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The Influence of Impurities on the Crystal Growth Kinetics According to a Competitive Adsorption Model

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ABSTRACT: A mathematical model describing the growth of crystals in impure solutions is presented. Evidence of competitive surface adsorption involving the crystallizing solute and impurities is discussed in terms of the adsorption isotherm in equilibrium and of the mechanism of occupation of active sites for growth. The impurity effect on crystal growth rates is characterized by the Langmuir adsorption constants and by the parameter β measuring the ability of the foreign species to move across the surface and occupy a stable position at the surface steps. Experimental growth rate data taken from the literature is used to test the proposed competitive adsorption model (CAM). The reported effects of the impurity concentration on the crystal growth rate at constant supersaturation are quantitatively described. Additionally, growth rate curves obtained in pure and impure solutions are used to investigate the influence of supersaturation on the relative growth rates. In all the examples considered, the CAM adequately describes the experimental data. An application example is given using the crystal growth rates of sucrose measured in a pilot evaporative crystallizer at different impurity concentrations. The kinetic effect of nonsucrose compounds existing in cane sugar solutions is characterized by estimating the average CAM parameters.

Introduction

The occupation by impurities of preferential places for solute incorporation into the crystal lattice is known to have a strong effect on crystal growth. Small quantities of specific impurities can suppress the growth, while others, being crystallographic face-selective, can be used as habit modifiers. Cabrera and Vermilyea introduced the pinning mechanism to explain the action of the impurities on the advancement of the surface steps.¹ They depart from the representation of crystal growth from pure solution due to the addition of new molecules at active sites (kinks) in the steps. When the impurity is adsorbed at those places, the steps flowing at the crystal surface are hindered and tend to curl around. If the average distance between adsorbed impurities along the step is smaller than $2 \times$ the critical radius for two-dimensional nucleation ($l < 2\rho_c$) the step will stop. The relationship between the velocity of advancement of steps and the radius of curvature is given by eq 1, also-called the Gibbs-Thomson formula:

$$\frac{v_\rho}{v_\infty} = 1 - \frac{\rho_c}{\rho} \quad (1)$$

where v_∞ stands for the movement of a straight step. At low supersaturations ($S \ll 1$) ρ_c is given by

$$\rho_c = \frac{\gamma\Omega}{kT} \frac{1}{S} \quad (2)$$

When, in eq 1 $\rho = l/2$, a minimum step velocity is reached (v_{\min}). Originally, Cabrera and Vermilyea considered the average step velocity during the time of step squeezing as the geometric mean of v_∞ and v_{\min} ($v = \sqrt{v_\infty v_{\min}}$),¹ so that,

$$\frac{v}{v_\infty} = \sqrt{1 - 2\frac{\rho_c}{l}} \quad (3)$$

More recently, Kubota and Mullin proposed the use of an arithmetic mean of the same limit velocities to describe v ($v = (v_\infty + v_{\min})/2$).² In this case,

$$\frac{v}{v_\infty} = 1 - \frac{\rho_c}{l} \quad (4)$$

and $l \geq \rho_c$. By assuming (a) the step advancement velocity, v , to be proportional to the face growth rate, R , and (b) infinite radius of curvature of the steps in pure system ($v_0 = v_\infty$), one can express eq 4 in terms of the growth rate ratio in impure and pure systems ($v/v_\infty \sim R/R_0$). The second assumption is open to criticism, particularly if spiral growth mechanisms are assumed.³ From simple geometric considerations, one can say that the equilibrium coverage of adsorption sites by impurities (θ_l) corresponds to the ratio of the average distance between active sites to the average distance between neighboring adsorbed impurities, $\theta_l = L/l$. This fraction is commonly given by a Langmuir adsorption isotherm:

$$\theta_l = \frac{K_a c_i}{K_a c_i + 1} \quad (5)$$

Nevertheless, Temkin isotherms⁴ and Freundlich isotherms⁵ also have been used. The typical form of the Kubota-Mullin equation is obtained by rewriting eq 4 as follows:

$$\frac{R}{R_0} = 1 - \alpha \frac{K_a c_i}{K_a c_i + 1} \quad (6)$$

with α being the “impurity effectiveness factor”, defined as

$$\alpha = \frac{\gamma\Omega}{kTL} \frac{1}{S} \quad (7)$$

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According to the value of α , equally adsorbed impurity species can affect very differently the growth kinetics. The determination of α and K_a is generally done by fitting the model equations to experimental data on the influence of c_i and S on the relative growth rates. Alternatively, K_a can be determined by performing independent adsorption experiments, where the impurity uptake into crystal is measured as a function of c_i .^{6,7}

Despite the current interest in this field of crystallization, the existing theories are not yet able to answer all questions.^{8–10} In this paper, a new engineering approach is proposed and validated against experimental growth rate data in the presence of impurities. The new model is believed to contribute to a better understanding of the mechanism by which impurities affect crystal growth from solution.

