

**DISSOLUTION OF MAGNESIUM FLUORIDE SALT IN THE
PRESENCE OF SOME AMINO ACIDS**

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ABSTRACT

The effect of some amino acids on the dissolution rate of magnesium fluoride crystals has been studied at under-saturation solutions using a constant-composition technique at 25 °C. The addition of amino acids to the reaction even at relatively low concentration (10^{-6} mol l⁻¹) markedly retards the rate of dissolution of the crystals. Moreover, the effect was more pronounced as the relative under-saturation increased. The retardation effect of these additives has been attributed to the blocking of active sites by adsorption of amino acids molecules at the crystals surfaces. Also, inhibition of dissolution reactions by amino acids can be interpreted in terms of Langmuir adsorption isotherm.

INTRODUCTION

Impurities play an important part in the theory of crystallization and dissolution in super-saturated or under-saturated solution [Hamza & Nancollas (1985); Hamza & Hamdona (1991); Weijinen et al., (1983) and Christoffersen et al., (1983)]. Nature continuously conducts large scale precipitation and dissolution processes in the atmosphere, soil and natural water [Stumm & Morgan (1981)]. The dissolution of fluoride salts of the alkaline earth is of importance in view of their applications in many fields, including fluoridation of water, electronics, spectroscopy, glass manufacture and dental caries. Amino acids are compounds of major importance for living organisms. Moving freely in blood

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circulation after digestion of proteins. Also, they enter into the cell, environment by simple diffusion, and thus their concentration is controlled by physiological mechanism. The factors that govern the mechanism of precipitation and dissolution of these fluoride salts are therefore of considerable interest, especially the influence of foreign additives which may exert a marked effect on the rates of crystallization or dissolution either through adsorption at the surface of crystals or by lattice substitution (Yoshikawa & Nancollas (1983); Abdul-Rahman *et al.*, (1985); Hamza & Hamdona (1992) and Chistoffersen & Christoffersen (1992)].

In present work, the kinetics of dissolution of magnesium fluoride have been investigated by the constant-composition method [Koutsoukos *et al.*, (1983)] in which the rate of reaction was measured for extended periods under conditions of constant ionic strength and solution composition. The effect of glycine [Gly], Lysine [Lys], Asparagine [Asn] and 8-amino-1-naphthol-3,6-disulphonic acid monosodium salt [AND] on the rate of dissolution has been investigated.

EXPERIMENTAL

Under-saturated solutions of magnesium fluoride were prepared in triply distilled deionised water using both ultrapure (Alfa Chemical) and reagent-grade (J.T. Baker) chemicals. Solutions were filtered (0.22 μm , Millipore Filters) before used. Metal ion concentrations were determined by passing aliquots through a cation-exchange resin (Dowex 50) in the hydrogen form and titrating the eluted acid with standardized potassium hydroxide. Solutions were stored in polyethylene bottles.

Seed crystals were prepared by adding 500 ml of (1.148 mol l⁻¹) potassium fluoride and 500 ml of (0.574 mol l⁻¹) magnesium nitrate to 100 ml of distilled water, under nitrogen, over a period of 6 h. The mixture was aged for 10 days before washing, the crystals were washed free of nitrate ion by decantation and stored in polyethylene bottles. The specific surface area (7.66 m² g⁻¹) of the crystals was measured using a single point nitrogen adsorption apparatus (30 nitrogen, 70 helium, quantasorb 11, quantachrome, Green vale, NY). The seed crystals were confirmed as magnesium fluoride by x-ray powder diffraction (Shimadzu XD-3 Diffractometer).

Dissolution experiments of the crystals were made in a polyethylene lined 300 ml double walled pyrex glass reaction cell

maintained at 25 ± 0.1 °C. Dissolution was made during magnetic stirring and bubbling with nitrogen gas. The fluoride-specific electrodes (Orion, Model 94-09) were calibrated using standard potassium fluoride solutions both before and at the end of each experiment. Subsequently under-saturated solutions of desired concentration were prepared by slow addition of magnesium nitrate solution to potassium fluoride solution. Following the introduction of the magnesium fluoride seed crystals, the activities of the magnesium and fluoride ions were maintained at constant levels by the addition of potassium nitrate as a diluent monitored by means of a pH-state (Model 632 Methrom + Impusomat 614 + Dosimat 665 + Labograph 586).

