Decrease in the Solubility Product of Hydroxyapatite by the Adsorption of Surface-Active Ion

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The solubility product (K_{sp}) of hydroxyapatite (HAP) in ionic surfactant solutions decreased with an increase in the adsorbed amount of the surface-active ions (dodecylammonium and dodecyl sulfate ions). In the presence of nonionic surfactant (polyoxyethylene(10) octylphenyl ether), K_{sp} was almost constant within the limit of experimental error. It was concluded that the decrease in K_{sp} is due to the decrease in the chemical potential of HAP through the adsorption of the surface-active ion on HAP, and due to the spontaneous change in the constituent ions of the HAP surface (*i.e.*, surface complex formation) by ion-exchange with the surface-active ion.

Keywords hydroxyapatite; solubility product; sodium dodecyl sulfate; dodecylammonium chloride; polyoxyethylene(10) octylphenyl ether; surfactant adsorption; ion exchange; chemical potential; surface complex

Introduction

Hydroxyapatite (HAP; $Ca_{10}(PO_4)_6(OH)_2$) is the major inorganic constituent of mammalian hard tissues. It is known that $Ca_{10}(PO_4)_6F_2$ and $Ca_2Sr_4(PO_4)_6(OH)_2$ are formed at the HAP surface in the presence of F^- and Sr^{2+}.[1,2] These surface complexes govern the dissolution rate of HAP through rapid re-formation at the dissolving site. In the previous papers,[3-5] it was shown that the solubility product of HAP (K_{sp}) regulated the concentrations of calcium and phosphate ions (Ca^{2+} and Pi) in ionic surfactant solutions in spite of the marked incongruent dissolution of HAP. However, precise calculation revealed that K_{sp} was not exactly constant but decreased with the adsorbed amount of the surface-active ions. In this paper, the effect of ionic and nonionic surfactants on K_{sp} will be discussed.

Experimental

Materials HAP (specific surface area: 28.4 m^2/g), dodecylammonium chloride (DAC), and sodium dodecyl sulfate (SDS) were the same samples as those used in the previous studies.[3-5] Polyoxyethylene (10) octylphenyl ether (TX100, critical micelle concentration at 30 °C: 0.26 mM) was purchased from Wako Pure Chemical Industries Ltd. and was of reagent grade.

Methods The experimental procedure employed for the TX100–HAP system was similar to those used in the previous studies.[3-5] The concentration of TX100 was determined at 276 nm by using a spectrophotometer (Shimadzu model UV-180). The determination of Pi by the molybdenum blue method[6] was performed after removing TX100 through decomposition by H_2SO_4 and H_2O_2. The method of calculation of $K_{sp}((Ca^{2+})^{10}(PO_4^{3-})^6(OH^-)^2)$ was described elsewhere.[3] The characterization of the HAP samples recovered from the surfactant-containing solutions was performed by X-ray powder diffractometry (Norelco Geiger counter diffractometer) using CuK_α radiation.

Results

The adsorbed amount of TX100 (X_{TX100}) on HAP from TX100 solution and the equilibrium concentrations of Ca^{2+} and Pi released concurrently from HAP ($C_{Ca^{2+}}$ and C_{Pi}) are plotted against the equilibrium concentration of TX100 (C_{TX100}) in Fig. 1. In contrast with the ionic surfactant–HAP systems,[3-5] X_{TX100} was very small and $C_{Ca^{2+}}$ and C_{Pi} were almost constant irrespective of C_{TX100}. However, no significant difference was observed in the X-ray diffraction patterns of the recovered HAP samples (data are not shown).

