$\Delta P/L$ = pressure drop per unit length
Re = Reynolds number defined as $Du\rho/\mu$
τ_w = wall shear stress defined as $\frac{D\Delta p}{4L}$
u = average velocity
u^* = friction velocity $\sqrt{\tau_w/\rho}$
ρ = density of the fluid mixture
μ = viscosity of the fluid mixture

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On Size-Dependent Crystal Growth Rates

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Several recent papers (Canning and Randolph, 1967; Abegg et al., 1968; Estrin et al., 1969) have contained expressions for size-dependent crystal growth rate which are used to describe the particle size distributions produced in a continuous mixed-suspension, mixed-product-removal (CMSMPR) crystallizer operating at steady state. These studies involved the use of population balance methods (Randolph and Larson, 1962) to treat experimental distributions which were not in accord with growth behavior suggested by McCabe's ΔL law (McCabe and Stevens, 1951). The paper by Abegg et al. (1968) lists the conditions necessary for the incorporation of a number of growth models into the population balance equation. These empirical growth rate expressions, however, are not related to specific crystal growth mechanisms.

In a suspension crystallizer, crystal growth is generally considered to involve three basic steps (Hixson and Knox, 1951), namely, diffusion of solute to the solid-liquid interface, followed by surface integration at the crystal surface and diffusion of heat of crystallization away from the interface. The effects of the third step on the overall growth processes are considered to be small in most systems exhibiting relatively low heats of crystallization. Lieb and Osmers (1973) recently studied the effects of diffusion and surface integration on the crystal size distribution in a CMSMPR crystallizer. They developed several mathematical growth rate models which reflect different mechanisms of diffusion and interfacial kinetics. The functional form of the growth rate expression was constrained by the requirement that the third moment of the distribution must converge. Their results showed that, under certain conditions, the size distribution may be greatly altered from the classic straight-line plot of logarithm of the particle density function versus particle size. In particular, a maximum exists in the distribution at a finite particle size when diffusion is dominant.

Recently, a rather unusual type of growth behavior has been obtained experimentally for ammonium sulfate and potassium sulfate crystals (Randolph and Cise, 1972; Youngquist and Randolph, 1972) which indicates that the growth rate of very tiny crystals is small but increases rapidly with size. Sikdar and Randolph (1974) observed the same phenomenon for magnesium sulfate heptahydrate crystals and indicated that such a size-dependent growth behavior for very tiny crystals cannot be described meaningfully by a slip velocity model as suggested by Rosen (1974). Neither can this behavior be explained by conventional diffusion and/or interfacial kinetics mechanisms (Lieb and Osmers, 1973). However, work by Wey and Estrin (1972), which takes into account the surface curvature effect (change of solubility with particle size), shows that the growth rate of small particles may indeed be a strongly increasing function of size. In this note, we (1) present a growth rate expression which includes the influence of surface curvature as well as those of diffusion and interfacial kinetics, and (2) study the effects of surface curvature on the behavior of the crystal size distribution in a CMSMPR crystallizer.

A description of the growth rate, which involves both diffusion and first-order interfacial kinetics, can be given by (Lieb and Osmers, 1973)

$$G = \frac{C_b - C_0}{\frac{1}{K_I} + \frac{\rho L}{D}} \tag{1}$$

The effect of surface curvature on the solubility of crystals in suspension is well known. The solubility of a newly formed nucleus is not the bulk solubility generally found in solubility tables but is a somewhat higher value expressed by the Gibbs-Thomson equation (Mullin, 1972). Therefore, in a given environment, the driving force for crystal growth is much lower for particles whose size is of the order of a nucleus than it is for macroscopic crystals. An equation relating particle size and the solute concentration in equilibrium with the solid phase, analogous to the Gibbs-Thomson equation, is

$$C_0 = C_e \, e^{\frac{\Gamma_D}{L}} \tag{2}$$

where C_e is the normal equilibrium solute concentration of large crystals and Γ_D is a capillary constant from the Gibbs-Thomson equation. In practice, Γ_D is a small parameter (typically $\Gamma_D \approx 10^{-7}$ cm) so that (2) can be reasonably represented by a simple linear expression (Mullins and Sekerka, 1963) for particles greater than about 100 Å in size.

$$C_0 = C_e\left(1 + \frac{\Gamma_D}{L}\right) \tag{3}$$

Substitution of (3) into (1) gives a growth rate expression which includes diffusion, interfacial kinetics, and surface curvature effects.

$$G = \frac{g\left(1 - \frac{L^*}{L}\right)}{1 + \epsilon L} \tag{4}$$

where

$$g = K_I(C_b - C_e) \tag{5}$$

$$L^* = \frac{C_e \Gamma_D}{C_b - C_e} \tag{6}$$

$$\epsilon = \frac{\rho K_I}{D} \tag{7}$$

g represents the size independent growth rate. L^* is equivalent to the critical size of a stable nucleus (determined from (3) for $L = L^*$ when $C_0 = C_b$) above which the particle grows spontaneously and below which it dissolves (Mullins and Sekerka, 1963; Wey and Estrin, 1972). ϵ represents the ratio of the relative resistance of diffusion to interfacial kinetics.

