Paper II

Modelling of mass transfer in facilitated supported liquid-membrane transport of palladium(II) using di-(2-ethylhexyl) thiophosphoric acid

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Abstract

The permeation of Pd(II) through supported liquid membranes (SLM) impregnated with di-(2-ethylhexyl) thiophosphoric acid (DEHTPA) in kerosene has been investigated. A model is reported describing the transport mechanism which consists of: diffusion process through the feed aqueous diffusion layer, fast interfacial chemical reaction and diffusion through the membrane. The experimental data is quantitatively explained by mathematical equations describing the rate of transport. Different rate-controlling processes take place as long the metal transport occurs. High selectivity in the separation of Pd(II) against Fe(III), Pt(IV), Rh(III) and Zn(II) is achieved and the lifetime of the membranes is also studied.

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1. Introduction

The use of liquid membranes containing a carrier metal has been proposed as an alternative to solvent extraction processes for the selective separation and concentration of metals from dilute aqueous solutions. In liquid membrane technology the extraction, stripping and regeneration operations are combined in a single stage (1-3).

Two configurations of liquid membranes are currently being investigated: supported liquid membranes (SLM) and liquid surfactant membranes (LSM). Each contains an extraction reagent incorporated into the organic phase similar to those used in conventional solvent extraction, and their use in membranes results in a large decrease in the solvent inventory. The metal extractant chemistry is identical to that found in solvent extraction but the overall process is governed by kinetic rather than equilibrium parameters. SLM consist of a thin high-microporous film in which the organic phase is adsorbed, on the other hand in the LSM type an organic membrane film is obtained by creating a water-in-iol emulsion with the strip liquor and the organic phase which is then suspended in the feed solution (4). From the engineering and practical standpoint, SLM are of particular interest because of its stability and simplicity. In this work, SLM are used for Pd(II) recovery from HCl solutions.

Palladium belongs to the precious metals (PM) group. The recovery of PM from primary and secondary sources is of great relevance since PM have specific properties and are fundamental metals for the production of new materials.

Several studies deal about the permeation of PM through SLM using different extactants: long chain amines (5-9), alkylated 8-hydroxyquinoleines (10-11) and phospholene derivatives (12). Sulphur-containing extractants are known to be highly selective for extraction of metals classified as soft Lewis acids, such as Pd(II) (13-14), and have been successfully applied for the separation of Pd(II) by SLM (15).

Di-(2-ethylhexyl) thiophosphoric acid (DEHTPA) is a new member of this class of sulphur-containing extractants and has been proved to be a selective reagent for Pd(II) when used in solvent extraction (16) as well as impregnated onto macroporous polymeric supports (17, 18).

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In the present paper, the transport of Pd(II) from HCl solutions through a SLM impregnated with DEHTPA is studied and a permeation model describing the transport mechanism is reported.

2. Experimental

2.1. Reagents and solutions

Di-(2-ethylhexyl) thiophosphoric acid (DEHTPA or HL) was kindly supplied by Bayer and was purified through a procedure consisting in the formation of its potassium salt as described elsewhere obtaining a product with a purity of 96.9 %. (17).

Kerosene, cumene and toluene (Fluka) were employed as organic diluents for DEHTPA.

Stock metal solutions were prepared by dissolving the required amount of $PdCl_2$, $PtCl_4$, $RhCl_3.3H_2O$ (Johnson Matthey) $ZnCl_2$ and $FeCl_3.6H_2O$ (Panreac) in hydrochloric acid solution.

All the other chemicals used in this work were of reagent grade.

2.2 Membranes

The flat-sheet supported liquid membranes were impregnated with carrier solution containing DEHTPA dissolved in kerosene, if not otherwise stated, by immersion for 24 h and then leaving it to drip for a few seconds before being placed in the transport cell.

The flat-sheet membranes used were Millipore Durapore GVHP 4700 of 12.5×10^{-3} cm thick microporous polyvinylidenedifluoride (PVDF) film with nominal porosity of 75% and effective pore size of 0.22 μm.

2.3. Transport Experiments

The batch transport experiments were carried out in a permeation cell consisting of two compartments made of methacrylate and separated by the microporous membrane. The membrane geometrical area was 11.3 cm^2 and the volume of the feed and stripping solutions 185 ml.

The experiments were performed at 25°C at a mechanical stirring speed of 1200 rpm in the stripping phase and 1000 rpm in the feed solution, except in the experiments where the stirring speed was varied.

The ionic strength in the feed and stripping phases was kept constant at 1 M in all the experiments.

The aqueous feed solutions contained 2.35x10^{-4} M of Pd(II), if not otherwise stated, in 1 M HCl. In the case of metal selectivity permeation test, Pd(II) and the other metals: Pt(IV), Rh(III), Zn(II) and Fe(III) were present initially in a concentration of 2.35x10^{-4} M.

In preliminary studies, thiourea and thiocyanate in HCl media, were tested as stripping reagents. Solutions of composition 0.9 M thiourea - 0.1 M HCl gave the best performance for palladium stripping and were employed as strippant phase in all the experimental runs.

