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A Level Chemistry B (Salters)

H433/02 Scientific literacy in chemistry

Advanced Notice Article

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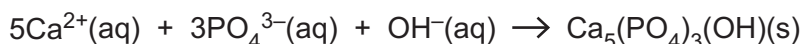
Fluoride compounds in dental hygiene

Extracted from 'The Chemistry of Dental Care' Parts 1 and 3 by Matthias Epple and Joachim Enax in *Chemistry Views* magazine, 2018.

Dental enamel is the hardest material in the human body. However, it is still possible for teeth to be damaged, for example, through cavities or consuming acidic foods. Therefore, modern dental hygiene is an important aspect of health care in general. In this article, we take a closer look at why fluoride is good for your teeth.

Enamel

The mineral phase of our teeth is based on calcium phosphate hydroxylapatite, $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$. This is precipitated under basic conditions according to the following equation:



Dental enamel consists of micrometer-sized, needle-like hydroxylapatite crystallites organized parallel to one another in crystallite bundles. It contains almost exclusively mineral components and only a small amount of protein. Due to its high mineral content and its specific microstructure, dental enamel is the hardest substance in the human body. Compared to a ceramic, dental enamel also possesses especially high resistance to breakage; that is to say, it is less brittle than tough. The outer surface of the enamel is coated with a thin protein layer (the pellicle).

Tooth decay (caries, cavities)

The most important dental disease worldwide is tooth decay.

A continuous process of de- and re-mineralization occurs within the oral cavity, on the surface of the tooth enamel. Upon consumption of acidic foods, the outer-most layer of the enamel becomes solvated and thus softened (demineralization). Fortunately, saliva is supersaturated with calcium phosphate, the result being a constant redeposition of calcium phosphate from this source (remineralization). Diseases are largely caused by bacterial biofilms (plaque). In the case of tooth decay (caries), bacteria such as *Streptococcus mutans* transform food components—mostly sugar—into acids (among others, lactic acid), which can then attack the teeth. For this reason, thoroughly cleaning the teeth is the chief goal of modern dental hygiene, in order to efficiently and effectively remove plaque deposits. If plaque is not effectively removed, calcium phosphate from saliva can be embedded within it, leading to the formation of tartar (a hardened form of dental plaque). Caries problems depend on the diet. The lower the sugar consumption, the lower the risk of caries. If acid attacks the hard material of teeth in the absence of bacteria (i.e., because of acidic dietary components such as soft drinks, fruit juice, or citrus fruits), or from gastric acid, one speaks of "acid erosion".

Fluoride compounds

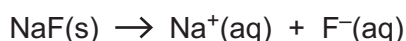
The use of fluoride-containing home tooth-care preparations is considered responsible for the considerable decrease in cases of cavities in recent decades. In Europe, however, oral hygiene agents are legally classified as cosmetic resources, and are thus subject to the European Cosmetic Ordinance. This, in turn, specifies a maximum allowed concentration of fluoride. Thus, the highest permitted fluoride level in toothpaste is 0.15% (calculated on the basis of F^-).

The amount actually present is made clear on the packaging of a fluoride toothpaste intended for adults; a typical value is 1450 ppm fluoride (i.e., 0.145%). Care is particularly called for with respect to children, since excessive fluoride levels can lead to fluorosis, a condition in which excess fluoride is incorporated into the teeth, leading to a yellowish discoloration.

Fluoride is the base corresponding to the moderately strong acid HF (hydrofluoric acid; $pK_a = 3.14$). Under the conditions normally present in the oral cavity ($pH = ca. 7$) the equilibrium lies fully on the side of the free fluoride ion. Even under acidic conditions, which can be encountered in plaque ($pH = ca. 5$), fluoride is present predominantly as the free anion, not in the form of HF. The fluoride in domestic products for dental hygiene may be introduced in the form of various compounds. In Germany, the most common fluoride source at present is sodium fluoride.

Sodium fluoride

The salt NaF is very water-soluble. In aqueous solution it dissociates into ions:



The nature of the counter-ion (sodium, potassium) here plays no significant role. Dissociation occurs immediately upon dissolution in water.

