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Effect of Added Salt on the Adsorption of Dodecyl Sulfate Ion and Concurrent Release of Phosphate and Calcium Ions at the Surface of Hydroxyapatite

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Concentrations of phosphate ion ($[Pi]_f$) and calcium ion ($[Ca^{2+}]_f$) liberated from the surface of hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$; HAP) during the adsorption of dodecyl sulfate ion (DS^-) onto HAP were determined at various concentrations of added salt (NaCl or Na_2HPO_4). The effects of added salt on the relationships among $[Pi]_f$, $[Ca^{2+}]_f$, the concentration of DS^- ($[DS^-]_f$), and the adsorbed amount of DS^- (X_{DS^-}) are discussed. The amount of X_{DS^-} increased monotonously with the concentration of NaCl added ($[NaCl]_i$). However, the equilibrium concentrations of phosphate ion (Pi) and calcium ion (Ca^{2+}) changed in a complex manner with $[NaCl]_i$. It was concluded that ions on the surface of HAP were partly ion-exchanged with those of sodium dodecyl sulfate and NaCl, and that Ca^{2+} and Na^+ were bound competitively as counter-ions to DS^- micelles. On the other hand, when Na_2HPO_4 was added to the solution, added Pi (*i.e.*, one of the lattice ions for HAP) had a drastic effect on X_{DS^-} and $[Ca^{2+}]_f$. The adsorbed amount of DS^- decreased with increasing concentration of added Na_2HPO_4 owing to competitive adsorption between DS^- and added Pi. The equilibrium concentration of Ca^{2+} , $[Ca^{2+}]_f$, decreased for two reasons. First, adsorbed Pi inhibits the release of Ca^{2+} from the surface of HAP by virtue of the electrostatic attractive force. Secondly, the excess Pi remaining in the solution prevents Ca^{2+} -release from the surface of HAP since the solubility product for HAP must remain constant.

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

Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$; HAP) is the main mineral component of mammalian hard tissues (teeth and bones) and human renal calculi. Thus, it is important to study the influence of organic ions on the surface properties of HAP in order to understand the processes occurring where the hard tissues contact body fluids and/or organic matrices in the human body.

In a previous study,²⁾ the influence of dodecyl sulfate ion (DS^-) on the HAP surface was studied at a constant mixing ratio of HAP to an aqueous solution of sodium dodecyl sulfate (SDS). It was found that phosphate ion (Pi) is released from HAP mainly by the mechanism of ion-exchange with DS^- adsorbed on HAP, whereas calcium ion (Ca^{2+}) is released mainly through its binding to DS^- micelles in the aqueous phase. The concentrations of released Pi and Ca^{2+} are restricted so as to keep the solubility product for HAP constant. Furthermore, the amount of DS^- adsorbed on the HAP surface and the amounts of Pi and Ca^{2+} released from the surface are also mutually balanced so as to maintain the electroneutrality of the surface phase of HAP.

In the present work, the effect of added salt (NaCl or Na_2HPO_4) on the adsorbed amount of DS^- and on the released amounts of the constituent ions of HAP (Pi and Ca^{2+}) was studied. The results are discussed, taking into account the competitive binding of counter-ions (Ca^{2+} and Na^+) to DS^- micelles, and competitive adsorption of DS^- and Pi on the surface of HAP.

Experimental

Materials—HAP and SDS were the same samples as those used previously.²⁾ Sodium chloride (NaCl) purchased from Nakarai Chemicals Ltd. was of reagent grade and was used after heating at 600 °C for 5 h to remove contaminating hydrochloric acid. Disodium hydrogen phosphate (Na_2HPO_4), purchased from Wako Pure Chemical Industries Ltd., was of reagent grade and was used without further purification.

Methods—HAP (0.7 g) was suspended in an SDS solution (35 ml) of a known concentration at 30 °C with or without added salt (NaCl or Na_2HPO_4), and the suspension was shaken vigorously at frequent intervals. No buffer solutions were used in order to avoid effects of buffering agents on the properties of the HAP surface and DS^- micelles. After at least 4 d, which was a sufficient time to reach 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 concentrations of dodecyl sulfate ion, phosphate ion, and calcium ion were determined by the same methods as before.²⁾ The adsorbed amounts of DS^- and Pi were calculated from the difference of the concentrations before and after addition of HAP. The pH of the filtrate was measured on a Toa HM-5ES pH meter.

