Chem. Pharm. Bull.
29(11)3090—3098(1981)

Adsorption of Hydroxyl Ion on Hydroxyapatite

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(Received May 15, 1981)

Hydroxyapatite (HAP) in water exhibited a buffer function in the region from weakly acidic through weakly alkaline pH. Equilibrium pH depends on the amount of HAP added, and on the species and concentration of added electrolyte. This function seems to originate from the ability of HAP to adsorb OH^- and/or from the protonation-deprotonation equilibrium of surface phosphate ion. Theoretical calculation of the suspension pH was attempted. The isotherm of OH^- adsorption from aqueous solutions of NaOH mixed with NaCl was of Langmuir type. The saturated amount of OH^- adsorption was almost constant irrespective of the amount of NaCl added, but the binding constant increased with the amount of added NaCl. The adsorption isotherms, however, formed just one curve irrespective of the amount of NaCl added when they were expressed as a function of the thermodynamic activity of NaOH. On the other hand, the amount of adsorbed OH^- increased with the amount of Ca^{2+} added, because Ca^{2+} is adsorbed on the HAP surface and forms a positively charged adsorption site for OH^-. An electrophoresis experiment confirmed that HAP particles have positive charges due to adsorbed Ca^{2+} even in solution at high pH.

Keywords——hydroxyapatite; suspension pH; pH calculation; adsorption of lattice ion; adsorption of hydroxyl ion; adsorption isotherm as a function of activity; protonation of surface phosphate; electrophoresis of hydroxyapatite

Hydroxyapatite(HAP), $Ca_{10}(PO_4)_6(OH)_2$, is a prototype of the inorganic constituent found in tooth, bone and renal calculi.[1] Thus, knowledge of the properties of HAP is of great physiological significance.

In the previous paper,[2] it was found that calcuim ion, one of the lattice ions of HAP, and sodium ion are more strongly adsorbed on HAP than any other di- and monovalent cations, respectively, because Ca^{2+} fits the adsorption sites formed by crystal defects or dislocations of Ca^{2+} on the HAP surface, and because the ionic size of Na^+ is almost the same as that of Ca^{2+}. It was also found that the suspension pH of HAP decreases with increasing concentration of metal chloride added, and that there is a small lag phase in the titration curve when HAP suspension is titrated with 1N NaOH. These results suggested that HAP adsorbs hydroxyl ions, one of the lattice ions of HAP, or releases protons corresponding to the amount of adsorption of metal ions added, which form positive charges on the HAP surface.

Physicochemical properties of HAP, such as buffer function against pH change or adsorption of OH^-, have not been well studied yet, although the effect of pH on the dissolution rate of HAP, especially in acidic media,[3,4] and phase equilibria diagrams for various kinds of calcium phosphates as a function of pH[5,6] have often been studied as basic research related to dental caries. The purpose of the present investigation was to gain a better understanding of the interactions between HAP and OH^- in water.

Experimental

Materials——All chemicals used were purchased from Nakarai Chemicals Ltd. or Wako Pure Chemical Industries Ltd. Water was doubly distilled. HAP was the same sample as that used in the previous paper.[2] It was confirmed that X-ray powder diffraction patterns of HAP were the same before and after soaking it in sample alkali solutions.

Methods——HAP(1g) was suspended in 20 ml of aqueous solution of NaOH or $Ca(OH)_2$ containing a neutral salt (NaCl or $CaCl_2$) of known concentration, and shaken vigorously at frequent intervals. After at least 3 days at 30°C, the filtrate through a Millipore filter (0.22 μm pore size) was analyzed by pH titration. The pH was measured by a pH-meter (TOA type HM-5A). The amount of OH^- adsorbed was calculated from the difference of OH^- concentration before and after addition of HAP. The adsorption isotherm was obtained as a function of free concentration of OH^-, or of the ionic product of free species, $[Na^+][OH^-]$. Reversibility of OH^- adsorption was confirmed.

Final pH, (pH)$_f$, of the suspension at equilibrium was measured in the supernatant, as functions of HAP concentration, neutral salt concentration, and initial pH, (pH)$_i$, of the medium solution adjusted by addition of a small amount of NaOH or HCl before HAP addition.

