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Extraction of 4-Hydroxycinnamic Acid from Aqueous Solution by Emulsion Liquid Membranes

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Abstract: This work reports a study of 4-hydroxycinnamic acid extraction by emulsion liquid membranes. The effect of the presence of additives in the membrane phase on solute permeation was tested. The membrane with 2 wt.% of isodecanol, 2 wt.% of ECA4360J, and Shellsol T as diluent was selected to examine the permeation of 4-hydroxycinnamic acid. The modeling of solute extraction was done by taking into account the mass transfer in the external phase and globule, and the reaction between the diffusing component and the stripping reagent. The agreement between the calculated results and the experimental data was found satisfactory.

Keywords: Emulsion liquid membranes, 4-hydroxycinnamic acid, phenols extraction, modeling

INTRODUCTION

Phenols are often present in wastewater streams from many industrial processes. For instance, in Portugal, phenols are typical pollutants that exist mainly in olive mill wastewaters and, on a minor scale, in other effluents produced by other industries like phenolic resin plants, pulp and paper industries, aniline production, and coal power plants. The toxicity of phenolic effluents is well known and their treatment must be accomplished. When

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the phenols content is less than 50 ppm, biological, chemical, or electrochemical oxidation processes can be used for their treatment. However, liquid-liquid extraction is the most economical non-destructive process at higher concentrations (1).

This work aims to study the extraction of one of the common polyphenols, 4-hydroxycinnamic acid, from aqueous solution by using emulsion liquid membranes. This phenolic compound, also known as *p*-coumaric acid, exists in olive oil, which is a typical component of the Mediterranean diet. This phenolic acid and other phenol derivatives are thought to be important to prevent severe diseases because they exhibit antioxidant activity (2, 3). However, the natural presence of phenols in olive mill wastewaters is a serious problem to the environment.

Emulsion liquid membranes (ELM) have demonstrated considerable potential as a technique for separating a large variety of solutes. Several studies have been published concerning the recovery and concentration of metal ions (4, 5) and biochemical products (6, 7) and the removal of pollutants from wastewaters such as metal species and phenols (8–10).

ELM have been tried as an alternative to the conventional liquid-liquid extraction due to their advantages, such as large specific surface area for extraction, simultaneous separation and concentration in a single step, and requirement of expensive carrier in small quantities. ELM is a three-phase dispersion system, where a primary emulsion is dispersed in a continuous phase, which is the feed phase to be treated. The liquid membrane refers to the phase that separates the external continuous phase from the encapsulated phase. During the contact between feed phase and emulsion, the solute is transported through the membrane into the internal phase droplets and is concentrated. After permeation, the emulsion is separated from the continuous phase and the splitting of the emulsion is usually performed by applying high voltage.

The liquid membrane consists of a diluent, a surfactant to stabilize the emulsion, and a carrier reagent (extractant) in the case of separation of solutes by chemical reaction. Thus, the solute is able to diffuse through the membrane phase due to its solubility (Type I facilitated transport) or it reacts with the extractant molecule giving a solute-carrier complex that is carried from the external phase to the inner interface (Type II facilitated transport).

The extraction of phenol with ELM is usually performed using membranes containing aliphatic diluents and a polyamine, ECA4360J, that acts as surfactant. The extraction of phenol, chlorophenols, and cresols, using this type of membranes has been interpreted with satisfactory results by considering Type I transport in the modeling (10–13). However, phenol derivatives such as phenolic acids can exhibit a different behavior. Since the surfactant ECA4360J has amino groups, the reactive extraction of phenolic acids cannot be ignored. Even though several works have been published reporting the carrier role of ECA4360J in the extraction of penicillin G (14–17), the reaction of surfactant with solutes with acidic properties is commonly neglected.

In the present work, it is thus intended to study the extraction of 4-hydroxycinnamic acid from aqueous solution by using emulsion liquid membranes with ECA4360J as surfactant. The modeling of mass transfer is also an aim in this study.

THEORY

Several mathematical models of mass transfer have been proposed to predict the solute extraction using ELM. Cahn and Li (18) were the first researchers to propose a simple model in which the extraction rate was assumed to be proportional to solute concentration difference between the internal and external phases. Matulevicius and Li (19) established a hollow sphere model and assumed that the mass transfer resistance was limited to the peripheral shell of the globule and kept constant during the extraction process. Kopp et al. (20) adopted a more complex but a realistic approach to model the permeation. They developed a shrinking core model that took into account the time dependency of the mass transfer resistance in the emulsion globule. This model was the basis for the advancing front model proposed by Ho et al. (21). The advancing front model was then extended to include external resistance of mass transfer (22, 23). Bunge and Noble (24) presented a so-called reversible model, which incorporated the reaction equilibrium between the solute and the internal reagent. Yan et al. (25) adopted the improved advancing front model and developed a model for Type I facilitated transport taking into account the reaction between the diffusing component and the stripping reagent in the globule. Yan (26) extended the latter model for Type II facilitated transport. This author assumed pseudo-first-order reactions, forward and stripping, since the concentrations of extractant and stripping reagent are in excess in most cases.

