Influence of Some Amino Acids on the Mechanism of Dissolution of Calcium Oxalate Monohydrate Crystals

N. S. Yehia, and D. I. Saleh

Department of Chemistry Faculty of Science, Shebin El-Kom, Menofia University, Egypt.
drnaemasalem@yahoo.com

Abstract: Mechanism of dissolution of calcium oxalate monohydrate (COM) crystals was studied in the absence and presence of Argnine (Arg), Aspartic acid (Asp), Alanine (Aln) and Asparagine (AS) at 37ºC, I=0.15 mol dm^{-3} and PH=6.5 from the study,it was obtained that concentrations as low as 10^{-6} mol dm^{-3} for each additive markedly reduce the dissolution rate of COM crystals. As the concentration of additive increase, the active sites on COM crystal surface are blocked through adsorption and the rate of dissolution of crystals decreased. This confirmed from the order of reaction (n=2), the value of activation energy, 7.14 Kcal / mol, and the validity of applying Langmuir-isotherm. The values of affinity constants in the presence of Arg, Asp, Aln and As are: 7.5,6.6,5.19 and 4.17 $\times 10^5$ dm^3 mol^{-1} respectively. The values of affinity constants (K_l) reflect the high adsorption at the same value of relative degree of undersaturation ($\sigma = 0.09$), and the order of inhibition was: Arg >Asp > Aln > As. The values of ΔG supported this order of inhibition of these additives. From the study, the anionic part of the additive molecule adsorbs onto Ca^{2+} active sites on the surface of COM crystals through electrostatic attraction. The molecular weight, molecular geometry, hydrophilicty and structure of the amino acid molecules were found to be the important factors affecting on the efficiency of the them.

Key words: dissolution, COM, amino acids, adsorption inhibition.

1.Introduction:

Calcium oxalate formation has been observed in species of several genera of fungi, for instance Aspergillus, penicillium, serpul, Beauveria, Acarospora and many lichen-forming fungi. The most common calcium oxalate monohydrate are, (COM) and calcium oxalate dihydrate (COD)[1].

In kidneys, the solution is always supersaturated with respect to COM crystals and supersaturation level is characterized by the COM crystal growth rate.

Stone formation in renal systems is one of the oldest and the most common form of crystal deposition disease. Calcium oxalate is one of the major inorganic components of renal stones and is found to be present in almost all kidney and bladder stones. Calcium oxalate is one of the main constituents of deposits in urinary tract.

The exact mechanism of intiation of CaO$_x$ stone formation is not completely understood. The mechanism of CaO$_x$ renal calculi formation has attracted the medical scientists because of its widespread clinical occurance and difficulty of treatment.

Calcium / oxalate specific proteins could be involved in the initiation of renal stone formation under altered physiological conditions. In hyperoxaluric condition, protein undergo peroxidation resulting in enhanced binding with calcium oxalate.

Understanding of the interactions between the stone crystals and the components of organic matrix is an important study of urinary stone formation.

Earlier studies from our laboratory on the effect of some amino acids[3], some extracts of Egyptian medicinal plants [4-6], some organic solvents[7] and some organic compounds[8,9] on the mechanisms of dissolution and crystallization of COM crystals were established.

Amino acids are compounds of major importance for living organisms moving freely in blood circulation after digestion of proteins in the body of vertebrates. So testing amino acids as possible inhibitors is advantageous compared to other compounds used in the past. Their concentration in blood or locally in tissues is controlled by physiological mechanism such as introduction into the cell and further metabolism or through the kidney function. Further charging of the liver function needs to be avoided; a fact which is a major problem when using synthetic drugs[10].

Inhibition of stone formation is another area of active interest because in normal urine, the product of ionic calcium and oxalate concentrations is more than one hundred times the value found in saturated solutions of the salt. Amino acids has been speculated that they may act as both as nucleation modifier and growth retardant.

The present work is an attempt to study the mechanism of dissolution of COM crystals in the

absence and the presence of Arg, Asp, Aln and As at 37°C, I=0.15 mol dm^{-3}, σ = 0.09, pH=6.5 using constant- composition method.

2. Materials:

Details concerning the preparation of COM crystals have been given elsewhere[11]. The seed material was examined using XRD, SSA, FTIR and scanning electron microscope (SEM) measurements. Solutions of Arg, Aln, Asp and As were prepared using either reagent grade (fisher scientific Co.,and J. T. Baker Co.) or ultra pore Alfa chemical Co. The chemicals are dissolved in triply distilled deionized water.

