



Extraction of molybdenum by a supported liquid membrane method

Carlos Basualto^{a,*}, José Marchese^b, Fernando Valenzuela^a, Adolfo Acosta^b

^a *Lab. Operaciones Unitarias, Fac. Ciencias Químicas y Farmacéuticas, Universidad de Chile, CC 233, Santiago, Chile*

^b *Laboratorio de Ciencias de Superficie y Medios Porosos, Dpto de Química, UNSL-FONCYT, C.C.256-5700, San Luis, Argentina*

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Abstract

This is a report on the extraction of molybdenum(VI) ions using a supported liquid membrane, prepared by dissolving in kerosene, the extractant Alamine 336 (a long-chain tertiary amine) employed as mobile carrier. A flat hydrophobic microporous membrane was utilised as solid support. Appropriate conditions for Mo(VI) extraction through the liquid membrane were obtained from the results of liquid–liquid extraction and stripping partition experiments. The influence of feed solution acidity, the carrier extractant concentration in the organic liquid film and the content of strip agent on the metal flux through membrane were investigated. It was established that maximal extraction of metal is achieved at a pH 2.0 if sulphuric acid is used in the feed solution and at a pH value over 11.0 if Na₂CO₃ is used as strip agent. Moreover, the molybdenum extraction through membrane is enhanced when a 0.02 mol l⁻¹ content of the amine carrier in the organic phase is used. The present paper deals with an equilibrium investigation of the extraction of Mo(VI) by Alamine 336 and its permeation conditions through the liquid membrane, and examines a possible mechanism of extraction.

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1. Introduction

The chief source of molybdenum now is molybdenite (MoS₂) the most valuable by-product of copper mining production. Molybdenite is by far the most important mineral of this metal and since is found associated with copper porphyry ores, many technical efforts has been developed in order

to separate both metals by efficient methods. Normally a molybdenite concentrate is obtained by a selective flotation. Usually the processing continues by roasting the sulphide concentrate to molybdenum trioxide in a step, which is highly demanding of energy and environmentally objectionable due to the production of sulphur oxides. Then, leaching of molybdenite concentrates and recovery of dissolved metals by solvent extraction (henceforth abbreviated as SX) has, therefore, become important as a promising industrial process.

* Corresponding authors. Fax: +56-2-222-7900.

E-mail addresses: cbasualt@uchile.cl (C. Basualto), marchese@unsl.edu.ar (J. Marchese).

The residual solutions generated in these leaching and SX steps contain variable but significant concentrations of molybdenum, copper, rhenium and other non-valuable metals. Many hydrometallurgical options can be employed to extract and separate the content of molybdenum from these solutions, among others, fractional crystallisation and conventional solvent extraction processes. SX technology offers a much greater flexibility in process design, being easier the latter conversion of MoS₂ to practical production of commercial molybdates. However, the current SX process presents serious limitations, as huge inventories of expensive solvent and crud formation at inter-phase and phase entrainment difficulties. Furthermore, sometimes due to its low content of molybdenum in waste leach solutions, the SX process in conventional mixer-settler reactors becomes economically inapplicable. Then, recovering of metals from this kind of solution by supported liquid membranes has, therefore, become important in recent years as an interesting practical process [1–4].

The novel membrane-based solvent extraction process has been shown as an effective alternative to current SX technology. Specifically, liquid membrane would present a high ability of separating selectively metal ions from aqueous solutions using a microporous solid support and a minimum quantity of expensive organic solvent in processes with considerable extraction extent [5].

Several studies on selective separation and enrichment of several compounds with solid supported-type liquid membranes have been formerly reported. Some of them are related to transport mechanism and permeability equations through membrane and others are concerned on practical applications of liquid membranes in diverse potential fields such as organic acid extraction, analysis of substances, nuclear waste processing, desalination of sea water, and others [6–9].