In this work, the prediction of solute depletion in the external phase is based on the pseudo-homogeneous description of the emulsion globule of Kopp et al. (20) and takes into account the mass transfer in the external phase and globule, and the stripping reaction resistance. The present model has the following assumptions:

1. The size distribution of emulsion globules and internal droplets are uniform and can be described by Sauter mean diameter.
2. No coalescence and redispersion occur between all emulsion globules.
3. There is no internal circulation and coalescence within the emulsion globule.
4. The diffusion in the emulsion globule can be described by the use of effective diffusivity. There is no transport resistance in the internal phase.
5. Emulsion breakage and swelling can be neglected.
6. At the globule surface, the concentrations in the membrane and external phases are in equilibrium.

7. Since far excess of internal reagent is used in most experiments, a pseudo-first-order stripping reaction is assumed. The stripping reaction rate per unit of internal interface is therefore given as

$$r_s = k_s c_C \tag{1}$$

where k_s is the stripping reaction rate constant and c_C is the concentration of the organic diffusing component. It is worth mentioned that the assumptions 1-6 are the same as in the treatment of the advancing front model.

The set of equations describing the mass transfer for a batch-type process of ELM is presented as follows:

- Mass transfer of the solute A in the external aqueous phase

$$-V_{III}\frac{dc_{A(III)}}{dt} = Sk_c(c_{A(III)} - c_{A(III),int}) \tag{2}$$

where the external surface of the emulsion globules (S) is obtained from the Sauter mean diameter (d_{32}):

$$S = \frac{6}{d_{32}}(V_I + V_{II}) \tag{3}$$

- Diffusion of species C in the emulsion phase

$$\frac{V_{II}}{V_I + V_{II}}\frac{\partial c_C}{\partial t} = D_{C,eff}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c_C}{\partial r}\right) - \frac{S'}{V_I + V_{II}}r_s \tag{4}$$

where S' is obtained from the Sauter mean diameter of the internal droplets (d_μ):

$$S' = \frac{6}{d_\mu}V_I \tag{5}$$

The initial and boundary conditions are as follows:
ICs:

$$c_{A(III)} = c_{A_{(III),0}} \quad \text{for } t = 0$$
$$c_C = c_{C,0} \quad \text{for } t = 0, \text{ all } r \tag{6}$$

BCs:

$$r = 0: \quad D_{C,eff}\frac{\partial c_C}{\partial r} = 0 \tag{7}$$

$$r = R: \quad D_{C,eff}\left.\frac{\partial c_C}{\partial r}\right|_{r=R} = k_c(c_{A(III)} - c_{A(III),int}) \tag{8}$$

Besides the above set of basic equations, it is necessary to establish the equilibrium relationship between the concentration of the solute in the external phase and the concentration of the diffusing component C in membrane to calculate $c_{A(\mathrm{III}),\mathrm{int}}$. It is worth mentioned that the concentration of the surfactant that can act as carrier is assumed to be constant within the emulsion globule.

The spatial derivative of the partial differential equation (Eq. 4) was discretized by the finite difference method and was transformed into a system of ordinary differential equations. The ordinary differential equations were solved by the subroutine DIVPAG from IMSL Math Library. The subroutine DUMPOL from the same Library was used to minimize the sum of the squared error (F) defined as

$$F = \sum (c_{A(\mathrm{III}),\mathrm{calc}} - c_{A(\mathrm{III}),\mathrm{exp}})^2 \tag{9}$$

to calculate the value of the constant k_s. All the other parameters of the model were obtained from experimental work and from correlations from literature. The size distribution of emulsion globules and the internal aqueous droplets were measured by the photographic method. Distribution data for the selected system were obtained from equilibrium experiments. The mass transfer coefficient of the solute in the external phase was estimated from the following correlation obtained by Levins and Glastonbury (27):

$$\frac{k_c d_{32}}{D} = 2 + 0.7\left(\frac{\rho_c d_{32}^{4/3}\varepsilon^{1/3}}{\mu_c}\right)^{0.62}\left(\frac{d_I}{d_T}\right)^{0.17}\left(\frac{\mu_c}{\rho_c D}\right)^{0.36} \tag{10}$$

where D is the diffusivity of the solute, d_I is the impeller diameter, d_T is the tank diameter, ρ_c and μ_c are the density and viscosity of the external phase, respectively, and ε is the energy dissipation rate per unit mass, which is related to the power number of the agitator used.

The effective diffusivity ($D_{C,\mathrm{eff}}$) was derived in a way similar to that developed by Teramoto and Matsuyama for phenol permeation (28), which was also reported by Lee et al. (17, 29). Thus, the effective diffusivity is given as

$$D_{C,\mathrm{eff}} = D_C\left[\frac{1}{x_e^{-1/3} - x_e^{1/3} + (k_s/D_C)x_e^{1/3}\left((\pi/6)d_\mu^3\right)^{1/3}} + 1 - x_e^{1/3}\right]^{-1} \tag{11}$$

The diffusivitiy of species C in the organic phase was estimated from the Wilke-Chang equation (30). The molar volume of the solute at its normal boiling point was determined to be 179.2 $\mathrm{cm}^3\ \mathrm{mol}^{-1}$ by using the Le Bas method (31).

