

Kinetic modelling of the facilitated transport of cadmium (II) using Cyanex 923 as ionophore

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Abstract

The facilitated transport of cadmium (II) from chloride through a flat-sheet supported liquid membrane is studied, using Cyanex 923 (phosphine oxides mixture) as ionophore, as a function of various experimental variables: hydrodynamic conditions, concentration of cadmium (II) (0.01–0.08 g l⁻¹) and HCl (0.1–5 M) in the feed phase, carrier concentration (2.5–40%, v/v) and diluent in the membrane phase. A model is derived that describes the transport mechanism, consisting of diffusion through a feed aqueous diffusion layer, a fast interfacial chemical reaction, and diffusion of carrier and the metal complexes through the organic membrane. The organic membrane diffusional resistance (Δ_{org}) and aqueous diffusional resistance (Δ_{aq}) were calculated from the model, and their values were 196145 and 260 s cm⁻¹, respectively, whereas the values of the bulk diffusion coefficient ($D_{\text{org,b}}$) and diffusion coefficient (D_{org}) also calculated from the model were 2.4×10^{-7} and 6.4×10^{-8} cm² s⁻¹. The separation of Cd(II) against Zn(II), Fe(III), Co(II) and Cu(II) is evaluated.

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1. Introduction

Cadmium occurs naturally widely dispersed in the environment and is produced as a by-product in the production of other metals, especially zinc. Human exposures occur principally as inhalation of Cd-containing dust in industry and orally as Cd-containing food in the general population. After uptake, cadmium in blood is initially taken up by the liver and subsequently slowly redistributed to the kidney where it is accumulate, resulting in various diseases; also Cd is considered carcinogenic to humans. Because of its toxicological properties, legislation implying considerable restrictions in its use and in the discharge of Cd-bearing effluents has been passed in a number of countries [1].

Several technologies can be used to remove these toxic metals from liquid effluents, including precipitation, solvent extraction, ion exchange, etc., among these, liquid membrane technique has acquired an importance for its use in separation, concentration or even analytical application. Though this technology is still

in the research or development stage, it holds a deserving position in the field of membrane separations due to its advantages over conventional separation operations. Including in the liquid membrane characteristics are their high specificity, low energy utilisation, ease of installation, etc.

The different types of liquid membranes are reviewed in the literature [2,3]. Supported liquid membranes and emulsion liquid membranes are the most commonly used. In supported liquid membranes, the extraction, stripping and regeneration of the organic phase are combined in a single stage. Moreover, from the engineering and practical standpoint, supported liquid membranes are of particular interest because of their simplicity.

The transport of Cd(II) from different aqueous solutions using this supported liquid membrane technology is reported in previous investigations (Table 1).

Before scaling up the flat-sheet supported liquid membrane, either in the form of the two others supported liquid membranes configurations: hollow fiber and spiral wound membrane extraction, a theoretical model of the liquid membrane system is needed in order to design an efficient recovery process.

This investigation presents the kinetic modelling of active transport of Cd(II) using Cyanex 923 (a commercially avail-

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Table 1
Selected carriers and aqueous systems used in supported liquid membranes for cadmium transport

| Carrier | Aqueous feed | Reference |
|---|------------------------------------|-----------|
| Tricaprylamine | Chloride | [4] |
| Tri- <i>n</i> -octylamine | Chloride | [5] |
| Cyanex 302 | Phosphoric acid | [6,11] |
| Aliquat 336 | HCl | [7,18] |
| TBP | Chloride | [8] |
| Kelex 100 | pH > 6 | [9] |
| Cyanex 923 | HCl/H ₃ PO ₄ | [10,19] |
| Polycyclic-carboxyl polyether derivative | Acidic | [12] |
| D2EHPA | Sulfate | [13,16] |
| D2EHPA | Nitrate | [14] |
| Cyanex 302 | Acidic | [15] |
| D2EHPA, PC88A | Sulfate | [17] |

able phosphine oxides mixture) immobilized on a microporous hydrophobic support. The organic membrane diffusional resistance (Δ_{org}) and the aqueous diffusional resistance (Δ_{aq}) were calculated from the proposed model. The influence of hydrodynamic conditions and chemical parameters were investigated in order to obtain efficient flat-sheet supported liquid membranes.

