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A multi-component mass transfer rate based model for simulation of non-equilibrium growth of crystals

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Abstract

A model based on multi-component mass transfer is proposed for modeling the non-equilibrium growth behavior of crystals during solution crystallization. The multi-component composition in crystals in any spatial location can thus be estimated at any time during a crystallization process. It can be applied to estimation of impurity content and assessing stability of crystalline pharmaceuticals. The multi-components are equally described by diffusion, adsorption and integration equations. The facet growth rates are estimated by the amount of materials grown on the surface divided by material densities and the surface areas. This is unlike conventional facet growth kinetic model in which the growth rate is correlated directly to supersaturation. The modeling method is illustrated by case studies of NaNO3 and KDP crystallization. The dynamic evolution of crystal composition and shape distribution is simulated.

Keywords: Crystal growth; multi-component mass transfer; non-equilibrium; crystal shape; crystal composition

1. Introduction

Considering that solution crystallization is regarded as a separation process for product purification in the chemicals, pharmaceuticals and food processing industries, its modeling and simulation should surely be able to estimate the composition of the multiple components in the final crystal solids as well as in the crystals at any time during the crystallization process. The most important modeling tool for crystallization, i.e. population balance (PB) modeling of crystallization however has focused on modeling crystal size and shape distributions, rather than the composition of multiple components in crystals. This means that the impact of process conditions (e.g. cooling rates in cooling crystallization) on the composition of a crystal solid, e. g. on the stability of the crystalline product in the case of a pharmaceutical, currently cannot be studied via process simulation, so can only be examined via experiments. This is in great contrast to the most important liquid-liquid separation process, distillation, where the most important task of modeling and simulation is to estimate the composition of components in the product streams. It seems illogical for the most important modeling tool for crystallization processes not to be able to estimate the composition of components in the crystals. As a matter of fact, some attention was paid to the study of crystal growth behavior in an impure media via simulation, but the focus was still on the size and shape of crystals, or more accurately, on how an impurity, often in a much smaller concentration in comparison with the material to be purified, affects the size and shape change of the crystal. There is limited simulation work on estimation of impurity content in the crystal solids which is often based on a partition coefficient which is obtained based on the assumption of solid-liquid phase equilibrium. Gu and Grant [1] investigated the amount of impurities through liquid inclusion, which means the solvent is incorporated into the host crystals as liquid inclusions containing dissolved impurities. Givand et al. [2-5] developed a thermodynamic model based on lattice substitution in which liquid inclusion and lattice substitution used equilibrium distribution coefficients of multiple solutes, which was based on phase equilibrium assumption. Some other researchers [6-8] considered adsorption models for impurities to improve the crystal growth rate (its unit is m/s) estimation; no the growth rate is not only a function of supersaturation but also depends on the impurity adsorbed onto the crystal. However, the adsorption model could not cover the modeling of impurity inclusion rate. To consider the incorporation rate of impurities, Borsos et al. assumed a concentration equilibrium between the incorporating impurities and the impurities in the solution [9]. Although the impurity incorporation was considered, the model was still based on the thermodynamic equilibrium while the kinetics of mass transfer was not taken into consideration. Considering cooling crystallization as an example, it is in essence a non-equilibrium operation – it only approaches phase equilibrium operation if the cooling time is indefinitely long or the cooling rate is close to zero which is however not allowed in practice.

Another observation motivated the current work is the way crystal growth rate (its unit is m/s) in population balance models is described. Currently a crystal face specific growth rate in morphological PB models, is a kinetic equation often directly correlated to supersaturation and other factors such as impurity content in the solution. The relationship with supersaturation is often in the form of $\mathrm{G} = \mathrm{k}\sigma^{g}$ where G is the growth rate in m/s, k is the growth rate coefficient in m/s, σ is the relative supersaturation and g is the growth exponent. The supersaturation and solubility here are about the main material to be purified, not about the impurity. This probably is alright if the impurity content is very low in comparison with the material to be purified. But how about co-crystallization in which there are two or three materials to be arranged in a crystal cell, and their compositions are of similar order of magnitude. In this case, when talking about the solubility and supersaturation which material they refer to? The treatment on the impact of impurity on growth rate is even more empirical. For example, in the work of Borsos et al.[9] the growth rate in the presence of impurity was estimated through multiplying the growth rate in the absence of impurity by a factor which relates to the concentrations of the impurities, there were no fundamental basis why the impurity affects growth in such linear manner.

In this work, a multi-component mass transfer rate based model for simulation of non-equilibrium growth of crystals is introduced. In the model, the multiple solute components are described by a set of diffusion, adsorption and integration equations to form a multi-component mass transfer system. Thus both the crystal growth in terms of size and shape and change of composition of all components in the crystal can be simulated simultaneously by solving the mass transfer equations.

