The Effect of Sodium Triphosphate on the Nucleation of Strontium Sulfate

By Hiromitu NAONO and Masaji MIURA

(Received July 7, 1964)

Since the patent of Rosenstein[1] was first presented, several investigators[2] have considered the inhibiting action of condensed phosphates on the crystallization of several sparingly soluble inorganic salts from their supersaturated solutions. In our previous papers[3] it has been reported that a supersaturated solution of strontium sulfate is perfectly stabilized for an extended period in the presence of a minute amount of sodium triphosphate. The concentration of the coexisting triphosphate is several hundred times less than that of strontium sulfate, and so the decrease in the concentration of free strontium ions by forming a complex with triphosphate may be regarded as negligibly small, despite the fact that the triphosphate is known to form a stable and soluble complex with strontium ion.[4] Under such conditions, it can not be expected that the concentration of strontium sulfate solution will be so reduced by the addition of triphosphate as to be unable to form nuclei.

In order to explain such observations, it has been proposed by some authors[2] that the phosphate ions are adsorbed on the surface of crystal nuclei born in the solution and that

---

[1] L. Rosenstein, U. S. Pat. 2038316 (1936).

[2] 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); R. F. Reitemeier and A. D. Ayers, *J. Am. Chem. Soc.*, **69**, 2759 (1947); B. Raistrick, *Discussions Faraday Soc.*, **5**, 234 (1949); E. J. Burcik, *Producers Monthly*, **19**, No. 1 (1954), p. 42.

[3] S. Otani, This Bulletin, **33**, 1544, 1549 (1960); M. Miura, S. Otani, M. Kodama and K. Shinagawa, *J. Phys. Chem.*, **66**, 252 (1962); M. Miura, S. Otani, Y. Abe and C. Fukumura, This Bulletin, **36**, 1091 (1963).

[4] A. Roppongi and T. Kato, ibid., **35**, 1086 (1962).

they prevent the further growth of nuclei. Our previous investigation[3] has shown that the surface of strontium sulfate particles is completely covered by a monomolecular layer of adsorbed triphosphate in the vicinity of the concentration where the triphosphate exhibits the inhibiting action. This finding seems to indicate that the adsorption plays a predominant role in the action.

According to the above assumption, the number of nuclei should increase rapidly and, after an extended period, a large number of the nuclei should be accumulated in the supersaturated solution, while the growth of nuclei is prevented by the triphosphate adsorbed on them. Contrary to these expectations, however, a small number of large, distorted crystals of strontium sulfate were found to be deposited by the supersaturated solution when the concentration of triphosphate is slightly lower than that which makes the supersaturated solution stable. Therefore, there still remain some problems to be solved concerning the major effect of triphosphate on the nucleation of some inorganic salts.

In this paper, two physico-chemical methods are employed to investigate and clarify the problems described above: (1) a light-scattering study of the supersaturated solution of strontium sulfate stabilized in the presence of triphosphate, and (2) a study of the nucleation rate of strontium sulfate from its supersaturated solutions containing various amounts of triphosphate.

Experimental

Materials.—The special grade reagents of strontium chloride and potassium sulfate were further purified by recrystallizing them from aqueous solutions. The method of the preparation and purification of sodium triphosphate has been described previously.[5]

Light Scattering.—The light-scattering measurements were performed at 25°C using a Shimadzu light-scattering photometer. All the solutions used in this work were filtered by a Cerafilter (its average pore diameter was 100—200 mμ). The values of the turbidity and of the dissymmetry coefficient of water were $5.4\times10^{-5}\,\mathrm{cm}^{-1}$ and 1.00 ± 0.01 respectively at 436 mμ. White light was used in place of monochromatic light in order to increase the intensity of the scattered light. Measurements were carried out in a semioctagonal cell for four samples: (1) 0.04 M $SrCl_2$; (2) 0.04 M K_2SO_4 containing 6×10^{-5} M $Na_5P_3O_{10}$; (3) a mixed solution containing equal volumes of solutions (1) and (2), and (4) 0.02 M $SrCl_2$ containing 3×10^{-5} M $Na_5P_3O_{10}$.