Results

Adsorption Isotherms of DS^- on HAP

Figures 1 and 2 show the adsorption isotherms of DS^- on HAP from an aqueous solution of SDS at constant concentrations of added NaCl (Fig. 1) and Na_2HPO_4 (Fig. 2). As shown in Fig. 1, the adsorbed amount of DS^- (X_{DS^-}) increased to a maximum, and then decreased with increasing concentration of free DS^- ($[\text{DS}^-]_f$). It was found that X_{DS^-} increased with increasing concentration of added NaCl ($[\text{NaCl}]_i$), and that the negative slope at high $[\text{DS}^-]_f$ became less steep as $[\text{NaCl}]_i$ increased.

On the other hand, when Na_2HPO_4 was added to an SDS solution (Fig. 2), X_{DS^-} decreased with increasing concentration of added Na_2HPO_4 ($[\text{Na}_2\text{HPO}_4]_i$) except in the region of low $[\text{DS}^-]_f$, where X_{DS^-} at $[\text{Na}_2\text{HPO}_4]_i = 13.6 \text{ mM}$ was larger than that at $[\text{Na}_2\text{HPO}_4]_i = 2.73 \text{ mM}$.

Concentration of Pi and Equilibrium pH of the Solution

Figure 3A shows the relationship between $[\text{DS}^-]_f$ and the concentration of phosphate ion released from the surface of HAP ($[\text{Pi}]_f$) in the presence of added NaCl. It was found that $[\text{Pi}]_f$ increased with $[\text{DS}^-]_f$. When $[\text{DS}^-]_f$ was low, $[\text{Pi}]_f$ increased with increasing $[\text{NaCl}]_i$, that is, in the order of $[\text{NaCl}]_i = 0, 25, 100$ and 450 mM . This order, however, was reversed gradually as $[\text{DS}^-]_f$ increased. When $[\text{DS}^-]_f$ became higher than 5.0 mM , $[\text{Pi}]_f$ decreased with increasing

Fig. 1. Adsorption Isotherms of DS^- on HAP from Aqueous Solution of SDS at Constant Initial Concentration of Added NaCl

Initial concentration of added NaCl, $[\text{NaCl}]_i$ (mM):
○, 0; ●, 25; ◐, 100; ●, 450.

Fig. 2. Adsorption Isotherms of DS^- on HAP from Aqueous Solution of SDS at Constant Initial Concentration of Added Na_2HPO_4

Initial concentration of added Na_2HPO_4 , $[\text{Na}_2\text{HPO}_4]_i$ (mM):
○, 0; ●, 2.73; ●, 13.6.

$[\text{NaCl}]_i$. The equilibrium pH, $(\text{pH})_f$, of the solution is plotted against $[\text{DS}^-]_f$ in Fig. 3B. It was found that $(\text{pH})_f$ increased with increasing $[\text{DS}^-]_f$, and the order of the effect of $[\text{NaCl}]_i$ was almost the same as that shown in Fig. 3A. This result shows that the increase of $(\text{pH})_f$ is closely related to the protonation of the phosphate ion released into the solution.

Figure 4 shows the relationship between $[\text{Pi}]_f$ and $[\text{DS}^-]_f$ at constant concentration of added Na_2HPO_4 . When $[\text{Na}_2\text{HPO}_4]_i$ was 0 mM (C) or 2.73 mM (B), $[\text{Pi}]_f$ increased with $[\text{DS}^-]_f$ by virtue of Pi-release from HAP. On the other hand, when $[\text{Na}_2\text{HPO}_4]_i$ was 13.6 mM (A), $[\text{Pi}]_f$ became less than $[\text{Na}_2\text{HPO}_4]_i$ owing to the adsorption of Pi. The equilibrium pH of the solution was almost constant (7.65–7.70 for $[\text{Na}_2\text{HPO}_4]_i = 2.73$ mM, 8.17–8.23 for $[\text{Na}_2\text{HPO}_4]_i = 13.6$ mM) irrespective of $[\text{DS}^-]_f$ due to the buffering function of Pi when enough Na_2HPO_4 was added (compare with the data in the absence of the added salt ($\circ$) in Fig. 3B).