The remaining part of this paper is organized as follows: Section 2 gives a detailed description of the proposed multi-component mass transfer models for modeling the non-equilibrium growth of crystals. Then in Section 3 a detailed case study on $NaNO_3$ crystallization in impure media is presented to illustrate the proposed modeling approach. A second case study, the crystallization of KDP in the presence of two impurities, is presented to further demonstrate the capability of the modeling technique. Finally in Section 4 conclusions will be drawn and pointers to future research will be provided. .

2. Multi-component mass transfer rate based model for single crystal growth

2.1 The "stage" model

The multi-component mass transfer rate based model takes inspirations from the non-equilibrium stage model for the distillation column simulation[10]. In our model, each "stage" stands for a discretized moment during simulation of the crystal growth. At each stage, mass transfer occurs between the solution and the crystal and leads to the growth of the crystal. **Error! Reference source not found.** shows the details of a stage in the model for crystal growth. The simulation of the crystal growth is discretized in time, j = 1～J. Therefore, the jth stage refers to the jth discrete time in the time span of the simulation of the crystal growth. In total there are C components, i = 1 ~ C. Stage j refers to the status of the crystal at time jth moment of the simulation, accordingly, stages j-1 and j+1 refer to the status of the crystal before and after moment j. At stage j, the liquid phase and the solid phase were considered separately. For the liquid phase at stage j, its status is defined by the total liquid mole number $L_{j,}$, the mole number of component i in the liquid phase on this stage (jth stage) $l_{i,j}$, the enthalpy of the liquid phase on stage j, H_j^L, and the temperature of the liquid phase on stage j, T_j^L. For the solid phase at stage j, its status is defined by the total solid mole number $S_{j,}$, the mole number of component i in the solid phase on this stage (jth stage), $s_{i,j}$, the enthalpy of the solid phase on stage j, H_j^S, and the temperature of the solid phase on stage j, T_j^L.

The status of the liquid phase at stage j-1 is defined by total mole number $L_{j-1,}$, component mole number $L_{i,j-1}$, the enthalpy H_{j-1}^L, and the temperature T_{j-1}^L. And the status of the solid phase at stage j-1 is described by solid mole number $S_{j-1,}$, the component mole number $s_{i,j-1}$, the enthalpy H_{j-1}^S, and the temperature T_{j-1}^L All the information about the status of the liquid phase about stage j-1 will be brought to the calculation of stage j, so it is in some way like mass and energy transfer from the tray (stage) above to the current tray (stage) in distillation column simulation. The information about stage j will be brought to the calculation for stage j+1. Similarly, information of the solid phase at stage j-1 is brought to stage j, and about stage j to be brought to stage j+1 calculation.

On stage j, the two phases are not at equilibrium because the process is moved to the next stage j+1 before they reach equilibrium – they can reach equilibrium at stage j only if the process stays sufficiently long at that stage. For example, in a cooling crystallization, is the cooling rate is close to zero, each stage can be considered as an equilibrium stage. There are mass transfers for each component between the liquid and solid phases in both directions. In Figure 1, $N_{i,j}$ is the net mass transfer rate of component i from the liquid phase to the solid phase, for stage j, in mol/s. This is for a crystallization process and one can image that for a dissolution process, the net mass transfer direction will be in the opposite direction. There is also energy transfer between the two phases. In Figure 1, e_j is the energy transfer rate, J/s, a positive value means energy transfer from liquid phase to solid phase, and a negative value means energy transfer from the solid phase to the liquid phase.

During the crystallization process, at stage j, energy and materials can be added or taken away from the liquid phase. In Figure 1, Q_j^L represents the energy added to (positive value) or taken away (negative) from the liquid phase of stage j. $f_{i,j}^L$ represents the mole number of component i added to (positive value) or taken away (negative) from the liquid phase of stage j. In this paper, we focus on the mass transfer in crystal growth and assume that the temperature in the crystallizer is homogeneous so the heat transfer can be ignored and Q_j^L is not considered. In the case studies, no materials are added after the crystallization begins so $f_{i,j}^L$ is not considered either.

2.2 The phase interface model

The interface model is shown in **Error! Reference source not found.**. In the solution, liquid mass transfer occurs due to the concentration difference between the bulk and the liquid interface. On the interface, ~~an~~ adsorption equilibrium prevails between the liquid interfacial concentration and the surface layer concentration. In the crystal, solid mass transfer occurs in the form of molecule integration from the surface layer to the crystal surface.

The total number of components including the solvent is C. The solvent is specially referred to as the Cth component. If proper parameters of the solvent are given, in principle, the solvent inclusion can also be modeled, in the same way as other components, although in the case study of this article, the solvent inclusion is ignored for simplicity and the parameters i.e. mass transfer coefficient corresponding to the solvent are assumed to be 0. It should be noted that **Error! Reference source not found.** and **Error! Reference source not found.** only represent a “stage” on one crystal face. For different crystal faces, different model parameters should be considered. The total number of faces is F.

