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Note

Limiting Partition Coefficient in a Tubular Ice System for Progressive Freeze-concentration

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A tubular ice system is effective for the scale-up of progressive freeze-concentration. The effective partition coefficient, *K*, as an index for the effectiveness of progressive freeze-concentration, is defined by the ratio of solute in ice and liquid phase. *K* is dependent both on the ice crystal growth rate and the mass transfer coefficient at the ice-liquid interface, as described by the concentration polarization model. The limiting partition coefficient, K_0, corresponds to *K* at the infinitesimal ice crystal growth rate and/or infinite mass transfer at the interface. K_0 is an important process parameter for progressive freeze-concentration. A method is proposed for determining K_0 experimentally for a tubular ice system. K_0 increased with increase in the concentration of solute, which suggests that K_0 is not determined by the equilibrium process but by the nonequilibrium process at the ice-liquid interface.

Keywords: progressive freeze concentration, scale-up, tubular ice system, limiting partition coefficient

Introduction

In the conventional method of freeze concentration, suspension crystallization (Huige and Thijssen, 1972), many small ice crystals are formed in the system, making the separation of ice crystals from the concentrated mother solution very complicated. Compared with this method, we proposed progressive freeze-concentration, in which only a single ice crystal is formed in the system. Since the separation of ice crystal from the concentrated mother solution is much easier in this method than that in the conventional method, the system is greatly simplified, reducing the process cost substantially (Miyawaki *et al.*, 1998). For the scale-up of progressive freeze-concentration, a tubular ice system was proved to be effective due to increased productivity (Shirai *et al.*, 1999). The effects of operating conditions have been analyzed on the effective partition constant of solute between ice and liquid phase for the tubular ice system (Miyawaki *et al.*, 2005). In this paper, a method is proposed for obtaining the limiting partition coefficient for the tubular ice system.

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Theoretical Considerations

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, *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 in consideration of 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).

$$K = K_o / [K_o + (1 - K_o) \exp(-U/k)] \quad (1)$$

where K_o is the limiting partition coefficient representing the partition coefficient of solute at the ice-liquid interface. K_o corresponds to the value of the partition coefficient at the infinitesimal rate of advance of the ice front ($U \to 0$) and/or at infinite mass transfer coefficient ($k \to \infty$) because at these conditions $K=K_0$ in Eq.(1). Equation (1) is rewritten as follows.

$$\ln[(1/K)-1] = \ln[(1/K_0)-1] - (U/k) \quad (2)$$

The mass transfer coefficient, k, is assumed to be proportional to the 0.8 power of the circulating flow rate, v, in turbulent flow (The Society for Chemical Engineers, Japan, 1988) giving Eq. (2) as:

$$\ln[(1/K)-1] = \ln[(1/K_0)-1] - (1/a)(U/v^{0.8}) \quad (3)$$

where a is an experimental constant. From this equation, it is easy to determine K_0 experimentally by linear extrapolation of the plot between ln $[(1/K)-1]$ and $(U/v^{0.8})$ to the intersection with the y-axis ($U/v^{0.8} \to 0$).

Materials and Method

Fig. 1 shows a schematic diagram of the experimental apparatus of the tubular ice system with a circulating flow inside. The apparatus comprised two straight pipes, 35.7 mm in diameter and 4 m long, curved pipes at the top and the bottom, and a pump for circulation. The straight pipes were cooled by the temperature-controlled coolant in the jacket. The curved pipes were thermally insulated to minimize heat transfer from the environment, which counteracts the ice crystal growth in the straight pipes.

In the tubular ice system, seed ice lining on the cooling surface is necessary to prevent initial super cooling, which causes serious contamination in ice crystal initially formed (Miyawaki *et al.*, 2005). Before starting freeze concentration, pure water was introduced into the system by a feed pump to form seed ice lining. When the seed ice volume went up to about 800 ml, the pure water initially introduced was removed and the system was filled with a sample solution to start progressive freeze-concentration. The sample solution was precooled to around -0.5 °C to avoid melting of seed ice crystal. At the top of the system, there was a small drain connected to a fine tube, through which overflow was discharged from the expansion in volume (8.5%) due to the phase change from water to ice. The volume of ice formed in the system was estimated from the volume of this overflow. Ice crystal growth rate and circulation flow rate were two important operating parameters; the former was controlled by the coolant temperature and the latter by the circulation pump.

After operation typically for 60 to 90 minutes, the circulation flow was stopped and the concentrated mother solution was removed, and its volume and concentration were measured. The bottom curved section of the system was then removed and the coolant was replaced with a warm medium to melt and remove the ice formed on the inner surface. After complete removal of the ice crystal, its total volume and concentration were measured.

