

Limiting Partition Coefficient in Progressive Freeze-concentration

X. GU, T. SUZUKI, AND OSATO MIYAWAKI

ABSTRACT: In the progressive freeze-concentration, limiting partition coefficient, K_o , is a very important process parameter, which corresponds to the partition coefficient of a solute between the ice and liquid phase assuming the infinitesimal ice growth rate and/or the infinite mass-transfer rate at the ice-liquid interface. K_o was determined for glucose and various electrolytes in the single-component and multi-component systems. K_o was dependent both on the concentration and the type of solute. In the single-component system, osmotic pressure was proved to be the major determinant of K_o . In the multi-component system, K_o for a solute was affected by the coexisting solute through the osmotic pressure of the total system. K_o was also dependent on viscosity when the change in the osmotic pressure was limited but the change in the viscosity was considerable because of the coexisting solute.

Keywords: progressive freeze-concentration, limiting partition coefficient, osmotic pressure, viscosity, concentration polarization

Introduction

There are 3 methods for the concentration of liquid food: evaporation, reverse osmosis, and freeze-concentration. Among these, freeze-concentration is known to give the best quality (Deshpande and others 1982). Freeze-concentration has been applied for the concentration of fruit juices (Omran and King 1974; Deshpande and others 1982; Bayindirli and others 1993) and dairy products (Hartel and Chung 1993; Hartel and Espinel 1993). Freeze-concentration is also proposed to be applicable to waste water treatments (Muller and Sekoulov 1992; Shirai and others 1999; Rodriguez and others 2000; Lemmer and others 2001; Wakisaka and others 2001).

The conventional method of freeze-concentration is based on suspension crystallization (Huige and Thijssen 1972), in which many small ice crystals are formed and are grown large by spending a long time through the Ostwald ripening mechanism in the system. In spite of this, the size of ice crystals is still limited so that the freeze-concentration based on this method needs a very complicated system composed of a surface-scraping heat-exchanger for the generation of seed ice, a recrystallization vessel for ice crystal growth, and a washing tower for separation of ice crystals from the concentrated mother solution. This complex system requires very high initial investment for the process.

On the contrary, progressive freeze-concentration has been proposed (Matthews and Coggeshall 1959; Bae and others 1994; Miyawaki and others 1998), in which a single ice crystal is formed in the system so that the process is expected to be much simpler, causing much lower initial investment compared with the suspension crystallization method. By using a tubular ice system, scale-up of the progressive freeze-concentration is easily done (Shirai and others 1999; Wakisaka and others 2001; Miyawaki and others 2005).

In the progressive freeze-concentration, a solute in the mother solution is separated at the ice-liquid interface so that the effective

partition coefficient of the solute between the ice and liquid phase is very important. This partition phenomena has been theoretically analyzed by the concentration polarization model (Miyawaki and others 1998). In this model, the limiting partition coefficient is a key process parameter, which could be obtained by the effective partition coefficient under the various operating conditions of ice growth rate and the mass-transfer rate at the ice-liquid interface (Pradistsuwana and others 2003).

In this article, the limiting partition coefficient in the progressive freeze-concentration is obtained for various systems containing various solutes for single- and multi-component systems to clarify the major determinant for the partition phenomena at the ice-liquid interface.

Theoretical considerations

In the progressive freeze-concentration, the effective partition coefficient of solute between the ice and liquid phase at the ice-liquid interface is defined as follows (Liu and others 1997):

$$K = C_S / C_L \quad (1)$$

where, C_S and C_L are the solute concentrations in the ice and solution phases, respectively. At the moment when the solution volume is V_L in the process of freeze-concentration, the following equation is obtained from the mass balance of the solute.

$$C_L V_L = -C_S dV_L + (C_L + dC_L)(V_L + dV_L) \quad (2)$$

From Eq. 1 and 2,

$$\frac{(dC_L/C_L)}{(dV_L/V_L)} = K - 1 \quad (3)$$

When the effective partition coefficient, K , is constant during the concentration process, Eq. 3 can be integrated to be:

$$(1-K) \ln(V_L/V_0) = \ln(C_0/C_L) \quad (4)$$

MS 20050252 Submitted 5/2/05, Revised 6/28/05, Accepted 8/11/05. Authors Gu and Suzuki are with Dept. of Food Science and Technology, Tokyo Univ. of Marine Science and Technology, Tokyo, Japan. Author Miyawaki is with Dept. of Food Science, Ishikawa Prefectural Univ., 1-308 Suematsu, Nonouchi, Ishikawa 921-8836, Japan. Direct inquiries to author Miyawaki (E-mail: osato@ishikawa-pu.ac.jp).

