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Original Scientific Paper

Formation and Aging Precipitates. Study on Nucleation of Strontium Sulfate from Solution

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The rate of precipitation of strontium sulfate from aqueous solutions was traced simultaneously by measurement of relative intensity of light scattering as well as by direct observation of particles by means of electron microscopy. Mechanisms for ionic crystal growth from solution were discussed and compared with experimental resulting precipitation rates. When the precipitate is formed by direct mixing of ions the nucleation occurs very rapidly. After the induction period the particles grow continuously, but a distinct crystal structure began to appear in particles whose length was bigger than 0.02 μm.

INTRODUCTION

Nucleation and crystal growth from solution have been subject of extensive investigations, both theoretical and experimental[1-5]. The vast majority of these studies have dealt with crystalline materials. This paper is concerned with the study of transition stages from homogeneous electrolyte solutions to heterogeneous precipitation systems. The paper is an extension of previous studies of kinetics of precipitation of barium, strontium and calcium sulfate[3,6,7,10], for which characteristic induction periods and growth surges were observed. It was observed that the rate of precipitation, number of particles and crystal size were quite different at high and low supersaturations. It was interesting to determine whether the growth of strontium sulfate from supersaturated solution was preceded by growth similar to that observed for the barium sulfate[8]. The relatively greater solubility of strontium sulfate makes it possible to follow the growth process with a greater precision. An attempt has been made in the present investigation to apply transmission electron microscopy and the electron diffraction method, with the intention of observing nucleation and the latter stages of formation of strontium sulfate precipitate which was obtained by the in statu nascendi technique.

EXPERIMENTAL

Materials

All chemicals used were analytical reagent grade without further purification. Standard 0.2 mol dm^{-3} solutions of strontium nitrate and sodium sulfate were prepared and standardized by gravimetric methods and by EDTA complexometric titration. More dilute solutions of these reagencis were prepared from standard solutions by addition of redistilled water. The precipitation systems were prepared by direct mixing of equal volumes of solutions of precipitating components in the usual experimental technique in statu nascendi.[9]

Relative intensity of scattered light (135 °) of systems was measured at various times by a Zeiss tyndallometer in connection with a Pulfrich light scattering photometer using blue, green and red filter. Temperature was kept in all experiments at 20 °C ± 0.01 by using a Höppler's ultrathermostat.

pH measurements were performed with a pH meter, Radiometer type TTT-11 with a combination glass and calomel electrode.

Electron microscopy observations. — The shape and size of strontium sulfate particles were determined by transmission electron microscopy using the Philips EM 300 electron microscope fitted with a goniometer stage. During the observation of the particles at various times each was subjected to the selected area diffraction method to be sure that every particle was a single crystal. Specimens were prepared by spraying supersaturated solutions onto carbon covered grids. Observed particles were not the result of precipitation on the grid, because the electrolyte was momentarily evaporated due to fine spraying.

RESULTS AND DISCUSSION

A major problem encountered in studies of nucleation from solution is the onset of phase transformation from liquid structure to solidus structure.

