



Modelling of zinc (II) transport through a PC-88A supported liquid membrane

Ana Maria Tarditi*, José Marchese, Mercedes E. Campderrós**

*Departamento de Química, Facultad de Química, Bioqca. y Farmacia. UNSL. CONICET, Chacabuco y Pedernera, 5700 San Luis, Argentina
Fax: +54 (2652) 422644; email: mcamp@unsl.edu.ar*

Received 3 November 2006; Accepted 10 October 2007

Abstract

Zinc has been permeated through a flat-sheet supported liquid membrane, using 2-ethylhexylphosphoric acid mono-2-ethylhexyl ester (PC-88A) in kerosene. Liquid–liquid experiments were conducted as a function of aqueous pH (1–6) to establish optimum conditions for both extraction and stripping of the metal. A mass-transfer model was developed to predict the extent of Zn(II) permeation through the supported liquid membrane (SLM) under different experimental conditions. The effect of stirring rate, carrier concentration and temperature upon metal transport has been evaluated. The metal flux has been derived taking into account stagnant layer aqueous diffusion and liquid membrane diffusion as controlling factors. The overall transport evaluated from the proposed resistances model was in reasonable agreement with those obtained from experimental data. Under the studied experimental conditions the resistance of the intrinsic organic phase is masked by the aqueous stagnant layer resistance; therefore the Zn (II) transport through the liquid membrane is mainly controlled by the hydrodynamic of the system.

Keywords: Supported liquid membrane; Zinc coupled transport; PC-88A; Mechanism

1. Introduction

The clean-up of sites where nuclear materials were used and the treatment of waste accumulation require the development of cost-effective

and efficient technologies. Liquid membrane technology has attracted increasing attention for its potential capability in the field of separation and has been demonstrated as an effective tool in many applications, such as resource recovery, pollutant removal and bioseparation [1–5]. This technology is particularly attractive when very dilute solutions are involved since the ratio between receiving phase and source phase can be drastically reduced.

*Fellow at the Instituto de Investigación en Catálisis y Petroquímica (FIQ, UNL, CONICET), Santa Fe, Argentina.

**Corresponding author.

The zinc ion is one of the most useful of all the metals in different industries as it is always present in polluted waters, sewage and industrial waste [6]. The extraction of Zn has been widely studied with different extractants. The use of organophosphorous compound in the liquid–liquid extraction of transition metals has been steadily increasing because of their excellent selectivity nature in forming complexes under different conditions. Typical extractants are di(2-ethylhexyl)-phosphonic acid (D2EHPA) [5,7–9] and bis (2,4,4-trimethylpentyl)-phosphinic acid (Cyanex 272) [10]. The extraction mechanism has been analyzed but relatively few studies with phosphonic acid monoester (PC-88A) have been reported [11]. PC-88A has a very similar chemical structure to D2EHPA but it was found that the first in n-heptane diluent is somewhat superior to D2EHPA with respect to separation of copper and zinc [12]. Furthermore, the transport and separation of Zn has been accomplished through different membrane configurations and different systems, the literature on this subject is numerous and only a few selected articles are referred here [13–19]. However, the elucidation of mass transfer mechanism for metal permeation through the liquid membrane with different commercial carriers is one of the important topics with lack of sufficient data.

In the present paper a model is proposed for the coupled co-transport across a supported liquid membrane (SLM) containing 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (denoted with the commercial name: PC-88A) as carrier. Furthermore, the possible rate-controlling step during the permeation process was estimated by studying resistances of aqueous film diffusion and complex diffusion through the SLM. Experimental conditions, i.e., stirring rate, carrier concentration, pH of the aqueous phases and temperature were systematically varied to determine their influence on the Zn (II) permeability and optimize the metal transport through the SLM.

2. Experimental

2.1. Materials and solutions physical properties

The carrier agent used was PC-88A, (Henkel Corp.), and the organic solvent was Kerosene JP1 grade (relative density: 825 kg m⁻³, viscosity: 0.15 kg m⁻¹s⁻¹, boiling point: 525–573 K) used without further purification.

The support was a microporous Teflon film, Goretex® S10187 of thickness $l = 44 \times 10^{-6}$ m with a nominal porosity (ϵ) of 87% and a tortuosity (τ) of 1.4. Filling the pores of this polymeric support with the carrier-kerosene solution was accomplished by immersing the membrane in the organic phase for at least 2 h before use, and then gently blotting it for few seconds with filter paper. The membrane serves both as a support for the organic phase, and as uniform barrier between two aqueous phases. This results in two aqueous–organic interfaces with well-defined transfer areas. All aqueous solutions were prepared with chemically pure Zn(II) (Merck, patron solution) HCl, CH₃COONa and distilled water saturated with kerosene.

Physical properties of both aqueous and organic solutions as a function of temperature are given in Table 1.

