

DETERMINATION OF CRYSTALLIZATION KINETICS FROM BATCH EXPERIMENTS

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Dedicated to Dr E. Erdős on the occasion of his 60th birthday.

Three types of batch crystallization model experiments are considered: *a*) crystallization in which a constant supersaturation is maintained throughout the experiment (*e.g.* by programmed cooling); *b*) crystallization during which supersaturation is produced at a constant rate; *c*) crystallization (*e.g.* by precipitation) in which an initial supersaturation produced at the beginning gradually decreases during the run. The kinetic data obtained in the first case are of the same kind as those obtained in a continuous MSMR (mixed suspension — mixed product removal) crystallizer. The two remaining types of experiment, on the other hand, can only provide relative kinetic data with respect to a reference run.

The measurements of crystallization rate on batch-operated crystallizers are attractive because of the ease of the experiments' performance and the simplicity of the experimental arrangement. However, unlike results from continuous model crystallizers which are easy to evaluate thanks to a simple mathematical description (constant supersaturation, constant suspension concentration, and constant crystal surface area in the steady state), adequate evaluation of results from batch experiments is mathematically complex and mostly very laborious¹. However, theoretical studies^{2,3} as well as results of model and full-scale experiments⁴ have shown that under certain circumstances the size distribution of product crystals from a batch-operated crystallizer may be formally described by the same relation as was theoretically derived for the continuous MSMR crystallizer. Thus, the relationships holding for a continuous crystallizer may formally be applied to batch crystallization^{3,5}. This, of course, greatly simplifies the treatment of data obtained by batch measurements. In principle, we can distinguish three typical cases: *a*) the crystallization is conducted in such a way as to keep the supersaturation of the solution constant throughout the experiment; *b*) the supersaturation is produced at a constant rate throughout the experiment, but as a result of increasing crystal area it reaches a maximum after a time and then gradually decreases; *c*) an initial supersaturation produced almost instantaneously at the beginning of the run decreases monotonously during the measurement.

The aim of this work is to compare the above batch procedures in regard of quantitative data they can provide on nucleation kinetics and crystal growth kinetics.

THEORETICAL

Batch Crystallization with Constant Supersaturation

If the crystallization process is conducted in such a way that the saturation rate is proportional to the crystal area, the supersaturation can be expected to be more or less constant during the run. This condition is met in the crystallization runs in which cooling is performed at a rate corresponding to the relation^{2,5}

$$(T_0 - T)/(T_0 - T_t) = (t/t_c)^4. \quad (1)$$

If the nucleation occurs at a constant supersaturation at a steady rate throughout the run, we can define the mean product crystal size (per mass) as

$$\bar{L} = L_N + \dot{L}t_c/4^{1/3}. \quad (2)$$

Comparison with the relationship holding for a continuous crystallizer⁶

$$\bar{L} = L_N + 3\dot{L}t_1 \quad (3)$$

gives the formal equation

$$t_c = 4.76t_1. \quad (4)$$

For continuous MSMRP crystallizer the following relations have been derived for the crystal population density⁷

$$f = f^0 \exp(-z) \quad (5)$$

and for the cumulative crystal size distribution^{7,8}

$$M(L) = 100(1 + z + z^2/2 + z^3/6) \exp(-z), \quad (6)$$

where

$$z = (L - L_N)/\dot{L}t_1. \quad (7)$$

It follows from Eq. (7) that in the $z-L$ coordinate system the size distribution of product crystals from a continuous MSMRP crystallizer will be represented by a straight line. If the size distribution of product crystals from a batch crystallizer fulfils the conditions (5) to (7), i.e., if it is likewise represented in the $z-L$ coordinate system by a straight line, then further relations derived from Eq. (5) for the continuous crystallizer can be expected to be formally valid for the batch process as well.