The values of pK_{sp} of HAP for the DAC–, SDS–, and TX100–HAP systems are shown against the adsorbed amounts (X) of the surfactant in Figs. 2A, B and C, respectively. Although the values are in the range of the literature values (108—125),[10] an increasing tendency with increase of the adsorbed amount of dodecylammonium and

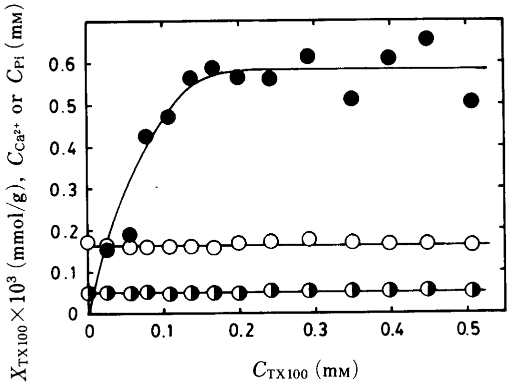

Fig. 1. Adsorption of TX100 on HAP and Concurrent Dissolution of HAP at 30 °C

Incubation time was 14 d. No buffer solution was used in order to avoid the effect of the buffering agents on the system. Solid/solution ratio = 40 g/l. ●, X_{TX100}; ○, $C_{Ca^{2+}}$; ◑, C_{Pi}.

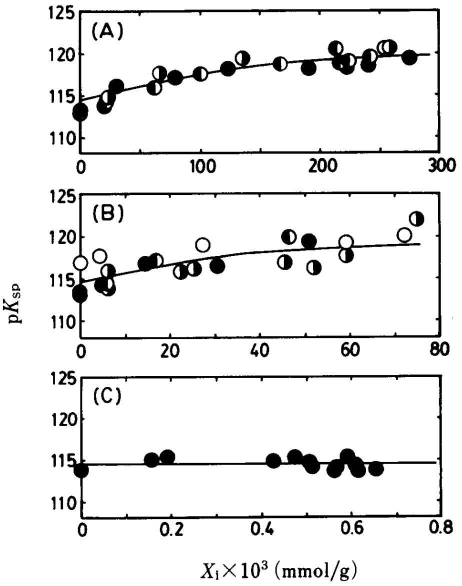

Fig. 2. Relationship between pK_{sp} of HAP and Adsorbed Amount of the Surface-Active Agent on HAP

In the case of the ionic surfactant solutions, pK_{sp} values were calculated in the concentration range less than the critical micelle concentrations of the surface active ions. (A) DAC–HAP system, (B) SDS–HAP system, (C) TX100–HAP system. Solid/solution ratio (g/l) = 10 (○), 20 (◑), 30 (◐), and 40 (●).

dodecyl sulfate ions (DA^+ and DS^-) was observed (Figs. 2A and B).

Discussion

The chemical potential of HAP determines the K_{sp} of HAP. This potential is approximately the sum of that relating to the surface phase and that relating to the bulk phase. The latter may be almost constant irrespective of the adsorption of the surfactant because the X-ray diffraction patterns of the HAP samples were not changed by the surfactant treatment. On the other hand, the former was considered to decrease with the adsorption of the surfactant. A simple physical adsorption model enables the estimation of its decrement, and consequently the increment of pK_{sp} by using the Ostwald–Freundlich and Gibbs equations.[8)] The calculated increments of pK_{sp} in the surfactant solutions from that in distilled water were 0.36 at $X_{DA^+} = 0.250$ mmol/g and 0.10 at $X_{DS^-} = 0.070$ mmol/g, for example. These values are much smaller than the observed values (see Figs. 2A and B). The simple physical adsorption model is, therefore, inadequate to explain the increase of pK_{sp} in ionic surfactant solutions.

Surface complex formation such as that proposed by Higuchi *et al.*[1,2)] was also observed when HAP was suspended in ionic surfactant solution (sodium oleate).[9)] Therefore, ion exchanges between DA^+ and Ca^{2+},[5)] and between DS^- and Pi[3,4)] were considered to result in the formation of surface complexes. These surface complexes might remain on the HAP surface and govern the apparent solubility of HAP even after attainment of dissolution equilibrium. As a result, the chemical potential and K_{sp} of HAP decreased with the progress of the ion exchange (*i.e.*, with the adsorbed amount of the surface-active ions). On the other hand, for TX100, no change of pK_{sp} was found because its adsorption is not accompanied with ion exchange and because the adsorbed amount was very small.

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