Techniques:

Dissolution experiments were carried out in double-walled pyrex-glass vessel thermostated at 37°±0.1ºC. A measured volume of sodium oxalate solution was transferred to the cell followed by known volume of NaCl solution, calculated volume of additive solution, definite volume of CaCl$_2$ solution and finally definite volume of deionized distilled water. The total volume was usually 300 ml and pH was adjusted to 6.5 ± 0.05 using standard NaOH and / or HCl solution. Satisfactory stability of under saturation solution was verified by constant e mf reading for at least 30 min, using Automatic titrator (718 titrino, Mettrohm CO.). The dissolution begins by adding definite weight of COM seed. Samples were periodically withdrawn and filtered through Millipore filters for solution analysis.

3. Results and Discussion:

Dissolution reactions are very important in technical and physiological systems. In the present study, COM crystals prepared and its structure elucidated using TGA, FTIR, XRD and SEM.

For many sparingly soluble salts Ma Ab, the rate of dissolution normalized for seed surface area, can expressed by equation:

$$R= [Ma\ Ab] / dt = k\ S\ \sigma^n \qquad (1)$$

Where:

k: is dissolution rate constant

S: is proportional to the number of dissolution sites available on seed crystals.

n: is the effective order of reaction.

σ: is the relative degree of undersaturation.

$$\sigma = (IP/K_{sp})^{1/n} \qquad (2)$$

Where:

IP:is the ionic product;the product of the activities of cation and anion.

K$_{sp}$:is the solubility product of the sparingly soluble salt at equilibrium.

The thermodynamic solubility product (Ksp):

$$K_{sp} = [Ca^{2+}]\ [C_2O_4]^{2-}.\ F_{Ca2+}.\ F_{C2O4}^{2-} \qquad (3)$$

Where:

F_{Ca}^{2+} and F_{C2O4}^{2-} are activity coefficient of Ca^{2+} and $C_2O_4^{2-}$ respectively

The activity coefficient of divalent cation or anino were assumed to be equal, so using extended Debye – Huckel equation proposed by Davis, F, can be determined.

$$Log\ f_2 = AZ^2\ (I^{1/2}/(1+I^{1/2}) - 0.3I^{1/2}) \qquad (4)$$

Where:

Z: is the charge of the ion (valence).

I: is molar ionic strength

A: is constant which can be calculated from the equation

$$A: 0.492 + 0.00063t + 0.0000054t^2 \qquad (5)$$

where: t is the temperature at which the reaction occur.

$$\sigma: ([Ca^{2+}]_t – [Ca^{2+}]_{eq}) / [Ca^{2+}]_{eq} \qquad (6)$$

Assuming at first approximation, simple spherical or Cubic particles, corrections were made for changes in the surface area during the dissolution reactions. But since the extent of dissolution reaction was very small (less than 5% of the total surface area of seed crystals)., the change in crystal surface area accompanying dissolution could be ignored.

Dissolution of COM crystals in the absence of additives:-

COM structure elucidated using TGA, FTIR, XRL and SEM.

The effects of change of degree of undersaturation, σ =0.07-0.2, the rates of dissolution of COM crystals at 37ºC, pH=6.5 and I=0.15 mol dm^{-3} were studied using constant- composition method. Dissolution experimental conditions are summarized in table (1), in which T$_{Ca}$ and T$_{ox}$ are total molar concentration of calcium and oxalate respectively.

Table(1): Dissolution of calcium oxalate monohydrate (COM) crystals, T$_{ca}$: T$_{ox}$=1:1, at t=37^{0}c and ionic strength, I=0.15 mol dm^{-3} using emf.

Tca/10-4 mol dm-3	10^{-2} σ	Seed/mg	Rate/10-8 mol min^{-1}m^2
1.854	7.0	10	1.990
1.794	10	10	5.093
1.714	14	10	8.217
1. 814	9.0	10	3.160
`1.814	9.0	50	3.135
1.814	9.0	90	3.120
1.814	9.0	100	3.118
1.814	9.0	200	3. 110
1.814	9.0	500	3.100
1.814	9.0	700	3.150
1.814(a)	9.0	10	3.069
1.814(b)	9.0	10	3.102

