

Transport of molybdenum with Alamine 336 using supported liquid membrane

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Abstract

The appropriate experimental conditions of Mo(VI) ion transport across a supported liquid membrane containing Alamine 336 as the mobile carrier dissolved in kerosene solvent have been investigated. The molybdenum flux has been studied as a function of the extraction solution acidity, the sodium carbonate concentration in the stripping solution and the carrier concentration in the liquid membrane. Suitable conditions for both feed and stripping solutions were achieved from analysis of experimental results of molybdenum transport through the liquid membrane. The permeation experiments showed that, at pH 2 with sulfuric acid in the extraction solution and at pH 11.5 with Na₂CO₃ in the stripping solution, an efficient transfer of the metal ion can be obtained. Furthermore, a maximum molybdenum transport was achieved at around 0.02 M of Alamine carrier in the organic phase. From these results, the extraction-stripping interface reactions for Mo(VI) permeation are proposed. An equation describing the permeation rate, taking into account the aqueous stagnant layers and liquid organic resistance as simultaneous controlling factors, has been derived. The validity of this model is evaluated with experimental data of mass transfer coefficient measured at different stirring rates.

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1. Introduction

Undoubtedly, the feasibility of separation and concentration of metals with liquid membranes must be considered as one of the most promising technological advances produced in the field of hydrometallurgical processes [1,2]. Especially, the use of solid supported liquid membranes under a hollow fiber or flat config-

uration has been successfully tested for recovery of metallic ions from aqueous solutions, becoming competitive with solvent extraction (SX) or ion-exchange (IX) processes [3].

It has been well documented that the employment of liquid membrane technology would offer several advantages compared with the current solvent extraction process in mixer-settlers, particularly huge savings in inventory of expensive solvent and smaller reactor size. Because no direct mixing between aqueous and organic phases occurs, crud formation and phase entrapment difficulties would be avoided. Many

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papers concerned with selective separation and concentration of metallic ions with liquid membranes have lately been reported [4–8]. Some of them are related to practical applications of liquid membranes in diverse potential fields and others are concerned with transport mechanism and permeability equations through membranes.

It is well known that molybdenum disulphide, MoS_2 , or molybdenite, is the main natural source of this metal, normally associated with porphyry copper ores, being separated by means of selective flotation. Generally, molybdenite concentrates are converted to molybdenum trioxide using a conventional oxidizing roasting, but the product is only a technical grade compound retaining most of the impurities of the initial concentrate after undergoing a highly contaminated process, which demands an enormous amount of energy too. This fact has produced a big interest in developing many options of leach processing for molybdenite concentrate and the subsequent recovery of dissolved metal by SX or IX processes [9,10]. The waste acid solution generated in these leaching and SX steps contains variable but significant concentrations of molybdenum, copper and rhenium as well as several non-valuable metals. This solution is rejected from conventional SX plants, due to the fact that its low content of metals make it economically inapplicable for the SX process. Recovering of metals from this kind of solution by supported liquid membranes has therefore become important in recent years as a promising practical process [11].

In the literature are reported many works on Mo(VI) solvent extraction from aqueous solutions using several extractants such as TBP, phosphine trioxide, sulphoxides, high-molecular weight alkylamines and alkylphosphoric acid esters [12–14]. Molybdenum chemistry is rather complicated. This metal exhibits several oxidation states in aqueous solution. Mo(VI) is usually the most stable in oxidizing conditions, but since it tends to hydrolyze and to form polyheteroacids, the number of species present in solution is large and it is not always possible to identify all of them, which makes it difficult to treat mathematically its reactions and products [15]. Then, it is interesting to study the permeation of this metal species through liquid membranes.

This communication describes the study of molybdenum transport using a supported liquid membrane

prepared by dissolving a high molecular weight tertiary alamine-type extractant in kerosene and a poly(tetrafluoroethylene) microporous flat membrane as support. The experiments were carried out with a permeation cell provided a continuous flow system. The information deduced from this work constitutes the basis for developing a practical membrane-based recovery process capable of achieving selective separation and enrichment of molybdenum from industrial waste solutions.