Glucose solution, purchased from Nacalai Tesque (Kyoto, Japan) was used as the sample solution for concentration. Solute concentrations in the feed solution, concentrated solution, and ice phase were analyzed by a refractometer (Atago N-1E, Tokyo).

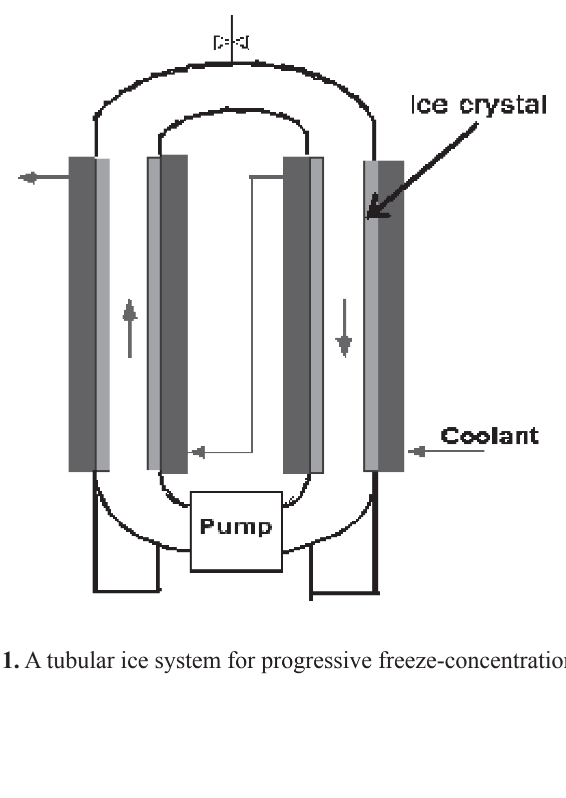

Fig. 1. A tubular ice system for progressive freeze-concentration.

Results and Discussion

In a tubular ice system, important parameters for determining the effective partition coefficient are the growth rate of ice (U) and the circulating flow rate (v) as is predicted by Eq.(1). The former is primarily determined by the coolant temperature, as shown in Fig. 2, where the growth rate of ice is plotted against time for various coolant temperatures. The growth rate of ice, however, is also strongly dependent on the circulation flow rate, as shown in Fig. 3, because the heat generation by the circulating flow affects energy balance in the ice formation. In practice, the mean advance rate of the ice front was determined from the ice thickness and the experimental time.

The effective partition coefficient has been measured at various coolant temperatures and various circulation flow rates to obtain $\ln[(1/K)-1]$, which was plotted against a lump parameter, $U/v^{0.8}$, as shown in Fig. 4. From this plot, $\ln[(1/K_0)-1]$ was determined by linear extrapolation to $U/v^{0.8} \to 0$, as

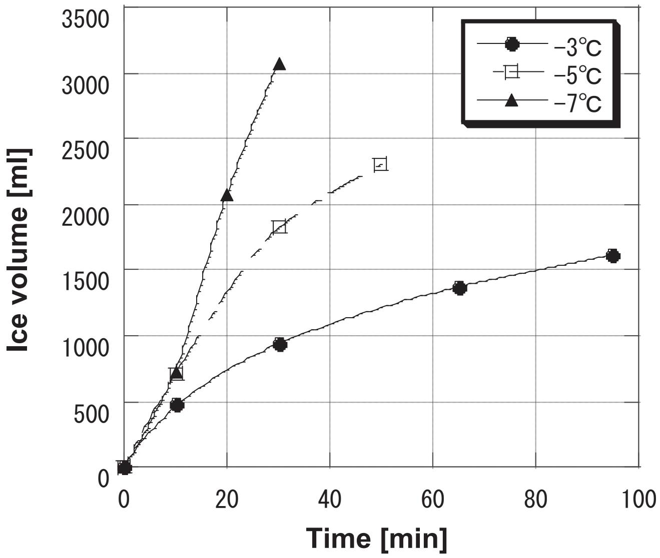

Fig. 2. The effect of coolant temperature on growth rate of ice from pure water in a tubular ice system (v =1.362m/s).

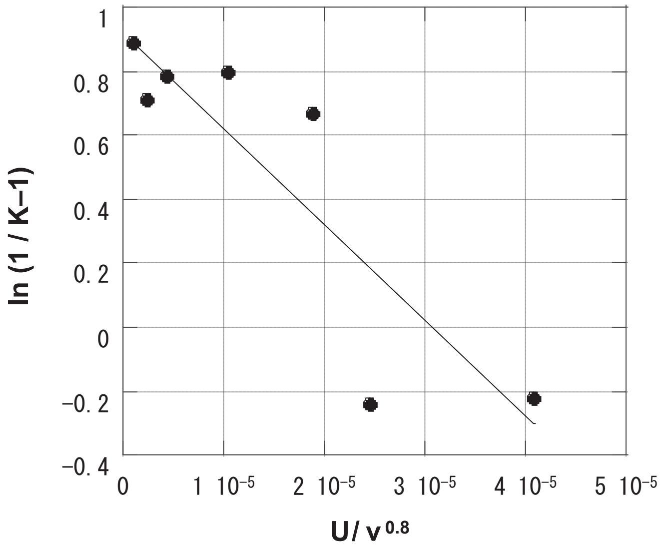

Fig. 4. Plot for limiting the partition coefficient for 10% glucose solution in a tubular system for progressive freeze-concentration.

