에멀젼형 액막계에서 중성물질의 추출 거동

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Extraction behavior of a neutral species in an emulsion liquid membrane system

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1. Introduction

Lately, special attention has been paid to recovery of biochemicals using ELM processes [1] because of a high extraction efficiency achieved using a large interfacial area, and a high concentration extent resulting from a high phase ratio between the feed and the receiving phases. Actually, all of the biochemicals extracted by the ELM processes were ionic products. However, saccharide, a neutral species, has not been extracted by the ELMs yet. In this work, therefore, we have tried to extract fructose by ELMs, which is the first attempt to develop the ELM system for extraction of a neutral species. Fructose is a hydrophilic diol-containing compound. A mixture of an organic boronic acid and a quaternary ammonium salt is well known to be one of the carriers suitable to transport the diol-containing compound. Here, we will describe in full detail our efforts to facilitate the transport of fructose in the ELM system with the carrier, changing various experimental conditions, and also will elucidate the transport mechanism of fructose in the system.

2. Experimental

A water-in-oil (w/o) type emulsion was made by slowly adding the internal phase to the organic membrane phase with intensive mixing provided by a homogenizer (high speed generator, T25, IKA Lab.). For each ELM experiment, 70cm^3 of the w/o emulsion was dispersed in 420cm^3 of the feed solution, where the concentration of fructose was 2 mmol/dm^3. The two phases were mixed by a turbine impeller of 4.5cm diameter in a batch-type glass cell of 10 cm inner diameter with four vertical baffles, which was setup in a water bath maintained at 25°C. All of the extraction runs were conducted at the stirrer speed of 330 rev/min. Samples were taken from the stirred cell periodically during the course of a run. The external phase of the samples was separated from the emulsion phase by filtration using a filter paper and was purified by a centrifugal separator (Hettich, Universal 32). The concentration of fructose in the external phase was analyzed using an HPLC apparatus equipped with a 7.8×300mm Cabosep Coregel-87H3 column (Transgenomic). The degassed and filtered eluent with a 0.45μm membrane filter (Supor(PES), Waters), containing 0.02 mol/dm^3 H_2SO_4, passed through the column at the flow rate of 0.8ml/min using a Waters 515 pump. Detection was achieved with a Waters 410 refractometer. The typical retention time of fructose was about 8 min. Unless otherwise stated, the initial concentrations of organoboronic acid and Aliquat 336 in the membrane phase was 20 and 50mmol/dm^3, respectively. In addition, the concentration of surfactant in the membrane phase was 3vol%, and w/o ratio (i.e. volume ratio of the internal phase to the membrane phase) was 1. The emulsification speed and time were 12,000 rev/min and 10 min, respectively. The external aqueous solution was 0.05 mol/dm^3 of sodium carbonate buffer solution (CarB, pH 10.3), and the internal aqueous solution was 0.0375 mol/dm^3 of ferrous sulfate solution.

3. Results and discussion

3.1. Transport mechanism of fructose

A tetrahedral transport mechanism has been used to analyze the same two-carrier LM system as our ELM system. In the tetrahedral transport mechanism shown in Fig. 1, a saccharide is transported as an anionic tetrahedral boronate salt, ion-paired with a lipophilic quaternary ammonium. Several workers [2] described the transport of saccharides by using the tetrahedral transport mechanism in which saccharides transport from an alkaline aqueous feed phase to a slightly acidic aqueous receiving phase. According to the mechanism, saccharide transport can be driven uphill via the application of a pH gradient across the membrane because every saccharide molecule is co-transported with a hydroxyl ion. Simultaneously, high concentration of anions in the receiving phase increases a driving force for stripping of saccharide at the interface between the membrane and the receiving phases.

