

Original Research Article

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## A STUDY ON INTERACTION DYNAMICS AND EFFECT OF TEMPERATURE ON HYDROXYAPATITE- FLUORIDE INTERFACE

Eiichi Akaho <sup>1\*</sup>, Masaki Kambara <sup>2</sup>

1. Faculty of Pharmaceutical Sciences, Kobe Gakuin University, 1-1-3 Minatojima, Chuo-ku, Kobe, 650-8586 Japan

2. Kambara Global Health Institute, Nishitani BII. 406, Minamihorie 1-10-11, Nishi-ku, Osaka, Japan, 550-0015

**ABSTRACT:** The amount of fluoride adsorbed onto hydroxyapatite increased as the aqueous fluoride concentration increased. When the aqueous fluoride concentration exceeded 100 ppm, the total amount of fluoride adsorbed onto hydroxyapatite decreased after being washed off with water three times. It is postulated that when the aqueous fluoride concentration exceeds 100 ppm, a multilayer structure of calcium fluoride formed around hydroxyapatite is washed off, resulting in the decrease of the fluoride adsorbed onto hydroxyapatite. It is also postulated that the fluoride multilayer consists of calcium fluoride- complex whose interaction force is weaker than ionic force created by replacing OH<sup>-</sup> with F<sup>-</sup>. One can rinse his/her mouth with fluoride solution of less than 100 ppm, 20 to 30 ppm preferably. And then one should rinse the mouth with water several times so as to achieve the fluoride concentration of 0.5 to 1 ppm in the mouth which is the WHO recommended fluoride concentration in drinking water. The thermodynamic study revealed that Langmuir isotherm can be applied for the adsorption of fluoride onto hydroxyapatite. The thermodynamic parameters indicated that the adsorption process is spontaneous and endothermic. The high degree of disorderliness exists between solid – solution interface upon the adsorption of fluoride onto hydroxyapatite.

**KEYWORDS:** Hydroxyapatite; fluoride; adsorption; thermodynamics; Langmuir isotherm; oral hygiene

**\*Corresponding Author: Dr. Eiichi Akaho** Ph.D.

Faculty of Pharmaceutical Sciences, Kobe Gakuin University, 1-1-3 Minatojima, Chuo-ku, Kobe, 650-8586 Japan.

\* E-mail Address: akaho@pharm.kobegakuin.ac.jp

## **1. INTRODUCTION**

### **Adsorption characteristics**

Various types of adsorption phenomena have attracted a special research interest because researchers observed unusual physico-chemical behaviors in it. [1] A scientific discernment on different definitions of physical adsorption was reported by Hill.[2] Adsorption is the adhesion phenomenon of atoms, ions, biomolecules or molecules of gas, liquid, or solids onto a surface of the adsorbent which can be solids or macromolecules. This process creates a film of the adsorbate, which can be molecules or atoms being accumulated, on the surface of the adsorbent. It differs from absorption, in which a fluid, gas or solid diffuses or permeates into a liquid or solid. A term sorption. Adsorption of adsorbate molecules including fluoride onto the adsorbent materials including hydroxyapatite is an interesting subject and studies have been conducted from various viewpoints such as adsorption phenomenon,[3-19] mechanism of adsorption,[20-23] adsorbate and adsorbent characteristics,[24-40] kinetic and equilibrium studies,[41-43] thermodynamic studies,[44-46] and synthesis of adsorbent.[47-49] This is a subject not only of physico-chemical aspects, but also of clinical and toxicological aspects. In other words, adsorption of fluoride comprehends basic sciences as well as applied sciences. This is another reason why this issue has attracted particular research interest in our scientific community.

### **Dental fluoride and its optimal concentration**

It was reported in the 1930's that certain areas of the United States had an unusually low incidence of tooth or dental caries and that these same regions had an unusually high concentration of natural fluoride in the water. Scientists argued that fluoride could replace the hydroxide ion in hydroxyapatite yielding new mineral which is intrinsically less soluble. However, it is noted recently that the incidence of dental caries has declined to a comparable extent both in communities where fluoridation is practiced and in the area where no fluoride is added to the water.[50] It might be pointed out that there exist conflicts between the two opposite claims. Many studies have shown that water fluoridation and dental fluoride treatment dramatically reduces dental caries,[51] although there are some other studies which report that there are no substantial association between dental fluoridation and occurrence of dental decay.[52]. As far as the concentration of fluoride in saliva is concerned, Featherstone JD reported that low but slightly elevated levels of fluoride in saliva and plaque help prevent and reverse caries by inhibiting demineralization and enhancing remineralization.[53] Sub ppm levels of fluoride in saliva are said to be effective in shifting the balance from demineralization to remineralization.[54] On the other hand, whether the systemic fluoride

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provide demineralization or remineralization is another question. Featherstone mentioned that the effect of systemically ingested fluoride on caries is minimal. Here we should notice the importance of the fact that one needs to achieve and maintain the optimal concentration of fluoride in saliva. As our preliminary study an adsorption of fluoride to hydroxyapatite was investigated. Hydroxyapatite is a main component of enamel. Therefore, it is assumed that the adsorption experiment of fluoride to hydroxyapatite will well represent the adsorption nature of fluoride onto enamel. Formation of hydroxyapatite, which exhibits mechanical properties in the range of those reported for dentin and bone, has been demonstrated. This is significant for the opportunity it affords to form synthetic analogs in vivo that are compositionally similar to hard tissue minerals.

