

CCA-436

546.431'226-182

Original Scientific Paper

## Monodisperse Sols of Barium Sulfate. I. Preparation of Stable Sols

J. Petres, Gj. Deželić, and B. Težak

Department of Physical Chemistry, Institute »Ruđer Bošković«, Department of Applied Biochemistry, »Andrija Stampar« School of Public Health, Faculty of Medicine, and Laboratory of Physical Chemistry, Faculty of Science, University of Zagreb, Zagreb, Croatia, Yugoslavia

Received July 22, 1966

Monodisperse sols of barium sulfate were prepared by a modified method of homogeneous precipitation and characterized by electron microscopy. The particles were spindle-shaped and of a rather uniform distribution when prepared with concentrations of barium and sulfate ions of  $4 \times 10^{-3}$  M. The degree of monodispersity obtained depends on the cleanliness of solutions and glassware, and good results were obtained by filtration of solutions and careful cleaning of glassware. Morphological changes in the particles during the reaction are studied. Monodisperse particles dispersed in the mother liquor are not stable, since they aggregate and recrystallize by aging. However, addition of nonionic detergents stabilizes the particles for longer periods, as detected by electron microscopy and ultramicroscopy. Stable sols of barium sulfate of particle size from 195 to 480 m $\mu$  for the longer axis, and from 95 to 188 m $\mu$  for the shorter axis, respectively, were prepared.

### INTRODUCTION

Several methods of homogeneous precipitation of barium sulfate were used in the past. There are<sup>1</sup> the LaMer-Dinegar method of homogeneously generated sulfate ion by the persulfate-thiosulfate reaction, the method by slow hydrolysis of sulfamic acid<sup>2</sup> and the method by hydrolysis of dimethyl sulfate<sup>3</sup>. The particles produced by these procedures were normally polydisperse considering the shape and the size. Andreasen<sup>4</sup> prepared nearly monodisperse particles by the hydrogen peroxide-thiosulfate reaction in the presence of sodium citrate. Takiyama<sup>5</sup> reported some preparations of rather monodisperse spindle-shaped particles by means of the decomposition of the complex of barium and ethylenediaminetetraacetic acid (EDTA) with hydrogen peroxide in the presence of sulfate ions.

In this work some monodisperse sols of barium sulfate were prepared by the Takiyama's method. An attempt was also made to stabilize barium sulfate sols using a nonionic detergent. A number of authors<sup>6, 7, 8</sup> have investigated the influence of surface-active agents on the stability of barium sulfate sols, but all of these papers were concerned with the peptizing properties of ionic detergents, e.g. dodecylpyridiniumhalides, sodium dodecylsulfate and potassium laurate. The stable sols of barium sulfate can be of great interest in some studies of physicochemical properties of colloidal solutions containing monodisperse spindle-shaped particles. These investigations are now in progress. In

the present communication some aspects of the preparation and characterization of monodisperse barium sulfate sols are described.

#### EXPERIMENTAL

##### *Preparation of Sols*

All chemicals used in this work were reagent grade. Standard 0.22 M solutions of barium chloride, sodium salt of EDTA and ammonium sulfate were prepared. Barium chloride and ammonium sulfate solutions were standardized by gravimetric methods, EDTA by complexometric titration. The more dilute solutions of these reagents were prepared from stock solutions by addition of redistilled water.

Hydrogen peroxide was taken from original packages of Merck's *Perhydrol* (E. Merck, Darmstadt, Germany) without dilution. The concentration of hydrogen peroxide was determined by an iodometric method and regularly controlled every week.

Nonionic detergents *Triton X-100* and *Triton X-305* were obtained by courtesy of *Rohm & Haas Co.*, Philadelphia, Pa., U.S.A. The water used for preparation of detergent solutions was specially cleaned from dust and other mechanical impurities by distillation from an all-glass still without glass joints.

The barium sulfate sols were obtained as follows: the reaction mixture was prepared by addition of the solution *B* to solution *A* at room temperature.