Nucleation Kinetics.—The rate of nucleation was measured by counting the number of crystals deposited from supersaturated solutions of strontium sulfate containing various amounts of sodium triphosphate. All the solutions used in this experiment were filtered according to the procedure used in the light-scattering measurements.

The supersaturated solution of strontium sulfate was prepared by adding 2.5 ml. of a 0.04 M strontium chloride solution to an equal volume of a 0.04 M potassium sulfate solution which also contained sodium triphosphate, the concentration of which varied from 0 to 3×10^{-5} M. The solution thus obtained was allowed to form nuclei for an appropriate period (nucleation time), during which time the degree of supersaturation remained nearly constant.

Preliminary experiments showed that, in the strontium sulfate solution of the above-described concentration, containing 3×10^{-5} M triphosphate, no crystals were formed for 1500 min., but the crystals placed in the solution grew slowly, although the number of crystals remained constant over the growth period. A solution of the same composition was used in this experiment as a growth medium. After the nucleation was over, the nuclei were transferred into a growth medium of a large volume and left to grow to crystals of a size large enough to be detected under a microscope (the growth time was about 1000 min.). The number of crystals thus grown was counted under a microscope using a Bürker counting room. In order to reduce the counting error, the average value of twenty-five runs was used to calculate the total number of crystals formed during nucleation.

Results and Discussion

The results of the light-scattering measurements are shown in Tables I, II and III, where i_θ is the scattering intensity in the θ direction and z_{45}, the ratio of i_{45} to i_{135}. As may be seen in Tables I and II, the value of i_{90} for the supersaturated solution stabilized with triphosphate show no appreciable increase with the lapse of time and takes, within the range of experimental error, the same value as that for each solution from which the supersaturated solution is prepared. The nucleation of the solution may, therefore, be almost completely prevented by the presence of triphosphate. In contrast to i_{90}, the value of z_{45} for the supersaturated solution changes with time. The two figures in the z_{45} column in Table II indicate the maximum and minimum values for one minute. The fluctuation of the values of z_{45} is mainly due to those of i_{45}. Even with the naked eye a small number of particles were observed to move at random by Brownian movement in the path of the incident beam. Scrupulous care was used to eliminate the traces of dusts in the solution, but the fluctuation in the values of i_{45} did not disappear. As is shown in Table III, this phenomenon was not observed in the system containing

---

[5] M. Miura, H. Naono and S. Otani, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **66**, 593 (1963).

TABLE I. LIGHT SCATTERING RESULTS OF THE SYSTEMS OF $SrCl_2$ (0.04 M) and K_2SO_4 (0.04 M)-$Na_5P_3O_{10}$ (6×10^{-5} M)

System	i_{90}	z_{45}
$SrCl_2$ (0.04 M)	13.5±0.2	1.00±0.01
K_2SO_4(0.04 M)- $Na_5P_3O_{10}$ (6×10^{-5} M)	13.5±0.2	1.00±0.01

TABLE II. LIGHT SCATTERING RESULTS OF THE SYSTEM OF $SrCl_2$ (0.02 M)-K_2SO_4 (0.02 M)-$Na_5P_3O_{10}$ (3×10^{-5} M)

Time min.	i_{45}	i_{90}	i_{135}	z_{45}
20— 21	27.6—30.0	13.6	27.0	1.03—1.12
25— 26	27.5—27.8	13.6	26.8	1.03—1.04
30— 31	27.6—28.7	13.7	27.0	1.02—1.06
38— 39	27.2—28.1	13.5	26.8	1.02—1.05
50— 56	28.1—30.5	14.0	27.6	1.02—1.08
60— 61	29.3	13.9	27.6	1.06
103—104	27.8—32.5	13.9	27.8	1.00—1.17
110—111	28.4—32.5	13.9	27.2	1.05—1.19
330—331	28.8	13.8	27.4	1.05

