Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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Online publication date: 29 January 1999

To cite this Article Kitamura, Yoshiro , Matsuyama, Hideto , Nakabuchi, Akihiro , Matsui, Nobuhiro , Doi, Yuji and Matsuba, Yorishige(1999) 'Separation of Ethyl Ester of Docosahexaenoic Acid by Facilitated Transport Membrane with High Stability', Separation Science and Technology, 34: 2, 277 — 288
To link to this Article: DOI: 10.1081/SS-100100650
URL: http://dx.doi.org/10.1081/SS-100100650

SEPARATION SCIENCE AND TECHNOLOGY, **34**(2), pp. 277–288, 1999

Separation of Ethyl Ester of Docosahexaenoic Acid by Facilitated Transport Membrane with High Stability

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ABSTRACT

The selective transport of the ethyl ester of docosahexaenoic acid (DHA-Et) was studied in the facilitated transport system where feed phase, membrane phase, and receiving phase had the same ethanol diluent. The carrier of DHA-Et was Ag^+, and a Nafion membrane was used as the support so that Ag^+ was immobilized in the support by electrostatic force. DHA-Et was sufficiently transported in this system due to the swelling of Nafion by ethanol, while the methyl ester of linoleic acid was hardly transported in a Nafion membrane containing aqueous Ag^+ solution (membrane solution). DHA-Et, which has six carbon—carbon double bonds, was transported fairly faster than the ethyl ester of oleic acid which has one double bond with a selectivity of about 10. This indicated that our membrane is useful for separating esters of polyunsaturated fatty acids based on the difference in the double-bond numbers. The effects of the water content in the ethanol solution used as diluent and the feed phase DHA-Et concentration on membrane performances were investigated. This type of facilitated transport membrane was stable for more than 200 days. This is because in addition to the immobilization of Ag^+ in the support membrane by the electrostatic force, the membrane phase had the same diluent as the feed and receiving phases so that leakage of the membrane solvent did not occur.

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Key Words. Facilitated transport; Polyunsaturated fatty acid; Silver ion; Docosahexaenoic acid; Oleic acid

INTRODUCTION

Polyunsaturated fatty acids (PUFAs), such as eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA), have favorable physiological activities and therapeutic advantages. These polyunsaturated fatty acids are contained in fish oils, such as bonito oil and sardine oil, together with many other fatty acids with different numbers of double bonds and carbon atoms. Therefore, EPA and/or DHA must be purified to be used as food additives or medical supplies. Several methods of vacuum distillation (1), liquid chromatography (2), supercritical fluid extraction (3), and so on were tested in an attempt to separate the desired components from fish oils.

Recently, separations of the ethyl esters of PUFAs were reported by the extraction methods with Ag^+ as the extractant (4–6). In this method the ethyl esters of PUFAs (PUFA-Ets) can be effectively extracted into the aqueous phase because Ag^+ reacts with the carbon—carbon double bonds of PUFAs to form hydrophilic complexes. Teramoto et al. indicated that the extracted complex was deduced to be $(\text{PUFA-Et}\cdot n\text{Ag})^{n+}$, where n is the number of the double bonds of PUFA-Et (6). Furthermore, the distribution ratio was found to increase drastically with a decrease in temperature and also to be highly dependent on the organic solvents used as the diluent of PUFA-Et. This extraction method is effective for the separation of PUFA-Ets with a high degree of unsaturation, such as EPA-Et and DHA-Et, from other PUFA-Ets in addition to the advantages that the solvent extraction method can be operated under mild condition and is suitable for mass production. However, this method requires a large amount of expensive Ag^+, which is a shortcoming from the economic standpoint.

