Growth phenomena and morphology of NaCl crystals in drowning-out precipitation operation

Hiroshi TAKIYAMA and Masakuni MATSUOKA
Department of Chemical Engineering, Tokyo University of Agriculture and Technology (TUAT)
184-8588, Tokyo, Japan

Drowning-out precipitation of the sodium chloride - ethanol - water system was carried out, and relationships between the supersaturation and the crystal morphology were examined under the various operating conditions. It was found that the crystal morphology changed as the degree of initial supersaturation ΔC_0 changed even if the initial supersaturation ratio σ_0 was the same. In order to control the crystal morphology, it was clear that both ΔC_0 and σ_0 should be specified. It also became clear that the number of crystal particles varied with the solution mixing conditions. The operating strategies of drowning-out precipitation were proposed.

1. INTRODUCTION

1.1. Drowning-out precipitation

The crystallization method which produces supersaturation by addition of another antisolvent is well known as the drowning-out precipitation. The advantages of this crystallization method are as follows: (1) The operations of crystallization are relatively simple. (2) It can be operated at room temperature condition. (3) The utility equipment can be simplified. (4) The product yield can be high. The drowning-out precipitation has the following disadvantages. (a) The product crystals are often too fine. (b) This crystallization method sometimes results in various crystal morphologies which depends on the operating conditions. The characteristics of the solid-liquid separation become poor because of those phenomena which lead to a decrease in product purity. Therefore, the control of the morphology and the size distribution of product crystals is essential in the drowning-out precipitation operation.

There are many studies on the drowning-out precipitation and various systems have been used. Jones et al. reported the possibilities of obtaining crystals similar to those from cooling crystallization of potassium sulphate and potash alum [1,2]. Oosterhof et al. discussed relationships between porous crystal morphology and the operating conditions in the case of sodium chloride precipitation [3]. In our previous work [4], surface appearance and morphology of crystals were classified, and relationships between them and the operating conditions were discussed. Franke et al. carried out a precipitation experiment of $CaSO_4 \cdot 2H_2O$ and $CaCO_3$ and proposed the design and operation scheme of the drowning-out precipitation [5].

1.2. Crystal morphology

Crystal morphology is often changed in various ways by the addition of antisolvents even when sodium chloride crystals were precipitated. When ethanol is used as the antisolvent, the morphology as shown in Fig.1 sometimes appears in addition to the cubic, plate and rod-like crystal shapes.

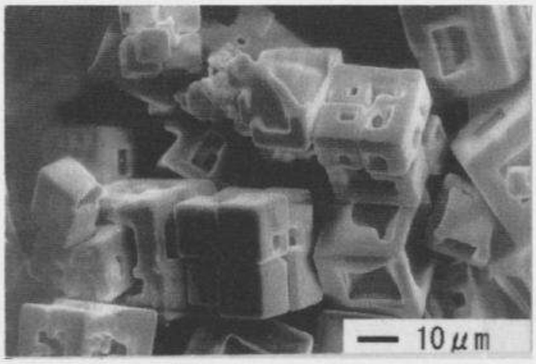

Figure 1. SEM photomicrograph of NaCl (NaCl - EtOH - H_2O system).

It seems that these crystals are agglomerated with eight constituent hollow cubic-like crystals. When methanol was added as the antisolvent, a different crystal morphology appears (Fig.2). When hydrochloric acid is added in order to generate supersaturation, the crystal morphologies also changed as shown in Fig.3. These crystal morphologies are very complex.

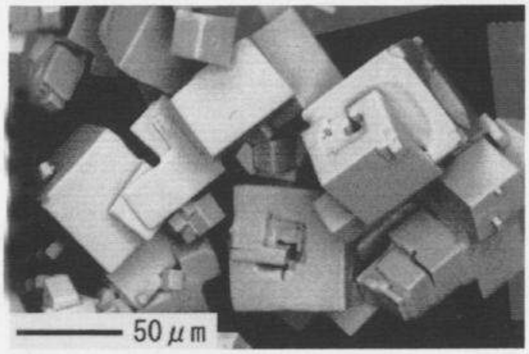

Figure 2. SEM photomicrograph of NaCl (NaCl - MeOH - H_2O system).