(a):stirring rate 300 rpm (b):stirring rate 500rpm

Plotting of – log R against – log σ is illustrated in fig (1). From the figure, the order of dissolution reaction of COM crystals (n) was found to be equal ≈2,which suggests that the dissolution of COM crystals follow surface- controlled mechanism.The independence of dissolution rates of COM crystals on the fluid dynamic (Table (1),(a)and(b)),supports the suggestion of the surface mechanism.
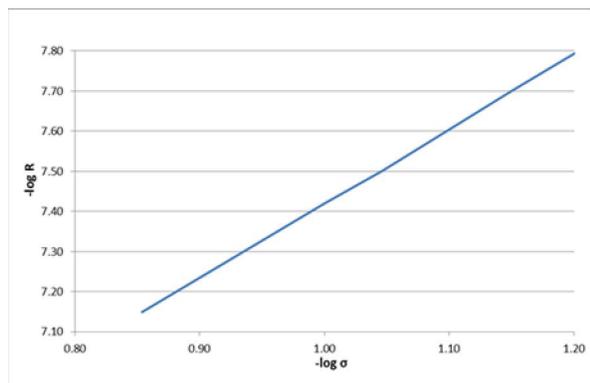

Fig. (1): Plots of – Log R against –Log σ for dissolution of calcium oxalate crystals at 37ºC

The effect of change of temperature on the rates dissolution on COM crystals illustrated in fig (2).

Linear relationship obtained with slope corresponding to the activation energy (Ea), Ea= 7.14 K cal / mol. The low value of Ea, supported the suggestion of surface- controlled mechanism.
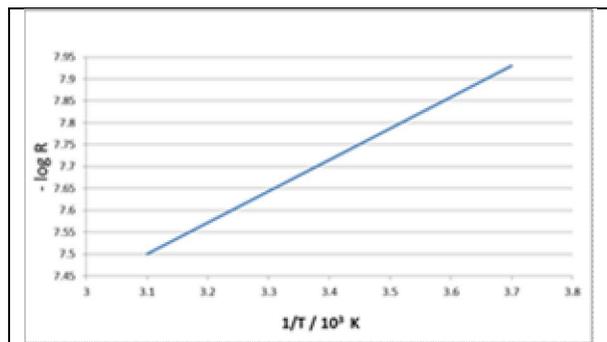

Fig. (2): Plots of – Log R against 1/T for dissolution of calcium oxalate crystals at σ= 0.9 using EMF

The effect of change of the values of ionic strength of the medium on the rates of dissolution was studied. It was found that the rates of dissolution of COM crystal increasing by increasing the value of ionic strength of the medium.

Dissolution of COM crystals in the presence of amino acids:

Natural materials contain impurities which are released by dissolution disintegration of the mineral there exist two possibilities:-
   i.   The impurities are released into the solution, from which they are adsorbed reversibly to the surface of the mineral acting there as inhibitors.
   ii. They are adsorbed irreversibly at the surface either directly from the disintegrating mineral or they are first released in the solution from which they are adsorbed to the surface [12].
      In case of (i),the surface concentration is related to impurity concentration in the solution by an adsorption isotherm.But the case (ii),complete irreversible binding released impurities to the universal surface was assumed, so the impurity concentration becomes zero. Increase of reversible adsorption of inhibitors should be reduced significantly.

In crystallization process, the additives have two functions: they inhibit crystal growth by binding themselves to the growth sites of the crystals; they enhance the heterogeneous nucleation, controlling and stabilizing the precipitated polymorph. It is generally accepted that the effect of minor amount of additives on the precipitation kinetics of mineral salts can be attributed to their preferential adsorption on the solid surface [13].

Additives may have number effects on the process of dissolution and crystallization:
1-changethe characteristics of adsorption layer of solid-liquid interface,
2-be adsorbed on the crystal surface physically and block the active dissolution or growth sites,
3-interactchemically with crystal surface to form complexes,
4-alter the surface charge or surface energy of the crystals.

The quality and intensity of the effect of amino acids on dissolution and precipitation of calcium oxalate depend on the concentration and chemical structure of these compounds It has been speculated that,the amino acid may act as both nuclear modifier and growth retardant in crystallization process by:
 1- Ion binding of amino acid with calcium or oxalate ions and subsequent change in growth rate, affects the crystal morphology. or
 2- Adsorption of amino acids on the specific crystal faces, can alter the nucleation rates of faces and control subsequent expansion of interpenetrants[14].

From the present study, the dissolution of COM crystals followed surface-controlled mechanism and the dissolution process affected by the ionic strength of the medium i.e it is electrostatic in its nature.So anions are adsorbed at cationic sites on COM crystal surface and vice versa. Anions slow dissolution of

COM crystals by adsorbing on crystal surface in competition with oxalate ions, so reducing the number of empty sites receive dissolving lattice oxalate anions.