The Competitive Adsorption Model

In the competitive adsorption model (CAM), crystal growth in the presence of an impurity is seen as a competition between the crystallizing solute units and the foreign species for the preferential adsorption sites. The factors determining the success of each type of molecule are related to their concentration, mobility, and physicochemical affinity with the crystal surface. When a simple Langmuir adsorption isotherm is considered (eq 5), θ_i is assumed to be exclusively dependent on the impurity concentration. This is not likely to be true since the number of kink sites occupied by impurities is certainly lowered as the supersaturation increases. For high supersaturation, all the active sites would be occupied by the crystallizing solute, and $\theta_i \sim 0$. The new perspectives on the impurity adsorption mechanism provided by the CAM will be complemented by an alternative description of the impurity effect on the crystal growth rate. This new approach considerably differs from the pinning mechanism proposed by Cabrera and Vermilyea and developed by Kubota and Mullin. In this regard, recent atomic force microscopy evidence go against the validity of the Gibbs-Thomson formula (eq 1) upon which the pinning mechanism is based.^{11–13} Instead of a gradual increase of v with ρ , an abrupt increase in v occurs when the step exceeds a critical dimension (ρ_c). The CAM is concerned with the impurity kinetic effect and not with modifications of the solution properties by the impurity.

The Langmuir adsorption isotherm is conventionally used to quantify the fraction of the solid surface covered by a monolayer of adsorbed species. As referred, crystal growth in impure solution comprises a multicomponent sorption phenomenon, where the adsorption sites are disputed by both the impurity and the pure solute. In equilibrium, the fraction of the surface occupied by impurities is given by the extension of the basic Langmuir model to competitive adsorption:¹⁴

$$\theta_s = \frac{K_i c_i}{K_i c_i + Kc + 1} \quad (8)$$

Expressing this equation as a function of supersaturation ($S = c/c^* - 1$) gives

$$\theta_s = \frac{k_i c_i}{k_i c_i + kS + 1} \quad (9)$$

where $k_i = K_i/(1 + Kc^*)$ and $k = Kc^*/(1 + Kc^*)$. Low surface impurity coverage ($\theta_s \ll 1$) is expected when the dimensionless

concentration $k_i c_i$ is also low. Even in these cases of barely adsorbed impurities, crystal growth rates can be drastically affected by impurities. This is certainly related to the mechanism of surface integration, and in particular, with the surface mobility of the different molecules.

According to the so-called Kossel model of a growing crystal face in pure solution, molecules entering a terrace near a step can be loosely adsorbed, diffuse across the surface, and reach an energetically favorable place (kink) to integrate the crystal. Although well-established in crystal growth from vapor, the existence of significant surface diffusion during solution growth is open to discussion.^{15–17} In the case of crystal growth in impure solution the kinetic effect of an impurity involves three analogous stages:⁴

- (1) Surface adsorption of the impurity molecules diffusing from solution.
- (2) Migration of impurity admolecules across the surface
- (3) Step/kink adsorption of impurity molecules migrating on the surface.

Each of these stages has an associated thermodynamic energy change, whose relative values determine if and how adsorption occurs. The coverage of active sites by an impurity (θ_i) will be proportional to the corresponding overall surface coverage (θ_s):

$$\theta_i = \beta \theta_s \quad (10)$$

The parameter β here introduced takes higher values when the second and third stages are thermodynamically favorable relative to the first one. For very mobile impurities, β is much greater than 1, i.e., impurities will be mainly concentrated in the preferential adsorption sites. Conversely, in the case of favorable surface adsorption and low mobility of the adsorbed impurities, β is expected to take small positive values. The density of adsorbed molecules of crystallizing solute at the surface (n_s) is generally thought to decrease toward the equilibrium concentration n_{se} as we approach the step. The intrusion of impurities on the adsorption equilibrium at the step will decrease n_{se} to $n_{se}(1 - \theta_i)$, and consequently, the growth rate perpendicular to the surface defined as³

$$R_0 = n_{se} \frac{\chi h D_s}{n_e x_s^2} \left(\frac{S^2}{C_1} \right) \tanh \left(\frac{C_1}{S} \right) \quad (11)$$

will decrease in the same proportion. Equation 11 results from the Burton Cabrera and Frank surface diffusion mechanism, wherein the constant C_1 is defined by

$$C_1 = \frac{2\pi\gamma\Omega}{kTx_s} \quad (12)$$

In accordance with what is stated, the ratio between growth rates in impure and pure solution is given by the following equation:

$$\frac{R}{R_0} = 1 - \theta_i \quad (13)$$

which, according to eqs 9 and 10 can be rewritten as

$$\frac{R}{R_0} = 1 - \beta \frac{k_i c_i}{k_i c_i + kS + 1} \quad (14)$$

New perspectives about the role of important variables in crystal growth from impure solutions (supersaturation, impurity

concentration, temperature, surface mobility, etc.) arise from eq 14. Nevertheless, evidence of competitive adsorption has been previously reported.¹⁸ For example, crystal growth stoppage after previous dissolution in contaminated solutions suggests the occupation by impurities of the active sites for pure solute integration.^{19,20} The observation of different growth rates when experiments are carried out at increasing or decreasing supersaturation indicates not only the existence of non-steady-state impurity adsorption,²¹ but also the competitive nature of this step and the crystallizing species attachment.²² Indeed, the theoretical treatment of the growth rate hysteresis proposed by Guzman et al.²¹ and Kubota et al.^{8,23} points out a time constant for impurity adsorption “ τ ” that is supposed to be a function of supersaturation. Such dependence can only be explained assuming that the adsorption isotherm is also a function of the crystallizing solute concentration.^{8,23} In the present study, we will not be concerned with non-steady state adsorption; therefore, equilibrium conditions are assumed.

