Crystal Growth Rates and Dispersion for *D*-Fructose from Aqueous Ethanol

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The growth of fructose crystals from aqueous ethanolic solutions was studied using a 1-L seeded batch crystallizer. The growth kinetics were found to linearly depend on the relative supersaturation of the crystallizing tautomer (β-D-fructopyranose). The growth-rate constant increased slightly with increasing temperature and increasing solvent ethanol content. The growth rates are lower than those for aqueous solutions of comparable supersaturations. Fructose displays significant growth-rate dispersion ($q = 0.35$) when crystallized from aqueous ethanolic solutions. The growth-rate dispersion is independent of solvent composition and temperature within the range studied, although it is slightly higher than is seen in crystallization from aqueous solutions.

Introduction

Fructose ($C_6H_{12}O_6$) is a monosaccharide that is widely used as a sweetener, in both liquid high-fructose corn syrup (HFCS) and solid forms. It is produced commercially through the enzymatic hydrolysis of starch into glucose, and subsequent isomerization of glucose to fructose (Ishakawa et al., 1978). This process produces an aqueous syrup of approximately 42% fructose, 52% glucose, and 6% other sugars on a dry weight basis. Chromatographic enrichment is used to generate a fructose-rich sidestream suitable for blending with the weak isomerized syrup to give a 55% HFCS syrup with a sweetness similar to cane sugar. The chromatographically enriched fructose stream is also a suitable feed for crystallization processes. Fructose may also be produced from plant inulins for hydrolysis, or by fermentation using strains of *Zymomonas mobilis*, which produce high concentrations of fructose and ethanol when grown on a sucrose medium (Edye et al., 1989).

Fructose has a very low solubility in ethanol compared to that in water. A saturated aqueous solution of fructose at 30°C contains 81.9 wt. % fructose (Bates et al., 1942), whereas in ethanol the solubility is 3.5 wt. % fructose (Flood et al., 1996a). The high solubility of fructose in water leads to high solution viscosity. The viscosity of a saturated aqueous fructose solution at 30°C is 1910 mPa·s, whereas a saturated ethanolic fructose solution has a viscosity of approximately 2

mPa·s. The benefits of a reduction in solubility and solution viscosity have led to the addition of lower alcohols, including ethanol, to concentrated fructose syrups to enhance crystallization (Mahoney, 1994; Day, 1985).

Fructose occurs naturally in solution in five tautomeric forms (Figure 1), yet only the *β-D-*fructopyranose form crystallizes. The tautomers interconvert in solution by mutarotation. In aqueous solutions the mutarotation rates are high (Cockman et al., 1987; Shallenberger, 1978) and the crystallization kinetics sufficiently slow (Shiau and Berglund, 1987) that the tautomeric equilibrium will be maintained during crystallization. However, it was shown by Flood et al. (1996b) that mutarotation in aqueous ethanolic solutions is sufficiently slow that crystallization can move the tautomeric equilibrium away from the equilibrium *β-D-*fructopyranose (the crystallizing tautomer) concentration. Hence it is important in aqueous ethanolic crystallizations of fructose to express the supersaturation in terms of the tautomer, *β-D-*fructopyranose, rather than total fructose.

Shiau and Berglund (1987) studied the crystal growth of fructose in aqueous solutions. The growth of fructose crystals in aqueous solutions was shown to be size independent, with significant growth-rate dispersion. The number mean growth rate, $\overline{G}$ (μm/min), in aqueous crystallization was determined to be:

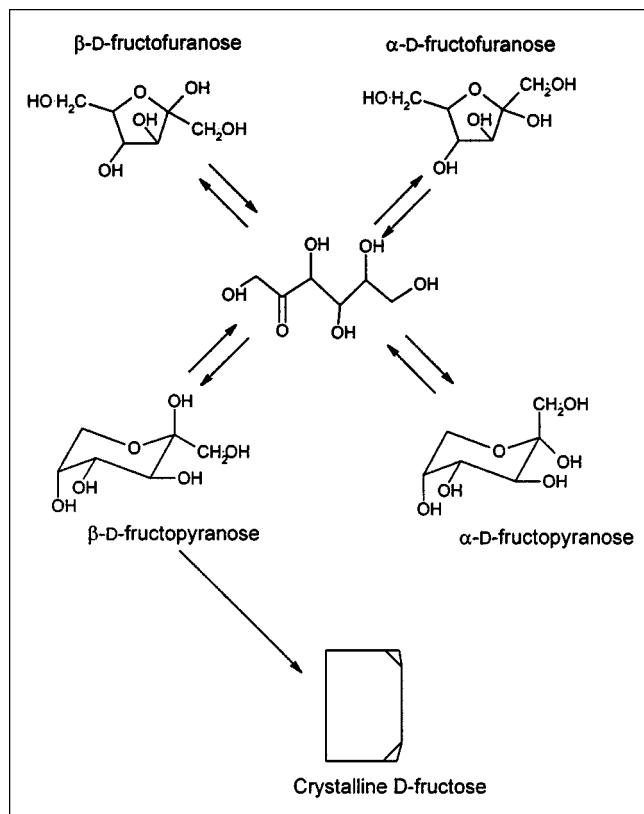$$\overline{G} = A \exp\left(\frac{-E}{RT}\right) \sigma^n,$$

