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Rapid Reaction-Diffusion Model for the Enantioseparation of Phenylalanine across Hollow Fiber Supported Liquid Membrane

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Abstract: This paper deals with the rapid reaction-diffusion model of the transport and enantioseparation factor of (D/L)-phenylalanine across hollow fiber supported liquid membranes. Mass transfer resistance of the boundary layer in the tube side and the boundary layer in the shell-side, diffusion in the membrane phase, and interfacial chemical reactions at the liquid membrane interfaces are taken into account in the model equations. The experimental results show that the proposed model can simulate the concentration of the (D/L)-phenylalanine and the separation factor of the enantioselective process satisfactorily. It is simply a mathematical model which can be easily used to predict the concentration of the enantiomers and the separation factor of the enantioseparation process.

Keywords: Enantioseparation, hollow fiber supported liquid membrane, phenylalanine, mass transfer, model

INTRODUCTION

It is widely known that different enantiomers of a drug can have vastly different pharmacological activities. So it is imperative to separate these

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closely related chiral isomers to obtain stereochemically pure drugs (1–3). Separation techniques such as crystallization, kinetic resolution, chiral chromatography, and membrane technology have been used for the production of pure drugs. Over recent years, attention has increased in the use of liquid membrane as selective enantioseparation barriers (4–6). Hollow fiber supported liquid membrane (SLM) is a kind of liquid membrane which offers many advantages such as high selectivity, high efficiency of separation, high enrichment efficiency and less use of the organic phase than in the classical solvent extraction process (7–11).

Hollow fiber SLM containing active chiral carriers provide a simple, stable means for studying the transport and selective separation of chiral drugs from dilute aqueous solutions. It is a promising enantioseparation method which has potential to scale-up. The most frequent applications of hollow fiber SLM systems for racemic resolution have been in the concentration and selective resolution of chiral amino acids (12–14). Hollow fiber SLMs are usually prepared by filling the pores with the organic liquid composed of the chiral carrier and the diluent.

Although mathematical models of liquid membrane systems for separation of heavy metal ions have been presented by some workers (15–18), few mathematical models for the enantioseparation of chiral drugs have been published at present.

In this work, a mathematical rapid reaction-diffusion model is presented for analyzing and predicting the transport of enatiomers of (D/L)-phenylalanine in a hollow fiber SLM process. The proposed model takes into account the mass transfer resistance of boundary layer in strip phase inside the hollow fiber and boundary layer in feed phase, diffusion in the membrane phase and rapid interfacial chemical reactions at the liquid membrane interfaces. It is simply a mathematical model which can be easily used to predict the concentration of the (D/L)-phenylalanine and the separation factor of the enantioseparation process.

THEORY

In this paper we propose a mechanism for the transport of enantiomers through a hollow fiber SLM. Consider a porous carrier-facilitated SLM used for separating D-phenylalanine and L-phenylalanine of the racemic mixtures. The membrane consists of a chiral carrier dissolved in a water immiscible organic diluent.

In order to simplify the mathematics and model development, the following assumptions are made:

1. An ideal system exists under complete mixing and constant temperature operation;
2. Constant physical and transport properties;

3. The membrane phase is completely immiscible with the aqueous phase;
4. The volume of the liquid membrane phase is neglected relative to the volume of the feed phase and the strip phase.
5. The reaction rate of formation of the enantiomer-carrier complex at the interface is rapid enough to ignore the influence of the reaction on the resistance of the process.