Concentration of Ca^{2+} Released from the Surface of HAP

Figure 5 shows the relationship between $[\text{DS}^-]_f$ and the concentration of calcium ion released from the surface of HAP ($[\text{Ca}^{2+}]_f$) at constant concentration of added NaCl. The curve consists of two branches: one is downward and another upward, and the slope of the latter decreases with increasing $[\text{NaCl}]_i$. The concentration of DS^- at the break point in Fig. 5 (6.7, 3.2, 2.0 and 1.1 mM for $[\text{NaCl}]_i = 0, 25, 100$ and 450 mM, respectively) is regarded as the critical micelle concentration for these systems.²⁾ It was found that $[\text{Ca}^{2+}]_f$ at $[\text{DS}^-]_f = 0$ mM increased with increasing $[\text{NaCl}]_i$. This increase can be explained in terms of ion exchange

Fig. 3. (A) Relationship between Concentration of Free DS^- and That of Phosphate Ion Released from HAP at Constant Initial Concentration of Added NaCl

(B) Relationship between Concentration of Free DS^- and Equilibrium pH of the Solution at Constant Initial Concentration of Added NaCl

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

Fig. 4. Relationship between Concentration of Free DS^- and That of Phosphate Ion at Equilibrium at Constant Initial Concentration of Na_2HPO_4 Added

The equilibrium concentration of phosphate ion was lower or higher than the initial concentration of Na_2HPO_4 added (shown by the triangle on the ordinate), depending on the experimental conditions. Initial concentration of Na_2HPO_4 added, $[\text{Na}_2\text{HPO}_4]_i$ (mM): (A) 13.6, (B) 2.73, (C) 0.

Fig. 5. Relationship between Concentration of Free DS^- and That of Calcium Ion Released from HAP at Constant Initial Concentration of Added NaCl

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

Fig. 6. Relationship between Concentration of Free DS^- and That of Calcium Ion Released from HAP at Constant Initial Concentration of Added Na_2HPO_4

All the symbols are the same as those in Fig. 2.

Fig. 7. Relationship between Equilibrium Concentration of Pi and the Adsorbed Amounts of DS^- , Pi and Ca^{2+}

○, $X_{\text{Ca}^{2+}}$; ●, X_{Pi} ; ○, X_{DS^-} . The initial concentration of SDS was 15 mM. All the equilibrium concentrations of DS^- for the data shown in this figure were higher than the cmc. The positive value in this figure (above the dotted line) shows the amount of adsorption, and the negative value (below the dotted line) gives the amount of ion released from HAP. The point A corresponds to the data on the ordinate in Fig. 4C, where neither Pi nor DS^- was added. The distance between point A and the curve for X_{Pi} (●) indicates the effect of the presence of Pi and DS^- .

between Na^+ (of NaCl) and Ca^{2+} (on the surface of HAP) because substitution of Ca^{2+} and Na^+ occurs at the surface of HAP.³⁾ In addition, an increase in the ionic strength and concomitant decrease in the activity coefficients on the addition of NaCl may increase the analytical concentration of Ca^{2+} at saturation.

Figure 6 shows the relationship between $[\text{Ca}^{2+}]_r$ and $[\text{DS}^-]_r$ in the presence of added Na_2HPO_4 . It shows that when Na_2HPO_4 was added to the solution, $[\text{Ca}^{2+}]_r$ decreased with increasing $[\text{Na}_2\text{HPO}_4]_i$. The break points in Fig. 6 (corresponding to the critical micelle concentration (cmc))²⁾ are 6.7 and 6.3 mM for $[\text{Na}_2\text{HPO}_4]_i = 0$ and 2.73 mM, but no break point was found in the case of $[\text{Na}_2\text{HPO}_4]_i = 13.6$ mM.