Figure 1. Mutarotation reactions and crystallization of *D*-fructose.

where $A = 4.0 \times 10^{-3}$ m/s, $E = 25.5$ kJ/mol, and $n = 1.25$. The variance of the growth rate distribution was evaluated as:

$$\sigma_G^2 = a\overline{G}^b,$$

where $a = 1.0 \times 10^{-7}$ $(m/s)^{0.65}$, and $b = 1.35$. Shiau and Berglund (1987) concluded that both surface integration and diffusion were important to fructose crystal growth from aqueous solutions. The study also showed that growth-rate dispersion can be observed in systems where the crystal growth was dominated by diffusion.

Chu et al. (1989) investigated the effect of additives on aqueous crystallization of fructose. It was found that glucose inhibited fructose crystal growth by increasing the solubility of fructose in water, thus reducing the effective supersaturation of fructose. Difructose dianhydrides inhibited the surface integration of fructose molecules due to their adsorption onto the crystal surface. Both additives were shown to significantly reduce the fructose crystal growth rate.

There are few published data on the crystal growth kinetics or growth dispersion of fructose in aqueous ethanolic solutions. Johns et al. (1990) and Addai-Mensah (1992) determined limited growth-rate kinetic and dispersion data; however, there are disagreements between the studies on the effect of temperature on crystal growth rates, and the magnitude of growth-rate dispersion effects.

Addai-Mensah (1992) noted an unusual period of crystal growth during the initial stages of batch aqueous ethanolic crystallizations, where the crystal grew at accelerated rates. Ignoring the initial stages, Addai-Mensah modeled the growth-rate kinetics as

$$G = k_G \sigma^{1.2},$$

where $\sigma =$ relative supersaturation, and G is the change in volume equivalent size with time, in μm/min units. The growth-rate constant k_G was equal to 2.5 and 3.0 μm/min at 30 and 40°C, respectively. The growth-rate dispersion at 30 and 40°C was found to be a function of the solvent composition

$$q = a_0[1 - a_1(E/W)],$$

where q is the change in standard deviation of the sample with change in size, and E/W is the mass ratio of ethanol/water in the solvent. The constants, a_0 and a_1 were evaluated as 0.7 and 0.1, respectively, for E/W values between 2 and 9.

The objective of this work described in this article was to determine the growth-rate kinetics and growth-rate dispersion of *D*-fructose over the range of temperature and solvent composition likely to be used in industrial aqueous ethanolic crystallization.

Materials and Methods

Materials

The fructose used in all experiments was anhydrous *D*-fructose (A.E. Staley, IL, USA). It was dried at 65°C under a vacuum of 600 mm Hg for 24 h before use, and after drying was stored in a desiccator over silica gel. This procedure was necessary, since fructose is hygroscopic at relative humidities greater than 50%. The fructose was analyzed by high-performance liquid chromatography (HPLC) analysis, and was found to contain no glucose or any other identifiable species. Ethanolic solutions were prepared from anhydrous ethanol (CSR Ltd., Sydney), which was determined to be $< 0.3\%$ water by Karl Fischer titration, and deionized water treated by reverse osmosis.

Seed crystal production

Seed crystals for the batch crystallizations were prepared by two methods, ball-milling and nucleation. The ball-milling of commercially produced fructose crystals was done using a 130 mm dia., 2-L glass Schott bottle containing 50 ceramic balls (10 mm dia.) and about 0.5 kg of crystalline fructose in fructose-saturated ethanol for 48 h. The ball-milled product size range was 10–200 μm. These crystals were wet sieved in fructose-saturated anhydrous ethanol, and the crystals in the 38–45-μm sieve cut were retained, washed, and kept in fructose-saturated ethanol at room temperature as the seed. The selected crystals had a size range from 10 μm to 90 μm (by Malvern Mastersizer/E), and a volume equivalent number mean size of 31 μm. Their particle-size distribution is shown in Figure 2.
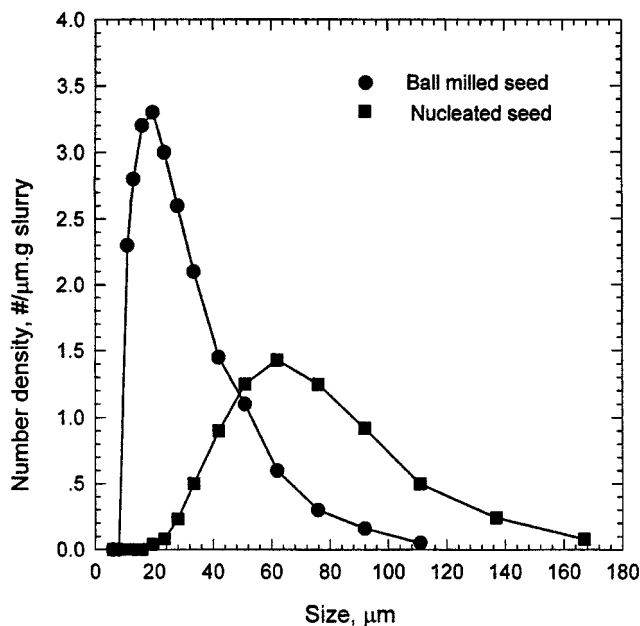
Figure 2. Particle-size distributions for seed crystals produced by nucleation, and by ball-milling.

