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Separation of Ethyl Esters of Eicosapentaenoic Acid and Docosahexaenoic Acid by Circulating Liquid Membranes Using Silver Nitrate as a Carrier. Uphill Transport by Use of Temperature and Solvent Dependencies of Distribution Ratio

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ABSTRACT

Experiments on the separation of ethyl ester of eicosapentaenoic acid (EPA-Et) and that of docosahexaenoic acid (DHA-Et) contained in ethyl ester of bonito oil (bonito oil-Et) were performed using circulating liquid membranes (CIRLMs) containing silver nitrate as a carrier. In this liquid membrane system an aqueous silver nitrate solution was circulated between a stirred vessel containing an organic solution of bonito oil-Et and another stirred vessel containing a receiving organic solvent. Using the CIRLM, two types of uphill facilitated transport of EPA-Et and DHA-Et in bonito oil-Et were demonstrated. The first type utilizes the distribution ratio of EPA-Et and DHA-Et, defined as the ratio of the concentration in the aqueous phase to that in the organic phase at equilibrium, which is remarkably dependent on the temperature, and the second uphill transport was based on the fact that the distribution ratio is considerably dependent on the solvent of the organic phase. A model of permeation through the circulating liquid membrane was proposed to explain the experimental results.

Key Words. Liquid membrane; Facilitated transport; Uphill transport; Polyunsaturated fatty acid; Silver nitrate

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INTRODUCTION

Fish oils have attracted attention as a source of ω-3 polyunsaturated fatty acids (PUFAs) such as eicosapentaenoic acid (EPA, C20:5ω3) and docosahexaenoic acid (DHA, C22:6ω3) since they have favorable physiological activities and therapeutic advantages (1). These polyunsaturated fatty acids are contained in various fish oils such as bonito oil and sardine oil. However, it is very difficult to separate the desired components from fish oils consisting of various fatty acids with different numbers of double bonds and carbon atoms.

Recently, it was found that ethyl esters of PUFAs (PUFA-Ets) such as EPA and DHA (EPA-Et and DHA-Et) could be selectively extracted into silver nitrate solutions since silver ion can complex with PUFAs (2, 3). In our previous paper (4) it was found that the extraction reaction and the distribution ratio D, which is defined as the ratio of the concentration of PUFA-Et in the aqueous silver nitrate solution to that in the organic phase at equilibrium, are respectively expressed as follows:

$$\text{PUFA-Et} + n\text{Ag}^+ \rightleftarrows (\text{PUFA-Et}\cdot n\text{Ag})^{n+} \tag{1}$$

$$D = \frac{[(\text{PUFA-Et}\cdot n\text{Ag})^{n+}]_{\text{aq}}}{[\text{PUFA-Et}]_{\text{org}}} = \alpha[\text{Ag}^+]^n \tag{2}$$

$$\alpha = m_1 \exp[(m_2/T) + m_3\phi]$$

Here, n is nearly equal to the number of carbon-carbon double bond of PUFA, $(\text{PUFA-Et}\cdot n\text{Ag})^{n+}$ is the complex between PUFA-Et and Ag^+, $[\text{Ag}^+]$ is the free silver ion concentration in the aqueous phase, T is the temperature, ϕ is the volume fraction of bonito oil-Et in the organic phase, and m_is are constants.

We also found two interesting characteristics of the present extraction system (4). The first is that the distribution ratios of EPA-Et and DHA-Et are remarkably dependent on the organic solvent in which PUFA-Ets are dissolved. For example, the distribution ratio of EPA-Et when *n*-dodecane is used as the solvent of EPA-Et is about 18 times that when *m*-xylene is used. The second is that the distribution ratio is highly dependent on the temperature. For example, the value of EPA-Et at 5°C is about 280 times that at 45°C when *n*-dodecane was used as the organic solvent. The values of the constants in Eq. (2) are summarized in Table 1.

In a liquid membrane system where the distribution ratio of a solute between a feed phase and a liquid membrane phase is higher than that between a receiving phase and a liquid membrane phase, uphill transport of the solute is possible. Therefore, by using liquid membranes containing silver nitrate as a carrier, PUFA-Ets such as DHA-Et and EPA-Et can

TABLE 1
Values of m, n, and α in Eq. (2)

PUFA-Et solvent	m_1 (—)	m_2 (K)	m_3 (—)	α[a]	n
EPA-Et *m*-xylene	3.36×10^{-20}	11,132	2.999	—	5
DHA-Et *m*-xylene	3.17×10^{-23}	13,304	2.896	—	6
EPA-Et *n*-dodecane	—	—	—	1.08×10^{-2}	5
DHA-Et *n*-dodecane				2.20×10^{-2}	6

[a] Values at 298 K and when the volume fraction of solvent is nearly equal to unity.

be transported against their concentration gradients from an *n*-dodecane solution to a *m*-xylene solution. Further, they can be pumped from their *m*-xylene solution (feed solution) to *m*-xylene (receiving phase) which is maintained at a higher temperature than the feed phase. The former type of uphill transport was demonstrated in a previous paper (5) which describes the uphill transport of EPA-Et from an *n*-dodecane solution to a *m*-xylene solution through a bulk liquid membrane and a supported liquid membrane. However, for demonstrating uphill transport driven by a transmembrane temperature difference, it appears difficult to use a usual bulk or a supported liquid membrane.

