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Adsorption of Dodecyl Sulfate Ion on Hydroxyapatite and Concurrent Release of Phosphate and Calcium Ions from the Surface of Hydroxyapatite

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Concentrations of phosphate ion ($[\mathrm{Pi}]_f$) and calcium ion ($[\mathrm{Ca}^{2+}]_f$) free from the surface of hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$; HAP) at the adsorption equilibrium of sodium dodecyl sulfate (SDS) were determined as a function of equilibrium concentration of dodecyl sulfate ion ($[\mathrm{DS}^-]_f$). When $[\mathrm{DS}^-]_f$ was lower than its critical micelle concentration (cmc), $[\mathrm{Pi}]_f$ increased with increase in $[\mathrm{DS}^-]_f$ owing mainly to the ion-exchange between dodecyl sulfate ion (DS^-) and surface phosphate ion. However, $[\mathrm{Ca}^{2+}]_f$ decreased with increase in $[\mathrm{Pi}]_f$ to maintain the solubility product of HAP constant. On the other hand, when $[\mathrm{DS}^-]_f$ was higher than the cmc, $[\mathrm{Ca}^{2+}]_f$ increased with increase in $[\mathrm{DS}^-]_f$ due to the binding of Ca^{2+} to DS^- micelles. Anionic species were concomitantly liberated from the surface of HAP to maintain the electroneutrality of the surface phase. Therefore, $[\mathrm{Pi}]_f$ increased and the amount of adsorption of DS^- decreased with increase in $[\mathrm{DS}^-]_f$.

Keywords——hydroxyapatite; sodium dodecyl sulfate; dodecyl sulfate ion; adsorption; ion-exchange; calcium ion release; phosphate ion release; calcium ion binding; solubility product; micelle

Introduction

Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$; HAP) is a major constituent of biological hard tissues (teeth and bones) and human renal calculi. Thus, knowledge of the interaction of HAP with organic compounds is of great importance.

It is known that phosphate and/or calcium ions are released from HAP when organic ions, such as acidic or basic homopolypeptides,[1] benzene polycarboxylic acids,[2] and phosphonylated polyelectrolytes,[3] are adsorbed on the surface of HAP. As for the adsorption of surface-active agents by HAP, some studies have been carried out mainly in the fields of caries prevention,[4] and mineral flotation.[5] However, there have been few studies concerning the relationship between the adsorption amount of surface-active agents and the amounts of release of phosphate and/or calcium ions from the surface of HAP.

In the present work, the amounts of phosphate and calcium ions liberated from the surface of HAP were determined as a function of concentration of dodecyl sulfate ion (DS^-) and/or adsorption amount of DS^- at a constant mixing ratio of HAP to an aqueous solution of sodium dodecyl sulfate (SDS). The results are discussed taking ion-exchange between DS^- and phosphate ion, binding of calcium ion (Ca^{2+}) to DS^- micelles, and the solubility product (K_{sp}) of HAP into account.

Experimental

Materials——HAP was prepared as described elsewhere.[6] The X-ray powder diffraction pattern was typical of HAP, and chemical analysis showed it to be almost stoichiometric ($\mathrm{Ca/Pi}=1.69$). SDS supplied by Nippon Oils and Fats Co., Ltd. was extracted with petroleum benzine in a Soxhlet's extractor for at least 20 h and recrystallized twice from *n*-butanol.

Methods——HAP was suspended in an SDS solution of known concentration at 30 °C, and the suspension was shaken vigorously at frequent intervals. After at least 4 d, which was sufficient to attain adsorption and dissolution equilibria, the suspension was filtered through a Millipore filter (0.1 μm pore size), and the filtrate was used for chemical analyses.

The concentration of DS^- was determined by the methylene blue diphasic titration method (Epton method) using a standard solution of cetylpyridinium chloride. The amount of DS^- adsorbed was calculated from the difference of DS^- concentration before and after addition of HAP. The concentration of phosphate ion released was determined according to the method of Gee *et al.*[7] The phosphate ammonium molybdate complex formed was reduced with stannous chloride. The absorbance of the resulting color was measured at 720 nm on a Shimadzu model UV-180 spectrophotometer after 15 min. The concentration of calcium ion released was determined by ethylenediamine tetraacetic acid (EDTA) chelatometry with 1-(1-hydroxy-2-naphthylazo)-6-nitro-2-naphthol-4-sulfonic acid (BT indicator) at pH 10. The pH of the filtrate was measured on a TOA type HM-5ES pH meter.

