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# A kinetics analysis applied to the recovery of Zn(II) content from mine drainage by using a surfactant liquid membrane

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## ABSTRACT

A kinetics analysis was conducted for the recovery of zinc (II) ions from a mine drainage sample by a liquid surfactant membrane containing di-(2-ethylhexyl)phosphoric acid as a carrier extractant and Span-80 as the surfactant. The extraction of metal was proportional to the concentration of carrier in the organic phase, inversely proportional to the zinc content in the feed solution, and was enhanced as the pH of the feed phase was increased. A minimum sulfuric acid content of 150 g/L in the stripping solution was necessary to favor the transport of metals from the external aqueous solution to the metal-receiving strip liquor. The experimentally observed results were analyzed by a metal extraction kinetics mechanism based on a facilitated transport model, which considers the interfacial chemical reaction between the metal and the carrier at the external interface of the liquid membrane as kinetic controlling step. The experimental results were fairly well explained by the model that takes into account the interfacial activity of both the surfactant and the carrier compound.

***Keywords:*** Surfactant liquid membrane; Zinc; Mine drainage; Kinetics

## 1. Introduction

A major concern in countries, like Chile, has been the determination of the ecological and economic need for more specific systems for the recovery of increasingly scarce metals and/or the removal of toxic metal ions from dilute solutions, which has led to the development of new extractants, ion exchangers, and adsorbents [1,2]. The introduction and application of these new products has improved significantly the selectivity and efficiency of a large number of separation techniques, such as solvent extraction in mixer-settler reactors (SX process) [3], ion-exchange (IX) [4], solvent-impregnated resins [5], and synthetic and natural adsorbents [6,7], among others. The theoretical principles that govern the operation of all these separation processes, as well as their practical technology, have been described in the technical literature, and it can be stated that all of them have some deficiencies that restrain their application under many operational and economic conditions.

In particular, waste and natural waters associated with mining activities are of great concern because of their load of surface and groundwater pollutants. These types of minewaters normally contain many and varied metallic ions. These ions are usually highly toxic

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and are present in such solutions in higher concentrations than those allowed by current regulations related to the emission and discharge of liquid industrial wastes (Standard No. 90/2000 of the Chilean Government). That is, for example, the situation of many waste solutions from industrial chemical processes or liquid residues from ore flotation, leaching, SX, filtration processes, and acid drainages in mining.

However, the metal content in these aqueous solutions is usually low, but often still higher than the legal standard. This makes its removal and recovery technically and economically difficult using available technologies, so there is an absolute and urgent need to introduce novel and improved technologies in this field.

One of the most promising methods that have been being studied in recent years is the use of emulsion liquid membranes (ELM). The ELM process is comprised of a double water-in-oil emulsion stabilized by appropriate surfactants and has several operational advantages, overcoming to a large extent the deficiencies indicated for SX and IX processing. Theoretically, the use of ELM would make it possible to obtain a high extent and rate of metal transport because it presents a higher interface surface area per unit volume compared to other extraction systems. This huge membrane surface area is made possible by the large number of small droplets generated in the double emulsion.

The studies of Li et al. [8] were the first of their kind on the industrial application of ELM, and they are commonly credited as the inventors of this process. Considerable progress has been reported recently by many investigators in the recovery and removal of metals by ELM. However, most of the research reported in the literature is related to work carried out using pure and ideal solutions prepared in the laboratory. Among them, the work of Melzner et al., who have studied the selective separation of Zn(II) from Co(II) and Cu(II) in pure acid solutions using D2EHPA as the carrier extractant and Span-80 as the surfactant [9]. The study of Goto et al. on the use of glutamic acid dialkyl ester and dialky type quaternary ammonium salts as new surfactants in metals extraction from synthetic solutions using an ELM is also of note [10]. Finally, the complete study of Nakashio on the role of surfactants in the behavior of ELMs [11] should be mentioned. Lorbach and Marr have reported a study concerning the recovery of zinc from a pure aqueous solution with water/oil/water ELMs also using dithio-D2EHPA as the extractant. They propose a mass transfer model for carrier-facilitated transport based on the extraction and stripping reaction between the $Zn^{2+}$ ions and the carrier molecules, as well as on the transient diffusion of the loaded carrier molecules into an emulsion globule. Their results indicated that the model was well suited for describing mass transfer phenomena in emulsion globules [12]. They used a single-drop apparatus to test model predictions for actual transfer rates, while our kinetics measurements were achieved using a stirred tank that simulates a conventional industrial membrane extractor. Draxler and Marr, in a study about the phenomenon and industrial applications of ELM, specifically talked about the separation of zinc and copper by this technology. Additionally, they reviewed the mass transfer mechanism of both metals through membranes using different surfactants, extractants, and diluents, and indicated that the practical operation of ELM in a large-scale plant should not generate major problems [13].