EXPERIMENTAL

Materials

The membrane phase consisted of a paraffinic solvent (Shellsol T, Shell Chemical Ltd.), 2 wt.% of a non-ionic surfactant (polyamine ECA4360J, Essochem Europe Inc.) and additives. Most experiments were carried out with an organic phase with 2 wt.% of a modifier (isodecanol, Riedel-de-Haën). The extractants tested (2 wt.% in the organic phase) were the tertiary amines Hostarex A327 (Höchst AG.) and Alamine 336 (tricaprilamine, Henkel), Aliquat 336 (ammonium quaternary salt, Henkel), and Cyanex 923 (Cytec) that consists of a trialkylphosphine oxides mixture.

A 0.2 kmol m^{-3} NaOH (Merck) solution was used as internal stripping phase in most experiments. The solute, 4-hydroxycinnamic acid, was of high purity analytical grade (Merck). The surfactant, diluent, and extractant reagents were used as supplied.

Methods

The emulsion was prepared by mixing the internal aqueous solution with the organic membrane phase using a rotor-stator type high-speed disperser (IKA Ultra Turrax T50) at 7000 rpm. The mixing time was 900 s. A predetermined volume ratio of 1.5 : 1 was maintained for organic phase to the internal stripping phase. The emulsion was dispersed in 800 mL of the external aqueous phase (100–500 mg L^{-1}) in a baffled glass reactor, with 85 mm internal diameter and 1 L capacity, immersed in a water bath with temperature control. The three-phase dispersion was stirred at 25°C (except when the temperature effect was tested) for 360–1200 s with a stainless steel paddle (45 × 45 × 1 mm) at 300 rpm. During permeation, samples and photographs for drop size measuring were taken periodically. Sampling was performed through inverted volumetric pipettes. Photographs were taken near the reactor wall by a Nikon F90X camera attached to a Nikon PB-6 and to a micro Nikkor 60 mm f/2.8D lens. A Nikon SB-26 flash was used as light source. After permeation the phases were settled and the emulsion was broken in a coaxial electrocoalescer. Details of this prototype are published elsewhere (32). Demulsification was performed by applying a 2 kV and 3–6 kHz electric field. Most experiments were carried out in duplicate.

The size of the emulsion globules was obtained by using the KS100 image analysis software (Kontron Elektronik GmbH) after the digitalization of the negatives (Epson FilmScan200). The size of the internal aqueous droplets was measured by taking microscopic pictures of the emulsion and analyzing the images with the software Olympus DP-SOFT.

The concentration of solute in the external and internal aqueous phases was measured with a double beam ultra-violet/visible spectrophotometer

(Hitachi U2000) at 308 nm. The pH value of the external phase was measured on a Metrohm 632 pH meter with a combined electrode. Distribution data were obtained by contacting the external aqueous phase with the membrane phase (with 0–2 wt.% of surfactant) for at least 16 h. The agitation of the phases, which was kept in a low level, was performed by an orbital shaker with temperature control. The time to attain the equilibrium was 4–5 h at 70 rpm. Equilibrium experiments were also carried out using an emulsion (without NaOH) as dispersed phase.

The molecular weight of the surfactant was determined by the method of lowering the melting point. The details of the experimental procedure are described elsewhere (17). The molecular weight of ECA4360J was estimated to be 680. This value is in agreement with the ones found by other authors, who obtained values in the range 630–760 (17, 33, 34).

RESULTS AND DISCUSSION

Exploratory ELM Tests

Several preliminary ELM tests were carried out to assess the influence of the membrane composition on 4-hydroxycinnamic acid extraction. Special attention was paid to stirring speed that was above the minimum for full dispersion but was kept in a low level to minimize the breakage of the emulsion. Higher stirring speeds increase the interfacial area of mass transfer but augment the non-ideal phenomena and decrease the efficiency of the process. The results obtained are presented in Table 1. It is shown that the extraction rate of the phenolic acid is very low using Shellsol T and surfactant in the membrane phase. The efficiency of extraction is as low as 50% after ten minutes of permeation. The extraction of 4-hydroxycinnamic acid is thus somewhat different from that of phenolic compounds that have been studied elsewhere (10, 11), whose permeation kinetics is considerably higher for the same organic membrane. The introduction of additives in the membrane phase was therefore tested to increase the extraction rate of the phenolic compound under study.

The addition of isodecanol in the organic phase containing diluent and surfactant made the extraction kinetics faster. Poposka et al. (35) reported a similar effect of this modifier on the citric acid extraction with trioctylamine. The presence of isodecanol also decreased the size of emulsion globules by about 30%, which augmented the interfacial area of mass transfer. In spite of alcohols being related to the deleterious effect of osmosis, the addition of a small amount as 2 wt.% of isodecanol in the membrane phase was found advantageous to the process.

