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Separation of L-Phenylalanine by Nondispersive Extraction and Backextraction. Equilibrium and Kinetic Parameters

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ABSTRACT

The objective of this work is the evaluation of the separation/concentration of L-phenylalanine by means of nondispersive extraction and backextraction in hollow fiber modules and the determination of the equilibrium and kinetic parameters, which will allow the description of the separation process. An organic solution based on Aliquat 336, 30% (v/v); isodecanol, 30% (v/v); and kerosene is used as a selective extraction medium. The extraction of L-phenylalanine takes place at pH 10.5, and the backextraction takes place at pH 0.5, with a sulfuric acid solution. The nondispersive extraction and backextraction process for the separation/concentration of L-phenylalanine is described by means of a mathematical model based on seven differential equations. Its resolution is performed by the gPROMS simulation package after introduction of the chemical equilibrium extraction parameters $K_{qE} = 1.32$ and $K_1 = 1.25 \times 10^{-3}$, allowing calculation of the optimum value of the mass transfer coefficient, $K_M = 1.12 \times 10^{-8}$ m/s, which is in the range of previously reported values. This model and its parameters are useful for establishing the viability of the industrial separation/concentration processes of L-phenylalanine.

Key Words. L-Phenylalanine; Hollow fiber; Nondispersive extraction and backextraction

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INTRODUCTION

Production of amino acids is carried out in one of two main ways: chemical or biochemical synthesis (microbial fermentation or enzymatic synthesis) (1). In the chemical process a racemic mixture of enantiomers is obtained, while the L-form is the main product of biochemical synthesis. In recent years the market for some L-amino acids has increased, and this has led to new manufacturing processes.

A new sweetener aspartame is L-aspartyl-L-phenylalanine methylester (1-methyl-*N*-aspartyl-L-phenylalanine). Its adoption in foods and especially in soft drinks has led to a major increase in the market for L-phenylalanine (L-Phe) from 50 tons in 1981, to over 3000 tons in 1984, to nearly 6000 tons in 1987 (2, 3).

Due to the low amino acid concentration in fermentation broths and enzymatic liquors, separation/concentration steps are required to reach the final conditions needed for commercial production. Different technological alternatives can be applied in the separation and concentration of amino acids: ion exchange, chromatography, adsorption, filtration, evaporation, reverse osmosis, electrodialysis, etc. These operations account for up to 50% of the production costs (4).

With regard to the separation/concentration of L-phenylalanine, it has been performed using such well-known technologies as ion exchange (5, 6) and reactive extraction (7–9). Recently, new separation technologies have been considered by differents authors: emulsion liquid membranes (3, 10–17), supported liquid membranes (18, 19), etc. Each technology has different limitations: the ionexchange of broth liquors requires extensive pretreatment, and a significant decrease in the adsorption capacity of the resin leads to a reduction of purification; in liquid–liquid extraction the formation of emulsions or microemulsions occurs when quaternary ammonium salts are used as reagents in stirred systems; in emulsion liquid membrane technologies, especially at high concentrations of the products, significant swelling effects of the membrane have been observed; and in supported liquid membranes the stability of the liquid membrane is the main drawback.

Nondispersive extraction in hollow fiber modules (NDX) combines the advantages of membrane processes with solvent extraction processes: 1) the possibility to contact organic and aqueous phases flowing at high velocities, even when their densities are similar; 2) a very high interfacial area per unit equipment volume, which allows a high rate in the separation step (20); 3) the capability of treating dilute solutions; 4) the reduction of solvent losses; and 5) a reduction in equipment volume. This technology has been widely reported for the extraction and recovery of metals

(21–23), extraction of proteins (24), acids (25), wastewater treatment (26), extraction of alcohol from fermentation broths (27), etc.

In hollow fiber contactors the aqueous and the organic solutions flow continuously, one through the lumen of the fibers and the other one by the shell side; both phases make contact through the pores of the fiber wall (24). Cussler et al. (28) reported that phase entrainment can be avoided by applying a differential static pressure in one of the phases.

To carry out the extraction and the backextraction processes simultaneously, two different configurations can be used: 1) contained liquid membranes in one module (29, 30) or 2) two different modules, one for the extraction process (EX) and the second for the backextraction (BEX), with the organic solution flowing in a closed cycle through both modules (24, 31, 32).

Several extractants have been reported in the literature for the selective extraction of L-phenylalanine: TOMAC (7), D2EHPA (8, 11, 16), ADOGEN 464 (13); AOT (33), and Aliquat 336 (3, 8–10, 18). In the application of Aliquat 336, the complex behavior of the quaternary ammonium salt has been widely mentioned in the literature (34–36).

