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Permeation of Mixtures of Four Phenols through a Supported Liquid Membrane in NaCl 1.0 mol·dm^{-3} Medium

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ABSTRACT

The permeation of four phenols (phenol, 2-chlorophenol, 2-nitrophenol, and 2,4-dichlorophenol) through a supported liquid membrane has been studied in NaCl 1.0 mol·dm^{-3} medium. The flux of each phenol was determined by measuring in real time the change of their concentration in the strip phase by making use of a fiber optic spectrophotometer and a multivariate calibration. The model for the permeation of phenol alone was first developed by making permeation experiments of a phenol, and then permeation studies of the mixture were carried out and the model was extended to those phenols. It was found that the permeation of a phenol is interfered with by the presence of other phenols.

Key Words. Phenols; Permeation; Liquid membranes; NaCl; Model

INTRODUCTION

Phenols are very common pollutants in many different industries (1), and therefore methods for their elimination and/or recovery have been sought for many years. Among the recovery methods, membrane processes, which can be considered clean and simple, have played an important role. Since the first use of a liquid membrane by Li et al. (2), many applications have appeared in the lit-

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erature (3–7). Some users have followed the initial application of an emulsion liquid membrane (ELM), while many others have used the supported liquid membrane (SLM) technique, mainly with hollow fibers. Thus, we thought a basic study on the permeation of mixtures of phenols in order to develop a model able to describe it would be of interest for future practical applications.

The only studies that have been carried out on mixtures of phenols use ELMs (3) and a hollow fiber module with the extracting organic phase flowing countercurrent to the feed phase (4), whereas in this work the transport of mixtures of phenols has been studied by means of batch experiments using flat SLMs, an aromatic solvent 95A 16/18, and a polypropylene support, which are most suitable for modeling of the transport because of the simpler geometry. The permeation experiments were carried out by measuring the variation of the concentration of the corresponding phenols using on-line spectrophotometrical measurements in real time both for the transport of phenol alone and in mixtures.

In order to develop a model which describes the permeation of phenols through the membrane, the experimental conditions that affect the transport were changed, i.e., the chemical and hydrodynamic conditions. Thus, the stirring rate, pH, phenol concentration, and other variables concerning the solutions were changed.

The permeation of phenol was first studied, and after developing a model which corresponded to its permeation, that model was applied to the transport of mixtures of four phenols (phenol, 2-chlorophenol, 2-nitrophenol, and 2,4-dichlorophenol), all of which are considered priority pollutants by the Environmental Protection Agency (EPA) of the United States.

THEORY

The transport of phenol across a membrane is a dynamic process. If the gradient of concentration, which is the driving force, is linear, then the process can be explained using Fick's first law. Usually this kind of permeation system is explained by using the resistances-in-series model, i.e., the different parts of the system can contribute to the overall resistance to transport, which can be calculated by measuring the change in the concentration of the solute either in the feed or in the strip phase. In the simplest cases the resistances that can be found are related to the following: the feed phase, the organic phase (the liquid membrane itself), and the strip phase. If both solutions are well stirred, the solute moves from the feed solution to the membrane and from the membrane to the strip solution only by diffusion, and it crosses the liquid membrane in the same way. The overall flux of the solute through the membrane can be expressed using

$$J = K([\mathrm{HB}]_f - [\mathrm{HB}]_s) \quad (1)$$

where K is the overall mass transfer coefficient, [HB] is the free concentration

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of the solute, and the subcripts f and s refer to the feed and strip solutions, respectively. The difference in the concentration is the driving force of the process. In a membrane with no carriers if steady state is attained, the following equation can be derived:

$$J = \frac{[\mathrm{HB}]_\mathrm{f} - [\mathrm{HB}]_\mathrm{s}}{\frac{1}{K_\mathrm{d}k_\mathrm{o}} + \frac{1}{k_\mathrm{f}} + \frac{1}{k_\mathrm{s}}} \tag{2}$$

where K_d is the distribution constant of the solute between the membrane phase and the aqueous phase; and k_o, k_f, and k_s are the individual mass transfer coefficients of the solute in the organic, feed, and strip phases, respectively. Thus, the total mass transfer coefficient is divided into three terms. In the case of phenols, which are weak acids, the free concentrations depend on the total concentration and the pH of the solutions. Therefore, by taking that into account the following expression can be obtained:

$$J = \frac{C_{\mathrm{HB_f}}\left[1 - \frac{C_{\mathrm{HB_s}}}{C_{\mathrm{HB_f}}}\frac{\left(1 + \frac{1}{\beta h_\mathrm{f}}\right)}{\left(1 + \frac{1}{\beta h_\mathrm{s}}\right)}\right]}{\left(1 + \frac{1}{\beta h_\mathrm{f}}\right)\left(\frac{1}{K_\mathrm{d}k_\mathrm{o}} + \frac{1}{k_\mathrm{f}} + \frac{1}{k_\mathrm{r}}\right)} \tag{3}$$

