

# Relationship between Recrystallization Rate of Ice Crystals in Sugar Solutions and Water Mobility in Freeze-Concentrated Matrix

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Published online: 25 April 2006  
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**Abstract** To better understand the relation between recrystallization rate and water mobility in freeze-concentrated matrix, isothermal ice recrystallization rates in several sugar aqueous solutions and self-diffusion coefficients of water component in corresponding freeze-concentrated matrix were measured. The sugars used were fructose, glucose, maltose, and sucrose. The sugar concentrations and temperature were varied so that ice contents for all samples were almost equal. Neither recrystallization rates nor diffusion coefficients depended uniformly on temperature. The recrystallization rates increased with increasing the diffusion coefficients, and a direct relationship was found between recrystallization rate and diffusion coefficient. This indicated that self-diffusion coefficient of water component in freeze-concentrated matrix is a useful parameter for predicting and controlling recrystallization rate in sugar solutions relevant to frozen desserts.

**Key words** Recrystallization · Water mobility · Ice crystal · NMR · Diffusion coefficient · Sugar

## Introduction

Recrystallization of ice crystals is one of the major causes of deterioration in frozen dessert such as ice cream during storage and distribution. Generally, the recrystallization of ice crystals in frozen food is characterized as an increase in mean size of ice crystals.<sup>1,2</sup> Recrystallization proceeds as a result of minimization of surface free energy of the entire crystal phase and the chemical potential is equalized among all phase.<sup>1,2</sup> There are three recrystallization mechanisms that are likely to occur in conventional storage of frozen dessert: migratory, isomass, and accretion.<sup>1,3</sup> Migratory recrystallization refers to the tendency for larger crystals in a polycrystal system to grow at the expense of small crystals. Smaller crystal cannot bind their surface water molecules as firmly as larger crystals because of the higher curvature and thus, larger surface free energy. Therefore, the water molecules on the surface of small crystals tend to migrate to the surface of larger ones through the freeze concentrated matrix, resulting in growth of larger crystals and disappearance of smaller ones. A similar process, called isomass recrystallization, can occur in a single crystal. Consider a single separated crystal with a rough surface. The part of surface with high curvature cannot bind surface water molecules as firmly as a smoother surface. As a result, the rougher surface becomes smoother. Accretion recrystallization is the process where two crystals that are in a point of contact grow together into one larger crystal. Because the contact point has apparently high curvature and is not as stable as the rest, formation of a neck eventually occurs by transportation of water molecules to this region, which leads to growth into one crystal.

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When ice crystals grow so large that they can be detected in the mouth, the smooth texture of a frozen dessert such as ice cream turns into a coarse, grainy, and icy texture, resulting in unacceptable product.<sup>2,3</sup> Therefore, the recrystallization process has been recognized as an important phenomenon to be considered for designing proper storage and distribution conditions for a frozen dessert.

Recrystallization of ice crystals in frozen food has been extensively studied. Zaritzky et al. studied the recrystallization of frozen beef and its model system, and they developed a model equation to predict the growth of ice crystals that assumes crystal growth by the difference of curvature of crystals.<sup>4–7</sup> Other researchers have performed quantitative analysis of recrystallization in ice creams to investigate the effect of storage temperature, temperature oscillations, sweeteners, and stabilizers on recrystallization rate.<sup>8–11</sup> Using experimental data, computer simulation of changes of ice crystal size in ice cream in practical storage and distribution conditions was also conducted.<sup>12</sup> Sutton et al.<sup>13–16</sup> reported the effects of sweeteners, stabilizers, and ice phase content on recrystallization rate by using several sugar solutions and ice cream with different composition. They also constructed a model to describe the recrystallization process that assumes diffusion-limited growth of crystals.<sup>17</sup> The mechanisms to explain the inhibition of ice recrystallization by addition of stabilizers have been also extensively discussed,<sup>10,11,14–16,18,19</sup> although the exact mechanisms seem to be unknown until now.<sup>3</sup>

Most of the studies mentioned above investigated the effect of practical production condition, such as temperature, temperature fluctuation, type of sweeteners, and stabilizers, etc. These studies have uncovered useful knowledge about manufacture and storage of frozen dessert; however, to better understand recrystallization phenomena, it is necessary to comprehend not only the correlation between production conditions and recrystallization rate, but also the molecular-level mechanisms accounting for different recrystallization rate. A better understanding of the molecular mechanisms of recrystallization will facilitate a systematic prediction and control of recrystallization behavior for various frozen desserts. It would be at least possible to reduce the extent of recrystallization experiments.

Considering the mechanisms of recrystallization noted above, the mobility of water molecules in a freeze-concentrated matrix may be one of the factors affecting recrystallization rate. Growth of ice crystals occurs with migration of water molecules. For example, in migratory recrystallization, water molecules migrate

from the surface of smaller ice crystals to that of larger ones by diffusion through the freeze-concentrated matrix. Therefore, increasing water mobility may increase the recrystallization rate. In the field of solution chemistry, it has been reported that mobility of water molecules in aqueous solution is affected by solute type, solute concentration, or temperature.<sup>21</sup> Some differences in recrystallization rate among frozen desserts may be explained systematically by the difference in water mobility in the freeze-concentrated matrix. This is also suggested by the fact that many experimental data of recrystallization of ice crystal<sup>8,9,11,13–16</sup> can be described well by the equation of diffusion-limited growth of crystals, which was originally derived to describe the growth of metal crystals.<sup>23,24</sup> However, there are few studies that experimentally investigate the relation between water mobility in freeze-concentrated matrix and recrystallization rate, and our understanding about this relation is insufficient.