The viability of the coupled process of extraction and backextraction of L-phenylalanine has been reported using an ammonium chloride solution as the stripping reagent [37]. In this process the chloride ion is exchanged by L-phenylalanine, and a maximum concentration of 44.60 g/L of L-phenylalanine was reached after 50 hours. However, due to crystallization of the amino acid salts in the organic phase, it was not possible to increase the L-phenylalanine concentration in the backextraction solution (37). In this study L-phenylalanine has been used as the production target molecule in the bioprocess, and it has been extracted by means of Aliquat 336, with sulfuric acid used as the stripping solution. The selection of the ammonium quaternary salt Aliquat 336 as the extraction reagent makes the transfer of the anionic form of L-phenylalanine necessary, which can be reached at a pH higher than 9 due to its zwitterionic character (18). The extraction takes place after ion exchange of the anionic amino acid by hydrogen sulfate according to the following equation:

$$\overline{(R_4N)^+(HSO_4)^-} + (\text{L-Phe})^- + OH^- \Leftrightarrow \overline{(R_4N)^+(\text{L-Phe})^-} + SO_4^{2-} + H_2O \quad (1)$$

Simultaneously, the amino acid is recovered in the second module by means of the ion-exchange reaction with sulfuric acid used as a backextraction reagent (BEX) according to the following equation:

$$\overline{(R_4N)^+(\text{L-Phe})^-} + 2HSO_4^- + 2H^+ \Leftrightarrow \overline{(R_4N)^+(HSO_4)^-} + (\text{L-PheH}_2)HSO_4 \quad (2)$$

In this work the equilibrium and kinetic parameters of the nondispersive extraction and backextraction of L-phenylalanine are presented. These results allow the separation process to be compared with existing technologies.

EXPERIMENTAL METHOD AND PROCEDURE

Aliquat 336 (Fluka), a commercial mixture of trialkylmethylammonium chlorides (trialkyl = C_8–C_{10}, mainly capryl) has been used as the extractant, and kerosene (Petronor, S.A.) has been used as the solvent. In order to avoid segregation of a third (second organic) phase, the addition of a modifier (a high molecular weight alcohol) was necessary. Isodecanol (30% v/v, Exxon Chemicals) was added to the organic phase. The feed solution contained 10 g/L L-phenylalanine (Aldrich). The pH of the solution was kept constant and equal to 10.5 by the addition of NaOH (1 M). Sulfuric acid (0.316 M) was used as the stripping solution, pH 0.5. A 1-to-2 ratio of feed solution volume to organic phase volume was employed. Two modules were used: the first one for the extraction process (EX) and the second one for the backextraction process (BEX). The aqueous feed (F) containing 10 g/L L-phenylalanine flows through the extraction module, and the stripping solution (S) flows through the backextraction module, while the organic phase (O) continuously flows in a closed cycle through both modules. The non-dispersive experimental system Liquid-Cel, commercialized by Hoechst-Celanese A.G., contains two gear pumps capable of flows up to 1 L/min for the organic and feed phases, and is powered by a variable speed DC motor. In order for the backextraction aqueous phase to flow, a diaphragm pump with a chemically inert PTFE diaphragm body and a valve seat was employed; it was capable of flows up to 0.8 L/min and was powered by a variable speed DC motor. A pulse dampener was used to eliminate pulsation in the output flow. Three Teflon flowmeters were equipped with backpressure control valves in order to maintain the appropriate differential pressure for the control of the aqueous–organic interface at each module. The inlet and outlet pressures of each stream were measured with stainless steel pressure gauges. The pressure of the aqueous phases was maintained 3 psi higher than the pressure of the organic phase, ensuring that displacement of the organic phase from the pores of the hollow fiber wall did not take place. Adjustment of pH in the aqueous phases was carried out by using a pH controller system (Methrom 691-01). The pH values were continuously monitored in the feed and stripping phases. The pH-meter signals activated peristaltic pumps (Eyela micro tube pump MP-3) for the addition of a 50% sodium hydroxide solution into the feed reservoir and the addition of sulfuric acid

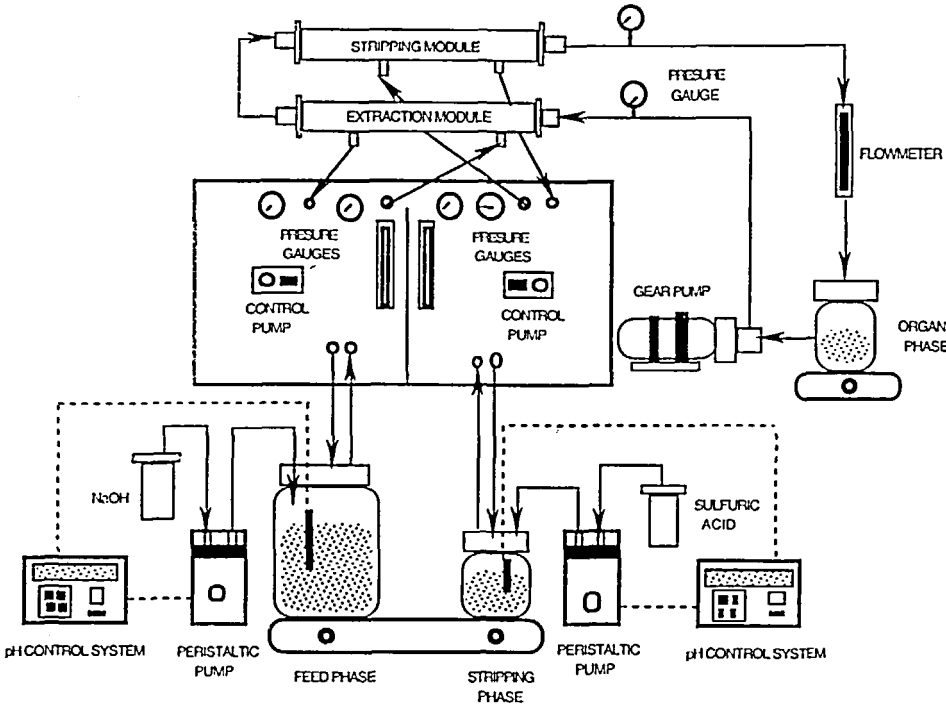

FIG. 1 Experimental setup of the coupled hollow fiber EX and BEX processes.

