The Effect of Several Condensed Phosphates on the Dissolution of Strontium Sulfate

By Masaji MIURA and Hiromitu NAONO

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The subject of the retarding action of several condensed phosphates on the crystallization of such sparingly soluble inorganic salts as strontium sulfate,[1-4] calcium carbonate[5] and calcium sulfate[6] has been investigated in our laboratory. It has been found that the retarding action is closely correlated with the adsorption of condensed phosphates on the crystal surface. In continuation of these works, we have studied the dissolution of strontium sulfate in the dilute solutions of several condensed phosphates and have found that the dissolution is considerably retarded in the presence of phosphates and inhibited almost completely under suitable conditions. Such a phenomenon as the inhibition of dissolution has not yet been investigated, however, although the retarding action of some additives on the dissolution of such crystals as lithium fluoride[7] and silver chloride[8] has been studied. In the present paper, some results will be given on the effect of condensed phosphates on the dissolution of strontium sulfate, and the mechanism of the dissolution will be discussed.

Experimental

Materials.—An analytical-grade reagent of sodium dihydrogen orthophosphate was further purified by recrystallization from its aqueous solution. Sodium pyro-, tri- and trimetaphosphate were prepared and then purified by the same procedure as has been described previously.[2,5] The powder of the strontium sulfate was the same as that used in the previous work;[2] its specific surface area was 0.29 m²/g.

Dissolution. — The dissolution process was followed by the conductance method at 25°C. Thirty milliliters of the phosphate solution was poured into a conductivity cell and then left to reach thermal equilibrium in a thermostat; then 1 ml. of the strontium sulfate sol was quickly added to the solution, the concentration of the sol being 1 mg. $SrSO_4$/ml. While the cell was being shaken continuously, the conductivity of the solution was measured at regular intervals.

Adsorption. — The adsorption of triphosphate on strontium sulfate was measured by the radio tracer method at 25°C with the aid of triphosphate labelled with ^{32}P. A known weight of the strontium sulfate powder was then added to 30 ml. of the triphosphate solution. The rate of the adsorption was determined by measuring the decrease in the radioactivity of the solution at intervals.

Results

The effect of ortho-, pyro-, tri- and trimetaphosphate on the dissolution of strontium sulfate is shown in Figs. 1—4, which give the increase in the specific conductance arising from the dissolution of strontium sulfate in the presence of various amounts of the phosphates. Curve A in each figure indicates the dissolution into pure water. The effect of these phosphates on the dissolution of strontium sulfate is summarized in Fig. 5, where the increase in the specific conductance after 50 min. is plotted against the phosphate concentration.

The adsorption rate of triphosphate on the surface of the strontium sulfate is shown in

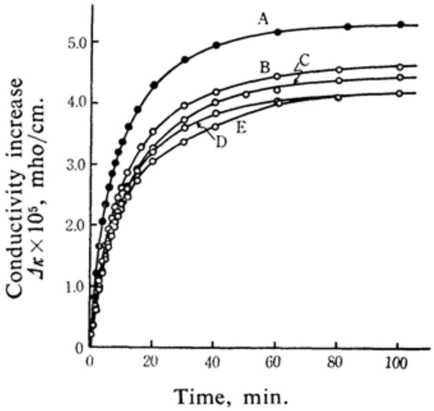

Fig. 1. Effect of sodium dihydrogen orthophosphate on the dissolution of strontium sulfate. Concentration of orthophosphate:
A) 0, B) 1.0×10^{-5} M, C) 4.0×10^{-5} M, D) 1.0×10^{-4} M, E) 4.0×10^{-4} M

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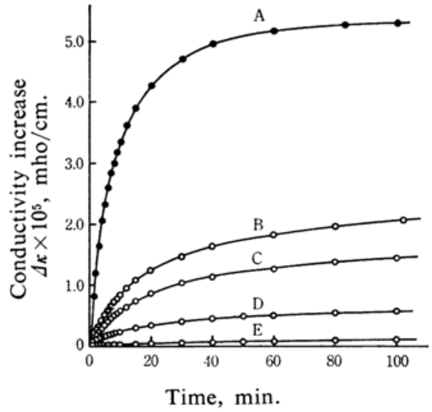

Fig. 2. Effect of sodium pyrophosphate on the dissolution of strontium sulfate.
Concentration of pyrohosphate:
A) 0, B) 5.0×10^{-6} M, C) 1.0×10^{-5} M,
D) 2.0×10^{-5} M, E) 4.0×10^{-5} M

