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Efficiency of Freeze Concentration with Ultrasonic Irradiation under Constant Freezing Rate　-Effect of Solute-

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Abstract: The performance of freeze concentration at constant freezing rate (40 mm/h) with/without ultrasonic irradiation was examined using three one-component solutions containing only one solute (mass concentration: 0.5, 5.0 kg/m^3 and ionic or molecular concentration: 0.03 mol/L) and a three-component solution containing three solutes (each component concentration: 0.01 mol/L).

Without ultrasonic irradiation the solutes are hardly concentrated at this freezing rate. On the other hand, with ultrasonic irradiation, the concentration efficiency is very good. In the equal mass concentration condition, the solutes of larger molecular weight are concentrated more effectively than solutes of smaller molecular weight. On the contrary, the solutes of smaller molecular weight are concentrated more effectively than solutes of larger molecular weight and the capture ability corresponds well to the magnitude of the diffusion coefficient of each solute in the equal ionic or molecular concentration condition. We should use these equal molar concentration solutions in comparing the freeze concentration characteristics of each solute.

The difference between the concentration efficiencies of each solute in the three-component solution is smaller than that between the concentration efficiencies in the one-component solution, but the order of the values of the efficiencies is the same.

Key words: Freeze concentration, Ultrasonic irradiation, Solute, Molecular weight, Diffusion coefficient

1. INTRODUCTION

In freezing aqueous solution slowly, pure ice is produced and most of the solutes are removed from the frozen solid phase (ice) and concentrated in an unfrozen liquid phase. This freeze concentration process can be used in the food industry [1] and for wastewater treatment [2−5].

There are two treatment methods; 1) suspension crystallization method [6, 7] where minute ice crystals are produced and their volumes are increased to be separated from mother liquor. 2) layer crystallization method [8, 9] where ice layer is formed and growing on the freezing plate, and solutes are concentrated into the unfrozen liquid phase. We choose 2) layer crystallization method because of the simplicity and the easiness of separation of the solid phase from the liquid phase. Liu *et al.* [1] showed that this method was very effective for tomato juice which contains various components. There is little, however, the report on the concentration efficiency of an individual solute in a multi-component solution.

At fast freezing rate which is needed for the practical treatment process, most of the solutes are captured into the freezing interface and the remained solution is not concentrated so much. In order to prevent this capture of the solutes into the freezing part, the strong agitation of the freezing interface is very effective [9−11]. We adopted an ultrasonic irradiation method as a simple and effective agitation means, and found that concentration efficiency of the solutes was considerably

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improved by this ultrasonic irradiation [12].

In this paper, the performance of freeze concentration was examined under various concentrations of three solutes (sodium chloride (NaCl), L-phenyl alanine (Phe), and saccharose (Sac)), using three one-component solutions containing only one solute and a three-component solution containing three solutes together.

2. Experimental

2.1 MATERIALS

We used three kinds of chemicals; NaCl, Phe and Sac as mentioned above. All chemicals (Hayashi and Wako Pure Chemicals) are of guaranteed reagent grade. The 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.

As the experiments of solutes' concentration, we used two standards: 1) Equal mass concentration condition; most of papers on freeze concentration used mass concentration, therefore, we used the solutions of 0.5 and 5.0 kg/m^3 in the first section (**3.1**). 2) Equal molar concentration condition; For NaCl solution, NaCl dissolves in water and is perfectly dissociated electrolytically to Na^+ and Cl^-. Therefore the ionic molar concentration of NaCl in aqueous solution is twice as much as the molar concentration of molecular NaCl. (The average molecular weight of these ions is about 29 (≈ (23+35.5)/2).) Consequently the mass concentration of 5.0 kg/m^3 corresponds to 0.171 mol/L (ionic concentration) for NaCl, 0.030 mol/L for Phe and 0.015 mol/L for Sac, which is very different for each solute. The order of molar concentration, that is the number of "the solute particle" (molecule or ion) dissolved in the unit volume of the aqueous solution, is NaCl > Phe > Sac. Therefore we examine the performance of freeze concentration for three solutions with the equal ionic or molecular concentration (0.03 mol/L) in the second section (**3.2**).

