Estimation of Crystallization Kinetics from Batch Cooling Experiments

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A direct optimization method to estimate nucleation and crystal growth rate parameters from seeded batch cooling crystallization experiments is evaluated. The experimental information applied comprises the concentration of the solution and the temperature as functions of time and the final product size distribution. Parameters in kinetic equations are determined by nonlinear optimization of a dynamic model of the experiment, by which intermediate approximations of experimental data are avoided. The optimization objective function includes both solution concentration data and product size distribution data. Kinetics are estimated for succinic acid crystallizing in aqueous solutions. Results from several different cooling crystallizations are simultaneously supplied into one single optimization to determine seven parameters.

Introduction

The crystal size distribution of the product produced by mass crystallization is usually of major importance. Ever since the pioneering work of Randolph and Larson (1962) and Hulburt and Katz (1964), population balance modeling has been used to increase the understanding for how size distributions arise and develop in crystallization processes. The primary kinetic processes are nucleation and crystal growth, usually strongly dependent on the solution supersaturation. At present the most important obstacle for design of crystallizers or prediction of crystallizer performance, by population balance modeling, is likely to be the problem of furnishing models with adequate kinetics. The traditional method to determine kinetics is to apply a continuous stirred vessel mixed suspension mixed product removal (MSMPR) crystallizer (Randolph and Larson, 1988). However, effort is devoted to develop methods based on batch crystallization experiments, by which the experimental work may become significantly more efficient.

Tanimoto et al. (1964) and Bujac and Mullin (1969) applied isothermal desupersaturation experiments to determine crystal growth rates. Seed crystals are added to an initially supersaturated solution and the concentration is measured during the experiment. By means of a mass balance, the crystal growth rate is related to the concentration decay. Garside et al. (1982) derived a method for obtaining the constants in the power law growth rate equation from only the initial derivatives of the supersaturation curve. Qiu and Rasmuson (1990) estimated the parameters in the two-step growth rate equation directly by fitting the mass balance equation to the experimental supersaturation data.

For the simultaneous estimation of growth and nucleation rates, information about the crystal size distribution has to be included. Misra and White (1971) and Ness and White (1976) used the population balance equation to obtain both the nucleation rate and the crystal growth rate from the measurements of crystal size distributions during the experiment. Tavare and Garside (1986) improved the accuracy of this method by Laplace transformation of the population balance equation. Qiu and Rasmuson (1991b) and Nyvlt (1989) measured the solution concentration during seeded batch cooling crystallizations and determined the product crystal size distribution. From these data the growth and nucleation rates during the process were calculated. The population balance is solved by the method of characteristics and a backward stepping procedure is adopted. Witkowski et al. (1990) used a nonlinear parameter estimation technique to estimate the nucleation and crystal growth rate parameters from the solution concentration and light obscuration measurements. Gutwald and Mersmann (1990) estimate growth and nucleation rates from batch experiments where the supersaturation is kept constant by a control system. The crys-

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tal size distribution is measured on-line. David et al. (1991) estimate some of the nucleation, growth, and agglomeration parameters from semi-batch isothermal reaction crystallization experiments. Both the concentration of the solution and the size distribution during the experiments are used in a step-wise optimization.

In the work of Qiu and Rasmuson (1991b), the experimental measurements on concentration vs. time and the product size distribution were approximated by polynomials, which were then applied in the evaluation of kinetic parameters for nucleation and growth. Unfortunately, significant parts of the experimental data of each experiment had to be excluded, because unrealistic results were produced otherwise. In a previous study (Qiu and Rasmuson, 1991a) on determination of crystal growth rate parameters from desupersaturation experiments, it was shown that polynomial fitting may distort important information. The purpose of the present study is to develop and examine the potential of a direct nonlinear optimization method to extract nucleation and growth kinetics from batch cooling crystallization experiments. The objective is to circumvent the need for approximation and for discrimination of experimental data. The method is adopted for the case where the concentration is recorded during the experiment, and the final crystal size distribution is determined by sieving. The study also includes the application of the method to experiments on succinic acid crystallizing in aqueous solutions. Kinetics for nucleation and growth are determined. The sensitivity of these parameters to the estimation procedure is analyzed as well as their possibility to accurately predict succinic acid batch cooling crystallization.

Parameter Estimation Technique

The estimation technique is based on a model for batch cooling crystallization and an optimization method which minimizes the difference between experimental data and those predicted by the model. The mathematical model comprises a population balance equation for the crystal size distribution and a mass balance equation which relates the total mass of crystals to the concentration change of the solution. The model also comprises kinetic equations for secondary nucleation and crystal growth, containing the parameters that are to be determined by the optimization. Consider a well-mixed batch cooling crystallizer in which crystal breakage, agglomeration, and crystal growth rate dispersion are negligible. Assume that evaporation of the solvent may be neglected and that nuclei are born at a negligible size. For this case the population balance equation can be written as (Randolph and Larson, 1971):

$$\frac{\partial n}{\partial t}+\frac{\partial (Gn)}{\partial L}=0 \tag{1}$$

with the initial condition:

$$n(0,L)=n_S \tag{2}$$

and the boundary condition:

$$n(t,0)=n^0(t)=B/G^0 \tag{3}$$

where n_S denotes the population density distribution of the seeds, which are added at $t=0$, and G^0 is the growth rate of nuclei. The crystal growth rate G depends on supersaturation, crystal size, temperature and degree of agitation, and the rate of secondary nucleation, B, is a function of supersaturation, magma density, temperature, and agitation:

$$G=G(\Delta c,L,N,T) \tag{4}$$

$$B=B(\Delta c,M_T,N,T) \tag{5}$$

Primary nucleation is assumed to be negligible. The total mass of solute substance is constant, but the solute concentration in the solution decreases during the process in proportion to the deposition of the solid phase. The mass balance equation can be written as:

$$c+M_T=c_0+M_0=\text{const} \tag{6}$$

The total crystal mass is obtained by integration over all crystals in the suspension:

$$M_T=\rho\int_0^\infty k_v L^3 n dL \tag{7}$$

The supersaturation driving force is the difference between the concentration and the solubility:

$$\Delta c=c-c^*(T) \tag{8}$$

For a given set of kinetics and process conditions this model can be solved for the concentration-time relation and the product size distribution. In the method of solution, the particle generation process is discretized into a generation of monosized pulses of nuclei, following the procedure used by Mullin and Nyvlt (1971), Jones and Mullin (1974), Janse (1977), and recently by Bohlin and Rasmuson (1992). One pulse of nuclei is formed during each time step, and the number within each pulse is determined by the prevailing conditions, such as supersaturation and so on. The method of characteristics (Randolph and Larson, 1988) transforms Eq. 1 formulated for each pulse, into ordinary differential equations of the particle characteristic and of the particle distribution along the characteristic. The resulting equations are $dL/d\xi=G$ and $dt/d\xi=1$, defining the characteristic, ξ, in the L-t plane (and corresponds to the common definition of the linear crystal growth rate: $dL/dt=G$). Along a characteristic curve the population density is given by $dn/d\xi=0$. These equations describe that a defined population of crystals of equal size (each pulse) travels along the size axis with the rate of crystal growth, keeping the number of particles constant. All nuclei generated within a time step are collected into one pulse. The complete set of equations is solved numerically by Euler's method using 240 time steps.

This simulation model is incorporated into a subroutine which defines the objective function in a NAG optimization routine (E04FCF) (Numerical Algorithms Group, Ltd., Oxford, U.K.). The objective function is composed of two parts. One part (F_c) contains the deviation between concentration measurements and the corresponding data from the simulation model, and the other part (F_W) contains the deviation between the measured and the predicted product size distribution. The parameters to be determined by minimizing the value of the objective function are the unknown kinetic constants embedded in Eqs. 4 and 5. The particular functions applied are given below. The optimization becomes a problem of nonlinear parameter estimation of a dynamic model (Bard, 1974). The routine E04FCF applies a combined Gauss-Newton and quasi-Newton method and the first derivatives of the objective function with respect to the parameters to be determined are calculated by the NAG library subroutine itself. This routine has successfully been used previously for a less complicated situation (Qiu and Rasmuson, 1990). The objective function is formulated either based on cumulative undersize product weight distribution data (Eq. 9) or based on product mass on each sieve (Eq. 10):

$$F=F_c+F_W=\frac{P}{m}\sum_{i=1}^{m}\left[\frac{c(t_i)-c_i}{c_0-c_f}\right]^2+\frac{1-P}{s}\sum_{i=1}^{s}\left[\frac{W(L_i)-W_i}{W_f}\right]^2 \qquad (9)$$

$$F=\frac{P}{m}\sum_{i=1}^{m}\left[\frac{c(t_i)-c_i}{c_0-c_f}\right]^2+\frac{1-P}{s}\sum_{i=0}^{s-1}\left[\frac{w(L_i)-w_i}{W_f}\right]^2 \qquad (10)$$

By dividing each concentration term by the maximum concentration change and each size distribution term by the total crystallized mass, the terms become dimensionless. Each sum is divided by the respective total number of data points, and a balancing of the two terms can be effected by choosing suitable values on the parameter P. The influence of P is analyzed below, as well as the choice of the objective function. The output data of the routine allow for computation of the inverse of the Hessian [approximated as $0.5\,(VS^{-1})(VS^{-1})^T$], from which the covariance matrix of the estimate is calculated. The standard deviations of the individual parameter estimates are obtained from the covariance matrix (Bard, 1974) and the ranges of confidence are calculated as suggested in the introduction to E04 routines of NAG.

