Effects of Some Cations on Dissolution Rate of Calcium Phosphate.

N. S. yehia ,A. M. EL Gamal

Department of chemistry, Faculty of science, Menofia University. Egypt
waelgcc@yahoo.com

Abstract: Dissolution of HAP crystals studied at   =0.6, temperature $37^{o}c$ and at I= 0.15 mal dm-3 using NaCl as electrolyte at pH= 7.4 using constant composition method. The HAP crystals prepared and confirmed using XRD, SEM, IR and chemical analysis .it was found that n 2 suggesting surface mechanism. The rate of dissolution increased with increasing PH and ionic strength of medicine. The Mg^{2+} , Zn^{2+} ,and Cd^{2+} rates of dissolution were studied . The order of inhibited the dissolution of HAP at the same conditions. the order of inhibition was; $Mg^{2+} > Cu^{2+} > Zn^{2+} > Mn^{2+} > Cd^{2+}$ the cations inhibited the dissolution by blocking the active sites on the surface of HAP crystal .From langmuir isotherm , K_L were found $12x10^{5,}$ $4.7x10^5$, $4.38 x10^5$, $3.85 x10^5$ and $1.8 x10^5$ for Mg^{2+} , Cu^{2+} ,Zn^{2+} , Mn^{2+} and Cd^{2+} respectively inhibition of the dissolution rates of HAP in the presence of Cd^{2+} was found increase with increasing ionic strength and PH of the medium . The inhibition was found to change the morphology of HAP crystals depending on the order of mixing the reagents at the begging of the dissolution process.
[N. S. yehia, A. M. EL Gamal. Effects of Some Cations on Dissolution Rate of Calcium Phosphate. Journal of American Science 2011;7(3):660-669]. (ISSN: 1545-1003). http://www.americanscience.org.

Keywords: Cations, calcium phosphate, HAP crystals, ionic strength.

1. Introduction

Hydroxy apatite (Ca_5 $(PO_4)_3OH$ HAP) is the most stable calcium phosphate salt under physiological conditions. This model compound has been used to study hard tissue calcification such as bone and teeth and in many undesirable cases of pathological mineralization of articulor cartilage [1& 2] cardiac valves [3] and kidney stones [4]. The precipitation of HAP is of great importance in a number of industrial purposes ranging from the water purification and fertilizer production.

Since hydroxy apatite is the most widely applied biomaterials various techniques have been developed to synthesize hydroxy apatite powders [5]. Alkaline earth cations present in biological fluids and in natural waters may play an important role in regulating the formation of calcium phosphate solid phases

Metallic materials have found wide application in restorative surgery as basic biomaterials for manufacturing implant pro stheses for skeletal replacement and fixtures [6]. The release rate of Ca and P from Fe – SHA (iron –synthetic hydroxyapatite) and Mn –SHA were in some cases greater than the result rates of Ca and P from pure SHA in distilled water Investigation was aimed to study the effect of Mg^{2+}, $Ca2^+$, Zn^{2+}, $Mn2^+$, and Cd^{2+} on the rate of dissolution and morphology of HAP crystals and the effects of changing the experimental conditions in the presence of additive on the rates and morphology of the HAP crystals.

2. Material and Methods:

Solutions were prepared from analytical grade chemicals (El- Naser Pharmaceutical Chemical Company) and distilled demonized water. Calcium chloride were analyzed by passing aliquots through ion exchange resin (Dewix – 50) in the hydrogen from and titrating the eluted acids with standardized sodium hydroxide solution of suitable concentration using phenolphthalein as indicator. All solutions prepared and stored in Pyrex vessels. Calcium phosphate seed was prepared in details by adding 1 L of (0.02 M) Calcium chloride solution to I L of sodium monohydrogene phosphate (0.012 M) after advanced the pH to 7.4 by using conc. HCL and the addition happen at room temperature and suddenly in 2 second. The seed solution was constantly stirred for one weak and was then filtered and the seed crystals washed with deionized distilled water to remove surface contamination due to chloride and sodium ions. The seed crystals were aged for one month then refiltered and carefully washed with deionized distilled water and this process was repeated several times. The seed was then filtered and dried. The seed crystal was characterized by X-ray powder diffraction, practical sizes, measured by single point BET nitrogen adsorption at 77 k was $0.36 m^2g^{-1}$.

3. Results and discussion:

Dissolution of HAP has already been performed to characterize the dissolution behavior of it. The term apatite describes a family of compounds having similar structures but not necessary having identical composition. HAP is the most stable phase of calcium phosphates having definite composition and definite composition and definite crystallographic structure. It is often as a proto type for bone and tooth mineral [7].

In the present work the dissolution of HAP crystals at σ = 0 – 6, t = 37°C, I = 0.15 mol dm^{-3}, using NaCl as background electrolyte, and pH = 7.4 using constant composition method which ensures that the factors which can influence, the under saturation such temperature, ionic strength and solution speciation remain constant during the entire experiments. So the rate reduction of dissolution of HAP crystals can not be attributed to alteration in HAP under saturation during the reaction.

