# Nucleation and Growth Rates of Ammonium Chloride in Organic Media: Development of an On-line Measurement Technique

Nucleation and growth rates of small ammonium chloride crystals precipitated from organic mother liquors were measured with an electronic particle counter using an on-line measurement and data reduction technique. Current values for nucleation and growth rates could be obtained within a period of 3 min, thus permitting rapid scanning of variables affecting crystal size distribution. Population average sizes of 1 to 3$\mu$ were typically measured in these organic liquors. The average size of particles increased with increase in ammonium chloride solubility. Addition of surfactants (sodium dodecylbenzene sulfonate, sodium oleate) either had no effect on nucleation or inhibited growth and nucleation equally, thus did not change particle size. The average size of particles was slightly increased with addition of magnesium chloride.

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## SCOPE

The on-line measurement of crystal growth and nucleation rates in a mixed suspension, mixed product removal (MSMPR) crystallizer has proved to be a versatile tool for studying nucleation/growth rate kinetics while directly observing the mechanisms underlying such kinetics (for example, Randolph and Cise, 1972; Sikdar and Randolph, 1976). Most previously studied systems are characterized by relatively high solubilities, low supersaturation, and the dominance of secondary nucleation. One of the goals of the present study was to extend this MSMPR technique to slightly soluble precipitation systems characterized by homogeneous nucleation mechanisms. An additional goal was to develop rapid on-line data processing techniques compatible with the on-line measuring capability of electronic particle counters. Development of this capability should prove useful in the study of fast reaction/precipitation systems. The present ammonium chloride study well illustrates such a reaction/crystallization system, where mixing and chemical reaction factors can also influence the crystal size distribution (CSD).

## CONCLUSIONS AND SIGNIFICANCE

Ammonium chloride nucleates by homogeneous mechanisms in slightly polar organic mother liquors. Agitation rate has no direct effect on nucleation but decreases the agglomeration of particles. Organic surfactants, which often act as crystal modifiers, do not affect ammonium chloride particle size. The addition of water in the organic medium increases solubility and results in a two to threefold increase in particle size. Higher solubility promotes mixing before reaction in the feed entrance zone, decreases locally high regions of supersaturation, and thus reduces nucleation. In such well-stirred reactor/crystallizers with a fast precipitation reaction, the crystals behave as an ideally mixed phase (obeying the exponential MSMPR distribution), while the reactants behave as a nonideal segregated phase. This behavior may characterize the essential difference between precipitation and crystallization systems. The on-line data measurement and reduction techniques developed in this study should be applicable to many other precipitation systems.

Most CSD studies deal with conditions of low supersaturation produced by either cooling or evaporation. Under these conditions, primary nucleation is negligible, and new nuclei are formed from existing particles by secondary nucleation. Furthermore, with highly concentrated slowly crystallizing systems, a uniform concentration exists throughout the crystallizer, and ideal mixing can be assumed. The MSMPR technique has proven useful in the analysis of such conventional crystallization systems (Randolph and Larson, 1971).

One purpose of this study was to apply the CSD analysis of the MSMPR crystallizers to precipitation systems where crystallization is due to chemical reaction. Design of such reactor/crystallizers is different from that of simple stirred-tank reactors because of the need to predict CSD as well as the extent of reaction. Similar factors, such as copre-

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cipitation, occlusions, and mother liquor additives, must often be considered in precipitation as well as crystallization studies.

In reactor/crystallizers, the direct mixing of two reactants often results in a region of high supersaturation, where particles are generated by primary nucleation mechanisms. This difference is obviously more significant with faster reactions and/or poorer mixing.

Precipitation due to chemical reaction has a wide range of applications. One example is the lime-soda water softening process, where the hardness producing ions (calcium and magnesium) are precipitated as calcium carbonate and magnesium hydroxide. Another industrially important example of a reactor/crystallizer is the digestion of phosphate rock to produce phosphoric acid with calcium sulfate (gypsum) as a waste by-product. Both the degree of reaction and the gypsum CSD are important variables. The precipitation of waste ammonium chloride in organic media, which is the system studied here, occurs with the amination of organic chlorides. The particular organic amination reaction which motivated this study occurs in the production of triamino-trinitro-benzene (TATB) by amination of trichloro-trinitro-benzene (TCTB). Both TCTB and TATB are explosive compounds. In this process, ammonium chloride is produced as a side product and sometimes cocrystallizes with TATB as an impurity at a level up to 1%. An assumed mechanism for this occlusion of impurity is that of attachment and overgrowth of small ammonium chloride particles in the TATB matrix. These fine particles embedded in TATB cannot easily be removed by washing. A practical solution to this problem might be to reduce nucleation, thus increasing ammonium chloride particle size. A goal of this study was to identify factors which influence ammonium chloride crystallization kinetics to increase particle size by inhibiting nucleation.