Surface is a boundary across which, there is a difference in concentration of some essential chemical constituent and across which there is in general an electrostatic potential difference associated with some kind of charge double layer. No surface could exist in true thermodynamic equilibrium; surface is at best steady state condition to which thermodynamic reasoning applies.

In heterogeneous reactions of solid- liquid systems, the soluble reactants diffuse across the interface and/or through the porous solid layer. Subsequently, chemical reactions occur, followed by desorption of soluble products, which diffuse away from the reaction surface. These steps take place consecutively, and one or more of them may be the rate-determining step [21].

The dissolution of number of sparingly soluble hydrated salts has been shown to be controlled by the diffusion of lattice ions from the crystal surface into the bulk solution.For anhydrous salts,however, the reaction may be controlled by taking place at.In these cases the rate of reaction is considerably smaller than that calculated on the basis of diffusion,following Fick, s law,of lattice ions away from the surface and for which the linear rate of dissolution will be inversely proportional to the crystal radius. For surface-controlled dissolution, the rate will be independent 0f the size of the crystals and of the fluid dynamics. Moreover, the concentration of electrolyte near the crystal surface will be the same as that in the bulk solution. In contrast to a bulk diffusion reaction, the surface polynuclear process is markedly inhibited by the presence of additives[22].

When a nucleus develops and transformations into a crystal, it exhibits different faces, the growth mechanisms and growth rates at which depend not only on the external factors (supersaturation, impurities, etc) but also on the internal factors (structure, bonds and defects).Discussion of the influence 0f crystal structure on the growth mechanism is very important to understand the growth state equations. For doing this periodic bond chain (PBC) theory must illustrated.This theory assumed that growth is a result of consecutive formation of strong bonds between growth units. A PBC is an uninterrupted chain of strong bonds which repeat periodically through the crystal. For complicated structures, there are three types of PBC, s, the complete PBC being the one which has the same composition as the crystal and electrostatic dipole moment perpendicular to the direction along which it

runs. According to this concept, three types of faces may be found in a crystal:

-F face (flat): they have PBC,s in at least two different directions in a slice of thickness d_{hkl} (interreticular distance;

-S faces (stepped): they contain only one PBC in the slice d_{hkl};

-K face (kinked): they contain no PBC in the slice d_{hkl}.

Since K faces contain only kinks, i.e growth sites, they grow by direct incorporation of atoms or molecules.Since F faces are flat, the number of kinks is very small in contrast with K faces.The growth rate of F faces should be much smaller than the growth rate of K faces.The S faces are intermediate between these two limiting cases.

When growth takes place in the presence of growth rates of the crystal can be greatly affected [23].

The effect of the inhibitor may be described as the prevention or strong retardation of the nucleation of etch pits in the areas around the adsorbed inhibitor.Due to interaction with inhibitor,lattice ions in these areas will be strongly attached to the crystal surface,the whole crystal may be inactivated and no dissolution will occur.Prevention or retardation of dissolution may occur by preferential adsorption of the inhibitor molecules at the edges of their development beyond the critical size [22].

Depending on the surface coverage, Θ, the rate of dissolution in the presence of additive (R_I) is given by:

$$R_I = R_0 (1 - \Theta) \qquad (7)$$

At the experimental conditions of the present work it was found that concentration of 8×10^{-6} mol.dm^{-3}, of Arg indicate complete inhibition.The fraction of the effective seed crystal surface covered by Arg molecules was only 1.6% assuming monolayer adsorption. The almost complete inhibition of dissolution indicates that only relatively small number of sites on the seed crystals was available for dissolution, this again points to surface-controlled dissolution mechanism. Adsorbed molecules could rotate freely around an axis vertical to the crystal surface and thus, the effective volume of a cone. There is, however, a special case, relatively characteristics of long- chain compounds, that pertains when the impurity is long –chain molecule, possessing many adsorption sites. Adsorption on the crystal is then never completely reversible. The impurity is always anchored at the crystal surface at several points [23].