Nucleated seed crystals were produced from a solution of ethanol/water mass ratio of 6, saturated at 60°C with *D*-fructose. This solution was cooled to 40°C while being stirred at 400 rpm. The solution was held under these conditions for 24 h, during which time nucleation occurred. The nucleated crystals had a number mean crystal size of 73 μm, and the same habit as was found in the product crystals of batch crystallization experiments. The particle-size distribution of these seed crystals is also shown in Figure 2.

Experimental apparatus

The seeded batch-crystallization experiments were performed in a 1-L glass vessel with a sealed glass lid to reduce ethanol loss (Figure 3). The crystallization slurry was agitated at 600 rpm by a centrally located, four-blade, 45° pitch impeller driven by a 70-W overhead mixer. The crystallizer was maintained at constant temperature (± 0.1°C) by immersion in a thermostatically controlled water bath.

Analyses

Total fructose concentration was measured using the total solids method for sugars (Anon., 1991). The concentration of β-*D*-fructopyranose was determined using gas chromatography (GC) of the trimethylsilyl derivatives of the fructose tautomers (Flood et al., 1996b). The mass of seed crystal charged was used with the seed-crystal size distribution to calculate the number of crystals per kg crystallizer slurry.

Crystallization solutions were checked for glucose contamination by HPLC. A 20-μL volume of the diluted solution was injected onto a Shodex S-801/S column (in the Na$^+$ form) operating at 75°C with a differential RI detector (Waters R401). The mobile phase was purified degassed water at a flow rate of 0.5 mL/min. Calibration standards were pro-

duced using analytical-grade glucose and fructose. Glucose could be detected to 5-mg/L solution.

The crystal-size distribution was measured using a Malvern Mastersizer/E with a 300-mm focal-length lens and a 15-mL stirred suspension cell. The volume fraction crystal-size distribution (CSD) was converted to a number CSD to allow its use in the population balance model. The mean crystal growth rate (G) was determined by the change in the number mean crystal size (L_{10}), and also through a mass-balance technique.

The crystal growth-rate dispersion was characterized by the coefficient, q, introduced by Larson et al. (1985) as the change in the standard deviation of the CSD with growth

$$q = \frac{\Delta \sigma_L}{\Delta L_{10}}.$$

Results and Discussion
Initial high crystallization rates

Crystallization experiments at 24, 30 and 40°C with relative supersaturations (σ) of up to 1.1 displayed no nuclei formation, crystal breakage, or agglomeration. The relative supersaturation was measured with respect to β-*D*-fructopyranose, the crystallizing tautomer. Figure 4 shows a typical set of CSD from a batch crystallization, plotted as cumulative number oversize against volume equivalent crystal size. This shows a substantially constant crystal number per g slurry as the crystallization proceeds. The CSD broaden with time, which indicates either size-dependent crystal growth, and/or crystal growth-rate dispersion.