It was confirmed that the adsorbed amount of DS^-, the equilibrium concentrations of phosphate and calcium ions, and the pH of the filtrate were independent of the mixing order of water, adsorbate solution, and HAP powder. On the other hand, the desorption experiment was carried out by diluting the suspension with water after adsorption equilibrium had been attained. The adsorbed amount of DS^- after re-equilibration was determined. These experiments showed that the adsorption of DS^- is reversible.

In the present work, no buffer solutions were used in order to avoid the effect of buffering agents on the properties of the HAP surface and DS^- micelles.

Results

Adsorption Isotherms of DS^- on HAP

Figure 1 shows the adsorption isotherms of DS^- on HAP from an aqueous solution of SDS at a constant mixing ratio of HAP to SDS solution (solid/solution ratio). When the concentration of DS^- was low, the adsorbed amount of DS^- (X_{DS^-}) increased with increase in the concentration of free DS^- ($[DS^-]_f$) but decreased with increase in the solid/solution ratio. However, when the concentration became high, X_{DS^-} decreased through a maximum with increase in $[DS^-]_f$; the slope depended on the solid/solution ratio.

Release of Phosphate Ion

It was found that phosphate ion (Pi) is released from HAP during the adsorption of DS^- on HAP. The concentration of phosphate ion released, $[Pi]_f$, is shown as a function of $[DS^-]_f$ in Fig. 2. It shows that $[Pi]_f$ increases with increase in $[DS^-]_f$ or the solid/solution ratio. This

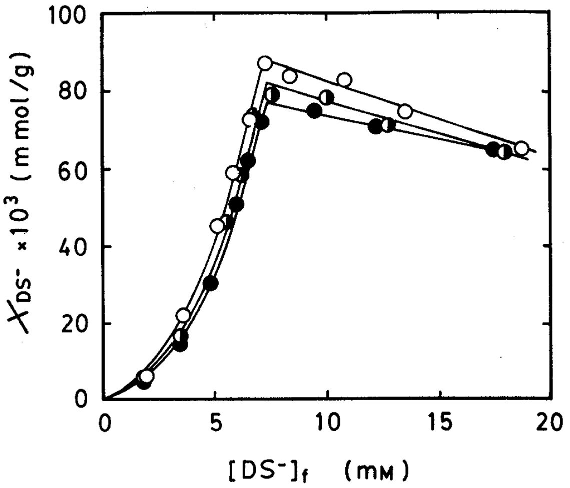

Fig. 1. Adsorption Isotherms of DS^- on HAP from Aqueous Solution of SDS at a Constant Mixing Ratio of HAP to SDS Solution

Solid/solution ratio (g/l): ○ 20, ◑ 30, ● 40.

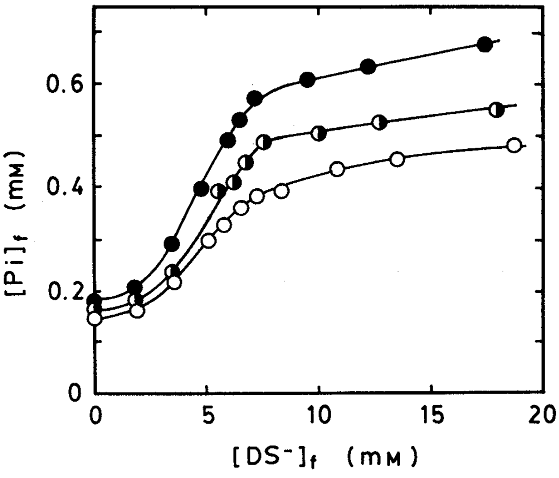

Fig. 2. Relationship between Concentration of Free DS^- and That of Phosphate Ion Released from HAP

All the symbols are the same as in Fig. 1.

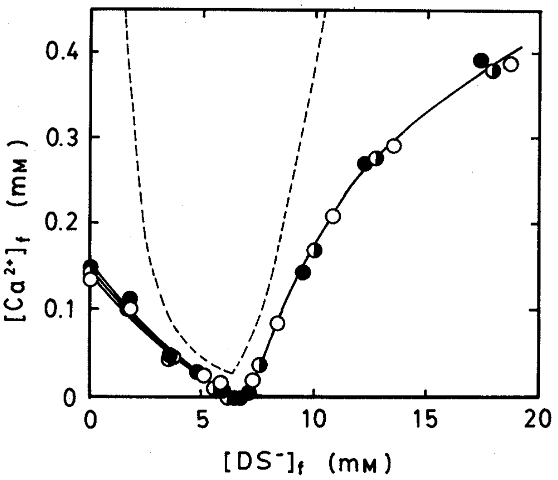

Fig. 3. Relationship between Concentration of Free DS^- and That of Calcium Ion Released from HAP

All the symbols are the same as in Fig. 1. The dotted line shows the solubility curve of calcium dodecyl sulfate as a function of the concentrations of calcium and dodecyl sulfate ions added.