In the present study, circulating liquid membranes were used in which an aqueous silver nitrate solution was circulated between a stirred vessel containing an organic feed solution and one containing an organic receiving solvent. The temperature of each vessel could be controlled independently. Simultaneous selective uphill transport of DHA-Et and EPA-Et from *n*-dodecane solutions of bonito oil-Et to *m*-xylene solutions were also investigated. Furthermore, the transport rates were analyzed by a proposed permeation model.

EXPERIMENTAL

Materials

EPA-Et and the ethyl ester of bonito oil (bonito oil-Et) were kindly supplied by Harima Kasei Co., Ltd. and Nihon Suisan Co., Ltd. The composition of bonito oil-Et is shown in Table 2. Organic solutions of these esters were prepared by dissolving them in *n*-dodecane or *m*-xylene. Silver nitrate solutions were prepared by dissolving silver nitrate in deionized water. The ionic strength of the aqueous solutions was adjusted at 4 mol/dm^3 by the addition of $NaNO_3$ when the silver nitrate concentration was lower than 4 mol/dm^3.

TABLE 2
Composition of Ethyl Ester of Bonito Oil

Component	Content (wt%)	Component	Content (wt%)
C14:0	3.58	C18:3ω3	0.56
C14:1	0.13	C20:1	1.11
C15:0	0.99	C20:4ω6	2.12
C16:0	18.63	C20:4ω3	0.39
C16:1	5.21	C50:5ω3 (EPA)	6.94
C18:0	5.04	C22:5ω3	1.43
C18:1	13.72	C22:6ω3 (DHA)	27.35
C18:2	1.29	Others	11.51

Circulating Liquid Membranes

The circulating liquid membrane system used in this work is schematically shown in Fig. 1. The system consists of a pair of stirred vessels between which a liquid membrane solution, i.e., an aqueous silver nitrate solution, is circulated. As shown in Fig. 2, two types of stirred vessels were used. Figure 2(a) shows a nondispersion-type stirred vessel. The

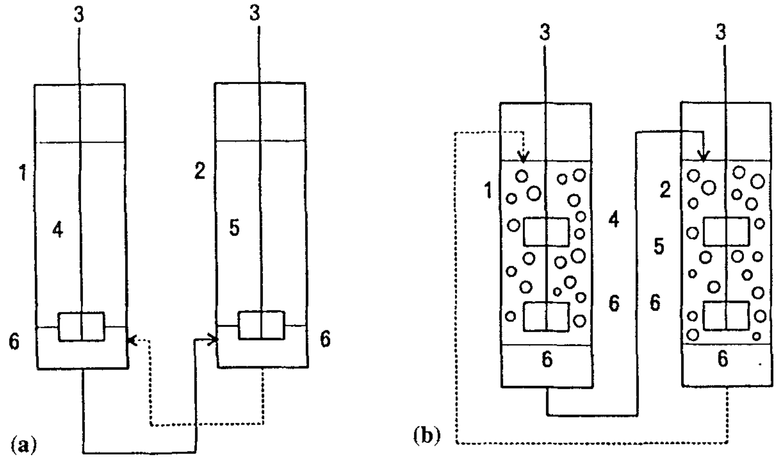

FIG. 1 Two modes of operation of the circulating liquid membrane systems. 1, stirred vessel containing feed solution; 2, stirred vessel containing receiving solvent; 3, stirrer; 4, feed solution; 5, receiving solution; 6, liquid membrane solution. (a) Nondispersion-type circulating liquid membrane (NDCIRLM). (b) Dispersion-type circulating liquid membrane (DCIRLM).

