CORRELATIONS BETWEEN CRYSTALLIZATION AND DISSOLUTION OF ALUMINIUM POTASSIUM SULPHATE

MASAMOTO NAKAJIMA, SYOUJI HIROTA
AND KEISUKE FUKUI

*Department of Chemical Engineering,
Himeji Institute of Technology, Himeji 671-22*

Growth and dissolution rates of a potash alum crystal have been measured at a constant temperature of 30°C. The diffusion theory for both growth and dissolution is discussed, based upon the experimental results. Based upon observations of the solution-crystal interfacial concentration for growth and dissolution, it is shown that the diffusion step in the growth process was second-order with respect to the driving force, and the presence of a separation step of solute or cluster from crystal lattice for the dissolution process is proposed because the interfacial concentration was not equal to saturated condition. Agreement between the dimensionless concentrations, which included the solution-crystal interfacial concentrations for growth or dissolution, related these phenomena and gave the relations among the transfer rate coefficients. And it was shown that the interfacial concentrations could be estimated even at a solution temperature other than 30°C by using the relations obtained at 30°C.

Therefore, the transfer coefficients of reaction and diffusion steps for the growth process can also be determined. The transfer coefficients of separation and diffusion steps for the dissolution process and interfacial concentration can also be calculated by measuring the overall rate coefficient for dissolution.

Introduction

It is important for studying crystallization phenomena in a supersaturated solution to measure the overall coefficients of crystal growth. Based upon the diffusion theory, the crystallization process consists of two steps, i.e. the diffusion step of solute or cluster from bulk solution to crystal surface and the surface integration or reaction step. This simple model has not been studied enough, but it has customarily been used. The measurement or estimation of the solution-crystal interfacial concentration is indispensable to a study of the kinetics of two processes occurring in series. The present authors tried to measure the interfacial concentration of the solution on the growing crystal surface of K-alum with the use of a Mach-Zehnder Interferometer and reported the surface reaction rate coefficient and the coefficient of diffusion step; they also showed correlations between the interfacial concentration and the solution velocity or mass transfer coefficients⁴⁾.

A few studies have been concerned with methods to estimate the rate coefficients for the surface reaction step or the interfacial concentration under some assumptions. That is, the rate coefficient for the sur-

face integration step is equal to the overall coefficient of mass transfer when the integration step controls the growth rate^{1,6,8)}. In another method, the rate coefficient for the diffusion step is equal to the overall dissolution rate coefficient^{2,5,9)}. Garside and Mullin²⁾ discussed each step of growth, using the second assumption, but could not reach a successful conclusion. Because the difference in mechanism between growth and dissolution phenomena is uncertain, assumptions made above come into question.

The present work proposes a method for estimating the interfacial concentration and for making clear the correlations between the mass transfer coefficients of the two steps for both growth and dissolution by measuring the overall growth and dissolution rates.

1. Experimental

Aluminium potassium sulphate was chosen as working material. Growth and dissolution rates have been measured at constant temperature of 30°C. **Figure 1** shows the apparatus used in this work. A solution of the desired concentration prepared with first-class K-alum and distilled water was circulated with the pump (1), through the rotameter (2) and heat exchanger (3) to the test section (5) and back to the reservoir (7). The test section was constructed of acrylic pipe of 3 cm inside diameter and about 70 cm

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1 pump	5 test section
2 rotameter	6 electric heater
3 heat exchanger	7 reservoir
4 chemical balance	

Fig. 1 Diagrammatic sketch of experimental equipment

Fig. 2 Effect of solution velocity upon overall coefficient K_o of growth rate and comparison of K_o with Eq. (4)

long, and the working temperature was kept constant with a heat exchanger. The solution in the reservoir was heated and controlled so that its temperature was about 6°C above the saturation temperature. The solution velocity at the test section was adjusted over the range 5 to 20 cm/sec, being the same velocity range with that of previous study⁴⁾. Seed crystals used in this work were about 1.5 cm long from edge to edge and were hung in the test section from a chemical balance with a nylon fish line. After stopping the pump, apparent weight change of the crystal was weighed in a stationary solution as quickly as possible at about five- to ten-minute intervals. The apparent changes of weight were plotted against elapsed time, from which the rates $dW/d\theta$ could be calculated by reading the gradients. Each surface area of a seed crystal was measured beforehand by the method previously reported³⁾. Experiments were carried out in a short time so that the rates of weight change might be linear with time; that is, the change of area was assumed to be negligible. During the runs, the change of concentration of bulk solution was negli-