Growth rates were calculated using the number mean crystal size. All crystallization experiments displayed high initial
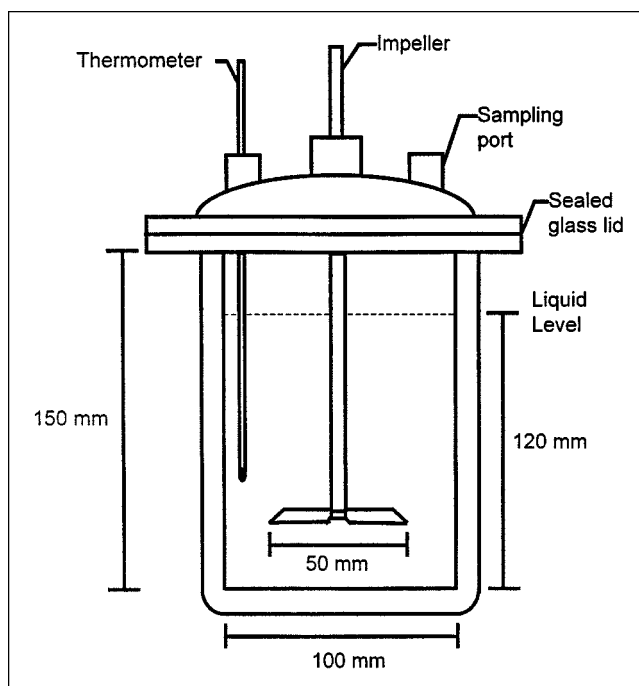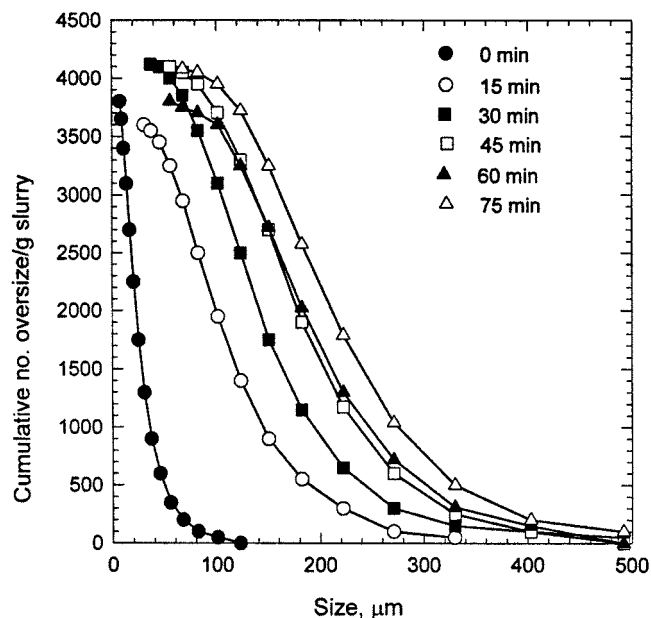

Figure 3. Batch crystallizer.

Figure 4. Change in crystal-size distribution with time for a typical batch crystallization.

mean crystal growth rates ($\overline{G}$ up to 6.5 μm/min). However, during the initial 30 min of batch experiments the mean crystal growth rate fell rapidly without a large change in the relative supersaturation (Figure 5). Furthermore, experiments differing only in respect of the initial relative supersatura-
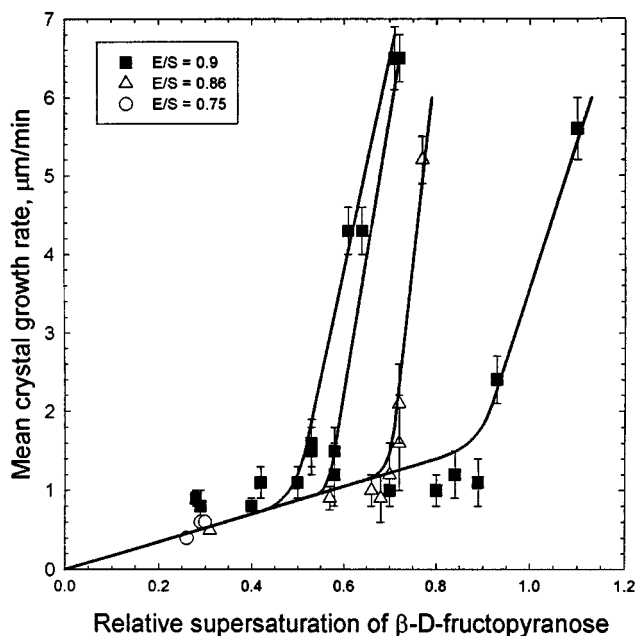

Figure 5. Mean crystal growth rates as a function of relative supersaturation (of the β-D-fructopyranose tautomer) at 24°C.

These experiments used ball-milled seed crystals. E/S refers to ethanol/(ethanol + water).

tions followed a different path of $\overline{G}$ vs. σ in the first 30 min of crystallization, but subsequently followed a common trend. These experiments were at 24°C, with an ethanol mass fraction in the solvent (ethanol and water) $E/S = 0.90$. Experiments with $E/S = 0.86$ and 0.75 are also shown in the figure.

This is the same phenomenon observed by Addai-Mensah (1992). He attributed this behavior to a history effect caused by ball-milling the seed crystals. The unusually high growth rates were observed until the crystals had grown by approximately 45 μm. Addai-Mensah showed that this effect was not due to size-dependent crystal growth, or to poisoning by difructose dianhydrides, which pose a particular problem in the aqueous crystallization of fructose (Chu et al., 1989). The results in Figure 4 also confirm that the effect was not due to size-dependent growth. The initial high growth rates could only be caused if small crystals were faster growing than large ones, which would cause the CSD to narrow with time, when in fact, they widen. Chu et al. (1989) showed that glucose poisoned aqueous fructose crystallization, but only significantly when glucose concentrations exceeded 0.05 g glucose/g water. This effect is not likely in this study, as the solutions used for crystallization in the current study were found to be free of glucose, at the 0.01 g/g level detectable by HPLC.

