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pH Dependence of Solubilities of (Ca + Ba + Mg) Hydroxylapatites

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The solubilities of solid solutions of calcium-barium-magnesium hydroxylapatites determined in the pH range 5.0–8.0 decrease with increase in pH of the dissolving medium. This is due to the dissolved phosphate ions function as proton-acceptors and being salts of weak acid undergoes hydrolyses in aqueous media and at a given pH also the solubility of the samples decrease with increase of mole content of barium and magnesium in CaHA.

INTRODUCTION

Calcium hydroxylapatite (CaHA), $Ca_{10}(PO_4)_6(OH)_2$, the principal inorganic constituent of human bones and teeth[1,2] belongs to an isomorphous series of compounds known as apatites. It forms solid solutions with its isomorph, barium hydroxylapatite (BaHA) and magnesium hydroxylapatite (MgHA). The $Ca^{2+} \rightarrow Ba^{2+}$ and/or Mg^{2+} replacement in CaHA is of extreme biological significance as it explains the mechanism of incorporation of barium and magnesium into human skeletal system according to the following equation :

$$Ca_{10}(PO_4)_6(OH)_2 + nBa^{2+} + mMg^{2+} \rightarrow Ca_{10-(n+m)}Ba_nMg_m(PO_4)_6(OH)_2 + {}_{(n+m)}\,Ca^{2+}$$

The present communication deals with investigations on the dependence of the solubilities of CaHA, BaHA and MgHA, and a series of their solid solutions on pH in the physiologically important range of 5.0–8.0 and the solubility effect with increase of Ba^{2+} and Mg^{2+} content in the solid solutions at fixed pH value.

EXPERIMENTAL

The details of preparation and identification of CaHA, BaHA, MgHA and a series of their solid solutions were reported earlier[3–5]. The solubility studies were based exclusively on the microanalytical determination of phosphate[6,7] in the solutions of the samples, the experimental weight per cent error of the determination being ± 0.125. Glass containers were found to be unsuitable for housing the systems due to interference by the dissolution of their ingredients. Potassium acid phthalate-sodium hydroxide and sodium diethylbarbiturate-hydrochloric acid were used as buffer combination of the medium of equilibration. The pH was measured with a line-operated. Beckman zeromatic pH meter before and after equilibration to ascertain its constancy. The buffer solutions were prepared in 0.165 M solution of sodium chloride to maintain the activity coefficients of the dissolving species of apatites effectively constant. The apatites get colloidally dispersed in their aqueous solutions due to their low solubilities and minute particle size. To test for efficient separation of the colloidal component, the suspensions of a series of saturated system of CaHA were filtered through a IG_4 sintered glass crucible (particle size retention, 5–10μ) and phosphorus contents of the filtrates compared with those of the corresponding filtrates obtained through a millipore filter (pore size, *ca* 10 mμ) fitted to a filter-holder attached to a hypodermic syringe. The phosphorus contents of the two filtrates were within limits of experimental error ($\pm$ 0.25 wt%). Extraneous ions dissolved due to the momentary contact of the colloidal suspensions with the glass crucibles were found to be too low to affect the accuracy of the subsequent analyses. Each system shaken mechanically at a regulated speed was set up by adding 0.2 g of 200 mesh (BSS) solute to 100 ml of the buffer solution prepared in CO_2-free water. The systems were housed in air-tight polyethylene containers to exclude the presence of carbon dioxide to avoid thereby alteration in the pH of the dissolving medium and to prevent the formation of carbonate-apatite. The assembly was kept in a thermally insulated cabin maintained at 37 ± 0.5°C to simulate biological conditions. The period of equilibration required for the attainment of saturation was determined through dissolution kinetics as described earlier[8] and maintained at 3 hrs for all the systems. A few ml each of chloroform and toluene were added to the stock solutions as well as to the systems to eliminate bacterial growth. The systems were separately filtered through IG_4 crucible and the phosphate content in the filtrate was determined complexometrically[6].

RESULTS AND DISCUSSION

Based on the fact that a mole of each sample has a total of 10 g atoms of calcium and/or barium and/or magnesium the molecular formulae of the samples were calculated. The g atom ratio, $\left(\frac{Ca + Ba + Mg}{P}\right)$ in a mole of each sample were calculated from the results of the chemical analyses and found to be 1.665 (theoretical 1.666). The effect of incorporation of barium and/or magnesium on the solubility of the bone mineral is represented in Fig. 1. The dependence of solubility on (i) the pH of the medium of equilibration in the physiologically important range of 5.0 to 8.0 and (ii) the barium and/or magnesium content in the sample at a given pH was investigated. The dissolution of CaHA can be considered to be initiated by the hydrolysis of PO_4^{3-} of the hydroxylapatite lattice which

