# *Crystal Habit Modification of Strontium Sulfate. II. Characteristic Effect of Sodium Triphosphate on Crystallization and Mechanism of Spherulite Formation*

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In the preceding paper[1] it was reported that the crystal habit of strontium sulfate was remarkably affected by a quite minute amount of sodium triphosphate (STP) added to the solution from which the crystals were deposited, and that the crystallization was retarded and finally came to be practically inhibited, as the amount of STP was increased, provided the concentration of the strontium ion was not over a given value.

Concerning the similar effect of condensed phosphates on the precipitation of various inorganic salts, many works have been published, mostly from the industrial point of view. For example, the effect of metaphosphates on the deposition of calcium carbonate was studied by several workers[2], and the action of triphosphate, metaphosphate, or Quadrafos on the precipitation of gypsum by Burcik[3]. Because of the minuteness of the amount of the phosphates effective in these cases, the prevention of the precipitation could not be ascribed to the sequestration of the component cations by complex formation. Some of the above authors, therefore, attributed the action of these phosphates to the adsorption of them on the crystal nuclei or the growing crystals.

However, the experimental evidences hitherto reported seem to be still insufficient for the reasonable interpretation of the mechanism of these phenomena, and concerning the effect of pure STP on the deposition of strontium sulfate, no work seems to be available in the literature. For the purpose of studying systematically the peculiar effect of STP on the deposition and the crystal habit of strontium sulfate, measurements were made in the present work on the following: (a) deposition rate and (b) dissolution rate of strontium sulfate at various STP contents, (c) surface adsorption of STP on strontium sulfate crystals, and (d) coprecipitation of STP with strontium sulfate. From the results of these experiments, the mechanisms of the habit modification, of the prevention of crystallization and of the spherulite formation will be discussed.

## Experimental and Results

**Inhibition of Crystallization by STP.**—To estimate quantitatively the retardation of the crystal deposition by STP, the rate of crystallization was measured by a conductance method. The reagents used were the same as those in the preceding work[1]. The solution to be examined was prepared

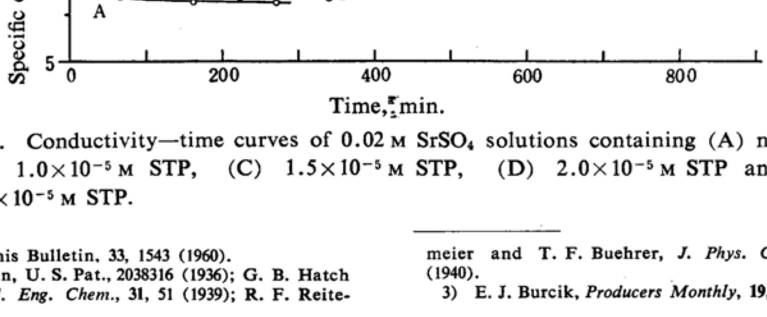

Fig. 1. Conductivity—time curves of 0.02 M $SrSO_4$ solutions containing (A) no STP, (B) $1.0\times10^{-5}$ M STP, (C) $1.5\times10^{-5}$ M STP, (D) $2.0\times10^{-5}$ M STP and (E) $3.0\times10^{-5}$ M STP.

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[1] S. Otani, This Bulletin, 33, 1543 (1960).

[2] L. Rosenstein, U. S. Pat., 2038316 (1936); G. B. Hatch and O. Rice, *Ind. Eng. Chem.*, **31**, 51 (1939); R. F. Reitemeier and T. F. Buehrer, *J. Phys. Chem.*, **44**, 535, 552 (1940).

[3] E. J. Burcik, *Producers Monthly*, **19**, No. 1, p. 42 (1954).

in a conductivity cell by mixing equal volumes of potassium sulfate and strontium chloride solutions of equivalent concentration, the latter containing an appropriate amount of STP. Being continuously shaken, the solution was put to the test as to its conductivity at intervals. The results of five runs with different concentrations of STP are illustrated in Fig. 1. The initial concentration of strontium sulfate was fixed at 0.02 M in all cases.