The mechanism and the concentration profiles are schematically illustrated in Fig. 1. The following steps are necessary:

First, the transport of the solute from the bulk of the feed phase to the interface with the liquid membrane, the flux of the solute is expressed by

$$j_f = k_f(C_f - C'_f) \tag{1}$$

Second, formation of the enantiomer-carrier complex at the interface, the flux of the solute is expressed by

$$j_{r1} = k_1 C'_f - k_{-1}C(0, t) \tag{2}$$

Third, diffusion of the complex through the liquid membrane phase to the interface with the strip phase, the flux of the solute is expressed by

$$j_{m1} = -D_e[\partial C(0, t)/\partial x] \tag{3}$$

$$j_{m2} = -D_e[\partial C(x_0, t)/\partial x] \tag{4}$$

Fourth, decomposition of the complex at the interface, the reaction flux of the solute is expressed by

$$j_{r1} = k_{-2}C(x_0, t) - k_2 C'_s \tag{5}$$

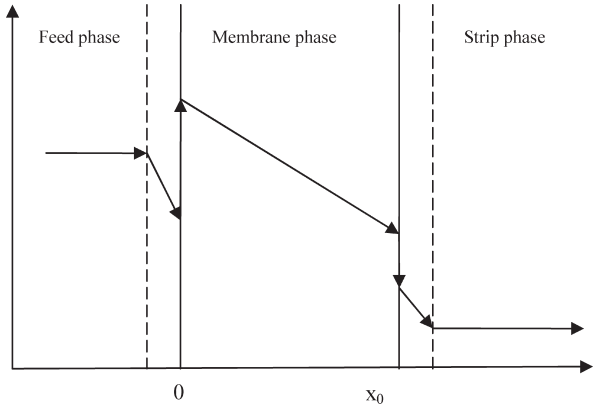

Figure 1. Schematic representation of the linear concentration profiles within the aqueous feed phase boundary layer, the organic membrane matrix, and the aqueous strip boundary layer.

Fifth, transport of the solute from the interface to the bulk of the strip phase, the flux of the solute is expressed by

$$j_s = k_s(C'_s - C_s) \tag{6}$$

where x_0 is the thickness of the membrane, x is the distance in the membrane, t is the time, c is the concentration of the enantiomers, $k_{1j}(k_{2j})$ and $k_{-1j}(k_{-2j})$ refer to the forward interfacial enantioselective reaction rate constants and the backward interfacial enantioselective reaction rate constants, respectively, k_f (19) and k_s (20) refer to the mass transfer coefficients in extraction boundary layer and strip boundary layer respectively.

$$k_f = 1.25\frac{D_f}{d_o}\left(Re\frac{d_o}{L}\right)^{0.93}Sc^{0.33} \tag{7}$$

$$k_s = 1.1615\frac{D_s}{d_i}\left(ReSc\frac{d_i}{L}\right)^{1/3} \tag{8}$$

Where d is the diameter, L is the length of the hollow fiber module, D is the free bulk diffusion coefficient for the solute calculated using the Wilke–Chang (21) equation, and D_e is the effective diffusivity in the membrane and is defined as

$$D_e = D \cdot \varepsilon'/\tau' \tag{9}$$

$$D = 7.4 \times 10^{-8}(\varphi M_B)^{0.5}T/(\mu_B V_A^{0.6}) \tag{10}$$

where ε' is the porosity of the membrane, and τ' is the tortuosity factor which takes into account the difference between the effective thickness and the physical thickness.

If the time is enough for these processes to reach a steady-state, the solute concentration of the feed phase, the liquid membrane phase, and the strip phase will come to a state of homeostasis. The mass-conservation equation and the concentration expression are given by:

$$V_f C_{f0} + V_s C_{s0} = V_f C_f + V_s C_s + V_m C_m \tag{11}$$

$$C_m = C_f K_{e1} = C_s K_{e2} \tag{12}$$

Then, for this pseudo steady-state assumption, the solute concentration expression of the feed phase (C_f), the liquid membrane phase (C) and the

strip phase (C_s) can be obtained as:

$$C_m = \frac{V_f C_{f0} + V_s C_{s0}}{V_f/K_{e1} + V_s/K_{e2}} \tag{13}$$

$$C_f = \frac{V_f C_{f0} + V_s C_{s0}}{V_f + V_s K_{e1}/K_{e2}} \tag{14}$$

$$C_s = \frac{V_f C_{f0} + V_s C_{s0}}{V_s + V_f K_{e2}/K_{e1}} \tag{15}$$

As for transitional state, equations describing the concentrations of the solute in the supported liquid membrane (SLM), the feed phase (FP), and the strip phase (SP) are as follows.

