Crystallization Kinetics of Potassium Chloride from Brine and Scale-up Criterion

A systematic study of potassium chloride crystallization shows that constant tip speed, $TIPS$, is the agitation criterion for scale-up. Three hydrodynamic regions are identified by a group $M_T \overline{TIPS}^3$. Thus, a new generalized kinetic equation is proposed: $B^o = KG^i(M_T \overline{TIPS}^3)^j$.

The values of the power index j are 0.7 and 1.2 for low and high ranges of $M_T \overline{TIPS}^3$, respectively. At even higher $M_T \overline{TIPS}^3$, j scatters due to the breakage of crystals. The power index i is independent of hydrodynamic conditions and depends only on the crystallization temperature, e.g., it is 2.8 at 313.2 K.

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Introduction

The production of potassium chloride through crystallization is one of the most important processes in industrial crystallization. However, very few kinetic studies of this process have even been briefly reported (Randolph et al., 1977, 1981), although there have been many papers on crystallization kinetics of various other systems. The operating conditions of most kinetic studies were rather narrow and far from industrial practice. The differences among the published values of the power indexes of suspension density and agitation speed in kinetic equations were pointed out in a review by Garside and Shah (1980). Some efforts have been made in the systematic kinetic study of potash alum and its scale-up (Garside and Jancic, 1979; Ottens and de Jong, 1973) and also of sodium chloride (Grootscholten et al., 1982). In three papers dozens of tests were reported, but they were still not enough to obtain satisfactory confidence limits of every power index and the coefficient in the kinetic equations.

In this paper a three-year study on the kinetics of potassium chloride crystallization from brine is reported. This work was done in two analogous mixed-suspension, mixed-product-removal (MSMPR) crystallizers, one of 2.5 dm³ volume and the other of 25 cm³. Five series of experiments were designed to study the individual effects of crystallization temperature T, suspension density M_T, agitation speed N, the scale of the crystallizer (impeller diameter) d, and their interaction. From these results the constant tip speed $TIPS$ was found to be the scale-up criterion, and the hydrodynamic conditions can be defined by a group $M_T \overline{TIPS}^3$. The nucleation rate B^o and growth rate G correlated well with this group in a general kinetic equation. 143 tests were made to obtain satisfactory standard deviations of all power indexes and the coefficient in the general kinetic equation.

Crystallizers and Hydrodynamic Experiments

Crystallizers and procedure

Two geometrically similar crystallizers are used, as shown in Figures 1 and 2, with active volumes of 2.5 and 25 dm³, respectively. In each there are a hollow draft tube, four baffles, and an impeller, all made of stainless steel. The vessels of the crystallizers are made of Pyrex glass and Plexiglas, respectively, and they have streamlined bottoms and plastic covers. For clear liquor drawoff, a separator is used in the 2.5 dm³ crystallizer, while a settling zone is provided in the 25 dm³ crystallizer. The diameters of the vessel, draft tube, and impeller are respectively 0.147, 0.068, and 0.060 m for the 2.5 dm³ crystallizer, and 0.300, 0.140, and 0.120 m for the 25 dm³ crystallizer. The heights of the draft tubes are 0.120 and 0.294 m, and the distances between the bottom of the draft tube and that of the vessel are 0.028 and 0.037 m, respectively. The cross-sectional area of the separator in the 2.5 dm³ crystallizer is 1.81×10^{-3} m², and that of the settling zone in the 25 dm³ crystallizer is 1.19×10^{-2} m².

The temperature of crystallization or saturation temperature of feed, the agitation speed, and the feed rate are controlled within ±0.1 K, ±1%, and ±2%, respectively. The feed is saturated with KCl and nearly saturated with NaCl (NaCl 13–16 wt. %, MgCl₂ 2.0–3.5 wt. %, Ca⁺⁺ 0.03–0.08 wt. %, and SO₄⁻ 0.06–0.20 wt. %).

After the system has reached the steady state, samples are taken, quickly filtered, washed once with 70% and then 100% ethanol in succession, and dried. Wet screen analysis is made in KCl-saturated ethanol, using 13 calibrated sieves from 16 to 400 mesh. Micrographs of crystals on each sieve are taken. When
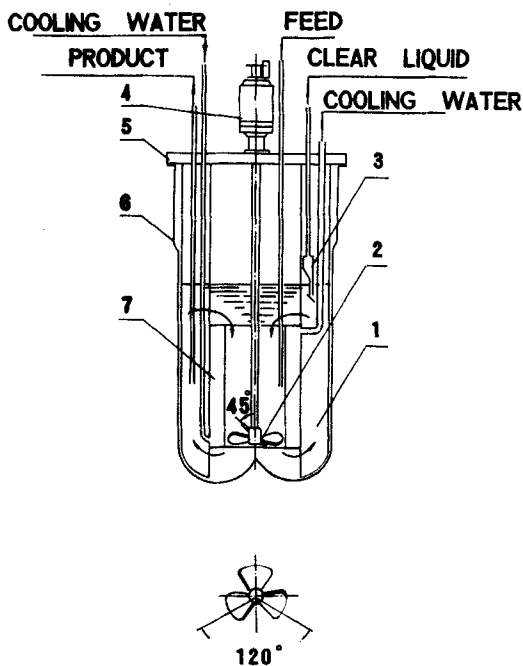
Figure 1. 2.5 dm³ crystallizer with clear liquor overflow.