where C_HB is the total concentration of the phenol, β is the protonation constant of the phenol, and h is the free concentration of protons in solution ($[\mathrm{H}^+] \approx {C_\mathrm{HB}}^{1/2}\ \beta^{-1/2}$, which is valid for the feed phase if no other acid or base is added). It can be seen from Eq. (3) that permeation against the gradient of the total concentration can be obtained if the pH of the strip solution is high enough, i.e., the free concentration of phenol in the strip solution becomes negligible no matter what the total concentration is. When the following condition is fulfilled

$$1/h_\mathrm{s} \gg \beta \tag{4}$$

the equation can be written as

$$J = \frac{C_{\mathrm{HB_f}}}{\left(1 + \frac{1}{\beta h_\mathrm{f}}\right)\left(\frac{1}{K_\mathrm{d}k_\mathrm{o}} + \frac{1}{k_\mathrm{f}} + \frac{1}{k_\mathrm{s}}\right)} \tag{5}$$

where the flux depends only on the total concentration of the solute in the feed solution. This situation, called facilitated transport with an irreversible reac-

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tion, is based on the insolubility of the phenolate ion in the organic membrane. Therefore, the driving force of the permeation is the concentration of a strong base in the strip solution. If the pH in the feed solution is low enough, the flux can be expressed in the following way:

$$J = \frac{C_{HB_f}}{\frac{1}{K_d k_o} + \frac{1}{k_f} + \frac{1}{k_s}} = KC_{HB_f} \tag{6}$$

where the transport depends only on the mass transfer coefficient of each solution. The inverse of the mass transfer coefficients are equivalent to the resistance due to each phase, and the overall resistance can be obtained by adding all resistances, like resistances in series, as in the following equation:

$$\frac{1}{K} = \frac{1}{K_d k_o} + \frac{1}{k_f} + \frac{1}{k_s} \tag{7}$$

The aqueous mass transfer coefficients can be defined as

$$k_f = \frac{D_{HB_f}}{\delta_f}; \qquad k_s = \frac{D_{HB_s}}{\delta_s} \tag{8}$$

where D_{HB} is the diffusion coefficient of the solute and δ is the thickness of the diffusion layer. For a liquid membrane the following definition is used (8):

$$k_o = \frac{D_{HB_o}\epsilon}{\delta_o \tau} \tag{9}$$

where ϵ is the porosity and τ is the tortuosity of the support.

If the concentration of the strong base is above a critical value, then the reaction front of the base with the phenol moves toward the interface and the thickness of the diffusion layer in the strip solution becomes negligible. This critical concentration can be calculated by using the following equation (9):

$$C_{NaOH} = \frac{qKC_{HB_f}}{k_B} \tag{10}$$

where q is the stoichiometric coefficient of the reaction and k_B is the mass transfer coefficient of the strong base. When this critical value is used, the flux is expressed by using

$$J = \frac{C_{HB_f}}{\frac{1}{K_d k_o} + \frac{1}{k_f}} = KC_{HB_f} \tag{11}$$

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where the overall mass transfer coefficient depends only on the feed and the membrane phases.

EXPERIMENTAL

Apparatus

- A Guided Wave 260 fiber optic spectrophotometer, which has as an optical probe a 2-cm light path that can be introduced into solutions and was used by us for measuring phenol concentrations.
- A stirring system consisting on two motors and a tachometer to measure and control the stirring rate.
- A Radiometer PHM84 pHmeter with a Ag/AgCl(s) Hanna Instruments HI 1310S combined electrode to perform the pH measurements.
- An Ecochemie Autolab voltammetric system with a Metrohm 663 VA electrolytic cell consisting on a gold electrode, a saturated calomel reference electrode, and a platinum auxiliary electrode to perform the chronoamperometric measurements.
- Scharlau DB-50 microburettes for the additions of the solution to the feed and strip phases.

Reagents and Solutions

The phenols used in this work were phenol (Merck, p.a.), 2-chlorophenol (Aldrich, >99%), 2-nitrophenol (Fluka, p.a.), and 2,4-dichlorophenol (Aldrich, 99%). Other reagents were sodium chloride (Merck, p.a.), sodium hydroxide (Merck, p.a.), and hydrochloric acid (Fluka, p.a.).

All solutions were prepared using MilliQ water. Stock solutions of the different phenols of 0.01 $mol \cdot dm^{-3}$ were prepared. 2-Nitrophenol and 2,4-dichlorophenol were dissolved in NaOH 0.01 $mol \cdot dm^{-3}$ medium in order to facilitate their dissolution. As the stripping phase, NaOH 0.1 $mol \cdot dm^{-3}$ and NaCl 0.9 $mol \cdot dm^{-3}$ solutions were used. The working solutions of the phenols were prepared in NaCl 1.0 $mol \cdot dm^{-3}$ medium. For the pH measurements, buffer solutions of pH 2.0, 4.0, 7.0, and 10.0 were used.

Procedure

Throughout this work a stripping solution of NaOH 0.1 $mol \cdot dm^{-3}$ and NaCl 0.9 $mol \cdot dm^{-3}$ was used. As feed phase solutions of different composition in phenols in NaCl 1.0 mol dm^{-3} medium were used, taking into account that the phenols give the acidic media required and in some cases a few drops of HCl 0.4 $mol \cdot dm^{-3}$ or NaOH 0.5 $mol \cdot dm^{-3}$ were added to change the pH of the solution. Therefore, an ionic medium of Na(OH, Cl) 1.0 $mol \cdot dm^{-3}$ was used

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throughout as the equilibrium constants used were previously experimentally determined in that medium (10).

