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The Effect of the pH Value on the Crystallization of Strontium Sulfate in the Presence of Triphosphate

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The crystallization of strontium sulfate has been conductometrically investigated in the presence of triphosphate under various pH values of the solution. The amount of triphosphate adsorbed on the crystal surface of strontium sulfate has been estimated as a function of the pH of the solution. The action of triphosphate in stabilizing the supersaturated solution of strontium sulfate and the amount of triphosphate adsorbed on the crystal surface depend remarkably on the pH of the solution; further, the two are closely correlated with each other. It has been concluded from these facts that the adsorption of triphosphate plays an important role in the stabilization of the supersaturated solution of strontium sulfate.

Several investigators have studied the characteristic phenomena caused by the action of condensed phosphates on the crystallization of sparingly-soluble inorganic salts from their supersaturated solution.[1-5] As has been reported previously,[2-4] the crystallization of strontium sulfate is extremely retarded and its supersaturated solution is stabilized by the coexistence of a minute amount of triphosphate. Recently, it has been clarified that the main function of triphosphate is the suppression of nuclei formation from the supersaturated solution of strontium sulfate.[6] On the other hand, such a stabilizing action is closely correlated to the adsorption of triphosphate on the crystal surface of strontium sulfate.[2-4]

The works mentioned above have treated the stabilizing action and the adsorptive behavior of triphosphate in a neutral solution.[2-4] It has been found, however, that when the pH of the solution is varied, remarkable differences arise in the stabilizing action, and also in the adsorptive behavior, of triphosphate. Accordingly, it seems of great interest to investigate these problems at various pH values.

Experimental

Materials.—Strontium chloride and potassium sulfate were purified by recrystallizing the special-grade reagents three times from their aqueous solutions. Pure sodium triphosphate labeled with ^{32}P was prepared by a procedure which has been described previously.[5] Strontium sulfate crystals used as an adsorbent were prepared by a procedure similar to that described in a previous paper,[3] except that the experiment was carried out in a nitrogen atmosphere in order to avoid the formation of strontium carbonate.

Crystallization.—The crystallization of strontium sulfate was traced by measuring the conductivity decrease in the supersaturated solution, which was prepared by mixing equal volumes of 0.02 M solutions of strontium chloride and potassium sulfate, the latter containing various amounts of triphosphate.

Adsorption.—The experiment of adsorption was carried out by a radiotracer method with the aid of triphosphate labeled with ^{32}P.[2]

The pH of the solution was adjusted by adding hydrochloric acid or sodium hydroxide. Crystallization and adsorption experiments were carried out at 25°C in a nitrogen atmosphere in order to restrain the pH change during the procedures.

Results and Discussion

As has been reported in the previous papers,[3,4] such a minute amount of triphosphate as 5×10^{-6} M practically inhibits the crystallization from a 0.01 M strontium sulfate solution when the solution is neutral. With its concentration kept at 5×10^{-6} M, the action of triphosphate on the crystallization of strontium sulfate was examined conductometrically at various pH values. As may be seen in Fig. 1, the stabilizing action of triphosphate becomes weak as the pH of the solution is lowered. In Fig. 3, the decrease in specific conductivity after 100 min, is plotted as a function of the pH of the solution. It must be emphasized that the stabilizing action changes abruptly within a certain pH range and practically disappears below pH 5. Figure 2 shows the pH dependence of the stabilizing

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[1] L. Rosenstein, U. S. Pat. 2038316 (1936); G. B. Hatch and O. Rice, *Ind. Eng. Chem.*, **31**, 51 (1939); R. F. Reitemeier and T. B. 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, 42 (1954).

[2] S. Otani, This Bulletin, **33**, 1544, 1549 (1960).

[3] M. Miura, S. Otani, M. Kodama and K. Shinagawa, *J. Phys. Chem.*, **66**, 252 (1962).

[4] M. Miura, S. Otani, Y. Abe and C. Fukumura, This Bulletin, **36**, 1091 (1963).

[5] M. Miura, H. Naono and S. Otani, *J. Chem. Soc. Japan, Ind. Chem. Sect.* (*Kogyo Kagaku Zasshi*), **66**, 597 (1963).

[6] H. Naono and M. Miura, This Bulletin, **38**, 80 (1965).

action of triphosphate, its concentration being 3×10^{-5} M. An abrupt change in the stabilizing action is also observed, but it occurs in a somewhat lower pH region than in the above case, as may be seen in Fig. 3.

Next, the crystallization of strontium sulfate was studied at various pH values in the absence of triphosphate. Figure 4 shows that the crystallizations are somewhat different at different pH values. The lower the pH of the solution, the more rapidly the crystallization begins, but the effect of pH on the crystallization is small compared with that in the presence of triphosphate mentioned above. Consequently, it is clear that the remarkable change in the stabilizing action with the pH value in the presence of triphosphate is mainly due to the change in the action of triphosphate with the pH.