Analysis of Literature Data

The following analysis is not intended to be a general review of the published work in the field (for this purpose, see the works of Kubota,²⁴ and Sangwal^{25,26}), but instead a selection of typical trends on the influence of supersaturation and impurity concentration on the relative growth rates R/R_0 . Our main emphasis is on the CAM differences and common aspects of existing theories, as well as on the contribution of the new model to solve unanswered questions. In the first phase, the case of weak impurity adsorption (low θ_s) is studied, since its quantitative treatment is analogous to the one followed in the Kubota-Mullin model. The novelty of the CAM is then highlighted by analyzing the growth rate dependence on the impurity concentration and supersaturation, when strong impurity adsorption occurs.

Barely Adsorbed Impurity. According to the definition of θ_s given in eq 9, low surface coverage is expected when the impurity affinity with crystal is low (low k_i), when the solubility of the crystallizing solute is high (high c^* , high k and low k_i) and for small impurity concentration (low c_i). Barely adsorbed impurities that impact on the crystal growth rates are called “active impurities”. If the conditions are such that $kS \gg (k_i c_i + 1)$, eq 14 simplifies to

$$\frac{R}{R_0} \approx 1 - \beta \frac{k_i c_i}{kS} \quad (15)$$

For this combination of factors, the relative growth rate measured at constant supersaturation is linearly dependent on c_i . This corresponds to the case shown in Figure 1 a, representing the crystal growth of sucrose in the presence of raffinose.²⁷ As expected, deviations from linearity start to be pronounced at low supersaturations and high c_i . From eq 15, it also arises that relative growth rates measured at constant c_i would be linearly dependent on the reciprocal of supersaturation (Figure 1b). The effect that trace amounts of raffinose have on R/R_0 is explained by the strong capacity of the impurity to occupy the active sites for growth, at the surface of the sucrose crystal (high β value). To provoke similar sucrose growth rate lowering, other impurities such as invert sugars, inorganic salts, oligosaccharides, and carbohydrates would have to occur in solution in much higher concentrations.²⁸

The behavior shown in Figure 1 was also identified for potassium sulfate growing in the presence of iron(III),²⁹ for

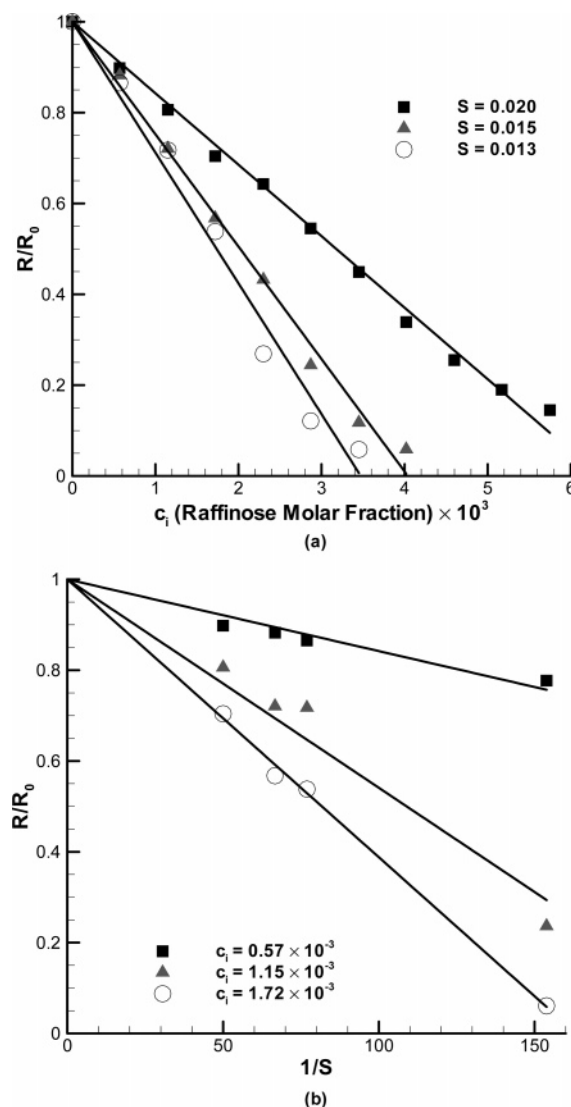


Figure 1. Effect of (a) the raffinose concentration and (b) the reciprocal of supersaturation on the relative growth rate of sucrose at 30 °C.²⁶

trinitrotoluene in the presence of 2,2-dinitropropane (R/R_0 vs c_i relationship)³⁰ and for NaClO_3 in the presence of $\text{S}_2\text{O}_6^{2-}$ (R/R_0 vs $1/S$ relationship).³¹ These results are as well explained by the Kubota-Mullin model, assuming $K_a c_i \ll 1$ in eq 5. Because of their high affinity to crystal growth sites, tailor-made additives can be considered as a particular case of active impurities.

Widespread Impurity Adsorption. Deviations from linearity on the representation of R/R_0 as a function of c_i are indicative of significant impurity adsorption at the crystal surface. When the crystal surface is extensively covered by the impurity (high θ_s), even moderately active impurities (low β) would influence the growth kinetics. In these cases, $k_i c_i$ is of comparable order of magnitude of $kS + 1$ in eq 9. The concept of competitive adsorption is here properly used since there is not a clear dominance of any of the adsorbates at the surface. Distinct supersaturation dependences of R/R_0 at constant c_i are expected by the CAM and by noncompetitive adsorption models, while the parameters of the Kubota-Mullin can be reinterpreted in the light of the CAM when analyzing the influence of c_i on R/R_0 at constant supersaturation.