Our objective is to provide reliable experimental information on the relation between recrystallization rate and water mobility in the freeze-concentrated matrix in various sugar (mono and disaccharide) solutions having relevance to frozen dessert. In this study, we measured isothermal recrystallization rate from observation of ice crystal development at constant temperature, whereas water mobility was estimated via the self-diffusion coefficient of water component obtained by pulse field gradient stimulated gradient echo proton NMR (PFGSTE <sup>1</sup>H NMR).

## Materials and methods

### Recrystallization rate measurement

Reagent grade sucrose, maltose, glucose, and fructose were purchased from Sigma (Pittsburgh, PA, USA) and dissolved in distilled water. Table 1 shows the details of the sample solutions. Values of ice content and concentration of freeze-concentrated matrix were calculated by using literature values of freezing point depression versus solute concentration.<sup>25–28</sup> We set the ice contents of all sample almost equal in this study. There have been several studies about how ice content affects recrystallization rate,<sup>10,11,13,16</sup> but the results are often contradictory. Therefore, to omit detailed discussion about effect of ice content, we set all of ice content value almost equal here.

Ice crystals during recrystallization process were observed by using similar cryomicroscope system as described in previous studies.<sup>8–11,29</sup> The system consisted of a light microscope (Labophot; Nikon Corp., Tokyo,

**Table 1** Sample sugar solutions

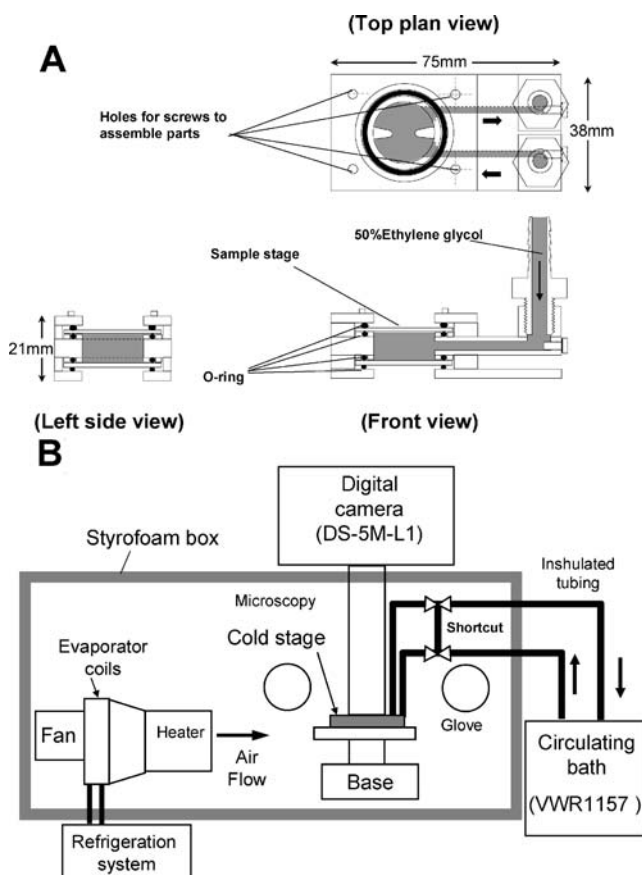
Sample	Temperature (°C)	Freeze-Concentrated Matrix Conc. (%)	Ice Content (%)	Water Frozen (%)
21.8% maltose	-4.4	40.0	45.4	58.1
22.45% sucrose	-4.6	41.1	45.4	58.4
18.5% glucose	-5.8	34.0	45.5	55.9
25.0% sucrose	-5.8	45.8	45.5	60.6
22.45% fructose	-8.0	41.1	45.4	58.6
28.6% sucrose	-8.0	52.4	45.4	63.6
25.0% fructose	-10.0	45.8	45.5	60.7
25.0% glucose	-10.0	45.9	45.4	60.8

Japan) placed in a refrigerated glove box, a digital camera (DS-5M-L1; Nikon Corp.) to photograph microscopic image, and a homemade cold stage. Figure 1A shows the schematic illustration of the cold stage. For the sample stage, sapphire glass disk plate (Edmund Industrial Optics, Barrington, NJ, USA) was used. Other parts, except tube fitting, O-ring, and assembling screw, were made out of an acrylic resin. Figure 1B shows the overall view of the system. The glove box was placed in an air-conditioned room ( $\sim 21^\circ\text{C}$ ). Tempera-

ture in the glove box was measured by a thermocouple located near the cold stage, and controlled to an accuracy of  $\pm 0.2^\circ\text{C}$  by a mechanical refrigeration system. A refrigerated bath (VWR1157; VWR International, West Chester, PA, USA) circulated 50% ethylene glycol through the cold stage to control temperature on the stage. The 50% ethylene glycol was thermostatted to an accuracy of  $\pm 0.01^\circ\text{C}$ . A dummy sample with a thermocouple was used to ensure that the set temperature and real sample temperature showed agreement before experiments. Using this system, sample temperature was controlled to an accuracy of  $\pm 0.1^\circ\text{C}$ .

