Agric. Biol. Chem., **51** (9), 2359～2366, 1987

Mechanism of Ice Growth in a Batch Crystallizer with an External Cooler for Freeze Concentration

Yoshihito SHIRAI,* Takayuki SUGIMOTO, Masayuki HASHIMOTO,
Kazuhiro NAKANISHI and Ryuichi MATSUNO**

Department of Food Science and Technology, Faculty of Agriculture,
Kyoto University, Sakyo-ku, Kyoto 606, Japan
**Department of Chemical Engineering, Faculty of Engineering, Kyoto University,*
Sakyo-ku, Kyoto 606, Japan

Received March 11, 1987

Two mechanisms of ice crystal growth were found in a batch crystallizer with an external cooler, that contained a large amount of ice crystals. With the first mechanism, the ice crystals grew larger by the usual kind of growth, governed by heat or mass transfer resistance, and with the second, the ice crystals agglomerated and the agglomerate fused into a very large ice crystal (1～3 mm in diameter). The conditions in which the second mechanism prevails were investigated extensively. The second mechanism occurred not because of the high concentration of ice crystals in the crystallizer but because of long residence time. Large ice crystal agglomerates were not produced when extremely small ice crystals were formed in the crystallizer at the start of the experiment.

In freeze concentration, large ice crystals with a sharp crystal size distribution are desirable to minimize loss of solutes. The larger the ice crystal, the smaller the amount of solute adhering to the surface. Huige and Thijssen[3,9] have studied ice crystal growth in several saccharide solutions with high ice-crystal concentrations in a continuous crystallizer equipped with a ripening tank. When the residence time of ice crystals was long enough, crystals as large as 1 mm were produced. Smith and Schwartzberg[4] also examined ice crystal size changes during ripening in freeze concentration. We have identified factors affecting the crystal size distribution in an adiabatic batch[1,7] or continuous[2] crystallizer. The distributions can be predicted in the crystallizer with a growth rate mechanism dependent on crystal size. These results were obtained in sample solutions that contained a few ice crystals (less than 0.3%). It is also necessary to investigate the behavior of ice crystals when the concentration of ice crystal in sample solutions is high.

Here, the mechanisms of ice crystal growth with high concentrations of ice crystals in sugar solutions were investigated in a batch crystallizer with an external cooler. The ice crystals formed were kept in the crystallizer throughout each experiment, and a sample solution was circulated between the crystallizer and the external cooler for heat exchange. We found that small ice crystals, 0.1～0.5 mm in diameter, agglomerated and changed into large ice crystals, 1～3 mm in diameter, with a sharp crystal size distribution when the crystals were kept growing in the crystallizer for a long time (1～2 hr).

MATERIALS AND METHODS

Materials. Lactose and glucose solutions of various concentrations were used. Skim milk was also used. Lactose and glucose of analytical grade were purchased

---

** To whom correspondence should be sent.

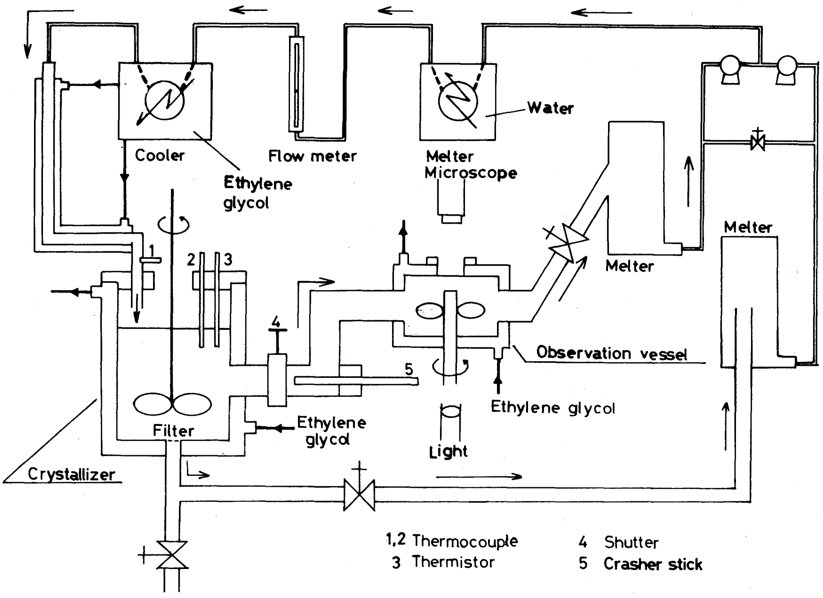

FIG. 1. Experimental Set-up.

from Wako Pure Chemicals; the skim milk was obtained from a market.