2. Experimental

2.1. Supported liquid membrane

The supported liquid membrane consisted of an organic phase that contained the carrier, supported on a polymeric porous membrane. Alamine 336 provided from Henkel was used as carrier of the liquid membrane without further purification. This tertiary amine, [tri-(C8–C10) amine], contains a basic nitrogen capable of forming amine salts with a wide variety of inorganic and organic acids. The organic extracting solutions were prepared by dissolving the extractant carrier in kerosene, an industrial diluent whose specifications averaged a specific gravity of 0.825 g/cm^3 , a viscosity value of 1.59 cP ($25 \text{ }^\circ\text{C}$) and a boiling point range between 200 and $300 \text{ }^\circ\text{C}$.

A flat hydrophobic microporous poly(tetrafluoroethylene) membrane supplied by Millipore was used as solid support. This support has a high porosity, low thickness and represents the most chemically inert and hydrophobic synthetic polymer. Its structural characteristics were provided by the supplier and they are: maximum pore size $r_m = 4.5 \cdot 10^{-7} \text{ m}$, porosity $\varepsilon = 0.80$ and thickness $l = 4.5 \cdot 10^{-7} \text{ m}$. The organic solvent containing the carrier was incorporated into the membrane support by capillary action.

2.2. Transport measurements

The experimental transport measurements were carried out with a stirred cell described elsewhere [16]. The membrane cell consisted of two hemicells, both provided with proper inlets and outlets for feed and stripping solution, being thus possible to operate the system in a continuous flow mode. The supported

liquid membrane was clamped between both hemi-cells resulting in a cross section area of $1.37 \cdot 10^{-4} \text{ m}^2$. The feed and stripping solutions were fed by a peristaltic pump with a volumetric flow rate of $8.33 \cdot 10^{-3} \text{ ml/s}$. The cell had a jacket for circulation of water to assure a constant temperature ($25 \text{ }^\circ\text{C}$) during the experiments. Both compartments were stirred with magnetic bars driven by synchronous motors. Solutions of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ dissolved in distilled water were used as feed phases. Stripping solutions were prepared by dissolving $\text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$ in distilled water. Molybdenum content was measured by atomic absorption spectrophotometry in a Varian AA50 apparatus.

3. Results and discussion

3.1. Molybdenum transport measurement

Metal ion transport through the membrane takes place with simultaneous extraction and stripping steps at both sides. Therefore, it is necessary to know the extraction and stripping reactions involved at the membrane interfaces since they are fundamental to understanding the transport phenomena of the metal ion through the supported liquid membrane. In order to determine the interfacial reactions and the best experimental conditions for Mo(VI) transport experimental runs changing the feed solution pH, sodium carbonate concentration in the permeate solution, carrier concentration and stirrer speed were designed.

3.2. Effect of feed solution pH

Several runs were accomplished varying the pH of the feed phase in a range between 2 and 5, adjusting it by controlled addition of H_2SO_4 and keeping constant both the metal content in the inlet feed solution (0.001 M) and the stirring rate (100 rpm). The stripping or receiving solution contained 1 mol/l Na_2CO_3 that gave a pH around 11.5. A solution 0.02 M Alamine 336 in kerosene was employed as the liquid membrane. Both aqueous phases were fed at a constant flow rate, F_v , of 0.01 ml/s. Fig. 1 shows the experimental results plotted as molar density of molybdenum transported through

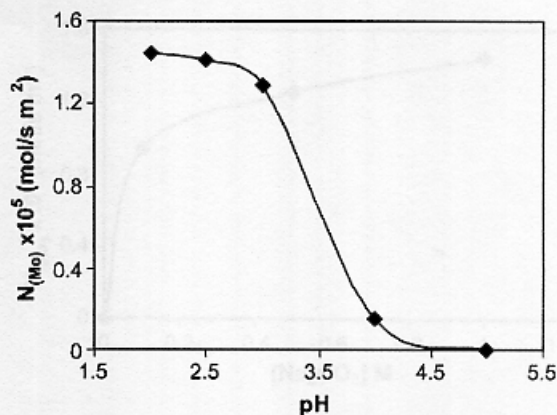


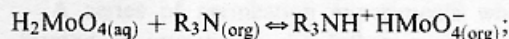
Fig. 1. Effect of feed solution pH on transfer rate of molybdenum. Stripping solution: 1 M Na_2CO_3 ; Alamine 336 concentration: 0.02 M.

the membrane, N_{Mo} , evaluated from the following expression

$$N_{\text{Mo}} = F_{v1}([\text{Mo}]_i - [\text{Mo}]_o)_1/A = F_{v2}[\text{Mo}]_{o,2}/A \quad (1)$$

where the subscripts “i” and “o” indicate the inlet and outlet conditions, respectively. Moreover, subscripts 1 and 2 denote feed solution and permeate (stripping) solution, respectively.