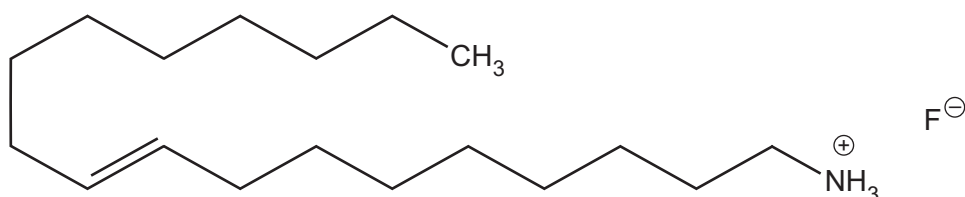
Tin difluoride

SnF_2 is a covalent material (i.e., not an ionic salt). The release of fluoride ions, in this case, requires hydrolysis.

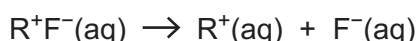
This occurs more rapidly at higher pH and higher temperature. Fluoride release here is clearly less rapid than with sodium fluoride, which dissociates into ions immediately upon dissolving.

Amine hydrofluorides

These are salts comprised of a cationic surfactant (ammonium salt) and the fluoride ion. A typical example is dactaflur:



Dissolution in water leads to immediate and complete dissociation, corresponding to:



This dissociation is independent of the nature of the ions, i.e., the same occurs with chloride instead of fluoride as the counterion.

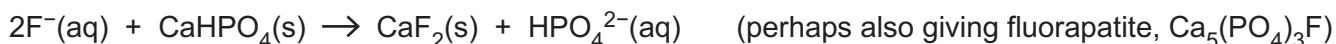
Effect of fluorine

Fluoride has a prophylactic effect against caries. The cationic surfactant plays a bacteriocidal role. Here, the bacteriocidal effect is not a function of the fluoride, as can be shown by the use of the corresponding amine hydrochloride.

It is also important to note that fluoride ions can be deactivated by calcium-containing cleansers, i.e., calcium carbonate:



or calcium hydrogen phosphate:



Solution and precipitation equilibria in the oral cavity

The mode of action of fluoride can be readily understood from a chemical standpoint in terms of the solid phases present and their solubility products. The source of the fluoride is irrelevant, incidentally; what is instead always important is fluoride ions in solution.

In what follows, we provide various calculations related to both dissolved and solid phases in the presence of fluoride in saliva. It is important to us in this context that these calculations – without complex numeric solution procedures – suffice for taking into account subsequent precipitation, protolysis, and complex-formation equilibria. They will, thus, rely on a few simplifying assumptions, but for this reason remain readily intelligible.

We assume in what follows that all ions are present in pure water. The following numerical values are thus employed in the calculations.

Compound	K_{sp} (M = mol dm ⁻³)
hydroxylapatite $\text{Ca}_5(\text{PO}_4)_3\text{OH}$	$1.58 \times 10^{-59} \text{M}^9$
fluorapatite $\text{Ca}_5(\text{PO}_4)_3\text{F}$	$9 \times 10^{-61} \text{M}^9$
calcium fluoride CaF_2	$3.9 \times 10^{-11} \text{M}^3$

Table 1.1

Ion	Concentration in saliva (M = mol dm ⁻³)
$[\text{Ca}^{2+}]$	$1.43 \times 10^{-3} \text{M}$
$[\text{PO}_4^{3-}]$	$2.55 \times 10^{-8} \text{M}$
$[\text{F}^{-}]$ after brushing with toothpaste containing 1500 ppm of fluoride, diluted ca. 1:10	150 ppm = $7.9 \times 10^{-3} \text{M}$

Table 1.2

The pH of saliva is assumed to be 7.0.

Let us consider the solubility equilibrium in saliva for **hydroxylapatite**, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$; the mineral substance in teeth.

For the ion product, IP, the following applies:

$$\text{IP} = [\text{Ca}^{2+}]^5 [\text{PO}_4^{3-}]^3 [\text{OH}^-] = (1.43 \times 10^{-3})^5 \times (2.55 \times 10^{-8})^3 \times 10^{-7} \text{M}^9 = 9.9 \times 10^{-45} \text{M}^9$$

$$K_{\text{sp}} = 1.58 \times 10^{-59} \text{M}^9$$

Supersaturation, as opposed to precipitation, can be calculated using:

$$\sqrt[9]{\frac{\text{IP}}{K_{\text{sp}}}} = \sqrt[9]{6.3 \times 10^{14}} = 44$$

At pH 7, saliva is therefore highly supersaturated with respect to hydroxylapatite. This is to be expected, since teeth do not dissolve under neutral conditions. However, it illustrates the possibility for remineralization of tooth enamel after attack by acid.