Solution *A* was composed of barium chloride solution, an ammonium chloride-ammonia buffer, EDTA and ammonium sulfate solutions mixed together in the same order. The molar concentrations of barium chloride, ammonium sulfate and EDTA were the same and ranged from  $2.2 \times 10^{-3}$  to  $8.8 \times 10^{-3}$  M. The ammonium chloride-ammonium buffer (pH = 10) was prepared as follows: 35 g. of ammonium chloride was dissolved in 285 ml. of concentrated ammonia (density 0.90 g. cm.<sup>-3</sup>), and made up with redistilled water to 500 ml. The volume of this buffer solution amounted always to 5% of the total volume of the reaction mixture.

The solution *B* consisted of hydrogen peroxide diluted with water to a constant concentration giving a value of 6% relative to the reaction mixture.

Both solutions (*A* and *B*) were clarified from dust particles by filtration through sintered glass filters G-5F, made by *Schott. & Gen.*, Mainz, Germany. All glassware were specially rinsed from dust and other impurities with redistilled dust-free acetone.

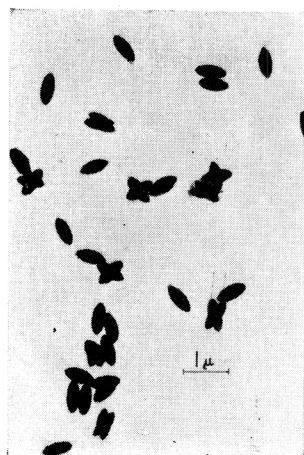
After mixing, the reaction mixture was put into a thermostat at  $(80.00 \pm 0.05)^\circ\text{C}$  and kept at this temperature during the course of reaction. The reaction was stopped at several reaction times by immersion of the container into ice water. The obtained sol was centrifugated at about  $4^\circ\text{C}$ . The times of centrifugation and RCF values were chosen appropriately to the particle size and varied from sample to sample. They ranged from 20 to 40 minutes and from  $384$  to  $950 \times G$ , respectively. After centrifugation the mother liquor was decanted and sedimented particles were peptized by addition of solutions of *Triton X-100* or *Triton X-305*.

##### *Observation of Sols and Particle Size Determination*

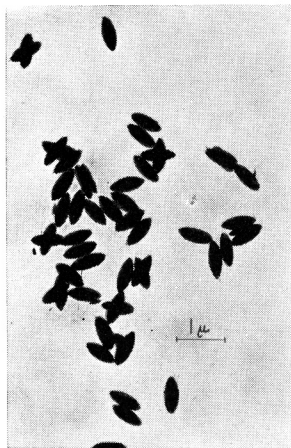
The shape and size of barium sulfate particles were observed by electron microscopy. A *Trüb, Täuber & Co.*, electron microscope (Model KM-4) was used. The specimens were prepared as described in Ref.<sup>5</sup> The measurements of particle size were made directly from electron micrographic plates using a calibrated low power microscope at a magnification of 25 times. For statistical analysis counts of about 200 particles were made except in two cases when no more than 120 particles were counted. The error of these measurements was about  $0.2 \Delta$ , where  $\Delta$  is the scale unit of the low power microscope. This corresponds to 2% of the minimal average particle size measured.

#### RESULTS

Trying to reproduce Takiyama's experiments on the formation of monodisperse barium sulfate sols, we found that the reproducibility of particle shape was poor. This was apparently caused by mechanical impurities, since filtration appreciably improved the situation. We found in a series of experiments that working with carefully filtered solutions of concentrations of barium and sulfate ions about  $4 \times 10^{-3}$  M gives the best results. Although the monodisper-



a



b



c



d



e

Figs. 1a—e. Electron micrographs of barium sulfate particles formed at several reaction times. a. 40 min; b. 60 min; c. 80 min; d. 100 min; e. 120 min; (concentration of reactants:  $4.4 \times 10^{-3} M$ )



Fig. 2.

