Growth Kinetics of Ammonium Sulfate in a Batch Cooling Crystallizer Using Initial Derivatives

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INTRODUCTION

A simple technique to deduce crystal growth kinetics from isothermal batch experiments performed in the integral mode was suggested by Garside et al. (1982). Evaluation of the zero time derivatives from the initial portion of a single seeded isothermal desupersaturation curve enabled the growth (or even dissolution) kinetic parameters to be determined directly. Although the technique is sensitive to experimental error in the measurement of the initial supersaturation decay, results reported (Garside et al., 1982; Palwe et al., 1983) show that the method appears reasonably reliable and the accuracy of the resulting kinetic responses is probably comparable to that obtained using more involved conventional techniques.

The purpose of this research note is to extend this analysis to a batch cooling crystallizer and show how the initial derivatives of the supersaturation and temperature profiles obtained in a series of integral batch experiments can be used to evaluate directly the kinetic parameters in crystal growth correlations. The technique will then certainly increase the experimental ease and flexibility with which the growth kinetics can be determined for many crystallization systems. Ammonium sulphate, an important inorganic bulk chemical, was chosen as a working system. The crystallization study of ammonium sulfate has received considerable attention, and some progress has been made in determining the applicable kinetic relationships (Mullin et al., 1970; Chambliss, 1966; Larson and Mullin, 1973; Klekar and Larson, 1973; Youngquist and Randolph, 1972; Bourne and Faubel, 1982).

THEORY

The overall crystal growth rate kinetics are assumed to be given by

$$R = k_g \exp(-E/R_gT)\Delta c^g \tag{1}$$

The effect of temperature on the overall growth rate is expressed in Eq. 1 by an Arrhenius-type relation. In general, the overall rate constant k_g then depends on crystal size, hydrodynamic situation, and presence of impurities. For a batch cooling crystallizer, the mass deposition rate can be expressed as

$$M_T = A_TR = A_Tkg \exp(-E/R_gT)\Delta c^g \tag{2}$$

where A_T is the total crystal surface area available for the growth and M_T is the total crystal mass both expressed per unit mass of solvent. The mass deposition as a result of nucleation process is assumed negligible. If the solubility relation for the crystallizing salt over the range of operation is represented by

$$c_s = aT + b \tag{3}$$

the supersaturation balance is then written as

$$\Delta\dot{c} + a\dot{T} + A_Tkg \exp(-E/R_gT)\Delta c^g = 0 \tag{4}$$

Differentiating Eq. 4. with respect to time and rearranging for $\dot{A}_T$ as

$$\dot{A}_T = -\frac{(\Delta\ddot{c} + a\ddot{T})}{R} - \frac{gA_T\Delta\dot{c}}{\Delta c} - \frac{EA_T\dot{T}}{R_gT^2} \tag{5}$$

Combining Eqs. 2 and 5 evaluated at $t = 0$

$$\left.\frac{dM_T}{dA_T}\right|_{t=o} = \alpha\overline{L}_o$$

$$= \frac{-\mathrm{A}_{To}[\mathrm{k_g} \exp(-E/R_gT_o)]^2\Delta c_o^{2g}}{\Delta\ddot{c}_o + a\ddot{T}_o + gA_{To}\Delta c_o^{-1}\Delta\dot{c}_oR_o + (A_{To}\dot{T}_o/R_gT_o^2)ER_o} \tag{6}$$

where $\overline{L}_o$ is an average size of the seed crystals and $\alpha = 1.5\rho/F$ (see Garside et al., 1982). Further rearrangement of Eq. 6 together with Eq. 2 evaluated at t = 0 gives the following expression for the kinetic parameters:

$$\frac{E}{R_g}x_1 + gx_2 + x_3 = 0 \tag{7}$$

where

$$x_1 = -\frac{(\Delta\dot{c}_o + a\dot{T}_o)\dot{T}_o\alpha\overline{L}_o}{T_o^2} \tag{8}$$

$$x_2 = -\frac{(\Delta\dot{c}_o + a\dot{T}_o)\Delta\dot{c}_o\alpha\overline{L}_o}{\Delta c_o} \tag{9}$$

$$x_3 = (\Delta\ddot{c}_o + a\ddot{T}_o)\alpha\overline{L}_o + [(\Delta\dot{c}_o + a\dot{T}_o)^2/A_{To}] \tag{10}$$

and

$$k_g = -\frac{(\Delta\dot{c}_o + a\dot{T}_o)}{[\Delta c_o^gA_{To} \exp(-E/R_gT_o)]} \tag{11}$$

Equation 7 is a linear equation in E/R_g and g. Both the kinetic parameters E/R_g and g can be determined from Eq. 7 by the least

