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Mass Transfer Resistance Analysis of L-Tryptophan Extraction in an Emulsion Liquid Membrane System

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ABSTRACT

The extraction of L-tryptophan with an emulsion liquid membrane containing di-2-ethylhexy phosphoric acid as a carrier, Span 80 as a surfactant, kerosene as a solvent, and hydrochloric acid solution as an internal phase stripping reagent, was studied. The effects of external phase pH, carrier concentration, internal stripping reagent concentration, and external initial solute concentration on the mass transfer flux were examined. The fractional resistances of external phase diffusion and emulsion globule diffusion to the overall process were defined and calculated by the proposed model. Thus, the rate-controlling steps for the overall process were quantitatively identified. For higher external phase pH and/or higher carrier concentration as well as lower external initial solute concentration, the overall process is mainly determined by the external phase diffusion. On the other hand, for lower external pH and/or lower carrier concentration, the emulsion diffusion is a rate-controlling step. However, in the majority of cases, the overall process is governed by the combined effects of both the external phase diffusion and the emulsion globule diffusion. Compared with the external phase pH and carrier concentration, the concentrations of internal stripping reagent and external initial solute are unimportant factors determining the overall process.

Key Words. Emulsion liquid membrane; Permeation; L-Trp; Fractional resistance; Rate-controlling step

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INTRODUCTION

Recently, increasing attention has been paid to the development of an efficient method for the separation and purification of biological products such as proteins and amino acids from fermentation broths. The application of emulsion liquid membrane (ELM) extraction has been considered as a promising approach to selective separation and rapid concentration of biological products because of the very thin liquid membrane, large interfacial area, and simultaneous reactive extraction and back-extraction in one unit. The ELM technique has already been applied in many bioseparation fields, including the extraction of amino acids (1–5), antibiotics (6–10) and other bioproducts (11–13).

Although many studies have been performed on the extraction of amino acids with ELM technique, few investigations concerning the mass transfer mechanism have been conducted because information is lacking on extraction equilibrium and extraction kinetics of the solute within such multiphase ELM systems. Therefore, for efficient application of ELM technique to amino acid extraction, it is very important to clarify the mass transfer mechanism in a wide range of conditions.

In this work, ELM extraction of L-tryptophan (L-Trp) was performed by using di-2-ethylhexy phosphoric acid (D2EHPA) as a carrier, Span 80 as a surfactant, kerosene as a solvent, and hydrochloric acid solution as an internal phase stripping reagent. First, the effects of various operating conditions, such as pH value of external phase, concentrations of carrier in the membrane phase, stripping reagent in the internal phase, and initial L-Trp in the external phase, on the mass transfer flux were examined. Then, the fractional resistances of the external phase diffusion and the emulsion globule diffusion to the overall process were defined and quantitatively studied. Finally, the rate-controlling step was identified.

MODELING OF ELM EXTRACTION PROCESS

Equilibrium of L-Trp Extraction with D2EHPA

As can be seen from Eq. (1), in aqueous solutions L-Trp exists in ionic forms of different charge depending on the pH value of the medium:

$$\underset{\substack{(A^+)\\ pH < pKa_1}}{H_2A^+} \overset{-H^+}{\underset{+H^+}{\Leftrightarrow}} \underset{\substack{(A)\\ pKa_1 < pH < pKa_2}}{HA} \overset{-H^+}{\underset{+H^+}{\Leftrightarrow}} \underset{\substack{(A^-)\\ pH > pKa_2}}{A^-} \tag{1}$$

where A^+, A, and A^- are the cation, zwitterion, and anion of L-Trp, respectively. For L-Trp, the dissociation constants, pKa_1 and pKa_2, are 2.38 and 9.38, respectively (14). When a cationic extractant such as D2EHPA is used as a

carrier, only the cation form of L-Trp can be extracted into organic phase from its acidic solution.

Shi et al. (15) studied the extraction mechanism of L-Trp with D2EHPA in detail and reported a general extraction equilibrium formulation. They found that the amino acid loading ratio (the molar concentration ratio of the equilibrium amino acid in the organic phase to the initial dimeric D2EHPA) has a great effect on extraction equilibrium. At a relatively low loading ratio ($<3 \times 10^{-3}$), the L-Trp extraction with D2EHPA can be expressed by the following formula:

$$H_2A^+ + 2\overline{(HL)_2} \Leftrightarrow \overline{H_2AL{\cdot}1.5(HL)_2} + H^+ \tag{2}$$