Membrane permeability was determined by monitoring palladium concentration by atomic absorption spectrophotometry (SpectroAA-640 Varian) in the source phase as a function of time. In the liquid membrane separation experiments of Pd(II) from several impurities, the metal mixtures were determined by ICP (Spectroflame of Spectro Analytical Instruments).

3. Modelling of the permeation rate

In the extraction process using SLM, the metal diffuses through the aqueous feed boundary layer and reacts at the interface, with the extractant which is placed in the pores of the support, resulting in the formation of metal complexes. Then, complexes diffuse through the membrane to the stripping phase because its concentration gradient is negative. Finally,

metal carrier complexes release metal ions into the aqueous strip solution at the liquid membrane-stripping interface.

Therefore, to model the mass transfer of Pd(II) it is necessary to consider diffusion of the solute through the aqueous feed boundary layer, reversible chemical reaction at the feed interface, diffusion of the metal complex species in the membrane and chemical reaction at the stripping interface.

3.1. Extraction equilibrium

The solvent extraction of Pd(II) by DEHTPA in kerosene has been studied previously (16). The extraction equilibrium can be described by the following reaction and equilibrium extraction constant:

$$PdCl_4^{-2}{}_{aq} + 2\,HL_{org} \Leftrightarrow PdL_{2\,org} + 4Cl^-{}_{aq} + 2H^+{}_{aq} \tag{1}$$
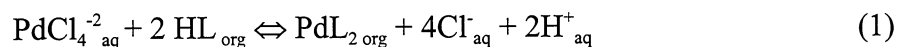
$$K_{ex} = \frac{\left[PdL_2\right]_{org}\left[Cl^-\right]_{aq}^4\left[H^+\right]_{aq}^2}{\left[HL\right]_{org}^2\left[PdCl_4^{-2}\right]_{aq}} \tag{2}$$

where HL is the organic extractant. At 1 M HCl, log K_{ex} was found to be 7.9. In this work, a conditional equilibrium constant, K^*_{ex}, will be used:

$$K^*_{ex} = K_{ex}\left[H^+\right]_{aq}^{-2}\left[Cl^-\right]_{aq}^{-4} \tag{3}$$

Taking into account the chemical equilibrium previously exposed, the mass balance equation for HL is described by the following expression:

$$\left[HL\right]_{org,o} = \left[HL\right]_{org,e} + 2K^*_{ex}\left[Pd\right]_{aq}\left[HL\right]_{org,e}^2 \tag{4}$$

where $[HL]_{org,o}$ is the analytical HL concentration, $[HL]_{org,e}$ is the concentration of HL not bound to palladium and $[Pd]_{aq}$ is the equilibrium Pd(II) concentration in the aqueous feed, where the symbol Pd represents the anion $PdCl_4^{-2}$.

3.2. Permeation model in solid-supported liquid membranes

The mass transfer of Pd(II) crossing the membrane is described considering only diffusional parameters. The interfacial flux due to the chemical reaction has been neglected since the chemical reaction is considered to occur instantaneously relative to the diffusion processes.

The overall membrane flux can be derived by applying the first Fick's diffusion law to the diffusion layer in the feed side and to the membrane when: a) the composition of the strip solution is such that equilibria 1 is completely shifted to the left at the membrane-aqueous strip interface, b) the membrane polarity is low enough to make negligible the concentration of charged species with respect to that of uncharged ones and c) there is no extraction of Pd(II) by the pure diluent. Assuming that the transport of Pd(II) occurs at the steady state and that concentration gradients are linear, the equations describing the aqueous diffusion film flux, J_a, and the membrane flux, J_o, are:

$$J_a = \frac{D_a}{d_a} \left([Pd]_{aq} - [Pd]_{aq,i} \right) \tag{5}$$

$$J_o = \frac{D_o}{d_o} \left([PdL_2]_{org,f} - [PdL_2]_{org,s} \right) \tag{6}$$

In Eq. 3 and 4, D_a is the aqueous diffusion coefficient of $PdCl_4^{-2}$, D_o is the membrane diffusion coefficient of PdL_2, d_a is the thickness of the aqueous stagnant film, d_o is the membrane thickness, $[Pd]_{aq}$ and $[Pd]_{aq,i}$ are the Pd(II) concentrations in the aqueous feed phase and in the feed solution-membrane interface respectively, and finally $[PdL_2]_{org,f}$ and $[PdL_2]_{org,s}$ are the PdL_2 concentrations at the membrane-feed solution and at the membrane-stripping phase interfaces respectively.

As the distribution coefficient of Pd(II) between the membrane phase and the stripping phase is considered much lower than that between the feed phase and the membrane, the concentration of the metal-extracted complexes in the membrane phase at the stripping solution side may be considered negligible compared with that at the feed solution side. Then, Eq. 6 can be written as:

$$J_o = \frac{D_o}{d_o}[PdL_2]_{org,f} \tag{7}$$

If the chemical reaction expressed by Eq. 1 is assumed to be fast compared to the diffusion rate, local equilibrium at the interface is reached and concentrations at the interface are related through Eq. 2. Thus, at steady state, $J_a = J_o = J$ and combining Eqs. 2, 3, 5 and 7, the following expression is obtained:

$$J = \frac{[HL]_{org,e}^2 K_{ex}^*}{\left(\frac{d_o}{D_o}\right) + \left(\frac{d_a}{D_a}\right)[HL]_{org,e}^2 K_{ex}^*}[Pd]_{aq} \tag{8}$$

