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EFFECT OF IMPURITIES ON THE CRYSTAL GROWTH FROM SOLUTIONS – A NEW KINETIC MODEL.

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ABSTRACT – A new approach to the phenomena of impurity adsorption during crystal growth is presented. We consider that the adsorption of elements onto the active sites of the crystal surface is a competitive process between the solute and the impurity molecules. Based on that, a general equation relating the face growth rates with the supersaturation and the impurity concentration is derived. The main experimental evidences known from the literature on crystal growth kinetics in the presence of impurities are used to test the proposed model. So far, we conclude that the theoretical statements of the competitive adsorption model are generally in agreement with the experimental facts.

KEYWORDS: crystal growth; impurity effect; competitive adsorption.

1.INTRODUCTION

The occupation by impurities of the preferential places for the incorporation of solute onto the crystal lattice (active sites) is known to have a strong effect on the growth of the crystal. Small quantities of specific impurities can suppress the growth, while others, being crystallographic face-selective, can be used as habit modifiers.

Cabrera and Vermilyea (1958) introduced the pinning mechanism to explain the action of the impurities on the displacement of the faces. They state that, when the impurities are adsorbed at actives sites, the flow of the steps at crystal surface is hindered. The impact of the impurity on the velocity of the step is assumed to be directly connected with the provoked decrease on the radius of curvature (r) relatively to the critical radius of curvature (r_c) for the pure system:

$$\frac{v_r}{v_0} = 1 - \frac{r_c}{r} \qquad (1)$$

Calling "l" to the average spacing between neighboring impurities, the velocity of the step will reach the minimum when the radius of curvatures is $l/2$,

$$\frac{v_{\min}}{v_0} = 1 - \frac{r_c}{l/2} \qquad (2)$$

Originally Cabrera and Vermilyea (1958) considered the average advancement velocity v as the geometric mean between v_0 and v_{min}. More recently, Kubota and Mullin (1995) proposed the use of an arithmetic mean of these velocities to describe v:

$$v = \frac{v_0 + v_{\min}}{2} \qquad (3)$$

Combining Equation 2 and 3 gives

$$\frac{v}{v_0} = 1 - \frac{r_c}{l} \qquad (4)$$

The fraction of the active sites covered with impurities can be approximated to the ratio of the average distance between active sites to the average distance between neighboring adsorbed impurities:

$$\theta = \frac{L}{l} \qquad (5)$$

In addition, according to the definition of critical radius of the two-dimensional nucleus given by Burton et al. (1951),

$$r_c = \frac{\gamma a}{kT\sigma} \qquad (6)$$

Therefore, Equation 4 can be written as,

$$\frac{v}{v_0} = 1 - \frac{\gamma a}{kT\sigma L}\theta \qquad (7)$$

From this equation one can expect that the action of a given impurity on the velocity of the steps is a function of:

a) The coverage of active sites (θ), which is described by an adsorption isotherm. Commonly it is adopted a conventional Langmuir isotherm, defined as

$$\theta = \frac{Kc_i}{Kc_i + 1} \qquad (8)$$

although, Temkin isotherms (Sangwal, 1999) and Freundlich isotherms (Sangwal and Mielniczek-Brzoska, 2002) were also studied.

b) The supersaturation-dependent factor α, defined as

$$\alpha = \frac{\gamma a}{kT\sigma L} \qquad (9)$$

Kubota and Mullin (1995) called to this parameter “impurity effectiveness factor”. Equation 7 can now be rewritten in the form

$$\frac{v}{v_0} = 1 - \alpha\theta \qquad (10)$$

This theory has been confronted with experimental kinetic data in several studies on the influence of supersaturation, impurity type and its concentration on crystal growth kinetics. The behavior of an impurity can be described by the values of α and K, estimated by fitting the equations of the model to v/v_0 vs. c_i or v/v_0 vs. σ data. Alternatively, adsorption isotherms can be determined separately from the kinetic research and then, the values of α corresponding to measured values of v/v_0 can be calculated using Equation 10 (Kubota et al., 2000). Currently, there is a great interest on this particular field of the crystallization but the existing theories are not yet capable to answer all questions (Kubota et al. 2003). The new model presented in this paper is expected to be a contribution for a better understanding of the unclear issues.

