

Contact Nucleation from Aqueous Dextrose Solutions

Contact nucleation studies were performed with the dextrose-water system. Under some conditions two crystallographic phases were formed, which were identified *in situ* using a laser Raman microprobe. In addition, the growth of the contact nuclei was monitored *in situ* using photomicroscopy. The results are discussed in the context of contact nucleation and growth models.

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Introduction

Dextrose is the common name for D-glucose, the pure crystalline solid recovered from almost completely hydrolyzed starch. Dextrose (corn sugar, starch sugar, blood sugar, grape sugar) is by far the most abundant sugar in nature and occurs either in the free state (monosaccharide form) or chemically linked with other sugar moieties. It can exist in three different crystalline forms: alpha monohydrate, alpha anhydrous, and beta anhydrous.

Contact nucleation is the primary source of new particles in many important industrial crystallizations. The exact source of these nuclei is not precisely known. This study focused upon such behavior in the important industrial process of dextrose crystallization. It was found by laser Raman microprobe that contact nuclei of both alpha monohydrate and alpha anhydrous dextrose result from the contact of an anhydrous parent crystal growing in pure solution. Under similar conditions using an industrial syrup, only one phase formed. These studies suggest that simple breakage from the parent crystal does not explain the source of contact nuclei. Both anhydrous and monohydrate dextrose contact nuclei exhibit growth rate dispersion wherein, under the same microscopic conditions, crystals grow at different rates.

Review of literature

Several researchers have attempted to prepare pure dextrose from starch conversion liquor either in syrup form or as a solid mass of crystals containing the mother liquor. The solubility curves of ice, alpha monohydrate, alpha anhydrous, and beta anhydrous dextrose were determined for the temperature range from -32 to 62°C by Young (1957). The shapes of these three crystals were reported by Becke (Newkirk, 1924) and the opti-

cal-crystallographic properties were determined by Dean (1974). The transitional temperature range between alpha monohydrate and alpha anhydrous in various concentrated solutions is 38 to 50°C (Dean, 1974; Edwards, 1982).

Behr (1881) crystallized individual crystals of anhydrous dextrose by seeding concentrated corn starch with a small amount of very pure anhydrous dextrose crystals. The seeded mother liquor was allowed to stand without agitation in heated rooms and care was taken to exclude any traces of dextrose hydrate crystals. This process was quite similar to that described by Soxhlet (1886).

In the early 1920's a successful commercial-scale method for production of pure dextrose monohydrate was invented by Newkirk (1936). Monohydrate dextrose crystals were produced by batch crystallization, wherein pure dextrose monohydrate seed crystals were added to a starch solution at a suitable temperature. A mixture of crystals and mother liquor was formed and the crystals were separated by centrifugation. At high supersaturation, nucleation of dextrose monohydrate was increased and the formation of many small crystals increased the surface area per unit weight of crystals. These small crystals required a large amount of wash water to remove the mother liquor and decreased the yields because of dissolution of crystals during centrifugation (Edwards, 1982).

The crystallization of anhydrous glucose required successive crystalline crops (Dean and Gottfried, 1950). Newkirk (1936) also invented methods for manufacturing alpha anhydrous and beta anhydrous dextrose in a crystalline form of high purity. However, Dean and Gottfried found that the concentration of impurities in the mother liquor was too great for successful operation. On the other hand, crystallization of dextrose in the monohydrate form proceeded satisfactorily despite the presence of impurities. Another advantage of the monohydrate was stronger temperature dependence of solubility as contrasted with that for the anhydrous form (Newkirk, 1936).

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Crystallization

Nucleation is the single most important phenomenon that controls the crystal size distribution. In most cases heavy suspensions do not support high supersaturation; therefore, homogeneous nucleation is probably insignificant. Nucleation that occurs at low supersaturations and requires the presence of growing crystals is called secondary nucleation. This has been observed to occur in carbohydrate systems and is usually referred to as false grain (Dean and Gottfried, 1950). In investigating the variables affecting the growth of dextrose crystals, Newkirk (1925) observed that great care was needed in cooling the mass in order to grow crystals properly without excessive formation of secondary nuclei.

Botsaris (1972) presented a comprehensive review of secondary nucleation, and de Jong (1979) reviewed the progress in understanding the phenomenon of secondary nucleation. Secondary nucleation itself has been confirmed by several investigators, including Timm and Larson (1968), Bennett et al. (1973), and Youngquist and Randolph (1972), when they noted the dependency of nucleation on the suspension density. The work of Randolph and Sikdar (1974) and Bauer et al. (1974) also indicated that crystals were being born into a measurable ($= 1-10 \text{ m} \times 10^{-6}$) size range.