2.2. Liquid–liquid partition measurements

The carrier PC-88A (denoted as HX), is known to dimerize in nonpolar aliphatic solvents [11]. Various authors have reported the formation of different Zn(II) species with organic compounds such as Zn X₂, Zn X₂(HX) and Zn X₂(HX)₂, especially the latter. We assume that the chemical reaction at the interface is governed by the equilibrium:

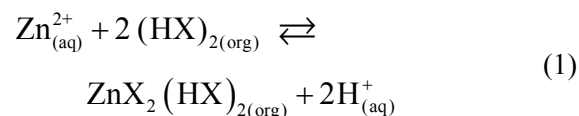


Table 1
Physical properties of the aqueous and organic solution as a function of temperature ($C^{\circ}_{\text{HX}} = 1.2 \text{ mol/dm}^3$)

T (K)	Aqueous phase		Organic phase	
	ρ (g/cm ³)	$\mu \times 10^2$ (g/cm s)	ρ (g/cm ³)	ρ (g/cm s)
289	0.998	1.08	0.857	0.067
298	0.997	0.88	0.852	0.043
305	0.995	0.78	0.848	0.04
314	0.992	0.644	0.836	0.035
328	0.985	0.506	0.825	0.031

The interfacial exchange equilibrium constant, K , can be represented by:

$$K = \frac{[\text{ZnX}_2 \cdot (\text{HX})_2][\text{H}^+]^2}{[\text{Zn}^{2+}][(\text{HX})_2]^2} \quad (2)$$

To evaluate the equilibrium constant (K) at different temperature, liquid–liquid extraction experiments were carried out. Equal volumes (0.01 dm³) of the two phases were equilibrated in separatory funnels at 298, 314 and 330 K. The organic phase consist of PC-88A 0.2M in kerosene. The aqueous phase was an aqueous solution of Zn(II) 0.1 g/dm³ at different pH values between 2–6, higher pH value may cause the ion to precipitate as Zn hydroxide. The Zn and proton concentrations were determined after and before the extraction by atomic absorption Varian Spectr AA-50 spectrophotometer and a Metrohm-Herisau pH meter, respectively. The results of Zn liquid–liquid extraction percentage (% E) at different temperatures as a function of pH are shown in Fig. 1, where

$$\%E = \frac{[\text{Zn}]_{\text{org}}}{[\text{Zn}]_{\text{org}} + [\text{Zn}]_{\text{aq}}} \times 100 \quad (3)$$

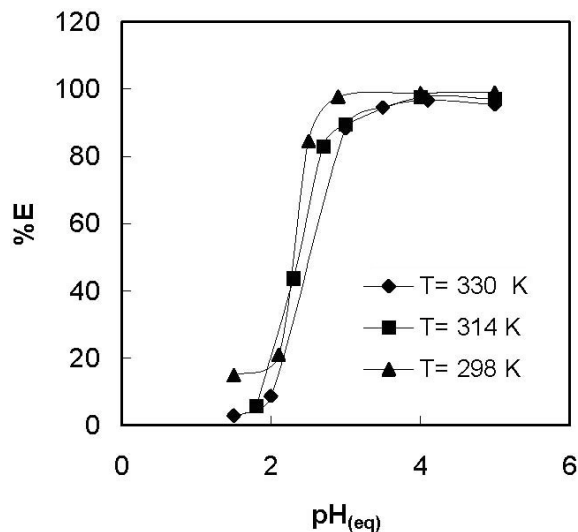


Fig. 1. Extraction of Zn(II) with PC-88A as a function of equilibrium pH at different temperatures.

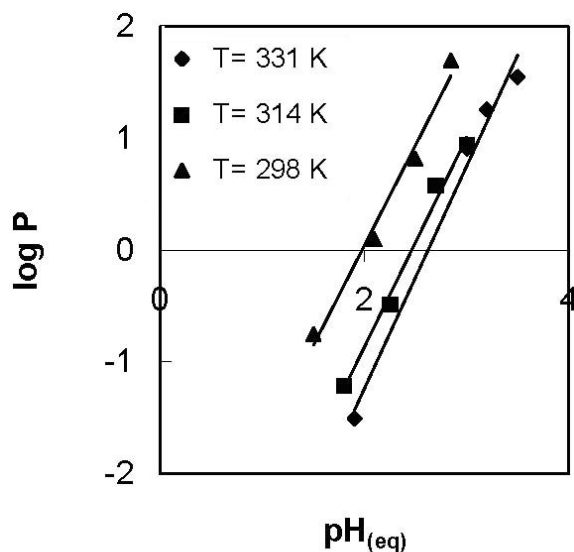
Fig. 1 shows that when the pH of the aqueous solution is between 4–5 high metal loading in the organic phase will be promoted and conversely, at pH lower than 2, metal complex will be dissociated.