2.2 METHODS

Fig. 1 shows an experimental apparatus of freeze concentration with ultrasonic irradiation at a constant freezing rate. The sample solutions (0 ^{o}C) were aerated in order to increase dissolved air concentration (*i.e.* dissolved oxygen concentration > 0.008 kg/m^3 (8 mg/L)), where the cavitation due to ultrasonic irradiation 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, 3 mm thickness and 320 mm height). The columns fell into a refrigerant (ethylene glycol solution, -16.5 ^{o}C) at a constant rate (40 mm/h) with ultrasonic irradiation. The intensity of irradiation was kept constant (30 W) throughout these experiments.

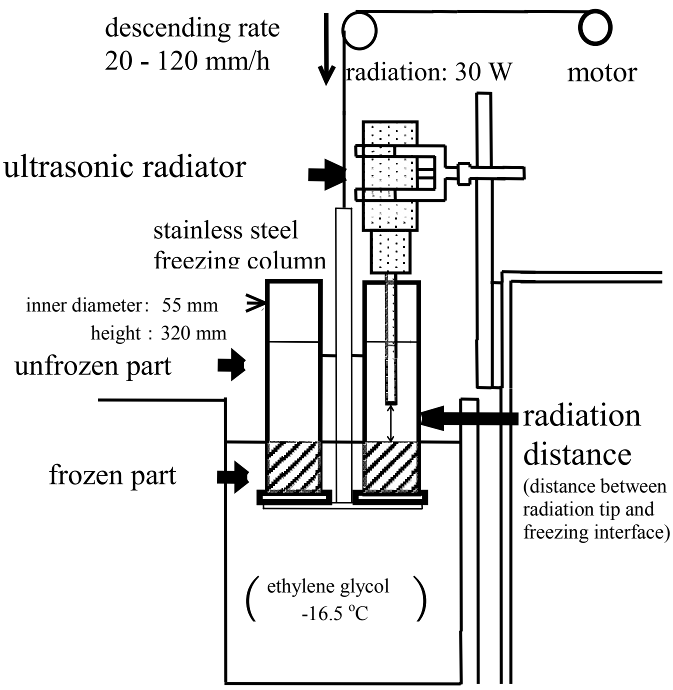

Fig. 1 Experimental apparatus of freeze concentration with ultrasonic irradiation at a constant freezing rate

The freezing columns were made of stainless steel, and the immersed solution part might be frozen rapidly. Therefore, the ice layer in the column would be considered to grow from the bottom, at the column descending rate (40 mm/h).

After 4.5 h freezing, these freezing columns were pulled out from the refrigerant (-16.5 °C) and the unfrozen liquid was poured out from the columns immediately. The frozen interface was washed with 0 °C distilled water to remove the unfrozen liquid. The volume and the solute concentration of the unfrozen part were measured. The frozen portion was taken out from the freezing column and melted to some parts from the bottom by an electric heating plate. The volumes and the solute concentrations of the all melted parts were measured. Thus, we could calculate the vertical solute concentration distribution in frozen portion and investigate the concentration process due to freezing. For reference, the experiments without ultrasonic irradiation were made simultaneously.

3. Results and Discussion

3.1 Equal mass concentration condition

In this section, we used mass concentration as mentioned in **2.1**.

3.1.1 Concentrations of solute during freezing progress

The concentrations of solute in the height of the frozen/unfrozen part are shown in **Fig. 2** (without ultrasonic irradiation), and **Fig. 3** (with ultrasonic irradiation). The Y-ordinate of these figures shows the distance from the horn tip of the ultrasonic radiator. The X-ordinate is the standardized concentration (C/C_0) of the frozen and the unfrozen parts, which is the concentration of each sample divided by the initial concentration. The concentration of the unfrozen part is the average mixed concentration which is calculated from the mass balance of solute when the freezing interface reaches the height of the Y-ordinate.

Without ultrasonic irradiation (Fig. 2), the standardized concentration of all the frozen and unfrozen parts are about 1.0, and the solutes are hardly concentrated and separated regardless of the kind of solutes. With ultrasonic irradiation (Fig. 3), the concentration ratios of the frozen parts decrease with the progress of freezing for all solutes. At the last stage of the freezing process, however, the concentration ratio of the frozen part changes little or increases slightly, while the ratio of the unfrozen part increases rapidly, because the solutes are moved into the unfrozen part [12 – 14]. Consequently the captured solute concentration of the frozen part may change with the concentration of the unfrozen part. As a result we evaluate the capture ability by "the distribution

solute		initial concentration Co [kg/m] 0.5	initial concentration Co [kg/m] 5.0
sodium chloride	frozen	○	☆
(NaCl)	unfrozen	●	★
L-phenyl	frozen	□	◇
alanine (Phe)	unfrozen	■	◆
saccharose	frozen	△	▽
(Sac)	unfrozen	▲	▼

