Generation and Growth of Secondary Ammonium Dihydrogen Phosphate Nuclei

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Introduction

The term "growth rate dispersion" (GRD) has been used to characterize two possible growth behaviors of crystals. Growth rate dispersion could be due either to fluctuations during the growth period of the crystals or to distinct growth rates between individual crystals under the same growth environment. The former approach constitutes the random fluctuation model proposed by Randolph and White (1977) whereas the latter corresponds to the constant crystal growth (CCG) model proposed by Ramanarayanan et al. (1985). Randolph and White used a parameter similar to the Taylor diffusion coefficient D_G to characterize the growth variations during the growth of the crystals. Although this approach seems plausible, there is very little experimental evidence to support this behavior for short periods of growth (Garside, 1985).

The CCG model proposed by Ramanarayanan et al. is a generalized model accounting for the three factors affecting crystal size distribution (CSD) under a given growth environment, namely, the birth size, the growth rate, and the residence time of the crystals. This model can be used to determine the growth kinetic parameters from batch crystallization experiments.

Starting with the CCG model, Eq. 1, and taking the expected values for both sides,

$$\ell = \ell_o + gt \tag{1}$$

$$\bar{\ell} = \bar{\ell}_o + \bar{g}t \tag{2}$$

the variance of the crystal population can be written as:

$$\sigma_L^2 = \sigma_{L_o}^2 + \sigma_G^2 t^2 \tag{3}$$

In the above equations it is assumed that the variables ℓ_o, g, and t are random independent variables. Thus by monitoring the crystal population in a batch crystallizer, a plot of the mean size of the population vs. time is a straight line with a slope equal to the mean growth rate of the crystals, and a plot of the variance of the population with square of the time is a straight line with the slope corresponding to the variance of the GRD.

Experimental

A diagram of the experimental setup is shown in Figure 1. The minicrystallizer consisted of a jacketed glass vessel with a capacity of 125 mL. The temperature of the solution was controlled by circulating water through the jacket of the vessel from two thermostatic baths for creating undersaturation and supersaturation, respectively, in an ammonium dihydrogen phosphate (ADP) solution. The temperature of the solution was controlled within ±0.1°C.

A stainless steel minicontactor was used to generate the secondary nuclei from the [100] face of an ADP parent crystal. The rod was 12.7 cm long and 3 mm in dia. The conical tip of the rod was flat. The total weight of the rod was 10.8 gm.

The CSD on the secondary nuclei was measured *in situ* using an ELZONE 80XY electronic particle counter from Particle Data, Inc. The system included a variable orifice tube, two platinum electrodes, and a glass stirrer. A TP 140 terminal/printer was used in conjunction with the particle counter to control its operation. In addition to these peripherals, an Apple II-Plus computer was interfaced with the 80XY counter for purposes of data storage and statistical analysis.

Ammonium dihydrogen phosphate was used as the solute for all the runs. The solubility data of Linke (1965) were used for the calculation of supersaturation.

Parent crystals of ADP were grown independently from filtered solutions of ADP. Typical size of the parent crystals was about 10 mm. The parent crystal was glued to the base of the contactor. Saturated solutions of ADP were prepared from distilled water at approximately 31, 32, and 33°C. These saturated solutions were filtered through a 0.2 micron Gelman filter to remove any solid particles and were used for the runs.

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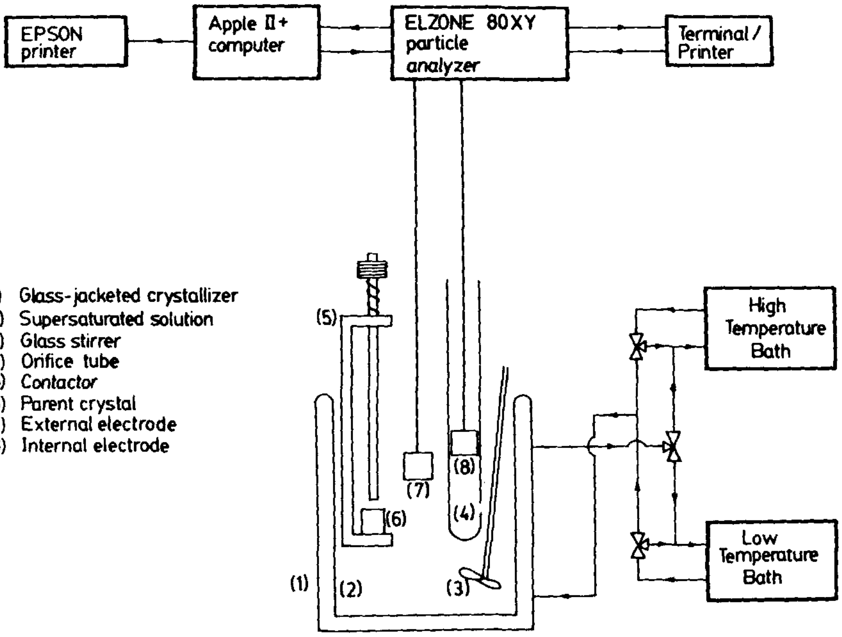

