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Crystallization of calcium sulfate crystals in simulated conditions of drinking water treatment

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Abstract: Mechanism of crystallization of calcium sulfate dihydrate (CSD) crystals was studied in the absence and presence of some amino acids; threonine (Thr), methionine, (Meth), asparagine (Asp), tyrosine, (Tyr) and alanine (Ala,) at t = 25 °C, ionic strength = 0.3 mol dm^{-3}, δ=1.32 and pH=7.5 from the study, it was obtained that concentrations as low as 10^{-5}mol dm^{-3} for each additive markedly reduce the crystallization rate of CSD crystals. As the concentration of additive increase, the active sites on CSD crystal surface are blocked through adsorption and the rate of crystallization of crystals decreased. This confirmed from the order of reaction (n=1), the value of activation energy, 250 Kcal / mol, and the validity of applying Langmuirisotherm. The values of affinity constants K_L were found 31.1, 25.00, 7.143, 5.00 and 2.19 x10^5 KJ/mol in case of the presence of Thr, Meth, Asp, Tyr and Ala respectively. The values of affinity constants (K_L) reflect the high adsorption at the same value of relative degree of supersaturation (δ = 1.32), and the order of inhibition was: Thr> Met > Asp > Tyr > Ala. 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 CSD 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.
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Key words: crystallization, CSD, amino acids, adsorption inhibition.

1. Introduction

Calcium sulfate minerals (i.e., gypsum, anhydrite and hemi-hydrate) are common scale-deposit minerals in water treatment plants [1-4] and oil and gas industry [5]. Crystallization of calcium sulfate dihydrate (gypsum) is of importance in view of their applications in a number of industrial and environmental precipitation processes. With increasing temperature, the solubility of all calcium sulfate forms decreases. This is the cause of calcium sulfate scale formation on heat transfer surface [6]. Crystallization can take place on foreign substance dust particles in the solution and it is very difficult to dust particles in the solution and it is very difficult to reproduce the results of such studies [7]. Earlier, many authors studied the growth of seed crystals of gypsum in super-saturation solutions [8 - 12], crystallization of gypsum on other crystal surfaces [13] and the precipitation on heated metal surface [14]. The factors that govern this mechanism of precipitation and dissolution of the sparingly soluble salts are therefore, of considerable interest, especially the influence of anions and cations which may exert a marked effect on the rate of precipitation, either through adsorption or by lattice substitution [15]. The present work aims at studying the Crystallization of calcium sulfate crystals in simulated conditions of drinking water treatment in case absence and presence some amino acids additives.

2. Experimental procedure

Analytical grade chemicals

Grade glassware and doubly distilled deionized water were used. Solutions of carbonate free sodium hydroxide (J. T. Baker chemical company) and hydrochloric acid (El-Naser pharmaceutical chemical company) were prepared. Solutions of calcium chloride (Fisher Scientic Company) and sodium sulfate (Baker chemical company) were prepared by weighing suitable amounts of the salts and dissolving in a definite volume of deionized distilled water. These solutions were then filtered through Millipore filter pads (0.22m, Millipore filters), quantitatively transferred to grade a volumetric flasks and diluted to the required concentrations using deionized distilled water concentration of CaCl2 was determined using atomic absorption and using cation exchange resin (Dowix-50). Na2SO4 concentration was determine dusing flame photometry.

Preparation of CSD crystals

The seed of CSD crystals were prepared and subjected to XRD, SEM, FTIR, TGA and chemical analysis.

Preparation of inhibitors:

Solutions of threonine, methionine, asparagine, tyrosine and alanine were prepared by taking suitable weights of reagents and dissolved in desired volumes of deionized distilled water.

The desired concentrations were prepared by diluting the stock solutions of the amino acids.

Crystallization experiments

Crystallization experiments of CSD crystals in the presences of additives were carried out as follows: in water thermostated double - walled pyrex glass vessel using potentiostatic measurements. Potentiostatic method used Metrohmcombititrator (model 718 stat titrino). Emf measurements were made by calcium ion – selective electrode in conjugation with Ag-AgCl electrode.

In crystallization experiments in the presence10^{-7}mol dm^{-3}, a measured volume of Na_2SO_4 was transferred to the cell followed by definite volume NaCl solution, then slow addition of known volume $CaCl^2$ of solution and the total volume of the cell completed using the suitable volume of deionized distalled water. The crystallization reaction starts by adding a suitable weight (0.05g) of prepared seed crystals. After the end of some experiments in the presences Thr, the precipitates were collected and exposed to analysis.

