Contact Nucleation from Aqueous Sucrose Solutions

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CONTINUOUS CRYSTALLIZATION STUDIES

The population balance technique developed by Randolph and Larson (1971) has been extensively used for both kinetic measurement and modeling of continuous mixed suspension, mixed product removal (MSMPR) crystallizers. When the assumptions of size-independent crystal growth, all crystals with equal growth (i.e., no growth rate dispersion) and all nuclei formed at a near-zero size, are invoked, a semilogarithmic relation is predicted between crystal population density and size. Evidence from continuous sucrose crystallization experiments (Hartel et al., 1980; Kuijvenhoven and de Jong, 1982), however, has shown that, at lower crystal sizes ($<50 \times 10^{-6}$ m), more crystals (orders of magnitude more) are present than are predicted by this relation. Clearly any or all of the assumptions may be in error.

The importance of the deviation from the model is that the semilogarithmic population density-crystal size plot is used to determine kinetic data. When the model holds and a straight line is produced, the growth rate is determined from the scope and the nucleation rate is determined from both the scope and intercept. When curvature occurs, the slope no longer has a single value and the intercept must be determined by some means of nonlinear extrapolation. In order to develop unambiguous kinetic models, it is necessary to understand the causes for curvature.

BATCH CONTACT NUCLEATION STUDIES

Gwynn et al. (1980) reported contact nucleation studies with the sucrose-water system wherein a single growing crystal was contacted and the subsequent size distribution was followed by a Coulter Counter. The results of their study confirmed that contact nucleation is the primary source of new particles and that contact nuclei of sucrose have an initial size distribution, not zero size as suggested by the MSMPR crystallizer model. In addition, by observing the size distribution at subsequent times they inferred size-dependent growth. Recently, Berglund and Larson (1982) demonstrated by use of a photomicroscopic technique that use of Coulter Counter data for determination of size-dependent growth can be in error. The reason is that the phenomenon of growth rate dispersion appears very similar to size-dependent growth when only the overall crystal size distribution is observed.

GROWTH RATE DISPERSION STUDIES

Most growth rate dispersion studies have been performed by seeding a batch crystallizer with a monodisperse size distribution and allowing it to grow without nucleation. Studies by White and Wright (1971) and Berglund (1980) demonstrated the presence of growth rate dispersion in the sucrose-water system. These experiments were conducted using fairly large ($> 100 \times 10^{-6}$ m) seed crystals and the effect of different size seeds was not established.

In the modeling of growth rate dispersion, two possibilities have been suggested in the literature. The first viewpoint is that growth rate dispersion is caused by random fluctuations in the growth rate of an individual crystal. This model was proposed and developed by Randolph and White (1977) and will be referred to as the "random fluctuation" model. A second model is based on the premise that each individual crystal has a constant growth rate but the growth rate of various crystals may be different causing a

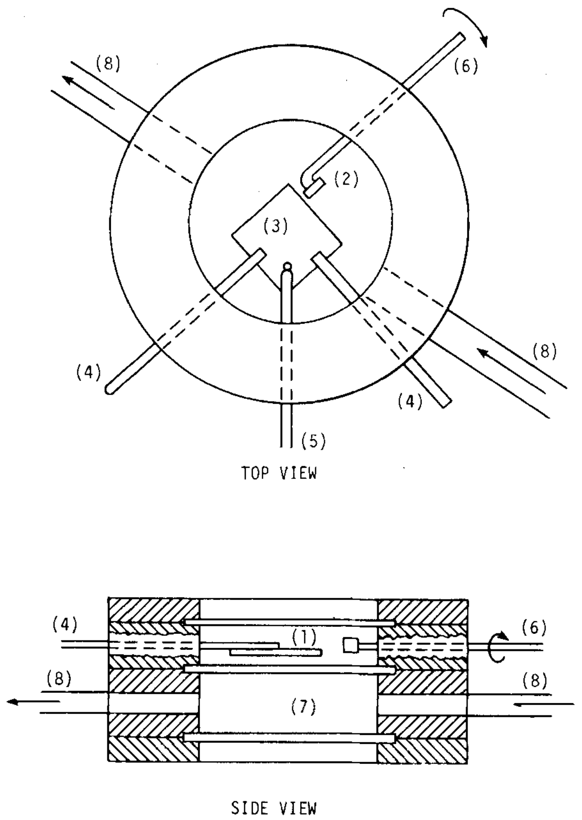

Figure 1. Schematic diagram of nucleation cell with the features: (1) chamber containing solution; (2) parent crystal; (3) glass cover slip where parent crystal is slid; (4) support rods for glass cover slip; (5) thermistor; (6) movable rod holding parent crystal; (7) chamber containing constant temperature water; and (8) water inlet and outlet.