Thus, the equilibrium constant for Eq. (2) can be expressed as

$$K_{ex} = \frac{[\overline{H_2AL{\cdot}1.5(HL)_2}][H^+]}{[\overline{(HL)_2}]^2[H_2A^+]} \tag{3}$$

where a component under a bar indicates the organic phase (membrane phase). However, at a high loading ratio ($>3 \times 10^{-3}$), the equilibrium formula, Eq. (3), did not hold. In addition to Eq. (2), two other parallel extraction equilibriums, Eqs. (4) and (5), exist at the same time:

$$H_2A^+ + \overline{H_2AL{\cdot}1.5(HL)_2} \Leftrightarrow \overline{2H_2AL{\cdot}HL} + H^+ \tag{4}$$

$$H_2A^+ + \overline{H_2AL{\cdot}HL} \Leftrightarrow \overline{2H_2AL} + H^+ \tag{5}$$

In a carrier-facilitated ELM system, the concentration of the solute–carrier complex in the membrane phase, generally, is much lower than that in a two-phase extraction system due to the existence of simultaneous extraction and stripping in the former system, consequently resulting in a relatively lower loading ratio of the amino acid. Therefore, the contributions of Eqs. (4) and (5) to the L-Trp extraction were reasonably neglected in this study, and only Eq. (2) was taken into account.

Mathematical Description of ELM Extraction Process

As shown in Fig. 1, L-Trp permeates from the external phase into the internal phase in five steps: (*a*) diffusion of A^+ in the stagnant layer of the external phase, (*b*) A^+/D2EHPA complex formation at the external phase/membrane phase interface; (*c*) diffusion of the complex in the thin oil layer; (*d*) diffusion of the complex in the inner core of the emulsion globule; and (*e*) stripping of A^+ at the membrane phase/internal phase interface. Hence, the overall permeation of L-Trp is determined by a number of resistances such as diffusion resistances of the external stagnant layer, thin oil layer, and the inner core of the emulsion globule as well as chemical reaction resistance. Teramoto et al. (5) reported that the chemical reaction resistance between A^+ and

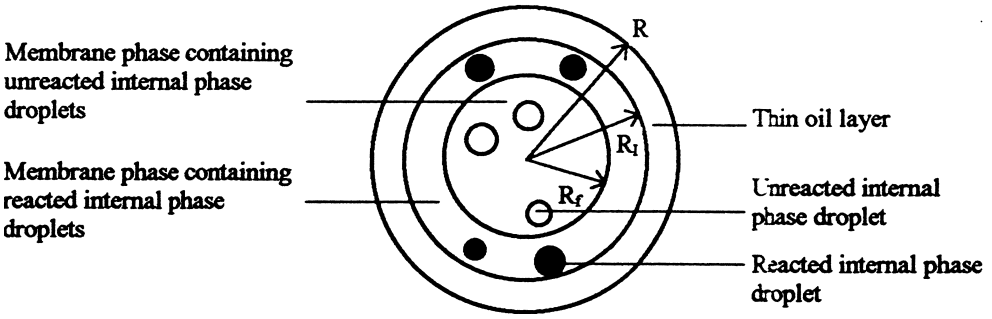

FIG. 1 Schematic description of an emulsion globule. R, R_I, and R_f represent the radius of w/o emulsion globule, inner core, and reaction front, respectively.

D2EHPA is negligible compared with the diffusion resistances. Therefore, among these resistances, only such resistances as the external phase diffusion and the emulsion globule diffusion are considered in the overall resistance in this study. Furthermore, when the extremely high internal reagent concentration, ionic nature of stripping reaction, and the large stripping interfacial area between the membrane and internal phase are considered, it may be assumed that the reaction between the complex and the internal stripping reagent is instantaneous, and the "advancing front model" (16) can be used to describe L-Trp ELM extraction.

As illustrated in Fig. 1, the overall diffusion resistance of the solute from the external to the reaction front can be expressed as

$$\frac{1}{K_T} = R_e + R_m = \frac{1}{k_e} + \left[\frac{\delta \cdot R}{D_c \cdot R_I} + \frac{R_I(R_I - R_f)}{D_{eff} \cdot R_f}\right] \cdot \frac{C_H}{K_{ex} C_{HL}^2} \qquad (6)$$

where K_T denotes the overall mass transfer coefficient; R_e is mass transfer resistance of the external phase; and R_m is diffusion resistance of the emulsion globule which combines the diffusion resistance in the thin oil layer and the effective diffusivity through the inner core of the emulsion globule. R, R_I, R_f, and R_i represent the radius of w/o emulsion globule, inner core, reaction front, and internal phase droplet, respectively.