gible. So initial surface area was used as the crystal area. Linear growth and dissolution rates were calculated by the following equation:

$$\frac{R}{R'} = \frac{dW}{d\theta} \frac{1}{(\rho_o - \rho_s)A}$$

where ρ_s was calibrated beforehand. The concentration of a solution was measured by evaporation to dryness. Ranges of experimental conditions were $0.73 < \Delta C < 4.9$ and $0.35 < \Delta C' < 4.7$ g hydrate/100 g H_2O for levels of supersaturation and undersaturation, respectively.

2. Experimental Results and Discussion

As is well known, the engineering diffusion model for crystallization is expressed by the following three equations:

$$R = K_o(C_b - C_s)^\alpha \quad (1)$$

$$= k_r(C_i - C_s)^\beta \quad (2)$$

$$= k_d(C_b - C_i)^\gamma \quad (3)$$

Present experiments showed the same results as those obtained from previous investigations^{3,4)}, i.e. the overall growth kinetics were second-order with respect to ΔC .

In Fig. 2, the overall growth coefficients K_o obtained in this study are plotted against solution velocity v , and the solid line shows the correlation obtained by previous work⁴⁾, that is,

$$K_o = (10.0 + 1.4 v^{0.53}) \times 10^{-7} \quad (4)$$

where $2 < v < 21$ cm/sec.

It is clear that the values of K_o observed in this research agree with Eq. (4) fairly well. Therefore the relations reported before⁴⁾ may be applied to the present research of single-crystal growth. And so $\beta=2$ and $k_r=2.2 \times 10^{-6}$ were also adopted. Although the exponent γ has been usually taken as unity even when $\alpha \neq 1$, it is difficult to interpret the rate coefficient k_d because it contains the concentration driving force as derived in previous paper⁴⁾;

$$k_{d(\gamma=1)} = \frac{K_o \sqrt{k_r} (C_b - C_s)}{\sqrt{k_r} - \sqrt{K_o}} \quad (5)$$

Hence, it may be more general to consider that the diffusion process is not first-order with respect to the driving force $C_b - C_i$. According to the experimental results $\alpha=\beta=2$, combining Eqs. (1) and (2) gives

$$\frac{C_i - C_s}{C_b - C_s} = \sqrt{\frac{K_o}{k_r}} \quad \text{or} \quad \frac{C_b - C_i}{C_b - C_s} = 1 - \sqrt{\frac{K_o}{k_r}} \quad (6)$$

$$R = K_o(C_b - C_s)^2 = \frac{K_o k_r}{(\sqrt{k_r} - \sqrt{K_o})^2} (C_b - C_i)^2 \quad (7)$$

Hence, comparing Eq. (7) with Eq. (3) gives the following relations if k_d is considered not to contain the driving force:

Fig. 3 Correlation of linear growth rate R with the driving force $C_b - C_i$ for diffusion step in growth process

$$\gamma=2 \text{ and } k_d = \frac{K_o k_r}{(\sqrt{k_r} - \sqrt{K_o})^2} \quad (8)$$

as reported in another paper⁷⁾, i.e. the diffusion step of growth should be second-order with respect to $C_b - C_i$. Using the experimental data obtained in previous work⁴⁾, growth rates R was plotted against $C_b - C_i$ as shown in Fig. 3, in which the straight line represents Eq. (8).

Linear dissolution rates R' were plotted against the overall-concentration driving force $C'_s - C'_b$ in Fig. 4, from which it was found that R' was proportional to $C'_s - C'_b$. Since the interfacial concentration was not equal to that at saturation according to the results through interferential observations, as shown in Fig. 5, the dissolution process seems to contain the separation step of solute from crystal lattice as well as the surface integration step for growth.

