The Effect of an Additive on Morphology of Sodium Chloride Crystals in Seeded Batch Cooling Crystallization

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Seeded batch cooling crystallization was performed to investigate the effect of an additive, citric acid, on the morphology of sodium chloride crystals in aqueous solution. The experimental results revealed that the amount of seed crystals plays an important role for the morphology of product crystals as well.

1. Introduction

We have studied seeded batch cooling crystallization, focusing on the effect of additives on crystallization process in many years. In seeded batch crystallization, the seed crystals, if the amount of them is sufficient, can be grown to the product of a desired size without secondary nucleation (Doki et al., 2003) (Doki et al., 2004a). And this seeding effect was applied to the polymorphic system Glycine to selectively obtain the unstable metastable α-form (Doki et al., 2004b). As for the effect of impurity on seeded batch cooling crystallization, Kubota and Takahashi (1987) reported the effect of Cr^{3+} on the crystal size of ammonium sulfate. The report describes the product size of ammonium sulfate is dependent on the timing of the addition of additive Cr^{3+}: the size became larger when Cr^{3+} was added after the occurrence of secondary nucleation. The effect of Bismarck Brown B on K-Alum crystal was investigated (Kubota and Oikawa, 1998): it is found that the shape of K-Alum crystal was modified from octahedron to truncated octahedron. Chianese (2003) reported the habit of hydroquinone crystal was modified by using pyrogallol the result was explained with the Kubota-Mullin's model of impurity effect on crystal growth (Kubota and Mullin, 1995).

Recently (Sasaki et al., 2006) (Sasaki et al., 2008), we investigated the effect of additive on crystal growth by measuring the growth-starting supercooling ΔT_G of a single crystal or the supercooling at which the crystal starts to grow when the aqueous solution is continuously cooled in the presence of additives. The experimental results obtained were that growth-starting supercooling ΔT_G depended on additive concentration in the case that the equilibrium adsorption onto the surface of a crystal was established.

In this study, seeded batch crystallization of sodium chloride was performed in an aqueous solution including citric acid as a modifier. The aim of this study is to show an important role of an additive in morphology modification in seeded batch system.

2. Experimental

2.1 Preparation for Measurement

Mixed aqueous solution of citric acid and hydroxide was prepared at T_s= 35 ℃ in a 500 mL glass crystallizer equipped with an agitator and a thermometer. An aliquot of sodium chloride powder was added into the solution and was agitated for more than 3 h. The working volume was 460 mL. The 35 ℃ saturated sodium chloride aqueous solution (pH = 4.5) was thus obtained. The solution was filtered through a filter paper (20 μm

pore size), and was cooled to an adsorption temperature, T_A= 34.5 ℃, lower than the saturation temperature 35 ℃.

The seeds of sodium chloride crystal were prepared by sieving recrystallized crystals with two successive sieves with openings of 180 and 150 μm. The arithmetic mean size of the sieves was L_S= 165 μm, which was considered to the average size of the seed crystals.

2.2 Seeded Batch Cooling Crystallization

Figure 1 shows the temperature profile in seeded batch cooling crystallization. This temperature profile was employed according to the precious studies (Sasaki et al., 2006) (Sasaki et al., 2008). The seed crystals (W_s in g/100 mL) were introduced into the solution during the temperature was kept at T_A=34.5 ℃ for 22 h in order to make citric acid adsorb seed crystals surface until an equilibrium state was established. After adsorption (t_{Aeq}= 22 h) was completed (Sasaki et al., 2006) (Sasaki et al., 2008), the slurry was cooled at a cooling rate of R = 0.23 ℃/h until a termination temperature of T_c= 29 ℃. The slow cooling rate minimizes second nucleation. The termination temperature T_c=29 ℃ was determined by considering the values of equilibrium growth-starting supercooling temperature ΔT_{Geq} for the (100) and (111) faces of a sodium chloride single crystal in our previous studies (Sasaki et al., 2006) (Sasaki et al., 2008). The growth-starting supercooling is the supercooling above which crystals can grow during cooling, the values of ΔT_{Geq} for the (100) and (111) faces at a citric acid concentration of c = 0.4 mol/L, were 3.7 ℃ for the (100) face and of ΔT_{Geq}= 4.2 ℃ for the (111) face, respectively (Sasaki et al., 2006) (Sasaki et al., 2008). From these data, it can be clearly concluded that the growth rate G of the (111) face is lower than that of the (100) face. Therefore, thus T_c= 29 ℃, which is lower than T_{Geq}= 30.8 ℃ (equilibrium growth-starting temperature) of the (111) face, is an effective temperature to grow preferentially the {111} faces. During the whole experiment, agitation speed was fixed at 200 rpm.

At the end of cooling, all the crystals were separated by filtration, and the crystals on the filter were washed by pure ethanol. After drying the crystals, the size distribution was determined by sieving, and crystal shape was observed through a microscope (OLYMPUS BX-P).