Inhibitor solutions were also introduced as titrant in order to compensate for dilution effects. In addition samples were periodically withdrawn and filtered at the reaction temperature through Millipore filters ($0.22 \mu\text{m}$), prior to solution and solid-phase analyses. The data confirmed that the lattice-ion and inhibitor concentrations were kept constant within 1 %.

RESULTS AND DISCUSSIONS

In order to be able to analyse the kinetics of the dissolution reaction in terms of the concentrations of free ionic species, it is necessary to take into account ion-pair and complex formation. Computations were performed, as described previously [Nancollas (1996)] by successive approximation for the ionic strength, ($I = 0.15 \text{ mol l}^{-1}$ in the present work) using the thermodynamic equilibrium constant, K , for the various associated species.

Activity coefficients were calculated from the extended form of the Debye-Huckel equation proposed by Davies [Davies (1962)].

For many sparingly soluble salts, M_aA_b , the rate of dissolution, R , normalized for seed surface area, can be expressed in terms of the relative under-saturation by Eq. (1):

$$R = dm/dt = k s \sigma^n \quad (1)$$

In which, m , is the number of moles dissolved at time t ; k , the rate constant; s , a function of the initial seed surface area and n , the apparent order of the reaction.

The relative under-saturation, σ , is defined in terms of the ionic product and the solubility product of magnesium fluoride by the following expression:

$$\sigma = (K_{so}^{1/3} - IP^{1/3}) / K_{so}^{1/3}$$

where the ionic product, IP and the solubility product, K_{so} are expressed in terms of the appropriate activities of the ionic species, $[(Mg^{2+})(F^-)]^{1/3}$ at time t and equilibrium, respectively.

Previous kinetic studies of the dissolution of magnesium fluoride indicate that at the same relative under-saturation ($\sigma = 0.3-0.75$) the rate of dissolution seems to be controlled by a poly-nuclear dissolution mechanism [Hamdona *et al.*, (2001)].

The crystal growth and dissolution rates of divalent metal ion salts in general are greatly inhibited by added substances [Nancollas *et al.*, (1982); Abdul-Rahman *et al.*, (1987); Hamza (1990); Koutsoukos *et al.*, (1981) and Hamza (1991)]. In the present work, the rate of dissolution of magnesium fluoride was studied in the presence of some amino acids as, Glycine (Gly), Lysine (Lys), Asparagine (Asn) and 8-amino-1-naphthol-3,6-disulphonic acid monosodium salt (AND).

Table 1 and Fig. 1. summarized the data for the dissolution of magnesium fluoride in the presence of additives at the same under-saturation for each additive, each experiment was made in duplicate or triplicate. It can be seen that concentrations as low as 5×10^{-6} mol l^{-1} for each, markedly reduce dissolution rates by as much as 52.3, 46.10 and 42.96 % in the presence of Lys, AND and Gly, respectively, whereas, low inhibition (37.5%) was determined for 5×10^{-5} mol l^{-1} of Asn. Table 1 shows that the rate of dissolution of magnesium fluoride in the presence of these amino acids decreases with successive additions of each and the effectiveness of inhibition follows the order: Lys > AND > Gly >> Asn.

In previous studies, concentration as low as 1.0×10^{-6} mol l^{-1} from Hydroxyethylidene -1,1-diphosphonic acid (HEDP) and Ethylenediamine tetra (methylene phosphonic acid) (ENTMP) reduced the dissolution of magnesium fluoride rates by at least 50% compared to that in the pure solution [Hamza & Nancollas (1985)]. Moreover, strontium fluoride showed more susceptibility to dissolution inhibition, 70% decrease in the rate of dissolution was exhibited by the addition of as low as 5×10^{-7} mol l^{-1} phosphonate [Hamza & Nancollas (1985)].

Table (1): Effect of some amino acid on the rate of dissolution of magnesium fluoride crystals, ionic strength = 0.15 mol l⁻¹ NaCl and $\sigma = 0.5$.