When the aqueous feed Pd(II) concentration is large enough to make $(d_a/D_a)[HL]_{org,e}^2 K_{ex}^* \ll (d_o/D_o)$ in the denominator of Eq. 8, i.e., $[HL]_{org,e}$ is negligible as compared to $2K_{ex}^*[Pd]_{aq}[HL]_{org,e}^2$ in Eq. 4, the membrane flux is equal to:

$$J = -\frac{d[Pd]_{aq}}{dt}\frac{V}{Q} = \frac{[HL]_{org,o}}{2}\frac{D_o}{d_o} \tag{9}$$

where V is the aqueous feed volume and Q can be computed by multiplying the geometrical area and the membrane porosity. Integrating Eq. 9:

$$[Pd]_{aq} = [Pd]_{aq,o} - \frac{[HL]_{org,o}}{2}\frac{D_o}{d_o}\frac{Q}{V}t \tag{10}$$

where $[Pd]_{aq,o}$ is the initial palladium aqueous feed concentration. In this situation, the flux is constant with time and plotting $[Pd]_{aq}$ versus time, a straight line must be obtained and therefore it is possible to evaluate D_o. The slope value of this straight line can be correlated to an initial membrane permeability coefficient, P_o, defined as:

$$P_o = \frac{J}{[Pd]_{aq,o}} = \frac{[HL]_{org,o}}{[Pd]_{aq,o}}\frac{D_o}{2d_o} \tag{11}$$

On the other hand, in the case that the Pd(II) concentration in the aqueous feed is so low that $[HL]_{org,e} \gg 2K_{ex}^*[Pd]_{aq}[HL]_{org,e}^2$ in Eq. 4, then Eq. 8 can be integrated to:

$$\ln\frac{[Pd]_{aq}}{[Pd]_{aq,o}} = -\frac{Q}{V}Pt \tag{12}$$

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where P is independent of the time and is defined as the permeability coefficient, which is expressed as:

$$P = \frac{J}{[Pd]_{aq}} = \frac{[HL]_{org,e}^2 K_{ex}^*}{\left(\dfrac{d_o}{D_o}\right) + \left(\dfrac{d_a}{D_a}\right)[HL]_{org,e}^2 K_{ex}^*} \qquad (13)$$

The permeability coefficient can be calculated from the slope of the plot ln $([Pd]_{aq}/[Pd]_{aq,o})$ versus time.

Finally, when total Pd(II) concentration in the aqueous feed is such that $[HL]_{org,e}$ falls between the above discussed extremes, a numerical solution for the integrated flux equations can be obtained:

$$\int_{[Pd]_{aq,o}}^{[Pd]_{aq}} \frac{d[Pd]_{aq}}{[Pd]_{aq}} \frac{V}{QP([Pd])} = t \qquad (14)$$

4. Results and discussion

The transport experiments performed in this work at 2.35×10^{-4} M Pd (II), gave in all the cases trends as those shown in Figure 4. As can be seen, at the beginning of the permeation process there is an induction period and the plots of ln $([Pd]_{aq}/[Pd]_{aq,o})$ versus time present an appreciable bending, but then in the course of the test a straight line is obtained. This pattern may be explained by the mass transfer modelling exposed previously. In the first portion of the graphs, the membrane permeability is entirely controlled by membrane diffusion, and a plot of $[Pd]_{aq}$ versus time should give a straight line as predicted by Eq. 10 allowing to calculate D_o and P_o. In the region where representing ln $([Pd]_{aq}/[Pd]_{aq,o})$ versus time a linear trend is observed, the permeability coefficient can be determined from the slope of the linear plot and Eq. 12. Out of these two limiting cases, the experimental points are justified by Eq. 14.

Similar mass transfer models have been also reported in the literature (19, 20) to explain the same type of experimental patterns.

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4.1. Influence of the stirring speed in the feed phase

Preliminary experiments were conducted to establish adequate hydrodynamic conditions. The permeability of the membrane was studied as a function of the stirring speed on the feed solution side, keeping constant the agitation of the stripping solution at 1200 rpm.

As can be seen in Figure 1, the Pd(II) permeability coefficient becomes virtually independent of the stirring speed above 750 rpm. This implies that d_a, which is the thickness of the boundary layer of Eq. 13 reached a minimum value.

The dependence of the initial permeability coefficient on the stirring speed is presented in Figure 2. This time, P_0 is not dependent of the aqueous feed stirring speed, as predicted by theory because terms containing d_a does not appear in Eq. 11.

4.2. Influence of the diluent

In Figure 3, the effect of the diluent on Pd(II) transport is illustrated and kerosene is the solvent giving the best permeability values compared with cumene and toluene. This is in accordance with previous Pd(II) liquid-liquid extraction results using DEHTPA (16).

4.3. Influence of DEHTPA concentration on Pd(II) permeation

ln ($[Pd]_{aq}/[Pd]_{aq,o}$) versus time plots at different extractant concentrations are reported in Figure 4. As mentioned before, two regions may be clearly differentiated in the experimental trends according to the proposed model.

