

Permeation study on the hollow-fiber supported liquid membrane for the extraction of Cobalt(II)

Ramakul Prakorn, Songkun Eakkapit, Pattawee Kongka Weerawat*, Hronec Milan** and Pancharoen Ura†

Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok, Thailand

*Department of Chemical Engineering, Faculty of Engineering and Industrial Technology of Silpakorn University, Sanam Chandra Campus, Nakhonphthom, Thailand

**Department of Organic Technology, Faculty of Chemical Technology, Slovak University of Technology, Bratislava, Slovak Republic

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Abstract—The transport of Co(II) through hollow-fiber-supported liquid membrane containing di-(2-ethylhexyl) phosphoric acid (D2EHPA) diluted in kerosene was examined. The mass transfer rate, expressed as permeability, P , focused on diffusion through the aqueous layer in the feed solution, the organic layer and the aqueous layer in the stripping solution. Experiments were performed as a function of aqueous feed solution velocity (100-500 ml/min), carrier concentration (0.1-20% v/v), aqueous stripping solution velocity (100-1,000 ml/min) and feed concentration (100-1,000 ppm) with 0.1 M HCl in the product phase. pH of the feed solution was 5.0. The measured permeabilities were compared to generally accepted mass transfer correlations. The validity of the prediction was evaluated with the experimental data, and the data were found to tie in well with the theoretical values. The model is the reported describing that the rate limiting step in the transport of the ion was the diffusion through both aqueous films, feed and stripping, whereas the organic resistance of the membrane was negligible. From this study, the model has good potential for the prediction of permeability of Co(II).

Key words: Cobalt, Hollow Fiber, Liquid Membrane, Modeling, Permeation

INTRODUCTION

The presence of metal ions in the environment is a major concern due to their toxicity to many life forms. For this reason, the separation of metal ions from solution is of great interest in hydro-metallurgical processes for recovering the metal values, as well as abating the environmental pollution problems. This separation can be achieved by liquid membrane systems that have been widely applied to the extraction and recovery of metal ions from solutions [Rathore, 2002; Campderros and Marchese, 2000]. A simultaneous extraction and stripping operation is very attractive because metal ions can move from low to high concentration solutions. The membranes contain an extractant or a carrier which possesses the potential for selective permeation by using the facilitated transport mechanism [Gherrou and Kerdjoudi, 2002; Porter, 1990]. This technique has been widely applied to the extraction and recovery of metal ions. One promising technique of liquid membrane is the use of micro-porous hollow fiber modules as liquid-liquid phase contactors. The basic principle of hollow fiber supported liquid membrane (HFSLM) is the immobilization of organic extractant into the pores of a hydrophobic membrane [Ramakul and Pancharoen, 2003; Sheng et al., 2004].

The potential advantages of HFSLMs over traditional separation techniques include lower capital and operating costs, low energy and low extractant consumption factors and high fluxes compared to solid membranes [Loiacono et al., 1986; Sheng et al., 2004]. Due

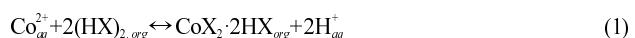
to these advantages, SLMs may be very useful for the recovery of metals from solutions.

In this study, we focused on the modeling of hollow fiber supported liquid membrane to recover cobalt ions. Knowledge of the rate determining step is of importance for designing or modeling the mass transfer process at large scale. The permeability of the ion was evaluated as a function of flow rate of both the feed and the stripping solution, as well as the extractant concentration. Mass transfer models have been used to describe the cobalt permeability through the supported liquid membrane.

THEORY

1. Liquid Membrane

The system consists of two aqueous phases, the feed solution (in the inner side of the fiber) and the stripping solution (on the outer side of the fiber). Both aqueous solutions are separated by the supported liquid membrane formed by the extractant denoted as (HX), and the organic diluent solution confined within the fiber pore via capillary action. This forms two aqueous-organic interfaces with well defined transfer areas. This system is represented in Fig. 1 and is referred to counter coupled transportation because the metal ion and the proton are transported simultaneously in opposite directions [Ramakul et al., 2004]. The reaction between the metal and the organic extractant is an ion-exchange reaction which can be described by an equation like the following [Drioli et al., 1989].



The extraction and stripping processes schematically illustrated in

†To whom correspondence should be addressed.