Additive/10 ⁻⁶ mol l ⁻¹	Rate/10 ⁻⁹ mol min ⁻¹ m ⁻²	% Inhibition
-----	14.376	-----
1.0 Lysine	11.500	20.01
2.0 Lysine	9.868	31.36
4.0 Lysine	7.374	48.71
5.0 Lysine	6.857	52.30
7.0 Lysine	5.113	64.43
1.0 AND	12.248	14.80
3.0 AND	9.489	33.99
5.0 AND	7.749	46.10
7.0 AND	6.482	54.91
1.0 Glycine	12.938	10.00
2.0 Glycine	11.350	21.05
3.0 Glycine	10.063	29.99
4.0 Glycine	8.735	39.24
5.0 Glycine	8.200	42.96
10.0 Asparagine	13.657	5.00
20.0 Asparagine	11.624	19.14
40.0 Asparagine	1.060	30.02
50.0 Asparagine	8.985	37.50
60.0 Asparagine	8.214	42.86

Applying a simple Langmuir adsorption model [Koutsoukos (1983)] the influence of these additives can be interpreted in terms of their selective adsorption at dissolution sites on the crystal surface of magnesium fluoride. The decreases in dissolution rate can be related to the crystal surface area covered by the adsorbed molecule. If R_0 and R_i are the rates of dissolution in absence and presence of inhibitors, respectively the Langmuir isotherm requires a linear relationship between the relative reduction rate $R_0/(R_0-R_i)$ and the reciprocal of the inhibitor concentration. Figure 2 confirms the applicability of this simple adsorption isotherm. The values of the adsorption affinity constant K_L are 2.08×10^5 , 1.67×10^5 , 1.43×10^5 and 1.28×10^4 l mol⁻¹ for Lysine, AND, Glycine and asparagin, respectively, at the same under-saturation $\sigma = 0.5$. These values reflect the high adsorption affinity which is the

same order of reactivity of amino acids related to the kinetic data in the following order: Lys > AND > Gly >> Asn.