The mass transfer modeling here is different from the work of Karpiński [11] and Rocha [12]~~and [10]~~. In Karpiński’s paper, crystal growth from solution was assumed to have consisted of a diffusion step and a “reaction” step when solute molecules arranged themselves into the crystal lattice [11]. Martins and Rocha proposed a model that treated crystal growth as a mass transport process consisting of solution diffusion, crystal surface adsorption and the integration of adsorbed growth elements into the crystal lattice. [12] However, their work was focused on single solute, i.e. the material to be purified, rather than considering multiple components and their goal was still limited to the modeling of the overall crystal growth rate. On the contrary, our model aims at modeling the mass transfer rate processes during the crystal growth. With the calculated mass transfer rate on each crystal face, both the facet growth rate and the crystal composition can then be derived. The equations in the model are introduced below.

2.3 Conservation relations

The mass balance for component i on stage j on crystal face k is: (i =1,2,…,C; j= 2,3, ...,J; k=1,2,..F)

$$M^{L}_{i,j} \equiv l_{i,j-1} - l_{i,j} - \sum_{k=1}^{F} N^{L}_{i,j,k} \Delta t = 0 \qquad (1)$$

$$M^{S}_{i,j,k} \equiv s_{i,j-1,k} - s_{i,j,k} + N^{S}_{i,j,k} \Delta t = 0 \qquad (2)$$

$$M^{I}_{i,j,k} \equiv N^{L}_{i,j,k} \Delta t - N^{S}_{i,j,k} \Delta t = 0 \qquad (3)$$

wherein $l_{i,j,}$ is the solution mole number of component i at moment j, $s_{i,j,k}$ is the crystal mole number of component i at moment j on face k. Initially (j=1) for the crystal seeds, $s_{i,1,k}$ represents the mole number of component i contained in the pyramid, of which the crystal center is the peak and face k is the base. If k stands for a group of symmetric-related faces, $s_{i,1,k}$ should also be the mole number component i contained in the pyramids corresponding to these faces. During the crystal growth, $s_{i,j,k}$ changes due to the mass transfer on face k. The crystal shape evolution can then be determined with the change of $s_{i,j,k}$. The details of shape evolution prediction will be discussed in Section 2.8. N^L and N^S are the liquid mass transfer rate and solid mass transfer rate separately (their units are mol/s).

In the following part of this model, the molar fractions of components in the liquid phase and solid phase are used to establish the mass transfer model. The component molar fraction in the bulk liquid phase can be expressed as:

$$x^{L}_{i,j} = \frac{l_{i,j}}{\sum_{i=1}^{C} l_{n,j}} \tag{4}$$

wherein $x^{L}_{i,j,k}$ is the molar fraction of component i in the solution at moment j on face k, $l_{i,j,k}$ is the mole number of component i in the solution at moment j on face k

In this model, the diffusion in the solid phase is simplified as negligible. Therefore, the growth of crystal is assumed to be purely the layer-by-layer stacking of crystallized material. The component molar fractions in the crystal layer formed at moment j can be expressed by:

$$y^{S}_{i,j,k} = \frac{s_{i,j,k} - s_{i,j-1,k}}{\sum_{n=1}^{C} (s_{n,j,k} - s_{n,j-1,k})}, \ j \geq 2 \tag{5}$$

wherein $y^{S}_{i,j,k}$ is the molar fraction of component i of the crystal layer formed at moment j on face k, $s_{i,j,k}$ is the mole number of component i at moment j on face k.

2.4 Transport relations

The mass transfer in the liquid phase is due to the diffusion of components in the solution, whose driving force is the molar fraction difference between the bulk ($x^{L}_{i,j}$) and interface ($x^{I}_{i,j,k}$) (i =1,2,…,C-1):

$$R^{L}_{i,j,k} \equiv N^{L}_{i,j,k} - k^{d}_{i,k} A_{k} (x^{L}_{i,j} - x^{I}_{i,j,k}) = 0 \tag{6}$$

wherein $k^{d}_{i,k}$ is the liquid phase mass transfer coefficient for component i corresponding to face k, in mol/(m^{2}s).

In this model, the diffusion in the solid phase is ignored. The mass transfer in the solid phase is a “reaction” process that the adsorbed solute molecules arrange themselves into the crystal lattice. The driving force of this step is the difference between the adsorption molar fraction ($z_{i,j,k}$) and the equilibrium molar fraction that depends on the solid interface molar fraction ($y^I_{i,j,k}$). (i =1,2,…,C)

$$R^S_{i,j,k} \equiv N^S_{i,j,k} - k^r_{i,k} A_k (z_{i,j,k} - K^r_{i,k} y^I_{i,j,k})^r = 0 \qquad (7)$$

wherein $k^r_{i,k}$ is the mass transfer coefficient for component i from adsorbed solute to crystallized solute in mol/(m^{2}s), $K^r_{i,k}$ is the equilibrium ratios of component i on crystal face k. r is the reaction order.