1. Baffle   5. Perspex cover
2. Impeller   6. Glass vessel
3. Separator   7. Draft tube
4. Motor
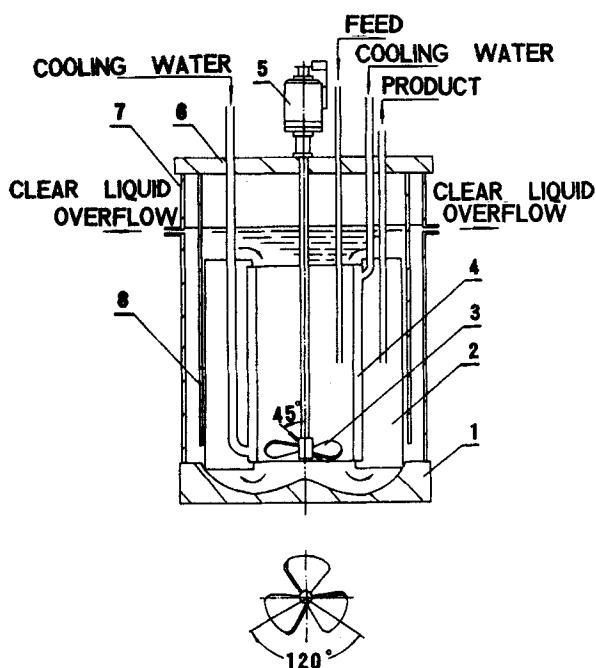
Figure 2. 25 dm³ crystallizer with clear liquor overflow.

1. Plastic bottom   5. Motor
2. Baffle   6. Plastic cover
3. Impeller   7. Plexiglas vessel
4. Draft tube   8. Plexiglas baffle

the tip speed is less than 3.1 m/s, the crystals are regular cubes in shape except those larger than 18 mesh. The linear relationship between ln n and L given by the population balance (Larson and Randolph, 1969) holds well in the whole size range except as indicated later. Correlation coefficients are better than 0.975, usually 0.99.

Hydrodynamic experiments

Experiments on residence time distribution (RTD) of solution give the dimensionless invariance 0.89 at a tip speed of 1.7 m/s. The turnover time is 2.6 ± 0.2 s at a tip speed of 2.6 m/s. The tip speed must be 2 m/s to have a quasihomogeneous state of glass beads-brine suspension, and 2.6 m/s for a well-mixed suspension in both crystallizers. The separation factors of −20 to +28 mesh glass beads and mixed glass beads (−18 to +160 mesh) are 0.97–1.03. These results show that all crystallization kinetics experiments described below were made in MSMPR crystallizers.

Experimental Results
Effect of crystallization temperature

Thirty-eight tests for crystallization kinetics in four series were run in the 2.5 dm³ crystallizer at 298.2, 313.2, 323.2, and 338.2 K, respectively. The tip speed was 2.58 m/s, i.e., the revolution speed was 13.67 rps. Temperatures in the saturator were 10.0 K higher than those of crystallization, i.e., 308.2, 323.2, 333.2, and 348.2 K, respectively. In every series, three sets of runs were done with different retention times. Duplicate runs were usually done in every set. No clear liquor was withdrawn, and the suspension density M_T were 15–20 kg/m³.

The results are given by Eqs. 1–4. At a crystallization temperature of 338.2 K, some very fine crystals formed during the filtration of samples. The regression of ln n vs. L is made only in the size range down to 100 μm.

The kinetic equations by regression of ln B^o/M_T vs. ln G are as follows:

At 298.2 K

$$B^o/M_T = 98.3 \, G^{1.74} \quad \text{correlation coefficient 0.961} \quad (1)$$

At 313.2 K

$$B^o/M_T = 1.12 \, G^{2.59} \quad \text{correlation coefficient 0.964} \quad (2)$$

At 323.2 K

$$B^o/M_T = 5.15 \, G^{2.09} \quad \text{correlation coefficient 0.964} \quad (3)$$

At 338.2 K

$$B^o/M_T = 15.3 \, G^{1.67} \quad \text{correlation coefficient 0.981} \quad (4)$$

The plot of ln B^o/M_T vs ln G is shown in Figure 3.