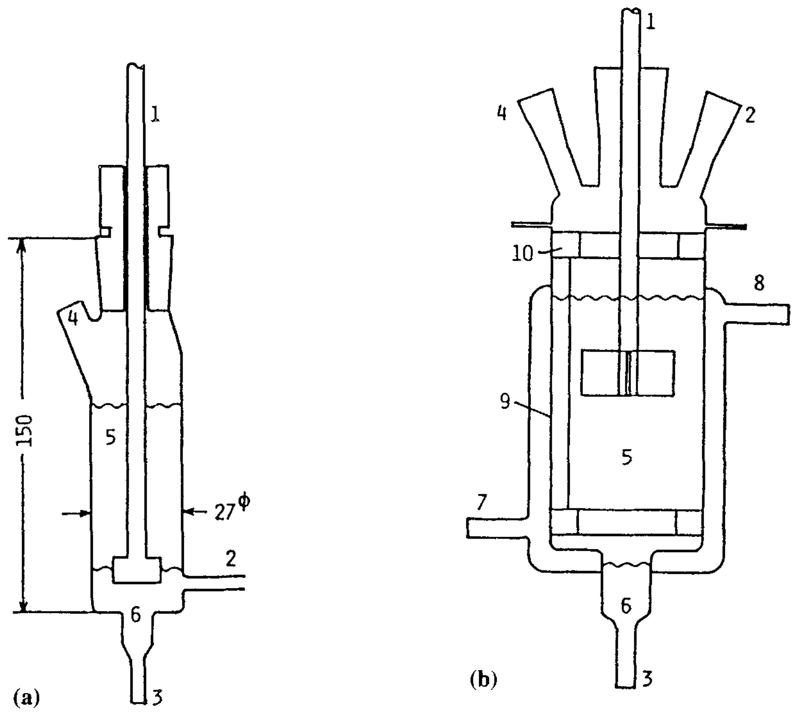

FIG. 2 Stirred vessels used in the circulating liquid membrane systems. 1, stirrer, 2, inlet of liquid membrane solution; 3, outlet of liquid membrane solution; 4, sampling port; 5, feed or receiving solution; 6, liquid membrane solution; 7, 8, inlet and outlet of water, respectively; 9, baffle plate; 10, support ring of baffle plate. (a) Nondispersion-type stirred vessel. (b) Dispersion-type stirred vessel.

vessel, of 2.7 cm inner diameter, was made of glass and equipped with a two-bladed stirrer. As shown in Fig. 1(a), since the liquid membrane solution is not dispersed in the organic solutions but is in contact with them at the free interface, this liquid membrane system is called a nondispersion-type circulating liquid membrane (NDCIRLM) here. Another type of the vessel is shown in Fig. 2(b). This vessel, 5.0 cm in inner diameter, was made of glass and equipped with two four-bladed stirrers and three baffle plates. In this vessel the liquid membrane solution was introduced continuously to the top of the vessel and dispersed in the organic phase as fine droplets so as to obtain a high transport rate due to the large liquid–liquid interfacial area. A liquid membrane system using two such vessels is called a dispersion-type circulating liquid membrane (DCIRLM).

In the circulating liquid membrane system, the permeant species are first transported from the feed to the liquid membrane phase in the feed vessel, then transferred to the liquid membrane phase in the receiving phase vessel by a reciprocating pump, and finally stripped to the receiving organic phase.

The circulating liquid membrane system was operated as follows. After an aqueous silver nitrate solution was charged into the two stirred vessel, an *n*-dodecane solution or a *m*-xylene solution of EPA-Et or bonito oil-Et was charged in the feed vessel F, and *m*-xylene was charged in the receiving vessel S. Then stirring was started, and the silver nitrate solution was circulated between the vessels by a reciprocating pump at the prescribed flow rate. The relative levels of the vessels were adjusted so that the two vessels contained approximately the same volume of the silver nitrate solution. The temperature of each vessel was controlled independently by a temperature controller. Samples were taken from the organic phases in the two vessels periodically and analyzed by a gas chromatograph equipped with an FID (Shimadzu GC-8A; column: ULBON HR-SS-10).

RESULTS

Uphill Transport Utilizing Temperature Dependence of Distribution Ratio

Figure 3 shows the time course of the feed and the receiving phase concentrations obtained with the NDCIRLM. Here, *m*-xylene was used as the solvent of both the feed and the receiving phase, and the feed solution was maintained at 295 K and the receiving solution at 314 K. When the silver nitrate concentration was 4 mol/dm^3, the distribution ratios of DHA-Et at 295 and 314 K were estimated as 8.9 and 0.58, respectively, from Eq. (2) using the parameters listed in Table 1. The corresponding values for EPA-Et were 1.53 and 0.156, respectively. It is clearly seen that DHA-Et and EPA-Et were transported against their concentration gradients. As far as we know, this is the first example of facilitated uphill transport by a liquid membrane which is effectively driven by the transmembrane temperature difference. It was also confirmed that the components other than DHA-Et and EPA-Et in the bonito oil-Et were not transported through the liquid membrane. Since the distribution ratio of DHA is higher than that of EPA-Et, DHA-Et was preferentially transported over EPA-Et.

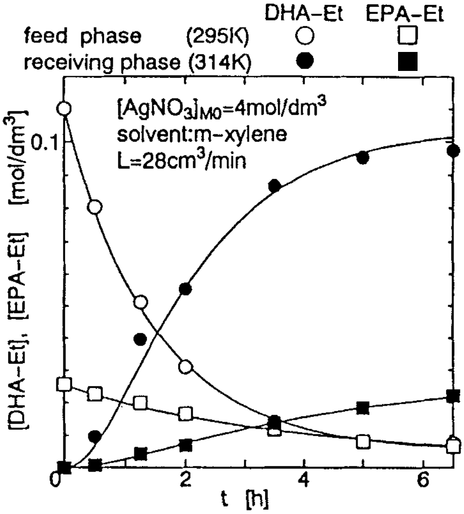

FIG. 3 Time courses of concentrations in the feed and the receiving phases obtained with NDCIRLM. Uphill transport driven by transmembrane temperature difference. Feed phase: *m*-xylene solution of bonito oil ethyl ester (volume ratio of bonito oil-Et to *m*-xylene = 0.25). Receiving phase: *m*-xylene. $V_F = 30$ cm^3, $V_S = 20$ cm^3, $V_M = 35$ cm^3, $L = 28$ cm^3/min, $T_F = 295$ K, $T_S = 314$ K, $N_F = N_S = 300$ rpm.