2.5 Interface model

The solid composition related to the mass transfer is equal to the composition of the crystal layer that formed in the last moment (i =1,2,…,C).

$$Q^S_{i,j,k} \equiv y^I_{i,j,k} - y^S_{i,j,k} = 0 \qquad (8)$$

For the adsorption phase, the model of a singular surface offering no resistance to the mass transport of adsorption is adopted and therefore the adsorption equilibrium between the liquid interface and the adsorption layer prevails. The adsorption equilibrium is modeled based on the Langmuir adsorption isotherms. The adsorption coverage is approximated by the adsorption layer composition (i =1,2,…,C-1), the adsorption of the solvent should be calculated by the summation relations.

$$Q^{ads}_{i,j,k} \equiv z_{i,j,k} - \sum_{n=1}^{C} y^I_{n,j,k} \frac{K_{i,n,k} x^I_{i,j,k}}{1+\sum_{m=1}^{C} K_{m,n,k} x^I_{m,j,k}} = 0 \qquad (9)$$

wherein $K_{m,n,k}$ is the Langmuir constant of adsorption of component m on component n on crystal face k. If the Langmuir constant is assumed to be identical for all the components on the same face, the $K_{m,n,k}$ can be replaced by $K_{m,k}$ and Eq. (9) can be simplified as

$$Q^{ads}_{i,j,k} \equiv z_{i,j,k} - \frac{K_{i,k} x^{I}_{i,j,k}}{1+\sum_{m=1}^{C-1} K_{m,k} x^{I}_{m,j,k}} = 0 \tag{10}$$

wherein $K_{i,k}$ is the simplified Langmuir constant of adsorption of component i on crystal face k.

2.6 Summation relations

The summations components of the liquid phase, solid phase and adsorption phase should be 1. The solid phase summation equations can be obtained from the summation of $Q^{S}_{i,j,k}$ so they are not independent equations and won't be listed here.

$$S^{L}_{j,k} \equiv \sum_{i=1}^{C} x^{I}_{i,j,k} - 1 = 0 \tag{11}$$

$$S^{ads}_{j,k} \equiv \sum_{i=1}^{C} z_{i,j,k} - 1 = 0 \tag{12}$$

2.7 Variables and functions for a single non-equilibrium stage

There are C+6FC unknown quantities for each stage j. These are the component liquid mole number ($l_{i,j}$: C in number), the solid mole number ($s_{i,j,k}$: CF), the liquid composition at the interface ($x^{I}_{i,j,k}$: CF), the solid composition at the interface ($y^{I}_{i,j,k}$: CF), the adsorption phase composition at the interface ($z_{i,j,k}$: CF), the mass transfer rate ($N^{L}_{i,j,k}$: CF and $N^{S}_{i,j,k}$: CF). The C+6CF independent equations that permits these unknown quantities include: component material balances for the liquid ($M^{L}_{i,j}$: C in number), component material balances for the solid ($M^{S}_{i,j,k}$: CF), component material balances around the interface ($M^{I}_{i,j,k}$: CF), the liquid phase mass transfer rate equations ($R^{L}_{i,j,k}$: (C-1)F), the solid phase mass transfer rate equations ($R^{S}_{i,j,k}$: CF), the interface solid component model ($Q^{S}_{i,j,k}$: CF), the interface adsorption equilibrium ($Q^{ads}_{i,j,k}$: (C-1)F), the summation equations ($S^{L}_{j,k}$:

F and $S^{ads}_{j,k}$: F).

2.8 Prediction of crystal shape and composition

Neither the face growth rate nor the normal distance straightforward appears in our model. However, based on the calculation of sold mole number of all components, the normal distance evolution can be obtained. The solid mole number $s_{i,j,k}$ on face k represents the mole number of component i that crystallized on face k. If k stands for a group of symmetric-related faces, $s_{i,j,k}$ also represents the mole number of component i that crystallized on these faces. With the change of quantities of all the components on face k known, if we assume the volume of the mixture is the sum of the volumes of pure substances, the relation between $s_{i,j,k}$ and $X_{j,k}$,, the normal distance of face k at moment j, can be established with the volume equations of pyramid as Eq~~t~~.(13).

$$\sum_{i=1}^{C} \frac{M_i (s_{i,j,k} - s_{i,j-1,k})}{\rho_i} = (X_{j,k} - X_{j-1,k}) A_k (X_{j-1,k}, k = 1, 2, \dots, F) \qquad (13)$$

wherein M_i is the molar weight and ρ_i is the density of component i, $X_{j,k}$ is the normal distance from the crystal center to face *k* at moment *j*, $A_j (X_{j,k}, j = 1, 2, \dots, F)$ is the area of face j when the values of $X_{j,k}, k = 1, 2, \dots, F$ are given, which can be obtained according to the geometric information of the crystal. If j stands for a symmetric-related face group, A_j should be the sum of all the face areas in that group,

According to Eq. (13), the evolution of normal distances of all the crystal faces can be obtained. Afterwards the crystal shape evolution can also be reconstructed.