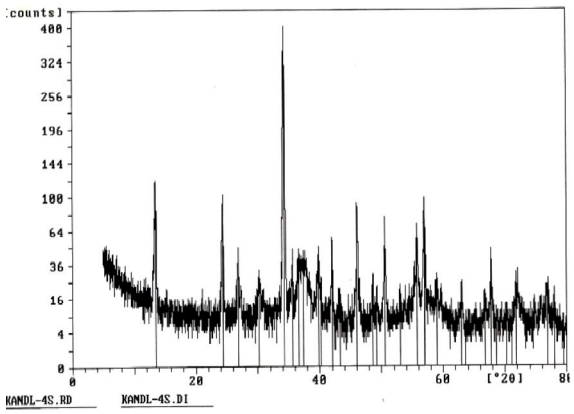


Fig (1): X-ray diffraction patterns of calcium sulfate dihydrate crystals

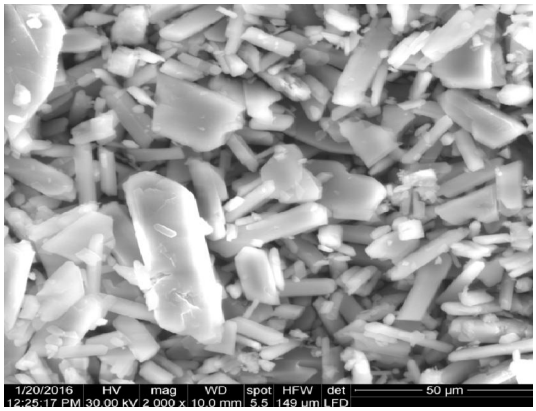


Fig (2): SEM micrographs of calcium sulfate dihydrate crystals

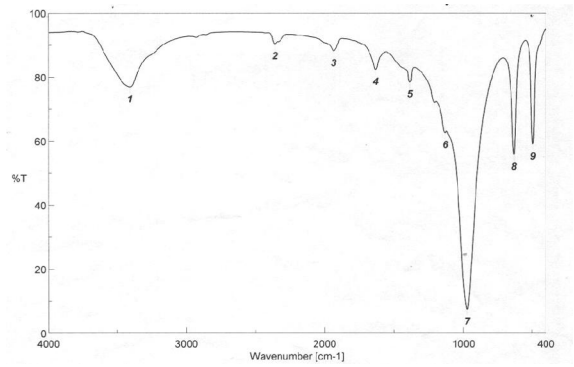


Fig (3): IR spectrum of calcium sulfate dihydrate crystals

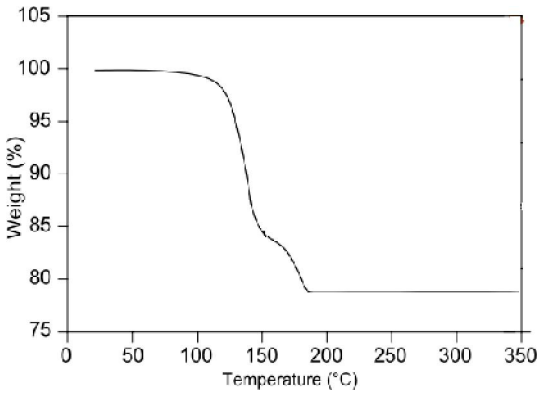


Fig (4): TGA of calcium sulfate dihydrate crystals

3. Results and Discussion

Concentrations of the ionic species in the mixed solutions of sodium sulfate and calcium chloride at any instant during the scaling experiments were computed by successive approximations for the ionic strength, I, as described previously [16] using activity coefficients calculated from the extended form of the Debye–Hückel equation proposed by Davies [17]. The rate of precipitation, R, may be expressed in terms of the degree of saturation by equation (1):

$$R = dm / dt = Rs\,\delta^{n} \qquad (1)$$

in which, m is the number of moles precipitated in time t. R, is the rate constant, n is the effective order

of reaction, and s is proportional to the number of growth sites available on the seed crystals. The degree of supersaturations is defined in terms of ionic products and solubility products for the calcium sulfate dihydrate salt as in equation (2):

$$\delta = \frac{(IP)^{1/2} - K_{SO}^{1/2}}{K_{SP}^{1/2}} \qquad (2)$$

Where, IP is the ionic products, and, K_{SP} is the solubility product, are expressed in terms of the appropriate activities of the ionic species [$(Ca^{2+})(SO_4^{2-})]^{1/2}$ at time, t, and at equilibrium, respectively.

The supersaturated degree of (δ) of the solutions, which is defined as the ratio of the activity products divided by the thermodynamic solubility product of the mineral (K_{sp}), is

$$\delta = \left\{ \frac{(Ca^{2+})(SO_4^{2-})}{K_{sp}} \right\}^{1/2} - 1 \qquad (3)$$

Where, parentheses denote to the activities of the respective ions and, $K_{sp,}$ is the thermodynamic solubility product of the precipitating solid. The activity coefficients of divalent cations and anions were assumed equal and were obtained using the extended Debye-Huckel equation of Davies: [18].

$$-\log f_Z = 0.5115 \; Z^2 \left\{ \frac{I^{1/2}}{\left(1 + I^{1/2}\right)} - 0.3 \; I \right\} \qquad (4)$$

Where "f" are the activity coefficients for the, Z, valent ions and, I is the solution ionic strength. The value of K_{sp} was calculated as a function of temperature by means of the following relationship obtained by Marshall and Shlusher[18] for calcium sulfate dihydrate in aqueous solutions from 0 to 110°C.

$$\log \left(K_{sp}\right) = 390.9619 - 152.6246 \; \log T - \frac{12{,}545.62}{T} + 0.0818493 \; T \qquad (5)$$

Crystal growth experimental conditions are summarized in TABLE 1 in which [Ca]t and [SO4]t are the total molar concentration of calcium and sulfate, respectively. Typical time plots of the amount of gypsum permoles precipitate, calculated from the titrants addition.

Table (1): The Crystallization of CSD crystals, T_{ca}^{2+}: T_{SO4}^{2-} = 1: 1 at t = 25 °C, 50 mg seed, 200 rpm, I = 0.3 mol dm^{-3} and pH = 7.5.

Exp. No	$T_{Ca^{2+}}$ x10^{-5} mol. dm^{-3}	Wt of seed g	δ	Rx10^{-6} mol min^{-1} m^{-2}	logδ x10^{2}	-log R
1	2.10	0.05	1.10	2.8000	04	5.5500
2	2.20	0.05	1.20	2.8500	08	5.5400
3	2.32	0.05	1.32	2.9400	12	5.5300
4	2.40	0.05	1.40	3.4200	15	5.4600
5	2.50	0.05	1.50	3.4670	18	5.4500
6	3.00	0.05	2.00	4.1680	30	5.3800
7	3.10	0.05	2.10	4.5490	32	5.3420
8	3.20	0.05	2.20	4.7863	34	5.3280
9a	2.32	0.05	1.32	2.9530	12	5.5297
10b	2.32	0.05	1.32	2.9682	12	5.53521
11c	2.32	0.05	1.32	2.9878	12	5.5399

9a, 10b and 11 c, experiments, the Stirring rates were 200, 400 and 500 rpm respectively.

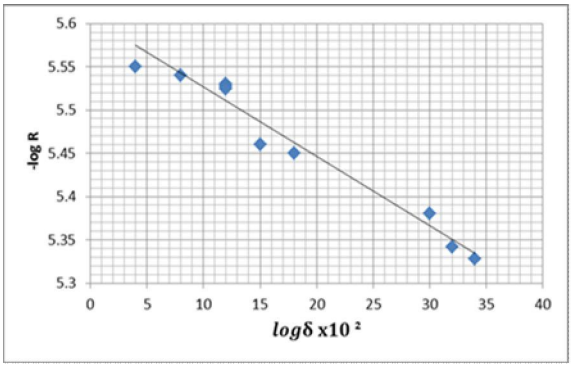


Fig (5): Plots of log R against log δ at t = 25 °C, 200 rpm, 50 mg seed, I = 0.3 mol dm^{-3} and pH = 7.5.

The results cited in TABLE 1 show that the rate of crystal growth of calcium sulfate dihydrate was proportional to the mass of seed crystals used to initiate the reaction. The suggestion of a predominantly diffusion mechanism over a range of relative supersaturations may also be supported by the observed dependence of the experimental rate of precipitation on changes in fluid dynamics, as shown in TABLE 1 (compare experiments a, b, c and d), which conclude that the reaction is a mass transfer limited [19]. A similar mechanism for the crystal growth of calcium sulfate dihydrate has been observed [19, 20]. The effective order of reaction was determined from the slope of typical plots of -log R against logδ, as depicted in Figure 1 which confirms a

first-order dependence upon relative supersaturation (n = 1) in Eq. (1).