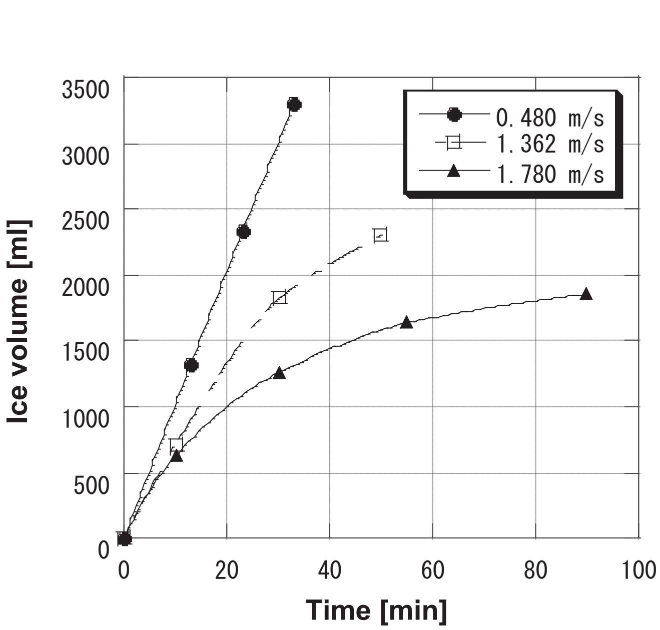

Fig. 3. The effect of circulation flow rate on growth rate of ice formation of pure water in a tubular ice system (coolant temperature = -5ºC).

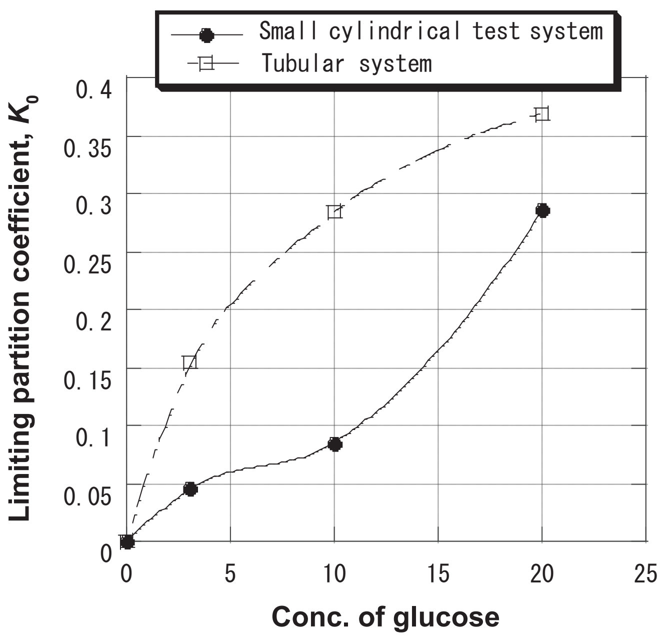

Fig. 5. The effect of solute concentration on limiting partition coefficient for a tubular system and a small cylindrical test system for progressive freeze-concentration.

predicted by Eq.(3), and the limiting partition coefficient K_0 was determined. In this procedure, the ice surface area was assumed to be constant, which is a prerequisite for Eq.(1). In practice, the ice surface area slightly decreased with increase in the ice volume. The thickness of the ice formed, however, was less than 0.5 cm in the present experiments so that the change in the ice surface area was negligible.

Fig. 5 shows K_0 thus obtained for glucose solution plotted against concentration. As was the case for the small cylindrical test apparatus (Miyawaki *et al.*, 1998), K_0 for the tubular system was strongly dependent on the solute concentration, although the absolute values of K_0 differed between the two systems. This concentration-dependence of K_0 suggests that K_0 does not necessarily represent the equilibrium partition phenomenon between the ice and liquid phases but K_0 rather reflects the nonequilibrium process at the ice-liquid interface with the multi-crystalline array of a dendritic ice structure (Gu *et al.*, 2005). The present result implies that the concentration efficiency (yield) decreases with increase in the concentration of solute in the progressive freeze-concentration. Multiple operations are therefore recommended when a complete yield for solute is required. The difference of K_0 between the small cylindrical test apparatus and the tubular system suggests a different ice structure because of the difference in flow conditions between the two.

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