The transport efficiency of Mo was found to be critically dependent on the pH of the feed solution. It is clearly observed that the permeation of molybdenum decreases as the pH of the feed solution increases. This fact could be explained considering that Mo(VI) in aqueous solutions exists in the form of a series of species, e.g., MoO_4^{2-} , HMoO_4^- , H_2MoO_4 and MoO_2^{2+} , increasing in the above order as the acidity of the aqueous solution increases. Different profiles of Mo(VI) species had been built using different initial Mo concentration in the aqueous extraction solution [15,17,18]. In all cases, the distribution of the Mo(VI) species shows that at pH 2 the predominant species is H_2MoO_4 . Then, it is appropriate to represent the Mo(VI) chemical reaction with alamine 336 carrier at the aqueous–liquid membrane interface as follows:



$$K_E = \frac{[\text{MoR}]}{[\text{H}_2\text{MoO}_4][\text{R}_3\text{N}]} \quad (2)$$

where the subscripts (aq) and (org) represent the aqueous and organic phases respectively; R_3N denotes the high-molecular weight tertiary alkylamine and $R_3NH^+ \cdot HMoO_4^-$ (or MoR) the amine salt formed during the interfacial reaction; K_E is the extraction equilibrium constant.

The expression given by Eq. (2) has been confirmed by the experimental results of Basualto [19], indicating that one mole of molybdenum would react with each mole of amine extractant. In his study, a value of $K_E = 734 \text{ (mol/l)}^{-1}$ was found.

Since the H_2MoO_4 species tends to disappear as the acidity of the solution diminishes, the amount of Mo transported through the SLM decreases.

3.3. Effect of sodium carbonate concentration in the stripping solution

As the extraction step occurs in the interface between the feed solution and the liquid membrane, the transport of metal necessarily requires a simultaneous back-extraction step at the opposite side of the membrane. In the back-extraction stage, the extractant carrier is regenerated and the metal is stripped. The literature contains many options for accomplishing the stripping of the molybdenum complex, among them, solutions of NH_4OH , ammonium salts as sulfate or nitrate, $NaOH$, Na_2CO_3 and some mixtures of these compounds have been used.

From this list, solutions of Na_2CO_3 were used as the stripping agent in the permeate side. The molarity of Na_2CO_3 was varied between 0 and 1.0 mol/l (pH range between 7.0 and 11.5). The feed was constituted by a 0.001 M Mo(VI) solution whose pH was adjusted to a value of 2.0 using sulfuric acid. A 0.02 M Alamine 336 solution in kerosene was utilized as the organic solvent to impregnate the membrane. The volumetric flow rate of the aqueous solution towards the membrane was about $8.33 \cdot 10^{-3}$ ml/s, while the stirring rate was kept constant (100 rpm).

In Fig. 2, it can be observed that when a neutral stripping solution (pH=7) is employed there is no transport of molybdenum, it being absolutely necessary to increase the pH of the permeate solution by raising the molarity of Na_2CO_3 .

It is well known that molybdate ion in basic aqueous solution exists in the form of MoO_4^{2-} [15,17,18], so it is reasonable to assume as the most

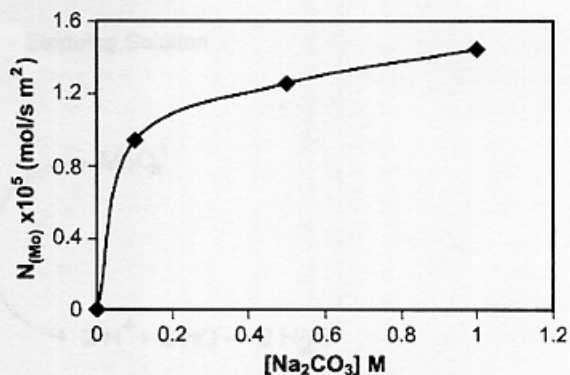
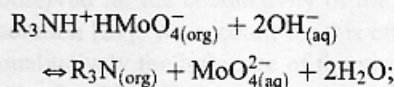


