STUDIES ON SOME PHYSICO-CHEMICAL ASPECTS OF SOLID SOLUTIONS OF PHOSPHATE AND ARSENATE APATITES OF STRONTIUM

SYNOPSIS

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Calcium hydroxylapatite, $Ca_{10}(PO_4)_6(OH)_2$, the principal inorganic constituent of human bones and teeth, belongs to an isomorphous series of substances known as apatites. It has been the subject of extensive investigations because of its biological significance and its remarkable ability to undergo a series of cationic and anionic exchange reactions, the criteria for such an exchange being the identity of charge and the proximity of ionic radii of the pairs of ions involved. Among such diverse exchange reactions a few have attained significance during the recent past consequent upon the toxicity of the elements involved, such an exchange being the mechanism of their incorporation into human skeletal system

Based on the contemporary importance given to the toxicity to the human system by arsenic and β-active Sr-90, a product of atomic explosions, studies on the replacement of calcium by strontium (ionic radii 0.99 and 1.13Å respectively) and of phosphate by arsenate covalent radii (1.10 and 1.18Å respectively) have been chosen for the present investigations. Among heteroionic cationic substitutions on calcium hydroxylapatite replacement of Ca^{2+} by Sr^{2+} is significant since it explains the mechanism of incorporation in the human skeletal system of β-active Sr-90. Such an incorporation even in trace amounts, can be fatal because of the long half-life period of Sr-90 (28.5 years). It is evident that a complete replacement of Ca^{2+} ions by Sr^{2+} ions leads to the formation of strontium phosphate apatite, $Sr_{10}(PO_4)_6(OH)_2$, while that of PO_4^{3-} by AsO_4^{3-} on strontium phosphate apatite leads to strontium arsenate apatite $Sr_{10}(AsO_4)_6(OH)_2$, both being iosmorphs of calcium hydroxylapatite. A partial replacement in either case leads to formation of solid solutions of the concerned end-members.

The toxicity of elemental arsenic and its salts is well known. There is prevalence of arsenic poisoning among workers employed in the manufacture of insecticides, paints and dyes containing the element. Inhalation of arsenic through nose and mouth and exposure of the skin to it are supposed to be responsible for the ailment. In spite of the fact that arsenic is distributed primarily throughout the soft tissues in living organisms its incorporation in the human skeletal system through $PO_4^{3-} \rightleftharpoons AsO_4^{3-}$ exchange on calcium hydroxylapatite of bone is probable.

It could be unambiguously established that ions incorporated in the human skeletal system through exchange reactions on calcium hydroxylapatite of bones play a significant role in two principal bone processes, namely, calcification and resorption, the deposition and dissolution respectively of calcium hydroxylapatite at the interface of bone and body fluids. Consequently, any attempt in the direction of elimination or minimization of such a toxicity is associated with a study of the solubility of calcium hydroxylapatite as well as of the products of the exchange reactions mentioned above under simulated biological conditions.

Prompted by such a consideration the present work which deals with the preparation, characterization and solubility equilibria of strontium phosphate apatite, strontium arsenate apatite and a series of six of their solid solutions spread over the entire compositional range, was undertaken. Adopting co-precipitation of the end-members in aqueous media through a judicious modification of the existing methods, the samples were prepared at 37°C to simulate biological conditions.

Characterization of these samples was brought about through sophisticated instrumental techniques such as x-ray diffraction, electronmicroscopy, i.r. and Laser Raman Spectral studies in addition to the conventional chemical analyses. Vegard's law demands that the unit cell volume of a homogeneous series of solid solutions varies linearly with the composition and offers a convenient method of scrutinizing their homogeneity. As is to be expected from the bigger size of the arsenate ion, a replacement of phosphate by it brings about a dilation of the unit cell. A systematic linear dependence of the unit cell volumes with the proportion of arsenate ion replacing phosphate ion ,observed in the present series of solid solutions,confirmed their homogeneity. The electronmicrographs of a few representative samples revealed the hexagonal pattern of the crystals confirming the absence of extraneous phases and enabling approximate calculation of the specific surface areas from the measured average dimensions of the individual crystals.