Comparing batch crystallization experiments seeded with ball-milled or nucleated seed crystals tested the hypothesis that the initial high crystal growth rates were due to a surface history effect. The nucleated seed crystals displayed a similar habit to product crystals from experiments using the ball-milled seed crystals, and had no apparent surface irregularities when viewed using light microscopy. Consequently, it was considered there would be no surface history effect from the use of this seed. Two experiments conducted at 24°C and $E/S = 0.90$ using the two types of seed (nucleated and ball-milled) are compared in Figure 6. The initial crystal growth rates determined from the nucleated seed experiment were significantly higher than would be expected by extrapolation of the relationship between $\overline{G}$ and σ found later in the crystallization, although not as high as for ball-milled seed. This demonstrates that the high initial growth rates were not solely due to a surface history effect caused by ball-milling.

It is probable that the severe reduction in the mean crystal growth rates in the first 30 min of batch crystallization is due to a slow poisoning effect that starts when crystals are added to solution. The poison could not be identified, although it could be an ethanol–fructose complex, or a noncrystallizing tautomer of fructose. This latter case would be analogous to the known inhibition of the growth rate of α-lactose by the noncrystallizing tautomer β-lactose, which is the predominant tautomer in aqueous solutions of lactose (van Kreveld, 1969). In aqueous ethanolic solutions of fructose, the noncrystallizing tautomers, principally α- and β-D-fructofuranose, make up 60% of the fructose in solution (Flood et al., 1996b). However, the most likely poison among the noncrystallizing tautomers is α-D-fructopyranose, as the furanose structure is significantly different to the pyranose structure. The concentration of this tautomer in aqueous ethanolic solutions is above the detection limits for gas chromatography of the Me_4Si derivatives, but less than 1% of total fructose in solution (Flood et al., 1996b).

The high initial mean crystal growth rates were observed for a period of 30 min for the ball-milled seed and 20 min for
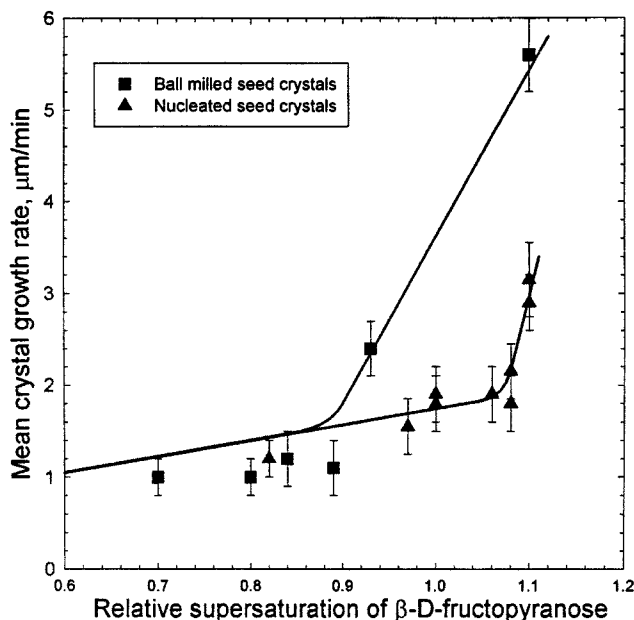
Figure 6. Crystallization experiments using ball-milled and nucleated seed at 24°C, $E/S = 0.90$.

Figure 7. Mean crystal growth rates of D-fructose from aqueous ethanolic solutions as a function of supersaturation of the β-D-fructopyranose tautomer, temperature, and solvent composition.

the nucleated seed. Subsequent to these periods, the relationship between the mean crystal growth rate and relative supersaturation was the same for both types of seed in all experiments (Figure 6). The shorter initial period of high growth rate observed for crystallizations performed with nucleated seeds may be due to poisoning that occurred during their growth in the nucleation vessel, before the seeds were added to the crystallization vessel.

The initial crystal growth rates were disregarded in subsequent analysis of the crystallization kinetics, but were up to four times greater than values predicted by the first-order rate equations used below to describe fructose crystallization in aqueous ethanol.

Growth kinetics

The crystallization kinetics was described for each set of conditions (temperature and E/S ratio) by the power-law model:

$$\overline{G} = k_G \sigma^n.$$

The relationship between $\overline{G}$ and σ at 24, 30 and 40°C for various solvent compositions is given in Figure 7. Batch crystallizations with $E/S = 0.75$ at 30 and 40°C required initial solution concentrations greater than 0.5 g fructose/g solution to achieve a suitable supersaturation due to the high solubility of fructose under these conditions. The resulting solutions were more viscous (> 20 mPa·s) and did not allow crystal separation from the solution quickly enough to achieve reproducible results. Hence these experiments were not included.

