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SOLUBILITY AND THERMODYNAMIC DATA OF CADMIUM HYDROXYAPATITE IN AQUEOUS MEDIA

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ABSTRACT

Solubility studies of cadmium hydroxyapatite, CdHA, precipitated in aqueous media at 37°C were made in a medium with a constant ionic environment of 0.165 M sodium nitrate. Purity of the sample was confirmed by analytical, X-ray and photomicrographic techniques. Dicadmium phosphate, $CdHPO_4$ and CdHA, were considered to be the virtual solid phases that controlled the solubility equilibria in the acidic and alkaline pH ranges, respectively. Thermodynamic quantities, ΔG^0, ΔH^0, ΔS^0 and ΔC_p^0 for the dissolution process of cadmium and calcium hydroxyapatites at a convenient pH of 5.0 were calculated and compared.

INTRODUCTION

Since it is known that cadmium can be incorporated into calcium hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, CaHA [1], the model system for the crystalline inorganic fraction for the skeletal system [2] causing "Itai Itai" [3] a very painful bone disease with osteoporetic-like effects, it would seem relevant to investigate the solubility behaviour of cadmium hydroxyapatite, $Cd_{10}(PO_4)_6(OH)_2$, CdHA, the final product of the $Ca^{2+} \rightarrow Cd^{2+}$ exchange reaction in CaHA according to the following equation

$$Ca_{10}(PO_4)_6(OH)_2 + n\,Cd^{2+} \rightarrow Ca_{10-n}Cd_n(PO_4)_6(OH)_2 + n\,Ca^{2+}$$

EXPERIMENTAL

A sample of CdHA was prepared in aqueous media at 37°C by the method of precipitation used earlier [4]. The sample was dried at 110°C for 6 h and was analysed complexometrically [5] for Cd and P contents. The weight percent errors in the determinations being ±0.4 for phosphorus and ±0.01 for cadmium. The X-ray powder diffraction pattern was obtained on a Debye Scherrer Unicam Camera with CuK_α radiation. The individual crystals were characterised by using a Meopta binocular research microscope. The solubility studies with the sample were made by the method of equilibration at 37°C [6,7] over a pH range 5.0 to 8.0 under a constant

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ionic environment using 0.165 M $NaNO_3$. Sodium acetate–acetic acid for pH 5.0–5.5 and borax–boric acid buffer combinations for pH 7.0–8.0 were used. Cadmium and phosphorus present in the saturated solutions were determined complexometrically [5]. The solid phases formed during equilibration were characterised by micro analytical determinations and from the constancy of their pK_{ip} values. Dicadmium phosphate. $CdHPO_4$ and an apatitic phase appear to dominate the solubility equilibria in the pH range 5.0–7.0 and 7.5–8.0, respectively. Standard thermodynamic parameters ΔG^0, ΔH^0, ΔS^0 and ΔC_p^0 for the species governing the solubility equilibria of CdHA and the dependence of solubility products, K_{sp} of the solute phase on temperatures between 37 and 52°C, at intervals of 5°C, and at a pH of 5.0 were investigated. Similar studies were repeated with a pure synthetic sample of CaHA and the results compared with those of CdHA.

RESULTS AND DISCUSSION

The experimental molar Cd/P g atom ratio of 1.68 is close to the theoretical Cd/P = 1.67 for pure CdHA. The lattice constants $a = 9.012$ Å, $c = 6.614$ Å (reported earlier $a = 9.01$ Å, $c = 6.61$ Å [8,9]) and the rod-like morphology of the crystals in the photomicrograph indicated that the sample of CdHA prepared is pure and free from other extraneous phases.