According to the concentration polarization model, the following equation is obtained from the mass balance equation of solute in the boundary layer near the ice-liquid interface in the solution phase (Burton and others 1953; Miyawaki and others 1998):

$$-D(dC/dx) + uC = uC_S \quad (5)$$

where D is the diffusion coefficient of solute, C is the solute concentration in the boundary layer, and u is the advance rate of ice front (ice growth rate).

The limiting partition coefficient of solute between ice and liquid phase at the ice-liquid interface is defined by:

$$K_0 = C_S/C_i \quad (6)$$

where, C_i is the solute concentration in the solution phase at the very interface between ice and liquid. Then, the effective partition coefficient (K) could be expressed as a function of the advance rate of the ice front and the mass transfer coefficient, k ($= D/\delta$; δ = thickness of boundary layer), at the ice-liquid interface as follows:

$$K = K_0/[K_0 + (1 - K_0)\exp(-u/k)] \quad (7)$$

where k has been correlated with the stirring rate, N , by the following equation (Miyawaki and others 1998):

$$k = aN^{0.2} \quad (8)$$

From Eq. 7 and 8, the following equation is obtained:

$$\ln(1/K - 1) = \ln(1/K_0 - 1) - (1/a)(u/N^{0.2}) \quad (9)$$

This means that a linear dependence of $\ln(1/K - 1)$ is expected to the combined parameter of $u/N^{0.2}$ and the limiting partition coefficient, K_0 , is obtained from the extrapolation of the linear plot to $u/N^{0.2} \rightarrow 0$, which corresponds to the infinitesimal ice growth rate and/or the infinite stirring rate at the ice-liquid interface.

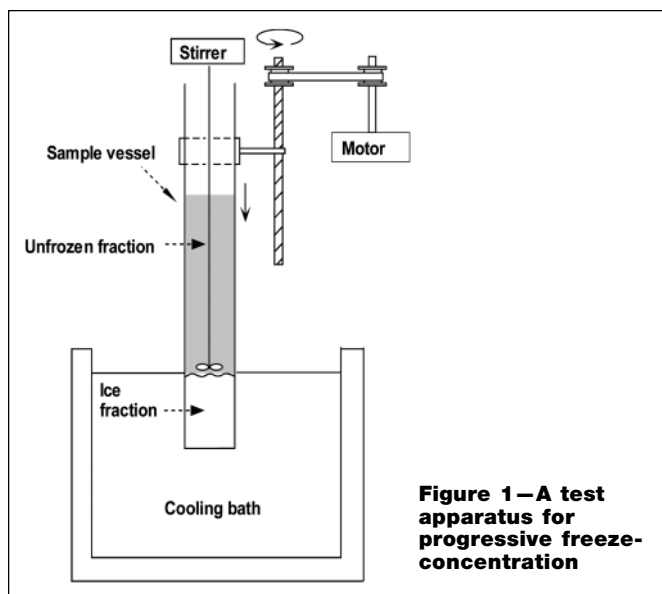


Figure 1—A test apparatus for progressive freeze-concentration

Materials and Methods

Materials

D-(+)-Glucose was purchased from Nacalai Tesque (Kyoto, Japan). Blue Dextran was obtained from Sigma Chemical (St. Louis, Mo., U.S.A.). Sodium chloride, potassium chloride, potassium nitrate, potassium fluoride, lithium chloride, and cesium chloride were purchased from Kanto Chemical (Tokyo, Japan). Dextran T2000 was from Pharmacia Biotech (Tokyo, Japan).

Apparatus and procedure for freeze-concentration

A small cylindrical test apparatus shown in Figure 1 was used for the progressive freeze-concentration (Miyawaki and others 1998). This apparatus consisted of a cylindrical sample vessel (48-mm dia, 197.5 mm height, 4-mm-thick plastic side with stainless-steel bottom), which was plunged into a cooling bath at a constant speed. The advance rate of the ice front was calculated from the thickness of ice and time for an experiment. The cooling bath equipped with a stirrer was kept at -15°C with a thermo-controller (NCB-3400, EYELA, Tokyo, Japan). The sample vessel was equipped with a 3-blade propeller, 3-cm in dia, for stirring the solution at the ice-liquid interface to control the mass-transfer.