2.COMPETITIVE ADSORPTION MODEL

The following steps can occur when an impurity molecule diffusing from solution, reaches the surface of a growing crystal (Sangwal, 1999):

Step 1: Surface adsorption.

Step 2: Surface diffusion of the adsorbed impurity molecule.

Step 3: Adsorption of the impurity at active sites.

Each of the mentioned steps has an associated thermodynamic energy change, whose relative values determine if and how adsorption occurs. The coverage of the active sites by an impurity, θ_l, will be proportional to the correspondent surface coverage, θ_s:

$$\theta_l = \beta\theta_s \tag{11}$$

The value of β here introduced, will take higher values when the second and third steps are thermodynamically favored relatively to the first step. On the contrary, in the case of favorable surface adsorption and low mobility of the adsorbed molecules, it is expected that β will tend to small positive values. Assuming a Langmuir type isotherm, it can be showed for a competitive adsorption that:

$$\theta_s = \frac{K_i c_i}{1 + K_i c_i + K_\sigma \sigma} \tag{12}$$

The occupation of active sites by impurities implies a proportional decrease of elements of solute integrating the crystal lattice per time unit, i.e.

$$\frac{v}{v_0} = 1 - \theta_l \tag{13}$$

Using Equations 11, 12 and 13 becomes,

$$\frac{v}{v_0} = 1 - \beta\frac{K_i c_i}{1 + K_i c_i + K_\sigma \sigma} \tag{14}$$

New ideas about the role of the most important variables on crystallization in the presence of impurities (impurity concentration, supersaturation, temperature, etc.) are introduced with Equation 14. The main experimental knowledge taken from literature will now be analyzed in the light of the new model, emphasizing the differences and common aspects to existing theories.

3.ANALYSIS OF LITERATURE DATA AND DISCUSSION

Typical experimental data on crystal growth in the presence of impurities will now be analysed and compared with the theoretical predictions of the competitive adsorption model. It will be focused the influence of supersaturation and impurity concentration on the relative growth rate.

3.1Dependence of v/v_0 on σ, at Constant c_i

Figure 1 represents the influence of the reciprocal of the supersaturation on the relative step velocity, according Equation 14.

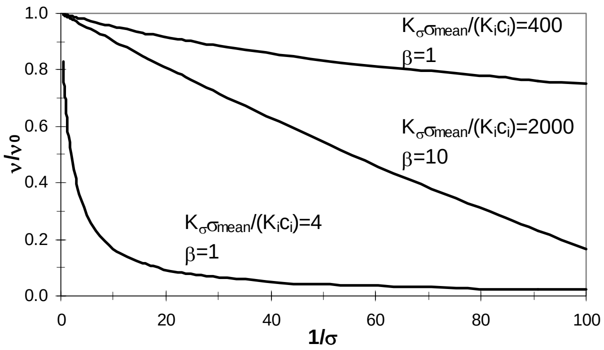

Figure 1 – Theoretical relationship between the relative step advancement and the reciprocal of the supersaturation for different combinations of the parameters $K_\sigma\sigma_{mean}/(K_i c_i)$ and β; σ_{mean} is the mean value of σ, evaluated for the considered range of supersaturations.

High values of $K_\sigma\sigma_{mean}/(K_i c_i)$, mean a linear dependence of v/v_0 on σ^{-1}. This kind of behavior is reported in literature by the works of Kubota et al. (1999) and Kubota (2001). Sometimes, the dispersion of the experimental data or the insufficient number of points does not allow being conclusive about this linearity. In the works of Albon and Dunning (1962) and Kubota et al. (2000) a curvature on the representation of v/v_0 vs. σ^{-1} is admissible. According to the competitive adsorption model this situation could roughly correspond to the case of Figure 1, when lower values of $K_\sigma\sigma_{mean}/(K_i c_i)$ are used. The models of Kubota-Mullin and Cabrera-Vermilyea do not admit this variation from linearity – See Equation 7. This happens because, according to the models, the effect of supersaturation is exclusively focused on the critical radius of the two-dimensional nucleus (Equation 6), being the coverage of the active sites on the crystal surface, independent of σ (Equation 8). Although the competition between the phenomena of impurity adsorption and solute adsorption/integration is conceptually admitted (Kubota et al., 1997), the mathematical models ignore it. Such is considered a limitation of these theories (Kubota et al. 2003).

