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Application of a Kinetic Model for Studying Impurities Effect on Crystallization of NaCl, KBr, ADP and Sucrose Solutions

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Abstract

Addition of impurities has an important role on the kinetic crystallization. Therefore, influence of impurities on the crystallization kinetics of NaCl, KBr, ADP and Sucrose solutions was investigated in a fluidized bed crystallizer. The growth and dissolution rates were related to the super saturation and impurity concentration. A strong mathematical model is applied to describe crystal growth rates within aqueous solutions as a function of impurity concentration. The model tries to relate the step velocity to the useful parameters such as the surface coverage (θ_{eq}), as well as the effectiveness factor of impurity, α. When $\alpha>1$, the step velocity is stopped at $\theta_{eq} <1$ (incomplete coverage of the active sites for adsorption). In the case of $\alpha=1$, the velocity reaches zero just at $\theta_{eq}=1$ (complete coverage) but approaches a limiting value. The value of α is changed by stereo chemical factors and decreases as the supersaturation is increased. The Langmuir adsorption isotherm is used to relate the relative step velocity with the impurity concentration in solution. Experimental results show that increasing the amount of impurity concentration leads to a decrease in the step velocity. Experimental data and model predictions have been compared to show that the agreement between them is very good. The obtained results are suitable for designing and quality control of the crystallization processes in chemical industries.

Keywords: *Crystal Growth Rate, Impurity Effectiveness Factor, Super Saturation, Step Velocity*

1. Introduction

Crystallization as a mass transfer process can be observed, especially when studying the different steps of crystal growth. In this case, diffusion phenomena have a key role to explain the kinetics of crystal growth [1-3]. The growth rate of a crystal is known to be reduced by traces of certain impurities. Selected impurities have been widely used in industry to change the shape of crystals and to improve the quality of crystalline products, powders or granular materials. In fact, comprehensive studies on the crystallization process can provide useful information with regard to design and quality control of the crystallization in the industrial crystallizers [4].

Impurity action on crystal growth has also been the subject of many experimental and theoretical studies in recent years [5-12]. The

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first models explain the adsorption of impurity species (ions, atoms or molecules) at kink, edge, and traces of a growing surface. They illustrate that an apparently flat crystal surface is in fact made up of moving layers (steps) of monatomic height which may contain one or more kinks. In addition, there will be loosely adsorbed growth units (atoms, molecules or ions) on the crystal surface and steps. Growth units are most easily incorporated into the crystal at a kink; the kinks move along the step and the face is eventually completed. A fresh step could be created by surface nucleation, and this frequently commences at the corners [13].

Davey and Mullin [14] reported the effect of $FeCl_3$ and $AlCl_3$ on the step velocity of ADP (ammonium dihydrogen phosphate). The step velocity in the directions of the faces of ADP crystals approached zero asymptotically as the impurity concentration was increased. Bliznakov and Nikolaeva [15], on the other hand, reported a different type of impurity actions of aliphatic carboxylic acids on the crystal growth of potassium bromide. The face growth rate approached asymptotically a non-zero value in this case.

Recently, Kubota and Mullin [14] advanced a new kinetic model of growth in the presence of impurities. The model describes the adsorption of any impurity along steps and introduces an effectiveness parameter α for the impurity adsorption. Nowadays, massive usage of crystal's impurities in crystallization phenomena are inevitable. Considering the above, an attempt was made to represent the effects of different impurities into some materials. An effectiveness factor is introduced to take into account the growth suppression ability of the impurity. The growth suppression effect is assumed to be determined by the effectiveness factor and fractional coverage of the crystal surface by the impurity adsorbed. The physical meaning of the effectiveness factor and step velocity will also be discussed. Furthermore, considering the important role of impurities actions in crystallization, the model is applied for KBr, ADP and Sucrose solutions. The experimental data and the model predictions are compared to show the ability of the model for the explanation of the kinetics of crystallization processes.