The liquid membrane method in which Ag^+ is used as a carrier of PUFA is an alternative way to separate EPA-Et and DHA-Et efficiently from fish oils. In this method the amount of Ag^+ used can be reduced because Ag^+ is incorporated only in the membrane phase. Nishi et al. demonstrated the facilitated transport of EPA-Et and DHA-Et through a supported liquid membrane where an aqueous Ag^+ solution was supported in pores of a microporous support membrane (4, 5). Teramoto et al. reported that EPA-Et was successfully transported against its concentration gradient from *n*-dodecane solution to *m*-xylene solution through a similarly supported liquid membrane (7). The principle of this uphill transport is that the distribution ratio of EPA-Et is highly dependent on the kinds of solvents of the organic phase. *n*-Dodecane gives a much higher distribution ratio than *m*-xylene. They said that it was

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the first demonstration of uphill transport by use of the solvent dependence on the distribution ratio. In a series of studies by Teramoto et al., separations of EPA-Et and DHA-Et by a circulating liquid membrane using Ag^+ as carrier was carried out (8). In this liquid membrane system, aqueous Ag^+ solution was circulated between stirred vessel containing an organic solution of bonito oil (feed phase) and another stirred vessel containing a receiving organic solvent (receiving phase). Uphill transport by the use of temperature dependence on the distribution ratio was also demonstrated.

Degradation of membrane performance by leakage of the aqueous carrier solution is a serious problem in supported liquid membranes from the standpoint of the commercial use. For the purpose of preventing such degradation, ion-exchange membranes were used as the supports for liquid membranes, mainly with respect to the separations of gas mixtures (9–13). The ionic carrier, such as Ag^+, was immobilized in these supports by electrostatic force, which provided longer operating lifetime. It was of interest to test the separation of PUFA by this type of facilitated transport membrane. As described below, however, when a Nafion membrane was used as the support ion-exchange membrane and aqueous Ag^+ solution was impregnated in the Nafion membrane, the methyl ester of linoleic acid was hardly transported. This is probably because PUFA is too large to be transported through the channels between the ionic clusters formed in a Nafion membrane (14–16).

In this work the selective transport of DHA-Et was investigated by a facilitated transport membrane using Nafion as the support. In this case, ethanol solvent was used as the membrane-phase solvent as well as for feed- and receiving-phase solvents. That is, the same solvent was used for the feed phase, the membrane phase and the receiving phase. This system is schematically shown in Fig. 1. The facilitated transport system shown in Fig. 1 is regarded as a extension of the normal liquid membrane system because this membrane consists of liquid and contains the carrier (Ag^+) as well as the normal liquid membrane. Although the support membrane used in this work was the ion-exchange membrane, the solute transport in this membrane is the carrier-mediated (facilitated) transport and is different from the transport mode of the ionic solute in the normal ion-exchange membrane. Therefore, our transport system can not be regarded as an extension of the normal ion-exchange membrane system. This type of facilitated transport membrane has the following two advantages: 1) the Nafion membrane is swollen by ethanol solution, which results in higher permeability of PUFA; there is enhancement of the membrane stability. Since the membrane-phase solvent is the same as the feed- and receiving-phase solvents, leakage of the membrane-phase solvent can be essentially prevented. This probably leads to the higher stability of this system.

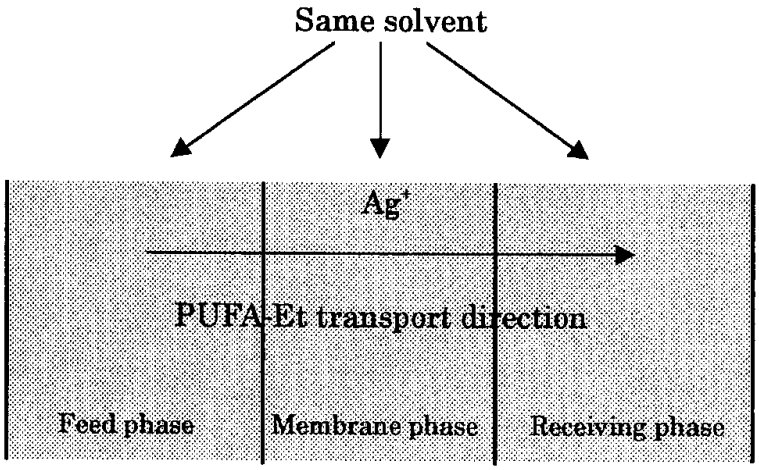

FIG. 1 Schematic setup of this facilitated transport system.