Until now, most papers concerning the practical applications of liquid membranes have been published for the recovery of metals from hydrometallurgical leach solutions or the removal of metal ions from acid waste streams [14,15]. An interesting report from Schugerl et al. about the application of the ELM system for the recovery of metals from mining waste waters and zinc liquors has been recently published [16], which constitutes the subsequent paper of these authors after a previous study using pure solutions [9]. Another important study is that reported by Teresa et al. related to the use of sulfur-containing carriers, such as thio-DEHPA and dithio-DEHPA, for the uptake of zinc from zinc plant effluent [17].

There are also numerous papers concerned with the mechanisms that govern metal transport through the membrane, many of them based on mass transfer with chemical reaction phenomena [18–20]. Many models for facilitating transport have been proposed to determine the mechanism of metal extraction. At first, Hochhauser et al. described the concentration of chromium by ELM containing an amine-carrier by considering that all chemical reactions in the membrane are so fast that it can be assumed that they are in equilibrium [21]. Most authors, however, have described the extraction of metals with ELM containing various carrier extractants by assuming that the chemical reactions between the metal ions and the extractant take place at the interface between the feed aqueous solution and the organic membrane [22,23]. Some studies have been published that interpret the experimental results of the extraction rate of metals by ELM by means of chemical models that take into account the interfacial reaction between the metal ions and the carrier [24,25]. Another group of studies are related to the selective transport mechanism of each species through the liquid film, including the effect of flow velocity and other hydrodynamics conditions on the mass-transfer coefficients [26–29].

However, as we mentioned above, most of this work refers to metal extraction from synthetic solutions whose experimental behavior is too ideal to make it comparable with actual industrial residual solutions.

Thus, the main objective of this paper is the application of a metal extraction kinetics mechanism to analyze the experimentally observed data obtained for the extraction of Zn(II) from an acid mine drainage (AMD) sample using an ELM in a stirred tank. The metal permeation mechanism is based on a facilitated transport model, which considers the interfacial chemical reaction between the metal and the extractant at the external membrane interface, as well as the interfacial activity of the carrier and the surfactant. From a practical standpoint, the ELM containing an alkyl-phosphoric carrier and a commercial surfactant allowed the extraction and concentration of most of the metal ions present in the aqueous feed solution.

## 2. Experimental

### *2.1. Materials*

Di-(2-ethylhexyl)phosphoric acid (D2EHPA) used as the carrier extractant for zinc was supplied by Daihachi Chem. Ind., and Span-80 (sorbitan monooleate), a well-known and one of the least expensive nonionic commercial compounds, was used as the surfactant. Span-80 has a molecular weight of 428.6 g/mol, with a suitable hydrophilic/lipophilic balance of 4.3. Industrial-grade aviation kerosene (Esso-Chile, 91% aliphatic compounds) was used as the organic diluent for both compounds, and has a low volatility that inhibits or reduces its loss by evaporation during the strong stirring steps needed to prepare the double emulsion. The extractant, the surfactant, and the diluent were used as received, without further purification. Considering the potential applications of this method in the field of wastewater treatment, the use of commercial compounds in this study was very important, although in this study the main goal was the kinetics analysis of the experimental results.

Samples of a copper extraction raffinate originating from a previous step designed to recover the Cu(II) ion content from the same AMD by ELM with an oximic extractant as carrier were used as the metal-containing feed solution that constituted the external aqueous phase of the liquid membrane system [30]. These acidic aqueous feed solutions had variable pH in the range of 1–4 and sulfate ion concentrations averaging 5 g/L. The original AMD samples had average chemical composition of Cu(II) 350 mg/L, Zn(II) 250 mg/L, Fe 280 mg/L, and minor quantities of other metals like Ca, Mg, Al, and As. The copper extraction raffinate had essentially the same composition, except for its copper concentration, which was almost zero due to its previous removal. In some experiments, the pH of all aqueous solutions was adjusted with sulfuric acid or sodium hydroxide solutions. Sulfuric acid solutions of various concentrations were used as the metal-acceptor stripping aqueous phase.