2. Materials and methods

The extractant Cyanex 923 was used as supplied by the manufacturer (CYTEC Ind.), it contains different phosphine oxides [20]. The average molecular weight is 348 and the density (20 °C) is 800 kg m⁻³. Solvesso 100 diluent was also used as supplied by the manufacturer (ExxonMobil Chem. Iberia) and contains >99% aromatics, boiling range 167–178 °C and flash point 48 °C; all other chemicals were of AR grade.

The flat-sheet membrane used was Millipore Durapore GVHP4700, a 125 × 10⁻⁴ cm thick microporous polyvinylidene fluoride film with nominal porosity (ϵ) of 75%, effective pore size (d_{org}) of 0.22 μm and tortuosity (τ) 1.67.

The membrane was impregnated with the corresponding carrier solution by immersion for 24 h and then leaving it to drip for 10 s before being placed in the transport cell. Previous tests demonstrated that longer immersion time do not influence metal transport.

The supported liquid membrane transport experiments were carried out at 20 °C with a two-compartment permeation cell consisting of a feed phase (200 cm³) separated from the receiving phase chamber (200 cm³) by the liquid membrane having an effective membrane area of 11.3 cm². The feed and receiving phases were mechanically stirred by using cylindrical Teflon impellers having a diameter of 2.4 cm at the stirring speeds of 1200 and 800 min⁻¹, respectively for the feed and receiving phases, unless otherwise stated, to avoid concentration polarization conditions at the membrane interfaces.

The cadmium (or metal) content of the aqueous phases was periodically determined by atomic absorption spectrometry. The

permeability coefficient, P , was calculated as

$$\ln \frac{[M]_t}{[M]_0} = -\frac{A}{V} Pt \quad (1)$$

where $[M]_t$ is the metal concentration in the feed solution at time t , $[M]_0$ the initial metal concentration in the same solution, A the effective membrane area, V the volume of the feed phase, and t is the elapsed time.

3. Results and discussion

3.1. Permeation model in solid supported liquid membranes

The mass transfer of Cd(II) crossing the membrane is described considering only diffusional parameters. The interfacial flux due to the chemical reaction is neglected, as the chemical reactions seem to take place at the interface feed phase/membrane and membrane/receiving phase interface, and it has been suggested that chemical reactions can be considered as occurring instantaneously relative to the diffusional process [21]. Thus, a model of the mass transfer of cadmium (II) may be derived by considering various steps:

- (i) diffusion of metal species from the bulk of feed solution to the aqueous feed boundary layer,
- (ii) diffusion of protons and chloride ions from the bulk of feed solution to the aqueous feed boundary layer,
- (iii) reaction between metal species, protons and chloride ions and carrier at the feed-membrane interface,
- (iv) diffusion of metal-carrier complexes from the feed-membrane interface to the membrane-receiving phase interface,
- (v) stripping of metal species at the membrane-receiving phase interface and diffusion of them to the bulk of the receiving solution, and
- (vi) diffusion of the regenerated carrier back to the feed-membrane interface, after which the process is repeated.

Fig. 1 shows a possible transport scheme for cadmium (II) across the supported liquid membrane. Such a process is called coupled co-transport, where the counterion (protons and chlo-

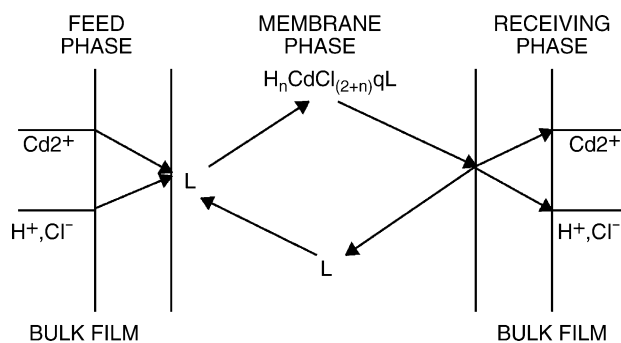
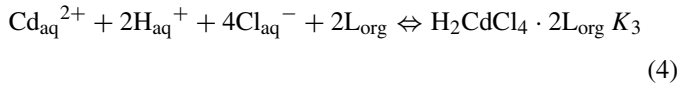
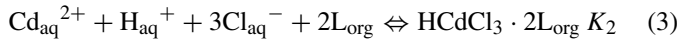
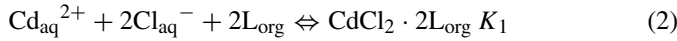


Fig. 1. Schematic concentration profile of the species across a flat-sheet supported liquid membrane containing Cyanex 923 as a mobile carrier. L: Cyanex 923.

ride ions) concentration in the feed solution is used as the driving force for metal transport.

