Thermochimica Acta, 52 (1982) 333–336
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

Note

SOLUBILITY OF HYDROXYAPATITE AND RELATED THERMODYNAMIC DATA

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(Received 4 June 1981)

Hydroxyapatite, $Ca_5(PO_4)_3(OH)$, is considered to be the model tooth and bone mineral [1] which controls the calcification and resorption process in vivo. Earlier studies [2–8] on the solubility of this compound do not convincingly establish the nature of the solid phase controlling the solubility equilibria of HA both in vivo and in vitro. We report in this paper that dicalcium phosphate dihydrate, $CaHPO_4 \cdot 2\ H_2O$, is formed during the dissolution of crystalline hydroxyapatite in the pH range 5.8–7.2 while at higher pH an apatite-like phase appears to dominate the dissolution.

A sample of hydroxyapatite was prepared at 37°C by the precipitation method as reported earlier [9]. Homogeneity and purity of the sample was confirmed by its molar Ca/P g atom ratio of 1.68 (theoretical 1.67) and by measurement of lattice constants ($a = 9.42$ Å and $c = 6.86$ Å). The electron micrograph also confirmed the presence of crystalline apatite. The solubility studies were made by the method of equilibration at 37°C as detailed earlier [10,11] in the presence of 0.165 M $NaNO_3$ to maintain the activity coefficients of the dissolving species constant [4]; sodium acetate–acetic acid for pH 5.8–6.8, and borax–boric acid buffer combinations for

TABLE 1

pH Dependence of the solubility equilibria of hydroxyapatite

Serial No	Final pH	Measured concn (g atoms l^{-1})		Calculated concn. (g ions l^{-1})			
		$Ca \times 10^3$	$P \times 10^3$	H_3PO_4 (moles l^{-1})	PO_4^{3-}	$HPO_4^{2-} \times 10^5$	$H_2PO_4^- \times 10^5$
1	5.2	2.71	2.80	2.324×10^{-6}	2.16×10^{-12}	2.882	276.65
2	5.8	2.44	2.50	4.887×10^{-7}	28.65×10^{-12}	9.600	231.59
3	6.1	2.04	2.01	1.896×10^{-9}	88.33×10^{-12}	14.833	179.32
4	7.2	1.10	0.90	3.703×10^{-9}	34.41×10^{-10}	45.90	44.08
5	7.25	0.80	0.62	4.7656×10^{-9}	62.56×10^{-10}	74.37	63.65
6	7.6	0.46	0.55	4.880×10^{-11}	74.14×10^{-10}	37.93	14.50
7	8.0	0.40	0.25	4.367×10^{-12}	10.21×10^{-9}	21.58	3.28
8	8.5	0.31	0.193	4.182×10^{-12}	27.12×10^{-9}	18.16	0.87
9	9.2	0.25	0.167	1.260×10^{-13}	12.39×10^{-8}	16.52	0.15

TABLE 2

Different phases expected to be formed

Sample No	$CaHPO_4$		$Ca_2HPO_4(OH)_2$		$Ca(H_2PO_4)_2$		$Ca_{10}(PO_4)_6(OH)_2$	
	K_{ip}	pK_{ip}	K_{ip}	pK_{ip}	K_{ip}	pK_{ip}	K_{ip}	pK_{ip}
1	0.78×10^{-7}	6.89	5.23×10^{-28}	27.27	2.07×10^{-8}	7.68	5.40×10^{-114}	113.26
2	2.34×10^{-7}	6.63	1.43×10^{-22}	21.84	1.30×10^{-8}	7.88	1.64×10^{-107}	106.78
3	3.02×10^{-7}	6.52	3.89×10^{-22}	21.41	6.55×10^{-9}	8.18	9.33×10^{-104}	103.03
4	5.04×10^{-7}	6.29	1.86×10^{-24}	23.73	2.13×10^{-11}	10.67	1.08×10^{-104}	103.96
5	6.23×10^{-7}	6.20	1.54×10^{-24}	23.81	3.28×10^{-10}	9.48	2.31×10^{-94}	93.63
6	1.74×10^{-7}	6.75	9.07×10^{-26}	25.04	9.67×10^{-12}	11.01	1.11×10^{-95}	94.95
7	0.87×10^{-7}	7.06	4.02×10^{-29}	28.39	4.30×10^{-13}	12.36	1.39×10^{-95}	94.85
8	0.56×10^{-7}	7.25	1.74×10^{-28}	27.76	2.34×10^{-14}	13.63	3.25×10^{-92}	91.49
9	0.41×10^{-7}	7.39	4.11×10^{-30}	29.39	5.62×10^{-16}	15.25	8.63×10^{-89}	88.06

the higher pH range 7.0–9.2 were used. The saturated solutions obtained were analyzed for Ca and P with the weight percent errors of ±0.1 and 0.4, respectively (Table 1). Since the ionic product K_{ip} is synonymous with the solubility product in the present context, the nature of the solid phase formed during dissolution of hydroxyapatite (HA) were characterized by chemical analysis and the calculated K_{ip} and pK_{ip} values. These values are included in Table 2. The constancy of the K_{ip} and pK_{ip} values with an average of 3.19×10^{-7} and 6.56, respectively, shows that dicalcium phosphate dihydrate (DCPD) is the phase governing the solubility equilibria in the pH range 5.8–7.2. Such a possibility is ruled out with other phases considered as shown by the wide variations in these values; our values are in close proximity to the values reported by La Mer [4] (3.36×10^{-7} and 6.66). A similar consideration of the results given in the last two columns of Table 2 confirms apatite as the solid controlling the solubility equilibria in the pH range 7.25–9.2.

The calculated free energy (ΔG) and entropy (ΔS) values for DCPD and HA at 37°C using the thermodynamic solubility products are reported in Table 3. The negative value of ΔG over the entire pH range investigated shows that dissolution is favoured throughout. The negative ΔG and the positive ΔS values for DCPD within the pH range 5.8–7.25 indicate that the formation of this species is favoured during dissolution of HA. The positive ΔG and negative ΔS values thereafter clearly demonstrate that DCPD is not formed in the alkaline region. This finding is in accordance with the $CaO-P_2O_5-H_2O$ phase diagram [12]. The increase in the positive values of ΔS for HA indicates that HA is less soluble with increase in pH of the dissolving medium. The above conclusion is further substantiated by the experimentally determined Ca/P atom ratio of 1.0 ± 0.1 and 1.70 ± 0.02 for the solid after attainment of saturation in both acidic and alkaline regions, respectively.

TABLE 3

Free energy and entropy of dissolution of HA and DCPD at 37°C over the pH range 5.8–9.2

Equilibrium pH	HA		DCPD	
	(−)ΔG (kJ mole^{-1} deg^{-1})	ΔS (J mole^{-1} deg^{-1})	ΔG (kJ mole^{-1} deg^{-1})	ΔS (J mole^{-1} deg^{-1})
5.8	33.2061	107.116	−0.558	+1.8019
6.1	41.1245	132.659	−1.194	+3.8540
7.2	67.1286	216.544	−2.473	+7.9760
7.25	67.9299	219.128	−3.002	+9.6830
7.6	64.3639	209.620	+0.179	−0.5790
8.0	67.2701	217.000	+1.908	−6.1570
8.5	74.2656	239.566	+3.007	−9.7020
9.2	87.0031	280.655	+3.785	−12.2100

ACKNOWLEDGEMENTS

We thank Principal Professor S. Dash for encouragement. P.P.M. and N.S.C. are thankful to the UGC, India, for a research grant.

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