

Crystallization as a Separations Process

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Crystallization as a Separations Process

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Foreword

THE ACS SYMPOSIUM SERIES was founded in 1974 to provide a medium for publishing symposia quickly in book form. The format of the Series parallels that of the continuing **ADVANCES IN CHEMISTRY SERIES** except that, in order to save time, the papers are not typeset, but are reproduced as they are submitted by the authors in camera-ready form. Papers are reviewed under the supervision of the editors with the assistance of the Advisory Board and are selected to maintain the integrity of the symposia. Both reviews and reports of research are acceptable, because symposia may embrace both types of presentation. However, verbatim reproductions of previously published papers are not accepted.

Preface

CRYSTALLIZATION IS AN IMPORTANT separation and purification technique used in a wide variety of industries. Interest in crystallization as a separations process has increased in recent years; as a result of this interest, important and significant research is being done in a number of countries. The international crystallization community has traditionally met every three years at the industrial crystallization meetings sponsored by the European Federation of Chemical Engineering. The most recent of these meetings was in Prague in September 1987; the next meeting is scheduled for September 1990 in the Federal Republic of Germany.

With the increased level of research and interest in the field, an additional international meeting held between the two European meetings seemed desirable. With this in mind, a symposium was organized as part of the International Chemical Congress of Pacific Basin Societies. The symposium included oral presentations and a poster session, with a total of 50 contributions. The contributions came from nine countries: 11 from the United States, 20 from Japan, 3 from Australia, 1 from the United Kingdom, 2 from Italy, 4 from the Federal Republic of Germany, 5 from the Netherlands, 3 from Sweden, and 1 from Czechoslovakia.

The presentations made at the symposium covered the broad spectrum of current research in crystallization. The contributions covered the major areas of current interest and research in crystallization.

This volume contains a selection of chapters presented at the symposium organized into four areas: basic studies, crystallizer operation and control, crystallization of organic molecules and biomolecules, and crystallization and precipitation of inorganic compounds. In addition, an overview chapter is included, which reviews important areas in the field.

We would like to thank the symposium contributors and participants, the contributors to this volume, and the organizing committee of the International Chemical Congress of Pacific Basin Societies for allowing us the opportunity to organize and conduct the symposium.

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Chapter 1

Crystallization Research in the 1990s

An Overview

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Crystallization from solution is an important separation and purification process in a wide variety of industries. These range from basic materials such as sucrose, sodium chloride and fertilizer chemicals to pharmaceuticals, catalysts and specialty chemicals. The major purpose of crystallization processes is the production of a pure product. In practice however, a number of additional product specifications are often made. They may include such properties as the crystal size distribution (or average size), bulk density, filterability, slurry viscosity, and dry solids flow properties. These properties depend on the crystal size distribution and crystal shape. The goal of crystallization research therefore, is to develop theories and techniques to allow control of purity, size distribution and shape of crystals.

The past 30 years have seen great advances in our understanding of the fundamentals of crystallization and has resulted in improved crystallizer design and operation. A dominant theme during this period was the analysis and prediction of crystal size distributions in realistic industrial crystallizers. This led to the development and refinement of the population balance technique which has become a routine tool of the crystallization community. This area is best described in the book of Randolph and Larson (1) which has been an indispensable reference and guide through two editions.

Another important development which altered our view of crystallization processes was the realization of the importance of secondary nucleation due to contact between crystals and the impeller and vessel. Secondary nucleation of this type has been shown (2-6) to often have a dominant role in determining crystallizer performance. Our understanding of crystal growth, nucleation, fluid mechanics and mixing have all greatly improved. A number of review (7-10) have appeared in recent years which describe the advances in these and

other areas. It is the purpose of this overview chapter to discuss areas which, in my opinion, will be of greatest interest and potential use in the 1990's. The list is by no means complete, however I believe that in the next decade much progress will be made in these areas and they will have a profound impact on industrial crystallization processes.