E-mail: ura.p@chula.ac.th

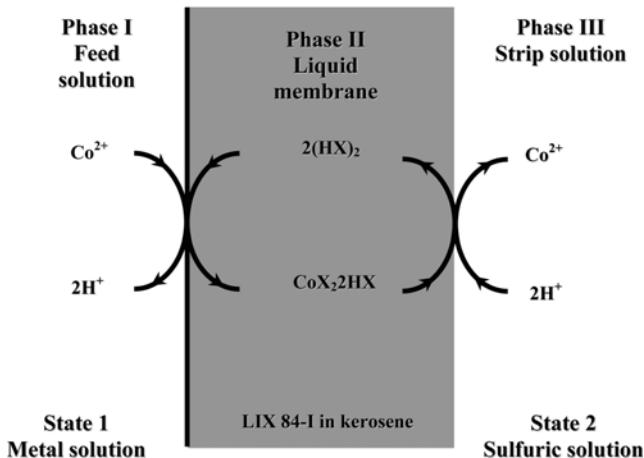


Fig. 1. Schematic representation of cobalt coupled transport with D2EHPA (HX).

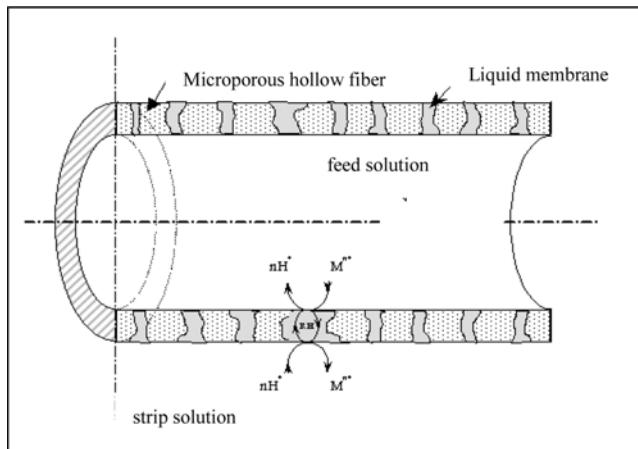


Fig. 2. Flow pattern in hollow fiber supported liquid membrane [Ramakul and Pancharoen, 2003].

Fig. 1 occurred in hollow fiber module as shown in Fig. 2 [Ramakul, 2002]. The inside of the hollow fiber module consists of a liquid membrane and two sides for aqueous solutions. The liquid membrane is trapped in hydrophobic micropore and this liquid membrane separates the feed and stripping solutions. The feed solution and the stripping solution flow countercurrently and the liquid membrane is between them.

2. Mass Transfer Modeling

The equilibrium constant, K_{eq} , can be represented by its logarithmic form:

$$K_{eq} = \frac{[\text{CoX}_2 \cdot 2\text{HX}_{org}][\text{H}^+]^2}{[\text{Co}_{org}^{2+}][(\text{HX})_{2,org}]^2} \quad (2)$$

The K_{eq} can be obtained by liquid-liquid extraction. The experimental data are shown in Fig. 3, from where the equilibrium constant is 9.0×10^{-6} and the value of the slope corroborates the proposed relationship [Eq. (1)].

A flux density equation was derived by Marchese [Marchese et al., 1993] for a flat-sheet supported liquid membrane. It can be used for the description of the permeability through hollow-fiber liquid membranes because the elementary steps are the same, except for

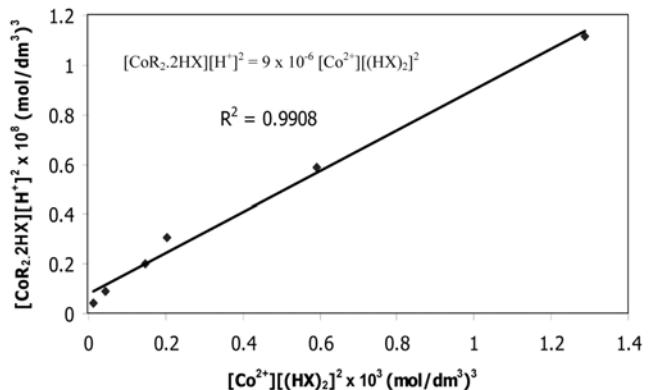


Fig. 3. Cobalt extraction with [D2EHPA] as a function of equilibrium $[\text{Co}^{2+}][(\text{HX})_2]^2$.

the correction of the cylindrical shape of the fibers. The mathematical model of a hollow fiber supported liquid membrane for the separation of cobalt using permeability coefficient depends on three of mass transfer resistances since the number of steps of transport mechanism is three. The model takes into consideration three resistances for transport:

One of them is the resistance when the liquid flowing through the hollow fiber lumen. The second resistance is the diffusion of the cerium complex across liquid membrane that immobilized in the porous wall of the fiber. The third resistance is due to the strip solution and organic interface at outside of fiber.