EXPERIMENTAL

Materials

DHA-Et of 95% purity was kindly supplied by Harima Kasei Co., Ltd. The ethyl ester of oleic acid (OLA-Et, purity: 95%) and the methyl ester of linoleic acid (LIA-Mt, purity: 95%) were purchased from Tokyo Kasei Kogyo Co., Ltd. Organic solvents used for the feed phase, the membrane phase, and the receiving phase were ethanol solutions containing different amounts of water. The water contents of the ethanol solution were determined by Karl-Fisher titration (Kyoto Electronics Co., Ltd., MKS-1).

Preparation of Facilitated Transport Membrane

Nafion 117 (1100 g equivalent molecular weight, 170 μm thickness) was purchased in the acid form from Aldrich Chemical Co. The membranes were converted to the Na salt form by soaking them in 1 mol/dm^3 NaOH solution overnight and then rinsing them in deionized water for more than 1 day. The membranes were then dried in vacuo. These Na-form membranes were used as nonreactive membranes to calculate the facilitation factor, which is defined as the ratio of the facilitated transport rate to the physical transport rate.

Ag-form membranes were prepared by soaking Na-form membranes in 1 mol/dm^3 $AgNO_3$ solution overnight, then rinsing them in water for more than 1 day, and drying them in vacuo. These Na- and Ag-form membranes were soaked and swollen in membrane-phase solution (mainly ethanol) before the transport experiments.

Flux Measurement

The permeation cell used for the transport experiment consisted of two chambers of the feed and receiving phases. The volumes of the feed- and receiving-phase solutions were about 70 cm^3. The feed phase contained PUFA-Ets and a standard substance for gas chromatography, while the receiving phase contained only the standard substance. The solvents were the same for the feed phase, the membrane phase, and the receiving phase. After sandwiching the membrane (area: 3.1 cm^2) between two chambers, the feed- and receiving-phase solutions were poured into the chambers, and the transport experiment was started.

The feed phase and the receiving phase were stirred by magnetic stirring bars. It was confirmed that the resistance of the stagnant films in the feed- and receiving-phase sides can be ignored because the permeation rates hardly changed when the stirring speed was decreased. Samples were withdrawn from the receiving phase, and the concentrations of PUFA-Et were measured by a gas chromatograph with a FID (Shimadzu Co., GC-14A). A capillary column (packing: DBWAX-M30-025, J&W Scientific Co.) was mainly used. The ethyl ester of lauric acid (Tokyo Kasei Kogyo Co., Ltd., purity: 99%) and the methyl ester of palmitic acid (Wako Pure Chemical Co., purity: 99.9%) were used as the standard substances in the transport of LIA-Mt and DHA-Et (OLA-Et), respectively. The permeation cell was immersed in water where the temperature was controlled at 30°C.

RESULTS AND DISCUSSION

Transport of PUFA in Normal Facilitated Transport System

The dried Ag-form membrane was soaked in water, and the facilitated transport membrane containing aqueous solution as the membrane phase was prepared. *n*-Hexane was used as solvent for both the feed and receiving phases. In this normal facilitated transport system, aqueous membrane solution existed between two organic solutions. When the transport of LIA-Mt (0.227 mol/dm^3) was measured in this system, no LIA-Mt transport into the receiving phase was detected even after 8 days. This means that the permeation rate of LIA-Mt was extremely small in this system. Certainly the use of an ion-exchange membrane as the support is considered to be useful for preventing degradation of the facilitated transport membrane. However, the normal system consisting of the organic feed phase, the aqueous membrane phase, and the organic receiving phase was found to be unsuitable for the transport of PUFA.

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Ion-exchange groups aggregate in perfluoronated polymers to form ionic clusters which are connected by short, narrow channels (14–16). The sizes of the channels and the clusters are about 10 A and 40 A, respectively. PUFA is a large molecule, so it is hardly transported in these structures, while small molecules, such as gases, are sufficiently transported (9–13).