This figure shows how the deposition rate is reduced by a minute amount of STP. Indeed, when the initial concentration of STP amounted to $3.0\times 10^{-5}$ M, no change could be detected for a period more than 70 hr. Even if some fine crystals of strontium sulfate were added to this solution, its conductivity remained unchanged for a long period. These facts show that not only the spontaneous crystallization but also the growth of the crystals added was inhibited by STP at this concentration.

The irregularities seen on curves C and D are caused by the stepwise deposition of crystals of two quite different types, one being spherulite and the other fine single crsytals. The comparatively steep decrease in conductivity in the earlier stage corresponds to the growth of the spherulites and that in the later stage to the deposition of fine single crystals.

**Effect of STP on Dissolution.** — The rates of dissolution of strontium sulfate into water and dilute STP solutions of various concentrations were measured by the conductance method at 25°C. The conductivity of the solvent was first measured with a glass-stoppered conductivity cell with 30.0 ml. of the solvent. Then 1.00 ml. of a solution containing 1.00 mg. of strontium sulfate was pipetted into the cell, and the resultant change in conductivity was traced, the solution being shaken continuously. The result is illustrated graphically in Fig. 2.

**Adsorption of STP on Strontium Sulfate.**—The adsorption of STP on strontium sulfate was measured by a radio tracer method with the aid of STP labeled with $^{32}$P.

The labeled STP was prepared, referring to the result of Edward and Herzog[4], by a thermal treatment of the orthophosphate mixture to which radioactive orthophosphate had been added. The product was then recrystallized from an aqueous solution by adding ethanol, and purity was found to be satisfactory for the purpose from a paper chromatographic test. The strontium sulfate used as the adsorbent was precipitated from an equivalent mixture of strontium chloride and potassium sulfate solutions, washed thoroughly with distilled water by decantation, and dried in an oven at 150°C. The particle size of strontium sulfate thus obtained was $3\sim5\ \mu$ in diameter.

The adsorbed amount of STP was determined by shaking 30.0 ml. of its solution of a known concentration with 0.1000 g. of the adsorbent for an appropriate period and by measuring the radioactivity of the solution before and after treatment. To avoid the dissolution of the adsorbent during the treatment, the STP solution used was prepared by diluting a measured small volume, say $0.1\sim1$ ml., of a rather concentrated stock solution with a given large volume, say $100\sim500$ ml., of a saturated solution of strontium sulfate.

The adsorption rate was estimated by measuring the radioactivity of the solution under investigation at intervals during the shaking. One of the results obtained at $1.0\times 10^{-5}$ M of the initial STP concentration at 30°C is shown in Fig. 3, in which the radioactivity is plotted against the time of shaking. The adsorption isotherm obtained at 30.0°C is also illustrated graphically in Fig. 4. It is ascertained

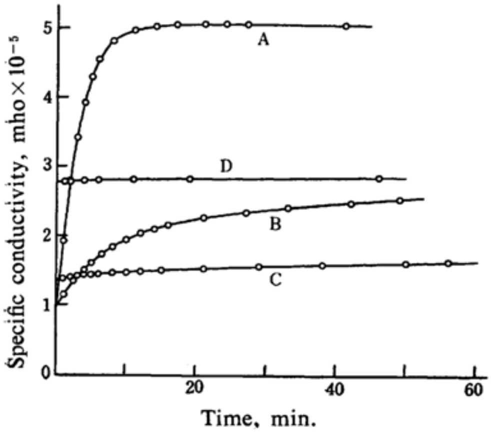

Fig. 2. Conductivity — time curves, showing the dissolution rate of $SrSO_4$ into water and STP solutions.
A: $H_2O$, B: $0.20\times 10^{-5}$ M STP, C: $1.0\times 10^{-5}$ M STP, D: $4.0\times 10^{-5}$ M STP