The resistance of other steps such as interfacial reactions of complexation and the diffusion of H^+ in both aqueous stagnant layers have been neglected. At low fractional saturation of the extractant species, the concentration of the free extractant (HX) is much higher than the concentration of the complexed extractant (CoX_2HX), valid that C_{HX}^0 (initial extractant concentration). In the mathematical description the transport process through the stagnant layer and organic phase is governed by Fick's law.

Equaling the different expression obtained for each step in steady state and adequate rearrangement, the overall permeability of cobalt P through the liquid membrane is given by [Marchese, 1993]:

$$P = \left[\frac{R_o}{([H^+]_1^2 + [H^+]_2^2)K_{eq}C_{0,HX}^2} + R_f + R_s \right]^{-1} \quad (3)$$

where R_f , R_o and R_s are the aqueous phase, organic phase and strip phase resistance, respectively, and they were defined as:

- organic phase resistance:

$$R_o = l_{ef}/D'_{\text{CoX}_2 \cdot 2\text{HX}} \quad (4)$$

- aqueous feed phase resistance:

$$R_f = 1/k_f \quad (5)$$

- aqueous stripping phase resistance:

$$R_s = 1/k_s \quad (6)$$

where l_{ef} is the effective thickness of the membrane, D'_{mem} the effective diffusion coefficient of the metal complex in the organic phase, k_f and k_s mass transfer coefficients of the feed and stripping phases, respectively. In accordance with our experimental conditions, the

proton concentration in both feed and stripping sides have been kept constant and $[H^+]_1 < [H^+]_2$, so the overall permeability of the metal can be written as:

$$P = \left[B + \frac{1}{k_f} + \frac{1}{k_s} \right]^{-1} \quad (7)$$

where

$$B = \left[\frac{l_{ef}}{D'_{CoX_2,2H^+} K_{eq} C_{0,H^+}^2 [H^+]_1^2} \right] \quad (8)$$

3. Evaluation of Effective Membrane Thickness, l_{ef}

The fiber geometry is known, but the membrane thickness has to be corrected for the spherical shape of the fiber by means of the inner and outer fiber diameter [Haan et al., 1989], as follows:

$$l_{ef} = r_i \ln \frac{r_o}{r_i} \quad (9)$$

where r_o is the radius of the fiber on the feed side and r_o and r_i refer to the outer and inner diameter of the fiber, respectively. The aqueous films are also spherically shaped, but this effect is already included in the mass transfer coefficient.

4. Evaluation of Effective Diffusion Coefficient in Liquid Membrane, (D'_{mem})

The effective diffusion coefficient through the supported membrane depends upon the diffusion coefficient of cobalt complex in the organic phase, D_{mem} , calculated by the Stokes-Einstein equation, as well as the tortuosity (τ) and the porosity (ε) of the support [Brembroek et al., 1998]

$$D'_{mem} = \frac{\varepsilon D_{mem}}{\tau} \quad (10)$$

5. Evaluation of the Mass Transfer Parameters

For the calculation of the permeability from Eq. (7), mass transfer rate parameters have to be known. These include the mass transfer through the aqueous film layer of the feed phase and the mass transfer through the aqueous film layer of the stripping phase. In this work the feed solution flowed inside the fibers and the stripping solution on the outer side of the fibers.

The flow through the hollow fibers, which is in the tube side, can be calculated to be always laminar. The following correlation is commonly used to describe the mass transfer coefficient (k_s) in the stripping solution [Bird, 2001; Brembroek, 1998]:

$$Sh = aGz' \quad (11)$$

$$\frac{k_s d_h}{D_{aq}} = a \left[\frac{d_h^2 \langle v_2 \rangle}{LD_{aq}} \right]^b \quad (12)$$

where Sh is the Sherwood number, Gz the Graetz number, d_h the hydraulic diameter defined as four times the cross-sectional flow area divided by the wetted perimeter, $\langle v_2 \rangle$ the mean liquid velocity in the outer side of the fibers and L their length, and D_{aq} the aqueous diffusion coefficient of the metal salt. For the feed solution, the mass transfer coefficient (k_f) is given by the equation.

$$\frac{k_f d_i}{D_{aq}} = m \left[\frac{d_i^2 \langle v_1 \rangle}{LD_{aq}} \right]^n \quad (13)$$

where $\langle v_1 \rangle$ is the mean liquid velocity inside the fibers.