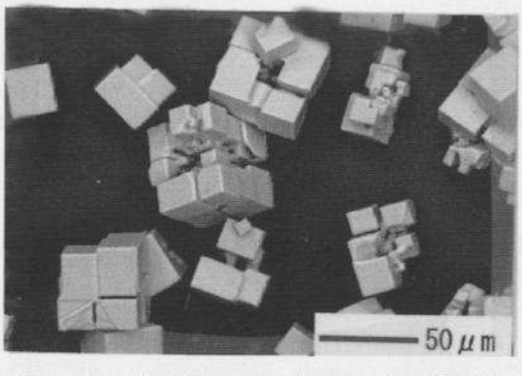

Figure 3. SEM photomicrograph of NaCl (NaCl - HCl - H_2O system).

As mentioned above, in the drowning-out precipitation the crystal morphology changes differently with the difference in the kinds of antisolvent and also in the operating conditions.

In this study, the relationships between the crystal morphology and the operating conditions, especially σ_0 and ΔC_0, are investigated. And the operating strategy of the drowning-out precipitation is discussed. The sodium chloride - ethanol - water system was used in the following discussion.

2. EXPERIMENTAL

2.1. Experimental methods

By mixing two ternary saturated aqueous ethanol solutions having different compositions (some of the solutions are binary), supersaturation was generated in order to precipitate sodium chloride crystals. The solubility and the solution density data were taken from the previous work [4]. The experimental procedures are as follows: (1) Two aqueous ethanol solutions saturated with sodium chloride (solution *a* and solution *b*) are prepared (see Table 1). The ethanol composition of solution *a* is higher than that of solution *b*. (2) One of the solutions was charged into a 10 ml crystallizer, and was stirred with a magnetic stirrer at predetermined speed. Then the other solution was fed into the crystallizer with a pipette at a ratio to provide a predetermined supersaturation to cause precipitation. The conditions of the mixing rate were also predetermined. All the experiments were carried out at room temperature (298K). (3) The slurry containing sodium chloride crystals was sampled and was filtered on a membrane filter (pore size 0.45 μm). (4) After drying, the crystals on the filter were observed with a scanning electron microscope (SEM: JEOL, JSM-3100LV).

Table 1
Solution combination group

	Solution *a*			Solution *b*		
	C_{NaCl}	C_{EtOH}	C_{H2O}	C_{NaCl}	C_{EtOH}	C_{H2O} [mass %]
Group A	0.04	99.96	0.0	26.35	0.0	73.65
Group B	0.04	99.96	0.0	2.24	8.20	89.56
Group C	0.04	99.96	0.0	8.12	46.20	45.68
Group D	8.12	46.20	45.68	26.35	0.0	73.65

2.2. Solution and operating conditions

Four groups (A to D) of solutions (*a* and *b*) shown in Table 1 were prepared. Some operating conditions were determined for each group to provide necessary supersaturations. Examples of the operating conditions are shown in Table 2. The relationships between ΔC_0 (= C_0 - C^*) and σ_0 (= ΔC_0 / C^*) for groups A and C are shown in Figs. 4a and 4b.

