Effects of Raffinose on Sucrose Crystal Growth Kinetics and Rate Dispersion

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Raffinose is a major impurity in sugar production from sugar beets. It exists to the extent of 0.3 to 1.2% of the sugar present in the beet (McGinnis, 1971). Previous research (Smythe, 1967b; Mantovani and Fagioli, 1964; Binder and Murphy, 1982; Vaccari et al., 1986) has shown that raffinose has a strong effect on both the habit and the growth rate of sucrose crystals grown in its presence. Powers (1960), Hungerford and Nees (1934), Smythe (1967a), and Vaccari et al. (1986) among others have shown that raffinose suppresses the deposition of sucrose on the faces parallel to the inclined axis such that plate- and needle-type crystals are formed. It has also been shown (Smythe, 1967b; Mantovani and Fagioli, 1964; Binder and Murphy, 1982; Vaccari et al., 1986) that low levels of raffinose can drastically reduce the growth rate of sucrose crystals. For example, 2 grams of raffinose per 100 grams of water has been shown to approximately halve the rate of growth.

The kinetics of sucrose crystal growth in the presence of raffinose have been studied by both Smythe (1967a) and Binder and Murphy (1982). Both studies showed that, in the presence of raffinose, sucrose crystals grew with approximately a second-order dependence on supersaturation. Their results suggested that the mechanism of the raffinose growth inhibition was due to the incorporation of the raffinose molecules into the sucrose crystal lattice, thereby impeding the orderly procession of sucrose molecules into the lattice. This has also been suggested by Aquilano et al. (1980), Black et al. (1986), and Vaccari et al. (1986) to explain the effect of certain "tailor-made" additives on the growth of crystals. This type of impurity has one component similar to the pure system (the fructose moiety of the raffinose) that can be incorporated into the lattice on certain faces with a second distinct component (the galactose moiety) that can disrupt further molecular incorporation. Both Murphy and Binder (1982) and Smythe (1967b) found that the effects of raffinose varied with temperature over the range 303–333 K. It was also found that the growth retardant effect of raffinose was slightly increased at the lowest temperatures.

Vaccari et al. (1986) carried out a detailed crystallographic study on the theoretical surfaces and face by face growth kinetics for both single and twin crystals. Their results showed that the growth rates from face to face are different. They found that the habit of sucrose was modified for twin crystals in the presence of raffinose since the elongation parameter (ratio of length to width of crystals) was quite different for pure and impure system, even for different levels of raffinose.

Since raffinose has such a large effect on the lattice incorporation of sucrose molecules, it has been suggested that the presence of raffinose would also affect the extent of growth rate dispersion (GRD). GRD is defined as the distribution of growth rates evident in a homogeneous sample of crystals growing in a uniform environment. That is, not all crystals grow at exactly the same rate. Binder and Murphy (1982) found that raffinose generally decreased the extent of GRD seen in pure solution (Berglund, 1980). However, the magnitude of this decrease could not be directly correlated to the level of raffinose present. They concluded that the resolution of their particle counting technique was inadequate to determine the extent of GRD precisely enough.

This work seeks to further the investigation of the effects of raffinose on both the crystallization kinetics and GRD of growing sucrose crystals. Measurements of the widening of the crystal size distribution (CSD) of suspension grown seed crystals, as well as direct photomicroscopic measurements of the growth of these seed crystals, were completed for this study. The range of supersaturation studied was 0.28 to 2.05 g sucrose per 100 g solution with a temperature range of 313 to 333 K. The results of a previous investigation (Liang et al., 1988) on the solubility of sucrose in raffinose solution were utilized for the kinetic determinations.

Experimental Studies

Supersaturated solutions of sucrose in the presence of raffinose were prepared in the following way. A raffinose solution of known concentration (ratio of raffinose to water) was prepared by adding a specified amount of reagent-grade raffinose to a specified amount of water. In consideration of the amount of raffinose in practical sugar production, the ratio of raffinose to water in solution was chosen as 2% and 4%. According to the solubility of sucrose in the presence of raffinose at each temperature (Liang et al., 1988), an excess of sucrose over saturation was added to the raffinose-water solution in a batch crystallizer, identical to that employed by Liang et al. (1987b). Following the dissolution of the sucrose crystals at elevated temperature, the solution was cooled and maintained at crystallization temperature in a constant temperature water bath.