On the other hand, based on the solid mass of each component, both the overall composition of the whole crystal or on a specific face normal direction, and the composition distribution along a specific face normal direction, can be obtained.

In the proposed models, there are some parameters for which their values need to be determined. $k^d_{i,k}$, the liquid phase mass transfer coefficient for the ith component can be measured by solid dissolution[13]. There are also correlations available for its estimation. For example, a correlation given by Geankoplis can be used to predict the mass-transfer coefficients from liquid phase to the surface of small catalyst particles, microorganisms other solids or liquid drops[14]. The parameters corresponding to mass transfer from the adsorption layer to solid phase, $k^r_{i,k}$ (the mass transfer coefficient from adsorbed solute to crystallized solute) and r (the reaction order) may be calculated with molecular simulation or regression of the proposed model with experimental data of measurement of single crystal growth.

$K_{i,k}$ (Langmuir constant of adsorption) and $K^r_{i,k}$ (the equilibrium ratios in Eq. (7)) can be correlated with the solubility data (In Section 3.1.1, an example will be given). $K_{i,k}$ can be obtained with molecular simulation and afterwards $K^r_{i,k}$ can be calculated using the correlation relations.

On the other hand, empirical estimation of the parameter values is also possible via model identification: we can firstly carry out crystallization experiments and analyze crystal shape and composition. Then we can use the data from the analysis to estimate the values of the model parameters via model identification.

It should be noted that accurate and fast determination of the model parameters is not an easy task and may need further research. In addition, whatever methods are used, it cannot completely avoid errors in the estimation of the parameter values. Therefore a sensitivity study on some parameters is given in last paragraph of Section 3.1.3.

2.9 Further discussion

The adsorption model was often used to relate the facet growth rate to the concentrations of impurities. Afterwards population balance equations (PBE) can be established for modeling crystal growth with impurities to predict the crystal size and shape distribution affected by the impurities.[9,15-18]. In the work of Borsos et al.[9] the incorporating rate of impurities was also discussed. However, their model has two main differences from our model.

Firstly, our model is based on multi-component mass transfer and the facet normal distance and growth rate are indirectly obtained from the calculated component mole number. In the adsorption-based crystal growth model, the growth rate of crystals was described by the conventional growth kinetics times a modification factor based on the multi-impurity adsorption model:

$$G_k = k_{g,k}\left(\frac{c - c_{sat}}{c_{sat}}\right)^{g_k} p_{imp,k} \qquad (14)$$

wherein $p_{imp,k}$ is the impurity coefficient on face k which is related to the impurity concentration. It is calculated based on an “equilibrium adsorption model”[9]. Although the difference between solute concentration and saturation concentration is similar to the mass transfer driving force and the growth rate coefficient $k_{g,k}$ equation of Eq. (14) can be regarded to imply the mass transfer coefficient, our model is comparatively closer to the first-principle.

Secondly, in our model, the mass transfer of all components are equally considered and described with the mass transfer equations. In the adsorption-based crystal growth model, the determination of incorporation rate of impurities was based on the assumption of impurity concentration equilibrium between the crystal and the solution, as Eqt. (15) and (16) shows [9]:

$$\frac{dc_{CGM,i}}{dt} = \frac{\chi_{c,i}}{1-\sum_i \chi_{c,i}} \frac{M_{CGM,i}}{M_C} \frac{dc}{dt} \tag{15}$$

$$\chi_{c,i} = \sum_k K_{d,i,k} \frac{c_{CGM,i}}{M_{CGM,i}} \left(\frac{c}{M_c} + \sum_i \frac{c_{CGM,i}}{M_{CGM,i}} \right)^{-1} \tag{16}$$

Eqt. (15) is the mass balance of the impurity concentration in the solution. The changing rate of the impurity concentration $c_{CGM,i}$ is proportional to the changing rate of the solute concentration c. $\chi_{c,i}$ is the mole fraction of impurities in the crystal phase. According to Eqt. (16), the mole fraction of impurities in the crystal phase is in equilibrium with the mole fraction in the solution based on the interfacial distribution coefficient $K_{d,i,k}$.. In other word, the mass transfer of the impurities was not considered and the incorporation of the impurities was based on an equilibrium assumption, which is different from the non-equilibrium mass transfer equations in our model.