The values of K_{ads} in case of the presence of Arg,Asp,Aln and As were calculated.These values supported the order of inhibition of the additives under study table(3), The driving force, ΔG, of dissolution process may be expressed as the free

energy of transfer from undersaturated solution to equilibrium.The values of ΔG in the presence of Arg,Asp Aln and As are summarized in table (3).
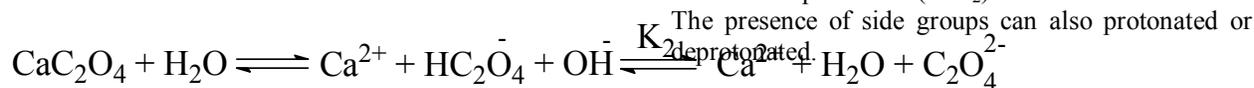
By similarly, cationic part of the additive molecule may adsorb on COM crystal surface competing with calcium ions on the surface, reducing their numbers on the surface.

The mechanism of dissolution of COM crystals in the presence of Arg,Aln, Asp and As was studied at the same experimental conditions of $\sigma = 0.09$, t = 37ºC, I=0.15 mol dm^{-3} and pH= 6.5 using constant-composition method. Fig (3), indicates typical plot of the dissolution rates of COM crystals against concentration of Arg,Asp,Aln and As at $\sigma = 0.09$. It was found that at concentration as low as 10^{-7} mol dm^{-3}, the inhibition values were 45.44, 42.24, 37.1 and 27.47% in case of the presence of Arg, Asp, Aln and As respectively which suggest order of inhibition of: Arg > Asp > Aln > As.

In absence of additive and during dissolution process of COM crystals at the conditions of study it was found that after 10 minutes the pH of the solution was found to increase from 6.5 to 6.87. This indicates that the free H$^+$ was also depleted. This suggested that the dissolution of COM water system was:
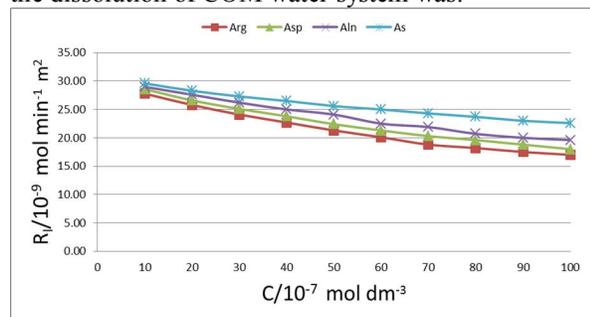
Fig(3) plots of rate of dissolution of calcium oxalate against additive for Asp, Arg, Aln and As.

/ or hydrogen bond[15]. Some specific anionic molecules in normal human urinc, inhibit this interaction by coating the COM crystal surface to prevent cell adhesion. Negatively charged macromolecules inhibit growth and aggregation of calcium oxalate crystals occurs most likely through calcium ions on the crystal surface [16].

The presence of a foreign compound in the supersaturated solution in which the HAP growth process is taking place, results in an interaction of the solute species with the precipitating solid When the solute species have functional groups as carboxyl and / or amino groups, they may adsorb reversibly onto the HAP crystal surface, which contains centers of positively and negative charged ions[10].

Incorporation of flurophores on growth of COM crystals indicated that dianionic and nonanionic species of these flurophores are present in the crystal growth solutions the negative charge on carboxyl and hydroxyl on the flurophores could also be attracted to positively charged calcium ions of the lattice.

Amino acids may be:-
  i. Non polar amino acids ex alanine.
  ii. Polar amino acids with positive charge ex arginine.
  iii. Polar amino acids with negative charge ex. aspartic acid.

The structure of amino acids depends on the pH of the solution in which they dissolved:-
  1. At low pH:- all acid groups (-COOH) are protonated, all amino groups are protonated (-NH$_3$).
  2. At neutral pH:- all acid groups are deprotonated (-COO$^-$), all amino groups are protonated(-NH$_3$).
  3. At high pH:- all the acid groups are deprotonated(-COO$^-$), all amino groups are deprotonated(-NH$_2$)

The presence of side groups can also protonated or deprotonated.

$$CaC_2O_4 + H_2O \rightleftharpoons Ca^{2+} + HC_2O_4^- + OH^- \xrightarrow{K_2} Ca^{2+} + H_2O + C_2O_4^{2-}$$

So the effective sites on COM crystals are $C_2O_4^{-2}$ and Ca^{2+}. Amino acids have carboxyl and amino groups, these functional groups may adsorb reversibly onto COM crystal surface, which contains centers of positively and negatively charged ions.