Seed crystals were prepared by sieving reagent-grade sucrose. The average size of the seed crystals as determined by Coulter Model Z_{BI} particle counter was 115 μm, with a range from 90 to 140 μm.

The apparatus and technique for both seed crystallization in the photomicroscopic cell and the batch crystallization process were identical to that employed in previous studies (Liang et al., 1987a,b). In the suspension crystallizer experiments, the change in size distribution of crystals during growth was used to obtain a measure of both the rate of crystal growth and the distribution of growth rates. Similar results were obtained from the photomicroscopic cell, in which growth rates of the individual crystals were determined. Further details of the apparatus and technique may be found in Liang et al. (1987a,b) and Berglund (1980).

In the photomicroscopic cell experiments, the projective images of sucrose crystals were obtained in the pictures. Because most crystals lie on either the 001 or 100 face, there were mainly two types (I and II) of projective image as shown in Figure 1. In this study, both the equivalent diameter based on the projective area and the dimensions along each axis (*a*, *b* for *Type I and c*, *b for* Type II) were determined by the image analysis. Therefore, growth rates based on the equivalent diameter and for each axis could be calculated. Because the evaluated number of crystals with projective Type I was low, analysis of mean growth kinetics for this image was not undertaken.

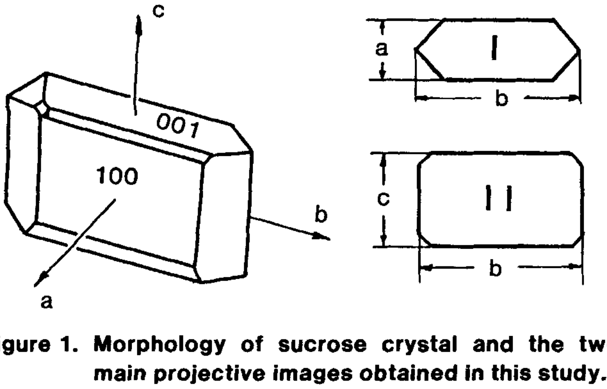

Figure 1. Morphology of sucrose crystal and the two main projective images obtained in this study.
Type I: lying on face 001; Type II: lying on face 100

Results and Discussion

Figure 2 shows examples of crystal size (area-based equivalent diameter) vs. time plots for individual seeds growing in the photomicroscopic cell in the presence of 2% raffinose under uniform conditions. The straight lines with varying slopes indicate that the sucrose crystals, in the presence of raffinose, grew in the same way as those in the pure system (Liang et al., 1987a). That is, each individual crystal grew at a constant rate; however, each crystal grew at a slightly different rate. For growth rates along the *c* and *b* axes, similar results were found for both pure and impure systems, and similar plots to Figure 2 were obtained. In the batch suspension crystallization experiments, the crystal size distribution (CSD) curves at sequential times displayed the same character as in the pure system (Liang et al., 1987b). That is, the variance (or spread) of the CSD increased with time. Therefore, growth rate dispersion was found to exist in the raffinose-sucrose-water system, similar to that shown in the pure sucrose-water system.

Morphology

In order to check the raffinose effect on the morphology of sucrose, the ratios of dimensions *b* to *a* or *b* to *c* for each crystal with projective image Type I or Type II were analyzed. These ratios are similar to the elongation parameter of Vaccari et al.