Regarding the additional extractants tested, the trialkylphosphine oxides mixture Cyanex 923 led to the greatest degree of phenolic compound recovery (93% for 6 min). The results obtained by using Alamine 336 and

Table 1. Effect of the presence of additives (2 wt.% isodecanol or 2 wt.% extractant) in the membrane phase (2 wt.% ECA4360+diluent) on 4-hydroxycinnamic acid extraction ($c_{III,0} = 0.2\,kg\ m^{-3}$, $V_{II}/V_I = 1.5$, $V_{III}/V_I = 10$, natural pH (3.7), 25°C)

Organic phase (additives)	c_{III} (3 min) (g m^{-3})	c_{III} (6 min) (g m^{-3})	c_{III} (10 min) (g m^{-3})	c_{III} (20 min) (g m^{-3})	c_I (kg m^{-3})	c_{II}[a] (kg m^{-3})
—	150	126	100	48	1.01	0.30
Isodecanol	4.0	2.4	3.1	3.6	1.57	0.32
Alamine 336, isodecanol	5.5	3.8	3.6	5.1	1.34	0.46
Aliquat 336, isodecanol	1.7	1.9	1.9	2.9	0.37	1.01
Aliquat 336, isodecanol	1.9	2.0	2.5	—	0.94[b]	0.47[b]
Cyanex 923, isodecanol	3.3	3.4	2.3	2.5	1.13	0.61
Cyanex 923	2.3	2.0	2.0	2.1	1.59	0.17
Cyanex 923	2.3	1.9	—	—	1.84[c]	0.08[c]
Hostarex A327, isodecanol	4.1	2.8	8.5	8.5	1.47	0.44

[a]Values obtained from mass balance for final permeation time.
[b]Time = 10 min, 0.2 kmol m^{-3} NaCl and 0.2 kmol m^{-3} NaOH in phase I.
[c]Time = 6 min.

Hostarex A327 are similar to the ones obtained with the simple system without these tertiary amines. The system with the ammonium quaternary salt Aliquat 336 produced a raffinate with a low concentration of phenolic acid. However, the occurrence of non-ideal phenomena was promoted. The emulsion presented a low stability and the globules were very small, which was also deleterious to the separation of phases after permeation. Moreover, the use of additional sodium chloride in the internal phase was necessary to reduce the accumulation of solute in the membrane.

Among the organic systems tested, the use of the membrane with 2 wt.% of isodecanol, Shellsol T, and surfactant allowed to obtain satisfactory results despite the absence of an additional extractant. Thus, it was selected to carry out the subsequent work.

Equilibrium Experiments

Several equilibrium experiments were carried out to assess the influence of isodecanol and surfactant on 4-hydroxycinnamic acid extraction. Table 2 shows the distribution ratios of 4-hydroxycinnamic acid, 4-hydroxybenzoic acid, and phenol, using organic phases with and without those additives. Both phenolic acids examined led to similar results. The distribution ratios of both phenolic acids strongly increased in the presence of the surfactant because of their acidic properties ($pKa1 \approx 4.5$). The contribution of isodecanol for extracting these phenols is almost negligible in terms of equilibrium. On the other hand, phenol ($pKa \approx 10$) exhibited a different behavior. It is worth mentioning that the extraction of both phenolic acids is strongly dependent on pH. The highest distribution ratios were obtained at natural pH. Above this value, a decrease of the extraction was observed reflecting the growing dissociation of these phenols. Figure 1 shows the equilibrium data for the extraction of 4-hydroxycinnamic acid in the range of pH 1.5–7.

Table 2. Distribution ratios of 4-hydroxycinnamic acid, 4-hydroxybenzoic acid, and phenol with additives (2 wt.% isodecanol and/or 2 wt.% ECA4360J) in the organic phase. Initial aqueous phase: 0.2 kg m^{-3} of solute, natural pH; $V_{aq}/V_{org} = 1$; 25°C)

	Organic phase			
Phenolic compound	Diluent	Diluent isodecanol	Diluent surfactant	Diluent isodecanol surfactant
4-Hydroxycinnamic acid	0.022	0.056	10	10
4-Hydroxybenzoic acid	0.010	0.025	8.3	7.5
Phenol	0.11	0.34	0.49	0.73

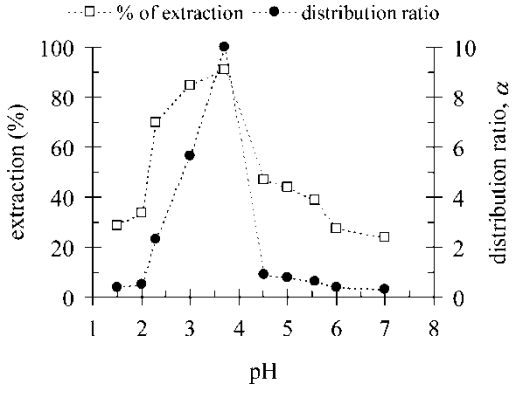

Figure 1. Influence of pH on the extraction of 4-hydroxycinnamic acid. Initial aqueous phase: 0.2 kg m^{-3} of solute, pH 1.5-7 (adjusted with H_2SO_4 or NaOH); organic phase: 2 wt.% of isodecanol, 2 wt.% ECA4360J, and diluent; $V_{aq}/V_{org} = 1$; 25°C).