The liquid membranes were made by using the industrial aromatic solvent 95A 16/18 produced by CEPSA (Spain), with a composition of mainly isomers of ethyltoluene and trimethyltoluene and a boiling point between 160 and 180°C, and a Celgard 2500 (Hoechst) polypropylene film as the support. Values of the experimentally determined distribution constants of the four phenols between the aqueous and the organic phase are shown in Table 1. Liquid membranes were prepared by immersion of the polypropylene film into the organic solvent for a few minutes, the time that proved to be long enough, and the excess solvent was wiped off with a tissue. Then the membrane was placed between two Viton rings of 4.2 cm diameter (i.e., the area of the membrane was 13.85 cm^2) which were tightly secured between the permeation cells following a system similar to that used at the University of Calabria (11). Both cells were filled with 131 cm^3 of the feed and strip solution by using a microburette and then immersed in a thermostatic bath of paraffin at 25 ± 0.1°C (see Fig. 1). Then the stirrers were connected and the spectrophotometric probe was introduced into the stripping phase, which was then stirred at 500 rpm and the blank was recorded. At that moment the permeation experiment was ready to begin and the feed phase was stirred at 1200 rpm. The variation in the concentration of phenol or phenols in the stripping solution, i.e., the increase in concentration, was measured by taking one spectrum every 30 seconds. The concentration of phenols was calculated in real time from each spectrum by making use of a multivariate calibration using partial least squares. For the experiments containing only phenol, spectra were collected between 260 and 320 nm; for the experiments with the four phenols, the 260 to 540 nm range was used. The stirring rate had been previously checked to be enough to minimize the effect of the diffusion layers of both phases. In previous experiments it had also been checked that the membrane was impermeable to inorganic solutes such as protons or other compounds insoluble in the organic solvent used.

TABLE 1
Distribution Constants of the Four Phenols between the Aqueous and Organic Phases (10)

Solute	K_d
Phenol	0.87 ± 0.02
2-Chlorophenol	19.6 ± 0.2
2-Nitrophenol	197 ± 2
2,4-Dichlorophenol	116 ± 2

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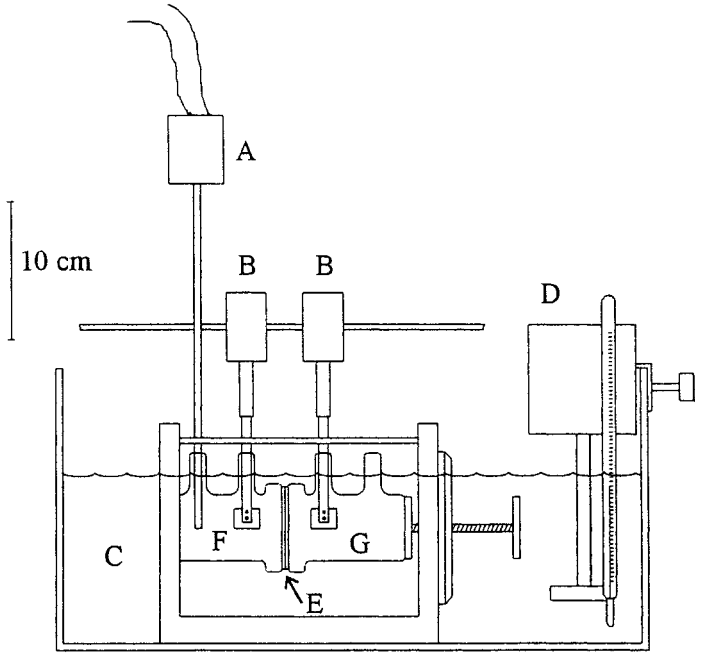

FIG. 1 Experimental setup of the liquid membrane permeation system. (A) Optical probe of the spectrophotometer, (B) motors and stirrers, (C) paraffin bath, (D) thermostatic system, (E) liquid membrane between 2 rings of Viton, (F) strip phase, (G) feed phase. Volume of feed and strip phase, 131 cm^3; area of membrane, 13.85 cm^2.

Throughout this work the variable determined in each permeation experiment was the initial flux by measuring the change in concentration of the solute or solutes in the strip solution. By plotting concentration versus time, the slope of the curve at 0 time gives the initial rate of the change in concentration, which is related to the flux as shown by the equation

$$J = \frac{d[\mathrm{HB}]}{dt}\frac{V}{A} \tag{12}$$

where V is the volume of the strip solution and A is the area of the membrane.

Different kind of experiments were performed in order to check the validity of the model described above and to calculate the values of the parameters of the model. First, all experiments were carried out with feed solutions containing only phenol (10^{-3} mol·dm^{-3}) in NaCl (1.0 mol·dm^{-3}) except where otherwise stated, and with NaOH (0.1 mol·dm^{-3}) and NaCl (0.9 mol·dm^{-3}) as the strip phase. Experiments at different initial concentrations of phenol were performed in order to check that the flux was directly proportional to that concentration. Some other experiments used a higher concentration of phenol in the strip solution in the alkaline medium mentioned. In order

to determine the values of the parameters of the model, several permeation experiments were carried out at different pH values of the feed solutions and with different polypropylene supports, i.e., with liquid membranes of different thicknesses.