If the membrane breakage and emulsion swelling are neglected, at the pseudo-steady state the mass balances of L-Trp in the external phase and the emulsion globule are expressed by

$$-V_e \frac{dC_e}{dt} = \frac{3(V_m + V_i)}{R} \cdot K_T \cdot C_{A^+} \qquad (7)$$

$$(C_{e0} - C_e) \cdot V_e = \frac{4}{3} \pi \cdot (R_I^3 - R_f^3) \cdot \theta_i \cdot C_{i0} \cdot n \qquad 0 \le R_f \le R_I \qquad (8)$$

where

$$C_e = C_{A^+}\,[1 + 10^{pH-pKa_1} + 10^{2pH-(pKa_1+pKa_2)}] \tag{9}$$

$$\frac{V_i}{V_i + V_m}\left(\frac{R}{R_i}\right)^3 = \theta_i \tag{10}$$

$$n = \frac{3(V_i + V_m)}{4\pi R^2} \tag{11}$$

The initial condition is

$$t = 0 \qquad C_e = C_{e0} \tag{12}$$

$$R_f = R_I \tag{13}$$

The fractional resistances of the external phase diffusion and the emulsion globule diffusion to the overall process were defined as

$$\Delta_e = \frac{R_e}{R_e + R_m} \tag{14}$$

$$\Delta_m = \frac{R_m}{R_e + R_m} \tag{15}$$

Obviously, Δ_e and Δ_m reflect the contributions of their respective diffusion steps to the overall resistance. If these parameters in Eqs. (6)–(11) are known, the set of Eqs. (6)–(8) can be solved numerically to obtain the Δ_e and Δ_m values. By comparing both the values, the rate-controlling steps for L-Trp extraction in the ELM system can be expected to be quantitatively identified.

EXPERIMENTAL METHODS

Aqueous L-Trp solution was prepared by dissolving L-Trp in distilled water. The membrane phase was prepared by dissolving D2EHPA as a carrier and Span 80 as a surfactant in a mixture of 80% (v/v) kerosene and 20% (v/v) paraffin oil as a diluent. An aqueous hydrochloric acid solution was used as the internal aqueous phase for stripping. The emulsions were made by vigorously mixing 50 cm^3 of the membrane phase and 40 cm^3 of the internal phase in an emulsifier at a stirring speed of 10,000 rpm for 10 min. The w/o emulsion operation was performed at room temperature by blending 50 cm^3 of the prepared emulsion and 200 cm^3 of the L-Trp aqueous solution in a batch-type stirred glass cell. The cell is 7 cm in inner diameter and 9 cm in depth. The solution in the cell was stirred at 250 rpm by a turbine impeller with six flat blades, each 3 cm in diameter. The aqueous L-Trp solutions were adjusted to the desired pH by chloroacetic acid buffer solution. A suitable amount of urea was added into the external phase to avoid swelling of the emulsion caused by the osmotic dif-

TABLE 1
Experimental Conditions

Factors	Conditions
Initial L-Trp concentration (mol/dm^3)	2×10^{-3}, 4×10^{-3}, 6×10^{-3}
Initial pH of external phase	1.5, 2.0, 2.5, 3.0
Carrier concentration (D2EHPA as dimer) (mol/dm^3)	0.032, 0.064, 0.096, 0.112
Initial concentration of internal stripping reagent (mol/dm^3)	1.0, 1.5, 2.0
Volume ratio of internal to membrane phase	4/5
Volume ratio of external phase to emulsion	4/1

ference. Samples were taken at a appropriate time interval and the external aqueous phase was immediately separated from the emulsion phase for analysis. Concentrations of L-Trp were determined by a spectroscopic method (17). Potassium ion concentration, which was dissolved in internal phase as trace, was measured by atomic absorption spectroscopy. The radius of the internal phase droplets, R_i, and radius of the emulsion globules, R, were determined by photography. The experimental conditions are listed in Table 1.

In all experiments, the breakage and swelling of the ELM were estimated as follows (3):

$$\mathrm{Br} = \frac{K_{ef}V_{ef}}{K_{i0}V_{i0}} \times 100\% \tag{16}$$

$$\mathrm{Sw} = \frac{K_{if}}{K_{i0}} \times 100\% \tag{17}$$

The following two parameters, extraction ratio, E, and initial mass transfer flux, J_0, were defined to evaluate the L-Trp extraction with the presented ELM system.

$$E = \frac{C_{e0} - C_e}{C_{e0}} \times 100\% \tag{18}$$

$$J_0 = -\frac{V_e}{S} \cdot \frac{dC_e}{dt} \tag{19}$$

where dC_e/dt can be obtained from the concentration in the initial period.