Transport of PUFA in New Facilitated Transport System

The transport of PUFA was studied in the new system where the feed phase, the membrane phase, and the receiving phase were the same ethanol solution (Fig. 1). As described above, the advantages of this system are that the permeation rate of PUFA is enhanced by the swelling of the membrane and the stability of the membrane increases due to suppression of leakage of the membrane solution.

Figure 2 shows the time course of concentrations of DHA-Et and OLA-Et transported into the receiving phase for Ag- and Na-form membranes when ethanol was used as solvent. Since the feed-phase solution was a mixture of DHA-Et and OLA-Et, the simultaneous transport of two PUFA-Ets was investigated in this experiment. As can be seen in this figure, DHA-Et and OLA-Et were sufficiently transported through the Ag-form membrane in this

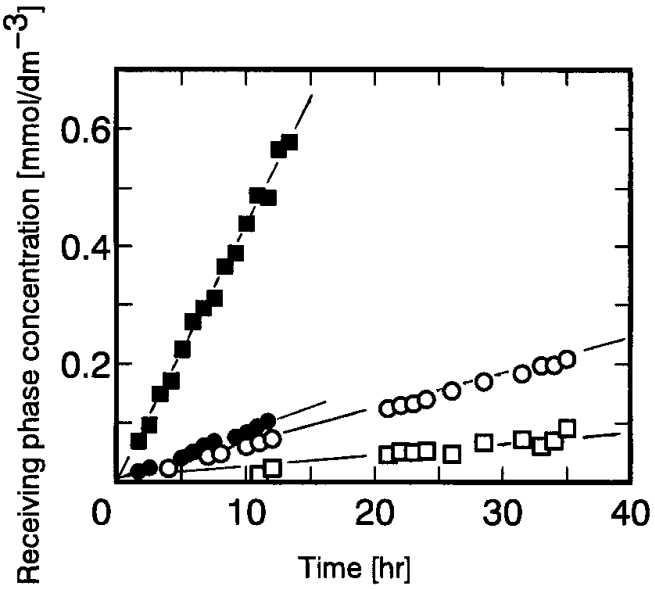

FIG. 2 Time course of concentrations of DHA-Et and OLA-Et transported into the receiving phase for Ag- and Na-form membranes. Solvent: ethanol (0.2 vol% water). Feed DHA-Et concentration = 6.2 mmol/dm^3, feed OLA-Et concentration = 12.5 mmol/dm^3. (■) DHA-Et/Ag-form membrane, (●) OLA-Et/Ag-form membrane, (□) DHA-Et/Na-form membrane, (○) OLA-Et/Na-form membrane.

TABLE 1
Permeances of DHA-Et and OLA-Et, Selectivities of DHA-Et to OLA-Et, and Facilitation Factor[a]

	DHA-Et permeance (m/s)	OLA-Et permeance (m/s)	Selectivity (—)
Ag-form membrane	4.55×10^{-7}	0.46×10^{-7}	9.90
Na-form membrane	0.27×10^{-7}	0.32×10^{-7}	0.84
Facilitation factor	16.5 (DHA-Et)	1.43 (OLA-Et)	

[a] Solvent: ethanol (0.2 vol% water); feed DHA-Et concentration = 6.2 mmol/dm^3; feed OLA-Et concentration = 12.5 mmol/dm^3.

system. Even in the case of the Na-form membrane where only passive transport occurs, transport of DHA-Et and OLA-Et into the receiving phase could be detected. This is due to swelling of the Nafion 117 membrane in ethanol. The solvent content (weight fraction) in Nafion 117 increased from 0.18 for water (17) to 0.36 for ethanol. The amount of Ag^+ leaked into the receiving phase was measured by an atomic absorption spectrophotometer (Hitachi Co., Z9000-S) after 12 hours in the experiment with the Ag-form membrane. The amount of Ag^+ in the receiving phase was only 0.2% of the total amount of Ag^+ in this system. Therefore, almost all the Ag^+ are immobilized in the membrane. The experiments with both Ag- and Na-form membranes were carried out twice. For all permeances, the differences between the two experiments were within 10% of the permeances.