The procedure used to observe the recrystallization process was similar to that in previous studies.<sup>13–15</sup> First, the glove box temperature was set to that of observation. The sample stage was cooled to  $-22.0^\circ\text{C}$  (the lowest temperature available in the system). Second, 2  $\mu\text{l}$  sample solution enclosed between two coverslips (diameter, 12 mm; Fisher Scientific International, Hampton, NH, USA; calculated sample thickness, 17.7  $\mu\text{m}$ ) was placed on the sample stage to be frozen and a glass coverslip (diameter 25 mm; Fisher Scientific International) was put over the sample chamber hole to prevent vaporization of water in the sample during the experiments. After 10 min, the temperature was elevated to the observation temperature ( $-4.0$ ,  $-4.4$ ,  $-5.8$ ,  $-8.0$ , and  $-10^\circ\text{C}$ ; see Table 1) at a rate of  $1.5^\circ\text{C}/\text{min}$ . Finally, after the observation temperature is reached, ice crystal images were periodically photographed using the digital camera and saved in digital format.

Size measurements were carried out by using the digital images. The photographed ice crystal image was first converted to a binary image. Then the projected area of each ice crystal was extracted. When clusters of ice crystals were observed, crystals that were stuck together, or those that were just in contact with each other, were considered as separated if a clear boundary line was visible in a similar manner as in previous studies.<sup>22</sup> The size of each crystal was calculated as the



**Fig. 1.** Schematic illustration of the experimental apparatus. (A) Cold stage, (B) overall view of the system.

radius of a circle having the equivalent projected area of the crystal. From the data set of each crystal size, the number-based mean crystal radius,  $r$ , was calculated. For these procedures, commercial image analysis software PopImaging (Digital being Kids Corp., Japan) and image handling software Photoshop (Adobe Systems Incorporated, USA) were used. Sometimes these programs did not extract the exact projection area of ice crystals. In such cases, the outline of the ice crystal was traced by mouse on the LCD monitor and the projected area was extracted manually.

To evaluate recrystallization rate, the theory based on the Ostwald ripening principle<sup>23,24</sup> was used, as in previous studies.<sup>8–11,13–16</sup> According to the theory, in the condition of isothermal system, the recrystallization process can be obtained by:

$$r^3 = r_0^3 + kt \quad (1)$$

where  $r$  is the number-based mean crystal radius,  $r_0$  is the number-based mean crystal radius at time  $t = 0$ , and  $k$  is the recrystallization rate. The recrystallization rate  $k$  is evaluated as the slope of the cube of the mean radius versus time.

All analyses were performed twice per sample and the averaged values were obtained.

In some cases, the measured crystal equivalent diameters exceeded the thickness of the sample solution enclosed between the two coverslips. Thus, the direction of the crystal growth was limited by coverslips. That is to say, ice crystals were restricted mainly to two-dimensional growth rather than three-dimensional one. Therefore, the recrystallization rate obtained in this study would be different from those in bulk at identical temperature conditions as shown by our previous studies.<sup>8,9</sup>

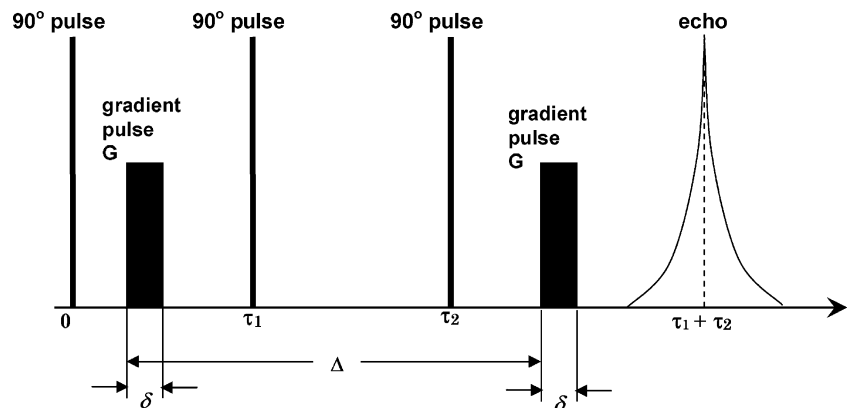
## Measurement of self-diffusion coefficient of water component

Sample concentration was set equivalent to the freeze concentrated concentration of sugar solutions at the temperature used in the recrystallization experiment (Table 1). To measure a self-diffusion coefficient of water component, PFGSTE was used.<sup>30</sup> The pulse sequence<sup>30</sup> shown in Figure 2 was used. Symbols  $\delta$ ,  $\Delta$ , and  $G$  represent the duration of field gradient pulse, the diffusion time, and the magnitude of the field pulse, respectively;  $\tau_1$  and  $\tau_2$  are the duration between the first and the second  $90^\circ$  pulses and between the first and the third  $90^\circ$  pulse, respectively.

Measurement was carried out on an Avance DRX300 (Bruker Japan Co., Tsukuba, Japan). The parameters were set as follows. The magnitude of the field gradient pulse  $G$  was changed in 32 increments. The minimum value of  $G$  was set at  $5.00 \times 10^{-2}$  T/m. The maximum  $G$  value and the duration of field gradient  $\delta$  were varied from  $6.00 \times 10^0$  to  $1.00 \times 10^1$  T/m and 1 to 2 ms, respectively, so that the echo intensity with maximum  $G$  was attenuated to below 10% of that with no applied gradient. Diffusion time  $\Delta$  was set to 10 ms. Values of  $\tau_1$  and  $\tau_2$  were automatically set by operation software of the apparatus (XWIN NMR; Bruker Japan Co.). The accumulation number of scans was 4 for each measurement.