Table 1. Experimental Parameters for the Simulation

Total time, t_f	5,400 s
Exponent of temperature profile, x	2
Initial temperature, T_0	30°C
Final temperature, T_f	20°C
Amount of seeds, W_0	0.16 g/kg water
Size range of seeds	250-355 μm
Initial concentration, c_0	108.95 g/kg water
(Initial supersaturation, $c^* = 104.29$)	4.66 g/kg water
Density of crystals, ρ	1,572 kg/m^3
Volumeric shape factor of the crystals, k_V	0.33

Evaluation of the Method

Theoretical experiment

Specify a set of nucleation and crystal growth parameters and simulate a batch cooling crystallization experiment. Discretize the calculated concentration vs. time curve and the final crystal size distribution and impose random errors on the specific data points. Apply the parameter estimation procedure to these theoretically produced experimental data. Compare the resulting kinetics with the values originally adopted and examine the range of confidence of each estimate.

For this simulation nucleation and growth kinetics are described by:

$$G=k_g\Delta c^g \qquad (11)$$

$$B=k_B\Delta c^b M_T^j \qquad (12)$$

and the kinetic parameters are given in Table 2, specified as "true value." Different parameters specifying the particular process being simulated are given in Table 1. The solubility

Table 2. Estimated Parameters for Theoretical Experiment*

P	F_c/F	k_B	b	j	k_g	g
			Using Eq. 9 as the Objective Function			
0.6	33%	3.02±0.43	2.39±0.17	0.839±0.149	4.46±0.44	0.995±0.194
0.7	18%	1.41±0.25	2.83±0.17	0.977±0.156	4.80±1.29	1.01±0.17
0.8	27%	1.38±0.23	2.85±0.17	0.981±0.144	4.81±1.09	1.01±0.14
0.9	46%	1.21±0.20	2.92±0.18	0.989±0.141	4.82±0.90	1.01±0.12
0.95	60%	1.15±0.21	2.93±0.21	0.997±0.156	4.92±0.85	1.01±0.10
0.98	79%	1.44±4.04	2.79±1.65	1.00±0.16	4.79±0.18	1.02±0.06
			Using Eq. 10 as the Objective Function			
0.6	17%	1.74±0.87	2.83±0.34	0.643±0.199	4.23±2.16	0.983±0.307
0.7	28%	1.79±0.40	2.77±0.27	0.699±0.175	4.58±1.83	0.945±0.235
0.8	20%	1.74±0.35	2.83±0.25	0.737±0.155	4.24±1.29	1.04±0.18
0.9	29%	2.41±0.65	2.54±0.24	1.04±0.22	4.15±1.32	1.12±0.19
0.95	47%	1.39±0.33	2.99±0.29	0.795±0.179	4.49±0.98	1.01±0.12
0.98	67%	1.32±0.38	2.96±0.31	0.781±0.215	4.79±0.97	0.987±0.106
0.99	76%	0.96±5.21	3.01±3.13	0.916±0.373	4.93±1.29	1.01±0.14
True Value		1.00	3.00	1.00	5.00	1.00

*G: ×10^{-8} m/s; Δc: g/kg water; M_T: g/kg water; B: No./kg water, s; ±95% confidence limits.

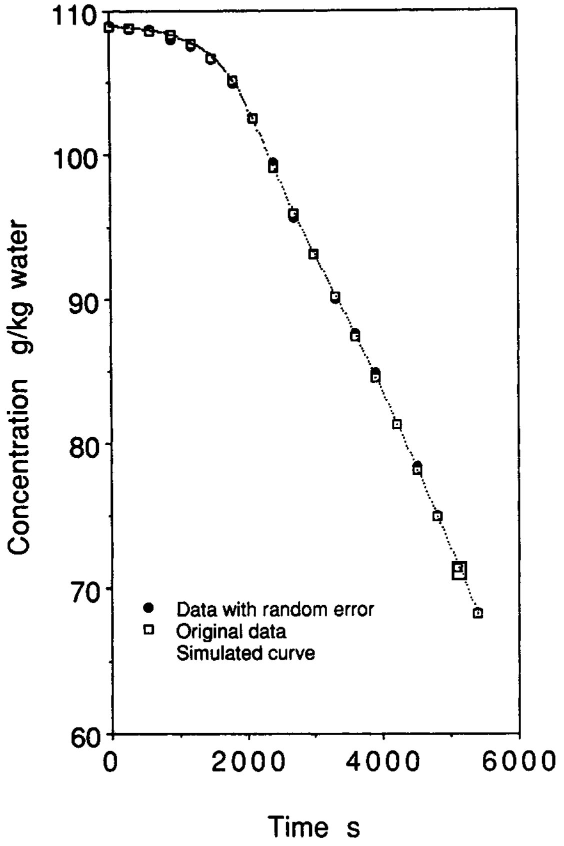

Figure 1. Concentration decay curve of theoretical experiment.

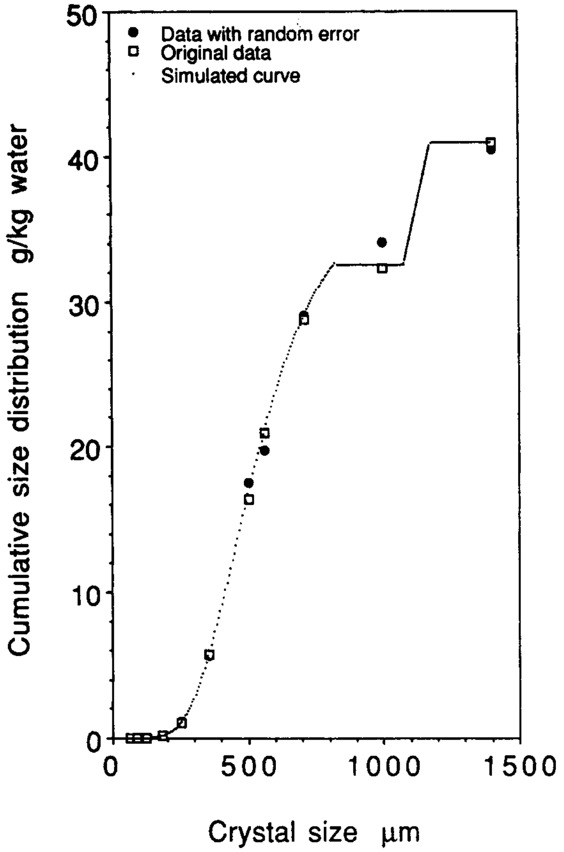

Figure 2. Product weight size distribution of theoretical experiment.

data of succinic acid (Qiu and Rasmuson, 1990) are adopted and the cooling curve follows the equation:

$$\frac{T_0 - T}{T_0 - T_f} = \left(\frac{t}{t_f}\right)^x \tag{13}$$

The process is simulated by the model given above and the concentration vs. time relation and the product size distribution are calculated. Random errors with zero mean are generated by a FORTRAN random number generation program and are added to these concentration and crystal size distribution data. The original and perturbed concentration vs. time data and product crystal size distribution data, respectively, are shown as data points in Figures 1 and 2. The perturbed data points are supplied to the parameter estimation program, and the resulting estimated kinetics are presented in Table 2. Equations 9 and 10 have been used as the objective function for the optimization, and the influence of different values of the weighting parameter P is shown. A low value on P reduces the importance of fitting the concentration curve and emphasizes the size distribution information, and vice versa. The results show that reasonable estimates are obtained for both objective functions over a wide range of P values. Considering the fact that five parameters are estimated from one experiment only, the confidence ranges are not discouraging. The results of the table also suggest that the value of P should result in a reasonable balance between the two terms of the objective function. When the two parts of the objective function are nearly equal at the optimum (F_c/F is approximately equal to 50%), the parameter estimations using both Eqs. 9 and 10 give a set of parameters very close to the true values. The parameter estimation using the cumulative size distribution (Eq. 9) in the objective function usually produces more narrow confidence ranges on the parameters and the parameters seem to be less dependent on P. The solid curves in Figures 1 and 2 are results predicted by the crystallization model using the estimated parameters, based on Eq. 9 and $P = 0.9$. Obviously, the parameter estimation is satisfactory.