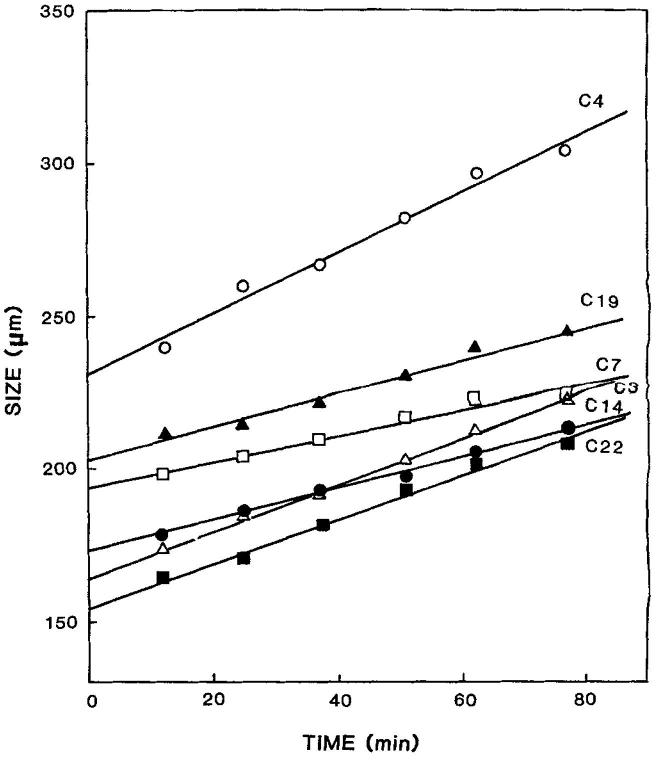

Figure 2. Characteristic size (area-based) vs. time plots for individual seed crystals growing in the photomicroscopic cell in the presence of 2% raffinose.
(ΔC = 0.99 kg/kg; T = 333 K)

(1986). The average dimension ratio, a:c:b, for the initial seeds in this study was obtained as 1:1.44:1.96 by image analysis. The rate of change of these ratios against time during the growth of each crystal in each run was calculated by performing linear regression using the morphology change of each seed crystal under each condition. The average results are plotted in Figure 3, where the hundreds of individual crystal data points are omitted. The rate of change of the b/c axis dimension ratio was found to change from 0.000508 min^{-1} at 0% raffinose to 0.000560 and 0.000822 min^{-1} at 2 and 4% raffinose, respectively. For the b/a axis dimension ratio, the rates of change were 0.000957, 0.00136 and 0.00251 min^{-1} at 0, 2 and 4% raffinose, respectively. It can be seen that the ratio of dimensions for both b to c and b to a axes, increases with time, even in the pure sucrose system. The presence of raffinose increases this trend, especially at the higher concentration of raffinose ($I/W = 4$).

The presence of raffinose decreases growth rate along all the axes—a, c and b. However, its effect on the a and c axes is stronger than that on the b axis. Based on these results, it may take a long period of time for a seed to become needle-shaped under these growth conditions, although it eventually will.

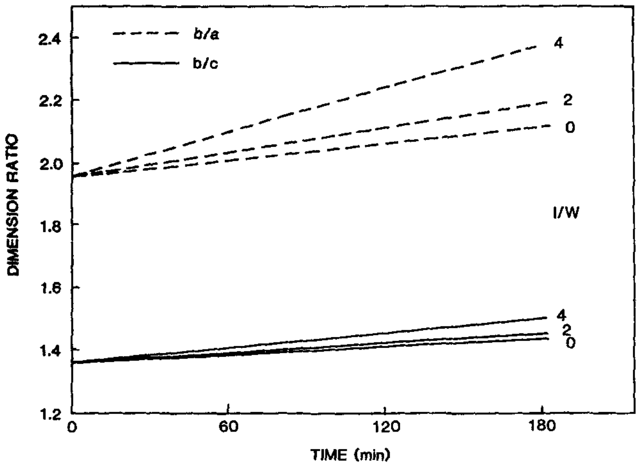

Figure 3. Average changes in dimension ratios for both the b to c and the b to a axes against time for seeds growing in the photo-microscopic cell.