The effect of change of degree of supersaturation, δ, on the rates crystallization on CSD crystals illustrated in fig (6). It was found that, increasing the degree of relative supersaturation (δ) lead to increase in the crystallization rates of calcium sulfate dihydrate crystals.

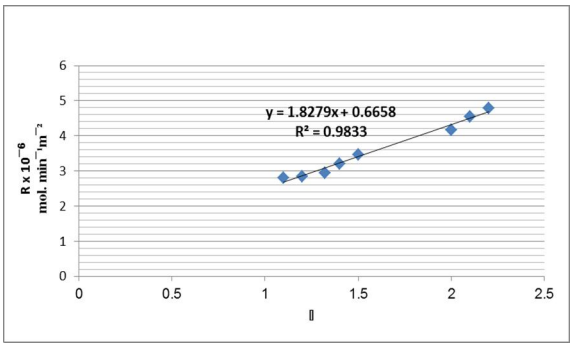


Fig (6): Effect of the degree of supersaturation, δ, on the rates of crystallization of CSD at t = 25 ° C, 200 rpm, 50 mg seed, I = 0.3 mol dm^{-3} and pH = 7.5.

The effect of change of pH of the medium on the crystallization growth of calcium sulfate dihydrate crystals in aqueous solution at 25°C I = 0.3 mol dm^{-3}, δ =1.32, weight of seed 50 mg and stirring rate = 200 rpm was studied at pH range (2 - 11).

From figure (7), the rates of crystallization on CSD crystals nearly independent on the change of the pH values of the medium in the present study. The effect of change of the pH values of the medium on, the rates of the crystallization of calcium sulfate dihydrate crystals is very low:

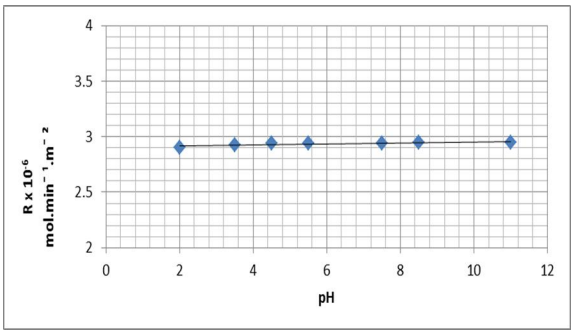


Fig (7): Effect of pH values of the medium on the rates of the crystallization of CSD crystals at t = 25°C, δ = 1.32, I = 0.3 mol dm^{-3}, 200 rpm and 50 mg seed.

The effect of stirring speed on the rates of crystallization of calcium sulfate dihydrate crystals has been examined by using 50 mg of seed crystals of calcium sulfate dihydrate, at temperature (25°C), solution (pH = 7.5), ionic strength (I = 0.3 mol dm^{-3}) and a relative supersaturation (δ = 1.32) while the stirring speed ranged from 200 - 500 rpm.

From the results, it was found that, the rates of crystallization of calcium sulfate dihydrate crystals increased from 2.9530 to 2.9878 mol min^{-1} $m^{-2}$by increases of stirring speed from 200 to 500 rpm. This ruled out that crystallization of calcium sulfate dihydrate crystals at 25 ° C, solution (pH = 7.5), ionic strength (I= 0.3 mol dm^{-3}) follow diffusion mechanism.

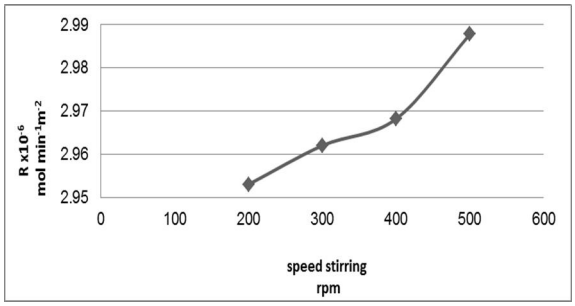


Fig (8): plot of stirring speed and the rate of crystallization of CSD crystals at t = 25 ° C, δ = 1.32, pH = 7.5, I = 0.3 mol dm^{-3} and 50 mg seed.

The effect of change of the ionic strength of the crystallization medium on the calcium sulfate dihydrate crystallization rates was studied in figure (9).

From the Figure (9), it was clear that as the ionic strength increased from 0.05 to 0.5 mol dm^{-3}, the calcium sulfate dihydrate crystallization rates increased from 2.578 to 3.061 mol min^{-1} m^{-2}. This means that, increasing the ionic strength of medium, increased the transport of Ca^{2+} and SO_4^{-2} ions from bulk to the surface of calcium sulfate dihydrate crystals leading to increasing of the rates of crystallization.

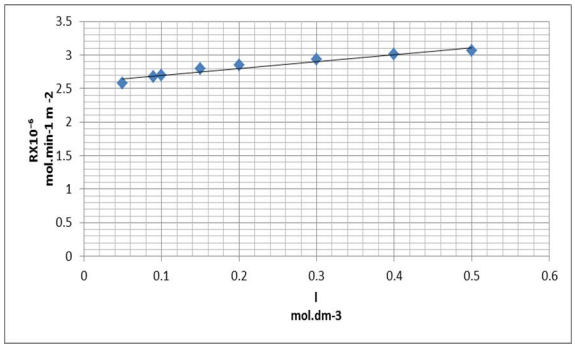


Fig (9): Plot of rates of crystallization of CSD crystals and The values of the ionic strength of the medium at t = 25° C, δ = 1.32, pH = 7.5, 200 rpm and 50 mg seed.

The effect of change of temperature on the rates crystallization on CSD crystals illustrated in fig (10).

It was found that the rates of crystal growth of calcium sulfate dihydrate crystals increased by increasing the temperature. From the figure, the activation energy of calcium sulfate dihydrate Ea_1 was calculated and found to be equal to 250 cal /mol. The lower value of activation energy supported the diffusion mechanism of crystallization of calcium sulfate dihydrate crystals.

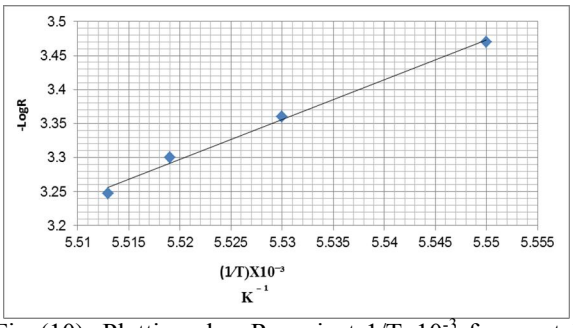


Fig (10): Plotting -log R against $1/Tx10^{-3}$ for crystal growth of calcium sulfate dihydrate crystals at δ = 1.32, pH = 7.5, 300 rpm, I = 0.3 mol dm^{-3} and 50 mg seed.