Before applying a sample into the sample vessel to start freeze-concentration, 1 mL of pure water was applied on the bottom (stainless steel) of the vessel to provide an ice lining, which prevented the initial supercooling (Liu and others 1998). Then 100-mL sample solution, precooled down to the freezing point, was poured into the sample vessel to start freeze-concentration. When the volume of ice crystal became 10 to 20 mL, the experiment was stopped and the ice crystal was separated from the concentrated mother solution to analyze the ice volume and the solute concentration in it, from which the solute concentration in mother solution, C_L , was calculated from the mass balance. Then, the effective partition coefficient, K , was calculated by Eq. 4.

Analytical method

The concentration of Blue Dextran was determined spectrophotometrically at 620 nm (Hitach U-1100, Tokyo, Japan). Glucose concentration was determined by a hand refractometer (N-10E, Atago, Tokyo, Japan). Concentrations of electrolytes were determined by a conductivity meter (CM-30S, DKK-Toa, Tokyo, Japan).

Measurement of viscosity

Viscosity was measured at 0°C by a dual-cylinder viscometer (Tokimek Type B, Tokyo, Japan) with a revolution speed that varied from 6 to 60 rpm to confirm the Newtonianity.

Estimation of osmotic pressure

To estimate osmotic pressure of a solution, the freezing point of the solution was obtained either by experiment or from the literature (Weast 1974). From the freezing point, water activity, A_w , was determined by the following equation (Hildebrand and Scott 1962; Chandrasekaran and King 1971):

$$\ln A_w = \frac{-\Delta H_f (T_f - T)}{R T_f T} + \frac{\Delta C_f}{R} \left[\frac{(T_f - T)}{T} \ln \left(\frac{T_f}{T} \right) \right] \quad (10)$$

where ΔH_f ($= 6008 \text{ J/mol}$) is the latent heat of water, T (K) is the freezing point of solution, T_f (K) is the freezing point of water, R is the gas constant, and ΔC_f ($= 38.7 \text{ J/mol/K}$) is the difference of the specific heat between water and ice.

From the water activity, the osmotic pressure, Π (MPa), was cal-

culated by the following equation:

$$\Pi = \frac{-RT}{v_W} \ln A_W = -126.02 \ln A_W \quad (11)$$

where v_W ($= 18.018 \text{ cm}^3/\text{mol}$) is the molar volume of water.

Results and Discussion

Limiting partition coefficient for glucose in the single-component system

The effective partition coefficient for glucose, K , in glucose solutions of 3% and 20%, was measured under various operating conditions of the ice growth rate, u , from 0.3 to 1.4 cm/h and the stirring rate, N , from 50 to 1000 rpm. K was dependent both on u and N as was expected by Eq. 7. To these data, Eq. 9 was applied to obtain linear lines with correlation coefficients of 0.955 and 0.962, respectively, for 3% and 20% glucose as shown in Figure 2. From the extrapolation of these linear lines to y-axis ($u/N^{0.2} \rightarrow 0$) based on Eq. 9, the limiting partition coefficient, K_0 , was obtained to be 0.0455 and 0.280 for 3% and 20% glucose, respectively.

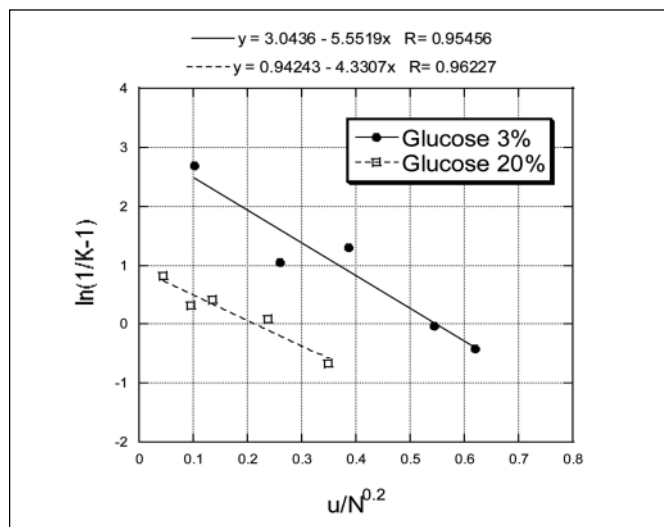


Figure 2—Determination of limiting partition coefficient for glucose solutions in progressive freeze-concentration

