What Is the Critical pH and Why Does a Tooth Dissolve in Acid?

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Abstract

This paper discusses the concept of critical pH for dissolution of enamel in oral fluids. The critical pH does not have a fixed value but rather is inversely proportional to the calcium and phosphate concentrations in the solution. The paper also discusses why teeth dissolve in acid, why remineralization of white-spot caries lesions is possible and why remineralization of teeth eroded by acid is not possible.

MeSH Key Words: *dental enamel solubility; hydrogen-ion concentration; tooth remineralization*

A recent article in this journal[1] referred frequently to the critical pH of dental enamel as 5.5, as though this were a fixed value, independent of the composition of the solution to which enamel is exposed. In fact, the critical pH varies over a wide range, its value depending on the concentrations of calcium and phosphate in the solution.
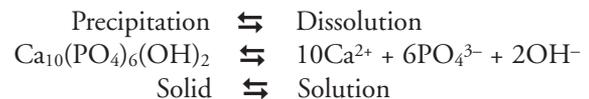
The critical pH is the pH at which a solution is just saturated with respect to a particular mineral, such as tooth enamel. If the pH of the solution is above the critical pH, then the solution is supersaturated with respect to the mineral, and more mineral will tend to precipitate out. Conversely, if the pH of the solution is less than the critical pH, the solution is unsaturated, and the mineral will tend to dissolve until the solution becomes saturated.

The concept of critical pH is applicable only to solutions that are in contact with a particular mineral, such as enamel. Saliva and plaque fluid, for instance, are normally supersaturated with respect to tooth enamel because the pH is higher than the critical pH, so our teeth do not dissolve in our saliva or under plaque. However, these fluids cannot be supersaturated with respect to individual ions, such as calcium or phosphate, as some authors state.[1]

Dental enamel is composed primarily of hydroxyapatite (HA), $Ca_{10}(PO_4)_6(OH)_2$, but it also contains several impurities such as carbonate and fluoride. Because the proportions of these impurities vary from person to person, and indeed from tooth to tooth, and because the impurities can influence enamel solubility, that solubility is not fixed

and varies slightly from person to person. Nevertheless, the factors that influence the solubility of enamel's primary component, HA, also influence the solubility of enamel.

When HA is in contact with water, the following reaction occurs:

$$\begin{array}{ccc} \text{Precipitation} & \rightleftarrows & \text{Dissolution} \\ Ca_{10}(PO_4)_6(OH)_2 & \rightleftarrows & 10Ca^{2+} + 6PO_4^{3-} + 2OH^- \\ \text{Solid} & \rightleftarrows & \text{Solution} \end{array}$$

A small amount of HA dissolves, releasing calcium, phosphate and hydroxyl ions. This process continues until the water is saturated with respect to HA. At that point, the rate of the forward reaction (mineral dissolution) is equal to the rate of the backward reaction (mineral precipitation).

The solubility of a substance such as HA, which can split into separate ions, is characterized by its solubility product, or Ksp, the product of the concentrations (mol/L) of the component ions, raised to the appropriate power, in a saturated solution. Thus, for a solution saturated with respect to HA, the Ksp is $[Ca]^{10}[PO_4]^6[OH]^2$. Strictly speaking, the values within brackets represent the activities (effective concentrations) of the component ions rather than their actual concentrations. The activities are inversely proportional to the concentrations of other ions, such as sodium and potassium, that are present. Because HA is a highly insoluble mineral, and because the activities of the 3 component ions are expressed in the large units of moles per litre, the measured value of Ksp for HA is very small, on the order of 10^{-117}. Although the Ksp is a constant, the

concentrations of each of the 3 component ions in a saturated solution can vary, provided that their product remains equal to the Ksp. Thus, in a more acidic solution, in which the hydroxyl concentration is reduced, the concentrations of the calcium or phosphate ions (or both) would have to increase if saturation were to be maintained.

For any given solution, such as saliva, plaque fluid, gastric juice or a soft drink, the ion product (Ip) is determined by means of a similar calculation, also based on the calcium, phosphate and hydroxyl concentrations. If Ip = Ksp, then the solution is just saturated with respect to HA. If Ip < Ksp, the solution is unsaturated, and if Ip > Ksp, the solution is supersaturated.

When a tooth is placed in distilled water of pH 7, a small amount will slowly dissolve (about 30 mg in 1 L of water).[2] The Ip for HA in distilled water is zero, because although the water contains hydroxyl ions, it contains no calcium or phosphate ions. Because Ip < Ksp, the water is unsaturated and the tooth will dissolve until Ip = Ksp. Likewise, a tooth will dissolve to some extent in any solution in which calcium and phosphate ions are not present, such as a sodium fluoride solution.

In contrast, saliva and plaque fluid do contain calcium, phosphate and hydroxyl ions, and most of the time Ip > Ksp for HA. Therefore, a tooth will dissolve in saliva or plaque fluid only if the pH is reduced to less than the critical pH. In people with low salivary concentrations of calcium and phosphate, the critical pH may be 6.5, whereas in those with high salivary calcium and phosphate concentrations, it may be 5.5.[3] The fluid phase of dental plaque contains much higher concentrations of calcium and phosphate than does saliva,[4] and its critical pH may be as low as 5.1.

Thus, the critical pH is not a constant, because the levels of calcium and phosphate in plaque fluid vary among individuals. The more calcium and phosphate that are present in a solution, the lower its critical pH.

Why Does a Tooth Dissolve in Acid?