The relation for the variation in the mean crystal size with the process parameters has been derived⁶ for the MSMPR crystallizer in the form

$$(\bar{L} - L_N)^{1+3g/n} f(z_N)^{g/n} = 3B_N m_c^{1-cg/n} \dot{m}_c^{g/n-1} \quad (8)$$

where

$$\dot{m}_c = m_c / \bar{t}_1 \quad (9)$$

$$f(z_N) = 1 + z_N + z_N^2/2 + z_N^3/6 \quad (10)$$

$$z_N = L_N / \bar{t}_1 \quad (11)$$

and

$$B_N = 4 \cdot 5^{g/n} \dot{L} m_c^{cg/n} / (\alpha Q_c \dot{N}_N)^{g/n} \quad (12)$$

Substituting the formal equation (4) into Eqs (9) and (8), we can write an analogous equation

$$(\bar{L} - L_N)^{1+3g/n} (f z_N)^{g/n} = 3B_N m_c^{(1-c)g/n} (t_c / 4.76)^{1-g/n} \quad (13)$$

which describes the behaviour of a batch-operated crystallizer under the given conditions.

The linear crystallization rate, \dot{L} , is calculated from Eq. (2):

$$\dot{L} = 4^{1/3} (\bar{L} - L_N) / t_c \quad (14)$$

From Eqs (12) and (14) we can derive for the nucleation rate

$$\dot{N}_N = \frac{m_c}{\alpha Q_c t_c (\bar{L} - L_N)^3 f(z_N)} \quad (15)$$

Batch Crystallization with a Constant Supersaturation Rate

When the supersaturation is produced at a constant rate during the whole process, first it increases almost linearly until a major portion of the crystals are produced spontaneously. During the rest of the process, *i.e.* practically for the batch time t_c , the crystals formed grow up, desupersaturating the solution. As the supersaturation decreases, so does the crystal growth rate, and if we replace the latter by the effective average rate \dot{L}_{av} , we can write⁹

$$\bar{L} = L_N + \dot{L}_{av} t_c \quad (16)$$

Identifying this average crystal growth rate with the linear crystallization rate from

Eq. (3), we can write the formal equation

$$t_c = 3\bar{t}_e. \quad (17)$$

Substituting into Eq. (8) we obtain

$$(\bar{L} - L_N)^{1+3g/n} f(z_N)^{g/n} = 3B_N m_c^{(1-c)g/n} (t_c/3)^{1-g/n}. \quad (18)$$

The only kinetic parameter which it seems reasonable to evaluate in this case is the mean linear crystallization rate

$$\dot{L}_{av} = (\bar{L} - L_N)/t_c, \quad (19)$$

while the nucleation rate expressed with respect to the whole batch time is of no real physical significance here. Since, however, the supersaturation-time curves for a series of runs carried out, e.g., at different supersaturation rates are of similar shapes and can be represented by equations which differ only in values of adjustable parameters¹⁰, we can choose one run of the series as a reference base (*) and compare kinetic parameters of the other runs with the reference values. The relative crystal growth rate will be expressed as a ratio of Eq. (19) to an analogous equation written for the reference run:

$$\dot{L}_{rel} = (\dot{L}/\dot{L}^*) = (\bar{L} - L_N)^*/(\bar{L}^* - L_N) t_c, \quad (20)$$

By analogy to the previous case, the nucleation rate is derived formally from Eqs (18) and (12):

$$\dot{N}_N = \frac{27m_c}{2\alpha Q_c (\bar{L} - L_N)^3 f(z_N) t_c} \quad (21)$$

The relative nucleation rate is then given as

$$\dot{N}_{N,rel} = \dot{N}_N/\dot{N}_N^* \simeq \frac{m_c (\bar{L}^* - L_N)^3 t_c^*}{m_c^* (\bar{L} - L_N)^3 t_c} \quad (22)$$

Batch Crystallization with One-shot Formation of Supersaturation

Precipitation is a typical example of crystallization with one-shot formation of supersaturation: the supersaturation is built up practically instantaneously on mixing the components, then crystals are formed after an induction period following which the supersaturation decreases monotonously until an equilibrium concentration is reached. Under these conditions neither the mean crystal growth rate nor the average nucleation rate can be defined since both the processes proceed at different supersaturations and

for different and, moreover, unknown times. As in the previous case, however, we can regard the curves for the supersaturation decay as similar to one another¹⁰, and taking one arbitrary run of the series as a reference base (*), express all the kinetic data with respect to this run¹¹.