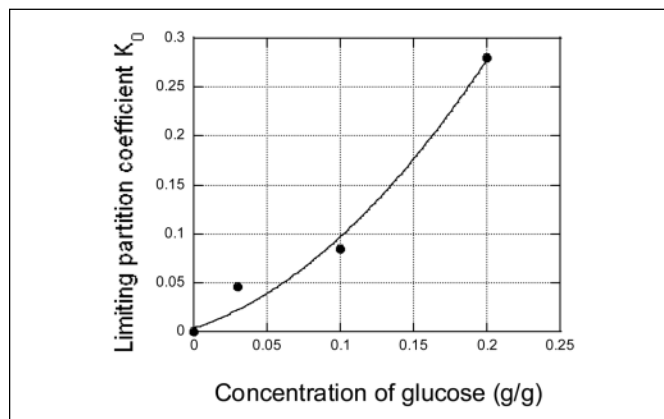


Figure 3—Effect of solute concentration on limiting partition coefficient of glucose

Figure 3 shows the effect of solute concentration on K_0 , which increased with an increase in the concentration of glucose although K_0 corresponds to the partition coefficient assuming the infinitesimal ice grow rate and/or the infinite mass-transfer rate at the ice-liquid interface. This suggests that the ice-liquid interface structure is dependent on the concentration of solute. The change in the ice-liquid interface structure would have affected the solute concentration polarization near the interface through the concentration polarization (Miyawaki and others 1998), which directly affects K and then K_0 . This means that K_0 does not necessarily represent the partition phenomenon between the ice and liquid phases at the thermodynamic equilibrium but K_0 is rather dependent on the nonequilibrium process at the ice-liquid interface. At the interface, a multi-crystalline array of dendritic ice structure would be formed so that a part of solute might have been trapped in a gap between the dendritic ice structures. Although a single ice structure is observed in the progressive freeze-concentration, the ice structure formed actually is an assemblage of multi-crystalline dendritic ice structures.

Because of this nonequilibrium process at the ice-liquid interface in the progressive freeze-concentration, solute-loss levels might be higher than the conventional method of suspension crystallization method, but this drawback would be easily overcome by a multistep operation or by a combination with other recovery system such as membrane process.

When K_0 is dependent on the concentration of solute, K is also dependent on the concentration so that the integration of Eq. 3 should be carried out numerically in consideration of the concentration effect on K . In the present case, however, the amount of ice crystal formed was small so that the change in the concentration of mother solution was kept low. Therefore, K could be assumed constant during the experiments so that Eq. 4 was considered to be applicable.

Figure 4 shows the effect of solute concentration on the osmotic pressure and viscosity of glucose solution. With an increase in the glucose concentration from 0% to 25%, viscosity increase was moderate only, from 1.52 to 3.05 mPa*s, whereas osmotic pressure increased from 0 to 15.06 MPa. This suggests that the osmotic pressure is the major reason that explains the change in K_0 along with the concentration of solute. Osmotic pressure would have affected the dendrite structure of the ice-liquid interface to change K and then K_0 .

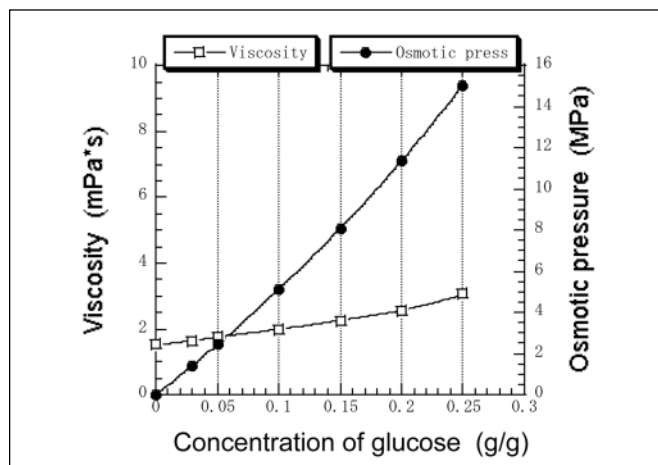


Figure 4—Viscosity and osmotic pressure of glucose solution

Table 1—Limiting partition coefficient for various solutes at various concentrations