### *2.2. Procedure*

First, the primary emulsion had to be prepared by vigorous mechanical agitation of the stripping internal aqueous phase and the organic phase. This organic solution was prepared by dissolving the extractant and the surfactant in kerosene. During this step, the stripping solution was dispersed in the organic phase using an OMNI ultrasonic agitator that produced an emulsion with small droplets whose diameter varied from 0.5 to 100 μm. Then, the double emulsion was prepared in a batch-type stirred tank whose temperature was kept constant at 30°C by a water bath. The inner volume of the tank was 1.0 L, with an inside diameter of 6.95 cm and a depth of 21.0 cm. A mixture of 50 mL of the primary emulsion and 250 mL of the feed solution were gently stirred with an IKA-Ruhrwerke RW20 stirrer equipped with a turbine impeller with eight flat blades. Although during the experiments we tested variable volume ratios to prepare the primary emulsion, in most of cases the primary emulsion was prepared using same volumes of organic and stripping solutions. The double emulsion was formed with the droplets of the primary emulsion encapsulated within the external aqueous phase globules. In this way, transport and enrichment of the metal ions from the external aqueous feed phase, across the membrane and to the inner strip liquor was achieved. Samples of all phases were taken at intervals and the metal content was measured by atomic absorption spectrophotometry on a Perkin Elmer 3110 instrument. Prior to the analysis, the raffinate was separated from the loaded primary emulsion by natural settling. In turn, the emulsion was broken using a high-voltage electrostatic coalescer. Adequate analytical reproducibility was achieved during the measurements, with an experimental error that averaged 0.3% taking into account the use of actual aqueous solutions. The acidity of the aqueous solutions was determined with an Oakton-500 pH meter.

## 3. Results and discussion

### *3.1. Zinc recovery from copper extraction raffinate*

After extracting the copper from the original AMD samples by a liquid membrane emulsion process using

5-nonylsalicylaldoxime as carrier [30], the raffinate produced during the extraction contained all the zinc, as well as other metal ions and impurities detected previously in the mine drainage sample. These remnants were not extracted by the oxime extractant at a pH range between 2.0 and 4.0. Therefore, it was necessary to carry out a second stage with a selective zinc extractant to recover it from this copper extraction raffinate.

The alkyl-phosphoric-type carrier D2EHPA was chosen, a widely used commercial acidic extractant [31,32] that, when dissolved in kerosene, is capable of forming a stable zinc-D2EHPA complex that has been widely used in different separations. From a chemical standpoint, this complex is very similar to PC-88A, an alkyl-phosphonic carrier that has been used in previous studies [33,34].

In all the experimental runs a 1,000 min$^{-1}$ stirring speed was used to prepare a stable primary emulsion, together with the use of 2% w/w of the commercial surfactant in the organic phase. The size of the primary emulsion globules was adequate, remained stable during the experiments, and had adequate rupture of the emulsion once the strip liquor was loaded and enriched with metal. Therefore, it was not necessary to increase the amount of Span-80 in the organic phase above 2% w/w, as this was enough to form the emulsion. With respect to the effect of stirring speed on the double emulsion, when using this reactor and the phase volumes indicated, a minimum of 350 min$^{-1}$ was required to assure an appropriate size of the double-emulsion droplets in the interface area for the carrier/metal reaction and to overcome the resistance of the external aqueous phase. Unnecessarily high stirring speeds caused coalescence of the globules, making the primary emulsion unstable and favoring the undesired transport of strip liquor towards the external continuous aqueous phase.

In initial studies concerning the use of ELM to uptake metal ions from aqueous solutions, we had used a multi-variable optimization method in order to get information about the main variables that affected the process and their relationships to each other [35,36]. In this work, and with the purpose of applying and validating the proposed kinetics model, we performed a significant number of experimental runs studying the effect of the most important variables observed in previous studies: the pH and initial metal concentration of the aqueous feed solution, the content of carrier extractant in the organic liquid membrane, and the concentration of the stripping agent in the inner aqueous receiving-solution.

In this type of surfactant liquid membrane, the acidity gradient between the acidic raffinate sample and the receiving strip liquor phase becomes one of the most important driving forces for the permeation of each metal through the organic liquid film. With the purpose of studying the influence of pH of the acidic feed solution on metal transport, several experiments were carried out varying the pH of the produced raffinate in the range of 0.3–5.3. The initial strip liquor consisted of a 150 g/L sulfuric acid solution, and the extractant used to prepare the organic solution was D2EHPA (3% w/w) and Span-80 (2% w/w) in kerosene. Fig. 1 shows the effect of the initial pH of the external aqueous solution, which was the raffinate produced during copper extraction, on the extraction of zinc. It is a plot of the disappearance of Zn(II) from the feed solution over time, expressed as the [Zn]/[Zn$_o$] ratio, where [Zn] and [Zn$_o$] are the remaining metal content in the raffinate and its initial content in the aqueous feed solution, respectively.