The extraction of cadmium (II) by Cyanex 923 dissolved in Solvesso 100 has been studied and described elsewhere [22]. The extraction equilibria at 5 M HCl (where maximum cadmium extraction is achieved) can be described by the following reactions and extraction constants:



$$K_1 = \frac{[\text{CdCl}_2 \cdot 2\text{L}]_{\text{org}}}{[\text{Cd}^{2+}]_{\text{aq}}[\text{Cl}^{-}]_{\text{aq}}^2[\text{L}]_{\text{org}}^2} = 7.9 \times 10^1 \quad (5)$$

$$K_2 = \frac{[\text{HCdCl}_3 \cdot 2\text{L}]_{\text{org}}}{[\text{Cd}^{2+}]_{\text{aq}}[\text{H}^{+}]_{\text{aq}}[\text{Cl}^{-}]_{\text{aq}}^3[\text{L}]_{\text{org}}^2} = 2.5 \times 10^1 \quad (6)$$

$$K_3 = \frac{[\text{H}_2\text{CdCl}_4 \cdot 2\text{L}]_{\text{org}}}{[\text{Cd}^{2+}]_{\text{aq}}[\text{H}^{+}]_{\text{aq}}^2[\text{Cl}^{-}]_{\text{aq}}^4[\text{L}]_{\text{org}}^2} = 7.9 \quad (7)$$

where L is the extractant.

The cadmium (II) transport rate is determined by the rate of diffusion of cadmium-containing species through the feed phase diffusion layer and the rate of diffusion of these species through the membrane. Then, the flux of cadmium (II) crossing the membrane may be derived by applying Fick's first diffusion law to the diffusion layer in the feed phase side and to the membrane. The diffusional fluxes at the feed phase boundary layer, J_{aq} , and at the membrane phase, J_{org} , can be expressed by the following equations:

$$J_{\text{aq}} = \Delta_{\text{aq}}^{-1}([\text{Cd(II)}]_{\text{TOT}} - [\text{Cd(II)}]_{\text{i,TOT}}) \quad (8)$$

$$J_{\text{org}} = \Delta_{\text{org}}^{-1}([\text{CdCl}_2 \cdot 2\text{L}]_{\text{i,f}} - [\text{CdCl}_2 \cdot 2\text{L}]_{\text{i,s}}) + \Delta_{\text{org}}^{-1}([\text{HCdCl}_3 \cdot 2\text{L}]_{\text{i,f}} - [\text{HCdCl}_3 \cdot 2\text{L}]_{\text{i,s}}) + \Delta_{\text{org}}^{-1}([\text{H}_2\text{CdCl}_4 \cdot 2\text{L}]_{\text{i,f}} - [\text{H}_2\text{CdCl}_4 \cdot 2\text{L}]_{\text{i,s}}) \quad (9)$$

The distribution coefficient of cadmium (II) between the membrane phase and the receiving phase is lower than that between the feed phase and the membrane; hence the concentration of the cadmium-extracted complexes in the membrane phase at the receiving phase side may be neglected compared with that at the feed phase side, then Eq. (9) can be rewritten as

$$J_{\text{org}} = \Delta_{\text{org}}^{-1}([\text{CdCl}_2 \cdot 2\text{L}]_{\text{i,f}} + [\text{HCdCl}_3 \cdot 2\text{L}]_{\text{i,f}} + [\text{H}_2\text{CdCl}_4 \cdot 2\text{L}]_{\text{i,f}}) \quad (10)$$