SLM:

$$\frac{\partial C_j}{\partial t} = D_e \frac{\partial^2 C_j}{\partial x^2} \quad (0 < x < x_0) \tag{16}$$

$$t = 0, \quad C_j = 0 \quad (0 < x < x_0) \tag{16a}$$

$$t \to \infty \quad C_j = \frac{V_f C_{f0j} + V_s C_{s0j}}{V_f/K_{e1j} + V_s/K_{e2j}} \quad (0 < x < x_0) \tag{16b}$$

$$x = 0 \quad D_e \frac{\partial C_j(0, t)}{\partial x} = k_f\left[C_j(0, t)(k_{-1j}/k_{1j}) - C_{fj}\right] \quad (t > 0) \tag{16c}$$

$$x = x_\phi \quad D_e \frac{\partial C_j(x_0, t)}{\partial x} = k_s\left[C_{sj} - C_j(x_0, t)(k_{-2j}/k_{2j})\right] \quad (t > 0) \tag{16d}$$

FP:

$$V_f \frac{dC_{fj}}{dt} = A \cdot D_e \frac{\partial C_j(0, t)}{\partial x} \tag{17}$$

$$t = 0, \quad C_{fj} = C_{f0j} \tag{17a}$$

$$t \to \infty, \quad C_{fj} = \frac{V_f C_{f0j} + V_s C_{s0j}}{V_f + V_s K_{e1j}/K_{e2j}} \tag{17b}$$

SP:

$$V_s \frac{dC_{sj}}{dt} = -A \cdot D_e \frac{\partial C_j(x_0, t)}{\partial x} \tag{18}$$

$$t = 0, \quad C_{sj} = C_{s0j} \tag{18a}$$

$$t \to \infty, \quad C_{sj} = \frac{V_f C_{f0j} + V_s C_{s0j}}{V_s + V_f K_{e2j}/K_{e1j}} \tag{18b}$$

Where A is the liquid membrane area, V_f and V_s are the volumes of the feed phase and the strip phase, respectively, c (x, t) is the solute concentration within the supported liquid membrane and is defined as the moles per unit

membrane volume, K_{e1} and K_{e2} refer to the equilibrium constant of interfacial chemical reaction in the feed phase side and the strip phase side respectively, subscript "j" refer to the enantiomeric form.

The equations can be cast into dimensionless form by defining:

$$y = x/x_0, \quad \tau = D_e \cdot t/x_0^2, \quad E_{fj} = C_{fj}/C_{f0j}, \quad E_{sj} = C_{sj}/C_{f0j}, \quad E_{mj} = C_j/C_{f0j} \tag{19a}$$

$$\beta = C_{s0j}/C_{f0j}, \quad K_{e1j} = k_{1j}/k_{-1j}, \quad K_{e2j} = k_{2j}/k_{-2j}, \quad K_f = k_f \cdot x_0/D_e \tag{19b}$$

$$K_s = k_s \cdot x_0/D_e, \quad \gamma_f = A \cdot x_0/V_f, \quad \gamma_s = A \cdot x_0/V_s, \quad \gamma_f/\gamma_s = V_s/V_f \tag{19c}$$

SLM:

$$\frac{\partial E_{mj}}{\partial \tau} = \frac{\partial^2 E_{mj}}{\partial y^2} \tag{20}$$

$$t = 0, \quad C_j = 0 \tag{20a}$$

$$t \to \infty, \quad E_{mj} = \frac{K_{e1j} \cdot K_{e2j}(\gamma_s + \beta\gamma_f)}{\gamma_f K_{e1j} + \gamma_s K_{e2j}} \tag{20b}$$

$$y = 0, \quad \frac{\partial E_{mj}(0, \tau)}{\partial y} = \frac{E_{mj}(0, \tau) - E_{fj} K_{e1j}}{K_{e1j}/K_f} \tag{20c}$$

$$y = 1, \quad \frac{\partial E_{mj}(1, \tau)}{\partial y} = \frac{E_{sj} K_{e2j} - E_{mj}(1, \tau)}{K_{e2j}/K_s} \tag{20d}$$