Many molybdenum species have been reported to exist in aqueous solution [10]. Commonly, the hexavalent form of this metal is the most stable, but since it presents the tendency to hydrolyse and to form polyhetero acids, identification of them used to be highly complicated that makes difficult the quantitative treatment of extraction equi-

librium information. As it has been reported before, polymolybdate anions predominate in the region above pH 3 being only possible to find cationic species of this metal at low pH zone [11]. Several authors have studied the extraction of Mo(VI) from aqueous solutions using different extractants such as TBP, phosphine trioxide, sulphoxides, high-molecular weight alkylamines and alkylphosphoric acid esters [12–15]. In a previous paper we studied quantitatively the extraction of this metal with PC-88A (an alkyl phosphonic acid) dissolved in Scaid-100 (Esso, Chile) from acid copper-containing solutions [16]. In other studies we have examined a practical procedure for recovery and separation of molybdenum(VI) and copper from acid leaching residual solution of Chilean molybdenite concentrate by SX [17]. The present paper deals with an equilibrium investigation of the extraction of Mo(VI) by Alamine 336 (a high molecular weight tertiary amine-type extractant) and its permeation conditions through a poly(tetrafluoroethylene) microporous flat liquid membrane, and examines a possible mechanism of extraction.

2. Experimental

2.1. Extraction and stripping equilibrium experiments

The aqueous solutions for Mo extraction were prepared by dissolving Na₂MoO₄ · 2H₂O in distilled water. The pH value in the range 1–7 was adjusted with sulphuric acid. The initial content of Mo(VI) in feed solution was set around 1×10^{-3} mol l⁻¹. Stripping solutions with pH ranging from 7 to 11 were prepared by dissolving the appropriate amount of Na₂CO₃ · 2H₂O in distilled water. The organic extracting solutions were prepared by dissolving the carrier extractant Alamine 336, [tri-C₈–C₁₀ amine] provided from Henkel S.A. in kerosene, an industrial diluent with a specific gravity of 0.825 and a viscosity value of 1.59 cP (25 °C). The amine was used without further purification. All the reagents were analytical grade products.

Molybdenum liquid–liquid extraction and equilibrium measurements were carried out by contacting in separator funnels equal volumes (20 ml) of the Mo solution and the organic solvent during 24 h enough to allow equilibrium to be reached. Back-extraction equilibrium experiments were made contacting the loaded organic phases with the $\text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$ aqueous solutions. These experiments were conducted at 25 °C.

2.2. Measurements of molybdenum permeation through membrane

The experimental permeation measurements of molybdenum were performed using a small stirred cell described elsewhere [18]. The membrane cell was conformed by two hemicells, both provided with proper inlets and outlets for feed and stripping solution, that makes possible to operate the system in a continuous flow way. The solid supported liquid membrane comprises of the organic phase that contains the carrier Alamine 336, supported on a polymeric porous membrane. As solid support a flat hydrophobic microporous poly(tetrafluoroethylene) membrane supplied by Millipore was utilised. This support presents excellent properties because of its flexibility, permeability and chemical and mechanical resistance. The main characteristics of polymeric membrane are: maximum pore size 4.5×10^{-7} m, porosity 0.80, and thickness 2×10^{-4} m. The organic solvent containing the carrier was incorporated into the support membrane by capillary action.

The supported liquid membrane was clamped between both hemicells resulting in a cross section area of 1.37×10^{-4} m². The feed and stripping solutions were fed by a peristaltic pump with a volumetric flow rate of 0.01 ml s^{-1} . The stirred cell was equipped with a water circulation jacket to assure a constant temperature (25 °C) during the experiments. Both compartments were stirred at 100 rpm with magnetic bars that were driven by synchronous motors.

Molybdenum content in both equilibrium and permeation experiments was measured by atomic absorption spectrophotometry in a Varian AA50 apparatus.

3. Results and discussion

3.1. Extraction equilibrium

To clarify the extraction mechanism of molybdenum ions through the liquid membrane it is first necessary to set the appropriate experimental conditions of liquid–liquid extraction and stripping partition steps and to assume the possible chemical reactions involved in them.