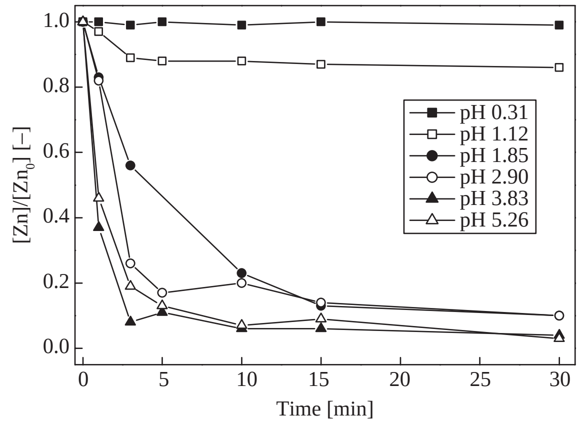

Fig. 1. Influence of feed solution pH on zinc extraction. Feed solution: 250 mg/L Zn; Stripping solution: 150 g/L $H_2SO_4$; organic solution: 3% w/w D2EHPA and 2% w/w Span-80 in kerosene.

The initial pH of feed solution was used because it was a controllable variable, but it became clear that what affected the transport of metal through the liquid membrane was the equilibrium pH. When a good extent of metal transport was achieved, the equilibrium hydrogen-ion concentration in the raffinate tended to increase due to the ion-exchange chemical reaction between the metal ion and the proton of the acid carrier used to prepare the liquid membrane.

From Fig. 1, it is clear that Zn(II) extraction increased with increasing pH of the outer aqueous solution, with transport of this metal to the strip liquor particularly remarkable above pH 2.9. However, zinc extraction was very fast and quantitative when the pH was increased to between 4.0 and 5.0. No important transport of this metal was observed at pH values lower than 1.8.

It has been reported that the transport efficiency of zinc ions through the membrane is strongly dependent

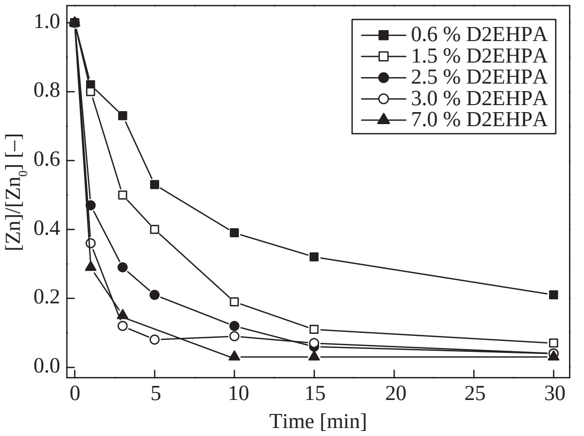

Fig. 2. Effect of carrier content of the organic solution on Zn(II) uptake. Feed solution: 250 mg/L Zn, initial pH 4.0; Stripping solution: 150 g/L $H_2SO_4$; organic solution: D2EHPA and 2% w/w Span-80 in kerosene.

on the type of ligand used as carrier in the organic phase. Among the different extractants used, D2EHPA, an alkyl-phosphoric compound, and PC-88A, an alkyl-phosphonic compound, have shown high efficiency for the permeation of zinc through the liquid membrane, extracting it as the $ZnX_2{\cdot}HX$ or $ZnX_2{\cdot}2HX$ complex. As has been established previously [37,38], this type of carrier normally dimerizes in aliphatic diluents. Both complex structures have been proposed, the prevalence of each depending on the metal to carrier ratio in the outer interface [37,39]. The most probable chemical reaction between the carrier extractant and the zinc ions at the outer interface of the organic liquid membrane is represented by Eq. (1), where HX denotes the acidic alkylphosphonic extractant, $(HX)_2$ is its dimer, and the subscripts ''aq'' and ''org'' denote aqueous and organic solutions, respectively, adjacent to the interface.

$$Zn^{2+}_{aq} + 2\,(HX)_{2org} = ZnX_2 \cdot 2HX_{org} + 2H^{+}_{aq}. \tag{1}$$

The influence of D2EHPA concentration in the organic phase used to prepare the liquid membrane on the extraction of zinc was also studied and the results are presented in Fig. 2. As shown, the results confirmed that the permeation of metal through the liquid membrane was strongly dependent on the concentration of carrier in the kerosene, with a maximum transport occurring at an extractant content above 3% w/w. An additional amount of carrier had no significant influence on the disappearance of metal from the aqueous feed phase. However, it was observed that, the higher the carrier/metal concentration ratio, the greater the possibility to form the $ZnX_2{\cdot}2HX$ complex.

