

TRANSPORT OF Zn(II), Cu(II), AND Ni(II) ON HOLLOW FIBERS-TYPE SOLID SUPPORTED LIQUID MEMBRANES

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ABSTRACT

This study reports on the transport and separation of Zn(II), Cu(II), and Ni(II) ions via a hollow fiber-type solid supported liquid membrane extractor. Alamine 336, a long chain tertiary amine was used as carrier extractant. The results of liquid-liquid extraction equilibrium measurements of these metals indicate that separation of zinc from copper and nickel is favored at a feed phase of acid concentration below 3.0 mol/L HCl using bidistilled water as acceptor solution. Measurements of permeations of these metallic ions through the liquid membrane indicate that the transport of metals is strongly affected by: the content of carrier extractant in organic solvent; the HCl concentration in the feed solution; and the volumetric flow rate of the stripping solution. By decreasing HCl concentration in the feed phase, the separation factor of Zn(II) from Cu(II) increases and the recovery of both metals decreases. Ni(II) ion was not transported during the entire experiment.

Key Words: Liquid membranes, hollow fibers, extraction, zinc, copper, nickel.

RESUMEN

En este estudio se informa sobre el transporte y la separación de los iones Zn(II), Cu(II) y Ni(II) en un extractor de membrana líquida de soporte sólido del tipo "fibras huecas". Como extractante transportador se utilizó Alamine 336, una amina terciaria de larga cadena alquílica. Los resultados de los experimentos de equilibrio de extracción líquido-líquido de estos metales indican que la separación de zinc de cobre y níquel es favorecida al emplear una solución de alimentación de 3,0 mol/L de HCl y al usar agua bidestilada como solución aceptora. Los experimentos de medición de permeación de estos iones metálicos a través de la membrana líquida indicaron que el transporte de los metales es fuertemente afectado por la concentración del extractante transportador en el

solvente orgánico, por la concentración de HCl en la solución de alimentación y por la velocidad de flujo de la solución de retroextracción. Al disminuir la concentración de HCl en la fase de alimentación, el factor de separación de Zn(II) de Cu(II) aumenta, disminuyendo la recuperación de ambos metales. Ni(II) no fue transportado bajo las condiciones experimentales de este estudio.

Palabras Claves: Membranas líquidas, fibras huecas, extracción, zinc, cobre, níquel.

INTRODUCTION

Membrane technology is slowly but continuously becoming a very important and promising alternative to the current processing practices normally employed for wastewater treatment, environmental decontamination, and, metals recovery from residual solutions generated by ores leached or from mine waters^{1,3}.

Particularly in the fields of valuable metals recovery and removal of undesired metals from mining or industrial solutions, techniques such as ion-exchange on solid resins, chemical precipitation, and solvent extraction are being regularly applied with many inconveniences and disadvantages^{4,5}.

In recent years these technological alternatives have incorporated liquid-liquid extraction processes using solid supported liquid membranes (SSLM). There are two kinds of liquid membranes that are capable of being used in hydrometallurgy: surfactant liquid membranes corresponding to double water-in-oil-emulsion^{6,7}; and solid supported liquid membranes. The solid support is constituted by a thin and microporous polymeric structure which is retained by capillary effect, an organic solvent containing a selective extractant that acts as carrier for metals. The metallic ions are carried from the feed donor solution through the solid membrane wall towards the acceptor strip liquor by coupled or facilitated transport mechanisms⁸⁻¹⁰.

In previous papers¹¹⁻¹⁷ we have investigated the extraction behavior of some metals by different extractants on solid supported liquid membranes using flat films and hollow fiber-types. We have attempted to elucidate the metal transfer mechanism. The results have been explained by a diffusion model which predicts that the extraction chemical reaction would occur at the interface of the liquid membrane. In another study we have explained the results through a heterogeneous interfacial reaction model that considers interfacial adsorption of extractant at the interface between the phases¹⁸.

The right choice of extractant and organic diluent and stripping agent was found to be the key factor in determining an effective liquid membrane system for the recovery of metals.

In this work, the transport and separation of Zn(II), Cu(II), and Ni(II) ions by Alamina 336 [tri.(C₈C₁₀)amine] -an ion-pair extractant- is studied using a hollow fiber-type solid supported liquid membrane extractor.

