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Determination of solubility products of phosphate and vanadate apatites of calcium and their solid solutions

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To understand the toxic effects of vanadium on the human skeletal system, the solubility products of phosphate and vanadate apatites of calcium and eight of their solid solutions, spread over the entire compositional range, were investigated at 37° C in 0.165 M sodium chloride solution. They were found to increase with increase in the vanadium content, the dissolution being found to be stoichiometric. A theoretical interpretation based on changes in lattice and hydration energies resulting from isomorphous ionic substitution is advanced.

1. Introduction

By virtue of its biological significance and its remarkable ability to undergo several isomorphous cationic and anionic substitutions involving toxic ions, calcium phosphate apatite, $Ca_{10}(PO_4)_6(OH)_2$ (CPA), the principal inorganic constituent [1] of human bones and teeth, has been the subject of extensive investigations to throw light on the mechanism of incorporation of such ions into the human skeletal system. It was established that the toxicity is controlled by the dependence of the principal bone processes, calcification and resorption, on the extent of incorporation of toxic ions. The present work dealing with the replacement of PO_4^{3-} by VO_4^{3-} resulting in the formation of its isomorph, calcium vanadate apatite, $Ca_{10}(VO_4)_6(OH)_2$ (CVA), was undertaken because the mechanism of occurrence of toxic effects [2, 3] of vanadium and its salts, such as paralysis, convulsions and sleepiness leading to bronchitis and bronchopneumonia caused when their proportion exceeds 1 mg kg^{-1} body weight, were not investigated earlier. In addition, these studies were intended to clarify a few ambiguities associated with the available results on the solubilities of apatites, especially in the context of its reported non-stoichiometric [4–6] dissolution.

2. Experimental details

CPA, CVA and a series of eight of their solid solutions, prepared through appropriate modifications of a wet method [7–9], were characterized through X-ray, infrared, electron microscopic and thermal analyses, in addition to conventional chemical analyses [8–11]. Their solubility products were determined in buffered 0.165 M sodium chloride solution at the biologically significant temperature of 37° C by analyses of their saturated solutions. Each system was set up by adding 0.2 g of apatite to potassium acid phthalate–sodium hydroxide or boric acid–borax buffer of required pH prepared in 200 ml of 0.165 M sodium chloride, the latter being needed to maintain the ionic strength during dissolution effectively constant [12]. The ionic strengths of the systems were found to range between 0.20 and 0.24. Further, an aqueous solution of 0.165 M sodium chloride, a solvent of biological importance, may be considered as a standard solution [13] of reference in which all activity coefficients of dissolved ionic species could be taken as unity. This avoids inaccuracies involved in the calculations of activity coefficients needed for the evaluation of solubility products of solutes containing polyvalent ions, and enables ionic products of saturated solutions of such substance to be taken as their solubility products. Equilibration took place in a thermally insulated cabin maintained at 37 ± 0.5° C for about 12 h, in air-tight polyethylene containers shaken at a regulated speed using a mechanical shaker. Attainment of saturation was confirmed separately by carrying out investigations on the dissolution kinetics of CPA, CVA and a representative solid solution of them as solutes at pH 5.2 and pH 7.5. The systems were equilibrated as above and the studies could be extended in each case to a total duration of 24 h by setting up ten identical systems, equilibration of each system being interrupted at convenient time-intervals. The equilibration time required for the attainment of saturation in each case was found to be 4 h. In order to be doubly sure about the attainment of saturation, a duration of 12 h was chosen for equilibration throughout the investigations. The colloidal component [14] of the solute was separated from the solution by filtration through a G4 sintered glass crucible under suction at the temperature of equilibration. From the saturated solutions thus obtained calcium was determined volumetrically [9] while phosphate [15] and vanadate [9, 16] were determined spectrophotometrically, a separate aliquot being taken each time. The effect of common ions on pK_{sp} of CPA and CVA was also investigated at convenient pH values.