HAP crystals are prepared; x-ray, IR, and SEM fig (1) analysis confirm the HAP structure. Chemical analysis showed the molar ratio of HAP of 1.69 using EDTA and atomic absorption for calcium and phosphate was determined spectro-photomatrically.
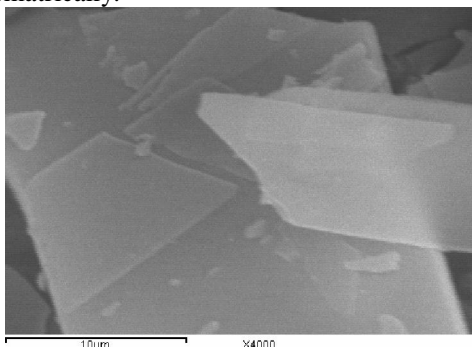
The rates of dissolution of HAP crystals, determined from the slops of lines from the plots of volume of titrant added to the cell with the time, are summarized in table (1) . Since the extent of the dissolution reaction was very small (less than 5% of the total surface area of seed crystals), so the change in the crystals surface area accompanying dissolution could be ignored. During the reaction the HAP crystals maintained their morphology as observed in SEM (fig. (1)). during experiments aliquots were drawn from time for (Ca^{2+}) and PO_4^{3-} . Each experimental were made triplicate for certainty.

Previous studies have noted that the dissolution rates of some sparingly soluble salts, such as DCPD, OCP and HAP microcrystals, decrease with the time at constant undersaturations. This was attributed to decrease in the density of active sites on the crystal surface or the smoothing of crystal surfaces [8].

The rates of dissolution of HAP crystals are plotting against the degree of undersaturation, (σ = 0.316 – 0.891) as shown in fig. (2).

The effective order of reaction was determined. Table (1) and fig (2). It can be seen that the dissolution reaction rates follow a parabolic rate law with n $\cong$ 2, which suggest surface- controlled mechanisms. For n $\leq$ 2 the suggested mechanism is transport and spiral mechanism. Previous studies showed that in dissolution of HAP, (n) = value between 4 and 6 at pH= 6.75, 6.3 and 7.15[9]suggesting poly nuclear mechanism, surface nucleation process[10, 11], surface processes combined with transport processes[12], both surface and diffusion mechanism[13,14,15] at higher temperature of 60°C, is mass transport while at lower HAP has generally been found tobe surface controlled with n>1, n>2[22-31),32,33,(34-41)]

The surface and transport mechanism over a range of relative under saturation can be supported as can be seen from table (1). From the table the rates of dissolution of HAP are independent on the changes in the rate of stirring (fluid dynamics)(exp (11) and (12)). This evidence may be inconclusive on such small particles for which changes in the stirring rate may have little influence on the fluids shear forces at crystal surfaces. The particles will tend to move with fluid flow. The rates of dissolution were also proportional to the weight of inoculating seed used to initiate the dissolution process which confirm the surface mechanism.

Table (4): Effect of under saturation on the rate of dissolution of calcium phosphate at 37°C.

Exp No		- log	R x 10^{-8}	- log R
1	0.891	0.05	35.481339	6.45
2	0.794	0.1	28.840315	6.54
3	0.70	0.155	22.6464	6.645
4	0.650	0.187	19.40886	6.712
5	0.603	0.22	17.37801	6.760
6	0.550	0.26	14.79108	6.830
7	0.501	0.3	11.29796	6.949
8	0.4	0.4	8.70964	7.06
9	0.355	0.45	6.76083	7.170
10	0.339	0.47	6.23735	7.205
11	0.316	0.5	5.55904	7.255
12	0.603			

a = stirring note = 500 rpm

The rate of dissolution of crystals in aqueous suspension is in general either controlled by surface processes, or by the transport of substance between the volume adjacent to the dissolving surface and the bulk

solution or by combination of such processes. In all cases the transport is taking with the rate controlled by diffusion (in a stagnant medium) or by convective-diffusion.
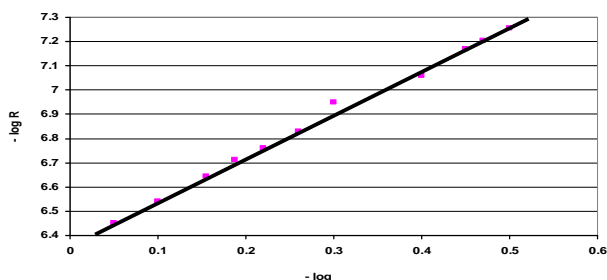
There is a change over from diffusion to convective- diffusion at about a certain crystal size, this depending on the statements is true:

(1) If surface processes are rate- controlling, the linear rate of dissolution is independent of the size of the crystals. The rate is also independent on the fluid dynamics. The concentration near the crystal surface is the same as in the bulk.

(2) If the rate is controlled by diffusion in stagnant medium, the linear rate of dissolution is inversely. propotional to the crystal radius. The rate independent of the fluid dynamics, if the mean distance between crystals is larger than about 20r. The concentration near the crystal surface is not the same as in the bulk.

(3) If convective diffusion is the determining process, the linear rate is inversely proportional to the square root of angular velocity.