Molybdenum chemistry is not easy. This metal has several oxidation states in aqueous solution, however, under normal conditions, the hexavalent form of molybdenum is the most stable in aqueous solution. Since Mo(VI) tends to form polyhetero acids and to be hydrolysed, the number of species present in solution is large and the identification of all of them is not always possible and the mathematical treatment of equilibrium data used to be rather complicated. It is well known that in aqueous solution the predominance of molybdenum species depends, among other factors, on the metal concentration, the pH of solution and the ionic strength. For instance, many polymolybdate anions predominate in the region of pH greater than 3 and that molybdenum forms cationic species only at a low pH. In Fig. 1 is shown a profile of abundance of each Mo(VI) species along the pH range, for a metal concentration of 0.001 mol l^{-1} . Fig. 1 was built from equilibrium equations and their respective constants, which are available in the literature [11,19,20]. It is well known that molybdate ion in basic aqueous solution exists in the form of MoO_4^{2-} and that a

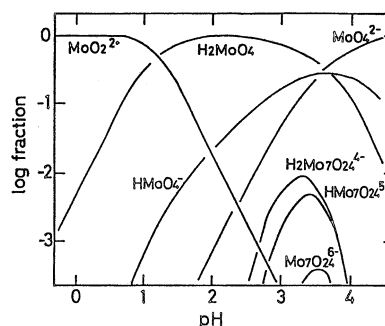
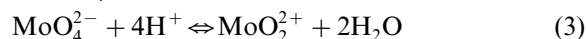
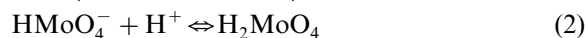
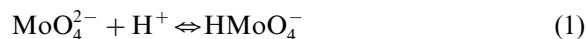


Fig. 1. Profile of abundance of Mo(VI) species along the pH range.

series of molybdenum species, e.g. HMoO_4^- , H_2MoO_4 and MoO_2^{2+} increase in the above order as the acidity of aqueous solution increases. In the zone under a pH value of 4.0 the following equilibria of Mo(VI) species are considered:



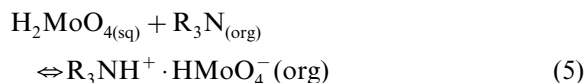
Some authors propose that MoO_2^{2+} species would exist in water as $\text{H}_4\text{MoO}_4^{2+}$ [21]. Moreover, polymerisation of Mo(VI) species depends on content of this metal in aqueous solution being highly probable as the concentration of molybdenum increases. Thus for example, the species MoO_4^{2-} tends to polymerise to $\text{Mo}_7\text{O}_{24}^{6-}$, $\text{HMo}_7\text{O}_{24}^{5-}$, $\text{H}_2\text{Mo}_7\text{O}_{24}^{4-}$ as can be appreciated in Fig. 1, and the cationic species MoO_2^{2+} , which exists at lower pH polymerise to the species $\text{Mo}_2\text{O}_5^{2+}$ and $\text{Mo}_3\text{O}_6^{2+}$. The tertiary amine, Alamine 336, used as extracting agent for molybdenum from acidic solutions contains a basic nitrogen capable of forming amine salts with a wide variety of inorganic and organic acids.

Several extraction equilibrium experiments were carried out changing both the metal and the amine initial concentration. Molybdenum content in the feed solution was varied between 50 and 450 mg l^{-1} meanwhile it was examined in a range of Alamine 336 concentration in organic phase between 1×10^{-3} and $1 \times 10^{-1} \text{ mol l}^{-1}$. Fig. 2 shows the Mo extraction data as a function of pH and Alamine concentration loaded in the organic phase. Molybdenum extraction extent, $\%E(\text{Mo})$, was calculated according to Eq. (4), where the subscripts 'in' and 'eq' indicate initial and equilibrium conditions, respectively, and 'aq' denotes aqueous solution.

$$\%E(\text{Mo}) = \frac{[\text{Mo}]_{\text{aq,in}} - [\text{Mo}]_{\text{aq,eq}}}{[\text{Mo}]_{\text{aq,in}}} 100 \quad (4)$$