Competitive Adsorption of DS^- and Pi

It is known that adsorption of phosphate ion on the HAP surface is specific⁴⁾ and stronger than those of other anions, such as chondroitin sulfate⁵⁾ and anionic salivary proteins.⁶⁾ Therefore, the effect of initial concentration of Pi on the amounts of adsorption and/or release of Pi, Ca^{2+} and DS^- was examined.

Figure 7 shows X_{DS^-} , X_{Pi} (the adsorbed amount of Pi), and $X_{\text{Ca}^{2+}}$ (the adsorbed amount

of Ca^{2+}) as a function of $[\text{Pi}]_f$, where Pi was supplied as Na_2HPO_4 and the initial concentration of SDS was kept constant at 15 mM. The value of $X_{\text{Ca}^{2+}}$ was negative because, as for Ca^{2+} , only release occurred. The value of X_{Pi} was also negative when $[\text{Pi}]_f$ was low. The results in Fig. 7 show that the release of Pi from HAP into the solution occurs during DS^- adsorption by the mechanism of ion-exchange between DS^- and Pi, as well as dissolution of HAP. The dissolved amount of Pi in the absence of both Na_2HPO_4 and SDS is shown by point A in Fig. 7 as a reference. The value of X_{Pi} increased with increasing $[\text{Pi}]_f$ and became positive when $[\text{Pi}]_f$ was higher than 6.2 mM. On the other hand, the released amount of Ca^{2+} decreased with increasing $[\text{Pi}]_f$, resulting in $X_{\text{Ca}^{2+}} = 0$ around $[\text{Pi}]_f = 7.8$ mM. The adsorbed amount of DS^- (X_{DS^-}) decreased monotonously with increase in X_{Pi} . The results show that competitive adsorption of DS^- and Pi takes place owing mainly to the mutual electrostatic repulsion between their negative charges.

Discussion

Effect of Added NaCl

Figure 8 shows the relationship between X_{DS^-} (taken from Fig. 1) and the increment of released amount of Pi due to the addition of SDS, $-\Delta X_{\text{Pi}}$, which was obtained from the difference of $[\text{Pi}]_f$ in the presence and absence of DS^- in the region of $[\text{DS}^-]_f < \text{cmc}$ in Fig. 3A. The graph shows that $-\Delta X_{\text{Pi}}$ increases almost in proportion to X_{DS^-} . However, $-\Delta X_{\text{Pi}}$ decreases with increasing $[\text{NaCl}]_f$. This can be explained in terms of electrostatic shielding effect of NaCl added, because Na^+ concurrently binds to the adsorbed DS^- and to the surface of HAP as a counter ion, and, as a result, electrostatic repulsion between adsorbed DS^- and surface Pi is suppressed.

When $[\text{DS}^-]_f$ is lower than the cmc, $[\text{Ca}^{2+}]_f$ decreases, as shown in Fig. 5, with increasing $[\text{Pi}]_f$ to keep the solubility product for HAP, K_{sp} , constant.²⁾ The values of $-\log(\text{Ca}^{2+})^{10}(\text{PO}_4^{3-})^6(\text{OH}^-)^2$, where () means the activity for the ion in the parenthesis, were obtained in the range of $[\text{DS}^-]_f < \text{cmc}$ according to the methods described previously.^{2,7,8)} The numerical values obtained were 113.1–117.6, 115.6–116.9, 117.9–119.3 and 127.6–128.4 for $[\text{NaCl}]_i = 0, 25, 100$ and 450 mM, respectively. These numerical values were somewhat scattered, although the values of $-\log K_{\text{sp}}$ should be constant irrespective of the ionic strength. However, these are in the range of the literature values ($= 108$ – 125)⁹⁾ except for the last ones (127.6–128.4). It is well-known that the Debye–Hückel approximation, which was used to obtain the activity coefficients in the present calculation, does not give the correct activity coefficient at high ionic strength. Therefore, the deviation of the calculated values from the literature values may be unavoidable since the ionic strength is as