Table 1. Property of hollow fiber module [Hoechst Celanese Corporation, 1995]

Properties	Description
Materials	Polypropylene
Inside diameter of hollow fiber	240 μm
Outside diameter of hollow fiber	300 μm
Size of pore	0.05 μm
Porosity	30%
Hydraulic diameter	488 μm
Surface area	1.4 m^2
Area per unit volume	29.3 cm^2/cm^3
Module diameters	6.3 cm
Module length	20.3 cm

EXPERIMENTAL

Di(2-ethyl hexyl) phosphoric acid (D2EHPA) from Fluka was used as the extractant. It is freely miscible with non-polar organic solvents in which it exists mainly as a dimer [Jakubec et al., 1986]. Kerosene was used as an organic solvent for its low solubility in water, high surface tension and low volatility, which makes the liquid membrane highly stable. The kerosene was JP1 grade used without further purification.

The aqueous feed solution was an aqueous solution of Co(II) as $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (Merck) at an ionic concentration of 100-1,000 ppm in distilled water buffered with acetic-acetate to keep the pH value near 5 where the extraction of cobalt ions is maximum. The stripping solution was distilled water buffered to an appropriate value (pH=1.0). Analytical grade reagents were used throughout. The hollow fiber membrane was microporous polytetrafluoroethylene fibers (Goretex, Japan). The support has excellent properties such as flexibility and high chemical and mechanical resistance. Some characteristics of the fibers are shown in Table 1.

The feed solution was made by dissolution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and pH was adjusted by HCl. The liquid membrane was made by dissolution of Di(2-ethyl hexyl) phosphoric acid (D2EHPA) in kerosene. The stripping solution was 0.1 M HCl and the organic solution containing D2EHPA was circulated in tube and shell side of the hollow fiber for 50 minutes. The experiment started by flowing the feed solution in the tube side. Simultaneously, stripping solution was pumped into the shell side countercurrently and one-through-mode operation was used. The flow diagram is shown in Fig. 5.

In this work, feed solution contains 100-1,000 ppm of cobalt(II) while the stripping solution containing 0.1 M HCl. A sample of 5 cm^3 was taken out at the end of each experiment from the feed and stripping tanks and the concentration of cobalt(II) ions was determined by Atomic Absorption Spectrophotometer (AAS).

1. Apparatus

- The Liqui-Cel® Laboratory Liquid/Liquid Extraction System which is composed of two gear pumps, two variable speed controllers, two rotameters and four pressure gauges was used.

- The Liqui-Cel® Extra-Flow module offered by CELGARD LLC (Charlotte, NC; formerly Hoechst Celanese), shown in Fig. 4, was used as a support material. This module uses Celgard® X-10 microporous polypropylene that are woven into fabric and wrapped

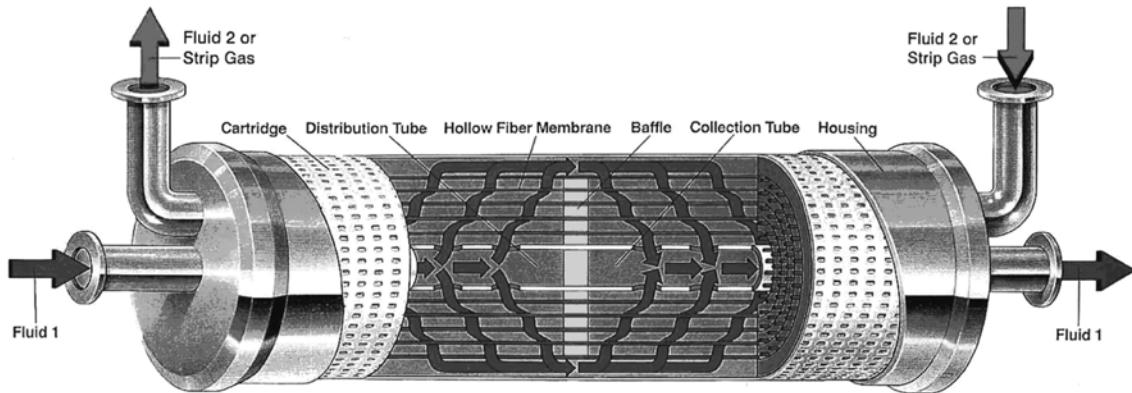


Fig. 4. The Liqui-Cel® Extra-Flow module.

around a central tube feeder that supplies the shell side fluid. Woven fabric allows more uniform fiber spacing, which in turn leads to higher mass transfer coefficients than those obtained with individual fibers. The property of hollow fiber module is shown in Table 1. The fiber is potted into a solvent-resistant polypropylene tube sheet and shell casing in polypropylene.