Consider now the solubility equilibrium for **fluorapatite**, $\text{Ca}_5(\text{PO}_4)_3\text{F}$.

For saliva containing 150 ppm fluoride after brushing, it remains true that:

$$\text{IP} = [\text{Ca}^{2+}]^5 [\text{PO}_4^{3-}]^3 [\text{F}^-] = (1.43 \times 10^{-3})^5 \times (2.55 \times 10^{-8})^3 \times 7.9 \times 10^{-3} \text{M}^9 = 7.8 \times 10^{-40} \text{M}^9$$

$$K_{\text{sp}} = 9 \times 10^{-61} \text{M}^9$$

with a supersaturation of:

$$\sqrt[9]{\frac{\text{IP}}{K_{\text{sp}}}} = \sqrt[9]{8.7 \times 10^{20}} = 212$$

In the presence of fluoride, saliva is thus very highly supersaturated relative to the precipitation of fluorapatite.

Finally, we consider the solution equilibrium of **calcium fluoride**, CaF_2 , in the presence of fluoride-containing saliva. Saliva containing 150 ppm fluoride ($7.9 \times 10^{-3} \text{M}$) after brushing can be shown to have a calcium fluoride supersaturation in double figures but much lower than fluorapatite.

After brushing with fluoride-containing toothpaste, it is thus possible that there will be precipitation of CaF_2 . But the supersaturation of fluorapatite is much greater.

The protective effect of fluoride against caries

Various mechanisms of action have been discussed with respect to the anticavity (anticaries) effect of fluoride (see **Table 1.3** below). The central point in this context is the accelerated crystallization (nucleation) of calcium phosphate during remineralization. However, the incorporation of fluoride into the enamel during routine daily tooth care is extremely limited (fluoride content of 500–1,000 ppm in the outer layer of solid tooth enamel; a stoichiometric fluorapatite would have a much higher ppm). There is also no detectable evidence for an acid-insoluble protective layer of calcium fluoride or fluorapatite. As a result, the activity of fluoride is apparently due to the effects of dental hygiene itself.

The discovery that the fluoride concentration is very low in the outermost enamel layer of the teeth, and that no crystalline calcium fluoride is detectable, indicates substoichiometric inclusion of fluoride in the hydroxyapatite lattice. Fluorapatite and hydroxylapatite are hardly distinguishable crystallographically, especially in the presence of extraneous ions. One can conclude that, due to its higher degree of supersaturation, fluorapatite crystallizes first, and acting as a seed, accelerates the further deposition of hydroxylapatite, without the incorporation of large amounts of fluoride.

Fluoride thus functions as a “catalyst” for the natural remineralization process from the saliva. Furthermore, the active agent fluoride requires saliva (i.e., the presence of calcium and phosphate ions) to be effective.

It is interesting to compare human teeth with shark teeth. The enamel of the shark tooth (enameloid) consists of almost stoichiometric amounts of fluorapatite, $\text{Ca}_5(\text{PO}_3)_3\text{F}$. Studies have shown that shark teeth, despite their high fluoride content, are subject to attack by acid. Shark teeth are just as hard as human teeth, so that one cannot assume hardening of the enamel through an integration of fluoride after use of a fluoride-containing oral-care product. The antibacterial effect of fluorides is due mainly to the counterion (with amine hydrofluorides, the cationic amine, with tin fluoride the Sn(II)), and not to fluoride itself. The fluoride concentration is too low to produce an effective antibacterial activity. The table below summarizes these findings.

Postulated mechanism of action for fluorides in home dental care, with comments from a chemical point of view:

Postulated mechanism	Comments
Improved remineralization	Yes, due to improved nucleation through precipitation of fluorapatite
Formation of a protective layer of fluorapatite and/or calcium fluoride to protect against erosion as a fluoride reservoir	No, because fluorapatite and calcium fluoride are both acid-soluble, i.e. no acid-stable shell forms around the tooth
Inclusion of fluoride in the enamel	Only on the surface to a very limited extent
Hardening of the enamel	Scarcely, even in the case of stoichiometric fluoride incorporation; even shark tooth enamel (fluorapatite) is not significantly harder than human tooth enamel
Antibacterial effects	At least with toothpaste, fluoride concentrations are too low; fluoride antibacterial activity is due mostly to the counterion (i.e. amine or tin), not to the fluoride

Table 1.3

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