Effect of Freezing Rate on Freeze Concentration Characteristics with Supersonic Radiation

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ABSTRACT

The capture of solute into freezing part is difficult due to vigorous agitation of the freezing interface during the freezing of solution. We have been studying the applicability of supersonic radiation to the agitating method, and found that the freeze concentration efficiency of solutes is improved greatly by this radiation. In this paper, the effect of the freezing rate on the freeze concentration characteristics is examined.

We modified the experimental apparatus where the distance between a supersonic transducer and freezing interface can keep constant (40 mm). Freezing columns (55 mm inner diameter and 320 mm height) made of stainless steel were descended in a refrigerator (-16.5 °C) at some prescribed rates (20, 40, 80, 120 mm/h) with/without supersonic radiation (54 W). This means freezing rate can be maintained almost prescribed constant values. From these experiments, it was found that the solute could hardly be concentrated in unfrozen part and the distribution factors of solutes were about 1.0 for all freezing rates without supersonic radiation. On the other hand, with supersonic radiation the distribution factors were much smaller than 1.0 at slower freezing rate (20, 40 mm/h) and were small up to 0.5 at faster freezing rate (80, 120 mm/h).

KEY WORDS
freeze concentration, supersonic radiation, freezing rate, solute

INTRODUCTION

In freezing water that includes solutes, pure ice is produced and most of the solutes are removed from the frozen phase and concentrated in an unfrozen liquid phase. The purpose of the freeze concentration process is the separation and concentration of solutes. The efficiency of the process is dependent on how to produce highly pure ice as fast as possible. This freeze concentration process, which is independent of the solutes, can be used for the food industry, seawater desalination and wastewater treatment etc.

At fast freezing rate, however, large part of the solutes from solution is captured into the freezing interface and then the solution is not concentrated. To prevent this capture of the solutes, the strong agitation of the freezing interface is very effective (Halde, 1979, Miyawaki, 1995, Shirai et al., 1998).

There are various means for agitating the freezing interface, and a common means is to stir the liquid near the ice-liquid interface by a propeller (Halde,1979, Bae et al.,1994, Yamazaki et al.,1998). But washing the device (propeller) is very troublesome and takes a long time, because this device is complex and has many moving parts. In addition, contamination of the freeze concentration equipment and process must be avoided. As a result, we used a supersonic radiation method as an alternative agitation means (Matsuda and Kawasaki, 1997), which is a simple and very easy operation. In this method, the immersion of only the radiator tip into the liquid is needed, and the washing operation becomes very easy. We found that freeze concentration efficiency of the solutes (sodium chloride and
glucose) is greatly improved by this supersonic radiation (Matsuda and Kawasaki, 1997). This efficiency is also dramatically improved by increasing the dissolved air concentration. These efficiencies increase as supersonic radiation intensity increases. The freeze concentration efficiency of suspended solids is also increased like as solutes. And this concentration efficiency of suspended solids decreases in solution (solute: sodium chloride, L-phenyl alanine and saccharose) than in pure water. As the molecular weight of solute is larger, the holding ability is lower.

In this paper, we try to examine clearly the effect of freezing rate on the concentration efficiency of three solutions with the constant ion or molecular concentrations (0.01 mol/L). The difference of concentration efficiency of each solute under various freezing rates is also investigated.

MATERIALS AND METHODS

Figure 1 shows an experimental apparatus of freeze concentration with supersonic radiation. The sample solutions (0 °C) were aerated in order to increase dissolved air (i.e. dissolved oxygen concentration > 0.008 kg/m³ (8 mg/L)), where the cavitation due to supersonic radiation could take place efficiently (Matsuda and Kawasaki, 1997). The solution, 0.5 kg, was poured into freezing columns made of stainless steel (55 mm inner diameter and 320 mm height). The columns descended down in a refrigerant (ethylene glycol solution, -16.5 °C) at various rates (20 - 120 mm/h) with/without supersonic radiation. The intensity of radiation was kept constant (54 W) throughout these experiments.

After the freezing columns descending down for 181 mm, these freezing columns were pulled out from the refrigerant (-16.5 °C) and the unfrozen parts were poured out.

Fig.1  Experimental apparatus of freeze concentration with supersonic radiation
from the columns immediately. The frozen interface was washed with 0 °C distilled water to remove the unfrozen sample.

The volume and the solute concentration of the unfrozen part were measured. The frozen portion was divided into six parts vertically. The volume and concentration of each part were measured to investigate the concentration process of freezing.

The samples used were one component solution which contains only L-phenyl alanine (0.01 and 0.03 mol/L), and three components solution. The latter sample contains three kinds of the solutes (sodium chloride (NaCl), L-phenyl alanine (Phe) and saccharose (Sac), the concentration of each solute particle is 0.01 mol/L). These solutes were dissolved together in water, and total mole concentration of the solute particle was 0.03 mol/L. The concentrations of solutes are NaCl: 0.005, Phe: 0.01, Sac: 0.01 mol/L.