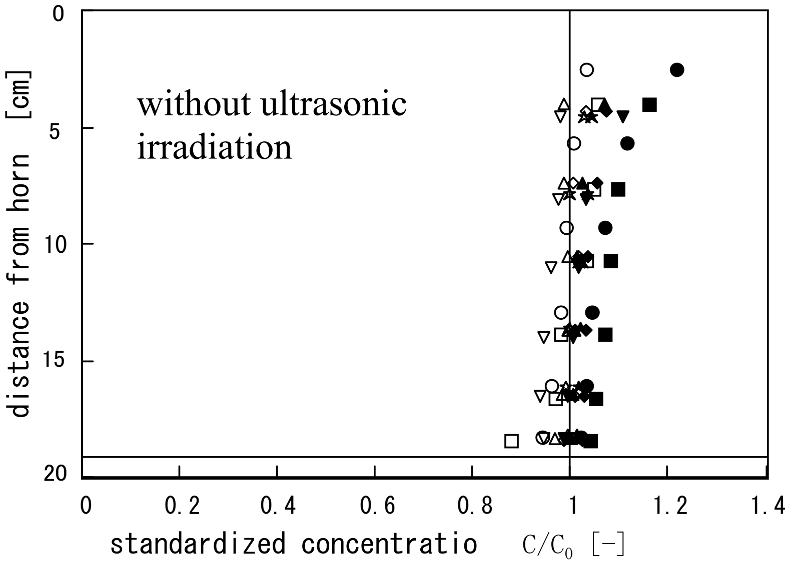

Fig. 2 Solute concentration varying with height, without ultrasonic irradiation

coefficient," as the ratio at which the solute in unfrozen part is captured by the freezing interface during freezing. This ratio is calculated by the following equation (1).

(distribution coefficient) = (concentration of a frozen part) / (average concentration of the corresponding unfrozen part) (1)

3.1.2 Distribution coefficients during freezing progress

Fig. 4 shows the calculation results of the distribution coefficient in the height of the frozen part. Without ultrasonic irradiation, the distribution coefficients are about 0.9 - 1.0 regardless of the kind or initial concentration of solute, and the solute can be hardly concentrated as shown in Fig. 2. This reason is considered to be that 40 mm/h freezing rate is too high to produce pure ice. Namely, needle-like ice crystals grow at the stagnant freezing interface and capture solutes easily.

With ultrasonic irradiation, the distribution coefficients for NaCl (5.0 kg/m^3) are largest, but the average value is about 0.4 (lower than 1.0) and the freeze concentration is effective. As the freezing interface approaches the horn tip in the progress of freezing, the distribution coefficient decreases rapidly. It is considered to be that the effect of cavitation by ultrasonic irradiation [12, 15] increases as the freezing interface approaches the horn tip and the agitating intensity per unit unfrozen volume increases as the unfrozen part volume

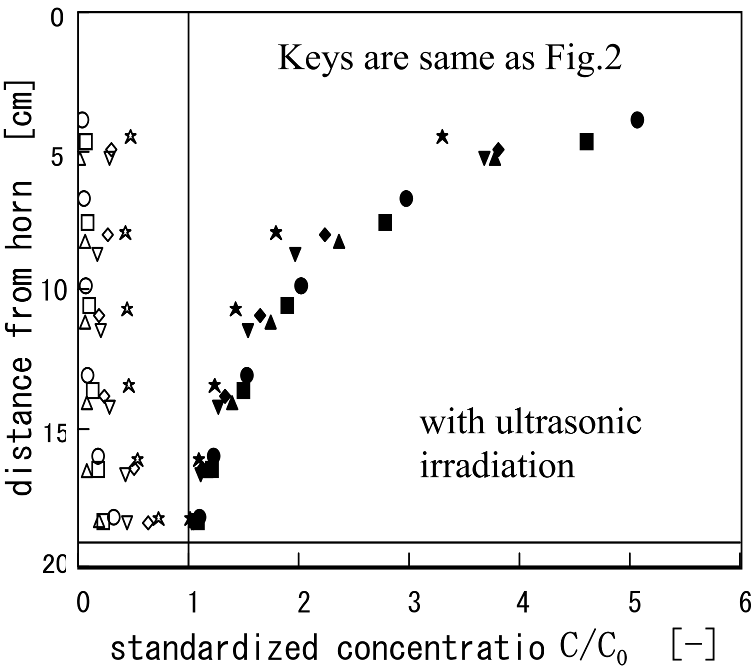

Fig. 3 Solute concentration varying with height, with ultrasonic irradiation

solute	ultrasonic irradiation	initial concentration Co [kg/m] 0.5	5.0
sodium chloride	without	☆	★
(NaCl)	with	○	●
L-phenyl	without	◇	◆
alanine (Phe)	with	□	■
saccharose	without	▽	▼
(Sac)	with	△	▲