Fundamental Research

Metastable Solution Structure

Classical nucleation theory has long postulated the existence of molecular clusters in supersaturated solutions (11, 12). This is the result of the size dependence of the free energy change between a small particle and the solution. A critical size exists above which a cluster of molecules will grow and below which the cluster will dissolve. The critical size is the maximum in the free energy curve where $d\Delta G/dr = 0$. Nucleation theory tells us that supersaturated solutions have a population of subcritical sized molecular clusters which form and dissolve. Nucleation occurs when one of these clusters reaches the critical size. Based on this concept the following questions arise.

1. Do these clusters actually exist?
2. What are the size distribution and/or average size of the clusters?
3. How do the clusters affect solution properties?
4. How do the clusters participate in the crystal growth process?

The last five years have seen an increasing level of research activity aimed at answering these questions which is likely to continue during the 1990's.

Indirect evidence of the existence of molecular clusters was reported by Mullin and Leci (13) who demonstrated that isothermal columns of aqueous supersaturated solutions of citric acid developed concentration gradients with higher concentrations in the bottom of the column, than at the top. No gradients were reported in saturated or undersaturated columns. These experiments were repeated by Larson and Garside (14) for a number of solutes with similar results. Larson and Garside (15) attempted to explain the gradient formation using a quasi-equilibrium theory which estimated an average cluster size of 1000 - 10,000 molecules. This is clearly far too large since clusters of this size would be easily detectable by light scattering and have not been detected in these types of experiments.

A number of investigators have attempted to obtain more direct evidence of cluster formation in supersaturated solutions by using spectroscopic techniques (16-22). Studies in bulk solutions and in highly supersaturated droplets using Raman and FTIR spectroscopy resulted in reports of features present in the supersaturated solution spectrum which were not present in the under-

saturated solution spectrum or in the crystalline material. Rusli et al. (19) used Raman spectroscopy to study NaNO_3 solutions. They reported that the clusters do not have a crystalline structure but are solvated consisting of clusters of solute and solvent molecules. They also reported that the clusters occur to a small degree in the undersaturated solutions.

While providing important evidence concerning the existence of the clusters and their structure, the spectroscopy work has not yet provided quantitative data on the cluster size and evolution.

Additional indirect evidence of cluster formation has been obtained through observed changes in the properties of supersaturated solutions. Myerson and coworkers (23-28) have demonstrated that diffusion coefficients of a variety of substances (urea, glycine, KCl, NaCl, valine) decline rapidly with increasing concentration in the supersaturated region. It has also been shown (27, 28) that the diffusion coefficients are a weak function of the solution 'age', declining with increasing age.

Employing experimental supersaturated solution diffusion coefficient data and the cluster diffusion theory of Cussler (29), Myerson and Lo (27) attempted to estimate the average cluster size in supersaturated glycine solutions. They estimated an average cluster size on the order of two molecules. Their calculations indicated that while the average cluster size was small, large clusters of hundreds of molecules existed, only there were very few of them. Most of the molecular association was in the form of dimers and trimers.

The current status of research in supersaturated solution structure centers on the direct determination of the cluster size and size distribution and the role of the clusters in crystal growth and nucleation. This will likely be accomplished through sophisticated spectroscopic and light scattering techniques using bulk solutions and using very highly supersaturated droplets suspended without a container using the electrodynamic balance technique (30, 31). Hopefully this will yield quantitative data which will answer some of the important questions relating to cluster size, form and evolution.

Growth Rate Dispersion

The development and refinement of population balance techniques for the description of the behavior of laboratory and industrial crystallizers led to the belief that with accurate values for the crystal growth and nucleation kinetics, a simple MSMR type crystallizer could be accurately modelled in terms of its CSD. Unfortunately, accurate measurement of the CSD with laser light scattering particle size analyzers (especially of the small particles) has revealed that this is not true. In many cases the CSD data obtained from steady state operation of a MSMR crystallizer is not a straight line as expected but curves upward (1, 32, 33). This indicates more small particles than predicted

by the population balance and could be the result of crystal breakage, size dependent growth or some other growth phenomenon.