Experimental. The experimental set-up is shown in Fig. 1. The sample solution was cooled to a constant temperature below the freezing point by the external cooler and fed into the crystallizer. Ice crystals that formed in the crystallizer were kept there throughout each experiment. The solution, which was separated from the ice crystals by a nylon filter at the outlet of the crystallizer, was recycled with a pump to the external cooler *via* an ice melter. The crystallizer contained 1.3 l of sample solution. The total amount of sample solution in the system was 3.2 l. The system was protected from heat loss with heat-insulating materials.

Experiments were done as follows:

1. The crystallizer and observation vessel were cooled to remove the heat produced by mixing with an agitator. The temperature of the ethylene glycol used for the refrigerant was set at 0.2°C below the freezing point of the solution since it is found from calculation that the heat generated by mixing is removed with this temperature difference. The revolution rate of the agitator was kept constant at 600 rpm.
2. The sample solution was circulated at a constant flow rate (usually 550 ml/min) among the crystallizer, the observation vessel, the melters, and the external cooler. The solution was cooled at 0.5°C below the freezing point by the external cooler and fed into the crystallizer. The temperature in the crystallizer decreased gradually.
3. A seed ice crystal with the volume of 10 μl was introduced into the crystallizer to start crystallization when the temperature in the crystallizer reached close to the freezing point.
4. The moment the seed crystal was introduced, a shutter placed between the crystallizer and the observation vessel was closed.
5. The ice crystals that formed were kept in the crystallizer for $10 \sim 120$ min of holding time. The ice crystals grew and nucleated during this period.
6. When the prescribed time had passed, the shutter was measured with a copper-constantan thermocouple into the observation vessel. Then, the feed solution was stopped and the ice crystals that floated in the vessel were observed with a microscope (Nikon SMZ 10) at 30 magnifications. The ice crystals in the observation vessel were agitated gently by a propeller to prevent agglomeration.

The change in temperature with time in the crystallizer was measured with a copper-constantan thermocouple and a thermistor (Ishizuka Denshi 512CT).

The amount of solute incorporated in the ice crystal was measured by the following procedure. Ice crystals that formed in the crystallizer were placed in a stainless steel net and washed for an appropriate length of time by being immersed in 20 vol of water at 0°C. After the interstitial water was drained off, the ice crystals were melted and the sugar was measured by the phenol sulfuric acid method.[10]

RESULTS AND DISCUSSION

Temperature changes during experiments

An example of the temperature change mea-

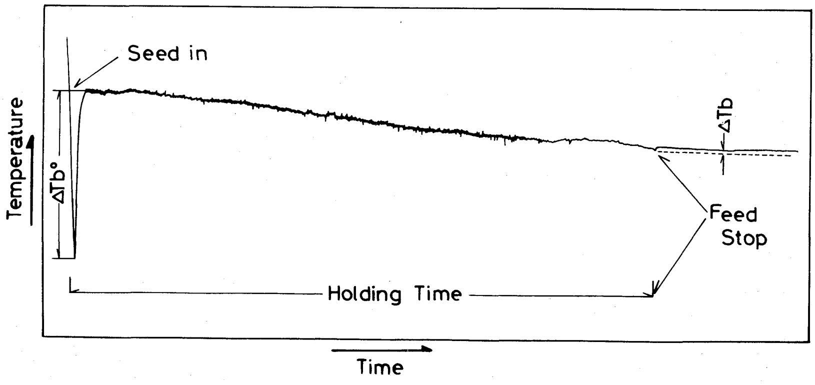

FIG. 2. Temperature Change during Crystallization of Ice Crystals in 10% Lactose Solution.
$\Delta Tb^{\circ}=0.148°C$; $\Delta Tb=0.003°C$; flow rate of sample solution, 550 ml/min.