PARAMETER ESTIMATION

Mass Transfer Coefficient of External Phase k_e

Teramoto et al. (5) experimentally determined the mass transfer coefficient of L-Trp in the external aqueous phase, and a k_e value was reported. Therefore,

TABLE 2
Values of Parameters Used in This Study

Parameters	Values				References
K_{ex} (mol/dm^3)	0.045				15
k_e (m/sec) $\times 10^5$	2.0				5
D_A+ (m^2/sec) $\times 10^{10}$	5.41				This study
C_{HL0} (mol/dm^3)	0.032	0.064	0.096	0.112	This study
$D_c \times 10^{10}$ (m^2/sec)	4.25	2.29	1.97	1.88	This study
$R \times 10^4$ (m)	2.15				This study
$R_i \times 10^6$ (m)	1.46				This study
$\delta \times 10^7$ (m)	7.66				This study

their reported value, as shown in Table 2, was used in this work to estimate the external phase diffusion resistance.

Thickness of the Surfactant Monolayer δ

Thickness of the thin oil layer, δ, was estimated according to the following equation (18):

$$\delta = \left(\frac{4\pi}{3}\right)^{1/3} R_i(\phi_i^{-1/3} - 1) \tag{20}$$

where

$$\phi_i = \frac{V_i}{V_i + V_m} \tag{21}$$

The estimated δ value is shown in Table 2.

Diffusivities

The Hayduk and Minhas correlation (19) was used to calculate the diffusivity of the solute-carrier complex in the membrane phase:

$$D_c = 13.3 \times 10^{-8} \left(T^{1.47}.\frac{\mu_m^e}{V_c^{0.71}}\right) \tag{22}$$

where

$$e = (10.2/V_c) - 0.791 \tag{23}$$

Here μ_m is the viscosity of the membrane phase, which is measured experimentally by viscometer, and V_c is the molar volume of the complex at its normal boiling point evaluated from the Schroeder rule (19).

The diffusivity of the solute in the aqueous phase was estimated by the Wilke–Chang equation (20). The effective diffusivity of the complex in the emulsion globule was estimated by the following Teramoto et al. correlation (5):

$$D_{\text{eff}} = \left[\frac{\phi_i^{1/3}}{\left\{ \frac{\phi_i^{2/3} D_A K a_1}{K_{ex} C_{HL}^2} + (1 - \phi_i^{2/3}) D_c \right\} + \left\{ \frac{\phi_i^{2/3} D_{A^+} K_{ex} C_{HL}^2 [Cl^-]_i}{(K_{ex} C_{HL}^2 + C_c)^2} \right\}} + \frac{1 - \phi_i^{1/3}}{D_c} \right]^{-1} \quad (24)$$

RESULTS AND DISCUSSION

Several experiments were performed to investigate the fractional mass transfer resistances and identify the rate-controlling step. By calculating the Δ_e and Δ_m values under the conditions investigated, and comparing both the values, the rate-controlling steps for the overall transport process can be expected to be quantitatively identified. Note that at a fixed stirring speed, the external diffusion resistance remains approximately constant throughout all the experiments, thus the overall resistance varies with the emulsion globule diffusion resistance. The effects of various experimental conditions such as external pH, concentrations of carrier, internal stripping reagent, and initial external L-Trp on the initial mass transfer flux were first studied. The experimental results were then interpreted in terms of the fractional mass transfer resistances calculated by the proposed model.

Figure 2 shows the initial fluxes through the emulsion globule at various external pH values. The initial flux increases sharply with increasing external pH up to 2.5, but slightly increases or almost remains constant in the higher pH range. Table 3 lists the variations of Δ_e and Δ_m with external phase pH under the same experimental conditions as shown in Fig. 2. Obvi-

TABLE 3
Fractional Resistances at Various

	$E = 1\%$		$E = 10\%$		$E = 30\%$	
pH	Δ_e	Δ_m	Δ_e	Δ_m	Δ_e	Δ_m
1.5	0.149	0.851	0.146	0.854	0.140	0.860
2.0	0.357	0.643	0.351	0.649	0.339	0.661
2.5	0.635	0.365	0.629	0.371	0.618	0.382
3.0	0.843	0.157	0.840	0.160	0.834	0.166

Note: $C_{e0} = 2 \times 10^{-3}$ mol/dm^3, $C_{HL0} = 0.096$ mol/dm^3, $C_{i0} = 1.5$ mol/dm^3.

