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Separation and Concentration of Phenylalanine by Emulsion Liquid Membrane in a CSTR Extraction Process

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ABSTRACT

The extraction and concentration of phenylalanine by the continuous CSTR emulsion liquid membrane (ELM) separation process has been evaluated. We discussed the influence of operating conditions on the separation and concentration efficiencies of phenylalanine. It was found that the extraction rate of phenylalanine increased as the amount of emulsion used and the internal concentration of H^+ increased. However, the concentration ratio of phenylalanine increased as the emulsion amount and acid concentration increased only up to a certain limit and then declined with further increases of these. The reduction of the concentration ratio is due to the swelling of the emulsion drops. Two effects, swelling owing to osmotic pressure and swelling caused by the entrainment of water due to mechanical agitation, are responsible for the swelling of emulsion drops. A mass transfer model for analyzing the extraction of phenylalanine by liquid surfactant membrane is presented. The model assumes that the extraction and stripping reactions are reversible, and that the reaction equilibrium exists in both the internal and the external interfaces. The scheme for mass transfer is based on a hollow sphere model. The phenomena of osmotic swelling, mechanical entrainment, and breakage are all considered in the mathematical treatment. The effects of operation parameters on the extraction efficiency and concentration ratio are discussed by simulation.

Key Words. Emulsion liquid membrane; CSTR; Phenylalanine; Extraction; Swelling; Entrainment; Breakage

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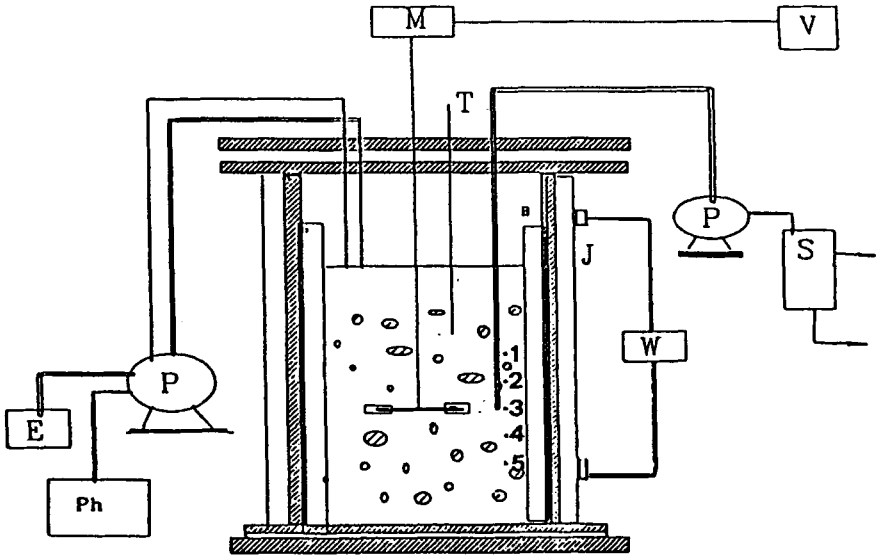
INTRODUCTION

Recently, the demand for L-amino acids has increased steadily. The main consumer is the food industry, but medical applications are also becoming increasingly significant. Amino acids, which are typical bioproducts produced on a large scale, are mainly separated and concentrated by ion exchange and crystallization. However, a drop in resin adsorption power results in the reduction of purification efficiency. As the need for a higher degree of purification becomes widespread, it is important to develop a more sophisticated novel separation which takes advantage of two or more properties at the same time or which has special selectivity.

The emulsion liquid membrane (ELM) technique, which was first developed by Li (1), is an attractive separation method with potential for a wide range of applications from wastewater treatments to biomedical applications (2–7). During the last decade the use of ELM has also been examined for the downstream processing of biochemicals owing to the potential for simultaneous separation and enrichment together with the avoidance of pretreatment. By applying ELM using an ionic carrier, thus taking advantage of the difference of both electrostatic charge and hydrophobicity, there is a possibility to increase selectivity and put several operations together. To date, the biochemicals treated by ELM processes are amino acids (8–12), organic acids (13–18), and antibiotics (19). However, most of these works were done on a batch scale, and there has been little research on a continuous process. In the present paper we study the separation and concentration of phenylalanine with ELM in a continuous CSTR process. The effects of operating conditions on the separation efficiency and concentration factor are discussed. A mathematical CSTR extraction model is also proposed, and the simulation results are compared with the experimental data.

EXPERIMENTAL

Figure 1 is a schematic diagram of the single-stage continuous CSTR apparatus used in this work. The 2-liter, acrylic-made extraction vessel is about 120 mm in diameter and 180 mm deep. Four equally spaced vertical baffles, 3 mm thick and 12 mm in width, were attached to the internal wall of the vessel to prevent vortexing. Vessel contents were agitated using a 5-cm standard, six disk-turbine type impeller. Impeller rpm was monitored by a tachometer. To maintain a uniform temperature in the vessel, it had a jacket through which water of constant temperature was circulated. A peristaltic pump equipped with a multichannel head delivered the emulsion and feed solutions through two lines mounted on the



B : Baffle
J : Water jacket
P : Peristaltic pump
S : Settler
V : Voltage stabilizer
E : Emulsion
M : DC stirrer
Ph : Phenylalanine solution
T : Thermometer
W : Water bath

FIG. 1 Schematic diagram of CSTR experimental apparatus.

top of the vessel. An outlet port fitted with a adjustable glass tube down to the liquid was also mounted on the top of the vessel. The outlet W/O/W emulsion flow was withdrawn continuously by a second peristaltic pump. After settling, the aqueous raffinate flow was separated from the W/O emulsion and collected at the bottom of the separator for analysis. Samples of W/O emulsion were also taken from the overflow at the top of the separator and demulsified by a microwave method to analyze the solute concentration and the change of the volume ratio. All chemicals were used as supplied. The membrane phase consisted of Span 80 and D2EHPA dissolved in kerosene solvent. The internal encapsulated reagent was HCl solution with which 500 ppm LiCl was dissolved as a leakage tracer. The membrane phase was prepared by blending all necessary components in advance, and the emulsion was made by addition of the internal phase under the intense shear provided by a Waring blender.