Comparison with previous method

In a previous method (Qiu and Rasmuson, 1991b), the product size distribution and the concentration data are approximated by spline functions. The total size range is discretized into a number of size steps and the product size distribution is displaced by horizontal translation towards decreasing sizes in specific size steps. The time corresponding to each step is determined by a mass balance and the concentration vs. time curve, by which the growth rate and the nucleation rate of each step can be calculated. In the Figures 3 and 4 nucleation and growth rates estimated by this method for the simulated experiment are shown. In applying the method, the product size distribution is approximated by a spline with two interior knots at 350 μm and 500 μm. The concentration vs. time curve is approximated by a spline with three interior knots at 1,900 s, 2,200 s, and 3,900 s. The size step is 4 μm. A comparison

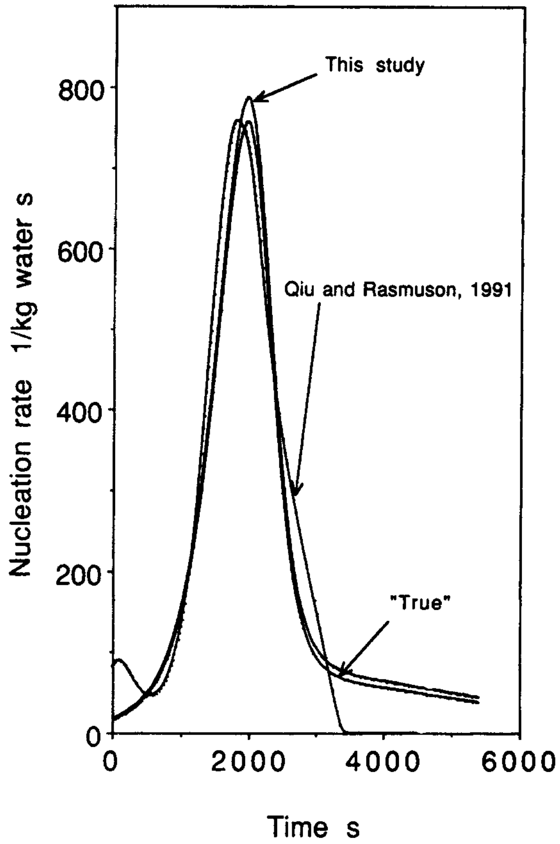

Figure 3. Nucleation rate vs. time of theoretical experiment.

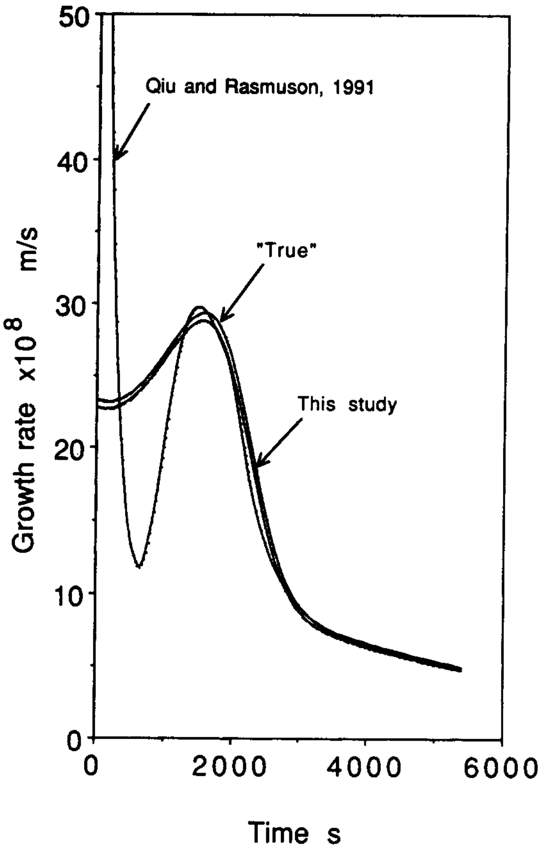

Figure 4. Growth rate vs. time of theoretical experiment.

is made with the "true" curves and with the corresponding data produced by the estimates of the nonlinear optimization method. By using the "true" constants of Table 2 we may predict "true" nucleation and growth rates vs. time. By replacing these constants by those of the optimization method ($P=0.9$, Eq. 9 of Table 2), we may critically examine the quality of the parameters extracted by this method. Figures 3 and 4 support that the optimization technique is successful since "true" growth and nucleation curves are well predicted by the estimated parameters. The figures furthermore reveal that the previous method fails to extract correct nucleation and growth rates in certain ranges of the experiment. For nucleation rates the agreement is acceptable only in the time range between 1,000 and 2,500 s. For growth rates the agreement is acceptable for times exceeding 1,500 s. In this previous method, calculated growth and nucleation rates are correlated to supersaturation and other parameters by equations in which kinetic constants are determined. Obviously, for determination of nucleation kinetics, both the early part and the final part of the experiment should be excluded, leaving only data from less than one-third of the total experimental time. For determination of growth kinetics, only data from two-thirds of the experimental time are useful. If this discrimination is used we obtain: $k_B=1.10$; $b=3.00$; $j=1.01$; $k_g=4.65$; $g=1.06$, which is close to the true values. Of course, the discrimination of the experimental information is rather arbitrary, and the amount of information applied becomes significantly reduced, making the experimental work less efficient. In seeded batch cooling crystallizations, the crystal growth rate is directly proportional to the first derivative of the concentration vs. time curve and the nucleation rate is directly proportional to the first derivative of the final cumulative crystal size distribution. By using the direct optimization method, the differentiation of experimental data that is done in our previous method (Qiu and Rasmuson, 1991b) is replaced by a mathematical-numerical integration of a set of differential equations being a mathematical model of the experiment. As a result, full account can be given to all experimental data without approximations or distortions.

Sensitivity analysis

It is of interest to analyze the importance of the design of experiments. Three experimental parameters are considered: the amount of seeds (W_0), initial supersaturation of the experiment (Δc_0), and the exponent of the cooling curve (x in Eq. 13), even though total time and temperature range also are of importance. The best design of an experiment (narrow confidence limits on good estimates) can be determined by maximizing the determinant of the approximated Hessian matrix at the optimization optimum (Draper and Smith, 1981), over the three-dimensional space (W_0, Δc_0, x). However, a more simple approach is applied here. The cooling crystallization experiment is simulated for different values of each of the individual variables (W_0, Δc_0 or x), while the other two variables, kinetic constants and conditions are kept constant as given by Table 1. On the data of each simulation (concentration vs. time and product size distribution), the same random number generation is applied and the resulting data are

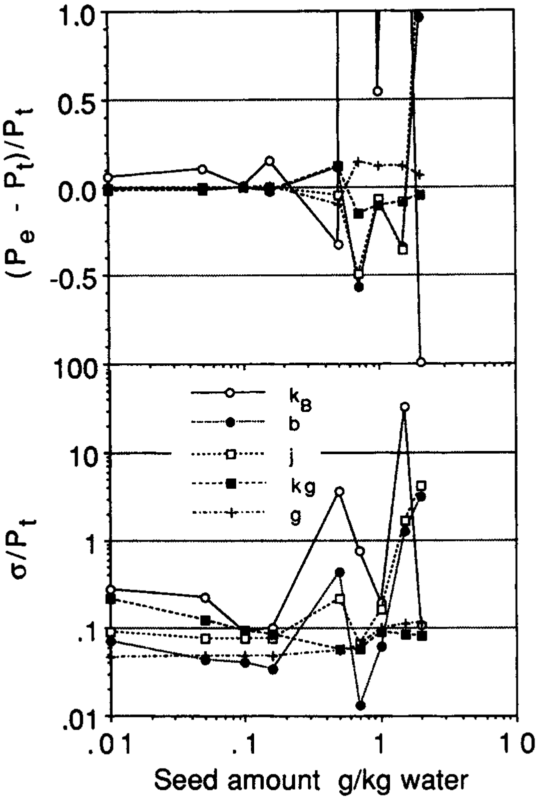

Figure 5. Parameter sensitivity to seed amount used in theoretical experiment.