TABLE 1
Characteristics of the Hollow Fiber Modules

Fiber type	X-10/polypropylene
Wall thickness	30 μm
Internal diameter	240 μm
Number of fibers	2100
Nominal porosity	30%
Shell material	Polypropylene
Potting material	Epoxy resin
Shell inner diameter	25 mm
Shell length	200 mm
Effective mass transfer length	160 mm
Effective mass transfer area	0.23 m^2

(6 M) into the stripping reservoir. The system allows the pH in the aqueous feed and stripping solutions to be controlled within a range of ± 0.1 pH units without any significant change in the total volume. The L-phenylalanine concentration in the aqueous phases was measured in a Perkin-Elmer Lambda 2 UV/V Spectrometer at a wavelength of 257.8 nm. The experimental setup is shown in Fig. 1, while the characteristics of the hollow fiber membrane modules are given in Table 1.

KINETIC MODELING

Mass separation devices used in nondispersive extraction usually contain a bundle of a large number of parallel hollow fibers. It is assumed that the conditions in each fiber are identical and independent of the other fibers. Thus, it is sufficient to solve the mass transfer equation for a single fiber in order to predict the overall performance of the mass separation device.

With regard to extraction processes and considering steady-state for the fluid phase containing the solute, Kim and Stroeve developed the mass transfer fundamentals of this systems, describing the velocity and concentration profiles along a hollow fiber by means of the continuity mass conservation equation and associated boundary conditions for the solute of the inner fluid (39). Alonso et al., working with the feed aqueous phase flowing through the lumen of the hollow fiber in a one-through operation mode, made a similar analysis and applied the continuity mass conservation equation satisfactorily to the modeling of the semicontinuous extraction process of Cr(VI) with Aliquat 336 as the organic carrier (40, 41).

For systems working in a nonsteady state, it is also necessary to describe the change of the solute concentration with time, which requires significant efforts in the solution of a system of differential equations. For simplicity, several systems have been described by means of macroscopic mass balances of the permeating solute applied to a certain volume of the fiber during a time interval. Urtiaga et al. (42) reported this approach in the modeling and parameter estimation of the recovery and concentration of phenol with hollow-fiber-supported liquid membranes, Alonso and Pantelides showed the modeling and simulation of a process plant for the removal and recovery of Cr(VI) with Aliquat 336 using hollow fiber modules (43); single and dual function membrane modules were considered, and the concentration profiles through the modules were simulated by solving mass transfer balances corresponding to all species involved in the process and considering convection and diffusion; a fully developed laminar flow inside the fiber was considered, whereas axial and radial

diffusion components were included. Overall mass balances were developed for the two hollow fiber modules employed in the non-steady extraction and backextraction of Cr(VI) by Ortíz et al. (42); considering that the mass transport resistance in both modules was due to the membrane, the system of differential equations was integrated by means of a Runge–Kutta algorithm.

In the present work the experimental system under study incorporates two hollow fiber modules and three reservoir tanks in which the liquids are mixed homogeneously. The organic phase flows from the extraction module to the backextraction one, is mixed in the organic-phase reservoir, and enters the extraction step again. For the description of the mass transport in this system, mass balance equations corresponding to the solute transport in the two hollow fiber modules must be combined with equations describing the change of solute concentration in the reservoirs.

The mass transfer rate in the extraction step depends on the mass transfer coefficient, K_M, and the concentration gradient, which can be obtained with the interfacial chemical equilibrium, assuming equilibrium conditions at the interface. Nonlinear chemical equilibrium systems would result in a more complex expression for the membrane resistance. It is assumed that the chemical equilibrium of L-phenylalanine extraction can be described by the mass action law, according to Eq. (1):

$$K_{Eq} = K[OH^-] = \frac{[\overline{(R_4N)^+(L\text{-}Phe)^-}][SO_4^{2-}]}{[\overline{(R_4N)^+(HSO_4)^-}][(L\text{-}Phe)^-]} \tag{3}$$

The low pH value of the backextraction solution may be responsible for the total neutralization of L-phenylalanine in the backextraction phase; for this reason, in this process it is considered that a maximum mass transfert gradient can be described by the concentration of L-phenylalanine in the organic phase.

For the development of the mathematical model, linear concentration gradients have been assumed. A differential mass balance for the tanks can be expressed by

$$\frac{\partial C}{\partial t} = \frac{Q}{V_T}(C_{in} - C_{out}) = \delta(C_{in} - C_{out}) \tag{4}$$

A differential mass balance for mass transfer in the modules can be expressed by

$$\frac{\partial C}{\partial t} + v\frac{\partial C}{\partial z} \pm \left(\frac{n2\pi r}{s}\right) K_M(C_0^* - C_0) = 0 \tag{5}$$

which after rearranging leads to

$$\left(\frac{V_M}{QL}\right)\frac{\partial C}{\partial t} + \frac{\partial C}{\partial z} \pm \left(\frac{n2\pi r}{Q}\right) K_M(C_0^* - C_0) = 0 \tag{6}$$

which can be expressed as

$$\alpha\frac{\partial C}{\partial t} + \frac{\partial C}{\partial z} \pm \beta K_M(C_0^* - C_0) = 0 \tag{7}$$

This equations can be applied to describe the mass transfer of L-phenylalanine in the modules and the tanks as follows.

