The Formation of Solvent Inclusions During Continuous MSMPR Crystallization

FAN WEIPING
and A. S. MYERSON

School of Chemical Engineering
Georgia Institute of Technology
Atlanta, GA 30332
Department of Chemical Engineering
Polytechnic Institute of New York
Brooklyn, NY 11201

INTRODUCTION AND BACKGROUND

The presence of pockets of solvent trapped as a second-phase impurity in crystals grown from solution and from the melt has been widely reported in the literature (Myerson, 1977; Myerson and Kirwan, 1977, Edie and Kirwan, 1973; Denbigh and White, 1966). These experimental studies have usually involved single crystals. Nidel (1977) attempted to reproduce experimental results reported for inclusion formation in single crystals employing a continuous mixed suspension, mixed product removal MSMPR crystallizer. At growth velocities similar to those used in single crystal studies. Nidel (1977) was unable to obtain any solvent inclusions. Slaminko and Myerson (1981) experimentally studied the formation of solvent inclusions in single crystals of potassium aluminum sulfate dodecahydrate and sodium chloride grown from aqueous solution. They reported a critical crystal size (at a given set of conditions) below which inclusions did not form. It was postulated from the results of Slaminko and Myerson (1981) that Nidel (1977) did not observe solvent inclusions in his continuous experiments because the crystals grown were all below the critical size.

The purpose of this work is to determine experimentally the critical size required for inclusion formation during the continuous growth of potassium aluminum sulfate dodecahydrate, sodium chloride, and potassium chloride in an MSMPR crystallizer and compare these results to those previously obtained in single crystal studies.

EXPERIMENTAL

Experiments were conducted in a continuous MSMPR crystallizer similar in design to those used by previous investigators (Shor and Larson, 1971. Nidel, 1977). The crystallization vessel was jacketed and contained a draft tube and baffles. Agitation was provided by a Lightnin Model 20 mixer. The jacket temperature was controlled by a Endocal refrigerated circulating bath (model RTE-5B), manufactured by Neslab, which allowed the jacket temperature to be controlled to within ±0.01°C. A schematic diagram of the MSMPR crystallizer appears in Figure 1.

The crystallizer was operated with supersaturations ranging from 0.5 to 3°C, at residence times ranging from 30 to 120 min. Steady state was assumed in each experiment after four residence times of operation at the desired temperature. Product crystals obtained were filtered and acetone-washed to remove adhering solution. The crystals were then sieved to separate them into size ranges. Crystals from each size range were analyzed for the percent entrapped solvent by atomic absorption spectroscopy. In those systems that form only hydrates, water exceeding the stoichiometric amount within the solid was taken as impurity. The accuracy of the excess water determination was no worse than ± 3% by weight. Crystal growth rates were calculated from the crystal size distributions employing methods described by Randolph and Larson (1971).

RESULTS AND DISCUSSION

Results are presented in Table 1 for the continuous growth of potassium aluminum sulfate dodecahydrate. The results demonstrate a critical crystal size between 2.8 and 3.35×10^{-3} m (second longest dimension) at crystal growth rates ranging from 1.05 to 3.9×10^{-8} m/s. This observed critical size is significantly larger than the largest crystals (2.2×10^{-3} m) examined by Nidel (1977) in a similar study employing an MSMPR crystallizer and explains the fact that no solvent inclusions were observed in his work. Slaminko and Myerson (1981) reported a critical crystal size of 2.8×10^{-3} at growth velocities ranging from 1.8 to 6.0×10^{-8} m/s during the growth of single crystals of potassium aluminum sulfate dodecahydrate. This result is essentially the same as observed in this work in a MSMPR crystallizer. Both the single crystal results of Slaminko and Myerson (1981) and the results presented in this work show that the critical size does not change significantly with increasing crystal growth rate. However, the amount of solvent inclusion in a crystal at a given size (above the critical size) increases with increasing crystal growth rate. This result is consistent with the results of Myerson and Kirwan (1977) and can be attributed to an unstable crystal-liquid interface.

A number of experiments were conducted employing sodium chloride in aqueous solutions at undercooling of 0.5–3°C and residence times of 30–120 min. The largest crystals obtained in any experiment were 1×10^{-3} m and no solvent inclusions were observed. Slaminko and Myerson reported a critical size of 2.0 ×

Correspondence concerning this paper should be addressed to A. S. Myerson.