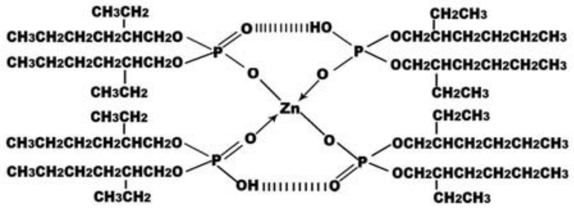

Fig. 3. Structure of the Zn(II)-extractant complex.

Only a carrier content sufficient to fulfill the 1:4 metal-extractant stoichiometry was required to prevent an increase in the membrane's viscosity, which would affect the diffusion of species in the system and, thus the transport of metal through the membrane. Depending on the structure of the metal–carrier complex, however, 4 mol of D2EHPA per mole of Zn(II) were required. It was advisable to avoid an excess of extractant with respect to the Zn ions existing in the raffinate because that would enhance the co-extraction of other metal ions present in the feed solution. Fig. 3 shows the structure of the complex of Zn(II) ions with the alkyl-phosphoric extractant. Two molecules of extractant participate, forming the complex binding the metal, and two other molecules act by forming a solvating structure.

To study the influence of zinc content on the aqueous feed phase, different experiments were carried out varying the metal concentration from 92 to 1,019 mg/L in the raffinate used in this study. Fig. 4 shows the results obtained when the zinc content was varied over the above range. In all the experiments, the same carrier concentration in the organic solution was used. As expected, the extent of extraction was higher

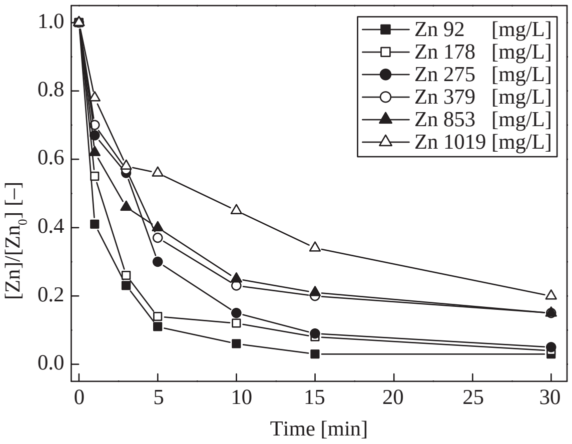

Fig. 4. Dependence of Zn(II) extraction on feed zinc content. Feed solution: initial pH 4.0; Stripping solution: 150 g/L $H_2SO_4$; organic solution: 3% w/w D2EHPA and 2% w/w Span-80 in kerosene.

as the level of metal in the feed solution decreased, which was reasonable considering the maximum metal loading capacity of the organic solution in the feed side of the membrane. In previous studies, however, it has been found that the metal flux [mol metal transported/s cm$^2$] was strongly affected by the initial metal concentration in the feed phase, indicating that an increase of metal content in the feed phase brought about a decrease in metal extraction while simultaneously enhancing the metal transport rate [32]. Unlike what happened in the SX process, when using ELM, it was not necessary to use a large inventory of extractant if there was a high metal content in the feed solution, because this compound was regenerated constantly as the extraction and stripping stages occur simultaneously on each side of the liquid membrane.

Once the metal had been transported to the organic phase of the ELM, it diffused as a metal–carrier complex species towards the inner interface of the emulsion droplet, where it underwent the back-extraction chemical reaction with the stripping agent. If the stripping stage did not proceed efficiently, the ELM became impractical. Several experiments were carried out to study the influence of sulfuric acid concentration in the stripping agent on Zn(II) ion transport with the alkylphosphoric extractant. Fig. 5 shows the effect of acid concentration on the back-extraction of metal at the inner membrane interface. Stripping efficiency increased nearly 100% when the concentration of sulfuric acid was over 150 g/L and when using times longer than 5 min. Further increases in acid concentration did not produce any measureable effect, but on the contrary, it could have contributed to the degradation of carrier and surfactant molecules. It is well known that during this step, the hydrogen ions supplied by the stripping agent displace the zinc ions from the organic–soluble complex. Thus, the metal–carrier complex is broken up and the carrier extractant is regenerated for a new extraction-stripping cycle. In general, it has been found that the stripping rate is very fast compared to the extraction rate at the outer interface of the emulsion droplets, so it can be assumed that the amount of extractant in the membrane is sufficient and practically constant. These observations would explain the possibility of achieving a huge number of extraction-stripping cycles by using the same primary emulsion stock, which was one of the major advantages of the SLM process with respect to conventional SX in mixer-settler reactors.