About 1 ml sample solution was put into an NMR sample tube (BMS-010BJ; outer diameter = 10 mm; Shigemi, Tokyo, Japan). Then the sample was tube was set to the apparatus. The sample temperature was controlled with Bruker's temperature control unit. During each experiment, sample temperature was continuously measured by optical fiber thermometer (FTP-3-003; Takaoka Electric MFG Co., Tokyo, Japan). In monitoring the measured temperature, setting temperature of the temperature control unit was

**Fig. 2.** Pulse field gradient stimulated echo pulse sequence.



manually adjusted to keep the sample temperature constant. By these procedures, temperature stability of the samples was within  $\pm 0.2^\circ\text{C}$  during the experiments.

In PFGSTE, when the sample consists of only single diffusion component, echo intensity  $I$  with the magnitude field gradient pulse  $G$  is expressed as follows:

$$I/I_0 = \exp(-D_i\gamma^2 G^2 \delta^2 (\Delta - \delta/3)) \quad (2)$$

where  $I_0$  is the echo intensity without applied field gradient pulse,  $\gamma$  is the gyromagnetic ratio of proton, and  $D$  is the diffusion coefficient.

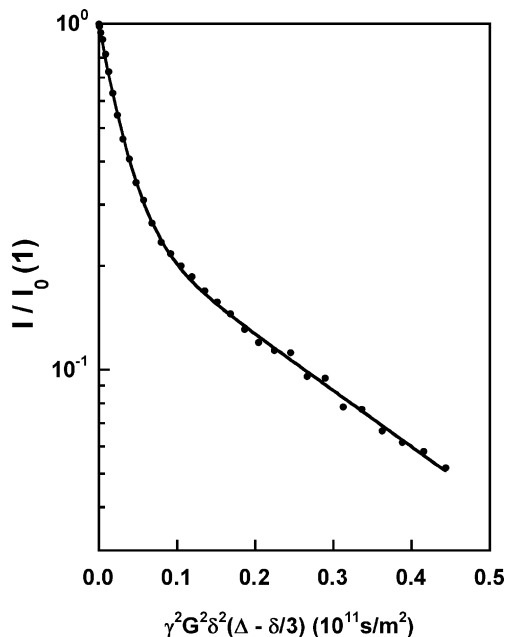
When the sample contains more than two diffusion components,  $I$  is expressed by the sum of the echo intensity from each component as follows.

$$I/I_0 = \sum_i F_i \exp(-D_i\gamma^2 G^2 \delta^2 (\Delta - \delta/3)) \quad (3)$$

Here,  $F_i$  is the fraction of the echo intensity attributed to the component  $i$ , which is expressed as follows.

$$\sum_i F_i = 1 \quad (4)$$

In Figure 3, a typical plot of  $(I/I_0)$  versus  $\gamma^2 G^2 \delta^2 (\Delta - \delta/3)$  in a semilogarithmic scale is presented. The plot was fitted well to the following equation of two components diffusing at different rates, and two diffusion coefficients  $D_1$  and  $D_2$  ( $D_1 > D_2$ ) were obtained.



**Fig. 3.** Typical plot of  $I/I_0$  versus  $\gamma^2 G^2 \delta^2 (\Delta - \delta/3)$  in a semilogarithmic scale. Sample: 21.8% maltose solution at  $-4.4^\circ\text{C}$ .

$$I/I_0 = F_1 \exp(-D_1\gamma^2 G^2 \delta^2 (\Delta - \delta/3)) + F_2 \exp(-D_2\gamma^2 G^2 \delta^2 (\Delta - \delta/3)) \quad (5)$$

The preceding studies also reported that two diffusion coefficient were observed in sucrose, trehalose, and fructose solutions by NMR.<sup>20,31</sup> These studies assigned the faster one to the water component (the weight average of the exchangeable sugar protons and the water proton) and the slower one to the sugar component (nonexchangeable sugar proton), respectively. We also judged that  $D_1$  was the self-diffusion coefficient of the water component and  $D_2$  was that of the sugar component.

All measurements were done three times per sample, and the averaged values were obtained.

## Results and discussion

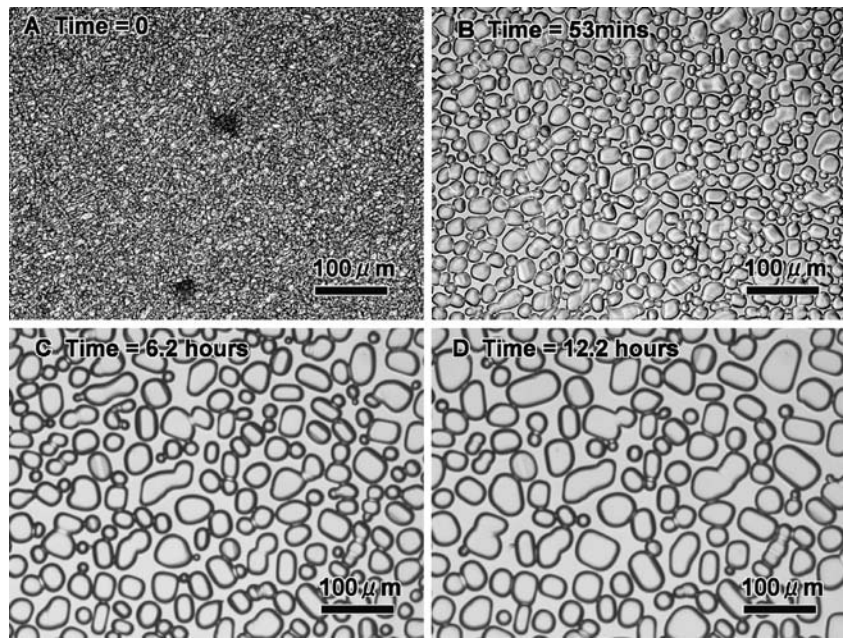
### Recrystallization rate

Figure 4 shows typical ice crystal images at various times. At time  $t = 0$ , very small crystals accreted extensively with each other. With increasing time, ice crystals grew in size and started separating from each other. Crystals that stuck together or in contact each other were considered as separated if a clear boundary line was visible. However, in the early stage of recrystallization, we were often unable to reach a reproducible decision because the ice crystals were so small that detailed structure could not be observed. Therefore, for evaluation of recrystallization rate, we only used the images of samples stored for at least 60 min in which ice crystals were large and sufficiently separated.