If the chemical reactions expressed by Eqs. (2)–(4) are assumed to be fast compared to the diffusion rate, local equilibria at the interface are reached and concentrations at the interface are related by Eqs. (5)–(7). At steady state, $J_{\text{aq}} = J_{\text{org}} = J$ and by

combination of Eqs. (5)–(8) and (10), the next expression is obtained

$$J = \frac{(K_1[\text{L}]_{\text{org}}^2[\text{Cl}^{-}]_{\text{aq}}^2 + K_2[\text{L}]_{\text{org}}^2[\text{H}^{+}]_{\text{aq}}[\text{Cl}^{-}]_{\text{aq}}^3 + K_3[\text{L}]_{\text{org}}^2[\text{H}^{+}]_{\text{aq}}^2[\text{Cl}^{-}]_{\text{aq}}^4)[\text{Cd(II)}]_{\text{TOT}}}{\Delta_{\text{org}} + \Delta_{\text{aq}}(K_1[\text{L}]_{\text{org}}^2[\text{Cl}^{-}]_{\text{aq}}^2 + K_2[\text{L}]_{\text{org}}^2[\text{H}^{+}]_{\text{aq}}[\text{Cl}^{-}]_{\text{aq}}^3 + K_3[\text{L}]_{\text{org}}^2[\text{H}^{+}]_{\text{aq}}^2[\text{Cl}^{-}]_{\text{aq}}^4)} \quad (11)$$

where Δ_{org} and Δ_{aq} are the transport resistances due to diffusion through the membrane and to diffusion by the feed phase boundary layer, respectively, and $[\text{Cd(II)}]_{\text{TOT}}$ is the total metal concentration in the feed phase. The permeability coefficient can be written as

$$P = \frac{(K_1[\text{L}]_{\text{org}}^2[\text{Cl}^{-}]_{\text{aq}}^2 + K_2[\text{L}]_{\text{org}}^2[\text{H}^{+}]_{\text{aq}}[\text{Cl}^{-}]_{\text{aq}}^3 + K_3[\text{L}]_{\text{org}}^2[\text{H}^{+}]_{\text{aq}}^2[\text{Cl}^{-}]_{\text{aq}}^4)}{\Delta_{\text{org}} + \Delta_{\text{aq}}(K_1[\text{L}]_{\text{org}}^2[\text{Cl}^{-}]_{\text{aq}}^2 + K_2[\text{L}]_{\text{org}}^2[\text{H}^{+}]_{\text{aq}}[\text{Cl}^{-}]_{\text{aq}}^3 + K_3[\text{L}]_{\text{org}}^2[\text{H}^{+}]_{\text{aq}}^2[\text{Cl}^{-}]_{\text{aq}}^4)} \quad (12)$$

This expression combines the equilibrium and diffusion parameters involved in the cadmium (II) transport process through a supported liquid membrane containing Cyanex 923 in Solvesso 100 as carrier.

3.2. Influence of the stirring speed (feed and receiving phases)

The influence of the stirring speed (feed phase) on cadmium transport was studied in order to optimize uniform mixing of the solution and to minimize thickness of aqueous boundary layer with feed and receiving conditions being maintained as 0.01 g l⁻¹ Cd(II) in 5 M HCl and water, respectively. The extractant concentration was 20% (v/v) in Solvesso 100 immobilized on a Durapore support. The metal flux, calculated as

$$J = P[\text{Cd(II)}]_{\text{TOT}} \quad (13)$$

becomes virtually independent of the stirring speed above 1200 min⁻¹, indicating a decrease in the aqueous boundary layer thickness, and then a minimum value of the thickness is reached at this agitation speed. Thus, a stirring speed of 1200 min⁻¹ (feed phase) was kept constant throughout the experiments conducted. On the other hand, the variation of the stirring speed in the receiving phase has a minor effect on the variation of cadmium transport.