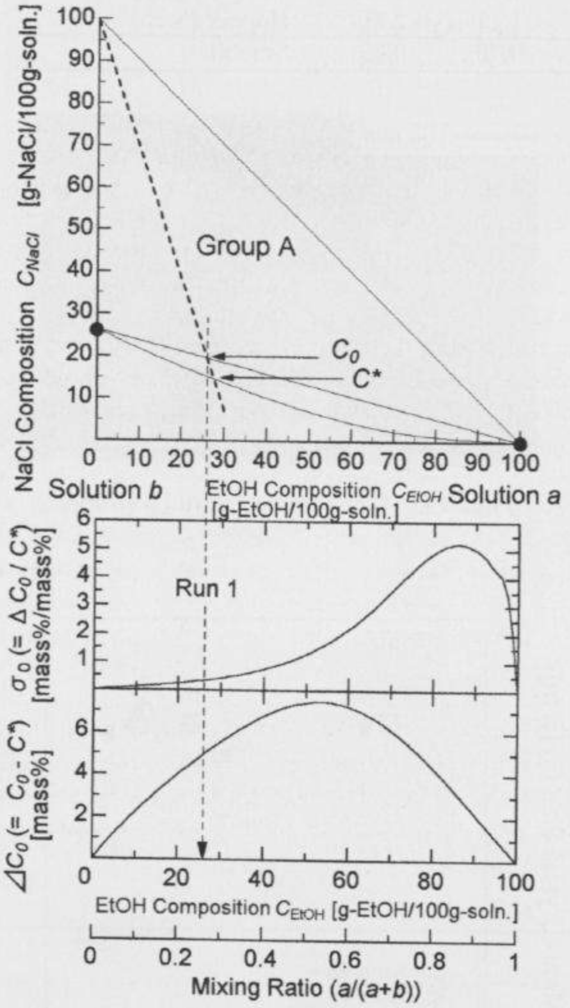

Figure 4a. Triangular phase diagram and operating condition of group A.

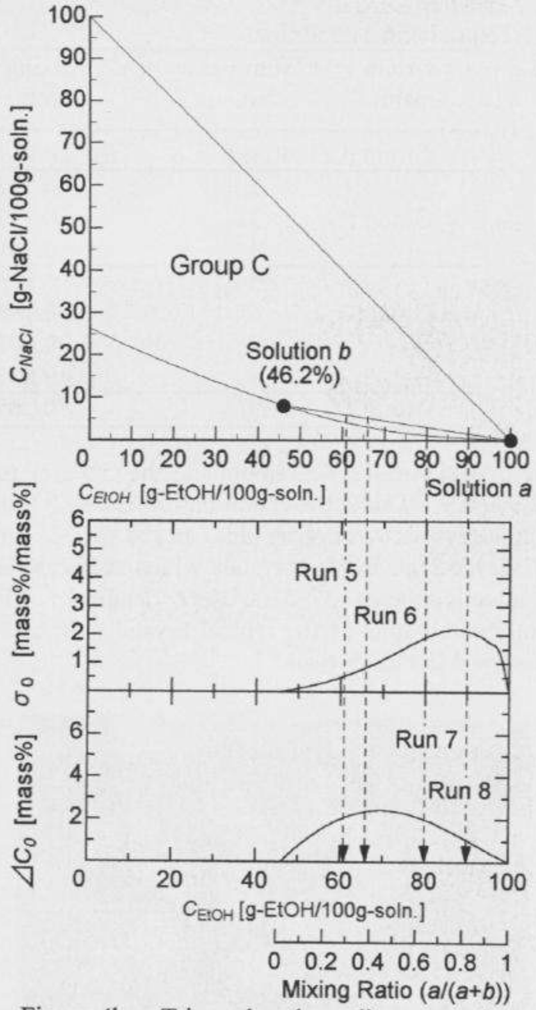

Figure 4b. Triangular phase diagram and operating condition of group C.

In the case of run 1 of group A, the composition of solution *a* and solution *b* were (0.04, 99.96, 0.0 (C_{NaCl}, C_{EtOH}, C_{H2O})) and (26.35, 0.0, 73.65) respectively. The mixing ratio (=(Mass of solution *a*)/(Mass of total solution) is 0.261. For this case σ_0 and ΔC_0 are 0.35 and 5.0 % respectively.

The operating conditions are quite evident from these diagrams even if the solutions are mixed at any arbitrary mixing ratio.