Figure 1. Experimental setup for batch growth rate dispersion studies.

Before each run, filtered saturated solutions and the contactor were placed in the minicrystallizer and held at a slightly higher temperature than the run temperature. This enabled the dissolution of stray crystallites. The solution temperature was then lowered to the run temperature of 30°C. The parent crystal was allowed to grow for a few minutes (typically 2 to 3 min) to generate a fresh surface for contact nucleation. The background count for the particle counter was taken at this juncture. After reproducible backgrounds were obtained, the parent crystal was contacted by dropping the rod from a height of about 1.5 to 2 mm. Typically, 10 contacts were made in quick succession within about 10 s. The contactor was then removed and the CSD measured within 30 to 60 s. CSD measurements were taken at regular intervals of time for a maximum of 20 min under certain cases so as not to change the supersaturation drastically.

After each sample was analyzed for CSD, the data were transmitted to the Apple II-Plus computer. A real-time clock was used to log the time at which the sample was taken for CSD analysis. Throughout the run the solution inside the orifice tube was flushed with a slightly undersaturated solution about 0.5°C above the saturation temperature of the solution used in the run. The system was flushed before and after sampling. Typical operating conditions for the runs are shown in Table 1.

Trial runs were conducted at each level of supersaturation to determine if primary nucleation was possible. Experiments were conducted without the parent crystal and the CSD was measured as a function of time. In each of these trial runs there was no significant change between the subsequent counts and the background count.

Results and Discussion

In order for the analysis presented in this paper to be valid, it is imperative that secondary nuclei of ADP follow the CCG model. This has been established by Ramanarayanan (1982) and confirms the validity of the CCG model for birth size and growth rate dispersions for the ADP-water system.

Figure 2 shows a plot of the mean size of the crystal population as a function of time for a number of runs at a supersaturation level corresponding to an undercooling of 2.1°C. The slope corresponds to the mean growth rate of the crystals at the supersaturation, and the intercept corresponds to the mean birth size of the crystals. Figure 3 shows a plot of the variance of the CSD as a function of the square of the time. The slope corresponds to the variance of the growth rate distribution, σ_G^2, and the intercept corresponds to the variance of the birth size distribution, $\sigma_{L_o}^2$. No attempts were made in these experiments to measure the energy of contact. This is evident from the mean and variance of the birth size distribution summarized in Table 2 for the three levels of supersaturation. The mean and the variance of the birth size distribution varied due to possible variation in the energies of contacts for the different runs. However, the growth parameters $\bar{g}$ and σ_G^2 do not seem to be affected by the energy of contact. This provides indirect evidence that the kinetic parameters for growth, $\bar{g}$ and σ_G^2, from laboratory experiments are not affected by the energy of contact and could be used for the design and

Table 1. Experimental Conditions for Growth Runs

Solution Saturation Temp., T °C	Degree of Under-cooling, ΔT °C	Relative Super-saturation σ	Orifice Size Dia., μm	Sampling Time, t s	Lower Size Limit μm
31.1	1.1	0.0145	76	28.5	3.57
32.1	2.1	0.0278	120	11.1	7.58
33.2	3.2	0.0423	150	7.1	8.82

Stirrer speed = 400 rpm
Area of contact = 7.9 mm^2
Energy of contact = 1.8×10^4 ergs
Sample size = 502.2 μL