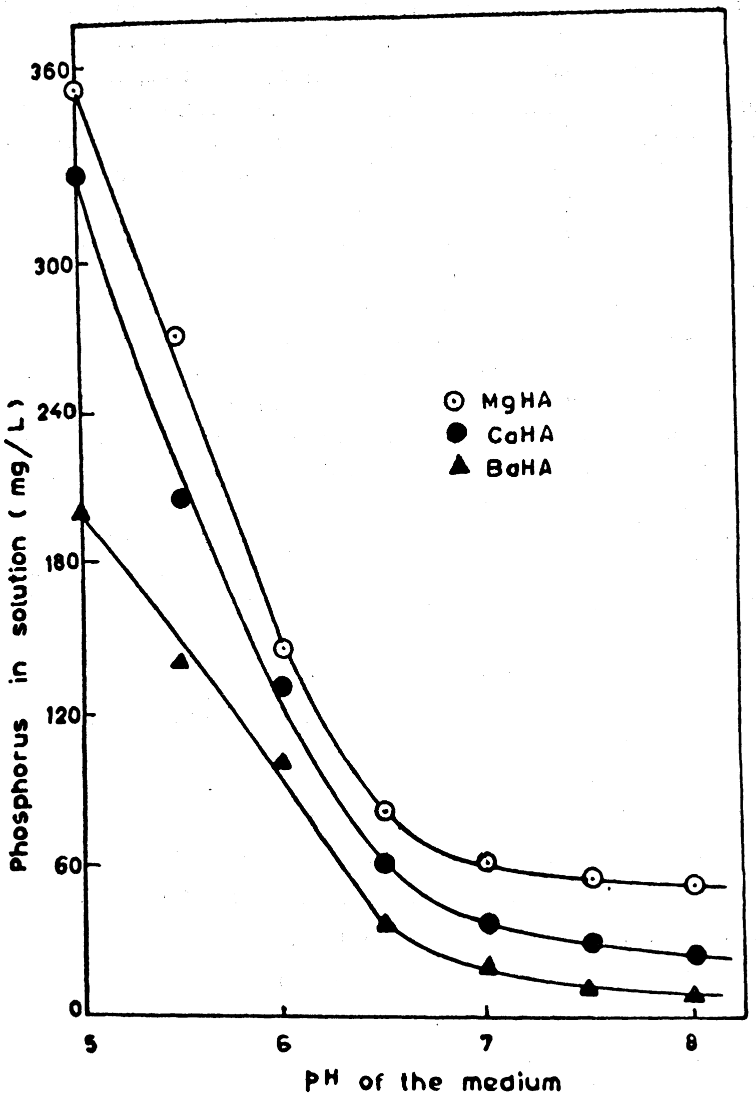

Fig. 1. Dependence of solubilities of solid solutions of (Ca + Ba + Mg) hydroxylapatites on the pH of the dissolving medium.

leads to the formation of $Ca_3(PO_4)_2$ and $Ca(OH)_2$ according to the following equations.

$$PO_4^{3-} + H_2O \rightarrow HPO_4^{2-} + OH^-$$
$$Ca_{10}(PO_4)_6(OH)_2 \rightarrow 3Ca_3(PO_4)_2 + Ca(OH)_2$$
$$Ca_3(PO_4)_2 + 2H_2O \rightarrow 3Ca^{2+}aq + 2HPO_4^{2-} + 2OH^- \text{ aq}$$
$$Ca(OH)_2 + H_2O \rightarrow Ca^{2+}aq. + 2OH^- \text{ aq.}$$

Exactly analogous equations can be proposed for the barium and magnesium species. So (Ca + Ba + Mg) HA basically undergo the same mode dissolution leading to the formation of corresponding tribasic phosphate and hydroxide, the solubility being given by the solubility product latter. It was observed that (i) the solubility of a given sample decreases with increasing pH of the dissolving medium (Fig. 1), which is due to the protonation of PO_4^{3-} in the dissolving medium[9] and (ii) at a given pH the solubility decreases with the barium and magnesium content in the solid solution.

This observation can be explained on the basis of (i) common ion effect applied to the solubility products of the solid solutions according to Milhofer[10] and (ii) due to formation of semi-covalent bonds on introduction of Ba^{2+} and Mg^{2+} in calcium hydroxylapatite[11].

The samples being salts of a weak acid undergo hydrolyses in aqueous media. The dissolved phosphate ions function as proton acceptors accounting thereby for the observed pH-dependence of the solubilities of the samples. The solubility at a given pH for the solid solutions decreases with increase in mole % of Ba^{2+} and Mg^{2+} in CaHA. This explains the role of incorporation of Ba^{2+} + Mg^{2+} in the solubility of the bone mineral.

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