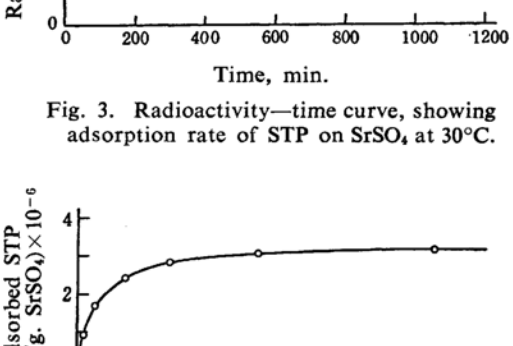

Fig. 3. Radioactivity—time curve, showing adsorption rate of STP on $SrSO_4$ at 30°C.

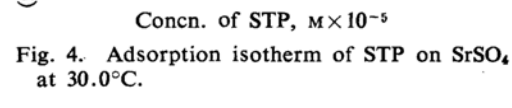

Fig. 4. Adsorption isotherm of STP on $SrSO_4$ at 30.0°C.

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4) J. W. Edwards and A. H. Herzog, *J. Am. Chem. Soc.*, **79**, 3647 (1957).

that this isotherm is in good agreement with Langmuir's equation.

**Coprecipitation of STP with Strontium Sulfate.** —The coprecipitation was studied with the aid of both the conductance method and the radiotracer technique. The procedures were as follows. Appropriate volumes of strontium chloride, labeled STP, and potassium sulfate solutions, all at 25°C, were pipetted into the conductivity cell in the order just mentioned, and shaken. The decrease in the concentration of strontium sulfate in the solution was traced by conductivity measurement. The radioactivity of the supernatant liquid was measured at intervals during precipitation to trace the decrease in STP concentration. Thus, both amounts of the strontium sulfate and STP precipitated within any desired period were determined simultaneously. One of the results obtained at 25°C is shown with curve A in Fig. 5. This curve illustrates how the amount of coprecipitated STP increases as the crystallization proceeds in a solution where the initial concentrations are 0.02 M with respect to both strontium chloride and potassium sulfate and $1.50\times10^{-5}$ M with respect to STP. In this experiment the solution was constantly shaken during crystallization.

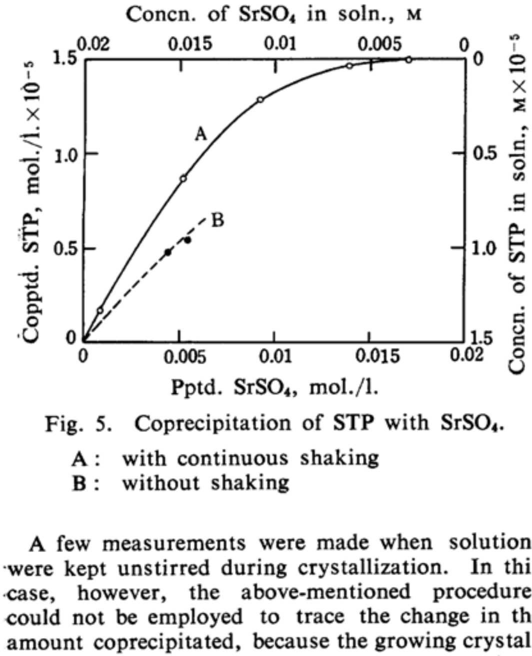

Fig. 5. Coprecipitation of STP with SrSO$_4$.

A : with continuous shaking
B : without shaking

A few measurements were made when solutions were kept unstirred during crystallization. In this case, however, the above-mentioned procedures could not be employed to trace the change in the amount coprecipitated, because the growing crystals were all sedimented at the bottom of the container, thus making the solution inhomogeneous. Therefore, the crystals deposited were filtered off at an appropriate time in the course of crystallization, and weighed after drying. The amount of coprecipitated STP was determined from the radioactivity of the filtrate. The two solid circles in Fig. 5 indicate the values obtained from two runs with solutions having the same composition as that mentioned above.