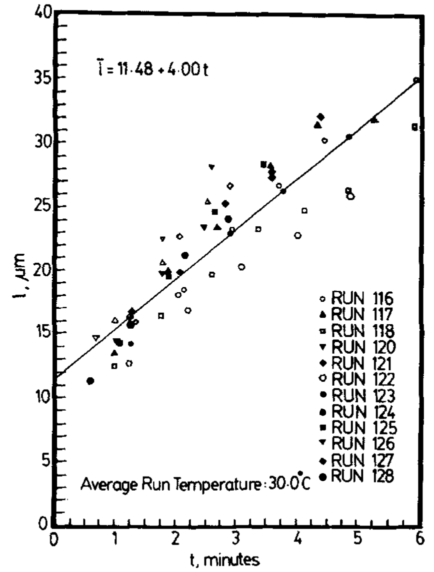

Figure 2. Mean size of secondary nuclei in a batch crystallizer at 2.1°C undercooling.

scale-up of crystallizers having a totally different mode for the generation of contact nuclei under similar conditions. This aspect needs to be studied in detail.

The growth rate dispersion parameters presented in Table 2 were correlated to supersaturation with the following equations:

$$\bar{g} = 9.31 \times 10^5 \sigma^{3.45} \quad (4)$$

$$\sigma_G^2 = 1.66 \times 10^8 \sigma^{4.74} \quad (5)$$

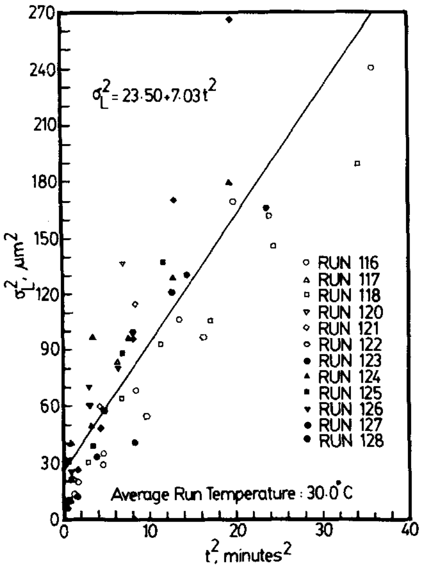

Figure 3. Variance of CSD in a batch crystallizer at 2.1°C undercooling.

Table 2. Birth Size and Growth Rate Dispersion Parameters for ADP-Water System

ΔT C°	σ	$\bar{\ell}_o$ μm	σ_{Lo}^2 μm²	$\bar{g}$ μm/min	σ_G^2 (μm/min)²
1.1	0.01451	6.87	20.72	0.35	0.13
2.1	0.02776	11.48	23.50	4.00	7.03
3.2	0.04227	9.42	10.93	16.97	51.37

In many cases the supersaturation is difficult to measure and is eliminated between Eqs. 4 and 5 to yield:

$$\sigma_G^2 = 1.045\,\bar{g}^{1.37} \quad (6)$$

Equations 4 and 5 indicate that the mean growth rate and the variance of the growth rate distribution increase with an increase in supersaturation. Growth rates have been established as increasing with an increase in supersaturation for a number of systems. From Eq. 5, it can be seen that σ_G^2 is a strong function of supersaturation. This implies that for a given initial size distribution, the CSD would widen to a greater extent for a higher level of supersaturation. Recently Berglund and Murphy (1984) and Rousseau and Girolami (1984) obtained similar results for the exponent in Eq. 6 for the sucrose-water and the potassium alum-water systems. The exponent of 1.37 in this work compares well with that of 1.74 for the sucrose-water system and 1.35 for the latter system. A typical value such as 1.5 for the exponent could be used with some degree of confidence for obtaining an order of magnitude value for the growth rate dispersion parameter σ_G^2. This would enable the characterization of growth rate dispersion for a number of systems for which the mean growth rate kinetics is available.

Conclusions

Batch crystallization experiments with the ammonium dihydrogen phosphate-water system indicate:

1. Secondary contact nuclei of ADP are born into a finite size range indicating birth size dispersion (BSD).
2. The crystals of ADP in the population grow and the mean and the variance of the CSD follow the statistical-mathematical extension of the CCG model.
3. The mean growth rate and the growth rate dispersion parameter can be determined from *in situ* CSD measurements from linear plots of the mean particle size vs. time and the variance vs. time squared, respectively, in a batch crystallizer.
4. It was observed in the range of experiments that the mean growth rate and the growth rate dispersion parameter are dependent on supersaturation and can be correlated with a power law.
5. The mean growth rate and the growth rate dispersion parameter do not seem to be affected by the number of contacts, i.e., the contact energy used for the generation of the nuclei. This aspect needs to be studied in greater detail.

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