The form of the growth rate expression and the magnitude of the parameters cannot be arbitrary. As indicated by Lieb and Osmers (1973), the growth rate expression must satisfy the constraint imposed by the material balance. In this study, we assume that nucleation occurs at size L^0 which is greater than the critical size of the stable nucleus, L^*. By following a procedure similar to that used by Lieb and Osmers, an expression for the growth rate constraint can be obtained

$$\lim_{L\to\infty}\left[L^3 \exp\left(-\frac{1}{T}\int_{L^0}^{L}\frac{dL}{G}\right)\right] = 0 \tag{8}$$

It can be shown that the growth rate expression given by (4) indeed satisfies this constraint.

Randolph and Larson (1962) have shown that the population balance equation for a simple CMSMPR crystallizer operating at steady state can be written as

$$\frac{d(Gn)}{dL} + \frac{n}{T} = 0 \tag{9}$$

Using the growth rate expression given by (4), Equation (9) can be integrated to give the steady state crystal size distribution.

$$\frac{n}{n^0} = \frac{L}{L^0}\left(\frac{1+\epsilon L}{1+\epsilon L^0}\right)\left(\frac{L^0 - L^*}{L - L^*}\right)^{\frac{L^*}{gT}(\epsilon L^* + 1) + 1} e^{-\frac{(L - L^0)}{gT}\left[\frac{\epsilon(L + L^0)}{2} + \epsilon L^* + 1\right]} \tag{10}$$

where n^0 is the nuclei population density which can be obtained from a material balance as suggested by Lieb and Osmers (1973).

Introducing the dimensionless variables and parameters

$$y = \frac{n}{n^0}, \quad x = \frac{L}{L^0}, \quad \alpha = \frac{L^*}{L^0}, \quad \beta = \frac{L^0}{gT}, \quad \gamma = \epsilon L^0$$

Equation (10) can be rewritten as

$$y = x\left(\frac{1+\gamma x}{1+\gamma}\right)\left(\frac{1-\alpha}{x-\alpha}\right)^{\alpha\beta(\alpha\gamma + 1) + 1} e^{-\beta(x-1)\left[\frac{\gamma(x+1)}{2} + \alpha\gamma + 1\right]} \tag{11}$$

The physical significance of the parameters α, β, and γ is as follows: α represents the surface curvature effect, which vanishes when $\alpha = 0$; β is related to the minimum crystal size; and γ represents the relative resistance of diffusion to interfacial kinetics so that when $\gamma = 0$, growth is controlled by surface integration, and when $\gamma >> 1$, by diffusion.

The dimensionless population distribution defined by (11) is shown in Figures 1 and 2 for selected values of the growth rate parameters. Figure 1 shows the effect of surface curvature on the steady state crystal size distribution in the CMSMPR crystallizer when growth is dominated by interfacial kinetics ($\gamma = 0$). With no surface curvature effect ($\alpha = 0$), the plot of ln y versus x gives the straight line consistent with the distribution predicted from McCabe's ΔL law. As surface curvature effects be-

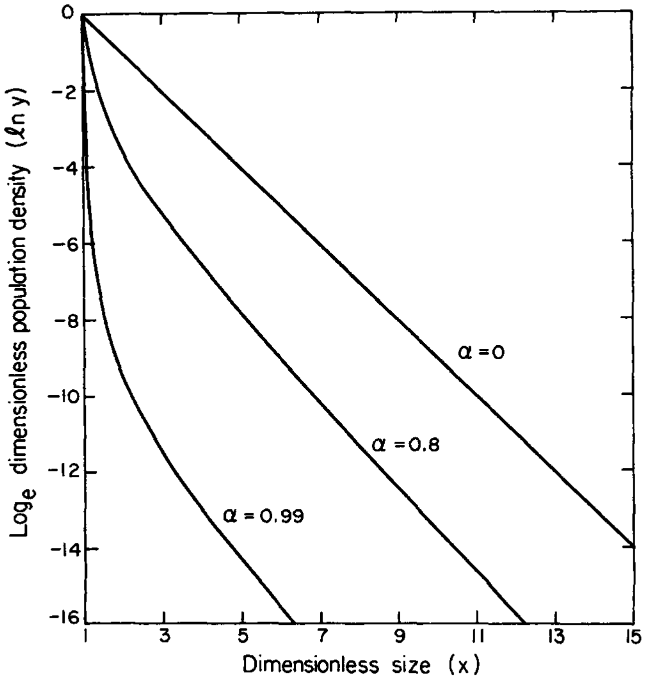

Fig. 1. Population density function for CMSMPR crystallizer—growth influenced by surface curvature ($\gamma = 0$, $\beta = 1$).

