

Note

Measurement of Limiting Partition Coefficient in Progressive Freeze-Concentration

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The limiting partition coefficient is the partition coefficient of a solute at the ice-liquid interface observed at an infinitesimal advance rate of the ice front or infinite mass transfer rate at the interface in progressive freeze-concentration. A method to determine the limiting partition coefficient was proposed based on the concentration polarization model. Electrolytes were concentrated at various operating conditions in advance rate of the ice front (*u*) and stirring rate (*N*) in progressive freeze-concentration. The limiting partition coefficients (*K*₀) of NaCl and KCl were obtained from the effective partition coefficients (*K*) observed under various operating conditions. From *K* experimentally determined, ln(1/*K*–1) was calculated and plotted against *u*/*N*^{0.2}. This plot showed a linear line, from which *K*₀ was obtained by extrapolation to *u*/*N*^{0.2}→0. The limiting partition coefficient was dependent both on the solute concentration and the chemical species of solute.

Keywords: progressive freeze-concentration, effective partition coefficient, limiting partition coefficient, ice crystal growth rate

Freeze concentration has been applied to the concentration of fruit juices, the concentration of dairy products, preconcentration of coffee extract before freeze-drying, preconcentration of solutes for analytical purposes, desalination, and waste water treatment (Muller, 1967; Deshpande *et al.*, 1982; Ramteke *et al.*, 1993; Muller & Sekoulov, 1992). For the industrial application of freeze concentration, the suspension crystallization method (Huige & Thijssen, 1972) has been extensively investigated because of its adaptability for scale-up. In this method, it is very important to grow ice crystals large enough to be easily separated from the mother solution (Omran & King, 1974; Shirai *et al.*, 1987). In this method, however, the entire system is complex, involving ice nucleation, ice-crystal growth, and ice separation processes so that the capital cost of the system is very expensive. Therefore, practical application of this method is still limited.

As an alternative approach to the suspension crystallization, progressive freeze-concentration is a concentration method in which only a single ice crystal is formed in the system. The separation of an ice crystal from the concentrated mother solution by this technique is much easier than that by the conventional suspension crystallization method (Bae *et al.*, 1994; Liu *et al.*, 1999). The entire system can be simplified to reduce the cost of freeze concentration substantially.

In progressive freeze-concentration, the effective partition coefficient of solute between ice and liquid phase is strongly dependent on the ice growth rate and the mass transfer at the ice-liquid interface. To analyze effects of these operating conditions on separation efficiency, a concentration polarization model has been successfully applied (Burton *et al.*, 1953; Miyawaki *et al.*, 1998). Using this model, the limiting partition coefficient of solute

at the ice-liquid interface has been found to be an important design parameter in progressive freeze-concentration. In this paper, we propose a method to determine the limiting partition coefficient of solute in progressive freeze-concentration.

Theoretical

The effective partition coefficient of solute between ice and liquid phases at the ice-liquid interface is defined as *K*=*C*_s/*C*_L, where *C*_s and *C*_L are the solute concentrations in the ice and liquid phases, respectively. The effective partition coefficient is determined by the following equation (Bae *et al.*, 1994),

$$(1-K) \ln (V_0/V_L) = \ln (C_L/C_0), \tag{1}$$

where *V*₀ and *V*_L are the liquid volume at time zero and at an arbitrary time, respectively, and *C*₀ and *C*_L are concentration of solute in the solution at the corresponding time. The effective partition coefficient, *K*, is an experimentally observable partition coefficient of solute between ice phase and bulk liquid phase. *K* has been analyzed by the concentration polarization model focusing on the solute concentration distribution near the ice-liquid interface, and expressed as a function of the advance rate of the ice front (*u*) and the mass transfer coefficient at the ice-liquid interface (*k*) by the following equation (Miyawaki *et al.*, 1998),

$$K = K_0 / (K_0 + (1 - K_0) \exp (-u/k)), \tag{2}$$

where *K*₀ is the limiting partition coefficient representing the partition coefficient of solute at the ice-liquid interface. *K*₀ corresponds to the value of the partition coefficient at an infinitesimal advance rate of ice front (*u*→0) and/or at infinite mass transfer coefficient (*k*→∞) because under these conditions *K*=*K*₀ in Eq. (2). The mass transfer coefficient has been experimentally determined and expressed as a function of stirring speed (*N*) as follows (Miyawaki *et al.*, 1998):

$$k = aN^{0.2}. \tag{3}$$

Using Eq. (3), Eq. (2) can be rewritten as:

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$$\ln(1/K-1) = \ln(1/K_0-1) - (1/a)u/N^{0.2} \quad (4)$$

From Eq. (4), it is easy to determine K_0 experimentally by linear extrapolation of the plot between $\ln(1/K-1)$ and $u/N^{0.2}$ to the intersect ion with y -axis ($u/N^{0.2} \rightarrow 0$).

Materials and Methods

Materials and sample preparation Sodium chloride and potassium chloride were obtained from Kanto Chemical Co., Tokyo, Japan. For preparation of the salt solution, each type of salt was dissolved in pure water to be 0.5, 2.5, and 10% (wt) and cooled to 0°C.

Progressive freeze-concentration Figure 1 shows a small test apparatus for progressive freeze-concentration similar to that used in the previous paper (Liu *et al.*, 1997). The apparatus consisted of a cylindrical sample vessel (48 mm inner diameter, 197.5 mm high) with acrylic or stainless steel wall and stainless steel bottom as a cooling plate. The sample vessel was plunged into a cooling bath (NCB-3400, EYELA, Tokyo) at a constant speed which corresponds to the advance rate of the ice front. The cooling bath was kept at -15°C. The sample vessel was equipped with a propeller for stirring the solution at the ice-liquid interface to enhance the mass transfer. Before applying a sample

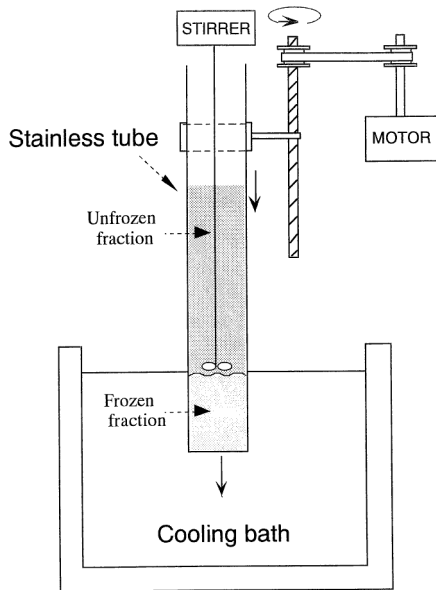


Fig. 1. Test apparatus for progressive freeze-concentration.

Table 1. Effective partition coefficient measured under various operating conditions in progressive freeze-concentration of 2.5% NaCl solution.

N [rpm]	u [cm/h]	K [-]
65	0.45	0.44
65	1.55	0.68
200	0.25	0.28
200	0.61	0.46
200	0.8	0.52
500	0.3	0.18
500	0.45	0.28
1000	0.18	0.32
1000	0.32	0.29
1000	0.5	0.36
1000	0.6	0.42

in the sample vessel, a small amount of pure water, typically 1 ml, was applied on the bottom of the vessel to provide an ice lining, which would prevent the initial supercooling (Liu *et al.*, 1998). The aqueous solutions of NaCl and KCl were used as test solutions with various concentrations. The salt concentrations in both ice and liquid phases were determined using a conductivity meter (CM-30S, DKK-TOA Corp., Tokyo).

Results and Discussion

The effective partition coefficient (K) of 2.5% NaCl aqueous solution during freeze concentration was measured under various operating conditions. The results are shown in Table 1. The partition coefficient was dependent both on the advance rate of the ice front and the stirring rate. From K thus measured, $\ln(1/K-1)$ was calculated and plotted against $u/N^{0.2}$. As was expected by Eq. (4), the plot was linear as shown in Fig. 2 and the limiting partition coefficient (K_0) was determined from the extrapolation of the linear line to $U/N^{0.2} \rightarrow 0$. By this method, the limiting partition coef-