After developing the model for the permeation of phenol, experiments with mixtures of the four phenols were carried out. In this case the compositions of the feed and strip solutions were the same as before but each phenol had a concentration of 10^{-3} mol·dm^{-3}. Again, permeation experiments in which the pH of the feed solution and the thickness of the membrane were varied were performed.

In order to determine the values of the diffusion coefficients in the NaCl 1.0 mol·dm^{-3} medium, chronoamperometric measurements were carried out with solutions of the different phenols in 10^{-3} mol·dm^{-3} concentration in the mentioned medium. A potential of 0.9 V, at which phenols are oxidized, was applied, and the diffusion coefficient was calculated by taking into account its relationship with the measured intensity.

RESULTS AND DISCUSSION

As a first check of the validity of the proposed model, the results obtained in the permeation experiments using only phenol at different concentrations in the feed phase showed that the flux is directly proportional to that concentration (if the rest of the parameters are kept constant). With a higher total concentration of phenol in the stripping phase the flux remained constant in spite of the gradient as long as the concentration of NaOH in that phase was high enough.

At optimum conditions the total mass transfer coefficient is about 1.3×10^{-5} m·s^{-1}. Taking into account that the mass transfer coefficient for NaOH in NaOH 0.1 mol·dm^{-3} medium is 1.519×10^{-5} m·s^{-1} according to Zha et al. (8), by making use of Eq. (10) a value for the critical concentration of NaOH of 4×10^{-4} mol·dm^{-3} was obtained. Therefore, the concentration used in the strip phase, 0.1 mol·dm^{-3}, is high enough so the effect of its diffusion layer is negligible, as was pointed out above.

In the permeation experiments carried out at different pH values in the feed phase containing only phenol, the voltmeter used for the pH measurements was calibrated on a daily basis by using buffer solutions with pH values of 2.0, 4.0, 7.0, and 10.0. Because the pH is related to the activity of protons, conversion to log h was carried out ($h = [H^+]$) by making use of the equation

$$-\log h = \text{pH} + \log \gamma_{H^+} \tag{13}$$

A value of $\gamma_{H^+} = 0.8570$ (12), which corresponds to the medium was used. In Fig. 2 the variation of flux with the concentration of protons in the feed phase

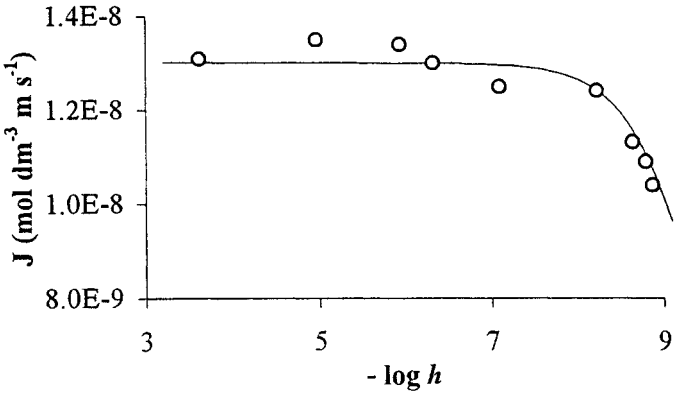

FIG. 2 Flux of phenol versus the variation of acidity of the feed phase: [Phenol] = 10^{-3} mol·dm^{-3}; feed phase, 1200 rpm; strip phase, 500 rpm; $-\log h_s \approx 13$.

is shown. In Fig. 3 the variation of flux is proportional to the number of supports used in the liquid membrane, i.e., the thickness of the membrane. The higher the pH, i.e., the lower the free concentration of phenol, the lower the flux; and the thicker the membrane, i.e., the higher the resistance due to the membrane, the lower the flux.

The theoretical lines drawn in Figs. 2 and 3 were calculated by using the program NLREG, which is a general purpose program for nonlinear regression calculations which minimizes the squared sum of errors, defined in this case as

$$U = \sum_{N_p} (J_{exp} - J_{calc})^2 \tag{14}$$

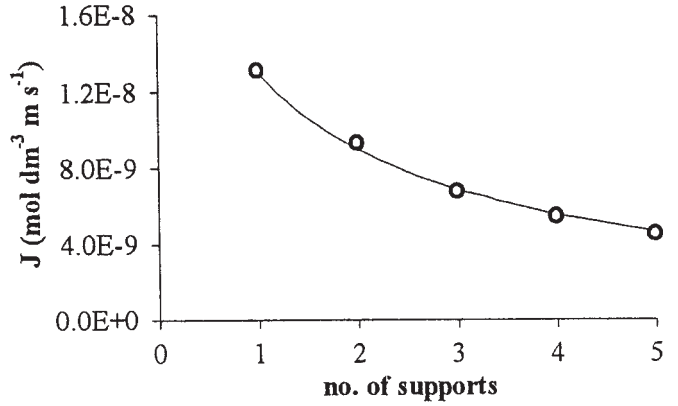

FIG. 3 Flux of phenol versus the number of supports of the liquid membrane. [Phenol] = 10^{-3} mol·dm^{-3}; feed phase, 1200 rpm; strip phase, 500 rpm; $-\log h_s \approx 13$; $-\log h_f \approx 5$.