By comparing the growth rates G and nucleation rates B^o at the same tip speed and retention time, as shown by the four dotted lines in Figure 3, we conclude that G increases and B^o decreases with an increase in crystallization temperature from 298.2 to 338.2 K. The slope of the dotted lines is −3, as predicted by theoretical calculation.
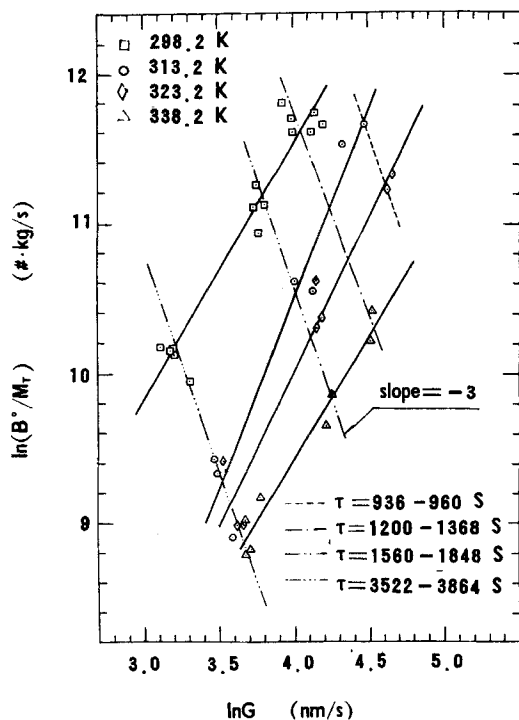
Figure 3. Effect of temperature on kinetics.

From Eqs. 1–4, the power index of growth rate varies in the range of 298.2 to 338.2 K and has a maximum value of 313.2 K.

Effect of suspension density

In this series of experiments the crystallization temperature was 313.2 K, and the temperature in the saturator 343.2 K. The suspension density in the 2.5 dm³ crystallizer was controlled by the ratio of flow rates of clear liquor drawoff to product withdrawal. An inverted pearlike bottle with a baffle near its inlet, which was immersed slightly below the level of suspension, was used as a separator. Large crystals in suspension were rejected by the baffle, fine crystals settled in the separator, and clear liquor was drawn off from the top of the separator. No crystals could be found in the clear liquor with a magnifier under strong light. The effect of the clear liquor drawoff on crystal size distribution (CSD) over the size range studied was negligible. The suspension density varied from 50 to 147 kg/m³ in three levels.

For every level of suspension density, three sets of different retention time experiments were run at a constant tip speed of 2.58 m/s. The results were obtained from 32 runs. Multiple regression of these runs gives the following equation

$$B^o = 0.126\ G^{2.95}\ M_T^{1.10} \quad \text{correlation coefficient } 0.924 \quad (5)$$

The F, F_i, and F_j are 84.7, 151.4, and 59.0, respectively, being greater than $10F_{0.01}(3, 32 - 3)$, $10F_{0.01}(1, 32 - 3)$, and $10F_{0.05}(1, 32 - 3)$, respectively. Hence, the model and its power index i are highly significant and the power index j is significant.

Comparing Eq. 5 with Eq. 2, we find that the power index of the growth rate is 2.78 ± 0.18 at 313.2 K. It is independent of suspension density in the range 15–147 kg/m³.

Effect of tip speed

In the 2.5 dm³ crystallizer the effect of tip speed was studied in the range of 2.04 to 4.01 m/s, i.e., 10.83 to 21.27 rps of the impeller. The temperature of the crystallizer was 313.2 K and that of the saturator was 343.2 K. The suspension density was controlled at a level of 133–175 kg/m³ by clear liquor withdrawal. The retention time was 3,610–3,680 s. These operating conditions are not far from those used in industrial crystallizers.

At tip speeds higher than 3 m/s coarse crystals were severely rounded. The regression of ln n vs. L was made only in crystal size ranges from 33 up to 810 μm for TIPS 3.08 m/s, 680 μm for TIPS 3.58 m/s, and 480 μm for TIPS 4.01 m/s. The results show that the scattering of data occurs at 4.01 m/s. Because crystals are severely rounded at that tip speed, only data in the tip speed range of 10.83 to 19.00 rps are correlated in Eqs. 6, 7, and 8.