3.2Dependence of v/v_0 on c_i, at Constant σ

Figure 2 shows the impact of the impurity concentration on the relative step velocity. Again, the plot is based on equation 14. A linear relation of the function $v/v_0(c_i)$ is here visible, even for moderate values of $K_\sigma\sigma/(K_i c_{i\_mean})$. Indeed, the experimental works in this field frequently confirm such profile (Mielniczek-Brzoska et al., 2000; Sangwal and Mielniczek-Brzoska, 2002; Kubota et al., 1999; Kubota, 2001). The curve of Figure 2 obtained with a lower value of $K_\sigma\sigma/(K_i c_{i\_mean})$ is also found in the works of Kubota et al. (2000) and Al-Jibbouri and Ulrich (2001). In both studies, the influence of impurities on the growth kinetics of sodium chloride crystals was investigated. The cases reported in Figure 2 are also expected by the models of Kubota-Mullin and Cabrera-Vermilyea by assuming suitable values for the adsorption isotherms constants and impurity effectiveness factor.

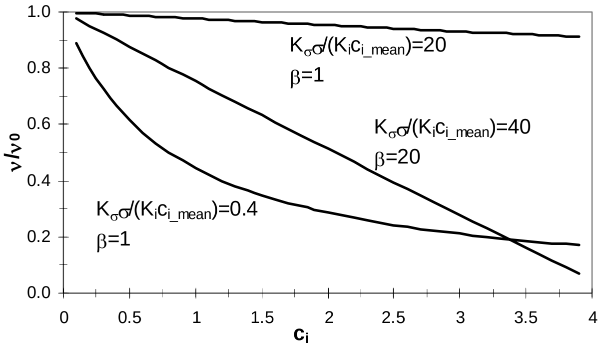

Figure 2 – Theoretical relationship between the relative step advancement and impurity concentration for different combinations of the parameters $K_\sigma\sigma/(K_i c_{i\_mean})$ and β; c_{i_mean} is the mean value of c_i, evaluated for the considered range of impurity concentrations.

In Figure 1 and 2, it is implicit the role of the β parameter. Although the langmuirian constants are not kept constant in all curves, one can infer the higher effect of an impurity when it has higher values of β. As it was presented, this is due to the mobility of the adsorbed impurity molecules, which can determine a strong tendency on occupying the active sites of the crystal.

4.CONCLUSIONS

The competitive nature of impurity adsorption during crystallization is consensual among the existing theoretical models. However, the predictions of these theories are not totally in accordance with this assumption, as it is the case of the role of the solute concentration (and supersaturation), whose effects are limited to the size of the critical radius. With the new model proposed, the dispute between solute and impurity is emphasized in the competitive adsorption isotherm equation. The experimental evidences documented in literature are here confirmed, not only in the case of the influence of impurity concentration on the relative crystal growth rate, but also on the effect of the supersaturation on this rate.

5.NOMENCLATURE

a	length the growth unit, m
c_i	impurity concentration, mg/dm^3 (ppm)
k	Boltzmann constant, J/K
K	Langmuir constant (Equation 8), dm^3/mg
K_i	impurity Langmuir constant (Equation 12), dm^3/mg
K_σ	solute Langmuir constant (Equation 12)
l	average spacing between neighboring impurities, m
L	average distance between step lines, m
v	average step velocity in the presence of impurity, m/s
v_0	step velocity for pure solution, m/s
v_{min}	minimum step velocity, m/s
v_r	velocity of a step with a given radius of curvature, m/s
r	radius of curvature of a growing step, m
r_c	critical radius of the two-dimensional nucleus, m
T	temperature, K
α	impurity effectiveness factor
β	proportionality constant in Equation 11
γ	edge free energy, J/m
θ	coverage of actives sites by adsorbed impurities (Equation 5)
θ_l	coverage of actives sites by adsorbed impurities (Equation 10)
θ_s	surface coverage by adsorbed impurities (Equation 11)
σ	relative supersaturation

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