Solute	Concentration of solute (wt%)				
	2%	3%	5%	10%	20%
LiCl	0.1193	—	0.2242	—	—
NaCl	0.0735	—	0.1730	0.2813	—
KCl	0.0530	—	0.1652	0.2223	—
CsCl	0.0259	—	0.1339	0.1063	—
KNO ₃	0.0719	—	0.0771	0.1376	—
Glucose	—	0.0455	—	0.0848	0.2804

Limiting partition coefficient for electrolytes in the single-component system

Figure 5 shows the effect of solute concentration on K_0 of NaCl in a single-component system. K_0 was more sensitive to the concentration of solute compared with the case of glucose in Figure 3. In Figure 6, K_0 was obtained for 4 different types of electrolytes, LiCl, NaCl, KCl, and CsCl at 5 wt%. Although the solute concentration was the same, K_0 was different depending on the type of solutes. K_0 was the highest for LiCl followed by NaCl, KCl, and CsCl. This order apparently seems to agree with the Hofmeister series (von Hippel and Schleich 1969).

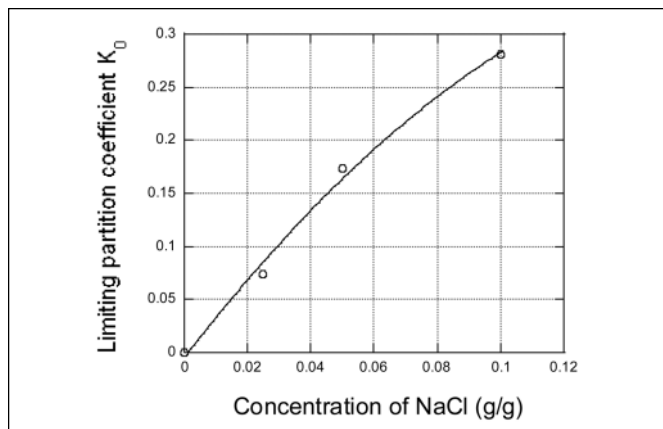


Figure 5—Effect of solute concentration on limiting partition coefficient of NaCl

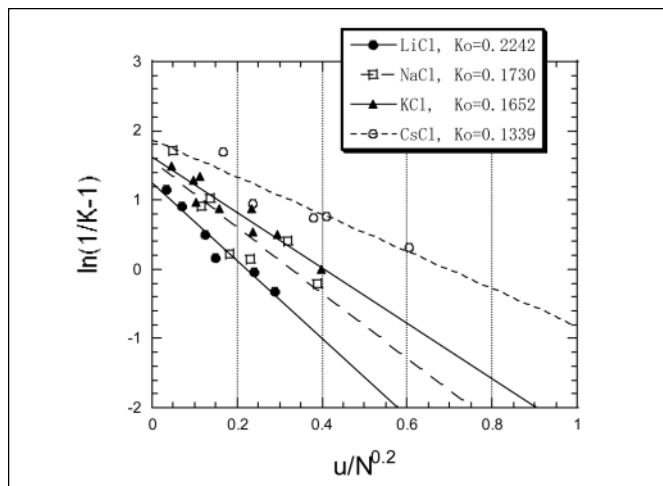


Figure 6—Determination of limiting partition coefficient for various electrolyte solutions at 5 wt%

Table 1 summarizes K_0 obtained for various electrolytes and glucose at various concentrations. For these solutions, the osmotic pressure was calculated based on the literature (Weast 1974) of the freezing point applying Eq. 10 and 11. Then K_0 was plotted against the osmotic pressure as shown in Figure 7, which include all the data in Table 1 except 20% glucose. A single correlation in Figure 7 between K_0 and the osmotic pressure strongly suggests that the osmotic pressure is the major determinant of K_0 . For 20% glucose solution, some different mechanism other than the osmotic pressure might have affected K_0 .