A number of investigators developed empirical growth rate expressions that included a size dependence. These models were summarized by Randolph (33, 34) who showed that they all produced a concave upward semi-log population density plot; thus are useful for empirical fits of non-linear MSMPR CSD data. These models however, supply no information on what is actually happening to cause the non-linear CSD.

The explanation which has emerged after a number of theoretical (35-40) and experimental studies (41-46) is known as growth rate dispersion. This unexpected concept says that crystals of the same size and material exposed to identical conditions of supersaturation, temperature and hydrodynamics do not necessarily grow at the same rate. This is not the same as size dependent growth (47) in which crystals of different sizes display differences in growth rate. The concept of growth rate dispersion was first used by White and Wright (41) to explain an observed widening of the size range during the batch growth of sucrose.

Studies of growth rate dispersion have resulted in two distinctly different mechanisms being proposed. In one mechanism it is assumed that crystals have a distribution of growth rates but each individual crystal grows at a constant rate (at a fixed set of conditions). This implies that nuclei are born with a distribution of growth rates and the observation of two nuclei in a crystallizer at steady state conditions will reveal each nuclei growing at a constant but different rate. This type of behavior has been demonstrated experimentally for crystal fragments produced by attrition (49), for secondary nuclei and (43, 44) for single crystal produced by primary nucleation (45).

The second mechanism for growth dispersion says that while all crystals have the same time averaged growth rate, the growth rates of individual crystals can fluctuate significantly with time. This mechanism, therefore, implies that the observation of two different crystals growing under identical conditions might be different at any time but that the time average growth rate over a long time period would be identical. Experimental evidence has also appeared (42-43) which supports this mechanism.

Explanations of growth rate dispersion which have appeared in the literature employ the surface integration step of the Burton Cabrera Frank (BCF) theory of crystal growth (50) as the primary cause of the observed phenomena. The BCF theory indicates that the growth rate of a crystal is dependent on screw dislocations which are present on the surface. Experimental work has shown that changes in the location or density of screw dislocations can cause large changes in the crystal growth rate. Collisions of the crystals with the impeller, walls and each other can result in damage to the dislocations and therefore changes in the crystal growth rate. This is especially true with secondary

nuclei which could display very different dislocation densities. In addition, the imperfect nature of the crystal growth process could lead to changes in the dislocations of the crystal faces. Zumstein and Rousseau (40) developed a model that includes both growth rate dispersion mechanisms. They found that both growth rate distribution and growth rate fluctuation could be observed in batch crystallizers experimentally by monitoring the increase in the variance of the CSD during growth periods. In continuous crystallization, however, only the growth rate dispersion mechanism could be observed through the upward curvature of the CSD plot.

Both experimental and theoretical work has demonstrated that growth rate dispersion exists, and has a measurable effect on the CSD in both batch and continuous crystallization processes. Further understanding of this phenomenon on a fundamental level will be required to develop methods to make use of or control growth rate dispersion and make it a tool in control of particle size and shape.

Impurity-Crystal Interactions and Crystal Morphology

The interaction of impurities (including the solvent) with growing crystals has long been of interest. A tremendous amount of qualitative data exists which shows the effect of many ionic and organic impurities on crystal habit, crystal growth rate and nucleation rate (51, 52). Industrially, impurities are used as scale inhibitors and habit modifiers in a number of processes. These additives, however, were developed through experimental programs which are essentially trial and error. There has not been a technique available to predict, in advance, the effect of impurities on the crystal morphology or growth rate. There is also no reliable method to choose an appropriate solvent to obtain desired solid properties. In recent years, however, progress has been made in these areas so that the concept of tailoring a solvent system and/or impurities to achieve a desired crystal morphology and size distribution seems a realistic goal.