Study of the rates of crystallization of calcium sulfate dihydrate crystals in presence of additives (some amino acids):

After drinking water treatment, there still present sulfate ions in it. The presence of Ca^{2+} or Mg^{2+} will form sulfate precipitates. It has been reported that large gypsum crystals are obtained in the presence of high sulfate concentration and thick crystals at low supersaturation ratio [21]. Sulfates are an important species and its mobility in natural. Systems are restricted by its conversion to organo-sulfer compounds and to precipitation. High sulfate content in most natural systems including fresh water peat are related to that presence of sulfate-enriched water [22].

Proteins are known to play a key role in regulating bio mineralization by controlling the shape, size and often the phase of inorganics crystals. Amino acids act as strong chelating agent which their advantages are the capability to be adsorbed on organic solid [23].

Previous work on the effect of amino acids on dissolution and crystallization of some sparingly soluble salts (ex. CaO_x, $CaCO_3$, HAP, CSD), illustrated that these amino acids were good inhibitors. [21-25].

Amino acids are compounds of major importance for living organisms moving freely in blood circulation after digestion of proteins in the body vertebrates. So testing amino acids as possible inhibitors are advantageous compounds to other compounds used in the past [25].

Additives may have number effects on the process of dissolution and crystallization:

1-change the 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-interact chemically 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.

2- Adsorption of amino acids on the specific crystal faces can alter the nucleation rates of faces and control subsequent expansion of inter penetrants [23].

In the present study, the effect of threonine, (Thr,), methionine, (Meth,), asparagine, (Asp,), tyrosine, (Tyr,) and alanine, (Ala,) on the rates of crystals growth of CSD crystals at conditions simulated to that of water treatment (t = 25 °C, pH = 7.5, and I = 0.3 mol dm^{-3}) was studied.

From fig (11), it was found that at concentration as low as 10^{-5}mol dm^{-3} decreased the crystallization rates of calcium sulfate dihydrate crystals by at least 31.30, 20.89, 17.520, 13.43 and 10.680 % in the presence of Thr, Meth, Asp, Tyr and Ala respectively, compared to that in the absence of them at the same relative supersaturation (δ = 1.32). The effect of low concentration of that additives on the rates of crystallization of calcium sulfate dihydrate crystals, indicate that they are good inhibitors. The order of inhibition of rates of crystallization of calcium sulfate dihydrate crystals in presence of these additives was:

Thr> Met > Asp > Tyr >Ala

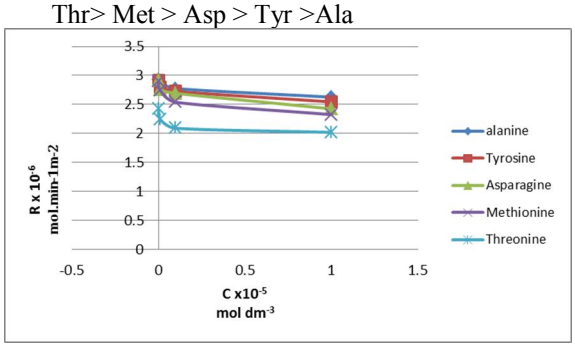


Fig (11): Effect of Thr, Met, Asp, Tyr and Ala on the rates of crystallization of CSD crystals, T_{ca}: Tso4 = 1: 1 at t = 25 °C, δ = 1.32, 50 mg seed, 200 rpm, I = 0.3 mol dm^{-3} and pH = 7.5.

The mechanism of crystallization of CSD crystals in the presence of additives under study:

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.

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 the surface of the crystals rather than by a transport mechanism. 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 wills be independent of 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.

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 of 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 dipolemoment perpendicular to the direction along which it runs. According to this concept, three types of faces may be found in a crystal:-F faces (flat): they have PBC, s in at least two different directions in a slice of thickness dhkl (inter reticular distance;

-S faces (stepped): they contain only one PBC in the slice dhkl;

-K face (kinked): they contain no PBC in the slice dhkl.

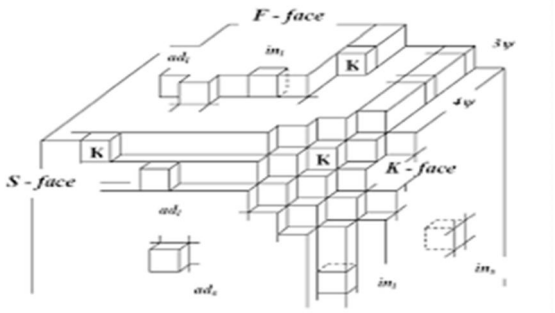


Fig (12): Schematic representation of a crystals exhibiting flat (F), stepped (s), and kinked (K) Faces. Front face exhibits a poly-gonized growth spiral, whereas top face exhibits a two-dimensional nucleus.

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. 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].

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 [23 - 26].

There are many previous studies on the inhibitory effect of some amino acids on the dissolution or crystallization of some sparingly soluble salts. 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:-

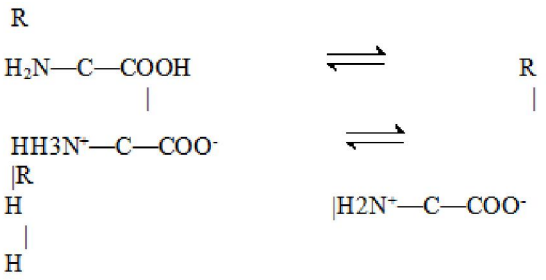
1. at low pH: -all acid groups (-COOH) are protonated, all amino groups are protonated (- $^{+}NH_3$).

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 cans also protonated or deprotonated. 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 rose, the–COOH group loses its proton at about pH = 2.

This point is calledPK_{a1}. As the pH is raised further, the –$^{+}NH_3$ group loses its proton at about pH = 9 or 10. This point is called PK_{a2}. An above this pH, the amino acid molecule has an overall negative charge.



(Cationic in acid) PK_{a1}=2 neutral PK_{a2}= 9-10 (anionic 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 zwitter ion, 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 molecul1eis (-COO^-), not free (-NH_2). The isoelectric 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 arginine: (pt = 10.8).

At (pt), the amino acid has net charge of zero. Amino acids with non – polar 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:-

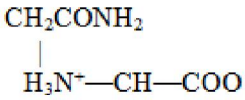


Table (2) some parameter of the amino acids under study.