Limiting partition coefficient in the multi-component system

The limiting partition coefficient was also measured for multi-component systems to investigate the effect of coexisting solute. Figure 8 compares the plots to obtain K_0 for Blue Dextran (BD) in a single component system of 0.05% BD and that in a double-component system of 0.05% BD with 20% glucose. K_0 for BD in the single-component system was much lower than that in the double-component system, reflecting the large difference in the osmotic

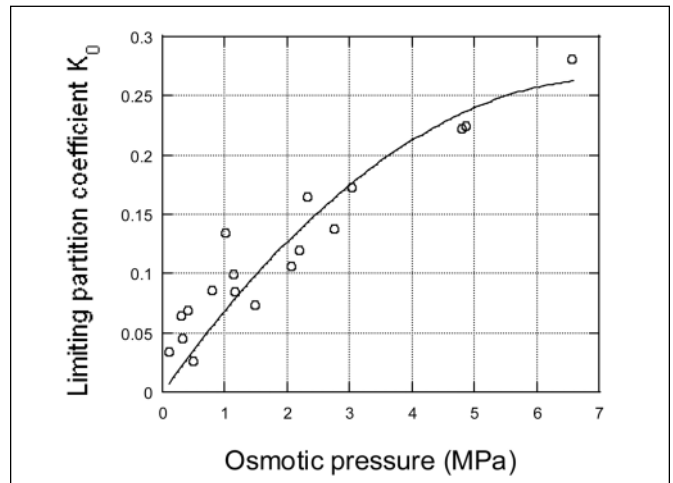


Figure 7—Effect of osmotic pressure on limiting partition coefficient for electrolytes and glucose solutions at various concentrations

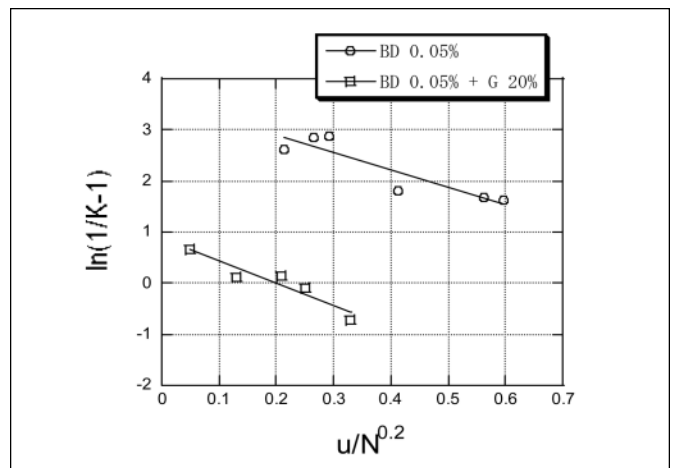


Figure 8—Limiting partition coefficient for Blue Dextran (BD) in the single-component system of 0.05% BD and in the mixed system of 0.05% BD plus 20% glucose (G)

Table 2—Comparison of limiting partition coefficients for Blue Dextran (BD) and glucose (G) between single component and mixed systems

	K_0 (G)	K_0 (BD)
Blue Dextran 0.05% (single component)	—	0.0274
Glucose 20% (single component)	0.2804	—
Glucose 20% ± Blue Dextran 0.05% (mixed system)	0.3090	0.2965

pressure between the 2 systems. Figure 9 compares the similar plots for glucose between a single-component system of 20% glucose and a double-component system of 20% glucose along with 0.05% BD. In this case, no substantial difference was observed between the 2 plots.

Table 2 summarizes K_0 in these cases. In the single-component system, K_0 for BD in 0.05% BD was very small (0.0274), reflecting the low osmotic pressure of the system, whereas K_0 for BD drastically increased to 0.2965 when 20% glucose coexisted in the mixed system. On the contrary, K_0 for glucose in the single-component system of 20% glucose and that in the mixed system with 0.05% BD were not much different because the addition of 0.05% BD scarcely

affected the osmotic pressure of the total system. These results suggest that K_0 in the multi-component system is dependent on the osmotic pressure of the whole system.

As for another example of multi-component system, a mixed system of NaCl and Dextran T2000 was tested. In this case, the concentration of NaCl was kept constant at 2.5% and the concentration of Dextran T2000 was varied from 0% to 8%. As shown in Figure 10, K_0 for NaCl increased much with an increase in the Dextran concentration. In this case, the osmotic pressure for the mixed system was almost constant as shown in Figure 11, but the viscosity changed from 1.82 to 52 mPa*s. This large change in the viscosity might have affected the flow properties at the ice-liquid interface to change the dendritic ice structure, which caused a change in the partition phenomenon at the interface.

