.0×10^{-3} M; temperature: 25.0° C. $\overline{D}_c$, $\overline{D}_b$ — arithmetic mean lengths of axes c and b, respectively; $s_r(D_c)$, $s_r(D_b)$ — corresponding relative standard deviations.

System	$c_{citrate}$ (moles/l.)	Age of systems															
		5 minutes				10 minutes				40 minutes				24 hours			
		$\overline{D}_c$ (mμ)	$s_r(D_c)$ (%)	$\overline{D}_b$ (mμ)	$s_r(D_b)$ (%)	$\overline{D}_c$ (mμ)	$s_r(D_c)$ (%)	$\overline{D}_b$ (mμ)	$s_r(D_b)$ (%)	$\overline{D}_c$ (mμ)	$s_r(D_c)$ (%)	$\overline{D}_b$ (mμ)	$s_r(D_b)$ (%)	$\overline{D}_c$ (mμ)	$s_r(D_c)$ (%)	$\overline{D}_b$ (mμ)	$s_r(D_b)$ (%)
D1	5×10^{-5}	2430	4.1	$=\overline{D}_c$		2500	4.0	$=\overline{D}_c$		2440	3.1	$=\overline{D}_c$		2450	4.1	$=\overline{D}_c$	
D2	1×10^{-4}	3210	2.1	2670	2.6	3240	2.9	2630	5.3	3260	2.7	2690	4.5	3230	1.6	2720	5.5
D3	5×10^{-4}	1490	2.5	1140	4.1	1530	1.2	1160	4.1	1480	2.1	1150	3.6	1460	3.3	1130	5.0
D4	5×10^{-3}	885	5.1	801	8.6	889	4.3	804	6.2	—	—	—	—	908	4.4	823	4.4

System C3 has particles with $D_c \sim 2\,\mu$ (compared with A1 having $\overline{D}_c = 1.43\,\mu$), but there is a particle, pointed by the arrow, positioned by chance in its b-a-profile. The detail of Fig. 4b shows the c-a-profile of big particles. All of these particles were formed within 3—5 minutes.

Precipitation of barium sulfate in the presence of citrate ions was investigated on several occasions. The first reports[2,18] have shown that citrate ions reduce the size of precipitated particles. It has also been claimed[19,20] that under suitable conditions spherical particles could be obtained.

Our experiments gave typical particles of rounded forms (Fig. 5a), and some of them appeared at first glance to be spherical (system D1). Data on particle sizes in relation to time are given in Table III. It is evident that these particles are almost completely formed in 5 minutes. A closer examination showed that even particles of D1, having $D_c = D_b$, were not spheres. This could be concluded directly by observing the particles in profile (detail of Fig. 5a), or from the shadow lengths. Calculations from shadows of six D1 particles gave a mean value $D_a = 1120$ mμ, which is in agreement with the directly measured value (from the c-a-profile) 1280 mμ, keeping in mind a rather poor accuracy (error about 10%) of determinations from shadow lengths. If the particles were spheres, their shadow would have a length approximately 4.5 times as great as it actually is.

Precipitation at elevated temperature (50.0° C) gives very complicated star-shaped particles, an example shown in Fig. 5b. Structures pointed by arrows are only apparently simple. Observed after the membrane breaking they show the same star-shaped structure as other particles. The particles are bigger than those precipitated at lower temperature.

TABLE IV

The Size of Barium Sulfate Particles (in mμ) Precipitated in the Presence of EDTA
Final concentration of sulfate ions: 2.2×10^{-3} M; concentration of barium ions: 2.0×10^{-3} M; temperature: 25.0° C. $\overline{D}_c$, $\overline{D}_b$ — arithmetic mean lengths of axes c and b, respectively; $s_r(D_c)$, $s_r(D_b)$ — corresponding relative standard deviations.

System	c_{EDTA} (moles/l.)	Age of systems							
		10 minutes				60 minutes			
		$\overline{D}_c$ (mμ)	$s_r(D_c)$ (%)	$\overline{D}_b$ (mμ)	$s_r(D_b)$ (%)	$\overline{D}_c$ (mμ)	$s_r(D_c)$ (%)	$\overline{D}_b$ (mμ)	$s_r(D_b)$ (%)
E1	2.2×10^{-4}	8000	—	5000	—	7500	—	4700	—
E3	8.8×10^{-4}	4720	2.5	2810	3.2	4600	4.4	2870	3.5
E4	2.2×10^{-3}	4450	2.2	2730	3.3	4550	2.0	2700	3.7
E5	4.4×10^{-3}	4500	2.4	2700	3.1	4520	2.2	2750	2.5
E6	8.8×10^{-3}	3120	2.2	1910	4.2	3080	2.0	1850	2.7
E7	2.14×10^{-2}	1640	3.5	1030	4.1	1650	2.6	1050	3.0
E8	8.54×10^{-2}	1740	1.7	1080	3.7	2160	1.9	1390	4.3