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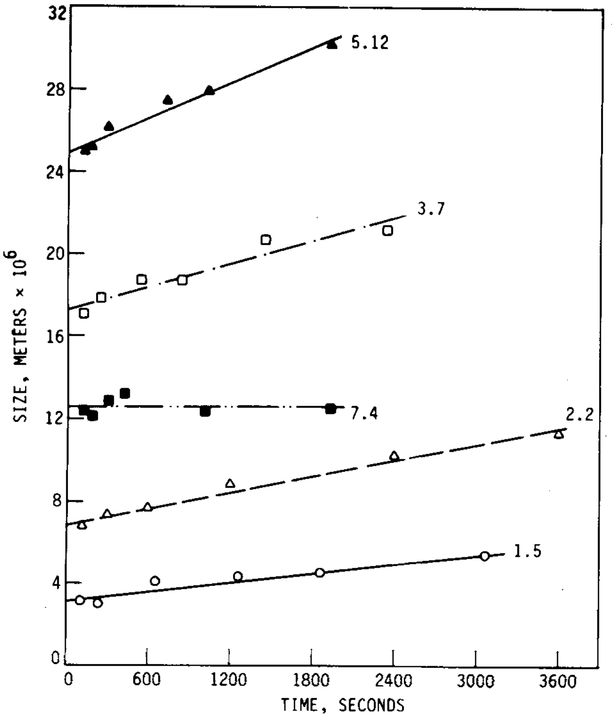

Figure 2. Size vs. time for contact nuclei of sucrose. Numbers refer to crystals measured.

growth rate distribution. This model was proposed by Ramanarayanan et al. (1982) based on the data of Berglund (1981) and will be referred to as the "constant crystal growth" model.

EXPERIMENTAL APPARATUS

The present study performed contact nucleation experiments using the same photomicroscopic technique applied to the citric acid monohydrate system by Berglund and Larson (1982). A schematic diagram of the nucleation cell with a description of features is shown in Figure 1. A parent crystal was glued to a movable rod prior to filling the cell. The nucleation cell was filled with sucrose solution of a known concentration. Initially after the cell was filled, it was heated above saturation to destroy any nuclei which may have occurred during transfer and to slightly dissolve the parent crystal. The solution, saturated at a known temperature, was then cooled and the parent crystal allowed to grow. After a short growth period, the parent crystal was slid aloing the glass cover slip in the cell to create contact nuclei. Photographs of the nuclei were then taken at timed intervals.

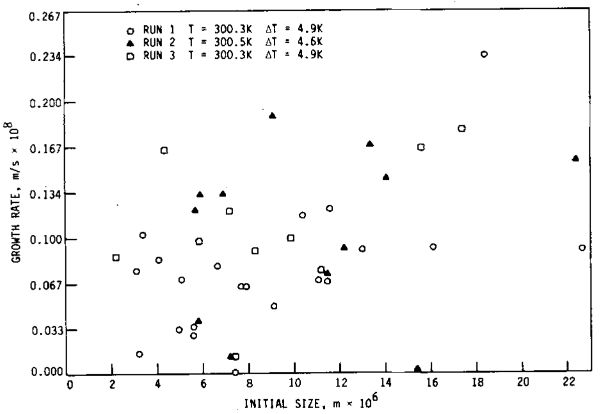

Figure 3. Growth rate vs. initial size for contact nuclei of sucrose from Runs 1, 2 and 3.

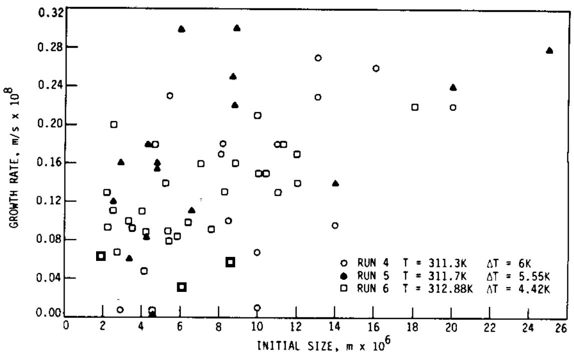

Figure 4. Growth rate vs. initial size for contact nuclei of sucrose from Runs 4, 5 and 6.

DATA ANALYSIS

The data from each experiment consisted of a series of photographs. To extract the size data use was made of an automatic image analyzer. The image analyzer determined the area of each crystal in the photograph. The characteristic size of each crystal was taken as the square root of the area or the geometric mean size. This is the value referred to as size in the subsequent discussion.