Contact nucleation is the most important type of secondary nucleation in many industrial crystallizations. In the work of Garside and Larson (1978), Garside et al. (1979), and Rusli et al. (1980), the contact nucleation process was observed both with photomicroscopy and with a Coulter counter. They used a contacting device in a batch crystallizer and found that a large

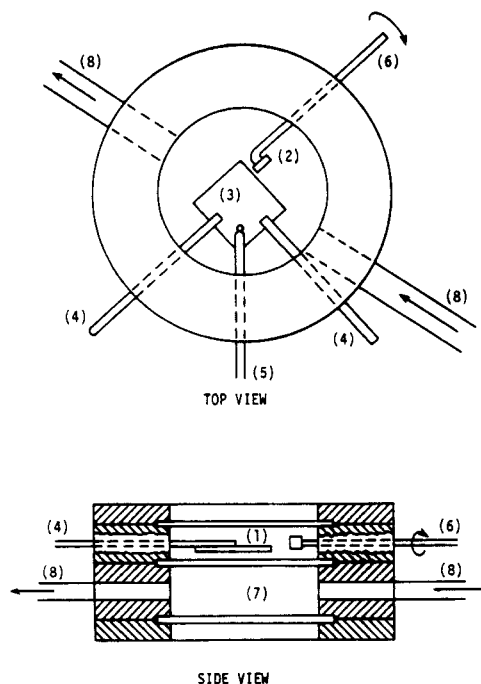


Figure 1. Nucleation cell.

1. Solution chamber
2. Parent crystal
3. Glass cover slip where parent crystal is moved
4. Support rods for glass cover slip
5. Thermistor
6. Movable rod holding parent crystal
7. Constant-temperature water chamber
8. Water inlet and outlet

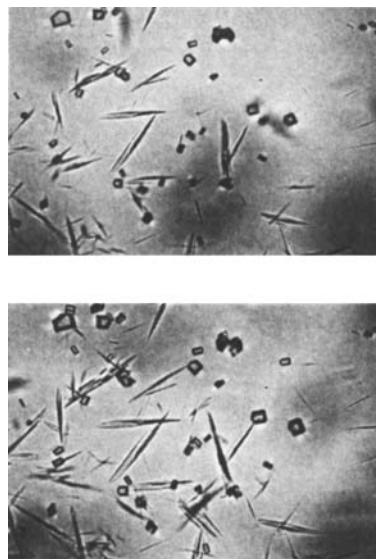


Figure 2. Typical photomicrographs of contact nuclei of dextrose.

Nuclei formed from pure solution at 314 K and 4 K supercooling
Elapsed time between photographs, 72 min; note the two different crystal forms present

number of microscopically visible nuclei were immediately formed, with a distribution of sizes as well as some anomalous growth behavior. Gwynn et al. (1980) reported contact nucleation studies with the sucrose-water system using the Coulter counter technique. These studies confirmed that contact nucleation is the primary source of new particles and that contact nuclei of sucrose have a measurable initial size distribution, not zero size as assumed in the mixed suspension, mixed product removal (MSMPR) crystallizer model. In addition, by observing the size distribution at subsequent times they inferred size-dependent growth.

Using the photomicroscopic technique, Berglund and Larson (1982) and Shanks and Berglund (1985) studied contact nucleation in the citric acid monohydrate-water and sucrose-water systems, respectively. These studies confirmed size-independent growth rate, growth rate dispersion, and initial nuclei size distribution. A linear regression analysis of time vs. size showed a constant growth rate for each crystal. Based on this premise, Ramanarayanan et al. (1982) proposed the constant crystal growth (CCG) model.

The occurrence of growth rate dispersion or size-dependent growth is important in modeling growth rate dispersion. The objective of this research was to study the growth rate and the initial size distribution of dextrose crystals in order to discriminate between these two phenomena. In addition, it was hoped that the study of contact nucleation would allow inferences to be made as to its mechanism.

