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Physico-chemical aspects of calcium vanadate apatite

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By appropriate modifications of existing precipitation methods, a sample of calcium vanadate apatite, $Ca_{10}(VO_4)_6(OH)_2$ was prepared at 110° C. It was characterized through X-ray, electron microscopic, infrared and thermoanalytical analyses in addition to chemical analysis. Equilibrating the sample in buffered aqueous media at 37° C, the solubility was measured using microanalytical techniques of Ca^{2+} and VO_4^{3-} present in the saturated solutions after separating the colloidal component of the solute. Duration of equilibration for the attainment of saturation of the solution of the sample was obtained from a study on its dissolution kinetics. The pK_{ip} of calcium vanadate apatite was found to be 107.09. The investigation showed that pK_{ip} was independent of the presence of the common ions.

1. Introduction

The toxicity of elemental vanadium and its salts [1–3] is well known. The mechanism of incorporation of vanadium in the human skeletal system may be supposed to be based on the isomorphous substitution of PO_4^{3-} by VO_4^{3-} in calcium phosphate apatite, $Ca_{10}(PO_4)_6(OH)_2$, (abbreviated as PHA), the principal inorganic constituents of human bones [4] and teeth [5]. A complete replacement of PO_4^{3-} by VO_4^{3-} (covalent radii of 0.110 and 0.122 nm, respectively [6]) leads to the formation of calcium vanadate apatite, $Ca_{10}(VO_4)_6(OH)_2$, (abbreviated as VHA) an isomorph of PHA. The physiology of bone and teeth, governed by calcification and resorption of PHA at the bone/body fluid and teeth/saliva interfaces, is greatly influenced by the formation of VHA which causes a disturbance to it leading to pathological conditions. It is evident that any attempt in the direction of the removal of the toxic ions, VO_4^{3-}, has to be based on a knowledge of the solubility phenomenon of VHA under simulated biological conditions. Since no literature is available to throw light on these aspects, the present investigation is significant in the study on incorporation of vanadium into the human skeletal and dental systems and the possibility of its elimination. Preparation, characterization, solubility of VHA as a function of pH and effect of common ions on solubility are reported in this paper.

2. Experimental details

A sample of VHA was prepared by modification of the existing wet method [7] and based on the following equation

$$10CaSO_4 + 6Na_3VO_4 + $$
$$+ 2NaOH = Ca_{10}(VO_4)_6(OH)_2 + 10Na_2SO_4$$

Stock solution of VO_4^{3-} was prepared by dissolving vanadium pentoxide in sodium hydroxide solution. The solutions of sodium orthovanadate and sodium hydroxide (0.5M) were preserved in polyethylene containers. The amounts of calcium and vanadium present in the solution were determined by gravimetric methods [8, 9]. The methods adopted for the preparation and purification of the samples were the same as those described elsewhere [10, 11]. The precipitated sample was washed with acetone and then air dried. A part of it was heated to about 300° C for about 6 h [12] and cooled in a desiccated atmosphere for use in chemical, X-ray and infrared analyses while the air dried sample was used for electron microscopic and thermogravimetric studies. The density of the sample was determined by a standard method [13] using toluene as a solvent [14]. A convenient weight (0.5 g) of the sample was dissolved in a minimum quantity of 5M nitric acid and the volume was made up to 500 ml in a standard flask. From an aliquot of this solution, calcium [8] and vanadium [9] were determined. The sample was characterized through X-ray, electron microscopic, infrared and thermogravimetric analyses, the experimental details being the same as those described elsewhere [15, 16]. The solubility studies carried out in buffered aqueous media, brought to a molarity of 0.165 with respect to sodium chloride, in the pH range 5.30 to 6.60 were based on the determination of calcium volumetrically [17] and vanadium spectrophotometrically [18] from the standard solution of the sample. While preliminary experiments indicated the suitability of the pH range for such solubility investigation, studies on dissolution kinetics provided the optimum period of equilibration for the formation of a saturated solution of the sample. It was found to be 4 h. In order to be doubly sure about the attainment of saturation, the equilibration period was extended to 12 h, the rest of the experimental details for solubility studies being the same as those described elsewhere [19, 20]. The effect of common ions on pK_{ip} of the sample was also investigated at convenient pH values.

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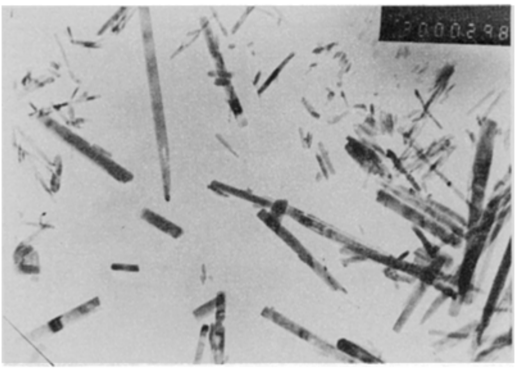

Figure 1 Electron micrograph of calcium vanadate apatite. × 30 000.