Fig. 2. The effect of Na_2CO_3 molarity (pH) on stripping rate of molybdenum. Feed solution pH: 2; Alamine 336 concentration: 0.02 M.

probable stripping reaction at the membrane–strip solution interface, the following equation:



$$K_S = \frac{[R_3N][MoO_4^{2-}]}{[MoR][OH^-]^2} \quad (3)$$

where K_S is the stripping equilibrium constant. The stoichiometry of Eq. (3) was corroborated by Basualto [19] obtaining a value of $K_S = 5.98 \cdot 10^4 \text{ (mol/l)}^{-1}$.

The result shown in Fig. 2 is consistent with the stripping reaction proposed. According to Eq. (3), the higher the OH^- concentration in the stripping solution, the greater will be the feasibility to break up the molybdenum–amine complex at the membrane–permeate solution interface.

The experimental results of this section and Section 3.1 indicate that the interfacial chemical reactions for Mo permeation through the supported liquid membrane, with the tertiary amine as carrier, can be schematized as shown in Fig. 3.

3.4. Effect of alamine concentration

A series of permeation experiments were performed to investigate the influence of the carrier concentration in the organic phase. In all the experiments, the feed solution in the extraction side of the membrane consisted of a 0.001 M Mo(VI) solution, at

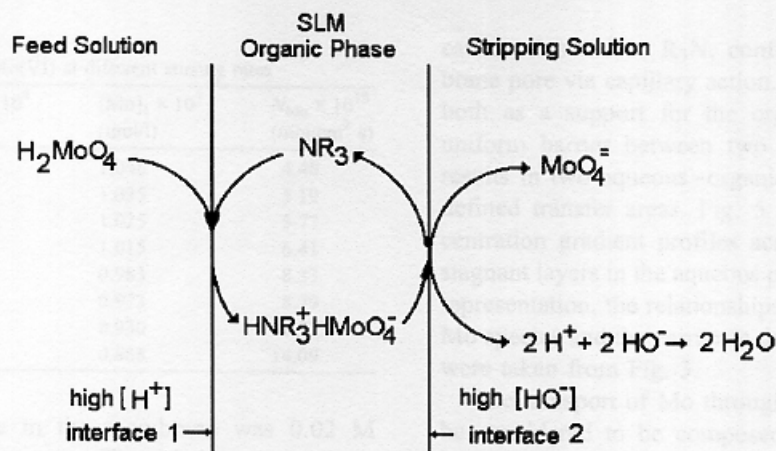


Fig. 3. Schematic representation of the interfacial chemical reactions for Mo permeation.

pH 2 adjusted with sulfuric acid. The acceptor stripping solution consisted of a 1.0 M Na_2CO_3 solution at pH 11.5. Both feed and permeate solutions were circulated at a flow rate of $8.33 \cdot 10^{-3}$ ml/s. The stirring rate in both compartments were kept constant (100 rpm). In Fig. 4 are shown the effects of the carrier concentration in the organic film on the transfer rate of molybdenum.

With increasing alamine concentration, initially, the metal transport increases, then goes through a maximum and finally decreases again. The maximum concentration of transported ion is reached at ca 0.02 M of Alamine 336 in kerosene. Some researchers explain this maximum by the increase of the organic

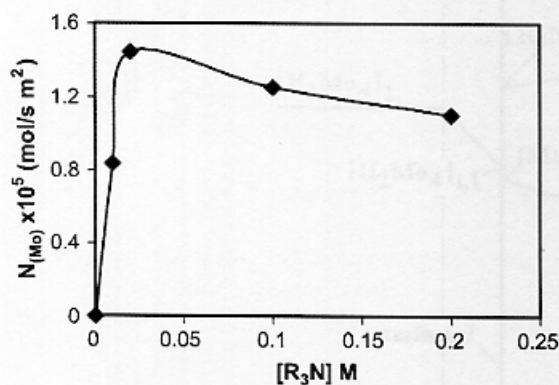


Fig. 4. Effect of Alamine 336 concentration in the organic phase on transfer rate of molybdenum. Feed solution pH: 2; stripping solution: 1 M Na_2CO_3 .