The batch cooling crystallization was performed repeatedly with different seed amounts, W_s from 0.1 to 0.5 g/100mL, at different citric acid concentrations of c = 0.1, 0.2, 0.3 and 0.4 mol/L.
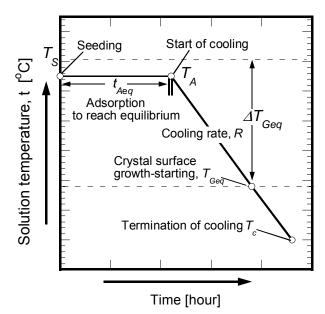

Figure 1: The Temperature Profile of Seeded Batch Cooling Crystallization.

2.3 Measurement of Transient Crystal Size Distribution

Transient crystal size distribution was measured. Sodium chloride crystals obtained in this study was not much in mass because the volume of crystallizer was small and supercooling was not large. Therefore, it was not possible to take samples of slurry successively at intervals from the crystallizer and to determine transient

crystal size distribution during cooling. Instead, the experiment was performed with various termination temperatures T_c at a seed amount of W_s = 0.30 g/100mL. And the whole crystals obtained in each experiment were analyzed by sieving. The termination temperatures T_c examined (and the corresponding supercoolings) were 34.5 °C (ΔT = 0.5 °C), 33.5 °C (ΔT = 1.5 °C), 32.9 °C (ΔT = 2.1 °C), 32.4 °C (ΔT = 2.6 °C), 31.9 °C (ΔT = 3.1 °C), 31.4 °C (ΔT = 3.6 °C) and 30.8 °C (ΔT = 4.2 °C). For all the experiments, the adsorption time t_A was 22 h.

3. Results and Discussion

3.1 Product Crystal Morphologies

Figure 2 shows the morphology map of the product crystals on the plane of seed amount and citric acid concentration. Circles denote truncated octahedron crystals (all faces are the (111)), whereas triangles denote those of truncated octahedral and cubic crystals, and crosses denote those of cubic crystals. It can be seen that the shape of product crystals are different depending on the seed amount and citric acid concentration. The {111} faces crystals were obtained at citric acid concentration c = 0.4 mol/L, over a wide range of W_s from 0.132 to 0.487 g/100mL. And, as citric acid concentrations is decreased, the range of W_s for {111} faces became steadily narrow, and then, cubic crystals become to be included in the product crystals. It is estimated that the effect of additive on the shape of crystals depend on the amount of seed crystals W_s.
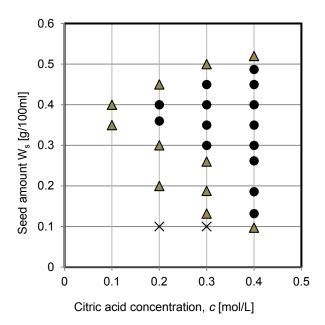

Figure 2: The product crystal morphologies at different seed amounts over a range of citric acid concentrations (c = 0.1, 0.2, 0.3 and 0.4 mol/L)

3.2 Distributions of Sizes and Shapes

In order to evaluate the influence of seed amount W_s on the shape of the product crystals, the following discussion is focused to the results of an additive concentration, c = 0.3 mol/L.
Figures 3a-3d show the size distribution and the mass fraction of truncated octahedral to cubic crystals. These crystals of the two shapes (truncated octahedron and cubic) were obtained at a one single operation of cooling crystallization. The product size (L_p) was determined by sieving, and the shape of crystals was classified with eyes to two types of truncated octahedron and cubic under microscope.
Truncated octahedron crystals were obtained at seed amounts W_s from 0.30 to 0.45 g/100mL. Figure 3a shows crystal size distribution at W_s = 0.30 g/100mL as a representative of the truncated octahedral product. As seen in Figure 3a, the size distribution is uni-modal and no crystals smaller than or equal to 50 μm (or much smaller than the size of seed crystals) are included. The distribution indicates that truncated octahedral crystals were all grown seed crystals, which were obtained without secondary nucleation during cooling.
And, Figure 3b shows the size distribution and the mass fraction at seed amount of W_s = 0.26 g/100mL. The product is a mixture of cubic and truncated octahedral crystals. The size distribution is bimodal. The smaller
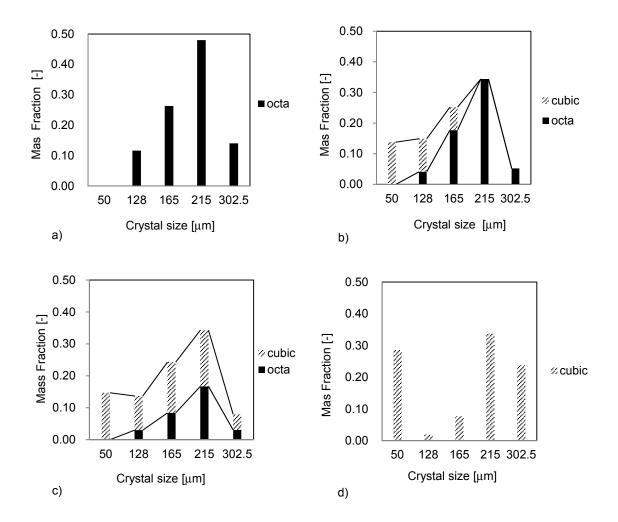
Figure 3: Distributions of size and shape of crystals obtained at: a) W_s= 0.30 g/100mL (W_s/W_p= 0.78, L_p/L_s= 1.17); b) W_s= 0.26 g/100mL (W_s/W_p= 0.66, L_p/L_s= 0.95); c) W_s= 0.50 g/100mL (W_s/W_p= 0.76, L_p/L_s= 0.99) and d) W_s= 0.10 g/100mL (W_s/W_p= 0.24, L_p/L_s= 1.05).