The size of the water droplets in the emulsion was measured by using a centrifugal automatic particle size analyzer (Horiba CAPA-300). The phenylalanine concentration was measured by UV spectrophotometry (HP 8452A) at a wavelength of 258 nm. Lithium concentration was measured by AA spectrophotometry (Hitachi Z-6100). The aqueous feed solution and prepared emulsion were combined in the extractor at a volume ratio equal to the volumetric flow-rate ratio, F/E. The pumps were then started, beginning with the continuous flow experiment. Aqueous and emulsion samples were collected from the effluent of the extractor every 5 or 10 minutes and analyzed. Steady-state was indicated when solute concentrations did not change over a period of two or three samples. Steady-state was usually reached after about 15 or 20 minutes. After recording the steady-state concentrations, the pumps and mixer were stopped to allow the emulsion and bulk phases to separate. The relative volumes of the emulsion to bulk phases were calculated from the thickness of the emulsion phase. In all experiments, mass balances were calculated on the total amount of phenylalanine in the system. Extraction efficiency and concentration ratio of phenylalanine were estimated as follows:

$$\text{Extraction efficiency} = (C_{10} - C_1)/C_{10} \tag{1}$$

$$\text{Concentration ratio} = C_3/C_{10} \tag{2}$$

EXPERIMENTAL RESULTS AND DISCUSSION

Typical experimental results using this ELM system in CSTR operation are shown in Fig. 2. As can be seen, the steady-state condition for each run was reached after about 15 or 20 minutes. The concentration ratio of phenylalanine in the internal phase was shown to be a factor of 3 or more. This demonstrated that, by using the ELM system, it was possible to separate and concentrate phenylalanine in the internal phase three times higher than the initial concentration of the external phase. This makes the ELM process more advantageous than conventional ion exchange because it is impossible to get such a high concentration of solute by the ion-exchange resin process.

Effect of Exit Position on the Effluent *F/E* Ratio

From the general characteristics of CSTR at steady-state operation, one might expect that the external aqueous phase to emulsion phase volumetric flow ratio of the outlet stream, $[F/E]_{out}$, should be equal to the ratio of that of the inlet stream, $[F/E]_{in}$. However, this is not always true in the ELM system. As shown in Fig. 2(b), it is found that the steady-state

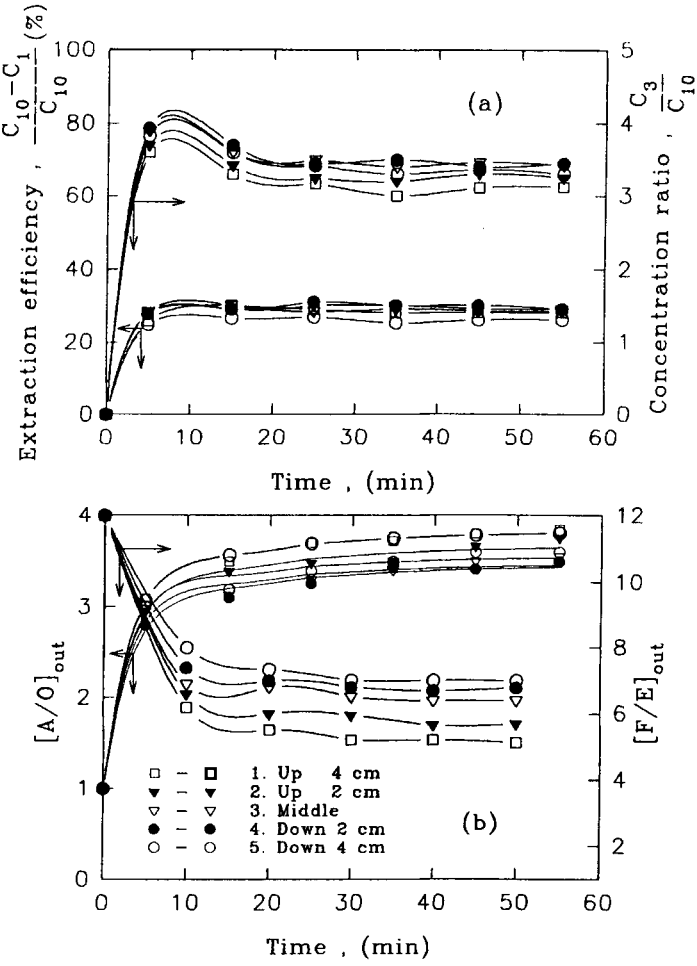


FIG. 2 Effect of different outlet positions.

outlet $[F/E]_{out}$ ratio (= 4–8) is significantly smaller than that of the inlet stream ($[F/E]_{in}$ ratio = 12). The reason for this phenomenon is due to the swelling and entrainment of water from the external phase into the internal phase of emulsion. This is also strongly supported by the results of Fig. 2(b). As can be seen, by breaking the emulsion sampled from the outlet stream and measuring the volume ratio of the internal aqueous phase to the membrane oil phase, it is found that the steady-state $[A/O]_{out}$ ratio in the outlet emulsion is also three times higher than that of the inlet emul-

sion. Figure 2(b) shows the results of a decrease of water content in the external aqueous phase and an increase of water content in the internal aqueous phase. Two mechanisms are suggested to be responsible for this water transport phenomena. One is the osmotic swelling and the other is the mechanical entrainment. Though the mechanisms are totally different, it is found that both phenomena are strongly influenced by the intensity of mechanical agitation. To study the effect of agitation more closely, five positions, as shown in Fig. 1, were chosen to be the outlet points for comparison. The results of these experiments are also shown in Fig. 2. As can be seen, different outlet points showed different degrees of the effects of water swelling and entrainment and thus gave different values of $[F/E]_{out}$ and $[A/O]_{out}$ ratios. Position 1, which had the least agitation intensity, was most influenced by these phenomena and gave the largest effects of water transfer. However, no attempt is made in this paper to distinguish between osmotic swelling and mechanical entrainment effects. A more detailed discussion of these phenomena will be present in a subsequent paper. The phenomenon of the difference between $[F/E]_{out}$ and $[F/E]_{in}$ in the ELM system should be seriously considered in the development of ELM separation process. For simplicity of operation, position 3 was chosen as the standard outlet position in this study.

Parameters Affect the Extraction and Concentration of Phenylalanine

Many factors have been proposed to be related to phenylalanine extraction, e.g., emulsion-to-feed treatment ratio, H^+ concentration, surfactant and carrier concentration, A/O phase ratio, agitation intensity, etc. only the two most important, treatment ratio and H^+ concentration, are studied in this paper regarding their effects on the efficiency of phenylalanine extraction and concentration.