sured in a 10% lactose solution during the experiments is shown in Fig. 2. Before the sample solution was seeded, its temperature decreased because subcooled solution at 0.5°C below the freezing point of the sample solution was continuously fed into the crystallizer. The decrease in the temperature continued even after the introduction of a seed ice crystal because there is an induction period[5~7)] during which ice nucleation occurs only from the seed crystal, and consequently the rate of release of latent heat is very low. At the end of the induction period, the temperature reaches a minimum and then rise abruptly until it reaches a plateau. The difference between the plateau and the minimum temperature is defined as the initial subcooling, ΔTb°. Even if the seed was introduced at the same temperature, the ΔTb° changed with the kind of solute and the concentration, on which the length of the induction period depends.[5,6)] Then the temperature decreased gradually because the freezing point decreased with the increase in the solute concentration. The temperature rose by 0.003°C to the freezing point when the feed solution was stopped. This difference in temperature, ΔTb, is the driving force for the growth and nucleation of the ice crystals.

Mechanism of ice crystal growth at high concentration of ice crystals

Ice crystals formed in the crystallizer were observed at different holding times and two mechanisms for ice crystal growth were found. In the first, the ice crystal increased its size by the usual growth process governed by heat or mass transfer resistance. In the second, the ice crystals agglomerated and the agglomerate fused into one very large ice crystal. Hereafter, the second mechanism will be called the agglomeration mechanism. In this article the conditions on which the second mechanism prevails were investigated extensively. Figure 3 shows changes in the ice crystal size in 10% lactose solution with increased holding time, in which the agglomeration mechanism is clearly seen. The initial subcooling, ΔTb°, was about 0.15°C. Ten minutes after the seeding, the ice crystals were disc-shaped, as observed before.[1,2,7~9)] Little agglomeration occurred among the ice crystals. As the holding time increased, the agglomeration increased, as shown in Fig. 3, with the boundaries of the agglomerated ice crystals seeming to melt into each other to make one crystal. At 120 min of holding time, the diameter of the agglomerated ice crystals reached 2 mm, and they were shaped like a disc. The size distribution of the ice crystals was very sharp.

With high solute concentration or high ΔTb°, agglomeration was not observed.

Effects of the amount of ice crystals in the crystallizer on growth mechanisms of the ice crystals