Raman Spectroscopy

Raman spectroscopy is a form of vibrational spectroscopy analogous to infrared (IR) spectroscopy. When visible radiation is incident on a sample, it is absorbed, transmitted, reflected, or scattered. The scattered radiation may be elastically scattered (Rayleigh scattering) at the frequency of the incident radiation or inelastically scattered (Raman scattering) at some shifted

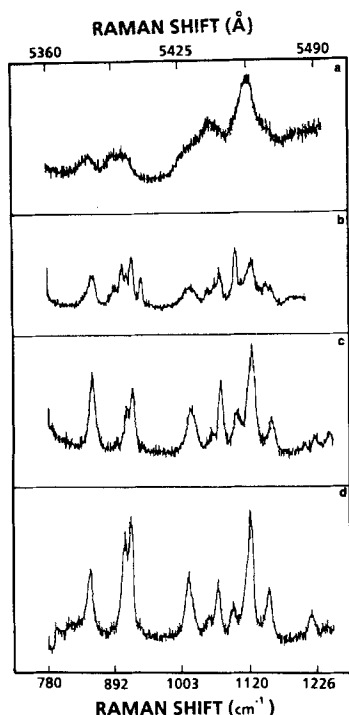


Figure 3. Raman shift of alpha monohydrate dextrose.

- A. Pure reagent grade
- B. Parent (needle) crystal
- C. Contact nuclei *in situ* at experimental conditions favorable to form two different phases
- D. Solution phase spectrum

frequency. Raman scattered light can be used to determine chemical structures by the study of molecular vibrations at characteristic frequencies.

Several features make Raman spectroscopy uniquely suited to the study of crystallization. The Raman spectrum of water does not obscure the spectrum of the dissolved species. The integrated intensity of a given Raman band is to a very good approximation linear, with molar concentration of the species in solution giving rise to the band. Micro-Raman spectroscopy permits *in situ* analysis of very small regions by focusing laser light through the objective lens of a microscope.

The laser Raman spectra of D-glucose, D-fructose, sucrose, cellobiose, maltose, and dextran for the 300 to 1,500 cm^{-1} region were respectively reported by Vasko et al. (1971, 1972), Cael et al. (1974), Mathlouthi et al. (1980), and She et al. (1974). D-glucose, cellobiose, maltose, and dextran consist of one or more D-glucose residues. Their vibrational spectra are very similar in this region (Vasko et al, 1971). Tu et al. (1978) used the advantages of laser Raman spectroscopy to study the mutarotation of D-glucose in aqueous solutions. Recent studies using the Raman effect provided information permitting reliable characterization of the anomers of D-glucose. In the analysis of alpha D-glucose, both as a crystalline solid and in aqueous solution, Vasko et al. (1972) obtained reasonable agreement between the calculated frequencies and those observed in the Raman spectrum.

Experimental Apparatus

Contact nucleation

In the present study, contact nucleation experiments were performed using the same photomicroscopic technique applied

to the citric acid monohydrate system by Berglund and Larson (1982). The photomicroscopic contact nucleation cell is shown in Figure 1. Experiments were conducted by first gluing a parent prism dextrose crystal (1–2 mm) to the movable rod. Growth of large crystals of dextrose was accomplished by carefully cooling a solution of dextrose to induce nucleation, then transferring a few nuclei to a slightly undercooled solution for growth.

After the parent crystal was obtained and mounted, a dextrose solution saturated at a known temperature was added to the cell. The solution was heated to destroy any nuclei that might have been generated by transferring the solution. Heating also slightly dissolved the parent crystal, insuring that no surface irregularities formed by washing and drying remained. The solution was cooled and the parent crystal allowed to grow. When the growth of the parent crystal was proceeding in a regular manner as evidenced by well-defined faces, it was slid approximately 0.5 cm across the glass plate shown in Figure 1 to generate contact nuclei. Contact nuclei were observed after a few minutes and the nuclei were photographed at time intervals by a camera-equipped microscope at 100 \times magnification. Dextrose solutions saturated at three different experimental temperatures and a standard industrial syrup saturated at 318 K were used in these studies.

Data analysis

An image analyzer was used to determine the area of each crystal in the photographs. The characteristic size of each crystal was taken as the square root of the area, i.e., the geometric mean size. This is the value referred to as size in the subsequent discussion.

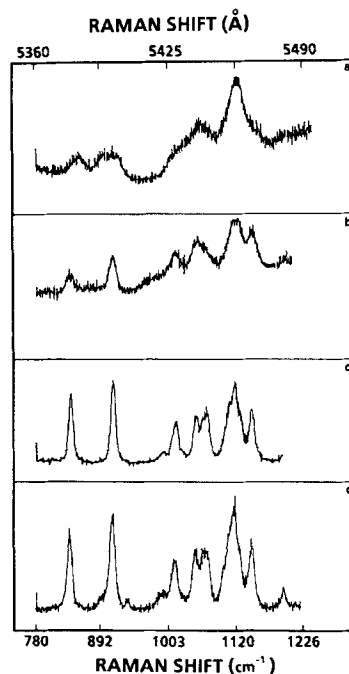


Figure 4. Raman shift of alpha anhydrous dextrose.