Again, the values of the mean crystal size \bar{L} (distribution mode) and of $\dot{L}t_c$ (straight line slopes) can be found from the graphical representation of product crystal size distribution in the $z-L$ coordinate system⁸. If the distribution is approximately linear, we can assume that the crystal population density is described, at least formally, by Eq. (5). The mass of the crystals formed is then given as

$$m_c = 2/9 N_c \alpha \rho_c \bar{L}^3. \quad (23)$$

The nucleation rate is formally expressed as

$$\dot{N}_N = 9m_c/[2\alpha\rho_c(\bar{L} - L_N)^3 t] \quad (24)$$

(compare with Eqs (15) and (21)), and the relative nucleation rate expressed with respect to a reference run (*) is given by

$$\dot{N}_{N,rel} = \dot{N}_N/\dot{N}_N^* = m_c(\bar{L}^* - L_N)^3/m_c^*(\bar{L} - L_N)^3. \quad (25)$$

For the mass of crystals formed we can write

$$m_c = \int_{L_N}^{\infty} k_G A_c \Delta w^{\#} dt, \quad (26)$$

where both the crystal area, A_c , and the supersaturation, Δw , are a function of time:

$$A_c = 2/9 \beta N_c (L_N + \dot{L}t)^2 \quad (27)$$

$$d\Delta w/dt = k_G A_c \Delta w^{\#} \quad (28)$$

The linear crystallization rate, \dot{L} , in Eq. (27) is also a function of supersaturation:

$$\dot{L} = k_G \beta \Delta w^{\#}/3\alpha\rho_c = k'_G \Delta w^{\#}. \quad (29)$$

Eq. (28) can be rewritten (for $L_N \rightarrow 0$) into the form

$$d\Delta w/\Delta w^{3\#} = 2/9 k_G \beta N_c (k_G/3\alpha\rho_c)^2 t^2 dt = K' t^2 dt \quad (30)$$

Integrating Eq. (30) within the limits $t = 0$, $\Delta w = \Delta w_0$ and $t = t_c$, $\Delta w = 0$, we ob-

tain¹¹

$$\Delta w_0^{1-3g} = [(3g - 1)/3] K' t_c^3. \quad (31)$$

Hence, the ratio of the slopes of the linearized particle size distributions for a given and the reference run may be written as

$$(\dot{L}t_c)_{rel} = \dot{L}t_c/(\dot{L}t_c)^* = (\dot{L}/\dot{L}^*) (\Delta w_0/\Delta w_0^*)^{(1-3g)/3}. \quad (32)$$

The relative linear crystallization rate is then defined by the equation

$$\dot{L}_{rel} = \dot{L}/\dot{L}^* = (\dot{L}t_c)_{rel} (\Delta w_0)_{rel}^{(3g-1)/3} \quad (33)$$

which gives \dot{L}_{rel} at same time as a function of the relative supersaturation

$$(\Delta w_0)_{rel} = \Delta w_0/\Delta w_0^*. \quad (34)$$

The nucleation rate varies with supersaturation according to the relation:

$$\dot{N}_N = k_N \Delta w^n, \quad (35)$$

and a similar expression may be written for the relative nucleation rate:

$$\dot{N}_{N,rel} = \dot{N}_N/\dot{N}_N^* = (k_N/k_N^*) (\Delta w_0)_{rel}^n \quad (36)$$