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where J_{exp} is the experimentally measured flux, J_{calc} is the value calculated using Eq. (11) with the corresponding parameters that have been calculated in the minimization process, and N_p is the number of points. All the data corresponding to both variations were treated together since all follow the same model. In the data from experiments of varying acidity, k_o was kept constant; in the data from experiments of varying membrane thickness, only δ_o was not kept constant. The results are shown in Table 2, where σ is the total error of the fit (in $mol \cdot dm^{-3} \cdot m \cdot s^{-1}$ units), R^2 shows the percentage of the variance explained by the model used, and K is the total mass transfer coefficient, calculated from the results of the regression, i.e., the values of k_f and k_o.

Once the value of the mass transfer coefficient of phenol in the feed phase is known, it is possible to calculate the value of the diffusion layer thickness if the diffusion coefficient is known. This diffusion coefficient was determined for the medium used by using a chronoamperometric technique described in the literature (13) by making use of Cottrell's equation:

$$i = nFAD^{1/2}\pi^{1/2}Ct^{-1/2} \tag{15}$$

where i is the intensity measured under the voltage applied, n is the number of electrons taking part in the oxidation reaction of phenol (2 in this case), F is the Faraday constant, A is the area of the electrode (0.07 cm^2), D is the diffusion coefficient, C is the concentration of the solute (10^{-3} $mol \cdot dm^{-3}$), and t is time. By plotting the intensity versus $t^{1/2}$, a straight lines crossing the (0, 0) point is obtained. From the slope of the plot the value of the diffusion coefficient is directly calculated. In this case the value for phenol in NaCl 1.0 $mol \cdot dm^{-3}$ medium is 5.38×10^{-10} $m^2 \cdot s^{-1}$. Taking into account the difference in medium, this value is comparable with the one estimated by Schlosser et al. in pure water (6) (9.98×10^{-10} $m^2 \cdot s^{-1}$). By using the value of this diffusion coefficient, the thickness of the diffusion layer of the feed phase was calculated as $(2.27 \pm 0.9) \times 10^{-5}$ m, which is similar to the value obtained for a LiCl 1.0 $mol \cdot dm^{-3}$ medium in a similar experimental setup, 2.13×10^{-5} m (14).

TABLE 2
Mass Transfer Coefficients of Phenol and the Parameters of the Fit to Eq. (11)

k_f ($m \cdot s^{-1}$)	$2.36 \pm 0.10 \times 10^{-5}$
k_o ($m \cdot s^{-1}$)	$3.33 \pm 0.15 \times 10^{-5}$
K ($m \cdot s^{-1}$)	1.30×10^{-5}
σ	2.75×10^{-10}
R^2	99.22%

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On the other hand, by taking into account the membrane support characteristics of porosity = 0.45 and thickness = 25×10^{-6} m, as stated by the manufacturer, and tortuosity = 2.25 (15), the diffusion coefficient of phenol in the organic solvent used was calculated by making use of Eq. (9). The value obtained was $(4.16 \pm 0.2) \times 10^{-9}$ $m^2 \cdot s^{-1}$.

Once the model for the transport of phenol was developed and the values of the parameters were known, it was possible to apply it to the permeation of mixtures of phenols. In this case a multivariate calibration was also used for the calculation of the change in the concentration of the four phenols in real time. In Fig. 4 the profile of concentrations of the four phenols in a permeation experiment is shown; it was therefore possible to measure the flux corresponding to each phenol separately. As before, different experiments were carried out by changing the pH of the feed phase and the thickness of the liquid membrane. In Figs. 5 and 6 the variation of the flux measured for each phenol with the variation of pH and thickness of the membrane is shown. It can be seen that the permeation of phenol is different from what was previously obtained, i.e., the value of the total mass transfer coefficient has changed in the presence of other phenols. On the other hand, variation in the thickness of the liquid membrane has little effect on the permeation of phenols with higher fluxes, which results in the determination of the mass transfer coefficient corresponding to the liquid membrane being more difficult if one of the two resistances is negligible compared to the other. This is due to the higher value of the distribution constants of the other phenols compared to that of phenol itself.

