The Effect of Crystal Size on Occlusion Formation During Crystallization from Solution

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Crystallization is an important industrial separation and purification process. The purpose of any crystallization process is the separation of solute and solvent upon freezing. The separations obtained should conform to those predicted by the equilibrium phase diagram. The degree of separation achieved, however, is often much less than predicted. Wilcox (1964) and Cheng et al. (1967) postulated that these nonequilibrium compositions could be the result of microscopic pockets of solvent being trapped inside the crystal as a second phase. These second phase impurities are called occlusions (inclusions).

The presence of occlusions in crystals grown from solution and the melt has been widely reported in the literature (Belyustin and Fridman (1968), Brooks et al. (1968), Denbigh and White (1966), Von Batchelder and Vaughan (1966), Pilkington and Dunning (1973), Baker and Cahn (1969), Hellawell (1965), Wilcox (1964), Edie and Kirwan (1973), Ozum and Kirwan (1976), Myerson and Kirwan (1977a)). Edie and Kirwan (1973) postulated that occlusion formation (hence solvent trapping) was the result of the crystal interface becoming unstable and growing dendritically with the dendrite arms impinging on one another in such a way as to form the occlusions. Edie and Kirwan (1973) used results from the literature on the radius and spacing of dendrites in metal systems to develop a quantitative relation between solvent trapping and various process variables (i.e., crystal growth velocity, interfacial temperature gradient). This relation was refined by Myerson and Kirwan (1977b), who obtained a relation that predicted increased trapping with increased crystal growth velocity and a decrease in the absolute value of the interfacial temperature gradient. This relation was shown (Myerson and Kirwan (1977a)) to adequately correlate experimental data for the growth of single crystals of sodium chloride, potassium aluminum sulfate dodecahydrate, and calcium sulfate dihydrate grown from aqueous solution, as well as literature data on melt crystallization.

Nidel (1977) attempted to reproduce experimental results on occlusion formation in single crystals in a continuous flow, MSMPR (mixed suspension, mixed product removal) crystallizer. In studies of the growth of potassium aluminum sulfate dodecahydrate in a suspension crystallizer at growth velocities employed in single crystal studies, no impurity trapping was observed. The occlusion-free crystals obtained in the MSMPR system, however, were significantly smaller than those with occlusions reported in single crystal studies. Previous investigators (Denbigh and White (1966), Brooks et al. (1969) have reported qualitative observations indicating that occlusion formation is a function of crystal size. Brice and Bruton (1974) developed a simple model which predicts that interfacial breakdown (hence unstable growth and occlusion formation) could only occur when the size of a crystal face exceeded some critical size, which is a function of the growth parameters. The model could explain the lack of trapping observed in Nidel's (1977) work.

The purpose of our investigation is twofold: (1) to experimentally determine the critical size required for occlusions to develop in potassium aluminum sulfate dodecahydrate and sodium chloride crystals at a variety of growth conditions; and (2) to determine the validity of the Brice and Bruton model.

THEORY

As previously mentioned, it has been postulated that the breakup of the stable crystal interface and its subsequent dendritic growth are the cause of occlusion formation. A simple macroscopic criterion for the stability of a planar crystal-liquid interface can be given the relation:

$$\frac{G}{VC_L(O)} > \frac{m(1 - k_o)}{D} \qquad (1)$$

where G is the interfacial temperature gradient, (measured from the solid to the solution) V the crystal growth velocity, $C_L(O)$ the interfacial solute concentration, m the slope of the liquidus line on the phase diagram, k_o the equilibrium distribution coefficient, and D mass diffusion coefficient. Analyses of the stability of a growing crystal face, whether employing Eq. 1 (Tiller, 1968), or using perturbation theory (Mullins and Sekerka, 1964), indicate that interfacial stability can only occur in the presence of a finite positive temperature gradient which must increase with increasing crystal growth rate. Such a stabilizing temperature gradient is not possible during crystallization from solution. The temperature gradient, in fact, is usually negative because of heat released upon crystallization. Brice and Bruton (1974) examined the problem of interfacial stability effect which decreases with increasing crystal size. They considered a perfect singular interface where growth occurred by nucleation followed by lateral spreading. For unstable growth to occur in this situation, a new nucleus must form before existing nuclei join or reach the edge. Employing this