The systems precipitated in the presence of EDTA are shown in Fig. 6. At low EDTA concentrations the precipitates generally consist of particles with complicated shapes. At EDTA concentrations exceeding 5×10^{-3} M the shape-controlling effects become pronounced. The particles become monodisperse and similar in size and shape like the corresponding particles grown
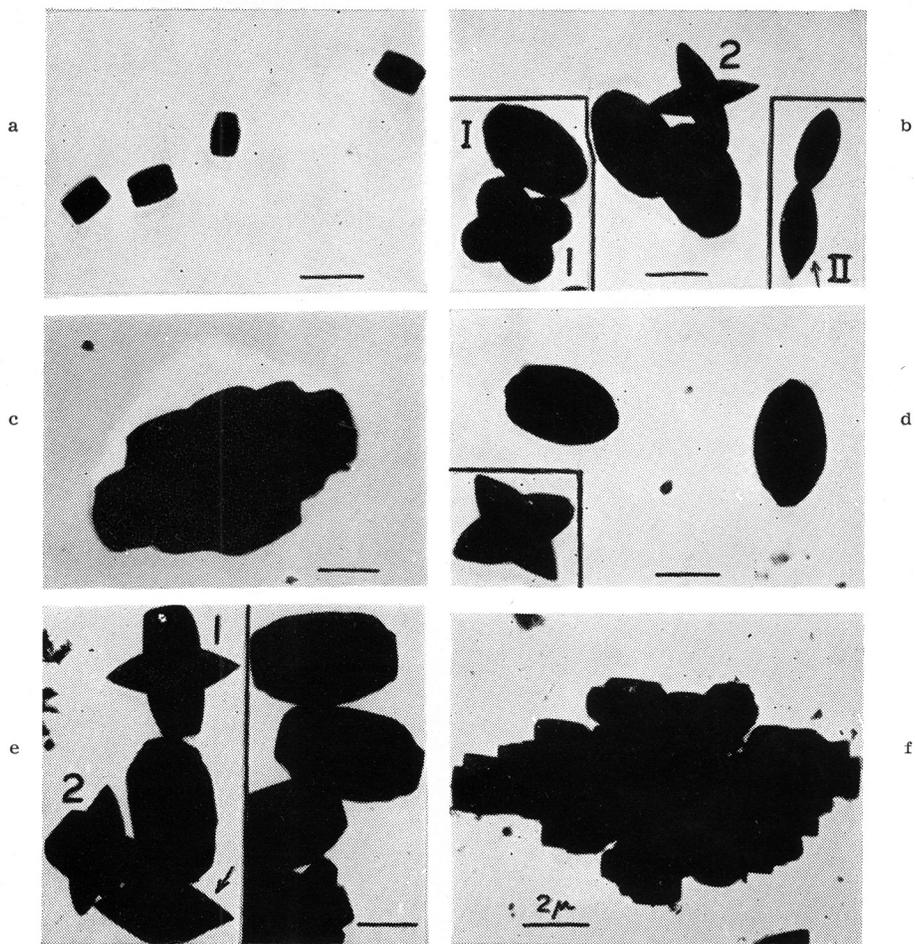
Fig. 1. Barium sulfate precipitated without the presence of foreign substances. Temperature 25.0⁰ C, age: 10 minutes; (a) System *A1*, 1×10^{-4} *M* BaCl$_2$, (b) *A3*, 1×10^{-3} *M* BaCl$_2$, (c) *A4*, 2×10^{-3} *M* BaCl$_2$, (d) *A7*, 4.4×10^{-3} *M* BaCl$_2$, (e) *A8*, 6×10^{-3} *M* BaCl$_2$, (f) *A9*, 2×10^{-2} *M* BaCl$_2$.