Figure 5 shows plots of the mean equivalent radius cubed against time for all samples. Solid lines in the plots resulted from fitting with Eq. (1). Correlation coefficients ( $R^2$ ) were generally over 0.95, with most over 0.99. The temperature dependence of recrystallization rate is shown in Figure 6. The value of  $k$  did not depend on temperature in a uniform fashion.

In a previous study, Sutton et al.<sup>13</sup> also measured the recrystallization rates in fructose solutions at the same temperature ( $-10.0^\circ\text{C}$ ). Their values of recrystallization rate were  $1972 \pm 61 \mu\text{m}^3 \text{h}^{-1}$  for 30% solution and  $878 \pm 34 \mu\text{m}^3 \text{h}^{-1}$  for 40% solution, respectively. They also found that at the same temperature, decreasing solution concentration resulted to an increase in recrystallization rate. Therefore, we initially expected that our recrystallization rate for 25.0% fructose at  $-10.0^\circ\text{C}$  would be larger than theirs because we used a lower sample concentration. The value

**Fig. 4.** Typical ice crystal images at different times. Sample: 28.6% sucrose 1solution at  $-8.0^{\circ}\text{C}$ .

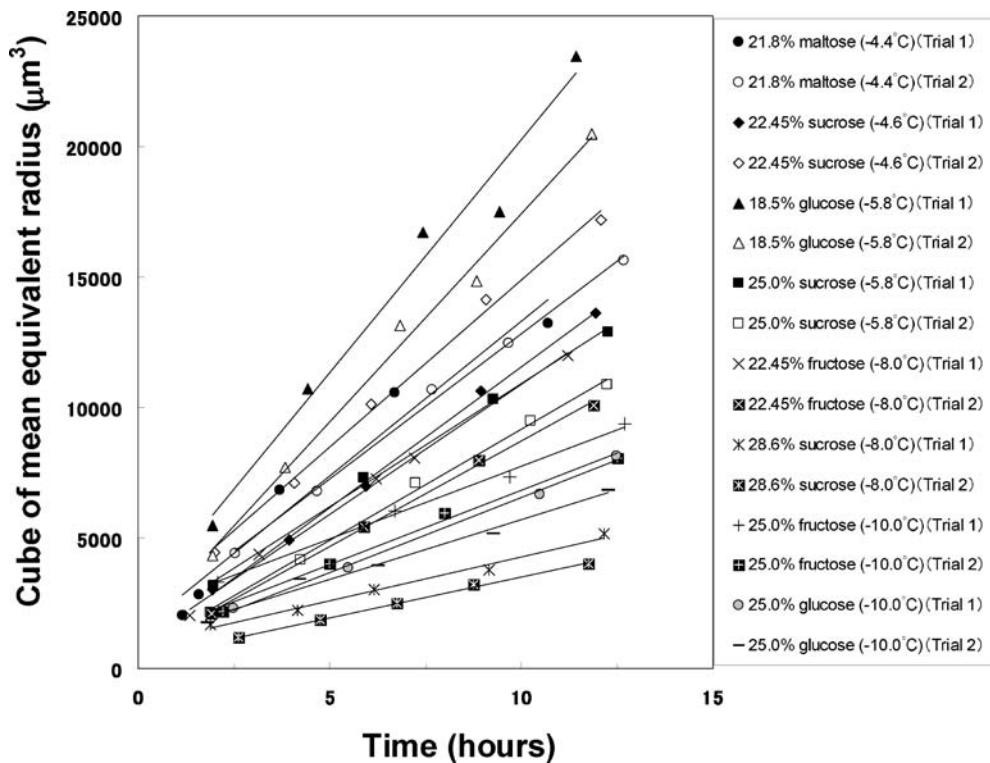


obtained from this study was, however, significantly smaller ( $566 \pm 9 \mu\text{m}^3 \text{h}^{-1}$ ). Although it is unclear why this smaller recrystallization rate was obtained in our case, it should be noted that there were many differences in experimental conditions between both studies, such as initial freezing temperature, sample volume, type of cold stage, and temperature elevation rate. These differences affect the development of ice

crystals, potentially resulting in significantly different recrystallization rate.

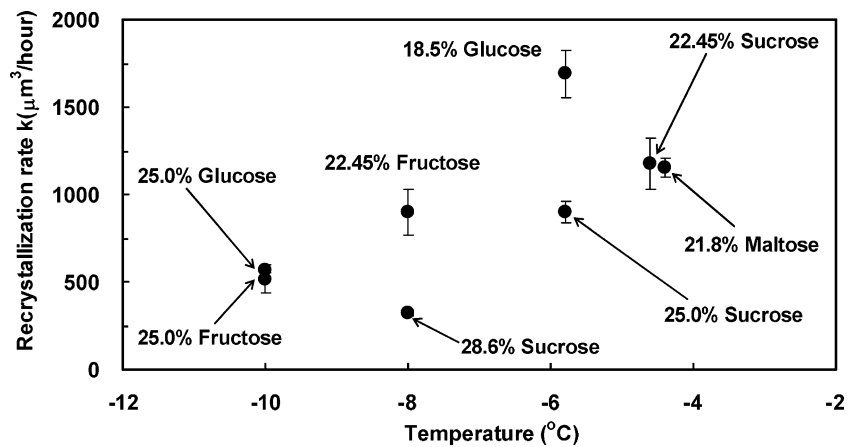
Diffusion coefficient

Figure 7A shows plots of the self-diffusion coefficient of the water component  $D_1$  as a function of temperature. Plots of the diffusion coefficient for the sugar



**Fig. 5.** Plots of the cube of the mean equivalent radius as a function of time. The solid lines represent results of fitting by Eq. (1).

