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Modeling of Facilitated Transport of Phenylalanine by Emulsion Liquid Membranes with Di(2-ethylhexyl)phosphoric Acid as a Carrier

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ABSTRACT

A mathematical model is developed in this paper to simulate the facilitated transport of phenylalanine (Phe) in emulsion liquid membrane (ELM) systems with di(2-ethylhexyl)phosphoric acid as a carrier. The model takes into account the mass transfer in both the external aqueous phase and the organic membrane phase interfacial reaction as well as membrane breakage during agitation. The model is tested by comparing theoretical predications with experimental results using Phe extraction by ELM processes. It is found that the model is valid for simulating the facilitated transport of Phe with ELM under various experimental conditions.

Key Words. Modeling; Facilitated transport; Phenylalanine; Emulsion liquid membrane; Di(2-ethylhexyl)phosphoric acid

INTRODUCTION

Recovery of amino acids from dilute aqueous solutions, such as fermentation broths and wastewaters, with concentrations lower than 10% (w/w) have high separation and purification costs due to complex and energy intensive recovery technology (1). Emulsion liquid membrane extraction has been tried as an alternative to the conventional process because of its outstanding advantages such as large specific surface areas for extraction, very fast extraction rates, simultaneous separation and concentration in a single step, and efficient

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recovery of solutes from low concentration streams. Recently, many studies have been carried out to extract amino acids from dilute aqueous solutions by the emulsion liquid membrane (ELM) process (2–6). Thus, a higher extraction ratio can be attained in a relatively short contact time under the optimum operation conditions in these reports, which shows the ELM process has now reached the practical application stage.

While considerable effort has been directed toward extracting amino acids by the ELM technique, very little attention has been paid to developing the mathematical model of facilitated transport of amino acids in ELM systems. In the present paper, in which di(2-ethylhexyl)phosphoric acid (D2EHPA) is used as the carrier molecule, Span 80 as the surfactant, kerosene as the membrane phase solvent, and chlorhydric acid as the stripping reagent, we propose a general mathematical model for the facilitated transport of amino acids. The model considers mass transfer in the external phase, the solute–carrier chemical reaction, diffusion in the globule as described by a advancing front model (7), and the stripping reaction. The leakage effect of the internal phase due to membrane breakage is also discussed in the model development. The proposed model satisfactorily predicts the experimental results of the batch extraction of phenylalanine (Phe).

MODELING DEVELOPMENT

Mechanism

The existing forms of an α-amino acid with a carboxylic group and an amino group in a aqueous solution are dependent on pH as follows:

$$\underset{(A^+)}{H_3N^+\,CHRCOOH} \underset{+H^+}{\overset{-H^+}{\Longleftrightarrow}} \underset{(A)}{H_3N^+\,CHRCOO^-} \underset{+H^+}{\overset{-H^+}{\Longleftrightarrow}} \underset{(A^-)}{H_2NCHRCOO^-} \tag{1}$$

$$K_a = \frac{[H_3N^+CHRCOO^-][H^+]}{[H_3N^+CHRCOOH]} \tag{2}$$

$$K_a' = \frac{[H_2NCHRCOO^-][H^+]}{[H_3N^+CHRCOO^-]} \tag{3}$$

Here A^+, A, and A^- are the cation, zwitterion, and anion of the amino acid, respectively. As long as a pH lower than the acid pK_a value is maintained, amino acid exists in the form of cation. The dissociated acid concentration present in the aqueous solution is related to the pH and acid pK_a according to the Hasselbach–Henderson equation:

$$[A^+] = [A]_t\left[1 - \left(\frac{1}{1 + 10^{pK_a - pH}}\right)\right] \tag{4}$$

where $[A]_t = [A^+] + [A] + [A^-]$. At pH − p$K_a$ = 2, A^+ represents

approximately 99% of the total acid present (dissociated plus undissociated forms).