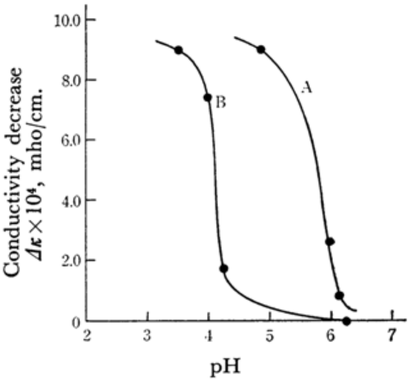

Fig. 3. Conductivity decrease after 100 min. Concentration of triphosphate:
A 5.0×10^{-6} M, B 3.0×10^{-5} M

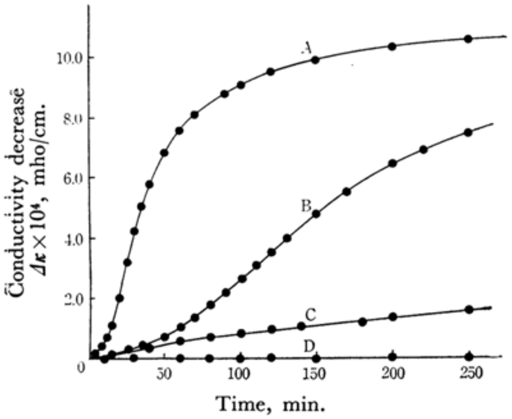

Fig. 1. Effect of pH on the crystallization of strontium sulfate from 0.01 M solution in the presence of 5.0×10^{-6} M triphosphate.
A pH=4.85, B pH=5.98, C pH=6.12, D pH=9.97

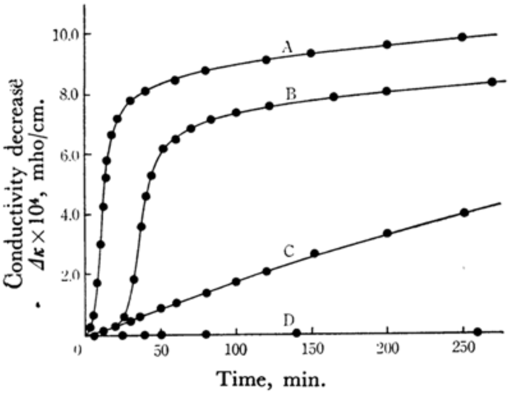

Fig. 2. Effect of pH on the crystallization of strontium sulfate from 0.01 M solution in the presence of 3.0×10^{-5} M triphosphate.
A pH=3.45, B pH=3.98, C pH=4.08, D pH=6.20

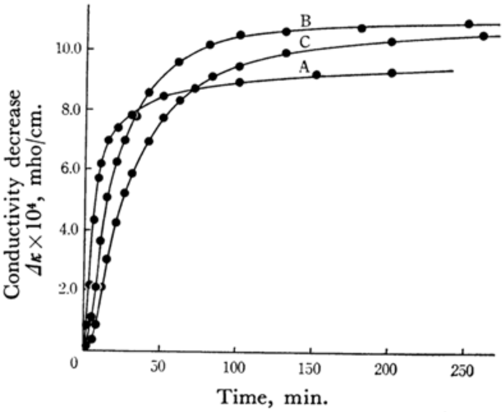

Fig. 4. Effect of pH on the crystallization of strontium sulfate from 0.01 M solution.
A pH=3.32, B pH=6.50, C pH=9.95

It has been considered so far that the stabilization of the supersaturated solution of strontium sulfate by triphosphate is to be attributed to the adsorption of triphosphate. It may, therefore, be expected that a remarkable difference will also appear in the adsorptive behavior of triphosphate on the surfaces of strontium sulfate crystals.

Adsorption isotherms of triphosphate at various pH's are shown in Fig. 5, in which the isotherms are divided roughly into three groups, namely, those in acidic, neutral and alkaline regions. The amount adsorbed increases with the rise in the pH of the solution. To make this relation clearer, the amounts adsorbed at the equilibrium concentration of 3×10^{-5} M were estimated as a function of the pH of the solution. The results are given in Fig. 6, which shows that abrupt changes in the amounts adsorbed occur in the vicinities of pH 4 and 11.