From Fig. 2 it can be observed that the highest Mo(VI) extraction was appreciated around pH 2.0, being the H_2MoO_4 (molybdic acid) one of most predominant species in that acidity range. Molybdenum extraction decreased as the pH of the aqueous solution was increased. This fact

could be attributed to the fact that H_2MoO_4 species tends to disappear as the acidity of solution diminishes, according with the experimental data of Fig. 2 and the species profile for Mo(VI) shown in Fig. 1. The anionic species (HMoO_4^- , MoO_4^{2-}) exist with predominance in a pH value range over 4 in which this metal extraction does not occur in great extension. Then, it is appropriate to represent the Mo(VI) extraction chemistry with Alamine 336 reagent as follows:



where the subscript 'org' represent organic phase, R_3N denotes the high-molecular weight tertiary alkylamine and $\text{R}_3\text{NH}^+ \cdot \text{HMoO}_4^-$ the amine salt formed during equilibrium. From this equation, the expression for extraction equilibrium constant, $K_{\text{eq,E}}$ can be written as:

$$K_{\text{eq,E}} = \frac{[\text{MoR}]_{\text{E}}}{([\text{Mo}][\text{R}]_{\text{E}})} \quad (6)$$

Where the subscript 'E' denotes extraction conditions. $[\text{MoR}]$ represents the concentration of molybdenum-amine salt formed at the organic phase, $[\text{Mo}]$ the molybdenum content as H_2MoO_4 species and $[\text{R}]$ the tertiary amine, once equilibrium is attained.

Then, Eq. (6) can be arranged as follows:

$$\log(D_{\text{Mo}})_{\text{E}} = \log K_{\text{eq,E}} + \log[\text{R}]_{\text{E}} \quad (7)$$

where D_{Mo} represents the metal distribution coefficient, defines as follows:

$$(D_{\text{Mo}})_{\text{E}} = \left(\frac{[\text{MoR}]}{[\text{Mo}]} \right)_{\text{E}} \quad (8)$$

In Fig. 3, all experimental results were correlated by Eq. (7). The slope value is nearly equal to 1.0, indicating that one mole of molybdenum would react with each mole of amine extractant, validating the equilibrium proposed in Eq. (5).

3.2. Stripping equilibrium

As the extraction step occurs in the interface between feed solution and the liquid membrane, transport of metal necessarily requires a simulta-

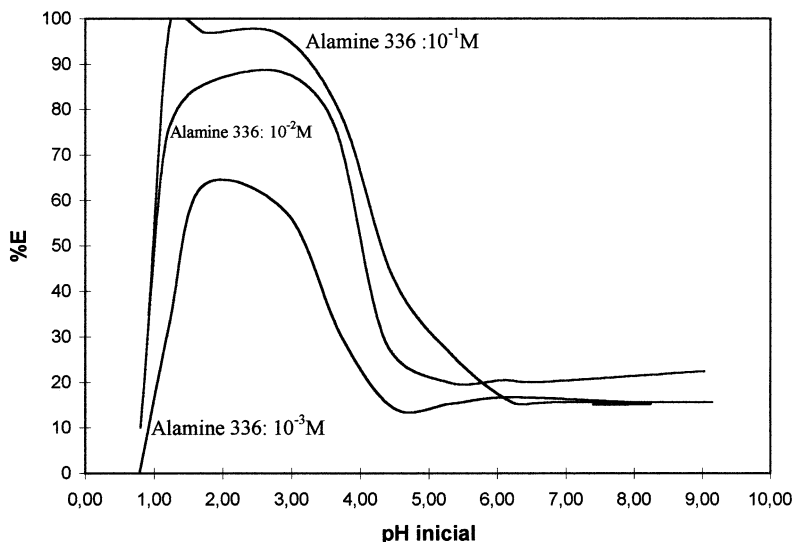


Fig. 2. Dependence of molybdenum extraction on pH and Alamine 336 concentration. Feed solution: $0.001 \text{ mol l}^{-1} \text{ Mo(VI)}$.

