ZETA POTENTIAL OF HYDROXYAPATITE IN THE PRESENCE OF HYDROXYPROPYLCELLULOSE AND SODIUM DODECYLSULFATE IN AN AQUEOUS PHASE (EFFECT OF FORMATION OF THE SURFACE COMPLEX)

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ABSTRACT: Adsorption of hydroxypropylcellulose (HPC) on hydroxyapatite (HAP) in the presence of sodium dodecylsulfate (SDS) and its effect on zeta potential of the HAP in an aqueous phase were studied. Although the adsorption amount of HPC was low in the absence of SDS, it increased with a concentration of SDS by virtue of formation of the complex between them on the surface. Zeta potential of the HAP was negative (-14 mV) in an aqueous solution of 0.9 % NaCl. Its absolute value decreased with a concentration of HPC because the slipping plane moves to the outside of the particle with the adsorption amount of HPC. The zeta potential, on the contrary, became more negative with a concentration of SDS after its adsorption and formation of the surface complex with HPC.

INTRODUCTION

When a nonionic and hydrophobic polymer captures an ionic surfactant in an aqueous phase through hydrophobic interaction, an intermolecular complex is formed, of which properties are quite similar to those of a polyelectrolyte. It is known that such a complex is formed between hydroxypropylcellulose (HPC) and sodium dodecylsulfate (SDS) as well as between polyvinylpyrrolidone (PVP) and SDS.1-4 On the other hand, we have precisely discussed the adsorption mechanism of SDS by hydroxyapatite (HAP) in an aqueous phase to date.5-8 It has been concluded that SDS or dodecylsulfate anion (DS-) is adsorbed to the surface of HAP through both electrostatic attractive force toward its calcium ion and isomorphous substitution for its
phosphate ion on the surface. After the adsorption, the hydrophobic group of SDS is protruding to an aqueous phase or lying on the surface. That is, the surface is modified to a hydrophobic one. We can expect that hydrophobic groups of the adsorbed SDS might easily interact with hydrophobic polymers such as HPC and PVP,\(^3,4\) resulting in formation of the surface complex. The objective of this paper is to study the complex formation between HPC and SDS on the surface and its effect on zeta potential of the HAP particle.

**EXPERIMENTAL**

HAP was from Nakarai, Ltd(Kyoto). Its specific surface area was 56.0 \(\text{m}^2/\text{g}\) by a N\(_2\) adsorption method, while its molar ratio of Ca\(^{2+}\)/PO\(_4^{3-}\) was 1.67 by chemical analyses. SDS was of an analaR grade of BDH, Ltd. HPC (M.W. =11-15 \(\times 10^5\)) was a product of Tokyo Kasei, Ltd. Average amount of its additional hydroxypropoxy groups was 3.4 mole for each sugar unit in mole. Concentrations of SDS and HPC were determined by Epton method and colorimetry at 620 nm by using anthrone and sulfuric acid, respectively. Adsorption amounts of SDS and HPC on HAP at 30 \(^\circ\)C were obtained from differences in their concentrations before and after the adsorption. Zeta poten-

![FIG. 1. Adsorption isotherm of HPC in the presence of SDS. [SDS]/(mmol/l) =0 (square), 1 (circle), and 4 (triangle). [HAP] =10g/dl. [NaCl]=0.9 %.](image)
tial was obtained at a room temperature by means of a Laser ZeeTM Model 501 (Pen Kem, Inc.) at various concentrations of SDS and HPC in an aqueous solution of 0.9 % NaCl. This concentration of NaCl was the same as that for the adsorption experiments of SDS and HPC. The HAP suspension (10 g/dl) containing given amounts of SDS and HPC was diluted 500 times just before the measurement with the SDS solution whose concentration was the same as that in the original suspension. This diluent was saturated with HAP.

RESULTS and DISCUSSION

Adsorption isotherms of HPC toward HAP in the presence or absence of SDS are shown in FIG.1. Dotted line is a hypothetical curve where all of the added HPC was adsorbed. The adsorbed amount of HPC in the absence of SDS was about 20 % of the added one. It was adsorbed owing probably to van der Waals interaction and hydrogen bonding between OH groups of HPC and OH⁻ 's on the surface of HAP. The adsorption amount of HPC, however, increased with an SDS concentration. Changes in the adsorption amount at a given concentration of HPC with that of SDS are shown in FIG.2. The left-hand side shows the adsorption amount in the unit of mg/g, while the right-hand side that relative to a total amount of the added HPC in the unit of %. The

FIG. 2. Effect of SDS on the adsorption amount of HPC. [HPC]/(g/dl) = 0.01(square), 0.1 g/dl (diamond), 0.5 g/dl(circle), and 1 g/dl(triangle). [HAP]= 10 g/dl. [NaCl]= 0.9 %. (Left) in the unit of mg/g, (Right) in %.
The adsorption amount of HPC increased with a concentration of added SDS. Exactly speaking, the adsorption amount slightly decreased after attaining a maximum when the concentration of added HPC was low. This is because the complex is more stable in an aqueous phase than on the surface when much amount of SDS, compared with that of HPC, is added. The initial slope in FIG.2 more declines with a concentration of HPC. This fact suggests that number of the adsorption sites for HPC is closely related to the amount of adsorbed SDS, that is, the SDS on HAP provides HPC its adsorption sites.