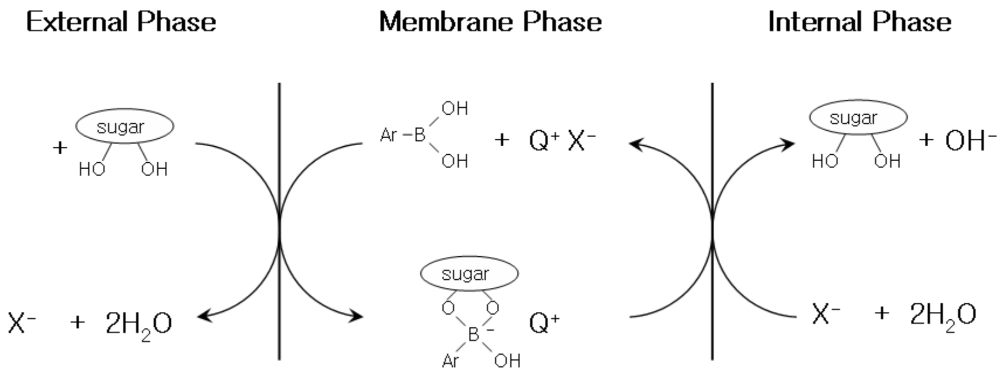

Fig.1 Tetrahedral transport mechanism of fructose in an ELM system ($ArB(OH)_2$: arylboronic acid, X^-: anion, Q^+Cl^-: quaternary ammonium salt).

3.2. Effect of various experimental conditions on extraction of fructose

3.2.1. Effect of type of organoboronic acid

Fig. 2 shows how organoboronic acids affect the transport of fructose in the present ELM system. Actually, PBA is the most widely used organoboronic acid for the investigation of the transport characteristics of saccharides through liquid membranes. Here we used PBA and three phenylboronic acid derivatives, BPBA, DCPBA and BTMPBA as organoboronic acids for the purpose. According to Westmark et al. [3], the transport rate of glucose through liposomes depends on both the lipophilicity of the boronic acid (as judged by hydrophobicity constant, in Table 1), as well as the acidity (as judged by pK_a in Table 1). They found that more lipophilic and acidic carriers were generally more effective for glucose transport. Referring to the pKa and values of four organoboronic acids in Table 1, we could conclude that the transport of fructose in our ELM system follows the similar extraction behavior as that of glucose does. In the ELM system, we used two different types of carriers, that is, an organoboronic acid (called the first carrier) and a quaternary ammonium salt (called the second carrier) together. One of the most effective boronic acids, BTMPBA, was used as the first carrier in the following ELM experiments.

Table 1. Values of pK_a and substituent hydrophobicity constants for various phenyl boronic acid derivatives [1]

Boronic acid	**pK_a**	**Sum of the π value***
3,5-bis(trifluoromethyl)phenylboronic acid (**BTMPBA**)	7.2	1.76
3,5-dichlorophenylboronic acid (**DCPBA**)	7.4	1.42
Phenylboronic acid (**PBA**)	8.9	0.0
4-tert-butylphenylboronic acid (**BPBA**)	9.3	1.98

*** Sum of hydrophobicity constants for aryl substituents excluding the boronic acid**

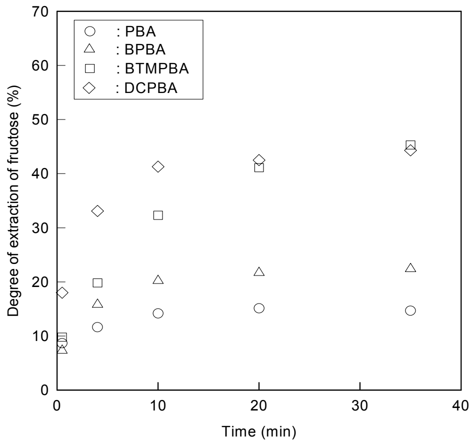

Fig. 2. Effect of organoboronic acid in the membrane phase on the extraction of fructose.

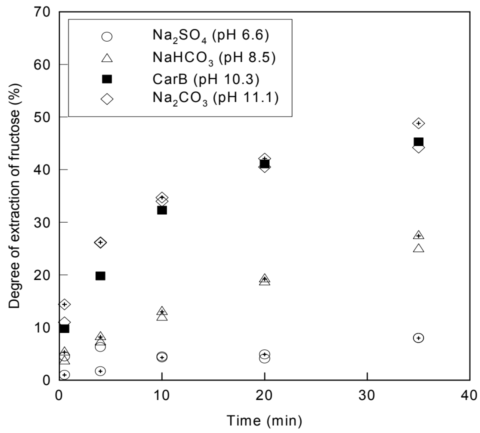

Fig. 3. Effect of inorganic salt in the external phase on the extraction of fructose

3.2.2. Effect of inorganic salt in the external aqueous phase

Fig.3 shows the effect of type of inorganic salt in the external aqueous phase on the extraction of fructose. CarB on the figure is the carbonate buffer solution with salt concentration of 0.05 mol/dm^3 and ionic strength of 0.12. Also, the hollow and the crosshair symbols are data obtained under the same salt concentration and under the same ionic strength as the CarB has, respectively. Actually, pH of each aqueous solution with 0.05 mol/dm^3 of salt concentration was given in parenthesis in Fig.3 and was almost constant independent of its salt concentration. The degree of extraction mostly increased with the increase in pH of the external phase, which can be explained well by the transport mechanism of fructose referred in Section 3.1.