• Brookfield Viscometer model LV-DVII+ was used to measure the viscosity of the liquid membrane.

• Atomic Absorption Spectrophotometer, Model IL551, AA/AE Spectrophotometer Instrumentation Laboratory Inc. was used to measure the concentration of cobalt ions.

• pH was measured by pH-meter HI8418A.

2. Procedure

The organic phase was introduced by capillary action by filling the fiber lumen with organic solution and maintaining it for 1 h; then the organic phase was removed from the module by gravity. A stream of water removes the excess. Feed and stripping solutions are fed concurrently upwards by two peristaltic pumps (Masterflex) at various flow rates. The feed solution was circulated through the inner

side of the fiber and the stripping one on the outer side. The flow diagram is shown in Fig. 5. Acidity was measured with a Metrohm-Herisau pH-meter and a combined glass Ag/AgCl electrode. The permeation of cobalt was monitored by periodically sampling both effluent solutions at steady state and was analyzed after appropriate dilution by a Varian AA 50 atomic absorption spectrophotometer. The measurements were made in duplicate, and the difference between the two values was less than 5%.

The experimental tests were carried out for 40-60 minutes. During the runs no substantial change in the SLM behavior because of breakdown, fouling or liquid depletion was noticed. The experimental mass balance with the assumption of instantaneous strip reaction [Kumar et al., 2000] was calculated by:

$$F_1([Co]_{in,1} - [Co]_{out,1}) = F_2[Co]_{out,2} \quad (14)$$

where F_1 is the volumetric flow rate; $[Co]$ is cobalt ion concentration at steady state and the subscripts in, out, 1, 2 refer to inlet, outlet, feed and stripping, respectively.

RESULTS AND DISCUSSION

Permeation experiments were performed to investigate both the influence of extractant concentration in the HFM (hollow fiber membrane) and the flow rate of solutions upon cobalt permeability. All of the feed solutions were an aqueous solution of Co at pH=5 and the stripping solution was 0.1 M of HCl. These conditions were established from liquid-liquid extraction determination. The extractant concentration in the fiber was varied between 0.1-20% v/v. The feed velocity was varied between 3.61×10^{-3} and 1.8×10^{-2} m/s (Reynolds number, $Re=12.6-62.8$) with constant stripping velocity, and then the latter was varied in the range of 6.95×10^{-4} to 6.95×10^{-3} m/s ($Re=27.3-272.8$) with constant feed velocity. The experimental value of permeability, P_{ex} [Marchese et al., 1993] was defined as Eq. (15)

$$P_{ex} = \frac{F_2[Co]_{ex,2}}{A_m[Co]_{m,1}} \quad (15)$$

The average value of $[Co]_{m,1}$ was also given as:

$$[Co]_{m,1} = \frac{([Co]_{in,1} - [Co]_{out,1})}{\ln([Co]_{in,1}/[Co]_{out,1})} \quad (16)$$

Substituting Eq. (15) by Eq. (14) and (16), then

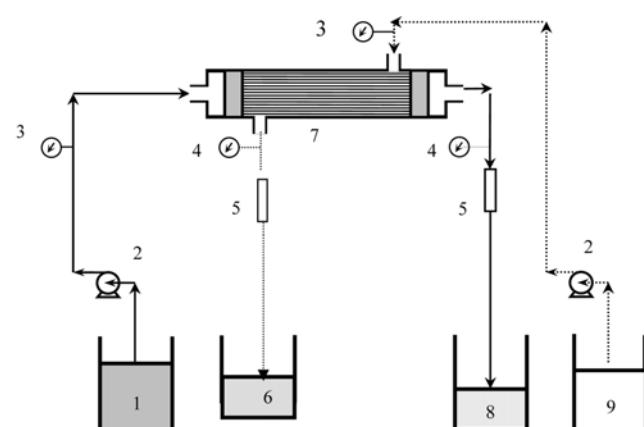


Fig. 5. Schematic counter-current flow diagram for one-through-mode operation in hollow fiber supported liquid membrane.