A group at the Weitzmann Institute in Israel has for a number of years been investigating the concept of crystal growth and morphology control through the use of tailor made additives (53-57). A tailor made additive is a molecule very similar to the crystallizing species in its structure but different in some specific way. The difference in the structural characteristics of the additive are such that once incorporated in the structure, the additive will disrupt the bonding sequences in the crystal and interfere with the growth process at the crystal surface. The Weitzmann group found that these additives could dramatically affect crystal growth and habit. The mechanism for the additive's effectiveness is based on two steps. The additive first adsorbs preferentially on specific crystal faces where the modified part of the additive points away from crystal interior. Once bound, the additive disrupts the layer growth of the particular face thus lowering the growth rate of the face. This results in an increased surface area of the faces in which the

impurity is adsorbed. By careful design of additives it is thus possible to design a crystal morphology. Examples of systems studies using this technique include the crystallization of benzamide from ethanol using benzoic acid and *o* and *p* toluamide as the additives (54), crystallization of racemic mixtures of amino acids using chiral additives which cause a kinetic resolution of the isomers by adsorbing only onto surfaces of similar chirality (55) and the use of 1-glutamic acid on 1-asparagine (58).

The use of tailor made additives holds great promise in the area of crystal growth and morphology control. The routine selection and use of these type of additives will require a fundamental understanding of the mechanism by which the additives work on a molecular basis. At the same time, the effect of solvent molecules on the crystal growth process is another related and important problem. In both instances, the relationship between internal crystal structure, crystal growth rate, solvent and impurities are needed to predict the habit of a crystal and thus allow selection of the proper conditions and components required to obtain a desired habit.

The early investigation of crystals led to interest in the correlation of crystal morphology (shape) with internal structure. A simple correlation was noticed by Donnay and Harker (59) in 1937 between the interplanar spacing of a crystallographic plane, d_i , and its area on an average crystal. Similar correlation holds between d_i and the frequency with which the plane (hkl) appears in an ensemble of crystals. Since the area of a plane is roughly proportional to the inverse of its linear growth velocity, R , the Donnay-Harker law is equivalent to stating that $R_i \sim 1/d_i$.

Hartman and Perdok (60-62) in 1955 developed a theory which related crystal morphology to its internal structure on an energy basis. They concluded that the morphology of a crystal is governed by a chain of strong bonds (called periodic bond chains (PBC)), which run through the structure. The period of these strong bond chains is called the PBC vector. In addition, Hartman and Perdok divided the crystal face into three types. These types are:

1. F-faces (flat) each of which is parallel to at least two PBC vectors.
2. S-faces (stepped) parallel to at least one PBC vector
3. K-faces (kinked) not parallel to any PBC vector.

If the sum of the energy within a slice (E_{slice}) of each type of face is compared, the F face will be the largest (followed by S and then K). the attachment energy (E^{att}), which is the difference between the crystallization energy and the slice energy will, therefore, be the smallest. A small attachment energy means a low growth velocity. The slow growth velocity of F faces means they will be the large faces on a grown crystal. The higher velocities of S and K faces mean they rarely (S) and almost never (K) develop.

The result of Hartman Perdok theory is to allow prediction of the growth shape of crystals from the slice energy of different F faces.

Hartman and Bennema (63) looked at attachment energy as a habit controlling factor. They found that the relative growth velocity always increases with increasing E^{att} , however, the relationships between the two depends on the mechanism of crystal growth and variables such as supersaturation, temperature and solid-fluid interactions. They demonstrated at low supersaturation, however, the relative growth velocity of a face is directly proportional to the attachment energy of that face. Hartman (64, 65) employed this assumption to calculate the habit of naphthalene and sulfur and had good agreement with observed forms.

A number of investigators (66, 67) have recently employed the critical Ising temperature (transition temperature from smooth to rough interface) to determine the relative importance of F faces. In general, results obtained by this method are quite similar to those obtained from attachment energy calculations.

A major weakness in the calculations described above is that they can only be used to represent vapor grown crystals. In crystals grown from solution, the solvent can greatly influence the crystal habit as can small amounts of impurities. Several investigators (68, 69) accounted for discrepancies between observed crystal habit and those obtained using attachment energies by assuming preferential solvent (or impurity) adsorption on crystal faces.