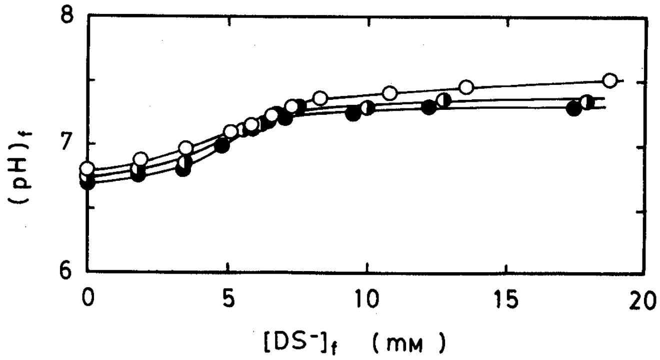

Fig. 4. Relationship between Concentration of Free DS^- and Equilibrium pH

All the symbols are the same as in Fig. 1.

result shows that the released amount of Pi increases with the surface area of HAP added. The effect of $[DS^-]_f$ on $[Pi]_f$ will be discussed later.

Release of Calcium Ion

Figure 3 shows the relationship between $[DS^-]_f$ and the concentration of calcium ion released, $[Ca^{2+}]_f$. The curve consists of two branches; one is downward and the other upward, resulting in a minimum at $[DS^-]_f = 6.7$ mM.

Equilibrium pH of the Solution

Figure 4 shows the equilibrium pH, $(pH)_f$, of the solution as a function of $[DS^-]_f$. The value of $(pH)_f$ increased with increase in $[DS^-]_f$ mainly through the protonation of phosphate ion released into the solution. However, $(pH)_f$ decreased with increase in the solid/solution ratio. This tendency was discussed elsewhere.[8]

Discussion

The value of $-\log(Ca^{2+})^{10}(PO_4^{3-})^6(OH^-)^2$, where ( ) means the activity of the ion in the parenthesis, was obtained from the analytical concentrations of each ion in the range of $[DS^-]_f < 6.7$ mM. To calculate the above product through the procedures described by Moreno *et al.*[9] and Smith *et al.*,[10] complex formation between phosphate and calcium ions (*i.e.*, $CaHPO_4$ and $CaH_2PO_4^+$) was taken into consideration as well as ionic strength and protonation of phosphate ion. The numerical values used here were as follows: the first, second and third dissociation constants for phosphoric acid are 7.08×10^{-3}, 6.31×10^{-8} and 4.17×10^{-13}, respectively[11]; and the formation constants for $CaHPO_4$ and $CaH_2PO_4^+$ are 244 and 8.20.[9,10] The activity coefficient (γ) for each ion was calculated through the Debye–Hückel equation (1);

$$\log \gamma = -\frac{Az^2\sqrt{I}}{1 + B\mathring{a}\sqrt{I}} \qquad (1)$$

where z is the valency of the ion, I is the ionic strength of the medium, A and B are constants ($A = 0.5161$ and $B = 0.3301$ at 30 °C for aqueous solution[12]), and $\mathring{a}$ is an ion-size parameter

(H^+ 9, OH^- 3.5, $H_2PO_4^-$ 4.25, HPO_4^{2-} 4, PO_4^{3-} 4, and Ca^{2+} 6[13]). The numerical values of $-\log(Ca^{2+})^{10}(PO_4^{3-})^6(OH^-)^2$ thus obtained were 116.5 ± 3.5, which is within the range of the literature values of $-\log K_{sp}$ for HAP (108—125).[14] This result suggests that the decrease of $[Ca^{2+}]_f$ in the region of low $[DS^-]_f$ (<6.7 mM) was caused by the increase in $[Pi]_f$ to maintain the solubility product of HAP, K_{sp}, constant.

On the other hand, in the region of $[DS^-]_f > 6.7$ mM, $[Ca^{2+}]_f$ increases with increase in $[DS^-]_f$, although $[Pi]_f$ also does so (see Fig. 3). As the solubility product of HAP should remain constant even in this region, it was concluded that the activity coefficient of Ca^{2+} decreases with increase in $[DS^-]_f$ owing mainly to binding of calcium ion to DS^- micelles. This conclusion may be supported by the fact that $[Ca^{2+}]_f$ depends only on $[DS^-]_f$, irrespective of the solid/solution ratio. Accordingly, the concentration of 6.7 mM, the break point in Fig. 3, is regarded as the critical micelle concentration (cmc) of this system.