2. The mathematical model

Davey and Mullin [15-16] derived the following expression for the step velocity V in the presence of impurity, assuming that the rate of surface diffusion of growth units to the steps, which is a rate determining process, is reduced by impurities adsorbed on the terraces, i.e., the flat faces between the steps,

$$V/V_0=1-\theta_{eq} \qquad (1)$$

Where V_0 is the step velocity in a pure system and θ_{eq} is the fractional coverage by adsorbed impurities on the surface. The relative velocity becomes zero just at $\theta_{eq}=1$. However, complete adsorption or complete coverage ($\theta_{eq}=1$) is not considered to be a necessary condition for the complete stoppage of crystal growth. The terms complete adsorption and complete coverage used here are only intended to mean the complete occupation of specific sites available for adsorption, since a specific impurity adsorbs at its own specific sites by a specific adsorption force, particularly in the case of chemisorptions. The site available for adsorption may be different with the combination of growing crystal and impurity. The number of the active sites changes for each combination. If the active site number is very limited, the separation of impurities adsorbed is relatively large, even at complete coverage. Under such a condition, the impurity may not stop the advancement of the step as indicated in the Cabrera-Vermilyea model [17], i.e., the step can easily squeeze out between the impurities. Furthermore, there are many kinds of active impurities e.g. macromolecules, organic compounds, metallic ions, and so on. The growth suppression characteristics of an impurity are also expected to depend on the size, shape, or orientation of the impurity molecules (a stereo chemical effect). Thus the general effectiveness of an impurity on crystal growth is considered to be determined by two characteristics: an adsorption factor (θ_{eq}) and an effectiveness factor (α).

$$V/V_0=1-\alpha\,\theta_{eq} \qquad (2)$$

Although Eq.2 might appear to be a simple modification of Eq.1 it does not necessarily carry the same assumption of a surface controlled growth mechanism since α can be derived independently. When α>1, the step velocity approaches zero at $\theta_{eq}<1$ (incomplete coverage). When $\alpha=1$ the velocity becomes zero just at $\theta_{eq}=1$ (complete coverage). And when $\alpha<1$, the step never approaches zero, even at $\theta_{eq}=1$ an adsorption isothermal is necessary to relate the relative step velocity (V/V_0) with the impurity concentration in solution. The Langmuir isotherm is assumed to apply here,

$$\theta_{eq}=Kx/(1+Kx) \qquad (3)$$

From Eqs.(2) and (3), the relative step velocity can be derived as a function of the impurity concentration x,

$$V/V_0=1-[\alpha Kx/(1+Kx)]. \qquad (4)$$

Where *K* is the Langmuir constant. The relative step velocity in Eq.(4) can be replaced by the relative face growth rate G/G_0 if the face growth rate is assumed to be proportional to the step velocity,

$$G/G_0=1-[\alpha Kx/(1+Kx)] \qquad (5)$$

In Fig. 1, the relative step velocities, calculated from Eq. 4 are shown for different effectiveness factors α as a function of dimensionless impurity concentration Kx; where α>1, the relative velocity decreases very steeply with increasing impurity concentration, reaching zero at a small value of Kx. For $\alpha=1$, the step velocity becomes zero asymptotically. For $\alpha<1$, however, the velocity never approaches zero but approaches a non-zero value asymptotically as Kx is increased.

3. Experimental procedure

The experimental setup of the fluidized bed crystallization system is shown in Fig. 2. It consists of a pump, two heat exchangers and a cell. The fluidized bed cell is made of acrylglas. The pump is a centrifuged pump. The two heat exchangers were connected to two water baths. One of them is suitable for keeping the solution under saturation in the vessel (heating), the second heat exchanger operates as a cooler or heater to create the required supersaturating or under saturation level in the growth and dissolution zones, respectively. One can find a similar setup in reference [19].