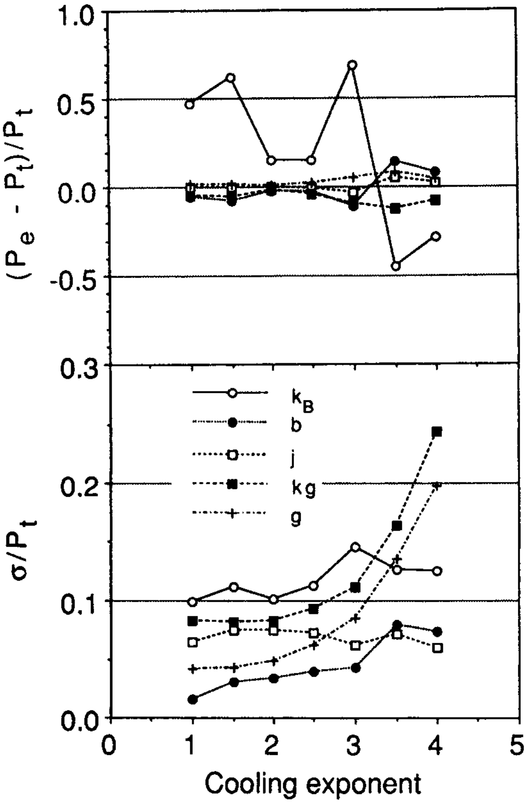

Figure 6. Parameter sensitivity to cooling profile used in theoretical experiment.

used for determination of kinetics adopting Eq. 9 and $P = 0.95$. The relative difference between estimate and correct value and the ratio of the standard deviation of the estimate to the true parameter value are plotted against each variable in Figures 5-7.

In Figure 5 the influence of the amount of seeds on the parameter estimation is shown. For the particular case the seed amount should not exceed 0.2 g/kg water. Below 0.2 g/kg water, the standard deviations for all the parameters are less than 30% of the true parameter values, and estimated values are very close to true values: the parameter estimation is successful. Above this value, all estimated constants commence to deviate significantly from the true values and in particular the ranges of confidence for nucleation parameters (k_B, b, and j) increases. Gradually, very large standard deviations on the parameters are obtained and the parameter estimation fails. When the seed amount is large most of the deposition of the crystallizing material takes place on the seeds. The seeded crystals become much larger than nucleated and the latter comprise a very low proportion of the total mass. Accordingly, the experimental data furnished to the estimation procedure mainly describes growth of seeds, and nucleation becomes difficult to characterize.

In Figure 6, the influence of the cooling order is shown. There is an influence of the cooling order on the estimated parameters, and for the particular case an order of 2 should not be significantly exceeded. By comparison with Figure 5 we may conclude, however, that the choice of cooling order is less important than the choice of seed amount. The influence on the ranges of confidence is much weaker. The standard deviations of the growth rate parameters increase when the cooling exponent increases. Probably, the range of supersaturation becomes more narrow at a high order of cooling. The supersaturation range should be as large as possible to make the parameter estimation well conditioned. However, as long as primary nucleation is not accounted for in the model, the supersaturation has to be kept within the metastable range.

The influence of the initial supersaturation on the parameter estimation is shown in Figure 7. The initial supersaturation is also much less critical than the seed amount. However, it seems to be favorable to have a high initial supersaturation. More correct estimates are obtained having reduced ranges of confidence. A high initial supersaturation can extend the supersaturation range. However, during the early stage of each experiment the magma density is low. Thus, the possibility to improve on the information concerning secondary nucleation by proper choice of initial supersaturation is limited.

Crystallization Kinetics of Succinic Acid

Experimental work on batch cooling crystallization of succinic acid has been reported (Qiu and Rasmuson, 1991b), previously. 12 seeded crystallizations were carried out in a 2.51 controlled cooling crystallizer. The amount of seeds varied from 0.12 to 2.0 g/kg water. The initial temperature was 30°C for all the experiments and the final temperature was either 20 or 15°C. Three impeller speeds, 400, 550, and 710 rpm were used. The cooling times were 1.5 or 2 h and different shapes of the cooling curve were used. During the experiments, the concentration of the solution was measured every five min

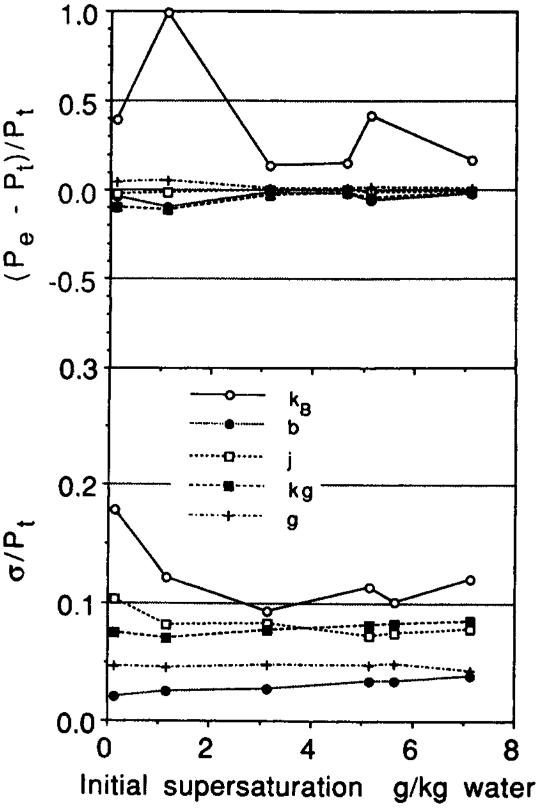

Figure 7. Parameter sensitivity to initial supersaturation used in theoretical experiment.

using a density meter and the temperature was recorded. At the end of each experiment, the product size distribution was analyzed by sieving. In all experiments, significant secondary nucleation took place and the seed crystals increased significantly in size. However, since the supersaturation was kept within the metastable zone, primary nucleation was negligible. The size distribution data applied in the present study has been corrected for losses the same way as in the previous work (Qiu and Rasmuson, 1991b).

The nonlinear optimization procedure can successfully extract the five parameters of Eqs. 11 and 12 from one experiment only for those seven experiments in which the amount of seeds is low (0.12–0.24 g/kg water). The ranges of confidence of the parameters become relatively narrow for $P = 0.95$, and these results are shown in Table 3. The table shows that the difference in parameter values obtained for different experiments often exceeds the range of statistical confidence of the estimations. It is possible that confidence intervals are underestimated, since linear statistics may be inadequate for characterizing regions of confidence for this problem. However, alternative possibilities are that there is experimental spreading, which significantly influences the value of the estimated parameters (compare the analysis of Qiu and Rasmuson, 1990), or that the model adopted does not fully account for all features. According to the results, there is no obvious reason to prefer one objective function (Eq. 9 or 10) over the other. Reliable nucleation parameters could not be estimated from those experiments where the amount of seeds (0.89–2.0 g/kg water) is large. The parameter estimation becomes ill-conditioned, as is discussed in the sensitivity analysis above.

All 12 experiments can be included in one single optimization. Kinetic relations have to be extended to account for the influence of the agitation rate on nucleation and growth:

$$G = k_g \Delta c^g N^p \tag{14}$$

and

$$B = k_B \Delta c^b M_T^j N^h \tag{15}$$

Thus, seven parameters are to be estimated. Results are presented in Table 4 for both Eq. 9 and Eq. 10 and for different values of P. All estimations produce reasonable values of parameters and ranges of confidence are reasonable as well. Rate constants vary considerably with the value of P, and ranges of confidence may become wide. However, it is our experience that values of the rate constants are sensitive to the values of the exponents on the independent variables in the rate equation.

Table 3. Parameter Estimation Based on Individual Succinic Acid Experiments*

No.	rpm	k_B	b	j	k_g	g
			Using Eq. 9 as the Objective Function			
E5	710	1.63±0.25	3.11±0.23	0.64±0.10	6.03±0.99	0.71±0.10
E6	710	1.44±0.12	3.20±0.21	0.55±0.12	4.66±0.82	0.98±0.10
E12	710	0.73±4.28	3.46±3.11	0.21±0.58	4.21±0.21	0.99±0.08
E11	550	6.40±1.13	2.14±0.19	0.57±0.16	1.86±0.62	1.23±0.19
E8	400	2.12±0.19	2.52±0.21	0.30±0.16	2.41±0.80	1.04±0.16
E9	400	1.80±4.12	2.71±1.13	0.58±0.21	1.88±0.06	1.31±0.04
E10	400	0.50±0.52	3.32±0.49	0.31±0.31	2.19±1.09	1.08±0.27
			Using Eq. 10 as the Objective Function			
E5	710	0.72±2.76	3.66±2.55	0.65±0.14	6.02±0.19	0.71±0.04
E6	710	2.01±2.88	3.06±0.87	0.52±0.12	4.82±0.74	0.96±0.11
E12	710	0.91±0.08	3.27±0.19	0.42±0.29	4.09±1.28	1.04±0.19
E11	550	10.6±41.6	1.83±2.03	0.71±0.35	1.75±0.70	1.29±0.23
E8	400	14.9±2.9	1.55±0.14	0.36±0.16	2.32±0.78	1.06±0.16
E9	400	0.75±1.67	3.06±1.11	0.62±0.33	1.95±0.47	1.31±0.12
E10	400	4.35±1.55	2.06±0.23	0.62±0.39	2.00±1.09	1.15±0.29

*G: $\times 10^{-8}$ m/s; Δc: g/kg water; M_T: g/kg water; B: No./kg water, s; ±95% confidence limits.