Feed Solution

Module mass balance:

$$-\alpha_{mA}\frac{\partial C_A^{mE}}{\partial t} - \frac{\partial C_A^{mE}}{\partial z} = \beta_{mA}K_M(C_0^{mE*} - C_0^{mE}), \quad z = 0,\ C_A^{mE} = C_{A,z=0}^{mE}$$

$$z = L,\ C_A^{mE} = C_{A,z=L}^{mE}$$

$$t = 0,\ C_A^{mE} = C_{Ai}^{mE} \tag{8}$$

Tank mass balance: $C_A^T = C_{A,z=0}^{mE}$

$$\frac{\partial C_A^T}{\partial t} = \delta_A(C_{A,z=L}^{mE} - C_{A,z=0}^{mE}), \quad t = 0,\ C_A^T = C_{Ai} \tag{9}$$

Organic Solution

EX module mass balance:

$$\alpha_{mO}\frac{\partial C_O^{mE}}{\partial t} + \frac{\partial C_O^{mE}}{\partial z} = \beta_{mO}K_M(C_O^{mE*} - C_O^{mE}), \quad z = 0,\ C_O^{mE} = C_{O,z=0}^{mE}$$

$$z = L,\ C_O^{mE} = C_{O,z=L}^{mE}$$

$$t = 0,\ C_O^{mE} = C_{Oi}^{mE} \tag{10}$$

BEX module mass balance:

$$-\alpha_{mO}\frac{\partial C_O^{mR}}{\partial t} - \frac{\partial C_O^{mR}}{\partial z} = \beta_{mO}K_M(C_O^{mR}), \quad z = 0,\ C_O^{mR} = C_{O,z=L}^{mE}$$

$$z = L,\ C_O^{mR} = C_{O,z=L}^{mR}$$

$$t = 0,\ C_O^{mR} = C_{Oi}^{mR} \tag{11}$$

Tank mass balance: $C_O^T = C_{O,z=0}^{mE}$

$$\frac{\partial C_O^T}{\partial t} = \delta_O(C_{O,z=L}^{mR} - C_{O,z=0}^{mE}), \qquad t = 0,\ C_O^T = C_{Oi} \tag{12}$$

Backextraction Solution

Module mass balance:

$$\alpha_{mR}\frac{\partial C_R^{mR}}{\partial t} + \frac{\partial C_R^{mR}}{\partial z} = \beta_{mR}K_M(C_O^{mR}), \qquad z = 0,\ C_R^{mR} = C_{R,z=0}^{mR}$$

$$z = L,\ C_R^{mR} = C_{R,z=L}^{mR}$$

$$t = 0,\ C_R^{mR} = C_{Ri}^{mR} \tag{13}$$

Tank mass balance: $C_R^T = C_{R,z=0}^{mR}$

$$\frac{\partial C_R^T}{\partial t} = \delta_R(C_{R,z=L}^{mR} - C_{R,z=0}^{mR}), \qquad t = 0,\ C_R^T = \chi^{\beta} \tag{14}$$

where the equilibrium amino acid concentration in the EX module is

$$C_O^{mE*} = \frac{K_{Eq}C_{OM}C_A^{mE}}{C_{Ai} + (K_{Eq} - 1)C_A^{mE}} \tag{15}$$

and the variables of operation in the experimental system are

$$\alpha_A = \frac{V_{MA}}{Q_A L}, \qquad \beta_A = \frac{2n\pi r}{Q_A}, \qquad \delta_A = \frac{Q_A}{V_{TA}}$$

$$\alpha_O = \frac{V_{MO}}{Q_O L}, \qquad \beta_O = \frac{2n\pi r}{Q_O}, \qquad \delta_O = \frac{Q_O}{V_{TO}}$$

$$\alpha_R = \frac{V_{MR}}{Q_R L}, \qquad \beta_R = \frac{2n\pi r}{Q_R}, \qquad \delta_R = \frac{Q_R}{V_{TR}}$$

There is less than a 10% fraction of the liquids in the flowmeters, tubes, etc; 5% of this volume has been assumed to be in the HF device (V_M) and 5% increases the real volume of the tank (V_T). Taking into account the residence time of these volumes, their influence in the mathematical modeling has been found to be negligible.

The set of first-order coupled differential equations (Eqs. 8–14) has been integrated by means of the gPROMS process modeling software to obtain the mass transport parameter from a comparison of the simulated results and the experimental data using the minimum standard deviation as a criterion in the optimization of the parameters. The gPROMS is a software package that provides a high-level language for the declarative description of mathematical models of unit operations, which can then be

combined hierarchically to form the description of the entire process; the mathematical models may involve mixed sets of nonlinear integral, partial and ordinary differential, and algebraic equations (43).

RESULTS AND DISCUSSION

Extraction Equilibrium

The system under study is the reversible extraction of L-phenylalanine with Aliquat 336. An intensive experimental study of the equilibrium at 20 ± 3°C was carried out, starting with an initial concentration of 30% (v/v) of the Aliquat 336 hydrogen sulfate form $\overline{((R_4N)^+[HSO_4]^-)}$, 30% (v/v) isodecanol, 40% (v/v) kerosene, and 10 g/L L-Phe. Three different volume ratios were used (V_A/V_O = 1, 2, and 3). The contacts were made in closed glass tubes in a rotatory SBS stirrer (50 rpm); the contact time was 1 hour. The organic and the aqueous phases were separated, and successive contacts (N) of the partially loaded organic phases with fresh aqueous solutions with the same volume ratios were made. The experimental results are shown in Fig. 2.