TABLE I

Availability of kinetic data from model experiments

Quantity	Batch			Continuous MSMPR
	I	II	III	
\dot{N}_N	+	-	-	+
\dot{L}	+	(+)	-	+
$\dot{N}_{N,rel}$		+	+	
\dot{L}_{rel}		+	(+)	
g/n	+	+	-	+
g	-	-	(+)	-
n	-	-	+	-

Elimination of the relative initial supersaturation, $(\Delta w_0)_{rel}$, from Eqs (33) and (36) yields

$$\dot{N}_{N,rel} = \text{const. } \dot{L}_{rel}^{3n/(3g-1)}. \quad (37)$$

DISCUSSION AND CONCLUSIONS

Let us now take a brief look at the information that can be obtained from the above types of experiments. Batch crystallization with constant supersaturation can provide data on the nucleation rate and the linear crystallization rate, though probably not so accurate, on account of the simplification inherent in Eq. (2), as can be expected for the continuous MSMPR crystallizer. When simplified for $f(z_N) \approx 1$ and $m_c = \text{constant}$, Eq. (13) gives a relationship for the ratio of the kinetic exponents of growth and nucleation, g/n ,

$$\frac{d \ln (\bar{L} - L_N)}{d \ln t_c} = \frac{1 - g/n}{1 + 3g/n}, \quad (38)$$

but we cannot establish individual values of g and n from equations of the type (29) and (35) unless we know the working supersaturation. The ratio n/g could alternatively be found by elimination of the unknown supersaturation from Eqs (29) and (35):

$$\dot{N}_N = \text{const. } \dot{L}^{n/g}. \quad (39)$$

Hence, a plot of $\log \dot{N}_N$ vs $\log \dot{L}$ will give a straight line of slope n/g .

In the case of batch crystallization with a *constant rate of supersaturation* we can use Eq. (19) to calculate the average linear crystallization rate, but this value is only of limited practical significance. For evaluating series of runs it is far more useful to determine the relative rates of growth (20) and nucleation (22). In addition, putting $m_c = \text{constant}$ in Eq. (18), we can derive Eq. (38) allowing us to estimate the ratio of the kinetic exponents g/n .

For the batch crystallization with *one-shot generation of supersaturation*, a logarithmic plot of the relative nucleation rate vs the initial supersaturation according to Eq. (6) will give a straight line of slope equal to the nucleation exponent n , a quantity which is generally difficult to determine by model experiments. For a series of runs we can get the relative nucleation rate (25), but evaluation of the relative crystal growth rate by application of Eq. (33) would require the knowledge of the exponent g based on independent measurements. As seen from Eq. (37), the value of the ratio of kinetic exponents which is important for crystallizer design, cannot be obtained directly in this case. However, knowing the value of n we can make a reasonable estimate of the value of g .

A summary of data which can be evaluated for the experimental arrangements considered is given in Table I.

LIST OF SYMBOLS

A_c	crystal area
B_N	system kinetic constant of crystallization
c	secondary nucleation exponent
f	crystal population density
f^0	crystal nuclei population density
$f(z_N)$	function defined by Eq. (10)
g	kinetic exponent of crystal growth
K'	constant defined by Eq. (30)
k_G	growth rate constant
k_N	nucleation rate constant
L	crystal size
L_N	initial crystal size
\bar{L}	mean crystal size (mode)
\dot{L}	linear crystallization rate
\dot{L}_{av}	average linear crystallization rate
$M(L)$	cumulative crystal size distribution
m_c	crystal mass, suspension concentration
\dot{m}_c	specific output of continuous crystallizer
N_c	number of crystals
\dot{N}_N	nucleation rate
n	kinetic exponent of nucleation
T	temperature
T_0	initial temperature
T_f	final temperature
t	time
t_c	batch time
\bar{t}_1	mean residence time of solution in continuous crystallizer
Δw	supersaturation
Δw_0	initial supersaturation
z	dimensionless residence time of crystals of size L
z_N	dimensionless initial crystal size
α	volume shape factor
β	surface shape factor
ρ_c	crystal density

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