Particle charge of the HAP suspension was qualitatively measured by using a microelectrophoretic apparatus (Mitamura Riken model 5-160) with a potential gradient of 5—6 V/cm at room temperature, as described elsewhere.[7]

Care was always taken not to cause the precipitation of $Ca(OH)_2$ by taking its solubility product into consideration when $CaCl_2$ was used as an added salt with NaOH.

Results

Buffer Function of HAP

It was found that when HAP is suspended in electrolyte solution, the pH of which is adjusted to (pH)$_i$, the pH decreases or increases to (pH)$_f$ at equilibrium. (pH)$_f$ depends on (pH)$_i$, on the amount of HAP added, and on the species and concentration of added electrolyte. The relationship between (pH)$_i$ and (pH)$_f$ is shown in Fig. 1. The dotted line in Fig. 1 shows the hypothetical relationship of (pH)$_i$=(pH)$_f$, which means HAP does not affect the suspension pH at all.

The (pH)$_f$ remains almost constant irrespective of (pH)$_i$ in the range from pH 5 through pH 11 for a fixed amount of HAP and a fixed concentration of added electrolyte, as shown in Fig. 1. On the other hand, the equilibrium pH, (pH)$_f$, decreases with the amount of added HAP (▲, △, ● and ○ at 1 M NaCl, for example) and of added electrolyte (◑ and ⊗ at 30 g HAP/dl in $CaCl_2$ aqueous solution, for example). The (pH)$_f$ decreases more strongly with 0.011 M $CaCl_2$ (◑) than with 1.0 M NaCl (○), even though the concentration of HAP is the same and much more NaCl is added than $CaCl_2$.

These results mean that HAP in electrolyte solution consumes OH^- and H^+ or releases H^+ and OH^- at the right side region or at the left side region of the dooted line in Fig. 1, respectively. Thus, HAP appears to be amphoteric, and this behavior of HAP is a kind of pH buffer function. Similar phenomena were also found in aqueous suspensions of kaolinite[7] and of Japanese acid clay,[8] as well as in aqueous suspensions of amorphous iron oxyhydroxide.[9]

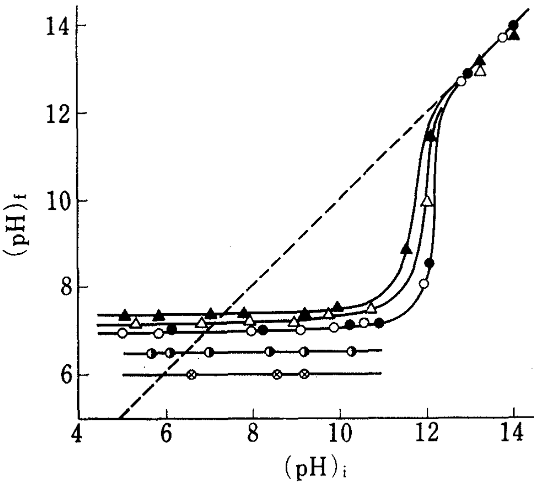

Fig. 1. Relationship between the Initial pH, (pH)$_i$, and the Final pH, (pH)$_f$

(pH)$_i$ was adjusted by addition of NaOH or HCl. HAP concentration (g/dl):
30 (○), 20 (●), 10 (△), and 5 (▲) in 1 M NaCl, 30 (⊗) in 0.10 M $CaCl_2$, and 30 (◑) in 0.011 M $CaCl_2$.

pH Increase by Dissolved HAP

Although (pH)$_f$ decreases with the amount of HAP added, as shown in Fig. 1, the value at the smallest amount of HAP (▲, 5 g HAP/dl, (pH)$_f$=7.40) is higher than the medium pH without HAP ((pH)$_i$=5.50 at 1 M NaCl, for example). It seems, therefore, that (pH)$_f$ increases to the maximum value at a HAP concentration below 5 g/dl, and then decreases with further increase of HAP concentration.