Taking the logarithm in Eq. (2) and rearranging with $C^{\circ}_{\text{HX}} \approx [\text{HX}]$, we obtain:

$$\log \frac{[\text{ZnX}_2 \cdot (\text{HX})_2]}{[\text{Zn}^{2+}]} = \log P = \log K + 2 \log C^{\circ}_{\text{HX}} + 2 \text{pH} \quad (4)$$

Experimental values of distribution coefficient (P) as a function of pH according Eq. (4) are plotted in Fig. 2. The slope values are nearly equal to 2, validating the extraction reaction proposed in Eq. (1). The calculated K values at different temperatures can be represented by:

$$\ln K = 13663 \frac{1}{T} - 50.343 \quad (5)$$



$$\log P_{331\text{K}} = 1.981 \text{ pH} - 5.203$$

$$\log P_{314\text{K}} = 1.879 \text{ pH} - 4.627$$

$$\log P_{298\text{K}} = 1.784 \text{ pH} - 3.253$$

Fig. 2. Distribution coefficient of Zn(II) as a function of equilibrium pH at different temperatures.

2.3. Transport measurements

The experimental transport measurement were carried out with a stirred cell described elsewhere [3]. The membrane cell consists of two half-cells, both provided with proper inlets and outlets for feed and stripping solutions, being thus possible to operate the system in a continuous flow way. The supported liquid membrane was clamped between both half-cells resulting in a cross section area of $1.37 \times 10^{-4} \text{ m}^2$. The feed and stripping solutions were fed by a peristaltic pump with a volumetric flow rate of $(8.16 \pm 0.5) \times 10^{-6} \text{ dm}^3/\text{s}$. The cell has a jacket for circulation of water to assure a constant temperature during the experiments. Both compartments were stirred with magnetic bars, which are driven by synchronous motors. The tests were carried out over periods of time of 4–5 h. During the runs no substantial

change in the SLM behavior because of breakdown, fouling or liquid depletion was noticed.

The metal flux, N_{Zn} , in steady state is calculated experimentally using:

$$N_{\text{Zn}} = \frac{F_{v2}}{A} ([\text{Zn}]_0 - [\text{Zn}]_1)_2 \quad (2)$$

where F_{v2} is the volumetric flow of the stripping solution; $[\text{Zn}]_{12}$, $[\text{Zn}]_{02}$ the average metal concentration in the inlet and outlet respectively of stripping solution at steady state. The mass balance closed within an error of $\pm 10\%$.

A systematic analysis of experimental parameters as performed such as stirring rate of aqueous solution, carrier concentration and system temperature. Following the results obtained in the liquid–liquid partition experiments, a pH 4 for feed solution and pH 1.8 for the stripping solution were used. The experimental conditions of all permeation analysis and results are showed in Table 2.

3. Modelling of zinc transport

The ion transport through the supported liquid membrane system is considered to be composed of many elementary steps [20,21] i.e., in the case of the system considered: (1) diffusion of zinc through the aqueous stagnant layer of feed solution; (2) diffusion of the extractant and the metal–carrier complex in the organic membrane phase; (3) diffusion of zinc through the aqueous stagnant layer solution of the stripping solution. The resistance of other steps such as interfacial reactions of complexation and diffusion of H^+ in both aqueous stagnant layers has been neglected. Fig. 3 shows the linear concentration gradient profiles across the SLM and the stagnant layer in the aqueous phase. The experiments demonstrated that the transport of Zn(II) is coupled by the counter-flow of H^+ , has been found with a similar system [19].

Table 2
Overview of the permeation experiments results

Stirring rate effect $C_{\text{HX}}^{\circ} = 1.2 \text{ (mol/dm}^3\text{)}$ $T = 298 \pm 1 \text{ K}$			Carrier concentration effect Stirring rate = $100 \pm 2 \text{ rpm}$ $T = 298 \pm 1 \text{ K}$				Temperature effect $C_{\text{HX}}^{\circ} = 1.2 \text{ (mol/dm}^3\text{)}$ Stirring rate = $110 \pm 2 \text{ rpm}$		
rpm (min^{-1})	$[\text{Zn}^{2+}]_{\text{O1}}$ $\times 10^3$ (mol/dm^3)	N_{Zn} $\times 10^9$ ($\text{mol/cm}^2 \text{ s}$)	C_{HX}° (mol/dm^3)	μ (g/cm s)	$[\text{Zn}^{2+}]_{\text{O1}}$ $\times 10^3$ (mol/dm^3)	N_{Zn} $\times 10^9$ ($\text{mol/cm}^2 \text{ s}$)	T (K)	$[\text{Zn}^{2+}]_{\text{O1}}$ $\times 10^3$ (mol/dm^3)	N_{Zn} $\times 10^9$ ($\text{mol/cm}^2 \text{ s}$)
0	1.596	0	0	0.013	1.710	0	289	1.201	1.79
25	1.514	0.62	0.2	0.014	1.427	1.56	298	1.213	2.06
50	1.324	1.13	0.8	0.034	1.451	1.71	305	1.185	2.22
110	1.324	2.07	1.2	0.043	1.447	1.92	314	1.133	2.50
230	0.842	2.37	2	0.055	1.444	1.80	328	1.127	2.54
335	0.797	2.46	3 (pure)	0.282	1.466	1.68			

$[\text{Zn}^{2+}]_{\text{I1}} = 0.1 \pm 0.015 \text{ g/dm}^3$ at pH 4; $[\text{Zn}^{2+}]_{\text{I2}} = 0$, distilled water buffered at pH 1.8.
 $F_{\text{v1}} \approx F_{\text{v2}} \approx 8.16 \pm 0.5 \times 10^{-6} \text{ dm}^3/\text{s}$.

