Note

Prevention of Initial Supercooling in Progressive Freeze-concentration

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A physical method is proposed that uses a cooling plate with many small holes to prevent initial supercooling in progressive freeze-concentration, and thus avoid serious contamination of the ice produced. The higher chance for ice nucleation of the water molecules in the holes due to the temperature gradient in the cooling plate resulted in the initial supercooling being completely prevented. Accordingly, the purity of the ice initially formed was substantially improved when compared with that by the standard vessel without holes in the cooling plate.

Key words: freeze concentration; supercooling; purity of ice; progressive freezing

Although freeze concentration is the most expensive of the methods for concentrating liquid food, it is also the best method for that purpose because of the high retention of flavor by thermally fragile components. The only method so far practically applied for freeze concentration is by suspension crystallization, in which small ice crystals are formed and removed from the mother solution. In contrast to this method, we have investigated the progressive freeze-concentration method in which only a single ice crystal is formed in the system as a layer on the cooling plate. This makes separation of the ice crystal much easier and makes the system simpler and cheaper than that for suspension crystallization. Progressive freeze-concentration has been successfully applied to model solutions containing Blue dextran, glucose, etc. The effective partition constant for the solute between the ice and liquid phases has been theoretically analyzed by a concentration polarization model.

Initial supercooling with progressive freeze-concentration contaminates the ice by the solute component to reduce its purity. To avoid this, an ice-lining process must be applied to the cooling surface, but this makes the operation complicated. In this note, a physical method to prevent this initial supercooling with progressive freeze-concentration is reported.

The apparatus for progressive freeze-concentration (Fig. 1A) consisted of a cylindrical sample vessel of acrylic resin (48 mm dia × 197.5 mm) with a stainless steel bottom without or with many small holes of 1.0 mm diameter and 6.0 mm depth (Fig. 1B), a cooling bath, and a driving system to plunge the sample vessel into the cooling bath at a constant speed to control the rate of advance of the ice front. The sample vessel was equipped with an agitator inside to stir the solution at the ice-liquid interface. Temperatures of the solution in the vessel and at the surface of the cooling plate were measured with a copper-constantan thermocouple. Glucose was

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analyzed by a refractometer (N-IE, Atago, Tokyo), and Blue dextran (Sigma, St. Louis) was measured as its optical absorbance at 600 nm by a spectrophotometer (DU-65, Beckmann, Tokyo).

Figure 2 shows the change in temperature of the solution and the cooling surface before and during initial freezing by the progressive freeze-concentration process. Figure 2A shows time-course plots of the temperature in the sample vessel without any holes at the bottom. Accompanying the decrease in temperature of the cooling plate, the temperature of the solution (1% glucose) dropped to −8°C and then both temperatures suddenly increased to freezing point. This temperature shift from −8°C to freezing point means that supercooling ceased at this moment and freezing was initiated.

Figure 2B shows a similar record of the temperature when using the vessel with holes in the bottom. Above freezing point, the temperatures of the cooling plate and the solution were similar, but they diverged below the freezing point. While the temperature of the cooling plate continued dropping below freezing point, the temperature of the solution stayed at freezing point, showing that no supercooling had occurred in this case.

Table 1 compares the probability for the occurrence of supercooling in vessels with and without holes, which was 97% and 0%, respectively. The mechanism for preventing supercooling in the vessel with holes in the

Table 2. Progressive Freeze-concentration of 5% Glucose*

<table>
<thead>
<tr>
<th>Temperature of initial freezing (°C)</th>
<th>Vessel without holes</th>
<th>Vessel with holes</th>
<th>Vessel with ice lining***</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration ratio**</td>
<td>1.08</td>
<td>1.23</td>
<td>1.22</td>
</tr>
<tr>
<td>Glucose concentration in ice phase (wt%)</td>
<td>4.2</td>
<td>1.8</td>
<td>1.9</td>
</tr>
</tbody>
</table>

* The coolant temperature was −15°C and the stirring rate at the ice front was 500 rpm.
** Volume ratio of the liquid phase before and after freeze-concentration.
*** A small amount of pure water was layered on the cooling plate to form an ice lining before the sample was applied.

Table 3. Progressive Freeze-concentration of 0.1% Blue Dextran*

<table>
<thead>
<tr>
<th>Temperature of initial freezing (°C)</th>
<th>Vessel without holes</th>
<th>Vessel with holes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration ratio**</td>
<td>1.15</td>
<td>1.16</td>
</tr>
<tr>
<td>Blue dextran concentration in ice phase (wt%)</td>
<td>0.0709</td>
<td>0.0156</td>
</tr>
</tbody>
</table>

* The coolant temperature was −15°C, and the stirring rate at the ice front was 400 rpm.
** Volume ratio of the liquid phase before and after freeze-concentration.

bottom is related to ice nucleation. The sample in the vessel is cooled from the bottom so that there is a temperature gradient in the bottom plate (cooling plate) of the vessel. Therefore, water molecules inside the holes in the bottom of the vessel are cooled to below the freezing point earlier than the average bulk water molecules in the vessel so that they have a higher chance of ice nucleation.

Table 2 shows a comparison of the performance during progressive freeze-concentration of a 5% glucose solution using vessels with and without holes in the cooling surface. The initial freezing temperature was much lower for the latter, showing the occurrence of supercooling in the vessel without holes. The ice purity was also very different between the two, and no concentration effect was apparent in the vessel without holes for glucose, while the ice purity was much higher in the vessel with holes. In this case, the ice purity was no different from that achieved with an ice lining.

Table 3 shows a similar comparison between the vessel with and without holes during the progressive freeze-
concentration of 0.1% Blue dextran. The vessel with holes was also effective for preventing initial supercooling to improve ice purity.

The absolute values of ice purity may not be enough for the purpose of freeze-concentration. The results in Tables 2 and 3, however, are only for the ice purity at the initial moment of ice crystallization with a very small concentration ratio. Increasing the operation time to increase the concentration ratio, has produced satisfactory results in progressive freeze-concentration as have been reported previously,2-4) because the initially formed ice has the highest chance of contamination by the solute.

In conclusion, a physical method involving small holes in the cooling surface proved effective to prevent the initial supercooling during progressive freeze-concentration that causes serious ice contamination by the solute component. The present method is expected to simplify the progressive freeze-concentration system by removing the necessity for the ice-lining step in its operation.

References