D2EHPA is a cation exchange extractant that has been used as a carrier to transport of amino acids (2, 3). Each amino acid has two types of functional groups: carboxylic (pK_a) and amino (pK'_a). These groups are affected by the pH. To ensure that these molecules are positively charged, in the ELM systems the pH in the external phase are chosen to be $pH < (pK_a + pK'_a)/2$. In this case, assuming that the organic phase and aqueous phase are immiscible and that the D2EHPA is insoluble in the aqueous phase, furthermore assuming that an equilibrium exists at the external phase–membrane phase interface, the proposed reaction for amino acid extraction by D2EHPA is

$$A^+ + 2\overline{(HL)_2} \Leftrightarrow \overline{AL(HL)_3} + H^+ \tag{5}$$

and the equilibrium constant for the above reaction is defined as

$$K_{ex} = \frac{[\overline{AL(HL)_3}]\cdot[H^+]}{[A^+]\cdot[\overline{(HL)_2}]^2} \tag{6}$$

Then the solute–carrier complex diffuses across the membrane to the internal phase reaction front, where the amino acid is immediately stripped into the internal phase by an instantaneous irreversible reaction since a high concentration of HCl is used in the internal phase as a stripping agent. Here $\overline{(HL)_2}$ and $\overline{AL(HL)_3}$ are the dimer of D2EHPA and solute–carrier complex in the membrane phase, respectively. K_{ex} is the equilibrium constant of Eq. (5). The distribution ratio α is defined as

$$\alpha = \frac{[\overline{AL(HL)_3}]}{[A_T]} = \frac{[\overline{AL(HL)_3}]}{[A] + [A^+] + [A^-]} = K_{ex}\cdot\frac{[\overline{(HL)_2}]^2}{[H^+] + K_a} \tag{7}$$

The overall transport of amino acids from the extemal aqueous phase to the internal aqueous phase can be described by the following transport and reaction processes.

1. Transport of amino acid from the external phase bulk to the aqueous boundary layer, and diffusion through it to the external–membrane interface.
2. Chemical reaction at the interface to form a complex with the carrier.
3. Diffusion of the carrier–solute complex through the membrane.
4. An instantaneous irreversible decomplexation reaction occurs at the internal phase–membrane interface with liberation of the solute and enrichment of the solute in the internal phase.
5. Diffusion of empty carrier back to the external–membrane interface.

The complex ($\overline{AL(HL)_3}$) under its own concentration gradient diffuses to the strip side, where A^+ is replaced by H^+. The amino acid is released in the

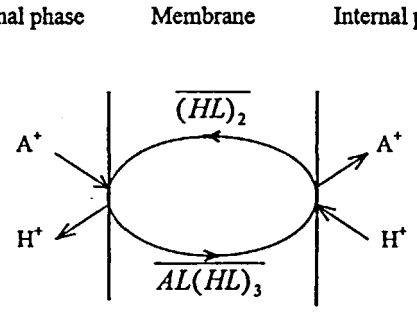

FIG. 1 Mechanism of amino acid facilitated transport by ELM.

internal phase and the carrier diffuses back to the feedside of the membrane. The total effect of this shuttle mechanism is the transport of amino acid from the external phase to the internal phase. The chemical potential gradient is ensured by a H^+ concentration difference between the external phase and the internal phase, which provides the driving force for the overall ELM extraction process.

Figure 1 shows the mechanism of facilitated transport of amino acids across an ELM with D2EHPA as the carrier.

Model Development

The following assumptions are made in this model development.

1. Isothermal batch operation process.
2. Constant physical and transport properties.
3. The membrane phase and external phase as well as the membrane phase and the internal phase are totally immiscible. The ion-exchange reaction takes place only at the interface. The solute is not very soluble in the membrane so that extraction by unfacilitated transport is negligible compared to facilitated transport.
4. The mean globule and internal phase droplet diameters are characterized using the Sauter mean diameter.
5. The internal phase droplets are immobile and there is no circulation of droplets within the emulsion globule because of the presence of surfactants on the globule surface and the relatively high internal viscosity.
6. The irreversible stripping reaction occurs at the interface and is very fast because the internal phase surface area is very large. As a result, it does not control the overall transport mechanism, while there is no internal

phase solute backdiffusion to the external phase. Further, it is assumed there is no other internal interfacial resistance.

7. According to the mass balance, the amount of loss of the solute in the external phase due to the facilitated transport equals the sum of the accumulated amounts of the solute in the membrane phase and in the internal phase. Considering that a high concentration of stripping agent is used, a relatively low volume ratio of the membrane phase to the internal phase (R_{oi}), as well as a lower ratio of the emulsion phase to the external phase (R_{ew}), is employed in the experiments. As a result, the accumulated amount of solute in the membrane phase can be negligible in comparison to that in the internal phase. In this case, at a constant given stirring speed, the flux of the solute due to leakage of internal droplets can be approximately expressed as $J_\varphi = \varphi V_e(C_{e0} - C_e)$, where φ denotes the membrane breakage coefficient (8).