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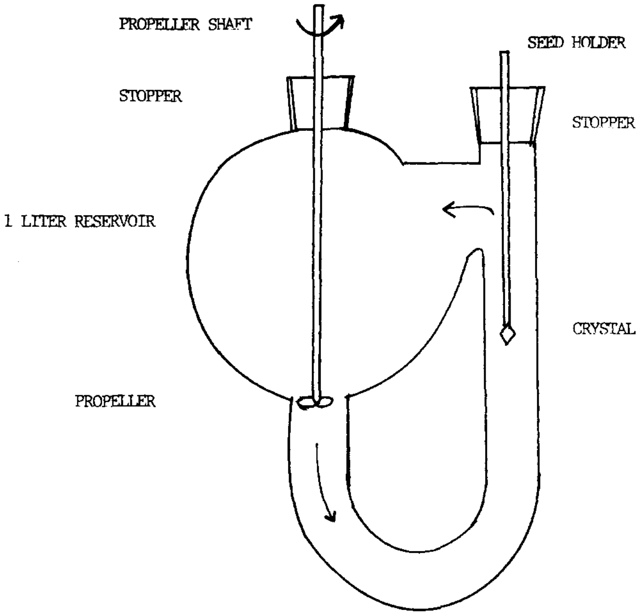

Figure 1. Apparatus for single crystal studies.

model Brice and Bruton (1974) obtained the following stability criterion:

$$L < \frac{V^*\lambda}{V} \qquad (2)$$

where L is the size of the growth face, V^* the spreading velocity, λ the height of the nucleus, and V the linear growth rate normal to the face. The spreading velocity, V^*, was given by the relation:

$$V^* = \frac{D}{\lambda}\,\frac{C_L(O) - C_{LE}}{C_L(O)} \qquad (3)$$

where C_{LE} is the equilibrium solute concentration. D here is taken to be the bulk solution diffusivity but could also be similar to a surface diffusion coefficient. Substitution of Eq. 3 into 2 yields:

$$L < \frac{D(C_L(O) - C_{LE})}{V\,C_L(O)} \qquad (4)$$

The purpose of this work is to experimentally verify Eq. 4 in the case of crystallization from aqueous solution. The experimental techniques employed and the results obtained are discussed in the next section.

SINGLE CRYSTAL GROWTH EXPERIMENTS

In order to experimentally measure solvent occlusion as a function of crystal size during the crystallization of solutes from aqueous solution, a flow crystallizer similar to one used by Botsaris and Denk (1970) was constructed. A schematic of the apparatus is shown in Figure 1. Solution at a controlled flow rate and supersaturation flows over a crystal suspended on the needle tip. Heat and mass transfer are well-defined in the geometry. The fluid velocity can be raised to a value where it does not affect growth rates indicating little mass transfer influence. The change in supersaturation in the solution during each experiment was small (2% or less) and should have had a negligible effect. The average growth rate was obtained from the weight gain of the crystal. The amount of solvent entrapped was obtained by analysis of the crystals employing atomic absorption spectrometry. In those systems that form hydrates, only water exceeding the stoichiometric amount within the solid was taken as impurity. The accuracy of the excess water determination was no worse than ±3% by weight. This apparatus was used to grow $KAl(SO_4)_2 \cdot 12\,H_2O$ and NaCl crystals from aqueous solution. Solubility data for these systems were

TABLE 1. DEPENDENCE OF OCCLUSION FORMATION DURING THE GROWTH OF SINGLE CRYSTALS OF POTASSIUM ALUMINUM SULFATE DODECAHYDRATE ON CRYSTAL SIZE

Applied Undercooling °C	Growth Velocity m/s × 10^8	Final Diameter m × 10^3	Mass Percent Occluded H_2O
1	2.4	1.2	0
1	1.0	1.7	0
1	2.2	2.3	0
1	1.8	2.6	0
1	1.5	2.8	8
1	1.9	3.3	15
1	1.6	3.4	13
1	1.9	3.6	17
2	3.6	1.3	0
2	3.9	2.1	0
2	5.3	2.8	0
2	3.7	2.8	0
2	3.0	3.0	6
2	4.0	3.1	7
2	4.9	3.2	19
2	4.4	3.4	12
2	3.7	3.7	12
2	4.0	3.9	15
2	3.6	4.1	16
2	4.9	4.2	14
3	6.9	2.5	0
3	5.9	2.7	0
3	5.8	2.8	0
3	5.4	3.2	8
3	7.5	3.5	13
3	9.7	3.8	10
3	8.5	5.2	12

TABLE 2. DEPENDENCE OF OCCLUSION FORMATION DURING THE GROWTH OF SINGLE CRYSTALS OF SODIUM CHLORIDE ON CRYSTAL SIZE

Applied Undercooling °C	Growth Velocity m/s × 10^8	Final Diameter m × 10^3	Mass Percent Occluded H_2O
0.5	2.1	2.0	0
0.5	2.3	2.1	0
0.5	2.0	2.2	0
0.5	1.8	2.3	9
0.5	2.1	2.3	6
0.5	2.4	2.4	8
0.5	2.0	2.4	9
0.5	2.6	2.4	12
0.5	2.2	2.5	10
0.5	2.4	2.5	12
0.5	1.8	2.6	14
0.5	2.2	2.6	12
1	3.5	1.8	0
1	3.0	1.9	0
1	3.4	2.0	0
1	2.5	2.2	6
1	2.4	2.2	9
1	3.8	2.2	6
1	4.0	2.4	8
1	3.5	2.5	8
1	4.0	2.6	10
1	3.4	2.7	11
1	3.4	2.7	9
1	3.6	2.8	8
1	3.0	3.0	13

obtained from Seidell and Link (1965). Further details may be found in Slaminko (1980).