1. Feed reservoir	6. Stripping outlet reservoir
2. Gear pump	7. Hollow fiber module
3. Inlet pressure gauges	8. Raffinate reservoir
4. Outlet pressure gauges	9. Inlet stripping reservoir
5. Flow meters	

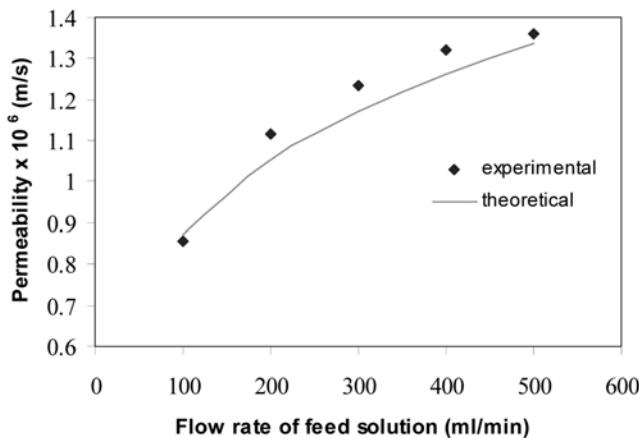


Fig. 6. Experimental permeability of cobalt ions as a function of flow rate of feed solution while the flow rate of stripping solution=100 ml/min, extractant concentration=20% v/v and feed concentration=1,000 ppm.

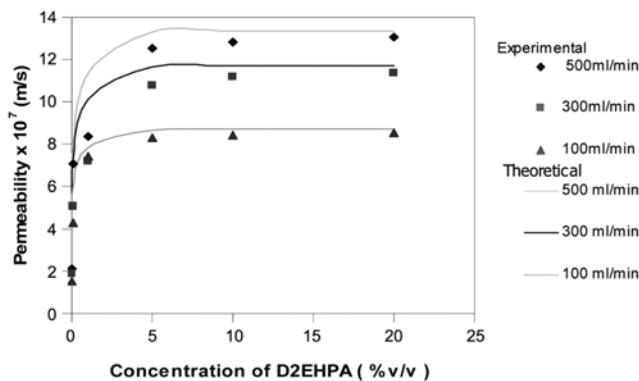


Fig. 7. Experimental permeability of cobalt ions as a function of extractant concentration and feed velocity while the flow rate of stripping solution=100 ml/min, flow rate of feed solution=100 ml/min and feed concentration=1,000 ppm.

$$P_{ex} = \frac{F_1 \ln([Co]_{in,0} - [Co]_{out,1})}{A_m} \quad (17)$$

where F_1 is the volumetric flow of the stripping solution and A_m is the mean surface of transfer area, $[Co]_{out,1}$ is the average cobalt ions concentration in the exit of the stripping solution and $[Co]_{in,1}$ the mean concentration of the cobalt ions in the feed. Cobalt permeation experiments and theoretical result are given in Fig. 6 and Fig. 7 as a function of flow rate of feed solution, respectively, with the flow rate of stripping solution was 100 ml/min, extractant and the feed concentration was 1,000 ppm.

The results show that the permeability is dependent on the feed flow rate but not on the extractant concentration when the concentration higher than 5% v/v. The transport rate is therefore limited through the aqueous film on the feed side of the membrane in this region. To calculate the permeability P from the model with Eq. (7), constant parameters are needed: $[H^+] = 1.00 \times 10^{-5}$ M, D_{aq} are 5.92×10^{-11} , 6.90×10^{-11} , 7.62×10^{-11} , 8.00×10^{-11} and 1.07×10^{-10} m²/s; when the concentration of feed is 1,000, 800, 500, 300 and 100 ppm, respectively. D_{mem} are 2.02×10^{-12} , 2.11×10^{-12} , 3.32×10^{-12} , 3.41×10^{-12} , 3.54×10^{-12} and 3.57×10^{-12} m²/s when the concentration of D2EHPA

are 20, 10, 5, 0.5 0.1% v/v respectively. The value of k_s can be obtained by calculation from Eq. (13), where m and n are well known the value of Leveque correlations [Leveque, 1928]: 1.62 and 0.33, respectively [Gabelman and Hwang, 1999]. This correlation was derived in analogy with the heat transfer correlation, and it is used to describe laminar flow through a tube.

To evaluate the parameters a and b for the mass transfer coefficient of stripping. The k_s experiments of Co(II) permeability as a function of stripping linear velocity $\langle v_2 \rangle$, with constant feed solution velocity of 1.8×10^{-2} m/s were carried out. The extractant concentration was 20% v/v. Then the fitting the parameters $a=4.83$ and $b=0.33$ for the mass transfer coefficient of stripping were evaluated from the logarithmic and represented in Eq. (12). The experimental data is fitting well as is shown in Fig. 8.