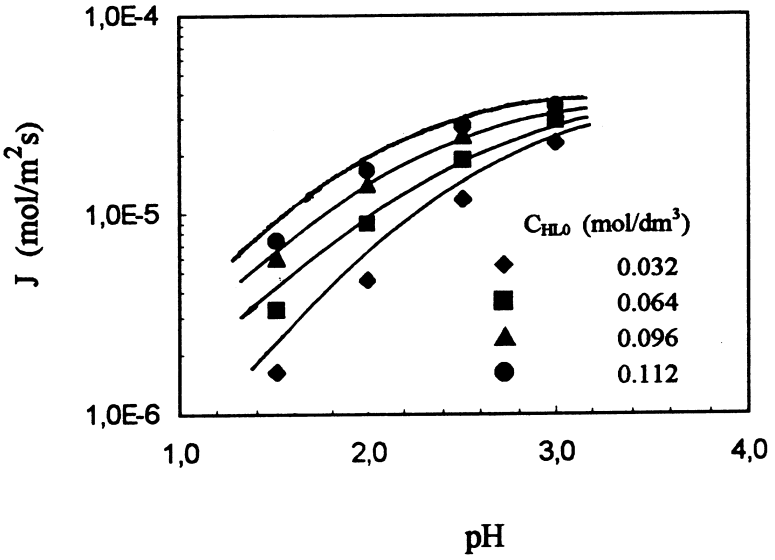

FIG. 2 Effect of pH in external phase on the initial mass transfer flux. $C_{e0} = 2 \times 10^{-3}$ mol/dm^3; $C_{i0} = 1.5$ mol/dm^3. The other operating conditions are as shown in Table 1.

ously, at the same external pH value, Δ_m increases gradually with an increase in extraction ratio, while Δ_e gradually decreases with the extraction ratio. This is because a higher extraction ratio corresponds to a longer diffusion distance within the emulsion globule, thus leading to an increase in emulsion globule diffusion resistance. On the other hand, at the same extraction ratio Δ_m decreases with increasing pH, indicating that the contribution of emulsion globule diffusion resistance to the overall resistance decreases, but that of external phase diffusion increases. In the lower pH range, it can be seen from Table 3 that the emulsion globule diffusion is important, thus the overall permeation process is mainly determined by emulsion gobule diffusion. In this case, the initial flux, as shown in Fig. 2, increases

External Phase pH Values

$E = 50\%$		$E = 70\%$		$E = 90\%$	
Δ_e	Δ_m	Δ_e	Δ_m	Δ_e	Δ_m
0.134	0.866	0.129	0.871	0.123	0.877
0.328	0.672	0.318	0.682	0.308	0.692
0.606	0.394	0.595	0.405	0.585	0.415
0.828	0.172	0.822	0.178	0.816	0.184

greatly with an increase in the external pH because of a decrease in the overall resistance. However, in the higher pH range, the external phase diffusion makes more contribution to the overall resistance than does the emulsion globule diffusion, showing that the external phase diffusion becomes a rate-controlling step. Therefore, the initial flux increases slightly with increasing pH. Especially under such extreme conditions as higher pH value and carrier concentration as well as lower initial external L-Trp concentration, the external phase diffusion resistance makes an overwhelming contribution to the overall resistance. Consequently, the overall permeation process is completely governed by the external phase diffusion and the overall resistance is approximately equal to the external phase diffusion resistance; thus, the initial flux is independent of the external pH. However, in the majority of cases, the overall permeation process is determined by the combined effects of both the external phase diffusion and the membrane phase diffusion. The solid lines in Fig. 2 represent the calculated results by the proposed model. The computed results are in satisfactory agreement with the experimental values.

The variation of the initial flux with carrier concentration at various external pH values is shown in Fig. 3. As the carrier concentration is increased, the initial flux also increases. Because the carrier concentration is relatively high (>0.096 mol/dm^3), an additional increase in carrier concentration does not yield significant increase in the initial flux, and the initial flux seems to reach a plateau value. Table 4 shows the calculated fractional resistances under the same experimental conditions as shown in Fig. 3. As is clear from Table 4, for the lower carrier concentration, the emulsion globule diffusion resistance is predominant. Thus, the overall permeation process is governed by the emulsion globule diffusion. Under this circumstance, increasing the carrier concentration leads to an increase in the initial flux. Note, however, that increasing the carrier concentration also lowers the effective diffusion coefficient,

TABLE 4
Fractional Resistances at

C_{HL0} (mol/dm^3)	$E = 1\%$		$E = 10\%$		$E = 30\%$	
	Δ_e	Δ_m	Δ_e	Δ_m	Δ_e	Δ_m
0.032	0.117	0.883	0.115	0.885	0.110	0.890
0.064	0.223	0.777	0.219	0.781	0.210	0.790
0.096	0.356	0.644	0.351	0.649	0.339	0.661
0.112	0.418	0.582	0.412	0.588	0.400	0.600

Note: pH = 2.0, $C_{e0} = 2 \times 10^{-3}$ mol/dm^3, $C_{i0} = 1.5$ mol/dm^3.

