Physicochemical Studies on Solid Solutions of Calcium Phosphorus Arsenic Hydroxyapatites

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Samples of arsenic hydroxyapatite and its solid solutions with calcium hydroxyapatite are synthesized in aqueous media. The samples are characterized by X-ray, infrared spectra, the assignments of phosphate, arsenate, and hydroxyl bands are recorded. The possibility of anion migration in the apatite lattice is proposed. Presence of water, adsorbed in nature, is indicated in the TGA and DTA analysis of the samples. The solubility product, K_{sp}, of the samples of arsenic hydroxyapatite $Ca_{10}(AsO_4)_6(OH)_2$, and the solid solutions, $Ca_{10}(PO_4)_{6-x}(AsO_4)_x(OH)_2$, ($x$=1 to 5) are determined considering the formation of ion pairs $[CaHAsO_4]^0$, $[CaHPO_4]^0$, $[Ca(H_2AsO_4)]^+$, and $[Ca(H_2PO_4)]^+$ in solution. The instability of the samples in solution is indicated from the experimental $\Delta G^0_{soln.}$ values.

Arsenic has been recognised as a toxic element, which causes poisoning in vivo.[1,2] It is deposited in bones and bony tissues[3,4] due to the possibility of $P^{5+} \rightarrow As^{5+}$ exchange reaction in the calcium hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, CaPHA of bone.[5] When this exchange reaction in calcium hydroxyapatite is complete, it leads to the formation of arsenic hydroxyapatite, $Ca_{10}(AsO_4)_6(OH)_2$, CaAsHA, isomorphous with $Ca_{10}(PO_4)_6(OH)_2$, CaPHA; while incomplete/partial substitution in it, results in the formation of solid solutions of calcium phosphorus arsenic hydroxyapatite, $Ca_{10}(PO_4)_{6-x}(AsO_4)_x(OH)_2$ (where x is the compositional parameters, ranges from 1 to 5). Though arsenic in naturally occurring phosphatic minerals is well-known[6] and formation of CaAsHA by solid state reaction[7] at high temperature and its characterization is well established, similar studies on CaAsHA and its solid solutions with CaPHA are not available. We, therefore, report here the formation of CaAsHA and calcium phosphorus arsenic hydroxyapatite samples, their characterization by X-ray, IR, and electron microscopy. Since the samples are synthesized in aqueous media at 100 °C, they are likely to carry attendent seats of water molecules with them. The nature of water present in the samples and their thermal stabilities are studied by TGA and DTA methods. The solubility of the samples of the solid solutions are investigated in the pH range 4.0 to 8.0 and their solubility products are reported.

Experimental

The chemicals used in the preparations of the samples were either BDH or E. Merck grade and the solutions are prepared in CO_2 free conductivity water. Calcium nitrate diammonium hydrogen phosphate and disodium hydrogen arsenate were used as desired by the stoichiometry for a sample of the general formula, $Ca_{10}(PO_4)_{6-x}(AsO_4)_x(OH)_2$ for an yield of 15 g. The method used for the preparation was reported earlier.[8] The samples after preparation were centrifuged, washed repeatedly with conductivity water until free from the adsorbed ions. Care was taken to exclude the possibility of incorporation of carbonate during preparation. The samples were dried (12 h) at 110 °C to constant weight and analyzed for Ca, P, and As complexometrically.[9] The X-ray diffraction patterns of the samples were recorded by a Debye-Scherrer powder diffraction instrument using Ni filtered Cu $K\alpha$ radiation. The electron microscopic patterns of acetone-washed samples were obtained using Simens Elminskop I by the method of electromagnetic disperson. The IR spectra of the samples, preheated at 800 °C, were recorded on a Perkin Elmer IR grating instrument. The range covered was from 4000—400 cm^{-1}. The thermal analyses of the samples were made on a Derivatograph (Budapest) which recorded simultaneous photographs of TG, DTA, and DTG of the samples. The samples were heated at a rate of 10° min^{-1} upto 1000 °C in a platinum crucible using Al_2O_3 as reference. The activation energy of dehydration of the samples was obtained by using Freeman and Carrol's equation[10] and also from Arrhenius plot obtained from DTA peaks.