The permeances of DHA-Et and OLA-Et for both the Ag- and Na-form membranes, the selectivity of DHA-Et to OLA-Et (which is defined as the ratio of DHA-Et permeance to OLA-Et permeance) and the facilitation factors are summarized in Table 1. The permeance was defined as the flux divided by the solute concentration in the feed phase. These values were obtained from the data shown in Fig. 2. First of all, in the Na-form membrane, the permeance of DHA-Et was lower than that of OLA-Et. This is probably because DHA-Et with its larger molecule weight has the lower diffusivity. The permeances of both DHA-Et and OLA-Et in the Ag-form membrane were fairly larger than those in the Na-form membrane. This is one indication that facilitated transport based on the interaction between the double bonds in PUFA-Et and Ag^+ occurred. The facilitation factor for DHA-Et was about 10 times higher than that for OLA-Et. This is because DHA-Et has six double bonds in its molecule while OLA-Et has only one. Therefore, selectivity increased in the Ag-form membrane and reached to about 10. This indicates that the facilitated transport membrane used in this work is useful for separating PUFA-Ets based on the difference in the number of double bonds.

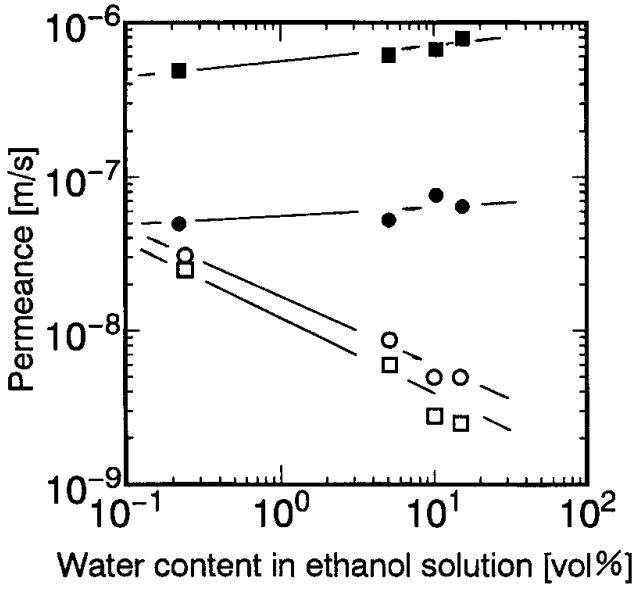

FIG. 3 Effect of water content in ethanol solution on permeances. Feed DHA-Et concentration = 1.14 mmol/dm^3, feed OLA-Et concentration = 2.29 mmol/dm^3. (■) DHA-Et/Ag-form membrane, (●) OLA-Et/Ag-form membrane, (□) DHA-Et/Na-form membrane, (○) OLA-Et/Na-form membrane.

Figure 3 shows the effects of water volume percent in ethanol solution on the permeances of DHA-Et and OLA-Et. The amount of water in ethanol is limited by the solubility of PUFA-Et. 15 vol% of water, which was the highest water content in this work, was close to such a limitation. The permeances of both DHA-Et and OLA-Et in the Ag-form membrane increased with an increase of water content, while those in the Na-form membrane decreased. Table 2 shows the solvent contents in the membranes, facilitation factors of

TABLE 2
Solvent Contents in Membrane, Facilitation Factors, and Selectivities[a]

Water content in ethanol solution (vol%)	Solvent content of Na membrane (vol%)	Solvent content of Ag membrane (vol%)	Facilitation factor of DHA-Et (—)	Selectivity of Ag membrane (—)
0.2	53	60	19.9	9.84
5.1	41	59	103	11.7
10.0	39	57	244	8.87
14.8	37	56	318	12.2

[a] Feed DHA-Et concentration = 1.14 mmol/dm^3; feed OLA-Et concentration = 2.29 mmol/dm^3.