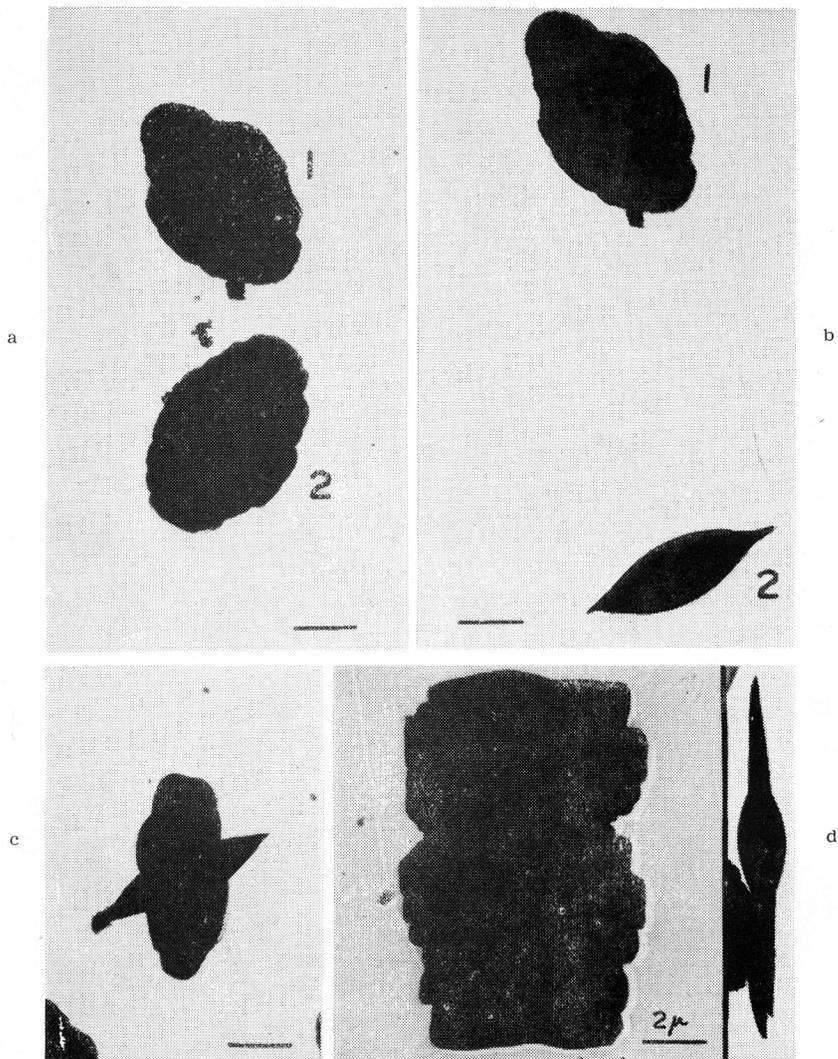
Fig. 2. Barium sulfate precipitated without the presence of foreign substances. Temperature: 25.0⁰ C, age: 10 minutes; (a), (b) and (c): System *A4*, 2×10^{-3} *M* BaCl₂, (d) Temperature: 50.0⁰ C, age: 10 minutes. *A4*, 2×10^{-3} *M* BaCl₂.
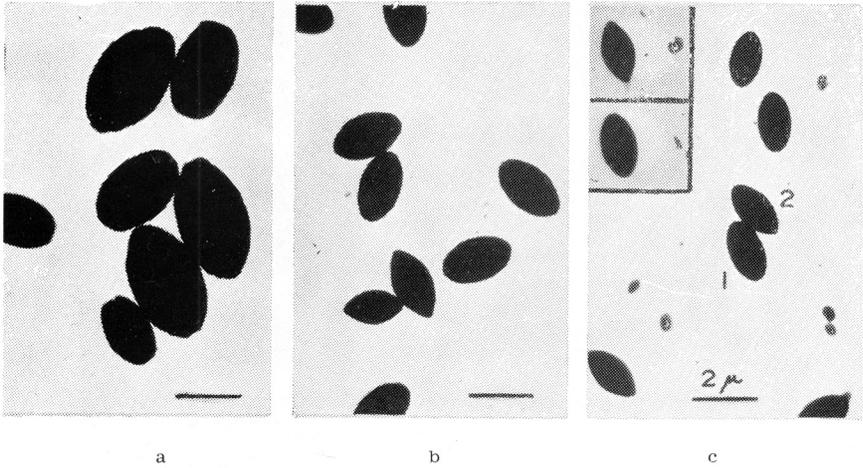
Fig. 3. Barium sulfate precipitated in the presence of *Triton X-100*. Temperature: 25.0⁰ C, age: 5 minutes, 4.4×10^{-3} *M* BaCl$_2$; (a) System *B7*, 0.001% *Triton X-100*, (b) *B4*, 0.05% *Triton X-100*, (c) *B3*, 0,1% *Triton X-100*
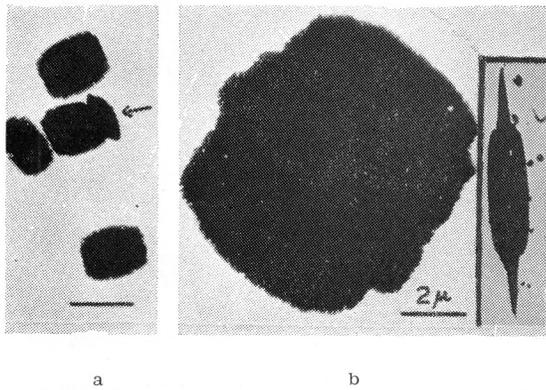