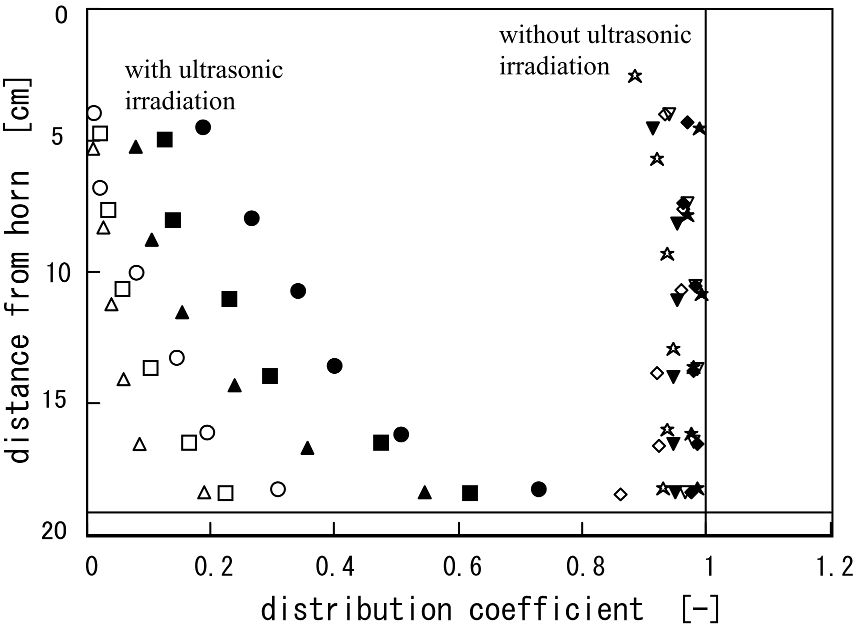

Fig. 4 Distribution coefficient varying with height with/ without ultrasonic irradiation (Equal mass concentration)

decreases. Consequently, the needle-like ice crystals formed without ultrasonic irradiation vanish, the freezing interface becomes smooth, and solutes are not easily captured in the frozen part. Moreover, the solutes concentrated near the interface are dispersed throughout the liquid by cavitation and agitation, and the interface concentration can be kept comparatively low during the freezing process.

For a fixed solute, the order of the distribution coefficient is 0.5 kg/m^3 > 5.0 kg/m^3. Consequently the lower mass concentration is clarified to improve the freeze concentration characteristics.

For a fixed mass concentration, the distribution coefficient of solutes has the following order; NaCl > Phe > Sac. The molecular weights of the solutes are shown in **Table 1**; NaCl < Phe < Sac. As a result, the solutes of larger molecular weights are more difficult to be captured by the frozen part, and more easily separated and concentrated than solute of smaller molecular weights under the same initial solute mass concentration, within these experimental conditions. The above results agree with the conclusion of Halde [10].

Table 1 Molecular weight and initial mass and molar concentration of solute

Solute	Molecular weight [-]	Initial mass concentration [kg/m^3]	Initial molar concentration [mol/L] One component solution	Three components solution
Sodium chloride (NaCl)	58.44	0.5, 5.0	0.015	0.005
L-phenyl alanine (Phe)	165.19	0.5, 5.0	0.030	0.010
saccharose (Sac)	342.30	0.5, 5.0	0.030	0.010

3.2 Equal molar concentration condition

The solutes must hit the freezing interface more frequently when the solution contains more solute particles (molecule or ion). Therefore, the solutes in high molar concentration solution may be easily captured into the freezing interface and we should compare the freeze concentration characteristics of various solutes under the equal molar concentration.

We used two kinds of solutions (described below), and the difference of concentration efficiency of each solute is investigated in the equal ionic or molecular concentration (0.03 mol/L condition).

1) **"one-component solution"** : This contains only one kind of solute (NaCl, Phe or Sac). The molar concentration of the solute particle (ion or molecule) in liquid is equal (0.03 mol/L).