A saturated solution of a solute (NaCl, ADP, KBr and Sucros) is prepared according to the solubility data. The solubility data has been presented in the handbooks of the chemical engineering field or references [13]. The solution was prepared by dissolving the required amount of one of our solutes (NaCl or ADP or KBr or Sucrose) in 7 liters of distillated water. The saturated solution is transferred to the reservoir of the crystallization system. The solution started circulation through the crystallization system. The temperature of the two water baths were adjusted to keep the solution under saturation in the reservoir (heating) and slightly supersaturated or under saturated in the growth and dissolution zone (cooling/heating). Usually 1-7 ^{0}C less than the saturation temperature is enough to have the solution in the met stable zone for the growth rate measurements. For dissolution rate measurements, a temperature of 1-6 ^{0}C higher than the saturation temperature is enough to create the required under saturation. In the case of growth rate measurements, independent of an impurity concentration, a carefully weighed amount of impurity is added to the solution. 7 g of well defined crystals of sieve cut of (NaCl or ADP or KBr or Sucros) were weighed and put into the cell. When the temperature of the solution reached the required temperature, the cell was fixed in its place. Adjusting the valve VI in the system controlled the fluidization velocity. A stopwatch was used to evaluate the operating time for each run. At the end of the run, valve VI was fully opened to keep the solution away from the cell then the cell content was filtered and washed with ethyl alcohol. The filtered crystals were dried at 70^{0}C for 4 hours. After that, the crystals were cooled to ambient temperature and weighed. The difference in weight of the crystals before and after the experiment is used in calculating the growth rate or dissolution rate, respectively.

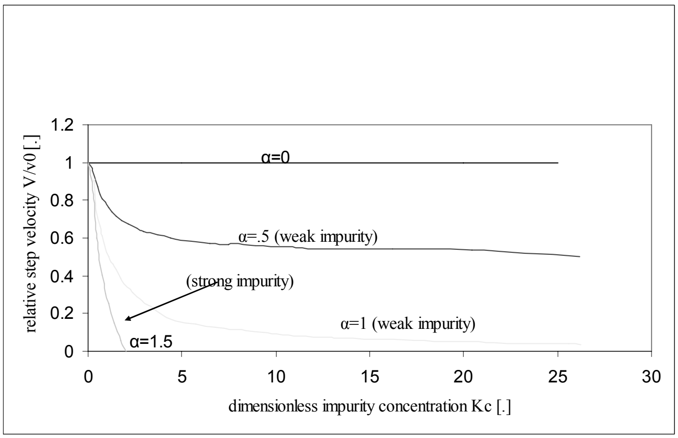

Figure 1. Theoretical relationship between the relative step velocity (V/V_0) and dimensionless impurity concentration Kx for different values of α

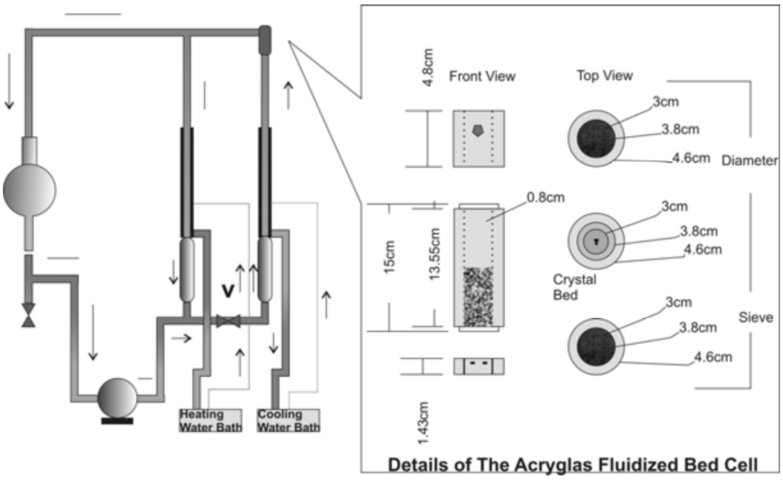

Figure 2. Fluidized bed experimental setup

All experiments were carried out in a fluidized bed, growth period has always been 17 minutes, saturation temperature was 30 ^{0}C and initial size range of the seed crystal was 315- 250 μm.

4. Results and discussion

The super saturation varied in the range of met stable zone where no nucleation occurred. Fig. 3 shows the thermodynamic effect on the NaCl growth rate in the presence $MgCl_2$. The experimental data of the system are presented in Table 1. By adding 50, 100, 250 ppm of the impurity $MgCl_2$ the saturation temperature will shift to 31, 33, 36^{0}C, respectively. This means that the solubility of NaCl is reduced with the increasing amount of $MgCl_2$ in the solution. Therefore the temperature should be raised to dissolve the total amount of NaCl added at 30^{0}C. Fig. 4 presents data given in Table 1 at the pure NaCl saturation temperature 30^{0}C. It seems obvious from Fig. 4 that the impurities are accelerating the growth rate of NaCl, but this is a misleading result. There is no kinetic acceleration of the growth rate of NaCl but rather a shift in the saturation temperature [18].