The results of the pH dependence of the solubility of CdHA are given in Table 1. From a knowledge of the total dissolved phosphorus (P total in g-atom l^{-1}), cadmium and the pH of the medium of equilibration, the concentrations of H_3PO_4, $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-} are evaluated and included in Table 1. The following relationships are considered

$$P_{total} = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}] \tag{1}$$

$$K_1 = \frac{[H_2PO_4^-][H^+]}{[H_3PO_4]} = 7.51 \times 10^{-3} \tag{2}$$

$$K_2 = \frac{[HPO_4^{2-}][H^+]}{[H_2PO_4^-]} = 6.57 \times 10^{-8} \tag{3}$$

$$K_3 = \frac{[PO_4^{3-}][H^+]}{[HPO_4^{2-}]} = 4.73 \times 10^{-13} \tag{4}$$

Where K_1, K_2 and K_3 are the three dissociation constants of orthophosphoric acid at 37°C [10–12]. The K_{ip} and pK_{ip} values for the species expected to be formed are included in Table 2. The calculated K_{ip} values are synonymous with the solubility product in the present context. By analogy with the dissolution of CaHA, the probable solid phases formed during the equilibration of CdHA in aqueous media are $CdHPO_4$, $Cd(H_2PO_4)_2$, and $Cd_2(HPO_4)(OH)_2$. The constancy of pK_{ip} values with an average of 2.0766×10^{-7} and 6.6982, respectively (for Nos. 1–5) in columns 9 and 10 show that $CdHPO_4$ is the virtual solid phase governing the

TABLE 1

pH Dependence of the solubility equilibria of cadmium hydroxyapatite

Sample no.	Final pH	$C_{H^+} \times 10^9$	$C_{OH^-} \times 10^7$	$Cd \times 10^3$	$P \times 10^3$	$C_{PO_4^{3-}} \times 10^{12}$	$C_{H_2PO_4^-} \times 10^5$	$C_{HPO_4^{2-}} \times 10^5$	$C_{H_3PO_4}$ (mole l^{-1})
		1	2	3	4	5	6	7	8
1	5.175	66.83	0.0149	6.41	2.215	1.5246	2.1541	219.1149	1.945×10^{-6}
2	5.70	19.95	0.0501	4.13	1.21	9.1425	2.8560	117.0880	3.1104×10^{-7}
3	6.25	5.623	0.1778	2.85	0.86	75.665	8.9950	76.9840	5.764×10^{-8}
4	6.80	1.585	0.631	1.31	0.731	639.1648	21.4181	51.6707	1.090×10^{-8}
5	7.125	0.7498	1.3336	0.97	0.450	1325.627	21.0138	23.9820	2.394×10^{-9}
6	7.60	0.2512	3.9809	0.332	0.395	5380.200	28.5730	10.9247	3.65417×10^{-10}
7	8.10	0.079	12.658	0.200	0.213	11383.190	19.0120	2.2860	2.4040×10^{-11}

TABLE 2

K_{ip} and pK_{ip} values of different phases expected to be formed during the dissolution of cadmium hydroxyapatite in aqueous media

Sample no.	$CdHPO_4$		$Cd_2(HPO_4)(OH)_2$		$Cd(H_2PO_4)_2$		$Cd_{10}(PO_4)_6(OH)_2$	
	$K_{ip} \times 10^7$	pK_{ip}	K_{ip}	pK_{ip}	K_{ip}	pK_{ip}	K_{ip}	pK_{ip}
	9	10	11	12	13	14	15	16
1	1.3807	6.8599	1.9649×10^{-27}	26.7066	3.077×10^{-8}	7.5119	3.6470×10^{-111}	110.4381
2	1.5925	6.7979	1.6502×10^{-26}	25.7823	5.662×10^{-9}	8.2471	2.1162×10^{-107}	106.6745
3	2.5635	6.5911	2.3097×10^{-25}	24.1629	1.689×10^{-9}	8.7724	2.0972×10^{-102}	101.6784
4	2.8057	6.5519	1.4634×10^{-24}	23.8346	3.497×10^{-10}	9.4564	4.0406×10^{-99}	98.3936
5	2.0407	6.6902	3.5169×10^{-24}	23.4538	5.5797×10^{-11}	10.2534	7.1178×10^{-98}	97.1476
6	0.9486	7.2291	3.9623×10^{-24}	23.3318	3.9623×10^{-12}	11.4021	5.9724×10^{-97}	96.2239
7	0.3802	7.4200	1.2184×10^{-23}	22.9142	1.0450×10^{-13}	12.9909	3.5691×10^{-97}	96.4475