Effect of [E/F] Treatment Ratio on the Extraction and Concentration Efficiency

The higher the value of the $[E/F]_{in}$ treatment ratio, the more emulsion is used, and the more liquid drops are formed; therefore, the mass transfer area enlarges and the extraction rate increases. This can be realized from Fig. 3(a) where the extraction rate grows noticeably with the increment of $[E/F]_{in}$. However, the increment of the $[E/F]_{in}$ ratio, although it helps to advance the extraction efficiency, has a detrimental influence on the concentration effect when it is boosted too much. It can also be seen in Fig. 3(a) that the concentration ratio is first heightened and then lessened when the $[E/F]_{in}$ ratio is increased. The reason may be that with an in-

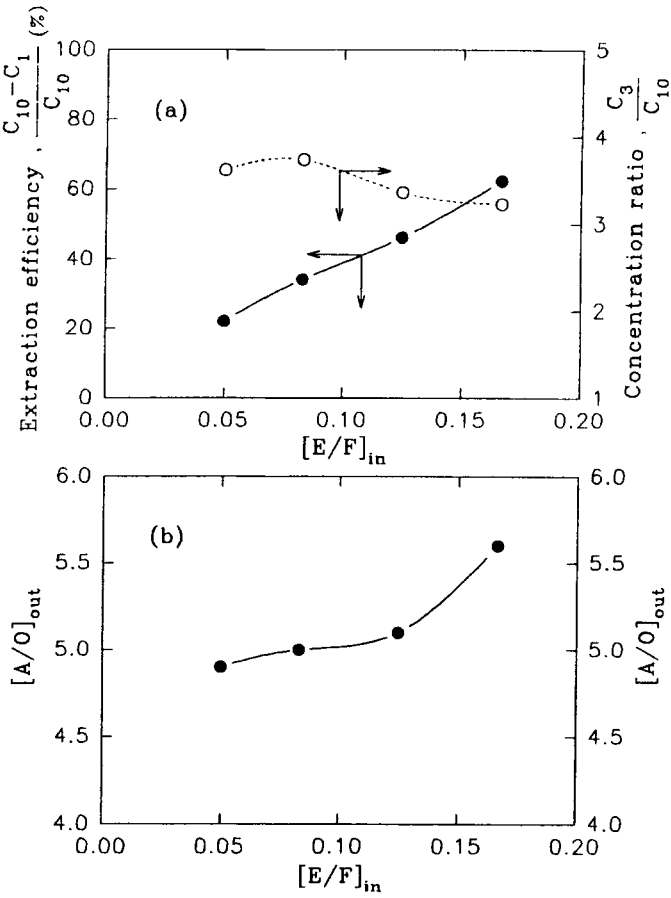


FIG. 3 Effect of $[E/F]_{in}$ treatment ratio.

crease of emulsion quantity, the extraction efficiency accelerates and causes a boost of the concentration effect. Figure 3(b) indicates that as the quantity of emulsion used increases, there is a gradual trend of enlargement of the swelling phenomena which becomes apparent when the $[E/F]_{in}$ treatment ratio is more than 0.1. This will dilute the materials which were originally extracted into the internal phase of the emulsion and cause a decrease of the concentration effect. Hence, with the increase of the $[E/F]_{in}$ treatment ratio, there is the possibility for concentration effect to first increase and later decrease.

Effect of Internal-Phase H^+ Concentration on the Extraction and Concentration Efficiency

Figure 4(a) shows that as the concentration of the internal-phase H^+ ions increases, extraction efficiency enhances accordingly. However, too high a concentration of H^+ ions is not absolutely helpful. If the concentration of inner H^+ ions grows to a certain degree, the increment of extraction efficiency slows, which will make the emulsion quite unstable and even broken. From Fig. 4(b) we see that as the concentration of H^+ ions height-

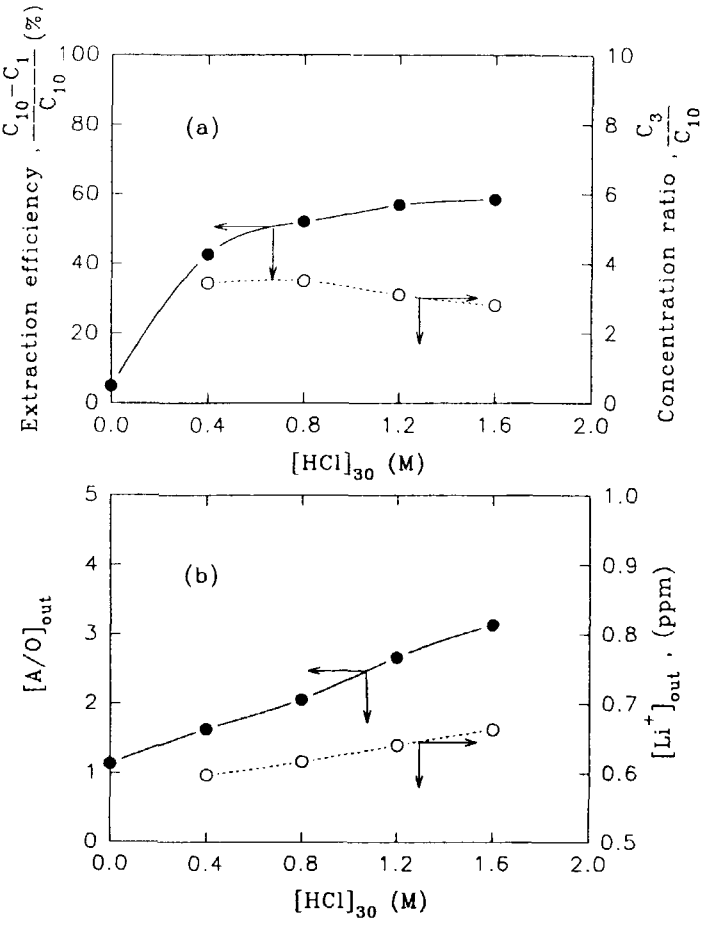


FIG. 4 Effect of internal-phase H^+ concentration.

ens, the leakage of inner solution obviously increases, which will do harm to the extraction efficiency. Further, another disadvantage will influence the extraction experiment through the increment of H^+ ion concentration; the swelling phenomenon will grow, as shown in Fig. 4(b), and this causes a decrease of the concentration effect. Figure 4(a) indicates that with the increment of H^+ ion concentration, the concentration effect of phenylalanine tends to increase first and decrease later. The reason may be that with the increment of H^+ concentration, the extraction efficiency is enhanced and the concentration effect increases accordingly. Later on, due to the noticeable growth of the swelling phenomenon, the concentration effect is reduced.