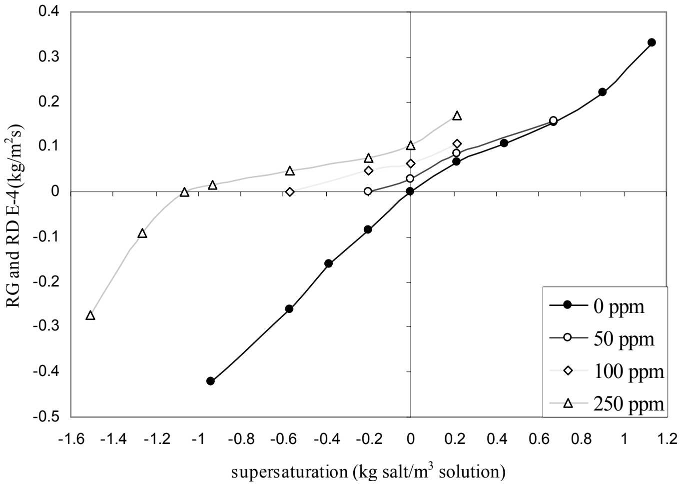

Figure 3. Growth and dissolution rates of NaCl in the presence of $MgCl_2$ (thermodynamic effect)

In order to determine the real influence on the growth rate, the saturation temperature must be corrected. This can be done by a correction of the temperature (rising temperature). This is necessary to dissolve the total amount of NaCl added at 30^0C, which is the basis to compare the different curves with each other. After the correction in temperature, the different corresponding saturation temperatures are 30, 31, 33 and 36^0C, for the impurity concentration 0, 50, 100, 250 ppm, respectively. In Fig. 5 the data of Table 1 are reported according to the new super saturation temperatures. The curves shown in Fig. 4 are the actual ones and show the kinetic effect on the growth rate. Therefore, the final result shows that the $MgCl_2$ will inhibit the growth rate of NaCl crystals.

Table 1. Experimental data for the mass growth rate of NaCl at different impurity concentration of $MgCl_2$ [19]

Temp ^{0} C	ΔC Kg_{salt}/m^3_{soln}	$R_g\times10^{-4}$ Kg/(m^2s)			
		I.C 0ppm	I.C 50ppm	I.C 100ppm	I.C 250ppm
36	-0.993				0.000
35	-0.871				0.019
33	-0.532			0.000	0.052
31	-0.185		0.000	0.50	0.077
30	0	0.000	0.032	0.065	0.105
29	0.202	0.068	0.087	0.108	0.173
28	0.410	0.106			
27	0.627	0.157	0.156		
26	0.840	0.220			
25	1.049	0.333			

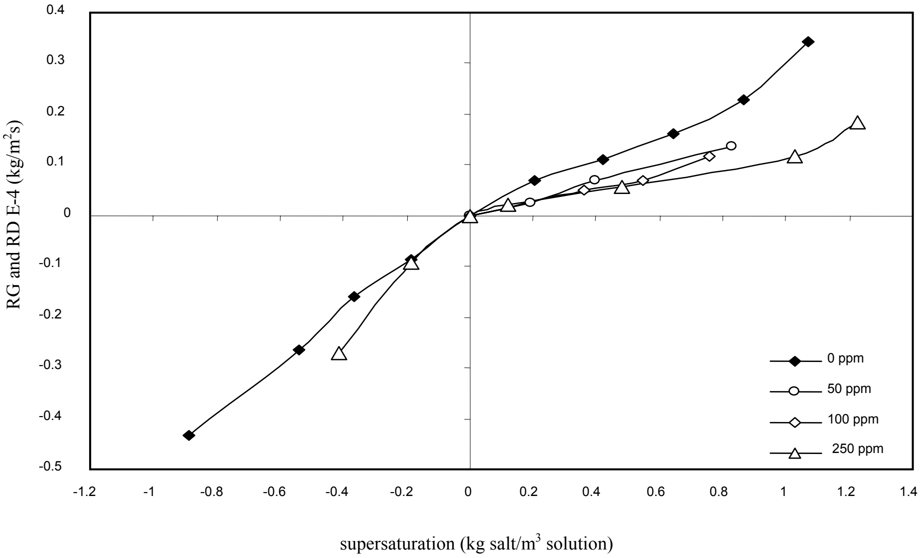

Figure 4. Growth and dissolution rates of NaCl in the presence of $MgCl_2$ after correction of the supersaturation (kinetic effect)