phase viscosity [20] and others with a maximum value observed for the conductivity of the Alamine organic solution [21]. We account for this effect by analyzing qualitatively the influence of the viscosity increase of Mo complex in the supported liquid membrane. From one point of view, the higher the carrier content in the liquid membrane the bigger should be the permeation of metal through it. A higher concentration of the tertiary amine in the organic phase should enhance the metal–extractant complex formation at the feed solution–liquid membrane interface, bringing about an augmentation of the driving force for metal ion permeation through the liquid membrane. However, it would not be recommended to increase indiscriminately the amine content of the organic phase because of the tendency to increase the viscosity of organic phase, the resulting low diffusivity of the Mo–amine complex, would cause a decrease in the transport rate. These opposing effects resulted in maximum transport at an alamine concentration around 0.02 M in kerosene.

3.5. Effect of the stagnant layer

A set of permeation experiments was performed to investigate the effect of stirrer speed (Ω) upon Mo transport. In all the experiments, the inlet feed aqueous solution was 0.001 M Mo(VI) at pH 2 and the stripping solution 1 M Na_2CO_3 at pH 11.5. The flow rate of both aqueous solutions was $8.33 \cdot 10^{-3}$ ml/s.

Table 1
Molar flux density of Mo(VI) at different stirring rates

Ω (s^{-1})	$[Mo]_2 \times 10^4$ (mol/l)	$[Mo]_1 \times 10^3$ (mol/l)	$N_{Mo} \times 10^{10}$ (mol/cm ² s)
0.58	0.737	1.046	4.48
0.70	0.853	1.035	5.19
0.83	0.948	1.025	5.77
1.13	1.053	1.015	6.41
1.67	1.369	0.983	8.33
2.11	1.474	0.973	8.79
2.7	1.896	0.930	11.53
4.17	2.317	0.888	14.09

The organic phase in the membrane was 0.02 M Alamine 336 in kerosene. The stirring rates of the aqueous solutions were varied between 35 and 250 rpm. Higher stirring speeds would promote both the formation of air bubbles and loss of organic phase, which in turn could mask the Mo transport process. The different operational conditions and Mo molar flux density (N_{Mo}) are shown in Table 1. In all cases, the N_{Mo} increases with increasing stirring rate, indicating a decrease in the stagnant layers thickness.

3.6. Modeling Mo(VI) transport

The system under study consists of two aqueous phases and an organic phase, which contains the

carrier, denoted as R_3N , confined within the membrane pore via capillary action. The membrane serves both as a support for the organic phase and as a uniform barrier between two aqueous phases. This results in two aqueous–organic interfaces with well-defined transfer areas. Fig. 5 shows the linear concentration gradient profiles across the SLM and the stagnant layers in the aqueous phase. In this schematic representation, the relationships involved between the Mo species and the carrier in the membrane interfaces were taken from Fig. 3.

The transport of Mo through the SLM system can be considered to be composed of many elementary steps [22]. In our theoretical considerations, the following steps are taken into account: (1) diffusion of H_2MoO_4 through the stagnant layer of feed solution; (2) diffusion of the carrier Alamine 336 and the Mo–carrier complex in the organic phase; (3) diffusion of MoO_4^{2-} through the stagnant layer of the stripping solution. In the present mathematical description, the following assumptions have been considered: (i) there is no interfacial resistance due to the extraction and stripping reactions; (ii) the reaction rates in the membrane are very much larger than diffusion rates. This assumption permits one to consider equilibrium everywhere within the membrane so the metal complex concentration at the interfaces can be correlated with