2) **"three-component solution"** : This contains three solutes (the concentration of each solute particle is 0.01 mol/L). These solutes are dissolved together in water, and total molar concentration of the solute particle is 0.03 mol/L. These concentrations of solutes are summarized in Table 1.

3.2.1 One-component solution

The experimental results with ultrasonic irradiation (open symbols) are shown in **Fig. 5** as the change in the distribution coefficient. For one-component solution, the distribution coefficients of solutes with ultrasonic irradiation have the following order; NaCl < Phe < Sac. The smaller the molecular weight of solute is, the more effectively the solute is separated and concentrated by freezing.

The capture ability of the solute by the freezing interface may depend on the mobility of the solute, and this mobility may be related to the diffusion coefficient of the solute in water. **Table 2** shows the values of the diffusion coefficients which are estimated for the infinite diluted solution at 0 ^{o}C. The value of NaCl is calculated with Nernst-Haskell Equation [16], and those of Phe and Sac with Wilke-Chang equation [17]. The diffusion coefficient of the solutes has the following order; NaCl

> Phe > Sac and this means that the solutes with smaller molecular weights can move faster in liquid. This corresponds well to the result that the solute of smaller molecular weight can be concentrated more effectively, as mentioned above.

3.2.2 Three-component solution

Most practical solutions applied to freeze concentration, like as wastewater and fruit juice *etc*, usually include multiple solutes. Therefore we should consider how to deal the multi-component solution. Consequently, we investigated the difference of the freeze concentration efficiency between the solutes in three-component solution.

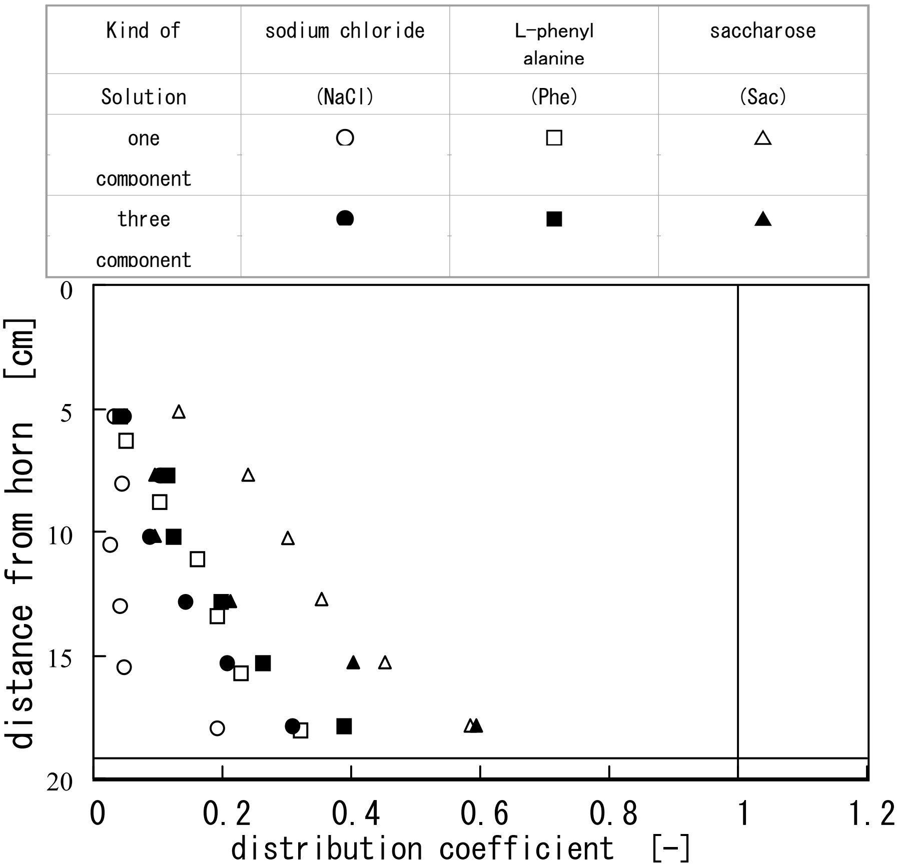

Fig. 5 Distribution coefficient varying with height with ultrasonic irradiation (Equal molar concentration)

The experimental results of the three-component solution with ultrasonic irradiation (solid symbols), are shown in Fig. 5, too. The distribution coefficient of solutes has the following order; NaCl < Phe < Sac, like as one-component solution. Therefore the order of concentration efficiency of individual solute are NaCl > Phe > Sac.