Some studies of precipitation kinetics using the MSMPR technique have been reported (Schierholz and Stevens, 1975), but the particle sampling and measuring techniques were laborious and often required electronic particle counting. Therefore, a final goal of this study was development of on-line CSD measurement and data reduction techniques as practical tools for the study of fine particle precipitation systems.

## RESEARCH APPROACH

After a series of introductory tests, a mixture of 50/30/20 vol % toluene/isobutyl alcohol/methyl alcohol was selected as the reaction medium. Three percent lithium chloride (which could be dissolved in the methanol) was added to provide conductivity for on-line sensing of particles. Isobutyl alcohol was used in the mixture to bridge the miscibility gap between toluene and methanol.

The mininucleator used in this study represented a modification of the apparatus developed previously for study of secondary nucleation in soluble conductive systems (Randolph and Cise, 1972). A schematic diagram of this nucleation system as used in the present study is shown in Figure 1. Briefly, the system operated as follows. Mother liquor from a surge tank was pumped at a rate of 95 to 120 ml/min with a positive displacement pump. This liquid passed through an adsorber containing an activated carbon bed, a fixed-bed saturator containing glass beads and ammonium chloride crystals, and a set of filters for removing particles larger than 0.2 μ. The filtered liquid was then introduced into the well-mixed crystallizer/reactor. Crystallizer discharge was returned to the surge tank via a level controller and a continuous flow cell which housed the orifice tube of the counter. Ammonia (excess reactant) was bubbled into the crystallizer through a fine fritted glass at a flow rate of 20 ml/min. Hydrochloric acid (limiting reactant) was prepared in a mother liquor solution with a known concentration and was metered into the crystallizer through a fine nozzle. Two different techniques were used for introduction of additives into the system. Additives which could be removed by adsorption on the carbon bed were continuously introduced to the crystallizer feed. This technique (Randolph and Koontz, 1976)provides an open loop of additive flow in the system. When adsorption was not possible, additive was introduced batchwise, and the carbon bed was bypassed.

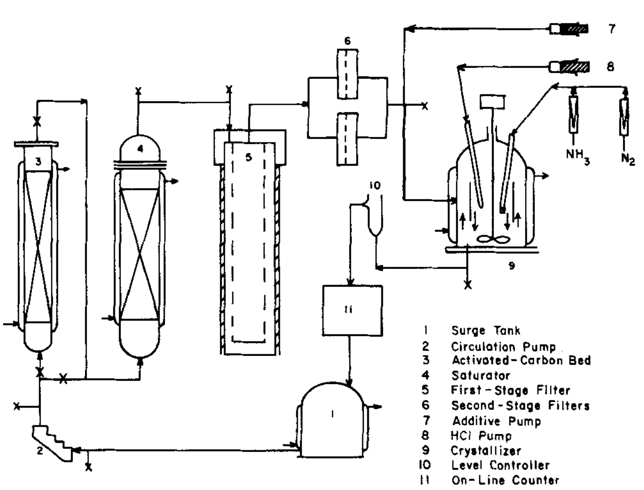

**Fig. 1. Schematic diagram of the apparatus.**

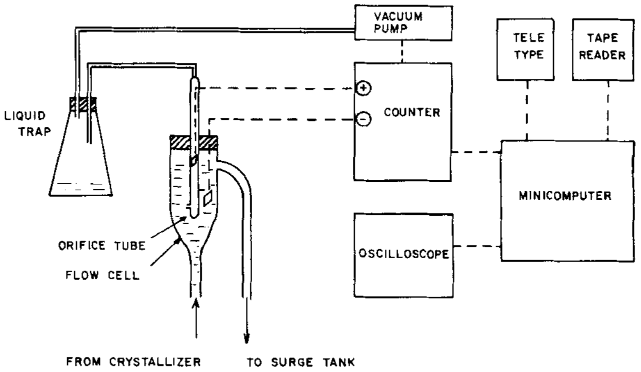

**Fig. 2. Arrangement for on-line measurement and analysis of the crystal size distribution.**

The on-line sampling technique used previously in similar studies (Randolph and Cise, 1972; Sikdar and Randolph, 1976) was implemented in this study. However, the capability of on-line regression of semilog population data to the theoretical MSMPR form was added utilizing the system shown schematically in Figure 2. The principal instrument consisted of an Electrozone Counter (Particle Data, Inc.) for particle sizing and counting, a PDP-8 minicomputer for CSD analysis and data reduction, a DEC-writer for input and output commands; and an oscilloscope for temporary display of data. In each sampling, 2 ml of the liquid were passed through the 95μ orifice tube of the counter. The counts and the distribution histogram were stored in the counter as the raw data. These data were then transferred to the minicomputer for calculation of population density, which was then displayed as a semilog plot. A representative population-density plot is shown in Figure 3. Using a linear regression subroutine, a straight line was fitted to this plot, and the