Although the solubility of some minerals, such as sodium chloride, is virtually independent of pH, the solubility of HA increases about 10-fold for each unit decrease in pH. At pH 7, the solubility of HA in water is about 30 mg/L, whereas at pH 4 it is about 30 g/L.[2]

There are 2 reasons for the increased solubility of enamel in acid. First, the hydrogen ions remove hydroxyl ions to form water, as follows: $H^+ + OH^- \leftrightarrows H_2O$. The product of $[H^+][OH^-]$ in water always equals 10^{-14} $(mol/L)^2$. Therefore, as the $[H^+]$ increases in an acid solution, the $[OH^-]$ must decrease in a reciprocal manner.

Second, the inorganic phosphate in any fluid such as saliva or plaque fluid is present in 4 different forms, namely H_3PO_4, $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-}, and the proportions depend entirely on the pH. **Figure 1** illustrates how the
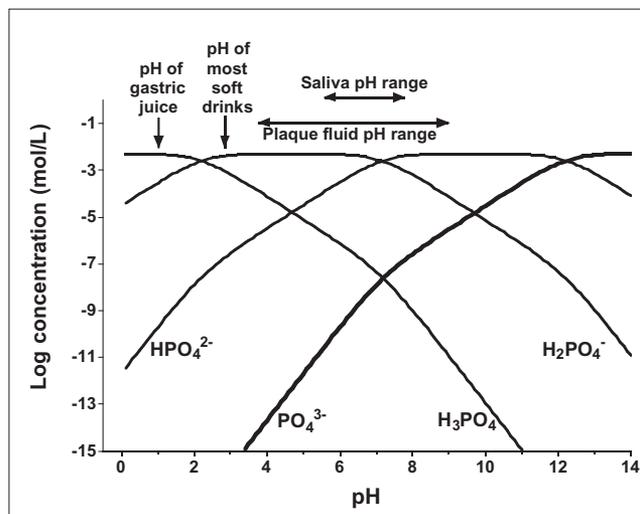
Figure 1: *The effect of pH on the concentrations of the various inorganic phosphate species in saliva containing a total phosphate concentration of 5×10^{-3} mol/L. There is a marked fall in the concentration of PO_4^{3-} (thick line) as the pH is reduced.*

proportions of the 4 phosphate species vary with pH when the total phosphate concentration is 5×10^{-3} mol/L, as is typical of saliva. The lower the pH, the lower the concentration of PO_4^{3-}, the only species that contributes to the Ip of HA.

Thus, as any solution is acidified, the calcium concentration is unaffected but the concentrations of both OH^- and PO_4^{3-} are reduced and so, therefore, is the Ip, often to a value less than the Ksp.

Clinically, there are 2 situations in which dentists place acid in contact with enamel and in which enamel dissolves. The first is the acid-etch technique, which usually employs 37% phosphoric acid. This solution contains no calcium and thus the Ip for HA is zero. Normally, though, the acid is applied for only about 10 s, so potential dissolution of the enamel is limited. The second situation is the use of acid fluorophosphate gels, which usually contain 0.1 mol/L phosphoric acid in addition to the sodium fluoride and which have a pH of 2.3. Again, these gels contain essentially no calcium and the Ip for HA is zero, which means that the tooth will begin to dissolve. Hence, to avoid excessive enamel loss, it is important not to exceed an exposure time of 4 min with these gels.

Patients, of course, may also introduce acid into their mouths, where it can cause erosion of enamel. The most devastating acid is gastric juice,[1] which contains hydrochloric acid and low concentrations of calcium and phosphate and which has a pH of about 1 (**Fig. 1**). Other sources of acid include fruit juices and soft drinks, which have great potential to cause erosion because many of them have a pH of less than 3 (**Fig. 1**).

Patients with severe xerostomia usually require daily exposure to fluoride rinses or gels to reduce the risk of caries to which they are susceptible. To avoid excessive enamel

decalcification in such patients, a neutral sodium fluoride gel or rinse rather than an acidulated fluorophosphate gel should be employed. The fluoride reacts with enamel to form fluorapatite which, being less soluble than hydroxyapatite, has the effect of reducing the critical pH.

Can Decalcified Enamel Be Remineralized?

In a white-spot caries lesion, the decalcification has occurred below the surface, and the lesion is covered by a virtually intact surface zone of enamel with a thickness of about 0.03 mm. There is very good clinical evidence that such lesions can be remineralized if the surface remains intact, provided they are kept free of plaque, salivary flow is adequate or is regularly stimulated by use of sugar-free gum, and topical fluoride treatments are given.[5] Such remineralization can take place only because saliva and plaque fluid are normally supersaturated with respect to tooth mineral, particularly when salivary flow is stimulated,[6] and because the subsurface lesion provides a suitable matrix for crystal growth after calcium and phosphate ions have passed through the pellicle and surface enamel.

In contrast, enamel that has suffered surface erosion by acid cannot be recalcified,[5] because there is no suitable matrix for crystal growth. An enamel surface eroded by acid becomes covered by an acquired enamel pellicle of salivary and bacterial proteins as soon as it contacts the saliva, and this pellicle inhibits mineral deposition. If saliva contacts enamel after acid etching, the pellicle that forms also reduces the strength of bonding to composite resin. In addition, the presence of the enamel pellicle prevents the teeth from enlarging continuously, even though they are bathed in saliva supersaturated with tooth mineral. Thus, contrary to some views,[1] enamel erosion is irreversible, which is why it is so important for dentists to check for its occurrence and thus allow patients to take appropriate measures to reduce further exposure of their teeth to acid.

Conclusions

In summary, the critical pH below which enamel dissolves is not constant but rather is inversely proportional to the concentrations of calcium and phosphate in the saliva and plaque fluid. Teeth with early subsurface caries lesions can be remineralized, but teeth that have suffered acid erosion cannot. ❖

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