When the pH is lower than 3.7, the distribution also decreased because the co-extraction of the other acidic species (H_2SO_4) occurred.

To confirm that the surfactant ECA4360J acted as an extractant of the solute under study (4-hydroxycinnamic acid) the equilibrium was carried out varying the concentration of the surfactant in the organic phase. A log-log plot of the distribution ratio α vs. the concentration of ECA4360J is shown in Fig. 2. As can be observed, a straight line with a slope of 1.4 was

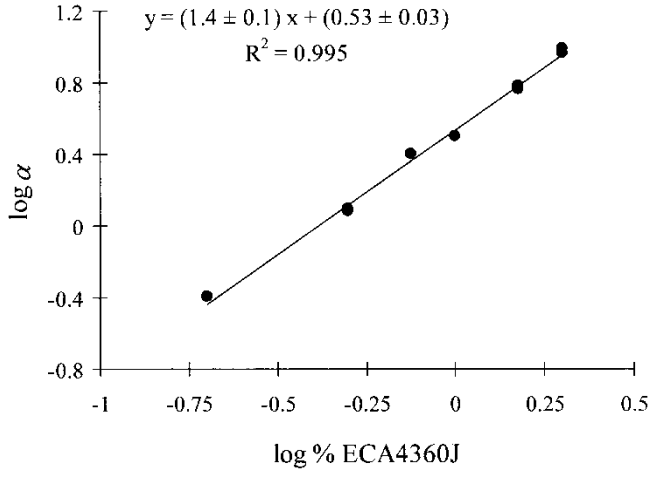

Figure 2. Distribution ratio (log) of 4-hydroxycinnamic acid vs. % of ECA4360J (log) in the organic phase. Initial aqueous phase: 0.2 kg m^{-3} of solute, natural pH (3.7); organic phase: 2 wt.% of isodecanol, 0.2–2 wt.% ECA4360J, and diluent; $V_{aq}/V_{org} = 5$; 25°C).

obtained thus indicating that 1 : 1 and 1 : 2 solute-extractant complexes might be formed. The extraction equilibrium is therefore formulated as follows:

$$A_{aq} + B_{org} \longleftrightarrow AB_{org}, K_{ex1} \quad (12)$$

$$A_{aq} + 2B_{org} \longleftrightarrow AB_{2\,org}, K_{ex2} \quad (13)$$

where B is the extractant ECA4360J, and K_{ex1} and K_{ex2} are the extraction equilibrium constants. The distribution ratio is thus given as

$$\alpha = \frac{c_{AB_{org}} + c_{AB_{2\,org}}}{c_{A_{aq}}} \quad (14)$$

The extraction equilibrium constants can be obtained from the following equation

$$\frac{\alpha}{c_{B_{org}}} = K_{ex1} + K_{ex2}\, c_{B_{org}} \quad (15)$$

The plot of α/c_B against c_B gives a straight line with a slope equal to K_{ex2} and an intercept equal to K_{ex1}, as is depicted in Fig. 3. The equilibrium constants, K_{ex1} and K_{ex2}, were evaluated to be $1.5 \times 10^2\,m^3\,kmol^{-1}$ and $1.19 \times 10^4\,m^6\,kmol^{-2}$, respectively. The contribution of species AB_2 to the distribution ratio increases with the concentration of surfactant in the organic phase. When the amount of surfactant exceeds 1.0 wt.% (0.011 kmol m^{-3}) in the organic solution, the contribution of 1 : 2 solute-ECA4360J complex to the partition ratio is greater than 50%. The results obtained in the present work are in agreement with the ones obtained by Lee et al. (17). These authors pointed out that the reaction of penicillin G with ECA4360J gives a 1:2

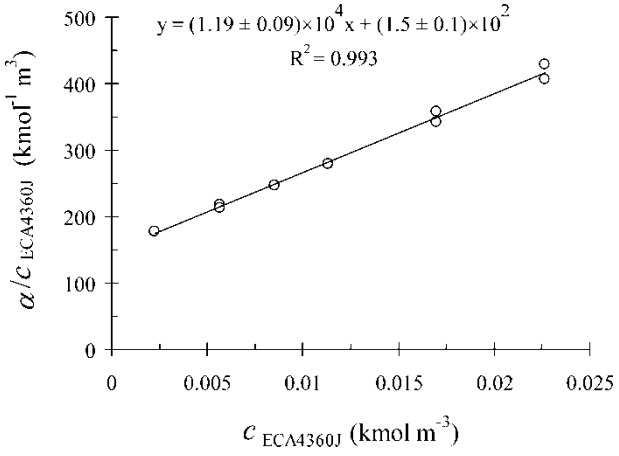

Figure 3. $\alpha/c_{ECA4360J}$ vs. concentration of ECA4360J in the organic phase. Experimental conditions: see Fig. 2.

solute-carrier complex. They investigated this equilibrium extraction using concentrations of surfactant around 0.1 kmol m^{-3}. Under these conditions, the contribution of 1 : 1 complex to the distribution ratio is then predicted to be about 10% from Eq. (15).