Amino acid	p_{Ka1} α-COOH	p_{Ka2} α-NH2	p_{Ka} Side -chain	P_t	Molecular weight
Thr	2.09	9.10	–	5.60	119.119 g/mol
Meth	2.13	9.28	–	5.71	149.210 g/mol
Asp	2.01	8.80	10.76	5.41	132.120 g/mol
Tyr	2.20	9.21	10.46	5.70	181.190 g/mol
Ala	2.35	9.87	–	6.11	089.090 g/mol

Inhibitor decreases the rates of the dissolution or crystallization of some sparingly soluble salts by different mechanisms:

1- By competitive of the cationic or anionic active sites depending 0n the chemical structure and charge of the additive molecule or ions. example, competition between citrate and oxalate, ions to bind to Ca^{2+} ions active sites on calcium oxalate crystals [27].

2- By chemical reaction forming complex with the cation active sites on the sparingly soluble salts.

3- By adsorption on the active sites physically blocking them and decrease the rates of the dissolution or crystallization of some sparingly soluble salts.

4- Change the characteristics of adsorption layers of solid solution interface.

Generally, the specific inhibition of the rates of the dissolution or crystallization is expected to take place at much lower concentrations of the additives molecules than for simple complexion, the inhibition of crystal growth by the additives ions or molecules is

due to surface adsorption of ions or molecules at growth sites.

On the crystal surface, some forms of a simple Langmuir-type isotherm must be applied.

$$R_o / (R_o - R_I) = 1 + (1/k_L x\ 1/C_i) \quad (6)$$

The affinity constant (k_L) is a measure of the affinity of additives for the surface of the adsorbate. Thus the affinity is related to an increased adsorption. If the intercept is less than one, this implying that this additive may cause complete inhibition of the precipitation process at concentrations lower than the one corresponding to mono layer coverage.

But if the intercept is more than one, thus means that in ability of additive to complete inhibition of crystal growth even at high concentration. Plotting $R_o / (R_o - R_I)$ against $1/C_i$ for all additives, a linear relation with intercept of unity indicated that Langmuir-isotherm satisfactory described the inhibitory effect of additives used. The best fit linear relation and an intercept of unity strongly suggested that the formation of a monomolecular blocking layer of additive ions or molecules at the growth sites on the CSD crystal surface.

The values of K_L in case of the presence of Thr, Meth, As, Tyr and Ala were: 31.1, 25.00, 7.143, 5.00 and 2.19×10^5 KJ/mol respectively supported the order of inhibition of the CSD crystal by these additives as

Thr> Met > Asp > Tyr >Ala

The growth inhibitors are able to retard or block growth process even if added in trace amounts for below the level required for sequestration. Their effectiveness can therefore only be explained by their preferential adsorption at active growth sites on the crystal surfaces. The degree of inhibition may be interpreted in terms of Langmuir adsorption isotherm. When solute crystallizes from supersaturated solution, the presence of a third component can often have a dramatic effect on the crystal growth, kinetics and habitually from the crystalline phase. Such a third component when is effectively at relatively low concentrations and exhibit a worked specificity in their action, factors have which led to the generally held conclusion that they are adsorbed onto the growing crystal surfaces [9, 26].

The adsorptions of additives onto crystal surface, changes the relative surface free energies of the faces and may block sites essential to the incorporation of new solute into crystal lattice. In general a specific inhibition of rate of crystallization or dissolution is expected to take place at much lower concentrations of additives is due to adsorption more than complexion of additive with the crystals growthed or dissolved [27].

In the present study, concentration as low as 10^{-5}mol dm^{-1} was markedly reduced the crystallization rates of calcium sulfate dihydrate crystals by at least 31.30, 20.89, 17.520, 13.43 and 10.680 % in the presence of Thr, Meth, Asp, Tyr and Ala respectively. The crystallization rates decreased by increasing the concentration of additive of CSD crystals due to the adsorption of it on the active sites on the surface of calcium sulfate dihydrate crystals, blocking them decreasing their numbers and decreasing the crystallization rates. The lower value of the activation energy of crystallization of calcium sulfate dihydrate crystals (250cal/mol) and observed dependence of the crystal growth rate of CSD crystals supported the diffusion as rate–determine step at the crystal face [29]. The observed dependence of the experimental rates of crystallization of CSD crystals of the present study, on the changes in fluid dynamics concluded that, the crystallization of CSD crystals in solutions, under the experimental conditions, was mass transfer limited [30,32]. The transport is taking place with the rate controlled by diffusion mechanism. The value of the order of crystallization of CSD crystals at the experimental conditions of the present study was first–order which confirms the diffusion mechanism [30,33,34]. In mass transport control in which the diffusion rate of material leaving the crystal surface, the temperature dependence of the diffusion coefficient should be important.

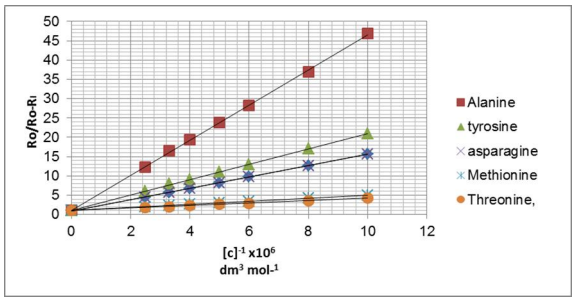


Fig (13): The effect of the Threonine, Methionine, Asparagine, Tyrosine and Alanine additives on the rates of crystallization of CSD crystals at same experimental conditions.

The molecular geometry, conformation and hydrophobicity of the amino molecules, used as inhibitor, are important factors affecting its degree of their inhibition. The hydrophobic one are less effective, linear polyelectrolyte allowing for maximum molecular flexibility are good inhibitors [27].

The factors that might govern the efficiency of the amino acid are:

1-The number of amino and carboxylic group content on the structure of amino acids.

2- The PKa values.

3-The molecular weight of the amino acids.

Amino acids act as strong chelating agents which their advantages are capability to be adsorbed on

inorganic solids[25,35]. It may cause the anions in stern layer to be released and becomes attached to the adsorption sites through amino acids/anion-exchange mechanism [36].