The equations of nucleation rate B^o and growth rate G with respect to tip speed TIPS are as follows:

$$B^o = 1.946 \times 10^5 (TIPS)^{2.10} \quad \text{correlation coefficient } 0.963 \quad (6)$$

$$G = 67.0(TIPS)^{-0.625} \quad \text{correlation coefficient } 0.952 \quad (7)$$

By regression of ln $(B^o/G^{2.78} M_T^{1.21})$ vs ln TIPS the kinetic equation can be expressed as:

$$B^o = 0.00381\ G^{2.78}\ M_T^{1.21}(TIPS)^{3.79} \quad (8)$$

The power index 2.78 of growth rate G has already been pointed out. The power index of suspension density M_T does not play an important role in the narrow M_T range of 133–175 kg/m³. However, the average value of 1.10 and 1.31, given by Eqs. 5 and 10, respectively, is used. The plot of ln $(B^o/G^{2.78} M_T^{1.21})$ vs. ln TIPS is shown in Figure 4. The correlation coefficient is 0.958. The F factor of 260 is greater than $10F_{0.01}(1, 25 - 2)$, which equals 78.8.

Equation 8 is valid in the range of suspension density 133–175 kg/m³ and tip speed 2.04–3.58 m/s at 313.2 K in the 2.5 dm³ crystallizer.

Effect of suspension density at low tip speed

At a tip speed of 2.04 m/s, i.e., impeller speed 10.83 rps, the suspension in the 2.5 dm³ crystallizer was under a quasi-homogeneous condition. The fine and intermediate crystals circulated through the draft tube, while the coarse crystals circulated in the annular space between the draft tube and the vessel. The product was withdrawn from the middle of the annular space. The straight-line relationship between ln n and L holds well.

The temperature of crystallization and that in the saturator was 313.2 and 343.2 K, respectively. Retention times varied in the range of 1,200 to 5,200 s. Three levels of suspension density of 53–171 kg/m³ were controlled by different ratios of clear liquor drawoff to product removal. The results of this series of 18 runs and 10 runs of TIPS 2.04 m/s in the last series give the effect of suspension density at tip speed of 2.04 m/s.

Using multiple regression of these 28 runs, we have

$$B^o = 1.51\ G^{2.58}\ M_T^{0.70} \quad \text{correlation coefficient } 0.949 \quad (9)$$

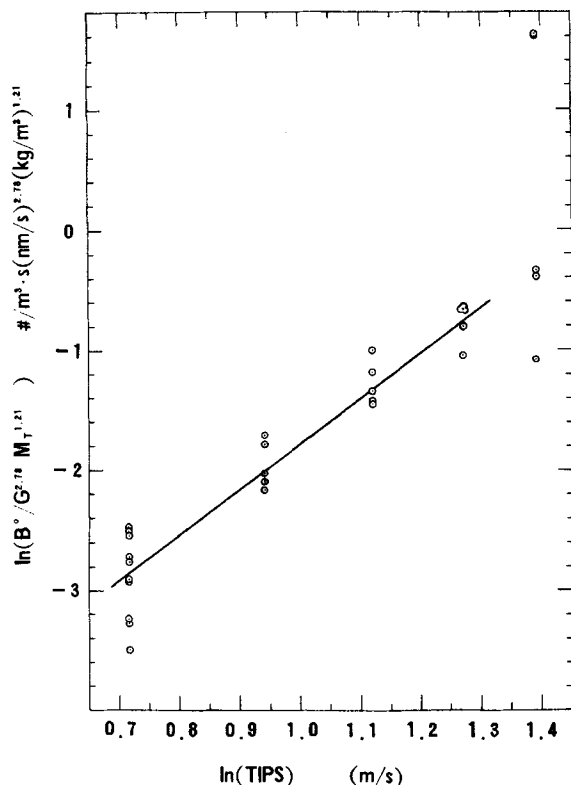The F, F_i, and F_j are 112.4, 224.3, and 37.0, respectively. The

Figure 4. Effect of tip speed on kinetics.

model and power index i are highly significant. F_j is a little less than $10F_{0.05}(1, 28 - 3)$ but much greater than $F_{0.01}(1, 28 - 3)$.

Comparing Eq. 9 with Eq. 5, we conclude that the power index i of growth rate is 2.78 ± 0.18 and is independent of tip speed, but the power index j of suspension density differs, from 1.10 to 0.70. Thus, the power index j is dependent on the hydrodynamic conditions.

Scale-up of crystallizers

Two agitation criteria were considered for scaling-up crystallizers: constant tip speed and constant energy input per unit volume. Three series of experiments were designed to match these two criteria: two series of kinetic studies at tip speeds of 2.6 and 2.0 m/s in the 2.5 dm³ crystallizer, and one series at a tip speed of 2.6 m/s in the 25 dm³ crystallizer. The first two series have been described above; here, the third series of experiments is reported. The temperature of crystallization and that in the saturator were 313.2 and 343.2 K, respectively. The tip speed of the impeller was 2.61 m/s, corresponding to 6.93 rps of the impeller. The range of retention time was 3,610 to 9,480 s. Three levels of suspension density of 55–146 kg/m³ were controlled by the rate ratio of clear liquor overflow from the settling zone to the flow of product withdrawal. The results of this series were obtained from 30 runs. Multiple regression of these results gives the following kinetic equation

$$B^o = 0.193 \, G^{2.60} \, M_T^{1.31} \quad \text{correlation coefficient } 0.916 \quad (10)$$

The F, F_i, and F_j are 70.0, 139.6, and 57.4, greater than $10F_{0.01}(2, 30 - 3)$, $10F_{0.01}(1, 30 - 3)$ and $10F_{0.05}(1, 30 - 3)$,

respectively. The model and its index i are highly significant and j is significant.