Fig. 2. Electron micrograph of a stable sol of barium sulfate.  
(concentration of reactants:  $4.4 \times 10^{-3} M$ )

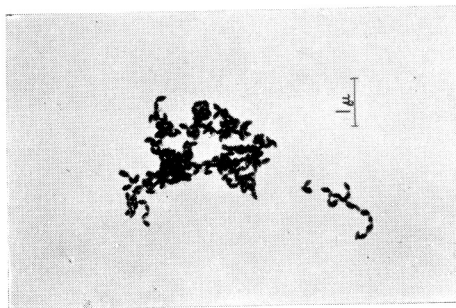


Fig. 3.

Fig. 3. A sol of barium sulfate (S-30) stabilized with Triton X-100 4 months after preparation.

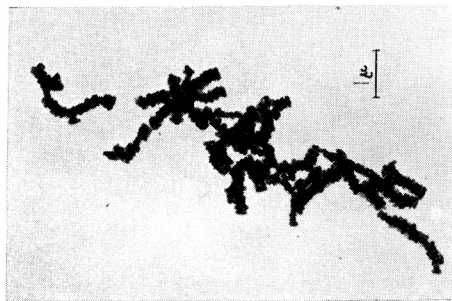


Fig. 4.

Fig. 4. A sol of barium sulfate (S-30) after aging of 4 months in mother liquor.

sity and shape were very reproducible, the particle size distributions varied somewhat.

Figs. 1a—e show a typical course of reaction followed during 120 minutes by use of electron micrography. The initial concentrations of barium chloride, ammonium sulfate and EDTA were  $4.4 \times 10^{-3} M$ . The micrographs of reaction times up to 40 minutes were morphologically the same as in Takiyama's paper<sup>5</sup>, thus only figures of reaction times uncovered by previous work are given. It can be seen that the particle size increases gradually with time and reaches an almost constant value after about 60 minutes. After 80 minutes the processes of aggregation take place, developing soon (after 100 minutes) a simultaneous recrystallization of particles. The recrystallization is indicated by a desintegration of spindle-shaped particles which starts with »dissolution« of the center of particle (see Fig. 1d, particle marked by the arrow), and ends by decay into chips of irregular size. The recrystallization process can also appear as the disappearing of particle tips and appearance of new rhombic forms (see Fig. 1e, arrow). The above results suggested that the reaction should be stopped at an early stage whilst the particles are still well shaped and nonaggregated, i.e. before 60 minutes. If the particles, after the reaction was stopped, were left in their mother liquor, the system was stable up to one day. After this period the particles started to aggregate and recrystallize. Whereas the recrystallization processes were easily recognizable by the electron microscope owing to the changes in particle shape, this method could not give any definite answer about aggregation. The method used for the detection of aggregates was ultramicroscopy.

In order to stabilize the barium sulfate sols, it was found that the addition of small amounts of nonionic detergents, after the mother liquor was eliminated, was capable of preserving sols from aggregation and recrystallization for longer periods. A typical stable sol is shown on Fig. 2. The sample was prepared by the reaction of  $4.4 \times 10^{-3} M$  of barium and sulfate ions and EDTA. The particles were centrifuged and redispersed in a  $10^{-3} M$  solution of Triton X-305, the concentration of particles being of the order  $10^{-4} g./ml$ . One can see almost perfect spindle-shaped particles of very uniform size. Table I gives particle

TABLE I  
Time Dependence of Particle Size of a Barium Sulfate Sol Stabilized by a  $10^{-3} M$  Solution of Triton X-305

Time of aging (hours)	$\bar{D}$ ( $m\mu$ )	$s(\bar{D})$ ( $m\mu$ )	$\bar{d}$ ( $m\mu$ )	$s(\bar{d})$ ( $m\mu$ )
0	484	22	189	14
19	475	18	188	15
40	481	26	188	12
87	471	20	185	11

size data for this preparation and its dependence on time. Arithmetic mean lengths of the long and short axes,  $\bar{D}$  and  $\bar{d}$ , respectively, characterize each preparation, and the respective standard deviations  $s(\bar{D})$  and  $s(\bar{d})$  are measures of the uniformity in size. These quantities are calculated as described previously<sup>9</sup>. Even after several months sols stabilized in this way showed almost

unaggregated particles of the same size, as it can be seen in Fig. 3 and from data in Table II (in this particular case the detergent used was *Triton X-100*