The solubility of the samples was investigated at 35 °C under a constant ionic environment[11] of 0.165 $mol\,dm^{-3}$ $NaNO_3$ by the method of equilibration. The different concentrations of As_2O_5 in doubly distilled water, for studies in pH range 4.0 to 6.0 and sodium hydroxide for pH 7.10 and 8.0 were used. Equilibration was done in air tight polyethylene thermostated flask containing 200 mg of the samples of particle size 200 μm in 50 ml of the desired solvent. Attainment of saturation was followed kinetically by analyzing in solution calcium, arsenic, and phosphorus content complexometrically.[9] The system attained saturation within ten hours of equilibration.

Calculations

The calculations used in the studies of the solubility are as follows. From the pH of the medium of equilibration and total calcium, arsenic, and phosphorus content, the concentrations of free ionic species XO_4^{3-}, HXO_4^{2-}, and $H_2XO_4^-$ were calculated using Eqs. 1 to 3 (where X=As or P).

$$[XO_4{}^{3-}]=[X]_{total}\Big/\left[\frac{(H^+)^3}{K_1K_2K_3}+\frac{(H^+)^2}{K_2K_3}+\frac{(H^+)}{K_3 f_{HAsO_4{}^{3-}}}+\frac{1}{f_{XO_4{}^{3-}}}\right] \quad (1)$$

$$[HXO_4{}^{2-}]=[X]_{total}\Big/\left[\frac{(H^+)^2}{K_1K_2}+\frac{(H^+)}{K_2 f_{H_2XO_4{}^-}}+\frac{1}{f_{HXO_4{}^{2-}}}\right] \quad (2)$$

$$[H_2XO_4^{-}]=[X]_{\mathrm{total}}/\left[\frac{(H^{+})}{K_1}+\frac{1}{f_{H_2XO_4^{-}}}\right] \tag{3}$$

Where K_1, K_2, K_3 are the three dissociation constants of orthoarsenic acid;[12,13) $f_{XO_4^{3-}}$, $f_{HXO_2^{2-}}$, $f_{H_2XO_4^{-}}$ are the activity coefficients of XO_4^{3-}, HXO_4^{2-}, and $H_2XO_4^{-}$ respectively. The quantity in the parentheses represented activities. Assuming the activity coefficients unity, approximate ionic strength, μ, was obtained using the equation.

$$\mu=\frac{1}{2}\sum C_iZ_i^2$$

The activity coefficients of the above ionic species of arsenic and phosphorus are obtained by the extended Debye equation.

$$\left(\log f_i=\frac{-A\sqrt{\mu}\;Z_i^2}{1+\sqrt{\mu}}+0.3\mu\right)$$

These were subsequently used and a fresh value of μ was calculated.

Following an iterative procedure, constancy in the value of ionic strength is obtained. The ion activity product, synonymous with the solubility product was calculated using the equation:

$$K_{sp}=[Ca]^{10}[AsO_4^{3-}]^{x}[PO_4^{3-}]^{6-x}\left[\frac{K_W}{(H^{+})}\right]^2 f_2^{10}f_1^{2-}f_{AsO_4^{3-}}^{x}f_{PO_4^{3-}}^{6-x}$$

where f_1 and f_2 stand for activity coefficients of the XO_4 (X=P or As) ions, H^+ and Ca^{2+} ions respectively. The solubility products are redetermined after considering the formation of the ion pairs $Ca(H_2AsO_4)^+$, $(CaHAsO_4)^0$, $Ca(H_2PO_4)^+$, $(CaHPO_4)^0$ in solution. The values of association constants used in the calculations are 8.71×10^{-3}, 0.108×10^{-6} for the arsenate[14,15) and 5.88×10^{2}, 7.49 for phosphate[16) species respectively. The solubility products of the samples after considering the ion pair formation are determined using the equation:

$$K_{sp}=[Ca-T]^{10}Y_2^{\,10}[PO_4^{3-}]_{IP}^{6-x}[AsO_4^{3-}]_{IP}^{x}Y_{PO_4^{3-}}^{6-x}Y_{AsO_4^{3-}}^{x}\left[\frac{K_W}{(H^{+})}\right]^2$$

where T is the total calcium involved in complex formation: $[PO_4]_{IP}$ and $[AsO_4]_{IP}$ refer to the concentration of the respective species after considering the ion pairs; Y_2, $Y_{PO_4^{3-}}$, and $Y_{AsO_4^{3-}}$, are the activity coefficients of Ca^{2+}, PO_4^{3-}, and AsO_4^{3-} species respectively; and (H^+) in the equation refers to the activity of H^+ ion.