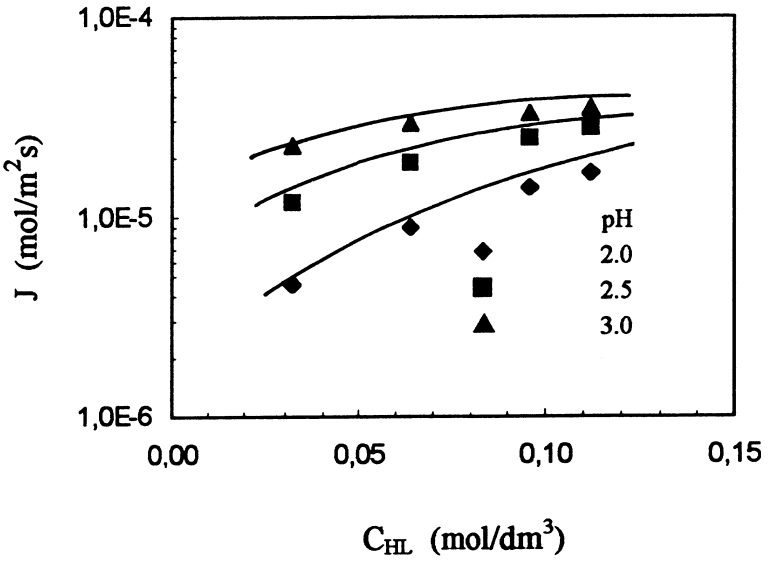

FIG. 3 Effect of carrier concentration on the initial mass transfer flux. $C_{e0} = 2 \times 10^{-3}$ mol/dm^3; $C_{i0} = 1.5$ mol/dm^3. The other operating conditions are as shown in Table 1.

D_{eff}, resulting in an increase in the emulsion globule diffusion resistance. Consequently, the overall process is controlled by the combined effects of both the external phase and emulsion globule diffusions. The computed results represented by the solid curves in Fig. 3 are in satisfactory agreement with the experimental data.

Figure 4 shows the variation of the initial flux with the stripping reagent concentration. Clearly, the computed results agree with the experimental values. The stripping reagent concentration seems to have little effect on the initial flux. This is because there is no obvious difference in the overall mass transfer resistance in the initial period. But as the permeation proceeds, it can

Various Carrier Concentrations

$E = 50\%$		$E = 70\%$		$E = 90\%$	
Δ_e	Δ_m	Δ_e	Δ_m	Δ_e	Δ_m
0.105	0.895	0.100	0.900	0.096	0.904
0.202	0.798	0.194	0.806	0.187	0.813
0.328	0.672	0.318	0.682	0.308	0.692
0.388	0.612	0.377	0.623	0.366	0.633

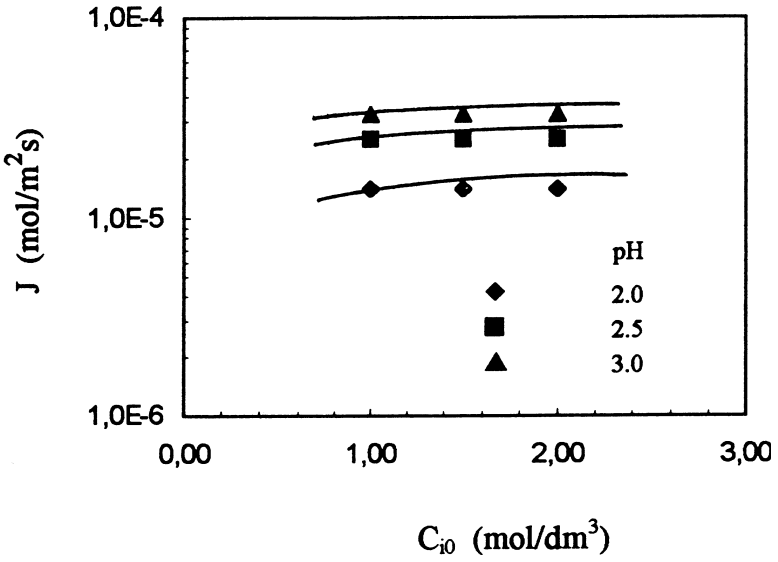

FIG. 4 Effect of internal stripping reagent concentration on the mass transfer flux. $C_{e0} = 2 \times 10^{-3}$ mol/dm^3; $C_{HL0} = 0.096$ mol/dm^3. The other operating conditions are as shown in Table 1.

be expected that the stripping reagent concentration has a positive effect on mass transfer flux due to an increase in the difference of hydrogen concentration between the external phase and the internal phase. Table 5 presents the tendencies of Δ_e and Δ_m with the internal stripping reagent concentration. At a lower extraction ratio the effects of C_{i0} on both the fractional resistances are indeed not significant because there is no great difference in the diffusion distance within the emulsion globule. It is known that a high concentration of stripping reagent corresponds to a larger stripping capacity, thus resulting in a slower advancement of the reaction front toward the center of the globule as

TABLE 5
Fractional Resistances at Various Internal

C_{i0} (mol/dm^3)	$E = 1\%$		$E = 10\%$		$E = 30\%$	
	Δ_e	Δ_m	Δ_e	Δ_m	Δ_e	Δ_m
1.0	0.356	0.644	0.348	0.652	0.331	0.669
1.5	0.356	0.644	0.351	0.649	0.339	0.661
2.0	0.357	0.643	0.352	0.648	0.344	0.656

Note: pH = 2.0, $C_{e0} = 2 \times 10^{-3}$ mol/dm^3, $C_{HL0} = 0.096$ mol/dm^3.