Figure 4 shows the plot of the concentration ratio R_S (= [DHA-Et]$_S$/[EPA-Et]$_S$) in the receiving phase against the extent of transport of DHA-Et, x (= 1 − [DHA-Et]$_F$/[DHA-Et]$_{F0}$). When x is small, R_S is larger than the initial concentration ratio in the feed phase R_{F0} (= [DHA-Et]$_{F0}$/[EPA-Et]$_{F0}$), i.e., 3.94. However, since the concentration ratio R_F (= [DHA-Et]$_F$/[EPA-Et]$_F$) in the feed phase decreases due to selective permeation of DHA-Et over DEPA-Et, R_S decreases with an increase in x and approaches R_{F0}. Therefore, the present circulating liquid membrane cannot be used for the mutual separation of DHA-Et and EPA-Et. However, it is applicable to the selective separation of DHA-Et and EPA-Et from bonito oil-Et.

Typical results obtained with the DCIRLM are shown in Fig. 5. The volume ratio of the feed to the membrane phase, V_F/V_M, in the DCIRLM was 3.75. Although this value was much higher than 0.86, the volume ratio in the NDCIRLM (see Fig. 3), the time required to decrease the DHA-Et concentration in the feed phase to half the initial concentration was shorter that for the NDCIRLM. This is attributable to a much larger

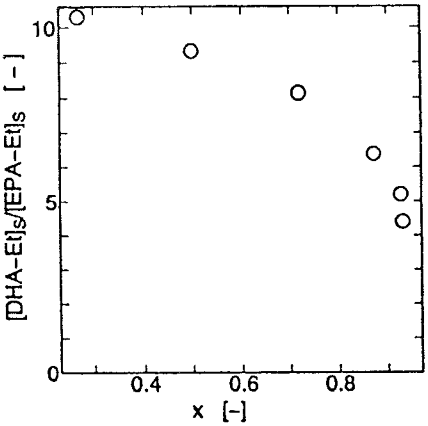

FIG. 4 Plot of $[\text{DHA-Et}]_S/[\text{EPA-Et}]_S$ against $x = 1 - [\text{DHA-Et}]_F/[\text{DHA-Et}]_{F0}$. The conditions are the same as in Fig. 3.

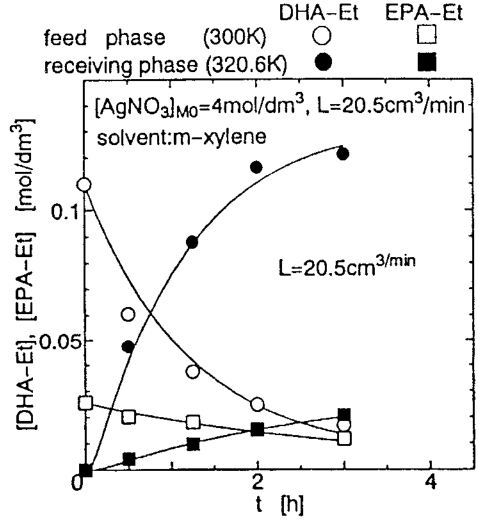

FIG. 5 Time courses of concentrations in the feed and the receiving phases obtained with DCIRLM. Uphill transport driven by transmembrane temperature difference. Feed phase: *m*-xylene solution of bonito oil ethyl ester (volume ratio of bonito oil-Et to *m*-xylene = 0.25). Receiving phase: *m*-xylene. $[\text{AgNO}_3]_{M0} = 4$ mol/dm^3, $V_F = 150$ cm^3, $V_s = 100$ cm^3, $V_M = 40$ cm^3, $L = 20.5$ cm^3/min, $T_F = 300$ K, $T_S = 321$ K, $N_F = 250$ rpm, $N_S = 410$ rpm.

aqueous–organic interfacial area and interfacial mass transfer rate in the DCIRLM.

Uphill Transport Utilizing Solvent Dependence of Distribution Ratio

The results obtained with the NDCIRLM are shown in Fig. 6. Here the feed phase was an *n*-dodecane solution of bonito oil-Et and the receiving phase was *m*-xylene. Both stirred vessels were kept at 298 K. In this figure the uphill transport of DHA-Et and EPA-Et from the *n*-dodecane to the *m*-xylene phase is clearly shown. The previous paper described the uphill transport of EPA-Et through a bulk and a supported liquid membrane (5); the principle of this uphill transport is that activity coefficients of PUFA-Et in *n*-dodecane are higher than those in *m*-xylene. In other words, the distribution ratio between the aqueous and *n*-dodecane phases is much higher than that between the aqueous and *m*-xylene phases. At $[AgNO_3]_M$ = 2 mol/dm^3, the distribution ratios of DHA-Et when *n*-dodecane and *m*-xylene are used as the solvent of bonito oil-Et are estimated as 1.41 and 0.089, respectively, and the those for EPA-Et for *n*-dodecane and *m*-xylene are 0.35 and 0.033, respectively (4).