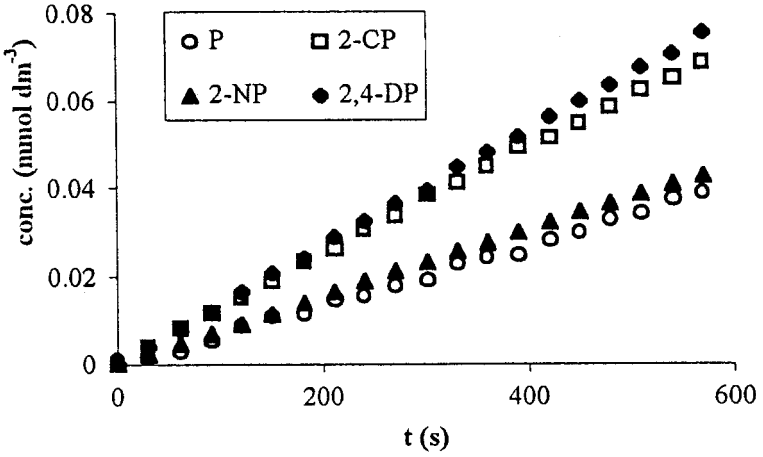

FIG. 4 Variation of the concentration of the four phenols in the strip phase. P = phenol, 2-CP = chlorophenol, 2-NP = 2-nitrophenol, 2,4-DP = 2,4-dichlorophenol. [P] = [2-CP] = [2-NP] = [2,4-DP] = 10^{-3} mol·dm^{-3}; feed phase, 1200 rpm; strip phase, 500 rpm; $-\log h_s \approx 13$; $-\log h_f \approx 4$.

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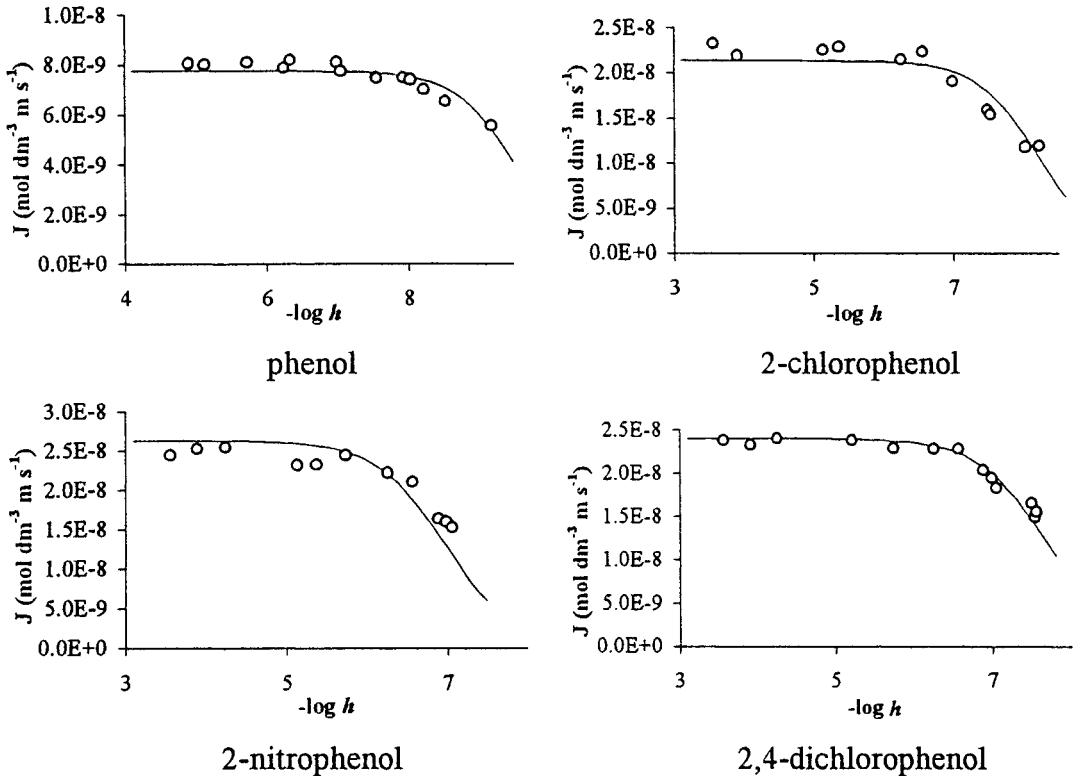

FIG. 5 Flux of each phenol versus the variation of acidity of the feed phase. Concentration of each phenol = 10^{-3} mol·dm^{-3}; feed phase, 1200 rpm; strip phase, 500 rpm; $-\log h_s \approx 13$.

The theoretical lines drawn in Figs. 5 and 6 were calculated by using the program NLREG and Eq. (11) as before, fitting the data corresponding to all the phenols together. The results are shown in Table 3.

By using the values of mass transfer coefficients corresponding to 2-chorophenol, 2-nitrophenol, and 2,4-dichlorophenol, the value of the thickness of the diffusion layer can be calculated if the diffusion coefficients are known. In this case also the same chronoamperometric technique was tried, but the results were not satisfactory due to adsoption processes on the electrode surface which had the result that the process was not controlled only by diffusion. In that case it is not possible to determine correctly the diffusion coefficient (13). However, by making use of the Wilke–Chang equation it is possible to calculate the diffusion coefficients of the other three phenols by making use of the previously calculated value of phenol. According to that equation, the diffusion coefficient is proportional to the following parameters:

$$D \propto \frac{\sqrt{M}T}{\eta\,(V_{\mathrm{M}})^{0.6}} \tag{16}$$

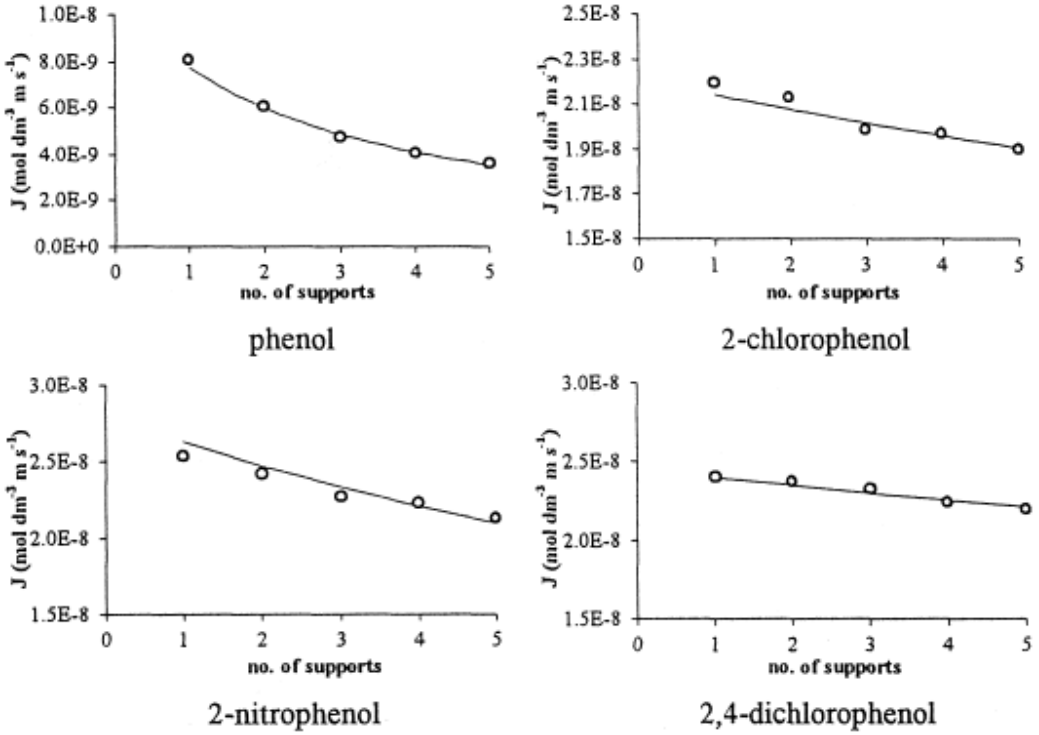

FIG. 6 Flux of each phenol versus the number of supports of the liquid membrane. Concentration of each phenol = 10^{-3} mol·dm^{-3}; feed phase, 1200 rpm; strip phase, 500 rpm; $-\log h_s \approx 13$; $-\log h_f \approx 4$.

where M is the molecular mass of the solute, T is the temperature, η is the viscosity of the solvent, and V_M is the molar volume. Taking into account that the only difference among the phenols are the diffusion coefficients, the molar volumes, and molecular masses, by knowing the last two it is possible to calculate the other. The molar volumes of the phenols were estimated by using the atomic contributions of Le Bas (16), and by taking as the reference value the experimentally determined value of the diffusion coefficient of phenol, the

TABLE 3
Mass Transfer Coefficients of the Feed Phase and the Organic Phase for Each Phenol and the Parameters of the Fit to Eq. (11)

	Phenol	2-Chlorophenol	2-Nitrophenol	2,4-Dichlorophenol
$k_f \times 10^5$ (m·s^{-1})	1.11 ± 0.18	2.21 ± 0.70	2.81 ± 0.07	2.45 ± 0.05
$k_o \times 10^5$ (m·s^{-1})	3.0 ± 1.2	3.4 ± 1.5	0.21 ± 0.04	0.97 ± 0.53
$K \times 10^5$ (m·s^{-1})	0.78	2.14	2.62	2.40
σ		1.14×10^{-9}		
R^2		97.63%		

TABLE 4
Molar Volumes and the Calculated Diffusion Coefficients

	Phenol	2-Chlorophenol	2-Nitrophenol	2,4-Dichlorophenol
V_M ($cm^3 \cdot mol^{-1}$)	103.4	124.3	125.0	145.2
D_{HB} ($m^2 \cdot s^{-1}$)	5.38×10^{-10}[a]	4.82×10^{-10}	4.69×10^{-10}	4.45×10^{-10}

[a] Experimental value.

others were calculated and the values are shown in Table 4. By using Eq. (8) the thicknesses of the diffusion layers of the feed phase according to the different phenols were calculated. The average value obtained was $2.0 \pm 0.3 \times 10^{-5}$ m, which is in agreement to the value obtained with phenol alone and thus shows the consistency of the calculations carried out.

In Table 3 it can be seen that the mass transfer coefficient of phenol in the aqueous phase has decreased whereas it is fairly constant in the organic phase. Since the experimental conditions are the same as in the permeation of phenol alone, except for the presence of the other phenols, it can be assumed the mass transfer coefficient has to be the same and that there must be an extra resistence which would explain the difference between the two experimental situations studied in this work. This extra resistance may be due to the presence of the other phenols, i.e., to a competitive interference of the other phenols to access the membrane interface. According to Want et al., in multicomponent systems the permeation of solutes with higher reactivities is not affected by the presence of solutes of lower reactivities, but the latter are affected by the presence of solutes of high reactivity. In this case the distribution constant of phenol is much smaller than that of the other phenols and, therefore, it can be assumed that there is an interference between them. Therefore, the permeation of phenol becomes slower due to the new resistance.