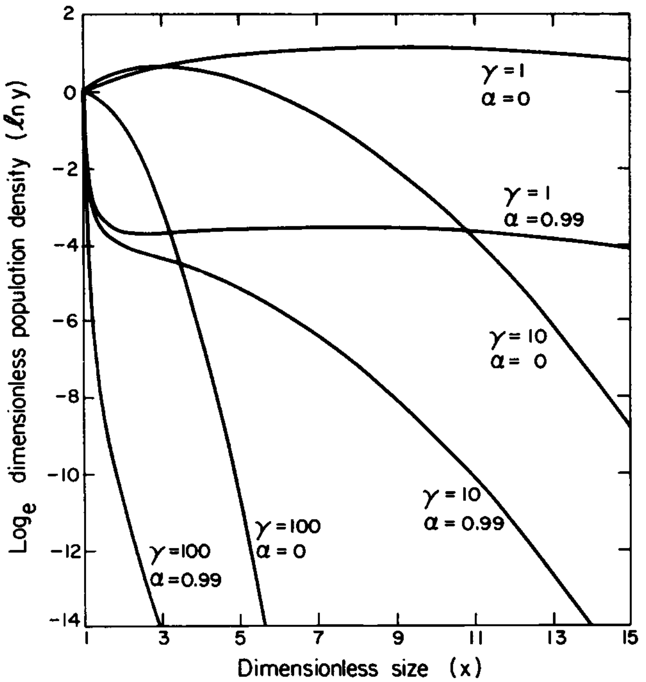

Fig. 2. Population density function for CMSMPR crystallizer—growth influenced by diffusion and surface curvature ($\beta = 0.01$).

come more important, the density function begins to deviate from the straight line behavior in the small particle size range. The concave nature of the distribution becomes more pronounced as α increases ($0 \leq \alpha < 1$). This type of distribution has been obtained experimentally (Canning and Randolph, 1967; Randolph and Cise, 1972; Youngquist and Randolph, 1972; Sikdar and Randolph, 1974). Although several empirical size-dependent growth rate expressions may be used to fit these data (Canning and Randolph, 1967; Abegg et al., 1968; Estrin et al., 1969), the proposed model, which includes the influence of surface curvature, offers a sounder theoretical basis for describing the potential growth mechanisms in the nucleus size range.

Figure 2 shows the steady state size distribution in the CMSMPR crystallizer when diffusion is also involved in the growth processes. Depending on the relative importance of diffusion, interfacial kinetics, and surface curvature, the distribution will exhibit a number of different shapes. When surface curvature is not important ($\alpha = 0$), the distribution shows a maximum at a finite particle size, consistent with the results of Lieb and Osmers (1973). However, when surface curvature becomes important, the distribution behaves differently in the small size region. For example, when $\alpha = 0.99$ and $\gamma = 1.0$, a local minimum and a local maximum exist in the same size distribution curve although the difference between the two extremes is not pronounced for these particular values of α and γ. The minimum occurs in the small size region and is due strictly to the surface curvature effect.

In summary, this work presents a crystal growth rate expression which includes diffusion, interfacial kinetics, and surface curvature effects. Incorporation of the surface curvature effect into the growth model shows that the theoretical crystal size distribution in a CMSMPR crystallizer can be altered significantly in the small size range from that predicted by conventional diffusion and/or surface integration controlled growth. This analysis may provide a better understanding of possible growth mechanisms and their effects on the crystal size distribution in the nucleus size range.

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NOTATION

C_b = bulk solute concentration
C_e = solute concentration in equilibrium with solid phase having flat surface
C_0 = solute concentration in equilibrium with solid phase having curved surface ($C_0 > C_e$)
D = mass diffusivity
G = linear crystal growth rate, Equation (1)
g = growth parameter, Equation (5)
K_I = surface integration growth coefficient
L = linear crystal size
L^0 = linear crystal size at which nucleation occurs
L^* = linear size of stable nucleus, Equation (6)
n = population density function
n^0 = nuclei population density
T = crystallizer residence time
x = dimensionless variable, L/L^0
y = dimensionless variable, n/n^0
α = dimensionless parameter, L^*/L^0
β = dimensionless parameter, L^0/gT
γ = dimensionless parameter, ϵL^0
Γ_D = capillary constant from the Gibbs-Thomson equation
ϵ = growth parameter, Equation (7)
ρ = density

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