Considering the straight line portions, it can be concluded that a limiting slope corresponding to a permeation coefficient is obtained in Figure 4 for all curves. This fact is corroborated in Figure 5, where the permeability coefficients at different extractant concentrations are represented. Because P is independent of DEHTPA concentration this region is representative of an aqueous diffusion film controlled permeation process. In these conditions, the term $(d_a/D_a)[HL]^2_{org,e}K^*_{ex} \gg (d_o/D_o)$ in the denominator of Eq. 13, and:

$$P = \frac{D_a}{d_a} \tag{15}$$

Assuming a typical value of 1×10^{-5} cm²/s for D_a and P equal to 0.002601 cm/s, the thickness of the aqueous diffusion film, evaluated from Eq. 15 is 3.8×10^{-3} cm. This value is the minimum thickness of the stagnant aqueous diffusion layer in our experimental conditions. In Figure 4 is also well noticed, that as expected from the developed model, the limiting P value indicating an aqueous diffusion film controlled permeability is reached earlier at higher mobile carrier concentrations.

At the other extreme of the curves, at short elapsed times, the membrane permeability is entirely controlled by diffusion. In this region, Eq. 10 holds and a plot of $[Pd]_{aq}$ versus time give straight lines as can be seen in Figure 6. Calculating the slopes of the lines, P_o values can be found by means of Eq. 11. The P_o versus $[HL]_{org,o}$ plot of Figure 7 indicates that a linear tendency is achieved in the DEHTPA concentration range 0.1 to 0.5 M as could be expected from Eq. 11 if it is supposed that D_o is concentration independent. However, at 1 M DEHTPA there is a noticeable deviation which can be explained by the following facts: a) probably D_o decrease when the concentration of extractant increase because of the membrane phase viscosity becomes higher (19, 20) and b) although the extent of DEHTPA aggregation in kerosene at low extractant concentrations is not significant (16), at 1 M DEHTPA the dimerization of the carrier is presumably important.

The slope of the straight lines and Eq. 10 allow also to evaluate the membrane diffusion coefficients of PdL_2 when all the carrier is bound to the metal. The calculated values are listed in Table 1. Although these values are approximate due to the assumptions involved in their calculation, it seems that D_o diminishes by increasing the DEHTPA concentration probably related to a viscosity increase in the organic phase.

The influence of the metal concentration on the membrane permeation was also investigated and the results are presented in Figure 8. When the Pd(II) concentration was ten times lower than the usual one, 2.35×10^{-5} M, the induction period was not observed with the experimental data available, owing to the low metal concentration which makes Eq. 12 valid during all the experiment.

4.4. Pd(II) permeation from solutions containing Fe(III), Pt(IV), Rh(III) and Zn(II)

The behaviour of Pd(II) together with other precious metals Pt(IV) and Rh(III) as well as some base metals Fe(III) and Zn(II) was examined in order to study the selectivity of DEHTPA supported liquid membranes. The results of metal permeability are shown in Figure 9, and clean permeation of Pd(II) over impurities is observed. Moreover, the Pd(II) permeation coefficient is not affected for the presence of the other metals since the limiting slope obtained has a similar value compared to that of single metal experiences.

4.5. Lifetime of the SLM

The lifetime of the SLM was evaluated by using the same support in several runs of 4 h duration. The membrane was stored in the same experimental set-up in contact with the air during the time that was not employed. Table 2 summarizes the results obtained where percentage extraction of Pd(II), E(%), was defined as:

$$E(\%) = 100 \frac{[M]_{aq,o} - [M]_{aq}}{[M]_{aq,o}} \tag{16}$$

at an elapsed time of 4 h. After three consecutive experiments (Exp. 1, 2 and 3) the metal extraction did not suffer a significant variation. In the following days a small extraction depletion was observed (Exp. 4 and 5), but finally the membrane efficiency fell to almost half of the initial value (Exp. 6). Regeneration of the membrane was successfully achieved by re-impregnating the support, since the percentage extraction was found to be again similar as that of the initial runs (Exp. 7).

5. Conclusions

The results of the permeation experiments confirm the validity of the derived physicochemical model.

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At the beginning of the transport tests, when the extractant is almost all bound to Pd(II), the flux is constant but the membrane permeability coefficient is function of time and the rate of metal transfer is controlled by the diffusion in the membrane. Then when Pd(II) concentration in the aqueous feed solution diminishes the flux tends to decrease and metal permeation can be described by a time independent permeability coefficient, being this situation representative of an aqueous diffusion film controlled permeation process.

On the other hand, SLM containing DEHTPA have been proved to selectively transport Pd(II) over Fe(III), Pt(IV), Rh(III) and Zn(II).

The membrane lifetime was evaluated and good performance in the metal transport was observed after five times usage of the same membrane. Once the Pd(II) membrane transport was significantly suppressed, by re-impregnation of the support metal transport ability was recovered.