Table 4. Parameter Estimation Based on all 12 Succinic Acid Experiments*

P	F_c/F	$k_B \times 10^{-4}$	b	h	j	$k_g \times 10^6$	g	p
				Equation 9 as the Objective Function				
0.40	43%	10,200 ± 7,000	2.63 ± 0.42	0.601 ± 0.520	0.462 ± 0.104	4.56 ± 1.32	1.35 ± 0.19	0.598 ± 0.177
0.80	77%	3,250 ± 603	2.53 ± 0.14	0.751 ± 0.516	0.498 ± 0.102	2.53 ± 0.52	1.28 ± 0.13	0.643 ± 0.178
0.85	78%	1,690 ± 360	2.55 ± 0.14	0.905 ± 0.477	0.531 ± 0.096	1.41 ± 0.27	1.26 ± 0.12	0.714 ± 0.170
0.90	86%	1,430 ± 509	2.50 ± 0.24	0.887 ± 0.392	0.525 ± 0.098	1.65 ± 0.30	1.26 ± 0.11	0.695 ± 0.166
0.95	73%	116 ± 11	2.18 ± 0.08	1.14 ± 0.42	0.632 ± 0.078	0.647 ± 0.074	1.12 ± 0.07	0.736 ± 0.118
0.98	82%	55.9 ± 5.8	2.11 ± 0.10	1.31 ± 0.60	0.732 ± 0.112	0.846 ± 0.110	1.16 ± 0.08	0.726 ± 0.156
				Equation 10 as the Objective Function				
0.80	10%	0.738 ± 0.505	2.15 ± 0.41	2.03 ± 0.37	0.716 ± 0.132	5.63 ± 1.71	1.35 ± 0.18	0.574 ± 0.190
0.85	13%	0.781 ± 0.284	2.16 ± 0.25	2.03 ± 0.57	0.718 ± 0.132	5.98 ± 1.44	1.35 ± 0.15	0.564 ± 0.262
0.90	19%	0.810 ± 0.273	2.16 ± 0.24	2.03 ± 0.57	0.718 ± 0.133	5.92 ± 1.26	1.35 ± 0.14	0.564 ± 0.244
0.95	31%	1.38 ± 0.421	2.23 ± 0.22	2.04 ± 0.62	0.755 ± 0.145	6.11 ± 1.10	1.34 ± 0.12	0.552 ± 0.226
0.98	52%	9.59 ± 2.99	2.33 ± 0.23	1.93 ± 0.75	0.868 ± 0.179	3.84 ± 0.62	1.34 ± 0.11	0.621 ± 0.222

*for dimensions: see list of notations; ±95% confidence limits.

The ranges of confidence of parameter values become more narrow when 12 experiments are included instead of only one, even though seven parameters are estimated instead of five. Equation 9 produces more narrow ranges of confidence than Eq. 10, for most of the parameters. However, the influence of the value of P is weaker for Eq. 10. Except for the parameter h, which describes the influence of stirring rate on nucleation, Eqs. 9 and 10 produce values for the constants that are reasonably close.

Principally, all parameter values in Table 4 are physically realistic and are at least close to the range of values reported for other substances. The growth rate is expected to depend on supersaturation to a power higher than 0.83, being the lower limit for the nuclei-above-nuclei model, and rarely values above 2 are reported. For the BCF theory the lower limit is unity. In this study, $g \approx 1.1$–1.4, indicating some influence of surface integration resistance. The dependence of growth rate on the stirring rate is here found to be: $p \approx 0.6$–0.7, which corresponds well to the dependence of ordinary mass transfer to particles in agitated suspensions. The dependence of secondary nucleation on supersaturation is $b \approx 2.1$–2.6, which is in accordance with results reported by others (values ranging up to 3 are expected (Garside and Davey, 1980)). The dependence of nucleation on the stirring rate (h) depends on the objective function chosen, which indicates a reduced reliability. h is in the order of unity for Eq. 9 and in the order of 2 for Eq. 10. Also the confidence range for this parameter is comparatively wide. Theoretical arguments suggest that the dependence of secondary nucleation on stirring rate should be of order 3-4 (Garside and Davey, 1980). Recent derivations by Polish and Mersmann (1988) suggest a value of 2.2, if fragmentation due to crystal-impeller collisions dominates. Experimental results range from 1.8 to 7.82 and several studies report $h = 2$–2.5 (Garside and Shah, 1980). However, Sikdar and Randolph (1976) found that the stirring rate did not effect the nucleation rate of citric acid and magnesium sulfate, and it has been reported (Mullin and Leci, 1972; Wang et al., 1981) that the influence of agitation on citric acid nucleation vanishes at increasing rotations per minute. A low order of dependence may reflect regeneration or survival limitation of the nucleation process. The dependence on magma density is found to be $j \approx 0.5$–0.8. The collision theory predicts a linear dependence if collisions with surfaces of the equipment dominate, but experimental results range from 0.14 to 1.21, with several correlations having j in the order of 0.5 (Garside and Shah, 1980). Again, a low value may indicate regeneration limited or survival limited nucleation.

The optimization attempts to correlate concentration and size distribution data of the experiments as well as possible. Figures 8 and 9 are the corresponding residual diagrams for the parameters that are obtained by adopting Eq. 9 and $P = 0.95$ (Table 4), shown as an example. With a few exceptions, size distribution residuals are evenly distributed, but the range is

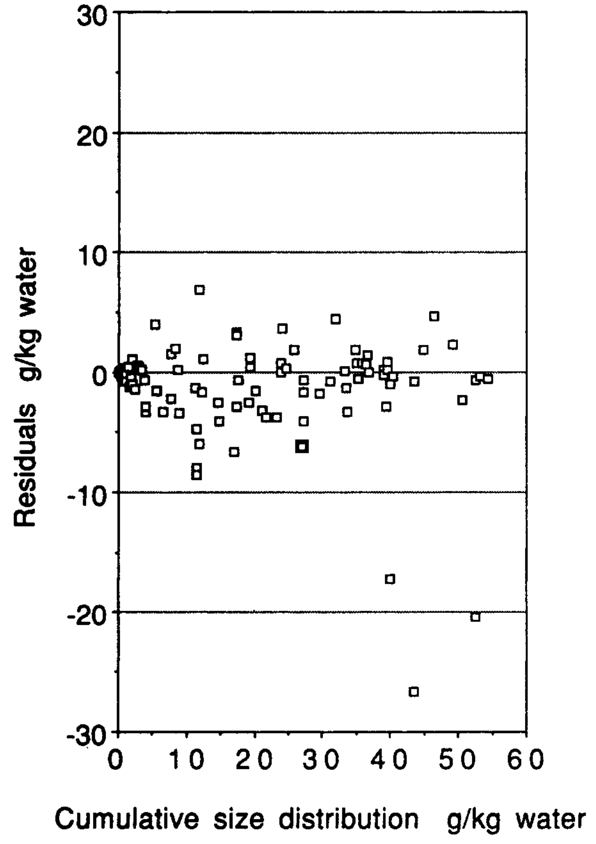

Figure 8. Size distribution residual diagram for succinic acid parameter estimation.

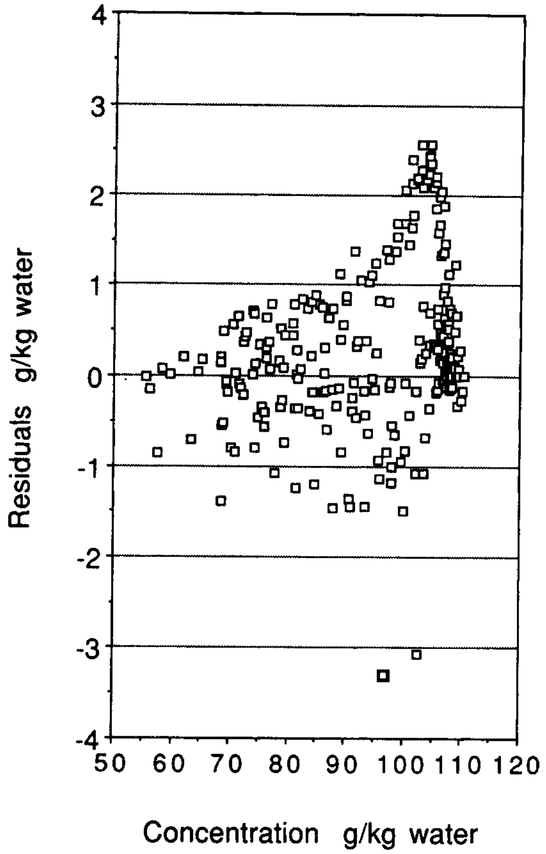

Figure 9. Concentration residual diagram for succinic acid parameter estimation.