The distribution coefficients of Sac (large molecular weight) in the three-component solution are smaller than those in the one-component solution, those of Phe are almost equal in both the solutions, and those of NaCl (small molecular weight) in the three-component solution is larger than that in the one-component solution. Therefore the difference of the distribution coefficients between each solute in the three-component solution is narrower than that in the one-component solution.

Table 2 Diffusion coefficient of solute estimated for infinite diluted solution (0 °C)

Solute	Molecular weight [-]	Diffusion coefficient [m^2/s]
Sodium chloride (NaCl)	58.44	6.73×10^{-10}
L-phenyl alanine (Phe)	165.19	3.57×10^{-10}
saccharose (Sac)	342.30	2.51×10^{-10}

Table 3 Change of diffusion coefficient of KCl in Sac-KCl-water solution containing saccharose (Sac) whose concentration changes (25 °C) (Henrion [18])

Concentration Sac [mol/L]	Concentration KCl [mol/L]	Diffusion coefficient of KCl [m^2/s]
0	1.00	18.92×10^{-10}
1.248	1.00	5.70×10^{-10}
1.748	1.00	2.94×10^{-10}
2.249	1.00	1.75×10^{-10}

The values of diffusion coefficient in a multiple solute system (in the three-component solution) may be different from those in a one solute system (in the one-component solution). There are few measured values of diffusion coefficient in a multiple solutes system. **Table 3** shows the change of the diffusion coefficients of KCl in the Sac-KCl-water solution [18]. The diffusion coefficient of KCl decreases with increasing Sac concentration. This decrease of the diffusion coefficient would be considered to be one of the reasons why the solute concentration efficiency in the three-component solution is less than that in the one-component solution.

On freezing the solution, needle-like ice crystals grow at the stagnant freezing interface toward the unfrozen part, and hold a part of the solution in the space between these ice crystals. The growth of these ice crystals is less in the case of freezing with irradiation than that without irradiation. During the freezing of the three-component solution, each solute concentration in the solution held in the space between the ice crystals will be roughly equal to that of the unfrozen solution and all solutes will be held together within the freezing part. Thus, the difference in concentration efficiency between each solute in the three-component solution is considered to be narrower than that in the one-component solution.

The recovery ratio of the solute is defined as the ratio of the mass of the solute remained in the unfrozen part after 4.5 h freezing to the mass of the initial dissolved solute. This ratio can be calculated by the volume and the concentration of the unfrozen part, and shown in **Table 4**. The recovery ratios without ultrasonic irradiation are about 0.2 regardless of the kind of solute and this means that the solutes are hardly concentrated. On the other hand, the recovery ratios with ultrasonic irradiation are more than 0.65 and therefore the solutes can be concentrated effectively. The ratios have the following order: NaCl > Phe > Sac. This result is well justified by the distribution coefficients, as shown above.

Table 4 Recovery ratio of solute in unfrozen part after 4.5 h freezing

	Recovery ratio [-]					
ultrasonic	One component solution			Three component solution		
irradiation	NaCl	Phe	Sac	NaCl	Phe	Sac
without	0.226	0.213	0.231	0.233	0.223	0.231
with	0.929	0.827	0.663	0.846	0.813	0.783

4. CONCLUSIONS

Using three one-component solutions containing only one solute (sodium chloride, L-phenyl alanine and saccharose) where mass concentrations and ionic or molecular concentrations of solutes in each solution were equal (0.5 & 5.0 kg/m^3, and 0.03 mol/L) and a three-component solution where ionic or molecular concentrations of solutes were equal (0.01 mol/L), the performance of freeze concentration of three kinds of solutes was examined at constant freezing rate (40 mm/h) with ultrasonic irradiation (30 W). The following results were obtained.

(1) For equal mass concentration solutions, the solutes of larger molecular weight were more easily separated and concentrated than those of smaller molecular weight.

(2) For equal ionic or molecular concentration solutions, the solutes of smaller molecular weight were separated and concentrated more effectively than solutes of larger molecular weight. This corresponded well to the magnitude of the diffusion coefficient of each solute. In order to compare the order of freeze concentration characteristics of each solute, we should use this condition.

(3) The difference between the concentration efficiencies of each solute in the three-component solution was narrower than that between the efficiencies of each solute in the one-component solution, but the order of the values of the efficiencies for three solutes was the same.

5. ACKNOWLEDGEMENTS

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