Since R' is proportional to overall driving force $C'_s - C'_b$, each step may be first-order with respect to driving force. Then the dissolution process will be given by the following three equations:

$$R' = K'_o (C'_s - C'_b) \quad (9)$$

$$= k'_r (C'_s - C'_i) \quad (10)$$

$$= k'_d (C'_i - C'_b) \quad (11)$$

The effect of solution velocity on K'_o is shown in Fig. 6, from which it was found that K'_o was proportional to $v^{0.6}$ (broken line) and expressed as

$$K'_o = 2.3v^{0.6} \times 10^{-6}, \quad 5 < v < 20 \text{ cm/sec} \quad (12)$$

The result agrees with that of Garside and Mullin²⁾.

3. Relations between Growth and Dissolution

As mentioned in the previous section, the interfacial concentration is necessary to obtain each rate

Fig. 4 Correlation of linear dissolution rate R' with overall driving force $C'_s - C'_b$

Fig. 5 Solution-crystal interfacial concentration for dissolution

Fig. 6 Effect of solution velocity upon overall coefficient K'_o of dissolution rate

coefficient for growth and dissolution. Although interfacial concentrations can be estimated from Eq. (6) at a constant temperature of 30°C, one must consider that k_r and K_o are functions of solution temperature in practical use. The temperature dependence on k_r and K_o is shown in Fig. 7 in the form of $(C_i - C_s)/(C_b - C_s)$, which is equal to $\sqrt{K_o/k_r}$. These observations of C_i were carried out at constant-solution velocity of 20 cm/sec, and then $(C_i - C_s)/(C_b - C_s)$ was independent of solution temperature. Solid line in Fig. 7 shows the value of $(C_i - C_s)/(C_b - C_s)$ calculated from Eqs. (4), (6) and $k_r = 2.2 \times 10^{-6}$ for solution temperature of 30°C. The solid line is in

Fig. 7 Effect of solution temperature upon the solution-crystal interfacial concentration at constant solution velocity of 20 cm/sec

good agreement with the experimental results, and so the value of $(C_i - C_s)/(C_b - C_s)$ for arbitrary solution temperature can be estimated by using the results for solution temperature of 30°C.

The measurements of interfacial concentration in the case of dissolution are plotted in Fig. 5, considering that $(C'_s - C'_i)/(C'_s - C'_b)$ would be independent of solution temperature as similar to growth process. The solid line in Fig. 5 was calculated by Eq. (6) for growth. Agreement between calculated line and the observations of $(C'_s - C'_i)/(C'_s - C'_b)$ gives the very interesting and useful relation

$$\frac{C'_s - C'_i}{C'_s - C'_b} = \frac{C_i - C_s}{C_b - C_s} = f(v) \quad (13)$$

where

$$f(v) = (0.45 + 0.064 \times v^{0.53})^{1/2} = \sqrt{\frac{K_o}{k_r}} \quad (13')$$

from which the correlations between growth and dissolution can be given.

From Eqs. (9) and (10),

$$\frac{C'_s - C'_i}{C'_s - C'_b} = \frac{K'_o}{k'_r} \quad (14)$$

Using the relation Eq. (13), combination of Eqs. (6) and (14) gives

$$\sqrt{\frac{K_o}{k_r}} = \frac{K'_o}{k'_r} \quad (15)$$

And also the following relation is introduced from Eqs. (1), (3), (9), (10) and (13):

$$\sqrt{\frac{K_o}{k_d}} = \frac{K'_o}{k'_d} \quad (16)$$

Consequently, when the overall rate coefficients, K_o and K'_o , at any solution temperature and velocity are measured, k_r and the interfacial concentration for growth and dissolution can be estimated from Eqs. (13) and (13'), respectively. Then k_d can be calculated from Eq. (8). And also the rate coefficients, k'_r and k'_d , of the separation and diffusion steps for dissolution process are given by Eqs. (15) and (16).

Thus the above method of estimating the rate coefficients of growth or dissolution can be adopted at an arbitrary solution temperature because the relation, Eq. (13), holds at an arbitrary temperature.

Conclusion

The relations between growth and dissolution kinetics are presented as follows:

- 1) The diffusion step in the growth process is second-order with respect to driving force.
- 2) The dissolution process also may be divided into two steps, just like the growth process.
- 3) Measurements of overall coefficients, K_o and K'_o , lead to estimation of the interfacial concentration and rate coefficients of growth and dissolution.
- 4) New correlations are presented between the rate coefficients of both phenomena.