- A. Pure reagent grade
- B. Parent (prism) crystal
- C. Contact nuclei *in situ* at experimental conditions favorable to form two different phases
- D. Solution phase spectrum

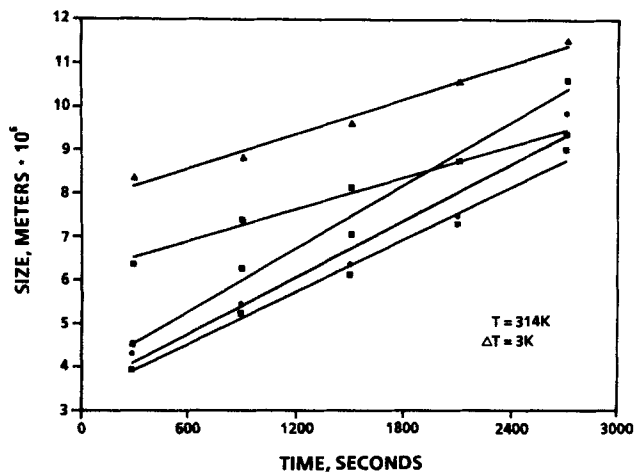


Figure 5. Size vs. time, alpha monohydrate dextrose contact nuclei in dextrose-water system.
Nuclei formed and grown at 314 K and 3 K supercooling.
Each line is for an individual crystal

Laser Raman spectroscopy

A laser Raman microprobe was used to identify different crystalline phases during contact nucleation. Dextrose solution was saturated at 318 K, filtered through a 0.45 m membrane, and the contact nucleation experiment was performed at 314 K as described above. The solution spectrum and the contact nuclei spectra were taken at a few locations after several hours. The Raman spectra of reagent alpha monohydrate dextrose, reagent alpha anhydrous dextrose, and the parent crystals (needle and prism) were also recorded. The spectrometer used was a

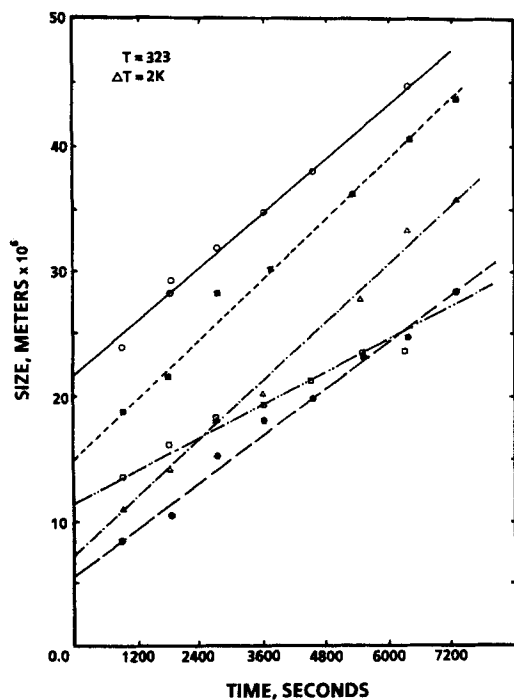


Figure 6. Size vs. time, alpha anhydrous dextrose contact nuclei.
Nuclei formed and grown at 323 K and 2 K supercooling
Each line is for an individual crystal

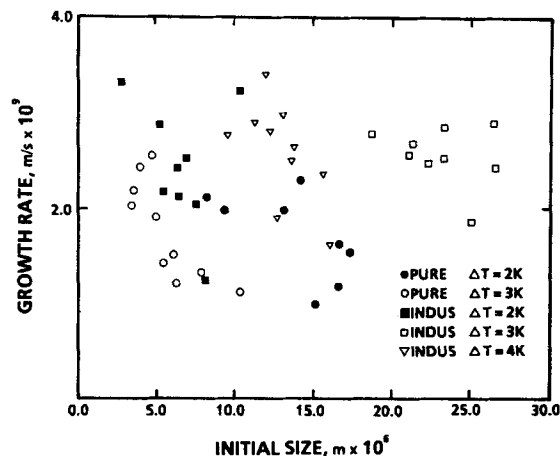


Figure 7. Growth rate vs. initial size, anhydrous dextrose contact nuclei.
Nuclei formed and grown at 314 K

Spex model 1406 equipped with a photomultiplier. All samples were illuminated with the 5145 Å line of a Coherent Radiation model CR-5 Ar⁺ laser using a SPEX Micramate. The recorded region was from 772 to 1,221 cm⁻¹ (5,360 to 5,490 Å) at a scan speed of 0.05 Å/s.