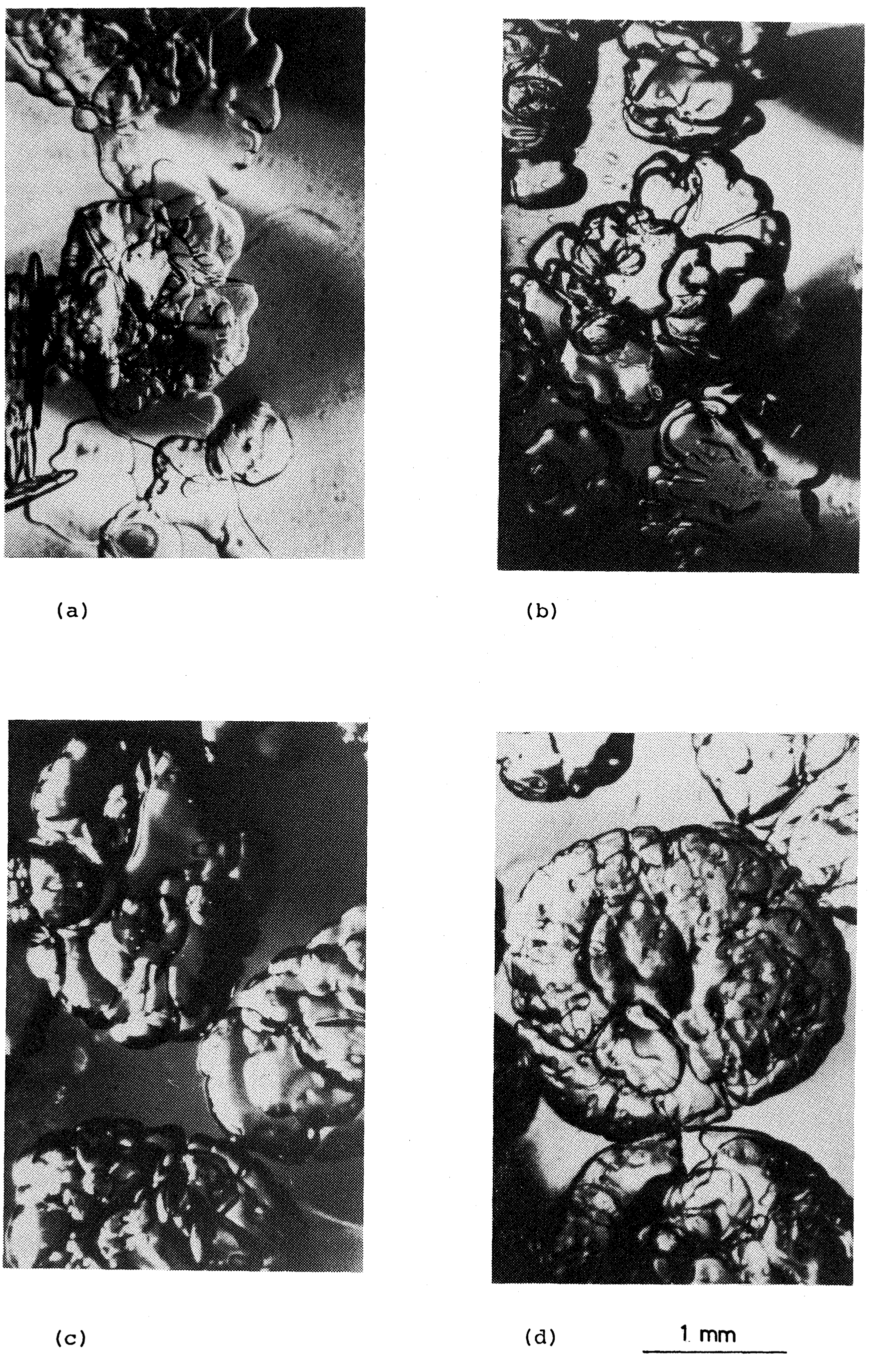

FIG. 3. Growth of Ice Crystals by the Agglomeration Mechanism in 10% Lactose Solution.
$\Delta Tb^{\circ} = 0.15^{\circ}C$; flow rate of sample solution, 550 mi/min; holding time, (a) 10 min; (b) 1 hr; (c) 1.5 hr; (d) 2 hr.

The feeding temperature of the sample solution was kept constant at 0.5°C below the freezing point, so the amount of ice crystals produced in the crystallizer was proportional to the feed rate and holding time. Figure 4 shows ice crystals formed in 10% lactose sc-

FIG. 4. Effects of the Amount of Ice Crystals on Their Growth in 10% Lactose Solution.

$\Delta Tb^\circ = 0.15^\circ C$; flow rate of sample solution, 160 ml/min; holding time, 2 hr.

FIG. 5. Effects of ΔTb° on the Growth of Ice Crystals in 10% Lactose Solution.

$\Delta Tb^\circ = 0.5^\circ C$; flow rate of sample solution, 550 ml/min; holding time, 2 hr.

lution when the solution was fed at 160 ml/min for 2 hr. Large ice crystals were formed by the agglomeration. The amount of ice crystals at 2 hr with this flow rate corresponded to that after about 30 min with the flow rate (550 ml/min) in the experiment shown in Fig. 3. However, judging from Fig. 3(a) and (b), large ice crystals were not found in such a short time as 30 min. This finding suggests that the formation of the large ice crystals caused by agglomeration was not due to the high concentration of the ice crystals but to the holding time.

Effects of the initial subcooling, ΔTb°, on the growth of the ice crystals

The ice crystals formed in 10% lactose solution at 2 hr after the start of crystallization with the initial subcooling of 0.5°C are shown in Fig. 5. Only small particles 0.5 mm in diameter were seen. In Fig. 6, ice crystals formed just after the start of crystallization with a ΔTb° of 0.152°C and 0.51°C are compared. The ice crystals formed with a ΔTb° of 0.51°C were much smaller than those with a ΔTb° of 0.152°C. Generally, the growth rate of ice crystals is proportional to the subcooling, whereas the nucleation rate is proportional to the second power of the subcooling.[9] Therefore, the greater the initial subcooling, the smaller the initial ice crystals. The small ice crystals shown in Fig. 5 seem to be formed only by the growth of the initial fine crystals without agglomeration. The initial crystal size distribution affected the growth mechanism; the agglomeration mechanism involves large initial crystals.