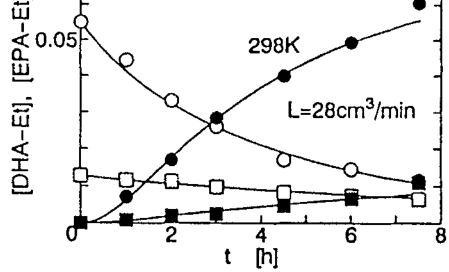

FIG. 6 Time courses of concentrations in the feed and the receiving phases obtained with NDCIRLM. Uphill transport by use of solvent dependence of distribution ratio. Feed phase: *n*-dodecane solution of bonito oil ethyl ester (volume ratio of bonito oil-Et to *n*-dodecane = 0.111). Receiving phase: *m*-xylene. $[AgNO_3]_{M0}$ = 2 mol/dm^3, V_F = 30 cm^3, V_S = 20 cm^3, V_M = 30 cm^3, L = 28 cm^3/min, T_F = T_S = 298 K, N_F = 300 rpm, N_S = 350 rpm.

Since *m*-xylene can form a complex with silver ion, it can be transported from the receiving phase to the feed phase by the facilitated transport mechanism. However, the amount of *m*-xylene transported was found to be very small.

The circulating liquid membrane process presented here seems to be similar to the usual solvent extraction process consisting of extraction and stripping units. However, the circulating liquid membrane operation differs from solvent extraction in that the amount of carrier (extractant) used in the circulating liquid membrane is small and is not enough to extract almost all of the desired solutes. Therefore, this type of liquid membrane is considered to be useful for cases where an expensive carrier is used, as in the present study. A much more efficient circulating liquid membrane system can be realized by redesigning the stirred vessel so a much higher interfacial mass transfer rate is obtained.

SIMULATION OF PERMEATION RATES

Transport Equations

A permeation model is proposed to simulate the time course of the concentrations of PUFA-Ets in the two vessels. The material balance equations for the *j*th species in the stirred vessels are expressed by the following equations.

$$\frac{d(V_F C_{F,j})}{dt} = -K_{F,j} S_F \left(C_{F,j} - \frac{C_{MF,j}}{D_{F,j}} \right) \tag{3a}$$

$$\frac{d(V_{MF} C_{MF,j})}{dt} = K_{F,j} S_F \left(C_{F,j} - \frac{C_{MF,j}}{D_{F,j}} \right) - L(C_{MF,j} - C_{MS,j}) \tag{3b}$$

$$\frac{d(V_{MS} C_{MS,j})}{dt} = L(C_{MF,j} - C_{MS,j}) - K_{S,j} S_S \left(\frac{C_{MS,j}}{D_{S,j}} - C_{S,j} \right) \tag{3c}$$

$$\frac{d(V_S C_{S,j})}{dt} = K_{S,j} S_S \left(\frac{C_{MS,j}}{D_{S,j}} - C_{S,j} \right) \tag{3d}$$

The fluxes of DHA-Et, EPA-Et, and Ag^+ are related as follows:

$$\sum_{j=1}^{2} n_j k_{MF,j}(C^*_{MF,j} - C_{MF,j}) = k_{F,Ag}([Ag^+]_{MF} - [Ag^+]^*_{MF}) \tag{4a}$$

$$\sum_{j=1}^{2} n_j k_{MS,j}(C^*_{MS,j} - C_{MS,j}) = k_{MS,Ag}([Ag^+]_{MS} - [Ag^+]^*_{MS}) \tag{4b}$$

Here subscripts 1 and 2 denote DHA-Et and EPA-Et, respectively. The conservation of silver in the liquid membrane phase is given by

$$[\mathrm{Ag}^+]_0 = [\mathrm{Ag}^+]_{\mathrm{MF}} + \sum_{j=1}^{2} n_j C_{\mathrm{MF},j} = [\mathrm{Ag}^+]_{\mathrm{SF}} + \sum_{j=1}^{2} n_j C_{\mathrm{SF},j} \quad (5)$$

The overall mass transfer coefficients, K_{F} and K_{s}, are expressed as

$$1/K_{\mathrm{F},j} = 1/k_{\mathrm{F},j} + 1/(D_{\mathrm{F},j}k_{\mathrm{MF},j}) \quad (6a)$$

$$1/K_{\mathrm{S},j} = 1/k_{\mathrm{S},j} + 1/(D_{\mathrm{S},j}k_{\mathrm{MS},j}) \quad (6b)$$

Here D is the distribution ratio at the aqueous–organic interface which depends on the temperature and $[\mathrm{Ag}^+]^*$, the silver ion concentration at the interface.

As the organic solution of bonito oil-Et was highly surface active, it was very difficult to keep the aqueous–organic interface flat in the NDCIRLM. It was also difficult to evaluate the liquid–liquid interfacial area in the DCIRLM. Therefore, simulation was limited to the single transport of EPA-Et from an *n*-dodecane solution containing only EPA-Et at low concentration to *m*-xylene, and simultaneous transport of DHA-Et and EPA-Et from a *m*-xylene solution of bonito oil-Et to *m*-xylene using the NDCIRLM.