Curve(A) in Figs. 2 and 3 shows the experimental relationship between (pH)$_f$ and the amount of HAP added to an aqueous solution of 1 M NaCl, for which (pH)$_f$ is 5.50. (pH)$_f$ of

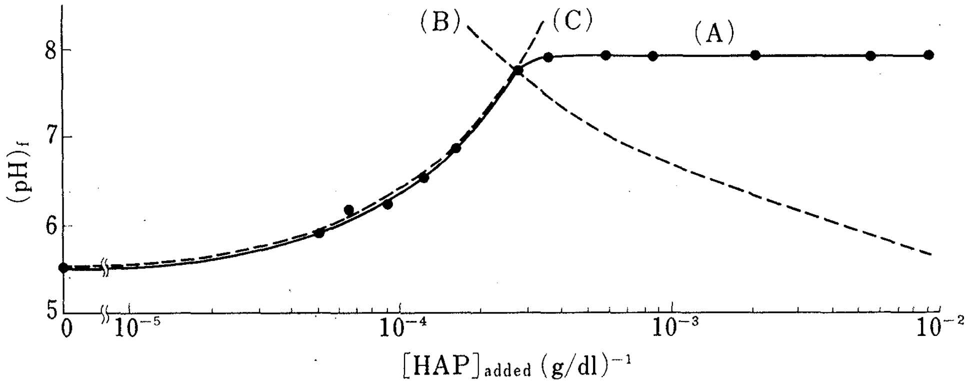

Fig. 2. Relationship between the Final pH, $(pH)_f$, and the Concentration of Added HAP, $[HAP]_{added}$

HAP was dissolved and/or suspended in 1 M NaCl. Curves(A), (B) and (C) show the experimental values of $(pH)_f$, of the solubility of HAP⁽¹⁰⁾ in the medium of $(pH)_f$, and of the calculated $(pH)_f$, respectively..

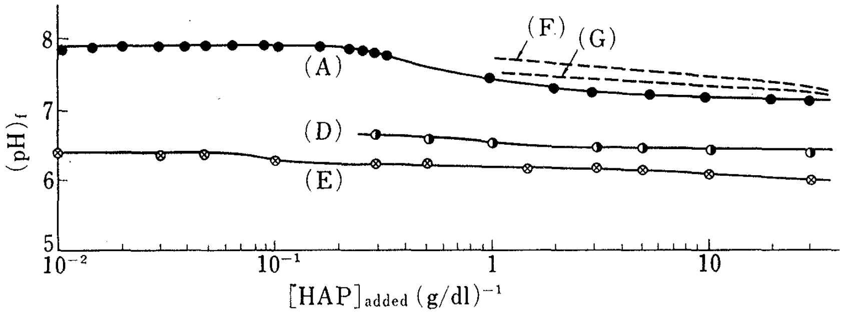

Fig. 3. Relationship between $(pH)_f$ and $[HAP]_{added}$

Almost all HAP added did not dissolve but remained suspended in the salt solution. Curve(A) in this figure is extended to higher concentration of HAP than curve(A) in Fig. 2. Curves(A), (D), and (E) show the experimental $(pH)_f$ in 1 M NaCl, in 0.011 M $CaCl_2$ and in 0.10 M $CaCl_2$, respectively. Curves(F) and (G) show the theoretical $(pH)_f$ assuming that the total concentration of CO_2 in 1 M NaCl is 2.50×10^{-5} M or 3.50×10^{-5} M, respectively. These concentrations are derived from medium at pH 5.50 and 5.40 before HAP addition.

the curve(A), shown in Figs. 2 and 3, first increases, then levels off at $(pH)_f = 7.90$, and finally decreases again with the amount of HAP added, as expected (see above). Curve(B) shows the solubility of HAP as a function of medium pH quoted from the literature,⁽¹⁰⁾ and shows that the solubility of HAP decreases with pH. Curves(A) and (B) cross nearly at the break point of the curve(A). This result suggests that the region of increasing $(pH)_f$, or leveling off and decreasing $(pH)_f$ is the region that corresponds to less than or more than the solubility limit of HAP, respectively. Curve(C) is theoretically calculated, and will be discussed later.

pH Decrease by Suspended HAP

$(pH)_f$ decreases with the amount of HAP added to an aqueous solution containing a constant concentration of NaCl(curve (A)) or of $CaCl_2$ (curves(D) and (E)), as shown in Fig. 3. The sequence of $(pH)_f$ at a given concentration of HAP is 1 M NaCl>0.011 M $CaCl_2$>0.10 M $CaCl_2$ through the whole range of HAP concentration investigated. The fact that the effect of $CaCl_2$ on $(pH)_f$ is stronger than that of NaCl, shown in Figs. 1 and 3, seems to be related to the fact that Ca^{2+} is more strongly adsorbed than Na^+ on HAP, as mentioned in the previous paper.⁽²⁾

Curves(F) and (G) in Fig. 3 are theoretically calculated $(pH)_f$ for the suspension in 1 M NaCl, and will be discussed later.