Time courses of desorption of SDS and HPC from the surface were studied after a ten-time dilution of the HAP suspension from 10 to 1 g/dl. The right-

FIG. 3. Time courses of desorption after the ten-time dilution. [HAP] = 10 g/dl, [NaCl] = 0.9 %, and [SDS] = 2 mmol/l before the dilution. (Left) Initial concentration of HPC = 0.5 g/dl. Open circle: after the dilution with a 0.9 % NaCl solution not containing SDS. Dotted bar: adsorption amount of HPC at [HPC]=0.05 g/dl, [SDS]=0.2 mmol/l, and [HAP]=1 g/dl for reference. Closed circle: after the dilution with a 0.9 % NaCl solution containing 2 mmol/l SDS. Broken bar: adsorption amount of HPC at [HPC]=0.05 g/dl, [SDS]=2 mmol/l, and [HAP]=1 g/dl for reference. These reference values were obtained from separate measurements.

(Right) Diluted with a 0.9% NaCl solution without HPC. Broken bar: adsorption amount at [SDS]=0.2 mmol/l, [NaCl]=0.9 %, and [HAP]=1 g/dl for reference, which was obtained from another experiment.
hand side of FIG.3 shows a desorption behavior of SDS after dilution with an aqueous solution of 0.9 % NaCl. SDS attained a new equilibrium value of the adsorption in a short period, which coincided with that obtained through the one-step adsorption. This fact suggests that adsorption of SDS is apparently reversible. On the other hand, desorption behavior of HPC is rather complicated, depending on a dilution method, as shown in the left-hand side. When the suspension is diluted by 10 times with a solution of 0.9 % NaCl not containing SDS, desorption of the polymer was observed. It took about 6 hrs to attain a new equilibrium. This is in contrast to the case of SDS mentioned above. To the contrary, the desorption was scarcely observed when the suspension was diluted with a solution of 0.9 % NaCl containing SDS of the same concentration as that in the original suspension before the dilution. This result shows that number of the adsorption sites for HPC for each gram of HAP was approximately kept constant by virtue of the fact that the total concentration of SDS in the system was kept constant. As a matter of fact, the equilibrium concentration of SDS should have been kept constant in order to make the number of the adsorption sites per unit weight of HAP constant.

Zeta potential of HAP was measured at various concentrations of SDS and HPC(FIG.4). It was negative in an aqueous solution of 0.9 % NaCl in the absence of both SDS and HPC at a neutral pH. The value became more negative with a concentration of added SDS due to its adsorption(see open circles).

FIG. 4. Zeta potential as a function of a concentration of SDS in the presence of 0.9% NaCl. Initial concentration of HPC/(g/dl) = 0 (circle),0.05(triangle),0.1(square), and 0.5(diamond). Original suspension of HAP(10 g/dl) was diluted 500 times with an aqueous solution of SDS containing 0.9 % NaCl. The polymer was scarcely desorbed after the dilution(see FIG.3).
Needless to say, the adsorption here includes hydrophobic interaction between the adsorbed SDS and those in the bulk solution (see INTRODUCTION). When HPC is added to the system, the potential increased algebraically with a concentration of HPC. This is because the slipping plane moves to the outside of the particle due to the adsorption of HPC with or without the aid of hydrophobic interaction with the adsorbed SDS. Polymer segments of the adsorbed HPC protrude into the bulk solution and capture further SDS by virtue of hydrophobic interaction again, resulting in more development of the surface complex of HPC-SDS. Therefore, the zeta potential became more negative again with a concentration of SDS.

Compared at a given concentration of SDS, an absolute value of the potential became small with a concentration and/or adsorption amount of HPC because of its thick adsorption layer (see FIGS. 1 and 2) and probably of the low charge density at the slipping plane. This tendency observed here is quite similar to that in the system of HAP-SDS-PVP, mentioned elsewhere. 4

CONCLUSION

Modification of the HAP surface to hydrophobic one by the adsorption of SDS and formation of the surface complex of SDS-HPC were studied. The adsorption amount of HPC increased after formation of the surface complex. Zeta potential of HAP was discussed, taking the effects of the surface complex, surface charge, and thickness of the slipping plane into consideration.

REFERENCES