THEORY

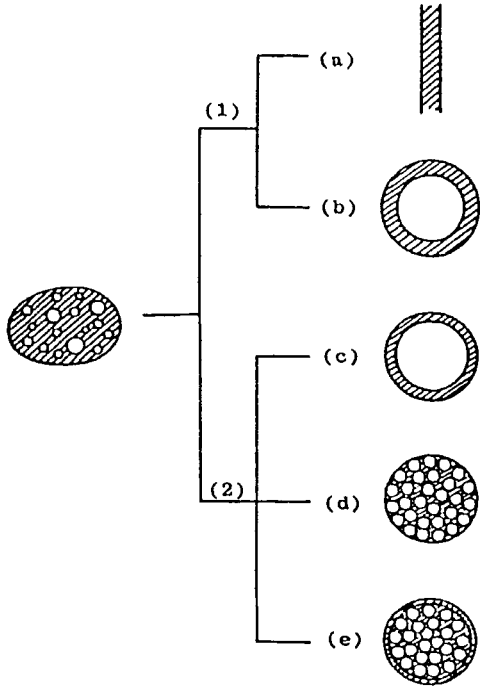
Mass Transfer Model of Emulsion Liquid Membrane

The development to date of emulsion globule models has two categories with a total of five simplified geometric structures (20, 21), as shown in Fig. 5.

First Category. Suppose the internal liquid microdroplets of a W/O emulsion can move freely and blend homogeneously with one another until they reach a congruent concentration. This category can be divided into two geometric models, the Uniform Flat-Plate and the Hollow Sphere, according to the relative size of the film thickness and the curvature of the globule.

Second Category. Suppose the internal liquid microdroplets of a W/O emulsion are immobilized and unable to blend with one another, and the concentration varies as the position changes. This category can also be divided into three geometric models: Immobilized Hollow Sphere, Immobilized Spherical Globule, and Immobilized Hollow Spherical Globule.

In the Hollow Sphere Model the internal liquid microdroplets of an emulsion can be combined into a big internal droplet surrounded by a liquid membrane. The Hollow Sphere Model, although unable to give a satisfactory description on the actual emulsion globule, has been widely adopted due to its mathematical simplicity. Therefore, our theoretical analysis is based on the Hollow Sphere Model. None of the modeling studies of CSTR operation in the literature include the effects of emulsion swelling, mechanical entrainment, and breakage, although there have been attempts to quantitatively describe emulsion swelling (11, 22). In this paper we propose a kinetic model which includes osmotic swelling, mechanical entrainment, and emulsion breakage for the extraction of phenylalanine in CSTR operation, and then compare with the actual experimental outcome to determine its practicality.



(a) Uniform Flat-Plate Model
(b) Hollow Sphere Model
(c) Immobilized Hollow Sphere Model
(d) Immobilized Spherical Globule Model
(e) Immobilized Hollow Spherical Globule Model

FIG. 5 Configurations of various emulsion drop models.

Phenylalanine, like other amino acids, is a zwitterion; it possesses a positive charge at low pHs (<3), no net charge at neutral pHs (3–9), and a negative charge at high pHs (>9). The dissociation equilibria are expressed as follows:

$$A^+ \overset{K_{a1}}{\rightleftharpoons} A + H^+, \qquad K_{a1} = \frac{[A][H^+]}{[A^+]} = 2.63 \times 10^{-3} \quad (25°C)$$

$$A \overset{K_{a2}}{\rightleftharpoons} A^- + H^+, \qquad K_{a2} = \frac{[A^-][H^+]}{[A]} = 5.75 \times 10^{-10} \quad (25°C) \tag{3}$$

Since phenylalanine is insoluble in the oil phase, an ion-exchange carrier (e.g., D2EHPA) must be added to the membrane phase in order to solubilize phenylalanine into the oil and transport it to the internal phase. A schematic diagram of the transport mechanism for phenylalanine in an ELM process is shown in Fig. 6. The overall reaction for phenylalanine extraction by the cation-exchange carrier D2EHPA can be expressed as follows:

$$A^+ + RM \underset{}{\overset{K}{\rightleftharpoons}} RA + M^+, \qquad K = \frac{[RA][M^+]}{[A^+][RM]} \tag{4}$$

Based on the hollow sphere model, as shown in Fig. 7, the flux of phenylalanine, J_1, from the bulk of the external phase to the interface with the membrane is given by

$$J_1 = k_{L1}([A^+]_l - [A^+]_{lm}) \tag{5}$$

where k_{L1} is the external phase mass transfer coefficient, $[A^+]_l$ is the phenylalanine concentration in the bulk of the external phase, and $[A^+]_{lm}$ is the concentration on the external phase side of the external phase-membrane phase interface.

By quasi-steady-state assumption, the diffusional flux, J_2, of the phenylalanine–carrier complex across the membrane phase is given by

$$J_2 = \frac{R_i D_{RA}}{R_o(R_o - R_i)}([RA]_{m1} - [RA]_{m3}) \tag{6}$$

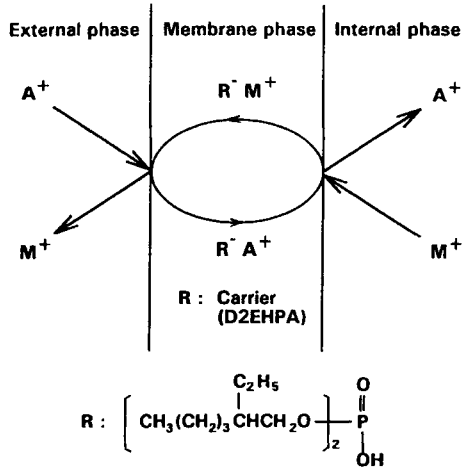


FIG. 6 Schematic diagram of the transport mechanism for phenylalanine.

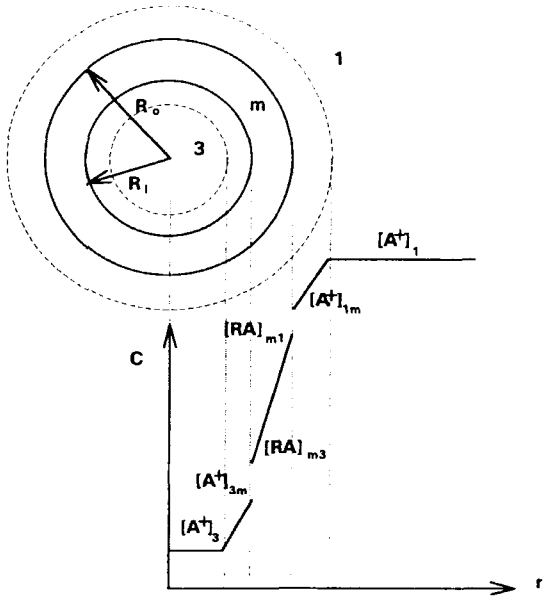


FIG. 7 Modeling of the emulsion drop.

where R_i and R_o are the inner and outer radius of emulsion globule, respectively, D_{RA} is the diffusivity of the complex, and $[RA]_{m1}$ and $[RA]_{m3}$ are the complex concentrations on the membrane phase side of the inner and outer interfaces, respectively.