The growth-rate exponent was determined to be 1.0 ± 0.2 (95% confidence range) for all conditions, which is close to the value of 1.2 ± 0.1 obtained by Addai-Mensah (1992) for a
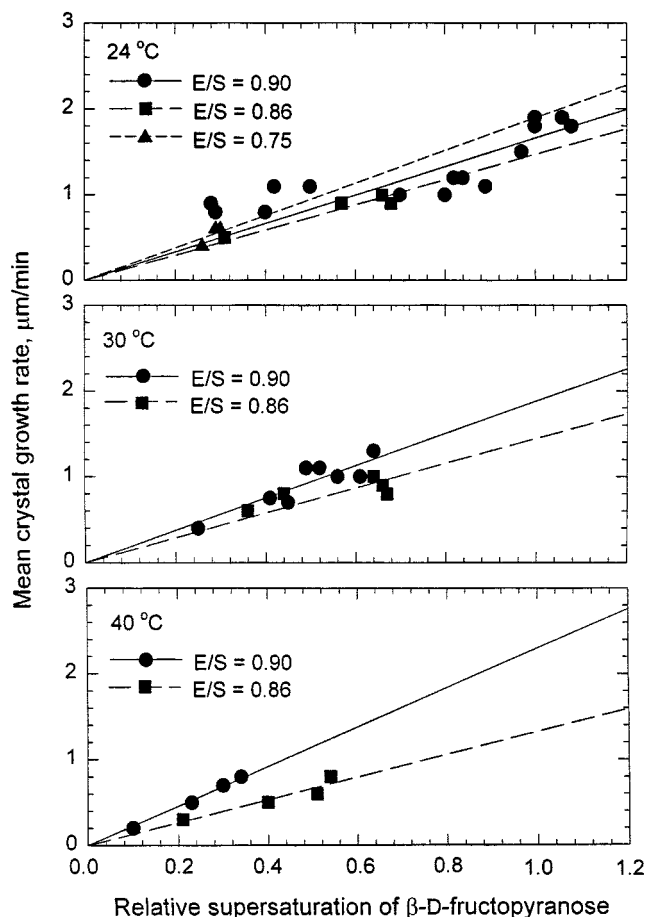
similar range of relative supersaturation. The difference in values may be due to Addai-Mensah determining the relative supersaturation in terms of total fructose, rather than β-D-fructopyranose. Flood et al. (1996b) showed that mutarotation of fructose in aqueous ethanolic solutions is sufficiently slow that seeded batch crystallization caused the β-D-fructopyranose tautomer to be depleted in solution.

It could be argued that since the tautomers may mutarotate in solution any tautomer that reaches the crystal surface may convert to the β-D-fructopyranose form in order to integrate into the crystal structure. However, the mutarotation reaction is acid/base catalyzed, and hence is faster when water molecules are available. As fructose molecules diffuse to the surface of the crystal, they lose their water of hydration, which could greatly reduce the rate of mutarotation.

For fructose crystal growth in aqueous (nonalcoholic) solution, the value of the growth-rate exponent n was found to be 1.25 (Shiau and Berglund, 1987). This value is not too dissimilar from the value of 1.0 found in this study. Shiau and Berglund suggested that both surface integration and diffusion may have been important. They expressed their relative supersaturation in terms of total fructose concentration, but
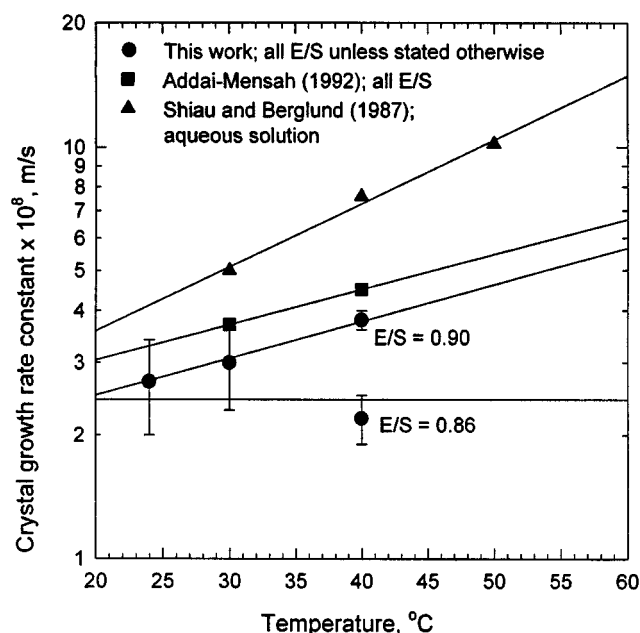
Figure 8. Crystal growth rate constant as a function of temperature.

All data has been modeled with a growth order of one.