A constant energy input per unit volume was designed for the pair of experiments in the 2.5 dm³ crystallizer at 2.04 m/s tip speed and in the 25 dm³ crystallizer at 2.61 m/s tip speed. Comparison of Eq. 10 with Eq. 9 shows that their power indexes of growth rate agree well and have an average value of 2.59, but their power indexes of suspension density are 1.31 and 0.70, respectively, the wide difference of which implies that a constant energy input criterion is invalid for scale-up.

The pair of experiments in the 2.5 dm³ crystallizer at a tip speed 2.58 m/s and in the 25 dm³ crystallizer at tip speed 2.61 m/s matches the constant tip speed criterion. Both power indexes of growth rate and suspension density in Eq. 5 agree with those in Eq. 10. The average values of these indexes are 2.78 for growth rate and 1.21 for suspension density. Thus, the constant tip speed criterion is valid for the scale-up of crystallizers.

Comparing Eqs. 5 and 10, we find that growth rate G and nucleation rate B^o are almost independent of crystallizer scale. Using the average power indexes of 2.78 and 1.21 for i and j, all data for Eqs. 5 and 10 can be correlated in the following equations:

For the 2.5 dm³ crystallizer

$$B^o = 0.152 \, G^{2.78} \, M_T^{1.21} \tag{11}$$

For the 25 dm³ crystallizer

$$B^o = 0.179 \, G^{2.78} \, M_T^{1.21} \tag{12}$$

The standard deviation of coefficients in Eqs. 11 and 12 is ± 0.041 and ± 0.042, respectively.

In accordance with a power index of tip speed 3.79 from Eq. 8, the coefficients corrected to the tip speed of 2.60 m/s are 0.157 for the 2.5 dm³ crystallizer and 0.176 for the 25 dm³ crystallizer. The t test on their difference of 0.019 shows that the effect of crystallizer scale may be neglected. Therefore, at the tip speed of 2.60 m/s the following equation

$$B^o = 0.166 \, G^{2.78} \, M_T^{1.21} \tag{13}$$

can be used for either the 2.5 dm³ or the 25 dm³ crystallizer. Considering the power index of tip speed for 3.79, we have

$$B^o = 0.00444 \, G^{2.78} \, M_T^{1.21} (TIPS)^{3.79} \tag{14}$$

Equation 14 is valid in the range of suspension density of 50–147 kg/m³ in either the 2.5 or 25 dm³ crystallizer at 313.2 K and tip speed near 2.60 m/s. Similarly, the difference between the coefficients of Eqs. 14 and 8 is considered to be within the limit of experimental error by t test.

General kinetic equation

The traditional general form of the kinetic equation is

$$B^o = K_1 \, G^i \, M_T^j \, N^k \, d^k \tag{15}$$

where N is revolutions per second of the impeller and d is the impeller diameter. There are five parameters in Eq. 15.

That the criterion for scale-up is constant tip speed implies

that the power indexes h and k are identical. Equation 15 then simplifies to

$$B^o = K \, G^i \, M_T^j \, (TIPS)^h \qquad (16)$$

In this equation, the power index i is independent of the suspension density, tip speed, and crystallizer scale. But both power indexes j and h increase when either the suspension density or the tip speed is increased. For example, from Eqs. 5, 9, and 10, j increases from 0.70 to 1.21 in the suspension density range of 50–171 kg/m³ when the tip speed rises from 2.04 to 2.60 m/s. And comparing B^o and G in the series of $TIPS$ 2.04 m/s with those of 2.58 and 2.61 m/s at each of the three suspension density levels of 50–55, 100–110, and 150–170 kg/m³, we also find that the power index h increases with increase in the suspension density. However, the ratio of h to j is approximately 3 in the wide ranges of M_T and $TIPS$; e.g., in Eqs. 8 and 14 this ratio is 3.13. Thus, Eq. 16 may be simplified to the following equation with only three parameters,

$$B^o = K \, G^i \, (M_T \, \overline{TIPS^3})^j \qquad (17)$$

This is the general kinetic equation we have obtained. To prove the validity of this equation, $\ln \, (B^o/G^i)$ is plotted against $\ln \, (M_T \, \overline{TIPS^3})$, and the values of j and K can be obtained by regression.