FP:

$$\frac{dE_{fj}}{d\tau} = \gamma_f \frac{\partial E_{mj}(0, \tau)}{\partial y} \tag{21}$$

$$\tau = 0, \quad E_{fj} = 1 \tag{21a}$$

$$\tau \to \infty, \quad E_{fj} = \frac{K_{e2j}(\gamma_s + \beta\gamma_f)}{\gamma_f K_{e1j} + \gamma_s K_{e2j}} \tag{21b}$$

SP:

$$\frac{dE_{sj}}{d\tau} = \gamma_s \frac{\partial E_{mj}(1, \tau)}{\partial y} \tag{22}$$

$$\tau = 0, \quad E_{sj} = \beta \tag{22a}$$

$$\tau \to \infty, \quad E_{sj} = \frac{K_{e1j}(\gamma_s + \beta\gamma_f)}{\gamma_f K_{e1j} + \gamma_s K_{e2j}} \tag{22b}$$

Then, using Laplace transform techniques, the dimensionless concentration of the enantiomers in the feed phase, the strip phase, and the

membrane phase can be obtained as:

$$E_{fj} = \frac{K_{e2j}(\gamma_s + \beta\gamma_f)}{\gamma_f K_{e1j} + \gamma_s K_{e2j}} + \frac{\gamma_f(K_{e1j} - \beta K_{e2j})}{\gamma_f K_{e1j} + \gamma_s K_{e2j}} \exp(-\lambda_j \tau) \quad (23)$$

$$E_{sj} = \frac{K_{e1j}(\gamma_s + \beta\gamma_f)}{\gamma_f K_{e1j} + \gamma_s K_{e2j}} - \frac{\gamma_s(K_{e1j} - \beta K_{e2j})}{\gamma_f K_{e1j} + \gamma_s K_{e2j}} \exp(-\lambda_j \tau) \quad (24)$$

where λ_j is defined as:

$$\lambda_j = \frac{\gamma_f K_{e1j} + \gamma_s K_{e2j}}{1 + K_{e1j}/K_f + K_{e2j}/K_s} \quad (25)$$

For the enantioselective separation process with selectivity for the D-isomer, the separation factor, α, defined by

$$\alpha = \frac{j_D}{j_L} = \frac{E_{sD} - E_{sD0}}{E_{sL} - E_{sL0}} \quad (26)$$

Then, combined with the Eq. (22), it can be obtained as

$$\alpha = \left(\frac{[K_{e1D}(\gamma_s + \beta\gamma_f) - \gamma_s(K_{e1D} - \beta K_{e2D}) \exp(-\lambda_D \tau)]}{(\gamma_f K_{e1D} - \gamma_s K_{e2D})} - E_{sD0} \right) / \left(\frac{[K_{e1L}(\gamma_s + \beta\gamma_f) - \gamma_s(K_{e1L} - \beta K_{e2L}) \exp(-\lambda_L \tau)]}{(\gamma_f K_{e1L} - \gamma_s K_{e2L})} - E_{sL0} \right) \quad (27)$$

since the solvent system of the feed phase is the same as that of the strip phase for the resolution of racemic (D/L)-phenylalanine, then Eqs. (24), (25), and (27) can be simplified as:

$$\lambda_j = \frac{\gamma_f + \gamma_s}{1/K_{e1j} + 1/K_f + 1/K_s} \quad (28)$$

$$E_{sj} = \frac{\gamma_s}{\gamma_f + \gamma_s} - \frac{\gamma_s}{\gamma_f + \gamma_s} \exp(-\lambda_j \tau) \quad (29)$$

$$\alpha = [1 - \exp(-\lambda_D \tau)]/[1 - \exp(-\lambda_L \tau)] \quad (30)$$

EXPERIMENTAL

The experiments were carried out on the resolution of racemic (D/L)-phenylalanine using copper(II) N-decyl-(L)-hydroxyproline as a chiral carrier in a membrane solvent (50%:50% volume basis hexanol:decane). The organic phase was prepared by adding CuN_2 (10 mM) to a 50%:50% (volume basis) mixture of hexanol/decane, and was then contacted with an equal volume of aqueous copper acetate solution (Cu^{2+}: 5 mM) at pH 4.8. The aqueous copper acetate solution was prepared by adding cupric sulfate to acetate buffer. The organic and aqueous solutions were contacted for 48 hours.