The fitting of the experimental data is very good as is shown in Fig. 6, 7 and 9. These results confirm the proposed model for cobalt coupled transport and the correlations used in the calculations of the mass transfer coefficients. The term B, which contains the organic resistance, is much lower than the other contributions, so it can be neglected.

With the mass transfer rate parameters determined, Eq. (7) was also used to fit the experimental value of permeability of cobalt through

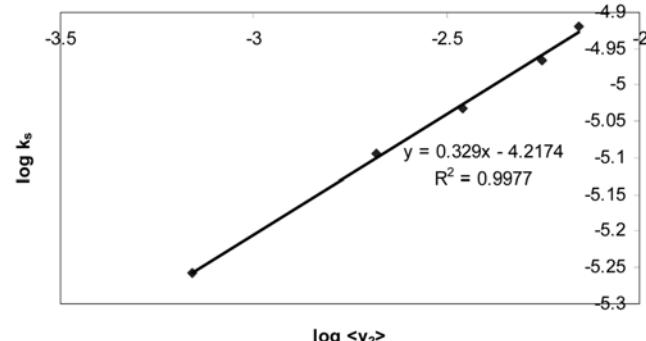


Fig. 8. Logarithmic representation of Eq. (12) for different stripping velocity ($\langle v_1 \rangle = 1.8 \times 10^{-2}$ m/s, [D2EHPA]=20% v/v).

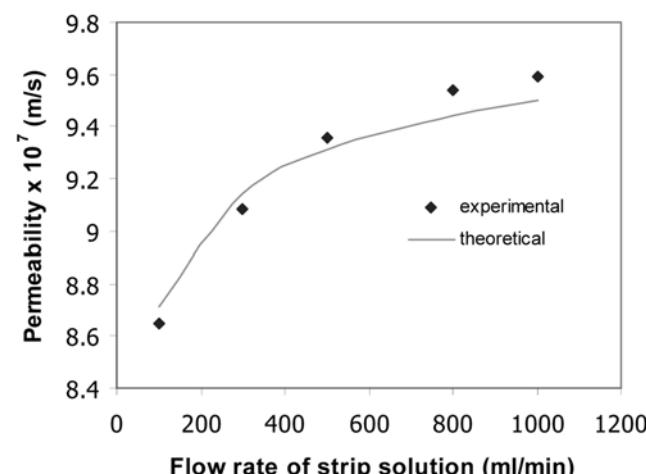


Fig. 9. Model fitting of cobalt ions permeability as a function of flow rate of stripping solution while the flow rate of feed solution=100 ml/min, extractant concentration=20% v/v and feed concentration=1,000 ppm.

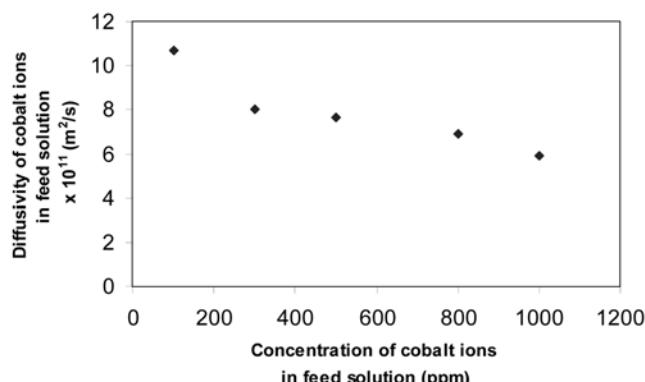


Fig. 10. The relation of Co concentration of feed solutions and diffusivity in feed solutions.