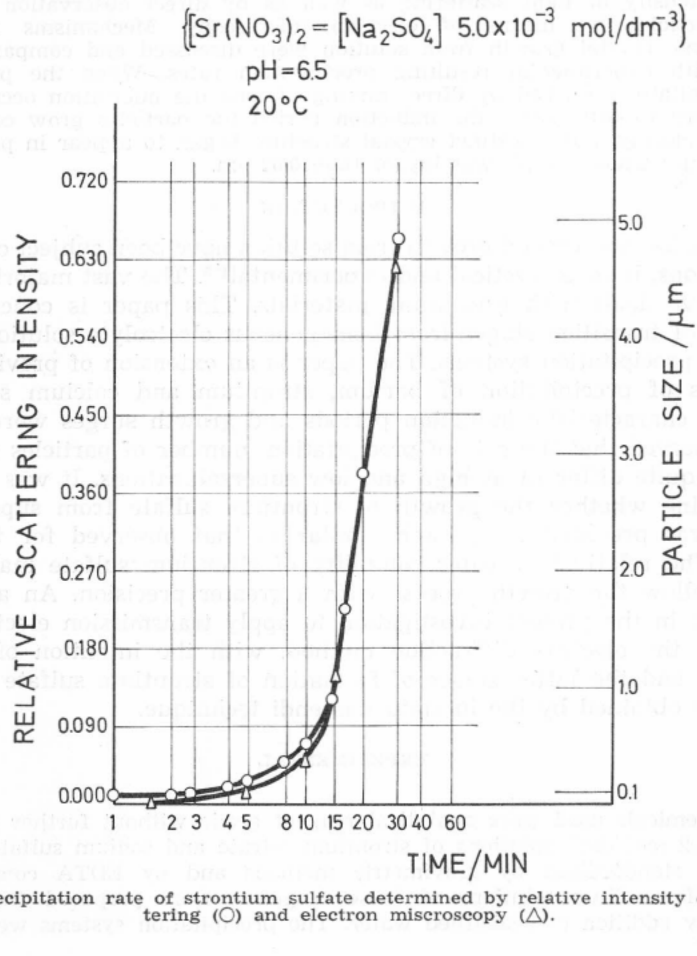


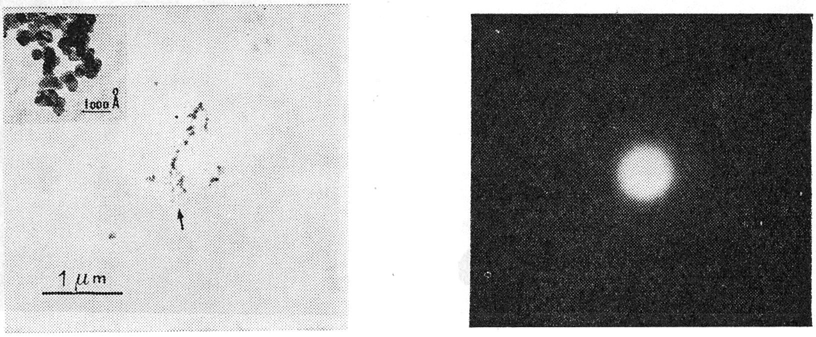
Figure 1. Precipitation rate of strontium sulfate determined by relative intensity of light scattering (○) and electron miscroscopy (△).

The rate of formation of precipitates of strontium sulfate in the system obtained by direct mixing of 5.0×10^{-3} mol dm^{-3} strontium nitrate and sodium sulfate solutions at 20 °C is shown in Figure 1. The method of mixing was the same in each experiment. The supersaturation was held constant and at such *c*/*s* (the concentration by the solubility) values, nucleation was usually heterogeneous. Essentially heterogeneous nucleation does not lead to the formation of particles. The activities of H^+ ions in solution were practically constant at 6.5.

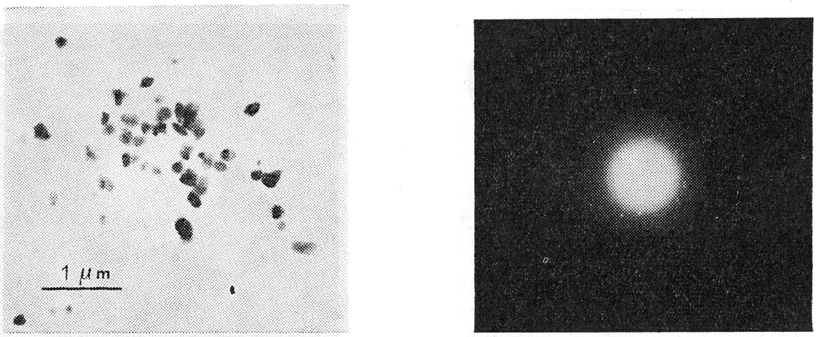
The plot »o« in Figure 1. shows dependence of relative light scattering intensities on time. After mixing the reaction components, a physical and chemical interaction occurs in solution, leading to the formation of precipitation species aggregates, Figure 2. a, b. These aggregates are unstable, have no crystalline structure and are transformed in nucleouses. At this time the core of the crystal structure appears, Figure 3. a, b. The time interval from the generation of critical supersaturation to the detection of the crystalline phase is called the induction period.

During this period the relative light scattering intensity changes only a little with time.

When the crystals are large enough their number can be measured by the optical microscopy. The number of growing crystals is roughly constant with time. After this period the relative light scattering intensities increase with the time due to the particle growth.



Figures 2a and 2b. »Aggregates« of strontium sulfate precipitate sampled after 1 minute. Electron micrographs and diffraction patterns of strontium sulfate precipitates.



Figures 3a and 3b. Crystal nuclei of strontium sulfate precipitate sampled after 5 minutes. Electron micrographs and diffraction patterns of strontium sulfate precipitates.

Variation of particle size of a compact fragment growing from solution with time is illustrated in Figure 1., plot »Δ«.

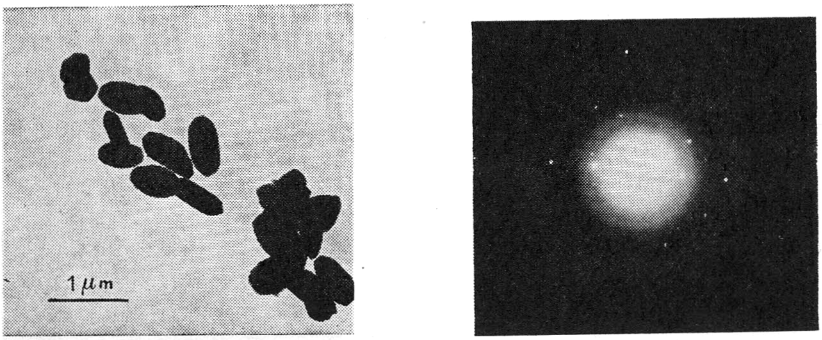
The existence of an induction period, during which no crystallization takes place until a certain »critical« size of nuclei is attained, is now experimentally found for the nuclei of strontium sulfate.