The calculations reported here satisfy the following conditions:

(i) Saturation with respect to the samples.

(ii) Congruent dissolution of the samples.

$$\frac{[Ca]}{([As]-[As]_0)+[P]}-\frac{5}{3}=0 \quad \text{for solid solutions, and}$$

$$\frac{[Ca]}{[As]-[As]_0}-\frac{5}{3}=0 \quad \text{for CaAsHA, and}$$

(iii) Electroneutrality, $E\pm=Z_iC_i=0$.

where $[As]_0$ is the molar concentration of initial arsenic in As_2O_5, as is the total arsenic in the medium after equilibration and $E\pm$ is the summation, which includes all the ionic species in the medium.

Results and Discussion

The results of chemical analyses of the samples are given in Table 1. Considering a total of six gram atoms of arsenic and phosphorus in a mole of the sample, chemical formulae are proposed from the analytical data. The [Ca]/[As] and [Ca]/([As]+[P]) gram atom ratio varying is found equal to 1.66±0.01 (Theo. 1.667) indicating the formation of apatite samples.

The X-ray powder diffraction pattern of all samples contained broad and diffused lines due to the colloidal dimensions of the crystals. Consequent upon substitution of a bigger AsO_4^{3-} ion in $Ca_{10}(PO_4)_6(OH)_2$ a dilation of the unit cell with an increase in the lattice parameters *a* and *c* (Table 1) resulted. These values when plotted against composition of the samples (Fig. 1) fell on a straight line (Vegard's law) indicating that

Table 1. Results of Chemical Analysis, Lattice Constant of Samples of Calcium Arsenic Hydroxyapatite and Its Solid Solution with Calcium Phosphorus Hydroxyapatite

Sample No.	Wt% Ca	Wt% P	Wt% As	Molecular formula	[Ca]/([P]+[As])	Lattice constants (Å) *a*	Lattice constants (Å) *c*
I	38.52	15.46	5.83	$Ca_{10}(PO_4)_{5.19}(AsO_4)_{0.81}(OH)_2$	1.66	9.47 (±0.01)	7.00 (±0.10)
II	36.58	11.13	14.14	$Ca_{10}(PO_4)_{3.93}(AsO_4)_{2.06}(OH)_2$	1.66	9.65 (±0.01)	7.14 (±0.05)
III	35.39	8.48	19.20	$Ca_{10}(PO_4)_{3.1}(AsO_4)_{2.9}(OH)_2$	1.66	9.76 (±0.02)	7.24 (±0.01)
IV	34.07	5.53	24.86	$Ca_{10}(PO_4)_{2.1}(AsO_4)_{3.9}(OH)_2$	1.66	9.9 (±0.04)	7.30 (±0.02)
V	32.79	2.69	30.31	$Ca_{10}(PO_4)_{1.06}(AsO_4)_{4.94}(OH)_2$	1.66	10.01 (±0.03)	7.45 (±0.03)
VI	31.26	—	35.00	$Ca_{10}(AsO_4)_6(OH)_2$	1.67	10.16 (±0.02	7.50 (±0.01)