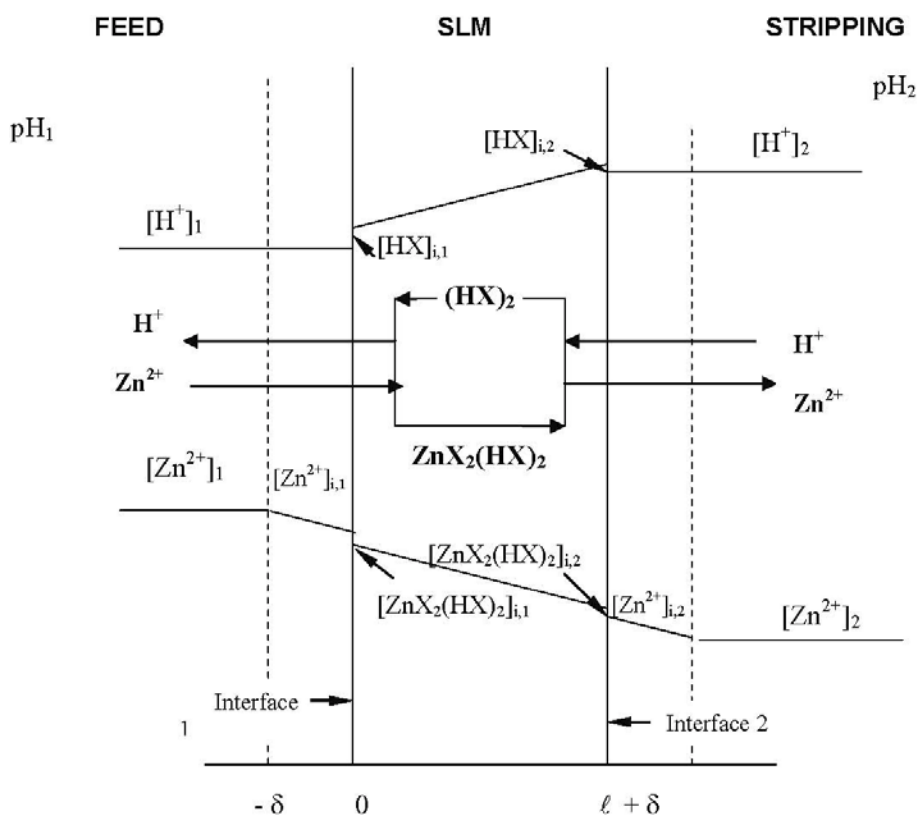


Fig. 3. Schematic representation of Zn(II) coupled transport through the SLM.

In this mathematical description the following assumptions were made:

- The transport process through the aqueous and organic phases stagnant layer is governed by Fick's law.
- The carrier and metal complex diffusivities in the SLM are approximately equal.
- The complexation and stripping reactions between the metal ions and the extractants do not show chemical limitations, so equilibrium is considered established everywhere within the membrane.
- Due to low fractional saturation of the carrier species, the concentration of the metal complex is much lower than the concentration of the free reagent HX; thus it is valid that $C_{\text{HX}}^o \approx [(\text{HX})_2]$.

At steady state the metal molar flux, N_{Zn} , across the SLM system for each step is expressed as follows:

- Step 1: Zn ion diffusion through the stagnant layer of feed solution:

$$N_{\text{Zn}} = \frac{D_{\text{Zn}}}{\delta} ([\text{Zn}^{2+}]_1 - [\text{Zn}^{2+}]_{i,1}) \quad (7)$$

$$= ka ([\text{Zn}^{2+}]_1 - [\text{Zn}^{2+}]_{i,1})$$

- Step 2: The metal complex diffusion through the supported liquid membrane is given by:

$$N_{\text{Zn}} = \frac{D_{\text{ZnX}_2} \varepsilon}{\ell \tau} K C_{\text{HX}}^{o2} \Delta \left(\frac{[\text{Zn}^{2+}]}{[\text{H}^+]^2} \right)_i \quad (8)$$

- Step 3: Metal ion diffusion through the stagnant layer of the stripping solution:

$$N_{\text{Zn}} = \frac{D_{\text{Zn}}}{\delta} ([\text{Zn}^{2+}]_{i,2} - [\text{Zn}^{2+}]_2) \quad (9)$$

$$= ka ([\text{Zn}^{2+}]_{i,2} - [\text{Zn}^{2+}]_2)$$

where D_{Zn} is the diffusion coefficient of Zn(II) ion in the aqueous phase, D_{ZnX_2} the diffusion coefficient of Zn complex in the organic phase, ka is the mass transfer coefficient and δ the stagnant aqueous layer thickness. The subscripts 1 and 2 indicate conditions in the bulk aqueous feed and stripping solutions respectively and the subscript i refers to interfaces.