The mole ratios of STP to strontium sulfate both in the precipitate and the solution were calculated from the data given on curve A in Fig. 5, and are plotted in Fig. 6. The upper curve indicates the value in the precipitate and the lower that in the solution.

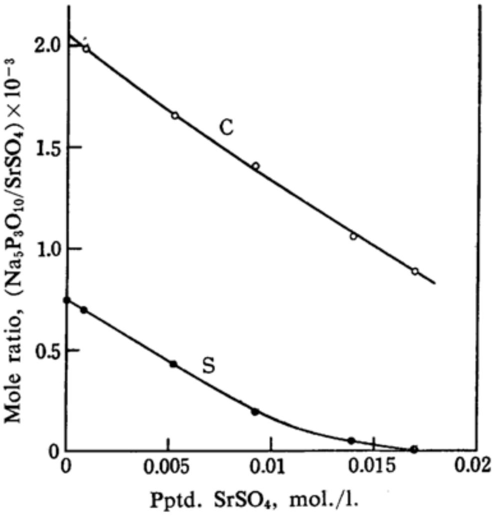

Fig. 6. Mole ratio of STP to SrSO$_4$ during crystallization.

C: in crystal S; in solution

## Discussion

From the measurements on the crystallization rate, a striking effect of STP was well noticed. As is seen in Fig. 1, an extremely small amount of STP ($3.0\times10^{-5}$ M in its concentration) is quite sufficient to prevent the deposition of crystals from the 0.02 M solution of strontium sulfate. This fact can not be attributed to the complex formation between strontium and triphosphate, in view of the extremely small mole ratio of triphosphate to strontium, namely, 1 : 670.

From the measurements on the dissolution rate, another striking effect of STP was observed. As is seen in Fig. 2, the dissolution of strontium sulfate was retarded by STP even when its concentration was as small as the one in the above-mentioned case. This evidence may possibly be attributed to the adsorption of STP on the crystal surface, because the dissolution can not be hindered directly by the STP existing in the bulk of the solution.

From the measurement of adsorption, the amount of STP adsorbed on strontium sulfate was found to be up to saturation at an extremely low concentration, namely $(2\sim4)\times10^{-5}$ M. Comparison of Fig. 4 with Figs. 1 and 2 reveals the fact that the concentration range within which the amount of adsorbed STP tends to be saturated agrees roughly with the one within which the retardation of crystallization and of dissolution becomes significant. The retardation or prevention of crystallization may accordingly be attributed to the adsorption of STP on the