Table 1. Crystal-Growth-Rate Constants (k_g) for Fructose Crystallized from Aqueous Ethanolic Solutions, with $\pm 95\%$ Confidence Intervals

Temp. (°C)	Rate Constant $\times 10^8$ (m/s)		
	$E/S = 0.75$	$E/S = 0.86$	$E/S = 0.90$
24	3.0 ± 0.7	2.5 ± 0.3	2.8 ± 0.3
30	—	2.5 ± 0.7	3.2 ± 0.3
40	—	2.2 ± 0.3	3.8 ± 0.2

Note: (—) Indicates no experiments at these conditions.

due to the very low crystal growth rates in their study and the higher mutarotation rates in aqueous solutions (Shallenberger, 1978; Cockman et al., 1987), it is likely that the tautomeric equilibrium would be closely maintained. Hence, for their experiments the two measures of supersaturation are equivalent.

The results of the three studies were compared (Figure 8) by recalculating the results of Addai-Mensah (1992) and Shiau and Berglund (1987), to determine the growth-rate constant for a crystal growth-rate order of one. For a given relative supersaturation, the growth rate of aqueous solutions appears to be approximately twice that of solutions with high ethanol content. Published kinetic studies comparing the crystallization of sugars from water and alcoholic solutions are rare. However, Gabas and Laguerie (1991) have shown that the crystal growth rate of D-xylose in aqueous solutions is 9 to 30 times faster than in aqueous ethanolic solutions for the same relative supersaturation.

Effect of temperature

The values of the rate constant (k_G) obtained from linear regression of the experimental data (Figure 7) are given in Table 1. At the higher ethanol contents ($E/S = 0.90$) the value of the growth-rate constant increases approximately 20% per 10°C rise in temperature. At the lower ethanol contents ($E/S = 0.86$) temperature has no measurable effect on the crystal growth kinetics. The results at the higher ethanol content are in agreement with Addai-Mensah (1992), who predicted a 20% increase in the growth rate constant between 30 and 40°C.

Flood et al. (1996a) showed that the viscosity of *saturated* aqueous ethanolic solutions of fructose with E/S larger than

0.85 decreases only slightly with increasing temperature, while the viscosity of those with E/S below 0.85 increases with increasing temperature. This unusual behavior is due to the large increase in fructose solubility with increasing temperature. Perhaps, the lack of crystal growth-rate dependence on temperature, especially at the lower ethanol contents, is due to the diffusivity of fructose in solution not increasing substantially with increasing temperature, as previously suggested by Johns et al. (1990).

Effect of solvent composition

There was no statistically significant effect of ethanol concentration on the growth kinetics of fructose from aqueous ethanolic solutions at 24 or 30°C, as seen by the value of growth-rate constants (Table 1). At 40°C, however, there is a significant increase (of 70%) in the crystallization rate constant as the E/S ratio is increased from 0.86 to 0.90.

Growth-rate dispersion

As seen from Figure 4, the CSD show a broadening with growth (growth-rate dispersion). The crystal growth-rate dispersion coefficient, q, was determined from the slope of a plot (Figure 9) of the standard deviation of the CSD against the number mean crystal size (L_{10}). The dispersion coefficients obtained are shown in Table 2. The dispersion coefficient is plotted against temperature in Figure 10. Temperature had no significant effect on q, hence, the results for different temperatures at the one E/S ratio are collected to give one data point. Figure 10 shows that in the current study, the solvent composition has no statistically significant effect on q. Since the variability in the value of the growth-rate dispersion coefficient is high, a constant value of 0.36 ± 0.10 is estimated for q independent of solvent composition and temperature.