Our model is based on the multi-component mass transfer and the organization form of the equations is inspired by the non-equilibrium stage model for distillation column proposed by Krishnamurthy and Taylor [10]. In their model, the mass and energy balance and transfer on each stage were considered for the liquid phase and the vapor phase separately. The transfer resistance on the interface between the liquid phase and the vapor phase was ignored. The incorporation of mass transfer rate equations makes it possible to consider the non-equilibrium between vapor and liquid on stages without incorporating the arbitrary and ambiguous stage efficiency.

There are several differences between the two non-equilibrium models. Firstly, unlike in the case of distillation, there are no column stages in the crystallizer and the crystallization system is not in a steady-state either. Therefore, variables change with time rather than spatial stages in our model. Secondly, solid phase shows much poorer diffusivity than vapor or liquid so in our model the mass transfer in the solid phase is ignored. Finally, unlike the non-equilibrium for distillation columns, the “streams” between stages in our model for crystallization are concurrent rather than countercurrent. Therefore our model can be solved stage by stage.

3. Case studies

3.1 $NaNO_3$ crystal growth with KNO_3

Sodium nitrate ($NaNO_3$) crystallization is selected for the case study of our proposed model. **Error! Reference source not found.** is the equilibrium morphology of a $NaNO_3$ crystal which was predicted by Benages-Vilau [19] and also observed by Wu et al [20]. As **Error! Reference source not found.** shows, a $NaNO_3$ crystal is rhombohedra with six faces. These faces can be classified into three groups of crystallographically equivalent faces, i.e. two {104}, two $\{\bar{1}14\}$ and two $\{0\bar{1}4\}$. The values of α, β, and γ are 90.57°, 102.72°, and 102.72°. Wu et al. also measured the crystal face specific growth kinetics of all the three faces.

Benages-Vilau et al. studied the morphology change of $NaNO_3$ from aqueous solution in the presence of K^+ or Li^+ ions. They found that the addition of these impurities led to a sudden decrease of the {104} face of $NaNO_3$ and caused the morphology change[21].

In the case study, we will use our proposed model to simulate the shape and purity evolution of a single $NaNO_3$ with or without the presence of KNO_3 as the impurity. A pure $NaNO_3$ crystal is loaded in the crystallizer as a crystal seed and the crystallization temperature is kept constant. KNO_3 is assumed to be adsorbed on {104} face only. The crystallization temperature is kept 218.15K. The initial solution consists of 181.14g of $NaNO_3$ and 188.86g of H_2O. The initial face normal distances of {104}, $\{\bar{1}14\}$ and $\{0\bar{1}4\}$ are 100.06μm, 216.83μm and 253.28μm respectively.

3.1.1 Model parameters

Although in our model, the adsorption constant $K_{i,k}$ and the equilibrium ratio $K^r_{i,k}$ take the place of solubility in conventional growth rate equation, the published solubility data are still helpful to estimate the values of $K_{i,k}$ and $K^r_{i,k}$. When a pure crystal of component i is in equilibrium with the component i solution, the mass transfer rate should be 0. That is to say, $x^L_{i,j,k}$, the molar fraction of component i of the solution bulk should be equal to the solubility X. According to Eqŧ. (6), (7), (8) and (10), the adsorption constant $K_{i,k}$ and the equilibrium ratio $K^r_{i,k}$, should satisfy the following relationship:

$$K^r_{i,k} = \frac{K_{i,k} X}{K_{i,k} X + 1} \qquad (17)$$

Xu and Pruess studied the solubility curve of $NaNO_3$ in water was measured and gave a linear dependence (molar fraction X vs absolute temperature T) when 278.15K<T<323.15K[22] as Eqŧ. (18)

$$X = 0.0022T - 0.1757 \qquad (18)$$

The solubility curve of KNO_3 can be described with a quadratic equation (solubility in $gKNO_3/100g\ H_2O$ vs absolute temperature)[23]:

$$m_{gKNO_3/100gH_2O} = 13.767 + 0.5588(T - 273.15) + 0.0178(T - 273.15)^2 \qquad (19)$$

With the solubility equations of Eq. (18) and (19) the relations between $K_{i,k}$ and $K^r_{i,k}$. can be related using Eq. (17).