White and Nancollas[13]. Found, the rate of dissolution of bovine enamel to be transport- controlled but with rate faster than expected for convective-diffusion. This was explain as a result of a couple transport of hydrogen ions inwards and dissolution product \s outwards. The rate of dissolution was found to be described by the empirical expression

$$R_d = [(HAP)_o - (HAP)] [a(H^+) + b] SD_{HAP} / \delta_N \quad ...(1)$$

Where:

R_d : is the rate of dissolution.,

S: area of enamel exposed.,

D_{HAP}: The overall diffusion coefficient.,

δ_N : The thickness of diffusion layer.,

(H^+): The activity of hydrogen ions

(HAP) is given by: $HAP = ([a^{2+}] f_2 / 5)^{5/9} [(PO_4^{3-}) f_3]^{3/9} ([OH^-] f_1)^{1/9}$

$(HAP)_o$ in saturated solution, it is independent on pH and composition of the saturated solution.

The rate of transport process is normally proportional to C - C$_o$, where "C" is bulk concentration of the dissolving substance and C$_o$ is the concentration near the dissolving surface. If transport of dissolved substance from the region near tooth surface into the bulk solution is the rate controlling process, the rate should be proportion to "C" whereas the rate given by:

Rd: $(HAP)_6 [a (H^+) + b] SD_{HAP} / \delta_N$ ....(2)

Assuming the solution next to the surface to be saturated and Ca/P = 1.67 and considering the transport of OH ions (PO_4^{3-}) ions from the surface and the transport of H$^+$ ions to the surface as a coupled diffusion phenomenon, H$^+$ ions are consumed in the boundary layer and H$_2$O, HPO_4^{2-} ions and $H_2 PO_4^-$ ions are formed. The result of this coupling is the effective distance that OH ions and PO_4^{3-} ions have to diffuse are shorted, because some the ions are transformed into other species. The effective distance the Ca^{2+} ions have to diffuse is independent of the coupling as the effective distance phosphate ions have to be diffuse if all the photolytic forms are considered as a whole. The bottle neck is the transport of H$^+$ ions to the crystalsurface. This bottle- neck is removed by using buffered solutions or by working with microcrystal [12].

Rotating disc method provided in case of dissolution of HAP about surface processes combined with transport processes [13]. For pH in the physiological pH controlled by surface processes [13].
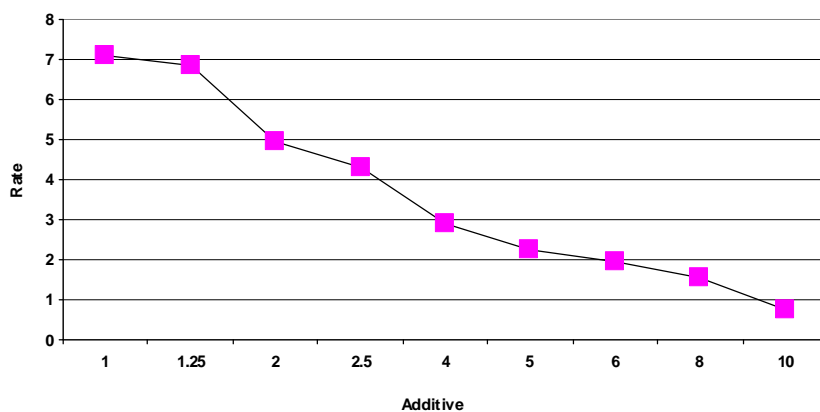
The rate of dissolution of HAP may be depend on the rate which H$^+$ ions can be delivered to the dissolving surface. H$^+$ ions as shown by Gray[21], be transported from the bulk. Solution to the crystal surface, either in the form of free ions or in the form of a weak acid which adissociates at the crystal surface. The rate-determining process for a rotating of HAP, as well as for suspensions of HAP may be:

(i)   transport of H$^+$ ions from the bulk to the crystal surface;
(ii) Surface processes;
(iii) Transport of dissolved substance from the volume or a combination of these processes [13].

Around pH = 7 about half the phosphate groups in the crystal surface should thus be in the form of hydrogen phosphate [9].

The rate controlled process can be significantly influenced by factors such as temperature, crystal size, fluid hydrodynamics and concentrations of the ionic species [22]. Surface charge is also an important property of solid. Since it can determine such processes as adsorption and surface properties. Indeed, processes such as adsorption, particularly of surfactants or macromolcules, can change the interfacial behavior of solids. Marisdly.

The affect of change of ionic strength on the dissolution Rates of HAP crystals was studied. It was found that the rates of dissolution increase with increasing ionic strength of mediums table (2) fig (3).