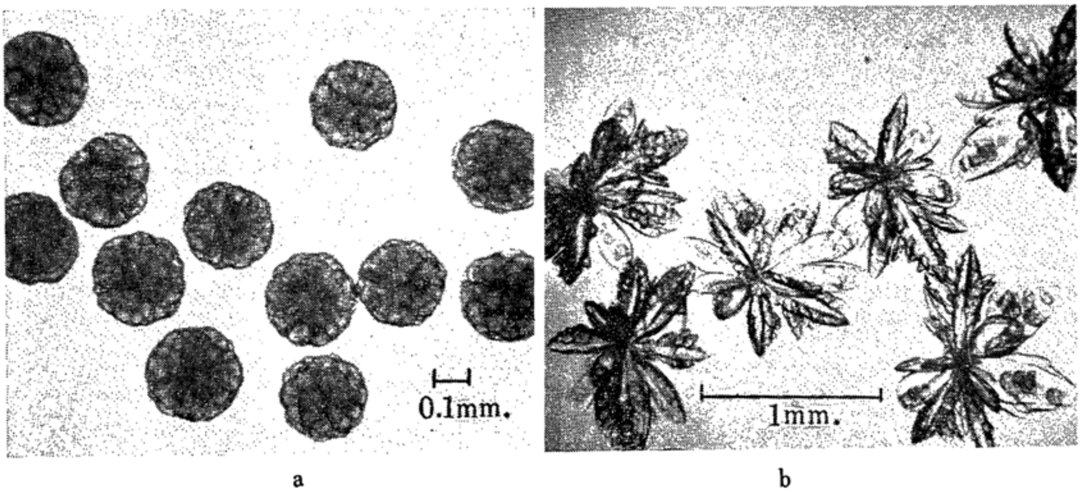

Fig. 7. Products grown from solutions of $SrSO_4$(0.02 M) containg STP ($1.5 \times 10^{-5}$ M).
a: with continuous shaking, b: without shaking

crystal nuclei or the growing crystals, and the following mechanism may be considered. The triphosphate ion may be adsorbed preferentially at the active centers of growth on the crystal nuclei or the growing faces of crystals, and the adsorbed triphosphate ion may act as a poison to the layer growth of the crystal faces. The larger the concentration of STP is, the more the active centers will be poisoned and the slower the growth rate will become, and finally, when the concentration of STP exceeds a given value, namely $(3\sim4) \times 10^{-5}$ M, at which the adsorption comes to be nearly saturated, all the active centers will be poisoned, and crystallization may be completely inhibited.

Strong interaction between STP and strontium sulfate may be reasonably recognized also from the measurements on coprecipitation. Fig. 6 shows that STP is coprecipitated almost completely with strontium sulfate, the mole ratio of STP to strontium sulfate in the crystal being several times as great as that in the solution.

As is seen from Figs. 5 and 7, agitation of the solution during crystallization has a considerable influence not only on the amount of coprecipitation but also on the crystal habit. Fig. 7a shows the spherulite obtained from a solution with continous shaking (corresponding to curve A in Fig. 5), and Fig. 7b the star-like aggregate from another solution of the same initial composition without shaking (corresponding to curve B in Fig. 5). The difference between the habits of these crystals may be due to the difference in the amount of coprecipitated STP, which can be possibly traced back to the difference in the mode of supply—one by agitation and the other merely by diffusion—of STP from the bulk on the crystal interface.

As already reported⁵⁾, the component crystallite of the spherulite or the star-like aggregate is elongated in the direction of *c* axis. This fact means that STP makes the growth rate predominant in the direction of *c* axis. From the above-mentioned poisoning action of the adsorbed STP upon the regular layer growth, it may be concluded that the adsorption of STP is at its minimum on the (001) face as compared with all the other faces, and accordingly the layer growth on this face is least retarded.

Next, the mechanism of spherulite formation will be considered. If radiating fibrillar growth starts from a common center in all directions with an equal growth rate, the growing aggregate will always be spherical. For this to occur, it is necessary to postulate the existence of a cluster of nuclei which has the ability to emit fibrillar crystallites in all directions. In practice, however, the formation of such a cluster of nuclei seems to be improbable, and it may be more acceptable to assume the branching of growing crystallite.

Keller and Waring⁶⁾ assumed a periodic branching of fibrils occurring at constant distances with a constant acute angle to explain the "sheaf" formation in the course of spherulitic growth of synthetic high polymers. They proved that the periodicity of branching is a necessary condition for the formation of Popoff's "Zweiblatt"⁷⁾ or Morse and Donnay's "sheaf"⁸⁾. Keller and Waring's illustration of

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5) Y. Takano and S. Otani, *J. Sci. Hiroshima Univ., Ser. A*, **23**, 109 (1959).

6) A. Keller and J. R. S. Waring, *J. Polymer Sci.*, **17**, 447 (1955).

7) B. Popoff, *Latv. Farm. Zurn.*, **1934**, 1.

8) H. W. Morse and J. D. H. Donnay, *Am. Mineralogist*, **21**, 392 (1936).