By repeated substitution and rearrangement of Eqs. (2), (7), (8) and (9), the transport rate of the metal ion is given by

$$N_{\text{Zn}} = \left(\frac{Ro}{\left([\text{H}^+]_1^{-2} + [\text{H}^+]_2^{-2} \right) K C_{\text{HX}}^{o2}} + Ra \right)^{-1} \quad (10)$$

$$\left(\frac{1}{[\text{H}^+]_1^2} + \frac{1}{[\text{H}^+]_2^2} \right)^{-1} \Delta \frac{[\text{Zn}^{2+}]}{[\text{H}^+]^2}$$

with

$$\Delta \left(\frac{[\text{Zn}^{2+}]}{[\text{H}^+]^2} \right) = \left(\frac{[\text{Zn}^{2+}]}{[\text{H}^+]^2} \right)_1 - \left(\frac{[\text{Zn}^{2+}]}{[\text{H}^+]^2} \right)_2 \quad (11)$$

Eq. (10) allows to evaluate the metal flux through the membrane; knowing K , the stagnant layer resistance $Ra = 1/ka$, and the intrinsic resistance of the organic phase Ro is given by:

$$Ro = \frac{\ell \tau}{D_{\text{ZnX}_2} \varepsilon} \quad (12)$$

The term $\Delta[\text{Zn}^{2+}]/[\text{H}^+]^2$ of Eq. (10) represents the driving force of the transport process. The difference of the ratio $[\text{Zn}^{2+}]/[\text{H}^+]^2$ across the membrane dictates the magnitude and direction of metal flux.

In accordance with our experimental conditions, $[\text{Zn}^{2+}]_1 > [\text{Zn}^{2+}]_2$ and $[\text{H}^+]_2 \gg [\text{H}^+]_1$, so:

$$\left(\frac{1}{[\text{H}^+]_1^2} + \frac{1}{[\text{H}^+]_2^2} \right) \gg \frac{1}{[\text{H}^+]_1^2} \quad \text{and}$$

$$\Delta \left(\frac{[\text{Zn}^{2+}]}{[\text{H}^+]^2} \right) \approx \left(\frac{[\text{Zn}^{2+}]}{[\text{H}^+]^2} \right)_1 \quad (13)$$

From Eqs. (10) and (13) the overall transfer resistance R_T , can be written as:

$$R_T \approx \frac{[\text{Zn}^{2+}]_1}{N_{\text{Zn}}} = Ro' + Ra \quad (14)$$

with the apparent organic resistance, Ro' , given by

$$Ro' = \frac{Ro [\text{H}^+]_1^2}{KC_{\text{HX}}^{\circ 2}} = \frac{\ell \tau}{D_{\text{ZnX}_2} \varepsilon KC_{\text{HX}}^{\circ 2}} [\text{H}^+]_1^2 \quad (15)$$

4. Analysis and discussion of Zn(II) coupled transport

4.1. Stirring rate effect

Several runs were accomplished varying the stirring rate of both aqueous compartment to analyze the effect of hydrodynamic of the system on Zn transport and the experimental conditions; results are given in Table 2. The mass transfer coefficient in the boundary layer as a function of both the geometry and hydrodynamics of the system can be interpreted by means of the following non-dimensional correlation:

$$Sh = \alpha Sc^\beta Re_\gamma \quad (16)$$

where Sh is the Sherwood number defined as (dka/D_{Zn}) , with d the impeller diameter ($d = 2$ cm); Sc is the Schmidt number defined as

(ν/D_{Zn}) where ν is the kinematics viscosity; Re is the Reynolds number defined as $(d^2 \Omega/\nu)$ where Ω is the impeller angular velocity. For laminar flow ($Re \leq 2 \times 10^4$), the following relation can be used:

$$ka = 0.081 \left(\frac{D_{\text{Zn}}}{d} \right) \left(\frac{\nu}{D_{\text{Zn}}} \right)^{0.33} \left(\frac{d^2}{\nu} \right)^{0.76} \Omega^{0.76} \quad (17)$$

The values of the coefficients $\alpha = 0.081$, $\beta = 0.33$, and $\gamma = 0.76$ were taken from Marchese et al. [22] which interpreted adequately the cell-stirrer geometry of this study.

The diffusion coefficients were calculated from Stoke-Einstein equation as:

$$D_i = \frac{k_B T}{6 \pi r_i \mu} \quad (18)$$

with k_B the Boltzmann constant and r_i the radius of the species i ($r_{\text{Zn}} = 0.74 \times 10^{-10}$ m).

Introducing the experimental parameter values and diffusivities obtained from Eq.(18) into Eqs. (15) and (17) the overall resistance for Zn transport can be predicted by:

$$R_T = Ro' + Ra = 2.416 \times 10^{-3} + 1283.6 \Omega^{-0.76} \quad (19)$$

Fig. 4 represents the results and the good correlation between the experimental values of R_T [Eq. (14)] and the theoretical line obtained from Eq. (19). The apparent organic resistance (Ro') is practically negligible in comparison with the aqueous layer resistance (Ra), masking from this way the intrinsic resistance of the organic phase (Ro).