Results and Discussion

For the purpose of discussion, the well-formed crystals are designated prisms and the elongated crystals designated needles. The parent crystals (prisms) were grown at 323 K with 3 K undercooling, which promoted the formation of the anhydrous form. An anhydrous crystal (as verified by Raman spectroscopy) was contacted in all experiments that were favorable to both alpha monohydrate and alpha anhydrous formation. At 314 K with 4 K undercooling two different polymorphs, needles and prisms, were observed in the pure solution. The photographs taken at two different times are shown in Figure 2. However, these two different kinds of nuclei were not obtained simultaneously in the other contact nucleation experiments, or in comparable conditions with industrial syrup. Apparently the impurities present in the industrial syrup are important in inhibiting formation of needle crystals.

The laser Raman microprobe technique was used to identify the two different phases in pure solution at 314 K and 4 K undercooling. The Raman shift obtained at two different locations *in situ* are given in Figures 3 and 4. The important differences in these figures are the Raman shifts and splits at about 918 and 1,078 cm⁻¹. The band assignments for these two wave numbers are C₁-H stretch and C-O-H deformation (Vasko et al., 1972). The additional water molecule present in alpha monohydrate forms a bond (probably a hydrogen bond) with the C-O. This bond causes splitting and shifting of the bands at these wave numbers. Upon comparison of these spectra with the others recorded for alpha monohydrate and alpha anhydrous crystals, it was concluded that there were two different growing phases present. One phase was primarily alpha monohydrate dextrose (needles) and the other was entirely alpha anhydrous dextrose (prisms). It appears that some other phase may also have been present in the needle, as suggested by Dean (1974) and evidenced by the additional band at 942 cm⁻¹. Since an anhydrous parent crystal was used in the contact and two dif-

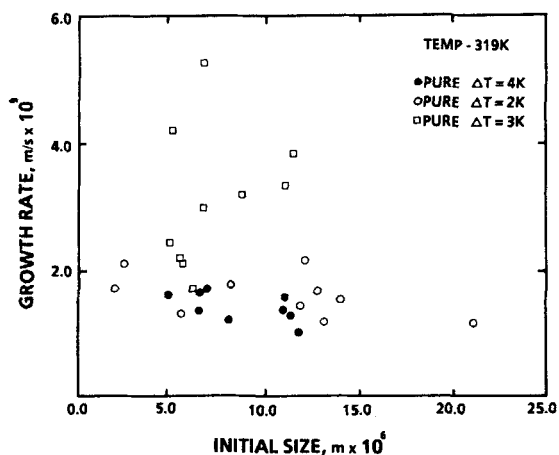


Figure 8. Growth rate vs. initial size, anhydrous dextrose contact nuclei.

Nuclei formed and grown at 319 K

ferent phases were formed, simple breakage cannot explain formation of the monohydrate phase. These results support the possibility that a semiordered layer is removed from the surface of a growing crystal in contact nucleation (Berglund and Larson, 1982). However, another possibility in the epitaxial growth of the monohydrate phase on an anhydrous nucleus. This should not be discounted since the Raman spectra indicate that the needles are not pure monohydrate. Clearly, the mechanism is still in question.

Figures 5 and 6 show examples of size vs. time plots for individual alpha monohydrate and alpha anhydrous crystals at different temperatures. The most important feature is their linearity, which indicates that each crystal grew at a constant but different rate. Each line has a correlation coefficient of at least 0.98. The intercepts of these plots also suggest that an initial size distribution may have been present. Unfortunately, it was not possible to study the genesis of the initial size distribution phenomenon due to the time resolution of this experiment. The growth rate was plotted against the apparent initial size and is presented in Figures 7, 8, and 9. The large amount of scatter in

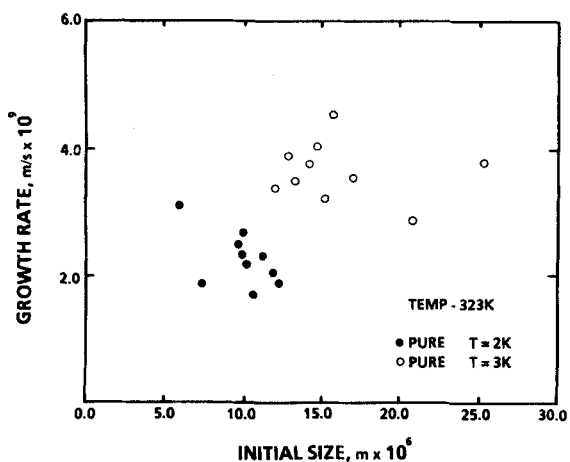


Figure 9. Growth rate vs. initial size, anhydrous dextrose contact nuclei.