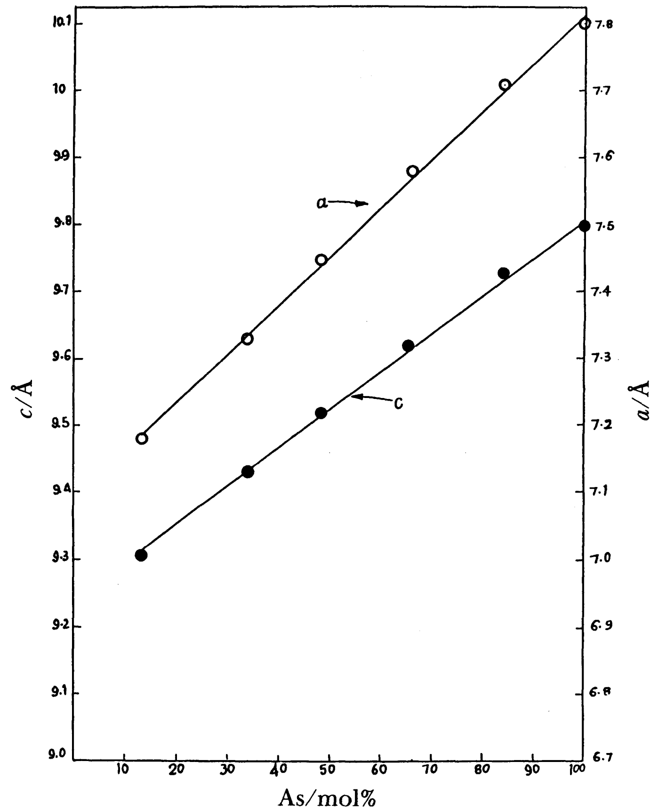

Fig. 1. Dependence of lattice constants a and c on the mole percent arsenic of the samples.

the samples are homogeneous solid solutions.

The electron microscopic patterns of the samples contained distinctly needle shaped crystals characteristic of apatites. The purity of the samples are indicated from the absence of extraneous phases in the microscopic patterns. With increase of AsO_4^{3-} in the samples, the crystals increased in size, the increase along the c-axis, however, is more pronounced than that along the a-axis.

The position in cm^{-1} and the assignments of the IR bands of the samples for $x=1$ to 5 are given in Table 2. The stretching hydroxyl bands appeared in the spectra of all the samples in the region 3560 to 3539 cm^{-1}. These bands are shifted with respect to the hydroxyl absorption in calcium hydroxide. This is indicated of a hydroxyl lattice interaction[17,18] and strongly suggest that the hydroxyl groups are situated within the three dimensional lattice. In fact, no vibrations at frequency about 3600 cm^{-1}, which are characteristics of hydroxyl group on the surface,[9] have been detected in the spectra.

A decrease of $\nu_s(OH)$ with an increase of the proportion of arsenate (AsO_4^{3-}) can be observed in Table 2. In addition, the phosphate vibrations also shifted to lower frequencies. These effects of substitution may be interpreted by considering that the interaction between OH group and the crystal becomes stronger as the arsenate content is increased, besides the effects of binding energies and atomic masses[20] respectively. The nonappreciable variance of the $\nu_t(OH)$ indicates that the relative positions of the OH group with respect to the particular plane varies from one sample to another.

Table 2. Positions (cm^{-1}) and Assignments of the Infrared Spectra of $Ca_{10}(AsO_4)_{6-x}(AsO_4)_x(OH)_2$

$x=$ 1	2	3	4	5	Assingment
3560	3555	3550	3554	3539	$\nu_s(OH)$
533	533	535	537	539	$\nu_t(OH)$
965	960	955	950	948	$\nu_1(PO_4)$
1080	1070	1060	1045	1030	$\nu_3(PO_4)$
1055	1055	1050	—	—	—
1044	1044	1035	—	—	—
465	463	455	450	450	$\nu_2(PO_4)$
605	605	600	600	600	$\nu_4(PO_4)$
575	580	575	567	570	
565	565	565	—	—	—
870	860	865	860	860	$\nu_3(AsO_4)$
855	850	855	850	850	
—	845	841	840	835	
430	430	420	425	420	$\nu_4(AsO_4)$

In the spectra of the samples, the ν_1 (As–O) mode cannot be detected, because the force constant of As–O and P–O are quite similar (k for P–O and As–O are 5.66 N cm^{-1} and 5.67 N cm^{-1} respectively) so that $\nu_1(As\text{–}O)/\nu_1(P\text{–}O)=[\mu_m(P\text{–}O)/\mu_m(As\text{–}O)]^{1/2}$, where μ_m is the reduced mass. In apatites, the ν_1(P–O) appears approximately around 950 cm^{-1}. The ν_1(As–O) appears in the IR region around 850 cm^{-1}, where the intense ν_3 mode of AsO_4 appeared. Therefore, the $\nu_1(As\text{–}O)\approx 850\ cm^{-1}$ is not observed due to the overlapping of ν_3 AsO_4 vibration in all cases.

The ideal symmetry of the tribasic phosphate ion in the free or undistorted state is tetrahedral i.e. it is a member of the T_d point group. In this ideal symmetry condition, absorptions corresponding to ν_3 and ν_4PO_4 mode should be observed. The appearance of ν_1 and ν_2 modes of phosphate in addition to the ν_3 and ν_4 modes in all cases indicate that T_d symmetry of the phosphate has been lowered to Cs site symmetry[21,22] consequent upon the substitution of the arsenate in CaPHA.

