Growth of Contact Nuclei of Potassium Nitrate

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In previous work by several authors (e.g., Sikdar and Randolph, 1976) experiments have been performed using the continuous mixed suspension, mixed particle removed (MSMPR) technique developed by Randolph and Larson (1971). In these works the results indicated marked deviation from linearity of the semilog plot of population density vs. size at small sizes ($<5 \times 10^{-5}$ m). This curvature has generally been attributed to size-dependent growth in this size range; however, the occurrence of growth rate dispersion, wherein nuclei exhibit a distribution of growth rates, may also be a factor.

In a batch study undertaken by Garside et al. (1979), it was shown that contact nuclei were born directly into a wide range of sizes ($2 \times 10^{-6} - 4 \times 10^{-5}$ m). These crystals' growth rates were determined by use of a Coulter Counter by taking samples at time intervals. From these data it was determined that a size-dependent growth rate model could be used to describe the subsequent size distributions from the initial size distribution.

Garside and Larson (1978) developed an alternate technique wherein an optical microscope was used in conjunction with a growth cell to monitor formation of contact nuclei. The advantage to this method lies in its ability to analyze individual crystals. Garside (1979) used this type of apparatus to measure the growth rates of potash alum crystals formed by contact nucleation. There was a marked spread in growth rates for crystals of the same size which is the phenomenon known as growth dispersion. In addition crystals of a fairly large size ($\approx 2 \times 10^{-5}$ m) did not appear to grow at all.

The objective of this study was to extend the use of the microscopic technique for an additional compound namely potassium nitrate. The focus of the study was the subsequent growth behavior of the nuclei.

EXPERIMENTAL EQUIPMENT AND PROCEDURE

The growth cell used for all experiments is the same as that described by Garside et al. (1979), Figure 1. It consists of two chamber: an upper one which is filled with solution and a lower one through which water from a constant temperature bath is circulated. The cell is mounted on the platform of an optical microscope equipped with a camera.

Solutions were prepared from reagent grade potassium nitrate. Solute concentration was established by allowing the solution to equilibrate at 31°C for several months. Supersaturation was then obtained by undercooling this solution in the cell.

Contacts were performed by lightly touching a growing parent crystal with a stainless steel rod. The secondary nuclei formed from this contact quickly settled to a lower plate in the cell, where their growth was monitored by photographs taken at timed intervals. Undercoolings studied were 0.9, 1.4, and 1.7°C. Further details are given by Kaufman (1980).

DATA ANALYSIS

The data consisted of series of photographs taken at timed intervals. Since the size data from other studies comes from a Coulter Counter measurement of equivalent spherical diameter, an equivalent measurement was developed. The photographs could be enlarged significantly with preservation of detail. The area of the crystal's projection was determined by use of a planimeter, and this area was converted to an equivalent circular diameter. The equivalent circular diameter was compared to a geometric mean size determined by using the largest dimension and the dimension at right angles to it. The geometric mean size was calculated by taking the square root of the product of the two dimensions. This value and the equivalent circular diameter were found to agree to within approximately 5%. Since the former value was much easier to determine it was used as the characteristic dimension, similar to the equivalent spherical diameter used in Coulter Counter analysis.

RESULTS AND DISCUSSION

Nineteen nuclei that were formed in the contact nucleation cell were analyzed. For each nucleus a plot of geometric mean diameter versus time was constructed using the photographic data and some examples are shown in Figure 2. The most interesting feature common to all of the plots is the linearity. This linearity indicates that each individual nucleus has its own constant growth rate since the slope is growth rate. In addition, the existence of a nonzero intercept (initial size) indicates that the nuclei are formed at a finite size and not at zero size as is assumed in an ideal MSMPR crystallizer. The undercooling, initial size, growth rate, and correlation coefficient for size vs. time for each nucleus are given in Table 1.

The constant growth rate of individual nuclei is an important result. Semilogarithmic plots of population density vs. size from continuous crystallization studies for this size range often demon-

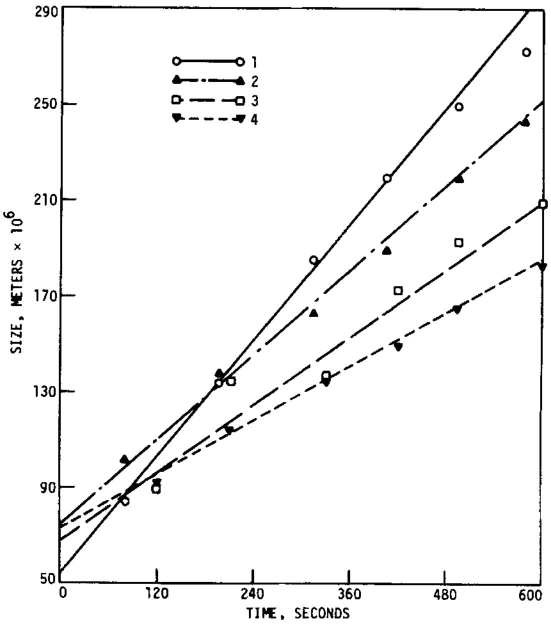

Figure 1. Batch contact nucleation cell used in the present study.