The concentration profiles of the solutes in an emulsion globule based on the above assumptions are schematically shown in Fig. 2.

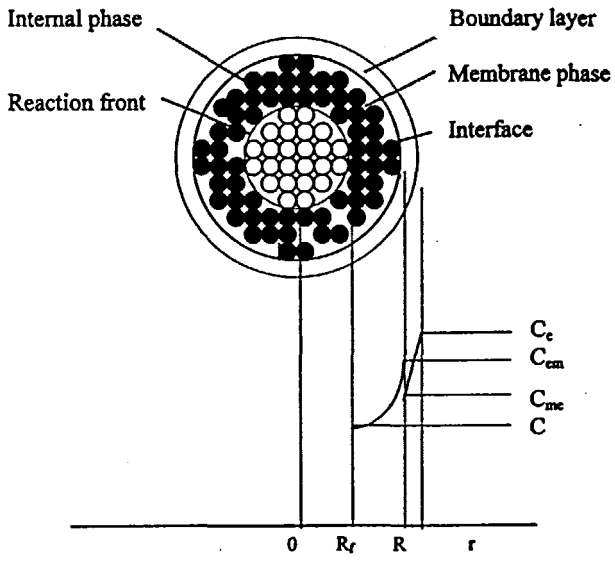

FIG. 2 Concentration profiles of the solute in an emulsion globule. The outer broken circle refers to the external phase boundary layer. R denotes the outer globule radius, and R_f the radius of the reaction front. The filled and open circles represent reacted and unreacted internal phase droplets, respectively.

At the steady state, the equations describing the solute amino acid in the external phase boundary layer, within the membrane phase of the emulsion globule, and at the external–membrane interface are, respectively, as follows.

The flux of the solute through the external boundary layer is given by

$$J_e = k(C_{em} - C_e) \tag{8}$$

Assuming that a steady diffusion into the globule exists and the reaction front moves slowly in comparison to solute diffusion, a quasi-steady-state solution gives the diffusional flux of the solute–carrier complex at the periphery of the emulsion globule as

$$J_m = \frac{R_f D_m}{R(R - R_f)} (C_{me} - C) \tag{9}$$

As a result of the leakage, both the radius of the emulsion globule, R, as well as the radius of unreacted core in emulsion, R_f, generally change slowly with time, i.e., R; $R_f = f(t)$. This effect is incorporated in the estimation of the diffusion distance $(R - R_f)$.

At the reaction front, the consumption rate of the solute–carrier complex by an irreversible stripping reaction is described as

$$(-r_f) = k_1 C \tag{10}$$

At the steady state, applying a material balance for the solute to Eqs. (8), (9) and (10), the following equations are obtained.

$$J \times 4\pi \times R^2 = J_e \times 4\pi \times R^2 = J_m \times 4\pi \times R^2 = \phi \times 4\pi \times R_f^2 \times k_1 \times C \tag{11}$$

$$J = k(C_e - C_{em}) = \frac{D_m}{R - R_f} \frac{R_f}{R} (C_{me} - C) = \phi k_1 \left(\frac{R_f}{R}\right)^2 C \tag{12}$$

where

$$C_{me} = \alpha \times C_{em}, \qquad \Phi = \frac{V_i}{V_m + V_i} \tag{13}$$

Rearranging the above equations, the flux of the solute can be obtained as

$$J = \left[\frac{1}{k} + \left(\frac{1}{\alpha \times D_m}\right)\left(\frac{R}{R_f}\right)(R - R_f) + \left(\frac{1}{\alpha \times \Phi \times k_1}\right)\left(\frac{R}{R_f}\right)^2\right]^{-1} C_e$$

$$t = 0, \qquad R_f = R, \qquad C_e = C_{e0} \tag{14}$$

A variable K is defined as

$$\frac{1}{K} = \frac{1}{k} + \frac{1}{\alpha}\frac{R}{R_f}\left[\frac{R - R_f}{D_m} + \frac{1}{\Phi \times k_1}\frac{R}{R_f}\right] \tag{15}$$