Adsorption Isotherm of OH^- from Aqueous Solutions of NaOH

Fig. 4 shows the amount of adsorbed OH^-, x_{OH^-}, as a function of equilibrium concentration of OH^-, c_{OH^-}, at constant Na^+ concentration adjusted by adding NaOH and NaCl. By means of this preparation method, the ionic strength, J, for each series can be kept constant before the adsorption, but at the adsorption equilibrium the ionic strength is not constant because ions, mostly OH^-, are adsorbed on HAP.

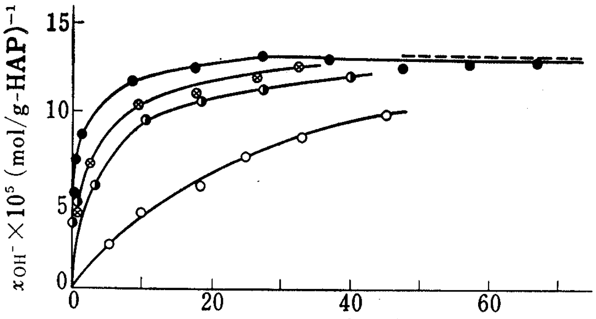

Fig. 4. Adsorption Isotherm of OH^- as a Function of Concentration of Free OH^-

Concentrations of added electrolytes (M): [NaOH]+[NaCl]=1.00 (●), 0.50 (⊗), 0.25 (◑), and [NaCl]=0 (○).

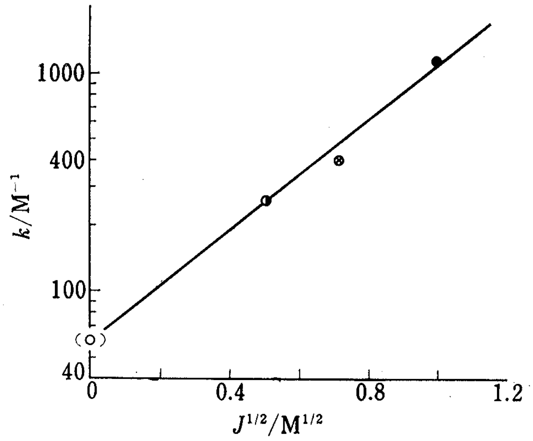

Fig. 5. Binding Constant, k, *vs*. Root of the Initial Ionic Strength, $J^{1/2}$

The parenthesized point (○) on the ordinate is the experimental point without NaCl. Experimental conditions for each symbol are the same as in Fig. 4. J was calculated from the total concentration of added electrolyte, instead of the ionic strength at equilibrium.

Each adsorption isotherm was confirmed to be of Langmuir type by the linearity of the reciprocal plot (Klotz plot) of the Langmuir equation (1),

$$x_{OH^-}=\frac{x_\infty\cdot k\cdot c_{OH^-}}{1+k\cdot c_{OH^-}}, \qquad (1)$$

from which the binding parameters, x_∞ and k, are obtained. The maximum amount of adsorption, x_∞, is almost constant (13.2×10^{-5} mol OH^-/gHAP), irrespective of the total concentration of added electrolytes, but the binding constant, k, increased with the total concentration of added electrolytes or the initial ionic strength, as shown in Fig. 5. Each curve in Fig. 4 is calculated with Eq. (1) using the numerical value of x_∞ obtained above, and k given in Fig. 5. Calculated curves are in fair agreement with the experimental values.

If the ion adsorption is dominated by electrostatic potential, the logarithm of the binding constant, log k, should decrease linearly with the root of the ionic strength, $J^{1/2}$, as previously mentioned in connection with counter ion binding to chondroitin sulfate.[11] However, as shown in Fig. 5, log k increases with $J^{1/2}$ almost linearly. Mechanisms for the adsorption of OH^- other than the electrostatic mechanism should therefore be considered.

Fig. 6 shows the adsorption isotherm for OH^- as a function of ionic product of free concentrations of Na^+ and OH^-, $[Na^+]$ $[OH^-]$, which is regarded as an approximation of the thermodynamic activity of NaOH at the adsorption equilibrium. All experimental points from Fig. 4 are strictly on one curve in Fig. 6, which is of Langmuir type again. This result shows that the adsorption of OH^- on HAP is dominated by the thermodynamic activity of the adsorbate, NaOH,[12] instead of by the electrostatic potential of the adsorbent.