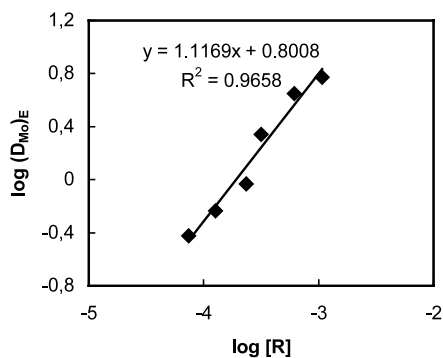
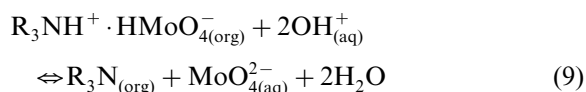


Fig. 3. Correlation of extraction experimental results according to Eq. (7).

neous back-extraction step at opposite side of membrane. In the back-extraction stage the extractant carrier is regenerated and the metal is stripped. In literature it has been reported many options to accomplish the stripping of molybdenum–amine complex, among them, solutions of NH_4OH , ammonium salts as sulphate or nitrate, NaOH , Na_2CO_3 , and some mixtures of these compounds, many of them under very special conditions [22–24]. All of them are employed in basic media that conduct to formation of respective molybdate salts.

Solutions of Na_2CO_3 with a pH value of 11.5 were used as stripping agent during the back-extraction equilibrium experiments. According to profile of distribution of Mo(VI) species presented in Fig. 1, it would be possible to assume as the most probable stripping equilibrium reaction in basic medium, the following equation:



with a stripping equilibrium constant $K_{\text{eq,S}}$, given by

$$K_{\text{eq,S}} = \frac{([\text{R}][\text{MoO}_4^{2-}][\text{H}_2\text{O}]^2)_{\text{S}}}{([\text{MoR}][\text{OH}^-]^2)_{\text{S}}} \quad (10)$$

where ‘S’ denotes stripping conditions and $[\text{MoO}_4^{2-}]$ represents the MoO_4^{2-} species concentration. Eq. (10) can be arranged as follows:

$$\log(D_{\text{Mo}})_{\text{S}} = \log\left(\frac{[\text{H}_2\text{O}]_{\text{S}}^2}{K_{\text{eq,S}}[\text{OH}^-]_{\text{S}}^2}\right) + \log[\text{R}]_{\text{S}} \quad (11)$$

where $(D_{\text{Mo}})_{\text{S}}$ denotes the metal distribution constant at stripping step, defined by the following expression:

$$(D_{\text{Mo}})_{\text{S}} = \left(\frac{[\text{MoR}]}{[\text{MoO}_4^-]}\right)_{\text{S}} \quad (12)$$

Results of the molybdenum stripping partitions experiments carried out at different extractant concentration are represented in Fig. 4 according with Eq. (11). The slope value is nearly equal to 1.0, indicating that one mole of molybdate will be produced for each mole of molybdenum–amine salt compound at the organic–aqueous interface validating the equilibrium proposed in Eq. (9).

3.3. Molybdenum permeation measurements

Probable expressions of the reactions involved in the molybdenum extraction and stripping steps were obtained from the results of extraction equilibrium experiments. The following experimental runs were designed in order to find out the best experimental conditions for molybdenum permeation through the liquid membrane.

The relation between the apparent permeabilities of molybdenum, P_{Mo} , and the concentration of carrier extractant is shown in Fig. 5. To evaluate the experimental results, the apparent permeability of metal was defined as follows:

$$P_{\text{Mo}} = \frac{J_{\text{Mo}}}{[\text{MO}]_{\text{i},1}} \quad (13)$$

where J_{Mo} is the molar flux of molybdenum transported through the membrane, obtained from the following equation:

$$J_{\text{Mo}} = \frac{Q_1([\text{Mo}]_{\text{i}} - [\text{Mo}]_{\text{o}})_1}{A} = \frac{Q_2[\text{Mo}]_{\text{o},2}}{A} \quad (14)$$

where Q is the volumetric flow rate of each aqueous phase, the subscripts 'i' and 'o' denote

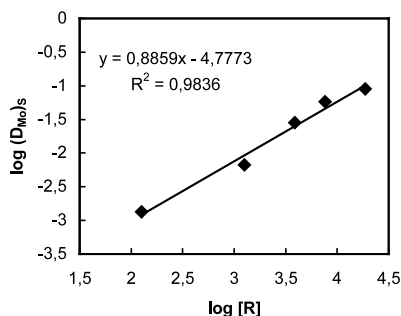


Fig. 4. Correlation of stripping experimental results according to Eq. (11).