Cell – crystal interaction is one of the major mechanisms of COM crystal adhesion at anionic sites on the surface of renal tubular cells. Several surface anionic molecules on renal tubular cell membranes may be responsible for this interaction. This cell-crystal interaction, may be due to ionic interaction and

The actual structure of amino acids is ionic and depends on pH of solution. The predominant form of amino acid depends on the pH of the solution: in acidic solution, the – COO$^-$ group is protonated to free –COOH, and the amino group is protonated to –$^+$NH$_3$, and the amino acid molecule has an overall positive charge. As the pH raised, the –COOH group loses its proton at about pH=2. This point is called PKa$_1$,. As the pH is raised further, the –$^+$NH$_3$ group loses its proton at about pH = 9 or 10. This point is called PKa$_2$. A bove this pH, the amino acid molecule has an overall negative charge.

(Cationic in acid)   PKa$_1$=2   neutral PKa$_2$= 9-10   (aminoic in base)
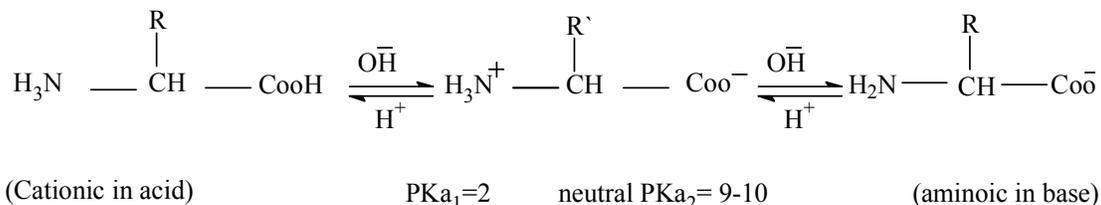
So, the amino acid bears a positive charge in acidic solution and negative charge in a basic solution. At intermediate pH, the amino acid is balanced between two forms, as dipolar zwitterion, with net charge of zero. In fact the acid part of amino acid molecule is (- $^+NH_3$) group not (-COOH) group and the basic part of the molecu11e is (-COO$^-$), not free (-NH$_2$).

The iosoelectric point of amino acids (pt), depend on the structure of them:
1. Acidic amino acids example aspartic acid pt=3
2. Neutral amino acids: pt=(5-6.3).
3. Basic amino acids example argnine:(pt=10.8).

At (pt), the amino acid has net charge of zero. Amino acids with non – polor side chain, have pt=4.8-6.3.

Acidic amino acids, are negatively charged at physiological pH, present as conjugate bases.

Polar uncharged, acidic and basic amino acids are hydrophilic the polar uncharged amino acids have polar side-chain are hydrophilic in its nature and can form H-bonding example, asparagine:-
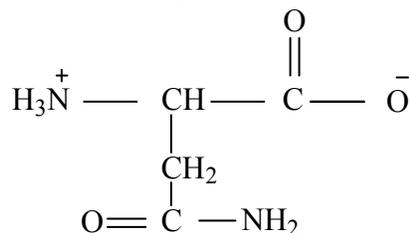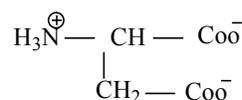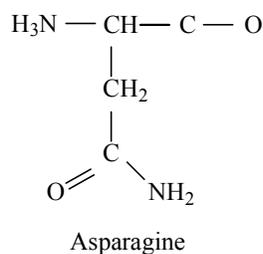

At physiological pH (7.3), the amino acid exists as a dipolar ion, z witter ion.

Amino acid	PKa$_1$,α-COOH	PKa$_2$ α-NH$_2$	PKa side - chain	pt
Argnine	2.17	9.01	12.48	10.67
Aspartic acid	2.09	9.82	3.86	2.77
Alanine	2.34	9.69	-----	6.01
Aspargine	2.02	8.84	------	5.41

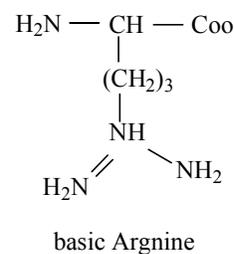At the pH of study (pH=6.5), zwitterions. At pH:-
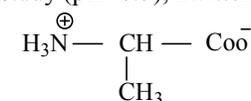
Charge= zero = neutral alonine

net charge = -(amionic form) Aspartic acid

Asparagine

basic Argnine

Arg and Asp at pH of study are charged and hydrophilic so, adsorbing on Ca^+ ion active sites of COM crystals through electrostatic attraction scince, the dissolution rates of COM. Crystals are affected by the change in the ionic strength of the medium which means that, dissolution is ionic in its nature. Inhibition may be due to the adsorption of $-COO^-$ groups on Ca^{2+} ions on the surface of COM crystals not through $-NH$ or NH_2 groups. This was proved from our previous study in which, the hydrazides of aniline and its derivatives when used as additives in dissolution of COM crystals they had little inhibitory effect than the aniline and its derivatives in spite of the increasing number of $-NH$ and $-NH_2$ in the hydrazides of them(8,9).