3. EXPERIMENTAL RESULTS

3.1. Crystal morphology

The observations of the crystal morphologies by SEM are shown in Table 2.

Table 2
Experimental conditions

Group name	Run No.	Mixing Ratio $a/(a+b)$	ΔC_0 [mass%]	σ_0 [-]	Surface appearance
Group A	Run 1	0.261	5.00	0.35	Smooth
Group B	2	0.577	6.29	2.03	Smooth
	3	0.732	5.00	3.61	Smooth
	4	0.741	4.65	3.90	Hollow
Group C	5	0.289	2.06	0.53	Hollow
	6	0.385	2.37	0.86	Hollow
	7	0.642	1.97	1.92	Hopper (Step)
	8	0.805	1.17	2.16	Hopper (Step)
Group D	9	0.167	0.70	0.03	Smooth

The crystal surface was smooth in the cases of runs 1,2,3 and 9. Under the conditions of runs 4, 5 and 6, hollow crystals were observed. In the case of run 7 and 8, the hopper type crystals which surfaces were negative pyramids of steps were obtained. SEM photomicrographs of the typical crystal morphology are shown in Figs 5, 6 and 7.

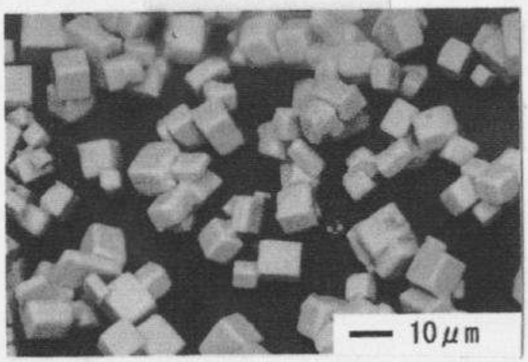

Figure 5. NaCl crystals in run 2 (Smooth).

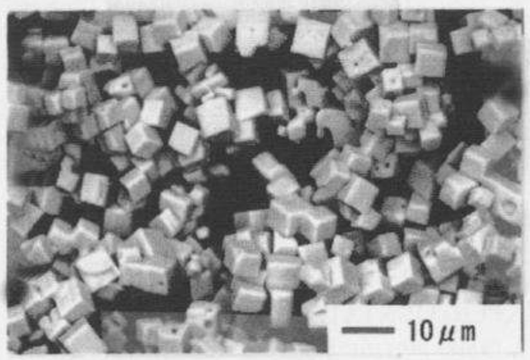

Figure 6. NaCl crystals in run 4 (Hollow).

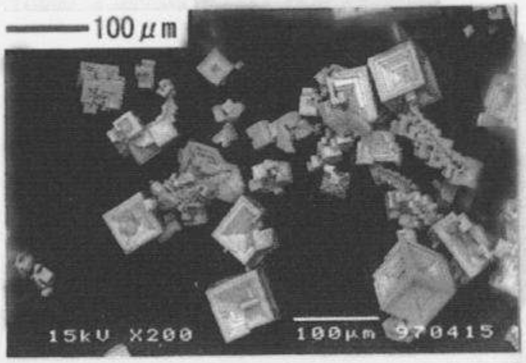

Figure 7. NaCl crystals in run 8 (Hopper).

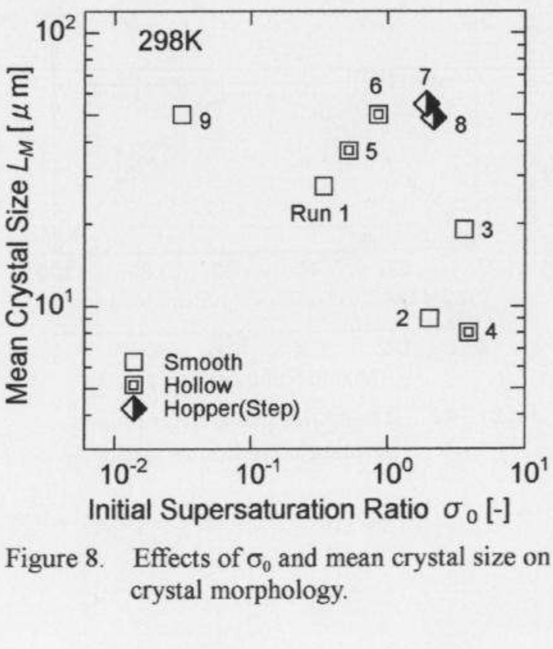

Figure 8. Effects of σ_0 and mean crystal size on crystal morphology.