Let us consider in the first place the example of Figure 2 about the influence of c_i on the relative growth rates of

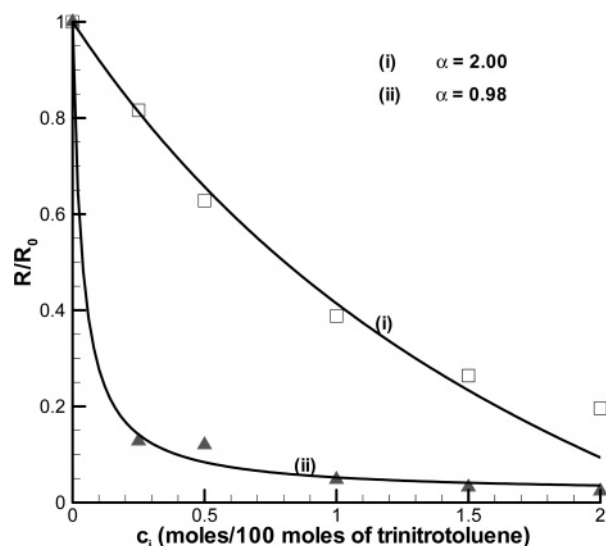


Figure 2. Effect of different additives on the relative growth rates of trinitrotoluene at 74.0 °C,²⁹ and respective fit to eq 6: (i) 2,4,6-trinitrodiphenyl ether; (ii) 2-chloro-2,4,6-trinitrostilbene.

trinitrotoluene growing in the presence of two distinct impurities.³⁰

As shown, the results follow the trend expected by eq 6 (Kubota-Mullin model) and the value of α obtained almost duplicates from one additive to the other. The difference between the effectiveness factors obtained should not be surprising, since different physicochemical properties of the additives are expected to influence differently the growth rate mechanism. Nevertheless, from the definition of the impurity effectiveness factor given in eq 7, α is a function of the molecular volume of the crystallizing solute, of the crystal surface and interfacial properties, and of temperature and supersaturation, but is not supposed to change with any characteristic property of the impurity. In other words, according to its classical definition, α is not expected to vary significantly with the impurity type. An alternative perspective of the physical meaning of α and K_a results from the competitive adsorption theory. At constant supersaturation, eq 14 of the CAM can be rewritten assuming kS as another constant:

$$\frac{R}{R_0} = 1 - \beta \frac{\frac{k_i}{kS+1}c_i}{\frac{k_i}{kS+1}c_i + 1} \quad (16)$$

By comparing this equation with the Kubota-Mullin definition given in eq 6, one realizes that $\alpha = \beta$ and $K_a = k_i/(kS + 1)$. The equivalence between the impurity effectiveness factor and the parameter β solves the dilemma of unchanging α among impurities. As referred, in the CAM β is a function of specific properties of the impurity (e.g., surface mobility), and thus it can be considered an intrinsic effectiveness factor of the pure solute-impurity system. The competitive adsorption constants k and k_i can be estimated either by fitting eq 14 to additional growth data on the influence of S on R/R_0 at constant c_i or by performing separate adsorption experiments.

When extensive impurity adsorption occurs, contrasting positions on the supersaturation dependence of the crystal growth rate result from the pinning mechanism theories and the CAM. The concept of critical supersaturation (S_c), defined by Kubota et al.²² as the limit supersaturation below which R

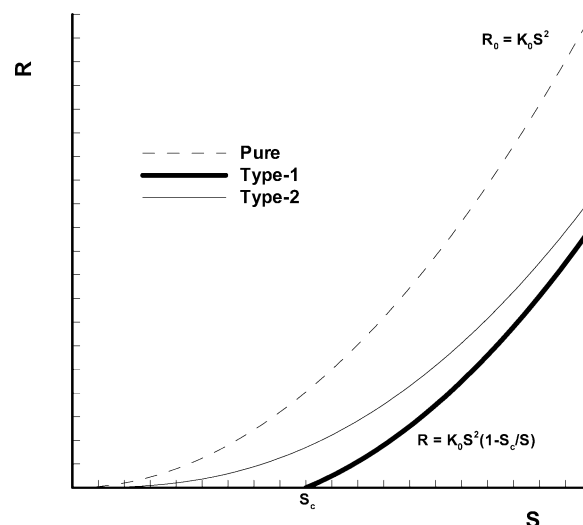


Figure 3. Typical growth rate curves in the presence of impurities.

= 0, can be conveniently used to illustrate the differences. In the Kubota-Mullin model, S_c is obtained by setting $R/R_0 = 0$ in eq 6 and using the definition of α given in eq 7, so that

$$S_c = \frac{\gamma\Omega}{kTL} \frac{K_a c_i}{K_a c_i + 1} \quad (17)$$

The stronger the impurity kinetic effect is, the wider is the supersaturation range of no growth, $0 \leq S \leq S_c$. The relative growth rate is easily expressed as a function of S_c using eqs 17 and 7:

$$\frac{R}{R_0} = 1 - \frac{S_c}{S} \quad (18)$$

In Figure 3, the type-1 curve represents the theoretical influence of an active impurity on the crystal growth kinetics as stated by the Kubota-Mullin model; crystals would start to grow at supersaturations above S_c , and for $S \gg S_c$ the growth rate curve is approximately parallel to the one of the pure system. In the example given, a second-order rate equation was used for the pure system. The behavior illustrated by type-1 curve can be found in the literature when very active impurities are investigated, such as in the case of ammonium oxalate monohydrate growing in the presence of Cr(III) ions,⁵ or the already mentioned example of the sucrose- α -D-glucose impurity system.²⁷ Even so, the other type of impurity-affected kinetics exemplified in Figure 3 (type-2 curve) is also frequently reported in the literature.^{28,32-34} Despite the marked growth rate lowering ($R/R_0 < 1$), there is not a clear supersaturation limit below which growth stops, which makes $S_c = 0$. This fact is not explained by pinning mechanism theories. Following, for example, the Kubota-Mullin model, if $S_c = 0$ it results from eq 18 that $R = R_0$, whichever the supersaturation considered.

