Coprecipitation of Cadmium with Hydroxyapatite

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The distribution behavior of the cadmium ion between hydroxyapatite precipitates and aqueous solution phase was studied, where the hydroxyapatite was prepared by the extremely slow addition of diammonium hydrogenphosphate to the solutions of cadmium and calcium nitrates buffered with ethylenediamine at 80°C. The cadmium ion was coprecipitated in the hydroxyapatite, obeying the Doerner and Hoskins logarithmic distribution law. Apparent distribution coefficient was remarkably affected by the ethylenediamine concentration and the pH value. The true distribution coefficient, $\lambda°$, was calculated by using the stability constants of proton and cadmium ion with ethylenediamine at 80°C, and its value gave a constant, about $10^{3.4}$, independently of the ethylenediamine amount and the pH value.

INTRODUCTION

The incorporation behaviors of metal ions and the radioisotopes into the bone structure of the body have been of great interest[1] since there release into the waste waters and atmosphere from chemical industry and nuclear reactors. Although the bone is not a single, homogeneous chemical substance, it is basically hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$ from its chemical composition and from X-ray diffraction analysis. Therefore, the apatite, which also exists in nature as the phosphate minerals and sediments, have been the subject of extensive biological and geochemical investigations.[2,3] However, experimental data on the coprecipitation of trace elements with hydroxyapatite are very scant.

Previously coprecipitation behaviors of copper,[4] zinc,[5] strontium,[6] and lead[7] with hydroxyapatite were investigated. In this paper, Author would like to deal with the coprecipitation of cadmium with the hydroxyapatite, because it is much interested in the incorporation of cadmium in human skeletal system which may lead to cadmium-poisoning.

EXPERIMENTAL

Apparatus and Reagents

Radioactivity countings were made with a Metro NaI(T1) (44.5 mm in diameter × 50.8 mm) well-type scintillation counter, Model PbW–6, connected with a Metro single channel pulse-height analyser, Model SP–6F.

A radioisotope, cadmium-115 m was supplied by New England Nuclear, Boston, Mass., U.S.A., as chloride in hydrochloric acid. This was converted into the nitrate and was diluted with 0.01 M of nitric acid to made the solution of about 1 μCi/ml. Stock

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solutions of calcium nitrate, $Ca(NO_3)_2$ $4H_2O$, and cadmium nitrate, $Cd(NO_3)_2$ $4H_2O$, were prepared and these metal contents were standardized complexometrically. Standard EDTA solution containing EDTA-Mg chelate was standardized with the standard calcium solution which was prepared from dry calcium carbonate.

All other reagents were reagent grade materials.

Coprecipitation Procedure

The coprecipitation procedure of cadmium was substantially the same as those described in the previous paper.[6] Five hundred milliliters of aqueous phase which contained 0.02 M of calcium nitrate and appropriate amounts of cadmium, cadmium–115 m and ethylenediamine was adjusted to a desired pH value, were taken into a 1.0 l Erlenmeyer flask equipped with a reflux condenser and regulated at 80°C. Stirring the solution constantly and passing the nitrogen gas in the flask, a 0.1 M diammonium hydrogenphosphate solution was added extremely slowly. An aliquot of the supernatant solution with the lapse of time was pipetted out. After the centrifugalous separation, the calcium ion in the solution phase was determined by EDTA titration and cadmium activities were counted.

The homogeneous[8,9] and logarithmic[10] distribution coefficients, D and λ, were calculated from the Eqs. (2) and (3).

RESULTS AND DISCUSSION

Precipitation Rate

The effect of the dropping rate of the hydrogenphosphate solution on the Ca/P ratio of the apatite precipitates was examined in the previous paper,[6] and in that case it was observed that the considerable line broadening of X-ray diffraction pattern occurred and the Ca/P ratio decreased when the dropping rate of the hydrogenphosphate solution increased.

The non-equilibrium distribution coefficient, λ', of microcomponent between precipitate and solution phases is related to the apparent distribution coefficient, λ, and to the degree of supersaturation, S, by the following equation, if the diffusion coefficients of micro- and macro-components is very nearly equal:[11]

$$\lambda' = \frac{\lambda S}{\lambda(S-1)+1} \tag{1}$$

The degree of supersaturation is directly related to the rate of precipitation. Therefore, the effect of precipitation rate on the coprecipitation behavior of cadmium was first of all determined.

In order to check the effect, the precipitation reaction was performed at the dropping velocities of 3.50, 10.0, and 30.0 ml of the hydrogenphosphate solution per hour; the concentrations of calcium, cadmium, and ethylenediamine were 2.0×10^{-2}, 1.0×10^{-5}, and 0.15 M, respectively; pH was 6.80 and the thermostat was regulated at 80°C. Figure 1 shows that the coprecipitation behavior of cadmium is scarcely influenced by the dropping velocity in the range studied.