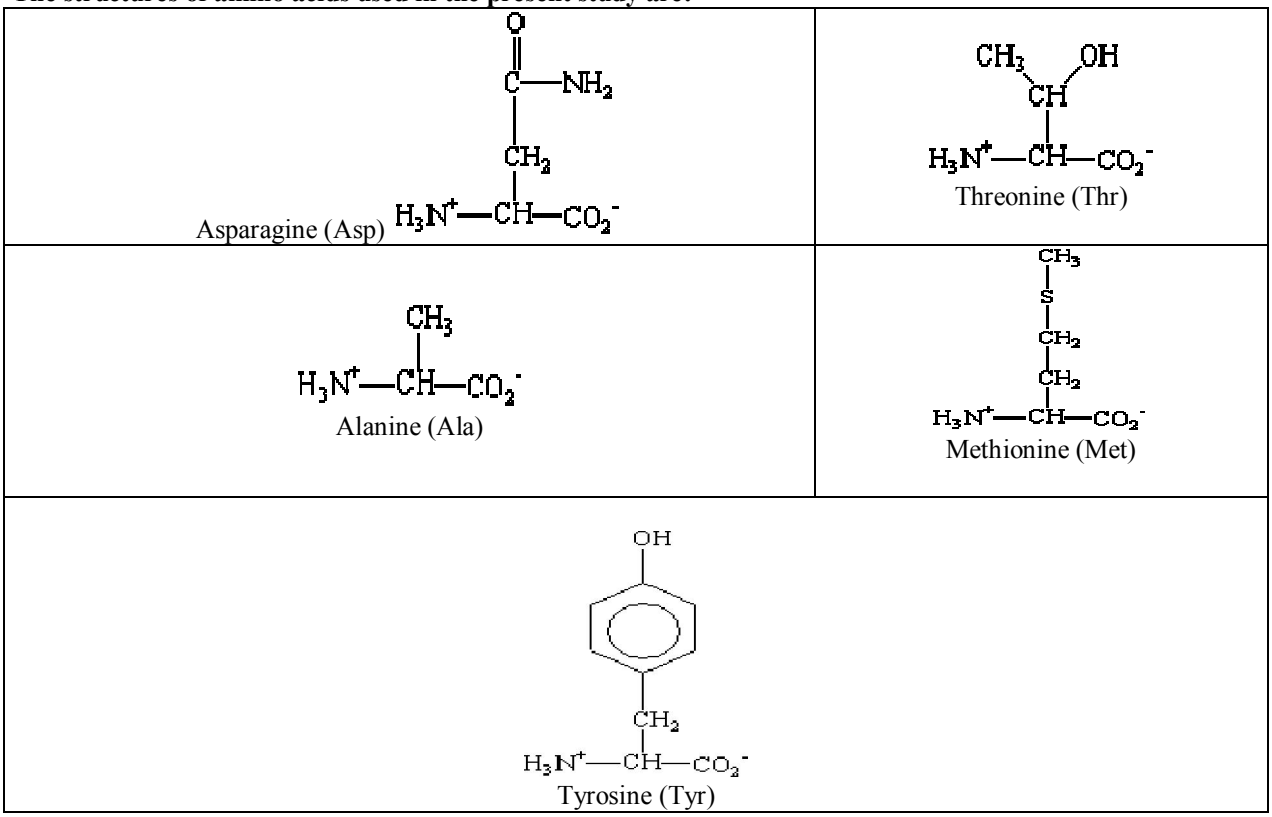
The amino acids may adsorb on the active site of inorganic solid as calcium oxalate mono hydrate or calcium carbonate by electrostatic attraction between the Ca^{2+}ion active sites and-NH_2or-NH groups of the amino acids, since the inhibition depended on the ionic strength of the medium.

If the inhibitor molecules are adsorbed on the crystal surface between the advancing dissolution or crystallization steps, the reaction can proceed provided that the adjacent adsorbed molecules are separated by a distance greater than that of the critical etch pit. The effect of the inhibitor may be described as the prevention or strong retardation of the nucleation of etches 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 or crystallization may occur by preferential adsorption of the inhibitor molecules at the edges of the sub critical etch pits forming on the surface, thus preventing their development beyond the critical size[24].

Adsorption process associated with the competition of at least two components: the solvent and the solute species. The surface of the mineral attracts the counter ions in the solution, and a layer is formed, which is firmly attached around the particle, called the stern. Additional counter ions are also attracted 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 equilibrium induces the formation of a diffuse layer of counter ions whose concentration is high to near to the surface; however is gradually decreased with the distance and reaches to equilibrium with the counter ions in the solution. In addition there is a lack of co-ions particle these ions are repelled by the surface [37].

In the present study, the inhibition of the crystallization of CSD crystals by the additives, Thr, Meth, Asp, Tyr and Ala can be suggested to be competition between the anionic parts of additive molecules and SO_4^{2-}ions for Ca^{2+}ions active sites on the crystal surface.

The structures of amino acids used in the present study are:



Threonine	-polar uncharged amino acid -hydrophilic -H-bonding to enzyme. -as H donor - soluble in water
Methionine	-polar uncharged α- amino acid -sulfur containing amino acid -cleating agents for heavy metals. -as methyl donor - soluble in water -hydrophobic -It is antioxidant -Buried in the core of proteins
Asparagine	-polar uncharged amino acids. -hydrophilic. -H-bonding in its group. -the side chain form H-bonding. - soluble in water. -has acidic side chain.
Tyrosine	-polar uncharged amino acids. -hydrophilic. -has polar side group -Aromatic amino acids.
Alanine	-hydrophilic. -important source of energy of muscle -Non-polar aliphatic reside

The amino acids under the study are polar uncharged, and Thr, Meth, and Asp are hydrophilic and all of them are (H -donor), so we can suggest, that the amino acid adsorbed on Ca^{2+} ion active sites, reduced their numbers and decreased the rates of crystallization of CSD crystals through preferential adsorption.

The hydrophilic amino acids are good inhibitors, since the active sites on the surface of CSD crystals are hydrated so, Methionine and Alanine must have lower inhibitory effect since they are hydrophobic. But Methionine has higher molecular weight, and the higher molecular weight of molecules of additive, the slower the growth kinetics and the most irreversible adsorption. Adsorption of macromolecules favors particle repulsion, and thus lowers the crystal aggregation [38].

Although Tyrosine has large molecular weight but the presence of aromatic ring may change the mode of adsorption and the respective efficiency. The aromatic ring laying on the surface of CSD crystals and prevent more additives molecules to reach the active sites on the surface of CSD crystals [39].

The presence of phenyl group decreases the inhibition capacity of the inhibitors. The presence of hydrophobic aromatic nuclei, affecting the configuration of the additive chains at gypsum/water interface yielding weaker interactions and therefore lowering the affinity of the additive for crystal surface of gypsum [40].

Methionine is hydrophobic amino acids [41] but it has higher molecular weight and is linear i.e., Allowing molecular flexibility in which the adsorbed molecules could rotate freely around the axis vertical to the crystal surface and thus effective volume of adsorption occur, so it has good inhibition capacity. Threonine has –OH group and Asparagine has –NH_2group and the presence of these functional groups increase the inhibitory effect of the additives Methionine is hydrophobic amino acids but it has higher molecular weight and is linear i.e., Allowing molecular flexibility in which the adsorbed molecules could rotate freely around the axis vertical to the crystal surface and thus effective volume of adsorption occur, so it has good inhibition capacity. Threonine has-OH group and Asparagine has –NH_2 group and the presence of these functional groups increase the inhibitory effect of the additives [22-25,27,42].