3.3. Influence of HCl concentration in the feed phase

To study the influence of the hydrochloric acid concentration in the feed phase on cadmium transport, a series of experiments were carried out at various HCl concentrations, keeping other variables constant. Thus, the single metal transport through the membrane of 0.01 g l⁻¹ Cd(II) from an aqueous feed phase of varying HCl concentrations was studied using water as strippant. Fig. 2 shows that the cadmium permeation increased as the HCl concentration of the phase was increased up to 2 M but above

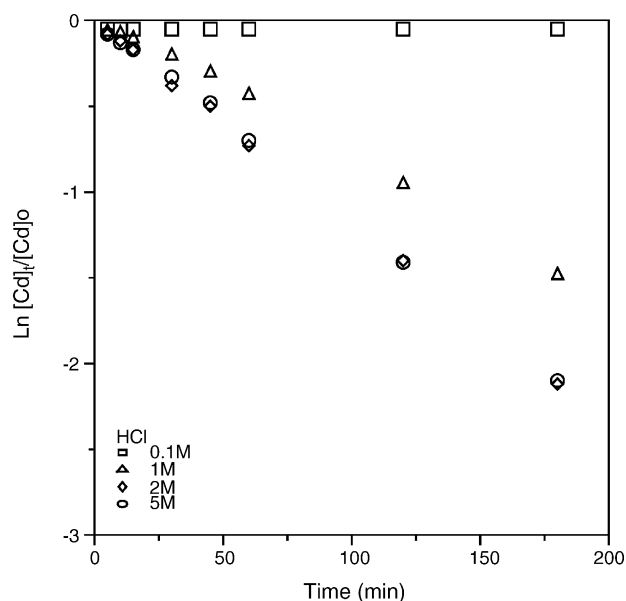


Fig. 2. Influence of HCl concentration (feed phase) on cadmium transport. Membrane phase: 20% (v/v) Cyanex 923 in Solvesso 100.

this value and up to 5 M HCl, the permeation coefficient then becomes constant.

At HCl concentrations above 5 M, the cadmium permeation decreases and this can be attributable to a competition between cadmium and HCl. It is known that Cyanex 923 extracted mineral acids [23].

3.4. Influence of cadmium (II) concentration in the feed phase

The influence of Cd(II) concentration on the membrane permeation was also investigated and the results are presented in Table 2. The results obtained revealed that the metal permeation coefficient is practically independent of the initial metal concentration, though the metal flux increased with the increase of the cadmium concentration in the feed phase, being this in accordance with the expected trend, since the flux of a solute varies in direct proportion with solute concentration [21,24].

Concentration profiles in the three bulk phases during the permeation experiments are shown in Fig. 3. From the initial stages of the experiment, the decrease in cadmium concentration in the feed phase was accompanied by a corresponding increase in the receiving phase concentration. It is also noted that, from near 60 min, cadmium (II) was being transported uphill against its

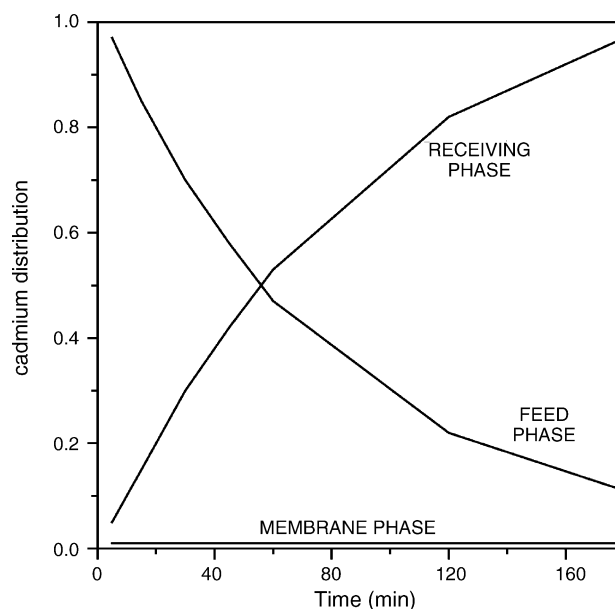


Fig. 3. Cadmium (II) concentration profiles in transport experiments. Feed phase: 0.02 g l⁻¹ Cd(II) and 5 M HCl. Membrane phase: 20% (v/v) Cyanex 923 in Solvesso 100. Receiving phase: water.

concentration gradient, driven by the co-current coupled transport of protons and chloride ions from the feed to the receiving phase.

3.5. Influence of membrane diluent on the transport of cadmium

The characteristics of the organic phase diluent have an influence on the performance of liquid–liquid extraction systems [25], thus a similar effect may be observed in liquid membranes [26–28]. A membrane diluent must fulfil a number of requirements, which are described in the literature [29,30].