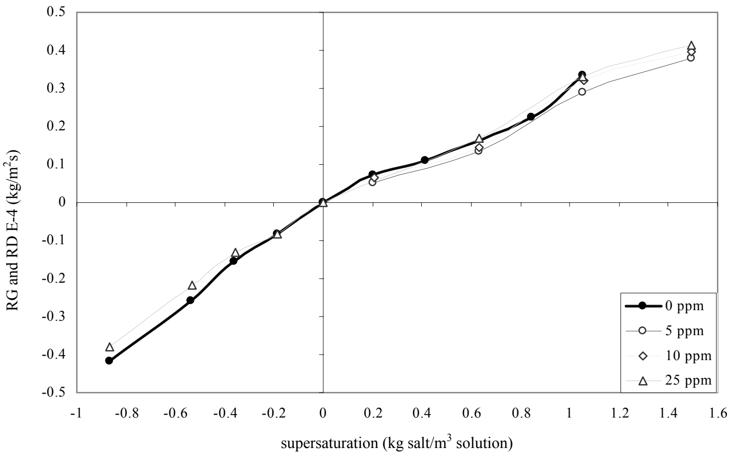

Figure 5. Growth and dissolution rates of Nacl in the presence of $CuSO_4*5H_2O$

For a simplified understanding, the process of crystal can be divided into two steps. The first step is the mass transport of the growth units by diffusion or convection from bulk of the solution to the crystal surface (the so-called diffusion step). The second step is the integration of the units into the crystal lattice (the so-called reaction step). The step with the lower rate determines the growth rate. Most crystal growth processes are dominantly either diffusion or reaction controlled. In the case of linear growth and dissolution rates, and an equal slope for the crystal growth can be called diffusion controlled. With the above assumption it has been shown that NaCl is diffusion controlled growing in the absence of impurities. However, with the used impurities a change in the dominating growth mechanism arises, i.e. the presence of certain impurities leads to the more important role of the reaction step. The suppression of the dissolution rates clearly indicates that the dissolution is the exact reverse of crystal growth; this means there is also a reaction (disintegration) step in dissolution. Fair addition of impurities into pure solute leads to a decrease in the crystal growth process, but during evaluation of the effect of impurities on crystal growth rate it faced an exception, the presence of $CuSO_4*5H_2O$ had no affect on the growth rates of NaCl. The kinetic effect in the presence of $CuSO_4*5H_2O$ is shown in Fig. 5. The results show a good agreement with the literature data[13], there was no effect on the single crystal growth rate of NaCl in the presence of the additive $CuSO_4*5H_2O$.

In order to verify our work a comparison between the experimental data with the model predictions was carried out for ADP, KBr, sucrose crystals in the presence of $FeCl_2$, $AlCl_3$; CH_3COOH, C_3H_7COOH and raffinose respectively as impurities.

During operation it was logical that the concentration of impurities ($MgCl_2$; $FeCl_2$, $AlCl_3$; CH_3COOH, C_3H_7COOH; raffinose) in NaCl, ADP,KBr, sucrose crystals respectively increased. The relative step velocity will vary in different amounts of α (impurity concentration factor) and θ_{eq} (fractional coverage by adsorbed impurities on the surface.

In Fig. 6, the impurity effect of raffinose ($C_{18}H_{32}O_{16}$) on the growth of sucrose ($C_{12}H_{22}O_{11}$) crystals has been shown. Fig. 7 shows the results of the relative step velocities (at 30 ^{0}C for σ=0.0065 (super saturation)) as a function of the dimensionless impurity concentration (*Kx*). In the case of *α*=0 the relative step velocity becomes constant at 1.