Determination of Mass Transfer Parameters

To obtain mass transfer parameters such as $k_{\mathrm{F}}S_{\mathrm{F}}$, $k_{\mathrm{S}}S_{\mathrm{S}}$, $k_{\mathrm{MF}}S_{\mathrm{F}}$, and $k_{\mathrm{MS}}S_{\mathrm{S}}$, batch experiments on the extraction of EPA-Et from its *n*-dodecane or *m*-xylene solutions to aqueous silver nitrate solutions and also on the extraction of DHA-Et and EPA-Et from *m*-xylene solutions of bonito oil-Et into aqueous silver nitrate solutions were performed using one of the nondispersion-type stirred vessels. The volumes of the organic and the aqueous phases were 20 and 7 cm^3, respectively. Samples (0.55 cm^3) were taken from the aqueous phase, diluted with water to lower the total silver concentration below 0.5 $\mathrm{mol/dm}^3$, and shaken with 1 cm^3 of *n*-dodecane to strip EPA-Et in the *n*-dodecane phase. The concentration of PUFA-Et in the *n*-dodecane phase was determined as described before. The feed phase concentrations were calculated by the material balance.

Typical results are shown in Fig. 7. The rate parameters were determined so that the results calculated by Eqs. (3a) and (3b) with $L = 0$ might fit the experimentally observed time course of the concentrations. The extraction equilibria given by Eq. (2) was modified so that the equilibrium concentrations calculated by the permeation model might fit the final concentrations obtained with the extraction experiments. The values of

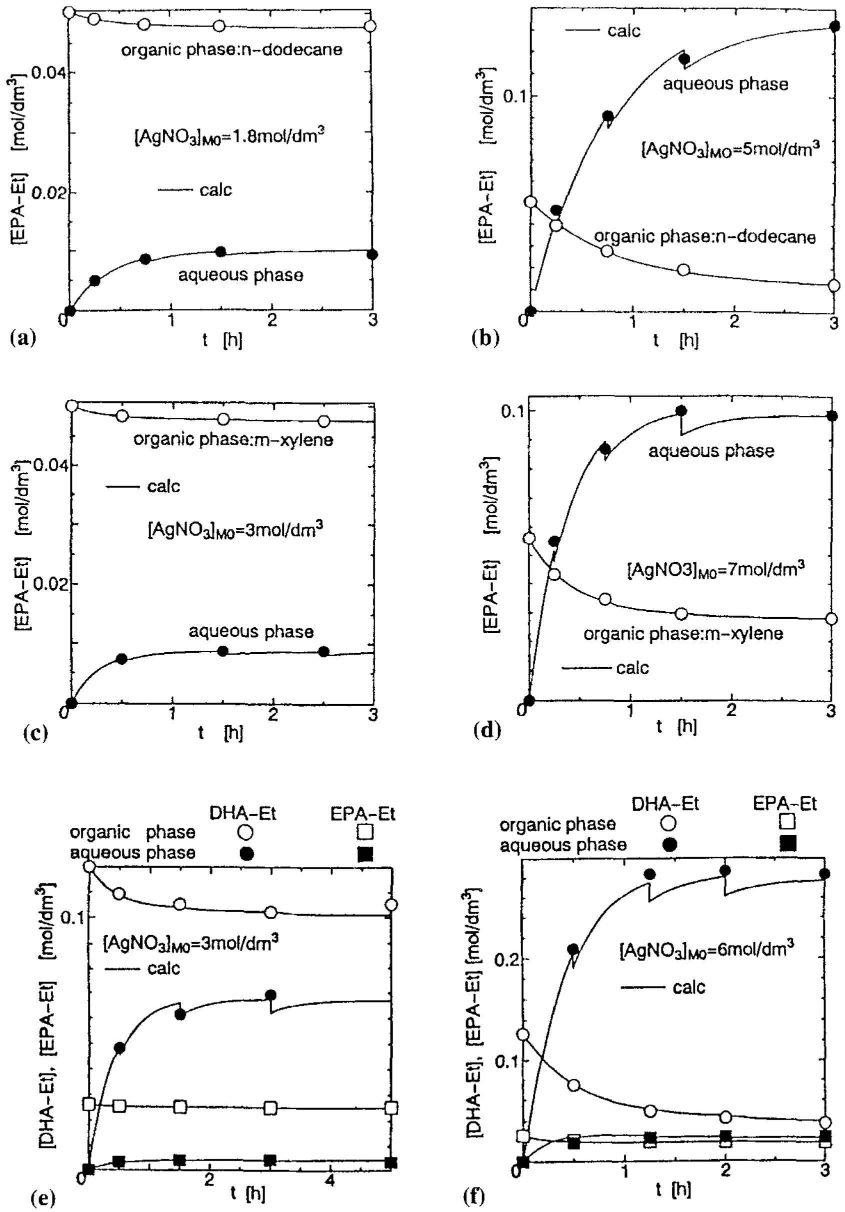

FIG. 7 Time courses of the concentrations in the feed and the aqueous phases in batch extraction of EPA-Et. V_F = 30 cm^3, V_M = 7 cm^3, 298 K, N_F = 300 rpm. (a) Feed phase: *n*-dodecane solution of EPA-Et, $[Ag^+]_{Mo}$ = 1.8 mol/dm^3. (b) Feed phase: *n*-dodecane solution of EPA-Et, $[Ag^+]_{Mo}$ = 5 mol/dm^3. (c) Feed phase: *m*-xylene solution of EPA-Et, $[Ag^+]_{Mo}$ = 3 mol/dm^3. (d) Feed phase: *m*-xylene solution of EPA-Et, $[Ag^+]_{Mo}$ = 7 mol/dm^3. (e) Feed phase: *m*-xylene solution of bonito oil ethyl ester, $[Ag^+]_{Mo}$ = 3 mol/dm^3. (f) Feed phase: *m*-xylene solution of bonito oil ethyl ester, $[Ag^+]_{Mo}$ = 6 mol/dm^3.