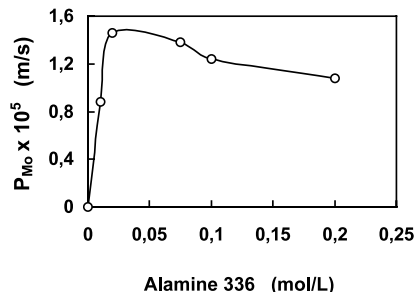


Fig. 5. Effect of Alamine 336 concentration in the organic phase on apparent permeability of molybdenum. Feed solution pH: 2. Stripping solution: $1 \text{ mol l}^{-1} \text{ Na}_2\text{CO}_3$.

the inlet and outlet conditions, respectively. Furthermore, subscripts 1 and 2 indicate feed solution and stripping (permeate) solution, respectively, being A, the effective membrane area. Feed solution at the extraction side of membrane consisted of a $0.001 \text{ mol l}^{-1} \text{ Mo(VI)}$ pure solution whose pH was adjusted at a value of 2.0 with sulphuric acid. A $1.0 \text{ mol l}^{-1} \text{ Na}_2\text{CO}_3$ solution was utilised as stripping phase, which gives a pH value around 11.5. The volumetric flow rates, Q_1 and Q_2 , of the feed and permeate aqueous solutions were about $1 \times 10^{-5} \text{ l s}^{-1}$.

Fig. 5 shows the effect of changing the carrier concentration in the organic film on permeation rate of metal. It is clearly observed that the molybdenum permeability increases as carrier content is augmented, reaching a maximum around a 0.02 mol l^{-1} of Alamine 336 in the organic film. However, when a higher molarity of extractant is used, a depressive effect on the apparent permeability of metal is observed. This maximum value has been explained due to the increase of the organic phase viscosity as carrier extractant content in the membrane is enlarged [25]. Although a bigger content of the carrier extractant in the liquid membrane makes possible a higher permeation of metal, it would enhance the metal–extractant complex formation at extraction-step interface. It would also imply an excessive enlargement of the viscosity of organic solvent producing a diminution of permeation rate of metal because of the decrease of diffusion of metal–amine complex through membrane. Then, the conjugation of these opposing effects, namely,

higher probability to form the extractable complex and a lower diffusion of this species because of a higher viscosity, as the extractant content in organic phase is increased, let to explain the experimentally observed maximum transport of metal when an Alamine 336 concentration around 0.02 M in kerosene is employed.

Fig. 6 presents the effect of feed solution pH on the permeability of molybdenum. These experiments were conducted employing a constant initial metal concentration in the feed solution around $1 \times 10^{-3} \text{ mol l}^{-1}$, an organic solvent prepared with a 0.02 mol l^{-1} Alamine 336/kerosene concentration and a receiving permeate solution consisting of a $1 \text{ mol l}^{-1} \text{ Na}_2\text{CO}_3$ solution (pH ca. 11.5). In Fig. 6 it is observed that the permeation rate of Mo(VI) depends on the acidity of feed solution. The maximum transport of molybdenum(VI) occurs in the vicinity of a pH range 2–3, but decreases with pH in the high pH range, accordingly with the results obtained in the liquid–liquid extraction equilibrium experiments (Fig. 2) and the extraction expression given by Eq. (5). Moreover, as can be observed in Fig. 1, H_2MoO_4 species tends to disappear as the acidity of solution decreases under a pH value of 1.0 and when the pH is raised over 3, then the metal ability to permeate through the liquid membrane decreases. On the other hand, Alamine 336 is an ion-pair-type of extractant which acts by following a mechanism based on the principle of ion