With increasing amount of α and *Kx*, the relative step velocity tends to reach to zero. In the amount of *Kx* =25 the relative step velocity will be 0.038. Therefore, these may be considered as an example of the case *α*=1. The same result can be obtained by applying the Eq. 4 for different amount of α in the mentioned material. The Figs. (7-9) below will prove good agreement with the model and the outcome results. The same studies on this issue confirm and support the results that have been shown here.

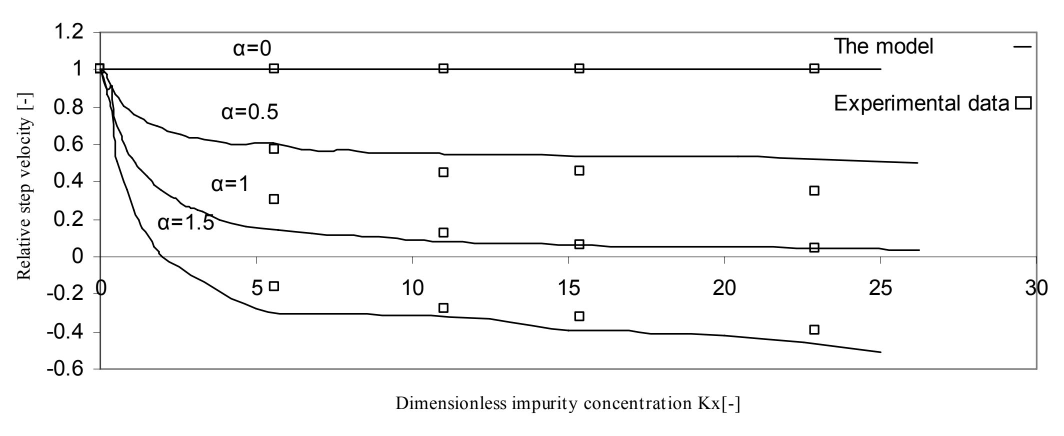

Figure 6. The relative step velocity of sucrose crystal in presence of raffinose as impurity

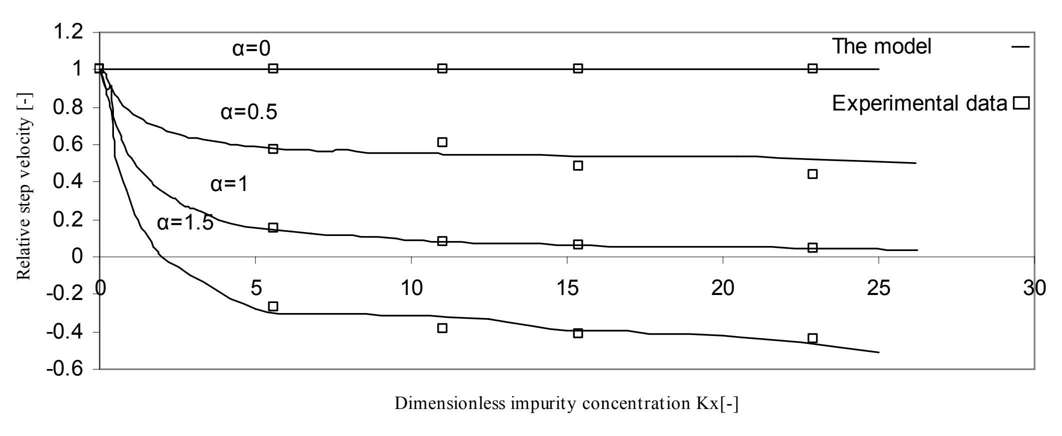

Figure 7. The relative step velocity of KBr crystal in presence of CH_3COOH as impurity