α in Eq. (2) for these experiments are listed in Table 3. By using the data obtained at low silver ion concentrations, the values of $k_{MF}S_F$ were determined since mass transfer resistance in the aqueous phase was rate-controlling under this condition. On the other hand, using the data obtained at high silver ion concentrations, the values of k_FS_F were obtained. These values are summarized in Table 3. The calculated results are shown by solid lines in Fig. 7. Agreement between the experimental and the computed results are excellent. The stepwise decrease in the calculated concentration in the aqueous phase at each data point is due to the dilution of the aqueous solution by addition of the silver nitrate solution (0.55 cm^3) to the aqueous phase to make up the amount of the withdrawn samples.

Simulation of Transport of DHA-Et and EPA-Et through Nondispersion-Type Circulating Liquid Membrane

The result of uphill transport of EPA-Et from an *n*-dodecane solution containing EPA-Et alone to a *m*-xylene solution is shown in Fig. 8. The volume of the organic phase in the stirred vessel was 20 cm^3. The total volume of the carrier solution was 20 cm^3. However, since some part of the carrier solution was contained in the tubes connecting the two vessels, the volume of the carrier solution in each vessel was about 7 cm^3. There-

TABLE 3
Mass Transfer Parameters Determined by Batch Extraction Experiments

$[AgNO_3]_{MO}$ (mol/dm^3)	Feed phase	K_FS_F (m^3/s)	$K_{MF}S_F$ (m^3/s)	α[a]
1.8	*n*-Dodecane + EPA-Et[b]	—	5.0×10^{-9}	1.31×10^{-2}
5.0	*n*-Dodecane + EPA-Et[b]	8.1×10^{-9}	—	9.58×10^{-3}
3.0	*m*-Xylene + EPA-Et[b]	—	7.0×10^{-9}	8.23×10^{-4}
7.0	*m*-Xylene + EPA-Et[b]	1.3×10^{-8}	—	3.70×10^{-4}
3.0	*m*-Xylene + bonito oil-Et[c]	—	6.1×10^{-9}	1.74×10^{-3} (EPA-Et) 2.67×10^{-3} (DHA-Et)
6.0	*m*-Xylene + bonito oil-Et[c]	1.1×10^{-10}	—	2.16×10^{-3} (EPA-Et) 3.45×10^{-3} (DHA-Et)

[a] $D_{EPA\text{-}Et} = \alpha[Ag^+]^5$, $D_{DHA\text{-}Et} = \alpha[Ag^+]^6$. Temperature: 298 K.
[b] $[EPA\text{-}Et]_{FO} = 0.055$ mol/dm^3.
[c] Volume % of bonito oil-Et = 0.20.

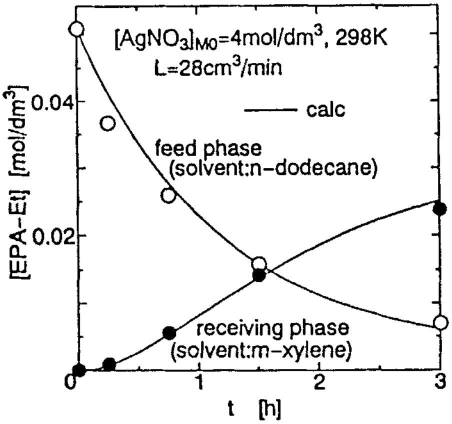

FIG. 8 Time courses of the concentration of EPA-Et obtained with NDCIRLM. Uphill transport by use of solvent dependence of distribution ratio. Feed phase: *n*-dodecane solution of EPA-Et. Receiving phase: *m*-xylene. $[AgNO_3]_{MO} = 4$ mol/dm^3, $V_F = 30$ cm^3, $V_S = 30$ cm^3, $V_M = 25$ cm^3, $L = 28$ cm^3/min, $T_F = T_S = 298$ K, $N_F = N_S = 300$ rpm. Values of parameters used in the calculation: $k_FS_F = 8.1 \times 10^{-9}$, $k_SS_S = 1.3 \times 10^{-8}$, $k_{MF}S_F = 5.0 \times 10^{-9}$, $k_{MS}S_S = 7.0 \times 10^{-9}$ m^3/s, $\alpha = 1.27 \times 10^{-2}$ (dm^3/mol)^5 for *n*-dodecane and 9.47×10^{-4} (dm^3/mol)^5 for *m*-xylene.

fore, the hydrodynamic condition in the stirred vessel was similar to that in the batch extraction experiments described before. Although the carrier concentration used in the experiment (4 mol/dm^3) was different from those employed in the batch extraction experiments, the values of $k_{MF}S_F$ and $k_{MS}S_S$ obtained with the batch extraction experiments listed in Table 3 were used as the approximate values of $k_{MF}S_F$. The solid lines are the results computed by Eqs. (3)–(6). The experimental results were satisfactorily simulated by the proposed permeation model.