Both Addai-Mensah (1992) and Johns et al. (1990) reported a small decrease in q with increasing ethanol content, although Addai-Mensah states that this is an unusual effect, since in his studies, the E/S ratio had no marked effect on the crystallization kinetics. Both these earlier studies also found no effect of temperature on q. The growth dispersion coefficients determined by Addai-Mensah (1992) and Johns et al. (1990), using an electronic sensing-zone device for CSD measurement, and Shiau and Berglund (1989), using a nucleation cell and light microscopy, are compared to those of the current study in Figure 10. The magnitude of q determined from the present study is similar to that found by Addai-Mensah (1992) and Shiau and Berglund (1989), but significantly higher than those found by Johns et al. (1990).
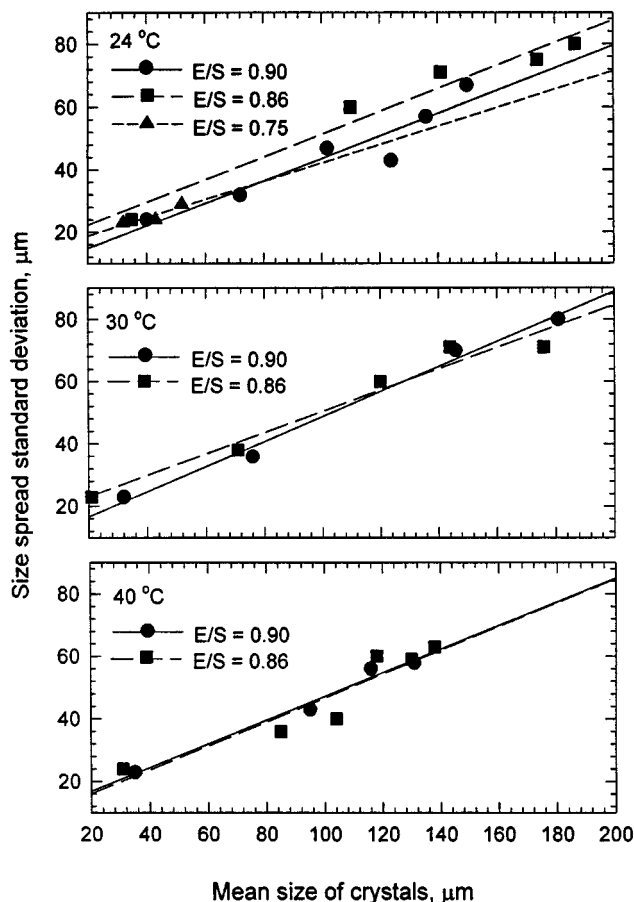
Figure 9. Relationship of size spread standard deviation with mean crystal size for *D*-fructose crystals grown in aqueous ethanolic solutions.
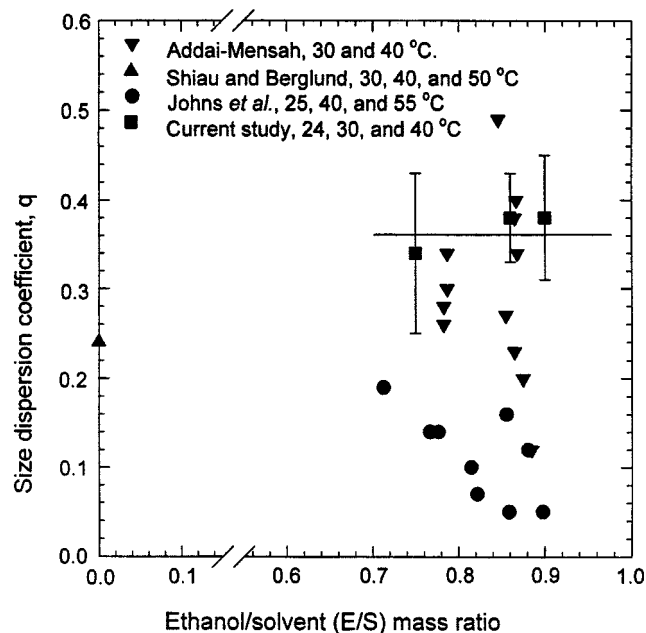

Figure 10. Size dispersion coefficient as a function of solvent composition for *D*-fructose grown from aqueous ethanolic solutions.

Conclusion

The crystal growth rate of fructose from aqueous ethanolic solutions displays a linear relationship with the relative supersaturation of the β-*D*-fructopyranose tautomer. The weak dependence on temperature suggests that the crystallization rate is at least partially dependent on the rate of diffusion of β-*D*-fructopyranose from solution. The significantly higher solubility at higher temperatures increases the viscosity of the crystallizing solution, thus minimizing the effect of increasing diffusivity with temperature.

The initial rate of crystal growth in batch experiments (for up to 30 min of growth) is significantly higher than subse-

quent crystal growth. This may be due to slow poisoning of crystallization either by noncrystallizing fructose tautomers, or by fructose-ethanol complexes present in solution at concentrations below detection limits.

Fructose crystallization displays significant growth-rate dispersion ($q = 0.35$). The values found are higher than those found for aqueous solutions. The growth-rate dispersion was not dependent on the solvent composition or crystallization temperature within the ranges studied.

Notation

$C =$ solution β-*D*-fructopyranose concentration, g β-*D*-fructopyranose/g solution
$C^* =$ equilibrium β-*D*-fructopyranose concentration, g β-*D*-fructopyranose/g solution
$E =$ mass of ethanol, g
$n =$ crystal growth rate order
$R =$ ideal gas constant, kJ/kmol·K
$S =$ mass of solvent (ethanol + water), g
$T =$ temperature, K
$\sigma_L =$ standard deviation of the crystal size distribution, μm

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Table 2. Size-Dispersion Coefficient, *q*, for Crystallization of Fructose from Aqueous Ethanolic Solutions, with ± 95% Confidence Intervals

Temp. (°C)	E/S = 0.75	E/S = 0.86	E/S = 0.90
24	0.28 ± 0.19	0.36 ± 0.11	0.36 ± 0.10
30	—	0.36 ± 0.06	0.41 ± 0.07
40	—	0.38 ± 0.09	0.38 ± 0.07

Note: (—) Indicates no experiments under these conditions.

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