At a crystallization temperature of 313.2 K, 112 runs were done. As shown in Figure 5, almost all the runs can be correlated well by the following equation:

$$B^o = K \, G^{2.78} \, (M_T \, \overline{TIPS^3})^j \qquad (18a)$$

For the first region, where $M_T \, \overline{TIPS^3} < 7.1 \; kg/s^3$

$$B^o = 0.162 \, G^{2.78} \, (M_T \, \overline{TIPS^3})^{0.70}$$

$$\text{correlation coefficient } 0.776 \qquad (18b)$$

The F factor of 94 is greater than $10F_{0.01}(1, 64 - 2)$, which is 70.7.

For the second region, where $9 > M_T \, \overline{TIPS^3} > 7.1 \; kg/s^3$

$$B^o = 5.00 \times 10^{-3} \, G^{2.78} \, (M_T \, \overline{TIPS^3})^{1.20}$$
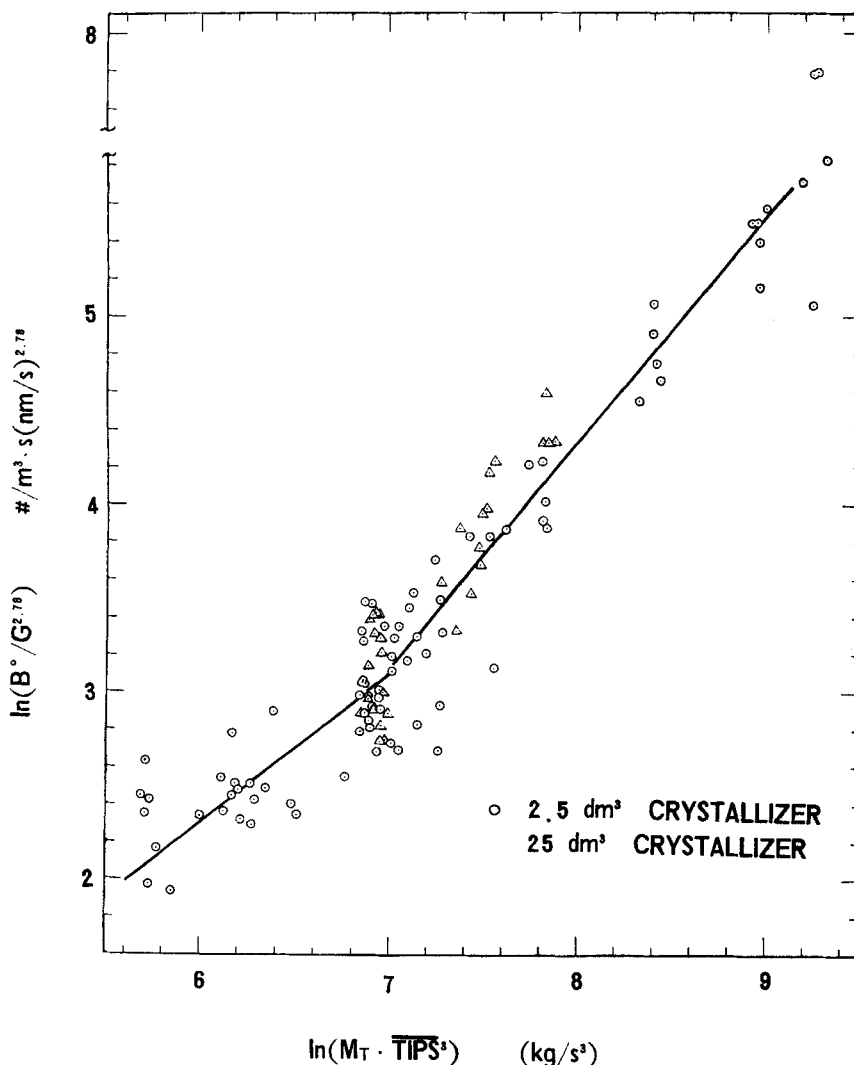
$$\text{correlation coefficient } 0.928 \qquad (18c)$$

Figure 5. Kinetics in different hydrodynamic regions.

The F factor of 250 is greater than $10F_{0.01}(1, 43 - 2)$, which is 73.0. In this region some large crystals are rounded.

For the third region, where $M_T \overline{TIPS}^3$ is greater than 9 kg/s^3, many crystals are severely rounded, and breakage of crystals occurs; j is even larger and scatters.

The F values of Eqs. 18b and 18c show that these equations are highly significant. Eq. 18a is valid at 313.2 K with suspension density in the range of 15–175 kg/m^3, tip speed 2–4 m/s, and crystallizer volume 2.5–25 dm^3. In Eq. 18a the effects of various factors, including retention time, suspension density, tip speed, and crystallizer scale, have been cross-checked well by all the series of experiments, Eq. 2 and Eqs. 5–14.