The influence of different variables such as extractant concentration in organic solvent, and the acidity of feed solution and flow rates of phases were analyzed.

This research will form the basis for developing a practical membrane-based solvent extraction process capable of achieving selective separation and enrichment of the above-noted metals from industrial waste solutions. The information deduced from this work will contribute to the construction of a pilot-scale extractor module.

EXPERIMENTAL

Materials

Alamine 336[tri-(C₈-C₁₀)amine], a tertiary amine from Chile Hartig-Henkel was used without further purification as the extractant of the organic solvent for distribution equilibrium measurements and for permeation experiments in the hollow fiber membrane extractor. n-Hexane of commercial GR grade was used as the amine diluent in all experiments. No phase modifier reagent was required during the extraction tests. A good phase separation was observed.

The aqueous feed solutions were prepared by dissolving ZnCl₂, CuCl₂, and NiCl₂ in hydrochloric acid at varying concentrations. The initial content of all metallic ions in feed solution was 100 mg/L. In order to determine the appropriate conditions for the stripping stage, the metal-loaded organic phases were contacted with HCl solutions and bidistilled water. These experiments were conducted at 25°C.

The permeation experiments were measured at the same temperature using the membrane extractor described in a previous paper⁶. The extractor is comprised of a glass shell and hollow fibers made of poly(tetrafluoroethylene). The fibers were supplied by Japan Goretex Co. Ltd. The inner and outer diameter of the hollow fibers used were 0.85 and 1.80 mm, respectively. Effective length of the fiber: being 0.20 m; the maximum membrane pore size: 2.0 μm.; porosity factor: 0.80. The inner diameter of the extractor glass tube: 10.0 mm.

Procedure

First of all, metal extraction equilibrium measurements were carried out by contacting in separatory funnels equal volumes of the feed solution and the organic solvent during six hour enough to allow equilibrium to be reached. Stripping equilibrium determinations were accomplished by following the same procedure; that is, by placing into contact equal volumes of the metal-loaded organic solution with the stripping solutions.

With respect to metals transport measurements, the experiments were carried out in an extractor module formed by five fibers arranged inside a jacketed glass shell to assure that the water carrying our the runs circulated at a constant temperature (25°C). Using microtube pumps, the aqueous feed solution was circulated through the inner side of the fibers and the stripping solution by the outer side in a cocurrent way. Previously, the organic solution had been circulated through the fibers. Due to the hydrophobic character of the fibers, the porous structure of the membranes are filled rapidly with the solvent containing the "carrier" extractant. Similar pressures at both side of membrane (fibers) were maintained in order to retain the organic solvent impregnated in the solid structure of membrane.

The metal concentrations were determined by atomic absorption spectrophotometry in a GBC-902 apparatus. The aqueous phase samples were measured directly. The content of metallic ions at the organic phase samples were calculated by mass balance considering metal concentrations at feed solutions and raffinates.

RESULTS AND DISCUSSION

Liquid-liquid extraction

In liquid-liquid extraction studies the results of distribution equilibrium are expressed as extraction extent, (%E), as follows:

$$\%E = \left(\frac{[Me]_{org}}{[Me]_{org} + [Me]_{aq}} \right) \cdot 100 \quad (1)$$

where $[Me]_{org}$ and $[Me]_{aq}$ denote metal concentration at equilibrium in organic and aqueous phases respectively. In Figure 1 is shown the extraction percentage of metals as a function of hydrochloric acid concentration.

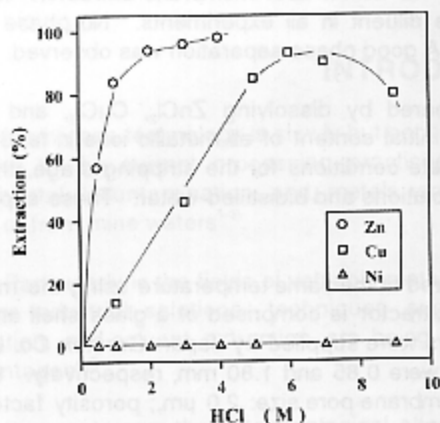
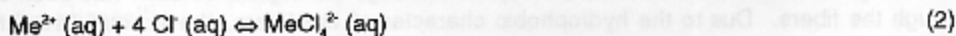


FIG. 1. The effect of hydrochloric acid concentration on metals extraction extent. Feed solution: 100 mg/L metal chloride; Organic phase: 5% v/v Alamine 336 in n-hexane.