**Fig. 6.** Temperature dependence of the recrystallization rate  $k$ .



component  $D_2$  are also presented in Figure 7B for comparison. Similar to recrystallization rate, both diffusion coefficients did not depend uniformly on temperature.

Using similar methods, Martin et al.<sup>20</sup> measured the self-diffusion coefficients of water and sugar components for sucrose and fructose solutions at  $-15^\circ\text{C}$ , solute concentration being the same as the freeze-concentrated matrix of these sugars at  $-15^\circ\text{C}$ . They reported that both diffusion coefficients for sucrose solution were smaller than those of fructose solution. In this study, the same trend can be seen for

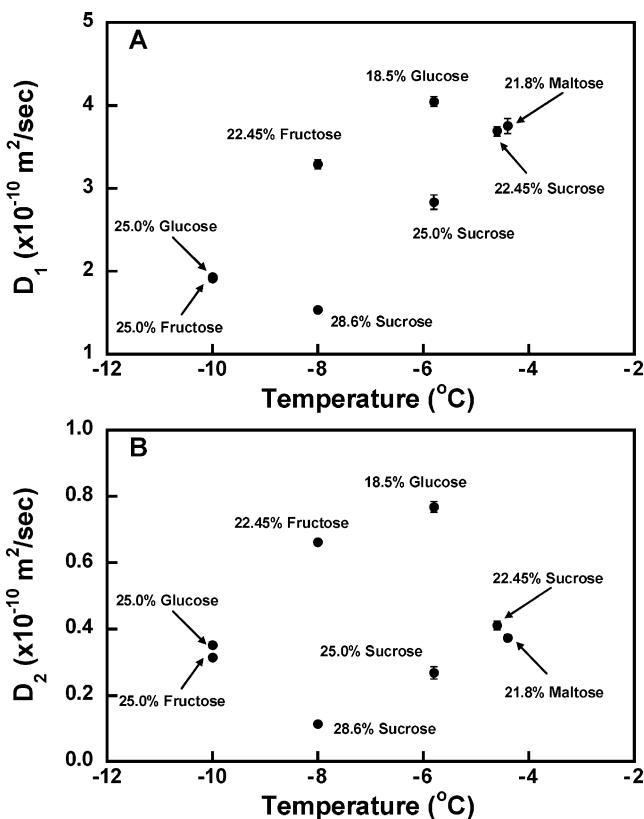
the data of 22.45% fructose and 28.6% sucrose measured at  $-8.0^\circ\text{C}$ .

#### Correlation between recrystallization and diffusion rates

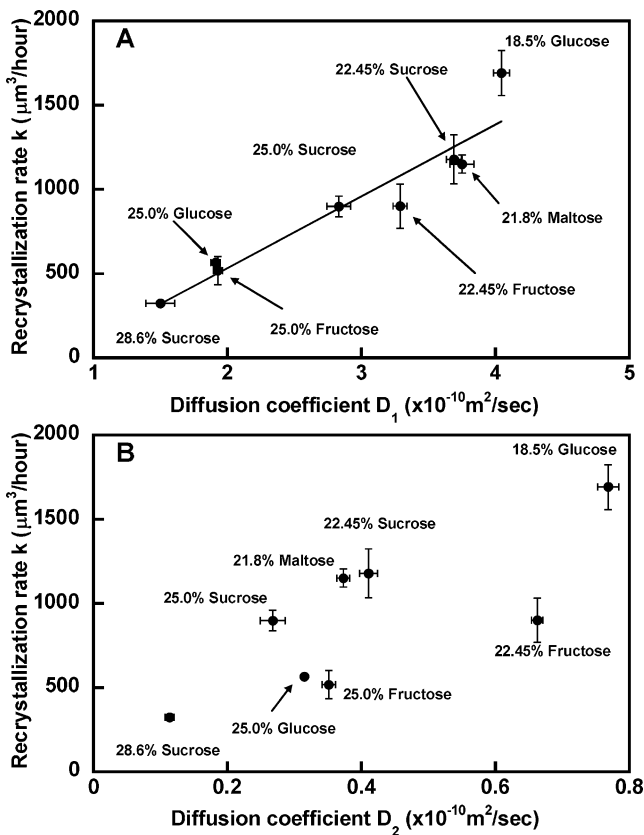
Figure 8A shows the recrystallization rate plotted as a function of  $D_1$ . Recrystallization rate  $k$  correlated well with  $D_1$ ; increasing  $D_1$  resulted to an increase in recrystallization rate  $k$ . This indicates that diffusion coefficient of water molecules in freeze-concentrated matrix is a useful parameter for predicting and controlling recrystallization rate in sugar solutions. Furthermore, the fitting result by a linear function was in reasonable agreement ( $R^2 = 0.90$ ), which suggested that the recrystallization rate examined in this study was approximated by a first-order kinetics with respect to the diffusion coefficient of water component.