In the IR spectra only one $\nu_s(OH)$ at about 3560 cm^{-1} and one $\nu_t(OH)$ at about 533 cm^{-1} appeared for all the samples. This indicates that three equivalent anions are situated in the normal plane to the hydroxyl rotation axis of each hydroxyl group. If this were not true, then more than one $\nu_s(OH)$ and $\nu_t(OH)$ should have resulted. Therefore, in order that this should not happen, the two exchanging anions (PO_4 and AsO_4) belonging to the unit cell of hydroxyapatite are equivalent and exchange their positions through an interplanar anionic migration, so that each anion site in the phosphorus arsenic hydroxyapatite is occupied by an effective anion, whose characteristics are an average of all the anions present in the unit cell.

In the thermographic analyses in all the samples a uniform loss in weight was observed upto 800 °C. TG curves (Fig. 2) have no distinct horizontals indicating nonappearance of a new stable phase during the thermal treatment. The possibility of decomposition appears unlikely since it has already been established that stoichiometric apatites decompose[23,24] at about 1200 °C. The total loss in weight may, therefore, be due to adsorbed water. The dehydration process in all cases is only of the type, a hydrate + water vapors is a two component system, where the dissociation pressure is a continuous uniform loss of water on dehydration. In each case an endothermic peak between 170—200 °C was detected. The IR peak at 1620 cm^{-1} in all the unheated samples disappeared after thermal treatment, which confirmed the presence of adsorbed water with the sample.[25] The activation energy of over all dehydration process from the TG

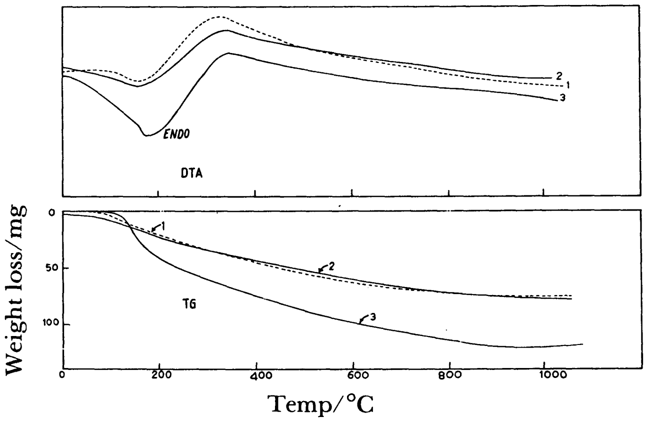

Fig. 2. Thermograms (TGA, DTA) of sample Nos. I, IV, and VI of Table 1.

Table 3. Activation Energies of Arsentic Hydroxyapatite(VI) and Solid Solutions of Calcium Phosphorus Arsenic Hydroxyapatites (Samples I and IV) by Freeman and Carrol's Equation and DTA

Sample No. as in Table 1.	Activation energy	
	Freeman and Carrol	DTA
	kJ mol^{-1}	kJ mol^{-1}
I	67.02	49.37
IV	59.20	48.53
$VI_{(CaAsHA)}$	70.83	72.80

Table 4. Solubility of $Ca_{10}(AsO_4)_6(OH)_2$ and Its Solid Solutions, $Ca_{10}(PO_4)_{6-x}(AsO_4)_x(OH)_2$ at 35 °C in the pH Range 4.0—8.0