Equilibrium extraction was also performed using an emulsion (without stripping reagent) as dispersed phase. Figure 4 shows the results obtained and illustrates the variation of the distribution ratio with the solute concentration. As the surfactant functions as emulsifier/carrier, the distribution ratios between the external phase and the organic phase decrease in the three-phase system. For instances, the distribution ratio is reduced from 10 (two-phase system, Table 2) to 6.5 (three-phase system) for a an external phase containing 0.2 kg m^{-3} of solute and an organic phase with 2 wt.% of ECA4360J. This indicates that the concentration of carrier available for reacting cannot be determined from the formal concentration of ECA4360J. Thus, it was decided to use, in the permeation model, the equilibrium function presented in Fig. 4 to calculate the solute concentration in the external phase at interface ($c_{A(III),int}$). The effect of temperature on the equilibrium was also checked and no significant changes were noticed in the range of 17–35°C. Therefore, the variation of distribution with temperature was neglected in the modeling.

Modeling of 4-Hydroxycinnamic Acid Permeation

The effect of several variables such as temperature, solute concentration in the external phase, external/internal volume ratio, and internal reagent concentration on the extraction rate of solute was studied. Table 3 lists the parameters and operating conditions of the experiments carried out. Concerning

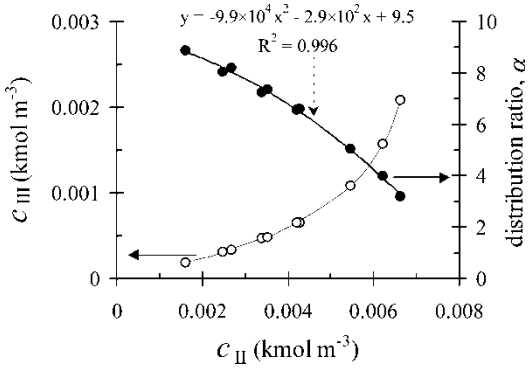

Figure 4. Distribution data of 4-hydroxycinnamic acid using an emulsion phase. Membrane phase: 2 wt.% of isodecanol, 2 wt.% ECA4360J, and diluent. Internal phase: deionized water. Initial external aqueous phase: 0.05–0.5 kg m^{-3} of solute, natural pH (3.7); $V_{III}/V_{I+II} = 5$; $V_{II}/V_I = 1.5$; 25°C).

Table 3. Parameters of the conducted experiments[a]

Run	Variable studied (relatively to run 1)		d_{32} (m)	k_c (m s^{-1})	D_C (m^2 s^{-1})	$D_{C,eff}$ (m^2 s^{-1})	k_s (m s^{-1})
1		—	4.31×10^{-4}	7.2×10^{-5}	2.36×10^{-10}	1.26×10^{-10}	2.4×10^{-8}
2	T	17°C	4.30×10^{-4}	6.0×10^{-5}	1.95×10^{-10}	1.04×10^{-10}	1.6×10^{-8}
3		30°C	4.31×10^{-4}	8.0×10^{-5}	2.67×10^{-10}	1.42×10^{-10}	3.0×10^{-8}
4		35°C	4.25×10^{-4}	8.9×10^{-5}	2.97×10^{-10}	1.58×10^{-10}	3.6×10^{-8}
5	$c_{III,0}$	0.1 kg m^{-3}	4.30×10^{-4}	7.2×10^{-5}	2.36×10^{-10}	1.26×10^{-10}	2.5×10^{-8}
6		0.5 kg m^{-3}	4.40×10^{-4}	7.2×10^{-5}	2.36×10^{-10}	1.26×10^{-10}	3.1×10^{-8}
7	V_{III}/V_I	20	3.53×10^{-4}	7.5×10^{-5}	2.36×10^{-10}	1.26×10^{-10}	2.3×10^{-8}
8		40	2.84×10^{-4}	7.8×10^{-5}	2.36×10^{-10}	1.26×10^{-10}	2.1×10^{-8}
9	NaOH(I)	0.1 kmol m^{-3}	4.21×10^{-4}	7.2×10^{-5}	2.36×10^{-10}	1.26×10^{-10}	2.3×10^{-8}
10		0.5 kmol m^{-3}	4.40×10^{-4}	7.2×10^{-5}	2.36×10^{-10}	1.26×10^{-10}	2.5×10^{-8}
11		1.0 kmol m^{-3}	4.46×10^{-4}	7.1×10^{-5}	2.36×10^{-10}	1.26×10^{-10}	2.5×10^{-8}

[a]Operating conditions of run 1: $c_{III,0} = 0.2$ kg m^{-3} (1.2×10^{-3} kmol m^{-3}); natural pH = 3.7; $V_{III}/V_I = 10$; $V_{II}/V_I = 1.5$; NaOH(I) = 0.2 kmol m^{-3}; 25°C. Aqueous droplets: $d_\mu = 2.3$ μm for all runs. Organic phase: density (25°C) = 769 kg m^{-3}; viscosity (25°C) = 1.79 mPa s.

the estimation of parameter D_C, the complex $AB_{1.5}$ was assumed to be the organic diffusing species for modeling the mass transfer.