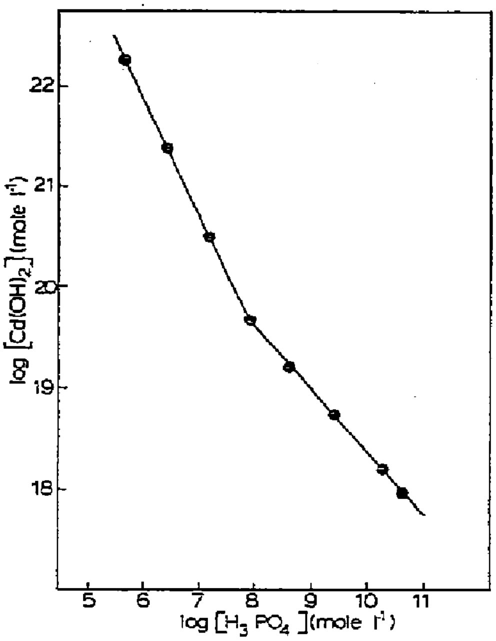

Fig. 1. Log-log plot of the solubility isotherm for dicadmium phosphate.

solubility equilibria in the pH range 5.0–7.0. The wide variation of the values of K_{ip} in columns 11, 13 and 15 in Table 2 rules out the possibility of $Cd(H_2PO_4)_2$, $Cd_2(HPO_4)(OH)_2$ and $Cd_{10}(PO_4)_6(OH)_2$ as the controlling solid phases. The sudden drop in the K_{ip} values of $CdHPO_4$ and the constancy of the K_{ip} and pK_{ip} values in columns 15 and 16 (for Nos. 6–7) indicate that CdHA is the controlling solid phase of the solubility equilibria in the alkaline pH range of 7.5–8.0. This latter observation can also be explained with the help of the solubility isotherm represented in Fig. 1.

The isotherm Fig. 1 represents the log–log plot of $Cd(OH)_2$ and H_3PO_4 for the dissolution of CdHA at 37°C. The lower region of the isotherm indicates composition of solution undersaturated with respect to CdHA, while that above the isotherm shows a region of supersaturation. In the lower portion of the curve the chemical potential of $Cd(OH)_2$ is relatively high in spite of the fact that the concentration of the Cd^{2+} ion is very low. As one moves up the curve in the direction of higher Cd^{2+} ion concentration, the chemical potential, i.e. the activity of $Cd(OH)_2$, decreases because of low pH values. The decrease in chemical potential of $Cd(OH)_2$ is compensated for by the increase in chemical potential of H_3PO_4, so that the quantity $10\,\mu\,Cd(OH)_2 + 6\,\mu\,H_3PO_4$ of the process

$$\Delta F^0_{\mathrm{CdHA}} + 18\,\mu\,H_2O = 10\,\mu\,Cd(OH)_2 + 6\,\mu\,H_3PO_4$$

remains constant, where ΔF^0 is the standard heat of dissolution of the process. It is evident that when the medium is basic the solution becomes supersaturated and results in precipitation of CdHA, while in acidic medium the solution behaves as undersaturated and the composition will not move further down the isotherm. These effects of the pH of the medium of equilibration are consequent upon the positive slope of the isotherm.

CdHA being the salt of a polybasic acid the following equilibria are considered to be established during its dissolution in the acidic pH range

$$Cd_{10}(PO_4)_6(OH)_2 \rightleftharpoons 10\,Cd^{2+} + 6\,PO_4^{3-} + 2\,OH^- \qquad (5)$$

$$PO_4^{3-} + H^+ \rightleftharpoons HPO_4^{2-} \qquad (6)$$

$$HPO_4^{2-} + H^+ \rightleftharpoons H_2PO_4^- \qquad (7)$$

$$H_2PO_4^- + H^+ \rightleftharpoons H_3PO_4 \qquad (8)$$

$$Cd^{2+} + HPO_4^{2-} \rightleftharpoons CdHPO_4 \qquad (9)$$

$$Cd^{2+} + 2\,H_2PO_4^- \rightleftharpoons Cd(H_2PO_4)_2 \qquad (10)$$

Since $Cd(H_2PO_4)_2$ formed according to eqn. (10) is converted into $CdHPO_4$ [13] in aqueous media, eqn. (9) can be considered to dominate. However, consequent upon the decrease of the chemical potential of H_3PO_4 in a more basic medium the solution tends towards the supersaturated region (Fig. 1) resulting in the precipitation of CdHA as a stable solid phase. Hence in the alkaline pH range investigated, CdHA is the virtual solid phase governing the solubility equilibria.