Effects of concentrations and kinds of sugar on the growth mechanisms of the ice crystals

Ice crystals as large as those shown in Fig. 3(d) also formed in 15% lactose and in 5%, 7.5%, and 10% glucose solutions 2 hr after the start of crystallization with the initial subcooling, ΔTb°, of 0.15°C. The ice crystals that formed in 10% skim milk were also large under

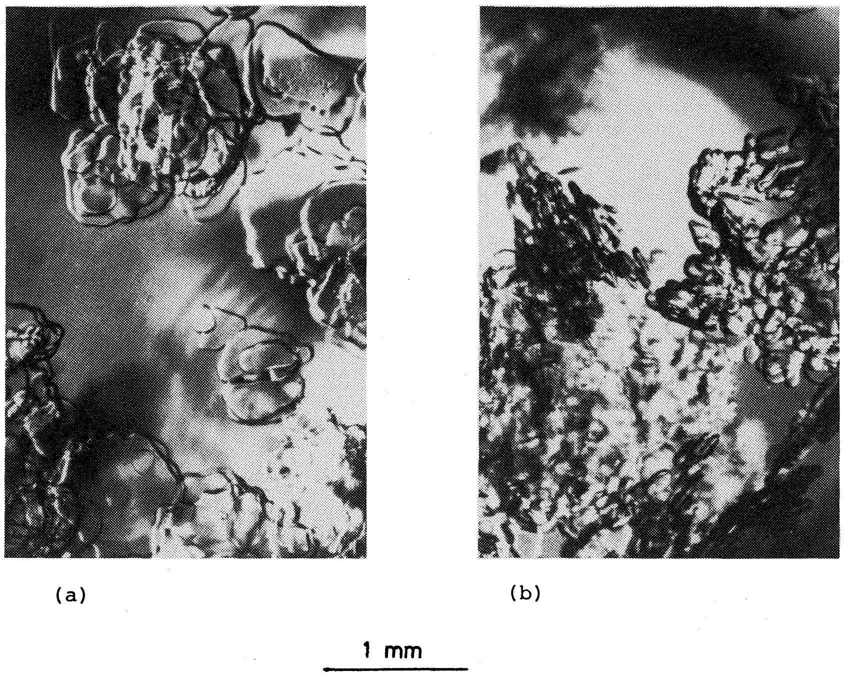

FIG. 6. Ice Crystal Shapes Just after the Start of Crystallization in 10% Lactose Solution. (a) $\Delta Tb^{\circ}=0.152^{\circ}\mathrm{C}$; (b) $\Delta Tb^{\circ}=0.510^{\circ}\mathrm{C}$; flow rate of sample solution, 550 ml/min.

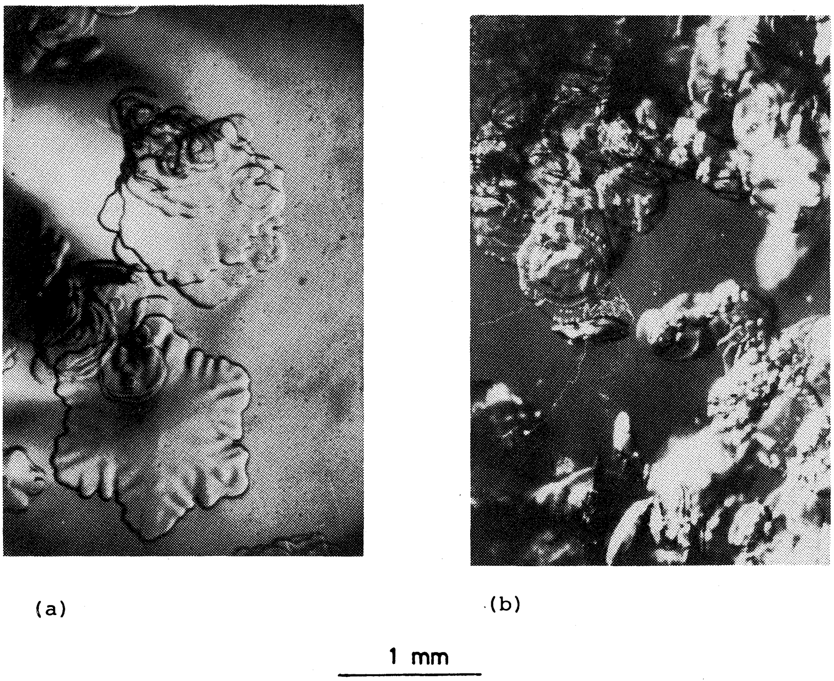

FIG. 7. Effects of Glucose Concentration on Ice Crystals Formed just after the Start of Crystallization. (a) 10% glucose solution, $\Delta Tb^{\circ}=0.153^{\circ}\mathrm{C}$; (b) 20% glucose solution; $\Delta Tb^{\circ}=0.156^{\circ}\mathrm{C}$; flow rate of sample solution, 550 ml/min.