Finally, the flux of phenylalanine, J_3, from the interface with the membrane phase to the bulk of the internal phase is given by

$$J_3 = k_{L3}([A^+]_{3m} - [A^+]_3) \tag{7}$$

where k_{L3} is the internal phase mass transfer coefficient, $[A^+]_3$ is the phenylalanine concentration in the bulk of the internal phase, and $[A^+]_{3m}$ is the concentration on the internal phase side of the internal phase–membrane phase interface.

Equation (8), created by combining Eqs. (3) to (7) and doing some mathematical manipulation, is the resulting mass transfer rate equation of phenylalanine which we attain by applying the hollow sphere model of emulsion globule in accordance with the chemical extraction equilibrium relationship and the dissociation equation of phenylalanine.

$$\frac{K^2}{R_o^2 R_i^2 k_{L1} k_{L3}}(-r_A)^3 + \left\{\frac{K^2[A^+]_3}{R_o^2 k_{L1}} - \frac{K^2[A^+]_1}{R_i^2 k_{L3}} + \frac{K[M^+]_{3m}}{R_o^2 k_{L1}} - \frac{K[M^+]_{1m}}{R_i^2 k_{L3}}\right\}(-r_A)^2 - \{K^2[A^+]_1[A^+]_3 + K[M^+]_{3m}[A^+]_1 + K[M^+]_{1m}[A^+]_3 + [M^+]_{1m}[M^+]_{3m}\}(-r_A) - \frac{R_i D_{RA} K[RM]_{m0}}{R_o(R_o - R_i)}\left\{\frac{[M^+]_{3m}}{k_{L1}} + \frac{R_o^2[M^+]_{1m}}{R_i^2 k_{L3}}\right\}(-r_A) + \frac{R_o R_i D_{RA} K[RM]_{m0}}{R_o(R_o - R_i)}\{[A^+]_1[M^+]_{3m} - [A^+]_3[M^+]_{1m}\} = 0 \quad (8)$$

where

$$4\pi R_o^2(-r_A) = 4\pi R_o^2 J_1 = 4\pi R_o^2 J_2 = 4\pi R_i^2 J_3 \quad (9)$$

$$[RM]_{m0} = [RM]_{m1} + [RA]_{m1} = [RM]_{m3} + [RA]_{m3} \quad (10)$$

Mass Balance of CSTR Operation

Mass Balance of Total Volumetric Flow Rate and Water Flow Rate

Referring to Fig. 8, under steady-state conditions the total volumetric flow rate of the inlet emulsion stream and aqueous stream is equal to the total flow rate of the outlet emulsion and aqueous streams. Therefore, the overall material balance equation is expressed by

$$q_{E,in} + q_{w,in} = q_{E,out} + q_{w,out} \quad (11)$$

For the water material balance in the aqueous stream, the outlet water flow rate is equal to the water inlet flow rate plus the water leakage rate

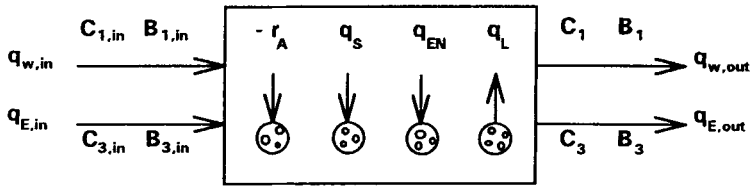


FIG. 8 Schematic diagram of material balance for CSTR.

due to the emulsion breakup (q_L) and minus the water entrainment rate (q_{EN}) and swelling rate (q_S) into the emulsion. Therefore, the water material balance equation is expressed by

$$q_{w,out} = q_{w,in} + q_L - q_{EN} - q_S \tag{12}$$

Mass Balance of Amino Acid

Under steady-state conditions, the overall mass balance of phenylalanine of all forms (i.e., A^+, A, A^-, and [RA]) in both the emulsion and external aqueous phases is given by

$$\begin{aligned} &q_{w,in}C_{1,in} + q_{E,in}(1 - \phi_{i,in})[RA]_{av,in} + q_{E,in}\phi_{i,in}C_{3,in} \\ &\quad = q_{w,out}C_1 + q_{E,out}(1 - \phi_i)[RA]_{av} + q_{E,out}\phi_i C_3 \end{aligned} \tag{13}$$

and that in the external aqueous phase side is given by

$$q_{w,out}C_1 = q_{w,in}C_{1,in} + q_L C_3 - q_{EN}C_1 - q_S C_1 - (-r_A)Va \tag{14}$$

where

$$C_i = [A^+]_i + [A]_i + [A^-]_i = \left(1 + \frac{K_{a1}}{[H^+]_i} + \frac{K_{a1}K_{a2}}{[H^+]_i^2}\right)[A^+]_i, \tag{15}$$

$$i = 1, 3$$

$$a = \frac{S}{V} = \frac{3V_E}{R_o V} \tag{16}$$

Mass Balance of Hydrogen Ion

As the same, under steady-state conditions, the overall mass balance of hydrogen ions of all forms (i.e., free H^+ ion and H^+ carried by A^+, A, and [RA]) in both the emulsion and external aqueous phases is given by

$$\begin{aligned} &q_{w,in}B_{1,in} + 2q_{E,in}(1 - \phi_{i,in})[RA]_{av,in} + q_{E,in}\phi_{i,in}B_{3,in} \\ &\quad = q_{w,out}B_1 + 2q_{E,out}(1 - \phi_i)[RA]_{av} + q_{E,out}\phi_i B_3 \end{aligned} \tag{17}$$

and that in the external aqueous phase side is given by

$$q_{w,out}B_1 = q_{w,in}B_{1,in} + q_L B_3 - q_{EN}B_1 - q_S B_1 - 2(-r_A)Va \tag{18}$$

where

$$B_i = [H^+]_i + [A]_i + 2[A^+]_i = [H^+]_i + \left(\frac{K_{a1}}{[H^+]_i} + 2\right)[A^+]_i, \tag{19}$$

$$i = 1, 3$$

Equations (8) to (19) may be solved simultaneously by the numerical method. The results of computation with various parameters are used to describe theoretically the behavior of phenylalanine extraction by ELM in a CSTR system.