The effect of temperature on the extraction rate of 4-hydroxycinnamic acid is shown in Fig. 5. As can be observed, the extraction rate increases with temperature in the range of 17–35°C and the present model describes the experimental data obtained quite well. The percentage of extraction was predicted with a standard mean deviation of 1.0% for this set of experiments. The extraction rate of solute augments with temperature mainly because the kinetics of stripping is faster. Increasing temperature also increased the diffusivity of solute-carrier complex through the membrane. The Arrhenius representation of the kinetic data gave the following straight line

$$\ln k_s = -\frac{(4.1 \pm 0.7) \times 10^3}{T} - (4 \pm 2) \qquad (16)$$

From the slope of the straight line obtained, the activation energy was calculated to be $34 \pm 6\,\text{kJ mol}^{-1}$, thus indicating the relevant effect of temperature on the extraction rate of this phenolic acid. A significant effect of the temperature on k_s was also obtained in a previous work concerning the extraction of a phenolic alcohol (36). The activation energy was found to be $48\,\text{kJ mol}^{-1}$ using a similar system (36).

Figure 6 illustrates the influence of the initial concentration of solute in the feed phase on the extraction rate of 4-hydroxycinnamic acid. The increase in the initial concentration lowers the degree of solute removal in the earliest stage of permeation, even though the flux of solute is increased. These results are caused by the variation of distribution ratio with solute concentration in the range studied. The higher value found for the parameter k_s ($3.1 \times 10^{-8}\,\text{m s}^{-1}$) for

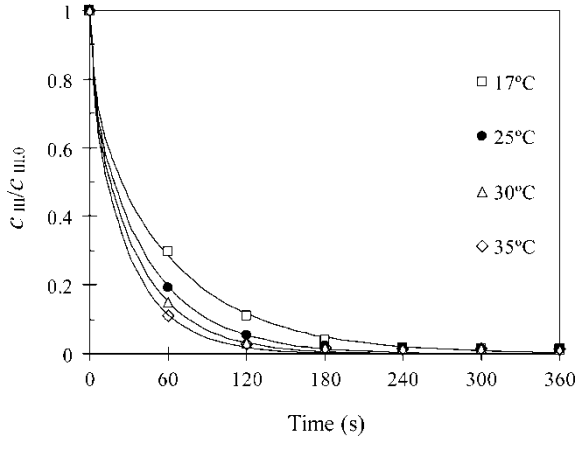

Figure 5. Effect of temperature on the extraction rate. $k_s = 1.6 \times 10^{-8}\,\text{m s}^{-1}$ (17°C), $k_s = 2.4 \times 10^{-8}\,\text{m s}^{-1}$ (25°C), $k_s = 3.0 \times 10^{-8}\,\text{m s}^{-1}$ (30°C), $k_s = 3.6 \times 10^{-8}\,\text{m s}^{-1}$ (35°C) (operating conditions: see Table 3; lines represent calculated results).

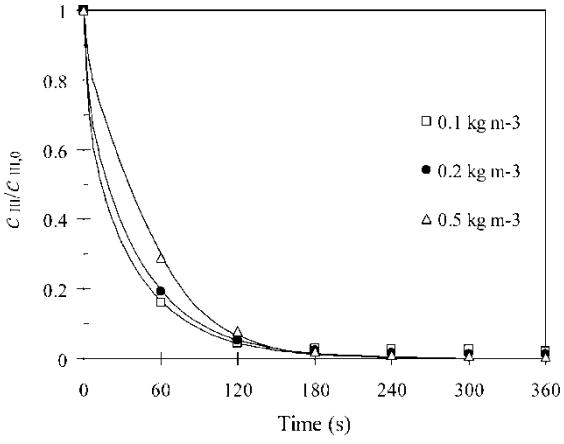

Figure 6. Effect of the initial concentration of solute in the external phase on the extraction rate. $k_s = 2.5 \times 10^{-8}$ m s^{-1} (0.1 kg m^{-3}), $k_s = 2.4 \times 10^{-8}$ m s^{-1} (0.2 kg m^{-3}), $k_s = 3.1 \times 10^{-8}$ m s^{-1} (0.5 kg m^{-3}) (operating conditions: see Table 3; lines represent calculated results).

the highest concentration is probably explained by the extent of non-ideal phenomena. Water transport occurred with different magnitudes because of the existence of different osmotic pressure gradients. As shown, after a few minutes, the solute concentration in the raffinate attained higher values when the feed concentration is 0.1–0.2 kg m^{-3}.