TABLE II  
Time Dependence of Particle Size of a Barium Sulfate Sol (S-30) Stabilized by a 0.05% Solution of Triton X-100

Time of aging	$\bar{D}$ ( $m\mu$ )	$s(\bar{D})$ ( $m\mu$ )	$\bar{d}$ ( $m\mu$ )	$s(\bar{d})$ ( $m\mu$ )
One day	195	11	95	7
4 months	198	13	94	7

of the concentration 0.05%). Clear evidence of the stabilizing action of the nonionic detergents can be seen in Fig. 4. It represents a micrograph of the same sol as in Fig. 3 after the particles had been kept for 4 months in their mother liquor. The particles are aggregated and have appreciably altered their shape.

Data for several monodisperse barium sulfate sols stabilized with *Triton X-100* are given in Table III.  $D_n$  and  $D_w$  are the number-average and weight-average long axes, respectively,  $d_n$  and  $d_w$  are the number-average and weight-average short axes, respectively,  $m_w/m_n = D_w^3/D_n^3$  is a quotient giving a measure of polydispersity<sup>9</sup>. Fig. 5 shows the histogram of one of these systems, which can be regarded as typical of these systems.

TABLE III  
Particle Size of Barium Sulfate Sols Stabilized by a 0.05% Solution of Triton X-100  
Long axis

Sample*	$\bar{D}$ ( $m\mu$ )	$s(\bar{D})$ ( $m\mu$ )	$D_n$ ( $m\mu$ )	$D_w$ ( $m\mu$ )	$m_w/m_n$
S-30	195	11	196	198	1.03
S-34	272	13	272	274	1.03
S-31	350	16	349	351	1.02

Short axis

	$\bar{d}$ ( $m\mu$ )	$s(\bar{d})$ ( $m\mu$ )	$d_n$ ( $m\mu$ )	$d_w$ ( $m\mu$ )	$m_w/m_n$
S-30	95	7	96	97	1.05
S-34	123	9	123	125	1.05
S-31	183	9	183	185	1.03

\* For all samples the concentration of reactants was  $4.4 \times 10^{-3}$  M.

DISCUSSION

From the influence of filtration on the uniformity of particles it is obvious that mechanical impurities are of importance in the initial stage of particle formation and growth. Nielsen<sup>10</sup> reported an interesting fact that careful cleaning of glassware used in precipitation experiments could lower the number

of formed barium sulfate particles by a factor of 10 or more. We found that the solutions could not be clarified by cleaning glassware only. It was also necessary to eliminate impurities having their origin in the solid chemicals. This suggests that rinsing of glassware and filtering of solutions are important operations in controlling the status of the reaction mixture prior to nucleation.

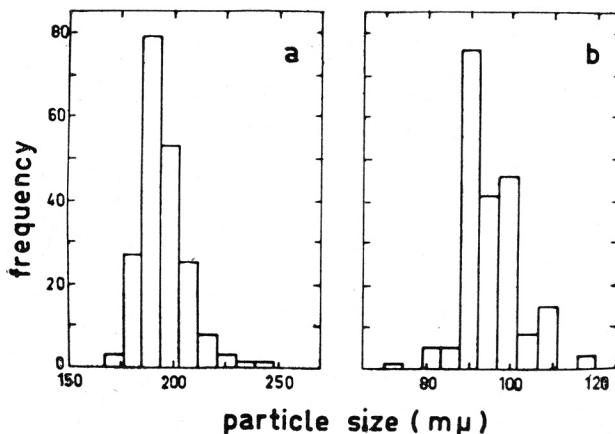


Fig. 5. Histogram of barium sulfate sol (S-30) stabilized with Triton X-100. a. Long axis; b. Short axis.

The mechanism of particle formation is obviously very complex. From the early stages where nucleation and primary growth are predominant the system soon develops pronounced aggregation and recrystallization phenomena. It is not clear whether the spindle-shaped single particles are grown from one or more nuclei. The last fact appears to be possible due to the mode of chipping of particles if aged in their mother liquor (Fig. 1d, arrow) or pure water<sup>11</sup>. All processes of aging, aggregation, and recrystallization are favoured by the high reaction temperature. This was shown by Fischer<sup>12</sup> on barium sulfate particles obtained by direct mixing of reagent solutions. At lower temperature these processes are slower and can be observed after a period of the order of a day or more.