Nuclei formed and grown at 323 K

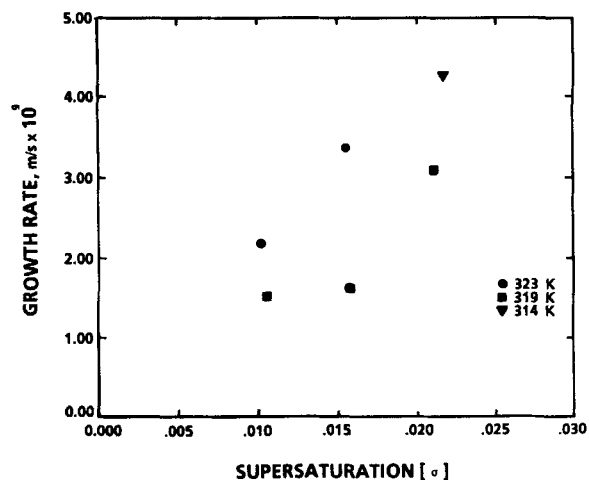


Figure 10. Mean growth rate vs. relative supersaturation, anhydrous dextrose contact nuclei.

Nuclei formed and grown at indicated temperatures

these data demonstrates little correlation between initial size and growth rate.

These results verify that the proper method to analyze the growth rate dispersion of this system is the constant crystal growth (CCG) model. Berglund and Larson (1984) showed in their analysis of citric acid monohydrate with the CCG model that the curvature in the semilogarithmic population density vs. size plot can be attributed to growth rate dispersion; the initial size distribution had a smaller effect. Figure 10 shows that an increase in supersaturation causes an increase in mean growth rate of anhydrous dextrose. It was not the purpose of this work to establish the correlation between growth rate and supersaturation. Figure 11 shows the trend between mean growth rate and variance of growth rate distribution. Faster growing crystals exhibit a larger variance of growth rate distribution. Further, these two figures indicate that growth rate dispersion may be correlated to supersaturation. To better understand or to further correlate this phenomenon, more experiments are needed.

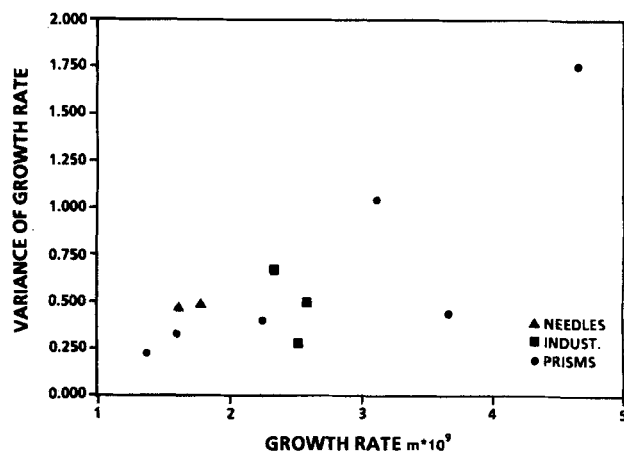


Figure 11. Variance of growth rate distribution vs. mean growth rate, anhydrous dextrose contact nuclei.

Nuclei formed and grown at various temperatures and supercoolings

Conclusions

1. Needle crystals are primarily alpha monohydrate and prism crystals are alpha anhydrous dextrose.
2. It is possible to form alpha monohydrate crystals by contacting alpha anhydrous parent crystals.
3. The laser Raman microprobe is a useful technique for *in situ* identification of the phases of alpha monohydrate and alpha anhydrous glucose.
4. Dextrose contact nuclei (anhydrous and monohydrate) appear to grow at a size-independent rate.
5. Initial size and growth rate distributions are observed for contact nuclei of both anhydrous and monohydrate phases of dextrose.
6. The constant crystal growth model should be used to model growth rate dispersion of contact nuclei in the dextrose water system.

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