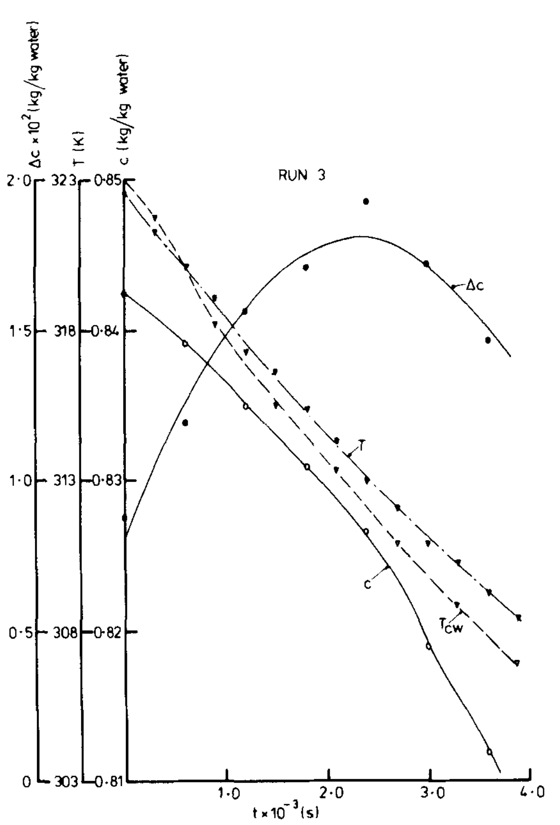

Figure 1. Concentration, temperature, and supersaturation profiles.

squares multiple linear regression analysis of a set of x_i data made available from a series of experiments. Equation 11 will also yield a set of k_g values, which in turn may be correlated with other variables by a least squares technique.

If the initial portions of measured supersaturation and temperature profiles are approximated by nth order polynomials as

$$\Delta c = \sum_{i=o}^{n} a_i t^i \tag{12}$$

and

$$T = \sum_{i=o}^{n} b_i t^i \tag{13}$$

and the zero time derivatives are given by

$$\Delta c_o = a_o;\ \Delta\dot{c}_o = a_1;\ \Delta\ddot{c}_o = 2a_2$$
$$T_o = b_o;\ \dot{T}_o = b_1;\ \ddot{T}_o = 2b_2 \tag{14}$$

EXPERIMENTAL

Experiments were performed in a 25 L agitated draft tube baffled (DTB) vessel fitted with a conical base baffle. Full details of the crystallizer have been reported elsewhere (Jones and Mullin, 1973). In a typical run a hot filtered solution of technical grade ammonium sulfate in distilled water having a concentration corresponding to a saturation temperature of about 50°C was charged into the crystallizer. The solution was maintained initially at about 55°C by circulating hot water through the crystallizer draft tube. A sample for the determination of initial solution concentration was taken. The solution was then cooled slowly to about 50°C. When the desired temperature was attained, the stirrer speed was adjusted to a desired level and presized, accurately weighed cured seeds of uniform size (retained between two successive sieves over the seed size range from 550 to 925 μm) were charged into the crystallizer, the overall crystal seed loading being about 20 kg/m³ of solution. This relatively high seed loading was used to reduce the homogeneous nucleation to a minimum, as only low levels of supersaturation were anticipated to be supported by the system. Seed curing was accomplished by keeping the seeds in a small amount (~300–400 mL) of saturated solution in a thermostatic bath with a gentle agitation for 2 h. The entire contents were then charged into the crystallizer at the start of the run. Just before starting the run, the heater in the circulating water thermostatic bath was switched off and the cooling water fed to coils in the bath was started at predetermined constant rate. The circulating water was thus cooled at a slow rate and this in turn would then cool the crystallizer contents.

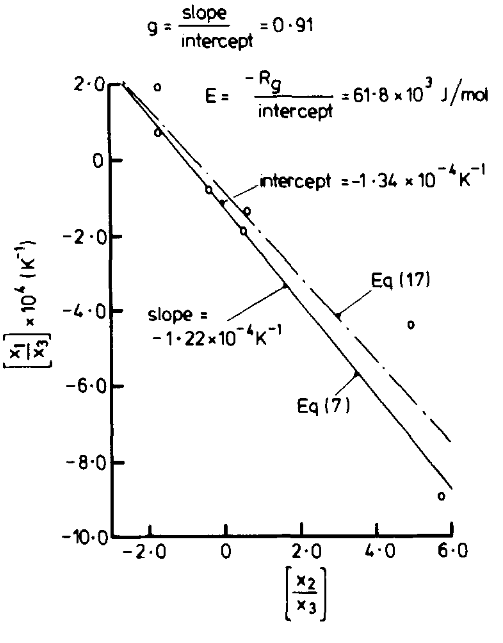

Figure 2. Graphical representation of parameter estimation.

At intervals of 10 min small (~15 mL) samples for concentration analysis were taken from the crystallizer by means of a pipette fitted with a cotton plug at the tip. Temperatures of the crystallizer and the cooling water bath were noted at 5 and 10 min intervals, respectively, with an accuracy of ±0.1°C and the difference between them at any time was always less than 2°C. Only the first 7 samples for concentration and 14 readings for temperatures were used. The concentration of solution samples was determined by evaporating the samples to dryness (a gravimetric analysis). This gave an estimated accuracy of better than $\pm 2 \times 10^{-4}$ kg/kg. The solubility at any time over the experimental range of temperature was determined from the linear relation

$$c_s = 0.00276T - 0.05669 \tag{15}$$

where c_s is the solubility (in kg salt/kg water) at temperature T (in K). The supersaturation at any time was then determined by subtracting the solubility from the actual concentration. The supersaturation level so determined for the technical grade ammonium sulfate was higher during all the experiments, the maximum being ~0.02 kg salt/kg water.