The experimental apparatus used in this enantioseparation process is shown in Fig. 2. In this case, the feed phase and the stripping phase were delivered by peristaltic pump in total-recycle mode, flows through the shell side and the tube side of the hollow fiber module in co-current mode.

The hollow fiber membrane was soaked in 0.1 mol/l Na_2HPO_4/H_3PO_4 buffer solution containing 2 mmol/l cetyl trimethylammonium bromide (CTMAB, surfactant) for at least 48 hours in order to strengthen its hydrophobility at the beginning. The solution of chiral selectors in the membrane pores was immobilzed by pumping the solution of chiral selectors into the tube-side of the hollow fiber module. This solution was circulated for 24 hours in order to distribute the dissolved CuN_2 molecules into the membrane pores. The organic phase can be excellent to dissolve the carrier and to separate the aqueous feed and stripping phase.

The feed and strip solutions were prepared by adding perchloric acid to deionized water until the solution pH was 2.0. A racemic mixture of the phenylalanine was dissolved in the feed solution (solute concentration: 10 mM). The feed phase was pumped into the shell-side while the strip solution into the tube-side. At various times, 100 μL samples were removed from the strip solution and the D and L-phenylalanine concentrations were determined using a C_{18} column. The HPLC used for amino acid analysis was a LC-2010A. The UV detector used a wavelength of 250 nm. The column temperature was maintained at 25°C.

RESULTS AND DISCUSSIONS

Determination of the Parameters

The polyvinylidene fluoride (PVDF) hollow fiber membrane used in this experiment has an effective area of 0.095 m^2. The configuration is shown in Table 1.

The equilibrium constant and the forward enantioselective reaction rate constants of both enantiomers were determined by equilibrium and kinetic studies detailed in Pickering and Chaudhuri (22). The assumed parameters characterizing this system are: $K_{e1L} = 0.149$, $K_{e2L} = 0.149$, $K_{e1D} = 0.228$,

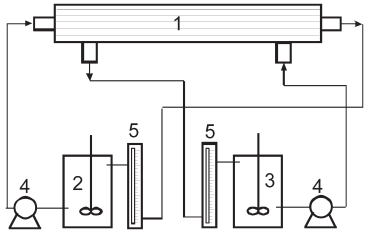

Figure 2. Experimental apparatus. 1. Hollow fiber membrane module; 2. Stripping phase container; 3. Feed phase container; 4. Peristaltic pump; 5. Flowmeter.

Table 1. Characteristics of PVDF hollow fiber membrane

External/ internal diameter	Temperature range	Pore size	PH range	Operation pressure
1.2/0.8 mm	5∼45°C	0.22 μm	2∼10	≤0.12 MPa

$K_{e2D} = 0.228$, $k_{1L} = 5.2 \times 10^{-4}$ m(sM)$^{-1}$, $k_{1D} = 8.5 \times 10^{-4}$ m(sM)$^{-1}$, $A = 950\ cm^2$, $x_0 = 0.02$ cm, $V_f = 200\ cm^3$, $V_s = 200\ cm^3$, $C_{f0} = 0.01$ M, $C_{s0} = 0.0$, $D_e = 1.3 \times 10^{-7}\ cm^2/s$, $k_f = 4.51 \times 10^{-6}$ cm/s, $k_s = 1.84 \times 10^{-4}$ cm/s.