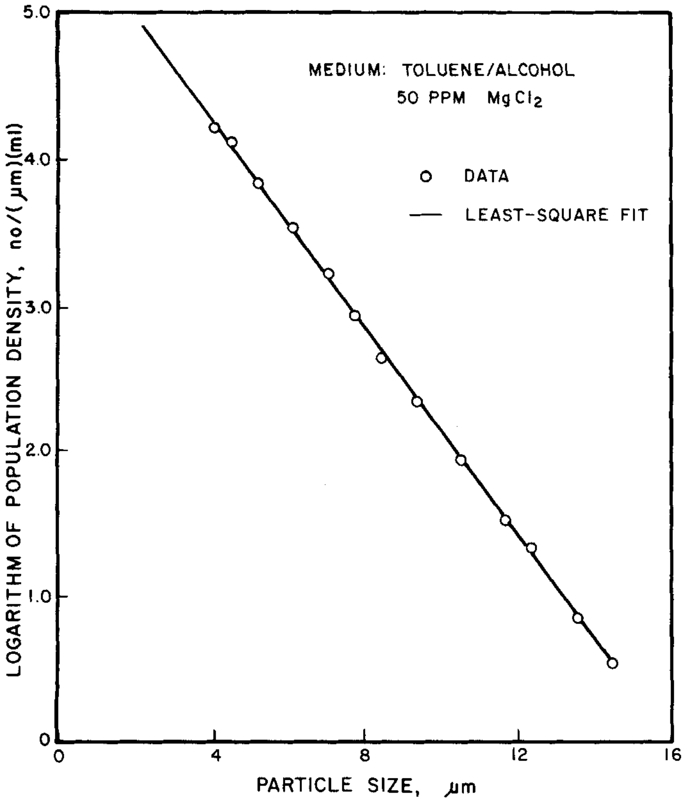

Fig. 3. Representative population density plot.

rate parameters were calculated and printed out. The entire process of counting and data analysis took less than 3 min for each sample. At least ten samples were analyzed in each experimental run after steady state was established.

To provide a basis for comparing the effect of reaction medium and additives on rate parameters, pure toluene was used as the reaction medium in several experiments. Owing to the small solubility of conductive salts in toluene, on-line CSD measurements could not be used in these runs. Thus, the tedious and time consuming technique of filtration and resuspension in a conductive solution was used.

## RESULTS

Rate parameters were obtained by data fitting to the well-known exponential population distribution of the mixed suspension, mixed product removal crystallizer (Randolph and Larson, 1971).

Thus

$$n = (B^\circ/G) \exp\left[-L/G\tau\right] \qquad (1)$$

where $\tau = V/Q$ is the mean residence time of the crystallizer.

Three other statistical properties of the particle distribution that were calculated (from the values of $B^\circ$ and $G$) were population average size, slurry density, and specific number defined as follows:

Population average size,

$$\bar{L}_{1,0} = \frac{\int_0^\infty L n dL}{\int_0^\infty n dL} = G\tau$$

Slurry density,

$$M_T = \rho k_v \int_0^\infty n L^3 dL = 6\rho k_v \frac{B^\circ}{G} (G\tau)^4$$

Specific number,

$$\nu = \frac{\int_0^\infty n dL}{M_T} = \frac{1}{6\rho k_v (G\tau)^3}$$

As previously discussed, one of the goals of this study was to find conditions for increasing ammonium chloride particle size. $\bar{L}_{1,0}$ and $\nu$ were utilized for comparison of particle size. Total nucleation rate $B^\circ$ and growth rate $G$ depend on the amount of precipitation and thus cannot be directly compared run to run, owing to the variable yield for each condition.

Among several factors influencing the particle size distribution, the reaction media, additives, and the degree of mixing were considered to be important. The effects of each of these factors were studied as follows.

### Effect of Reaction Medium

The reaction medium was found to have a significant effect on precipitation kinetics. For example, the average size of particles produced in toluene/alcohol mixture was about 30% larger than that of particles produced in pure toluene. The log $n$ vs. $L$ population plots of the resuspended samples from the pure toluene runs exhibited a characteristic two-slope shape above and below 8 $\mu$ particle size. The first section (up to 8 $\mu$) was taken as representative of the particle distribution. The larger $G\tau$ value from the distribution segment above 8 $\mu$ was assumed to be due to agglomeration and/or recrystallization in the supersaturated IPA/LiCl/$NH_4Cl$ counting solution. The effect of reaction medium on size distribution can be seen from Table 1. Note the small characteristic particle sizes of 1 to 3 $\mu$ in these organic media.