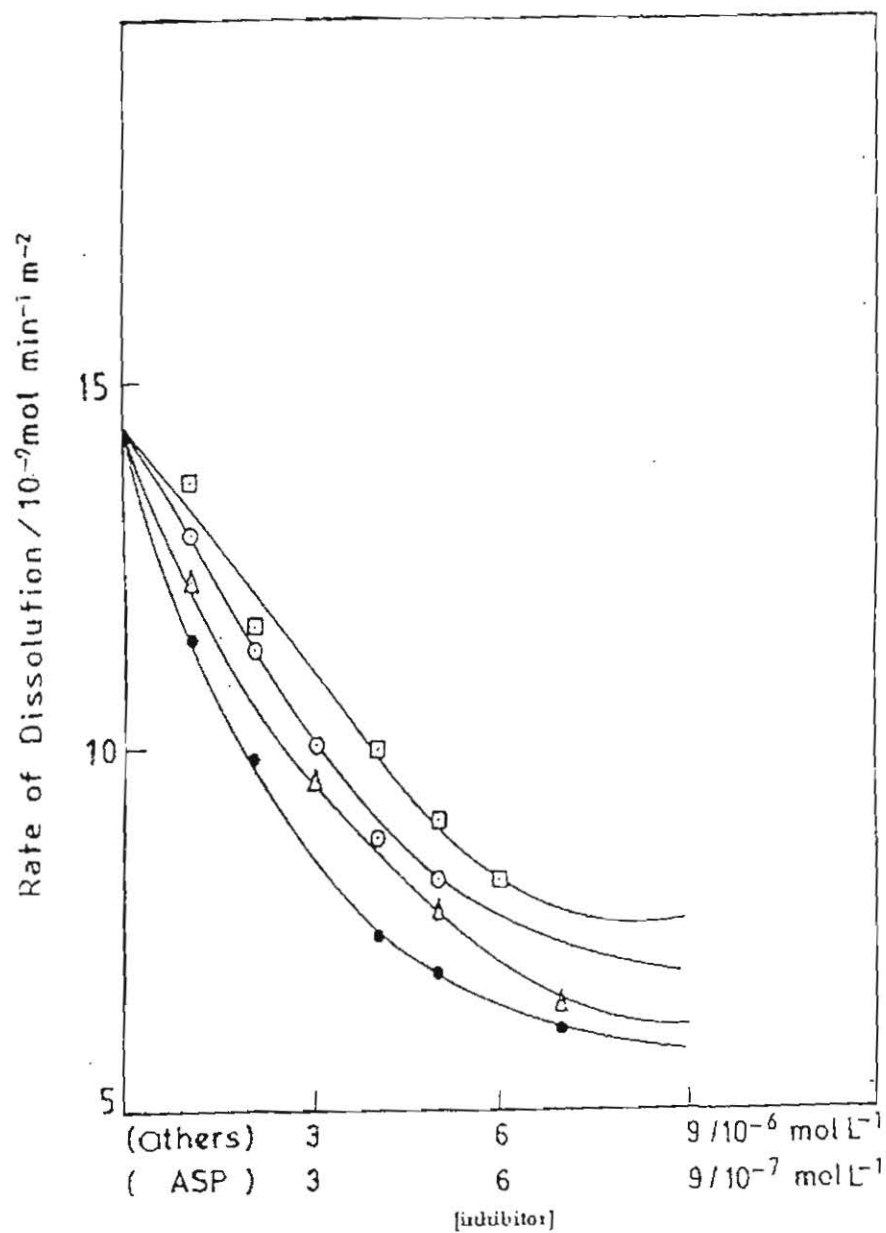


Fig. (1): Rate of dissolution of magnesium fluoride crystals against the concentration of amino acids; Lys(●), AND(Δ), Gly(○) and Asn(□).

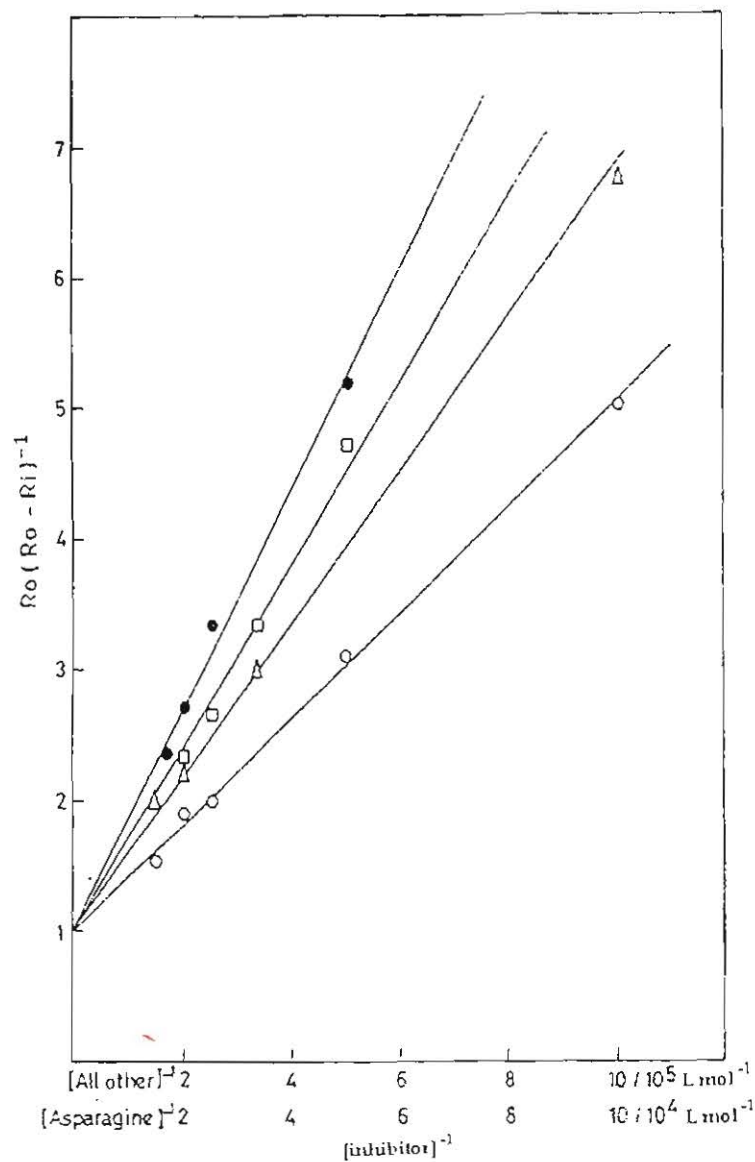


Fig. (2): Plots of $R_o(R_o - R_i)^{-1}$ against $[Amino\ acids]^{-1}$ for the dissolution of magnesium fluoride crystals; Lys(○), AND(△), Gly(□) and Asn(●).

