The Effect of Tri-, Tetra-, Penta- and Hexaphosphate on the Crystallization of Strontium Sulfate

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It is a well-known fact that a very small amount of various condensed phosphates exhibits a striking effect on the stabilization of supersaturated solutions of various inorganic salts, especially those of sparingly soluble calcium salts.(1) In many papers emphasis has been laid on the superior of effect of " hexametaphosphate," a mixture many homologues of polyphosphates, but no work seems to have been done with its individual constituents.

In our previous works,[2,3] the effect of ortho-, pyro-, tri- and trimetaphosphate on the crystallization of strontium sulfate has been investigated in relation to the adsorption of these phosphates on the crystals of strontium sulfate. The purpose of the present work is to study the effect of the higher homologues of polyphosphates, which are the main constituents of the " hexametaphosphate."

Experimental

Radioactive tri-, tetra-, penta- and hexaphosphate were separated by anion-exchange chromatography from a " hexametaphosphate glass " prepared by pyrolysis from a mixture of sodium dihydrogen phosphate and disodium hydrogen phosphate containing ^{32}P.(4) Since these phosphates are gradually hydrolyzed in a solution,(4) all measurements were made with solutions newly prepared and stocked in a cold place. The other reagents used were the same as those used in the previous works.[2,3] The strontium sulfate crystals used as the adsorbent were prepared in a way similar to that used in a previous work,(3) but the crystal size of the product was somewhat larger than that used before.

The effect of the phosphates on the crystallization rate of strontium sulfate was examined by measuring the conductivity decrease in equivalent mixtures of strontium chloride and potassium sulfate solutions containing various amounts of the phosphates. The techniques employed in measuring the conductivity and the adsorption of the phosphates on strontium sulfate have been described in the previous papers.[2,3]

Results and Consideration

The effect of the four kinds of phosphates on the crystallization rate of strontium sulfate is represented by the conductometric data shown in Fig. 1—4. The ordinate of these graphs represents the percentage decrease in the specific conductivity with reference to the total decrease when no phosphate is added.

Figure 5 shows the adsorption isotherms obtained at 25°C and pH 7. This figure shows that the number of moles adsorbed per gram of strontium sulfate decreases with the increase in the chain length of polyphosphate.

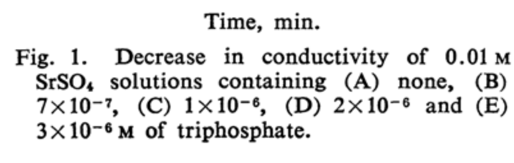

Fig. 1. Decrease in conductivity of 0.01 M $SrSO_4$ solutions containing (A) none, (B) 7×10^{-7}, (C) 1×10^{-6}, (D) 2×10^{-6} and (E) 3×10^{-6} M of triphosphate.

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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. F. Buehrer, *J. Phys. Chem.*, 44, 535, 552 (1940); E. J. Burcik, *Producers Monthly*, 19, 42 (1954).

2) S. Otani, This Bulletin, 33, 1543 (1960).

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

4) W. Wieker, *Z. Elektrochem.*, 64, 1047 (1960); S. Otani, M. Miura and T. Doi, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), 66, 593 (1963).

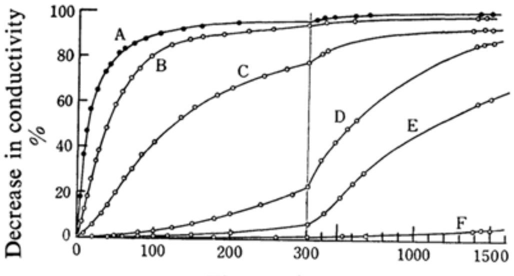

Fig. 2. Decrease in conductivity of 0.01 M $SrSO_4$ solutions containing (A) none, (B) 5×10^{-7}, (C) 1×10^{-6}, (D) 1.5×10^{-6}, (E) 2×10^{-6} and (F) 2.5×10^{-6} M of tetraphosphate.

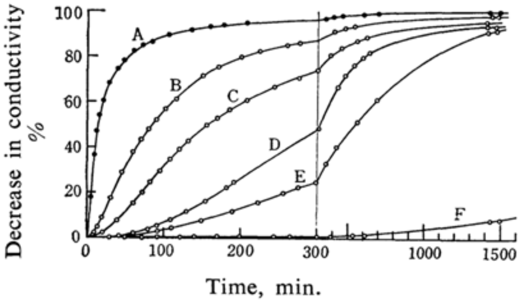

Fig. 3. Decrease in conductivity of 0.01 M $SrSO_4$ solutions containing (A) none, (B) 5×10^{-7}, (C) 7×10^{-7}, (D) 1×10^{-6}, (E) 1.5×10^{-6} and (F) 2×10^{-6} M of pentaphosphate.