Fig. 4. Barium sulfate precipitated in the presence of *Aerosol MA*. Temperature: 25.0⁰ C, age: 10 minutes, 0.05% *Aerosol MA;* (a) System *C3*, 1×10^{-4} *M* BaCl$_2$, (b) *C2*, 5×10^{-4} *M* BaCl$_2$.
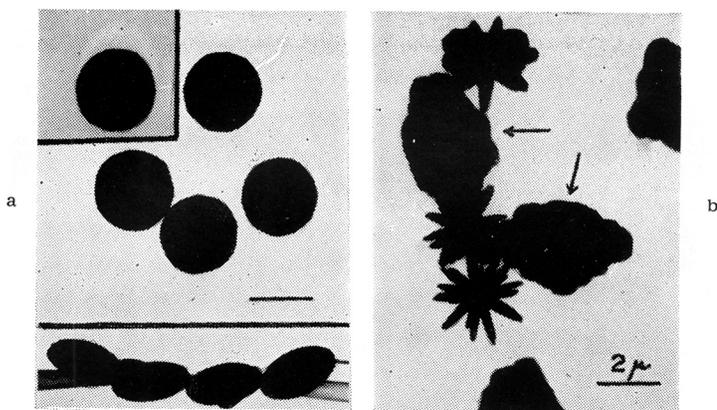
Fig. 5. Barium sulfate precipitated in the presence of sodium citrate. Age: 10 minutes, 2×10^{-3} M $BaCl_2$; (a) Temperature: 25.0⁰ C, System *D1*, 5×10^{-5} M sodium citrate, (b) Temperature: 50.0⁰ C, *D2**, 1×10^{-4} M sodium citrate.
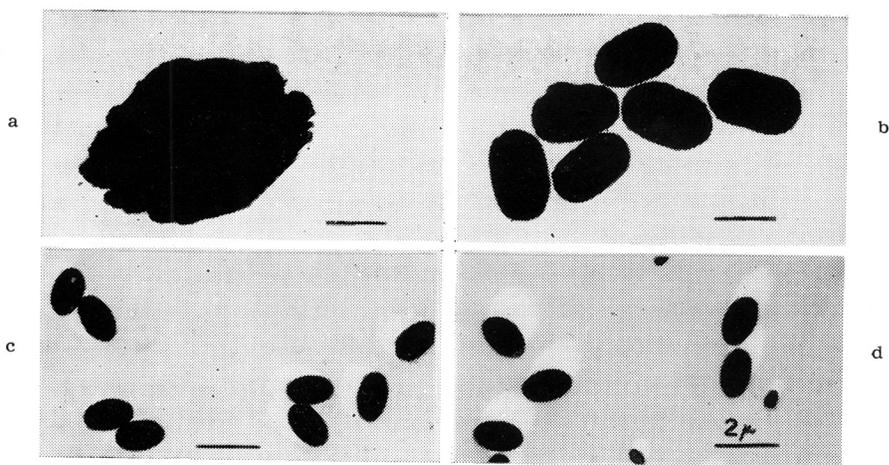
Fig. 6. Barium sulfate precipitated in the presence of EDTA. Temperature: 25.0⁰ C, age: 10 minutes, 2×10^{-3} M $BaCl_2$; (a) System *E1*, 2.2×10^{-4} M EDTA, (b) *E6*, 8.8×10^{-3} M EDTA, (c) *E7*, 2.14×10^{-2} M EDTA, (d) *E8*, 8.54×10^{-2} M EDTA.