3.2 Crystal size

Feret's diameters of the crystals were measured by a digitizer from the photomicrographs and the volume based average size was calculated. Relationships among σ_0, the average size and the surface appearance of crystals are shown in Fig. 8. It is clear that the higher σ_0 and the larger the crystals are, the rougher the crystal surface becomes. These relationships agree with the previous experimental results [4].

4. DISCUSSION

4.1. Crystal morphology and operating conditions

Even if one combination group of solutions is chosen, σ_0 and ΔC_0 can be different by changing the mixing ratio of the two solutions. It was summarized how the crystal morphology changed when σ_0 and ΔC_0 were determined as the operating conditions in each group. The results are shown in Fig. 9. The solid curves show relations between σ_0 and ΔC_0 for the same group, that is, any point of these curves corresponds to one mixing ratio of solutions in one group. The broken lines show various equilibrium concentrations C^*. The slope of the broken line corresponds to the reciprocal of C^*.

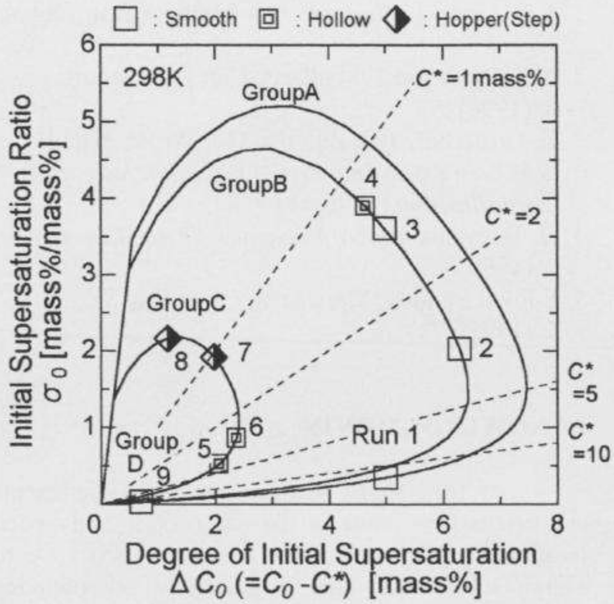

Figure 9. Relationships among ΔC, σ_0 and crystal morphology.

From Fig. 9 the following conclusions can be drawn. (1) The crystal morphology changes with the mixing ratio even for the same combination group. (2) The crystal surface shows a tendency to become hopper like when σ_0 is higher, even if the precipitation is carried out as the same ΔC_0. (3) The crystal surface becomes smooth when ΔC_0 is higher as the same σ_0. It is clear that a crystal morphology can not be predicted by only controlling either σ_0 or ΔC_0. It is understood that the crystal surface is kept smooth if the operating conditions were in the range of high ΔC_0 values.

4.2. Number of crystal particles

It is important to prevent producing small sized crystals in order to make solid-liquid separation easy for industrial application. In the drowning-out precipitation, it is necessary that the number of crystal particles is reduced to obtain larger crystals. So, the influence of the mixing conditions of two solutions on the number of crystal particles was investigated. The results are shown in Fig.10.