### **Removal of fluoride**

The adsorption of fluoride onto hydroxyapatite can be applied for the removal and defluoridation of fluoride from aqueous solutions. There has been a considerable number of reports related to this area in recent years.[55-63] Sternitzke et al. reported that fluoride uptake on hydroxyapatite can occur through different mechanisms which are influenced by solution composition.[64] They also stated that a fluoride surface layer with a thickness of several nanometers is formed on nanosized hydroxyapatite when the fluoride uptake study was conducted by nano secondary ion mass spectroscopy. Poinern et al. studied defluoridation behavior of nanostructured hydroxyapatite synthesized through an ultrasonic and microwave combined technique, and reported that the intra-particle diffusion process played a significant role in determining the rate of defluoridation.[49]

### **Dental fluoride and the mechanism of fluoride adsorption onto hydroxyapatite**

A large number of studies on the hydroxyapatite in relation to fluoride have been performed and a model for the mechanism of the fluoride uptake by hydroxyapatite has been proposed.[49, 65-74] Leamy et al. reported that the extent of hydroxyl replacement by fluoride ranged from 17 to 72% and correlated it with the surface area of the parent hydroxyapatite. In addition, there are some unknown factors as to the extent of the adsorption of fluoride to the teeth enamel.[69] Thus it is worth carrying out an investigation to study an interaction of fluoride to hydroxyapatite as well as the extent of absorption of fluoride to hydroxyapatite which is one of the major components of the teeth enamel.

### **Thermodynamics**

Thermodynamics, equilibrium isotherm, and adsorption mechanism of small and large molecules including fluoride onto large molecules including hydroxyapatite, aluminum and chitin have been studied extensively.[20-23, 41-43] Thermodynamics of adsorption of statherin onto hydroxyapatite crystals have been characterized by isothermal titration calorimetry and equilibrium adsorption

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isotherm analysis by Goobes et al.[46] They found that statherin adsorption is characterized by an exothermic enthalpy of  $\sim 3$  kcal/mol that diminishes to zero at  $\sim 25\%$  surface coverage. Thermodynamics of fluoride adsorption shows different pattern depending upon types of adsorbent. Goswani et al. pursued the kinetic and equilibrium study for the fluoride adsorption using pyrophyllite.[75] They reported the negative  $\Delta H_o$  value which signified that the adsorption process is exothermic. The other study referring to the exothermic nature of fluoride adsorption is conducted by using a new metal ion-loaded (Zr(IV), Al(III), Fe(III)) fibrous protein.[76] On the other hand, Mourabet et al. investigated the adsorption potential of Brushite for the removal of fluoride from aqueous solution and reported that the adsorption of fluoride ions on the Brushite is feasible, spontaneous, and endothermic.[77] The adsorption study using graphene as adsorbent also revealed that the adsorption process is endothermic in nature.[78]. De Leeuw et al. conducted molecular dynamics simulations of the interaction of citric acid with the hydroxyapatite and reported that the calculated average adsorption energies were  $+291.4$  kJ mol<sup>-1</sup> for the hydroxyapatite.[79] Studies on adsorption dynamics and the effect of temperature of fluoride showed that the adsorption process is endothermic and occurs spontaneously.[45, 80] Nelson et al. investigated the mechanism of fluoride uptake by hydroxyapatite from acidic fluoride solutions and found that fluoride and acid diffuse into the reaction site and phosphate diffuse out as the reaction proceeds.[81]

### **Equilibrium isotherms**

Equilibrium isotherms were studied for the adsorption of various dyes on chitin and theoretical isotherms have been compared with experimental data. It was then found that a good agreement was obtained using a composite isotherm of the general form.[82] Sundaram et al. reported that the fluoride sorption was reasonably explained with Langmuir, Freundlich and Redlich-Peterson isotherms.[42]

## **2. MATERIALS AND METHODS**

### **Experimental and Materials**

#### **Determination of fluoride concentration**

A fluoride stock solution was prepared in the ultra-pure water where ion resistance was less than 18 m $\Omega$ . Fluoride solutions of various concentrations were then prepared in centrifuge tubes which contained 200 mg of hydroxyapatite. At different time intervals fluoride concentrations were measured by the ion chromatography after shaking the centrifuge tube for a specific period of time. The ion chromatograph conditions were as follows:

- a) ion chromatograph model: Dionex DX-100
- b) eluent solution: 0.1M sodium tetraborate
- c) flow rate of the eluent solution: 1 ml/min

d) column used : Ionpac AS4-SC

e) detector: an electric conductivity meter

f) the injection port: 0.7 ml

### **Fluoride in-take to hydroxyapatite**

Sodium fluoride was used for making a fluoride solution. Fifty ml of the ultra-pure water was added to 0.995 g of sodium fluoride in order to make 9000 ppm of fluoride stock solution.. A fluoride solution of different concentration was prepared by diluting the 9000ppm fluoride parent solution. Zero point two gram of hydroxyapatite was placed in the centrifuge test tube, and then ten ml of the fluoride solution of different concentrations was added. The entire content of the test tube was shaken in the shaker for a given period of time. At the specified time interval, the test tube was taken out and the entire solution was filtered. The remaining filtered hydroxyapatite was washed off by 10 ml of ultra-pure water for three times. The one filtrate and three washed-off solutions were analyzed to determine the fluoride concentration by the ion chromatography.

### **Extent of fluoride adsorption onto hydroxyapatite**

Zero point two gram of hydroxyapatite was placed in the test tube and ten ml of the fluoride solution of different concentrations was added to it. Fluoride solutions containing hydroxyapatite were kept shaking overnight (12 hours), one day (24 hours), two days (48 hours) and so on. At the end of each time interval, the amount of fluoride in the solution was measured by ion chromatography and the amount of fluoride taken up by hydroxyapatite was calculated.

### **Perturbation Experiments**

Twelve Erlenmeyer flasks containing 80 ml of  $3.46 \times 10^{-5}$  M fluoride solution and 80 mg of hydroxyapatite were agitated in a water bath for 1 h at 30°C, and then the temperature was shifted from 30°C to 50°C, 40°C, 30°C, and 40°C at one hour interval. At the end of each interval, two flasks were removed and the contents were assayed for fluoride concentration.

## **3. RESULTS AND DISCUSSION**

### **Measurement of fluoride by ion chromatography**

One of the popular methods to measure the concentration of fluoride in the aqueous solution is an ion electrode method. However, the minimum concentration of fluoride measurable by fluoride electrode is about 100 ppm, which is well above the concentration one needs to know in the dental hygienic setting. An alternative, convenient and reliable method to measure the fluoride concentration is

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 ion chromatography, by which one can measure a concentration of fluoride as low as 0.05 ppm.