Considering Assumption 6, the chemical reaction resistance can be neglected, and Eq. (15) is further simplified as

$$\frac{1}{K} = \frac{1}{k} + \frac{1}{\alpha}\cdot\frac{R}{R_f}\left[\frac{R - R_f}{D_m} + \frac{1}{\Phi \times k_1}\cdot\frac{R}{R_f}\right] \approx \frac{1}{k} + \frac{[H^+] + K_a}{K_{ex}\cdot[\overline{(HL)_2}]^2}\cdot\frac{R}{R_f}\cdot\frac{R - R_f}{D_m} \tag{16}$$

where $1/k$ is the external phase mass transfer resistance across the boundary layer, $1/D_m$ approximately represents the membrane phase diffusion resistance within the emulsion globule, $1/k_1$ is the interfacial reaction resistance, and $1/K$ is the combined overall resistance of these three effects which comprehensively includes thermodynamical parameters such as K_a and K_{ex} and kinetic parameters such as k and D_m. Therefore, the overall mass transfer resistance can accurately reflect the mass transfer capacity of the chosen ELM system under the operation conditions.

According to the material balance, the following equations can be obtained.

$$-V_e\frac{dC_e}{dt} = \frac{3}{R}(V_i + V_m)J - \varphi\cdot V_e\cdot(C_{e0} - C_e) \tag{17}$$

$$\frac{R}{R_f} = \left(1 - \frac{V_e(C_{e0} - C_e)}{C_{i0}V_i}\right)^{-1/3} \tag{18}$$

Rearranging Eq. (15):

$$\frac{dC_e}{dt} + \varphi\cdot C_e = \varphi\cdot V_e\cdot C_{e0} - \frac{3}{R}\frac{V_i + V_m}{V_e}\cdot J \tag{19}$$

Equations (14), (18), and (19) may be solved simultaneously by using a Runge–Kutta algorithm method if all the above parameters are known. C_e, the concentration of solute in the external phase at any contact time, can be obtained by Eqs. (14), (18), and (19).

EXPERIMENTAL

Emulsion Preparation

Several experiments were carried out to test the validity of the developed model. Phe was chosen as a model amino acid in the experiments. The membrane phase was composed of di(2-ethylhexyl)phosphoric acid (D2EHPA) as

the carrier, Span 80 (sorbitan monooleate) as the surfactant, and kerosene as the solvent. The internal phase stripping reagent was 1.5 mol/L HCl solution.

The water-in-oil emulsions were prepared by first mixing together the oil and the surfactant. Then the membrane phase and the internal phase were added to a blender and emulsified for 10 minutes at a stirring speed of 10,000 rpm.

ELM Extraction

The experimental apparatus used for Phe extraction with ELM was a batch-type stirred cell equipped with four glass baffles. The inner diameter and the depth of the tank were 7 and 9 cm, respectively. A measured volume of the prepared emulsion was added to the stirred cell containing the feed aqueous solution of Phe, and the mixture was stirred at 250 rpm. The cell was placed in a thermostatted bath maintained at 298 K. Lithium chloride was used as a tracer in the internal phase solution to measure the degree of membrane breakage. Samples were withdrawn at given intervals and analyzed with a spectrophotometer after the external phase was separated from the emulsion. The diameter of the W/O emulsion globules was measured by a photographic method. Because it is very difficult to measure the change of the radius of unreacted core in the emulsion, R_f, with time in the experiments, it is assumed that the change of R_f with time is negligible. Therefore only the change of emulsion globule radius R with time is considered.

RESULTS AND DISCUSSION

Parameters Evaluation

The following physical properties must be known to compare experimental and theoretical results.

Equilibrium Constant for Phe-D2EHPA Reactive Extraction. Equilibrium constant for Phe-D2EHPA reactive extraction, K_{ex}, was obtained from the literature as 0.117 dm^3/mol (2).

Acid Dissociation Constant of Phe. The literature value of the Phe dissociation constants K_α was 1.0×10^{-2} mol/dm^3 (9).

External Phase Mass Transfer. The emulsion globule may be treated as a rigid spherical particle existing in the agitated vessel because sufficient surfactant is contained in the membrane phase. Therefore the external phase mass transfer coefficient, k, may be estimated by the correlation reported in the literature (10). For the purpose of estimating the mass transfer coefficient, it was assumed that the membrane phase consisted of 100% kerosene. Thus, the external phase mass transfer coefficient was estimated to be 3.6×10^{-3} cm/s.

Membrane Phase Diffusion Coefficient. In this study the membrane phase diffusion coefficient D_m was estimated to be 3.9×10^{-5} cm^2/s by using the Wilke–Chang equation.