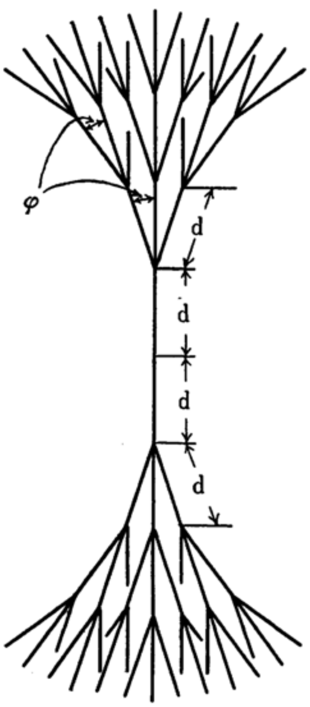

Fig. 8. Schematic diagram showing the sheaf formation through periodic branchings (after Keller and Waring).

the sheaf formation through the periodic branching is reproduced in Fig. 8.

In the present case, the branching of crystallite were recognized from a microscopic observation of the growth process. Fig. 9 shows the development of a seed in a solution containing an appropriate amount of STP. Fig. 9a shows the seed which is one of the splinters obtained by crushing a well-developed spherulite, and Fig. 9b and 9c illustrate the successive stages of its growth. By crushing the product (Fig. 9c), a large number of wedge-shaped smaller crystallites resulted. These are shown in Fig. 9d. By comparing these photographs with each other, it may be seen that radiating crystallization started everywhere on the surface of the seed. This fact may certify that branching of crystallite is induced by STP.

No indication of sheaf formation was observed either in this experiment or in many others mentioned before. However, the formation of spherulite can be interpreted on the basis of the above-mentioned evidence that, under the influence of STP, branchings are accompanied by the growth of strontium sulfate crystal and its growth rate is highly predominant in the direction of *c* axis. Under this condition, the crystal growth must proceed as follows. Starting from a single nucleus, an aggregate crystallites will be formed as a result of successive branchings during the growth, and the number of the crystallites will increase acceleratedly as the growth proceeds. On the other hand, the growth of each crystallite must inevitably be restricted by the steric hindrance of the adjacent ones, and, as a result, only those crystallites of which the direction of the fastest growth happened to coincide nearly with the radial direction may survive. Thus, sooner or later, the aggregate changes to be constructed of a great number of crystallites directed radially, at least near the periphery. Hereafter, the