Because NaCl is almost entirely dissociated electrolytically to Na⁺ and Cl⁻ ions in water, the solute particle concentration of NaCl in water is shown as the concentration of total ion (Na⁺ and Cl⁻), but not as molecule (NaCl). Therefore the ionic mole concentration of NaCl in aqueous solution is twice as much as the mole concentration of molecular NaCl. The concentration of molecule, NaCl, is consequently a half of the other solute (Phe and Sac) concentration, but the mole concentrations of solute particles are kept constant in all solutions.

The solute concentration of NaCl was analyzed with a conductivity method, that of Phe with an absorptiometric method at 258 nm and that of Sac with a total organic carbon concentration analyzing method. For reference, the experiments without supersonic radiation were made simultaneously. Details of the experiment have been described in a previous paper (Matsuda et al., 1999).

RESULTS AND DISCUSSION

One component solution

As the sample freezes, the concentration of the unfrozen part increases because the solutes are moved into the unfrozen part (Corte, 1950, Matsuda and Kawasaki, 1994, Matsuda and Kawasaki, 1997, Matsuda et al., 1999). Consequently the holding ability of the solute into ice solution interface may change with the concentration of the unfrozen part. As a result we evaluate this holding ability by calculating "the distribution factor," as the ratio of solute held into the frozen part by the freezing interface. This ratio is the value of the concentration of a frozen part divided by the average concentration of the corresponding unfrozen part. The calculation method is as follows (Matsuda and Kawasaki, 1997).

The frozen part is divided into n segments vertically. While the m'th segment from the bottom of the freezing column is freezing, the concentration of the unfrozen part changes from Cu,m-1 to Cu,m. The concentration of m'th segment of frozen part, Cf,m, are obtained from the observed value, and Cu,m-1 and Cu,m are calculated by the assumption of complete mixing of unfrozen part. Therefore the distribution factor of m'th segments, Φ_m, can be calculated by Eq.(1).

\[ \Phi_m = \frac{C_{f,m}}{\{(C_{u,m-1} + C_{u,m})/2\}} \]  

A small value of the distribution factor means that solutes are less likely to be held by the freezing interface.

The experimental results for one component solution (0.01 mol/L) with/without supersonic radiation at various freezing rates are shown in Fig.2 as the change of the distribution factor. The distribution factors without supersonic radiation in Fig.2 are about 0.9 - 1.0 regardless of the kind of solute, and the solutes are hardly concentrated. On the other hand, the distribution factors of solutes
with supersonic radiation are much less than 1.0, and have the following order; 20 < 40 < 80 < 120 mm/h. The slower the freezing rate is, the more easily the solute is separated and concentrated by freezing.

Table 1. Overall distribution factor (DF)

<table>
<thead>
<tr>
<th></th>
<th>freezing rate [mm/h]</th>
<th>Cfav $\times 10^{-4}$ mol/L</th>
<th>Cun $\times 10^{-4}$ mol/L</th>
<th>overall DF [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>one component solution</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(A) Phe 0.01 mol/L</td>
<td>20</td>
<td>0.88</td>
<td>150.1</td>
<td>0.007</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>2.1</td>
<td>177.2</td>
<td>0.015</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>6.2</td>
<td>194.5</td>
<td>0.041</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>11.8</td>
<td>183.7</td>
<td>0.083</td>
</tr>
<tr>
<td>(B) Phe 0.03 mol/L</td>
<td>40</td>
<td>38.0</td>
<td>836.8</td>
<td>0.067</td>
</tr>
<tr>
<td><strong>three components solution</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C) each 0.01 mol/L</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaCl</td>
<td>40</td>
<td>5.5</td>
<td>156.5</td>
<td>0.053</td>
</tr>
<tr>
<td>Phe</td>
<td>40</td>
<td>17.3</td>
<td>311.5</td>
<td>0.083</td>
</tr>
<tr>
<td>Sac</td>
<td>40</td>
<td>18.1</td>
<td>282.6</td>
<td>0.095</td>
</tr>
</tbody>
</table>
Table 1 (a) shows the overall distribution factor (DFoa) that means the distribution factor of unfrozen part and whole frozen part at the end of freezing when the freezing columns descended down into the refrigerant (-16.5 °C) for 181 mm. And this DFoa can be calculated by Eq.(2).

\[
DFoa = \frac{2 \cdot C_{fav}}{(C_0 + C_{un})}
\]

where \(C_{fav}\): average concentration of whole freezing part [mg/L]

\(C_0\): initial concentration of sample solution [mg/L]

\(C_{un}\): concentration of n’th segment [mg/L].