Experimental Data and Model Prediction of the Dimensionless Concentration in the Feed Phase and the Strip Phase

The validity of Eq. (29) has been demonstrated by experiments. By using those parameters, the computational results are shown by solid line and dot line in Fig. 3 which are in good agreement with the experimental data. Therefore, it can be concluded that Eq. (29) can simulate the dimensionless concentrations well.

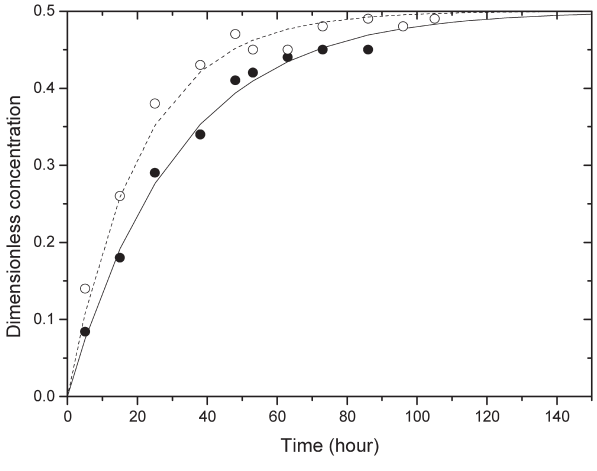

Figure 3. The model prediction of dimensionless concentration of (D/L)-phenylalanine vs. the experimental data. ● dimensionless concentration of L-phenylalanine in the stripping phase (E_{sL}); ○ dimensionless concentration of D-phenylalanine in the stripping phase (E_{sD}); Solid line: model prediction of E_{sL}; Dot line: model prediction of E_{sD}.

It indicates that the dimensionless concentrations change rapidly in the first few hours of operation and then change slowly to reach equilibrium. The equilibrium dimensionless concentration of E_{sD} and E_{sL} are equal to 0.5 because the solvent system of the strip phase is the same as that of the feed phase. As for the solution used in this system, the dimensionless concentration of the L-phenylalanine in the striping phase can be received as:

$$E_{sL} = 0.5 - 0.5\exp\left(-9.2 \times 10^{-4}t\right) \tag{31}$$

And it also indicated that the concentration of D-phenylalanine is higher than that of L-phenylalanine. The slope of D-phenylalanine is steeper than the slope of L-phenylalanine. The concentration difference between the D- and the L-phenylalanine in the strip solution shows a maximum. This maximum concentration difference is determined by the ratio of the enantioselective equilibrium constants of the two enantiomers. In this case, the maximum was shown at the time of 30 hours. This result can be used as a guideline to determine the optimum operation time for the process.

Experimental Data and Model Prediction of the Separation Factor

Figure 4 shows the separation factor of the enantioselective separation process. The computational results are shown by a solid line which is in good agreement with the experimental data. Therefore, it can be concluded that Eq. (30) can simulate the dimensionless concentrations well.

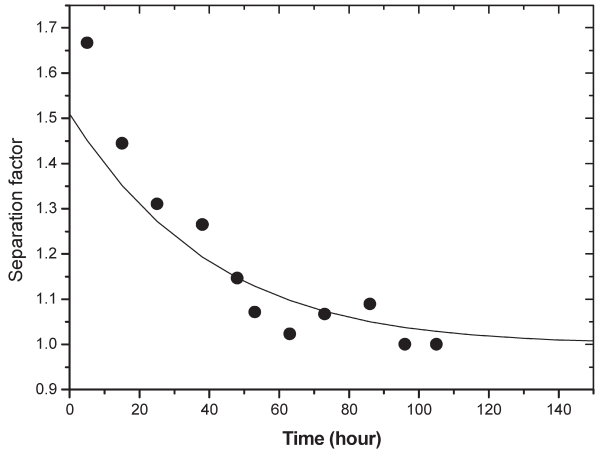

Figure 4. The model prediction of separation factor vs. the experimental result. ● experimental data of separation factor; Solid line: results computed by Eqs. (30).

