Solubilization of hydroxyapatite at neutral pH by an anionic ionic exchange resin

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Sucrose, induced dental plaque has been shown to contain high amounts of lipoteichoic acids, a bacterial anionic polymer with chemical properties similar to ionic exchange resins. The present study describes an in vitro experiment where a commercial resin Amberlite IR 120 was shown to dissolve hydroxyapatite at neutral pH.
The resin binds calcium and the dissociation of the hydroxyapatite

$$Ca_5(PO_4)_3OH \rightarrow 5Ca^{++} + 3\ PO_4^{-3} + OH^-$$

is driven to the right as long as the resin takes up calcium. The dissociation of the hydroxyapatite was monitored by electrical conductivity and pH of the aqueous phase. It is suggested that this mechanism may be of some significance *in vivo*.

Key-words: Dental caries, chelation; preventive dentistry

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The concept of chelation as a possible mechanism in dissolution of mineralized tissues in dental caries is well established (3), and several in vitro experiments have in fact demonstrated that amino acids and lactic acid, at neutral pH, can remove calcium from enamel (4, 5, 6, 9, 10).

Recent research has shown that an other potential chelating agent, lipoteichoic acid, is present in relatively high amounts in sucrose plaque (8). Lipoteichoic acids are extracellular bacterial products which are thought to form complexes with the glucan molecules present in the intermicrobial matrix (8). They are polymers of glycerol and ester-bound phosphate, are strongly negatively charged at all physiological pH levels, and have high affinity for cations, (1). This activity is presumably based on charge (7).

The aim of the present study was to demonstrate that hydroxyapatite can be solubilized in the presence of an anionic commercial ionic exchange resin which has chemical properties similar to lipoteichoic acids.

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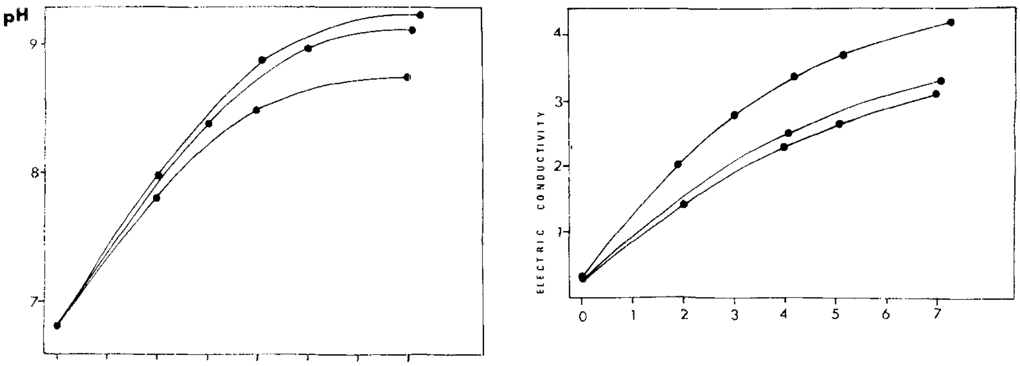

Fig. 1. Solubilization of hydroxyapatite in presence of an anionic ionic exchange resin (Amberlite I.R. 120). The disintegration of the mineral was monitored by release of OH^- ions (top), and by ions in the aqueous phase giving increased electric conductivity (bottom).
Conductivity is expressed as $\varkappa_{20} \cdot 10^4$ ohm^{-1} cm^{-1} and the abscissa is expressed in hours after start of the experiment.

MATERIAL AND METHODS

Different amounts of sodium saturated Amberlite IR 120 resin (10, 5 and 3 meq.) in 20 ml of distilled water were shaken overnight, and 50 mg of hydroxyapatite (Bio-Gel HTP, Bio-rad Laboratory, Richmond, California) was then added. The shaking continued, and electrical conductivity and pH were monitored to measure the solubilization of the hydroxyapatite. Hydroxyapatite with Ca/P ratio of 1.63 and surface area of 36 m^2 (a gift from Dr. G. Ingram) was also tested in the same system.

RESULTS

Both pH and conductivity increased rapidly as seen in Fig. 1. pH increased from 6.8 to 7.8 and 8.0 respectively in the experiments where 3 meq. and 5 or 10 meq. of Amberlite was added, and conductivity showed a similar pattern. Apatite samples with different Ca/P ratios and surface areas gave similar results.

DISCUSSION

The results can be interpreted as follows:

The first step in the dissociation of hydroxyapatite is presumably

$$\text{(I)}\ Ca_5(PO_4)_3OH \rightarrow 5Ca^{2+} + 3PO_4^{-3} + OH^-$$

(the charge of the phosphate ion dependent on pH).

After addition of the suspension of sodium saturated Amberlite resin the dissociated calcium ion will displace the sodium bound to the resin, because divalent cations in general have a higher affinity for the anionic resin, and sodium will be released into the aqueous phase. Reactions (I) as described above will be driven to the right with increased release of ions as a result. Sodium, phosphate and hydroxyl ions will increase in the solution whereas the released calcium will be taken up by the resin material as described. Increased concentrations of sodium and phosphate will give increased conductivity whereas OH^- will cause a rise in pH. This process will continue until all the available sites on the resin are saturated with calcium.

Processes of this kind are known to

proceed much faster if a direct contact between the mineral and the ionic exchange resin can be achieved. In this case ions are thought to be transferred directly from the mineral to the resin without entering the aqueous phase (2).

Whether such processes take place in dental plaque or not is not known, but it seem possible. However, the presence of adsorbed proteins on the enamel and of structural proteins in the enamel together with the relatively small available surface area of the teeth may limit its importance *in vivo.*

It seems, however, clear that ionic exchange resins with chemical properties similar to anionic polymers present in sucrose plaque can dissolve hydroxyapatite rapidly *in vitro at neūtral pH.*

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