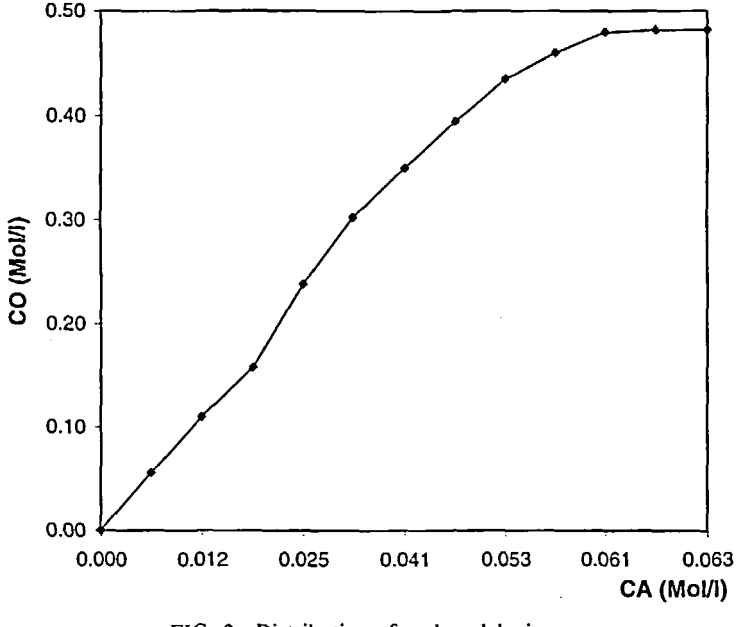

FIG. 2 Distribution of L-phenylalanine.

After applying the mass action law and mass balances to describe the chemical equilibrium, the equilibrium equation should be

$$K_{Eq} = \frac{\left[\sum_{N=1}^{N} (C_{Ai} - C_{AN}) \frac{V_A}{V_O}\right] [C_{Ai} - C_{AN}]}{[C_{AN}]\left[C_{OM} - \sum_{N=1}^{N} (C_{Ai} - C_{AN}) \frac{V_A}{V_O}\right]} \tag{16}$$

where N is the number of contacts, C_{OM} is the initial concentration of the carrier, C_{Ai} is the initial concentration of L-phenylalanine in the aqueous phase, C_{AN} is the equilibrium concentration of L-phenylalanine in the aqueous phase in N contacts, and V_A and V_O are the volumes in the aqueous solution and in the organic phase, respectively. Equation (16) can be rearranged to

$$\sum_{N=1}^{N} (C_{Ai} - C_{AN}) \frac{V_A}{V_O} = C_{OM} - \frac{1}{K_{Eq}} \left\{ \frac{\left[\sum_{N=1}^{N} (C_{Ai} - C_{AN}) \frac{V_A}{V_O}\right] [C_{Ai} - C_{AN}]}{[C_{AN}]} \right\} \tag{17}$$

Figure 3 shows the linear plot from which the values of K_{Eq} and C_{OM} are obtained from the origin ordinate and the slope of the regression fitting: $K_{Eq} = 1.32$, $C_{OM} = 0.5035$ M, and $R^2 = 0.99$.

Kinetics

Kinetic experiments were carried out starting with a 10 g/L concentration of L-phenylalanine in the feed solution and an organic mixture of Aliquat 336, 30% (v/v) isodecanol, and 30% (v/v) kerosene, with sulfuric acid (pH 0.5, 0.316 M) as the stripping reagent.

Experiments were carried out to study the extraction and backextraction of L-phenylalanine. The same organic phase was maintained during the process, while both the feed and backextraction aqueous solutions were renewed using fresh solutions of the same composition.

Both EX and BEX steps were carried out while working in a recirculating mode, and the fluid phases flowed cocurrently. The batch time was 48 hours in each experiment. When the concentration in the feed solution decreased below 700 mg/L, a new batch with a fresh aqueous feed solution and a fresh aqueous stripping solution were supplied. The experimental conditions are shown in Table 2. Samples were taken at different times

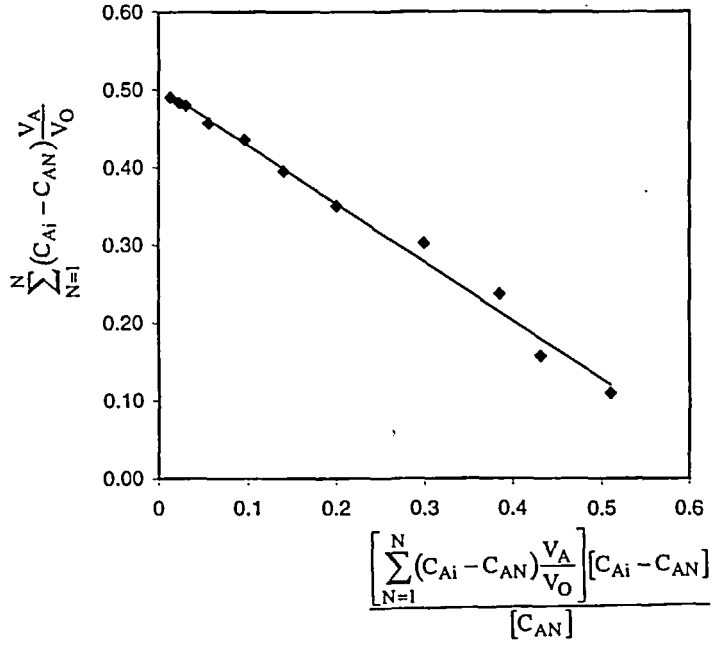

FIG. 3 Linear fitting of the equilibrium results (Eq. 17).

from the aqueous reservoirs, and the L-phenylalanine concentration was analyzed after each experiment.