the same conditions. However, the ice crystals did not agglomerate in 15% glucose solution; they remained small, like those shown in Fig. 5. The ice-crystal growth rate decreased with increasing concentration of the solution because of a decrease in the diffusion rate of the solutes, but the nucleation rate increases greatly.[9] This yields small initial ice crystals in solutions with high concentrations. Figure 7 compares ice crystals that formed just after the start of crysrallization in 10% and 20% glucose solutions. The ice crystals that formed in 20% glucose solution were much smaller than those in the 10% glucose solution and almost the same size as those in the 10% lactose solution with the initial subcooling of 0.51°C. The ice crystals that formed in the 15% glucose solution did not agglomerate into the large ice crystals, because large ice crysrals were not formed at the start of crystallization. Thus, it probably depends on the initial crystal size in the crystallizer whether agglomeration occurs or not, and a critical crystal size on which the growth mechanisms depend might exsist.

Incorporation of solutes into the agglomerated ice crystals

The formation of large ice crystals by agglomeration is useful for freeze concentration only if the solute is not incorporated into the ice crystal during the agglomeration process. Figure 8 shows the relationship between the numbers of washings and the concentration of lactose in melted ice crystals, that had been formed by crystallization with 10% lactose for 2 hr. If the solute is incorporated homogeneously in the ice, the concentration of lactose should be constant whatever the washing time. However, the concentration of lactose in the ice decreased sharply with an increase in the numbers of washings. This suggested that the solute adhered only to the surface of the ice crystals.

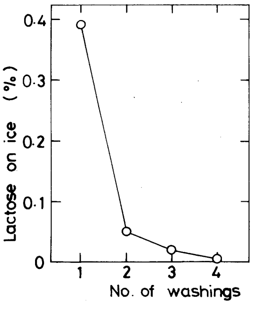

FIG. 8. Relationship between the Lactose Concentration in Large Ice Crystals that Had Agglomerated and the Washing Time.

The ice crystals formed in 10% lactose solution after 2 hr of the start of crystallization was analyzed.

In the agglomeration process, it was observed that boundaries of ice crystals fused as if they have melted. The solute which had adhered on the large ice crystals might have washed away from the agglomerated spot with the melted water.

In this study, we observed an agglomeration mechanism that resulted in the formation of large ice crystals, and investigated the conditions under which the mechanism occurred. Only the initial crystal size distribution was extracted as an dominating factor for the agglomeration growth mechanism. However, the effect of other properties than the initial ice crystal size should become clearer after further work.

The findings should be taken into consideration when designing freeze concentration system.

Acknowledgments. This work was supported in part by a Grant-in-Aid for Scientific Research (No. 59040022) from the Ministry of Education, Science and Culture of Japan.

REFERENCES

1) Y. Shirai, K. Nakanishi, R. Matsuno and T. Kamikubo, *AIChE J.*, **31**, 676 (1985).
2) Y. Shirai, K. Sakai, K. Nakanishi and R. Matsuno, *Chem. Eng. Sci.*, **41**, 2241 (1986).
3) N. J. J. Huige and H. A. C. Thijssen, *J. Cryst. Growth*, **13/14**, 483 (1972).
4) C. E. Smith and G. Schwartzberg, *Biotechnology Progress*, **1**, 111 (1985).
5) A. M. Omran and C. J. King, *AIChE J.*, **20**, 795 (1974).
6) J. H. Stocking and C. J. King, *AIChE J*, **22**, 131 (1976).

7) Y. Shirai, K. Nakanishi, R. Matsuno and T. Kamikubo, *J. Food Sci.*, **50**, 401 (1985).
8) G. Margolis, T. Sherwood, P. L. Brian and A. F. Sarofim, *Ind. Eng. Chem. Fundam.*, **10**, 439 (1971).
9) N. J. J. Huige, Nucleation and growth of ice crystals from water and sugar solutions in continuous stirred tank crystallizers, Ph. D. Dissertation, Univ. Eindhoven, The Netherlands (1972).
10) M. Dubios, K. A. Gilles, J. K. Hamilton, P. A. Rebers and F. Smith, *Anal. Chem.*, **28**, 350 (1956).