**Table 1.** Percent of fluoride washed off from the hydroxyapatite after mixing fluoride in the aqueous solution with hydroxyapatite for 24 hours

| initial concentration of fluoride (ppm) in the aqueous solution (10 ml) | number of washings(0, 1, 2, 3) and percent (%) of fluoride washed off |      |      |      |
|---|---|------|------|------|
|   | 0   | 1    | 2    | 3    |
| 10  | 9.18  | 1.73 | 2.10 | 2.54 |
| 25  | 6.96  | 1.32 | 1.49 | 1.30 |
| 50  | 7.59  | 2.43 | 1.49 | 1.13 |
| 75  | 18.2  | 5.13 | 2.11 | 1.90 |
| 100   | 30.0  | 8.26 | 2.54 | 1.90 |
| 150   | 50.8  | 14.0 | 4.20 | 2.21 |
| 200   | 59.7  | 15.6 | 3.59 | 1.83 |
| 250   | 65.5  | 17.0 | 4.59 | 2.24 |
| 300   | 70.9  | 14.7 | 3.34 | 2.22 |
| 310   | 70.5  | 18.6 | 4.33 | 2.20 |
| 320   | 72.4  | 18.9 | 4.07 | 1.92 |

(Note)

1. Two hundred milligram of hydroxyapatite was placed in each test tube to which the different concentration of fluoride solution (10ml) was added. The entire solution was then shaken for 24 hours.
2. The fluoride concentration of the shaken solution was determined by ionchromatography, and the percent of fluoride washed off was obtained as follows: .

$$[ \text{Fluoride concentration of each filtrate (ppm)} / \text{the initial fluoride concentration in the aqueous solution(ppm)} ] \times 100$$

Table 1 shows the percent of fluoride washed off from the hydroxyapatite after shaking the fluoride solution of different concentrations containing hydroxyapatite for 24 hours. When the initial fluoride concentration in the aqueous solution was in the lower range, less than ten percent of fluoride in the solution was filtered out at the zero time washing. This means that more than 90 percent of the fluoride initially added was adsorbed on the surface of the hydroxyapatite in those concentration ranges. For example, the percent washed off at the zero time washing for 10 ppm, 25 ppm, and 50 ppm, the concentration of fluoride solutions were in the lower range, that is, 9.18%, 6.96%, and 7.59%, respectively. On the other hand, when

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the initial fluoride concentration was higher, more than 70% of the fluoride was washed out. Seventy point nine percent, 70.5% and 72.4% of fluoride adsorbed onto hydroxyapatite were washed out at the zero washing time for 300 ppm, 310 ppm, and 320 ppm fluoride solutions respectively. In any case, this result clearly indicated that a fairly distinctive adsorption took place between fluoride and hydroxyapatite.

**Figure 1.** A total amount of fluoride adsorbed to hydroxyapatite after being washed off with water three times.

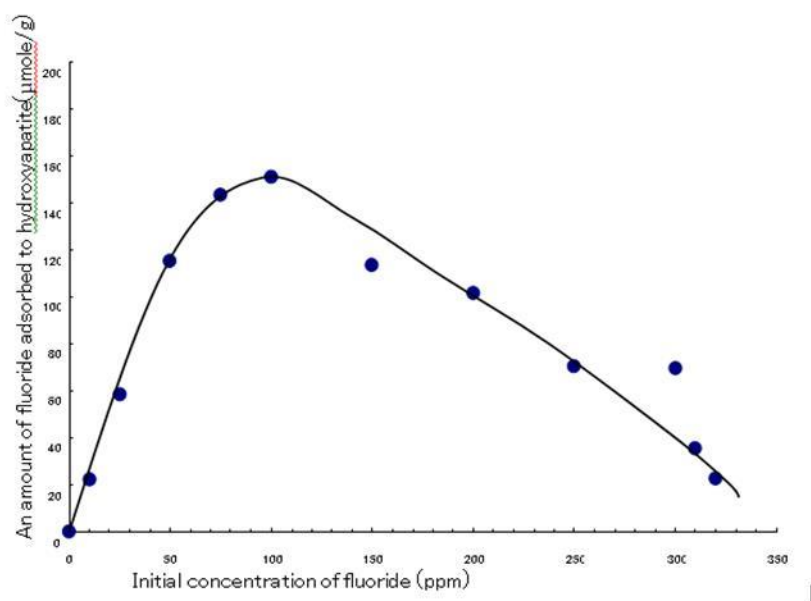
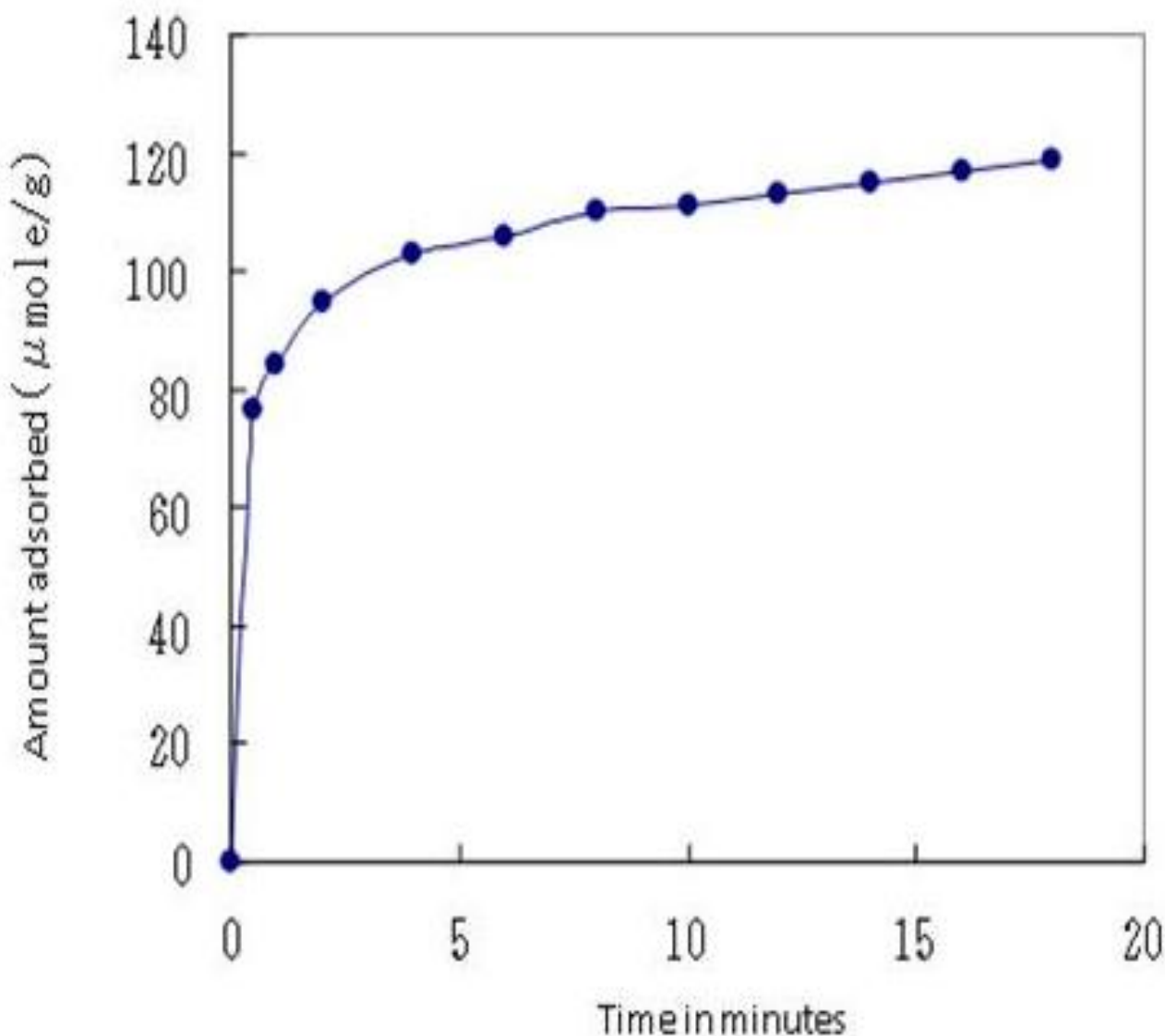