### Effect of Additives

The effect of water on ammonium chloride size distribution is shown by Figures 4, 5, and 6. The data show that water enhanced nucleation at low concentrations (up to

Table 1. Rate Parameters for Crystallization of Ammonium Chloride in Different Media

| | $T = 25°C$ | | Rev/min = 800 | | | |
|---|---|---|---|---|---|---|
| Medium | Residence time, $\tau$ (min) | Growth rate, $G$ ($\mu$m/min) | Nucleation rate, $B^\circ \times 10^{-5}$ (No./$\mu$m-ml) | Slurry density, $M_T \times 10^6$ (g/ml) | Specific number, $\nu \times 10^{-11}$ (No./g) | Population average size, $\bar{L}_{1,0}$ ($\mu$m) |
| Gaseous* | 0.17 | 2.32 | 2 000 | 10.0 | 34.00 | 0.40 |
| Toluene | 10.50 | 0.08 | 0.035 | 0.1 | 3.67 | 0.84 |
| Toluene/alcohol | 10.00 | 0.12 | 1.30 | 10.7 | 1.20 | 1.20 |
| Toluene/alcohol/2% water | 9.70 | 0.14 | 1.30 | 14.7 | 0.83 | 1.36 |
| Toluene/alcohol/4% water | 8.77 | 0.34 | 0.15 | 16.7 | 0.08 | 2.98 |

* After Stone and Randolph (1969).

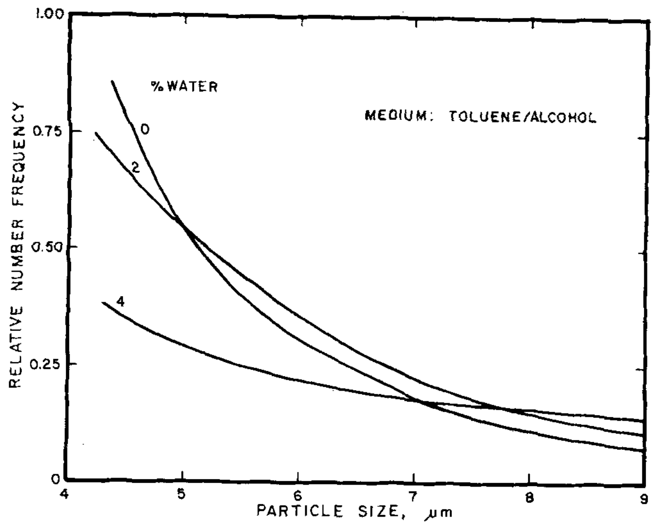

Fig. 4. Characteristics CSD's at three concentrations of water.

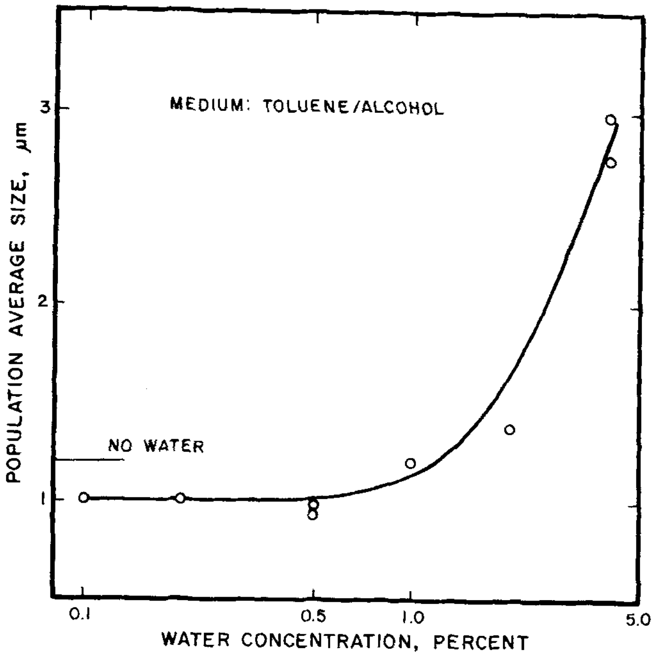

Fig. 5. Effect of water addition on average particle size of crystals.

0.5% water) but decreased nucleation in higher concentrations. Addition of 2 to 4% water caused a significant increase in the average size and a decrease in the specific number of particles. The improvement in the distribution of particles is clear in Figure 4, which shows a decrease in the relative number of fine particles and an increase in the number of large particles when 2 to 4% water was added to the system. Thus, larger particles were grown in a more waterlike mother liquor.