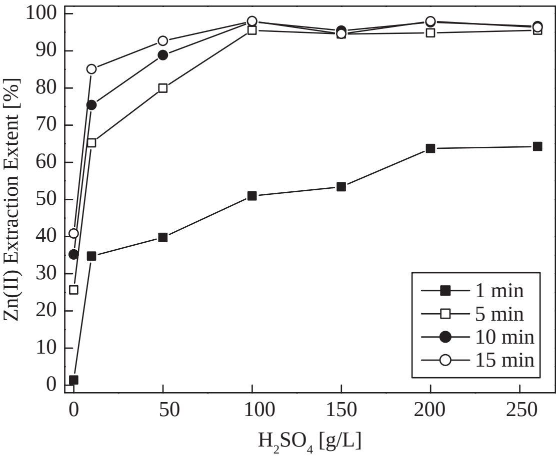

Fig. 5. Influence of sulfuric acid content in internal aqueous solution on zinc removal. Feed solution: 250 mg/L Zn, initial pH 4.0; organic solution: 3% w/w D2EHPA and 2% w/w Span-80 in kerosene.

Some experiments were carried out to measure the enrichment of the strip liquor with metal. For that purpose, the same fraction of primary emulsion was treated with fresh zinc feed solution at pH 4.5, containing a Zn(II) level of approximately 1.76 g/L in the final strip liquor, which is a several-fold enrichment with respect to the initial Zn(II) content in the AMD sample. Copper had been extracted in the former stage, and most of the iron, present as Fe(III), precipitated around pH 3.0, which made it necessary in some cases to filter the aqueous solution before its treatment in the ELM extractor. It was found that Ca and Mg could only be extracted by using a carrier above pH 6.0, and arsenic, which is usually present in this kind of acid solution as an anionic species, was not extractable by this cation-exchange extractant. No detectable aluminum was extracted under these conditions.

### *3.2. Kinetics analysis of experimental results*

In order to account for the experimental results obtained in this study, a mechanism for the metal permeation through the membrane was studied. The model was based on a facilitated transport model that considered the interfacial reaction between the metal and the carrier at the outer interface of the membrane. This information, in turn, was deduced from the extraction kinetics information obtained in our previous work, and from analogous models found in the literature. The model assumed that the water droplets inside the emulsion globule moved freely, contained a uniform average zinc content [18,30] and that the permeation of the metal would occur through an interfacial reaction mechanism due to the interfacial activity of the alkylphosphoric carrier. The zinc extraction mechanism by a liquid membrane containing the carrier extractant D2EHPA was predicted to proceed by: (1) metal ions diffusing from the bulk feed solution to the external interface of the emulsion droplet; (2) reacting zinc ions at the external interface with the dimer of D2EHPA as described by Eq. (1), which represents the metal extraction equilibrium; (3) the diffusion of the zinc-extractant complex into the emulsion droplet; and (4) the occurrence of an interfacial stripping reaction between the metal complex and the stripping agent, sulfuric acid, at the interface of the internal aqueous droplet in the emulsion globule.

In the organic phase, the dissolved carrier extractant, HX, dimerizes, and is then adsorbed at the interface according to the following reactions [40]:

$$2\mathrm{HX}_{\mathrm{org}} \leftrightarrow (\mathrm{HX})_{2\mathrm{org}}, K_{\mathrm{D}} \tag{2}$$

$$(\mathrm{HX})_{2\mathrm{org}} \leftrightarrow (\mathrm{HX})_{2\mathrm{ad}}, K_{(\mathrm{HX})_2} \tag{3}$$

where $K_{\mathrm{D}}$ represents the dimerization constant of the carrier, $K_{(\mathrm{HX})2}$ is the adsorption equilibrium constant of the dimer, the subscript ''ad'' denotes adsorbed species at the interface, and ''org'' denotes the organic solution adjacent to the interface.