In Figure 8B, the graph for sugar component diffusion coefficient  $D_2$  is also presented for comparison. For  $D_2$ , there was no direct correlation with recrystallization rate  $k$ . Solute must be rejected near the surface of ice crystals as the crystals grow. Therefore, not only the diffusion rate of water molecules but also that of solute can affect recrystallization rate in principle. However, results of Figure 8A and B suggested that contribution of solute diffusion rate was much smaller than that of water molecules.

Under the condition where solute type and solute concentration are similar, a decrease in temperature will result to a decrease in the self-diffusion rate of water molecules. Also, at constant temperature, changing solute type or solute concentration will alter the diffusion rate because of the different interaction between solute and water. The result in Figure 8 indicates that the difference in recrystallization rate can be explained well by the difference in the diffusion rate caused by a difference in sugar type, concentration,



**Fig. 7.** Plots of measured diffusion coefficients  $D_1$  (A) and  $D_2$  (B) as a function of temperature.



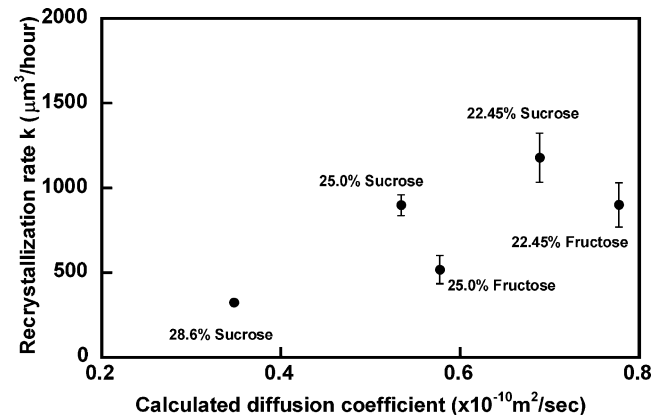
**Fig. 8.** Correlation between recrystallization rate  $k$  and measured diffusion coefficients  $D_1$  (A) and  $D_2$  (B). The solid line represents result of linear fitting.

temperature, or their combination. From this result, the following question arises: what are the dominant factors that determine the diffusion rate of water molecules?

Sutton et al.<sup>13,17</sup> tried to systematically describe the recrystallization process of ice crystals in sugar solutions (fructose and sucrose) and ice cream by using a model based on an assumption of diffusion-limited growth of crystals. Their model attempted to describe the effect of not only the diffusion rate of the water component, but also of ice content. However, results of the model fitting were unsatisfactory in most cases, and the correlation between the diffusion rate of the water component in freeze-concentrated matrix and recrystallization rate was obscure. A possible explanation for these results is that the diffusion coefficients of the water component used for model fitting were inadequate. Sutton et al. did not measure the actual self-diffusion coefficient of water component themselves, but rather extrapolated the reported mutual diffusion coefficients of sucrose or glucose solutions measured at 25, 35, and 1°C<sup>32,33</sup> to lower temperatures. For comparison, we followed their method to calculate the diffusion coefficients for sucrose and fructose

solutions used in this study. The calculated values are significantly different, a factor of 3.3 to 5.3 smaller, than our measured values of  $D_1$ . The correlation of extrapolated values with recrystallization rate  $k$  was also not very good (Figure 9). The original mutual diffusion coefficients of English and Dole<sup>32</sup> and Gladden and Dole<sup>33</sup> were evaluated from macroscopic diffusion experiments of sucrose or glucose in water, which were based on classical Fick's law that assumes coupling of water and sugar motion. If this assumption holds, the evaluated diffusion coefficient would also correspond to diffusion motion of water molecules. In recent years, however, it has been recognized that diffusion of water molecule in concentrated sugar aqueous solution does not couple with that of sugar molecules, because of the different diffusion mechanism of each molecule.<sup>31,34</sup> According to Ekdawi-Sever et al.<sup>31</sup> diffusion of sugar appears continuous, whereas that of water consists of random jumps followed by rapid vibrations within transient cages created by surrounding molecules. From these aspects, it appears that the diffusion coefficients evaluated by extrapolation did not reflect the true diffusion motion of water molecules, which would render the effect of diffusion of water component unclear.

Results of the current study show the usefulness of the self-diffusion coefficient of the water component in a freeze-concentrated matrix as an indicator to estimate the recrystallization rate of ice crystals in mono- or disaccharide solutions. It would be interesting to know the effect of stabilizers such as locust bean gum or guar gum on diffusion rate of water component. It has been suggested that stabilizers increase local viscosity and would thereby reduce water molecule mobility, which leads to lower recrystallization rate.<sup>11</sup> However, Martin et al.<sup>20</sup> reported that the diffusion coefficient of water molecules in freeze-concentrated



**Fig. 9.** Plots of recrystallization rate  $k$  as a function of the diffusion coefficient calculated by the method of Sutton et al.<sup>13</sup>



matrix of fructose solution were not influenced by the addition of locust bean gums, although recrystallization rate was decreased significantly. As for the mechanism of reduction of recrystallization rate by addition of stabilizers, several hypotheses have been proposed, although the exact mechanism is still unknown. Sutton et al.<sup>14–16</sup> proposed that the reduction of recrystallization is brought about by the adsorption of stabilizer onto the surface of the ice crystal, not a retardation of water molecule movement. A physical hindrance against the growth of ice crystal by weak stabilizer gel structure has been also suggested.<sup>35</sup> Sahagian and Goff<sup>36</sup> postulated that a mechanism of stabilizer action at subzero temperature involves a modification of the kinetic properties of the freeze-concentrated matrix rather than thermodynamic parameters. Other factors rather than water mobility in freeze-concentrated matrix may also have a significant effect in determining recrystallization rate in the presence of a stabilizer. Since our systematic understanding of fundamental properties of the solutions at subzero temperature is very limited until now, further studies are needed to solve this problem. Results of this study will be a basis for considering the effect of stabilizer addition.