Magnesium chloride was another additive which influenced ammonium chloride precipitation. At a concentration of 50 ppm, magnesium chloride reduced nucleation and slightly increased the average particle size. This effect, shown in Figures 6 and 7, was observed in both toluene/alcohol and toluene/alcohol/water media.

Sodium oleate was studied as a possible crystallization modifier. As this compound had little solubility in the organic media, 1% water was added to increase its solubility in the additive feed solution, which was then metered into the circulating liquor. Seventy parts per million of sodium oleate in the final crystallizer mixture decreased nucleation rate considerably. However, slurry density was reduced in nearly the same proportion. That is, growth and nucleation rates were reduced in the same proportions. Thus, the net effect on particle size was not significant.

Sodium dodecylbenzene sulfonate had limited solubility (about 25 ppm) in the medium with or without water. This concentration was added uniformly to the circulating liquor and did not show any effect on ammonium chloride precipitation.

Sodium hexametaphosphate was more soluble than the other two sodium salts, but no significant change was observed, even with 160 ppm of this additive in the circulating liquor.

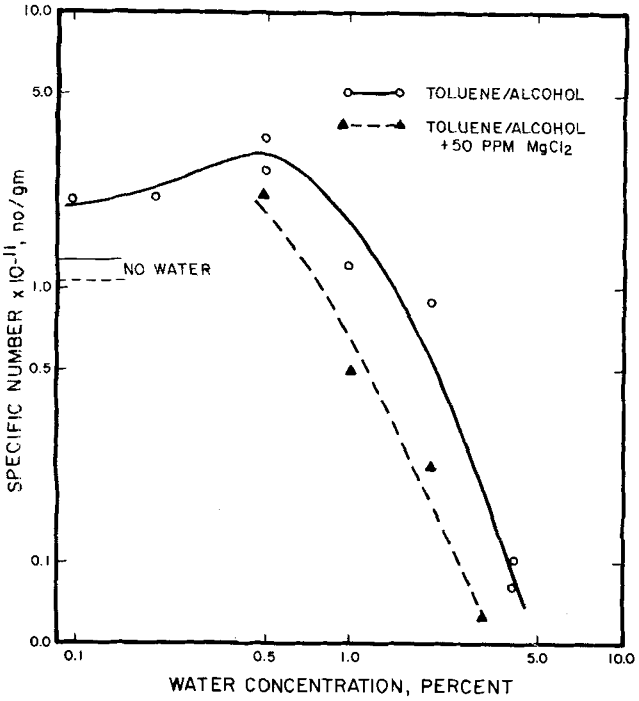

Fig. 6. Effect of water addition on specific number of crystals.

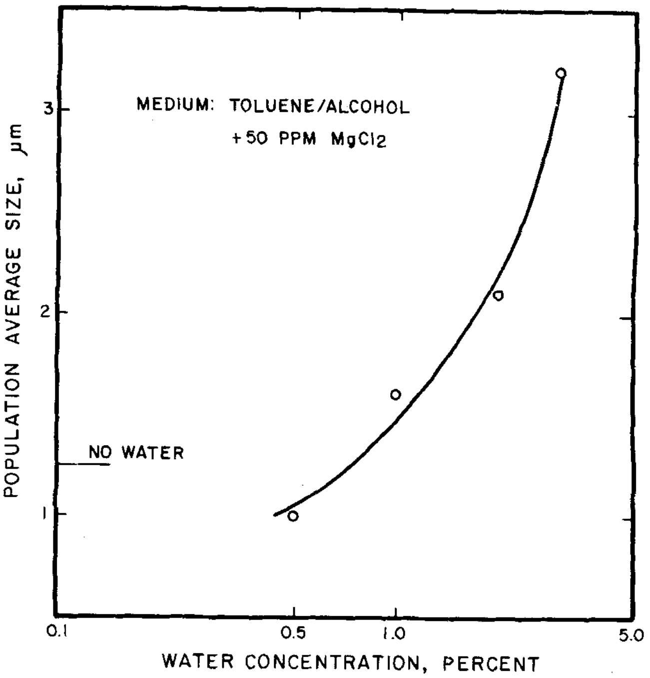

Fig. 7. Effect of water addition with 50 ppm magnesium chloride.