In a recent paper (70) Hartman studies the effect of surface relaxation on the habit of corundum and hematite. The habits observed on natural and synthetic crystals of these systems did not agree with calculated relaxed equilibrium or growth habits. Hartman concluded that these observations could be understood by invoking specific solvent adsorption on (111) faces.

The work discussed in the previous paragraphs provides the framework for the prediction of crystal habit from internal structure. The challenge is to add realistic methods for the calculation of solvent and impurities effects on the attachment energies (hence the crystal habits) to allow this method to provide prediction of crystal habit. Initial attempts of including solvent effects have been recently described (71, 72). The combination of prediction of crystal habit from attachment energies (including solvent and impurity effects) and the development of tailor made additives (based on structural properties) hold promise that practical routine control and prediction of crystal habit in realistic industrial situations could eventually become a reality.

Crystallizer Design and Operations

The design and operation of industrial crystallizers is where developments in the laboratory are confirmed and their practical significance determined. In recent years, crystallization processes involving specialty chemicals and pharmaceuticals have increased. This has led increased interest in batch crystallization operation, optimization and design. At the same time, the advent of powerful computers and their routine availability has stimulated interest in the area of on-line control of crystallization process (both batch and continuous). Progress in batch crystallization is summarized in a number of recent papers and reviews (73-80). In this section I will discuss two areas which I think will have an impact in the next decade.

Crystal Growth and Nucleation Kinetics from Batch Experiments

The measurement of crystal growth and nucleation kinetics is a fundamental problem which confronts everyone interested in crystallizer process design and development. Application of the population balance model to analyze and/or predict the CSD requires knowledge of the kinetic constants. Crystallizer design also requires some knowledge of kinetic parameters, particularly the ratio of the exponents of nucleation to crystal growth. The standard method for the determination of growth and nucleation kinetics is the use of the CSD obtained from a steady state MSMR crystallizer. At steady state, assuming size independent growth and clear feed, the population balance equation can be written as:

$$G\tau \frac{dn}{dL} + n - n_0 = 0 \quad (1)$$

where G is the crystal growth, τ the residence time, n the population density and L the crystal size. The solution to equation 1 is

$$n = n_0 \exp(-L/G\tau) \quad (2)$$

A plot of the $\ln n$ versus L yields a straight line where the slope is $-1/G\tau$ and the intercept is n_0 (the population density of nuclei). Since the MSMR is at steady state, the supersaturation is known. This experiment can then be repeated at a number of different supersaturations and fit to growth and nucleation expressions of the form below:

$$G = k_g \Delta C^g \quad (3)$$

$$B = k_b \Delta C^b \text{ or } k_b^1 M_T^j \Delta C^b \quad (4)$$

where ΔC is the supersaturation, M_T the slurry density, k_g , k_b and k_b^1 the kinetic constants and g , b and j the kinetic orders.

This is the standard method for obtaining growth and nucleation kinetics. While not difficult (for those with experience in crystallization) the technique is very time consuming, uses up significant amounts of material and data analysis often presents problems (because of a concave upward CSD). Because of these factors, industrial investigators often do not attempt to obtain growth and nucleation kinetics in crystallization process development and design. This had led to interest in the development of methods to employ batch crystallization to obtain the needed data. The simplest method which can be used to obtain kinetic data from a batch crystallizer, involves measurement of the desupersaturation curve in a seeded isothermal experiment. If a small supersaturation is employed it is assumed that nucleation is negligible. Garside et al. (81) developed a method to employ the initial derivatives of the desupersaturation curve to obtain growth and dissolution kinetics. The experimental technique and analysis required for this technique are simple however, as in most techniques that employ derivatives, there is a large variability in the results. The technique is useful in estimating growth and dissolution kinetics with small amounts of material and is relatively quick to do.

