EFFECT OF POTASSIUM POLYVINYL SULFATE OF VARIOUS DEGREES OF SULFATION ON THE FORMATION OF HYDROXYAPATITE IN AN AQUEOUS PHASE

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Abstract: Effect of potassium polyvinylsulfate(Sulf. PVA) on the formation of hydroxyapatite(HAP) via amorphous calcium phosphate (ACP) in an aqueous phase was studied in the presence of 0.9 % NaCl at 35 °C. Sulf. PVA retarded the transformation of ACP to HAP, although polyvinylalcohol(PVA) showed no effects on the formation. This effect became more significant with increases in the concentration and degree of sulfation(α) of Sulf. PVA. This was explained in terms of (1)the crystal poisoning through isomorphous substitution and (2)electrostatic repulsion against Pi in the adsorption layer of Sulf. PVA on the HAP seed surface.

INTRODUCTION

Chemical structure and size of sulfate ion(SO₄²⁻) are quite similar to those of phosphate ion(PO₄³⁻, Pi). That is, these are of tetrahedral oxoacids and the interatomic distance between S and O(= 0.149 nm) are almost the same as that between P and O(= 0.155 nm). Therefore, Pi on the surface of HAP is easily exchanged to sulfate ion(SO₄²⁻)¹ or sulfate
group($R\cdot SO_4^-)^2$. 3 through isomorphous substitution although their valencies are different with each other. In the previous paper, the effect of Sulf.PVA($\alpha = 0.922$) on the transformation of ACP to HAP was compared with that of phosphorylated polyvinylalcohol(Phos. PVA). The effect of the former was weaker than that of the latter, because the affinity of sulfate group for the seed/nucleus of HAP is lower than that of phosphate group. In addition to these results, it was found that the mother compound, polyvinylalcohol(PVA), showed no effects on the formation of HAP. In the present paper, the effect of degree of sulfation($\alpha$) of PVA was studied, taking into consideration the facts mentioned above.

EXPERIMENTAL

Sulf. PVA(Wako Pure Chemical Industries, Ltd., Osaka) was used as a potassium salt($\alpha = 0.922$), of which degree of polymerization was ca. 1500, as was converted to PVA. This is the same sample as that used before. After hydrolysis of Sulf. PVA(concentration = 1 %) in the presence of 70 mmol/dm$^3$ H$_2$SO$_4$ at 100°C for 5 minutes, another sample of Sulf. PVA of low degree of sulfation($\alpha = 0.321$) was obtained. PVA, for the reference, was purchased from Wako Pure Chemical Industries, Ltd., of which viscosity-average molecular weight and degree of saponification were $1.6 \times 10^4$ and ca. 100 %, respectively.

Time courses of calcium ion activity(Ca$^{2+}$-selective electrode, Orion) and pH(H$^+$-selective electrode) of the solution were traced with a 2-pen recorder after mixing 1.25 mmol/dm$^3$ CaCl$_2$, 2.50 mmol/dm$^3$ K$_2$HPO$_4$, and an additive in an aqueous solution of 0.9 %(= 154 mmol/dm$^3$) NaCl. The induction time($T$) to HAP from ACP was determined from an intersection of the tangents drawn to the curves of Ca$^{2+}$-activity and pH just before and after the second steep decrease, as was shown elsewhere. The induction time obtained from these two curves agreed reasonably well with each other. Data of the induction time($T$) in the present paper were
shown as those relative to the standard induction time without an additive \(T_0 = 20\) min, i.e., \(T/T_0\).

**RESULTS AND DISCUSSION**

Figure 1 shows the effect of \(\text{Na}_2\text{SO}_4\) and Sulf. PVA on \(T/T_0\) as a function of a concentration of sulfate ion or group. Although PVA (data not shown here) and \(\text{Na}_2\text{SO}_4\) did not affect at all, both of Sulf. PVAs retarded the transformation of ACP to HAP. The effect became stronger with increases in their concentration and degree of sulfation, \(\alpha\).

Figure 2 is showing the effect of degree of sulfation \(\alpha\) on \(T/T_0\). Data were quoted from Fig. 1 at 0.075 mmol/dm³ of a repeating-unit concentration of PVA which was converted from a concentration of Sulf. PVA by virtue of the \(\alpha\)-values. This concentration of the repeating unit was chosen as a common scale for Sulf. PVA with a different \(\alpha\)-value.