3. Results and discussion

3.1. Chemical analysis

Based on the chemical analysis the amount of calcium and vanadium were found to be 35.03 and 26.58 wt %, respectively which amounted to a g atom ratio, Ca/V, equal to 1.67, in agreement with the stoichiometric value of 1.67. A striking agreement between the experimental and the stoichiometric value justifies the purity of the samples and the suitability of the method adopted for preparation as well as for chemical analysis.

3.2. X-ray data

The lattice parameters *a* and *c* of the sample were found to be 0.972 and 0.698 nm, respectively. A comparison of these values with those of PHA ($a = 0.943$ and $c = 0.692$ nm) suggests a dilation of the unit cell as is to be expected by the replacement of PO_4^{3-} by VO_4^{3-} (covalent radii 0.110 and 0.122 nm, respectively). In addition, molar volumes of the sample obtained from both X-ray data as well as from density measurements were found to be 343.00 and 306.09 ml mol^{-1}, respectively suggesting a good agreement. The density of VHA was found to be 3.68 g ml^{-1}.

3.3. Electron microscopic studies

The electron micrograph of the sample shows hexagonal shape [21, 22] crystals characteristic of apatites which substantiates the homogeneity of the sample (Fig. 1). The average dimensions, both length and breadth of the individual crystals, were measured taking into consideration the extent of magnification and were found to be 626.6 and 39.3 nm, respectively.

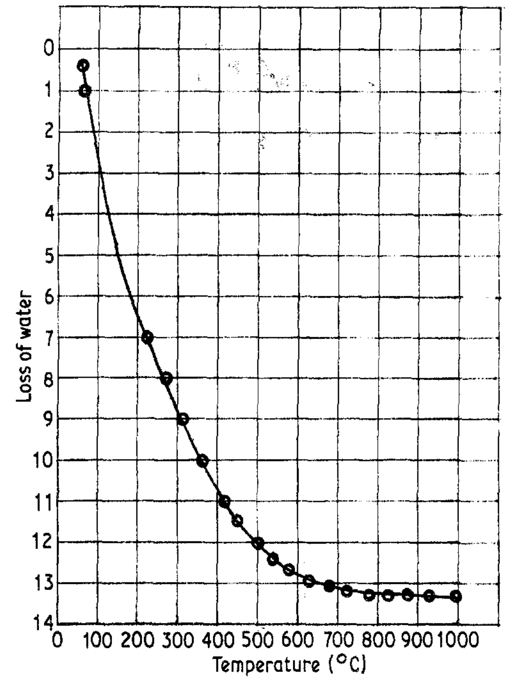

Figure 2 Pyrolysis curve of calcium vanadate apatite.

From the average dimensions of the individual crystals of the sample, the specific surface area of VHA was calculated and its value was found to be 28.50 m^2 g^{-1}.

3.4. Infrared data

The infrared absorption spectra of the sample exhibited characteristic peaks at 830 800 cm^{-1} due to VO_4^{3-}, and 3550 and 3460 cm^{-1} due to OH^-. The last band represents the characteristic of the O–H stretching mode of the hydroxyl ion of the apatites [23]. The persistence of the peak at about 3550 cm^{-1} in spite of sintering at 1000° C confirms the thermal stability of the sample up to this temperature.

3.5. Thermogravimetric analysis

Thermogravimetric analysis of the sample confirmed its thermal stability up to a temperature of about 1000° C. The temperature dependence of the wt % loss curve (Fig. 2) of VHA was found to be free from discontinuities unlike those of the samples containing water of crystallization [24]. It is evident from the foregoing theoretical considerations that the pyrolysis curve, based on the thermogravimetric analysis of the

TABLE IA pH dependence of the solubility equilibria of calcium vanadate apatite (VHA)

Sample number	Final pH	Measured concentration (g atoms l^{-1})		g atom ratio, Ca/V	Calculated concentration (mol or g ions l^{-1})			
		Ca $\times 10^{+3}$	V $\times 10^{+3}$		H_3VO_4	$H_2VO_4^-$ $\times 10^{+5}$	HVO_4^{2-} $\times 10^{+6}$	VO_4^{3-} $\times 10^{+13}$
1	5.33	8.27	5.15	1.60	5.96×10^{-5}	507.90	14.30	3.06
2	5.53	7.88	4.41	1.78	3.23×10^{-5}	436.50	19.49	6.60
3	5.90	7.12	3.92	1.64	1.22×10^{-5}	387.00	40.50	32.20
4	6.60	3.78	2.25	1.68	1.34×10^{-6}	213.00	112.00	448.00

Solute: 0.2 g of $Ca_{10}(VO_4)_6(OH)_2$, 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 (potassium acid phthalate–sodium hydroxide or boric acid–borax) maintained at a molarity of 0.165 with respect to NaCl.