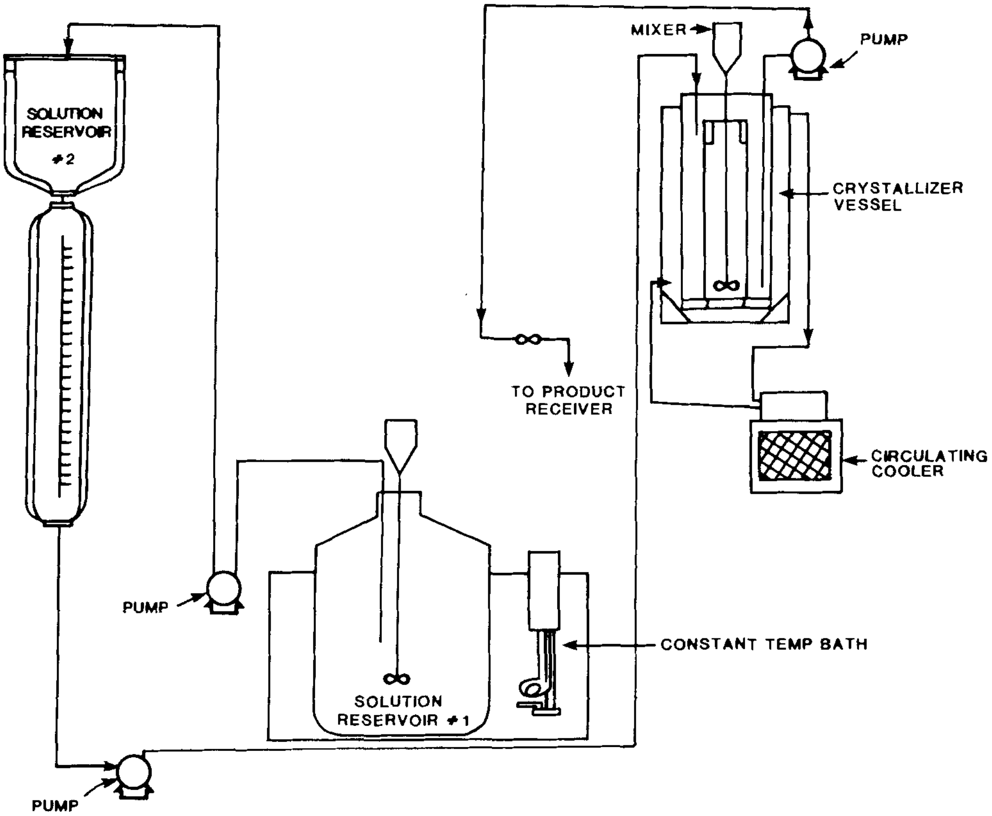

Figure 1. Continuous MSMPR crystallizer.

10^{-3} for the growth of single crystals of sodium chloride, which explains the lack of inclusions observed in this study. Results are presented in Table 2 for the continuous growth of potassium chloride. The results demonstrate a critical crystal size ranging between 1.2 and 2.4 × 10^{-3} m. The results in the KCl system show dependency of critical size on crystal growth rate with the critical size increasing with increasing crystal crystal size. This result has been predicted theoretically (Brice and Bruton, 1974) but attempts to employ theory to predict the critical size have met with little success.

TABLE 1. FORMATION OF SOLVENT INCLUSIONS DURING THE CONTINUOUS GROWTH OF POTASSIUM ALUMINUM SULFATE DODECHYDRATE

Run	Under-cooling °C	Residence Time, min.	Growth Rate m/s × 10^8	Mesh No.	Crystal Dimen. m × 10^3	Solvent Incl. wt. %
1	0.5	60	1.05	≤5	≥4.0	0
1	0.5	60	1.05	4	4.25	7
2	1.0	60	1.66	≤7	≥2.8	8
2	1.0	60	1.66	6	3.35	6
2	1.0	60	1.66	5	4.0	7
3	2.0	60	2.1	≤7	2.0	0
3	2.0	60	2.1	6	3.35	5
3	2.0	60	2.1	5	4.0	7
3	2.0	60	2.1	4	4.75	10
4	1.0	30	3.4	≤7	≥2.8	0
4	1.0	30	3.4	6	3.35	7
4	1.0	30	3.4	5	4.0	10
4	1.0	30	3.4	4	4.75	13
5	2.0	30	3.9	≤7	≥2.8	0
5	2.0	30	3.9	6	3.35	7
5	2.0	30	3.9	5	4.0	12
5	2.0	30	3.9	4	4.75	14

The results of this study have demonstrated a critical crystal size for the formation of solvent inclusions in a continuous MSMPR crystallizer. The results have also shown that critical size data obtained from single crystal studies is essentially the same as that obtained in continuous MSMPR experiments. This suggests the control of solvent inclusions industrially by laboratory measurements of the critical crystal size for the system of interest,

TABLE 2. FORMATION OF SOLVENT INCLUSIONS DURING THE CONTINUOUS GROWTH OF POTASSIUM CHLORIDE

Run	Under-cooling °C	Residence Time, min.	Growth Rate, m/s × 10^8	Crystal Dimen., m × 10^3	Solvent Incl. wt. %
1	1	40	1.9	≥2	0
1	1	40	1.9	2.4	5
1	1	40	1.9	2.8	8
2	2	40	2.6	≥2.0	0
2	2	40	2.6	2.4	7
3	3	40	3.2	≥1.2	0
3	3	40	3.2	2.0	4
3	3	40	3.2	2.4	8
4	2	60	1.6	≥2.4	0
5	3	60	2.1	≥2.0	0
5	3	60	2.1	2.4	6
5	3	60	2.1	2.8	8

followed by control of the crystal size to minimize crystals above this critical size.

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