In these experiments more than 90% of the L-phenylalanine of the feed solution was extracted, while the backextraction yield was nearly 100%; This shows that the organic phase was regenerated and ready for further

TABLE 2
Experimental Conditions

Phase	V_M (L)	V_T (L)	Q (L/s)	α ($s \cdot m^{-1}$)	β ($s \cdot m^{-2}$)	δ (s^{-1})	Flow
Feed	0.055	0.400	5.8×10^{-3}	0.592×10^{2}	3.39×10^{5}	1.45×10^{-2}	Outside fiber
Organic	0.024	0.145	5.8×10^{-4}	0.258×10^{3}	3.39×10^{6}	4.0×10^{-3}	Inner fiber
Stripping	0.055	0.160	1.8×10^{-3}	0.185×10^{3}	1.07×10^{6}	1.15×10^{-2}	Outside fiber

use. This would allow the hollow fiber extraction and backextraction process to be applied for the continuous concentration of L-phenylalanine using Aliquat 336 as the carrier.

The calculation of the mass transport coefficient in the membrane, K_M, requires the integration of the differential Eqs. (8)–(14) by means of the gPROMS simulation package (43) after introduction of the mathematical model and the chemical equilibrium extraction parameters (K_{Eq} = 1.32 and C_{OM} = 0.5035 M). K_M was considered the optimization parameter in a comparison of the experimental and the simulated data of the extraction and backextraction processes. Optimization was done on the basis of the minimum weighted standard deviation for the dimensionless concentration of L-phenylalanine in the EX solution and the dimensionless concentration of L-phenylalanine in the BEX solution. The weighted standard deviation is defined as

$$\sigma = \sqrt{\frac{\sum \left(\frac{C_{exp} - C_{sim}}{C_{exp}} \right)}{M - 1}} \tag{18}$$

After comparison of the experimental data of the kinetic runs (EX and BEX data) with the simulated values, the optimum value of K_M obtained

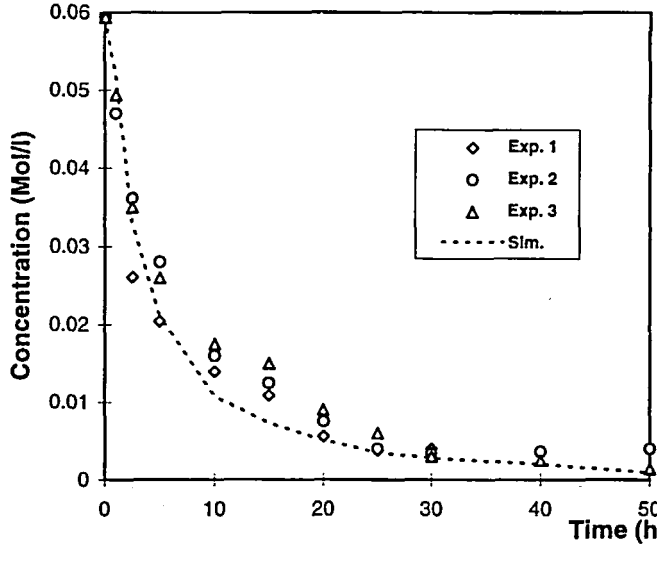

FIG. 4 Experimental and simulated results of L-phenylalanine extraction.

was 1.12E-8 m/s, with a minimum standard deviation of 33.52%. Experimental and simulated results are shown in Figs. 4 and 5 for the extraction and stripping solutions, respectively.

The mass transfer coefficient K_M is in the range of magnitude of previously calculated parameters for the nondispersive extraction and backextraction of chromate using the same extraction agent (K_M is in the range between 8.8×10^{-8} and 0.106×10^{-8} m/s, depending on the extraction agent concentration) in hollow fiber systems (41). This could indicate that only changes in the diffusivity of the complex specie have an influence on the mass transfer coefficient in the hollow fiber modules.