The adsorbed dimer species would react with zinc ions at the interface following an ion-exchange reaction to form the metal complex extracted into the organic phase as follows:

$$\mathrm{Zn}^{2+}_{\mathrm{aq}} + (\mathrm{HX})_{2\mathrm{ad}} \leftrightarrow \mathrm{ZnX}_{2\mathrm{ad}} + 2\mathrm{H}^{+}_{\mathrm{aq}}, K_{\mathrm{ZnX}_2}, \tag{4}$$

$$\mathrm{ZnX}_{2\mathrm{ad}} + (\mathrm{HX})_{2\mathrm{org}} \overset{k}{\longleftrightarrow} \mathrm{ZnX}_2\ 2\mathrm{HX}_{\mathrm{org}}, \tag{5}$$

where $K_{\mathrm{ZnX2}}$ corresponds to the equilibrium constant of the reaction represented by Eq. (4), and $k$ is the forward reaction rate constant of Eq. (5). It was clear that, in the ELM process, the surfactant, an interfacially active compound, competed with the carrier for the vacant active adsorption sites. In this sense, Eq. (6) expresses the adsorption equilibrium of surfactant at the interface, where $K_{\mathrm{S}}$ is the adsorption equilibrium constant of the surfactant

$$Sf_{\mathrm{org}} \leftrightarrow Sf_{\mathrm{ad}}, K_{\mathrm{s}}. \tag{6}$$

Analyzing the metal extraction mechanism shown above, the diffusional resistances in the aqueous phases (step 1) and membrane (step 3) would be rather small [41]. Then, the interfacial reaction step shown by Eq. (5), i.e., the formation of the metal–carrier complex at the interface (step 2), could be considered the rate-controlling step, because $\mathrm{ZnX}_{2\mathrm{ad}}$ would also have interfacial activity. Furthermore, the stripping reaction (step 4) was very fast, as the experimental results showed, making it possible to neglect the reverse reaction in Eq. (5).

Therefore, the calculated reaction rate, $J_{\mathrm{Zn,\ calc}}$, could be expressed as follows:

$$J_{\mathrm{Zn,calc}} = \frac{k[\mathrm{ZnX}_2]_{\mathrm{ad}}[(\mathrm{HX})_2]_{\mathrm{org}}}{\Theta_{\mathrm{ad}}}, \tag{7}$$

where $J_{\mathrm{Zn}}$ is expressed in [mol/cm$^2$ s] and the species concentrations in [mol/cm$^3$]. In this equation, $\Theta_{\mathrm{ad}}$ is the total number of vacant adsorption sites for the adsorption interfacial reaction, which includes, according to Langmuir's adsorption isotherm, the fractions of interfacial area covered by the carrier HX, its dimer $(\mathrm{HX})_2$, the metal–carrier complex $\mathrm{ZnX}_2$, and the surfactant $S_f$. Combining Eq. (4) and Eq.(3) it is possible to obtain an expression for $[\mathrm{ZnX}_2]_{\mathrm{ad}}$, and Eq. (7) can be rewritten as:

$$J_{\mathrm{zn,calc}} = \frac{kK_{\mathrm{ZnX}_2}K_{(\mathrm{HX})_2}}{\Theta}\frac{[\mathrm{Zn}^{2+}][(\mathrm{HX})_2]^2}{[\mathrm{H}^+]^2}. \tag{8}$$

The hydrogen-ion concentration, $[\mathrm{H}^+]$, was calculated using the initial pH and the stoichiometry of the metal-extraction chemical reaction involved in the process. This value was then compared with the experimentally measured values.

Assuming Langmuir's adsorption isotherm, $\Theta_{\mathrm{ad}}$ can be expressed as follows:

$$\begin{aligned}\Theta_{\mathrm{ad}} = 1 &+ K_{\mathrm{HX}}\ [\mathrm{HX}] + K_{(\mathrm{HX})_2}\ [(\mathrm{HX})_2] \\ &+ K_{\mathrm{ZnX}_2}\ [\mathrm{ZnX}_2] + K_{\mathrm{s}}[Sf].\end{aligned} \tag{9}$$

Considering the important interfacial activity of the surfactant and that of the carrier, which in this study, exists basically as the dimer under these experimental conditions, the third and fifth terms of Eq. (9) would be considerably bigger than the others [10]. With this information, Eq. (9) could be rewritten in the following simplified form:

$$\Theta_{\mathrm{ad}} = K_{(\mathrm{HX})_2}[(\mathrm{HX})_2] + K_{\mathrm{s}}[Sf]. \tag{10}$$

Introducing Eq. (10) into Eq. (8), the following expression for the calculated reaction rate was obtained:

$$J_{\mathrm{Zn,calc}} = \frac{k_f[\mathrm{Zn}^{2+}][(\mathrm{HX})_2]^2[\mathrm{H}^+]^{-2}}{K_{(\mathrm{HX})_2}[(\mathrm{HX})_2] + K_{\mathrm{s}}[Sf]}, \tag{11}$$

where $k_f = [(kK_{\mathrm{ZnX2}}K_{(\mathrm{HX})2})/S_{(\mathrm{HX})2}]$ corresponds to the overall rate constant, i.e., the interfacial reaction constant calculated considering the interfacial