Tavare and Garside (82) developed a method to employ the time evolution of the CSD in a seeded isothermal batch crystallizer to estimate both growth and nucleation kinetics. In this method, a distinction is made between the seed (S) crystals and those which have nucleated (N crystals). The moment transformation of the population balance model is used to represent the N crystals. A supersaturation balance is written in terms of both the N and S crystals. Experimental size distribution data is used along with a parameter estimation technique to obtain the kinetic constants. The parameter estimation involves a Laplace transform of the experimentally determined size distribution data followed by a linear least square analysis. Depending on the form of the nucleation equation employed four, six or eight parameters will be estimated. A nonlinear method of parameter estimation employing desupersaturation curve data has been developed by Witkowski et al (85).

The availability of computers and sophisticated parameter estimation techniques have led to interest in other methods for the estimation of growth and nucleation kinetics. These methods include measurement of the desupersaturation curve and/or size distribution in a seeded batch crystallizer undergoing controlled cooling and in a non-seeded batch crystallizer undergoing controlled cooling (83-84). The parameter estimation techniques being proposed to analyze these systems are quite complex and non-linear. With the advances in computing and the availability of advanced numerical programs, it should be possible to do these calculations on a PC.

The determination of kinetics from batch experiments and parameter estimation is experimentally easy but involves difficult and sophisticated calculations. The accuracy of the results, however, is not significantly worse than obtained in MSMR experiments in many systems. Development of standard calculation techniques and software should make this method of kinetics determination routine in the next decade.

On-Line Control of Crystallizers

The development of the population balance approach has done much to further our understanding of CSD transients and instabilities which are observed in the plant and the laboratory. Advances in computing and control technology which have occurred in the chemical process industry together with the recognition that on-line CSD control might be achievable has led to an increased level of interest and investigation of this area.

Until recently most work on CSD control was theoretical with not attempt at implementation, since measurement of the necessary variables employed in these theoretical studies was usually not possible. Descriptions of many of the theoretical studies are summarized in several places (1, 86, 87).

One approach which has resulted in experimental implementation is that of Randolph and co-workers (88-92). Using a simulation (91) Randolph and Beckman demonstrated that in a complex RTD crystallizer, the estimation of nuclei density could be used to eliminate cycling or reduce transients in the CSD. Randolph and Low (88) experimentally attempted feedback control by manipulation of the fines dissolver flow rate and temperature in response to the estimated nuclei density. They found that manipulation of fines flow rate upset the fines measurement indicating that changes in the manipulated variable disturbed the measured variable. Partial fines dissolution resulting from manipulation of the fines dissolver temperature appeared to reduce CSD transients which were imposed upsets in the nucleation rate. In a continuation of this work Randolph et. al. (92) used proportional control of inferred nuclei density to control an 18 liter KC1 crystallizer. Nuclei density in the fines loop was estimated by light scattering. This technique was shown to be effective in minimizing the effect of disturbances in nucleation rate of the product CSD.

Another experimental approach (93, 94) to CSD control involved the use of on line solution and slurry density measurements as measured variables with jacket temperature and residence time as manipulated variables. This was attempted in a 10 liter MSMR crystallizer employing K-alum. Results showed that this scheme was able to return the crystallizer to a steady state after the introduction of an upset and that on-line density measurements of solution and slurry could be obtained and used.

A group at Delft University (95-97) has for several years been involved in

experimental and theoretical studies of on-line control of crystallization processes. Their control scheme involves the on-line measurement of the CSD by light scattering or by Fraunhofer diffraction. The main experimental implementation problem is that neither of these techniques work with concentrated slurries so that dilution is necessary. The Delft group has designed an automatic dilution unit which employs saturated mother liquor as the dilution liquid which is separated from the product using a hydrocyclone and filters. A semibatch dilution mode has been employed, however complete implementation of this system with control results has not yet been reported.

The future of on-line control of crystallization should see the use of parameter estimation for estimation and correction of model parameters along with higher level nonlinear control schemes. The major challenge continues to be realistic measurement of the necessary variables such as the CSD or its moments.

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