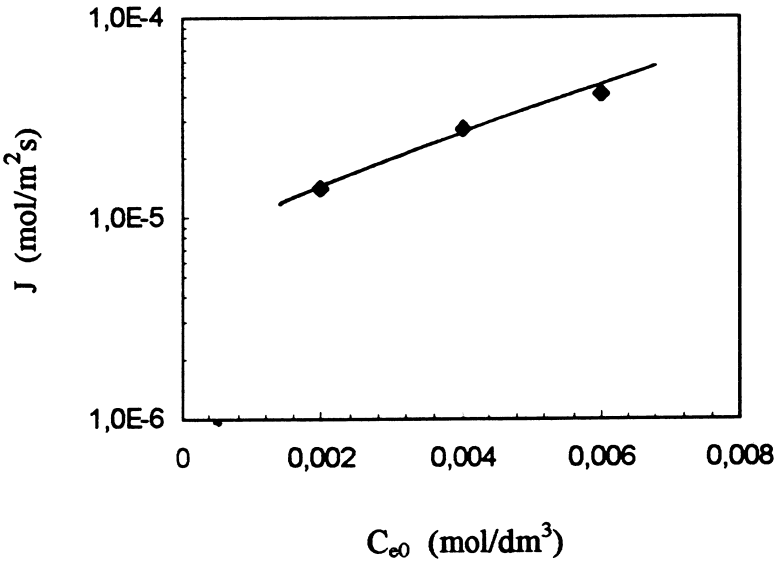

FIG. 5 Effect of initial solute concentration in the external phase on the mass transfer flux. pH = 2.0; C_{i0} = 1.5 mol/dm^3. The other operating conditions are as shown in Table 1.

the process continues. Therefore, it is reasonable that the emulsion globule diffusion resistance decreases with increasing internal stripping reagent concentration. However, compared with the external phase pH and the carrier concentration, it seems that the concentration of internal stripping reagent is a less sensitive factor affecting the values of Δ_e and Δ_m, implying that it is not a key factor determining the overall process.

The effect of initial L-Trp concentration in the external phase on the initial flux is shown in Fig. 5. The initial flux increases linearly with increasing initial L-Trp concentration. Table 6 shows the variations of both the fractional resistances with initial L-Trp concentration. Both the fractional

Stripping Reagent Concentrations

E = 50%		E = 70%		E = 90%	
Δ_e	Δ_m	Δ_e	Δ_m	Δ_e	Δ_m
0.315	0.685	0.301	0.699	0.288	0.712
0.328	0.672	0.318	0.682	0.308	0.692
0.335	0.665	0.327	0.673	0.319	0.681

TABLE 6
Fractional Resistances at Various Initial

C_{e0} (mol/dm^3)	E = 1%		E = 10%		E = 30%	
	Δ_e	Δ_m	Δ_e	Δ_m	Δ_e	Δ_m
2.0×10^{-3}	0.356	0.644	0.351	0.649	0.339	0.661
4.0×10^{-3}	0.355	0.645	0.344	0.656	0.322	0.678
6.0×10^{-3}	0.354	0.646	0.338	0.662	0.307	0.693

Note: pH = 2.0, C_{HL0} = 0.096 mol/dm^3, C_{i0} = 1.5 mol/dm^3.

resistances seem to be independent of the external initial L-Trp concentration in the initial period. Thus, the initial flux is proportional to the external L-Trp concentration, as shown in Fig. 5. In addition, Table 6 shows that at the same extraction ratio, the emulsion globule diffusion resistance increases slowly with increasing initial L-Trp concentration. From the viewpoint of kinetics, the initial solute concentration, like the internal stripping reagent concentration, is not a key factor governing the overall process compared with the external phase pH and carrier concentration. The computed results represented by the solid curves are in very close agreement with the experimental data.

Because the effects of membrane breakage and emulsion swelling on mass transfer were neglected in the mathematical development, the stability of emulsion was also examined. Table 7 shows the breakage and swelling of emulsion under typical conditions with increasing stirring speed. These results are relatively lower compared with Shen's data (4), showing a higher emulsion stability. Although the breakage and swelling somewhat reduces the extraction ratio of L-Trp, it can be reasonably predicted that the effects of these factors on the Δ_e and Δ_m values are very small under the present experimental conditions.

