FORMATION OF INTERMOLECULAR COMPLEX BETWEEN POLYVINYLPYRROLIDONE AND
SODIUM DODECYLSULFATE THROUGH HYDROPHOBIC INTERACTION ON THE SURFACE
OF HYDROXYAPATITE IN AN AQUEOUS PHASE

— flocculation of the HAP particles by the surface complex —

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Abstract: Formation of an intermolecular complex between sodium dodecylsulfate(SDS) and polyvinylpyrrolidone(PVP) on the surface of hydroxyapatite(HAP) and its effect on dispersion/flocculation of the HAP particles were studied in an aqueous phase. PVP alone was scarcely adsorbed on HAP. However, it was adsorbed in the presence of SDS bound on the surface of HAP, forming the surface complex between PVP and SDS by virtue of hydrophobic interaction.

In the absence of SDS, PVP did not affect the mean diameter(d) of secondary particles of HAP irrespective of its concentrations. The d -value, however, decreased after attaining a maximum with a concentration of PVP when a certain amount of SDS was added. These facts mean that the SDS-PVP complex behaves as dispersing and flocculating agents for the HAP particles. The d -values were measured as a function of concentrations of SDS and PVP.

INTRODUCTION

It is known that sodium dodecylsulfate(SDS) forms an intermolecular complex with polyvinylpyrrolidone(PVP) owing to hydrophobic interaction in an aqueous phase.¹ Complex similar to the above is also formed on the surface of hydroxyapatite(HAP). In the previous papers,^{2,3,4} it was shown that SDS is adsorbed on HAP by the mechanisms of electrostatic attraction

between negative charge of dodecylsulafte ion(DS) and positive one localized on the surface of HAP and of ion-exchange (isomorphous substitution) of DS with a surface phosphate ion. SDS thus bound on HAP captures PVP segments through the hydrophobic interaction, resulting in formation of the surface complex although PVP is hardly adsorbed on HAP without SDS.

In the present paper, effects of the adsorbed PVP on stability of an HAP suspension were discussed. PVP exhibited bridging/flocculating and dispersing effects on the suspension after the adsorption, depending on its concentration and a binding ratio of SDS/PVP.

EXPERIMENTAL

The samples of HAP(Ca/P = 1.66) and PVP(M.W. = 1.19×10^6) were the same as those used in the previous papers.^{2,3,4} SDS was of BDH analaR. An HAP suspension(10 g/dl) was prepared in an aqueous solution of 0.9 % NaCl containing known amounts of SDS and PVP. Three days after the prepa-

FIGURE 1. The d-value as a function of concentrations of PVP and SDS

ration, the suspension was diluted ca. 3000 - 4000-fold with its suspending medium. Immediately after the dilution, a mean diameter(d) of secondary particles of HAP in the suspension was measured a few times at time intervals of one minute by a Coulter counter(type TA-II) at room temperature. The d -value in the original suspension just before the dilution was estimated by extrapolation of its time-course back to zero time.

RESULTS AND DISCUSSION

The d -value for HAP particles in an aqueous solution of PVP mixed together with SDS is shown in FIG. 1 as a function of their concentrations. FIGURE 2 is a map of the contour lines obtained from FIG. 1. PVP did not show any effects over the concentrations studied in the absence of SDS. This is because PVP is not bound by HAP without the assistance of SDS.³ On the other hand, the d -value gradually increased with an added concentration of SDS in the absence of PVP. This is probably because hydrocarbon chains of DS adsorbed on the HAP particles, which are protruding from the surface, associate with each other to form the bridges among the particles through hydrophobic interaction(FIG. 3), resulting in the aggregation of the primary particles and, therefore, the increase in the d -value.

The d -value exhibited a maximum at 0.02 - 0.03 % of PVP in the presence of SDS. This fact means flocculation of HAP occurs due to the co-

FIGURE 2. Contour lines for the d -values. Figures on respective curves refer to the d -values in a unit of μm .

operative contribution of SDS with PVP toward the interparticle bridging. There might be two modes for the interparticle bridging(see FIG. 3):

(1) PVP molecule adsorbed on a particle spreads out its polymer chain to the neighboring particles to be adsorbed, resulting in the interparticle bridging by PVP itself. As for SDS, it offers the adsorption site for PVP on the surface of HAP; (2) PVP loops and tails protruding from an HAP particle are bound to those from another particle with the assistance of SDS in the manner of "HAP-PVP-SDS-PVP-HAP", resulted in the interparticle bridging. In this case SDS play a role in jointing the PVP segments with each other at a location remote from the surface of HAP. This mechanism might be less important because SDS does not behave as an accelerator to connect PVP directly to the surface of HAP.

When both concentrations of SDS and PVP were high enough, the d-value decreased again(see FIGS.1 and 2). This is because the primary particles of HAP became repulsive each other due to the effects of (1)high charge density owing to DS adsorbed on the surface and of (2)steric hindrance of the loops and tails of PVP adsorbed via SDS implanted on the surface. The relationships among the binding ratio of SDS/PVP, concentrations of added SDS and PVP, and the d-values were furthermore discussed elsewhere.^{2, 3}

FIGURE 3. Scheme for the formation of the secondary particle in the presence of PVP and SDS. (1) HAP particle, (2)adsorbed DS, (3)surface complex of PVP and SDS, (4)hydrophobic segments of PVP

REFERENCES

- 1 M.Nakagaki and S.Shimabayashi, Nippon Kagaku Kaishi, 1972, 1496.
- 2 S.Shimabayashi, T.Uno, and M.Nakagaki, Colloids and Surfaces, in press
- 3 S.Shimabayashi, Y.Yoshida, K.Arima, and T.Uno, Phosphorus Research Bulletin, 4, 89(1994).
- 4 S.Shimabayashi, H.Tanaka, and M.Nakagaki, Chem. Pharm. Bull., 34, 4474 (1986).