Considering now the new model, the CAM mathematical definition of critical supersaturation is obtained by setting $R/R_0 = 0$ in eq 14,

$$S_c = \frac{k_i c_i (\beta - 1) - 1}{k} \quad (19)$$

By combining this equation with eq 14, an alternative equation for R/R_0 results:

$$\frac{R}{R_0} = 1 - \frac{1 + k_{si}S_c}{1 + k_{si}S} \quad (20)$$

with

$$k_{si} = \frac{k}{1 + k_i c_i} \quad (21)$$

From eq 19 one can establish two distinct situations: (i) if besides being extensively adsorbed (high $k_i c_i$ product), the impurity is also active ($\beta > 1$), S_c will assume positive values; (ii) if the impurity is slightly active, $\beta < 1$, and the critical supersaturation given by eq 19 will be negative. The first case roughly corresponds to the type-1 curve in Figure 3. As for the Kubota-Mullin model, there is a zone of no growth for $S < S_c$, and for $S \gg S_c$ R tends to be parallel to R_0 . Despite the common limit cases, distinct supersaturation dependences of R are expected by the two theoretical models for intermediate supersaturations. Comparing eqs 18 and 20, one finds that a linear R/R_0 vs $1/S$ relationship is expected by the Kubota-Mullin model, while in the CAM, the relative growth rates decrease with $1/S$ in a more gradual way. Both trends are represented in Figure 4 for the case of sodium chloride growing in the presence of lead(II).⁶ As shown, the results are very well described by the CAM. The parameters of eq 20 that best fit the data are $k_{si} = 699$ and $S_c = 8.6 \times 10^{-4}$, indicating that lead(II) is an active impurity during the growth of sodium chloride ($\beta > 1$).

The other situation resulting from the CAM definition of critical supersaturation corresponds to poorly active impurities, so that $\beta \leq 1$ and $S_c \leq 0$. In physical terms, negative critical supersaturations mean that growth will always occur at positive supersaturations, even at growth rates much smaller than R_0 (see type-2 curve in Figure 3). As mentioned before, this behavior is not expected by the traditional pinning mechanisms, despite the great number of published studies reporting it. Examples of type-2 curves can be found for the sodium chloride growth in the presence of impurities like MgCl_2 , PbCl_2 , $\text{K}_4\text{Fe}(\text{CN})_6 \cdot \text{H}_2\text{O}$,³² for potassium sulfate growth in the presence of chromium(III),³³ for hydroxyapatite (0001) face growth in the presence of magnesium and zinc,³⁴ and for sucrose crystal growth in the presence of several poorly active impurities.²⁸ A particular case of impurity affected growth curves is observed when the growth kinetic order remains unchanged in pure and impure solutions, i.e., when R/R_0 is independent of supersaturation, even at low S . In the following example, one of these situations is used to illustrate the CAM applicability to industry purposes.

Application Example

So far, we have discussed the action of single impurities during crystal growth, but in most applications, different impurities are present simultaneously and have a combined effect on the growth kinetics. In the industrial crystallization of sucrose, empirical equations are used to describe the variation of sucrose solubility and growth rate with the solution purity, generally expressed in terms of the nonsucrose to water ratio (NS/W). The estimated empirical parameters are valid for the specific composition of the syrup used on the measurements. It is reported that in the beet sugar industry, raffinose is the most influencing impurity, while in cane sugar, oligosaccharides and the dextran polysaccharide are suspected to be the ones having a determinant role.³⁵ From the already mentioned study on the isolated influence of some of these species on sucrose growth,²⁸ one may expect active sugar beet impurities (high β) and poorly

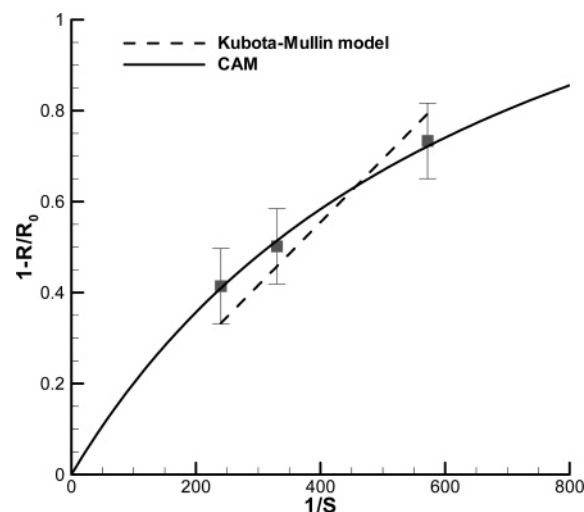


Figure 4. Representation of eqs 18 (Kubota-Mullin model) and 20 (CAM) for the set of parameters that best fit the data of Kubota et al.⁶ on the effect of lead(II) on the growth of sodium chloride crystals at 35 °C. The results are estimated for $c_i = 0.25 \times 10^{-6}$ mol/dm.³ The vertical error bars indicate standard errors.