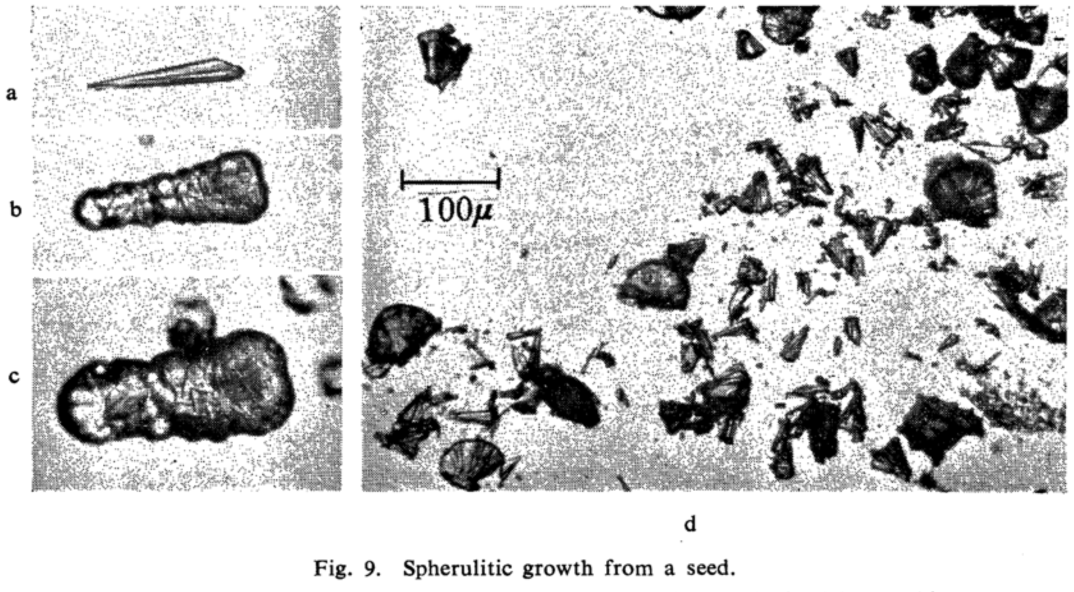

Fig. 9. Spherulitic growth from a seed.
a: seed, b: after 48 min., c: after 190 min., d: splinters obtained by crushing c

shape of the aggregate must gradually approach a sphere, because the growth rate is uniform in all directions in the radial growth.

The above-mentioned concept may explain why such a star-like aggregate as that shown in Fig. 7b is produced, when the solution is kept unstirred. For a moment just after a crystal nucleus begins to grow, it may be supplied with enough STP to cause frequent branchings regardless of the solution being stirred or not. However, as the growth proceeds, the concentration of STP at the immediate vicinity of the growing aggregate may be reduced rapidly because of the consumption of STP due to the selective adsorption (cf. Fig. 6). If the solution is not stirred, STP is supplied merely by diffusion, and hence the branching may ocurr less frequently. Accordingly the resultant aggregate, being composed of a relatively small number of radiated crystallites, gives a star-like appearance.

As to the mechanism of the branching of crystallite, Keller and Waring[6] mentioned twinning and rupture of distorted crystal as possible causes. In the present work, branching is induced by STP, and may be attributed to the adsorption of the latter onto the crystallite. The mechanism of branching may be considered as follows. The adsorbed triphosphate ion could hardly enter into the regular crystal lattice of strontium sulfate because of the unfitness of the size and ionic charge. The crystal lattice may be distorted in the vicinity of the adsorbed triphosphate ion. As the amount of adsorbed triphosphate increases, many ruptures of lattice may appear on the crystal faces owing to the distortions of the lattice. These ruptures may cause branchings of crystallite.

From the above discussion, we may conclude that we shall have a possibility of preparing spherulites of any substance, if we can find an impurity that has the following properties. (1) The impurity is intensely and preferentially adsorbed by the particular crystal faces of the substance in question and (2) the impurity can not make a solid solution or mixed crystal with the substance. A clue to finding such a suitable impurity may possibly be obtained from the knowledge of the relation between the molecular or ionic structure of the impurity and the crystal structure of the substance in question. For the preparation of a spherulite of an inorganic salt, there may be found some suitable impurities among those polyatomic complex ions which have a strong affinity to either of the component ions of the salt.

## Summary

1) The peculiar effect of sodium triphosphate (STP) on the crystallization and the crystal habit of strontium sulfate was studied systematically by measuring (a) the deposition rate and (b) the dissolution rate of strontium sulfate at various STP concentrations, (c) the surface adsorption of STP on strontium sulfate crystal, and (d) the coprecipitation of these salts.

2) The inhibiting action of STP on the deposition and dissolution of strontium sulfate is attributed to the adsorption of STP.

3) The fact that STP makes the growth rate predominant in the direction of $c$ axis of strontium sulfate is ascribed to the small adsorption of STP on the (001) faces compared with that on the other faces.

4) The occurrence of the branching of crystallite was ascertained experimentally, and attributed to the ruptures appearing on the crystal faces as a result of the unfitness in the size and ionic charge of the adsorbed triphosphate.

5) The formation process of the spherulite can be interpreted from the fact that the frequent branchings are accompanied by the nearly one-dimentional growth of crystallite.

6) Possibilities of preparing spherulites from other substances are discussed.

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