Particles began to be observed with an electron microscope 1 minute after the solution had been mixed. On the electron micrograph, Figure 2a, a group of particles can be seen, obtained from the 1 minute specimen, which have a radius of about 0.02 μm. On the corresponding diffraction pattern (Figure 2b) only diffuse rings of amorphous carbon film are visible.

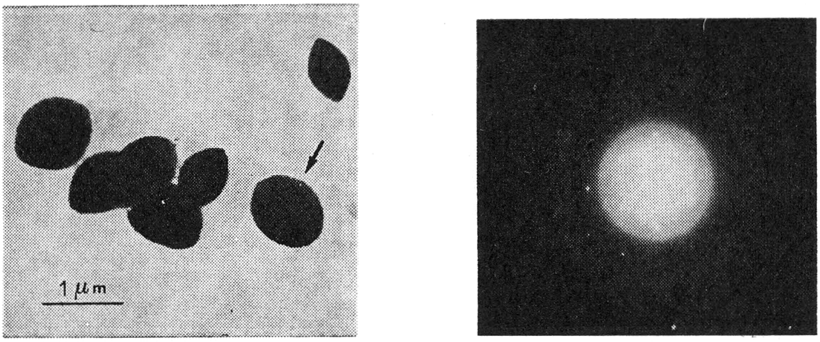
Particles in a 5 minute specimen (Figure 3a), radius about 0.16 μm, began to be spindle shaped. The electron diffraction pattern obtained from these particles (Figure 3b) is composed of many spots belonging to different crystals.

In a 10 minute specimen particles have a long axis of 0.70 μm and they are spindle shaped as shown in Figure 4a. These particles have a well defined crystal structure as shown by diffraction maxima in the diffraction pattern in Figure 4b.

A few particles in the 15 minute specimen, also spindle shaped, are visible on Figure 5a. The length of the long axis is about 1.1 μm. Electron diffraction was made of one of these particles (labeled with arrow) as shown in Figure 5b.

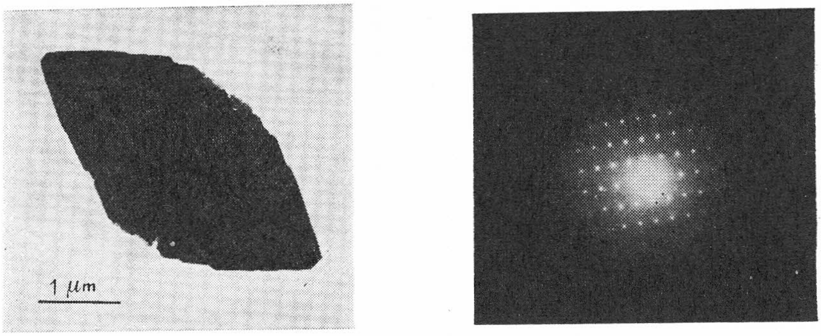


Figures 4a and 4b. Crystals of strontium sulfate precipitate sampled after 10 minutes. Electron micrographs and diffraction patterns of strontium sulfate precipitates.



Figures 5a and 5b. Crystals of strontium sulfate precipitate sampled after 15 minutes. Electron micrographs and diffraction patterns of strontium sulfate precipitates.

This diffraction was analysed by measuring (regularly) spaced diffraction maxima, and calculated »*d*« was compared to known ASTM values for strontium sulfate. Values corresponded with a derivation of 2%.



Figures 6a and 6b. Single crystal of strontium sulfate precipitate after 30 minutes. Electron micrographs and diffraction patterns of strontium sulfate precipitates.

Size of particles measured in the 30 minute specimen was about 4.45 μm in long axis. One of these particles is shown on Figure 6a. There is no doubt that the particle in Figure 6a is one single crystal. This is proved by the corresponding single crystal diffraction pattern shown in Figure 6b.

This was also confirmed by observing the particles using the dark field technique.

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SAŽETAK

Nastajanje i starenje taloga. Studij nukleacije stroncium sulfata iz otopine

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Brzina taloženja stroncij sulfata iz vodene otopine bila je proučavana mjerenjem relativnog intenziteta rasipanog svjetla te direktnim promatranjem čestica pod elektronskim mikroskopom. Prodiskutiran je mehanizam ionskog kristalnog rasta iz otopina i uspoređen s eksperimentalnim rezultatima brzine taloženja. Kada talog nastaje direktnim miješanjem reakcijskih komponenata, nukleacija nastaje vrlo brzo. Nakon indukcijskog perioda čestice kontinuirano rastu, no kristalna struktura počinje se pojavljivati tek kod čestica većih od 0,02 μm.

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