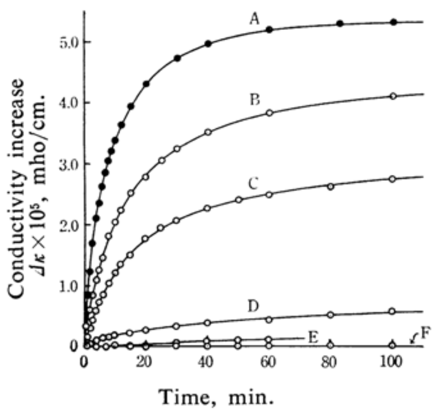

Fig. 3. Effect of sodium triphosphate on the dissolution of strontium sulfate.
Concentration of triphosphate:
A) 0, B) 5.0×10^{-7} M, C) 1.0×10^{-6} M,
D) 5.0×10^{-6} M, E) 2.0×10^{-5} M,
F) 4.0×10^{-5} M

Fig. 6, where the initial concentration of triphosphate is 1.0×10^{-5} M, the equilibrium concentration, 3.6×10^{-6} M, and the weight of strontium sulfate, 150 mg.

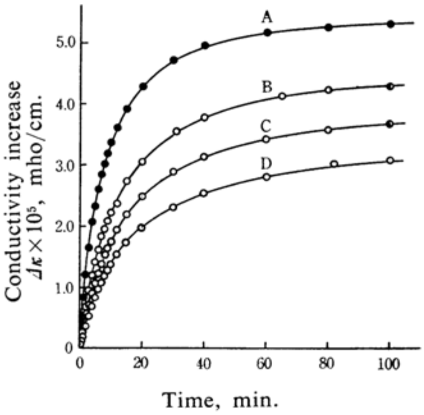

Fig. 4. Effect of sodium trimetaphosphate on the dissolution of strontium sulfate.
Concentration of trimetaphosphate:
A) 0, B) 2.5×10^{-5} M, C) 1.0×10^{-4} M,
D) 2.0×10^{-4} M

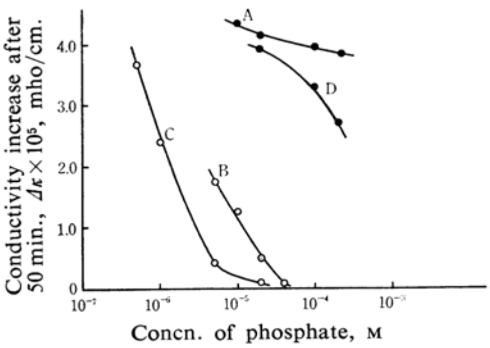

Fig. 5. The retarding action of several condensed phosphates on the dissolution of strontium sulfate.
A) ortho-, B) pyro-, C) tri-,
D) trimetaphosphate

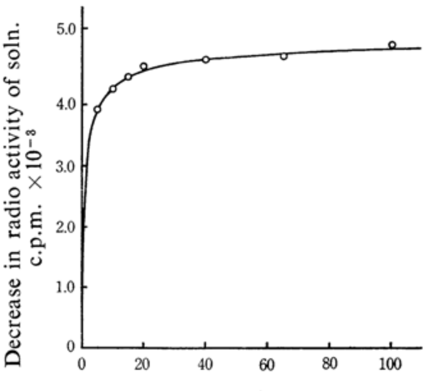

Fig. 6. Adsorption rate of triphosphate on the surface of strontium sulfate.

Discussion

As may be seen in Figs. 1—4, pyro- and triphosphate, even in their dilute solutions, exert a profound influence upon the dissolution of strontium sulfate, and an increase in the concentration of these phosphates brings about an increase in the retarding action until finally it practically inhibits the dissolution. Moreover, when a small amount of triphosphate is added to a system in which strontium sulfate has been dissolving in water, the dissolution of the substance is immediately and almost completely inhibited, as may be seen in Fig. 7. On the other hand, the effect of

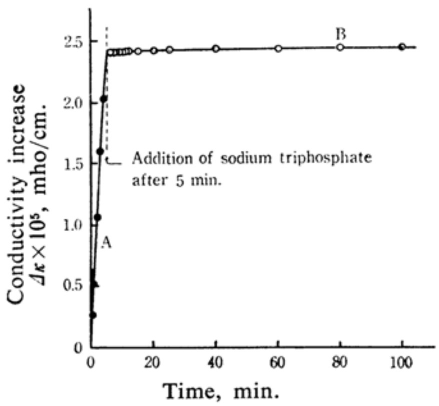

Fig. 7. Effect of sodium triphosphate on the dissolution of strontium sulfate.
Concentration of triphosphate:
A) 0, B) 1.0×10^{-5} M

ortho- and trimetaphosphate is not so large as that of the other phosphates.