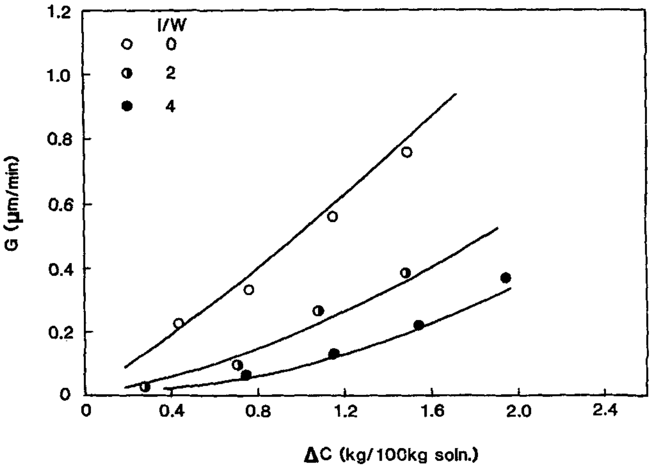

Figure 4. Mean growth rate along axis c vs. supersaturation at various raffinose levels for seeds growing in the photomicroscopic cell at 323 K.

Growth kinetics

Figure 4 shows the growth rate as a function of supersaturation and impurity level at 323 K for growth of seeds along the c axis in the photomicroscopic cell. Figure 5 shows growth kinetics of the c axis as a function of temperature at an impurity level of $I/W = 2$. Similar graphs were obtained for all other cases studied as well. It was found that the decrease in growth rate observed with increasing raffinose level occurred in both the suspension reactor and the photomicroscopic cell. For example, at a supersaturation of $\Delta C = 1$ kg sucrose/100 kg solution and a temperature of 323 K, the growth rate in the suspension reactor was retarded by approximately a factor of 5 in the presence of 4% raffinose. The growth retardant effect of raffinose was also seen to be slightly greater at lower temperatures. These results are in accord with the previous results of Smythe (1967b) and Binder and Murphy (1982).

The growth data were analyzed according to the standard growth kinetic model given as

$$G = A \exp(-E/RT)\, \Delta C^n \tag{1}$$

Values of the frequency factor, A, activation energy, E, and the supersaturation exponent, n, for the present conditions at a fixed I/W were obtained using the nonlinear regression procedure. The results of this statistical analysis for each condition of impurity level, temperature, growth environment and growth axis are shown in Table 1.

Under pure conditions, sucrose growth in the stagnant environment of the photomicroscopic cell was influenced significantly by a mass transfer mechanism. This was evident from an activation energy of 28.9–33.1 kJ/mol and a supersaturation exponent near unity for Cases II and III ($I/W = 0$) in Table 1. The addition of raffinose, however, raised the activation energy to 45.6–57.7 kJ/mol and the supersaturation exponent to about 1.5 for $I/W = 2$ and 2 for $I/W = 4$. This suggests that surface integration of molecules into the lattice had become a more important factor in the growth mechanism in the presence of

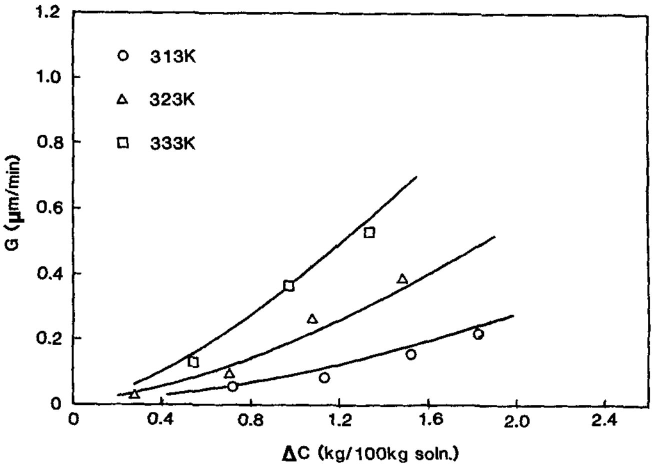

Figure 5. Mean growth rate along axis c vs. supersaturation at various temperatures for seeds growing in the photomicroscopic cell at $I/W = 2$.