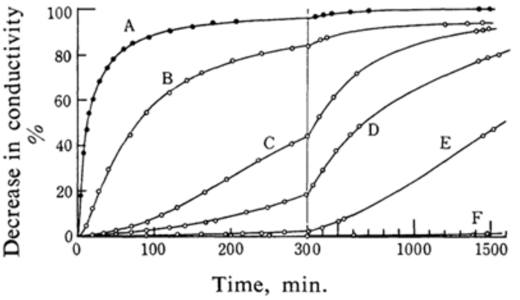

Fig. 4. Decrease in conductivity of 0.01 M $SrSO_4$ solutions containing (A) none, (B) 5×10^{-7}, (C) 1×10^{-6}, (D) 1.25×10^{-6}, (E) 1.5×10^{-6} and (F) 2×10^{-6} M of hexaphosphate.

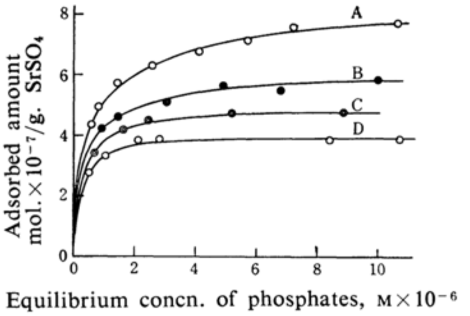

Fig. 5. Adsorption isotherms of tri- (A), tetra- (B), penta- (C) and hexaphosphate (D) at 25°C, pH 7.

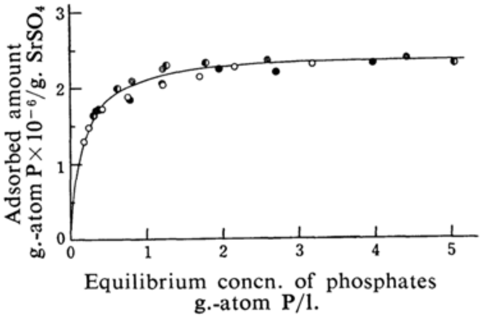

Fig. 6. Adsorption isotherms expressed in terms of the monomer unit.
○ Tri ● Tetra ◎ Penta ◐ Hexa

If, however, we represent the same data in terms of the monomer unit, as in Fig. 6, the adsorbed amounts of these phosphates can be illustrated by a common curve almost within the range of experimental error. This fact shows that a tetrahedral PO_4 unit of the polyphosphates adsorbed always occupies, on the average, about the same area of the crystal faces, independent of the chain length of the phosphates examined.

As has been mentioned previously,³⁾ the average area occupied per triphosphate ion adsorbed on strontium sulfate is 37 Å²; hence, we can estimate the area occupied per PO_4 tetrahedral unit of the phosphates as roughly 12 Å², independent of their chain length. On the other hand, the areas occupied per ion pair of strontium sulfate on the (1 0 0), (0 1 0) and (0 0 1) faces of its crystal (celestine) were found to be 18.4, 28.7 and 22.4 Å² respectively.⁵⁾ Since the adsorption of phosphates is considered to be caused by some bonding between phosphate anions and Sr^{2+} cations on the crystal face, the above-mentioned data suggest that more than one PO_4 tetrahedral unit may be bound to an Sr^{2+} ion on the crystal faces.

As has been discussed in previous papers,²,³⁾ the inhibition of the crystallization of strontium sulfate due to the phosphates added may be caused by their adsorption on the crystal nuclei or growing crystals of strontium sulfate. From the similar behavior of the four phosphates in their adsorption on strontium sulfate, their effect on the crystallization rate may be expected to be nearly equivalent in all cases. That this is true may readily be realized if the phosphate concentrations are expressed in monomer units and Figs. 3—6 are then compared with one another. Independent of the

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5) S. Otani and M. Miura, *J. Sci. Hiroshima Univ., Ser. A-II*, **27**, 11 (1963).

chain length of the phosphates, each monomer exhibits almost the same effect on the crystallization rate. The effects of these phosphates on the habit of the crystals deposited are also similar to one another; spherulites having a nearly spherical shape were obtained from 0.01 M strontium sulfate solutions containing $(5\sim9)\times10^{-6}$ g.-atom P/1. of each phosphate.

In so far as the present work is concerned, " hexametaphosphate " can not be expected to exhibit a far greater effect on the crystallization of strontium sulfate if there is no cooperative effect among the individual constituents.

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