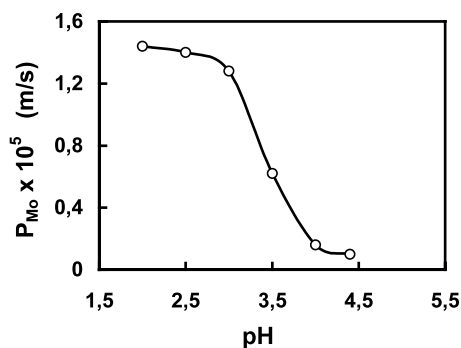


Fig. 6. Effect of feed solution pH on apparent permeability of molybdenum. Stripping solution: $1 \text{ mol l}^{-1} \text{ Na}_2\text{CO}_3$. Alamine 336 concentration: 0.02 mol l^{-1} .

association whereby a large and positively charged organic species produces the extraction of a large and anionic metal complex toward the organic phase. However, the anionic species of Mo(VI) (molybdate and polymolybdates-type species) which could be theoretically extracted and transported by the tertiary amine extractant, exists with predominance in a pH range ≥ 3.5 .

Metal permeation through liquid membranes requires a simultaneous stripping step at opposite side of membrane. Among different chemical compounds possible to use as strip agent when a basic carrier as Alamine 336 is employed, commonly basic substances used to present the better performance. In Fig. 7 is represented the effect of the sodium carbonate concentration—the chosen reagent in this study—in the stripping solution on the apparent permeability of molybdenum(VI). The feed solution was conformed by a $1 \times 10^{-3} \text{ mol l}^{-1}$ Mo(VI) solution whose pH was adjusted to a value of 2.0 using sulphuric acid. The liquid membrane was prepared by dissolving 0.02 mol l^{-1} Alamine 336 in kerosene. No transport of Mo(VI) through the membrane was detected under neutral stripping conditions, i.e. when the pH of strip solution is close to 7, being indicative of the fact that a stronger basic medium is necessary to promote the permeation of metal towards the receiving solution. As can be appreciated, the higher the concentration of sodium carbonate in the back-extraction solution the higher is the permeability of Mo(VI) to the opposite side of membrane. Eq. (9) supports these

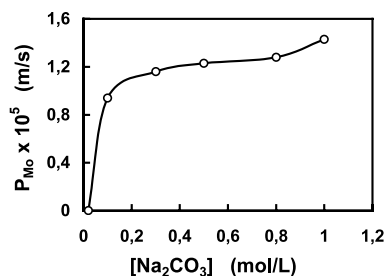


Fig. 7. The effect of Na_2CO_3 molarity on apparent permeability of molybdenum. Feed solution pH: 2. Alamine 336 concentration: 0.02 mol l^{-1} .

results, since as can be observed in it, the rupture of metal–extractant complex formed in the extraction step is enhanced by increasing the basic character of stripping medium when a bigger hydroxyl ions concentration is used. Thus, metal is stripped and the extractant carrier is regenerated and pumped to the extraction interface.

4. Conclusions

A solid supported liquid membrane method of extraction of molybdenum(VI) from acid aqueous solution has been described. A long-chain tertiary amine (Alamine 336) was used as carrier extractant. The following information was obtained:

- 1) Beforehand, the liquid–liquid extraction and back-extraction equilibria behaviour of the carrier were studied in order to establish the suitable conditions for Mo(VI) permeation through the membrane. Taking into account the extraction and stripping equilibria information of Mo(VI) with Alamine 336, a possible mechanism of extraction is examined. The proposed chemical reactions are validated from the experimental results obtained in this study and from a profile of abundance of species of Mo(VI) along the pH range.
- 2) The effect of variation of feed solution acidity, the content of strip agent and the carrier extractant concentration in the organic liquid membrane have been studied with an aim to optimise the metal permeation extraction process. The maximal apparent permeability of molybdenum was achieved when the pH of feed solution is adjusted around a value of 2.0 with sulphuric acid and if a 1.0 mol l^{-1} Na_2CO_3 is employed as stripping solution. The molybdenum(VI) permeation through the liquid membrane was enhanced when a 0.02 mol l^{-1} concentration of the amine carrier in the organic film was used. It was not possible to rise it indiscriminately because a lower transport of metal-complex species occurs due to an important increase of viscosity of the organic phase. The experimental results related with the metal permeation through the