Acknowledgments

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TABLE 1
Diffusion coefficients of PdL_2 complexes at different carrier concentrations

$[HL]_{org,o}$	D_o (cm^2/s)
0.1	1.31×10^{-8}
0.15	1.23×10^{-8}
0.25	1.18×10^{-8}
0.3	1.10×10^{-8}
0.4	1.23×10^{-8}
0.5	1.11×10^{-8}
1	7.32×10^{-9}

TABLE 2
Lifetime of SLM

Experimental conditions. Feed phase: $[Pd]_{aq,o} = 2.35 \times 10^{-4}$ M in HCl 1 M, 1000 rpm stirring speed. Membrane phase: 0.5 M DEHTPA.
Stripping phase: 0.9 M thiourea - 0.1 M HCl, 1200 rpm stirring speed.

Experiment Number	Membrane usage before the test (h)	Membrane Age (Days)	Pd(II) Ex(%) at an elapsed time of 4 h
1	0	0	80
2	4	0	81
3	8	0	82
4	12	1	74
5	16	2	74
6	20	5	44
7	Re-impregnation	6	83
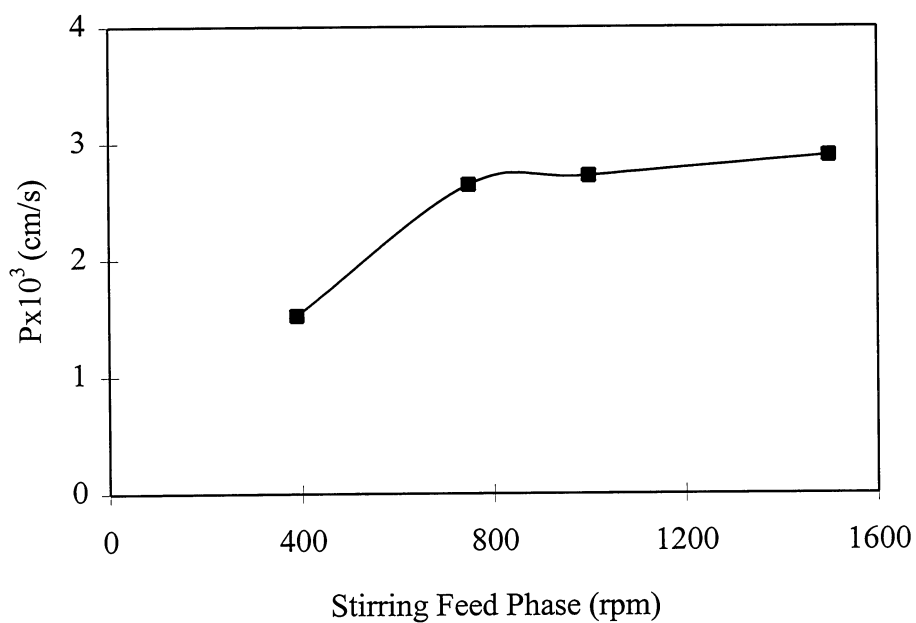
FIGURE 1. Influence of feed phase stirring speed on permeability coefficient of Pd(II). Experimental conditions. Feed phase: $[Pd]_{aq,o}=2.35 \times 10^{-4}$ M in HCl 1 M. Membrane phase: 0.25 M DEHTPA in kerosene. Stripping phase: 0.9 M thiourea - 0.1 M HCl, 1200 rpm stirring speed.