Table 1. Kinetic Model (Eq. 1) for Different Raffinose Levels in Suspension Reactor and Photomicroscopic Cell

Case*	I/W [%]	A [μm/min]	E* [kJ/mol] Est.	Std.	Low.	Upp.	n** Est.	Std.	Low.	Upp.	RSS† [$\mu m^2/min^2$]
I	0	$9.9(10)^9$	28.4	3.35	55.2	70.3	2.0	0.1	1.8	2.2	0.122
	2	$1.9(10)^{11}$	72.8	4.2	63.6	82.0	1.9	0.2	1.5	2.3	0.019
	4	$2.1(10)^{10}$	69.0	6.7	55.2	82.8	2.2	0.3	1.6	2.7	0.032
II	0	$1.1(10)^5$	33.1	2.1	28.0	38.1	1.1	0.03	1.1	1.2	0.021
	2	$4.3(10)^8$	57.7	5.4	45.6	70.3	1.5	0.2	1.1	1.9	0.009
	4	$3.8(10)^6$	47.3	3.3	39.7	54.4	2.0	0.2	1.6	2.4	0.005
III	0	$3.9(10)^4$	28.9	1.7	25.1	32.6	1.2	0.01	1.2	1.2	0.039
	2	$3.9(10)^8$	56.5	7.9	38.1	74.5	1.6	0.3	1.0	2.3	0.059
	4	$4.2(10)^6$	45.6	2.9	38.9	52.7	2.1	0.2	1.6	2.7	0.034

*Case I – in suspension reactor
Case II – in photomicroscopic cell, along *c* axis
Case III – in photomicroscopic cell, along *b* axis
†RSS – residual sum of squares

**Est. = estimated value
Std. = asymptotic standard error
Low. = approximate lower value of asymptotic 95% confidence interval
Upp. = approximate upper value of asymptotic 95% confidence interval

raffinose and that bulk diffusion had become less important. Under these conditions, both surface incorporation of sucrose into the crystal lattice and volume diffusion of sucrose molecules to the crystal surface were important factors in crystal growth.

In the agitated environment of the suspension reactor, pure sucrose grew by predominantly a surface integration mechanism. The activation energy for these conditions was about 62.8 kJ/mol with a supersaturation exponent of two as seen in Case I ($I/W = 0$) in Table 1. The addition of raffinose, in this case, had negligible effect on both the supersaturation exponent and the activation energy.

Growth rate dispersion

A power law model of the form

$$\sigma_G^2 = \alpha G^\beta \tag{2}$$

was used to determine the extent of growth rate dispersion under various conditions. The parameters α and β were obtained for each experimental condition, both in the suspension reactor and the photomicroscopic cell, by using a linear regression on the logarithmically transformed coordinates. In order to compare the model fit at different conditions, a series of T-tests on the slopes and intercepts were performed.

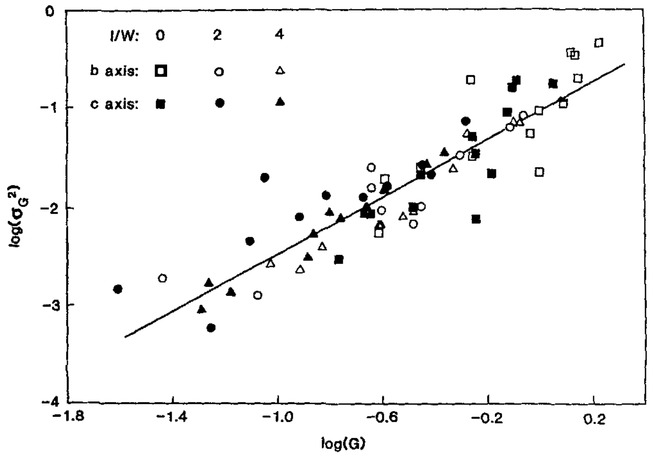

Figure 6. Relationship between variance of the growth rate distribution and mean growth rate for seed growth in the photomicroscopic cell.

The T-tests for *b* or *c* axis growth in the photomicroscopic cell indicated that there was no significant difference in the dependent of σ_G^2 on G for different raffinose content levels ($I/W = 0, 2, 4$). Further T-tests for all the raffinose content levels showed that there was no significant difference in GRD between *b* axis growth and *c* axis growth. Therefore, the model fits could be considered statistically identical, and the extent of GRD for sucrose seed crystal growth in the photomicroscopic cell under all conditions studied can be represented by a single expression given as

$$\sigma_G^2 = 0.09\, G^{1.46} \tag{3}$$

and shown in Figure 6.