Amino acids could act as strong chelating agents. Their advantages over the latter class of ligand is their capability to be adsorbed on inorganic solids. The model proposed suggests that as the amino acids molecule approaches the particle surface it causes the anions

in the Stern layer to be released and become attached to the adsorption sites through amino acids/anion-exchange mechanism [Rawis *et al.*, (1982)].

The factors that might govern the efficiency of amino acids are: (a) the number of amino and carboxylic groups, (b) the molecular size, (c) the pK_a and pK_b values, (d) the PI values. The first three factors can be ruled out since: (a) the number of amino and carboxylic groups is not a decisive factor with regard to its reactivity, as the most and less efficient amino acid in the present work, Lysine and Asparagine contain two amino groups and one carboxylic group. No parallelism exists between the reactivity and amino groups and carboxylic groups, content. The molecular size has no bearing on the reactivity. The order of increase in molecular size of the amino acids can be given as follows: AND > Lys > Asn > Gly, which is not the order of their reactivities; (c) the reactivity is not dependent upon the pK_a or pK_b as shown in Table 2 [David (1992)].

A better assessment could only be gained by a comparison of the PI values of these amino acids since the isoelectronic point has to be taken into account as seen in table 2. The values of PI for the present amino acids fall in the following order: Lys > Gly > Asn, which is the same order of reactivity in inhibiting the dissolution rate of magnesium fluoride crystals. Therefore, the order of decreasing reactivity of amino acids may be related to its PI values.

Table (2): Constant of some amino acids.

	Pk_a	Pk_b	PI
Lysine	2.18	8.95	9.74
Glycine	2.34	9.60	5.97
Asparagine	2.02	8.80	5.41

On the assumption that the degree of inhibition may be affected by the degree of relative under-saturation, the dissolution of magnesium fluoride in the presence of some amino acids has been investigated at different relative under-saturations ($\sigma = 0.6, 0.5$ and 0.4), as shown in Table 3. It can be seen that the rate of dissolution of magnesium fluoride decreases with the progressive addition of amino acid (AND) to the medium at all levels of relative under-saturation studied, and the degree of inhibition increases with increasing the relative under-saturation of the

dissolution reactions. It was observed that concentration as low as $5 \times 10^{-6} \text{ mol l}^{-1}$ reduces the dissolution rates by at least 65.08, 46.10 and 29.09 % compared to that in pure solution at that relative under-saturation, $\sigma = 0.6, 0.5$ and 0.4 respectively. Figure 3 Shows that the values of the adsorption constants K_L are $5.00 \times 10^5, 1.67 \times 10^5$ and $8.13 \times 10^4 \text{ l mol}^{-1}$ at that relative under-saturations studied, respectively. A similar dependence of the degree of inhibition with change in driving force has been observed for the influence of some phosphonate on the kinetics of dissolution of strontium fluoride crystals [Hamza and Nancollas (1985)].

The marked dependence upon degree of saturation (σ) of the effectiveness of growth and dissolution inhibitors has important consequences in assessing the usefulness of these compounds for biological and industrial applications. It is clearly insufficient to base this assessment on the results of a limited number of threshold precipitation and dissolution experiments.

Table (3): Effect of AND on the dissolution of magnesium fluoride crystals at different relative under-saturation.

Additive/ $10^{-6} \text{ mol l}^{-1}$	σ	Rate/ $10^{-9} \text{ mol min}^{-1} \text{ m}^{-2}$	% Inhibition
-----	0.6	22.857	-----
1.0	0.6	15.094	33.33
2.0	0.6	12.219	46.03
3.0	0.6	9.704	57.14
4.0	0.6	8.646	62.17
5.0	0.6	7.907	65.08
6.0	0.6	7.245	68.30
----	0.5	14.376	----
1.0	0.5	12.164	15.387
3.0	0.5	9.488	33.99
5.0	0.5	7.748	46.10
7.0	0.5	6.766	52.935
----	0.4	7.907	----
1.0	0.4	6.900	12.73
3.0	0.4	6.182	21.82
5.0	0.4	5.607	29.09
7.0	0.4	5.037	36.297
9.0	0.4	4.776	39.598