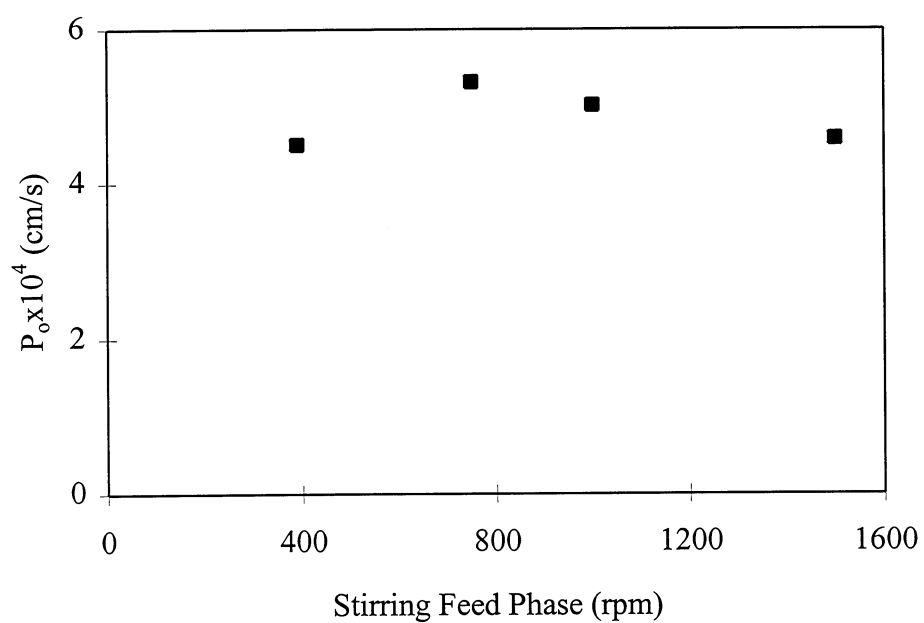
FIGURE 2. Influence of feed phase stirring speed on initial permeability coefficient of Pd(II). Experimental conditions: as in Figure 1.
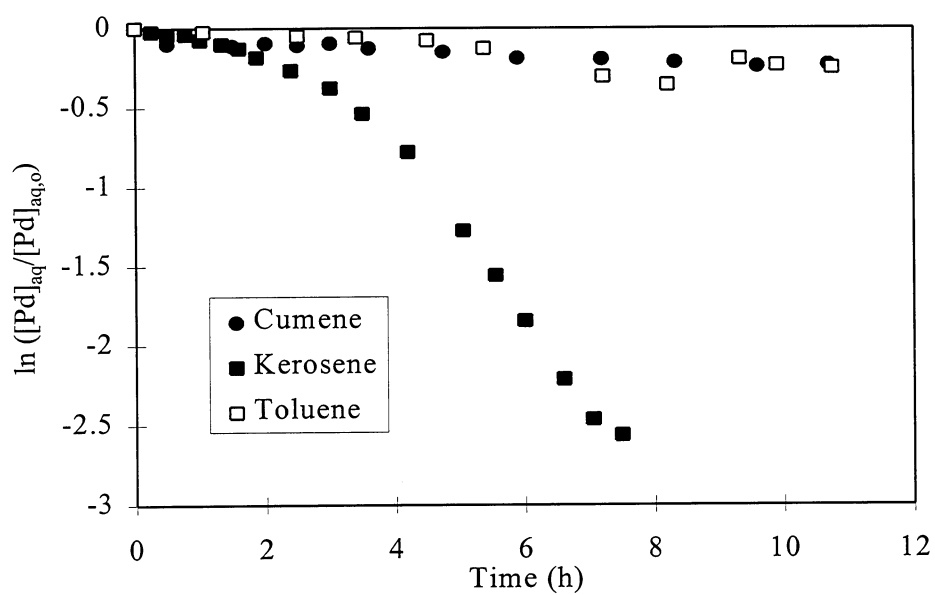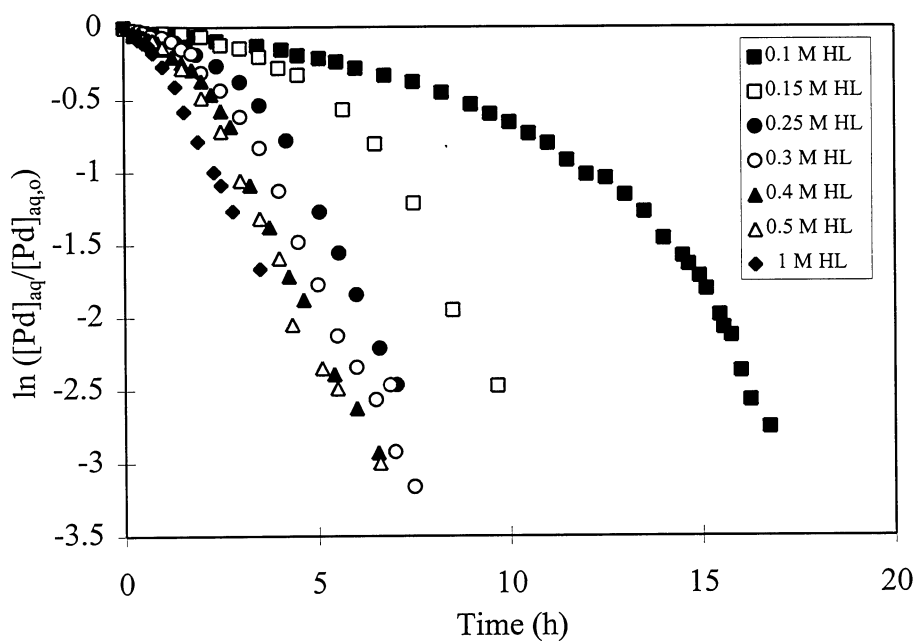
FIGURE 3. Influence of the diluent in the membrane phase on Pd(II) transport. Experimental conditions. Feed phase: $[Pd]_{aq,o}=2.35x10^{-4}$ M in HCl 1 M, 1000 rpm stirring speed. Membrane phase: 0.25 M DEHTPA. Stripping phase: 0.9 M thiourea - 0.1 M HCl, 1200 rpm stirring speed.
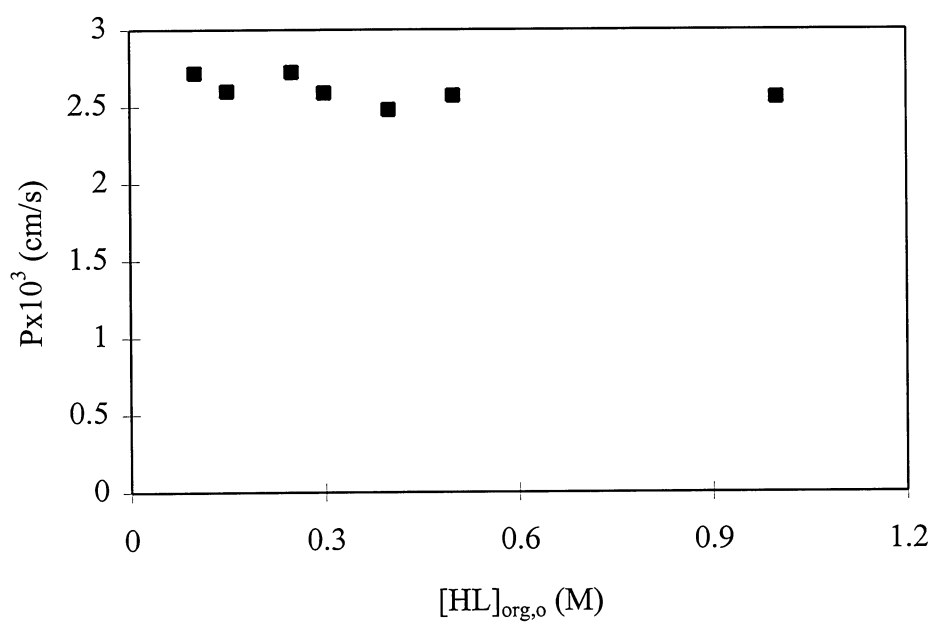
FIGURE 4. Influence of DEHTPA concentration in the membrane phase on Pd(II) transport. Experimental conditions. Feed phase: $[Pd]_{aq,o}=2.35\times10^{-4}$ M in HCl 1 M, 1000 rpm stirring speed. Membrane phase: DEHTPA in kerosene. Stripping phase: 0.9 M thiourea - 0.1 M HCl, 1200 rpm stirring speed.