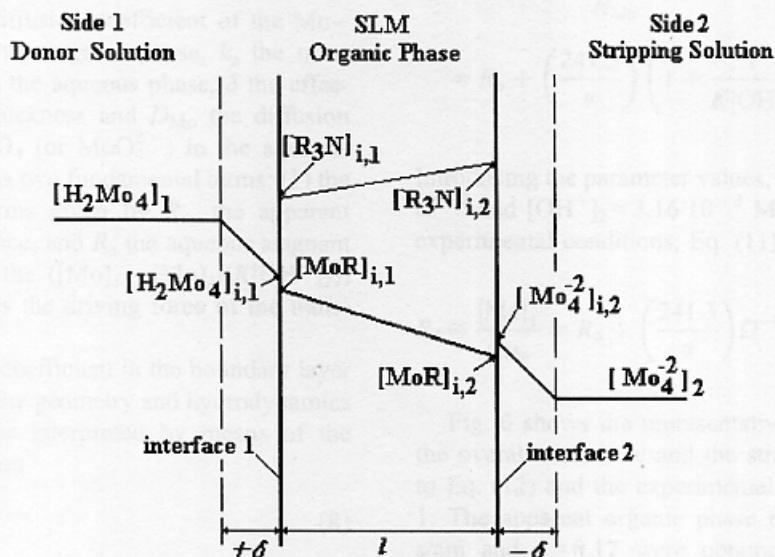


Fig. 5. Schematic representation of Mo and R_3N concentration profiles for SLM system.

the aqueous operational conditions through Eqs. (2) and (3); (iii) at low fractional saturation of the carrier species, the concentration of the metal complex [MoR] is much lower than the concentration of free reagent [R₃N], thus it is valid to consider that $C_R^\circ \cong [R_3N]$; (vi) the transport process through the stagnant layers and organic phase is governed by Fick's law.

From these assumptions, the following expression of the Mo molar flux density at steady-state across the SLM system is obtained:

$$N_{\text{Mo}} = \left[R_o + R_a \left(1 + \frac{1}{K[\text{OH}^-]_2^2} \right) \right]^{-1} \cdot \left([\text{Mo}]_1 - \frac{[\text{Mo}]_2}{K[\text{OH}^-]_2^2} \right) \quad (4)$$

with

$$K = K_E \cdot K_S \quad (5)$$

$$R_o = l\tau / D_{\text{MoR}} \varepsilon K_E C_R^\circ \quad (6)$$

$$R_a = 1/k_a = \delta / D_{\text{Mo}} \quad (7)$$

where D_{MoR} is the diffusion coefficient of the Mo–alamine complex in the organic phase, k_a the mass transfer coefficient in the aqueous phase, δ the effective stagnant layer thickness and D_{Mo} the diffusion coefficient of H₂MoO₄ (or MoO₄²⁻) in the aqueous phase. Eq. (4) contains two fundamental terms: (1) the overall resistance terms given by R_o , the apparent organic phase resistance, and R_a the aqueous stagnant layer resistance; (2) the $([\text{Mo}]_1 - [\text{Mo}]_2 / (K[\text{OH}^-]_2^2))$ term which represents the driving force of the transport process.

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 dimensional correlation

$$Sh = \alpha Sc^\beta Re^\gamma \quad (8)$$

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

the Schmidt number defined as (ν / D_{Mo}) with $\nu=0.896 \cdot 10^{-2}$ cm²/s the kinematic 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:

$$k_a = \alpha (D_{\text{Mo}})^{0.67} (\nu)^{-0.41} d^{0.48} \Omega^{0.74} \quad (9)$$

The values of the coefficients $\beta=0.33$ and $\gamma=0.74$ were taken from Marchese and Quinn [23], which interpreted adequately the cell-stirrer geometry of this study.

The Mo diffusion coefficient in the aqueous phase was calculated from the Stoke–Einstein equation as

$$D_{\text{Mo}} = \frac{k_B T}{6\pi r_{\text{Mo}} \mu} \quad (10)$$

with k_B the Boltzmann constant and r_{Mo} the radius of the species H₂MoO₄ ($r_{\text{Mo}}=2.54 \cdot 10^{-8}$ cm), $D_{\text{Mo}}=9.61 \cdot 10^{-6}$ cm²/s.

Introducing the experimental parameter values and diffusivity obtained from Eq. (10) into Eqs. (9), (7) and in the rearranged Eq. (4), the following expression of the overall resistance for Mo transport (R_T) is obtained:

$$R_T = \frac{[\text{Mo}]_1 - [\text{Mo}]_2 / K[\text{OH}^-]_2^2}{N_{\text{Mo}}} = R_o + \left(\frac{241.3}{\alpha} \right) \left(1 + \frac{1}{K[\text{OH}^-]_2^2} \right) \Omega^{-0.74} \quad (11)$$