The equilibrium stability of HAP is greatly increased by lowering the PH of the medium. The dissolution rates of HAP crystals were found to increase with increasing PH of the medium fig(4)
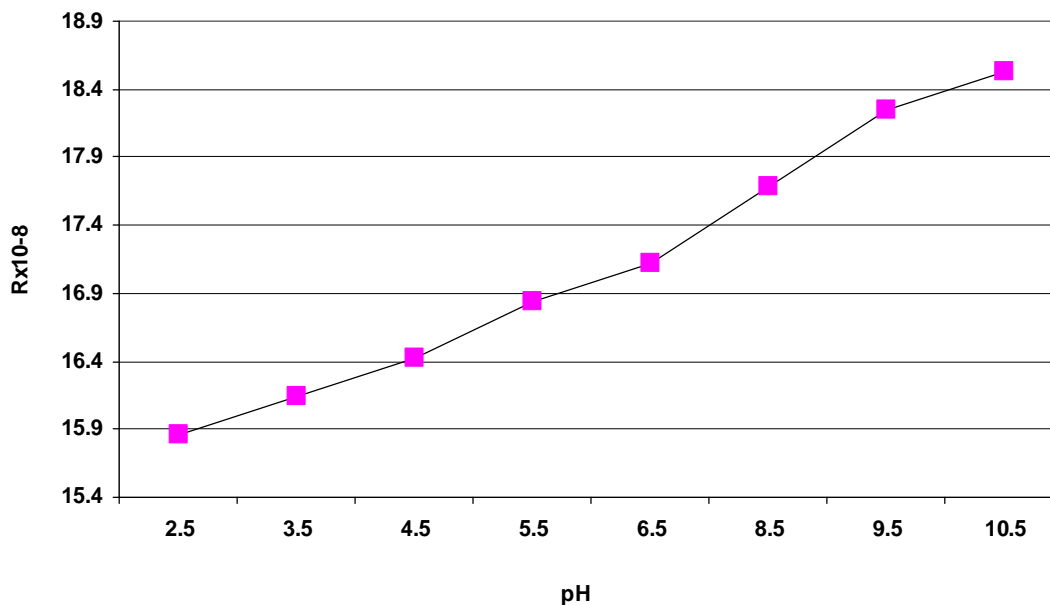
Dissolution of HAP may depend on the rate by which hydrogen ions can be delivered to the dissolving surface. Hydrogen ions may, as shown by Gray, be transported from the bulk solution to the crystal surface, either in the form of free ions or in the form of a weak acid which dissociates at the crystal surface. The rate controlling Process for a rotating disc of HAP may be

(I) trans port of hydrogen ions from the bulk to the crystal surface

(II) surface processes

Transport of dissolved substance from the volume adjacent to the crystal surface to the bulk solution. Or a combination of these processes [22] in the case of HAP , information a bout surface processes combined with transport processes .as shown later , for PH in the physiological PH range , the rate of dissolution of HAP microcrystal sin on aqueous suspension is controls by surface processes. These processes can therefore be studied without interference from transport processes by investigation such suspensions. [22]

Inhibition

The rate of dissolution of HAP crystals are studied in the presence of some cations like Mg^{2+} ,Cu^{2+} ,Zn^{2+} ,Mn^{2+} and Cd^{2+} .

The dissolution inhibition in the presence of these metal ions, the order of inhibition of dissolution of HAP crystals are in the order