Discussion

Effect of temperature

The temperature effect on crystallization in some systems has been studied in a few works (Helt and Larson, 1977) and has been discussed by Wey and Terwilliger (1980). In this work, the dependence of the power index i on crystallization temperature shows a maximum i value of 2.78 at 313.2 K and lower values of 1.74, 2.09, and 1.67 at 298.2, 323.2, and 338.2 K, respectively. The physical meaning of this dependence is not yet clear, but one possible explanation may be that it is due to the considerable change occurring in the structure of the aqueous solution in this temperature range (Chernov, 1973; Wojciechowski, 1981).

The value i of 2.78 at 313.2 K agrees well with 2.77 at 311 K (Randolph et al., 1981), but not with their previously obtained value of 4.99 at 305 K (Randolph et al., 1977).

The data of B^o, G, and M_T from the 38 above-mentioned tests for the effect of crystallization temperature and the i values from Eqs. 1–4 are correlated in a general equation, using the Simplex algorithm on the computer as follows

$$B^o = \frac{12.5}{(6,067)^i} G^i M_T^{0.70} \exp\left[\frac{2,777}{RT} i - \frac{-5,858}{RT}\right] \quad (19)$$

where the power index 0.70 of the suspension density is given by Eq. 18b, and the gas constant per mole R is 1.9865 cal/mol · K.

When the crystallization temperature rises at constant supersaturation, the growth rate G increases, as indicated by $\exp(-2,777/RT)$. This tendency agrees with that published in most works, as mentioned by Wey and Terwilliger (1980). The nucleation rate B^o, however, decreases at constant supersaturation when temperature T rises as indicated by $\exp(5,858/RT)$. This relationship has also been reported by Helt and Larson (1977) for potassium nitrate, as well as by Sikdar and Randolph (1976) for magnesium sulfate. This reveals the complexity of the secondary nucleation.

Effects of suspension density and tip speed

The effect of mechanical contact on the nucleation rate of growing crystals was first investigated by Clontz and McCabe (1971). In crystallizers this effect for a given system depends mainly on the suspension density and agitation, besides supersaturation. In some works (Bennett et al., 1973) the second or fourth moment was used instead of the suspension density. But we find that our data correlate better with the suspention density than with these moments. Agitation can be expressed by specific energy input (Ottens and de Jong, 1973; Ploss et al.,

1986), tip speed (Bennett et al., 1973; Bourne and Hungerbuehler, 1980), or revolution speed of the impeller. As mentioned above, the expression with tip speed is the best. The power indexes of the suspension density or tip speed in published kinetic equations do not agree with one another (Garside and Shah 1980). However, in most works, the indexes j and h are not far from 1 and 3, respectively. Either of these values was used for the derivation of kinetic equations (Ottens and de Jong; Bennett et al.). Only in a few works (Juzaszek and Larson, 1977; Randolph et al., 1981; Grootscholten et al., 1982) were the original data and correlation coefficients of the kinetic equations published. But the deviations of individual power indexes are still unknown, and the individual indexes often contradict the corresponding series of data or the indexes estimated by multiple regression. No connection between indexes j and h was considered in the limited ranges of suspension density and agitation speed in previous works.

In this work we find a good correlation of nucleation rate B^o and growth rate G with the group $(M_T \overline{TIPS}^3)$. The standard deviations of i and j in Eq. 18a are 0.2 and 0.1, respectively. The relative standard deviation of K is 25%. Even the equations obtained by multiple regression agree fairly well with Eqs. 18b and 18c. They are as follows:

For the first region

$$B^o = 0.261 G^{2.69} M_T^{0.61} \overline{TIPS}^{2.35} \quad (20a)$$

For the second region

$$B^o = 0.0155 G^{2.22} M_T^{1.40} \overline{TIPS}^{3.42} \quad (20b)$$

The indexes in Eqs. 20a and 20b differ from the corresponding indexes in Eqs. 18b and 18c by only 20% or less.

The increase of j in Eq. 18a from 0.70 in the first region to 1.20 in the second region seems to reflect the nucleation mechanism changing from crystals-crystallizer collision to crystals-crystals collision. It may also explain that the divergence of published j and h values is not only due to experimental error but also to the different regions in which the experiments were done.