The dotted line in Fig. 3 shows the precipitation boundary curve (PBC) of the $CaCl_2$–SDS system at 25 °C obtained by Subbadin *et al.* by turbidity measurement.[15] Baviere *et al.* had obtained a similar PBC for the same system.[16] The region below the PBC is monophasic, whereas calcium dodecyl sulfate precipitates in the region above the PBC. The experimental points in Fig. 3 are obviously in the monophasic region. The PBC quoted in Fig. 3 is available as a criterion for precipitate formation even at 30 °C (present work), because PBC shifts upwards with temperature.[17] It was, therefore, concluded that calcium dodecyl sulfate would not precipitate in the solution of the present work.

Figure 5 shows the relationship between X_{DS^-} (quoted from Fig. 1) and the increment of released amount of Pi due to the addition of SDS, $-\Delta X_{Pi}$, which was obtained from the difference of $[Pi]_f$ in the presence and absence of DS^- in the region of $[DS^-]_f <$ cmc in Fig. 2. All the experimental points in Fig. 5 are almost on one curve irrespective of the solid/solution ratio. This result suggests that the increase in $[Pi]_f$ with increase in $[DS^-]_f$ ($<$cmc) in Fig. 2 is caused by the mechanism of ion exchange between Pi on the surface of HAP and DS^- adsorbed on HAP. However, the initial slope (dotted line) was *ca.* 0.175 and the curve deviated downwards from the dotted line. These facts can be explained by taking the electroneutrality with respect to the surface phase of HAP into consideration. That is, the increase of negative charge on the surface of HAP owing to the adsorption of DS^- is compensated for by simultaneous binding of Na^+ as a counter-ion for the adsorbed DS^- as well as by increase of the amount of ion exchange of Pi with DS^- and by decrease of the amount of Ca^{2+}-release. The concentrations of released Pi and Ca^{2+} ($[Pi]_f$ and $[Ca^{2+}]_f$) are, as mentioned before, restricted by the solubility product of HAP (K_{sp}). Another lattice anion, OH^-, may also be released from the surface of HAP concomitantly with DS^- adsorption. The valence of surface Pi at approximately neutral pH (see Fig. 4) is less than -3 by virtue of protonation. These facts make the ratio of $-\Delta X_{Pi}/X_{DS^-}$ smaller than 1/3 (see the dotted line).

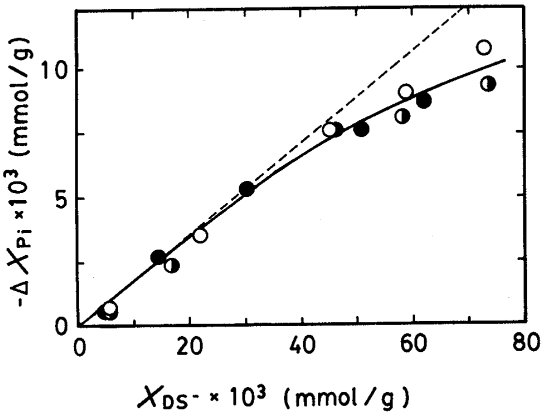

Fig. 5. Relationship between the Adsorbed Amount of DS^- and the Amount of Phosphate Ion Released through the DS^- Adsorption

All the symbols are the same as in Fig. 1. Concentrations of DS^- corresponding to X_{DS^-} (Fig. 1) and $[Pi]_f$ (Fig. 2) for this figure are less than the cmc. The dotted line shows the initial slope of the curve (=0.175).

When $[DS^-]_f$ becomes higher than the cmc, Ca^{2+} is captured by DS^- micelles as a counter-ion. Therefore, $[Ca^{2+}]_f$ increases with increase in $[DS^-]_f$, depending only on $[DS^-]_f$ and not on the solid/solution ratio (Fig. 3). Negative charge density on the surface of HAP might increase with decrease in the solid/solution ratio because the amount of Ca^{2+} released from unit weight of HAP increases with decrease in the solid/solution ratio. However, this negative charge is compensated for by a decrease of X_{DS^-} (Fig. 1) and by release of Pi from the surface of HAP (Fig. 2) with increase in $[DS^-]_f$. Accordingly, the decrease of X_{DS^-} (*i.e.*, negative slope in Fig. 1) becomes steeper as the solid/solution ratio decreases, and Pi-release continues above the cmc (Fig. 2) by a mechanism different from that below the cmc.

However, there is another reason for the maximum in X_{DS^-} (Fig. 1). That is, the single-ion activity of DS^- decreases through a maximum with increase in $[DS^-]_f$.[18)] Both reasons (*i.e.*, compensation of excess negative charges on HAP and a maximum in the ion activity of DS^-) may contribute to the maximum in X_{DS^-}.

These results on the influence of organic ions on the surface of HAP crystallites are important as a basis for understanding the formation of hard tissues in organic matrices and the binding of connective tissues with hard tissues in the human body.

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