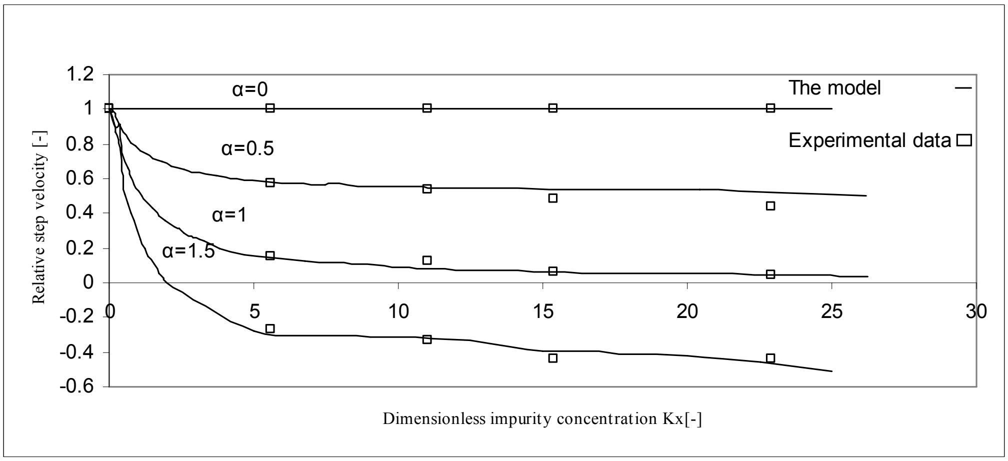

Figure 8. The relative step velocity of KBr crystal in presence of C_3H_7COOH as impurity

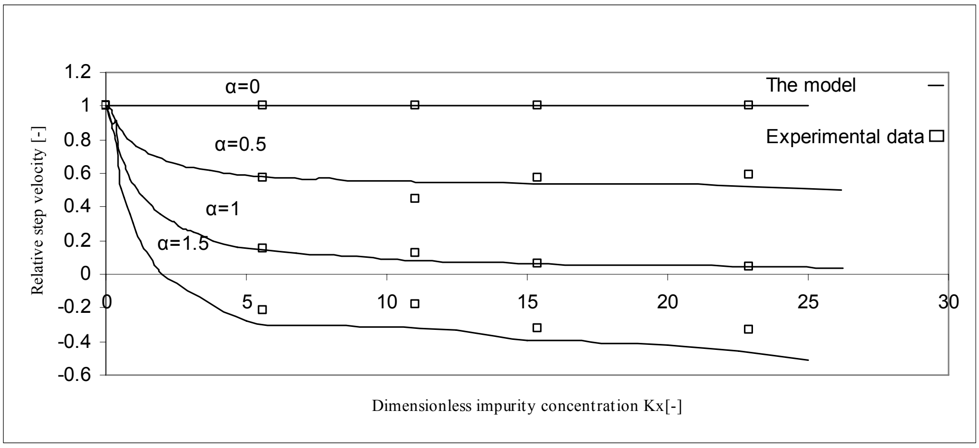

Figure 9. The relative step velocity of ADP crystal in presence of $AlCl_3$ as impurity

5. Conclusions

The crystal growth rate of NaCl, ADP, KBr and sucrose is diffusion controlled in the absence of impurities. However, a change arises in the growth mechanism with the used impurities, i.e. the presence of the impurities leads to a more important role of the reaction step. The effect of different impurities on the growth rate of the mentioned crystals can be divided into:

1. Thermodynamic effects, where the impurities affect the solubility of the crystals solution as in the case of NaCl in the presence of $MgCl_2$.
2. Kinetic effects, where the impurities will reduce the crystal growth rate of NaCl, ADP, KBr, and sucrose compared to pure solutions.

The model can be used to show that the general relationship of crystallization kinetics with impurity content was valid not only for single crystals but also for many systems in an industrial crystallizer where many crystals are growing in a suspension. The knowledge of these interdependencies allows crystallization conditions to be controlled so as to yield a product with a desired size distribution and shape. It was found that when α is equal to one, full coverage of the crystal surface leads to growth rates (relative step velocity) equal to zero. And α less than one leads to relative growth rates (the relative step velocity) decreasing as the impurity concentration increased, approaching a limiting non-zero value asymptotically.

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Nomenclature

θ	The coverage of the surface
V	Step velocity for impure solution (m/s)
V_0	Step velocity for pure solution (m/s)
V_∞	limiting step velocity for impure solution (m/s)
K	Langmuir constant (ppm^{-1}).
C	Impurity concentration (ppm).
α	The impurity effectiveness factor.
θ_{eq}	The fractional coverage by adsorbed impurities on the surface.
R_G	Mass growth rate for impure solution (kg/m^2s)
R_{G0}	Mass growth rate for pure solution (kg/m^2s)

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