The values of solubility products (in terms of $-\log K_{sp}$) for CdHA and CaHA are calculated by the equations

$$-\log K_{sp} = A/T + B + CT \qquad (11)$$

TABLE 3

Comparison of experimental and calculated values of $-\log K_{sp}$ of cadmium and calcium hydroxyapatites at different temperatures and pH = 5.0

	$-\log K_{sp}$			
	37°C	42°C	47°C	52°C
CaHA System				
Experimental	6.4104	6.4299	6.5211	6.5962
Theoretical	6.4221	6.4358	6.4940	6.5945
CdHA System				
Experimental	6.8599	7.0036	7.0283	7.1256
Theoretical	6.8229	6.9774	7.0907	7.1649

TABLE 4

Thermodynamic quantities of cadmium hydroxyapatite system at pH = 5.0, and temperature between 37 and 52°C

Temp. (°C)	$\Delta G^0 \times 10^4$ (J mole^{-1} deg^{-1})	(−) $\Delta H^0 \times 10^4$ (J mole^{-1})	(−) ΔS^0 (J mole^{-1} deg^{-1})	(+) $\Delta C_p^0 \times 10^2$ (J mole^{-1} deg^{-1})
37	4.0491	6.4664	320.2702	27.5839
42	4.2075	5.0761	294.7324	28.0288
47	4.3438	3.6635	250.2422	28.4737
52	4.4558	2.2287	205.7520	28.9186

For CaHA

$$-\log K_{sp} = \frac{27803.65}{T} - 172.3795 + 0.28746\,T \qquad (12)$$

For CdHA

$$-\log K_{sp} = \frac{-25711.466}{T} + 161.80711 - 0.2324\,T \qquad (13)$$

The experimental and the calculated values are compared in Table 3. Both CdHA and CaHA show retrograde solubility. Since in $CaHPO_4$ [14] and $CdHPO_4$, the solid phases considered to control the solubility equilibria exhibit retrograde solubility, our observation of temperature dependence of the solubility of CdHA and CaHA are understandable.

The thermodynamic quantities ΔG^0, ΔH^0, ΔS^0 and ΔC_p^0 for the process of dissolution of CdHA and CaHA at pH 5.0 given in Tables 4 and 5 are obtained from eqns. (14)–(17).

$$\Delta G^0 = 2.3026\,R(A + BT + CT^2) \qquad (14)$$

TABLE 5

Thermodynamic quantities for calcium hydroxyapatite system at pH = 5.0 and temperature between 37 and 52°C

Temp. (°C)	$\Delta G^0 \times 10^4$ (J mole^{-1} deg^{-1})	$\Delta H^0 \times 10^3$ (J mole^{-1})	(−)ΔS^0 (J mole^{-1} deg^{-1})	(−)$\Delta C_p^0 \times 10^2$ (J mole^{-1} deg^{-1})
37	3.8113	+3.421	111.9077	34.1190
42	3.8810	−13.775	166.9385	34.6693
47	3.9782	−31.247	221.9693	35.2196
52	4.1030	−48.994	277.0000	35.7699

$$\Delta H^0 = 2.3026\, R(A - CT^2) \tag{15}$$

$$\Delta S^0 = -2.3026\, R(B + 2\, CT) \tag{16}$$

$$\Delta C_p^0 = -2.3026\, R(CT) \tag{17}$$

where A, B and C are the empirical constants of eqn. (11).

The negative values of ΔH^0, indicating that the process of dissolution for both the apatites is exothermic, explain the decrease in solubility with the increase in temperature. The higher negative value of ΔS^0 of the species for the CdHA system indicates that the order produced by the Cd^{2+} ions in solution is greater than that for Ca^{2+} in aqueous media during dissolution. This can be understood by considering the size of the Cd^{2+} and Ca^{2+} ion (0.97 Å and 0.99 Å, respectively); the former being a smaller ion with a high charge results in higher entropy in solution and hence CdHA is less soluble than CaHA under chosen conditions. The values of ΔG^0, ΔH^0 and ΔS^0 are higher for CdHA than CaHA in aqueous media, indicating that the dissolution process for the former is more energy consuming and hence it is less soluble.

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