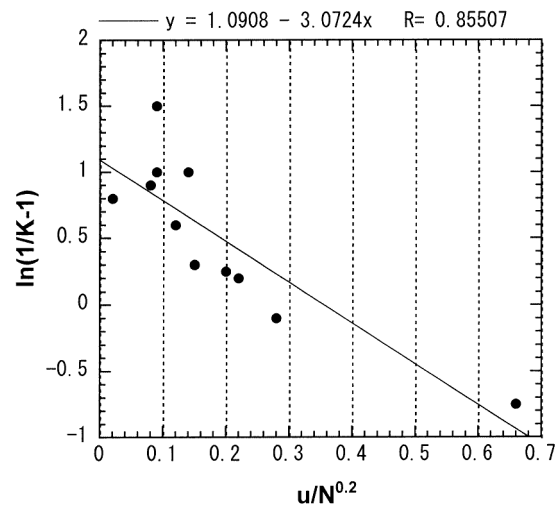


Fig. 2. Determination of limiting partition coefficient for 2.5% NaCl solution in progressive freeze-concentration.

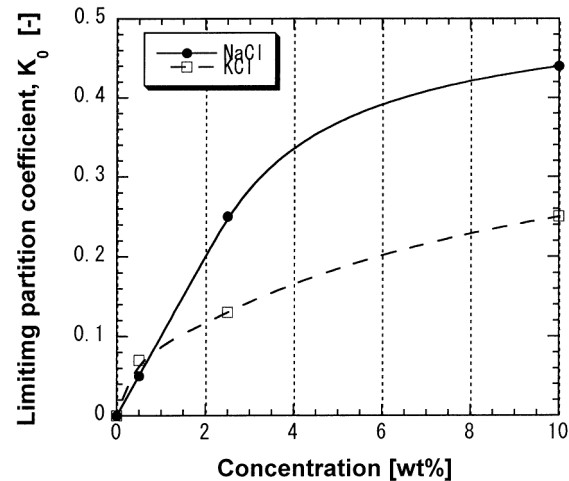


Fig. 3. Effect of solute concentration on limiting partition coefficient for NaCl and KCl in progressive freeze-concentration.

ficient was obtained for NaCl and KCl in solutions with various concentrations.

The limiting partition coefficient was found to be dependent on the solute concentration as shown in Fig. 3, where K_0 for solute concentration at zero was intuitively assumed to be zero because K_0 monotonically decreased with a decrease in solute concentration. K_0 represents the affinity of a solute to ice so that this parameter was expected to be independent from the concentration of solute. However, K_0 was strongly dependent on the concentration of solute.

When K_0 is dependent on solute concentration, the effective partition coefficient, K , should also be dependent on the concentration through Eq. (2). This means that K in Eq. (1) is not constant during the progressive freeze-concentration process. In practice, however, Eq. (1) has been applied to determine K only for the initial concentration process with a small amount of ice crystal formation, typically less than 10% in volume ratio. Therefore, the effect of concentration on K was negligible in the present case. If Eq. (1) is applied for a process with much higher concentration ratio, the effect of solute concentration on K through a change in K_0 should be taken into account.

K_0 was also different between NaCl and KCl as shown in Fig. 3. The hydration state of Na^+ is much stronger than K^+ , which affects the aqueous solution structure through the hydrogen bonding. Na^+ is so-called "water-structure-forming" while K^+ is "water-structure-breaking" (Kaminsky, 1957; Herscovits & Kelly, 1973). The interfacial water molecules adjacent to Na^+ are less mobile and their entropy is lower than those adjacent to K^+ (Collins & Washabaugh, 1985). The viscosity of NaCl solution is higher than KCl solution at the same molar concentration (Kaminsky, 1957). These differences correspond to the difference in the solution structure between the two solutions, and this difference in structure might have affected the difference in K_0 observed in the present case.

Conclusion

By applying the concentration polarization model, the limiting partition coefficient (K_0) was successfully determined from the experimentally determined effective partition coefficient for the progressive freeze-concentration under various operating conditions. The limiting partition coefficient was found to be dependent both on the solute concentration and the chemical species of solute. K_0 provides an important design parameter in the progres-

sive freeze-concentration process under various operating conditions.

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