The i.r. and Laser Raman spectra could confirm the identity of the samples. The predominant absorption peaks recorded in the traces of the samples were found to be due to the PO_4^{3-}, AsO_4^{3-} and OH^- ions.

Studies on the solubility of the samples were undertaken at 37°C in order to investigate its dependence on the replacement of PO_4^{3-} ion by AsO_4^{3-} ion on strontium phosphate apatite. Since it was intended to determine the solubility product of each sample from data resulting from the chemical analyses of the saturated solutions a buffered dissolving medium was used to maintain constancy of the activity of OH^- ions involved in such calculations. In order to investigate the reproducibility of the solubility product so determined, the studies in each case were extended to a few chosen pH values, the range being restricted to the limits, 5.5 and 8.0. In addition all such buffered dissolving media were maintained at a molarity of 0.165 with respect to sodium chloride to simulate biological conditions. By adopting such a medium of dissolution the complicated process of evaluating accurately the activity coefficients of polyvalent ions could be avoided by assuming all of them to be unity without foregoing accuracy. It is evident that such calculations make the solubility product, Ksp, and the ionic product, Kip, synanymous.

Each one of the powdered samples was equilibrated with the chosen buffer combination as the medium of dissolution at a controlled rate of shaking using a constant temperature shakerbath. The colloidal component of the solute present in its saturated solution due to its low solubility was separated by filtration at 37°C through a $1G_4$ sintered glass crucible before the solutions were analyzed for the products of dissolution. A separate experiment could prove the suitability of such crucibles for colloidal separation.

While phosphorus and arsenic were determined spectrophotometrically, atomic absorption spectroscopy was adopted for the determination of strontium, the attainable accuracy in all the cases being scrutinized by analyses of solutions of known compositions.

A scrutiny of attainment of saturation and the minimum period of equilibration required for the purpose were determined through dissolution kinetics of a couple of representative samples. From among the concentrations of the products of dissolution, the measured total dissolved phosphorus was subdivided into the proportions of orthophosphoric-acid and its three dissociation products, $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-}. Using the three dissociation constants of the acid and the equilibrium pH of the system, the latter being required also for evaluating OH^- ion concentration needed for the calculation of solubility product. Similar calculations were done with orthoarsenic acid in the case of systems having arsenate -

containing samples as solutes.

There exists an ambiguity in the earlier literature regarding the solute phase likely to control the solubility of apatite systems since the dissolution involved is hydrolytic. That the apatites exhibit stoichiometric dissolution could not be unambiguously established by the earlier workers. In order to investigate this significant aspect of dissolution of apatites, the solubility data of the present investigations were subjected to calculations to establish which among the possible phases exhibited a constancy for the activity product of its ions. It is evident that for the phosphate containing apatites such phases are the primary and secondary phosphates of the metal concerned in addition to the apatite phase. By analogy with a double salt, $Ca_2(HPO_4)(OH)_2$, a phase reported to control the solubility product of calcium hydroxyl apatite by functioning as a surface coating, the ionic product of its strontium counterpart, $Sr_2(HPO_4)(OH)_2$, was also calculated for the present systems. Examination of the data on solubility of all the phases mentioned above reveals that the ionic product of apatite showed a constancy over the entire pH range investigated and the calculated set of values were found to lie within the error limits. It is evident that the corresponding arsenate phases are relevant for strontium arsenateapatite while the phases of both phosphate and arsenate are to be considered for the systems involving the solid solutions. Such calculations were done on the data of solubility of all these samples. That the apatite phase controlled the solubility was further supplemented by the fact that the g atom ratio, Sr/(P+As), of the saturated solutions of all the samples was in the proximity of the theoretical value (1.67) confirming unambiguously the occurrence of stoichiometric dissolution of apatites.

It could be established further that the solubility product of each sample of the series while remaining constant at all the pH values investigated, decreased systematically with an increase in the extent of replacement of PO_4^{3-} by AsO_4^{3-}. An interpretation of these results could be provided by the concept of alterations in lattice and hydration energies of ionic crystals consequent upon isomorphous substitution.