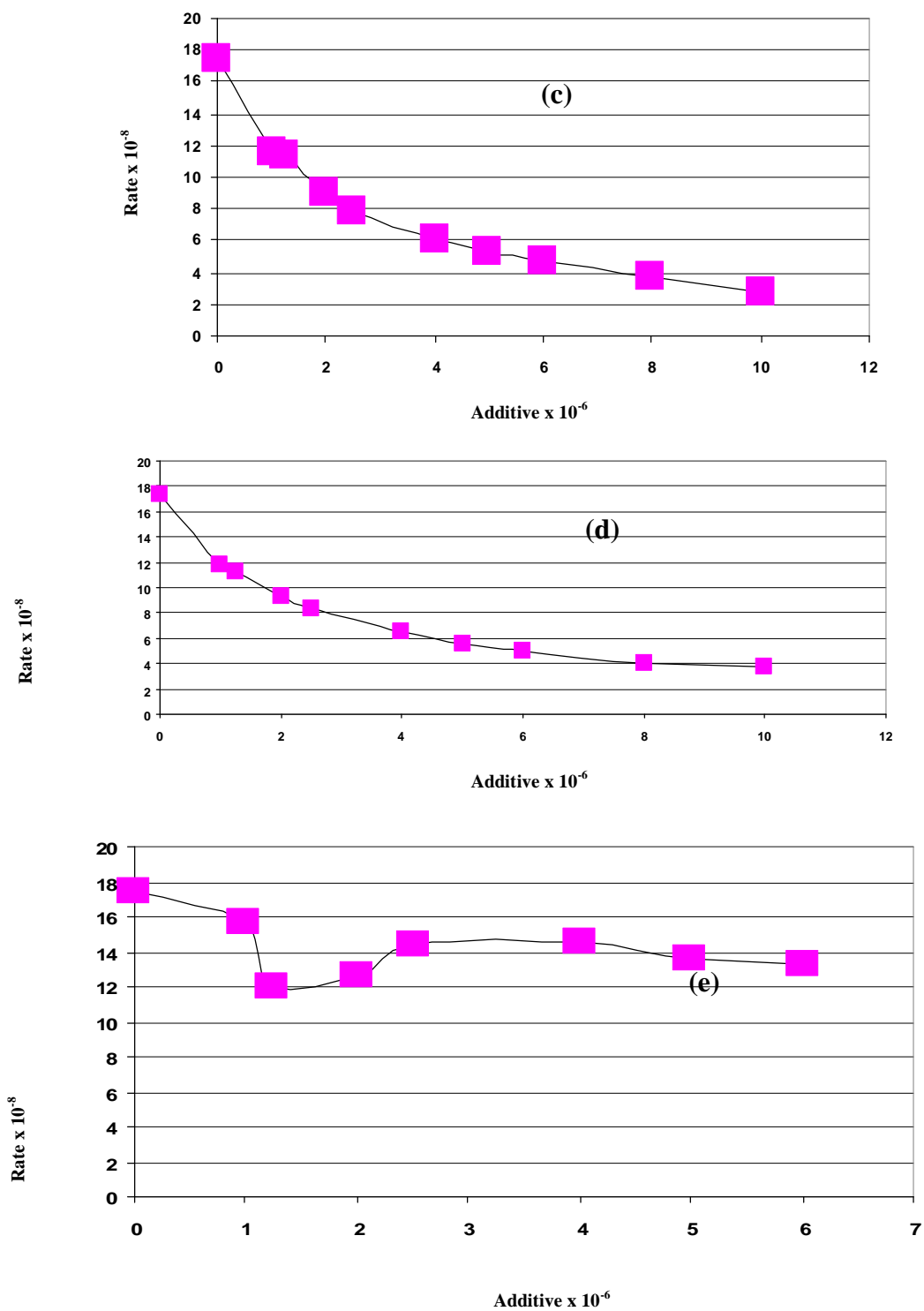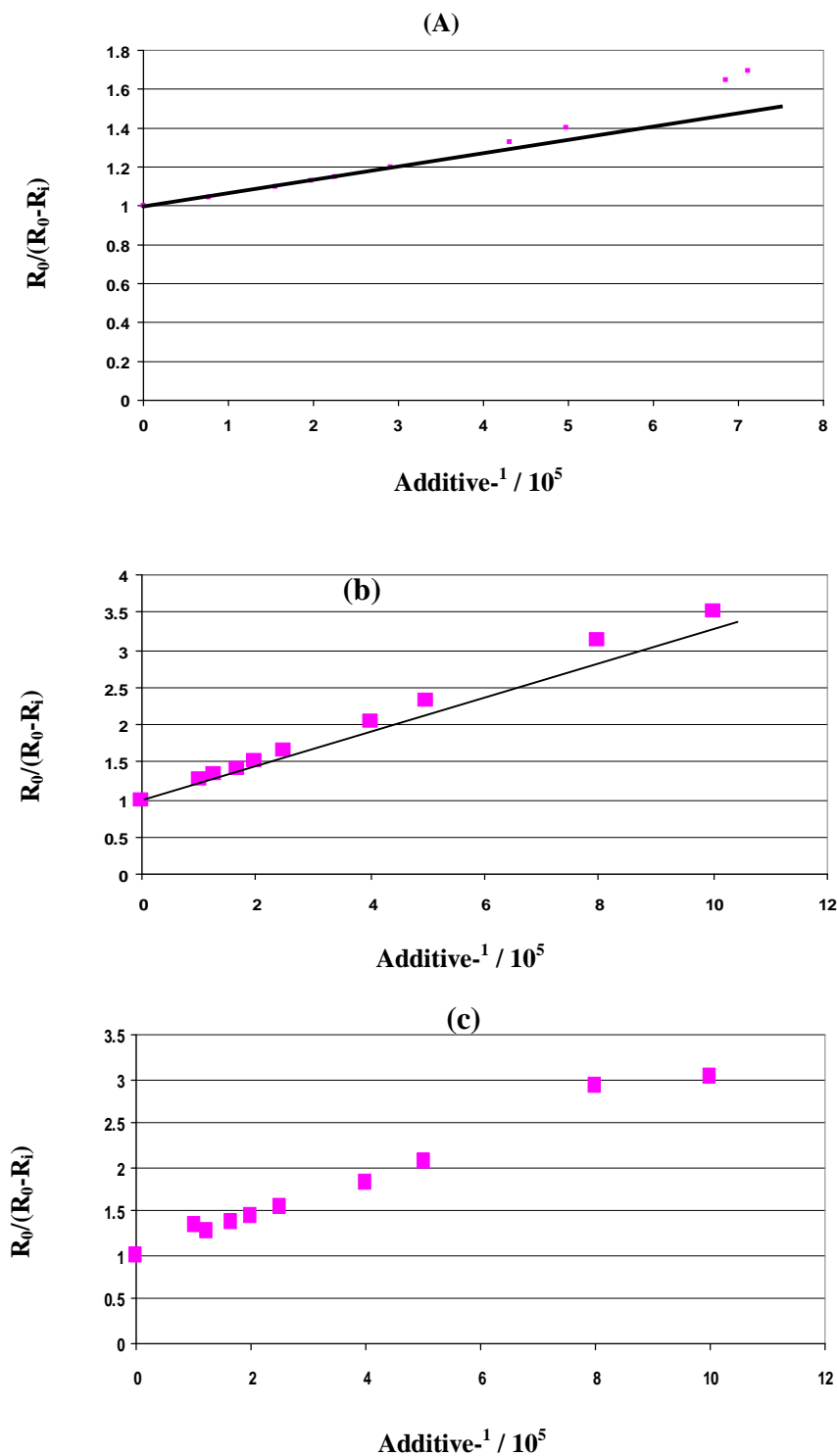$Mg^{2+} > Cu^{2+} > Zn^{2+} > Mn^{2+} > Cd^{2+}$ fig (5)