The simulation of extraction results in Fig. 4 shows a decrease of the extraction rate, which cannot be described by the model. The accumulation of sulfuric acid and amino acid salt in the stripping phase may be responsible for a new equilibrium which leads to a concentration decrease of the $\overline{((R_4N)^+(\text{L-Phe})^-)}$ form:

$$4OH^- + \overline{(R_4N)^+(HSO_4)^-(\text{L-Phe}\cdot H_2)\cdot HSO_4} \Leftrightarrow \overline{(R_4N)^+(\text{L-Phe})^-} + 2SO_4^{2-} + 4H_2O \quad (19)$$

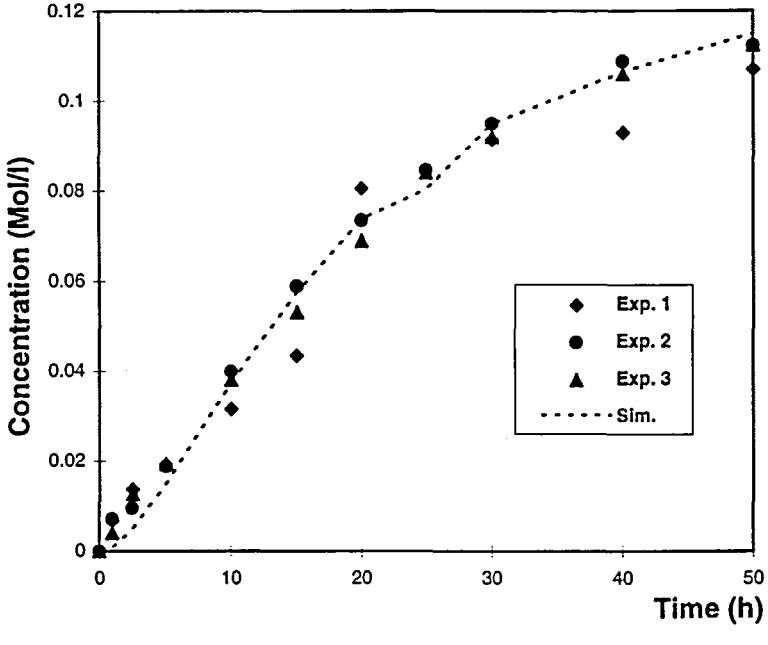

FIG. 5 Experimental and simulated results of L-phenylalanine backextraction.

where

$$K_1 = \frac{[\overline{(R_4)^+(\text{L-Phe})^-}]\cdot[SO_4^{2-}]^2}{[(R_4N)^+(HSO_4)^-(\text{L-Phe}\cdot H_2)\cdot HSO_4]} \tag{20}$$

leading to an equilibrium concentration in the organic phase given by

$$C_O^{mE*} = \frac{K_{Eq}C_{OM}C_A^{mE}}{C_{AE} + K_{Eq}/K_1(C_{AE})^2C_A^{mE} + K_{Eq}C_A^{mE}} \tag{21}$$

An optimized simulation of the process model introducing this new equilibrium parameter leads to the fitting shown in Figs. 6 and 7, where $K_M = 1.12 \times 10^{-8}$ m/s, $K_{Eq} = 1.32$, $K_1 = 1.25 \times 10^{-3}$, and $\sigma = 0.287$, which is the range of experimental error. The parity plot of the simulated and experimental data is shown in Fig. 8.

From the fundamentals:

$$K_M = D\epsilon/\lambda\tau \tag{22}$$

After substitution of $\epsilon = 0.30$ and $\lambda = 3 \times 10^{-5}$ (m):

$$D/\tau = 1.12 \times 10^{-12} \text{ (m}^2\text{/s)}$$

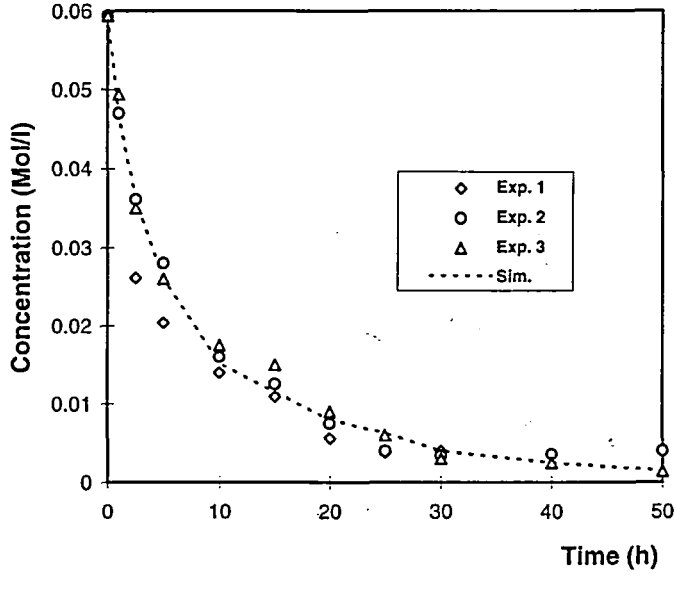

FIG. 6 Two equilibria model. Experimental and simulated results (EX).

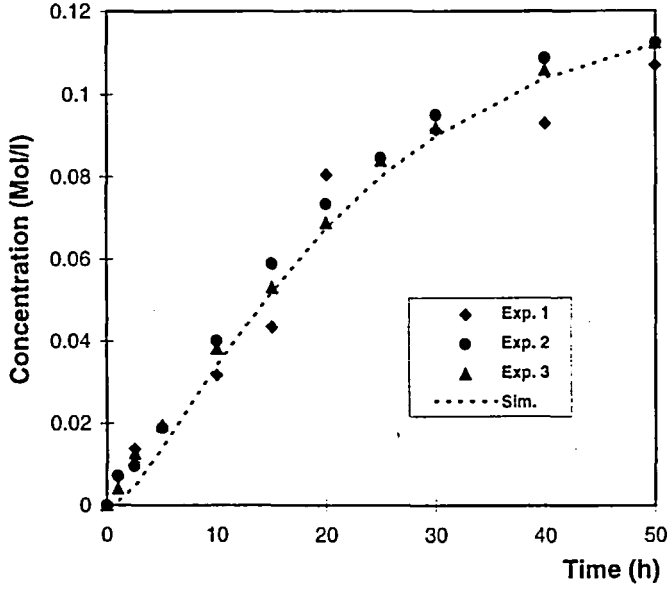

FIG. 7 Two equilibria model. Experimental and simulated results (BEX).