Membrane Breakage Coefficient. The membrane breakage coefficient was obtained in order to measure the leakage rate of tracer from the emulsion globule to the external phase. In this study LiCl was intentionally encapsulated in the internal phase only for purpose of the measurement, i.e.,

$$V_e \cdot \frac{d[\mathrm{LiCl}]}{dt} = \varphi \cdot V_i \cdot [\mathrm{LiCl}]_{i0}$$

Thus, the membrane breakage coefficient φ was determined experimentally to be 2.2×10^{-4} s^{-1}.

Sauter Mean Diameter of Emulsion Globule. The Sauter mean diameter of an emulsion globule was measured to be 0.41 mm.

Comparison between Model and Experimental Results

The validity of the proposed model was investigated by comparing the calculated results with several experimental data.

The calculated and experimental results at the various pH values in the external phase are shown in Fig. 3. It is seen that there is good agreement

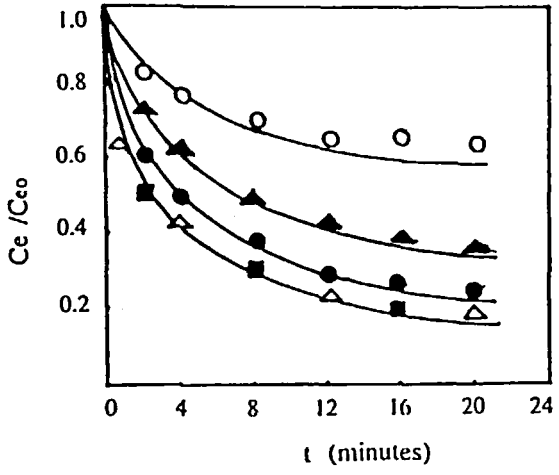

FIG. 3 The effect of pH in the external phase on Phe extraction. (○) pH 1; (▲) pH 2; (●) pH 3; (△) pH 3.5; (■) pH 4; Span 80, 3.0% (v/v); D2EHPA, 4.0% (v/v); kerosene, 93% (v/v); HCl, 1.5 mol/L; $R_{oi} = 5/4$; $R_{ew} = 1/4$. The solid lines represent the model's predications.

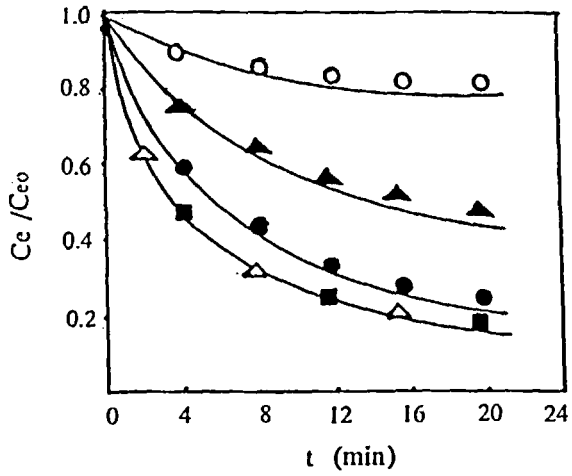

FIG. 4 The effect of D2EHPA concentration on Phe extraction. (○) 2.0%; (▲) 3.0%; (●) 4.0%; (△) 4.5%; (■) 5.0% (all in v/v); pH 3.0; Span 80, 3.0% (v/v); kerosene, 92–95% (v/v). The solid lines represent the model's predications. Other conditions as in Fig. 3.

between experiment and theory. The figure shows that an increase of pH in the external phase in a relatively low pH range has a positive effect on the transport of Phe, which is in agreement with the model predication. However, for pH > 3, a further increase in pH has little effect on the extraction of Phe. The reason for this can be explained by the proposed model. When $[H^+]$ is much higher than K_a in Eq. (16), the overall mass transfer resistance is proportional to $[H^+]$ of the external phase. Thus the extraction ratio decreases with decreasing pH. On the other hand, when $[H^+]$ is much lower than K_a, the overall mass transfer resistance is almost independent of $[H^+]$. In this case an increase of pH has no effect on the extraction of Phe, which means that under the operation conditions the mass transfer in the external phase boundary layer may be the rate-controlling step for the transport of Phe.