Table 1. Experimental Conditions of the Sucrose Growth Experiments

exp no.	NS/W	syrup	average temp (°C)	crystal content (%)	
				min	max
1	0	synthetic	62.3	0	13.6
2	0	synthetic	62.3	13.6	22.5
3	0.058	blended	62.1	0	17.1
4	0.434	cane	62.0	0	11.0
5	0.490	cane	65.6	8.1	16.9
6	0.597	cane	62.2	18.5	31.0

active sugar cane impurities (low β). Using crystal growth rates of sucrose measured in a pilot vacuum pan (evaporative crystallizer), an application example of the CAM is now given to characterize the kinetic influence of nonsucrose compounds in typical cane sugar syrups.

Experimental. Crystal growth rates of sucrose were measured in a 50 L pilot vacuum pan at different NS/W levels. The detailed procedure and experimental apparatus are described elsewhere.³⁶ Growth experiments were carried out at a constant amount of water by means of an automatic control of the microwave density. Water was continuously admitted into the pan to balance the evaporation rate. Three types of syrups were used: industrial syrup from Cora Texas mill (Louisiana), synthetic syrup, prepared with refinery white sugar and tap water, and blended syrup obtained by adding 1 part of the industrial syrup to approximately 8 parts of synthetic syrup. Composition analysis indicated that the industrial syrup has 87.7% apparent purity (sucrose content measured by the polarization method), 65.4% dissolved solids measured by refractometry, 1.12% glucose and 1.16% fructose measured by HPLC, and 2.2% ash content. In the experiments with industrial syrup, different NS/W levels correspond to different boiling stages. Initially, the crystallized matter content is lower and the mother liquor purity is higher; as the crystallization proceeds, supersaturation is achieved by means of increasingly higher amounts of evaporated water, and the NS/W level is increased. Table 1 summarizes the main experimental conditions at which growth rates were measured.

Previous growth experiments at laboratory scale suggest a linear dependence of the overall growth rate of sucrose (R_G) on

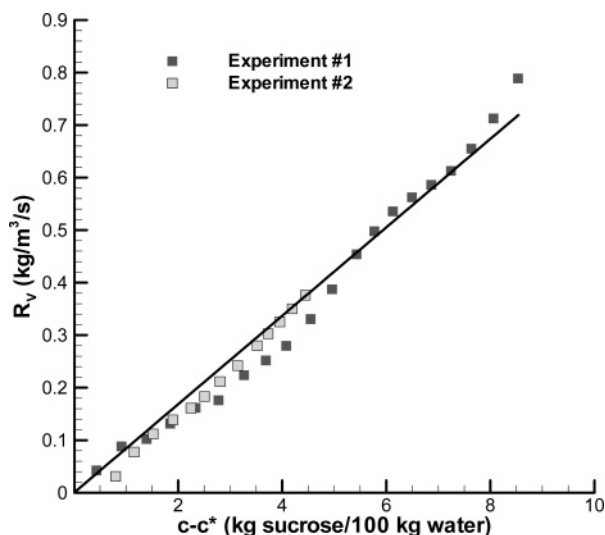


Figure 5. Volumetric growth rates of sucrose obtained with synthetic syrup (NS/W ~ 0).

the instantaneous crystal size (L).³⁷ On the basis of this premise, the kinetic effect of crystal size was normalized by calculating the crystal growth rates in a volumetric basis:³⁷

$$R_v = \frac{f_s}{f_v} \frac{R_G}{L} = 6\rho_s \frac{R}{L} \quad (22)$$

where f_v and f_s are the volume and surface area shape factors. The volumetric growth rate is directly computed from the variation of the mass of crystals, regardless of their size, number, and surface area during the experiments, according to the following definition.³⁷

$$R_v = \rho_s \frac{\Delta \ln m}{\Delta t} \quad (23)$$

The average supersaturation in the time interval Δt is calculated from the average dissolved sucrose concentration (c) in the same period and from the sucrose solubility (c^*) obtained for the set of conditions of each experiment.³⁸

Results and Discussion

Figure 5 shows the growth rate curves obtained with synthetic syrup ("pure" case) at different experimental conditions (see Table 1). Equally spaced data points are considered. Both curves are in good agreement, despite the differences in crystal size and mass fraction and hydrodynamic conditions. This fact sustains the use of volumetric growth rates to account for the kinetic influence of crystal size, as well as our previous results reporting almost invariable mass transfer resistances at different hydrodynamic conditions inside the pan.³⁸

Variations in the volumetric growth rate of sucrose with NS/W can therefore be attributed to the impurities influence on the crystal growth kinetics. The differences found are represented in Figure 6. All the curves were fitted by a rate law of the form

$$R_v = K_v \Delta c \quad (24)$$

A linear relationship between crystal growth rates and supersaturation was already reported by Wright and White in their mathematical model of vacuum pan crystallization.³⁹ At

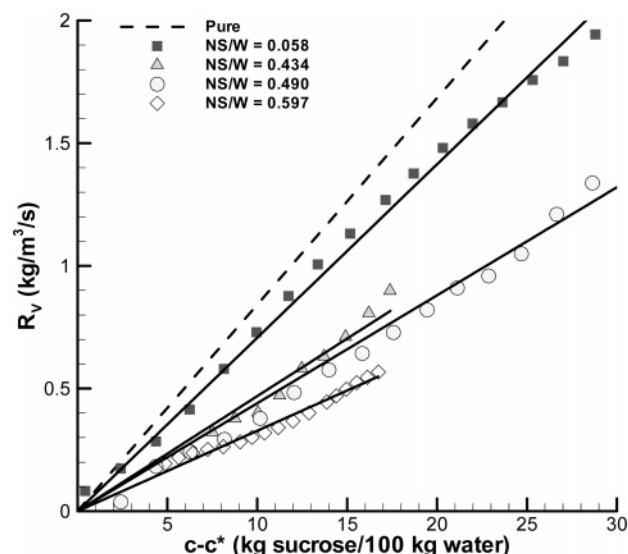


Figure 6. Volumetric growth rates of sucrose obtained at different NS/W levels.