The effects of Sulf. PVAs were compared with those of Phos. PVA⁵ in Fig. 3, where \(T/T_0\) is shown as a function of a concentration of phosphate or sulfate group. Data of inorganic sulfate ion were also shown here as a reference, quoted from Fig. 1. Sodium chondroitin-6-sulfate (\(\text{Na}_2\text{Chs}\), data not shown here)⁶ as well as \(\text{Na}_2\text{SO}_4\) did not delay the transformation over the concentration range shown in Fig. 3. This was probably because \(\text{Na}_2\text{Chs}\) is hydrophilic and easily desorbable from the

**FIGURE 1.** Effect of concentration of sulfate ion/group on the relative induction time, \(T/T_0\).
- ◆: \(\text{Na}_2\text{SO}_4\)
- ○: Sulf.PVA\((\alpha = 0.321)\)
- □: Sulf.PVA\((\alpha = 0.922)\)
seed surface when Pi, as one of the component ions for HAP, approaches and gets contact with the surface to compete for the growth/adsorption sites with the sulfate group of Na₂Chs.

The retardation by polymers was observed at concentrations higher than ca. 10⁻³ mmol/dm³ of phosphate or sulfate groups irrespective of the degree of esterification of the polymers and of the electric charge of the groups. The effect of Phos. PVA was the most remarkable although its degree of esterification (α = 0.0817, ○) is far less than Sulf. PVA (α = 0.922, ●).

FIGURE 2. Effect of degree of sulfation, α, on the relative induction time, T/T₀.

FIGURE 3. Effect of concentration of sulfate or phosphate group on the relative induction time, T/T₀.

○: Phos. PVA (α = 0.0817)
●: Sulf. PVA (α = 0.922)
○: Sulf. PVA (α = 0.321)
●: Na₂SO₄
Mechanism for the retardation is as follows (see Figure 4): some of the sulfate/phosphate groups of the polymer chain occupy the Pi sites on the seed surface through isomorphous substitution, while the others on the same polymer chain are unattached but close to the surface, forming an adsorption layer. Negative charges in and on the adsorbed layer repel Pi approaching its site on the seed surface, resulting in the inhibition/retardation of the transformation of ACP to HAP. Effect of the polymer layer is important, because Sulf. PVA affects significantly T/T₀ while Na₂SO₄ showed no effect even at the same concentration (see Fig. 3).

Phosphate group of Phos. PVA is more firmly bound to the seed surface than sulfate group of Sulf. PVA, because the size of phosphate group of Phos. PVA is closer to that of inorganic phosphate ion (Pi) than that of sulfate group of Sulf. PVA is. Therefore, rate of desorption of the phosphate group is lower than that of the sulfate group when Pi approaches the seed surface from a bulk solution to repel the phosphate/sulfate groups bound on the seed surface. That is, the difference in retarding efficiencies between these groups are explained in terms of the affinity to the seed surface. On the other hand, the difference in the effect between high and low degree of sulfation of Sulf. PVAs is explained in terms of efficiency of rejection against Pi in the adsorption layer. That is, the higher the degree of sulfation (α), the higher the

FIGURE 4. Schematic illustration for the competition between sulfate group of the adsorbed Sulf. PVA and inorganic phosphate ion for the active growth sites on the surface of HAP nucleus.
electric charge density and the repelling efficiency are. As for PVA, it has no charged groups along the polymer chain, and its amount of adsorption by HAP was low\(^5\). Therefore, the retardation effect was little.

**CONCLUSION**

1. Na\(_2\)Chs, Na\(_2\)SO\(_4\), and PVA did not show any effects on the transformation of HAP from ACP in an aqueous phase.

2. The retardation effect (i.e., crystal poisoning) of Sulf.PVA increased with the degree of sulfation (\(\alpha\)) and its concentration.

3. The retardation effect of Phos. PVA (\(\alpha = 0.0817\)) was stronger than that of Sulf. PVA (\(\alpha = 0.922\)), even though the \(\alpha\)-value of the former is lower than that of the latter.

4. The retardation effect was explained in terms of two factors cooperative on the seed surface: (1) isomorphic substitution of sulfate/phosphate group for inorganic phosphate ion, and (2) electrostatic repulsion against Pi in the adsorption layer of the polymer.

5. Significance of the polymer effect (comparing to that of Na\(_2\)SO\(_4\)) and that of the charge effect (comparing to that of PVA) were emphasized.

**REFERENCES**