Adsorption Isotherm of OH^- from Aqueous Solutions containing Ca^{2+}

Curves (a) and (b) in Fig. 7 show the adsorption isotherms of OH^- from aqueous solutions of NaOH mixed with 110 mM $CaCl_2$, and from aqueous solutions of $Ca(OH)_2$ without any added

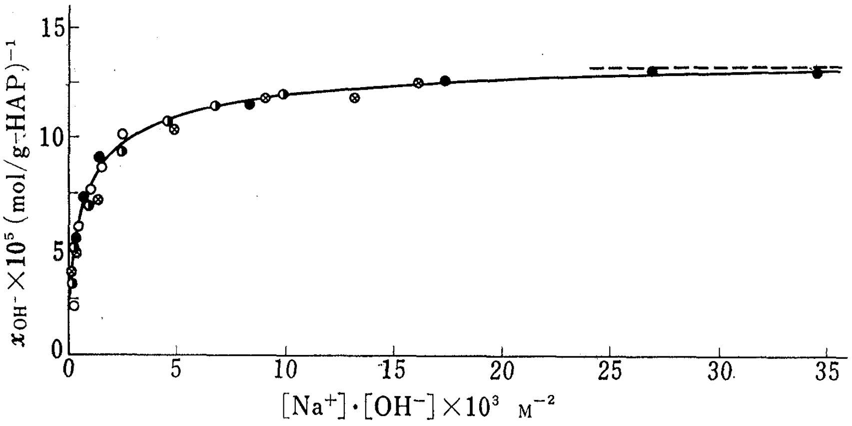

Fig. 6. Adsorption Isotherm of OH^- as a Function of Ionic Product of $[\mathrm{Na}^+][\mathrm{OH}^-]$

All the symbols and data are the same as in Fig. 4.

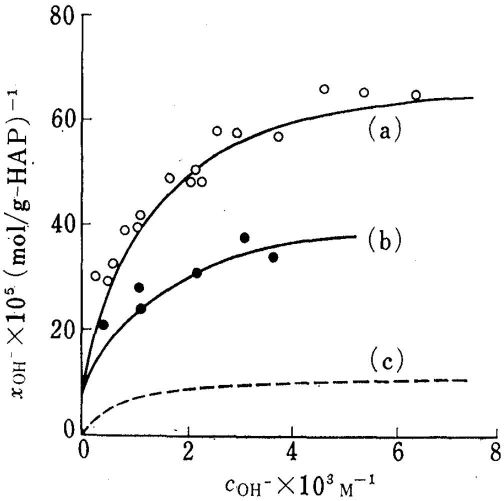

Fig. 7. Adsorption Isotherm of OH^- from Aqueous Solution Containing Calcium Ions

Curves(a) and (b) are adsorption isotherms of OH^- from aqueous solutions of NaOH with 110 mM $\mathrm{CaCl_2}$, and of $\mathrm{Ca(OH)_2}$, respectively. Curve(c) is the same adsorption isotherm as that shown with closed circles in Fig. 4, which is drawn for comparison with curves(a) and (b).

salt, respectively. Curve(c) is the same adsorption isotherm as that shown by closed circles in Fig. 4, and is included for comparison with curves(a) and (b).

The amount of adsorbed OH^- shown by curves(a) and (b) is strikingly larger than that shown by curve(c), and the saturated amount of adsorption, x_∞, seems to depend on the amount of Ca^{2+} added. This result is in contrast with the results in Figs. 4 and 6, where x_∞ was experimentally constant, irrespective of the concentration of Na^+ added.

Curves(a) and (b) were theoretically calculated with Eq. (1) for $x_\infty=71.4\times10^{-5}$ mol OH^-/gHAP and $k=1.12\times10^3\ \mathrm{M}^{-1}$, and for $x^\infty=41.6\times10^{-5}$mol OH^-/gHAP and $k=1.33\times10^3\ \mathrm{M}^{-1}$, respectively. These calculated curves are not in very good agreement with the experimental values. When the agreement of the data in the range of lower concentration of free OH^- is improved by adjusting the numerical values of x_∞ and k, the agreement in the range of higher concentration of free OH^- becomes worse, and *vice versa*. The values given above are, therefore, not entirely satisfactory.