The mass transfer coefficients from the solution to the crystal surfaces can be predicted using a correlation given by Geankoplis[14] as Eq. (20):

$$k'_{i,k} = \frac{2D_i}{d_k} + 0.31 N_{Sc}^{-2/3}\left(\frac{\Delta\rho\mu_c g}{\rho_c^2}\right)^{1/3} \qquad (20)$$

wherein D_i is the diffusivity of component i in the solution in m^2/s, d_k is the equivalent diameter of the crystal in the direction of face k in m. For the modeling of $NaNO_3$ crystal growth, d_k is assumed to be the normal distance from face k to the crystal center times 2. N_{Sc} is the Schmidt number given by $N_{Sc}=\mu_c/\rho_c D_i$, μ_c is the viscosity of the solution in kg/(m•s), $g=9.80665\ m/s^2$, $\Delta\rho=\rho_p-\rho_c$, ρ_p is the density of the crystal in $kg/m^3$and ρ_c is the density of the solution in kg/m^3.

The unit of the mass transfer coefficient in Eqt. (20) should be translated from m/s to mol/(m2 •s) with Eq. (21) before it can be used in the corresponding equations in our model:

$$k_{i,k}^{d} = \frac{k'_{i,k}\,\rho_c}{\sum_{i=1}^{C} x_i^L M_i} \qquad (21)$$

wherein M_i is the molar weight of component i.

Graber et al. proposed the diffusivity, density and viscosity equations of aqueous $NaNO_3$ and KNO_3 at 25℃[24], which can be used to determine the property parameters in Eqt. (18). Because in the case study the amount of KNO_3 is much smaller than $NaNO_3$, μ_c and ρ_c can be approximately calculated by the corresponding equations of aqueous $NaNO_3$. Meanwhile, D_i is calculated using the diffusivity equation of aqueous $NaNO_3$ or KNO_3 assuming that the diffusivity would not affected by the other nitrate salt.

According to Karpiński’s suggestion, assigning the reaction order r=2 would be the most appropriate choice in the light of BCF growth theory, the previous intuitive trials and the experimental data[11].

3.1.2 $NaNO_3$ crystal growth in the absence of impurities

Through regression based on Wu's measurement of growth of single $NaNO_3$ crystal, the parameters corresponding to $NaNO_3$ which were not yet determined can now be obtained. The values of these parameters are listed in Table 1.

Table 1 Model parameters corresponding to $NaNO_3$

Parameter	{104}	$\{\bar{1}14\}$	$\{0\bar{1}4\}$
$K_{i,k}$	77.68	109.32	114.78
$K^r_{i,k}$	0.927	0.947	0.950
$k^r_{i,k}(10^3 mol \cdot m^{-2} \cdot s^{-1})$	0.650	1.520	1.801

Then a simulation is run in $NaNO_3$ solution without impurities with the same initial conditions as Wu's experiment. The comparison of simulated and experimental normal distance evolution is shown in **Error! Reference source not found.**. It can be seen that the two sets of curves fit well which indicates that our proposed model can be a good alternative to describe the growth of a single crystal.

3.1.3 $NaNO_3$ crystal growth with KNO_3

The parameters corresponding to KNO_3 need to be determined when the crystal growth with KNO_3 impurity is simulated. According to the experiment results of Benages-Vilau et al., the addition of KNO_3 impurity poisoned the {104} face growth rate[21]. Therefore, KNO_3 is assumed to affect the {104} face only and the parameters corresponding to other faces are assumed to be 0. The values of $K_{i,k}$, $K^r_{i,k}$ and $k^r_{i,k}$ are estimated as 776.8, 0.9805 and 64.97 $mol \cdot m^{-2} \cdot s^{-1}$ respectively. The molar number of $NaNO_3$, total molar number of all the solution components, and the shape of crystal seed are the same as they are in the growth in the absence of impurities. Therefore, the molar fractions of NaNO3 of all the simulation have the same initial value of 0.1689. KNO_3 is added with

$NaNO_3/KNO_3$ molar ratio of 10^{-3} and 10^{-5}. Because of the parameter setting of KNO_3 on $\{\bar{1}14\}$ and $\{0\bar{1}4\}$, the normal distance evolutions of faces $\{\bar{1}14\}$ and $\{0\bar{1}4\}$ show no differences from simulation in the absence of KNO_3. The normal distance evolution of face {104} and shape evolution during crystallization are shown in **Error! Reference source not found.**.

The overall molar fraction of KNO_3 of the growing $NaNO_3$ can also be predicted with the proposed model as is shown in **Error! Reference source not found.**(a). On the other hand, due to the change of solution phenomenon, the composition of crystal in the normal direction of {104} is different at different locations and the distribution of KNO_3 molar fraction in the normal direction of {104} can also be simulated with the proposed model, as is shown in **Error! Reference source not found.**(b). In **Error! Reference source not found.**, the molar fraction is normalized through dividing the molar fraction by the initial molar ratio of $KNO_3/NaNO_3$ (i.e. 10^3 or 10^5)