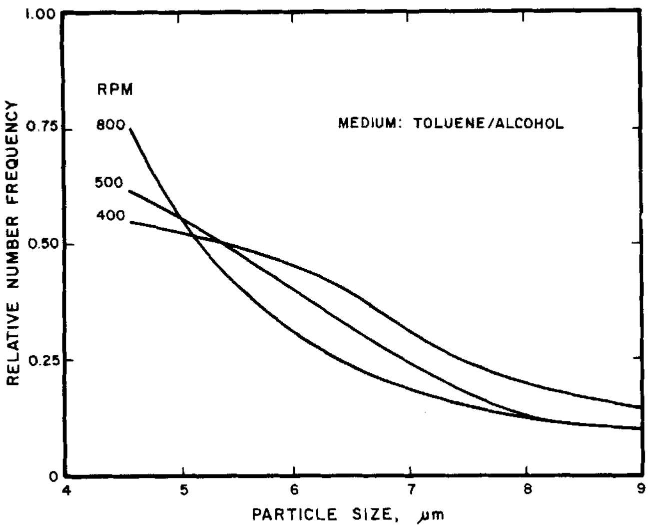

**Fig. 8. Characteristic CSD's at three stirring speeds.**

### Effect of Mixing

Figure 8 exhibits the size distribution of particles at three different stirring speeds. At speeds above 800 rev/min, the distribution was close to an exponential function, which is characteristic of a true MSMPR crystallizer. However, as the revolutions per minute decreased, agglomeration of particles changed the distribution function significantly. At low stirring rates, for example, 400 rev/min, a large number of agglomerates was visible (appearing as black specks in the counter microscope). The increase in agglomeration with lowering of revolutions per minute also resulted in larger apparent growth rate and average particle size with smaller apparent specific number as shown in Figures 9 and 10.

## DISCUSSION OF RESULTS

The formation and growth of ammonium chloride particles in the reactor/crystallizer are due to four processes occurring simultaneously: chemical reaction, nucleation, growth, and sometimes agglomeration.

As the two reactants come in contact, a fast chemical reaction takes place, and a relatively high concentration of $NH_4^+$ and $Cl^-$ is produced in the contact zone, resulting in high local supersaturation. These regions of high supersaturation give rise to homogeneous nucleation as the primary seed source. The rate of homogeneous nucleation is conventionally represented by

$$B^\circ = a(s) \exp\left[-\ b\sigma^3/\log^2 s\right] \tag{2}$$

where $a(s)$ and $b$ are functions of temperature and system physical properties.

The growth rate of crystals also depends on supersaturation according to

$$G = ks^i \tag{3}$$

where $i \simeq 1$ to 2.

The dependence on $s$ of $B^\circ$ is stronger than that of $G$; therefore, higher supersaturation enhances nucleation relative to growth, thus decreasing $\overline{L}_{1,0}$.

The particle distribution is significantly influenced when conditions are such that agglomeration occurs. The occurrence of agglomeration in this system appeared to be favored by high rates of make (higher number and mass density) and low agitation rates. In general, conditions were found where agglomeration did not occur for the study of additives.

The major factors affecting CSD are discussed as follows.

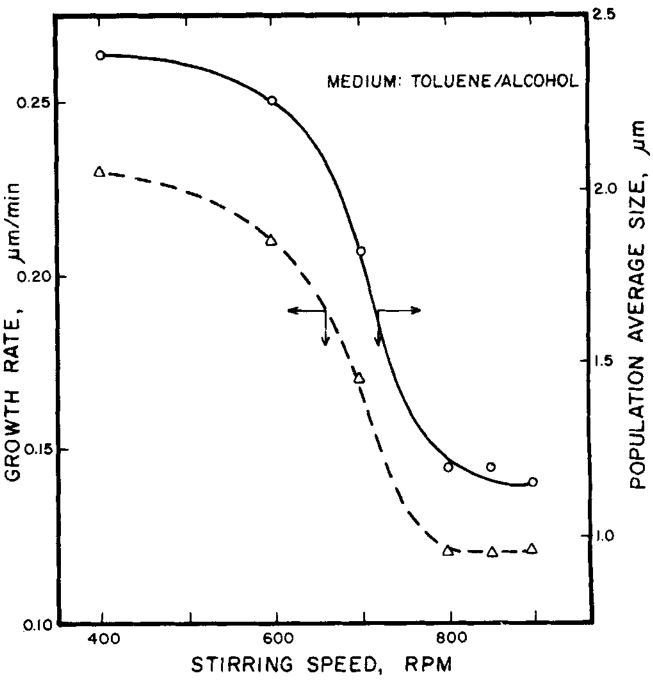

**Fig. 9. Effect of stirring speed on apparent growth rate and average particle size of crystals.**

### Effect of Reaction Medium

Nucleation, growth, and agglomeration rates all depend on the properties of the medium in which crystallization takes place. Comparing crystallization in different reaction media, one may conclude that as the solubility in the reaction medium increases, the rate of nucleation decreases, and larger particles are obtained. This is probably due to the fact that a more powerful solvent can absorb locally high levels of supersaturation in the reagent entrance region without generating bursts of homogeneous nucleation. This higher level of tolerance provides a greater chance to dilute the high supersaturation regions by mixing.