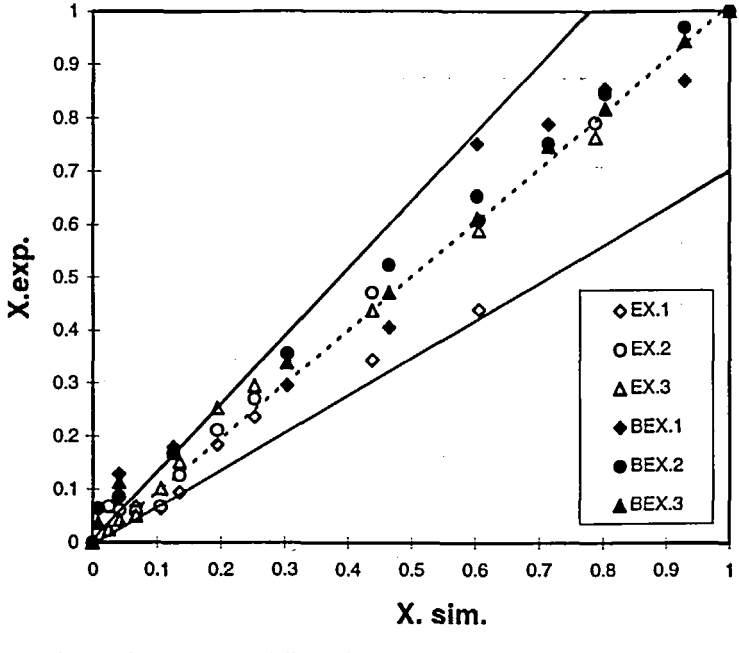

FIG. 8 Parity graph, experimental dimensionless concentration of L-phenylalanine vs simulated dimensionless concentration of EX and BEX for the two equilibria model.

This low value of the effective diffusion coefficient in the filled pores of the fiber, nearly 100 times smaller than the diffusion coefficient of L-phenylalanine in water, can be justified by taking into account that:

1. The viscosity of the Aliquat 336 concentrated solutions (30% v/v) is much higher (by nearly 50 times) than the water solutions. Correlations usual consider the product (diffusion coefficient) × (viscosity) to be a constant.
2. The diffusing specie is not L-phenylalanine. It is the complex of amino acid with Aliquat 336.
3. Solutions of high viscosity which fill the pores of the membrane may interact with the surface, leading to lower diffusion values.

An experimental determination of the diffusion coefficcient of the amino acid–Aliquat 336 complex in high viscosity solutions will apparently be necessary to correlate the experimental mass transfer parameter with the diffusion coefficient.

CONCLUSIONS

This work has shown the viability of the separation/concentration process of L-phenylalanine using nondispersive extraction and backextraction in hollow fiber modules.

A closed cycle organic phase based on Aliquat 336 (30% v/v), isodecanol (30% v/v), and kerosene was used as the extraction reagent. Sulfuric acid was the stripping agent.

The main parameters of the process (equilibrium constants, $K_{Eq} = 1.32$, $K_I = 1.25 \times 10^{-3}$, and membrane mass transfer coefficient, $K_M = 1.12 \times 10^{-8}$ m/s) were evaluated. They allow a good description of the experimental results as shown in the parity graph.

These results allow evaluation of this technology against other separation processes.

NOTATIONS

C	solute concentration (mol/L)
C_{OM}	maximum concentration of the extraction reagent in the organic phase (mol/L)
D	effective diffusivity (m^2/s)
K_{Eq}	chemical equilibrium constant (Eq. 3)
K_M	membrane mass transport coefficient (m/s)
K_I	chemical equilibrium constant (Eq. 20)
L	length of a fiber in the module (m)

M	number of experimental points in the EX and BEX process
N	number of succesive contacts in the extraction equilibrium
n	number of fibers in the modules
Q_A, Q_O, Q_R	flow rate of the feed, organic, and BEX solutions (L/s)
R^2	regression coefficient
r	radius of the fiber (m)
s	cross-sectional area for the phase in the module (m^2)
t	time (s)
V_{TA}, V_{TR}, V_{TO}	volume of the feed, BEX, and organic solutions in the tanks (L)
V_{MA}, V_{MR}, V_{MO}	volume of the feed, BEX, and organic solutions in the modules (L)
v	average linear velocity in the phase (m/s)
X	dimensionless concentration of L-phenylalanine (C_A/C_{Ai}).
z	axial distance in the module (m)

Greek Letters

α	variable of operation in the experimental system (s. m^{-1})
β	variable of operation in the experimental system (s. m^{-2})
δ	variable of operation in the experimental system (s. m^{-1})
ϵ	nominal porosity of the fiber
λ	wall thickness of the fiber (m)
σ	weighted standard deviation (Eq. 18)
τ	tortuosity

Subscripts

A	solute in the feed solution
O	solute in the organic solution
R	solute in the BEX solution

Superscripts

*	equilibrium
T	tank

mE	extraction module
mR	backextraction module

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