Experiments were conducted at several undercoolings (1-3°C) and a variety of growth times so as to obtain crystals at a variety of sizes at each undercooling. The crystallization temperature was 28 or 29°C. A flow rate of 0.04 m/s was used to minimize mass transfer effects. Crystals were initially about 5×10^{-4}m in equivalent spherical diameter based on their mass.

RESULTS AND DISCUSSION

Results are presented in Tables 1 and 2 and indicate a critical size below which no trapping occurs. The critical size observed for the growth of $KAl(SO_4)_2 \cdot 12\ H_2O$ crystals at an average growth velocity of 4.2×10^{-8} m/sec was 2.8×10^{-3} m. This observed critical size is significantly larger than the largest crystals (2.2×10^{-3} m) examined by Nidel (1977) in his study of the growth of $KAl(SO_4)_2 \cdot 12\ H_2O$ crystals in an MSMPR crystallizer at approximately the same growth rates. This result, therefore, explains the fact that no trapping was observed by Nidel (1977) since all crystals examined in his study were below the critical size.

Previous work (Myerson (1977)) has indicated that the degree of trapping in $KAl(SO_4)_2 \cdot 12\ H_2O$ crystals larger than 3.6×10^{-3}m and NaCl crystals larger than 3.2×10^{-3} are not a function of size. The degree of trapping was found to depend only on process variables (crystal growth velocity, agitation, etc.). If the degree of trapping is constant with size in large crystals (crystals significantly larger than the critical size) it indicates that a constant percentage of new crystalline material added during the growth process is trapped solvent. When a crystal reaches its critical size, therefore, a fixed percentage of all new crystalline material added to the crystal should be trapped solvent. The overall degree of trapping in a crystal growing from its critical size therefore, should start at zero, increase with increasing crystal size, and asymptotically approach a constant maximum value. This increase in trapping with increasing crystal size up to a maximum value was experimentally observed and is shown in Tables 1 and 2.

In order to apply Eq. 4 it is necessary to obtain values for the interfacial concentration and the diffusion coefficient. The interfacial concentration was obtained by equating the mass transfer flux of solvent from the crystal surface to the rate of rejection of solvent by the growing crystal. At the solution velocities employed good mass transfer conditions prevailed so that the interfacial concentration was quite close to the bulk value. The diffusivities of potassium aluminum sulfate dodecahydrate were reported by Mullins et al. (1965). For 30°C near saturation conditions D is about 5×10^{-10} m^2/sec. For the observed growth velocities in Table 1 of about 1.8×10^{-8}, 4.0×10^{-8}, and 6.0×10^{-8} m/s, Eq. 4 predicts critical crystal dimensions between 1.5×10^{-3} m and 3×10^{-4} m. This is to be compared with the experimentally observed values of about 2.6×10^{-3} m, 2.8×10^{-3} m, and 2.8×10^{-3} m.

Employing the results of Table 2 for the growth of sodium chloride crystals along with the diffusivity near saturation conditions (Tyrrell (1961)), Eq. 4 predicts critical crystal dimensions between 9×10^{-5} m and 5×10^{-5} m as compared with the observed critical dimensions of 2.2×10^{-3} m and 2.0×10^{-3} m.

In both systems studied the critical size predicted by Eq. 4 was significantly smaller than the observed critical size. In addition, the decrease in critical size with increasing crystal growth velocity predicted by the Brice and Bruton theory was not observed. This lack of correlation of experimental data with the Brice and Bruton theory may, however, be the result of observing overall crystal growth rates based on equivalent spherical diameter instead of growth rates of the individual crystal faces. A more accurate test of the theory would involve the measurement of crystal growth velocities for the individual faces along with the size at which the faces begin to grow unstably. Experiments designed to make these measurements are currently under construction.

NOTATION

$C_L(O)$ = interfacial solute concentration (kg-mol/m^3)
C_{LE} = equilibrium solute concentration (kg-mol/m^3)
D = diffusivity (m^2/s)
G = interfacial temperature gradient (°C/m)
k_o = solute equilibrium distribution coefficient
L = crystal face dimension (m)
m = slope of liquidus curve (°C-m^3/kg-mol)
V = linear growth velocity normal to crystal face (m/s)
V^* = nuclei spreading velocity (m/s)
λ = height of nucleus (m)

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