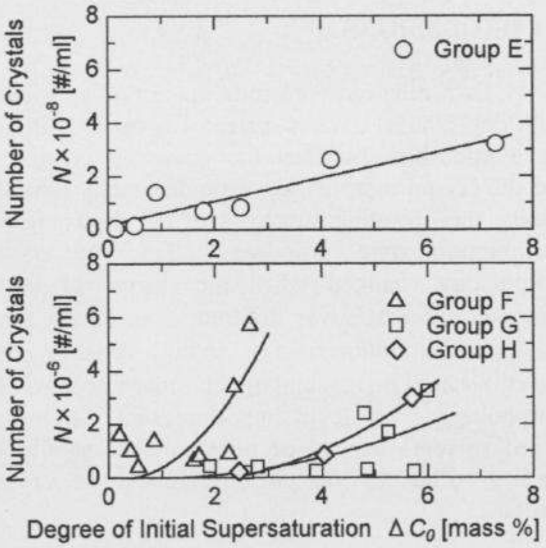

Figure 10. Relationships between solvent composition and number of crystals.

Table 3
Ratio of solvent composition

Group name	Solution *a*			Solution *b*			Mixing ratio
	C_{EtOH}	C_{H2O}	M_a [%]	C_{EtOH}	C_{H2O}	M_b [%]	$a/(a+b)$
Group E	99.9	0.0	100	0.0	73.8	0	0.02 ~ 0.97
F	99.9	0.0	100	45.9	45.9	50	0.05 ~ 0.97
G	89.5	9.9	90	0.0	73.8	0	0.08 ~ 0.89
H	94.8	5.0	95	7.7	69.2	10	0.15 ~ 0.73

$M_i = C_{EtOH}\text{-solution } i \,/\, (C_{EtOH}\text{-solution } i + C_{H2O}\text{-solution } i) \times 100 \quad (i = a \text{ or } b)$

The experimental conditions were the same as in the previous work [4]. The ratio of the solvent composition of each group is shown in Table 3. There is a larger number of crystal particles in the case of group E in comparison with other groups as the same ΔC_0. It was assumed that physical properties of the solution such as density and solution structure influenced mixing behavior. The reason for these phenomena needs further discussion however the number of crystal particles could be reduced by using binary mixed solvents instead of pure solvents.

5. CONCLUSIONS

Drowning-out precipitation of the sodium chloride - ethanol - water system was carried out and the relationships between the operating conditions and the crystal morphology were discussed. As the results, the operating strategies of the drowning-out precipitation were proposed. (1) The crystal morphology changed when the degree of initial supersaturation ΔC_0 was different even as the same initial supersaturation ratio σ_0, so both variables (ΔC_0 and σ_0) should be manipulated in order to control the morphology. (2) It is important that the binary mixed solvents instead of pure solvents should be used in order to reduce the number of crystal particles.

NOMENCLATURE

C_0 initial concentration of NaCl in solution, mass %

C_{EtOH} concentration of ethanol in solution, mass %

C_{H2O} concentration of H_2O in solution, mass %

C_{NaCl} concentration of NaCl in solution, mass %

C^* equilibrium concentration (solubility), mass %

ΔC_0 degree of initial supersaturation ($= C_0 - C^*$), mass %

M_i ethanol composition of mixed solvent in solution i ($i = a, b$), %

σ_0 initial supersaturation ratio ($= \Delta C_0 / C^*$)

REFERENCES

1. A.G. Jones, J. Buds and J.W. Mullin, *Chem Eng Sci*, 42(1987)619
2. A.G. Jones and J. Mydlarts, *Can J Chem Eng*, 68(1990)250
3. H. Oosterhof, T.G. Zijlema, G.J. Witkamp and G.M. van Rosmalen, *Proc 13th Symp. Ind. Crystallization* (1996)613
4. H. Takiyama and M. Matsuoka, *Trans IChemE*, 76(1998)809
5. J. Franke and A. Mersmann, *Chem Eng Sci*, 50(1995)1737

ACNOWLEDGMENTS

This study summarizes the experiments and discussions made in the consortium "Advanced purification in crystallization" during March 1996 to March 1999. The authors gratefully acknowledge the members of the consortium.