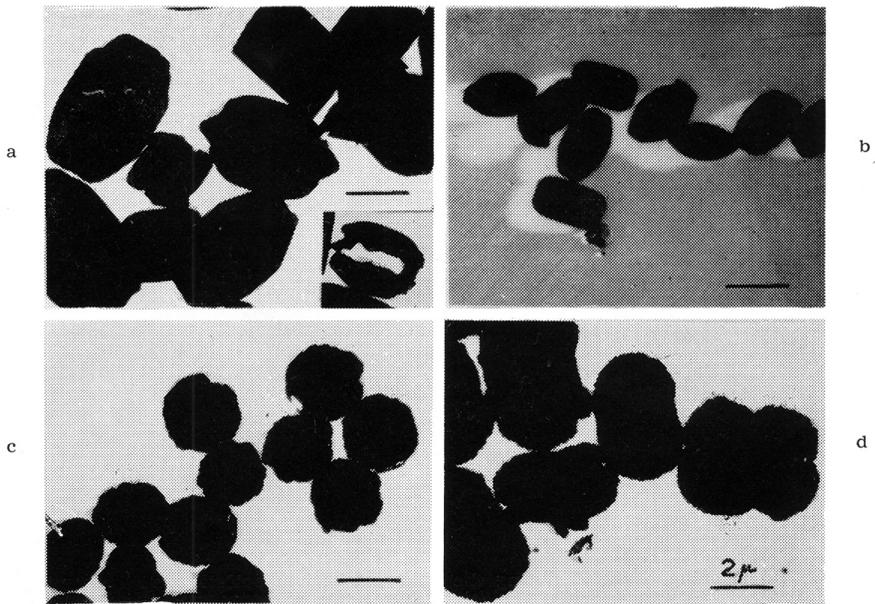
Fig. 7. Barium sulfate particles aged in their mother liquor at room temperature. (a) System *A7*, age: 3 days, (b) *B4*, age: 3 days, (c) *D1*, age: 5 days, (d) *E5*, 4.4 × 10⁻³ *M* EDTA, age: 7 days.
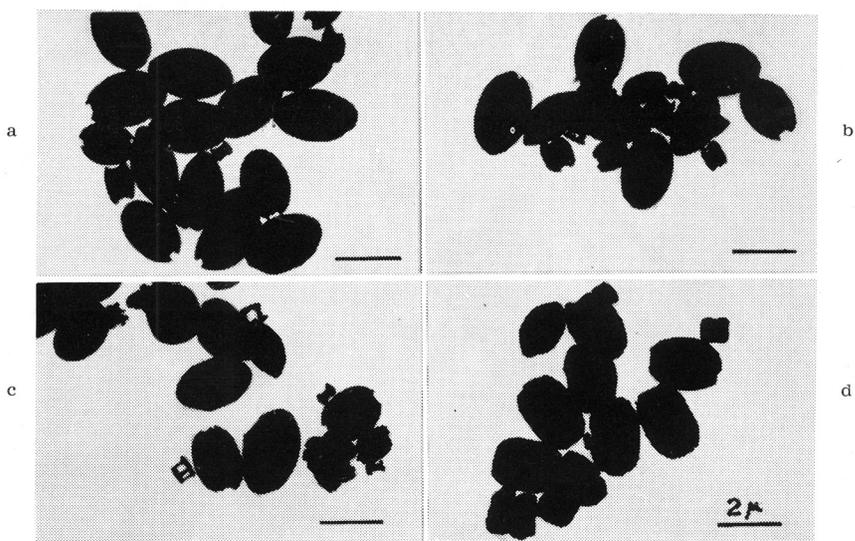
Fig. 8. Ostwald ripening observed during the aging of barium sulfate particles. System *B21'*, 3×10^{-3} *M* BaCl$_2$, 0.05% *Triton* X-100, age: (a) 2.5 hours, (b) 5.5 hours, (c) 24 hours, (d) 5 days.
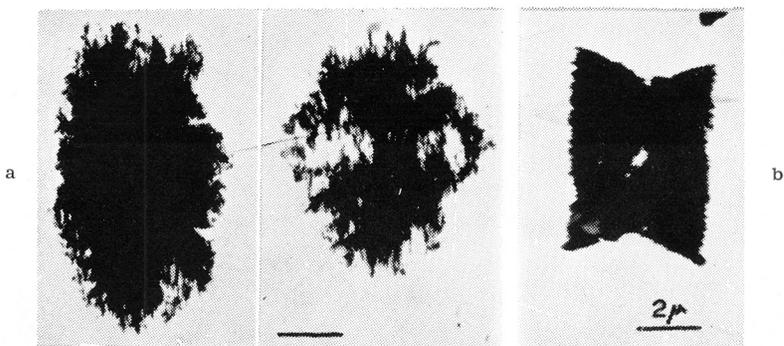
Fig. 9. Dissolution of barium sulfate particles in water. (a) System *A4*, 2×10^{-3} *M* BaCl₂, dissolution time: 1 hour, (b) System *C2.1* prepared at 50.0⁰ C, 0.05⁰/₀ *Aerosol MA*, 5×10^{-4} *M* BaCl₂, dissolution time: 2.5 hours.