Figure 1 shows a total amount of fluoride adsorbed onto hydroxyapatite applying aqueous washing for three times in the mixed solution of fluoride with hydroxyapatite. When the concentration of fluoride was 100ppm, the total amount of fluoride absorbed to hydroxyapatite showed the maximum value. When the concentration of fluoride exceeded 100ppm, the total amount of fluoride adsorbed onto hydroxyapatite decreased.

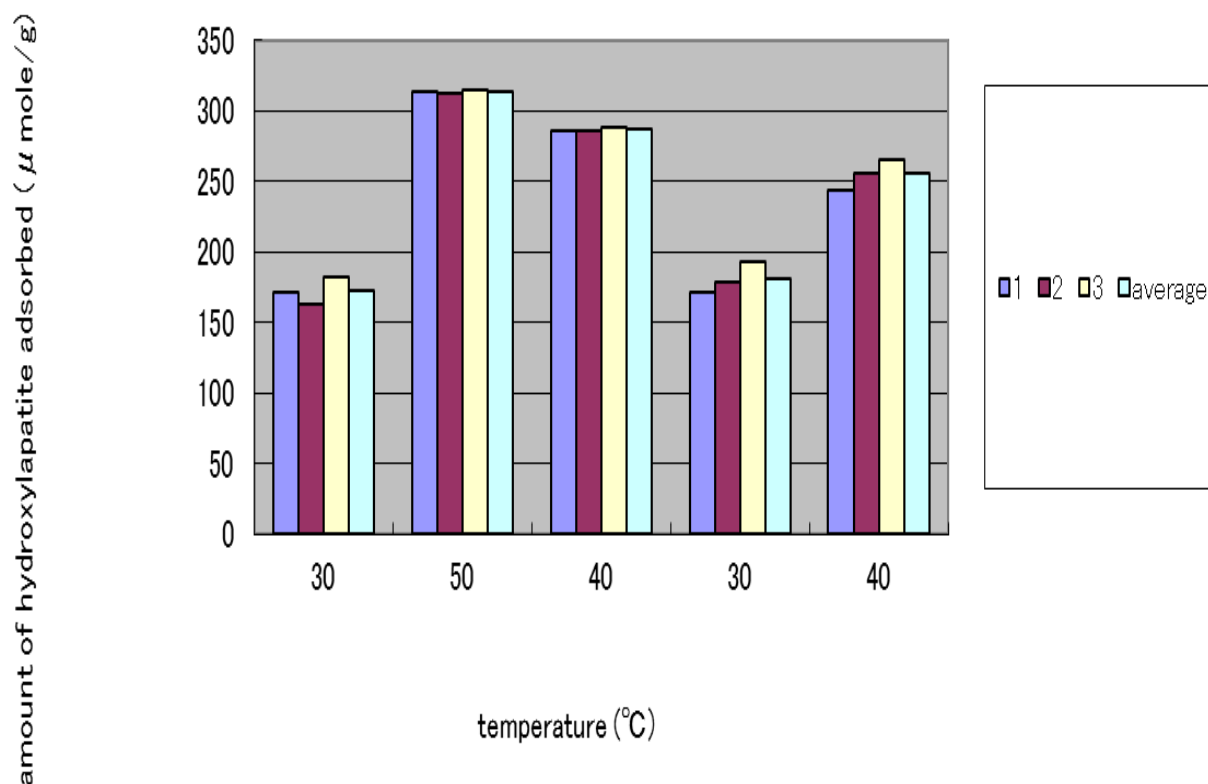


**Figure 2.** Adsorption of fluoride on hydroxyapatite with time from aqueous solution

Figure 2 shows the time dependent interaction of fluoride with hydroxyapatite. The concentration of fluoride in the aqueous solution used was 100 ppm which was found to be the maximum concentration of fluoride up to whose concentration hydroxyapatite keeps adsorbing fluoride. The result indicates that the adsorption level reached the plateau in about five minutes. When the adsorption process is ionic and chemical in nature, the interaction of the system should be irreversible.[83,84] The perturbation method to check whether the system is reversible or irreversible was reported by Ohkura et al.[83,84] and the perturbation experiment for the present system was conducted by the method described by them.[83,84] When the temperature of fluoride solutions with hydroxyapatite was shifted from 30°C, to 50, to 40, to 30, and to 40°C, the amount of fluoride adsorbed to hydroxyapatite was observed to increase as the temperature increases as shown in Figure 3.