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TABLE I Solubility products of phosphate and vanadate apatites* of calcium and their solid solutions in 0.165 M sodium chloride solution

Serial no.	Final pH	Measured conc. (10^3 mol l^{-1})			Calculated activities (mol l^{-1})			Mole ratio, Ca/(P + V)	pK_{sp}	Average pK_{sp}
		Ca	P	V	$a_{(OH^-)}$† $\times 10^8$	$a_{(PO_4^{3-})}$ $\times 10^{12}$	$a_{(VO_4^{3-})}$ $\times 10^{13}$			
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
Solute:	*calcium phosphate apatite,* $Ca_{10}(PO_4)_6(OH)_2$									
1	4.77	3.36	2.06	–	0.16	0.21	–	1.62	118	114
2	4.94	3.17	1.87	–	0.25	0.42	–	1.69	116	
3	5.20	2.67	1.53	–	0.46	1.14	–	1.74	114	
4	5.65	2.30	1.29	–	1.28	7.50	–	1.78	109	
Solute:	*solid solution no. 1,* $Ca_{10}(PO_4)_{5.7}(VO_4)_{0.3}(OH)_2$									
5	5.48	1.03	0.55	0.06	0.87	1.47	0.08	1.69	118	114
6	5.85	0.71	0.38	0.05	2.04	5.56	0.36	1.60	115	
7	7.01	0.14	0.05	0.03	29.5	107.0	39.7	1.65	112	
8	7.20	0.12	0.04	0.03	45.7	164.0	76.7	1.65	111	
Solute:	*solid solution no. 2,* $Ca_{10}(PO_4)_{5.4}(VO_4)_{0.6}(OH)_2$									
9	5.54	1.17	0.56	0.14	1.00	1.89	0.23	1.64	116	113
10	5.90	0.82	0.42	0.10	2.29	7.55	0.84	1.58	114	
11	7.01	0.18	0.06	0.05	29.5	120.0	59.7	1.64	111	
12	7.20	0.15	0.05	0.04	45.7	182.0	123.0	1.66	110	
Solute:	*solid solution no. 3,* $Ca_{10}(PO_4)_{4.9}(VO_4)_{1.1}(OH)_2$									
13	5.22	2.60	1.24	0.37	0.48	1.01	0.13	1.60	116	113
14	5.62	1.84	0.80	0.34	1.20	4.01	0.78	1.62	113	
15	6.05	1.10	0.37	0.31	3.23	13.2	5.12	1.61	112	
16	7.01	0.36	0.05	0.02	29.5	95.2	21.5	1.62	109	
Solute:	*solid solution no. 4,* $Ca_{10}(PO_4)_{3.7}(VO_4)_{2.3}(OH)_2$									
17	5.03	5.32	1.64	1.57	0.31	0.56	0.23	1.72	116	112
18	5.17	5.09	1.34	1.47	0.43	0.87	0.41	1.80	115	
19	5.40	4.47	1.16	1.37	0.72	2.16	1.13	1.76	112	
20	6.03	3.42	0.71	1.29	3.09	22.8	19.3	1.70	106	
Solute:	*solid solution no. 5,* $Ca_{10}(PO_4)_{3.1}(VO_4)_{2.9}(OH)_2$									
21	5.08	5.89	1.16	2.25	0.35	0.49	0.42	1.72	116	111
22	5.27	5.52	0.96	2.11	0.54	0.99	0.95	1.79	114	
23	5.57	4.75	0.79	1.96	1.07	3.21	3.53	1.72	111	
24	6.17	4.19	0.47	1.88	4.26	28.3	53.2	1.77	104	
Solute:	*solid solution no. 6,* $Ca_{10}(PO_4)_{2.3}(VO_4)_{3.7}(OH)_2$									
25	5.19	6.73	0.96	2.94	0.45	0.69	0.91	1.72	115	111
26	5.39	6.24	0.87	2.61	0.71	1.55	2.05	1.79	112	
27	5.65	5.46	0.56	2.48	1.29	3.26	6.46	1.79	110	
28	6.61	1.99	0.07	1.17	11.7	28.5	244.0	1.59	106	
Solute:	*solid solution no. 7,* $Ca_{10}(PO_4)_{1.6}(VO_4)_{4.4}(OH)_2$									
29	5.27	7.21	0.78	3.43	0.54	0.81	1.54	1.71	115	109
30	5.40	6.73	0.64	3.14	0.72	1.20	2.58	1.77	112	
31	5.79	6.01	0.42	2.98	1.77	4.67	14.8	1.76	108	
32	6.42	5.07	0.19	2.75	7.58	33.7	242.0	1.72	101	
Solute:	*solid solution no. 8,* $Ca_{10}(PO_4)_{0.8}(VO_4)_{5.2}(OH)_2$									
33	5.33	7.78	4.52	3.92	0.62	0.61	2.33	1.78	113	107
34	5.52	7.45	3.55	3.83	0.95	1.14	5.46	1.78	111	
35	6.14	6.78	2.01	3.76	3.98	10.5	9.28	1.70	103	
36	6.65	2.95	0.12	1.72	12.8	6.02	429.0	1.69	102	
Solute:	*calcium vanadate apatite,* $Ca_{10}(VO_4)_6(OH)_2$									
37	5.33	8.27	–	5.15	0.62	–	3.06	1.60	112	107
38	5.53	7.88	–	4.41	0.98	–	6.60	1.78	110	
39	5.90	7.12	–	3.92	2.29	–	32.2	1.64	106	
40	6.60	3.78	–	2.25	10.9	–	448.0	1.68	100	