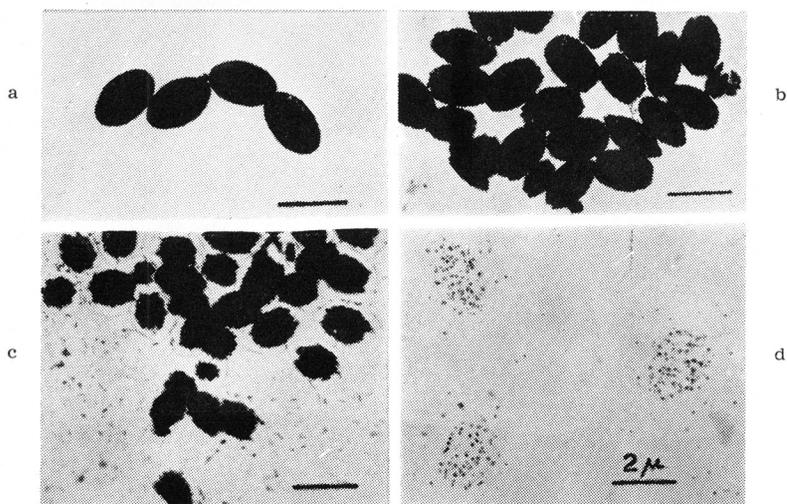
Fig. 10. Dissolution in water of barium sulfate particles prepared in the presence of *Triton X-100*. System *B17*, 2×10^{-3} *M* BaCl₂, *Triton X-100* 0.01⁰/₀; (a) untreated sample, (b) dissolution time: 1 hour, (c) dissolution time: 2.5 hours, (d) dissolution time: 5 hours.
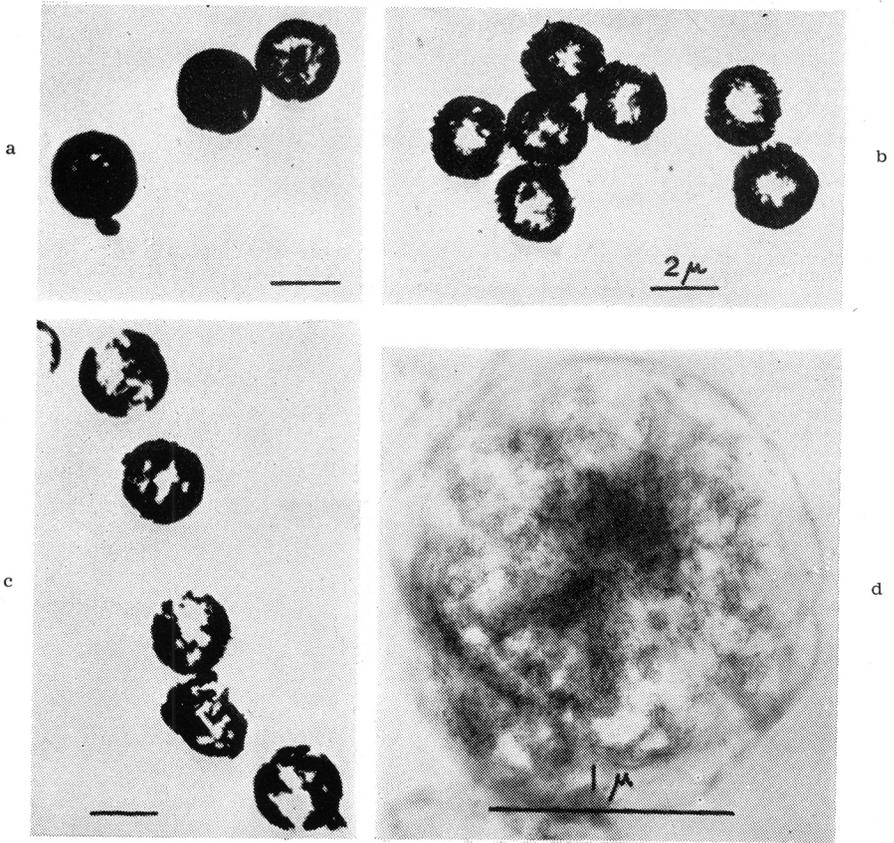
Fig. 11. Dissolution in water of barium sulfate particles prepared in the presence of sodium citrate. System *D1*, 2×10^{-3} *M* BaCl₂, 5×10^{-5} *M* sodium citrate; dissolution time: (a)4 hours, (b) 6.5 hours, (c) 9.5 hours, (d) 22 hours.