From Fig. 5 it may be seen that the retarding action of these four phosphates increases in the order of ortho-, trimeta-, pyro- and triphosphate and that there is a great difference in the retarding action between the former two phosphates and the latter two ones. The same tendency has been observed in the retarding action of these phosphates on the crystallization of strontium sulfate.²⁾

The retarding action of phosphates may be considered to be caused by the covering of the surface of particles by the phosphates adsorbed, thus preventing the escape of ions from the surface of crystal into the solution. The adsorption of phosphates on the surface of crystal seems, then, to play a predominant role in the retarding action. According to the results of the measurements of the adsorption of these phosphates on the strontium sulfate particles previously reported,²⁾ the adsorbed amount of tri- or pyrophosphate is much larger than that of trimeta- or orthophosphate. The results of the adsorption reveal that the retarding action on the dissolution of strontium sulfate is closely related to the adsorption of phosphates.

It is of much interest to discuss the retarding action by combining the dynamic behavior of the dissolution of strontium sulfate with the rate of the adsorption of phosphate. Let us now consider the case where 1 mg. of strontium sulfate is dissolved in 30 ml. of a solution. The initial slope of the dissolution curve in water gives the initial rate of the dissolution. From the initial rate, the increase in the concentration of strontium sulfate in the solution is calculated to be 1.9×10^{-4} M per minute, where a linear relationship is assumed between the specific conductance and the concentration. On the other hand, the average area occupied per ion pair of strontium sulfate on the (001), (010) and (100) faces of its crystal was found to be 23.2 Å^2.³⁾ The suface area of 1 mg. of strontium sulfate was also found to be 2.9×10^{-4} m^2 from its specific surface area.²⁾ If the outermost layer of the crystal surface dissolves into 30 ml. of the solution, it can be calculated from the above two data that the increase in the concentration of strontium sulfate is 6.9×10^{-8} M. The time necessary for removing the outermost layer of the particle surface is approximately 3.6×10^{-4} min., by which time the surface layer of particles is uniformly removed by the dissolution. As is shown in Fig. 6, the amount of adsorbed triphosphate increases rapidly within the first few minutes, but it needs at least more than ten minutes to reach the adsorption equilibrium.

From these results, it is clear that there is an extremely large difference between the time required to remove one layer of the crystal surface of strontium sulfate by dissolution and that required to cover the surface by a monomolecular layer of triphosphate. In spite of such a large difference between these two times, the dissolution is greatly retarded. In order to explain such facts, the following mechanism may tentatively be proposed for the dissolution of strontium sulfate.

The surface of crystal may not be uniform; the special places may play a predominant role for the dissolution. On the other hand, the fact that the adsorption isotherm of triphosphate on strontium sulfate approaches the saturation point in an extremely dilute concentration, namely, ca. 10^{-6} M, shows that a strong interaction exists between the surface of strontium sulfate and triphosphate. The adsorbed triphosphate may form a fairly strong bond with the strontium ions of the crystal surface, presumably forming a compound such as the surface complex. When such places as the active sites for the dissolution are covered by the adsorption of triphosphate, the dissolution may be remarkably retarded. Such places may be kinks or steps on the crystal surface, as has been presumed by Sears et al.⁷⁾ in the case of the dissolution of lithium fluoride poisoned by a trace of ferric fluoride. It may be inferred that the adsorption on the kinks or steps prefers the adsorption on the flat surface of the crystals. The probability that such places are covered increases with the increase in the concentration of triphosphate, resulting in the strong retarding action. A similar consideration may be applied to the case of pyrophosphate.

The insignificant effect of ortho- and trimetaphosphate may be attributed not only to the small adsorption amount, but also to the weak bond between these phosphates and the crystal surface in comparison with the case of tri- or pyrophosphate.

Summary

The effect of ortho-, pyro-, tri- and trimetaphosphate on the dissolution of strontium sulfate has been studied. Pyro- and triphosphate remarkably retard the dissolution, even in an extremely dilute solution, while ortho- and trimetaphosphate exhibit only an insignificant effect. From the results of the measurements of the adsorption of these phosphates onto the crystal surface, it is considered that the retarding action of these phosphates is to be attributed to the adsorption. The kinetic treatments of the dissolution and adsorption lead to the conclusion that the dissolution may be controlled by the specific places on the crystal surface and that such places may be the rate-determining sites for the dissolution.

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Department of Chemistry
Faculty of Science
Hiroshima University
Higashisenda, Hiroshima