Electrophoresis of HAP Particles

When a small amount of HAP particles was placed in an electrophoresis cell containing 15 mM NaOH, it was found that the HAP particles are negatively charged, confirming the adsorption of OH^-. On the other hand, the mobility of HAP in 15 mM NaOH containing Ca^{2+} increases with the amount of Ca^{2+} added. When enough Ca^{2+} (15 mM, for example) is added, it was found that the HAP particles have positive charges. This result confirms excess adsorption of Ca^{2+} rather than OH^-, in accord with Spiering's result for $\mathrm{Ca_3Al_2(OH)_{12}}$.13) This behavior is also similar to Tung's results.14) He found that compressed HAP membrane was amphoteric in its permselective properties. In KCl solution, HAP was more cation selective as the pH of the solution was increased, but in $CaCl_2$ solution, a HAP membrane was anion selective with no significant pH effect.

Discussion

Numerical Calculation of $(pH)_f$ Increase

In the concentration range lower than the solubility of HAP, ionic species affecting $(pH)_f$ are H^+, OH^-, HPO_4^{2-}, and $H_2PO_4^-$ from dissolved HAP, and HCO_3^- and H_2CO_3 from dissolved CO_2 of air. The effect of other species, such as CO_3^{2-}, PO_4^{3-} and complex species ($CaH_2PO_4^+$, for example) listed in the literature,3,5) can be neglected in the calculation of $(pH)_f$ on the assumption that their amounts are small in 1 M NaCl solution. The equations to be considered are as follows, where [i] is the molar concentration of the i-th species.

By the dissociation-association equilibrium of proton,

$$k_p = \frac{[H_2PO_4^-]}{[H^+][HPO_4^{2-}]} = 1.58 \times 10^7, \tag{2}$$

$$k_c = \frac{[H_2CO_3]}{[H^+][HCO_3^-]} = 0.219 \times 10^7, \tag{3}$$

and

$$K_w = [H^+][OH^-] = 1.86 \times 10^{-14}, \tag{4}$$

where association constants, instead of dissociation constants,15) are used for convenience of derivation of the result, Eq. (10).

By mass balance,

$$[H_2PO_4^-] + [HPO_4^{2-}] = 6[HAP], \tag{5}$$

$$[Ca^{2+}] = 10[HAP], \tag{6}$$

$$[H_2CO_3] + [HCO_3^-] = [\text{total } CO_2], \tag{7}$$

and

$$[Na^+] = [Cl^-], \tag{8}$$

where [HAP] is the concentration of dissolved HAP in 1 M NaCl solution, and 6 and 10 are stochiometry factors for phosphate ion and calcium ion, respectively.

By electroneutrality,

$$\begin{aligned}&[H_2PO_4^-] + 2[HPO_4^{2-}] + [HCO_3^-] + [OH^-] + [Cl^-]\\&= 2[Ca^{2+}] + [H^+] + [Na^+].\end{aligned} \tag{9}$$

The following equation is obtained from the above equations,

$$[HAP]\left(\frac{6}{k_p[H^+]+1}\right) - 14 = ([H^+]-[OH^-]) - \frac{[\text{total } CO_2]}{k_c[H^+]+1}. \tag{10}$$

The value of [total CO_2] is obtained from the pH of the medium (pH 5.50 for 1 M NaCl) as 2.50×10^{-5} M, and is assumed to be constant in the calculation of $(pH)_f$, neglecting the dependence of CO_2 solubility on $(pH)_f$. Putting the numerical values given above into Eq. (10), the dependence of $[H^+]$, and then $(pH)_f$, on [HAP] is obtained, as shown by curve(C) in Fig. 2, where the concentration of HAP is converted to weight concentration of added HAP, $[HAP]_{added}$. The curve(C) slopes upwards with increasing concentration of dissolved HAP in accordance with the experimental curve(A). It is, therefore, concluded that the increase and subsequent leveling off of $(pH)_f$ with increase of [HAP] is due to the dissociation-association equilibria of both phosphate and carbonate ions in the solution.

Numerical Calculation of $(pH)_f$ Decrease

In this section, carbonate ions and bicarbonate ions are assumed not to be adsorbed to HAP surface or replaced by the lattice anions (OH^- and PO_4^{3-}) on the surface of HAP.16,17) It is, henceforth, assumed as a matter of convenience that they exist stably in the bulk solution (1 M NaCl) without any interaction with HAP and only affect the pH of the solution by their buffer function.