3.2.3. Effect of inorganic salt in the internal phase

Generally, the ionic strength of the internal phase in ELM systems is one of the most dominant factors to increase emulsion swelling. Thus we investigated the effect of pH of the internal phase on the extraction of fructose under the same ionic strength of the phase. Three different salts containing sulfate ion were used to obtain the internal phase. A lower pH of the internal phase gave a higher degree of extraction as shown in Fig. 4, but the pH of the internal phase had a little effect on the degree of extraction. In the similar way, the effect of four different salts containing sodium ion on the extraction was investigated, as shown in Fig. 5. Despite that all of their pHs are between 6 and 7, their degrees of extraction was not much lower than that obtained with ferrous sulfate solution of pH 3.6 in Fig. 4, except sodium perchlorate. In conclusion, the pH of the internal phase did not affect the degree of extraction of fructose as much as the pH of the external phase did.

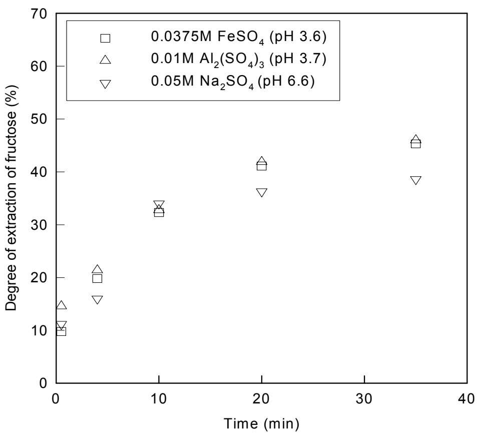

Fig. 4. Effect of sulfate salt in the internal phase on the extraction of fructose.

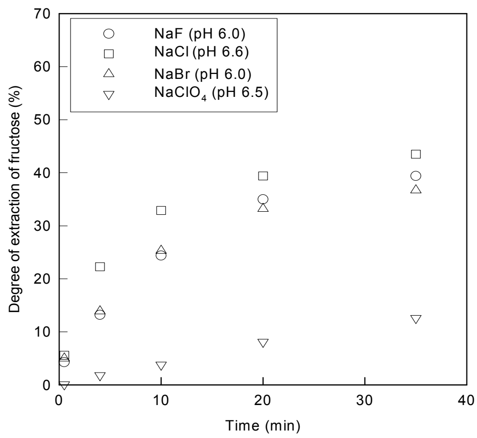

Fig. 5. Effect of sodium salt in the internal phase on the extraction of fructose (Salt concentration: 0.15 mol/dm3).

4. Conclusions

A monosaccharide, fructose was extracted by the ELM using a mixture of an organoboronic acid and a quaternary ammonium salt as a carrier. When a mixture of BTMPBA and Aliquat 336 was used as the carrier, the best degree of extraction of fructose was obtained. Also, the effects of various experimental conditions on the extraction of fructose were investigated, and its degree of extraction was dependent on pH of the external phase most sensitively. The transport of fructose by the ELM could be explained by the tetrahedral boronate pathway, which described the experimental results well. Even though the present ELM system was adequate to extract the neutral species, an internal reagent to strip fructose more strongly was needed for development of a practical ELM system.

REFERENCES

[1] Yordanov, B. and Boyadzhiev, L., "Pertraction of citric acid by means of emulsion liquid membranes", *J. Membr. Sci.*, **238(1-2)**, 191 (2004).

[2] Sinbo, T., Nishimura, K., Yamaguchi, T. and Sugiura, M., "Uphill transport of monosaccharides across an organic liquid membrane", *J. Chem. Soc., Chem. Commun.*, **349**, (1986).

[3] Westmark, P.R., Gardiner, S.J. and Smith, B.D., "Selective monosaccharide transport through lipid bilayers using boronic acid carriers", *J. Am. Chem. Soc.*, **118**, 11093, (1996).