FIGURE 5. Influence of DEHTPA concentration in the membrane phase on permeability coefficient of Pd(II). Experimental conditions: as in Figure 4.
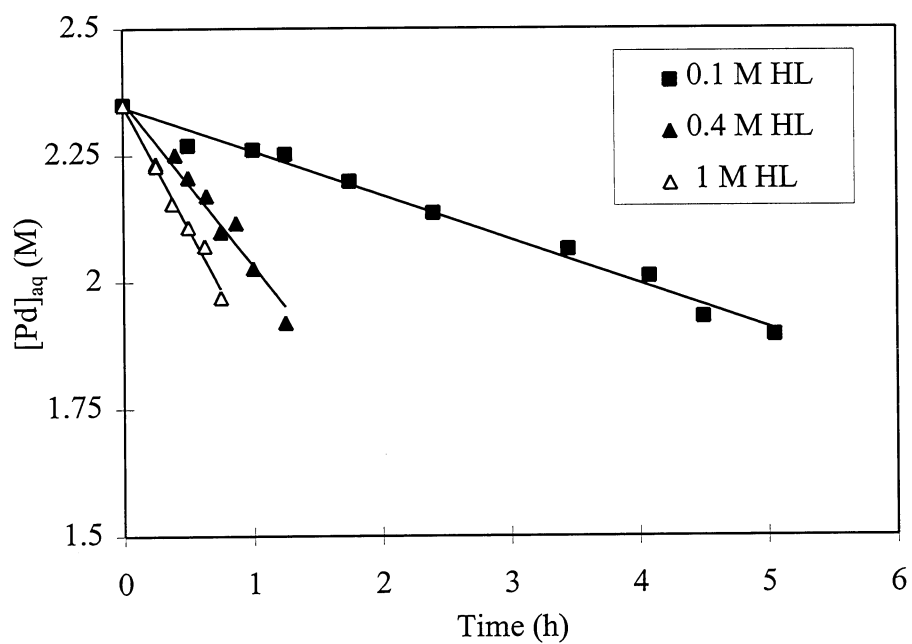
FIGURE 6. Total Pd(II) concentration in the aqueous feed versus time at the beginning of the experimental runs. Experimental conditions: as in Figure 4.
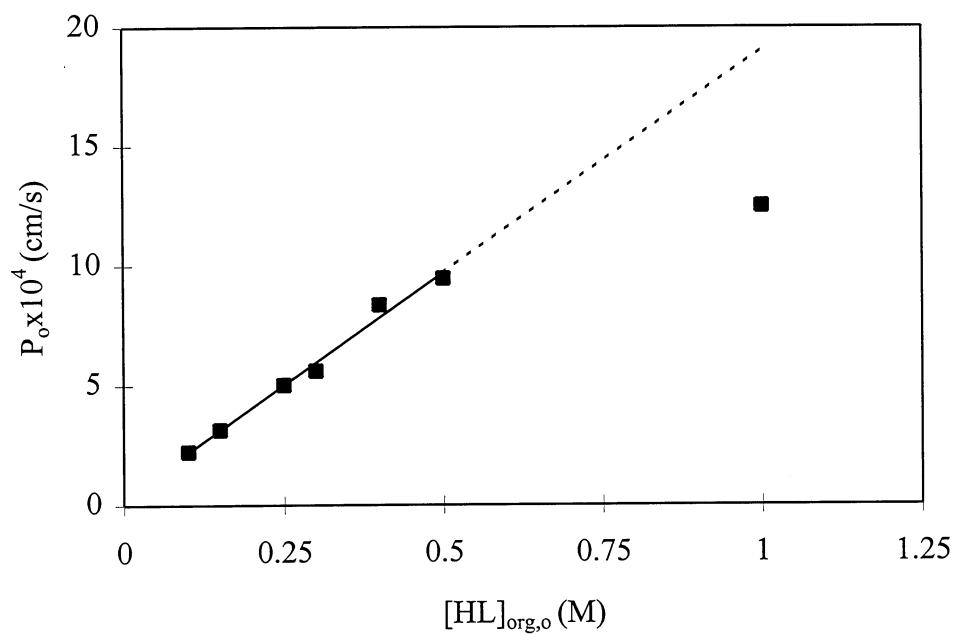
FIGURE 7. Influence of DEHTPA concentration in the membrane phase on initial permeability coefficient of Pd(II). Experimental conditions: as in Figure 4.
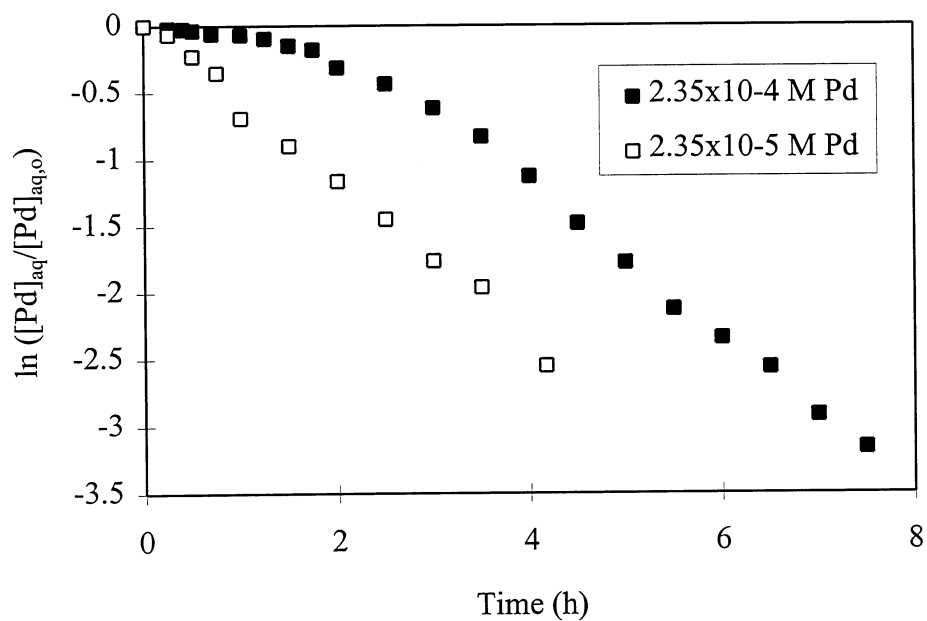