in the presence of *Triton X-100*. If the EDTA concentration is increased, new, smaller particles appear and the systems become bidisperse. The particle size data are summarized in Table IV (data for *E8* belong to the population of bigger particles). The particles were fully developed in 10 minutes, except system *E8* in which the particle size continued to increase.

Aging of Barium Sulfate Particles

Soon after the barium sulfate particles were formed, usually after a few hours, aging can be noted, consisting basically of recrystallization and dissolution of formed particles. The rate of these processes, as well as the final habit of aged particles, is strongly dependent on the type of foreign substance present during the particle formation. Fig 7 shows a survey of most characteristic shapes selected from a number of aged systems observed. These systems were precipitated (a) without the presence of foreign substances (system *A7*), (b) in the presence of *Triton X-100* (system *B4*), (c) in the presence of sodium citrate (system *D1*), and (d) in the presence of EDTA (system *E5*). It is typical for particles of the *A* and *B* series that the aged particles have smooth surfaces with clear tendency to develop crystal facets, whereas for particles of series *C* (precipitated in presence of *Aerosol MA*, picture not shown), *D*, and *E* jagged surfaces are most frequent. Smaller particles ($< 4 \mu$) are often subject to a specific dissolution beginning from the inner part of particles (detail in Fig. 7a).

Of all systems studied, fastest aging was observed on particles formed in the presence of *Triton X-100*. Fig. 8 shows typical recrystallization of particles of the *B* series. The first phase of aging consists of a characteristic mode of dissolution from particle tips, predominantly observed on smaller particles. In 5.5 hours crystal facets begin to appear. In 24 hours only skeletons of smaller particles are left over, whereas bigger particles are approaching the final shapes similar to those in Fig. 7b.

Dissolution of Barium Sulfate Particles

Dissolution of particles in water proceeds by irregular tearing over the whole particle surface. Some typical features found in dissolution experiments are shown in Figs. 9, 10, and 11. The process of particle dissolution in systems of series *A* (Fig. 9a) and *B* (Fig. 10) proceeds predominantly from the outside, leading finally to a disintegration into very small chips. Particles belonging to series *C* (Fig. 9b) and *D* (Fig. 11) show most frequently dissolution from the particle inside. The contours of particles which are observable after exhaustive dissolution (Figs. 10c and d, Fig. 11d) are a result of the deformation of the *Mowital* membrane due to the weight of the particle.

It is interesting to note that if the particles were once irradiated by the electron beam (i. e. if the sample was used for observation in the electron microscope), they showed a remarkable resistance to dissolution.

DISCUSSION

The most intriguing question concerning the formation of precipitated particles is the understanding of the mechanism of their growth. Much work has been devoted to the study of the growth of barium sulfate particles, as recently reviewed by Walton[21]. There is a big dilemma whether a stable particle should always be formed from one nucleus, or several nuclei can form small primary particles which can aggregate to final structures. In the basic

assumptions of the nucleation theories applied to sparingly soluble hetero-polar precipitates[16] the models used are simplified, and little attention is paid to several important factors encountered in phase transition phenomena of these substances, as adsorption of ions and molecules in the methorical layer, coulombic interactions between nuclei or particles, etc. These factors were discussed in detail elsewhere[22]. It should be noted that direct experimental proofs supporting either one or the other concept are still lacking. So we will try to reach some conclusions on the mechanisms of the formation of barium sulfate particles, although the present experiments were not primarily designed for the elucidation of nucleation problems. We should always keep in mind the specificity of our systems, taking into consideration the method of their preparation, and this discussion should not be understood to be generally applicable to precipitation systems of different genesis (e. g. systems prepared by diffusion mixing). However, remembering the fast generation of sulfate ions in the Andreasen reaction, we can try to compare our results with the results from direct mixing precipitation.

On the basis of Nielsen's experimental data[23] the nucleation in the range of concentrations studied in this paper should be heterogeneous, i. e. the par-ticles should start to grow on mechanical impurities already present in the system, the homogeneous nuclation being of negligible importance. Nielsen's data were obtained by direct mixing of precipitating ions at equimolar concen-trations, with N having a constant value in the range from 3×10^5 to 3×10^6 ml.$^{-1}$ for the heterogeneous nucleation region. Data from Table I indicate that only when the particles were precipitated at equimolar concentrations, the values of N are comparable in order with Nielsen's data. The systems having different barium and sulfate ion concentrations appear to have a significantly higher N. Since there is no reason to assume that the number of mechanical impurities changes from system to system, it seems that a direct diffusion growth of particles from heterogeneous nuclei cannot be considered as the only mechanism responsible for the formation of barium sulfate particles.

Similar discontinuities in N related to the concentration of a precipitating ion were reported by Mealor and Townshend[24]. They also found remarkable differences in N (belonging to the heterogeneous precipitation region) for different sparingly soluble salts and are claiming that heterogeneous nuclei are not equally efficient for all substances. It is possible, however, to explain these results by the existence of two parallel mechanisms. One of them is the formation of primary particles by direct diffusion growth, and the other consists of the aggregation of these primary particles, thus controlling the final N of barium sulfate particles. Here heterogeneous nuclei are also influenc-ing N, as is seen from the experiments with filtered solutions (Table II), and are playing an important role in the aggregation process.

The discontinuities of N values can be explained by different coulombic interactions of primary particles. The system $A4$ was formed under almost isoelectric conditions which favor aggregation processes, whereas the other systems are stabilized by excess electrical charges, arising from the prevalence of either barium or sulfate ions in the methorical layer. If the concentration of barium ions exceeds a certain value (system $A9$), aggregation is very evident and the effect greatly resembles that of coagulation.