Additive x 10^{-6}
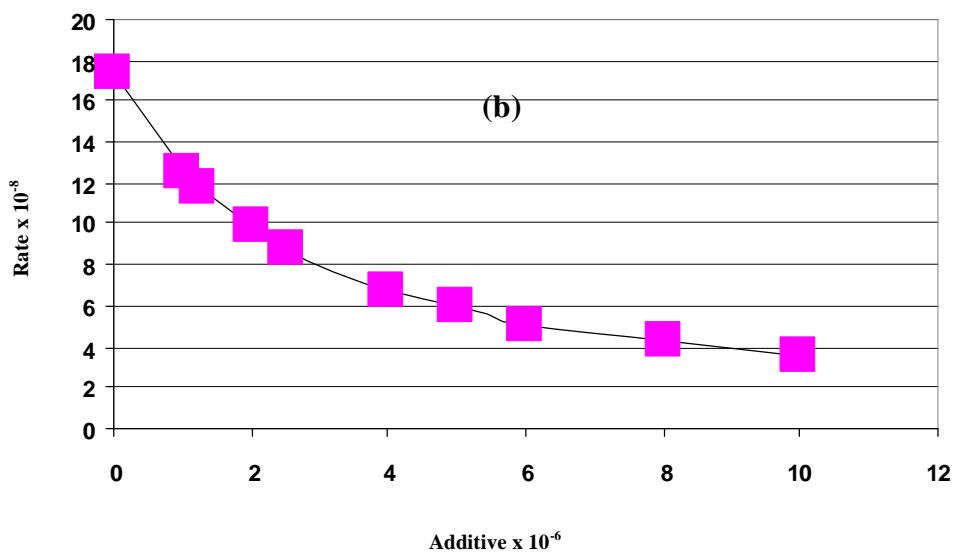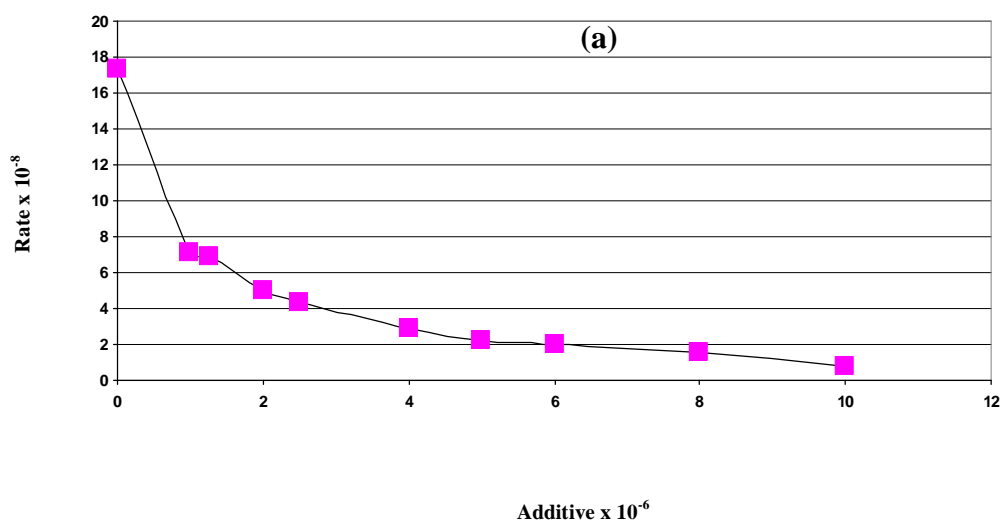
Additive x 10^{-6}

Figure 5 (a,b,c,d, e): Plot of Rate x 10^{-8} against Additive x 10^{-6} in the presence of Mg^{2+}, Mn^{2+}, Cu^{2+}, Zn^{2+},Cd^{2+}

The decrease of rate of dissolution of HAP crystals can be interpreted in terms of blocking of active sites through adsorption of the metal ions at crystal surface during dissolution this can b interpreted in terms of Langmuir isotherm. Fig (6).
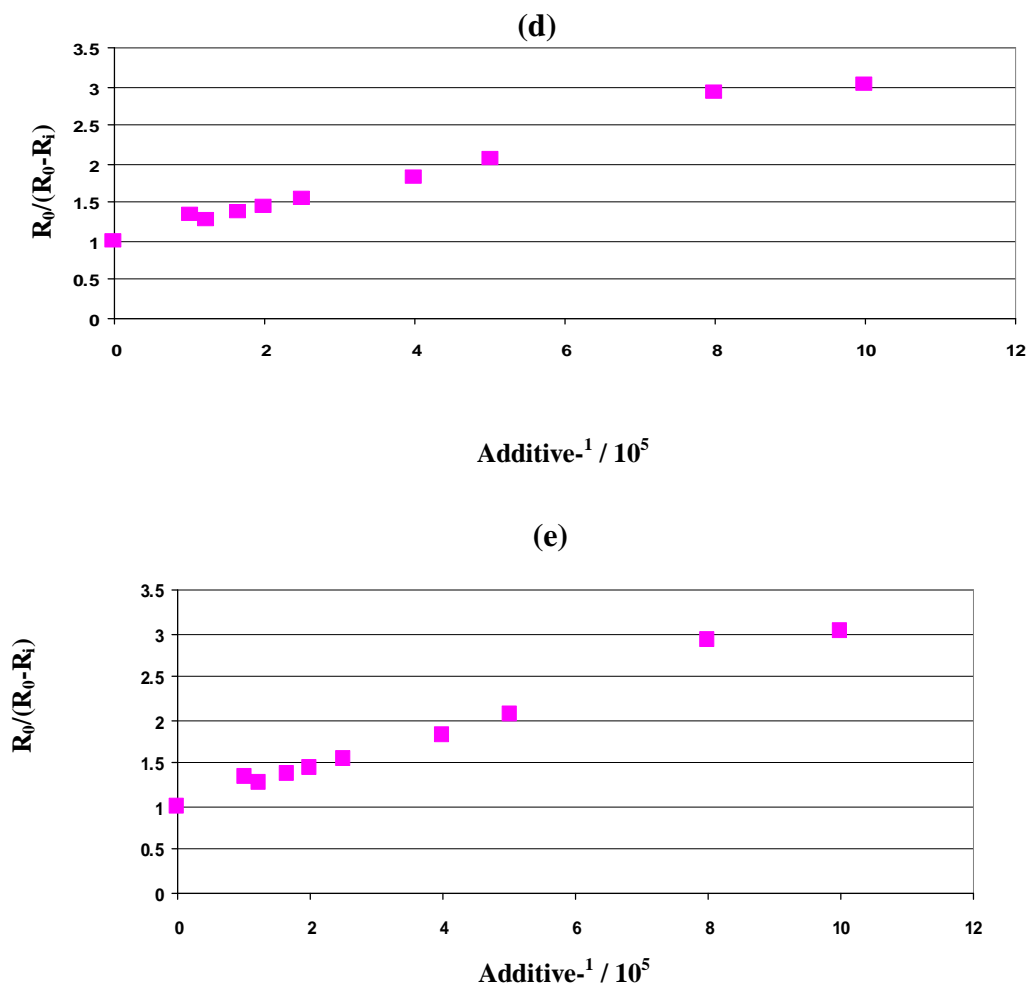
(d)