part consists of cubic crystals (50-128 μm), which is not affected by the presence of additive, and the larger part consists of truncated octahedral crystals. From the results shown in Figure 3b, it is suggested the nuclei generated by secondary nucleation mechanisms grew to cubic during cooling because of insufficient adsorption time of citric acid.

Figure 3c shows the distribution of crystal size and shape for the case that the seed amount was increased to W_s = 0.50 g/100mL. Cubic crystals are obtained over the all crystal size range. This is because a large number of secondary nuclei were generated by the increased seed crystals. It is known that seed mass density (or magma density) has an effect on secondary nucleation (Doki et al., 2003) (Doki et al., 2004a). Because of insufficient adsorption time, the effect of citric acid did not appear and hence the nuclei-grown crystals were all cubic. In Figure 3c, truncated octahedron crystals are also seen. These crystals are considered to be grown seed crystals, for which sufficient adsorption time is guaranteed.

In case that the seed amount was reduced to W_s = 0.10 g/100mL, all the product crystals are cubic (Figure 3d). In this case, the secondary nuclei-grown crystals became cubic for the same reason as mentioned above. That is, citric acid was not given enough time for adsorption and, hence, secondary nuclei grew without the effect of citric acid. While, the seed crystals are considered not to have grown virtually, because the surface of a small number of seed crystals were covered enough with citric acid and growth was suppressed.

In summary, in seeded batch cooling crystallization of sodium chloride aqueous solution in the presence of citric acid, secondary nucleation plays a key role for morphology change. A small amount of seed crystals,

which do grow virtually because of suppressive effect of citric acid, leads to a high supersaturation and large numbers of secondary nuclei are generated. These nuclei-grown crystals are all cubic. This is because adsorption time for citric acid is insufficient. A large number of seed crystals generate many secondary nuclei. These nuclei are not affected by the presence of citric acid. Grown-secondary nuclei are cubic. Simultaneously, the added seed crystals can grow and become truncated octahedral. A medium amount of seed crystals grow to octahedral shape with suppressed secondary nucleation. Thus, an optimal seed amount is considered to exist for a large amount of octahedral sodium crystals.

3.3 Behavior of Crystal Growth

Figure 4 shows the transient size distribution of crystals during cooling for seed amounts of W_s = 0.30 g/100mL, at a citric acid concentration of c = 0.3 mol/L. In Figure 4, particles less than 100 μm size are not observed. It is clear that the seeds grew without secondary nucleation and their morphology was modified. In our previous studies (Sasaki et al., 2006) (Sasaki te al., 2008), the values of ΔT_{Geq}, the growth-starting supercooling above which crystals can grow during cooling, for the (100) and (111) faces were 3.1 and 3.6 ℃ at a citric acid concentration of c = 0.3 mol/L. And, from the transient crystal size distribution (Figure 4), it can be seen clearly that the seed and secondary nuclei started to grow at ΔT = 3.1 ℃.
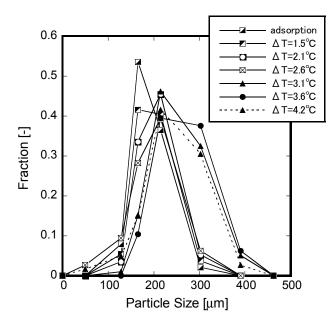

Figure 4: Transient Particle Size Distribution (c = 0.3 mol/L, seed size = 165 μm, W_s = 0.30 g/100mL).

4. Conclusions

Seeded batch cooling crystallization of sodium chloride was performed in an aqueous solution doped with citric acid as a morphology modifier. The experimental results reveal that morphology of sodium chloride crystals can be changed to octahedral. The concentration of citric acid and the seed amount both play an important role for morphology modification

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