To investigate the effect of the circulation rate L on the permeation rate, an experiment was performed where L was reduced from 28 cm^3/min (Fig. 8) to 14 cm^3/min. However, the decrease in the permeation rate was very slight. This suggests that the rate-limiting step is not the convective transfer of the EPA-Et·Ag complex from the feed to the receiving vessel by the pump but the interfacial mass transfer between the organic and membrane phases.

Figure 9 shows the result of the transport of DHA-Et and EPA-Et in a *m*-xylene solution of bonito oil-Et to a *m*-xylene (receiving phase). Here, since both the feed and the receiving solutions were kept at 25°C, passive facilitated transport occurred, and the transport stopped when the concen-

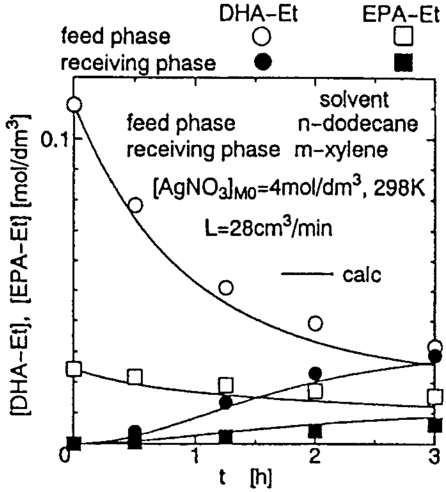

FIG. 9 Time courses of concentrations in the feed and the receiving phases obtained with NDCIRLM. Feed phase: *m*-xylene solution of bonito oil-Et (volume ratio of bonito oil-Et to *m*-xylene = 0.25). Receiving phase: *m*-xylene. $[AgNO_3]_{M0} = 4$ mol/dm³, $V_F = 30$ cm³, $V_S = 30$ cm³, $V_M = 25$ cm³, $L = 28$ cm³/min, $T_F = T_S = 298$ K, $N_F = N_S = 300$ rpm. Values of parameters used in the calculation: $k_F S_F = k_S S_S = 8.6 \times 10^{-9}$, $k_{MF} S_F = k_{MS} S_S = 6.1 \times 10^{-9}$ m³/s, $\alpha = 1.74 \times 10^{-2}$ (dm³/mol)⁶ for EPA-Et and 2.67×10^{-3} (dm³/mol)⁶ for DHA-Et.

tration in the receiving phase approached that in the feed phase. Here again, the computed results are in good agreement with the experimental results.

The simulation of uphill transport driven by transmembrane temperature difference was not carried out because the interfacial temperature which has a remarkable influence on the distribution ratio could not be estimated accurately.

CONCLUSION

Using silver nitrate as a carrier, two types of uphill transport of DHA-Et and EPA-Et were demonstrated with the two types of circulating liquid membranes, i.e., the nondispersion-type liquid membrane and the dispersion-type liquid membrane.

The first type of uphill transport utilizes the temperature dependence of the distribution ratios of these PUFA-Ets, and these esters were transported against their concentration gradients from their *m*-xylene solution (feed phase) to the *m*-xylene phase (receiving solution) which was maintained at a higher temperature than the feed phase. This may be the first demonstration of uphill facilitated transport driven by a transmembrane temperature difference which utilizes the fact that the distribution ratios of these PUFA-Ets are higher at lower temperature.

Another type of uphill transport utilizes the solvent dependence of the distribution ratios of PUFA-Ets. DHA-Et and EPA-Et contained in bonito oil-Et were selectively transported against their concentration gradients from their *n*-dodecane solution to the *m*-xylene phase.

A model of permeation through the circulating liquid membrane was proposed. Some of the experimental data could be satisfactorily simulated by the proposed permeation model using the mass transfer parameters determined by the batch experiments on the extraction of PUFA-Ets with aqueous silver nitrate solutions.

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SYMBOLS

C	concentration (mol/m^3)
D	distribution ratio
DCIRLM	dispersion type circulating liquid membrane
DHA	docosahexaenoic acid
EPA	eicosapentaenoic acid
Et	ethyl ester
K	overall mass transfer coefficient (m/s)
k	liquid film mass transfer coefficient (m/s)
L	volumetric circulation rate of liquid membrane phase (m^3/s)
m_1, m_2, m_3	constants in Eq. (2)
N	stirring speed (rpm)
n	number of carbon-carbon double bonds in PUFA-Et
NDCIRLM	nondispersion-type circulating liquid membrane
PUFA	polyunsaturated fatty acid
R	[DHA-Et]/[EPA-Et]
S	aqueous–organic interfacial area (m^2)
T	temperature (K)
t	time (s)

V	liquid volume (m^3)
x	degree of transport of DHA-Et defined by $1 - [\text{DHA-Et}]_F/[\text{DHA-Et}]_{F0}$

Greek Letters

α	coefficient in Eq. (2)
ϕ	volume fraction of bonito oil-Et in organic phase

Superscript

*	value at aqueous–organic interface

Subscripts

F	feed phase
MF	liquid membrane phase in feed vessel
MS	liquid membrane phase in receiving vessel
S	receiving phase
0	initial value

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