4.2. Carrier concentration effect

A series of permeation experiments at 100 rpm were performed to investigate the influence of carrier concentration (C_{HX}°), in the organic phase.

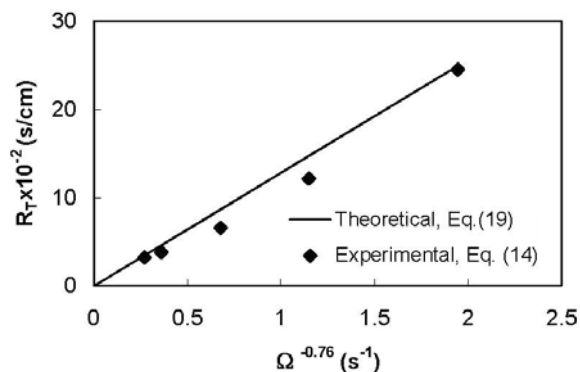


Fig. 4. Overall transfer resistance as a function of stirring rate ($C_{\text{HX}}^{\circ} = 1.2 \text{ mol/dm}^3$, $T = 298 \pm 0.5 \text{ K}$).

The experimental conditions and transport results are given in Table 2. Introducing the constant parameter values and the diffusion coefficient from Eq. (18) with $r_{\text{ZnX}_2} = 7.95 \times 10^{-10} \text{ m}$ into Eqs. (15) and (17), the following expression of R_T as a function of C_{HX}° is obtained:

$$R_T = \frac{3.061 \times 10^{-9}}{C_{\text{HX}}^{\circ} D_{\text{ZnX}_2}} + 856.86 \quad (20)$$

Fig. 5 shows the effect of carrier concentration on Zn(II) transport calculated from the theoretical assumption [Eq. (20)] and experimental results [Eq. (14)]. The values obtained indicate that the carrier concentration has no effect on the Zn transport. The results confirm that in this operating conditions the apparent organic resistance is negligible compared with the aqueous layer resistance.

4.3. Temperature effect

Experiments were oriented towards determining the temperature effect on Zn transport. The results of fluxes at different temperatures are shown in Table 2.

The temperature affects the viscosities of both aqueous and organic solutions, which in terms

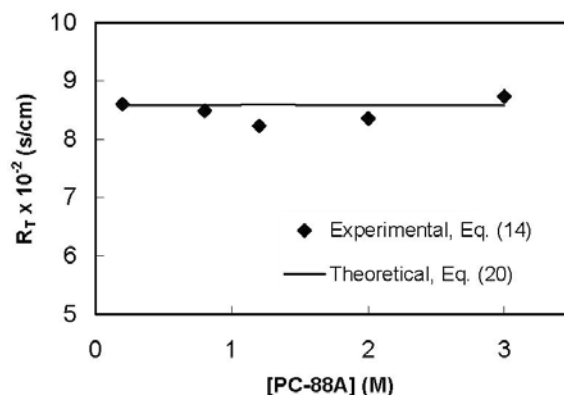


Fig. 5. Overall transfer resistance as a function of carrier concentration (stirring rate = $100 \pm 5 \text{ rpm}$, $T = 298 \text{ K} \pm 0.5 \text{ K}$).

affect the diffusion coefficients. The dependence of the organic and aqueous solutions diffusivities with temperature is given by Eqs. (21) and (22). They were obtained by fitting the experimental values of viscosities as a function of temperature shown in Table 1 and from the Stoke–Einstein expression [Eq. (18)].

$$D_{\text{ZnX}_2} = 1.842 \times 10^{-20} T^{5.44} \quad (21)$$

$$D_{\text{Zn}} = 3.298 \times 10^{-23} T^{7.28} \quad (22)$$

Considering that the aqueous solution density (ρ) is practically unaffected by the temperature, and introducing Eqs. (5), (21) and (22) into Eqs. (15) and (17), the following correlation between the overall resistance and the temperature is obtained:

$$R_T = 1.172 \times 10^{31} e^{-13663/T} T^{-5.44} + 2.481 \times 10^{22} T^{-7.58} \quad (23)$$

For the experimental temperature range of this study, the term of apparent organic resistance is much lower than the aqueous layer resistance

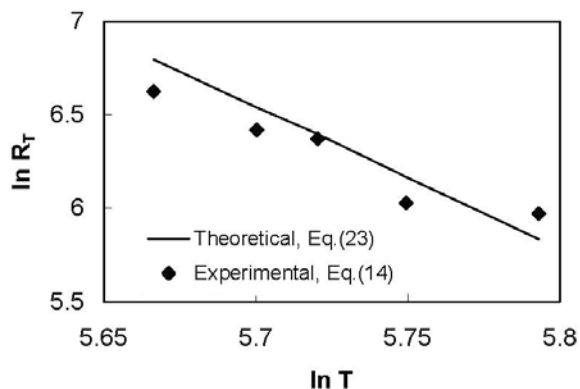


Fig. 6. Overall transfer resistance as a function of temperature ($C_{\text{HX}}^{\circ} = 1.2 \text{ mol/dm}^3$, stirring rate = $110 \pm 5 \text{ rpm}$).