Table 2. Volumetric Rate Constants That Best Fitted the Results of Figures 5 and 6, and Relative Volumetric Growth Rates, at Different NS/W Levels

exp no.	NS/W	K_v	R^2	R_v/R_{v0}
1	0	0.0842	0.974	1
3	0.058	0.0707	0.994	0.840
4	0.434	0.0469	0.948	0.557
5	0.490	0.0440	0.980	0.522
6	0.597	0.0328	0.971	0.390

same time, they found an exponential dependence of the growth rate on NS/W:

$$\frac{R_1}{R_2} = \exp\left\{-1.75\left[\left(\frac{NS}{W}\right)_1 - \left(\frac{NS}{W}\right)_2\right]\right\} \quad (25)$$

Since the publication of the work of Wright and White, other authors have proposed alternative empirical parameters for the same relationships.^{40,41} Using eq 25 and the equivalence given in eq 22, one can estimate the relative growth rate in impure and pure solutions, irrespective of the crystal size:

$$\frac{R_v}{R_{v0}} = \exp\left(-1.75 \frac{NS}{W}\right) \quad (26)$$

The form of eq 26 can be tested against the results of Figure 6. With that purpose, the relative volumetric growth rates were calculated using the rate constants that best fit the experimental curves (Table 2). The obtained results are plotted as a function of NS/W in Figure 7. A fairly good adjustment was obtained using an exponential constant of -1.45 . This indicates a somewhat lower growth rate variation with NS/W than eq 26.

Although useful for the sugar industry, the exponential-type equation correlating the relative growth rates and the impurity concentration lacks physical meaning. The competitive adsorption theory can be applied to sugar crystallization by characterizing the overall action of the nonsucrose compounds through average CAM parameters. Because of the large number and variety of impurity species (which can be grouped as polysaccharides and other organic compounds, invert sugars, color and ash) it is not feasible to distinguish the competitive adsorption parameters for each component in sugarcane syrups.

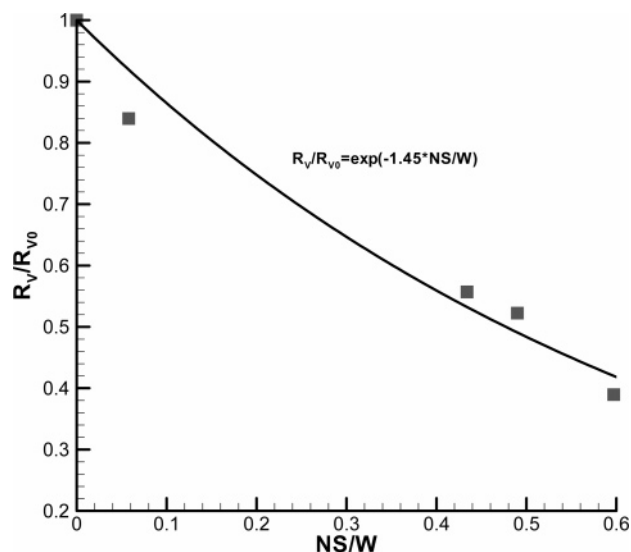


Figure 7. Influence of NS/W on the relative volumetric growth rates of sucrose and respective fit using an exponential curve.

Linearizing eq 14 and expressing it in terms of volumetric rates yields:

$$\frac{1}{1 - R_V/R_{V_0}} = \frac{1 + kS}{\beta} \frac{1}{k_i c_i} + \frac{1}{\beta} \quad (27)$$

The dimensionless impurity concentration $k_i c_i$ can be conveniently given as a function of the nonsucrose to water ratio, by letting $k_i c_i = k'_i(NS/W)$. The relative growth rates of sucrose (R_V/R_{V_0}) are a strong function of NS/W but did not change significantly with supersaturation. At low supersaturations, this fact is explained by the simplified form of eq 27 admitting $kS \ll 1$:

$$\frac{1}{1 - R_V/R_{V_0}} = \frac{1}{k'_i \beta} \frac{1}{NS/W} + \frac{1}{\beta} \quad (28)$$

The parameters β and k'_i are easily obtained by fitting eq 28 to the data of Table 2. In so doing, the average impurity activity of the compounds in the cane solutions is characterized by $\beta = 0.90$ and $k'_i = 2.64$. In Figure 8, the obtained influence of NS/W on the relative growth rates can be compared with that given by the CAM using the fitted parameters.

The good agreement found confirms that the new model is a valuable alternative to the empirical correlations used so far in the sugar industry. As expected, the impurities in sugar cane solutions are moderately active in suppressing the sucrose growth rate. Since $\beta < 1$, this example corresponds to a system exhibiting negative S_c (eq 19). The marked growth rate decrease is due to the extensive impurity adsorption in the considered range of NS/W. For example, for NS/W = 0.6, the overall surface coverage is given by

$$\theta_s \approx \frac{k'_i(NS/W)}{k'_i(NS/W) + 1} = 0.61 \quad (29)$$

which is equivalent to say that, under these conditions, more than 60% of the sucrose crystal surface is covered by nonsucrose compounds.