The amino acid adsorbed on Ca^{2+} ion sites, on the surface of COM crystals, blocking them and reducing their numbers and reducing the rates of dissolution of the crystals.

The change of ionic strength of the medium from this study affect the rate of dissolution of COM crystals which means that the adsorption of the amino acid onto Calcium ions of COM crystal surface is electrostatic interaction.The crystallization of hydroxyapatite in the presence of polymer containing $C\equiv N$ functional group was investigated.

It was found that the polarity of $-C=N$ bond in which negative charge is sighted towards the nitrogen atom suggested that, the positively charged Ca^{2+} ions was attracted by electric field[19].

In general, inhibitor molecules exert their influence through adsorption at active dissolution sites on the crystal surfaces. Anionic side chain group may be adsorbed at cationic (Ca^{2+}) sites and inhibit the dissolution when present at very low levels. The adsorption can be interpreted in terms of a Langmuir – type isotherm leading to an equation of the form:-

$$R_o / (R_o - R_I) = (K_L C)^{-1} \qquad (8)$$

Where:

R_o and R_I are the rates of dissolution in absence and the presence of inhibitor respectively.

K_L: is affinity constant.

C: is the concentration of the additive.

Typical plots according to the last equation, fig(4), confirmed the applicability of this simple adsorption isotherm at $\sigma = 0.09$. The value of K_L were: 7.5, 6.6, 5.19, and 4.17×10^5 dm^3 mol^{-1} were calculated from the slope of lines in case of the presence of Arg, Asp, Aln and As respectively. These values reflect the high adsorption affinity at low undersaturation in the presence of these additives which runs in the order.

Arg > Asp > Aln > As

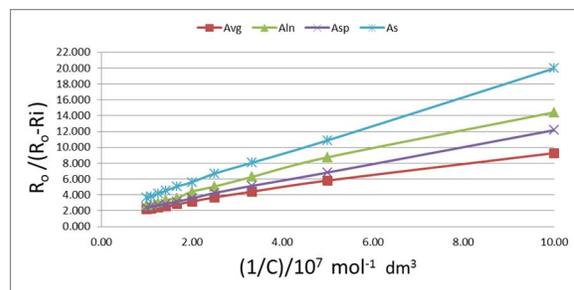**Fig (4) Plots of $R_o/(R_o-Ri)$ against [additive]$^{-1}$ of dissolution of calcium oxalate in precence of Arg, Asp, Aln and As.**

If the inhibitor molecules are adsorbed on the crystal surface between the advancing dissolution steps, the reaction can proceed provided that the adjacent adsorbed molecules are separated by a distance greater than that of the critical etch pit [20].The effect of the inhibitor may be described as the prevention or strong retardation of the nucleation of etch pits in areas around the adsorbed inhibitor or molecules. Due to interaction with the inhibitor, lattice ions in these areas will be strongly attached to the crystal surface. If sufficient inhibitor molecules are adsorbed onto the surface, the whole crystal may be inactivated and no dissolution may occur by preferential adsorption of the inhibitor molecules at the edges of the subcritical etch pits forming on the surface, thus preventing their development beyond the critical size.

Adsorption from solutions containing several ions is complicated process associated with the competition of at least; the two solvent and the solute species. The surface of the mineral attracts the counterions in the solution, and a layer is formed, which is firmly attached around the particle, called the stern layer. Additional counterions are also attached by the surface, but they are repelled immediately by the stern layer as well as by other counter ions trying to approach the particle. This dynamic equilibriums induces the formation of a diffuse layer of counterions whose concentration is high near to the surface; however it is gradually decreased with the distance reaches equilibrium with the counterions in the solution. In addition, there is a lack of Co-ions in the neighborhood of the particle, since these ions are repelled by the surface[21]. The surface charge of calcium oxalate would be either due to either the hydrolysis of surface ions or the adsorption od species like $(HC_2O_4^-, C_2O_4^{2-}, Ca^{2+}, CaHC_2O_4^+, OH^-$ and H_3O^+ formed in the solution during its dissolution. Such species play a more or less important role in the surface charging mechanism; however Ca^{2+} and CO_3^{2-} are considered to be important surface ions.