If the molar concentrations of occupied and unoccupied adsorption sites for OH^- on the surface of HAP are expressed by $[YOH^-]$ and $[Y]$, respectively, the equilibrium of OH^- adsorption can be written as follows,

$$Y + OH^- \rightleftarrows YOH^-,$$

$$k = \frac{[YOH^-]}{[Y][OH^-]} = 1.13 \times 10^3, \tag{11}$$

where k is the binding constant of OH^- adsorption at 1 M NaCl, which is shown in Fig. 5. Eq. (11) is a different form of the Langmuir equation, Eq. (1). $[Y]$ and $[YOH^-]$ are related to the concentration of suspended HAP, $[HAP]_{solid}$, as follows,

$$[Y] + [YOH^-] = B[HAP]_{solid} = 13.2 \times 10^{-2}[HAP]_{solid}, \tag{12}$$

where $B(=13.2 \times 10^{-2}$ mol OH^-/mol HAP) is the saturated amount of adsorption of OH^- expressed in mol OH^-/mol HAP unit, which is converted from the value of x_∞ $(=13.2 \times 10^{-5}$ mol OH^-/gHAP) in Fig. 4.

By mass balance of dissolved HAP,

$$[H_2PO_4^-] + [HPO_4^{2-}] = 6S, \tag{13}$$

and

$$[Ca^{2+}] = 10S, \tag{14}$$

where S is the molar concentration of HAP dissolved in the suspending medium, which depends on $(pH)_f$.

By electroneutrality of dissolved and adsorbed species,

$$\begin{aligned}&[H_2PO_4^-] + 2[HPO_4^{2-}] + [OH^-] + [YOH^-] + [HCO_3^-] + [Cl^-]\\ &= 2[Ca_2^+] + [H^+] + [Na^+].\end{aligned} \tag{15}$$

The following equation can be obtained from Eqs. (2)—(4), (7), (8), and (11)—(15),

$$\begin{aligned}&[HAP]_{solid}\left(\frac{Bk[OH^-]}{1+k[OH^-]}\right)\\ &= S\left(14 - \frac{6}{k_p[H^+]+1}\right) + ([H^+]-[OH^-]) - \frac{[\text{total } CO_2]}{k_c[H^+]+1}.\end{aligned} \tag{16}$$

This equation shows the relationship between $[HAP]_{solid}$ and $[H^+]$, and, therefore, $(pH)_f$ at the adsorption equilibrium. When the numerical values given above are used and the solubility of HAP, S, at each $(pH)_f$ is read out from the solubility curve(B) in Fig. 2, the numerical relationship between $[HAP]_{solid}$ and $(pH)_f$ is obtained.

The concentration of the suspension of solid HAP in molar unit, $[HAP]_{solid}$, is converted to that of added HAP in weight unit, $[HAP]_{added}$, by assuming that the amount of dissolved HAP is very small compared with the total amount of added HAP. Curve(F) in Fig. 3 is the relationship between $[HAP]_{added}$ (g/dl) and $(pH)_f$ obtained by using the value of 2.5×10^{-5} M for $[\text{total } CO_2]$ consistently in the calculation of curve(C) in Fig. 2. Curve(F) decreases with $[HAP]_{added}$, but the agreement between the calculated and found values (Curve(A)) is not good. If a value of 3.5×10^{-5} M (assuming pH 5.40 for 1 M NaCl) is used for $[\text{total } CO_2]$, curve(G) in Fig. 3 is obtained. Curve(G) approximates curve(A) better than curve (F), but the agreement between curves(A) and (G) is still not good.

The fact that Eq. (16) lacks a term taking account of the adsorption equilibrium of H^+ on solid HAP may be one of the reasons for the poor agreement between the calculated(curves(F) and (G)) and found values (curve(A)), but it is practically difficult to obtain the adsorption constants for H^+ experimentally because the lower the pH of the suspending medium, the more HAP dissolves. Another reason may be uncertainty in the estimation of the amount of solubilized CO_2, which may be larger than in the case of curves(A) and (C) in Fig. 2 because of the vigorous shaking carried out after preparation of the sample suspension in order to reach equilibrium rapidly. Furthermore, some portion of Ca^{2+} dissolved into water from HAP may be re-adsorbed on the solid HAP surface and form adsorption sites for OH^-, as mentioned later.