RESULTS AND DISCUSSION

Figure 2 shows examples of size vs. time plots for individual crystals. The most striking feature of these plots is their linearity. Since the slope of the line is equal to growth rate, these plots imply a single, size-independent growth rate. A second aspect is the variation in intercept, which corresponds to an initial size distribution. Finally, it should be noted that these lines have different slopes indicating a distribution of growth rates.

A further substantiation of the observation of size-independent growth can be seen in Figures 3, 4 and 5. Here growth rate (the slope of the size vs. time plot) is plotted against the apparent initial size (the intercept of the size vs. time plot). These figures show little correlation, if any, between initial size and growth rate as evidenced by the large amount of scatter. What is indicated is a distribution of initial sizes (as was found by Gwynn et al., 1980) and a distribution of growth rates.

The results presented indicate that the proper method of analysis of the growth rate dispersion present is the "constant crystal growth" (CCG) model. Berglund and Larson (1983) performed an analysis with the CCG model using initial size and growth rate distributions. Their results indicated that the curvature in the semilogarithmic population density-size plot can be attributed mainly to growth rate dispersion, while initial size distribution had a smaller effect.

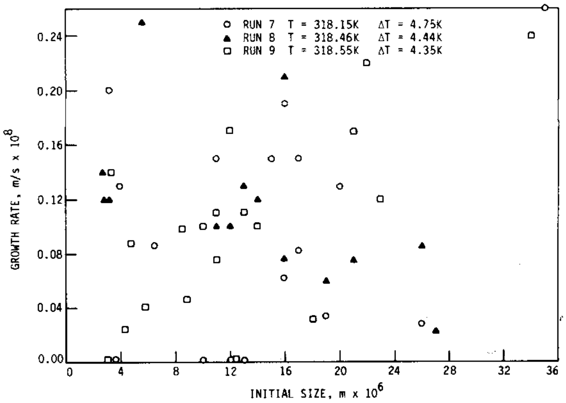

Figure 5. Growth rate vs. initial size for contact nuclei of sucrose from Runs 7, 8 and 9.

The causes for the presence of growth rate dispersion have been listed previously (Garside, 1977). The most likely cause is a variation in dislocation density on the surface of various nuclei resulting in different growth rates. This would be true if the growth followed a Burton-Cabrera-Frank surface diffusion mechanism, which was demonstrated for larger sucrose crystals by Valcic (1975). The mechanism of contact nucleation is still in question and further experimentation is necessary.

CONCLUSIONS

1. Sucrose contact nuclei appear to grow at a size independent rate.
2. Both initial size and growth rate distributions are observed for contact nuclei of sucrose.
3. The "constant crystal growth" model should be used to model growth rate dispersion in the sucrose-water system.
4. Curvature in semilogarithmic population density-size plots from continuous sucrose crystallization studies is probably due to growth rate dispersion and not size dependent growth.

ACKNOWLEDGMENTS

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Solubilities Near the Solvent Critical Point

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INTRODUCTION

Solubilities of gases in liquids are needed for the design of reactors and separation equipment. High-temperature data are rarely available and are difficult to measure. Hayduk and Laudie (1973) observed that all gas solubilities in a solvent tend towards a common value as the solvent critical temperature is approached. Beutier and Renon (1978) showed that this is due to the thermodynamic relationship for the solute (2):

$$H_2 = \phi_2 P_{c_1} \tag{1}$$

at the solvent (1) critical point. This is a very useful relationship for the extrapolation of solubilities to high temperatures. Beutier and Renon attempted also to derive an expression for the variation with temperature at the solvent critical point:

$$\frac{d(H_2/\phi_2)}{dT} = -\infty \tag{2}$$

Although the final result is correct, their derivation is questionable as will be shown below. The vapor-liquid equilibrium equation for the solute is:

$$y_2 \phi_2 P = H_2 x_2 \gamma_2^* c_2 \tag{3}$$

where c_2 is the Poynting correction:

$$c_2 = \exp\left[\int_{P_1^0}^{P} \frac{\bar{v}_2}{RT}\, dP\right] \tag{4}$$

Equation 3 can also be written as

$$\frac{y_2}{x_2} P = \frac{H_2}{\phi_2} \gamma_2^* c_2 \tag{5}$$

Similarly for the solvent:

$$\frac{y_1}{x_1} P = \gamma_1 \frac{\phi_1^0}{\phi_1} P_1^0 c_1 \tag{6}$$

where

$$c_1 = \exp\left[\int_{P_1^0}^{P} \frac{\bar{v}_1}{RT}\, dP\right] \tag{7}$$