Table(2): Values of surface coverage, Θ, in case of the presence of Arg, Asp, Aln and As at σ =0.09, t=37⁰c, 10^{-7} mol.dm⁻³ additive, I= 0.15 mol dm⁻³ and pH =6.5 using emf.

conc/10^{-7} mol.dm⁻³ (1)-Arg	R_I/10^{-9} mol.min⁻¹.m²	Θ /10^{-2}	C_{inh} /Θ /10^{-5}
100	17.0	45.4	2.20
90	17.5	43.8	2.05
80	18.2	41.6	1.92
70	18.8	39.7	1.77
60	20.1	35.5	1.69
50	21.3	31.6	1.58
40	22.7	27.2	1.47
30	24.1	22.7	1.32
20	25.8	17.2	1.16
10	27.8	10.8	0.93
(2)-Asp			
100	18.0	42.2	2.37
90	18.8	39.7	2.27
80	19.6	37.1	2.16
70	20.3	34.9	2.01
60	21.3	31.6	1.89
50	22.4	28.1	1.78
40	23.8	23.6	1.69
30	25.1	19.5	1.54
20	26.6	14.6	1.37
10	28.6	8.2	1.22
(3)-Aln			
100	19.6	37.1	2.69
90	20.0	35.2	2.51
80	20.7	33.6	2.38
70	21.9	29.8	2.36
60	22.5	27.8	2.16
50	24.1	22.7	2.21
40	25,0	19.8	2.02
30	26.2	15.9	1.89
20	27.6	11.4	1.75
10	29.0	6.9	1.44
(4)-As			
100	23.0	27.5	3.64
90	23.0	26.2	3.44
80	23.7	23.9	3.34
70	24.3	22.0	3.18
60	25.0	19.8	3.04
50	25.6	17.8	2.80
40	26.5	15.0	2.67
30	27.3	12.4	2.42
20	28.3	9.2	2.18
10	29.6	5.0	1.99

Table (3): Values of K_{ads} and ΔG,in dissolution of COM crystals using some amino acids at experimental conditions using emf.

Additive	K_{ads} /10^4 J/mol	Δ G KJ/mol
Arg	12.05	- 40.5
Asp	9.26	- 39.8
Aln	7.14	- 39.1
AS	5.70	- 38.6

Conclusion:-

1. Dissolution of COM crystals were studied using constant - composition method.
2. Dissolution of COM crystals at experimental conditions of t=37ºC, I=0.15 mol dm^{-3},σ=0.09 and 0.01g of seed was followed surface-controlled mechanism.
3. The effect of some amino acids, Arg, Asp, Aln and As on the mechanism of dissolution of COM crystals was studied.
4. Concentration as low as 10^{-7} mol dm^{-3} reduced the rates of dissolution of COM crystals by 45,42,37 and 27% in case of the presence of Arg, Asp, Aln and As respectively.
5. The low values of concentration of inhibitor effectively reduced the dissolution rates of COM crystals,indicates the surface adsorption of inhibitor molecules on the active sites on the surface of the COM crystals.
6. The validity of applying Langmuir - isotherm, supported the physical adsorption of the inhibitor molecules on COM crystal surface.
7. The effect of change of the values of ionic strength of the medium on the rates of dissolution of COM crystals, indicating that the adsorption of inhibitor molecules on active sites of COM crystals are ionic in its nature.
8. The anionic part of inhibitor attracted to the Ca^{2+} active sites on COM crystal surface decreasing their numbers and decrease the dissolution rates.
9. The molecular weight, the molecular geometry, hydrophilicity and structure of the additive molecules are the main factors affecting the efficiency of the amino acids used in this study.
10. At concentration of 8×10^{-6} mol dm^{-3}, in case of the presence of Arg additive for example, complete adsorption of the additive molecules occur on COM surface and only 1.6 % of the COM crystal surface, covered by Arg molecules, assuming monolayer adsorption. Relatively small number of sites on COM crystal surface available for dissolution, again points to surface – controlled dissolution mechanism.
11. The values of K_{ads} and ΔG supported the order of inhibition: Arg > Asp > Aln > As

This order of inhibition supported by the high values of affinity constants; 7.5, 6.6,5.19 and 4.17×10^5 dm^3 mol^{-1} in case of the presence of Arg, Asp, Aln, and As respectively.

12. The high values of affinity constants in the case of the presence of these additives reflects that they are good inhibitors of dissolution of COM crystals at experimental conditions of the study.

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