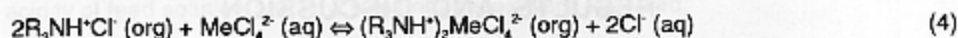
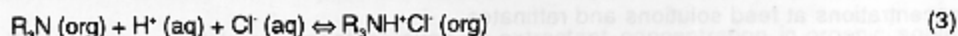
Figure 1 shows that the influence of HCl concentration on extraction extent is different for each metal. A quite good extraction is reached for zinc when HCl concentration is as low as 0.1 mol/L. The extraction of copper into organic phases can be increased by increasing HCl concentration to a maximum value of 5.0 mol/L, while nickel extraction is negligible over all acid concentration ranges studied. Hence, these results support the feasibility of bringing about the separation of these metals with Alamine 336.

This unlike behavior in the extraction of these metallic ions can be ascribed to the fact that in the HCl aqueous medium, Zn(II) and Cu(II) are capable of forming very stable $MeCl_4^{2-}$ -type anionic complexes according to the following equation:



Nickel ions do not have the tendency to form such anionic chloro complexes which is clearly exhibited in Figure 1.

The extraction mechanism of Zn(II) and Cu(II) by the tertiary amine in HCl aqueous solutions may be explained by the following equations:



Equation 3 represents simple amine salt formation while Equation 4 represents true ion exchange. Alamine 336 contains a basic nitrogen capable of forming amine salts with a wide variety of inorganic acids -as HCl- and organic acids. This extractant acts on the principle of ion association. R_3NH^+ , a large positively-charged organic species, produces the extraction of a large anionic metal complex ($MeCl_4^{2-}$) in the organic phase and at the same time causes the expulsion of a small common chloride anion to the raffinate.

Thus, the $(R_3NH^+)_2MeCl_4^{2-}$ species is formed, which is soluble only in the organic solution. A greater affinity of Cl for the amine implies a larger amine salt formation. The bigger the stability of $MeCl_4^{2-}$ anion in the aqueous medium, the bigger the extent of anion exchange reaction. In the same way, as the relative affinity of $MeCl_4^{2-}$ for the organic cation (R_3NH^+) increases, the extraction reaction indicated in Equation 4, proceeds largely and fastly.

Several tests of zinc stripping were carried out using HCl solutions and bi-distilled water. The results shown in Table I indicate that the back-extraction of this metal increases as the HCl concentration in the stripping solution decreases. Amine type extractants can be stripped with a wide variety of inorganic ions solutions such as Cl^- , OH^- , CO_3^{2-} or SO_4^{2-} . The right choice of stripping agent depends on the overall recovery process, but it is obvious that the performance of this back-extraction step is favored when the deprotonation of amine is facilitated.

The results of Table I agree with equations 3 and 4 which indicate that the stripping of metal anionic complexes is enhanced at low HCl concentration. Under that condition the free base is regenerated.

TABLE I. Stripping extent of zinc.

Stripping solution	Zinc stripping extent (%)
Bi-distilled water	90
2 M HCl	80
8 M HCl	0

An analysis of Figure 1 allows us to select the best experimental conditions to operate the permeation tests in the membrane extractor with the view toward optimizing the selective extraction and selective separation of metals.

The figure indicates that, it is convenient to maintain a low hydrochloric acid concentration, around 2.0 mol/L, at donor feed solution in the inner side of the membrane. The level of HCl promotes a higher extraction rate of zinc towards the organic phase and makes possible a bigger Zn/Cu separation, while nickel is not extracted at all. The different extraction order is an effect of the ease of formation of the anionic metal chloride species.

If the purpose was to separate nickel from copper, the optimal concentration of HCl at feed solution would be around a value of 5.5 to 6.0. Larger concentrations of HCl should produce a lower copper extraction extent due mainly to the competitive extraction of the acid, probably polyprotonated anionic species as HCl_2^- .

In the case of stripping solution to be circulated by the outer side of fibers, the results obtained suggest that the hydrochloric acid concentration should be kept at a very low level, yielding even better results when water is used as the strip agent.