It has been reported previously that triphosphate adsorbed from a neutral solution forms a monomolecular layer on the surfaces of strontium sulfate crystals.[3)] It is, therefore, apparent from the

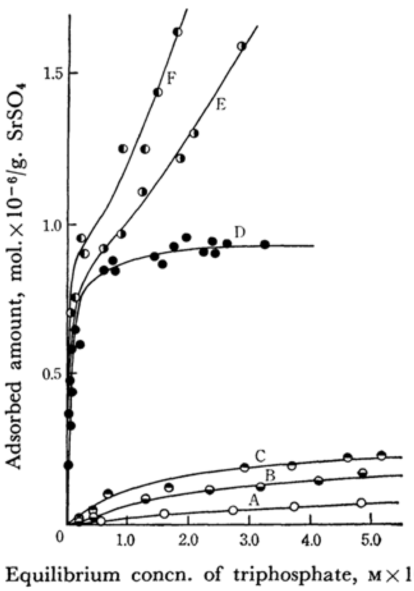

Fig. 5. Adsorption isotherms of triphosphate at various pH.
A pH=2.5, B pH=3.2, C pH=3.5,
D pH=6.8, E pH=10.9, F pH=11.3

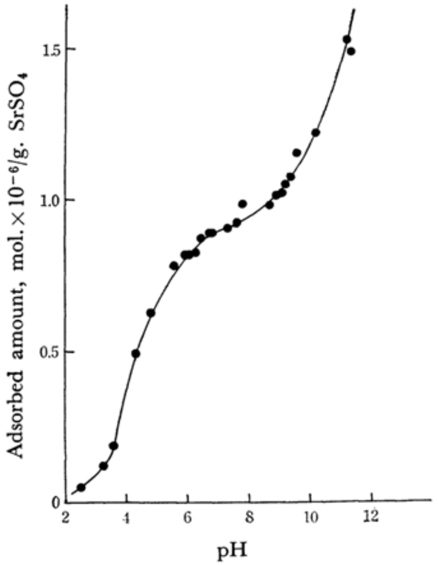

Fig. 6. Relation between adsorbed amount and pH of solution at the equilibrium concentration of 3×10^{-5} M triphosphate.

isotherms in the acid region that the adsorbed triphosphate covers merely a small fraction of the adsorbent surface. On the other hand, on the alkaline side the amount adsorbed far exceeds that corresponding to the monomolecular layer.

Now, let us discuss the pH dependence of the stabilizing action of triphosphate in connection with that of the amount adsorbed at the concentration of triphosphate, 3×10^{-5} M. It is obvious from Figs. 2 and 6 that both the stabilizing action and the adsorbed amount change remarkably in the vicinity of pH 4; that is, the stabilizing action increases rapidly with the abrupt change in the adsorbed amount. This fact indicates that the adsorption plays an important role in the stabilizing action, as has been considered previously. In the present work, no large difference in the stabilizing action was observed on the alkaline side, though the amount adsorbed was far larger than that in the neutral region.

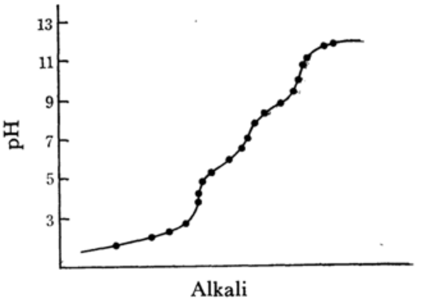

Fig. 7. Titration curve of triphosphoric acid with tetramethyl ammonium hydroxide. After J. I. Watter et al.7)

When triphosphoric acid is titrated with alkali, three inflection points can be obtained, corresponding to three different ionic species, namely, $H_2P_3O_{10}^{3-}$, $HP_3O_{10}^{4-}$ and $P_3O_{10}^{5-}$, as may be seen in Fig. 7.7) A comparison between the titration (Fig. 7) and the adsorption (Fig. 6) curves shows that the ionic species, $HP_3O_{10}^{4-}$ and $P_3O_{10}^{5-}$, have a much greater ability to be adsorbed on the crystal surface than does $H_2P_3O_{10}^{3-}$. On the other hand, the stability of the complex between strontium and triphosphate ions increases with an increase in the pH of the solution.8) Therefore, triphosphate ions of a higher valency may be adsorbed on the strontium sulfate crystal, forming a surface complex with strontium ions and thus playing an important role in stabilizing the supersaturated solution of sutrontium sulfate.

Summary

The pH of the solution exerts a profound influence on the action of triphosphate in stabilizing the supersaturated solution of strontium sulfate, and also on the amount of triphosphate adsorbed on its crystal surface. Both of these functions of triphosphate show a remarkable change in the vicinity of pH 4 when the concentration of triphosphate is 3×10^{-5} M. Above pH 4, the stabilizing action and the amount of triphosphate adsorbed

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7) J. I. Watters, S. M. Lambert and E. D. Loughran, *J. Am. Chem. Soc.*, **79**, 3651 (1957).

8) A. Roppongi and T. Kato, This Bulletin, **35**, 1086 (1962).

increase remarkably. On the other hand, it has been reported that the stability of the strontium complex with triphosphate increases with the increase in the pH. These facts have led us to the conclustion that the stabilizing action in the higher pH range is mainly due to the strong interaction between triphosphate ions of a higher valency and the surfaces of strontium sulfate crystals.