Figure 3. Perturbation experiments on the adsorption of fluoride by hydroxyapatite from aqueous solution - the temperature was shifted at 1-h intervals.



This result indicates that adsorption process is irreversible and the mechanism of adsorption is of chemisorption type. The similar type was reported for the aminopurine adsorption study onto activated carbon.[84]

#### **Adsorption of fluoride to hydroxyapatite and the effect of aqueous washing on the extent of fluoride adsorption onto hydroxyapatite**

When hydroxyapatite is soaked in the sodium fluoride solution, the hydroxyl group is replaced by fluoride and, fluorapatite is formed. This phenomenon is regarded as F-/OH- exchange process. After all the hydroxyl group are replaced by the fluoride group on the surface of hydroxyapatite, it is

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assumed that fluorides are adsorbed on the surface of fluorapatite forming the calcium fluoride layers  
In other words, at the higher fluoride concentrations calcium fluoride is formed on the surface of  
hydroxyapatite by a surface precipitation process.

### **Calcium Fluoride formation**

As far as the effect of aqueous washing over the surface of fluoride-adsorbed hydroxyapatite is concerned, only small percent, less than two percent, of fluoride was washed off when the initial aqueous fluoride concentration was in the lower range. Besides, there was no practical difference in the washed-off percent among the first, the second and the third washings. This indicates that the adsorption of fluoride to hydroxyapatite is strong enough to stand for the physical aqueous washing when the initial aqueous fluoride concentration is in the lower range. When the initial aqueous fluoride concentration was in the higher range, the percent of fluoride washed off at first washing was more than ten times higher than those in lower concentration range of fluoride in the aqueous solution; 14.7% for 300ppm, 18.6% for 310ppm, and 18.9% for 320ppm, respectively, while 1.7% for 10 ppm, 1.32% for 25 ppm, and 2.43% for 50 ppm, respectively in the lower concentration range of fluoride in the aqueous solution. The percent of fluoride washed off in the higher concentration range of fluoride in the aqueous solution decreased to approximately one quarter at the next washing and to approximately one half at the last washing. This suggests that more than one layers of adsorbed calcium fluoride were created on the surface of hydroxyapatite. The second and higher layers of calcium fluoride are apparently loosely bound on the surface of fluorapatite so that a fairly substantial percent of fluoride are washed off at the first washing. It is postulated that when the fluoride concentration is above 100 ppm, more than one layers of calcium fluoride are formed on the surface of Fluorapatite as stacking layers which are washed off as chunks of calcium fluoride. It is also postulated that the binding force between fluorides in the stacking layer should be weaker than the force formed following F<sup>-</sup>/OH<sup>-</sup> ion exchange process because substantial amounts of fluoride adsorbed on fluorapatite as stacking layers were washed off.

### **Incorporation of fluoride onto hydroxyapatite**

It is shown that as time goes the extent of fluoride adsorption to hydroxyapatite increased. This indicates that some kind of time-dependent interaction between fluoride and hydroxyapatite took place. Hydroxyl group of the hydroxyapatite is replaced by fluoride in accordance with the increased shaking time. Therefore, the more fluoride is taken up by hydroxyapatite the more shaking time is spent.

### **Elimination of fluoride adsorbed onto hydroxyapatite**

Fluoride is certainly adsorbed substantially on hydroxyapatite. A question now comes as to how fluoride is taken up on or to hydroxyapatite. It is thought that interaction between fluoride and hydroxyapatite is created after the ionic displacement between fluoride and hydroxyl group of hydroxyapatite up to a certain concentration of fluoride in the aqueous solution which was found to be about 100ppm. More than one layers of fluoride are formed creating stacking layers of calcium fluoride whose binding force should be weaker than that of calcium fluoride and hydroxyapatite. Therefore, stacking layers of fluoride are easily washed off. Our finding indicated that fluoride adsorbed on the surface of the hydroxyapatite as calcium fluoride stacking layers are washed away quite easily by simple aqueous rinsing. This finding is very important in the area of dental hygiene, because it indicates that calcium fluoride does not stay long enough on the surface of teeth enamel when the fluoride concentration in the aqueous solution exceeds 100 ppm. We previously noticed that Featherstone found that low but slightly elevated levels of fluoride in saliva help prevent and reverse the formation of caries by inhibiting demineralization and enhancing remineralization.[53] He also stated that sub ppm levels of fluoride is effective in shifting the balance from demineralization to remineralization. Their findings coincide with our finding. Besides, our finding is more specific in terms of fluoride concentration needed to prevent dental caries. Featherstone stated that the effective concentration needed to prevent caries is sub ppm levels, which is rather ambiguous. We quantitatively found that fluoride concentration of 100 ppm or less is optimum to prevent caries.

### **Langmuir equilibrium and thermodynamic characteristics---**

$$\frac{c}{M} = \frac{1}{ab} + \frac{1}{a}c \quad \cdot \cdot \cdot \cdot \cdot \quad (1)$$

Equation (1) represents Langmuir equation, where M (mg/g) is the amount of fluoride adsorbed; c (g/L), equilibrium concentration; a, Langmuir constant for the amount adsorbed at saturation; and b, Langmuir equilibrium constant. A plot of c/M versus c should give a straight line with a slope of 1/a and an intercept of 1/ab (Figure 4). Since adsorption is often an irreversible process, affinity constants derived from the Langmuir equation should only be considered as apparent values. For the same reason, any thermodynamic parameters derived from the apparent affinity constant should also be considered as apparent values. The thermodynamic equilibrium constant,  $K_0$ , can be obtained by plotting  $\ln(M/c)$  versus M and extrapolating the curve to M being zero, as shown in Figure 5.<sup>44</sup>