We calculated the mass transfer coefficient of this new resistance. First, new resistances inversely proportional to the distribution constants of the phenols (as is the resistance due to the organic phase) were tried, but the model was not able to properly explain the data. Therefore, a different model which only included the new resistance was investigated to explain the permeation of phenol in the presence of the other phenols, whereas the same model developed before was kept for the other phenols. The model used for phenol is

$$J = \frac{C_{HB_f}}{\frac{1}{K_d k_o} + \frac{1}{k_f} + \frac{1}{k_i}} \tag{17}$$

where k_i is the mass transfer coefficient due to the interference of the other

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TABLE 5
Mass Transfer Coefficients of the Organic Phase for Each Phenol and of the Interference of Phenol Calculated Using Eqs. (11) and (17) and the Parameters of the Fit

	Phenol	2-Chlorophenol	2-Nitrophenol	2,4-Dichlorophenol
$k_o \times 10^5$ (m·s^{-1})	3.0 ± 0.9	3.6 ± 0.9	0.21 ± 0.02	1.0 ± 0.3
$k_i \times 10^5$ (m·s^{-1})			2.1 ± 0.6	
σ			1.1×10^{-9}	
R^2			97.63%	

phenols. By using this new model and keeping the value of k_f for phenol constant at the same value obtained in the experiments for phenol alone, the parameters were calculated as before. The results are shown in Table 5. These values were used to draw the theoretical lines in Figs. 5 and 6. By making use of the mass transfer coefficients of the phenols in the membrane phase, it is possible to calculate their diffusion coefficients in the organic solvent. The values are shown in Table 6. The value for phenol has a much higher uncertainty than before and they overlap. The others are not very well defined due to their higher distribution coefficients which makes the resistance due to the liquid membrane smaller. Therefore, there is not much change in the flux in spite of changing the thickness of the membrane, and the values thus obtained have lower reliability.

It is possible to define the selectivity coefficient with the total mass transfer coefficient obtained for each phenol according to

$$S_{12} = K_1/K_2 \tag{18}$$

where S_{12} is the selectivity coefficient of Solute 1 with respect to Solute 2 in permeation through the liquid membrane, and K_1 and K_2 are the overall mass

TABLE 6
Calculated Diffusion Coefficients of the Phenols in the Solvent 95A 16/18

Solute	$D_{HBo} \times 10^9$ (m^2·s^{-1})
Phenol	3.7 ± 1.2
2-Chlorophenol	4.4 ± 1.1
2-Nitrophenol	0.26 ± 0.03
2,4-Dichlorophenol	1.21 ± 0.40

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TABLE 7
Selectivity Coefficients, S_{12}, of the Phenols

	Phenol	2-Chlorophenol	2-Nitrophenol	2,4-Dichlorophenol
Phenol	1	0.36	0.30	0.32
2-Chlorophenol	2.74	1	0.82	0.89
2-Nitrophenol	3.36	1.22	1	1.09
2,4-Dichlorophenol	3.08	1.12	0.92	1

transfer coefficients of the two solutes. This coefficient can predict the preconcentration ratio of one of the solutes with respect to the other in the strip phase. The calculated selectivity coefficients are shown in Table 7. It can be seen that only phenol can be separated from the others, but the separation is not good.

SYMBOLS

A	surface of the membrane
C_{NaOH}	critical concentration of NaOH
C_{HB_f}	total concentration of the feed phase
C_{HB_s}	total concentration of the strip phase
D_{HB_f}	diffusion coefficient in the feed phase
D_{HB_o}	diffusion coefficient in the organic phase
D_{HB_s}	diffusion coefficient in the strip phase
F	Faraday's constant
$[HB]_f$	free concentration of the feed phase
$[HB]_s$	free concentration of the strip phase
h_f	free concentration of protons in the feed phase
h_s	free concentration of protons in the strip phase
J	flux through the liquid membrane
K	overall mass transfer coefficient
k_f	mass transfer coefficient in the feed phase
k_B	mass transfer coefficient of the strong base
K_d	distribution constant
k_i	mass transfer coefficient due to the presence of the other phenols
k_s	mass transfer coefficient in the strip phase
k_o	mass transfer coefficient in the organic phase
M	molecular mass
n	number of electrons
q	stoichiometric coefficient
R^2	percentage of the variance explained by the model

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T	temperature
U	squared sum of errors
V	volume of the strip phase
V_M	molar volume
β	protonation constant
δ_f	thickness of the diffusion layer in the feed phase
δ_o	thickness of the membrane
δ_s	thickness of the diffusion layer in the strip phase
ϵ	porosity of the support
γ_{H^+}	activity coefficient of the protons
η	viscosity of the solvent
σ	total error of the fit
τ	tortuosity of the support

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