We must know more clearly, from future studies, the diffusion mechanism of solute, particularly in the form of cluster, for the case of both crystal growth and dissolution in order to determine whether the diffusion step of growth is first-order or second-order with respect to driving force. The two steps of dissolution proposed here will be also discussed more precisely.

Nomenclature

A	= surface area of a crystal	[cm ²]
C	= concentration in reference to growth	[g hydrate/100g H ₂ O]
C'	= concentration in reference to dissolution	[g hydrate/100g H ₂ O]
ΔC	= level of supersaturation $C_b - C_s$	[g hydrate/100g H ₂ O]
$\Delta C'$	= level of undersaturation $C'_s - C'_b$	[g hydrate/100g H ₂ O]
$f(v)$	= function of v defined by Eq. (13')	[—]
K_o	= overall growth rate coefficient	[(cm/sec)/(g hydrate/100g H ₂ O) ^{α}]
K'_o	= overall dissolution rate coefficient	[(cm/sec)/(g hydrate/100g H ₂ O)]
k_d	= mass transfer coefficient for diffusion step of crystal growth	[(cm/sec)/(g hydrate/100g H ₂ O) ^{γ}]
k_r	= surface integration rate coefficient	[(cm/sec)/(g hydrate/100g H ₂ O) ^{β}]
k'_d	= mass transfer coefficient for diffusion step of crystal dissolution	[(cm/sec)/(g hydrate/100g H ₂ O)]
k'_r	= rate coefficient for separation step of crystal dissolution	[(cm/sec)/(g hydrate/100g H ₂ O)]
R	= linear growth rate	[cm/sec]
R'	= linear dissolution rate	[cm/sec]
v	= relative velocity between crystal and solution	[cm/sec]
W	= apparent weight of a crystal	[g]
α	= exponent of $C_b - C_s$ in Eq. (1)	[—]
β	= exponent of $C_i - C_s$ in Eq. (2)	[—]
γ	= exponent of $C_b - C_i$ in Eq. (3)	[—]
θ	= time	[sec]
ρ_c	= crystal density	[g/cm ³]
ρ_s	= solution density	[g/cm ³]

<Subscripts>

- b* = bulk solution
i = solution-crystal interface
s = at saturation

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EFFECTIVE DIFFUSIVITIES OF HEAVY WATER IN ACTIVATED CARBON PELLETS BY TRANSIENT MEASUREMENTS USING THE WICKE-KALLENBACH APPARATUS

HIROMITSU SHIBUYA AND KUNITARO KAWAZOE

*Department of Chemical Engineering,
University of Tokyo, Tokyo 113*

A dynamic Wicke-Kallenbach method to obtain effective diffusivities is presented.

The method is carried out by performing curve-fitting between measured breakthrough curves and calculated ones obtained numerically by use of the Fourier inverse transform technique.

The major advantage of this transient method is that it is possible to determine effective diffusivities within a short measuring time.

The method is illustrated with experimental data for heavy water diffusing through activated carbon pellets. The values of effective diffusivity obtained for heavy water are reasonable ones and are in good agreement with those obtained previously using the breakthrough method.

Introduction

Several experimental techniques have been proposed to measure effective diffusivities in porous solids.

From the point of view of obtaining accurate values of effective diffusivity, the static counterdiffusion technique of Wicke-Kallenbach⁽¹⁾ is an excellent one since it never includes other mass transport processes other than intraparticle diffusion. The techniques have widely been used for gases.

On the other hand, dynamic methods using moment analysis have recently been used^(1-3,8) to obtain highly accurate values of effective diffusivity. The most excellent feature of the method is that it needs only first moment calculations and increases the accuracy of the calculated values of effective diffusivity. However,

for liquids the Wicke-Kallenbach apparatus has been only slightly used^(5,9) due to the defects that they need too long a measuring time, of the order of several hundred hours, for example, since for liquids time constant of diffusion through the porous solid is much larger than that for gases. Moment analysis also needs a sufficiently long time when the tail of the peak vanishes. Long-time measurements should be avoided since they are likely to cause unstable operation of experimental equipment, leading to erroneous results.

Another obstacle frequently encountered for liquids is that the magnitude of a response peak is too weak to obtain a complete data chart for moment analysis.

In this paper, a dynamic method to obtain effective diffusivities is proposed. The major advantage of the method is that it can save a considerable amount of measuring time.

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