A sensitivity analysis for this case study is conducted and the result is summarized below. In the test the liquid mass transfer coefficient and the mass transfer coefficient from adsorbed solute to crystallized solute of KNO_3 are changed to examine their effects. If the value of $k^d_{i,k}$ (the liquid mass transfer coefficient) for KNO_3 on face {104} is multiplied by 0.1, i.e. increased by 10%, the prediction on composition and crystal size and shape doesn't show significant change. That might be because with the parameter settings in the case study the mass transfer is controlled by the mass transfer resistance from adsorbed solute to crystallized solute, rather than the mass transfer in the liquid phase. Even if the value is multiplied by 10^{-4}, the normal distance of {104} at the moment of 10th hr will be reduced by only 5.1% and the molar fraction of KNO_3 on face {104} at that moment will be reduced by only 0.37%. On the other hand, if $k^r_{i,k}$ (the mass transfer coefficient from adsorbed solute to crystallized solute) for KNO_3 on face {104} is multiplied by 0.1, the normal distance of {104} and the molar fraction of KNO_3 on face {104} at that moment will reduce by 27.81% and 20.79% separately. Here in this paper we limit our discussion on sensitivity analysis in order to not divert the focus from the introduction of this new modeling technique.

3.2 KDP crystal growth with crystal growth modifier

A case study on the potassium dihydrogen phosphate (KDP) crystal growth in the presence of two impurities (aluminum sulfate and sodium hexametaphosphate) is performed. KDP crystal has two independent crystal faces, the {100} face and the {101} face. The distances from the crystal center to {100} and {101} are separately denoted as x_1 and x_2. According to Borsos's work, divalent and trivalent metal ions (aluminum sulfate) preferably adsorb on the {100} face of KDP crystal, which leads to decreased growth rate of the corresponding characteristic length. Anionic growth modifiers (sodium hexametaphosphate) preferentially adsorb on the {101} face, resulting in growth rate inhibition for the corresponding characteristic length [9].

The crystallization is run at a constant temperature of 25℃. The initial solution contains 150g of KDP and 400g of water. One crystal seed with $x_1=x_2=2$ mm is loaded. In the impure solution, both aluminum sulfate and sodium hexametaphosphate are added at concentrations of 12.5ppm. The duration of crystallization of each batch is 2000 seconds. The values of model parameters are as Table 2 shows.

Table 2 Parameter values for KDP crystal growth modeling

Parameter	Face	KDP	aluminum sulfate	sodium hexametaphosphate
$k^d_{i,k}$ (mol•m^{-2}•s^{-1})	{100}	10^4	10^4	10^4
	{101}	10^4	10^4	10^4
$K_{i,k}$	{100}	90	3×10^4	0
	{101}	90	0	3×10^4

$K^{r}_{i,k}$	{100}	0.753	0.909	0
	{101}	0.753	0	0.909
$k^{r}_{i,k}$ ($mol\bullet m^{-2}\bullet s^{-1}$)	{100}	1	0.02	0
	{101}	3	0	0.05
r	{100}	2	2	2
	{101}	2	2	2

3.2.1 Evolution of distances from crystal center to crystal faces

The evolution of face normal distances is as **Error! Reference source not found.** shows. Aluminum sulfate and sodium hexametaphosphate decrease the growth rate of {100} and {101} separately. Therefore crystal in the presence of aluminum sulfate has a higher aspect ratio and crystal in the presence of sodium hexametaphosphate has a lower aspect ratio. Because the consumption rate of solute is also decreased, the growth rate of the other face becomes higher.

3.2.2 Evolution of impurity content

The evolution of impurity content in the whole crystal is shown in **Error! Reference source not found.** (a). The molar fraction of impurities in the whole crystal firstly increases and then decreases due to the consumption of impurities. Due to the changing solution phenomenon, the composition of crystal on each face normal direction is also different in different locations. With our model, the impurity molar fraction distribution along face normal direction can also be predicted as **Error! Reference source not found.**(b) shows.

4. Conclusion

In this work, a multi-component mass transfer model is proposed for modeling the crystal growth of multi-component systems. In the model, all the solutes are equally described by a set of diffusion, adsorption and integration equations. The equations are organized in the form of the non-equilibrium stage model including the conservation relations, transport relations, interface model and summation relations. Through solving the equations, evolution of both the crystal shape and composition can be predicted.

A case study of $NaNO_3$ crystal growth in the presence of KNO_3 is conducted. The shape and composition evolutions of $NaNO_3$ crystals of crystallization with different initial KNO_3 concentrations are modeled. A second case study of KDP crystal growth in the presence of two different impurities is presented to show the influence of different impurities on different crystal faces.

The main contribution of this work is the proposal of a novel model for the prediction of composition evolution of multi-component crystallization processes. Although in this article only case studies on crystallization in impure media are given, the model can be expected to work on other multi-component crystallization processes like co-crystallization. In future work, the model will also be incorporated into the morphological population balance (MPB) model [25,26] to enable MPB in predicting the crystal compositions.

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