TABLE III. LIGHT SCATTERING RESULTS OF THE SYSTEM OF $SrCl_2$ (0.02 M)-$Na_5P_3O_{10}$ (3×10^{-5} M)

Time min.	i_{45}	i_{90}	i_{135}	z_{45}
25— 26	26.3	13.0	26.0	1.01
45— 46	26.1	12.9	25.7	1.01
53— 54	26.4	12.9	26.1	1.01
145—146	26.6	13.2	26.4	1.01
153—154	26.8	13.0	26.4	1.01

both sodium triphosphate and strontium chloride. From these observation it has been concluded that the fluctuation is caused by a small number of crystallites of strontium sulfate formed in the supersaturated solution.

The effect of triphosphate upon the nucleation rate of strontium sulfate is shown in Table IV, where the nucleation rate, J, is defined as the rate of nuclei formation per unit volume (ml.) per unit time (sec.). In Fig. 1 the nucleation rate is plotted against the concentration of triphosphate in a log-log scale. The explosive formation of nuclei occurs in the absence of triphosphate, but the nucleation rate is markedly reduced by an increasing concentration of triphosphate. Within the concentrations of triphosphate ranging from 0.2×10^{-5} M to 1.5×10^{-5} M, the curve in Fig. 1 obeys the equation:

$$J=Kc^{-9.5}$$

where K is a constant and c, the molar concentration of triphosphate. The equation shows that a tenfold increase in the concentration of triphosphate reduces the nucleation rate to approximately one-several thousand millionth.

TABLE IV. INFLUENCE OF TRIPHOSPHATE ON THE NUCLEATION RATE OF STRONTIUM SULFATE

Concn. of triphosphate, M	Nucleation time, sec.	Nucleation rate (J)
0	10	$(8\ \pm3\ )\times10^{6}$
2.0×10^{-6}	30	$(2.0\pm0.7)\times10^{6}$
5.0×10^{-6}	100	$(1.0\pm0.5)\times10^{3}$
1.0×10^{-5}	180	$(1.5\pm0.6)\times10^{-1}$
1.5×10^{-5}	600	$(5\ \pm1\ )\times10^{-3}$

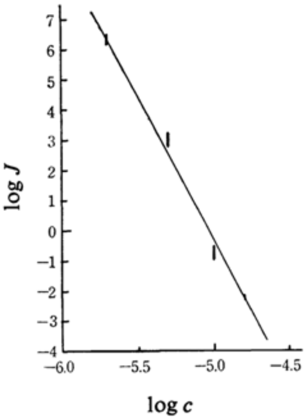

Fig. 1. Relation between the nucleation of strontium sulfate and the concentration of triphosphate.

It is now clear from these results that the minute amount of triphosphate greatly suppresses the nucleation of strontium sulfate. In the previous papers of our laboratory[3,5] it was reported that the inhibiting action of condensed phosphates was closely related to the adsorption of phosphates onto the crystal surface in the cases of strontium sulfate and calcium carbonate.

By combining the finding concerning light scattering and the nucleation rate with those of adsorption, we may consider that the clusters of strontium sulfate with the embryonic dimension which are generated in the supersaturated solution may be broken into separated ions by the adsorption of triphosphate and that such a probability increases with the increase in the concentration of triphosphate.

Summary

The nucleation from supersaturated solutions of strontium sulfate containing various amounts of triphosphate has been investigated by means of light scattering and nucleation kinetics. The nucleation rate is remarkably reduced by the increase in the concentration of triphosphate and may be represented by an empirical expression, $J=Kc^{-9.5}$. Light-scattering measurements have confirmed that practically no

nucleation occurs in the supersaturated solution stabilized in the presence of triphosphate.

The authors wish to express their thanks to Dr. Otani for his helpful discussions.

Department of Chemistry
Faculty of Science
Hiroshima University
Hiroshima