($Ro' \ll Ra$) so it can be neglected from Eq. (23). Fig. 6 shows good agreement between experimental results calculated from Eq. (14) and the theoretical correlation given by Eq. (23) as a logarithmic form.

5. Conclusions

Transport of zinc(II) from aqueous solutions through SLM containing PC-88A in kerosene was investigated. The results obtained in this study provide important information about the adequate experimental conditions for Zn(II) transport through a SLM. The experimental results indicate that the highest Zn(II) extraction occurs when the pH of the feed and stripping solutions are adjusted to a value of 4 and 2 respectively. The interfacial chemical reactions between Zn(II) and PC-88A extractant [Eq. (1)] was corroborated by liquid–liquid extraction experiments. From these experiments an expression was obtained, which gives the temperature dependence of the equilibrium constant.

The effect of carrier concentration, stirring rate and temperature on Zn(II) transport through the SLM was analyzed. It was found that increasing the impeller rotation and the system temperature produces an increase on metal transport,

whereas the carrier concentration effect was negligible.

A mass transfer model to predict the extent of Zn(II) permeation through the SLM was proposed. From this, a general expression of Zn permeation rate taking into account aqueous stagnant layer and organic resistances as controlling factors was derived. The evaluated resistances were in reasonable agreement with the overall resistance evaluated from experimental data. It was shown that for the studied operating conditions aqueous stagnant layer resistances mainly controlled the Zn(II) transport using PC-88A in high concentrations, a similar behavior was found for special conditions of Zn(II)-D2EHPA transport ($[\text{Zn}] \leq 1.74 \times 10^{-3} \text{ M}$, $[\text{H}^+] \leq 1.6 \times 10^{-3}$ and $[(\text{RX})_2] \leq 2.66 \times 10^{-2} \text{ M}$) [21].

6. Symbols

A	—	Membrane cross transfer area, cm^2
C_{HX}°	—	Initial concentration of the carrier, mol/dm^3
d	—	Impeller diameter, cm
D_{Zn}	—	Diffusion coefficient of the Zn(II) ion in the aqueous phase, cm^2/s
D_{ZnX_2}	—	Diffusion coefficient of metal complex in the organic phase, cm^2/s
D_{ZnX_2}'	—	Effective diffusion coefficient of metal complex in the organic phase, cm^2/s
$\%E$	—	Liquid–liquid extraction percentage
F_{v2}	—	Volumetric flow, cm^3/s
K	—	Equilibrium constant, Eq. (2)
ka	—	Mass transfer coefficient, cm/s
k_B	—	Boltzmann constant
ℓ	—	Membrane thickness, cm
N_{Zn}	—	Metal flux, $\text{mol/cm}^2 \text{ s}$
P	—	Distribution coefficient
Ra	—	Aqueous resistance, s/cm
Re	—	Reynolds number
Ro	—	Organic resistance, s/cm
Ro'	—	Apparent organic resistance

R_T	— Overall resistance, s/cm
r_{Zn}	— Ionic radius of Zn^{2+} , cm
r_{ZnX2}	— Zn complex radius, cm
Sc	— Schmidt number
Sh	— Sherwood number

Greek

α	— Dimensionless coefficient, Eq. (17)
β	— Dimensionless coefficient, Eq. (17)
δ	— Stagnant layer thickness
ε	— Support porosity
γ	— Dimensionless coefficient, Eq (17)
μ	— Viscosity, g/s cm
ρ	— Density, g/cm ³
τ	— Support tortuosity
ν	— Kinematics viscosity, cm ² /s
Ω	— Impeller angular velocity, rev/s