FIGURE 8. Influence of metal concentration on Pd(II) transport. Experimental conditions. Feed phase: Pd(II) in HCl 1 M, 1000 rpm stirring speed. Membrane phase: 0.25 M DEHTPA in kerosene. Stripping phase: 0.9 M thiourea - 0.1 M HCl, 1200 rpm stirring speed.
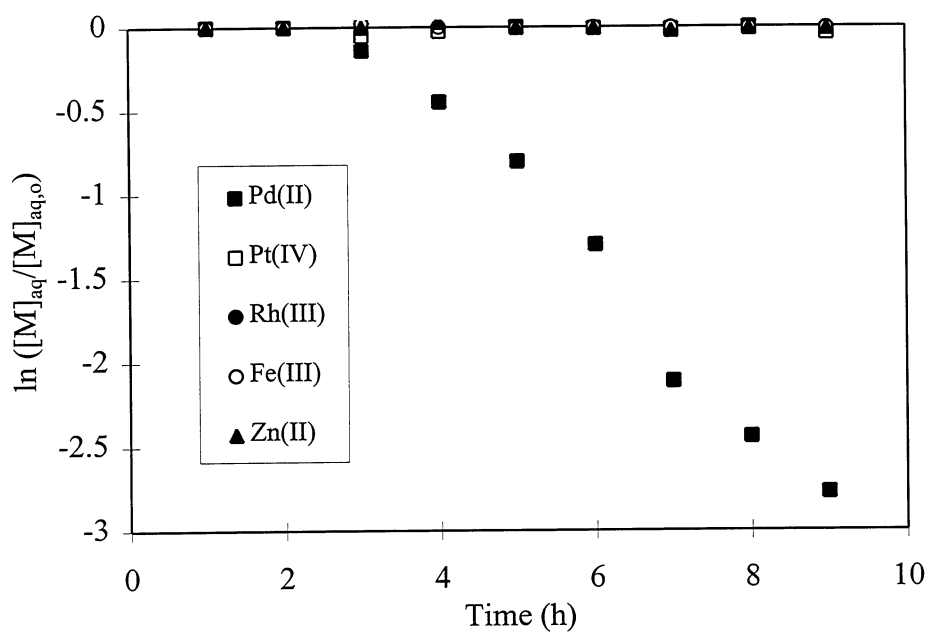
FIGURE 9. Metal transport for Pd(II) and some impurities. Experimental conditions. Feed phase: $[M]_{aq,o}$=2.35x10^{-4} M in 1 M HCl, 1000 rpm stirring speed. Membrane phase: 0.25 M DEHTPA in kerosene. Stripping phase: 0.9 M thiourea - 0.1 M HCl, 1200 rpm stirring speed.