A comparison of the calculated results with experimental data at various carrier concentrations is shown in Fig. 4. The experimental data are in good agreement with the model predications. It is seen that as the carrier concentration increases, the overall mass transfer resistance as expressed by Eq. (16) decreases, which results in an increase in the extraction ratio of Phe. This indicates that the transport of Phe seems to be governed by diffusion within the emulsion globule. Besides, as depicted in Fig. 4, when the carrier concentration is higher that 4% (v/v), a further increase in the carrier concentration seems to have little effect on the extraction of Phe, which shows that the

mass transfer in the external phase boundary layer may be a rate-controlling step for the extraction of Phe in this case.

CONCLUSION

A mathematical model is developed to analyze and predict the transport of Phe from an aqueous solution by an emulsion liquid membrane in a batch separation process. The proposed model takes into account the external phase mass transfer resistance, the interfacial reaction resistance, the diffusion within the emulsion globule, as well as the leakage effect of the internal phase due to membrane breakage. The overall mass transfer resistance includes these three resistances. Under various experimental conditions the transport of Phe can be governed by either of them, by mass transfer in the external phase boundary layer, by diffusion within the membrane phase, or by a combination of these effects. The parameters required for modeling could easily be obtained without using adjustable parameters. The validity of the model was investigated experimentally. The proposed model satisfactorily predicts the experimental results.

SYMBOLS

A	amino acid or zwitterion of amino acid
A^+	cation of amino acid
A^-	anion of amino acid
C	solute mean concentration within emulsion globule (mol/dm^3)
C_e	solute concentration in external phase (mol/dm^3)
C_{em}	solute concentration at external–membrane phase interface (mol/dm^3)
C_{me}	solute–carrier complex concentration at membrane–external phase interface (mol/dm^3)
D_m	diffusivity of solute–carrier complex in membrane phase (m^2/s)
D2EHPA	di(2-ethylhexyl)phosphoric acid
$(HL)_2$	dimer of D2EHPA
J	flux (m^2/s)
K	overall mass transfer coefficient defined by Eq. (15) (s/m)
K_{ex}	extraction equilibrium constant defined by Eq. (6)
K_a	acid dissociation constant defined by Eq. (2) (mol/dm^3)
K'_a	acid dissociation constant defined by Eq. (3) (mol/dm^3)
k	external phase mass transfer coefficient (m/s)
k_1	pseudo-first-order forward reaction rate constant (m/s)
R	Sauter mean radius of W/O emulsion globule (m)

R_{ew}	volume ratio of emulsion to external phase
R_f	radius of unreacted core in emulsion (m)
R_{oi}	volume ratio of membrane phase to internal phase
r	radial distance (m)
r_f	consumption rate of the solute by stripping reaction defined by Eq. (10)
t	time (s)
V_e	volume of external phase (cm^3)
V_i	volume of internal phase (cm^3)
V_m	volume of membrane phase (cm^3)

Greek Letters

α	distribution ratio of solute between organic phase and aqueous phase defined by Eq. (7)
Φ	volume fraction of internal phase in W/O emulsion defined by Eq. (13)
φ	membrane breakage coefficient (s^{-1})

Subscripts

e	external phase
i	internal phase
m	membrane phase
T	sum of A^+, A^-, and A
0	initial value

REFERENCES

1. T. B. Vickroy, "Lactic Acid," in M. Moo-Young (Ed.), *Comprehensive Biotechnology, Vol. 3*, Pergamon Press, 1985, p. 761.
2. M. Teramoto, T. Yamashiro, A. Inoue, A. Yamamoto, H. Matsuyama, and Y. Miyake, *J. Membr. Sci., 58*, 11 (1991).
3. S.-A. Hong and J.-W. Yang, *Ibid., 86*, 181 (1994).
4. H. Yong and S.-A. Hong, *Biotechnol. Bioeng., 39*, 125 (1992).
5. M. P. Thien and T. A. Hatton, *Sep. Sci. Technol., 23*(8/9) 819 (1988).
6. M. P. Thien, T. A. Hatton, and D. W. Wang, *Biotechnol. Bioeng., 32*, 604 (1988).
7. W. S. Ho, T. A. Hatton, E. N. Lightfoot, and N. N. Li, *AIChE J., 28*, 662 (1982).
8. G. Zhongmao, Z. Hefei, D. T. Wasan, and N. N. Li. *J. Chem. Ind. Eng. (China)*, (1)1 (1986).
9. S. Tong and W. Jingyan, *Biochemistry*, 2nd ed., High Education Press, Beijing, 1990, p. 93.
10. C. C. Chan and C. J. Lee, *Chem. Eng. Sci., 42*, 83 (1987).

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