The relationship between $(pH)_f$ and $(pH)_i$, shown in Fig. 1, also has to be analyzed quantitatively. In principle, the relationship between them is obtained when $[OH^-]$ in Eq. (16) is expressed as a function of the concentration of initial OH^- added to adjust $(pH)_i$. However, there is some ambiguity in Eq. (16), as mentioned above, and a detailed discussion is not appropriate at present.

Comparison of the Effects of Na^+ and Ca^+

Davis *et al.*[9] studied the adsorption of Cu^{2+} on iron hydroxide, and showed that it is consistent with the experimental finding that some portion of adsorbed Cu^{2+} forms a hydrolytic complex of $CuOH^+$ on the particle surface. In a similar manner, OH^- is assumed to be adsorbed on Ca^{2+} on the surface of HAP, and the number of sites increases with the adsorption of Ca^{2+}. Ca^{2+} adsorbed on HAP forms an adsorption site for OH^- by producing positive charges on the surface, and x_∞ increases with the amount of Ca^{2+} added, as shown in Fig. 7. Strictly speaking, the isotherm of OH^- adsorption in the presence of Ca^{2+} in solution, therefore, cannot be expressed by a simple Langmuir equation, Eq. (1), which is only applicable to the case of a constant number of adsorption sites. This may be the reason why the experimental points in Fig. 7 deviates from the curve calculated with Eq. (1).

Ca^{2+} is regarded as binding directly to the HAP surface or as staying in the inner Helmholtz layer, because Ca^{2+} was assumed to be dehydrated when it is adsorbed on HAP,[2] and because HAP particles have positive charges even in high-pH solution when it contains sufficient Ca^{2+}, as mentioned in the section on electrophoresis.

Na^+ is also regarded as being adsorbed on the HAP surface.[2] If the amount of Na^+ adsorbed is large enough, the saturated amount, x^∞, of OH^- adsorption from a solution of NaOH containing NaCl should increase with the concentration of Na^+ in much the same way as in the case of Ca^{2+} adsorption. However, the value of x^∞ obtained experimentally is almost constant, irrespective of the concentration of Na^+ added, as mentioned before. It is, therefore, concluded that the amount of Na^+ adsorbed in the inner Helmholtz layer or bound directly to the HAP surface is very small, and that almost all Na^+ is present in the electric double layer (*i.e.* Stern layer) as counter ions for adsorbed OH^-, or remains in the bulk solution. Added Na^+ seems just to increase the thermodynamic activity of NaOH, which is approximately expressed as ionic product of $[Na^+]\cdot[OH^-]$, as used in Fig. 6.

Adsorption Sites for OH^-

It seems that there are several kinds of sites for OH^- adsorption on the surface of HAP. OH^-, the lattice ion of HAP, may be adsorbed on the site of an OH^--defect and/or OH^--dislocation, and in the neighborhood of Ca^{2+} on the HAP surface, the amount of the latter sites being increased by the adsorption of Ca^{2+}, as mentioned above.

Ca^{2+} adsorption, furthermore, may cause the ion-exchange with H^+ of protonated phosphate ion on the surface. Consumption of OH^- by released protons is apparently assumed to be equivalent to the adsorption of OH^- by HAP. Addition of Ca^{2+}, thus, increases the total amount of OH^- adsorption and/or decreases the $(pH)_f$, as shown in Fig.s 1, 3 and 7. On the other hand, the effect of Na^+ on decreasing $(pH)_f$ is small, as mentioned above and in the previous paper,[2] because Na^+ is not as tightly adsorbed on HAP as Ca^{2+} and the amount of ion-exchange between Na^+ and surface H^+ is assumed to be small.

The association-dissociation equilibrium of H^+ involving the surface phosphate ions must also be taken into consideration, even if Ca^{2+} is not added. Davis *et al.*18) showed that anion protonation occurs more easily on the surface than in the bulk solution. Consumption of protons from the bulk solution by the protonation of surface phosphate ions on HAP may be responsible for the fact that $(pH)_f$ is larger than $(pH)_i$ in the range of the lower $(pH)_i$ in Fig. 1.

Acknowledgement We are grateful to Mr. K. Kimura, Faculty of Technology, Kyoto University, for measuring the X-ray powder diffraction pattern of HAP.

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