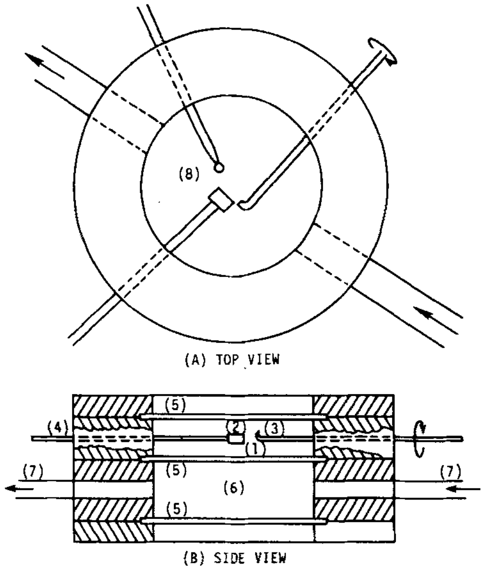

Figure 2. Geometric mean size vs. time for contact nuclei of potassium nitrate at an undercooling of 1.7°C.

strate curvature which has been interpreted as size-dependent growth. From the present results of size-independent growth rate it appears necessary to search for an alternate explanation of the curvature.

Another important result of the present work is the wide variation in growth rates for nuclei at the same undercooling. Table 1 gives the gowth rates and indicates to what extent the values vary. The growth rates were compared using a t-test at the 95% confidence level and were found to be significantly different. While the various crystals were found to be significantly different at a given undercooling, when it was attempted to correlate growth rate to the variable undercooling it was found that this variation was too large to give any meaningful result.

Some crystals have growth rates listed in Table 1 that are zero. These crystals do not appear to grow and are 2.5×10^{-5} to 4.5×10^{-5} m in size. This size range rules out the Gibbs-Thomson effect as a possible explanation. It would appear the zero growth rate of these crystals is related to some other factor, perhaps structure.

TABLE 1. RESULTS OF STATISTICAL ANALYSIS OF SIZE VS. TIME REGRESSIONS

Crystal No.	ΔT °C	Initial Size, m/s × 10^6**	Growth Rate m/s × 10^6**	Correlation Coefficient
1	1.7	53.1	23.6	0.993
2	1.7	74.2	17.6	0.997
3	1.7	68.9	14.3	0.975
4	1.7	72.4	11.1	0.998
5	1.7	71.5	11.5	0.996
6	1.7	78.9	21.6	0.992
7	1.7	26.8	0.00	0.000
8	1.7	34.4	0.00	0.000
9	1.7	42.1	0.00	0.000
10	1.4	23.9	0.00	0.000
11	1.4	63.6	8.80	0.971
12	1.4	49.9	0.773	0.902
13	1.4	81.1	2.21	0.999
14	1.4	63.0	2.42	0.986
15	0.9	36.5	2.40	0.974
16	0.9	43.9	4.18	0.996
17	0.9	40.9	1.19	0.960
18	0.9	37.4	7.80	0.995
19	0.9	33.0	8.17	0.983

* Intercept of regression line.
** Slope of regression line.

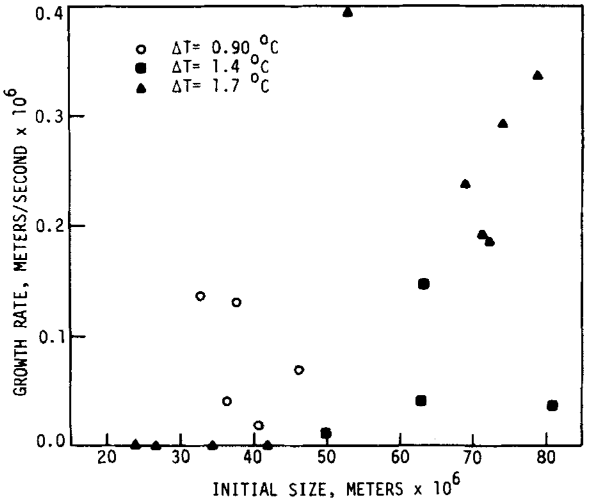

Figure 3. Growth rate vs. initial size for contact nuclei of potassium nitrate.

In an attempt to correlate the growth rate to some experimental measured value, the growth rates were plotted against initial size, Figure 3. From this plot it is clear that the contact nuclei are formed with both an initial size distribution and a growth rate distribution. This plot also indicates there may be some dependence of growth rate on initial size; however, there are insufficient data to prove this.

The data present some interesting points. It seems that curvature at lower sizes in the semilog population density plots is not simply due to size dependent growth rate. Upon viewing the data presented, it would appear that growth dispersion combined with an initial size distribution would provide a more viable explanation. If the initial size distribution is not important the growth rate dispersion phenomenon may also be important in systems which exhibit primary nucleation.