References

- [1] N.S. Rathore, J.V. Sonawane, A. Kumar, A.K. Venugopalan, R.K. Singh, D.D. Bajpai and J.P. Shulka, Hollow fiber supported liquid membrane: a novel technique for separation and recovery of plutonium from aqueous acidic wastes, *J. Membr. Sci.*, 189 (2001) 119–128.
- [2] M. Teramoto, S.S. Fu, K. Takatani, N. Ohnishi, T. Maki, T. Fukui and K. Arai, Treatment of simulated low level radioactive wastewater by supported liquid membranes: uphill transport of Ce(III) using CMPO as carrier, *Sep. Pur. Technol.*, 18 (2000) 57–69.
- [3] M.E. Campderrós and J. Marchese, Facilitated transport of niobium(V) and tantalum(V) with supported liquid membrane using TBP as carrier, *J. Membr. Sci.*, 164 (2000) 205–210.
- [4] N.M. Kocherginsky and A.B. Grishchenko, Mass transfer of long chain fatty acids through liquid–liquid interface stabilized by porous membrane, *Sep. Pur. Technol.*, 20 (2000) 197–208.
- [5] J. Macanás, D. Oleinikova, M. Muraviev and M. Muñoz, Separation of zinc and bismuth by facilitated transport through activated composite membranes, *Solvent Extr. Ion Exch.*, 24 (2006) 565–587.
- [6] L. Boyadzhiev and Z. Lazarova, Liquid membranes (liquid pertraction), in: *Membrane Separations Technology, Principles and Applications*, R.D. Noble and S.A. Stern, eds., Elsevier, New York, 1995, pp. 321–322, and references therein.
- [7] L.A. Ajawin, E.S. Pérez de Ortiz and H. Sawistowski, Kinetic of extraction of zinc by di(2-ethylhexyl)phosphoric acid in n-heptane. *Proc. Internat. Solvent Extraction Conf.*, 3 (1980) 80–112.
- [8] I. Ortiz Uribe, S. Wongswan and E.S. Pérez de Ortiz, A systematic method for the study of the rate-controlling mechanisms in liquid membrane permeation processes. Extraction of zinc by bis(2-ethylhexyl)phosphoric acid. *Ind. Eng. Chem. Res.*, 27 (1988) 1696–1701.
- [9] D.B. Dreisinger and W.C. Cooper, The kinetic of zinc, cobalt and nickel extraction in the D2EHPA-heptane-HClO₄ system using the rotating diffusion cell technique, *Solv. Extn. Ion Exch.*, 7 (1989) 335–339.
- [10] S.B. Kanungo and R. Mohapatra, Coupled transport of Zn(II) through a supported liquid membrane containing bis (2,4,4-trimethylpentyl) phosphinic acid in kerosene. II Experimental evaluation of model equations for rate process under different limiting conditions, *J. Membr. Sci.*, 105 (1995) 227–235.
- [11] Y. Sato, K. Kondo and F. Nakashio, Extraction kinetic of zinc with 2-ethylhexyl phosphonic acid mono-2ethylhexyl ester using a hollow-fiber membrane extractor, *J. Chem. Eng. Japan*, 22 (1989) 686–689.
- [12] F. Nakashio, K. Kondo, A. Murakami and Y. Akiyoshi, Extraction equilibrium of copper and zinc with alkylphosphonic acid monoester, *J. Chem. Eng. Japan*, 15 (1982) 274–279.
- [13] P.R. Danesi, R. Chiarizia and A. Castagnola, Transfer rate and separation of Cd(II) and Zn (II) chloride species by a triaurylammonium chloride-triethylbenzene supported liquid membrane, *J. Membr. Sci.*, 14 (1983) 161–174.
- [14] M. Goto, H. Yamamoto, K. Kondo and F. Nakashio, Effect of new surfactants on zinc extraction with liquid surfactant membranes, *J. Membr. Sci.*, 57 (1991) 161–174.
- [15] W. Mickler, A. Reich, E. Uhlemann and H.J. Bart, Liquid membrane permeation of zinc, cadmium and

- nickel with 4-acyl-5-pyrazolones and β -diketones, *J. Membr. Sci.*, 511 (1996) 91–97.
- [16] C. Corsi, G. Cnagnarelli, M.J. Slater and F. Veglio, A study of the kinetics of zinc stripping for the system $\text{Zn}/\text{H}_2\text{SO}_4/\text{D2EHPA}/\text{n-heptane}$ in a Hancil constant interface cell and a rotating disc contactor, *Hydrometallurgy*, 50 (1998) 125–141.
- [17] A.R. Fakhari, A.R. Khorrami and M. Shamsipur, Selective uphill Zn^{2+} transport via bulk liquid membrane using an azacrown ether carrier, *Sep Purif. Technol.*, 50 (2006) 77–81.
- [18] Y. Yulizar, A. Ohashi, H. Nagatani and H. Watarai, Kinetic study of $\text{Ni}(\text{II})$ and $\text{Zn}(\text{II})$ complexation with a pyridylazo extractant by a centrifugal liquid membrane method, *Anal. Chim. Acta*, 419 (2000) 107–114.
- [19] D. He, X. Luo, C. Yang, M. Ma and Y. Wan, Study of transport and separation of $\text{Zn}(\text{II})$ by a combined supported liquid membrane/strip dispersion process containing D2EHPA in kerosene as the carrier, *Desalination*, 194 (2006) 40–51.
- [20] J. Marchese, M.E. Campderrós and A. Acosta, Mechanistic study of cobalt, nickel and copper transfer across a supported liquid membrane, *J. Chem. Tech. Biotechnol.*, 57 (1993) 37–42.
- [21] T-C Huang and R-S Juang, Transport of zinc through a supported liquid membrane using di(2-ethyl-hexyl)phosphoric acid as a mobile carrier, *J. Membr. Sci.*, 31 (1987) 209–226.
- [22] J. Marchese and J. Quinn, Interfacial transfer kinetics studied with immobilized liquid membranes, *Lat. Am. J. Heat Mass Transf.*, 9 (1985) 167–183.