The apparent homogeneous and logarithmic distribution coefficients, $D^{8,9}$ and $\lambda,^{10}$ can be calculated from the following expressions:
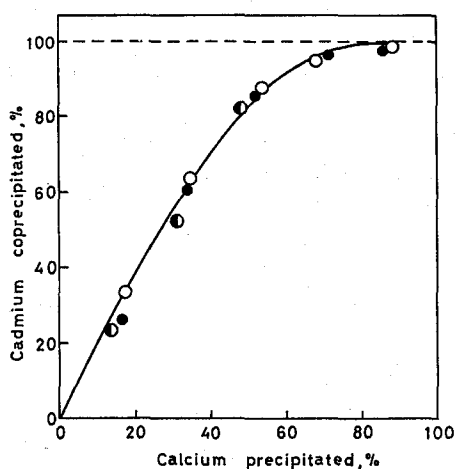
Fig. 1. The coprecipitation of cadmium with hydroxyapatite formed at various precipitation rates.

Ca^{2+}, 0.02 M; Cd^{2+}, 10^{-5} M;
ethylenediamine, 0.15M; HPO$_4{}^{2-}$, 0.1M;
dropping velocity, ◑, 3.5 ml/hr;
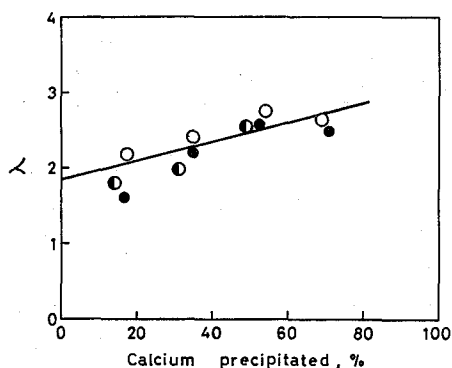○, 10 ml/hr; ●, 30 ml/hr; pH, 6.80;
temperature, 80°C.

Fig. 2. The apparent logarithmic distribution coefficients at each percentage of precipitated calcium.

◑, λ at 3.5ml/hr of the dropping velocity;
○, λ at 10 ml/hr; ●, λ at 30 ml/hr.
Others are the same as indicated in Fig. 1.

$$D = \frac{C_{Ca} \cdot M_{CdPh}}{C_{Cd} \cdot M_{CaPh}} \tag{2}$$

$$\lambda = \log \frac{C_{Cd,initial}}{C_{Cd,final}} \Big/ \log \frac{C_{Ca,initial}}{C_{Ca,final}} \tag{3}$$

where C_{Ca} and C_{Cd} are the total concentration of calcium and cadmium ions in the solution phase. M_{CaPh} and M_{CdPh} are the mole fractions of calcium and cadmium in the apatite phase.

Figure 2 shows the relationships between the distribution coefficients and the precipitated calcium. As Fig. 2 shows, the distribution of cadmium obeys considerably well the logarithmic distribution law. Strictly speaking, the logarithmic distribution coefficient, λ, does not seem to be constant; it tends to increase slightly as the precipitation proceeds. But this is considered to be caused by the slight shift of pH to lower side during the reaction progress refer to the effect of pH.

Chelate Formation with Ethylenediamine

The logarithmic distribution coefficient in a state of non-equilibrium approaches unity as the degree of supersaturation, S, increases as shown in Eq. (1). This indicates that the observed distribution coefficient becomes difficult to be influenced by the degree of supersaturation if the apparent distribution coefficient can approach unity by controlling the activity of a trace metal ion in the solution phase with a suitable chelating agent.

In the present system, ethylenediamine which is used as a buffering agent reacts with the cadmium ions to form the stable chelate compounds, while the reagent scarcely reacts with calcium ions. The formation of the cadmium ethylenediamine chelate undoubtfully

has a profound effect on the apparent distribution coefficient; with increasing the concentration of ethylenediamine in the solution phase, the activity of cadmium dissolved in the solution decreases and the value of the apparent distribution coefficient of cadmium must decrease.

When there exist complex-forming ions like ethylenediamine in the solution phase, in general, total concentrations of calcium, cadmium and the ligand, C_{Ca}, C_{Cd}, and C_L, respectively are given by the following expressions:

$$C_{Ca} = M_{Ca} \{1 + \sum \beta_i{}^{CaL} m_L{}^i\} \tag{4}$$

$$C_{Cd} = M_{Cd} \{1 + \sum \beta_i{}^{CdL} m_L{}^i\} \tag{5}$$

$$C_L = M_L \{1 + \sum \beta_i{}^{LH}[H]^i\} + m_{Ca} \sum \beta_i{}^{CaL} m_L{}^i + m_{Cd} \sum \beta_i{}^{CdL} m_L{}^i \tag{6}$$

where M_L is the molar concentration of ligand, and $\beta_i{}^{LH}$, $\beta_i{}^{CaL}$ and $\beta_i{}^{CdL}$ denote the cumulative or gross stability constants of proton, calcium and metal complexes with the ligand, respectively.