Although it is difficult to explain the influence of foreign substances in the mechanism of the formation of barium sulfate particles, yet some conclu-

sions can be drawn from our micrographs. It is well known from the literature (see e. g. Refs. 17, 20, 25, 26) that precipitated particles always contain copre-cipitated (occluded) foreign matter. It should therefore be expected that foreign substances strongly influence the methorical layer and change the growth and aggregation rate. If the substance is pronouncedly surface active, a strong influence on particle formation can be expected. In this respect experiments with nonionic detergents are very illustrative. Low concentrations of *Triton X-100* do not influence the shape or size of particles, but an increased detergent concentration causes a decreased particle size (and, consequently, an increased N, since solubility does not change appreciably). Finally, at highest detergent concentrations new particles are formed, having predomi-nantly a rectangular shape normaly observed in highly diluted systems. This might be explained either as a delayed nucleation, or, in terms of our aggre-gation concept, as an inhibited aggregation. It is interesting to note that EDTA, as a typical complexing agent, produces very similar effects (Figs. 6c, d), although at concentrations higher by an order of magnitude. The presence of big anions markedly influences both the shape and size of particles. It is also clear that formation of barium complexes with citrate and EDTA is influencing the particle formation. In all cases the precipitated material is genotypically barium sulfate, but foreign substances figure as strong phenotypical factors influencing both the mechanism and the kinetics of precipitation.

If the concentration of barium ions is around 10^{-4} M, foreign substances have no or only little influence on the shape and size of particles (Fig. 1a, Fig. 4a, system B15 prepared in the presence of 0.01% *Triton X-100* — the micro-graph not shown). This suggests that at low supersaturation ratios particles tend to develop crystal facets, and the mechanism of direct diffusion growth seems to prevail over aggregation mechanisms.

Dissolution experiments are again supporting the importance of consider-ing aggregation during particle formation. Our results show two different mechanisms of dissolution, depending on the type of foreign substance present during particle formation. Presence of big anions (dihexylsulfosuccinate, citrate, EDTA) seems to favor dissolution from the particle inside, whereas particles grown in the presence of nonionic detergents or small anions (thiosulfate, tri-thionate, *etc.*) are dissolved primarily from the outside. This peculiar behavior was already reported[10,25], but was not recognized as being dependent on the type of foreign substance. This phenomenon seems to be related to the chemical reactivity of big anions (i. e. their complexing ability). It is interesting to note that particles with occluded complex species are showing a highly ordered structure, as revealed by electron diffraction experiments[10], and even advanced dissolution does not disturb this order. In the last phase of the dissolution process only primary particles remain, as shown in Figs. 10d and 11d. These particles are dispersed without order over the whole area occupied previously by the original particle.

The aging phenomena are in agreement with previous observations[1,27,28] and indicate the occurrence of Ostwald ripening in systems with smaller par-ticles (Fig. 8). There are differences in aging behavior depending on the foreign substance present during particle formation. Again as in dissolution experi-ments, two different mechanisms can be distinguished, provoked by big anions on the one hand, and by small anions or nonionic detergents on the other.

The experiments at elevated temperature, leading as a rule to coarser and more complicated forms, are showing the predominance of aggregation processes.

From the results presented in this paper it can be concluded that the concepts of previous workers[26,29,30], who consider precipitation as a process passing through phases of formation of primary particles and their aggregation to secondary structures, should not be underestimated. The aggregation concept is not in conflict with the fact that barium sulfate particles are predominantly morphologically well defined. They can be regarded as real crystals with an »inner organization«, frequently called »mosaic crystals«. It is clear that primary particles should be anisotropic in shape and capable of being arranged into secondary structures by vectorial ordering. Many authors explain this »inner organization« as a result of the mechanism of the so-called »dendritic growth«[21]. It is not difficult to understand that these dendritic structures can be formed by aggregation, too. A final decision in this highly controversial question can be expected only by collecting additional experimental data, as well as by developing suitable theoretical models for ionic solutions and phase transitions of heteropolar sparingly soluble substances.

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IZVOD

Monodisperzni solovi barium-sulfata. II. Morfološke karakteristike, starenje i otapanje čestica

J. J. Petres, Gj. Deželić i B. Težak

Proučavana je morfologija čestica barium-sulfata dobivenih precipitacijom iz homogene otopine kod 25⁰ i 50⁰ C u prisutnosti raznih stranih supstancija, kao i bez njih. Kao strane supstancije uzeti su ovi tipovi spojeva: neionski detergent (*Triton X-100*) anionski detergent (*Aerosol MA*), supstancije koje kompleksiraju (citrat i EDTA). Čestice su bile promatrane elektronskim mikroskopom. U svim slučajevima nastale su anizotropne čestice više ili manje definirane strukture, a većina sistema bila je monodisperzna. Opaženo je stvaranje sraslaca sraštenih u različitim profilnim ravninama. Proučavano je starenje čestica u matičnici i njihovo otapanje u vodi. Mehanizam stvaranja čestica razmatran je na osnovu podataka o veličini čestica, njihovoj morfologiji, kao i njihovu starenju i otapanju. Promatran je utjecaj stranih supstancija u vezi s njihovim kemijskim svojstvima. Na osnovu dobivenih rezultata je pretpostavljeno da se čestice barium-sulfata pretežno stvaraju agregacijom primarnih čestica, dok do čistog difuzijskog rasta dolazi samo pod posebnim uvjetima.

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