Conclusions

The limiting partition coefficient, K_0 , as an important process parameter for progressive freeze-concentration, was determined for glucose and various electrolytes based on the concentration polarization theory in the single-component and multi-component systems. The osmotic pressure of a solution was proved to be the major determinant of K_0 . In some cases, however, K_0 was also dependent on viscosity when the change in the osmotic pressure was limited but the change in the viscosity was considerable because of the coexisting solute. From K_0 , the effective partition coefficient, K , can be theoretically estimated at any operating conditions of the ice growth rate and the mass-transfer rate at the ice-liquid interface in the progressive freeze-concentration.

Although the solute-loss level may be larger for the progressive freeze-concentration compared with the conventional method of suspension crystallization, the system will be much simpler for the former. Scale-up of the progressive freeze-concentration is easily carried out by a tubular ice system (Miyawaki and others 2005). The operational mode of the progressive freeze-concentration is a repeated batch with a relatively short cycle, whereas that of the suspension crystallization is a continuous mode with very long residence time. This means that the former is much flexible than the latter. Therefore, the progressive freeze-concentration is an effective option of freeze-concentration with a high practical potential when an appropriate operating condition is used.

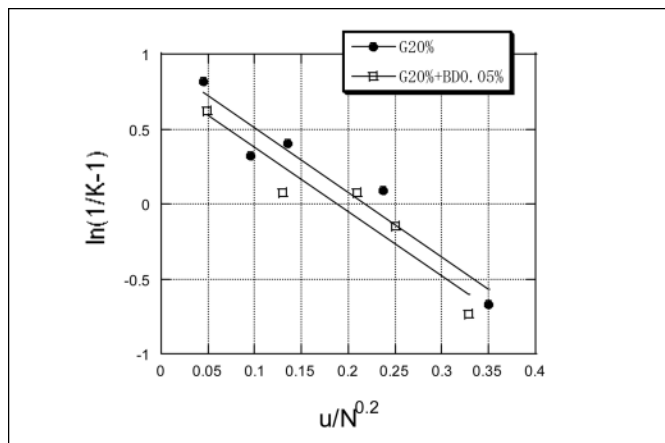


Figure 9—Limiting partition coefficient for glucose (G) in the single-component system and in the mixed system of 20% G plus 0.05% Blue Dextran (BD)

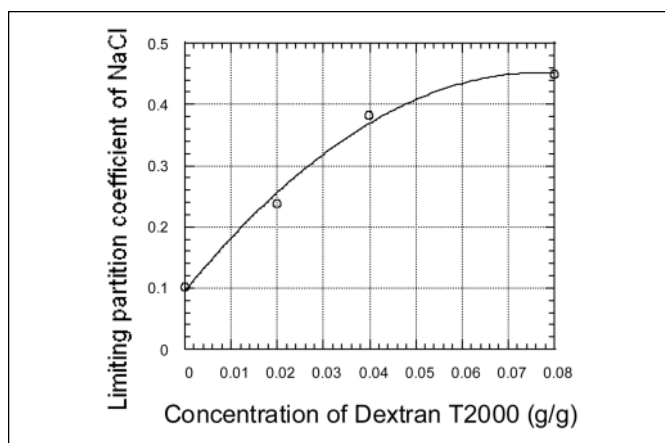


Figure 10—Effect of concentration of Dextran T2000 on the limiting coefficient of NaCl in the mixed system of 2.5% NaCl and Dextran T2000 at various concentrations

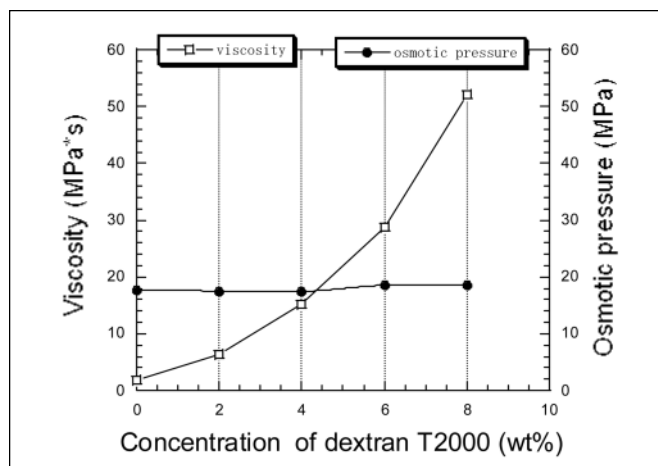


Figure 11—Viscosity and osmotic pressure of the mixed system of 2.5% NaCl and Dextran T2000 with concentration varied