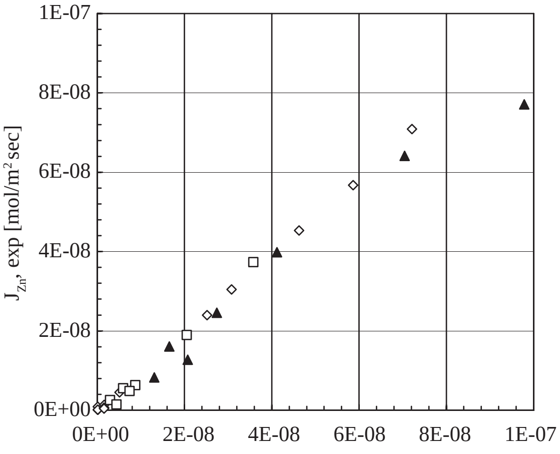

Fig. 6. Comparison between the calculated and experimentally observed values of the extraction rate.

area occupied by one mole of the interfacially active dimer, $S_{(HX)2}$[42].

On the other hand, the experimentally observed transfer rate of Zn(II) ions per unit surface area of emulsion droplet, $J_{Zn,\ exp}$, could be determined as

$$J_{Zn,exp} = -\frac{V_{aq-ex}}{A_{em}}\frac{d[Zn^{2+}]}{dt}, \tag{12}$$

where $V_{aq\text{-}ex}$ is the volume of external aqueous phase, $A_{em}$ is the total surface area of the emulsion droplets, and $d[Zn]/dt$ was the change in metal concentration over time. $A_{em}$ could be estimated from the total volume of the emulsion droplets, $V_{em}$, and the surface area and volume of each drop, $S_{drop}$ and $V_{drop}$, as explained previously [30].

The flux of metal could then be rewritten as

$$J_{Zn,exp} = -\frac{V_{aq-ex}}{V_{em}}\cdot\frac{D}{6}\cdot\frac{d[Zn]}{dt}, \tag{13}$$

where $D$ denotes the average emulsion droplet diameter. Using the values of $k_f = 1 \times 10^{-3}$ cm/s and $K_{(HX)2} = 1.8 \times 10^6$ cm$^3$/mol reported by Nakashio [43] $K_S$ becomes $5.2 \times 10^7$ cm$^3$/mol [24], and the experimental parameters measured in this study ($V_{aq\text{-}ex}$, $V_{em}$, $D$). Fig. 6 compares the experimentally obtained values $J_{Zn,\ exp}$ obtained from Eq. (13) with the calculated values $J_{Zn,\ calc}$, according to the interfacial reaction mechanism of metal extraction by ELM expressed by Eq. (11). Fig. 6 shows a good correlation between the experimental results and those calculated using the mechanism indicated in this study, which accounted for the obtained results and validated the theoretical assumptions made to explain the recovery of Zn(II) from the copper extraction raffinate. There was a slight disagreement between the calculated and the experimental metal flux values in the region of higher reaction rates, which in general, corresponded to values found when a greater extractant content was used to prepare the liquid membrane, or when a higher metal concentration was present in the external aqueous solution.

## 4. Conclusions

Important mechanistic data was generated from the study of the recovery of Zn(II) ions from a mine drainage by means of an ELM process using an alkyl-phosphoric extractant (D2EHPA) as metal carrier through the liquid membrane. It was found that the extraction of zinc increased as the initial pH of the aqueous feed solution increased, and the extraction was very fast and quantitative when the pH was adjusted to a value of 4.0. Zn(II) transport through the membrane was found to be proportional to the concentration of alkyl-phosphoric carrier in the organic phase and inversely proportional to the zinc content in the metal-containing solution.

The metal stripping reaction at the internal interface of the liquid membrane was very fast, with zinc extraction favored when the sulfuric acid concentration in the metal-receiving aqueous phase was higher than 150 g/L. In addition, the alkyl-phosphoric carrier extractant transported zinc selectively, achieving a substantial degree of enrichment from the feed solution to the strip liquor when a low inventory of extractant and a suitable volume ratio of the two aqueous solutions was used.

Finally, a mechanism for the facilitated transport of metal in the membrane was proposed for analysis of the observed experimental results. It was found that the results could be explained by considering the interfacial reaction between the metal and the extractant at the outer membrane interface, taking into account the interfacial activity of the surfactant and of the carrier that existed as a dimer in the organic phase.

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