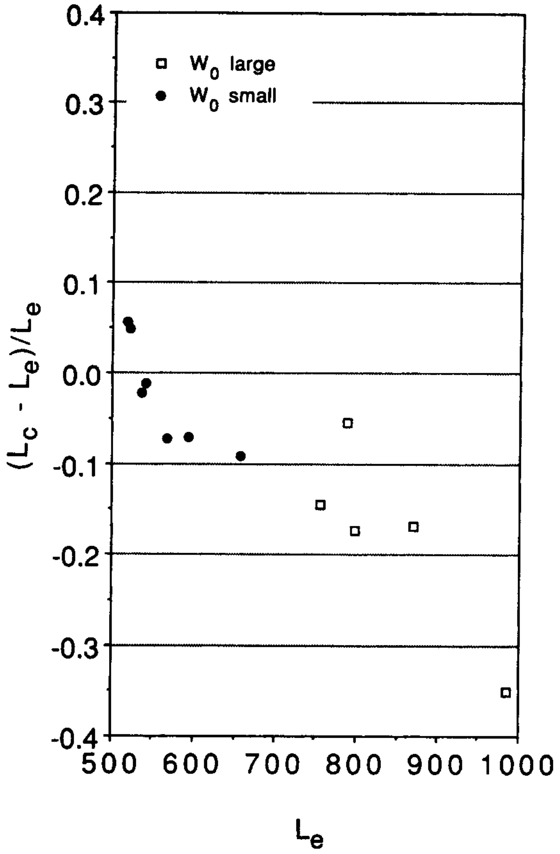

Figure 10. Prediction of experimental product weight mean size by estimated parameters.

rather wide. Concentration residuals are not entirely evenly distributed. At high concentrations, that is, normally early in the experiments, predictions tend to underestimate the concentration. The concentration decay is in practice slower than predicted, which indicates that the mass increase of seeded crystals might be overestimated.

Parameters determined by the optimization technique can be inserted into the model described above and used for prediction of batch cooling crystallizations. The prediction capability of the kinetics can be tested by simulation of the experiments. Strictly, additional experiments not included in the parameter estimation should be used, but in this case this is not critical, since the experimental program covers a wide range of different conditions. Figures 10 and 11 show whether experimental weight mean sizes and size distribution coefficients of variation can be accurately predicted by parameters of Eq. 9 and $P = 0.95$. In comparison to the previous method (Qiu and Rasmuson, 1991b), the prediction of mean sizes is improved. The mean sizes of the 7 experiments having a low amount of seeds are predicted within 10%. The predictions for those experiments having a large amount of seeds are, however, still not satisfactory. Concerning coefficients of variation there is a significant improvement, since now all values are predicted correctly almost within 20%, and for those experiments having a low amount of seeds the deviation is less than 15%. If parameters obtained by adopting Eq. 10 (and the same P-value) are used, the prediction of mean sizes is less accurate. Even for some of the low seed amount experiments, and prediction of CV values is not improved over that shown in Figure 11. In Figures 12 and 13 the prediction, by parameters of Eq. 9 and $P = 0.95$, of complete size distributions and concentration curves are shown for two experiments, one of low seed amount (E5) and the other of high seed amount (E3). Points are experimental data and dotted lines are predictions. The reason for the improved prediction of CV values seems to be an improved prediction of the distribution of the mass between nucleated and seeded crystals. However, it is quite clear that the overall prediction of E3 is unsatisfactory, while E5 is predicted well.

A few alternatives to Eqs. 14 and 15, to represent the kinetics have been evaluated. First, the activation energies for nucleation and crystal growth have been included in Eqs. 14 and 15 in a regression to estimate nine parameters. However, the obtained confidence limits on these activation energies are not acceptable, probably reflecting that the temperature range is too narrow. Secondly, the crystal growth rate is normally assumed to be limited by two resistances to mass transfer: diffusion through the boundary layer and surface integration into the lattice. A simple representation of this is (Qiu and Rasmuson, 1990):

$$\frac{G}{k_{d0}(N/550)^{0.62}} + \left(\frac{G}{k_r}\right)^{\frac{1}{r}} = \Delta c \qquad (16)$$

containing three parameters to be determined by optimization: k_{d0}, k_r, and r. A regression based on Eq. 16 and the nucleation

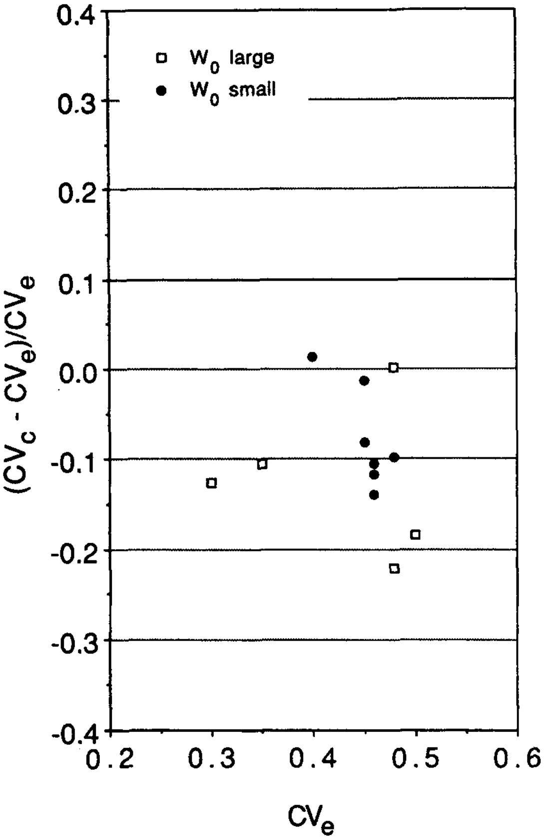

Figure 11. Prediction of experimental product coefficient of variation by estimated parameters.

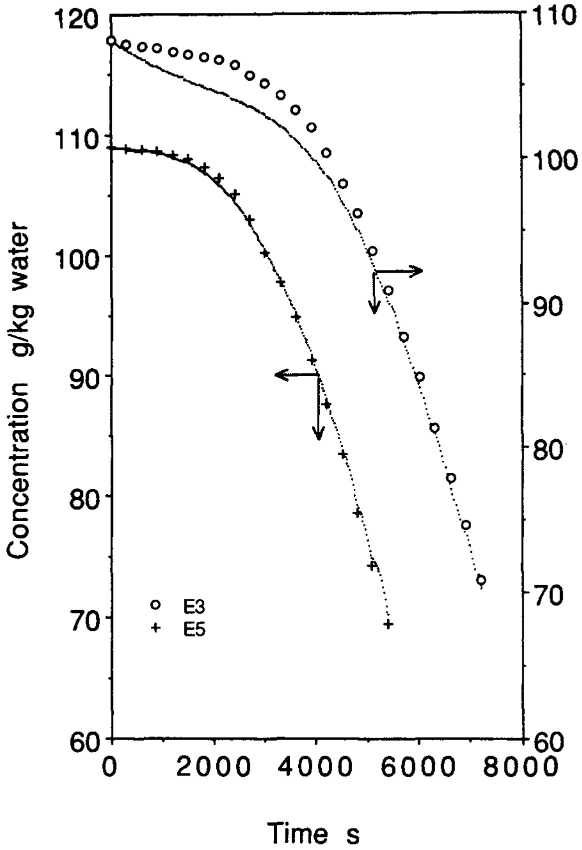

Figure 12. Prediction of complete experimental concentration vs. time by estimated parameters.

rate equation, Eq. 15, to determine seven constants, was unsuccessful. The value obtained on r, the order of dependence of the surface integration rate on supersaturation, is unreasonably high. Thirdly, secondary nucleation caused by collisions with the impeller or with other crystals may produce nuclei that at least initially have growth properties different from large crystals grown for some time, washed, dried, sieved, and washed again (that is, seeded crystals). In a previous study (Qiu and Rasmuson, 1990), growth of seeds were studied using the same crystallizer and stirrer as in the present work. The results were correlated by a two-step equation similar to Eq. 16 (Eq. 19 in that article; unfortunately the equal sign just before the Δc disappeared at printing). This equation can be included to describe the growth behavior of the seeds, while kinetics for nucleation and nuclei growth described by Eq. 14 and 15 are extracted by optimization. The constants obtained by this procedure do not differ significantly from those of Table 4, but in some cases the confidence in the values disappears completely. It seems as this operation withdraws too much information from the parameter estimation. If the parameters that are obtained by adopting Eq. 9 and $P = 0.95\%$ (disregarding a low confidence in two of the parameters) are used and the growth of the seeds is still described by the previous two-step equation, the prediction of mean sizes and coefficients of variation is worse than that shown in Figures 10 and 11. Even the seven experiments of low seed amount are less correctly predicted. One reason why the previous equation may be incorrect in predicting the behavior of the seeds in the present experiments is that the size-increase is very significant, and we suspect that a shape change takes place. In the experiments, from which the two-step equation is determined, the size-increase is limited.