The hydroxyl group in the molecular backbone, it is a key factor in the effectiveness of tri carboxylic acids as inhibitors, [43] and the presence of –NH_2group also increase the inhibition of the additive [27]

The inhibition of some organic acids on crystals growth of calcium phosphate dihydrate was found to be due to an interaction between the anionic functional

groups and Ca^{2+} ions active sites on the surface of the calcium phosphate dihydrate crystals [44].

The hydrophilic amino acids (Thr and Asp) form H-bond with water molecules of hydrated active sites on the surface CSD crystals, most of these amino acids are H -donor, so, on making H-bond with water molecules, leaving the side chain negatively charged which preferential adsorbed on Ca^{2+} ions active sites electrostatically since crystallization process in this study affected by the ionic strength of the medium. the order of one, the low value of activation energy and the validity of applying Langmuir–isotherm confirm the physical adsorption of the molecules or ions of additive on the active sites on the surface CSD crystals. The adsorption of anions of amino acids on Ca^{2+} ion active sites decreased their numbers so, decreased the rates of crystallization of CSD crystals anions of amino acids adsorbed on Ca^{2+} ions in competition of SO_4^{2}.

The sorption process can be described by four consecutive steps:

1-Transport in the bulk of solution.

2- Diffusion through the solution to the external surface of crystal surface (also called diffusion of additive molecules).

3- Particle diffusion in the liquid contained in the pores and in the sorbate along the pore walls.

4- Sorption and desorption within the particle and on external surface. Generally, steps (1) and (4) occur rapidly so that the rate–controlling steps become step 2, step 3, or the combination of them. Since, the mechanism was surface – controlled one, so we suggest that step (3) may be the rate–determining step. In the classic description of Pinng mechanisms is based on impurity adsorption at surfaces, step or kinks In this case, impurities act as blockers at the sites where they adsorb, preventing the crystal step from propagating locally and thus causing a straight step to become scalloped. As step curve, their velocity is reduced until they eventually stopped when their radius of curvature reaches the critical radius. In this model, the degree of inhibition, depends on the under saturation or supersaturation and the blocker concentration on the surface. Higher concentration of adsorbed make greater reduction in velocity and this effects is more pronounced at lower supersaturations or undersaturations. A good model crystal for studying the several aspects of interactions between additives and crystals, Skirtic *et al* had summarized following:

1) Importance of molecular size of the additive i.e. small or macromolecules, number of functional groups in the molecules and the overall charge in the growth or dissolution of crystals.

2) Importance of a structural fit between the organic molecules and the ionic structure of a particular crystal face, this decides the order of inhibition or reaction at a particular crystalline face. It may affect various crystalline face expected to the solution. As a result, it may change the morphology of the growing crystal.

3) Influence of the hydration layer exposed on the surface of the crystals. Such structural hit exists between distances of carboxylic groups in the polaspartic β-sheet and distance of neighboring calcium ions from two adjacent layers constitute one Ca-HPO_4 bi-layer lying beneath the hydrated layer parallel to be (010) plane. In adsorption of Phosphonates on gypsum, the suggested mechanisms of the process were:

1) Chemical bonding (complexion) of Ca^{2+} ions at the crystal surface with the phosphonate group.

2) Formation of hydrogen bridges between the hydroxyl groups and either the sulfate ions or the crystal water molecules at the gypsum crystal surface. The inhibition of growth rates of HAP by serine explained by attraction of positively charged protonated anion group adsorbed on the negatively sites on HAP crystal surface, in dissolution of CSD crystal in the presence of $Mg^{2+,}$ $Zn^{2+,}$ $Mn^{2+,}$ Cu^{2+} and Cd^{2+} it was found that the rates of dissolution decreased due to adsorption of metal ions on active sites on the surface of the crystals blocking them so decreasing their numbers on the crystal surface. The molecular weight, the atomic size of the cations in the inhibitors affected their inhibitory effect of them. Adsorption of the inhibitor on the surface of may occur by competition between the active sites on the surface of crystal similar to that of the inhibitor charge [45]. In dissolution of CSD crystals in the presence of some cations, it was interpreted as competition between the cation and Ca^{2+} ions active sites on surface of CSD crystals which depended on the size of cations replace the Ca^{2+} ions at the surface [30]. Sulfonic anions replaced the sulfate lattice of gypsum crystal surface enhancing the inhibiting capacity of the additive [46]. In the presence of additive (adsorbate), the rate, Ri, is proportional to the fraction of the surface free from adsorbed additive (1- θ) and given by:

$$R_I = R_o (1- \theta) \quad (7)$$

Where R_o: is the rate of reaction in the absence of additive. On substituting in eq (7) and upon further rearrangement yields:

$$R_O (R_O - R_i) = 1/ (K_I [c]) + 1 \quad (8)$$

From eq (8), this model predicts a linear relationship between Ro (Ro-Ri) and 1/[c], with an intercept of unity. That the Langmuir- isotherm satisfactory described the inhibitory effect of the additive ions. Fig (11) indicated the relation between R_o (R_o - R_i) and 1 / [c], in the case of the presence of Thr, Meth, Asp, Tyr and Ala at the experimental conditions. The best fit linear relation and an intercept

of unity, strongly suggested that the mechanism of inhibition involves that proposed for the Langmuir adsorption namely the formation of a mono molecular blocking layer of additive ions at the growth sites on CSD the crystal surface.

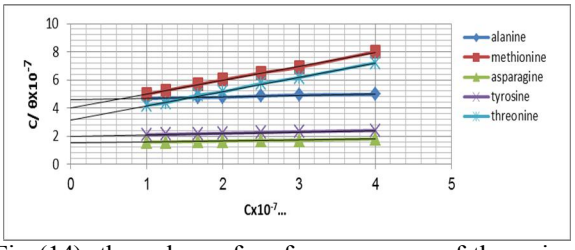


Fig (14): the values of surface coverage of threonine, asparagine, methionine, tyrosine and alanine additives on the surface of CSD crystals at different concentrations of the additives at experimental conditions.

The values of Kl, ΔG and K_{ads} reflected the good adsorption of these additives on growth sites on CSD crystal surface, blocking them and reducing the crystallization rates. The amino acids act as strong chelating agents which their advantages is capability to be adsorbed on inorganic solids. The model proposed suggested that as the amino acids molecule approaches the particle surface. it cause the anions in stern layer to be released and become attached to the adsorption sites through amino acids/ anion-exchange mechanism[47].