The T-tests also showed that, for growth in the suspension reactor, the fits of σ_G^2 vs. G could be considered statistically identical for the conditions with raffinose level of $I/W = 2$ and 4, but significantly different between pure ($I/W = 0$) and impure ($I/W = 2, 4$) systems. This comparison is shown in Table 2, Cases A and B, and shown in Figure 7.

Comparing the GRD for the photomicroscopic cell and the suspension reactor, it was found that a significant difference existed for the impure system with the presence of raffinose. This is unlike for the pure system in which the extent of GRD was statistically identical (Liang et al., 1987b) between cell and reactor. This difference can be seen in Table 2, Case A and C,

Table 2. Parameters in Eq. 2 for Different Cases of Sucrose Growth

Case*	log(α) Est**	Std.†	α	β Est.**	Std.†
A	−0.751	0.220	0.18	1.51	0.11
B	−0.973	0.179	0.11	1.63	0.14
C	−1.118	0.260	0.08	1.32	0.11

*A – suspension reactor growth in the presence of raffinose
B – suspension reactor growth in pure system
C – photomicroscopic cell growth of seeds (*b* and *c* axes) in the presence of raffinose
**Est. – estimated value
†Std. – standard error

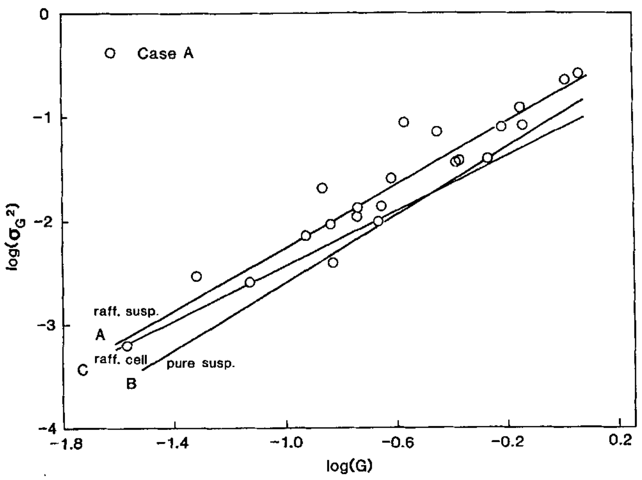

Figure 7. Comparison of dependence of variance of the growth rate distribution, σ_G^2, on the average growth rate, G, for different growth conditions.

and in Figure 7. Comparing line A and C, at lower mean growth rates, the magnitude of GRD was increased only slightly by the presence of raffinose. At higher mean growth rates, however, this difference was increased. That is, as the crystals grew faster, the effects of raffinose on GRD were increased. These results may be attributable to the incorporation of raffinose into the lattice of growing sucrose crystals, although further research is necessary to verify this effect. New experimental techniques are necessary to demonstrate these effects more clearly.

The above results suggest an interesting anomaly. It can be seen that GRD in the cell for impure system is identical to that for the pure system in the cell, yet different from the pure system in the suspension reactor. Logically, one might conclude then that the GRD in the cell is different from that in the reactor for pure sucrose. This would appear to contradict our previous results (Liang et al., 1987b) which suggest that these were the same. This anomaly may be due to the different experimental methods involved in determining growth rate (*b* and *c* axis changes in this work vs. changes in equivalent circular diameter in previous work) or it may be due to the tenuous nature of these statistical comparisons. It is apparent that more sensitive techniques for investigating GRD changes must be developed.

Acknowledgement

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Notation

A = frequency factor, μm/min
ΔC = supersaturation, kg sucrose/100 kg solution
E = activation energy for growth, kJ/mol
G = mean growth rate, μm/min
I/W = mass ratio of raffinose to water in solution, %
n = supersaturation exponent in Eq. 1
R = ideal gas constant, 8.314 kJ/mol · K
T = temperature, K
α = constant in Eq. 2
β = exponent in Eq. 2
σ_G^2 = variance of growth rate distribution, $\mu m^2/min^2$

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