Permeation experiments in the membrane extractor

Several experimental runs were accomplished in order to study the transport of Zn(II), Cu(II) and Ni(II) through the hollow fiber-type membrane using Alamine 336 as carrier. A feed solution containing 100 mg/L of each metal as chloride in 3.0 mol/L HCl aqueous solution and bi-distilled water as stripping phase were circulated through the extractor. The volumetric flowrates of both solutions were about $1 \cdot 10^{-6}$ m³/sec. The results of transport using the hollow fiber-type liquid membrane impregnated with organic solvents containing different proportions of Alamine 336 in n-hexane are presented in Figure 2.

The average transport percentage of ions, %T, is given by the following equation:

$$\%T = \{1 - ([Me]_{out}/[Me]_{in})\} \quad (5)$$

$[Me]_{out}$ and $[Me]_{in}$ being the metal concentration of donor solution at outlet and inlet of extractor respectively. In Figure 2 it is observed a transport (%T) enhancement of Zn(II) and Cu(II) as the carrier concentration at liquid membrane increases, being reached a maximum value when the pore structure of fiber was impregnated with a concentration of Alamine 336 around a value of 30%. After this point the transport extent of these metals decreases, probably because an important rise of the viscosity of organic phase occurs which implies a strong diminution of diffusion rate of the extractant and its complex with metals species. It can be observed that nickel was not transported through the membrane for the entire range of amine concentrations which is consistent with the extraction equilibrium study. Similar results were described in a previous report but using a flat-type solid supported liquid membrane¹³.

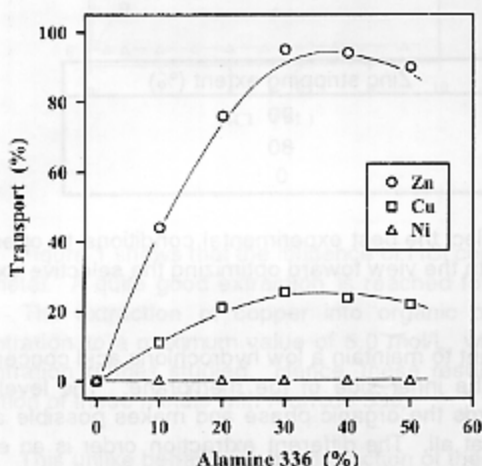


FIG. 2. Dependence of metals transport on concentration of extractant Alamine 336. Feed solution: 100 mg/L metal chloride in 3.0 M HCl; Stripping solution: bi-distilled water.

Experiments were also performed in order to measure the transport of these metals varying the volumetric flowrate of stripping solution. Feed solutions consisted of 100 mg/L of each metal in 3.0 mol/L HCl, using bi-distilled water as the receiving strip liquor.

The fibers were impregnated with a 30% v/v Alamine 336 dissolved in n-hexane. Feed solution was circulated at $1 \cdot 10^{-5}$ m³/sec and the strip liquors were pumped in a range of $1 \cdot 10^{-6}$ and $2.5 \cdot 10^{-5}$ m³/sec at 25°C. Figure 3 shows the experimental results reached in these runs.

From Figure 3, it is observed a decrease of metal transport for Zn(II) and Cu(II) as the stripping solution volumetric flowrate is increased, which is explained due the shortening of residence time of this phase in the extractor bringing about less contact time between this aqueous phase and the liquid membrane.

However, these results must be considered together with the fact that a similar pressure should be assured on both sides of the membrane in order to retain the impregnated carrier in the pore structure of the fiber. Further experiments have to be carried out addressing this point to prevent leakage of organic solvent from the fiber wall and a faulty performance of liquid membrane.

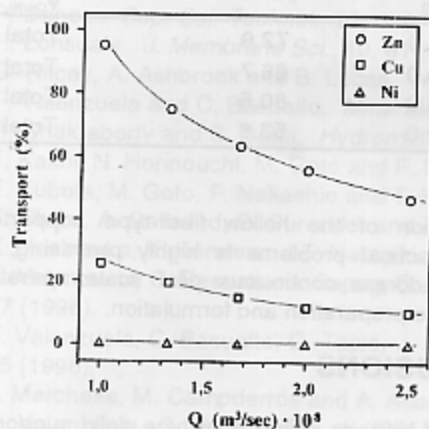


FIG. 3. Change of metals transport with volumetric flowrate of stripping solution. Feed solution: 100 mg/L metal chloride in 3.0 M HCl. Stripping solution: bi-distilled water; organic phase: 30% v/v Alamine 336 in n-hexane.