References

- Bae SK, Miyawaki O, Arai S. 1994. Control of freezing front structure and its effect on the concentration-efficiency in the progressive freeze-concentration. *Cryobiol Cryotechnol* 40:29–32.
- Burton JA, Prim RC, Slichter WP. 1953. The distribution of solute in crystals grown from the melt. Part I. Theoretical. *J Chem Phys* 21:1987–91.
- Chandrasekaran SK, King CJ. 1971. Solid-liquid phase equilibria in multicomponent aqueous sugar solutions. *J Food Sci* 36:699–704.
- Deshpande SS, Bolin HR, Salunkhe DK. 1982. Freeze concentration of fruit juices. *Food Technol (May)*:68–82.
- Hartel W, Chung MS. 1993. Contact nucleation of ice in fluid dairy products. *J Food Eng* 18:281–96.
- Hildebrand JH, Scott RL. 1962. *Regular solutions*. Engelwood Cliffs, N.J.: Prentice Hall. p 20.
- Huige NJJ, Thijssen HAC. 1972. Production of Large crystals by continuous ripening in a stirred tank. *J Crystal Growth* 13–14:483–7.
- Lemmer S, Klomp R, Ruemekorf R, Scolz R. 2001. Preconcentration of wastewater through the Niro freeze concentration process. *Chem Eng Technol* 24:485–8.
- Liu L, Fujii T, Hayakawa K, Miyawaki O. 1998. Prevention of initial supercooling in progressive freeze-concentration. *Biosci Biotechnol Biochem* 62(12):2467–9.
- Liu L, Miyawaki O, Hayakawa K. 1999. Progressive freeze-concentration of tomato juice. *Food Sci Technol Res* 5(1):108–12.
- Matthews JS, Coggeshall ND. 1959. Concentration of impurities from organic compounds by progressive freezing. *Anal Chem* 31:1124–5.
- Miyawaki O, Liu L, Nakamura K. 1998. Effective partition constant of solute between ice and liquid phases in progressive freeze-concentration. *J Food Sci* 63(5):756–8.
- Miyawaki O, Liu L, Shirai Y, Sakashita S, Kagitani K. 2005. Tubular ice system for scale-up of progressive freeze-concentration. *J Food Eng* 69:107–13.
- Muller M, Sekoulov I. 1992. Waste water reuse by freeze concentration with a falling film reactor. *Wat Sci Technol* 26:1475–82.
- Omran AM, King CJ. 1974. Kinetics of ice crystallization in sugar solution and fruit juices. *AIChE J* 20:795–803.
- Pradistsuwana C, Theprugsa P, Miyawaki O. 2003. Measurement of limiting partition coefficient in progressive freeze-concentration. *Food Sci Technol Res* 9(2):190–2.
- Ramteke RS, Singh NI, Rekha MN, Eipeson WE. 1993. Methods for concentration of fruit juices: a critical evaluation. *J Food Sci Technol* 30:391–402.
- Rodriguez M, Luque S, Alvarez JR, Coca J. 2000. A comparative study of reverse osmosis and freeze concentration for the removal of valeric acid from wastewaters. *Desalination* 127:1–11.
- Shirai Y, Wakisaka M, Miyawaki O, Sakashita S. 1999. Effect of seed ice on formation of tube ice with high purity for a freeze wastewater treatment system with a bubble-flow circulator. *Wat Res* 33:1325–9.
- von Hippel PH, Schleich T. 1969. Ion effects on the solution. *Acc Chem Res* 2:257–65.
- Wakisaka M, Sirai Y, Sakashita S. 2001. Ice crystallization in a pilot-scale wastewater treatment system. *Chem Eng Process* 40:201–8.
- Weast RC, editor. 1974. *Handbook of chemistry and physics*. Cleveland, Ohio: CRC Press. p 218–67.