The slower the freezing rate is, the lower \(C_{fav}\) and the higher \(C_{un}\) are. Consequently DFoa decreased as the freezing rate decreased. This corresponds well to Fig.2. The distribution factors for 20 & 40 mm/h are very smaller than those for 80 & 120 mm/h. Using this experimental apparatus, therefore, we can make sufficiently good concentration of Phe under freezing rate less than 40 mm/h.

Three components solution

Under the constant mole concentration of solute particles in liquid, the concentration characteristics in "one component solution" were discussed in One component solution. However, solutions include multiple solutes in practical freeze concentration, such as seawater and fruit juice etc. Consequently the difference of the freeze concentration efficiency among the solutes in three components solution must be examined.

The experimental results of the solution included three solutes, which were measured with/without supersonic radiation for Phe solution, are shown in Fig.3. Without supersonic radiation, the distribution factors are about 0.9 - 1.0 regardless of the freezing rate, as shown in Fig.2. The distribution factors of Phe have the following order; 20 < 40 < 80 < 120 mm/h. The slower the freezing rate is, the more easily the solute is separated and concentrated by freezing, as mentioned in One component solution.
In considering the effect of the kind of solutes, Fig 4 shows the distribution factor of solutes with supersonic radiation, at 40 mm/h freezing rate. This distribution factor has the following order; NaCl < Phe < Sac. The solutes of smaller molecular weights are more easily concentrated than solute of larger molecular weights. The ability of holding the solute on the freezing interface may be dependent on the movability of the solute, and this movability may be related to the diffusion coefficient of the solute in water.

Table 2 shows molecular weights and the values of the diffusion coefficients which are estimated for the infinite diluted solution at 0 °C. The value of NaCl is calculated with Nernst-Haskell Equation (Oe, 1985), and those of Phe and Sac with Wilke-Chang equation (Wilke and Chang, 1955). The diffusion coefficient of the solutes has the following order; NaCl > Phe > Sac and this means that the solute of smaller molecular weight can move more freely in liquid. This corresponds well to the result that the solute of smaller molecular weight can be concentrated and separated easily, as mentioned above.

<table>
<thead>
<tr>
<th>solute</th>
<th>molecular weight [-]</th>
<th>diffusion coefficient [m$^2$/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>sodium chloride (NaCl)</td>
<td>58.44</td>
<td>$6.73 \times 10^{-10}$</td>
</tr>
<tr>
<td>L-phenyl alanine (Phe)</td>
<td>165.19</td>
<td>$3.57 \times 10^{-10}$</td>
</tr>
<tr>
<td>saccharose (Sac)</td>
<td>342.30</td>
<td>$2.51 \times 10^{-10}$</td>
</tr>
</tbody>
</table>

Table 1 (C) shows DFoa at 40 mm/h freezing rate, and Dfoa’s have the following order; NaCl < Phe < Sac. The solutes of smaller molecular weights are more easily concentrated than solute of larger molecular weights.
Comparison between "one component solution" and "three components solution"

In order to compare the difference of concentration and separation efficiency of each solute in "one component solution" and "three components solution", the distribution factors are shown in Fig. 5 for Phe at freezing rate of 40 mm/h. The experimental results for one component solution (0.03 mol/L) are also plotted together. The values of the distribution factors in Fig. 5 have the following order: one component solution (0.01 mol/L) < one component solution (0.03 mol/L) ≈ three components solution. 

DFoa for Phe solution are shown in Table 1 (A,B,C), and these values corresponds well to the results, as mentioned above.

![Fig.5 Distribution factor with height in the one & three components solution (Phe, 40 mm/h)](image)

CONCLUSIONS

Under the condition where ion or molecular concentrations of solutes in each solution are constant (0.01 mol/L), the effect of freezing rate and the kind of solutes was examined with supersonic radiation, and the following conclusions were obtained.

1. The slower the freezing rate is, the more easily the solute is separated and concentrated by freezing. Using our experimental apparatus (55 mm inner diameter and 320 mm height freezing column made of stainless steel), we can make sufficiently good concentration of L-phenyl alanine under freezing rate less than 40 mm/h.

2. The solutes of smaller molecular weights are more easily concentrated than solute of larger molecular weights. This corresponds well to the order of the diffusion coefficient of the solute.

3. Using our experimental apparatus, the distribution factors of L-phenyl alanine in the three components solution (total concentration is 0.03 mol/L and L-phenyl alanine concentration is 0.01 mol/L) are almost equal to those in the one component solution (0.03 mol/L), but those in the one component solution (0.01 mol/L) are smaller than those in the one component solution (0.03 mol/L).
ACKNOWLEDGMENTS

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REFERENCES