*0.2 g apatite, washed with a 2% solution of EDTA maintained at pH 10 using ammonium chloride and ammonium hydroxide, is taken in 200 ml of an appropriate buffer combination of potassium acid phthalate and sodium hydroxide or boric acid and borax brought to a molarity of 0.165 M with respect to sodium chloride.

†Calculated from the measured final pH of the equilibrated system.

TABLE II Studies on the effect of common ions on the solubility equilibria of calcium phosphate apatite

Serial no.	Common ion added ($mg\,l^{-1}$)		Final pH	Measured conc. ($10^3\,mol\,l^{-1}$)		Mole ratio: Ca/P	Calculated activity ($10^{12}\,mol\,l^{-1}$)	Solubility product of solute,
	Ca	P		Ca	P		$a_{(PO_4^{3-})}$	pK_{sp}
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
1	10	–	5.62	3.23	1.19	2.71	6.03	108
2	30	–	5.62	4.44	0.79	2.46	4.01	108
3	–	10	5.48	2.49	1.59	6.87	4.26	110
4	–	30	5.48	1.75	2.58	11.1	6.91	110
							Average	109

$K_{sp} = (Ca^{2+})^{10}(PO_4^{3-})^6(OH^-)^2$.

Solute: 0.2 g $Ca_{10}(PO_4)_6(OH)_2$ washed with a 2% solution of EDTA maintained at pH 10 using ammonium chloride and ammonium hydroxide.

Dissolving medium: 200 ml of an appropriate buffer combination of potassium acid phthalate and sodium hydroxide brought to a molarity of 0.165 M with respect to sodium chloride.

Temperature: 37 ± 0.5° C; $pK_w = 13.54$.

3. Results

A few representative sets of results on the determination of the solubility products of CPA, CVA and eight of their solid solutions are given in Table I. Experimentally determined concentrations of calcium, phosphorus and vanadium for each sample at a measured pH are given in columns 3 to 5. While the activities of OH^- and Ca^{2+} ions were thus available directly from the measured pH and concentrations of Ca^{2+}, respectively, those of PO_4^{3-} and VO_4^{3-} could be calculated from the total concentrations of phosphorus and vanadium given in columns 4 and 5, the details of the calculations being given later.

The activities of PO_4^{3-} and VO_4^{3-} thus calculated for each sample at the chosen pH values are given in columns 7 and 8, respectively, the corresponding activities on the other ionic species shown in Equation 7 being omitted.

Results on the determination of solubility products of CPA, CVA and their solid solutions involving microanalytical determination of their constituent ions, known for their mutual interference [8], are vulnerable to errors. In addition, these errors become magnified in the evaluation of solubility products because of the high powers to which the activities of some of the constituting ions are to be raised. Keeping these limitations in view, the activity products of all the possible solute phases likely to control the solubility equilibria of CPA and CVA and their solid solutions such as $CaHPO_4$, $Ca_2HPO_4(OH)_2$, $Ca(H_2PO_4)_2$, $CaHVO_4$, $Ca_2HVO_4(OH)_2$ and $Ca(H_2VO_4)_2$ were calculated in the light of their hydrolytic dissolution. For the sake of brevity the calculated data of phases other than CPA, CVA and their solid solutions are not given in the present communication, because the divergence of the K_{sp} values calculated was much more for them in comparison with those of the above phases. Consequent upon the errors involved, the divergence in K_{sp} of CPA, CVA and their solid solutions is still considerable, although it is found to be lower than the values for the other phases. The pK_{sp} values of the phases are given in column 10 of Table I.