DHA-Et, and selectivities of DHA-Et to OLA-Et when ethanol solutions with various water contents were used. The decrease of the permeances in the Na-form membrane with an increase of water content, as shown in Fig. 3, can be explained by the decrease of solvent contents in the membrane; that is, the decrease of membrane swelling. In the Ag-form membrane the permeances increased despite the decrease of solvent contents. Hartley et al. measured the stability constants of complexes of Ag^+ with unsaturated alcohols in a number of solvents (18). They showed that the stability constants depend on the solvents in the order water $>$ methanol $>$ ethanol, which was ascribed to competition between an olefin and the solvents for coordination of Ag^+. Therefore, with an increase of water content in ethanol solution, the stability constant of the Ag–PUFA complex is expected to increase. This is the reason why the permeances increased with the water contents for the Ag-form membrane. Thus, since the tendency of the permeance change in the Ag-form membrane is opposite that in the Na-form membrane, the facilitation factors increased with the water contents and a maximum value of more than 300 was obtained in ethanol solution involving 15 vol% water.

Figure 4 shows the effect of DHA-Et concentration in the feed phase on DHA-Et fluxes for both the Ag- and Na-form membranes. The fluxes in a Na membrane is a linear function of feed DHA-Et concentration, which is evidence of Fickian diffusion. On the other hand, in the Ag-form membrane,

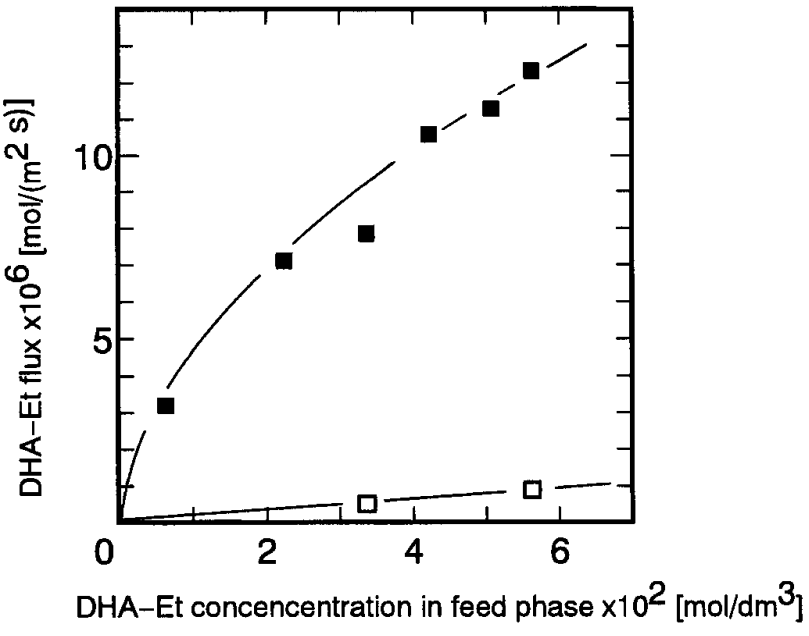

FIG. 4 Effect of DHA-Et concentrations in feed phase on DHA-Et fluxes. Solvent: ethanol (0.2 vol% water). (■) DHA-Et/Ag-form membrane, (□) DHA-Et/Na-form membrane.