Expt. No.	Sample	As_0 (M×10^3 in As_2O_5 soln.)	pH	C_{Ca}×10^3 mol dm^{-3}	C_{As}×10^3 mol dm^{-3}	C_P×10^3 mol dm^{-3}
1	I	0.36	4.0	0.94	0.076	0.47
2		0.11	5.0	0.90	0.07	0.47
3		0.01	6.0	0.86	0.07	0.44
4		—	7.1	0.82	0.065	0.425
5		—	8.0	0.79	0.064	0.414
6	II	0.36	4.0	1.100	0.23	0.45
7		0.11	5.0	1.0	0.21	0.392
8		0.01	6.0	0.98	0.206	0.384
9		—	7.1	0.96	0.202	0.376
10		—	8.0	0.94	0.198	0.368
11	III	0.36	4.0	1.30	0.38	0.40
12		0.11	5.0	1.20	0.37	0.35
13		0.01	6.0	1.10	0.34	0.33
14		—	7.1	1.0	0.30	0.30
15		—	8.0	0.99	0.30	0.30
16	IV	0.36	4.0	1.40	0.48	0.36
17		0.11	5.0	1.24	0.42	0.32
18		0.01	6.0	1.12	0.40	0.27
19		—	7.1	1.02	0.37	0.25
20		—	8.0	1.01	0.36	0.25
21	V	0.36	4.0	1.52	0.71	0.21
22		0.11	5.0	1.26	0.62	0.14
23		0.01	6.0	1.13	0.57	0.11
24		—	7.1	1.06	0.54	0.10
25		—	8.0	1.01	0.50	0.10
26	VI	0.36	4.0	1.70	1.024	—
27		0.11	5.0	1.28	0.88	—
28		0.01	6.0	1.14	0.698	—
29		—	7.1	1.08	0.64	—
30		—	8.0	1.02	0.61	—

Table 5. Electroneutrality $E_\pm$ Solubility Product (K'_{sp} and K_{sp}) and Free Energy (ΔG°_{soln}) Calculated from Table 4

Expt. No.	Sample	pH	$E_\pm$	K'_{sp} (without ion pair)	K_{sp} (ionpair)	ΔG°_{soln} kJ mol^{-1}deg^{-1} ($-RT \ln K_{sp}$)
1	I	4.0	0.012	6.85×10^{-107}	5.84×10^{-107}	626.38
2		5.0	0.009	6.69×10^{-107}	5.73×10^{-107}	626.43
3		6.0	0.008	6.58×10^{-107}	5.89×10^{-107}	626.36
4		7.1	0.008	5.79×10^{-107}	5.00×10^{-107}	626.78
5		8.0	0.008	4.52×10^{-107}	3.80×10^{-107}	627.47
6	II	4.0	0.010	6.01×10^{-103}	5.57×10^{-103}	602.92
7		5.0	0.010	6.01×10^{-103}	4.99×10^{-103}	603.20
8		6.0	0.010	5.37×10^{-103}	4.56×10^{-103}	603.44
9		7.1	0.009	4.82×10^{-103}	4.04×10^{-103}	603.74
10		8.0	0.009	4.20×10^{-103}	3.60×10^{-103}	604.04
11	III	4.0	0.013	2.92×10^{-100}	2.24×10^{-100}	587.56
12		5.0	0.012	2.75×10^{-100}	2.34×10^{-100}	587.45
13		6.0	0.011	2.51×10^{-100}	2.12×10^{-100}	587.70
14		7.1	0.010	2.54×10^{-100}	2.09×10^{-100}	587.74
15		8.0	0.010	2.54×10^{-100}	2.09×10^{-100}	587.74
16	IV	4.0	0.014	9.79×10^{-98}	8.50×10^{-98}	572.35
17		5.0	0.013	8.94×10^{-98}	8.41×10^{-98}	572.38
18		6.0	0.011	9.06×10^{-98}	8.20×10^{-98}	572.45
19		7.1	0.011	8.68×10^{-98}	7.60×10^{-98}	572.64
20		8.0	0.010	8.59×10^{-98}	8.15×10^{-98}	572.46
21	V	4.0	0.015	6.34×10^{-94}	6.10×10^{-94}	549.62
22		5.0	0.013	7.08×10^{-94}	6.00×10^{-94}	549.66
23		6.0	0.012	6.83×10^{-94}	6.28×10^{-94}	549.54
24		7.1	0.010	5.66×10^{-94}	5.43×10^{-94}	549.92
25		8.0	0.010	5.80×10^{-94}	5.40×10^{-94}	549.93
26	VI	4.0	0.014	3.61×10^{-91}	3.57×10^{-91}	533.30
27		5.0	0.013	3.85×10^{-91}	3.79×10^{-91}	533.15
28		6.0	0.011	3.88×10^{-91}	3.80×10^{-91}	533.14
29		7.1	0.011	5.01×10^{-91}	4.97×10^{-91}	533.45
30		8.0	0.010	5.56×10^{-91}	3.52×10^{-91}	533.34

curves and DTA curves are given in Table 3. The nonuniformity in the values obtained by both the methods is due to difficulty in fixing the base line in DTA curve.