One of the more important variables influencing the permeation rate of metals and the feasibility of separating them by using liquid membranes is the acidity of the feed solution, as was noted in distribution equilibrium studies. Some experiments varying the concentration of hydrochloric acid at feed solutions to a range between 0.5 to 3.0 mol/L utilizing water as the acceptor solution were carried out. Metallic ions content at feed phase were 100 mg/L running both extractor at intervals of one hour. In these experiments, the impregnation of hollow fibers porous structure was accomplished with an organic solvent containing 30% v/v Alamine 336 in n-hexane.

Separation factors, (ϕ_{A-B}) , were calculated by the following expression:

$$\phi_{A-B} = \left(\frac{[A]_{SL}}{[A]_R} \right) \cdot \left(\frac{[B]_R}{[B]_{SL}} \right) \quad (6)$$

where A and B represent metals A and B respectively, suffixes "SL" and "R" denote strip liquor (acceptor solution) and raffinate (donor solution), being all the concentrations measured at extractor outlets.

In Table II is shown the effect of hydrochloric acid concentration at feed solution on the recovery extent (%) and separation factors of each metal. We can clearly appreciate that the increase of acidity of feed phase strongly influences the recovery of Zn(II), while the Cu(II) extraction is only moderately affected and Ni(II) was not completely recovered. These results are in agree with the observation that Ni(II) can be selectively separated from a solution containing the other metals. The feasibility of separating zinc from copper is good, being improved by lower HCl concentrations at feed solutions.

Further studies on solid supported liquid membranes processes (SSLM) are required, however these results confirm that this technology is an interesting alternative to current conventional solvent extraction (SX) and ion-change (IX) processes for valuable metals recovery or undesired ions removal, especially from dilute solutions. SSLM is a simpler process than SX and IX, since the extraction and stripping operation are combined and considerably less solvent or resin is required.

TABLE II. Metal recovery (%) and separation factor (ϕ)

HCl (M)	Metal Recovery (%)			ϕ_{Zn-Cu}	ϕ_{Zn-Ni} ϕ_{Cu-Ni}
	Zn	Cu	Ni		
0.5	77.8	4.2	0.0	72.9	Total
1.0	81.0	6.5	0.0	66.7	Total
2.0	87.9	14.3	0.0	60.5	Total
3.0	94.9	25.6	0.0	53.8	Total

Therefore, we believe that the application of the hollow fiber-type supported liquid membrane technology for resolving industrial practical problems is highly promising, although further studies are necessary that particularly address continuous pilot scale operations and improvements in process equipment and membrane preparation and formulation.

CONCLUSIONS

A process of transport of Zn(II), Cu(II) and Ni(II) on hollow fiber-type solid supported liquid membranes has been studied. Measurements of liquid-liquid extraction equilibrium and permeation of these metals with Alamine 336 in n-hexane were accomplished at 25°C. From the distribution equilibrium results could select the best permeation conditions. It was found that separation of zinc from copper and nickel is favored at a feed phase with an acid concentration below 3.0 mol/L HCl and using bi-distilled water as the acceptor solution.

In the continuous membrane extractor it was noted that the effect of hydrochloric acid concentration at feed solution presented the following effects: the recovery of Zn(II) is enhanced when increasing the acid content at feed phase; the copper transport reaches a maximum around 5.5 mol/L HCl being observed a diminution of this metal permeation for higher acidity; while nickel is not completely extracted in all the range studied.

The separation factors indicate that it is possible to separate totally Ni(II) from Zn(II) and Cu(II). The separation of Zn(II) from Cu(II) is enhanced as HCl content at feed solution decreases.

The transport of Zn(II) and Cu(II) is positively influenced by the extractant concentration used to impregnate the solid support of liquid membrane. However, a maximum value of 30% Alamine 336 must be utilized because a decrease of permeation is produced probably due to the excessive increase in viscosity of the organic phase, thus reducing the diffusivity of extractant and metallic species in the porous structure of fibers.

Finally, a higher volumetric flowrate of receiving strip solution produces a lower metal permeation, due the shortening of residence time of this phase in the extractor bringing about less contact time between this aqueous phase and the liquid membrane. Special care must be taken in order to assure a good pressure balance at both sides of the membrane to prevent organic solvent leakage from the fiber wall.

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