COMPARISON BETWEEN THEORETICAL MODEL AND EXPERIMENTAL RESULTS

We can obtain the separation efficiency and the concentration ratio of phenylalanine with Eqs. (8) to (19). We then make a comparison between

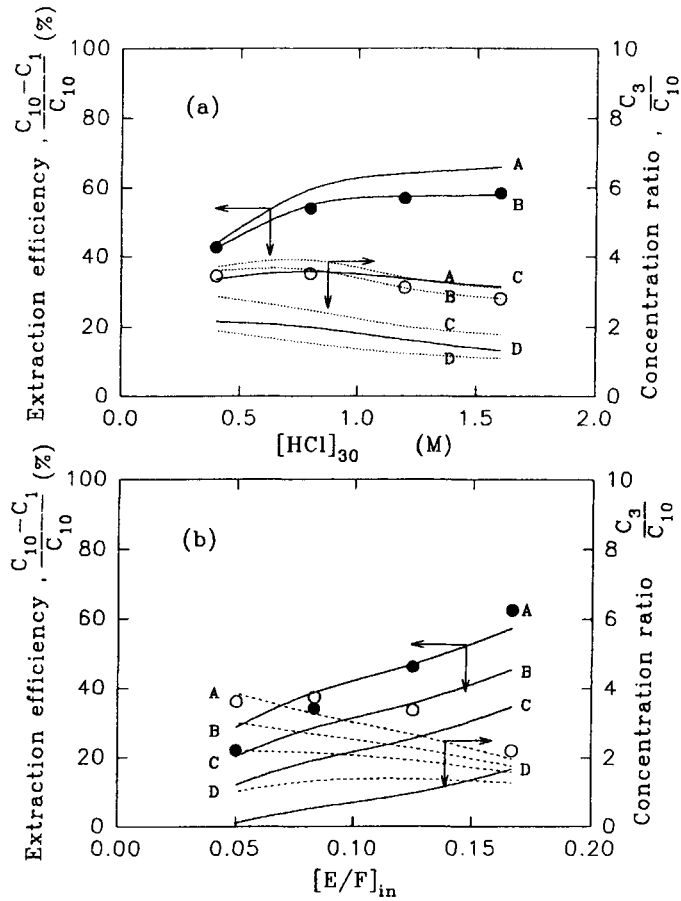


FIG. 9 Effect of emulsion drop size. A: R_o = 0.02 cm. B: R_o = 0.05 cm. C: R_o = 0.1 cm. D: R_o = 0.3 cm.

the outcome calculated from the theoretical model and the experimental data in order to study the applicability of the theoretical model. By changing the concentration of the internal hydrochloric acid and the emulsion flow rate, the effects of such operating parameters as emulsion globule diameter, extraction equilibrium constant, mass transfer coefficients, and diffusion coefficient on the separation efficiency and concentration ratio

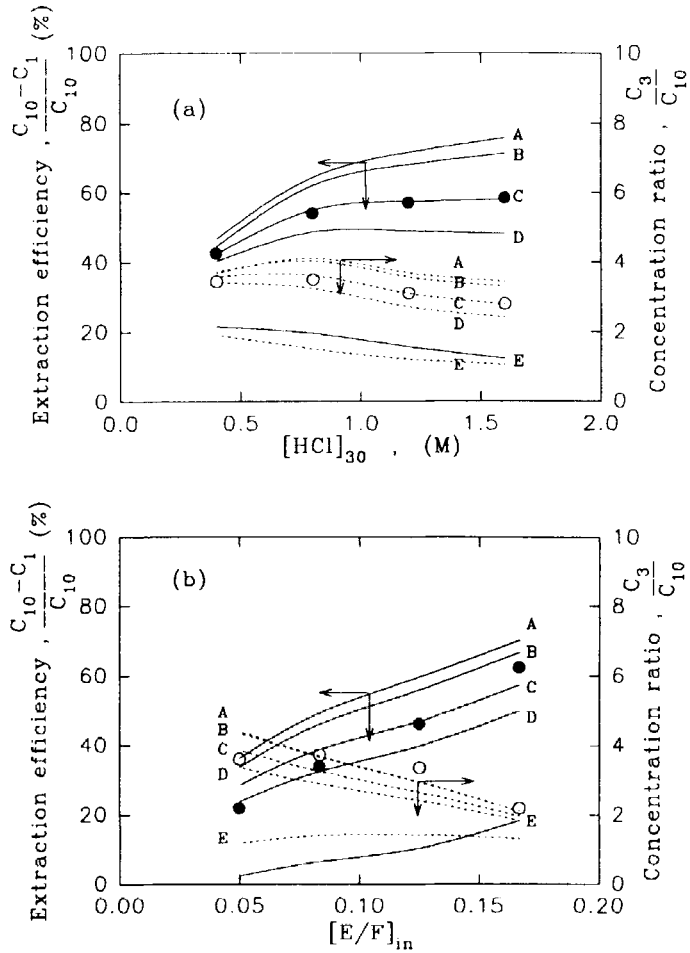


FIG. 10 Effect of extraction equilibrium constant. A: K = 0.1. B: K = 0.01. C: K = 0.002. D: K = 0.001. E: K = 0.0001.

of phenylalanine can be seen. Figure 9 shows that as the drop diameter of the emulsion dwindles, the extraction efficiency and concentration ratio apparently heighten. This is because the mass transfer area expands and the extraction efficiency and concentration ratio increase accordingly with a decrease in the drop diameter of the emulsion. In Fig. 10 it is shown that with the increment of the extraction equilibrium constant, the extraction