It also can be seen that the initial separation factor is the highest one achieved during the run, and it declines rapidly in the first few hours, then it approaches to the value of 1 as time going on. According to the Eq. (30), the initial separation factor can be deduced as:

$$\lim_{\tau \to 0} \alpha = \frac{\lambda_D}{\lambda_L} \tag{32}$$

In this case, because the solvent system of the feed solution is the same as that of the strip solution, the equations $\gamma_f = \gamma_s$ can be deduced, and Eq. (32) can be simplified as:

$$\lim_{\tau \to 0} \alpha = \frac{1/K_{e1L} + 1/K_f + 1/K_s}{1/K_{e1D} + 1/K_f + 1/K_s} \tag{33}$$

This result is similar as that studied by Jason D. Clark (13) but contains more factors. It means that the ratio of the enantioselective equilibrium constants for the D- and L-phenylalanine of amino acids may be used to predict the maximum degree of separation that could be expected under ideal conditions. For an organic phase consisting of 50–70% decane:50–30% hexanol (v/v) solvent, this initial separation is calculated to be about 1.5.

It also indicates that there is an obvious deviation of the computational results from the experimental data in the first few hours of the experiment. It is because that K_{eL} and K_{eD} include the distribution coefficient of the uncomplexed enantiomers, they are not real equilibrium constants and will vary with the organic solvent and the pH in the aqueous phase during the first stage of the operation.

CONCLUSION

A rapid reaction-diffusion model has been developed to analyze the mass transfer rates and the separation factor of D- and L-phenylalanine across hollow fiber supported liquid membranes containing chiral carrier. The mass transfer resistance of the boundary layer in the strip phase inside the hollow fiber and the boundary layer in the feed phase, the diffusion in the membrane phase and the rapid interfacial chemical reactions at the liquid membrane interfaces are taken into account comprehensively. The model was found to be a very useful design equation, the experimental results show that the proposed model can simulate the concentration of the enantiomers and the separation factor of the enantioselective process satisfactorily. And the model can be easily used to predict the concentration and the separation factor of the enantioseparation process. It is expected that the model could be applied to the separation of other chiral drugs by changing a few parameters such as diffusion coefficient and equilibrium constant, depending on the chiral carrier and the enantiomers of interest.

LIST OF SYMBOLS

A	membrane area (cm^2)
C	concentration within membrane (moles per unit volume of membrane)
C_f	bulk concentration in the feed phase (moles per unit volume)
C_s	bulk concentration in strip phase (moles per unit volume)
E	dimensionless concentration within membrane
E_f	dimensionless concentration in the feed phase
E_s	dimensionless concentration in the strip phase
D_e	effective diffusivity (cm^2/s)
D_0	free bulk diffusion coefficient (cm^2/s)
FP	the feed phase
j	solute flux (mol/cm^2s)
k_1	forward interfacial enantioselective reaction rate constants in feed phase (m/sM)
k_{-1}	backward interfacial enantioselective reaction rate constants in feed phase (m/sM)
k_2	forward interfacial enantioselective reaction rate constants in strip phase (m/sM)
k_{-2}	backward interfacial enantioselective reaction rate constants in strip phase (m/sM)
k_f	mass transfer coefficient in extraction boundary layer (cm/s)
k_s	mass transfer coefficient in strip boundary layer (cm/s)
K_{e1}	equilibrium constant of interfacial chemical reaction in feed phase
K_{e2}	equilibrium constant of interfacial chemical reaction in strip phase
SLM	supported liquid membrane
SP	the strip phase
t	real time (hour)
T	absolute temperature
V_f	volume of feed phase (cm^3)
V_s	volume of strip phase (cm^3)
x_0	membrane thickness (cm)
x	spatial coordinate
y	dimensionless coordinate, x/x_0

Greek Letters

α	separation factor
β	initial dimensionless concentration
γ	constant containing area, thickness and volume

λ	constant containing γ, A, and K_e
τ	dimensionless form of time
ε'	porosity of the membrane
τ'	tortuosity of the membrane pores

Subscripts

0	initial concentration
f	denotes feed phase
j	enantiomeric form
m	membrane
r	reaction
s	denotes strip phase

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