The results of solubility of the samples obtained at a series of pH are summarized in Tables 4 and 5 together with the calculated quantities $E_\pm$, K'_{sp}, and ΔG^0. Table 5 shows that $E_\pm$ is within the anticipated experimental error, indicating no gross error in the analytical figures, calculations, and model used. It is seen from Table 4 that the samples exhibited a stoichiometric dissolution,25—28) represented by the reaction:

$$Ca_{10}(PO_4)_{6-x}(AsO_4)_x(OH)_2 \rightarrow 10Ca^{2+} + (6\text{-}x)PO_4^{3-} + xAsO_4^{3-} + 2\ OH^-$$

(where x=1—6). The saturation condition is evidenced by the smooth curves obtained in the plots of calcium concentration, versus pH (Fig. 3) for all samples and a reasonable constancy in K_{sp} for the solid solutions. The solubility product (K'_{sp}) without considering the presence of ionpairs and (K_{sp}) after considering ion pairs are given in Table 5. From the K_{sp} values of each solid solution over the entire pH range, the free energy of the solution ΔG°_{soln} have been calculated and are given in Table 5. The investigations indicate that the solubility of solid solutions decreased with increase of OH^- concentration of the medium of dissolution. This observation is understandable from the considerations of alteration in chemical potential8) of $Ca(OH)_2$, H_3AsO_4, and H_3PO_4 with increase of pH. The solution with increase in OH^- concentration becomes supersaturated and decrease in solubility is therefore resulted.

From the K_{sp} values of the sample given in Table 5 it can be concluded that the solubility of the samples increased with increase in proportion of arsenate. At the first instance, this could reasonably be due to the higher dissociation constant of H_3AsO_4 than H_3PO_4 at a given temperature. This, however, can be substantiated from the possible alteration of lattice energy of the solid solutions consequent upon the replacement of bigger arsenate (1.18 Å) ion in place of phosphate

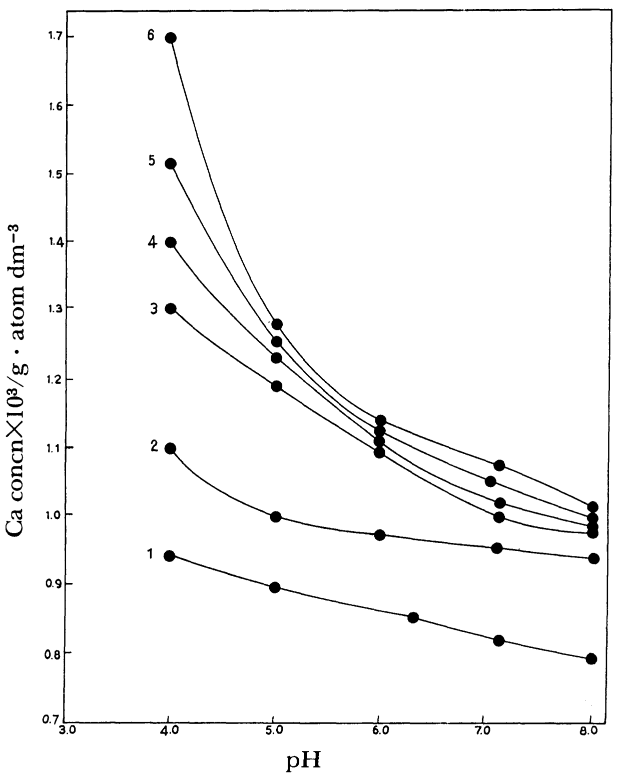

Fig. 3. Solubility equilibria of samples of calcium arsenic phosphorus hydroxyapatite in the pH range 3.0 to 8.0.
(1) Sample No. I, (2) Sample No. II, (3) Sample No. III, (4) Sample No. IV, (5) Sample No. V, (6) Sample No. VI. Sample Nos. indicate the numbers of Table 1.

(1.10 Å) ion in calcium hydroxyapatite. Thus, the loose packing crystalline structure of the solid solution with decreased lattice energy supports the observed increasing solubility trend of the solid solutions with higher proportion of arsenate ions. The decreasing stabilities of the solid solutions is also evidenced from the experimental $\Delta G^{\circ}_{\text{soln}}$ values.

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