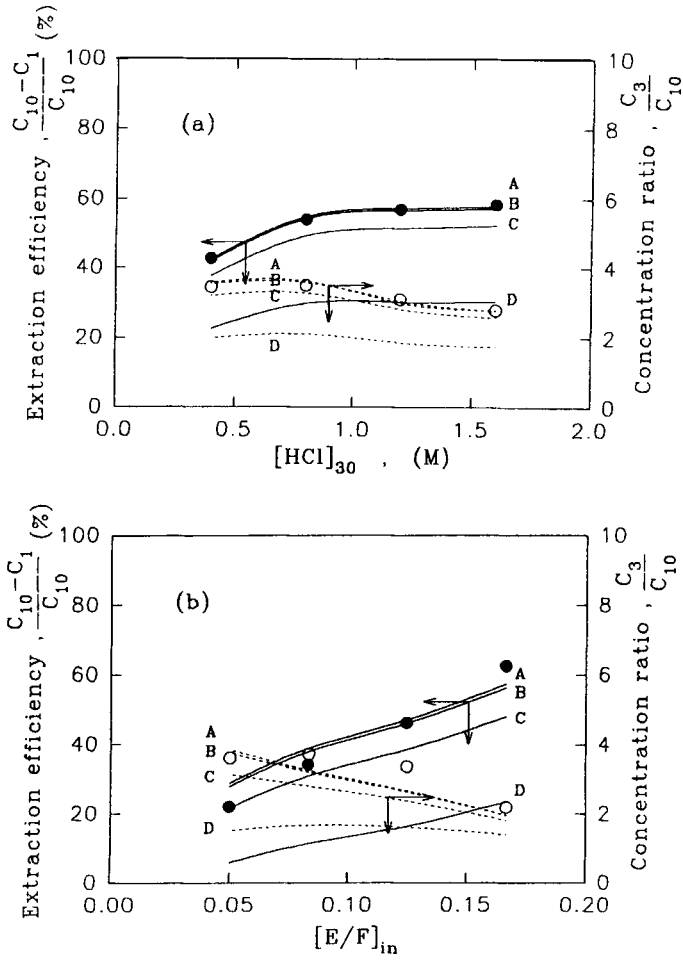


FIG. 11 Effect of internal-phase mass transfer coefficient. A: $k_{L3} = 10^{-3}$ cm/s. B: $k_{L3} = 10^{-4}$ cm/s. C: $k_{L3} = 10^{-5}$ cm/s. D: $k_{L3} = 10^{-6}$ cm/s.

efficiency, and the concentration ratio have a noticeable growth. Likewise, Figs. 11 and 12 show that as the mass transfer coefficients of the internal and external phases increase, the extraction efficiency and concentration ratio also tend to increase but do not change as much. Figure 13 shows that the extraction efficiency and concentration ratio gradually grow with the increase of the diffusion coefficient of the liquid membrane.

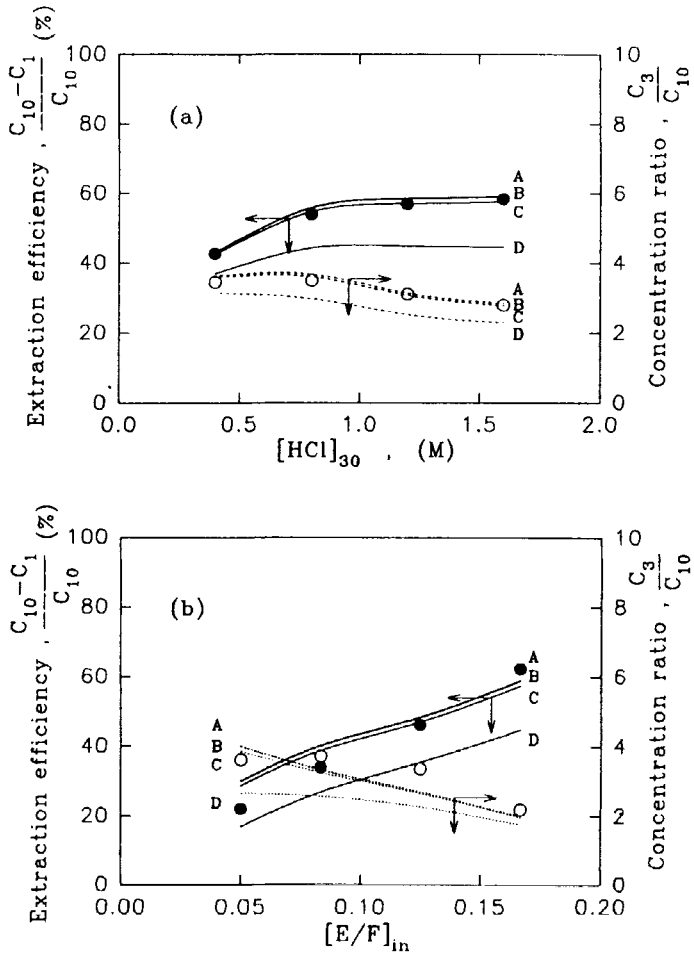


FIG. 12 Effect of external-phase mass transfer coefficient. A: $k_{L1} = 10^{-1}$ cm/s. B: $k_{L1} = 10^{-2}$ cm/s. C: $k_{L1} = 10^{-3}$ cm/s. D: $k_{L1} = 10^{-4}$ cm/s.

In summary, with decreasing R_o value and increasing K, k_{L1}, k_{L3}, and D_{RA} values, the extraction efficiency and concentration ratio of phenylalanine will also grow.

Figures 14(a) and 14(b) present optimum model calculations and experimental results for two different sets of operating conditions. The figures show that the theoretical model calculations, although they do not fit the

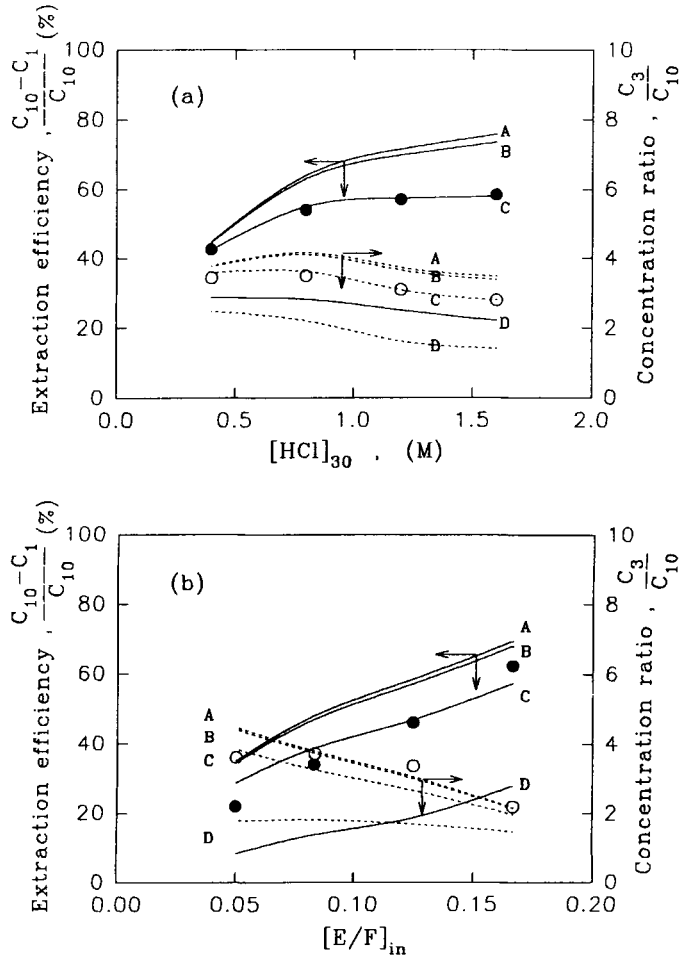


FIG. 13 Effect of membrane-phase diffusion coefficient. A: $D_{RA} = 10^{-4}$ cm²/s. B: $D_{RA} = 10^{-5}$ cm²/s. C: $D_{RA} = 10^{-6}$ cm²/s. D: $D_{RA} = 10^{-7}$ cm²/s.