Introducing the parameter values, $K=K_E K_S=4.29 \cdot 10^7$ M⁻² and $[\text{OH}^-]_2=3.16 \cdot 10^{-3}$ M for the stirring rate experimental conditions, Eq. (11) can be reduced to:

$$R_T \cong \frac{[\text{Mo}]_1}{N_{\text{Mo}}} = R_o + \left(\frac{241.3}{\alpha} \right) \Omega^{-0.74} \quad (12)$$

Fig. 6 shows the representative linear behavior of the overall resistance and the stirrer speed according to Eq. (12) and the experimental data given in Table 1. The apparent organic phase resistance $R_o=183.1$ s/cm and $\alpha=0.17$ were obtained from linear last-squares regression analysis. Introducing these parameters into Eq. (12), the overall resistance for Mo

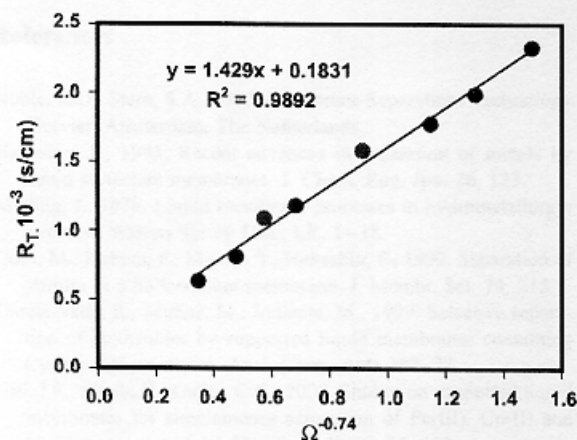


Fig. 6. Effect of stirrer speed on the Mo overall resistance.

transport as a function of the stirring rate can be predicted by

$$R_T \text{ (s/cm)} = 183.1 + 1429\Omega^{-0.74} \quad (13)$$

From Eq. (6), the apparent organic resistance $R_o = 200.2$ s/cm was evaluated. For that, values of $D_{\text{MoR}} = 2.68 \cdot 10^{-6}$ cm²/s (from Eq. (10) with $r_{\text{MoR}} = 7.5 \cdot 10^{-8}$ cm), $l = 4.5 \cdot 10^{-5}$ cm, $\tau = 1.4$, $\varepsilon = 0.8$, $K_E = 734$ M⁻² and $C_R^\circ = 0.02$ M were used. This apparent organic resistance value is in reasonable agreement with the R_o evaluated from the y -axis intercept according with Eq. (13), confirming the validity of the resistance model proposed.

4. Conclusions

The results obtained in this study provide important information about the right experimental conditions for the facilitated transport of molybdenum using a supported liquid membrane. The experimentally observed results indicate that the highest extraction of molybdenum occurs when the pH of the feed solution is adjusted to a value of 2.0. Under such a condition, Mo(VI) exists predominantly as the H_2MoO_4 (molybdic acid) species. An equimolar relationship was found between this species and the carrier agent when they reacted to form the metal complex at interface. An increase in the metal transport was also observed as the alkalinity of the stripping solution was

increased to around pH 11.5. The results suggest a stripping reaction at the membrane-stripping solution interface, which produced the rupture of the molybdenum complex, releasing the Mo(VI) as molybdate ion into the receiving aqueous phase and subsequently the regeneration of amine carrier extractant.

The effect of the extractant concentration in the organic solutions on the permeation of metal through the membrane was also investigated. It was found that increasing amine content in the liquid membrane increased the metal transport. However, it not possible to raise the amine concentration indefinitely since the diffusion rate of the carrier–metal complex through the membrane decreases as the viscosity of organic film increases. The maximum Mo(VI) ion transport was achieved at an Alamine carrier concentration around 0.02 M in kerosene.

The effect of stirring rate on Mo permeation through the SLM was analyzed. Increasing impeller rotation produced an increase in Mo transport. A mass transfer model to predict the extent of Mo(VI) transport was proposed. From this, a general expression of Mo permeation rate, taking into account the aqueous stagnant layer and the organic phase resistance as controlling factors, was derived.

The capacity of the supported liquid membrane technique to generate strip solutions with enriched concentrations of solute attest to the potential usefulness of this separation process in hydrometallurgy and decontamination of industrial wastewater. However, it is absolutely necessary to get more information about the long-term period stability of the membrane and the durability (lifetime) of the support material.

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