TABLE 7
Stability of Emulsion with Stirring Speed

Stirring speed (rpm)	150	200	250	300	350
Sw	5%	7%	10%	12%	17%
Br	7%	9%	11%	14%	18%

Note: pH = 2.0, $C_{e0} = 2 \times 10^{-3}$ mol/dm^3, C_{HL0} = 0.096 mol/dm^3, C_{i0} = 1.5 mol/dm^3.

L-Trp Concentrations

$E = 50\%$		$E = 70\%$		$E = 90\%$	
Δ_e	Δ_m	Δ_e	Δ_m	Δ_e	Δ_m
0.328	0.672	0.318	0.682	0.308	0.692
0.303	0.697	0.285	0.715	0.270	0.730
0.281	0.719	0.259	0.741	0.240	0.760

CONCLUSIONS

The extraction of L-Trp with the ELM process using D2EHPA as a carrier was performed. The effects of various operational conditions on the initial mass transfer flux were investigated. Furthermore, the fractional resistances of external phase diffusion and emulsion globule diffusion to the overall permeation process were calculated by the proposed model. Thus, the rate-controlling steps for the overall process were identified. For higher external phase pH and/or higher carrier concentration, the overall process is mainly governed by the external phase diffusion. Thus, the overall resistance is approximately equal to the external phase diffusion resistance, and the initial flux is almost independent of the external pH and the carrier concentration. On the other hand, for lower external pH and/or lower carrier concentration, the emulsion globule diffusion is a rate-controlling step for the overall permeation process. Therefore, increasing the external pH and/or the carrier concentration leads to an increase in the initial flux. However, in the majority of cases, the overall process is determined by the combined effects of both the external phase diffusion and the emulsion globule diffusion. Compared with the external phase pH and carrier concentration, the concentrations of internal stripping reagent and the external initial solute are unimportant factors determining the overall process. When the calculated results by the proposed model were compared with the experimental data, it was found that the present model can be applied to the analysis of the mass transfer resistance in L-Trp ELM extraction.

NOMENCLATURE

A	zwitterion of L-Trp
A^-	anion of L-Trp
A^+	cation of L-Trp
Br	breakage (%)
C_{A^+}	concentration of L-Trp cation (mol/dm^3)

C_c concentration of L-Trp-carrier complex in membrane phase (mol/dm^3)
C_e concentration of L-Trp in external aqueous phase (mol/dm^3)
C_{e0} initial concentration of L-Trp in external aqueous phase (mol/dm^3)
C_H concentration of hydrogen ion in external phase (mol/dm^3)
C_{HL} concentration of carrier concentration in membrane phase (mol/dm^3)
C_{i0} initial concentration of internal phase stripping reagent (mol/dm^3)
D_A diffusivity of L-Trp zwitterion in aqueous phase (m^2/sec)
D_{A^+} diffusivity of cation of L-Trp in aqueous phase (m^2/sec)
D_c diffusivity of the complex in membrane phase (m^2/sec)
D_{eff} effective diffusivity of L-Trp—carrier complex through membrane phase (m^2/sec)
E extraction ratio of L-Trp defined by Eq. (13)
HL carrier D2EHPA in organic phase
J_0 initial flux (mol/m^{2}sec)
Ka_1 dissociation constant of cation of L-Trp
Ka_2 dissociation constant of zwitterion of L-Trp
k_e external phase mass transfer coefficient (m/sec)
K_e potassium ion concentration in the external phase (mol/dm^3)
K_{ex} extraction equilibrium constant
K_i potassium ion concentration in the internal phase (mol/dm^3)
K_T overall mass transfer coefficient defined by Eq. (16) (m/sec)
n number of emulsion globules
R Sauter mean radius of w/o emulsion globule (m)
R_e external diffusion resistance (sec/m)
R_f radius of reaction front (m)
R_i radius of internal phase droplet (m)
R_I radius of inner core of emulsion globule (m)
R_m emulsion globule diffusion resistance (sec/m)
Sw swelling (%)
T temperature (K)
t time (sec)
V_e volume of external aqueous phase (m^3)
V_i volume of internal aqueous phase (m^3)
V_m volume of membrane phase (m^3)

Subscripts

0 initial value
c solute–carrier complex
e external aqueous phase
f final value

i	internal aqueous phase
m	membrane phase
T	sum of all values

Greek Letters

δ	thickness of the thin oil layer (m)
ϕ_i	volume fraction of internal phase to emulsion globule defined by Eq. (21)
θ_i	volume fraction of internal phase droplets defined by Eq. (10)
Δ_e	fractional resistance of external phase diffusion to the overall process defined by Eq. (12)
Δ_m	fractional resistance of membrane diffusion to the overall process defined by Eq. (13)

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