Results of the effect of common ions on the solubility equilibria of CPA and CVA are given in Tables II and III respectively. It was found from these results that the pK_{sp} values (column 9, Tables II and III) of the apatite phase exhibited a constancy proving the response of the solubility of apatites to the common-ion effect. As expected, the mole ratios, Ca/P (column 7, Table II) and Ca/V (column 7, Table III) in these cases were found to diverge from the stoichiometric values in accordance with the principle of solubility product.

4. Discussion

It is evident that the solubility product, K_{sp}, of CPA is equal to the product of the concentrations of the

TABLE III Studies on the effect of common ions on the solubility equilibria of calcium vanadate apatite

Serial no.	Common ion added ($mg\,l^{-1}$)		Final pH	Measured conc. ($10^3\,mol\,l^{-1}$)		Mole ratio: Ca/V	Calculated activity ($10^{13}\,mol\,l^{-1}$)	Solubility product of solute,
	Ca	V		Ca	V		$a_{(VO_4^{3-})}$	pK_{sp}
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
1	10	–	5.70	8.41	2.94	2.85	9.63	107
2	30	–	5.70	10.7	1.76	6.07	5.78	109
3	–	10	5.79	6.42	4.22	1.52	20.90	107
4	–	30	5.79	4.71	5.69	0.83	28.20	108
							Average	108

$K_{sp} = (Ca^{2+})^{10}(VO_4^{3-})^6(OH^-)^2$.

Solute: 0.2 g $Ca_{10}(VO_4)_6(OH)_2$ washed with a 2% solution of EDTA maintained at pH 10 using ammonium chloride and ammonium hydroxide.

Dissolving medium: 200 ml of an appropriate buffer combination of potassium acid phthalate and sodium hydroxide brought to a molarity of 0.165 M with respect to sodium chloride.

Temperature: 37 ± 0.5° C; $pK_w = 13.54$.

dissolved ions raised to appropriate powers, as given by the products $(Ca^{2+})^{10}(PO_4^{3-})^6(OH^-)^2$. While the concentrations of Ca^{2+} and OH^- were available directly from the measurements, that of PO_4^{3-} was calculated as shown below from the overall analytical concentration of PO_4^{3-} represented as P_{total}.

Orthophosphoric acid, being a tribasic acid, dissociates as shown below:

$$H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+ \qquad (1)$$

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

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

It is evident that the H^+ ion in the above equilibria exists as H_3O^+ ion in aqueous media. The total amount of phosphorus present in a solution of CPA, represented as P in the tables, can be subdivided as shown below into (i) the undissociated acid, and (ii) its dissociated ionic species $(H_2PO_4^-)$, (HPO_4^{2-}) and (PO_4^{3-}), making use of the pH of the system and three dissociation constants [17, 18], K_1, K_2 and K_3 of the acid:

$$K_1 = \frac{a_{(H_2PO_4^-)}a_{(H^+)}}{a_{(H_3PO_4)}} = 7.51 \times 10^{-3} \qquad (4)$$

$$K_2 = \frac{a_{(HPO_4^{2-})}a_{(H^+)}}{a_{(H_2PO_4^-)}} = 6.33 \times 10^{-8} \qquad (5)$$

and

$$K_3 = \frac{a_{(PO_4^{3-})}a_{(H^+)}}{a_{(HPO_4^{2-})}} = 4.73 \times 10^{-13} \qquad (6)$$

The activity coefficients of all these ions were considered to be unity in a 0.165 M sodium chloride solution as suggested by La Mer [13]. Thus the total dissolved phosphorus is given by the expression,

$$a_{(P_{total})} = a_{(H_3PO_4)} + a_{(H_2PO_4^-)} + a_{(HPO_4^{2-})} + a_{(PO_4^{3-})} \qquad (7)$$

where the activities are expressed in moles/litre.