RESULTS AND DISCUSSION

A series of seven batch experiments was performed. Typical variations of concentration and temperature during the initial period of run 3 are shown in Figure 1. Second-order polynomials in time were fitted by a linear least-squares technique for both supersaturation (7 data points at 600 s intervals) and temperature profiles (14 data points at 300 s intervals) in order to evaluate the zero time derivatives and hence the coefficients x_i in Eq. 7 for each run. The values of the growth rate order g and the activation en-

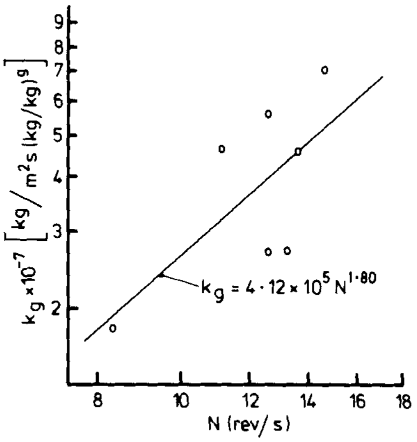

Figure 3. Relation between growth rate coefficient and stirrer speed.

ergy E were then determined by the linear least-squares technique using the coefficients x_i determined in seven runs. Overall rate constants for individual runs were determined from Eq. 11 and subsequently correlated in terms of a power law term of stirrer speed by a linear least-squares technique. The final kinetic correlation is

$$R = 4.12 \times 10^5 N^{1.8} \exp\left(-\frac{7.44 \times 10^3}{T}\right) {}_{\Delta c}0.91 \tag{16}$$

Alternatively, Eq. 7 may be rearranged as

$$\frac{x_1}{x_3} = \left(-\frac{gR_g}{E}\right)\frac{x_2}{x_3} - \frac{R_g}{E} \tag{17}$$

Equation 17 is a linear relation in x_2/x_3 and x_1/x_3; the corresponding experimental data are plotted in Figure 2. The solid line in Figure 2 is drawn using the least-squares estimates of g and E obtained from Eq. 7 in Eq. 17, and the dotted line represents the best fit (in a linear least-squares sense) of Eq. 17 through the data points. The correlation between the rate coefficient determined by Eq. 11 and the stirrer speed is depicted in Figure 3.

The order of the growth process as presented in Eq. 16 is around unity. Similar near-first-order growth kinetic results have been reported by Mullin et al. (1970) and Klekar and Larson (1973). The activation energy is about 62 kJ/mol, which is higher than that for the diffusional process (<~25 kJ/mol). Although the scatter in the correlation represented in Figure 3 is apparent, the stirrer speed shows a near-second-order dependence, indicating stronger influence on the overall growth rate. The overall growth rates predicted by Eq. 16 (~0.01–0.08 μm/s) over the range of variables are comparable to those derived from the population density information from the batch experiments (~0.005–0.1 μm/s) and from the continuous MSMPR crystallizer experiments (~0.02–0.25 μm/s (Mullin and Larson, 1973; Chambliss, 1966; Bourne and Faubel, 1982)).

CONCLUSIONS

The method presented here to evaluate the crystal growth kinetics from the integral mode batch experiments performed in a cooling crystallizer required the determination of the first two initial derivatives of supersaturation and temperature profiles with time. The order of the growth process for ammonium sulfate was about unity and activation energy about 60 kJ/mol. The kinetic results were comparable to those obtained using conventional techniques based on solid-side information.

NOTATION

a = temperature coefficient in solubility relation (Eq. 3), kg/kg·K
a_i = coefficients in polynomial (Eq. 12)
A_T = total crystal surface area, m²/kg solvent
b = constant in solubility relation (Eq. 3), kg/kg
b_i = coefficients in polynomial (Eq. 13)
Δc = concentration driving force, kg solute/kg solvent
c_s = solubility, kg solute/kg solvent
E = activation energy for growth process, J/mol
F = overall shape factor (ratio of surface to volume shape factor)
g = growth order
i = index variable
k_g = growth rate coefficient, Eq. 1, kg/m²s (kg/kg solvent)^g
L_o = average seed crystal size, m
M_T = total crystal mass in suspension, kg/kg solvent
N = stirrer speed, rps
R = growth rate, kg/m²s
R_g = gas constant, J/mol/K
t = time, s
T = temperature, K
x_i = variables in Eq. 7
α = $3\rho/2F$, kg/m³
ρ = crystal density, kg/m³

Subscript and Superscripts

0 = value at $t = 0$
· = derivative with respect to time
— = average quantity

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