Figure 4. Langmuir isotherm plots for the adsorption of fluoride on hydroxyapatite

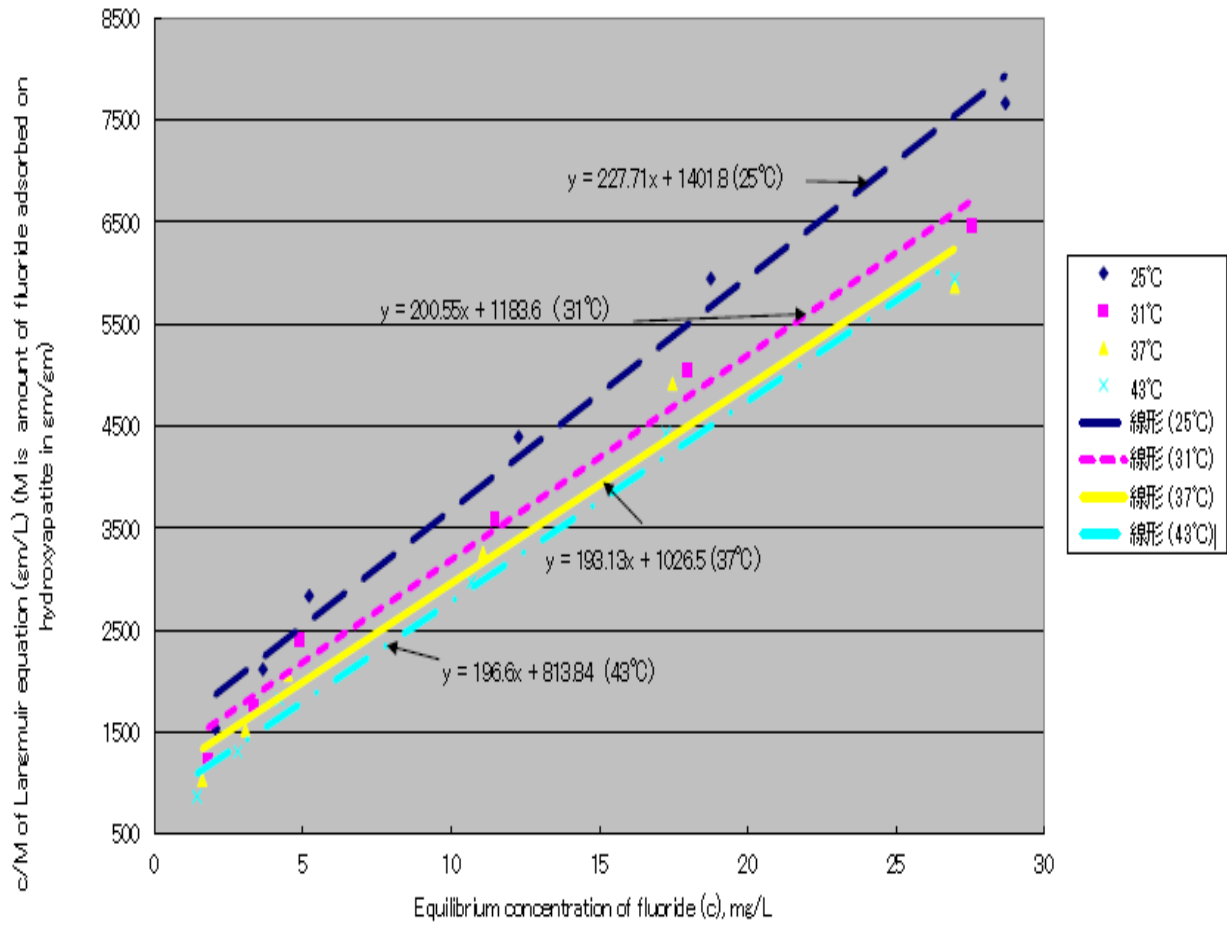
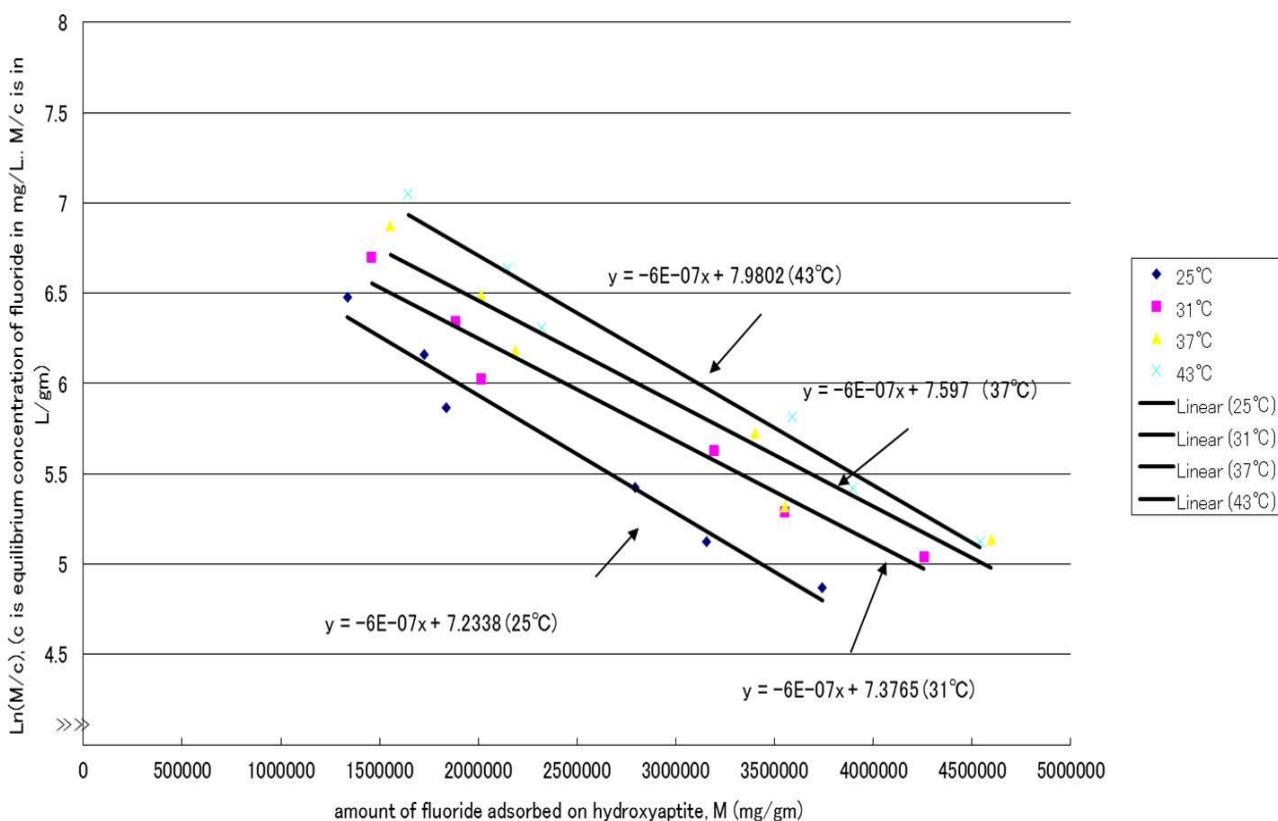