Additive^{-1} / 10^5

(e)

Additive^{-1} / 10^5

Figure 6 (a,b,c,d, e): Plot of $R_0/(R_0-R_i)$ against Additive^{-1} / 10^5 in the presence of Mg^{2+}, Mn^{2+}, Cu^{2+}, Zn^{2+},Cd^{2+}

From the fig (5) K_L= adsorption affinity constant are 12×10^5, 3.85×10^5, 4.38×10^5, 4.7×10^5, and 1.8×10^5 in the case of the presence of Mg^{2+}, Mn^{2+}, Zn^{2+}, Cu^{2+} and Cd^{2+} respectively. The radii of these metal ions are smaller than that of Ca ions and from K_{so} values of $MgPo_4$, $CuPo_4$, $ZnPo_4$, $MnPo_4$ and $CdPo_4$ are less than that of HAP so the validity of formation of their phosphate salt is big. Also the bond between Cu^{2+}, Zn^{2+}, Mn^{2+}, and phosphate ions are strong than that between Ca^{2+} and phosphate . so these metal ions are adsorbed on to phosphate active sites leading decrease the number of active sites, leading decrease the dissolution rates of HAP crystals . Cd^{2+} make strong bond with phosphate ions, but the K_{so} of $CdPo_4$ nearly equal to that of HAP and ionic radii OF Ca^{2+} and Cd^{2+} nearly the same so the affect of Cd^{2+} as inhibitor is less than the other additives.

To discus the effect of experimental condition on the inhibition activity of additive Cd^{2+} was taken as example. The effect of change of   on the rates of dissolution of HAP crystals in the presence of Cd^{2+} was studied. From fig (7)

The order was found   2 , suggesting surface controlled mechanism at active sites on the surface .
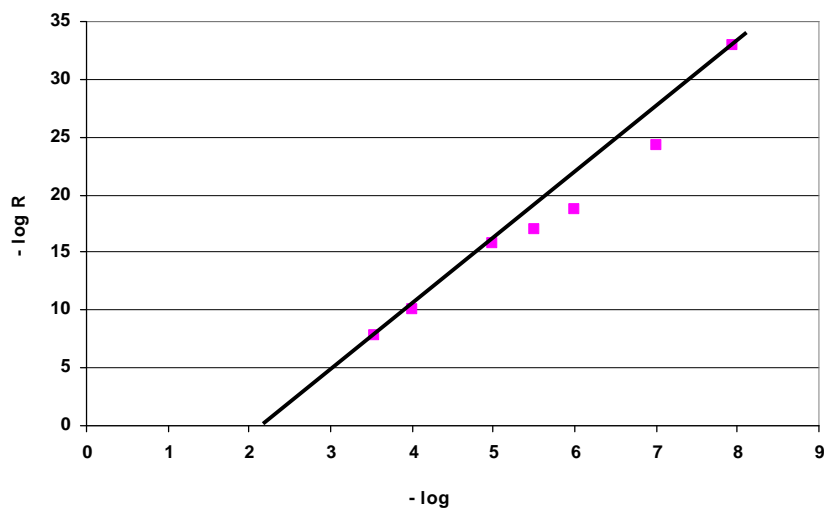
The effect of change of pH on the rates of dissolution of HAP crystals in the presence of Cd^{2+} was studied. From fig (8) was found that rate of dissolution of HAP crystals decrease with increasing the pH of the medium.
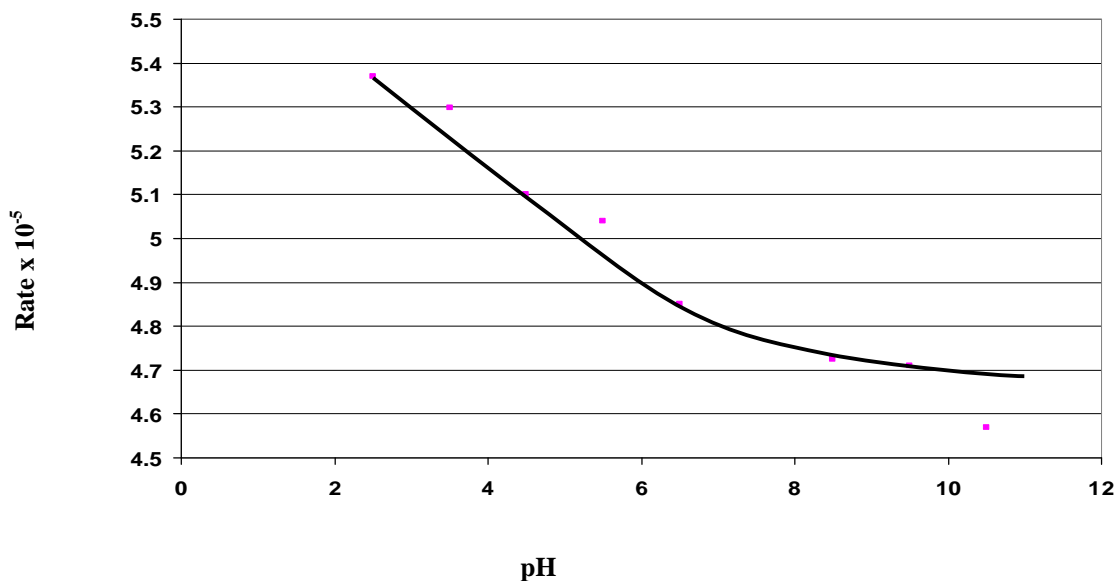
References