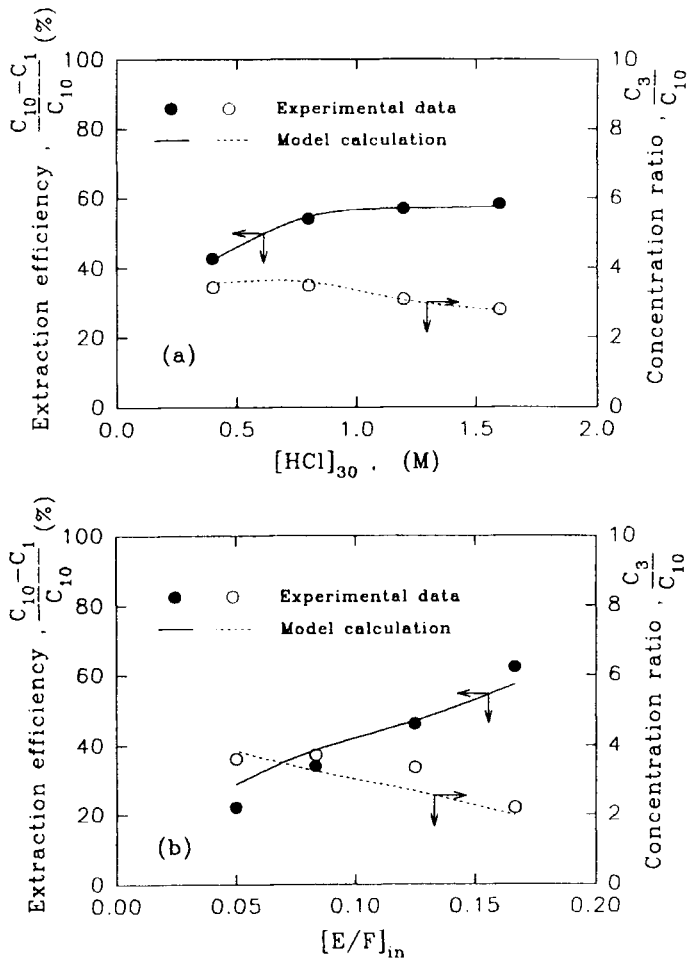


FIG. 14 Comparison of model simulation with experimental data.

experimental outcomes very well, can still be used to predict the trend of the extraction and concentration phenomena of phenylalanine, thus showing the applicability of the theoretical model.

CONCLUSION

According to the preliminary research results of this paper, it is feasible to apply the ELM system in a continuous CSTR operation to separate

and concentrate amino acids. This study has chosen phenylalanine as the model amino acid and D2EHPA as the carrier which, under proper operating conditions, can extract and concentrate phenylalanine from the external-phase solution into the internal-phase solution. The extraction efficiency can to reach 70% while concentration ratio is increased fourfold. For this paper we adopted the hollow sphere emulsion globule model, based on chemical extraction equilibrium and the mass balance equations of CSTR operation, to study the extraction and concentration efficiency of phenylalanine. We also made a comparison between the model calculations and the experimental results to determine the feasibility of applying the mathematical model to the ELM system we studied. The results show that the theoretical model calculations can predict the trend of extraction and concentration of phenylalanine. It was found that the flow rate ratios of the external phase and the emulsion phase at five different outlet positions do not agree with the flow rate ratio of the inlet streams during the extraction process. It was also discovered that the emulsions obtained from five different outlet positions became glutinous. This indicates that the emulsion creates the osmotic swelling phenomenon during CSTR operation. This phenomenon not only decreases the extraction efficiency and concentration ratio but, what is worst, affects the operationability of CSTR. Therefore, if a way could be found to reduce the occurrence of the osmotic swelling phenomenon, the CSTR operation be helped and the extraction and concentration efficiency of phenylalanine would be increased.

NOTATION

A	phenylalanine zwitterion
A^+	positively charged phenylalanine
A^-	negatively charged phenylalanine
a	interfacial area per unit volume (cm^2/cm^3)
B	total concentration of hydrogen ion in all forms (mol/dm^3)
C	total concentration of phenylalanine in all forms (mol/dm^3)
D_{RA}	diffusion coefficient of RA in membrane phase (cm^2/s)
E	emulsion flow rate (cm^3/s)
F	external aqueous phase flow rate (cm^3/s)
H^+	hydrogen ion
J_1	mole flux of phenylalanine in external phase ($mol/cm^2 \cdot s$)
J_2	mole flux of phenylalanine in membrane phase ($mol/cm^2 \cdot s$)
J_3	mole flux of phenylalanine in internal phase ($mol/cm^2 \cdot s$)
K	extraction equilibrium constant (—)
K_{a1}	first dissociation constant of phenylalanine (mol/dm^3)
K_{a2}	second dissociation constant of phenylalanine (mol/dm^3)

k_{L1}	mass transfer coefficient of phenylalanine in external phase (cm/s)
k_{L3}	mass transfer coefficient of phenylalanine in internal phase (cm/s)
M^+	counterion
q_E	volume flow rate of emulsion (cm^3/s)
q_w	volume flow rate of external aqueous phase (cm^3/s)
q_{EN}	volume flow rate of aqueous phase due to mechanical entrainment (cm^3/s)
q_L	leakage rate of internal phase (cm^3/s)
q_S	osmotic swelling rate (cm^3/s)
R_i	inner radius of emulsion globule (cm)
R_o	outer radius of emulsion globule (cm)
RM	counterion–carrier complex
RA	phenylalanine–carrier complex
$-r_A$	extraction flux of phenylalanine ($mol/cm^2 \cdot s$)
S	total interfacial area (cm^2)
V	total volume (cm^3)
V_E	emulsion volume (cm^3)
[A]	concentration of A in aqueous phase (mol/dm^3)
$[A^+]$	concentration of A^+ in aqueous phase (mol/dm^3)
$[A^-]$	concentration of A^- in aqueous phase (mol/dm^3)
$[H^+]$	concentration of H^+ in aqueous phase (mol/dm^3)
$[M^+]$	concentration of M^+ in aqueous phase (mol/dm^3)
[RA]	concentration of RA in membrane phase (mol/dm^3)
[RM]	concentration of RM in membrane phase (mol/dm^3)
ϕ_i	volume fraction of internal phase in emulsion (—)

Subscripts

0	initial value
1	external phase
3	internal phase
av	average value
in	inlet
m	membrane phase
out	outlet

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