To refine the estimation of kinetics for growth and nucleation of succinic acid, the five experiments containing a large amount of seeds are excluded from the optimization, and the result is presented in Table 5. Notably, the influence of choice of objective function has virtually disappeared. Furthermore, the values of these constants are close to those obtained by incorporating the previous two-step equation as discussed earlier (third case), and not too strongly deviating from those of Table 4. If the parameters of Table 5 and Eq. 9 are used for prediction, the result becomes very close to that presented in Figures 10 and 11. There is only a slight removal of each point in these diagrams. In using Eq. 10, the seven low seed amount experiments are better described if the parameter estimation is based on these experiments only.

Discussion

Method

This study concerns nonlinear optimization estimation of kinetics from seeded batch cooling crystallizations, in which the concentration and temperature are recorded and the product crystal size distribution is determined. In all work on determination of crystallization kinetics, the accuracy of the supersaturation determination is critical. Accurate character-

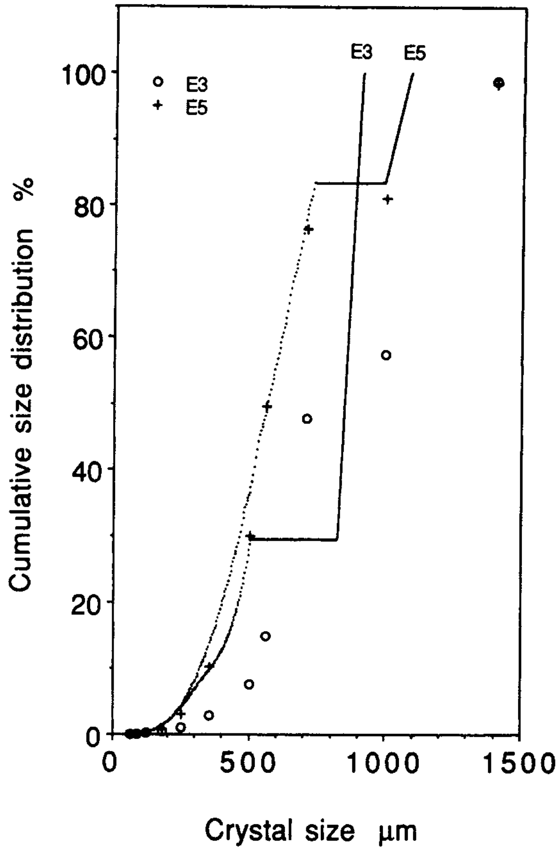

Figure 13. Prediction of complete experimental product size distributions by estimated parameters.

ization of the particle size distribution is also of importance. In the present study, the result should be comparatively insensitive to the characterization of the small size fraction. However, the distribution comprises seeded as well as nucleated crystals and attention should be devoted to the range comprising seeded crystals. Crystalline products often range up to sizes of a few millimeters, and sieving becomes the choice for size distribution determination. Normally, sieving has a moderate resolution, that decreases with increasing size, and the fraction of the product corresponding to seeded crystals tends to become poorly characterized. In calculating the mean size and the CV of the product of the succinic acid experiments, the size of each sieve fraction is chosen as the arithmetic mean of the upper and the lower sieve. Uncertainties in mean size and CV arise when a significant proportion of the mass is allocated into a rather narrow size range in the upper region, that is, when the product is dominated by seeded crystals.

Concerning the choice of objective function, in Eq. 10 the product size distribution is accounted for as the mass between two sieves, which is the original experimental data at hand. In the simulation (in the optimization subroutine), monosized subpopulations of crystals are generated, and these subpopulations become distributed over the size scale, due to differences in birth time. At the end, all pulses within each sieve range are summed and the mass is compared with experimental data. By using Eq. 9, the cumulative weight below each sieve is used in the objective function. Since the absolute deviation is minimized, the relative error tends to become larger for those experimental values that are low. In this respect, Eq. 9 puts increased emphasis *on* the upper region of the cumulative size distribution, that is, increased interest into the behavior of the seeded crystals. Equation 10 emphasizes the size range where most of the mass is found. Equation 10 seems to have properties that are favorable over those of Eq. 9. However, this has not been confirmed in the present work. Equation 9 is less sensitive to disturbances in the experimental data. The parameters obtained by using Eq. 9 and all 12 experiments do as well in predicting all experimental mean sizes and coefficients of variations, as those parameters obtained by using Eq. 10 and the seven more favorable (low seed amount) experiments. A reduced sensitivity is of course not necessarily a positive feature, but we have not been able in the present study to expose the opposite. Since the objective functions are different, the ranges of confidence of parameters are not in detail comparable, and should not directly be used for discrimination of objective function. In conclusion, we cannot form a definite judgment on the choice of the objective function, and we believe that the applicability of the crystallization model is a more important issue for the succinic acid case.

The optimization identifies the values of the parameters that minimizes the collected discrepancies between the model predictions and the experimental data. The parameter P can be used to increase the importance of fitting the size distribution at the expense of fitting the concentration data, or vice versa. However, when P goes to zero, only the product crystal size distribution data are considered, and in the case of single experiment this information can only allow for determination of an average (over time) growth rate and an average nucleation rate. When P goes to unity, only concentration vs. time data

Table 5. Parameter Estimation Based on the Seven Succinic Acid Experiments with Small Amounts of Seeds*

P	F_c/F	$k_B \times 10^{-6}$	b	h	j	$k_g \times 10^6$	g	p
				Equation 9 as the Objective Function				
0.60	40%	1.70 ± 0.23	2.42 ± 0.10	1.18 ± 0.27	0.543 ± 0.059	0.495 ± 0.155	1.19 ± 0.11	0.827 ± 0.119
0.85	71%	1.70 ± 0.19	2.42 ± 0.09	1.18 ± 0.32	0.543 ± 0.065	0.495 ± 0.080	1.19 ± 0.09	0.827 ± 0.120
0.90	62%	1.05 ± 0.20	2.33 ± 0.06	1.22 ± 0.35	0.593 ± 0.095	0.718 ± 0.120	1.19 ± 0.10	0.773 ± 0.138
0.95	77%	1.29 ± 0.23	2.44 ± 0.13	1.37 ± 0.52	0.667 ± 0.111	0.657 ± 0.105	1.21 ± 0.09	0.807 ± 0.142
				Equation 10 as the Objective Function				
0.85	53%	0.903 ± 0.588	2.34 ± 0.36	1.24 ± 0.35	0.579 ± 0.082	0.692 ± 0.119	1.19 ± 0.10	0.777 ± 0.114
0.90	64%	0.903 ± 0.648	2.34 ± 0.40	1.24 ± 0.38	0.579 ± 0.088	0.692 ± 0.124	1.19 ± 0.10	0.777 ± 0.110
0.95	75%	0.732 ± 0.649	2.44 ± 0.49	1.44 ± 0.48	0.651 ± 0.104	0.685 ± 0.113	1.21 ± 0.10	0.798 ± 0.114

*for dimensions: see list of notations; ±95% confidence limits.

are considered, and it becomes extremely difficult to obtain nucleation information (regardless of parameter estimation method). When the model correctly describes all important features of the kinetics and the process, the resulting parameters should be rather insensitive to the value of P, within reasonable limits. However, when the model is not sufficiently accurate or flexible, or in case of systematic errors in experimental data, the value of F at the optimum may be governed by systematic deviations. The value of P determines how these deviations are distributed between the two terms, and the estimates depend more strongly on the particular value chosen. However, no particular value is more correct than other values, as long as a reasonable weight is given to both terms. The key issue is not to determine, in some sense the best value on P, but rather to identify the reason behind the systematic deviations and deal with that.

Kinetics of succinic acid

The direct nonlinear optimization method successfully estimates seven kinetic parameters for nucleation and growth of succinic acid, and in particular the parameters for nucleation are improved in comparison to our previous method (Qiu and Rasmuson, 1991b). However, in using these estimates, the prediction of those experiments that involves a large amount of seeds is still unsatisfactory. Uncertainties in the experimental characterization of the mean size and CV is not a sufficient explanation. As shown in Figures 12 and 13 (experiment E3), the extent of the underestimation of the final size of the seeded crystals is outside the range of the uncertainty of the corresponding sieve fraction size.