The plots of $\{(R_o / R_o - R_i)$ and $(R_o / R_o - R_i)^2$ against $[C]^{-1}x10^6)\}$ of crystallization of CSD crystals in the presence of additives fig (15, 16) according to the models involving impurity adsorption (n = 1) and the surface terrace (n = 2) respectively. The values of Q_{diff} (The differential heat of adsorption corresponding to impurity coverage θ) for kinks and terrace are similar predicted from Langmuir adsorption model table (4).

Table (3): Values of Kads and ΔG, in crystallization of CSD crystals using some amino acids at experimental conditions

Additive	Kads x105 KJ / mol	Kl x105 KJ / mol	Δ G KJ/mol
Thr	30.77	31.10	- 48.86
Meth	24.60	25.00	- 48.28
Asp	6.67	7.143	- 44.92
Tyr	4.97	5.00	- 44.16
Ala	2.14	2.19	- 42.05

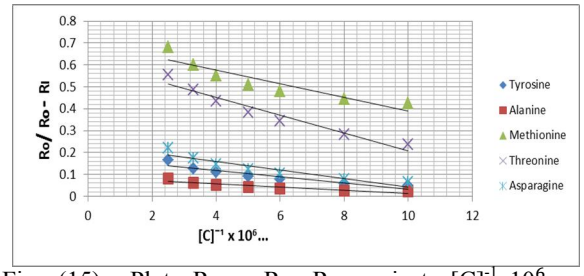


Fig (15): Plot $R_o / R_o - R_i$ against $[C]^{-1}x10^6$ of crystallization of CSD crystals in the presence of additives in case of kink sites at experimental conditions.

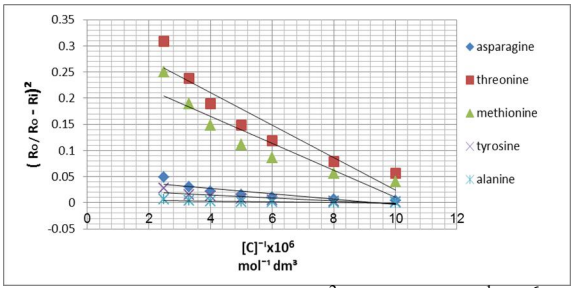


Fig (16): plot $(R_o / R_o - R_i)^2$ against $[C]^{-1}x10^6$ of crystallization of CSD crystals in the presence of additives in case of terrace site at experimental conditions

Table (4): The differential heat of adsorption of additives on the surface of CSD crystals.

Inhibitor	Q_{diff} kink Cal/mol	Q_{diff} terrace Cal/mol
Threonine	17.304	9.744
Methionine	17.647	10.097
Asparagine	17.166	9.600
Tyrosine	17.104	16.900
Alanine	17.245	17.432

From the values of Q_{diff} Langmuir and Q_{diff} Temkin terrace; it was found that:

1- In case of threonine, The differential heat of adsorption of kink sites are larger than that of terrace, so, Threonine favored adsorption in kink sites more than in terrace sites.

2- In case of Methionine favored adsorption on kink sites more than in terrace.

3- In case of Asparagine favored adsorption in kink sites, than terrace ones.

4- In case of Tyrosine favored the two sites approximately.

5- In case of Alanine favored the two sites.

At concentration of $5x10^{-7}$mol dm^{-3} of threonine 7.97 % of CSD crystals surface is complete inhibited. The low number of active sites on the surface of CSD

crystals means that the reaction between the inhibitor molecules and CSD crystals surface is physical in its nature in which the additive ions or molecules adsorbed on the active sites, blocking them and reduced their numbers.

From SSA measurements it was found that SSA of CSD crystals seed was The total pore volume of the surface of CSD crystals was reduced from $7.5e^{-o2}$ to $1.4e^{-o1}$ and the average pore radius also reduced from $3.8e^{+o1}$ A^o to $3.61e^{+o1}$ A^o in the absence and the presence of threonine. From the results, the molecules of inhibitors adsorbed on the pores of CSD crystal surface, reducing their volume and their radii. The reduction of size of pore on CSD crystal surface in the presence of additives supported the suggestion of physical adsorption of molecules or ions of additives on active sites (kink and terrace).

Conclusion

1. The crystallization of CSD crystals was studied at t =25 ^oC, δ=1.32, pH = 7.5 and I=0.3 mol $dm^{-3.}$
2. The crystallization of CSD crystals followed first-order reaction and the rates of crystallization were increased by increasing the fluid dynamics which supports the surface diffusion mechanism.
3. The rates of crystallization of CSD crystals were found to be increased slightly with increasing the pH values of the medium.
4. The rates of crystallization of CSD crystals were increased by increasing of the values of ionic strength of the medium.
5. The low value of activation energy (250 Cal/mol) supported the surface diffusion mechanism.
6. The effect of Thr, Meth, Asp, Tyr, and Ala amino acids on the mechanism of crystallization of CSD crystals at experimental conditions of the study was studied. They were found to be good inhibitors and concentration as low as10^{-5}mol dm^{-3} inhabited the rates of crystallization of CSD crystals. The order of increase of inhibition was:

Thr> Met > Asp > Tyr >Ala

7. Applying Langmuir-isotherm supported the physical adsorption of the molecules or ions of additive on the actives sites on the surface of CSD crystals blocking them and reduced their numbers. The values of K_L were found 31.1, 25.00, 7.143, 5.00 and 2. 19 $x10^5$ KJ/mol in case of the presence of Thr, Meth, Asp, Tyr and Ala respectively. The higher values of K_L indicated the higher affinity of these additives to adsorb on the surface of CSD crystals.
8. Calculated of values of ΔG and K_{ads} values in the presence of these amino acids supported the order of inhibition of CSD crystals in the presence of these additives.
9. The active sites on the surface of CSD crystals at the experimental conditions were found to be mainly kinks and terrace.
10. The effect of change of pH values of the medium on the crystallization rates of surface of CSD crystals in the presence of 10^{-7} mol dm^{-3} was studied. From which the rates were slightly increased with increasing the pH values of the medium.
11. The ionic strength of the medium when increased the crystallization rates of surface of CSD crystals in the presence of 10^{-7} mol dm^{-3} of Thr decreased i.e. the inhibition increased.
12. Concentration of 5 x 10^{-7}mol dm^{-3} of Thr,7.97 % of surface of CSD crystals completely inhibited meaning the low numbers of the active sites on the surface of CSD crystals and the reaction is physical adsorption and electrical in its nature since The rates of crystallization of CSD crystals affected by the ionic strength of the medium.
13. The value and the radii of the pores of CSD surface decreased in the presence of 10^{-7} mol dm^{-3} of threonine which explained by a physical adsorption of molecules or ions of threonine on this pores (actives sites) blocking them and reducing their numbers, so reduced the crystallization rates of CSD crystals.

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