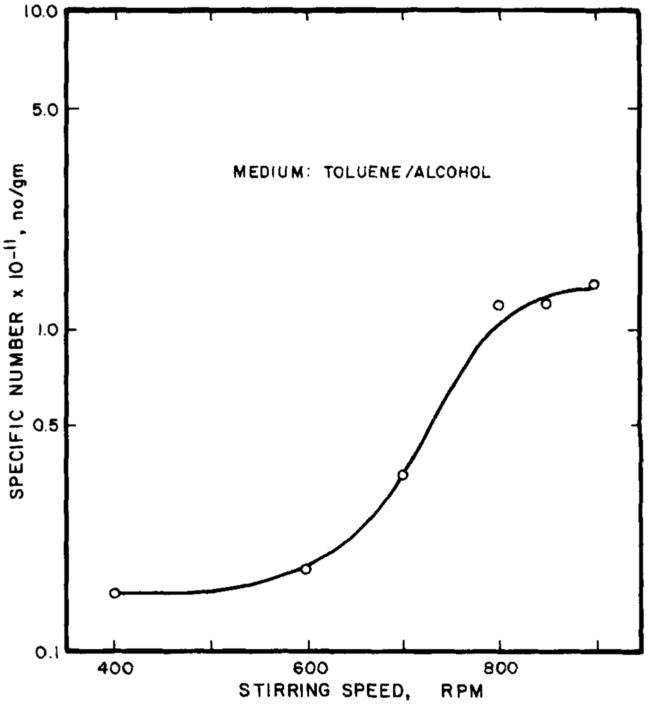

**Fig. 10. Effect of stirring speed on apparent specific number of crystals.**

It should be noted that the total mixed volume $V$ was used to obtain the growth rate $G$ from the size parameter $\overline{L}_{1,0} = GV/Q$. Undoubtedly, higher supersaturations and, hence, higher growth rates existed in the reagent entrance region. Significantly, even with such nonuniform regions of growth in the crystal magma, a near perfect fit to the MSMPR exponential population distribution was obtained under the proper conditions of agitation, rate of make, and total run time. Thus, as the suspension turnover time was much shorter than the 10 min retention time, crystals circulated randomly through high and low growth regions. The mixed discharge sets the exponential form of the distribution, and the reported growth rate is, in fact, the average over the suspension. Another way of saying this is that the crystals (due to the long retention time) behave as an ideal mixed phase, while the reagents (due to their fast reaction) behave as a segregated phase. This difference in supersaturation uniformity, which often spawns homogeneous nucleation, largely explains the differences in behavior between precipitation and soluble cooling systems. The MSMPR technique allows data interpretation for both systems, but growth rates are relative (to the assumed mixed volume) in the former case.

### Effect of Additives

Additives affect the crystallization kinetics in different ways. The mechanism in most cases is not clearly known. In this study, small concentrations of water (less than 0.5%) enhanced nucleation, while high concentrations had an opposite effect. This is probably due to the fact that water has two different effects: lowering the crystal/solution surface energy and increasing the solubility. At low concentrations of water, the first effect is dominant, and results in an increase in nucleation rate, as shown by Equation (2). However, at higher concentrations, the solubility effect becomes dominant, and the nucleation rate decreases. This dual effect results in the maximum shown in Figure 6.

Among the other additives tested in this study, $Mg^{++}$ showed some nucleation inhibition. This effect might be attributed to ion coordination effects. Sodium oleate, sodium dodecylbenzene sulfonate, and sodium hexametaphosphate are all effective modifiers in various aqueous systems, for example, borax and sodium bicarbonate (Randolph and Koontz, 1976). The former two additives are effective in aqueous solutions because of their surface active properties, while the latter is a powerful complexing agent. Neither surface active nor complexing effects of these three additives were of significance in the organic media studied.

### Effect of Mixing

Mixing affects the rate parameters and the CSD in two ways: it changes the extent of nonuniform supersaturation caused by the fast reaction and also effects the rate of agglomeration. This latter effect was only significant below a certain agitation level (800 rev/min in the present system).

In this study, the revolutions per minute were always 800, except for experiments performed to study these mixing effects. Under these conditions, no agglomeration was observed, and the CSD was close to the MSMPR exponential distribution. However, nonuniform supersaturation was probably not eliminated by increased agitation, as evidenced by the effect of reaction medium and the reduced nucleation that was observed when the reagent stream was diluted.

At low stirring speeds, agglomeration prevailed, and multicrystalline particles were visible with viewing microscope. As shown in Figure 8, the CSD deviated from the exponential form especially at the small size end of the distribution.