In conclusion, the difference in recrystallization rate of ice crystals in various sugar solutions with different sugar type, concentration, and temperature, correlated well with the self-diffusion coefficient of the water component in the freeze-concentrated matrix. That is, the recrystallization rate in the sugar solution used in this study depended strongly on water mobility in the freeze-concentrated matrix. Thus, the self-diffusion coefficient of the water component in the freeze-concentrated matrix is a useful parameter to predict and control recrystallization rate.

**Acknowledgments** This research was supported by the College of Agricultural and Life Science at the University of Wisconsin. The authors also wish to thank Dr. Baomin Liang for his technical support to the present research. T. H. is also grateful to the Ministry of Education, Culture, Sports, Science, and Technology of Japan that made possible this research.

## References

- O.R. Fennema, In: *Low-temperature Preservation of Foods and Living Matter*, edited by O.R. Fennema, W.D. Powrie, E.H. Marth (Marcel Dekker, New York, 1973)
- R.W. Hartel, In: *The Properties of Water in Foods: ISOPOW 6*, edited by D.S. Reid (Blackie Academic & Professional, London 1998)
- R.W. Hartel, *Crystallization in Foods* (Aspen Publisher, Gaithersburg 2001)
- A.E. Bevilacqua and N.E. Zaritzky, *J Food Sci* **47**, 1410–1414 (1982)
- M.N. Martino and N.E. Zaritzky, *Science des Aliments* **7**, 147–166 (1987)
- M.N. Martino and N.E. Zaritzky, *J Food Sci* **53**, 1631–1637, 1649 (1988)
- M.N. Martino and N.E. Zaritzky, *Cryobiology* **26**, 138–148 (1989)
- D.P. Donhowe and R.W. Hartel, *Int Dairy J* **6**, 1191–1208 (1996)
- D.P. Donhowe and R.W. Hartel, *Int Dairy J* **6**, 1209–1221 (1996)
- T. Hagiwara and R.W. Hartel, *J Dairy Sci* **79**, 735–744 (1996)
- T. Miller-Livney and R.W. Hartel, *J Dairy Sci* **80**, 447–456 (1997)
- E. Ben-Yoseph and R.W. Hartel, *J Food Eng* **38**, 309–329 (1998)
- R.L. Sutton, A. Lips, G. Piccirillo, and A. Sztzheho, *J Food Sci* **61**, 741–745 (1996)
- R.L. Sutton, A. Lips, and G. Piccirillo, *J Food Sci* **61**, 746–748 (1996)
- R.L. Sutton, D. Cooke, and A. Russell, *J Food Sci* **62**, 1145–1149 (1997)
- R.L. Sutton and J. Wilcox, *J Food Sci* **63**, 104–107 (1998).
- R.L. Sutton, I.D. Evans, and J.F. Crilly, *J Food Sci* **59**, 1227–1233 (1994)
- A. Regand and H.D. Goff, *Food Hydrocolloids* **17**, 95–102 (2003)
- A.K. Carrington, H.D. Goff, and D.W. Stanley, *Food Res Int* **29**, 207–213 (1996)
- D.R. Martin, S. Ablett, A. Darke, R.L. Sutton, and M. Sahagian, *J Food Sci* **64**, 46–49 (1999)
- M. Rampp, C. Buttersack, and H.-D. Lüdemann, *Carbohydr Res* **328**, 561–572 (2000)
- S. Bolliger, H. Wildmoser, H.D. Goff, and B.W. Tharp, *Int Dairy J* **10**, 791–797 (2000)
- I.M. Lifshitz and V.V. Slyozov, *J Phys Chem Solids* **19**, 35–50 (1961)
- C. Wagner, *Z Elektrochem* **65**, 581–591 (1961)
- F.E. Young and F.T. Jones, *J Phys Chem* **53**, 1334–1350 (1949)
- F.E. Young, F.T. Jones, and H.J. Lewis, *J Phys Chem* **56**, 1093–1096 (1952)
- F.E. Young, *J Phys Chem* **61**, 616–619 (1957)
- CRC Handbook of Chemistry, Physics, 84th Ed., edited by D.R. Lide (CRC Press, Boca Raton 2003)
- D.P. Donhowe, R.W. Hartel, and R.C. Bradley Jr, *J Dairy Sci* **74**, 3334–3344 (1991)
- J.E. Tanner, *J Chem Phys* **52**, 2523–2526 (1970)
- N. Ekdawi-Sever, J.J. de Pablo, E. Feick, and E. von Meerwall, *J Phys Chem A*, **107**, 936–943 (2003)
- A.C. English, M. Dole, *J Am Chem Soc* **72**, 3261–3267 (1950)
- J.K. Gladden, M. Dole, *J Am Chem Soc* **75**, 3900–3904 (1953)
- C.J. Roberts, P.G. Debenedetti, *J Phys Chem B* **103**, 7308–7318 (1999)
- A.H. Muhr and J.M.V. Blanshard, *J Food Technol* **21**, 683–710 (1986)
- M.E. Sahagian and H.D. Goff, *Food Res Int* **28**, 1–8 (1995)