From Equations 4 to 6 it can be shown that

$$a_{(H_3PO_4)} = \frac{a_{(P_{total})}a_{(H^+)^3}}{q} \qquad (8)$$

$$a_{(H_2PO_4^-)} = \frac{a_{(P_{total})}K_1\,a_{(H^+)^2}}{q} \qquad (9)$$

$$a_{(HPO_4^{2-})} = \frac{a_{(P_{total})}K_1K_2a_{(H^+)}}{q} \qquad (10)$$

$$a_{(PO_4^{3-})} = \frac{a_{(P_{total})}K_1K_2K_3}{q} \qquad (11)$$

where $q = a_{(H^+)^3} + K_1a_{(H^+)^2} + K_1K_2a_{(H^+)} + K_1K_2K_3$. A similar set of calculations [19] could be done to obtain the activity of the vanadate ion, $a_{(VO_4^{3-})}$, from its ionization constants [9], K_1, K_2 and K_3 taken, respectively, as 3.98×10^{-4}, 1.32×10^{-8} and 1.00×10^{-13}. A combination of these two sets of calculations could be made for the solid solutions.

The pK_{sp} values of the phases given are only a few among a total of about ten determinations made in each case, the individual values being found to differ from the average by about ± 7%. Within these limitations it could be concluded that the samples exhibited stoichiometric dissolution [9, 10, 20–24] contrary to the results reported in the earlier literature [4–6]. This is further substantiated by the proximity of the observed mole ratios, Ca/(P + V), of the systems with the stoichiometric value of 1.67. An additional substantiation of the stoichiometric dissolution of apatites could be provided by the remarkable regularity with which the end-members responded to the common-ion effect.

While the pK_{sp} of a given solute is supposed to be independent of the pH of the dissolving medium at a given temperature, it was found to decrease systematically with an increase in pH in all the solutes reported in this work. Substantiation of such results in the case of apatite systems was provided by Larsen [25, 26]. Based on an established fact that an apatite exists as a colloidal component in its saturated solution, Larsen supposed it to behave like an amphoteric colloid such that in highly acidic media the observed pK_{sp} is lower than expected while in alkaline media the converse is the case. The reason suggested by him was the occurrence of negative and positive adsorption of anions, respectively above and below the isoelectric point which is supposed to be in the vicinity of pH 5. However, further clarification can be provided by subsequent investigation.

A theoretical interpretation of the dependence of solubility of an ionic crystal on anionic replacement is possible through thermodynamic considerations [27]. For an ionic compound, change in the Gibbs energy accompanying dissolution, ΔG_{soln}, is related to K_{sp} as shown below, at a given temperature, T, and can be calculated by the expression

$$\Delta G_{soln} = -RT \ln K_{sp} \qquad (12)$$

using the experimental value of K_{sp}. Alternatively, it can be evaluated by considering dissolution of an ionic compound to consist of (i) breaking down of its crystal architecture, and (ii) the hydration of the constituent ions thus set free, resulting in the expression

$$\Delta G_{soln} = \Sigma \Delta G_{hi} - \Delta G_{lattice} \qquad (13)$$

where $\Sigma\Delta G_{hi}$ is the sum of the Gibbs energy changes of hydration of the constituting ions of the solute, while $\Delta G_{lattice}$ is the Gibbs energy change of formation of the lattice. The terms on the right-hand side of Equation 13 can be calculated [27] for an ionic crystal and can be shown to be dependent on the replacement of a given anion by another of a divergent ionic radius, as is the case with PO_4^{3-} and VO_4^{3-} ions.

It can be concluded that while the overall change in the solubility of an ionic compound depends exclusively on the relative variations in $\Delta G_{hydration}$ and $\Delta G_{lattice}$ terms, as mentioned above, the latter becomes more dominant for sparingly soluble salts such as apatites. This can be justified by the fact that the alterations in hydration energies [28] for the pair of anions involved, i.e. PO_4^{3-} and VO_4^{3-} in the substitution investigated, are of a very small magnitude [29]. That CVA is more soluble than CPA under a given set of experimental conditions could be substantiated by the fact that the lattice energy of CVA is expected to be lower than that of CPA because the covalent radius of VO_4^{3-} (0.122 nm) is greater than that of PO_4^{3-} (0.110 nm). The decomposition temperature from thermogravimetric analysis [9, 30] was of the order of 1000 and 1300° C, respectively, for CVA and CPA. These theoretical considerations are adequate to explain qualitatively the dependence of solubility of ionic crystals on ionic replacement.

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