Fig. 8. Relationship between the Adsorbed Amount of DS^- and the Amount of Phosphate Ion Released through the Adsorption of DS^- at Constant Initial Concentration of Added NaCl

All the symbols are the same as those in Fig. 1. Concentrations of DS^- corresponding to X_{DS^-} (Fig. 1) and to $[\text{Pi}]_f$ (Fig. 3A) for this figure are less than the cmc (6.7, 3.2, 2.0 and 1.1 mM for $[\text{NaCl}]_i = 0, 25, 100$ and 450 mM, respectively). The ordinate value, $-\Delta X_{\text{Pi}}$, was obtained from the data shown in Fig. 3A through the following equation, $-\Delta X_{\text{Pi}} = ([\text{Pi}]_f \text{ in the presence of } \text{DS}^- - [\text{Pi}]_f \text{ in the absence of } \text{DS}^-) / (\text{weight of HAP added})$.

high as 450 mM NaCl.

On the other hand, in the region of $[DS^-]_f > \text{cmc}$, $[Ca^{2+}]_f$ increases with $[DS^-]_f$ by virtue of the binding of Ca^{2+} to DS^- micelles.²⁾ When NaCl was added to the solution, this increasing tendency of $[Ca^{2+}]_f$ (i.e., positive slope of the curve) was suppressed as shown in Fig. 5. This can be explained in terms of the competitive binding of Ca^{2+} and Na^+ to DS^- micelles. That is, the ratio of the amount of Ca^{2+} -binding to that of Na^+ -binding to the surface of micelles decreases when the concentration of added Na^+ increases. The negative charge remaining on the surface of HAP caused through Ca^{2+} -release from HAP to DS^- micelles is compensated by release of negative charges, i.e., decreasing X_{DS^-} (Fig. 1) and releasing Pi (Fig. 3A). Accordingly, the negative slope of X_{DS^-} in Fig. 1 and the positive slope of $[Pi]_f$ in Fig. 3A above the cmc became less steep with increasing $[NaCl]_f$.

Effect of Added Na_2HPO_4

When $[DS^-]_f$ is lower than the cmc, $[Ca^{2+}]_f$ becomes too low to be detected in the presence of enough phosphate ion (Fig. 6). This may be explained as follows: adsorbed Pi prevents the release of Ca^{2+} from the surface of HAP owing to the electrostatic attractive force between them, and excess Pi in the solution suppresses Ca^{2+} -release because the concentrations of Pi and Ca^{2+} in the solution are mutually restricted so as to keep the solubility product for HAP constant.

Even in the region of $[DS^-]_f > \text{cmc}$, the Ca^{2+} -release from the surface of HAP is strongly depressed (Figs. 6 and 7). The competitive binding of Na^+ (from Na_2HPO_4) and Ca^{2+} (from HAP) to DS^- micelles takes part in this depression. Of course, two mechanisms, as mentioned above (adsorbed Pi and excess Pi in the solution), are also available. The latter makes the equilibrium concentration of Ca^{2+} free from both micelles and HAP low owing to the restriction of the constant solubility product of HAP.

Added Pi makes the adsorbed amount of DS^- (X_{DS^-}) decrease by competing for the adsorption sites on HAP, as shown in Fig. 7. On the other hand, Na^+ makes X_{DS^-} increase by reducing the electrostatic repulsion among dodecyl sulfate ions adsorbed on the surface of HAP by virtue of counter-ion binding and/or increasing the ionic strength. These opposite effects of Na^+ and Pi result in the complex behavior of the amount of adsorbed DS^- , as shown in Fig. 2.

In summary, the amount of DS^- adsorbed and the amounts of the lattice ions (Ca^{2+} and Pi) released synchronously from HAP depend on the species and concentration of added salt and on the concentration of DS^- micelles present in the solution.

The results mentioned above suggest that, in the human body, the affinity of organic ions for hard tissues is affected by the species and concentration of electrolytes present in the body fluids, and that some of the constituent ions of the hard tissues are released by the mechanisms of ion-exchange when organic ions are bound to the surface of hard tissues.

References and Notes

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