The effect of the volume ratio of external phase to internal phase on the extraction rate is depicted in Fig. 7. As the treatment ratio V_{III}/V_I increases, the extraction rate decreases, which is caused by the reduction of the specific volume of emulsion globules. The reduction in the hold-up decreases the interfacial area of mass transfer and decreases the capacity of the internal phase for trapping solute simultaneously. As displayed in Fig. 7, the model closely predicts the experimental data with $k_s = 2.3$-2.4×10^{-8} m s^{-1}, excepting the experiment with $V_{III}/V_I = 40$, for which the optimal value of k_s was about 13% lower.

Finally, the influence of the concentration of the internal reagent (sodium hydroxide) on the extraction of 4-hydroxycinnamic acid was tested. The increase in the stripping reagent concentration from 0.1 to 1.0 kmol m^{-3} NaOH had no significant effect on the extraction. The parameter k_s was evaluated to be 2.3-2.5 $\times 10^{-8}$ m s^{-1} for this set of experiments (see Table 3). Thus, a first overall stripping reaction order was verified.

CONCLUSIONS

The effect of the presence of additives in the membrane phase on solute permeation was tested. The use of the membrane with 2 wt.% of isodecanol,

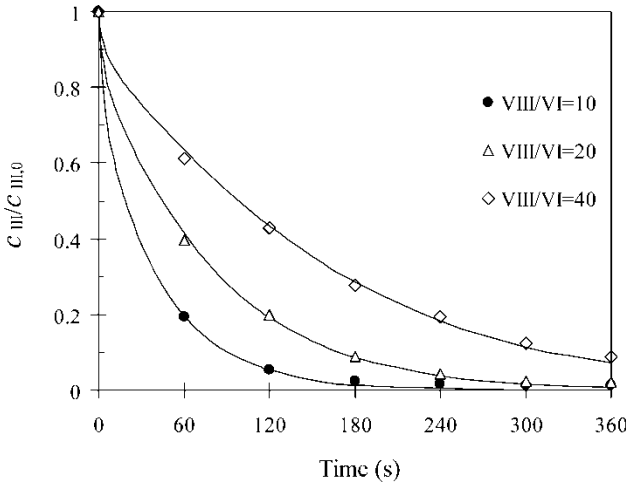

Figure 7. Effect of the volume ratio of external phase to internal phase on the extraction rate. $k_s = 2.4 \times 10^{-8}$ m s^{-1} ($V_{III}/V_I = 10$), $k_s = 2.3 \times 10^{-8}$ m s^{-1} ($V_{III}/V_I = 20$), $k_s = 2.1 \times 10^{-8}$ m s^{-1} ($V_{III}/V_I = 40$) (operating conditions: see Table 3; lines represent calculated results).

Shellsol T, and surfactant allowed to obtain satisfactory results despite the absence of an additional extractant. This system was selected to examine the extraction of 4-hydroxycinnamic acid. It was confirmed that the surfactant ECA4360J also acted as carrier of 4-hydroxycinnamic acid. The equilibrium data indicated that 1 : 1 and 1 : 2 solute-extractant complexes might be formed.

The modeling of solute permeation was done by taking into account the mass transfer in the external phase and globule, and the reaction between the diffusing component and the stripping reagent. The partition data between the solute and ECA4360J obtained from three-phase system were used in the modeling. The agreement between experimental and calculated results for solute extraction was found satisfactory. The percentage of extraction was predicted with a standard mean deviation of 1.3% for a total of 66 experimental points.

NOTATION

A	solute
B	extractant
c	concentration on the molarity scale, kmol m^{-3}
d_I	impeller diameter, m
d_T	tank diameter, m
d_μ	Sauter mean diameter of internal droplets, m

d_{32}	Sauter mean diameter of emulsion globules, m
D	molecular diffusivity, $m^2\ s^{-1}$
$D_{C,eff}$	effective diffusivity of solute-carrier complex, $m^2\ s^{-1}$
K_{ex1}	equilibrium constant of Eq. (12)
K_{ex2}	equilibrium constant of Eq. (13)
k_c	mass transfer coefficient of solute in the external phase, $m\ s^{-1}$
k_s	stripping reaction rate constant, $m\ s^{-1}$
R	emulsion globule radius, m
r	radial co-ordinate, m
r_s	stripping reaction rate per unit of interface, $kmol\ m^{-2}\ s^{-1}$
S	total interfacial area between the external phase and emulsion globules, m^2
S'	total interfacial area between the membrane phase and internal droplets, m^2
t	time, s
V	volume, m^3
x_e	volume fraction of phase I in the emulsion, $V_I/(V_I + V_{II})$

Greek Letters

α	distribution ratio between the external phase and the membrane phase
ε	energy dissipation rate/unit mass ($m^2\ m^{-3}$)
μ_c	viscosity of continuous phase ($kg\ m^{-1}\ s^{-1}$)
ρ_c	density of continuous phase ($kg\ m^{-3}$)

Subscripts

aq	aqueous phase
C	complex in the organic phase
org	organic phase
I	internal aqueous phase
II	organic membrane phase
III	external aqueous phase
calc	denotes a calculated value
exp	denotes a experimental value
int	interface
0	initial value

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