Dimensionless group for the hydrodynamics in crystallizers

The secondary nucleation rate is sensitive to the hydrodynamic condition, which depends on three factors: flow of suspension, gravity force, and probability of collision. The flow of suspension is usually characterized by the Reynolds number of particles, Re_p. The Froude number of particles, Fr_p, is used, as in fluidization, to characterize the suspension of crystals. The probability of collision can be expressed by the volume fraction of crystals in suspension as $(1 - e)$, where e is voidage of suspension. A new dimensionless group χ is now introduced

$$\chi = (1 - e)Fr_p Re_p \quad (21)$$

The velocity of suspension flow is in proportion to the tip speed $TIPS$, and $TIPS$ is used as the characteristic velocity in Fr_p and Re_p. Therefore,

$$\chi \propto (1 - e)\left(\frac{\overline{TIPS}^2}{L_D g}\right)\left(\frac{\overline{TIPS} L_D}{\nu}\right) \propto \frac{M_T \overline{TIPS}^3}{\rho_s \nu g} \quad (22)$$

The group χ is also proportional to the collision power on the unit surface area of crystals.

Thus, χ is in proportion to the group $(M_T \overline{TIPS^3})$ and seems to be a dimensionless group, characteristic of the hydrodynamic condition of crystallizers. Equation 17 can then be expressed as the dimensionless equation

$$\frac{B^o}{K'G^i} = \chi^j \qquad (23)$$

where j is 0.70 in the first region and 1.20 in the second region.

The coefficient of kinetic equations

The coefficient K in Eq. 15 is highly sensitive to the structure and dimensions of crystallizers. The published values of K differ widely (Garside and Shah, 1980). The great influence of the clearance between the impeller and the draft tube was pointed out by Scrutton et al. (1982) and Grootscholten et al. (1985). Our value of K in Eq. 18a is much less than that reported by Randolph et al. (1981).

A series of 13 tests was done in another 25 dm³ crystallizer. At a tip speed of 2.61 m/s, suspension density 16–19 kg/m³, crystallization temperature 313.2 K, and retention time between 1,020 and 3,980 s, we find the i value to be 2.74. It again agrees well with 2.78 ±0.2 in Eq. 18a. However, K is found to be only one-sixth of that in Eq. 18a. The correlation coefficient is 0.917. Thus, geometrical analogy is necessary for the scale-up of crystallizers.

The effects of physical properties on the coefficient K in Eq. 17 or K' in Eq. 23 cannot now be predicted. To tackle this problem, a precise method for determining suspersaturation in crystallizers is required, and then the nucleation rate and growth rate can be correlated with supersaturation. From this point of view, the kinetic equation that can correlate different systems would not be established until the precise measurement of supersaturation for various systems was developed.

Conclusions

1. The general kinetic equation for secondary nucleation is expressed more reasonably by the equation

$$B^o = KG^i(M_T \overline{TIPS^3})^j$$

rather than by the traditional empirical equation

$$B^o = K_1 G^i M_T^j N^k d^k$$

2. The power index i is independent of M_T, N, and d; however, it depends on the crystallization temperature.

3. The constant $TIPS$ is the scale-up criterion for geometrically similar crystallizers. The hydrodynamic conditions of crystallizers are identified by the group $M_T \overline{TIPS^3}$. The three hydrodynamic regions are found to correspond with the three levels of $M_T \overline{TIPS^3}$. The power index j is larger in the second region than in the first region. In the third region, where $M_T \overline{TIPS^3}$ exceeds a certain limit, many crystals are rounded, breakage of crystals occurs, and the value of j tends to be divergent.

4. When the crystallization temperature T rises, the growth rate G increases, while the temperature effect on the nucleation rate B^o is quite the reverse, i.e., when T increases, B^o decreases.

Notation

B^o = nucleation rate, no./m³ · s
d = impeller diameter, m
e = voidage of suspension
F = F factor of the regression equation
F_i, F_j = F factor with respect to power indexes i, j
Fr_p = Froude number of particle, $u^2/L_D g$
G = growth rate, nm/s
g = acceleration of gravity, m/s²
h = power index of impeller revolution in kinetic equation
i = power index of growth rate in kinetic equation
j = power index of suspension density in kinetic equation
K = coefficient, Eqs. 16, 17, 18a, no./m³ · s(nm/s)^i(kg/s³)^j, no./m³ · s(nm/s)^i(kg/m³)^j(m/s)^k
K' = coefficient, Eq. 23, no./m³ · s(nm/s)^i
K_1 = coefficient, Eq. 15, no./m³ · s(nm/s)^i(kg/m³)^j(s^{-1})^k · m^k
k = power index of impeller diameter in kinetic equation
L = crystal size, m
L_D = dominant crystal size, m
M_T = suspension density, kg/m³
N = revolutions per second of impeller, s^{-1}
n = population density, no./m⁴
Re_p = Reynolds number of particle, uL_D/ν
T = crystallization temperature, K
$TIPS$ = tip speed of impeller, m/s
u = velocity of suspension, m/s

Greek letters

ν = kinetic viscosity of solution, m²/s
ρ_s = density of crystals, kg/m³
τ = retention time, s
χ = dimensionless group, Eq. 21

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