Various commercial diluents for Cyanex 923 were investigated in the present supported liquid membrane system. Fig. 4 shows the effect of the diluent on the transport of cadmium. Diluents xylene, cumene and Solvesso 100 gave best permeability values and even better than *n*-decane and *n*-heptane. With a straight chain configuration, these two aliphatic diluents has a relatively regular structure with strong Van der Waal's forces between the molecules, and suffer more disruption on transport of bulky complexes.

3.6. Influence of carrier concentration

The influence of the membrane composition on cadmium transport was studied using different carrier concentrations in the membrane phase. Fig. 5 shows the variation in the metal transport through a supported liquid membrane impregnated with solution 2.5–40% (v/v) Cyanex 923 in Solvesso 100. Lower concentrations of carrier were investigated, and near no-transport was achieved. The metal permeation increased with the phosphine oxide concentration up to near 25% (v/v) and then decreases, this being typical of a process controlled by diffusion in the stagnant film of the feed phase, whereas the decrease in the

Table 2
Influence of initial cadmium (II) concentration on metal transport

| [Cd(II)] (g l ⁻¹) | $P (\times 10^3 \text{ cm s}^{-1})$ | $J (\times 10^9 \text{ mol cm}^{-2} \text{ s}^{-1})$ |
|-------------------------------|-------------------------------------|--|
| 0.01 | 3.5 | 0.31 |
| 0.02 | 3.7 | 0.65 |
| 0.04 | 3.5 | 1.2 |
| 0.08 | 3.2 | 2.3 |

Feed phase: Cd(II) in 5 M HCl. Membrane phase: 20% (v/v) Cyanex 923 in Solvesso 100. Receiving phase: water.

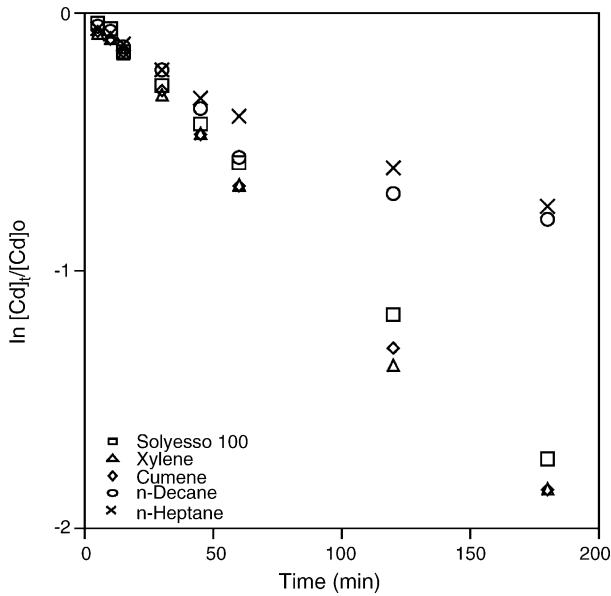


Fig. 4. Influence of the diluent in the membrane phase on the transport of cadmium. Feed phase: 0.01 g l^{-1} Cd(II) in 5 M HCl. Membrane phase: 10% (v/v) Cyanex 923 in each diluent. Receiving phase: water.

metal transport at higher carrier concentration can be attributed to an increase in the membrane phase viscosity which increases the membrane resistance to transport.

3.7. Evaluation of the mass transfer resistances

To determine the value of the resistances to the mass transfer, the next expression, derived from Eq. (12), has been used:

$$\frac{1}{P} = \Delta_{\text{aq}} + \frac{\Delta_{\text{org}}}{K_1[L]_{\text{org}}^2[\text{Cl}^-]_{\text{aq}}^2 + K_2[L]_{\text{org}}^2[\text{H}^+]_{\text{aq}}[\text{Cl}^-]_{\text{aq}}^3 + K_3[L]_{\text{org}}^2[\text{H}^+]_{\text{aq}}^2[\text{Cl}^-]_{\text{aq}}^4} s \quad (14)$$