In particular, the result shown in Figures 12 and 13 suggests that there are aspects of the process which are not covered by the model. In particular, it has been assumed that the shape is constant and that growth dispersion is negligible. A constant volume shape factor of 0.33 is adopted. The actual value of the volume shape factor does only influence on the value of the nucleation rate constant. The nucleation rate constant is inversely proportional to the volume shape factor. Other parameters of the nucleation rate equation and the parameters of the growth rate equation do not depend on the particular value of the shape factor. Even though the shape factor relates the linear crystal growth rate to the mass consumption (Eqs. 4, 6, and 7), it also relates the mass distribution determined by sieving to the population density distribution. Hence, during estimation of kinetics from the experimental data, the influence of the shape factor value cancels out. Thus, the particular value of a constant shape factor is not very important here. A changing shape can be accounted for in the model. However, shape information cannot be extracted within the optimization simultaneously with nucleation information, but has to be determined directly by laboratory work. Growth dispersion can be included in the model, and information can in principle be obtained within the optimization from the present experimental data. At least one extra parameter has to be estimated. In the size range covered by nucleated crystals, we cannot distinguish growth rate dispersion from the nucleation process. However, in the size range covered by seeded crystals only, exclusive information on the growth process is at hand. By comparison of the initial seed size distribution and the part of the product distribution that corresponds to seeded crystals, information on growth dispersion may be extracted. The reliability of this information is critically dependent on the quality and resolution of the determination of the size distribution in the upper region. Furthermore, the phenomenon of growth rate dispersion is usually regarded as being related to the surface integration process, that is, to variations in the rate of integration of molecules into the lattice of the crystal faces. If this is the case, growth rate dispersion may very well be accompanied by simultaneous variations in crystal shape, that is, shape dispersion. Thus, if growth rate dispersion is to be included in the evaluation of kinetics, we should also question the assumption of a constant crystal shape.

Stored product samples from the previous experiments have been reexamined by sieving using a refined set of sieves in the upper region, and the crystal shape of each fraction has been determined. In Figure 14, the volume shape factor of each sieve fraction is plotted vs. arithmetic mean size of the upper and lower sieve for several experiments. The shape factor is determined by counting and weighing. Normally each determination is based on about 100 crystals. Obviously, a significant variation in shape is at hand. Either 100 particles are far from sufficient to obtain a statistically reliable value, indicating a significant spread within each fraction, or the variations among different fractions are significant. We believe that the variations cannot be explained by size variations within each fraction. There is maybe a tendency of a maximum shape factor value in the upper size region, but due to the lack of clear, systematic behavior, no shape variation effect has been included in the evaluation of kinetics. Resieved size distributions

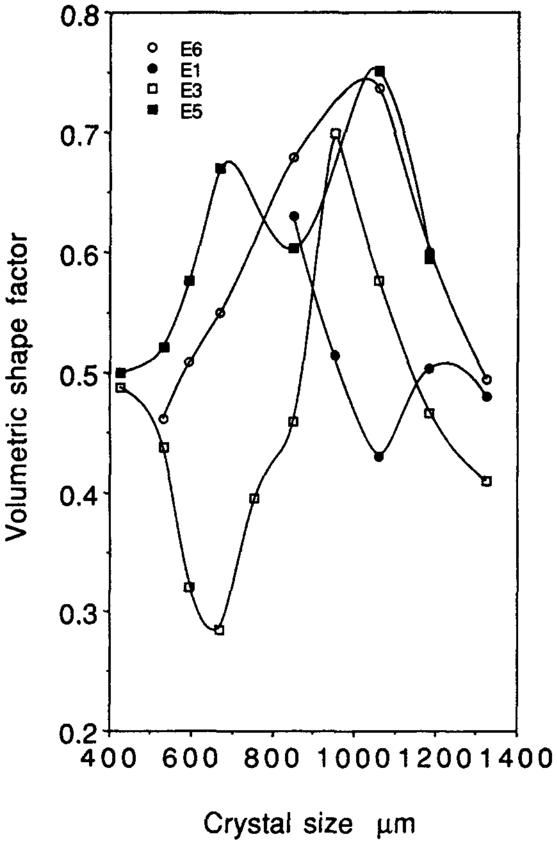

Figure 14. Experimental product volume shape factor for different sieve fractions.

indicate, at least in some experiments, a presence of growth rate dispersion. However, again the picture is not entirely clear, and unfortunately the agreement of these refined distributions with those originally obtained is not always acceptable. Thus, these refined size distributions cannot with confidence be applied for extraction of kinetics. Further work has to be based on experiments in which the crystalline product is characterized more carefully.

In our previous communication (Qiu and Rasmuson, 1991b), seven parameters could not be confidently estimated simultaneously. Thus, nucleation was given a linear dependence on magma density. This assumption has experimental and theoretical support, and is often used by others. For comparison the corresponding estimation ($j=1$) has been performed by the nonlinear regression method and Eq. 9 for $P=0.95$. The values obtained are $g=1.37$, $p=0.87$, $b=2.72$, and $h=1.31$ in comparison to $g=1.05$, $p=0.63$, $b=4.01$, and $h=2.28$ previously reported (Qiu and Rasmuson, 1991b). Obviously, the parameter values obtained are sensitive to the method of evaluation, in particular concerning nucleation.

Conclusions

Seeded batch cooling crystallization experiments have the potential of being very efficient for determination of crystallization kinetics. However, this potential can only be exploited successfully if the experimental information is handled adequately. In this work, a direct nonlinear optimization method to evaluate crystal growth and secondary nucleation kinetics simultaneously is developed and evaluated. The underlying experimental data comprise concentration and temperature vs. time measurements, and the product crystal size distribution. Kinetic parameters are estimated by fitting a mathematical model of the crystallization experiment to experimental data. To evaluate the method, experimental results are produced theoretically by simulation and perturbation, and it is shown that the method can generate reliable estimates of kinetics. Furthermore, it is shown that this estimation is not very sensitive to the design of the experiments. As opposed to our previous method (Qiu and Rasmuson, 1991b), this optimization approach can give full account to all experimental data without approximations or distortions, and as a result more information of higher accuracy concerning kinetics can be determined.

The direct optimization method is applied for determination of kinetics of succinic acid crystallizing in aqueous solutions. The results of 12 seeded batch cooling crystallization experiments at different conditions are simultaneously supplied into one single optimization. Seven kinetic parameters for nucleation and growth are successfully estimated, and in particular the parameters for nucleation are improved in comparison to our previous method. Estimated parameters allow for an improved prediction of mean sizes and in particular of the mass distribution between nucleated and seeded crystals in the product. Experiments in which the product is dominated by nucleated crystals can be predicted very well by these parameters. Weight mean size is predicted accurately within 10% and coefficient of variation within 15%. Experiments in which the product is dominated by seeded crystals are not predicted satisfactorily. A refined characterization of the size distribution and analysis of variations in crystal shape are needed for further developments.

Acknowledgments

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Notation

b = order of nucleation rate with respect to Δc
B = nucleation rate, 1/s kg solvent
c = concentration, kg/kg solvent
c^* = solubility, kg/kg solvent
Δc = supersaturation, kg/kg solvent
CV_c = coefficient of variation of predicted product weight distribution
CV_e = coefficient of variation of experimental product weight distribution
F = objective function for the optimization
F_c = solution concentration part of objective function
F_W = product size distribution part of objective function
g = order of growth rate with respect to Δc
G = crystal growth rate, m/s
h = order of nucleation rate
j = order of nucleation rate
J = Jacobian matrix of the residual function for the optimization
k_B = nucleation rate constant
k_{d0} = volume diffusion rate constant at 550 rpm, m/s (kg/kg solvent)
k_g = overall growth rate constant
k_r = surface integration rate constant
k_V = volume shape factor
L = characteristic crystal size, m
L_c = predicted product weight mean size, μm
L_e = experimental product weight mean size, μm
m = number of the concentration measurements
M_T = total crystal mass, kg/kg solvent
n = population density of crystals, 1/m·kg solvent
n_S = population density of seeds, 1/m·kg solvent
N = impeller speed, rpm
p = order of growth rate with respect to N
P = weighting parameter in objective function
P_e = estimated parameter value
P_t = true parameter value
r = order of surface integration rate with respect to Δc
s = number of sieves used to analyze the product
S = vector of singular values of the estimated Jacobian matrix
t = time, s
T = temperature, °C
V = matrix of orthonormalized eigenvectors of J^TJ
x = exponent for the temperature profile

Greek letters

ξ = characteristic
ρ = density of crystalline material, kg/m^3
σ = standard deviation of parameter

Superscripts

0 = at zero size

Subscripts

f = final
0 = initial

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