Figure 5. Plots of  $\ln(M/c)$  versus  $M$  of Langmuir equation for the adsorption of fluoride on hydroxyapatite



It is said that the endothermic nature of adsorption is indicated by an increase in  $K_0$  with rise in temperature.[80] Our result showed the increase of  $K_0$  from the value of 7.23 to 7.98 as the temperature rises from 25 °C 43 °C representing that the system is endothermic. Plaut et al. reported that the standard enthalpy associated with the sorption process of fluoride digluconate from aqueous solution by PHEM (poly (2-hydroxyethyl methacrylate) powder was zero over the temperature range of 20 ~ 50°C.[85, 86] They concluded that the sorption process of this system was associated with ion exchange interaction whose standard enthalpies are generally zero or very small. To make this type of thermodynamic assumption for the sorption process of fluoride onto hydroxyapatite in the present system, the following equations were applied.

$$\Delta G = -RT \times \ln K_0 \quad \cdot \cdot \cdot \cdot \cdot \quad (2)$$

$$\Delta H = d(\Delta G/T)/d(1/T) \quad \cdot \cdot \cdot \cdot \cdot \quad (3)$$

$$\Delta S = (\Delta H - \Delta G)/T \quad \cdot \cdot \cdot \cdot \cdot \quad (4)$$

$$\ln K_0 = \Delta S_0/R - \Delta H_0/RT \quad \cdot \cdot \cdot \cdot \cdot \quad (5)$$

$\Delta G$  is free energy change;  $\Delta H$ , enthalpy change;  $T$ , absolute temperature; and  $\Delta S$ , entropy change. A plot of  $\ln K_0$  versus  $1/T$  by applying equation (5) was linear. Therefore,  $\Delta S$  and  $\Delta H$  were determined

Eiichi Akaho & Masaki Kambara RJLBPCS 2017 www.rjlbpcs.com Life Science Informatics Publications from Y axis intercept and the slope of the line as shown in Table 2.

Birch et al. reported that the standard enthalpies of ion exchange interaction are generally within the range of 0.0 to 10 KJ/mol or -0.024 to 2.4 Kcal/mol.[87] The enthalpy change ( $\Delta H$ ) in the present study was obtained by plotting  $\ln K_o$  vs  $1/T$  which was linear (Figure 6).  $\Delta H$  and  $\Delta S$  (entropy change) were determined from the slope and intercept of the plot, and  $\Delta H$  was 4.23 Kcal/mol which is a little larger than the range reported by Birch et al. Plaut et al. also calculated the entropy by using poly (2-hydroxyethyl methacrylate) instead of hydroxyapatite, obtained the value of 5.02 e.u., and referred it as the driving force behind ionic interactions associated with the disruption of the hydration shells of the ions.[85,86,88] In the present system, the entropy value was 30.5 e. u. This is probably because the hydration shells of the ions in the present system is more randomly formed than the system reported by Plaut et al.[85,86,88] The small enthalpy value and the positive entropy values of 30.5 e. u. in the present system suggests that the interaction of fluoride with hydroxyapatite was mainly ionic interaction in nature.[33-35, 85,86,88]

Figure 6 Plot for  $\ln(K_o)$  versus  $1/T$  to determine thermodynamic parameters