Thus, by plotting $1/P$ versus the denominator of the above equation for different carrier concentrations and $[\text{HCl}] = 5 \text{ M}$, a straight line should be obtained with slope Δ_{org} and intercept Δ_{aq} . From Fig. 6, Δ_{org} and Δ_{aq} were found to be $19,6145$ and 260 s cm^{-1} , respectively. By substituting these values of transport resistance, the validity of Eq. (12) was determined. In Fig. 7, the experimental and calculated values using Eq. (12) have been plotted as a function of the carrier concentration, and it can be seen that the models fits reasonably well the data obtained within the experimental conditions. Assuming a value of $6.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for D_{aq} , a value of $1.7 \times 10^{-3} \text{ cm}$ is obtained for d_{aq} (thickness of the aqueous boundary layer). On the other hand, the calculated value of the diffusion coefficient (membrane phase) was $6.4 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$.

The diffusion coefficient of the cadmium-complexes in the bulk organic phase ($D_{\text{org,b}}$) can be evaluated from the diffusivity in the membrane (D_{org}) with micropores from the following expression [31]:

$$D_{\text{org}} = \frac{\varepsilon}{\tau^2} D_{\text{org,b}} \quad (15)$$

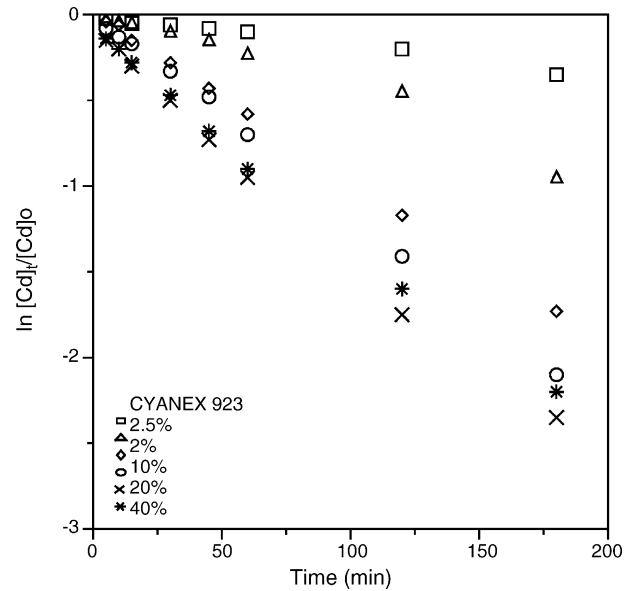


Fig. 5. Metal transport vs. carrier concentration. Feed phase: 0.01 g l^{-1} Cd(II) and 5 M HCl. Receiving phase: water.

The value of $D_{\text{org,b}}$ was found to be $2.4 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$. It should be noted that in the present system, D_{org} presents a lower value than that of the bulk diffusion coefficient, this is attributable to diffusional resistance caused by microporous thin membrane placed between the feed and receiving phases.

3.8. Influence of co-ions in the feed phase

Since cadmium-bearing effluents are produced in a number of industries, it is interesting to compare the performance of the present system against the presence of other heavy metals in the wastewater. Table 3 shows results obtained in the transport of cadmium (II) when the feed phase also contained other accompanying metals. It can be seen that within the experimen-

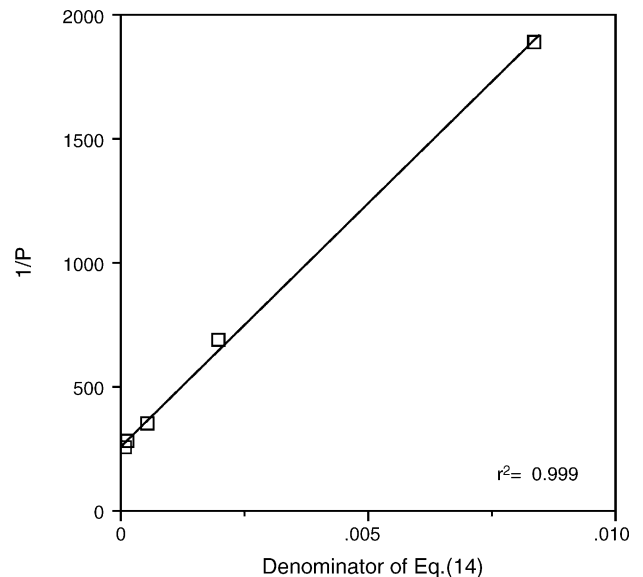


Fig. 6. $1/P$ plotted vs. the denominator of Eq. (14) for experimental data.