In the present system, calcium ion scarcely reacts with ethylenediamine, and C_{Cd} is negligible compared with C_L. Then, the values of M_{Ca} and M_{Cd} were obtained from the following equations:

$$M_{Cd} = C_{Cd} / \{1 + \sum \beta_i{}^{CdL} m_L{}^i\} \tag{7}$$

$$M_{Ca} = C_{Ca} \tag{8}$$

$$M_L = C_L / \{1 + \sum \beta_i{}^{LH}[H]^i\} \tag{9}$$

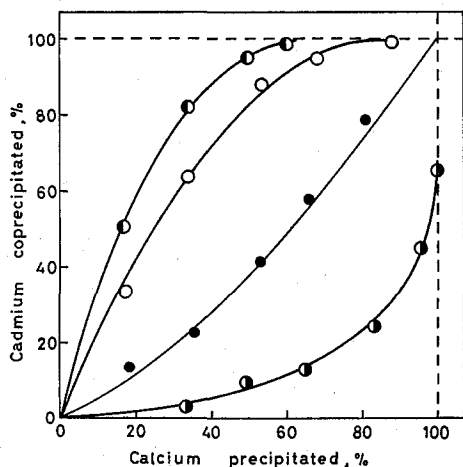The true distribution coefficient, $\lambda°$, for the present system can be calculated from

Fig. 3. The coprecipitation of cadmium at various ethylenediamine concentrations.

Ethylenediamine, ◑, 0.10M; ○, 0.15M; ●, 0.25 M; ◐, 0.50 M; dropping velocity, 10 ml/hr.
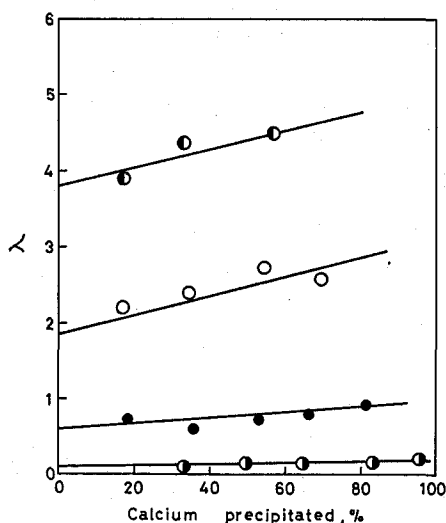
Others are the same as indicated in Fig. 1.

Fig. 4. The apparent distribution coefficient at various ethylenediamine concentrations.

Ethylenediamine, ◑, 0.10M; ○, 0.15M; ●, 0.25M; ◐, 0.50M; dropping velocity, 10 ml/hr.

Others are the same as indicated in Fig. 1.

these values and Eq. (3) or the apparent distribution coefficient calculated, assuming the all activity coefficients are equal to unity.

To examine the influence of the chelate formation on the apparent and true distribution coefficients, the coprecipitation of cadmium was made with the solutions containing 0.10, 0.15, 0.25, and 0.50 M of ethylenediamine. The results are shown in Fig. 3, where the percentages of the coprecipitated cadmium are plotted against the fractions of the precipitated calcium. It is found, as may be expected, that the coprecipitation of cadmium considerably increases as the ligand concentration decreases. The apparent logarithmic distribution coefficients in this system were calculated and plotted against the precipitation percentages of calcium in Fig. 4.

To calculate the true distribution coefficients, $\lambda°$, it is necessary to have the equilibrium constants of proton and cadmium with ethylenediamine at 80°C. The following values were used which were estimated from the values of stability constants and enthalpies:[12]

$$\beta_1^{CdL}=10^{4.62}, \quad \beta_2^{CdL}=10^{8.37}, \quad \beta_3^{CdL}=10^{10.12} \quad K_1^{LH}=10^{8.60} \quad K_{12}^{LH}=10^{5.65}$$

where K_1^{LH} and K_{12}^{LH} denote $[LH]/[L][H]$ and $[LH_2]/[LH][H]$ (L=ethylenediamine), respectively.