The population density plots (log $n$ against $L$) for CSD's at low stirring speeds were not linear over a wide range of particle sizes. The calculation of $\overline{L}_{1,0}$ and rate parameters were based on a relatively small section of the curve at the small size end, where the plot was linear and the scatter was minimum. Therefore, the growth rates reported include the net effect of both crystal growth and agglomeration. These data show increasing values of $G$ and $\overline{L}_{1,0}$ with lower revolutions per minute. Calculation of the actual linear growth rate and single crystal particles size is not feasible with this on-line technique when significant agglomeration occurs.

### Evaluation of the Experimental Technique

On-line measurement of CSD combined with the on-line data processing technique used in this study is a powerful tool for studying the kinetics of crystallization. In fact, this technique can be utilized for certain studies which have not been practical so far, owing to experimental limitations. Some of the advantages of the present method over batch sampling and separate data analysis are as follows:

1. The entire measurement and analysis takes only a few minutes.
2. The on-line technique eliminates sampling errors inherent with other batch techniques.
3. The capability of the system in displaying the intermediate results during CSD analysis saves time in checking the sampling accuracy and observing the system behavior.
4. The technique of on-line measurement and data reduction, if further developed, is a necessary prerequisite for the ultimate control of CSD in industrial crystallizers.

Obviously, there are limitations and problems which have to be resolved. The conductivity requirement of the mother liquor is a limitation in application of this on-line measurement. Other limitations are particle number density and orifice plugging. Other particle sizing instruments of the laser light scattering type (having no small apertures to plug) might prove more feasible in an industrial application. Finally, this on-line technique does not distinguish between single crystals and agglomerates; formation of the latter would be likely in organic media at industrial rates of make.

## ACKNOWLEDGMENT

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## NOTATION

$a$ = parameter in Equation (2)
$b$ = parameter in Equation (2)
$B^\circ$ = nucleation rate, No./(ml) (min)
$G$ = linear growth rate, $\mu$m/min
$i$ = parameter in Equation (3)
$k$ = parameter in Equation (3)
$k_v$ = shape factor for volume
$L$ = particle size, $\mu$m
$\overline{L}_{1,0}$ = population average size, $\mu$m
$M_T$ = solid concentration, g/ml
$n$ = population density, No./(ml) ($\mu$m)
$Q$ = volumetric flow rate, ml/min
$s$ = supersaturation, g of ammonium chloride/ml of medium
$V$ = crystallizer volume, ml
$\nu$ = specific number, No./g

$\rho$ = density of crystals, g/ml
$\sigma$ = surface energy, erg/cm$^2$
$\tau$ = residence time, min

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# The Mechanisms of Transfer of Hydrophobic Coated Mineral Matter Particles from a Hydrocarbon to an Aqueous Phase

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**A solid/liquid separation process based on the transfer of hydrophobic coated mineral particles from a hydrocarbon to an aqueous phase is described. This process could be used, for example, to remove mineral matter from coal derived liquids in order to meet fuel specifications. A model system which involves hydrophobic, asphaltic, coated mineral matter particles in a model liquid, xylene, was used in conjunction with the mechanistic studies. The mineral matter distribution coefficient to the aqueous phase decreases rather than increases with time in batch experiments. Five asymptotic models based on the fate of the surface active chemical at long time are investigated. Included were adsorption on the mineral matter particle, adsorption at the oil/water interface, distribution of the surfactant to the aqueous phase, complete detergency, and partial detergency. Experimental data on the influence of surfactant concentration, contact time, water/oil ratio, and shear are consistent only with the partial detergency model.**

## SCOPE

An extractive method is presented for the transfer of solid particles from one liquid stream to another. The process is based on the surface characteristics of the particle. Albertsson (1958, 1971) and Raghavan and Fuerstenau (1975) have previously demonstrated this process. This paper deals with the case where the particles are naturally wet by the original stream due to an acquired carbonaceous matter coating.

An experimental system consisting of an oil phase (xylene), an aqueous phase ($p$H adjusted water), and composite particles is studied. A composite particle consists of a mineral matter core which is surrounded by a hydrophobic layer. The composite particles are obtained from a coal derived liquid. Particle removal from coal derived liquids is a potential application of this process.

A surface active agent is used in order to promote particle transfer from the oil phase to the aqueous phase. The surfactant can function either by adsorbing onto the particle surface, making it hydrophilic, or by removing the hydrophobic coating (detergency), thereby exposing the more hydrophilic mineral matter surface. The liquid phases have been chosen so that the surface properties of the composite particles will dominate the experimental system.

Five mechanistic models based on the fate of surfactant at long time are proposed. These include adsorption onto the composite particle, adsorption at the oil/water interface, distribution of the surfactant to the aqueous phase, complete detergency of the hydrophobic layer, and partial detergency. These models are compared with data from batch experiments in which mixing time, mixing speed, surfactant concentration, and water/oil ratio are varied. The asymptotic models permit an unambiguous interpretation of the qualitative parameter dependences.

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