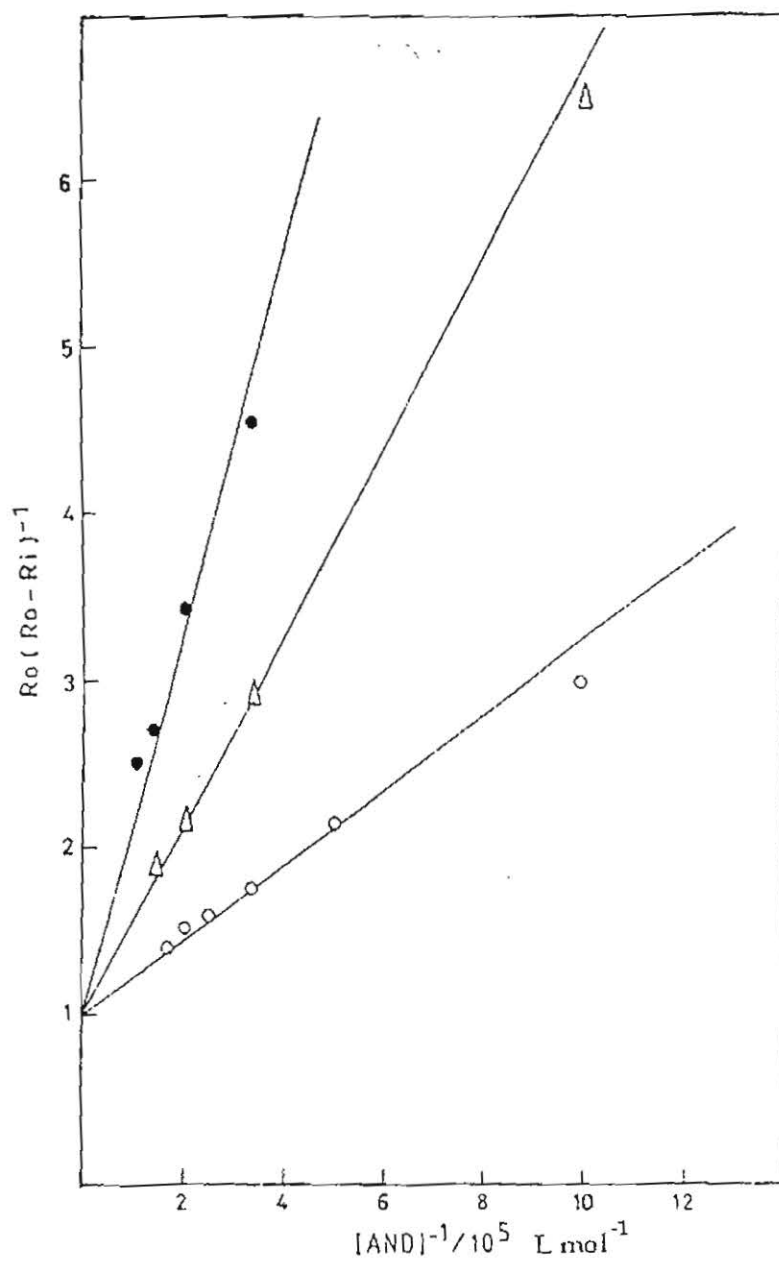


Fig. (3): Plots of $R_o(R_o - R_i)^{-1}$ against $[AND]^{-1}$ for the dissolution of Magnesium fluoride crystals; $\sigma = 0.6$ (\circ), $\sigma = 0.5$ (Δ) and $\sigma = 0.4$ (\bullet).

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ذوبان ملح فلوريد الماغنيسيوم في وجود بعض الأحماض الأمينية

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تمت دراسة تأثير بعض الأحماض الأمينية على سرعة ذوبان بلورات فلوريد المغنيسيوم في محاليل تحت التشبع بواسطة طريقة التركيب الثابت عند ٢٥ درجة مئوية وقد لوحظ أن إضافة الأحماض الأمينية ولو بتركيزات في حدود الجزء في المليون تثبط سرعة ذوبان البلورات . وعلاوة على ذلك فإن درجة التثبيط تكون أكثر وضوحاً كلما زادت درجة تحت التشبع وقد عزى التأثير المتثبط لتلك المواد المضافة لإمصاص تلك المواد المضافة على البقع النشطة على السطح البلوري . وقد خسرت النتائج على ضوء منحنى لانجمير .