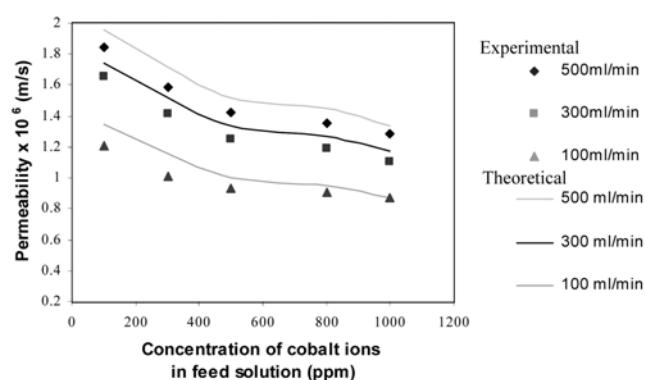


Fig. 11. Model fitting of cobalt ions permeability as a function of feed concentration while the flow rate of stripping solution=100 ml/min, the flow rate of feed solution=100 ml/min and the extractant concentration=20% v/v.

the aqueous feed. The results are shown in Fig. 9 for an extractant concentration of 20% v/v. The predicted mass transfer rate parameters adequately interpreted the experimental permeability values calculated from Eq. (14), validating the model. The results confirm that in these operating conditions the aqueous layer resistances are the dominant step in cobalt transfer through the liquid membrane.

When the concentration of feed solution was increased the diffusivity of feed solution decreased as shown in Fig. 10. From this result and Eq. (13), the mass transfer coefficient also decreased. Consequently, in Fig. 11, the permeability decreased by Eq. (7).

To obtain a higher mass transfer rate, the flow rate of the feed can be increased, but the higher the flow rate, the higher the pressure drop over the module and the larger the possibility of the leaching of the extractant. The optimal flow rate will be a balance between pressure drop and mass transfer rate. The extractant concentration can be kept low (0.5-1.0 M) because the reaction rate and the diffusion through the membrane are not rate limiting.

CONCLUSIONS

The permeation of cobalt ions was investigated with D2EHPA as the extractant in a hollow fiber module. It was found that the rate limiting step in the transport of the ion was the diffusion through both aqueous films: the feed and the stripping sides of the mem-

brane. The permeation of Co(II) is increased with the increase in the flow rate which makes evident the existence of boundary layers in the aqueous phase. The organic resistance of the membrane was negligible since the permeability of cobalt is practically constant with the variation of extractant concentration in the fiber above 0.2 M.

A mass transfer model to predict extent of Co(II) permeation was proposed, taking into account resistances typically present in a coupled transport process: aqueous stagnant layer and organic resistances. Accepted mass transfer correlations were used and the fitting parameters were evaluated to compare the measured permeability. The results were in reasonable agreement for the experimental conditions examined and confirm that the permeation rate was limited by diffusion through aqueous film, irrespective of the extractant concentration. The proposed model permits the calculation of cobalt permeability for different feed and stripping rate velocities in a hollow-fiber system like that used in this work. The studied system was effective for performing a reduction of cobalt content in water to permit levels without any contamination of the environment and was fast and economical; however, it is necessary to perform a complete analysis of the experimental conditions such as extractants, organic solvent, pH of aqueous phases, membrane stability, and transfer area in order to obtain a process more suitable for industrial operations.

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NOMENCLATURE

A_m	: mean surface of mass transfer [m^2]
B	: term defined in Eq. (8)
C_{HX}^0	: initial concentration of the extractant [M]
d	: diameter [m]
D_{aq}	: aqueous diffusion coefficient of the metal salt [$m^2 s^{-1}$]
D_{mem}	: diffusion coefficient through in liquid membrane [$m^2 s^{-1}$]
D'_{mem}	: effective diffusion coefficient in liquid membrane [$m^2 s^{-1}$]
F_v	: volumetric flow [$m^3 s^{-1}$]
K_{eq}	: equilibrium constant, Eq. (2)
k_f	: mass transfer coefficient of the feed phase [$m s^{-1}$]
k_s	: mass transfer coefficient of stripping phase [$m s^{-1}$]
l_{ef}	: membrane thickness [m]
L	: length of fiber [m]
P	: permeability [$m s^{-1}$]
r_i	: internal radius of the fiber [m]
r_o	: internal radius of the fiber [m]
R_f	: aqueous feed phase resistance [$s m^{-1}$]
R_0	: organic phase resistance [$s m^{-1}$]
R_s	: aqueous stripping phase resistance [$s m^{-1}$]
$\langle v \rangle$: mean liquid velocity through fibers [$m s^{-1}$]

Greek Letters

ε	: porosity
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ν : kinematic viscosity [Pa s]

τ : support tortuosity

Subscripts, Superscripts

a, b : exponential and pre-exponential factors in Eq. (12)
m, n : exponential and pre-exponential factors in Eq. (13)

Dimensionless Numbers

Gz : Graetz number ($d^2 \langle v \rangle / LD_{eq}$)

Re : Reynolds number ($d \langle v \rangle / \nu$)

Sh : Sherwood number ($k_s d / D_{eq}$)

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