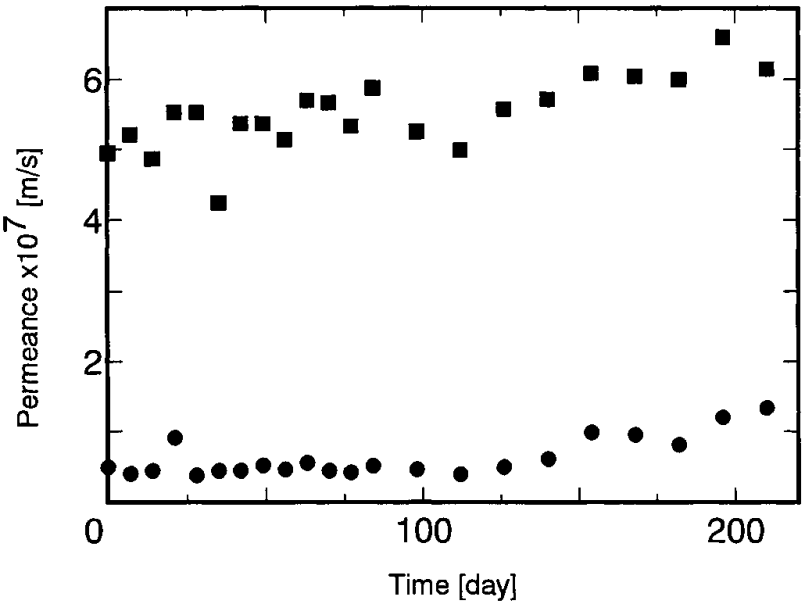

FIG. 5 Stability test of Ag-form facilitated transport membrane. Solvent: ethanol (0.2 vol% water), Feed DHA-Et concentration = 1.14 mmol/dm^3, feed OLA-Et concentration = 2.29 mmol/dm^3. (■) DHA-Et/Ag-form membrane, (●) OLA-Et/Ag-form membrane.

fluxes are a highly nonlinear function of feed DHA-Et concentration. This is because the carrier is saturated at a higher solute concentration, and this is characteristic of the facilitated transport mechanism.

A stability test of this type of facilitated transport membrane was carried out. The result is shown in Fig. 5. The membrane was placed in the permeation cell only when the permeances were measured. In other cases the membrane was soaked in ethanol which was used as the solvent. As can be seen in Fig. 5, the permeances of both DHA-Et and OLA-Et hardly changed up to 150 days. Although slight increases in both permeances were observed after 150 days, high selectivity was maintained for more than 200 days. Nishi et al. carried out the separation of PUFA-Et with the normal type of facilitated transport membrane where an aqueous Ag^+ solution was impregnated in pores of the porous support membrane. They reported the membrane performance decreased after only 10 hours (4, 5). This is probably because aqueous membrane solution leaked to the organic feed and receiving phases. As shown in Fig. 1, in our facilitated transport system the feed phase, the membrane phase, and the receiving phase were the same solvent. This essentially leads to prevention of leakage of the membrane solution to the feed and receiving phases. In addition, the immobilization of Ag^+ in a Nafion membrane by the electrostatic force may be another reason for the high stability.

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CONCLUSION

In a normal facilitated transport system where the membrane phase was an aqueous Ag^+ solution and the feed and receiving phases were organic solutions, the methyl ester of linoleic acid was hardly transported through a Nafion membrane. This is probably because PUFA is too large a molecule to be transported in the channel and cluster parts of Nafion.

The transport of PUFA-Ets was studied in a system where the feed phase, the membrane phase, and the receiving phase were the same ethanol solution. DHA-Et and OLA-Et were sufficiently transported in a Ag-form membrane due to swelling of Nafion by ethanol. DHA-Et, which has six carbon—carbon double bonds, was transported fairly faster than OLA-Et, which has one double bond, with a selectivity of about 10. This shows that the facilitated transport membrane used in this work is useful for separating PUFA-Ets based on the difference in the number of double bonds. With an increase of the water content of the ethanol solutions used as solvents, the permeances of PUFA-Ets increased in the Ag-form membrane due to an increase of the complexation ability between Ag^+ and PUFA-Ets, while they decreased in the Na-form membrane. The facilitation factors increased with the water content and reached more than 300 in an ethanol solution involving 15 vol% water.

This type of facilitated transport membrane was found to be very stable. This is because the membrane phase was the same solvent as the feed and receiving phases, so that leakage of the membrane solution did not occur. This high stability is one of the advantages of this facilitated transport membrane.

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Received by editor January 4, 1998
Revision received April 1998

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