The apparent and true distribution coefficients in the present system are shown in Table I. Though the apparent coefficient varies from 3.80 to 0.115 as ethylenediamine increases from 0.10 to 0.50 M, the true distribution coefficient is scarcely affected by the concentration of ethylenediamine in the parent solution, as shown in the Table I. This suggests that it is not necessary to take account of the influence of the degree of supersaturation on the distribution coefficient in the present system.

pH Effect

The change of the apparent distribution coefficient in the pH value at 0.25 M of ethylenediamine is shown in Fig. 5, in which the percentages of coprecipitated cadmium at pH 6.50, 6.80, 7.15, and 7.50 are plotted against the fractions of precipitated calcium. The apparent distribution coefficient which is extrapolated to zero per cent of precipitated calcium, is plotted against the pH value in Fig. 6. As shown in these figures, the extent of cadmium coprecipitation decreases rapidly as the pH rises. This is caused by the increase of the ethylenediamine concentration with the rise of pH. However, as seen in Table I, the true distribution coefficient, $\lambda°$, becomes scarcely affected by the pH and showed a constant value, about $10^{3.5}$.

Table I. Apparent and Thermodynamic Distribution Coefficients at Various Concentrations

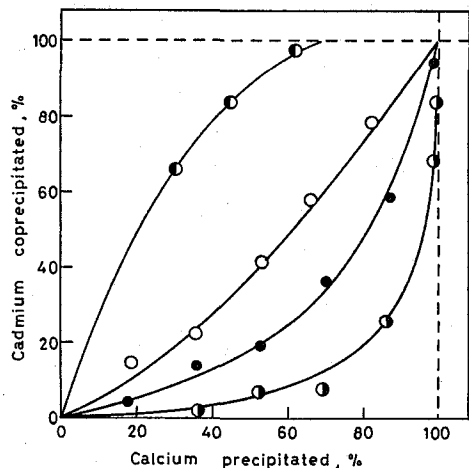| Total ethylenediamine,M	pH	λ	$\log \lambda°$
0.10	6.80	3.80	3.40
0.15	//	1.85	3.45
0.25	//	0.60	3.42
0.50	//	0.115	3.36
0.25	6.50	2.90	3.64
//	7.15	0.22	3.35
//	7.50	0.012	3.53

Ca 0.02 M, Cd 10^{-5} M, temperature 80°C

Fig. 5. The coprecipitation of cadmium at various
pH values.

pH, ◑, 6.50; ○, 6.80; ●, 7.15; ◐, 7.50;
ethylenediamine, 0.25 M; dropping veloc-
ity, 10 ml/hr.
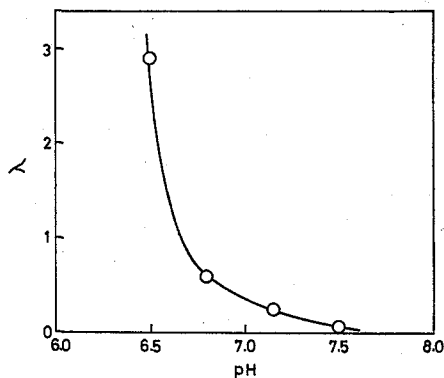Others are the same as indicated in Fig. 1.

Fig. 6. The effect of pH on the apparent distri-
bution coefficient.

Ethylenediamine, 0.25 M;
dropping velocity, 10 ml/hr.
Others are the same as indicated in Fig. 1.

Cadmium Concentration

To investigate the effect of molar ratio between cadmium and calcium, the hydroxy-
apatite was precipitated at pH 6.80 from the solution containing cadmium ranging from
10^{-2} M to 10^{-8} M. The results are shown in Fig. 7; there are no significant changes
in the apparent distribution coefficient when the initial cadmium concentration is less than
10^{-4} M. However, the apparent distribution coefficient tends to decrease at higher con-
centration than 10^{-4} M of cadmium.

In principle the distribution coefficient is independent of the molar ratio between
micro- and macro-components for the system formed the isomorphous mixed crystals.
Since there does not exist the apatite structure of cadmium, the micro- and macro-
components are essentially immiscible. Therefore, in such an anomalous mixed crystal,
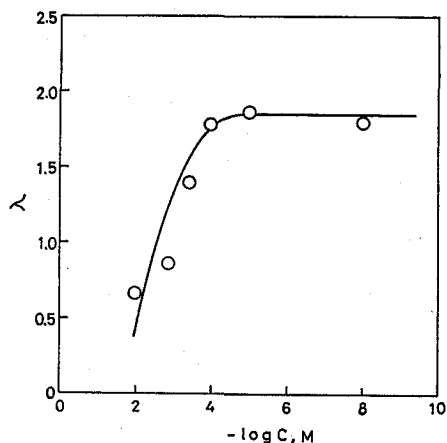

Fig. 7. The effect of cadmium concentration on
the apparent distribution coefficient.

it is considered the crystal lattice of the apatite becomes saturated with cadmium in the presence of tracer level. Further increase of cadmium ion perhaps results in the post precipitation of a second solid phase.

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