Data in Table III show that the stable barium sulfate sols have a narrow distribution and can be regarded as monodisperse. It is interesting to note that the shorter axis has always a higher  $m_w/m_n$  value suggesting a triaxial ellipsoidal form of particles, although both of the shorter axes are almost equal.

*Acknowledgment.* The authors wish to thank Dr. M. Wrischer for many helpful suggestions in the application of the electron micrographic techniques and the preparation of some electron micrographs.

#### REFERENCES

1. V. K. LaMer and R. H. Dinegar, *J. Am. Chem. Soc.* **73** (1951) 380.
2. W. F. Wagner and J. A. Wuellner, *Anal. Chem.* **24** (1952) 1031.
3. P. J. Elving and R. E. van Atta, *Anal. Chem.* **22** (1950) 1375.
4. A. H. M. Andreasen, K. Skeel-Christensen, and B. Kjaer, *Kolloid — Z.* **104** (1943) 181.
5. K. Takiyama, *Bull. Chem. Soc. Japan* **31** (1958) 950.
6. N. A. Held and K. N. Samochwalov, *Kolloid — Z.* **72** (1935) 13.
7. B. D. Cuming and J. H. Schulman, *Australian J. Chem.* **12** (1959) 413.

8. M. Miura, H. Fujita, and Y. Watari, *J. Sci. Hiroshima Univ., Ser. A-II.* **28** (1964) 41.
9. Gj. Deželić, M. Wrischer, Z. Devidé, and J. P. Kratochvil, *Kolloid. — Z.* **171** (1960) 42.
10. A. E. Nielsen, *Acta Chem. Scand.* **11** (1957) 1512.
11. K. Takiyama, *Bull. Chem. Soc. Japan* **32** (1959) 442.
12. R. B. Fischer, *Anal. Chem.* **23** (1951) 1667.

### IZVOD

#### Monodisperzni solovi barium-sulfata. I. Priređivanje stabilnih solova

*J. Petres, Gj. Deželić i B. Težak*

Modificiranom metodom homogene precipitacije prema Takiyami priređeni su monodisperzni solovi barium-sulfata i karakterizirani metodama elektronske mikroskopije. Čestice su bile vretenastog oblika i imale su dosta uniformnu raspodjelu, naročito ako su bile priređene s koncentracijama od oko  $4 \times 10^{-3}$  M barium i sulfat-iona. Nađeno je da mehaničke nečistoće prisutne u reakcionim otopinama znatno utječu na monodisperznost, pa su dobri rezultati postignuti upotrebom filtriranih otopina i posebno očišćenog posuda. Studirane su morfološke promjene na česticama u toku reakcije.

Monodisperzne čestice dispergirane u matičnom lugu nisu stabilne, jer se starenjem agregiraju i rekristaliziraju. Međutim, ako se čestice redispergiraju u vodenim otopinama neionskih detergenata relativno niskih koncentracija, mogu ostati stabilne kroz dulje vrijeme, što je utvrđeno elektronsko mikroskopskim i ultramikroskopskim istraživanjima. Tako su priređeni stabilni solovi barium-sulfata s veličinom od 195 do 480 m $\mu$  za dužu os čestice, odnosno od 95 do 188 m $\mu$  za kraću os.

ODJEL FIZIČKE KEMIJE  
INSTITUT »RUĐER BOŠKOVIĆ«

I

ODJEL ZA PRIMIJENJENU KEMIJU  
ŠKOLA NARODNOG ZDRAVLJA »ANDRIJA ŠTAMPAR«  
MEDICINSKI FAKULTET

I

ZAVOD ZA FIZIČKU KEMIJU  
PRIRODOSLOVNO-MATEMATSKI FAKULTET  
SVEUČILIŠTE U ZAGREBU  
ZAGREB

Primljeno 22. srpnja 1966.