SUMMARY AND CONCLUSIONS

The experimental evidence presented suggests that size-dependent growth does not occur for contact nuclei in the potassium nitrate-water system. Rather, the data show that a wide range of growth rates occurs in crystals growing under identical conditions. In addition each crystal seems to possess some constant inherent growth rate. In view of these results it is suggested that interpretation of curvature in the semilog population density-size plot from MSMPR crystallizers should focus on the phenomenon of growth rate dispersion instead of size dependent growth.

ACKNOWLEDGMENTS

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Vapor-Liquid Equilibria for NH_3 and H_2O in the 100 to 150°C Region: Effect of Low Levels of Phenol on Partial Pressure of Ammonia

Experimental results are reported for the partial pressure of ammonia in water solutions containing low concentrations of phenol. Experiments were performed in 0.6 molal phenol at 100 and 150°C. Results at 150°C indicate that the very small effect of phenol on the partial pressure of ammonia is within the limit of experimental error, 3%, and therefore could not be established from the data. However, at 100°C, the partial pressure of ammonia was decreased by nearly 10%. Computer program TIDES—a computerized thermodynamic framework for calculating vapor-liquid equilibria for volatile weak electrolytes and other common gases—has been revised to account for the effect of low concentrations of phenol.

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INTRODUCTION

Chemical and related industries frequently use water to cool and wash process streams. For example, in coal-gasification processing, water absorbs not only small quantities of nitrogen, carbon monoxide, hydrogen, argon, lower hydrocarbons, and phenolics, but also sizable quantities of ammonia, carbon dioxide, hydrogen sulfide, hydrogen cyanide, and sulfur dioxide. Describing phase equilibria for aqueous solutions of volatile, weak electrolytes have been the subject of several recent studies (Edwards et al., 1978; Renon and Beutier, 1978); however, these studies do not account for the presence of phenol, which is nearly nonvolatile but partially dissociates in water. Growing interest in coal gasification has motivated questions regarding the effect of phenol on the degree of dissociation of volatile, weak electroytes. We have performed some experiments on ammonia-phase equilibria in water containing low levels of phenol. The temperature range of 100 to 150°C was chosen to correspond to industrial coal-gasification operating conditions. For typical coal-gasification processes, concentrations of 0.07 to 0.2 molal phenol have been reported for wastewater streams (Div. of the Bureau of Mines, 1974). Our experiments were performed with 0.6 molal phenol solutions to amplify the phenol's effect.

REVISION OF PROGRAM TIDES

To calculate the effect of phenol on ammonia partial pressure, Program TIDES (a computerized molecular thermodynamic correlation for phase equilibria of aqueous volatile, weak electrolytes as described by Pawlikowski, 1981) has been revised to account for phenol dissociation. Phase-equilibrium and chemical-equilibrium expressions for phenol are incorporated into the solution schemes for bubblepoint, dewpoint, and flash calculations. Table 1 provides the phenol dissociation constant and its temperature dependence as reported by Tsonopoulos (1976). Henry's constant for phenol is also given as a function of temperature. Because there are no data available, all binary interaction parameters for phenol and phenolate ion and all other species were set equal to zero.

To examine Program TIDES' capability to predict phase equilibria for solutions containing phenol, some experiments for NH_3 and phenol in water were performed.

EQUIPMENT AND PROCEDURE

A static experimental apparatus was used for measurements on both liquid- and vapor-phase compositions. Details of the experimental apparatus are described elsewhere (Pawlikowski, 1981). Gas-liquid chromatography was used for sample analysis.

After the equilibrium cell was thoroughly cleaned, it was filled with 0.6 molal phenol solution. The solution was degassed by pulling a vacuum for several hours. The cell is then pressurized with NH_3, and the solution was allowed to equilibrate overnight. Samples of both liquid and vapor phases were taken using the technique outlined by Pawlikowski. Phenol levels in the vapor phase were below the detection limit of the chromatograph. After sampling was completed, the pressure in the cell was adjusted by the addition of more ammonia vapor.

Anhydrous ammonia (purity better than 99.99%) was obtained from Matheson Gas Co. Water was obtained from a reverse-osmosis

TABLE 1. PROPERTIES OF PHENOL IN WATER*

Dissociation Equilibrium:

$$C_6H_5OH \overset{K_{EQ}}{\rightleftharpoons} C_6H_5O^- + H^+$$

$$ln\ K_{EQ} = -00669.42/T \qquad -27.7262\ ln\ (T) + 174.133$$

K_{EQ} is mol/kg H_2O
for a temperature range of 25 to 250°C

Henry's Constant

$$ln\ H\ (\text{bar kg/mol}) = -58.808 + 0.26613T - 0.31628E - 3T^2$$

for a temperature range of 0 to 100°C

Phenol-Phenol Interaction Parameter, β_{tt} in kg H_2O/mol

$$\beta_{tt} = 42.979 - 0.25389T + 0.3698E - 3T^2$$

for a temperature range of 0 to 100°C

Henry's constants and β_{tt} parameters obtained from data of Good and Millay (1956) and Hirata (1975).

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* Temperature T in K.