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

Dissociation constants: Acid = H_3VO_4; $K_1 = 3.98 \times 10^{-4}$; $K_2 = 1.32 \times 10^{-8}$; $K_3 = 1.00 \times 10^{-13}$.

TABLE IB Phases expected to be formed

Sample number	$Ca_{10}(VO_4)_6(OH)_2$		$CaHVO_4$		$Ca_2HVO_4(OH)_2$		$Ca(H_2VO_4)_2$	
	K^*_{ip}	pK_{ip}	$K^\dagger_{ip}$	pK_{ip}	$K^\ddagger_{ip}$	pK_{ip}	$K^\S_{ip}$	pK_{ip}
1	4.66×10^{-113}	112.33	1.18×10^{-7}	6.92	3.71×10^{-26}	25.42	2.13×10^{-7}	6.67
2	7.37×10^{-111}	110.13	1.53×10^{-7}	6.81	1.15×10^{-25}	24.93	1.50×10^{-7}	6.82
3	1.96×10^{-106}	105.70	2.88×10^{-7}	6.53	1.07×10^{-24}	23.96	1.06×10^{-7}	6.97
4	5.85×10^{-101}	100.23	4.23×10^{-7}	6.37	1.92×10^{-23}	22.71	1.71×10^{-8}	7.76

$^*K_{ip} = (Ca^{2+})^{10}(VO_4^{3-})^6(OH^-)^2$.
$^\dagger K_{ip} = (Ca^{2+})(HVO_4^{2-})$.
$^\ddagger K_{ip} = (Ca^{2+})^2(HVO_4^{2-})(OH^-)^2$.
$^\S K_{ip} = (Ca^{2+})(H_2VO_4^-)^2$.

sample, confirm convincingly that the water associated with them is a non-essential type.

3.6. Solubility equilibria

The results on the solubility product of the sample at a series pH values are given in Table IA. The phases expected to be formed are given in Table IB. Knowing the total vanadium content of the saturated solution of the sample at different pH values, the concentrations of H_3VO_4, $H_2VO_4^-$, HVO_4^{2-} and VO_4^{3-} were calculated using the values of three dissociation constants of H_3VO_4 and pK_w. The values of the dissociation constants of H_3VO_4 at 25° C were used for calculations since the values at 37° C are not available in literature. It could be found that data on an analogous system, H_3PO_4, exhibited insignificant temperature dependence in the range, 25 to 37° C. For the entire series of concentrations of common ions investigated, the pK_{ip} values of the apatite phase exhibited a reasonable constancy proving the response of the solubility of apatite to the common ion effect reported in Table II. As expected the g atom ratio, Ca/V, in these cases were found to be divergent from the stoichiometric value, confirming the solubility product principle.

It is evident that the pK_{ip} value and the g atom ratio, Ca/V, of VHA, reported in Table I provides unambiguous evidence for the stoichiometric dissolution of the samples the average pK_{ip} value being 107.09. Arguments in favour of such a theoretically favoured stoichiometric dissolution were advanced independently by Clark [25], Moreno *et al.* [26] and Wier *et al.* [27]. The higher solubility of VHA than its phosphorus counterpart, PHA (average pK_{ip} value being 113.80) could be explained on the basis of the concept of lattice and hydration energies [28, 29] of ionic solids consequent upon isomorphous anionic [30] substitutions.

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TABLE II Miscellaneous studies on the solubility equilibria of VHA

Sample number	Common ion added ($mg\,l^{-1}$)		Final pH	Measured concentration (g atoms l^{-1})		g atom ratio, Ca/V	calculated concentration (mol or g ions l^{-1})				Ionic product of solute	
	Ca	V		Ca $\times 10^{+3}$	V $\times 10^{+3}$		H_3VO_4 $\times 10^{+5}$	$H_2VO_4^-$ $\times 10^{+3}$	HVO_4^{2+} $\times 10^{+5}$	VO_4^{3+} $\times 10^{+13}$	K_{ip}	pK_{ip}
1	10	–	5.70	8.41	2.94	2.85	1.46	2.90	1.91	9.63	2.98×10^{108}	107.52
2	30	–	5.70	10.73	1.76	6.07	0.87	1.74	1.17	5.78	1.57×10^{-109}	108.80
3	–	10	5.79	6.42	4.22	1.52	1.69	4.17	3.39	20.90	3.17×10^{-108}	107.50
4	–	30	5.79	4.71	5.69	0.83	2.29	5.62	4.57	28.19	8.66×10^{-109}	108.00

$K_{ip} = (Ca^{2+})^{10}(VO_4^{3-})^6(OH^-)^2$; average $pK_{ip} = 107.95$.

Proof for constancy of pK_{ip} values and response of g atom ratio, Ca/V, to addition of common ions Ca^{2+} and VO_4^{3-}.

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

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

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

Dissociation constants: Acid = H_3VO_4; $K_1 = 3.98 \times 10^{-4}$; $K_2 = 1.32 \times 10^{-8}$; $K_3 = 1.00 \times 10^{-13}$.

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