supported liquid membrane are concordant with those obtained in the liquid–liquid extraction equilibrium step.

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References

- [1] C. Yang, E.L. Cussler, *J. Membr. Sci.* 166 (2000) 229.
- [2] S.W. Park, G.W. Kim, S.S. Kim, I.J. Sohn, *Sep. Sci. Technol.* 36 (2001) 2309.
- [3] F. Valenzuela, H. Aravena, C. Basualto, J. Sapag, C. Tapia, *Sep. Sci. Technol.* 35 (2000) 1409.
- [4] F.J. Alguacil, A.G. Coedo, M.T. Dorado, *Hydrometallurgy* 57 (2000) 51.
- [5] Y. Sato, K. Kondo, F. Nakashio, *J. Chem. Eng. Jpn.* 23 (1990) 23.
- [6] N. Tbeur, T. Rhlalou, M. Hlaibi, D. Langevin, M. Metayer, J.F. Verchere, *Carbohydr. Res.* 329 (2000) 409.
- [7] G.O. Yahaga, *Sep. Sci. Technol.* 36 (2001) 3563.
- [8] J. Trocewicz, *J. Sep. Sci.* 24 (2001) 587.
- [9] J. Melling, *Liquid Membrane Processes in Hydrometallurgy: A Review*, Warren Spring Lab., LR, 1979, pp. 1–18.
- [10] M. Ardon, A. Pernick, *J. Less Common Metals* 54 (1977) 233.
- [11] Y. Sato, F. Valenzuela, T. Tsuneyuki, K. Kondo, F. Nakashio, *J. Chem. Eng. Jpn.* 20 (1987) 317.
- [12] J.J. Cruywagen, H.A. McKay, *J. Inorg. Nucl. Chem.* 32 (1970) 255.
- [13] T. Sato, H. Watanabe, H. Suzuki, *Hydrometallurgy* 23 (1990) 297.
- [14] L. Karagiozov, C. Vasilev, *Hydrometallurgy* 12 (1984) 111.
- [15] G.S. Dai, B.Y. Xuan, Y.F. Su, *Hydrometallurgy* 13 (1984) 137.
- [16] F. Valenzuela, S. Poblete, J. Sapag, C. Tapia, C. Basualto, *Bol. Soc. Chil. Quim.* 40 (1995) 25.
- [17] F.R. Valenzuela, J.P. Andrade, J. Sapag, C. Tapia, C. Basualto, *Miner. Eng.* 8 (1995) 893.
- [18] M.E. Campderros, J. Marchese, *J. Membr. Sci.* 164 (2000) 205.
- [19] A.S. Reddy, B.R. Reddy, *Ind. J. Chem.* 19A (1980) 200.

- [20] Y. Sasaki, I. Lindqvist, L. Siller, *J. Inorg. Nucl. Chem.* 9 (1959) 93.
- [21] *Gmelin Handbook of Inorganic Chemistry, Supplement*, vol. B 3b, eighth ed., Springer, Berlin, 1987, p. 67.
- [22] A.N. Zelikman, V.M. Nerezov, *Russ. J. Inorg. Chem.* 14 (1969) 685.
- [23] M.B. MacInnis, T.K. Kim, *J. Chem. Tech. Biotechnol.* 29 (1979) 225.
- [24] L. Karagiosov, Ch. Vasilev, *Hydrometallurgy* 4 (1979) 51.
- [25] M.E. Campderrós, J. Marchese, *Indian J. Chem. Tech.* 1 (1994) 35.