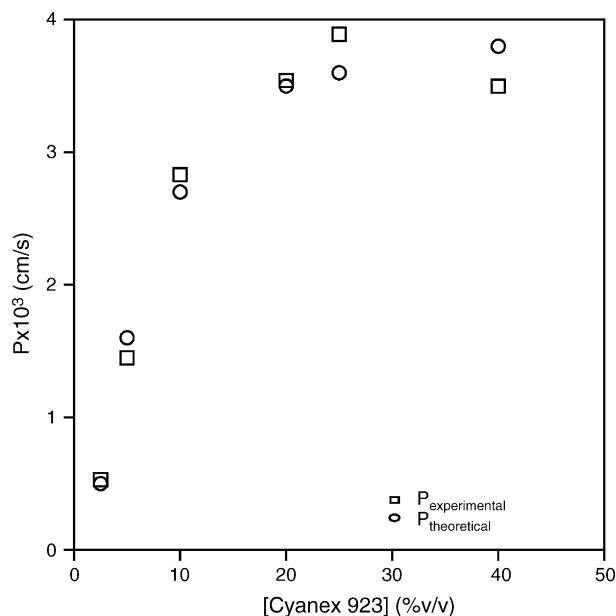


Fig. 7. Influence of the concentration of carrier in the supported liquid membrane phase on the permeability of cadmium. Circle points: experimental data. Square points: calculated values. Experimental conditions as in Fig. 5.

tal conditions, cadmium (II) is transported preferably against the other metals presented in the initial feed phase. The separation factor cadmium-metal, $\beta_{Cd/M}$, defined as the ratio of permeabilities cadmium-metals:

$$\beta_{Cd/M} = \frac{P_{Cd}}{P_M} \quad (16)$$

shows the possibilities of the separation of cadmium from other metals presented in the feed phase using Cyanex 923 dissolved in Solvesso 100 as carrier: $Co(II) > Cu(II) > Cr(VI) > Fe(III) > Zn(II)$. In any case, the permeability value of cadmium obtained from these binary systems also presented a minor value than that obtained from a mono-elemental solution; this can be attributable to a multi-ion effect or crowding ion effect, observed in a number of permeation systems [32].

Table 3
Cadmium (II) transport in presence of different metals (binary solutions)

| System | P_M ($\times 10^3$ cm s $^{-1}$) | $B_{Cd/M}$ |
|---------|--------------------------------------|--------------|
| Cd(II) | 3.5 | |
| Cd(II) | 3.2 | 1.19 |
| Zn(II) | 2.7 | |
| Cd(II) | 3.4 | 11.3 |
| Cr(VI) | 0.3 | |
| Cd(II) | 3.2 | 2.29 |
| Fe(III) | 1.4 | |
| Cd(II) | 3.4 | Quantitative |
| Co(II) | No permeation | |
| Cd(II) | 3.4 | Quantitative |
| Cu(II) | No permeation | |

Feed phase: 8.9×10^{-5} M each metal in 5 M HCl. Membrane phase: 20% (v/v) Cyanex 923 in Solvesso 100. Receiving phase: water.

4. Conclusions

Cyanex 923 dissolved in Solvesso 100 is an effective carrier for cadmium (II) from hydrochloric acid solutions. Metal transport is influenced by a number of variables of the feed phase: stirring speed and HCl concentration, and of the membrane phase: carrier concentration and membrane diluent. From experimental data, it is inferred that metal permeation can be described by a time-independent permeability coefficient, this situation being representative of an aqueous diffusion film controlled permeation process. Mass transfer coefficients were calculated as 5.1×10^{-6} and 3.8×10^{-3} cm s $^{-1}$ for the organic and aqueous phases, respectively; whereas the thickness of the feed phase boundary layer was estimated as 1.7×10^{-3} cm. The system presented good selectivity against the presence of different base metals in the feed phase and is convenient in using water as receiving solution.

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