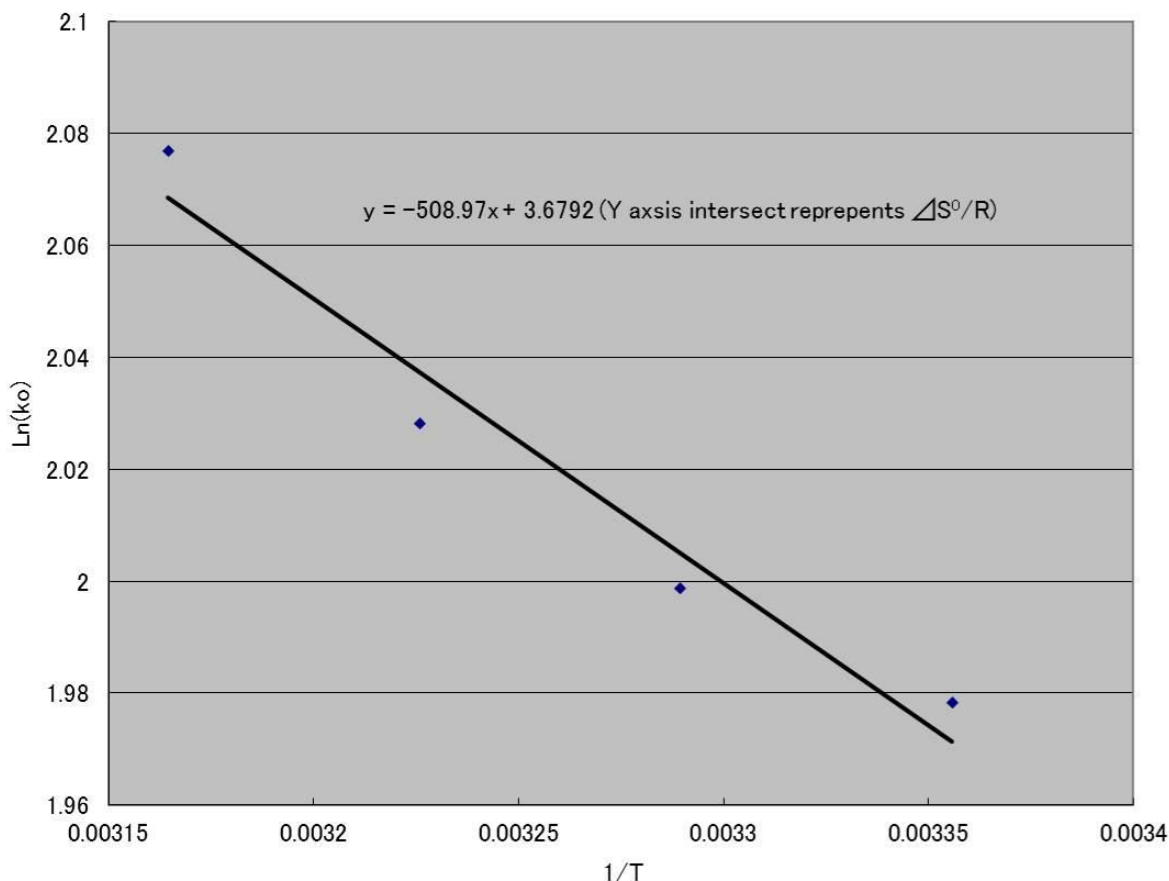


Table 2 shows the results of apparent thermodynamic functions of the adsorption of fluoride onto hydroxyapatite. The negative value of the standard free energy changes ( $\Delta G$ ) indicates that the adsorption of fluoride onto hydroxyapatite is spontaneous. The value of  $\Delta H_0$  is positive and this is

Eiichi Akaho & Masaki Kambara RJLBPCS 2017 www.rjlbpcs.com Life Science Informatics Publications characteristic to the endothermic reaction. It agreed with the previous argument in that the endothermic reaction represents an increase in  $K_0$  with rise in temperature. The value of entropy change was 30.5 e. u. suggesting that the high degree of disorderliness exists at the solid-solution interface during the adsorption of fluoride onto hydroxyapatite as is previously delineated.

Table 2. Thermodynamic functions of adsorption of hydroxyl apatite from aqueous solution containing fluoride

| Temperature(°C) | $K_0$ | $\Delta G$<br>(Kcal/mol) | $\Delta H$<br>(Kcal/mol) | $\Delta S$ (e.u.)<br>J/ mol x k |
|-----------------|-------|--------------------------|--------------------------|---------------------------------|
| 25              | 7.23  | -4.90                    | 4.23                     | 30.5                            |
| 31              | 7.38  | -5.05                    | —                        | —                               |
| 37              | 7.60  | -5.22                    | —                        | —                               |
| 43              | 7.98  | -5.45                    | —                        | —                               |

### Fluoride in the mouth and in the drinking water

An excess amount of fluoride in drinking water, which is reported in India, Brazil, and other countries, causes various detrimental effects such as dental, skeletal fluorosis, fluoride enamel opacity, bone fracture, decreased birth rates, child birth with insufficient weight, Down's syndrome, and other bone-related damages.[89,90] When one wants to use fluoride solution for hygienic purpose, he/she can rinse his/her mouth with fluoride solution of less than 100 ppm keeping it as less as possible, preferably to 20 to 30 ppm. And then one should rinse the mouth with water several times so as to achieve the fluoride concentration of 0.5 to 1 ppm in the mouth which is the WHO recommended fluoride concentration in drinking water.[91-95]

### 4. CONCLUSION

The amount of fluoride taken up by the hydroxyapatite increased up until about 150 $\mu$ moles of fluoride per gram of hydroxyapatite and then it decreased as the concentration of fluoride increased. One hundred ppm was the maximum aqueous concentration of fluoride in order for the fluoride to be taken up by hydroxyapatite. Adsorption of fluoride to hydroxyapatite was time dependent, when the fluoride concentration of 100 ppm was applied. It is postulated that ion exchange takes place between fluoride and hydroxyl group of hydroxyapatite when the concentration of fluoride solution, in which fluorapatite is held, is 100 ppm or less. This ion-exchange complex fairly well stands for a regular aqueous washing and most of fluoride in the fluorapatite is kept as intact. As the concentration of fluoride solution, in which hydroxyapatite is held and shaken, increases, fluoride forms more than one layers of calcium fluoride around fluorapatite as stacking layers. This

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fluoride stacking layers should hold together by fluoride-fluoride interaction. These stacking layers of fluoride are easily scaled off by an aqueous washing especially when the fluoride concentration in an aqueous solution is 100 ppm or more. An excess amount of fluoride in drinking water causes various harmful effects<sup>89,90</sup> It is reported that fluoride in drinking water should be kept in the range of 0.5 – 1.0 ppm, and to provide safe drinking water an excess amount of fluoride in water has to be removed by some physical methods including adsorption techniques which is most widely used.[91-95]. The value of the standard free energy changes ( $\Delta G$ ) was negative and the adsorption process of fluoride on hydroxyapatite is considered to be spontaneous. A positive value of  $\Delta H_0$  and an increase in  $K_0$  with rise in temperature are characteristic to the endothermic reaction. The value of entropy change was 30.5 e. u. suggesting that high degree of disorderliness exists at the solid-solution interface during the adsorption of fluoride onto hydroxyapatite. For the dental hygienic purpose, the concentration of fluoride should be kept at 100 ppm or less. If it exceeds 100 ppm, the fluoride will be scaled off extensively and comprehensively by rinsing the mouth with water. Since the experiment in aqueous media represents a homogeneous environment, and our study was designed to investigate the adsorption nature of fluoride to hydroxyapatite in this aqueous homogeneous environment. We hope that this result will further promote a study in saliva or other physiological heterogeneous media.

#### **CONFLICT OF INTEREST**

The authors declare that they have no competing financial or non-financial interest.

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