1- A.L. Boskey . P.G. Ballogh , Scanning Electron Micros . 28 (1984) 511.

2- C.V. Gordon, T. Villanveva , H.R . Shumacher v. J. Gohel Rheumatology 11(1984) 861

3- E. J. Schoen, R. J. Levy, Cardiol. Clin. 2(1984)713

4- G.H. Nancollas, J Crystal. Growth. 42(1977)185

5- Mosahiro. yoshimura , Pornapasujari .Jwor- akun, Fukoh , T. Fujiwara , Materials Science and Engine ringc .24 (2004)521

6- Ricardo – M. Souto, Maria M .Laz, and Rui . L. Ries . biomaterial 24(2003) 4213-4221

7- Barone , J . P. NANACOLLAS, G. H, AND TOMSON, M.JCALCIF- Tissue Res. 21 ,17 (1976)

8- E. J. Schoen, R. J. Levy, Cardiol. Clin. 2(1984)713

9- C.V. Gordon, T. Villanveva , H.R . Shumacher v. J. Gohel Rheumatology

10- G.H. Nancollas, J Crystal. Growth. 42(1977)185

11- S.Koutsopou(os, E. Dalas . J . of crystal Growth .217 (2000) 410

12- Mosahiro . yoshimura , Pornapasujari .Jwor- akun, Fukoh , T. Fujiwara , Materials Science and Engine ringc .24 (2004)521

13- H , Aoki , Science . and Mejical Application of hydroxyapatite , JASS, Tokyo ,1991

14- Barone , J . P . NANACOLLAS, G . H, AND TOMSON, M.JCALCIF- Tissue Res. 21 ,17 (1976)

15- G. H. Nancollas , Pare Appl . Chem . 64 (1992) 1673.

16- J. Christoffersen , M . R. Christoffersen, J, Crystal Growth, 43. (1978) , 501

17- M.B. Fawzi, F- L. Fox, M . G .Ded hiya, W .I. Higuchi and J. Coll. Int . Sci, 67, (1978),304

18- H.E. Buckely , In. Crystal Growth (1951)

19- G. H. Nancollas , Ceromic Tran S, l ,(1988),8.

20- J.A.Budzand . G. H. Nancollas ,J ,cryst. Growth, 91, (1988) , 490.

21- w. Joshimura , H .Suda , Hydroxyapatite and relatej Compound , CRC. Press ,Cleveland ,OH ,(1994) P45

.

22- Jorgen Christoffersen. Margarct R .Christoffersn and Niels KJAERGAAARO .J .of Crystal Growth

23- W. Suchank , M. Yoshimura , J. Mater . Res 13(1) (1998) 94-117

24- P.Koutsoukos,Z.Amjad,M.B.Tomson, and G.H.Nancllas, J.of the American Chemical society, 102,1980.

25- A. W.Bamforth "Industrial Crystallization" Macmillan Co.,N.y. ,(1966).

26- A.Van. Hook,"Crystallization theory and practice". Reinhold Publishing Co., N.Y., (1963).

27- P.E.Colld "Chemical Oceanography ",P.Diley and G. Skirrow, Eds.,A Cademic Press, N.Y., (1965)

28- K.S.Spiergler "Salt WaterPurification" Wiley, N.Y., (1962).

29- M.N.Elliot, Desalination,6,(1989),87,8,(1970),2.

30- G.H. Nancollas, A.E.Eralp and J.S.Gill,J. Ptroleum Eng., 18,(1978) 133.

31- G.H.Nancollas and M.P.Tomson, Faraday Discussions, Chem. Soc.,61,(1976),175.

32- G.H.Nancollas."Biological Mineralization" Colston Res. Symposium,Bristol, (1977),245.

3/3/3011