Conclusions

An expression establishing the dependence of the relative growth rates in impure and pure solutions on supersaturation

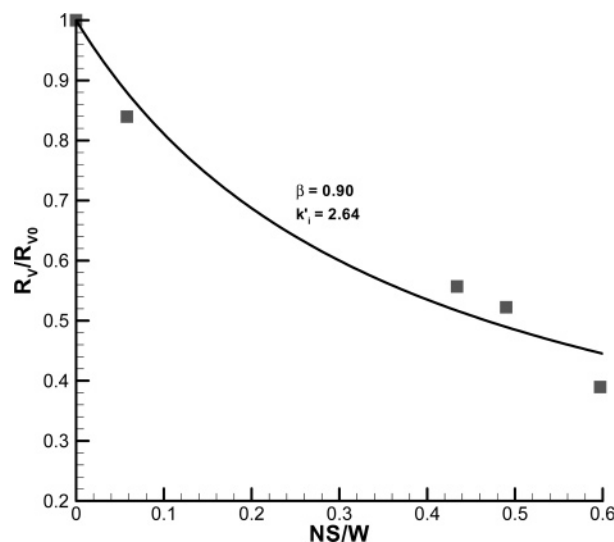


Figure 8. Experimental and theoretical influence of NS/W on the relative volumetric growth rates of sucrose. The CAM curve is represented for the parameters of eq 28 that best fit the experimental data.

and impurity concentration is proposed (eq 14). A mechanism of competitive adsorption is assumed, where the crystallizing solute and the impurity dispute (1) the coverage of the crystal surface and (2) the occupation of energetically favorable places at surface steps. The first stage is quantified by a Langmuir isotherm for competitive adsorption, while the second is a function of the thermodynamic energy change of the surface processes. According to classical theories of crystal growth, the growth rate varies in the same proportion as the number of adsorbed molecules at the step. At a given surface coverage, the impurity activity reflects the tendency to replace the crystallizing solute at the active sites and is measured by means of the parameter β . In systems exhibiting $\beta > 1$ the fraction of active sites occupied by the impurity is higher than the surface coverage. This can lead to crystal growth suppression at supersaturation below a critical limit given by eq 19. For $\beta < 1$, crystal growth can be slowed by the presence of impurities but is not suppressed. The role of supersaturation and impurity concentration on the crystal growth rates significantly changes with the impurity adsorption extension and impurity activity. Published experimental data showing different types of impurity-affected kinetics was adequately described by the CAM. Differences and common aspects between the new competitive model and existing theories based on the pinning mechanism were discussed, and the CAM contribution to solve unanswered questions was highlighted. Crystal growth rates of sucrose measured in a pilot vacuum pan at different impurity concentrations were well described by the CAM. The average activity of the nonsucrose compounds in cane sugar syrups was estimated to correspond to $\beta = 0.90$, which confirms the low kinetic effect predicted in literature for these compounds. This application example illustrates the robustness of the new model and demonstrates the CAM to be a valuable alternative to the empirical correlations used so far in the sugar industry.

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Notation

Roman Symbols

C_1	constant of the BCF equation, eq 12
c	solute concentration, mole fraction or kg of sucrose/100 kg of water
c_i	impurity concentration, mole fraction or mol/dm ³
D_s	surface diffusion coefficient, m ² /s
f_s	surface area shape factor
f_v	volume shape factor
h	elementary height, m
K_V	volumetric growth constant, eq 24
K_a	Langmuir constant in the Kubota-Mullin model, eq 5
K_i	Langmuir constant in the CAM, eq 8
K	Langmuir constant in the CAM, eq 8
k	Boltzmann constant, J/K
k_i	parameter of the CAM, $k_i = K_i/(1 + Kc^*)$
k'_i	parameter of the CAM, $k'_i c_i = k'_i(NS/W)$
k	parameter of the CAM, $k = Kc^*/(1 + Kc^*)$
k_{si}	parameter of the CAM, $k_{si} = k/(1 + k_i c_i)$
L	crystal size, m
L	average distance between active sites in a step, m
l	average distance between adsorbed impurities in a step, m
m	mass of crystals, kg
n_e	density of molecular positions at crystal surface, m ⁻²
n_s	density of surface adsorbed molecules, m ⁻²
n_{se}	density of surface adsorbed molecules in equilibrium, m ⁻²
NS/W	non-sucrose to water ratio, kg of nonsucrose/kg of water
R	growth rate perpendicular to the crystal surface, m/s
R_G	overall growth rate, kg/m ² /s
R_V	volumetric growth rate, kg/m ³ /s
S	supersaturation
T	temperature, K
t	time, s
v	step advancing velocity, m/s
x_s	mean displacement of adsorbed molecules, m

Greek symbols

α	impurity effectiveness factor in the Kubota-Mullin model
β	impurity effectiveness factor in CAM, eq 10
γ	interfacial tension, J/m ²
Δ	difference/variation
θ_i	coverage of adsorption sites by impurities in a step
θ_s	overall surface coverage
ρ	radius of curvature of a step, m
ρ_s	crystal density, kg/m ³
χ	constant of the BCF equation, eq 11
Ω	molecular volume, m ³

Indices and exponents

c	critical
min	minimum
*	saturation
∞	straight step
0	pure system

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