Selective Emulsion Liquid Membrane Extraction of Cu(II) Mediated by a Schiff Base Ligand

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ABSTRACT: *This study concerns the application of a Schiff base ligand of type N_3O_2 as a carrier in a water-in-oil emulsion liquid membrane for the selective transport of copper ions. A hydrochloric acid solution formed the internal aqueous phase (receiving phase), and the membrane was composed of a Schiff base ligand called bis(1'-hydroxy-2'-acetonaphthone)-2,2'-diiminodiethylamine (**L**) in dichloromethane and the non-ionic surfactant Span® 80 in paraffin. By applying the optimum conditions, a quantitative uptake of copper ions (initial concentration 5 mg L^{-1}) from the aqueous feed phase (pH 5) into the receiving phase (hydrochloric acid 0.7 mol/L), after 10 min was attained. The optimal value determined for the treat ratio allows achieving a concentration factor of >6 for the copper ions in the receiving phase. The proposed emulsion liquid membrane provided an excellent selectivity towards copper ions with respect to some associated metal ions including Cd(II), Ni(II), Zn(II), Co(II), Fe(II), and Cr(III). However, such selectivity was not observed in the competition of Cd(II) and Pb(II) ions. The breakage of emulsions and recovery of the internal phase from the membrane was performed by freezing the internal solution. The expansion of the frozen internal phase volume results in the breakage of the emulsions. The applicability of the proposed procedure was appraised by employing the method for the recovery of copper from the leached solutions of the cobalt and nickel-cadmium filter cakes of a zinc production plant.*

KEYWORDS: *Facilitated transport; Phase dispersion liquid membrane; Copper recovery; N-O donor phase transfer agent.*

INTRODUCTION

Hydrometallurgical methods are the main techniques used for metal production from both primary and secondary sources [1]. The simplicity requires low-cost equipment and high selectivity of the solvent extraction, making this technique is considered and applied, rather than other hydrometallurgical methods, in a wide metal production plants [2]. Despite the advantages, diversity, and the general applicability of solvent extraction methods for the separation, purification, and recovery of metals, they suffer from some inconveniencies including the need
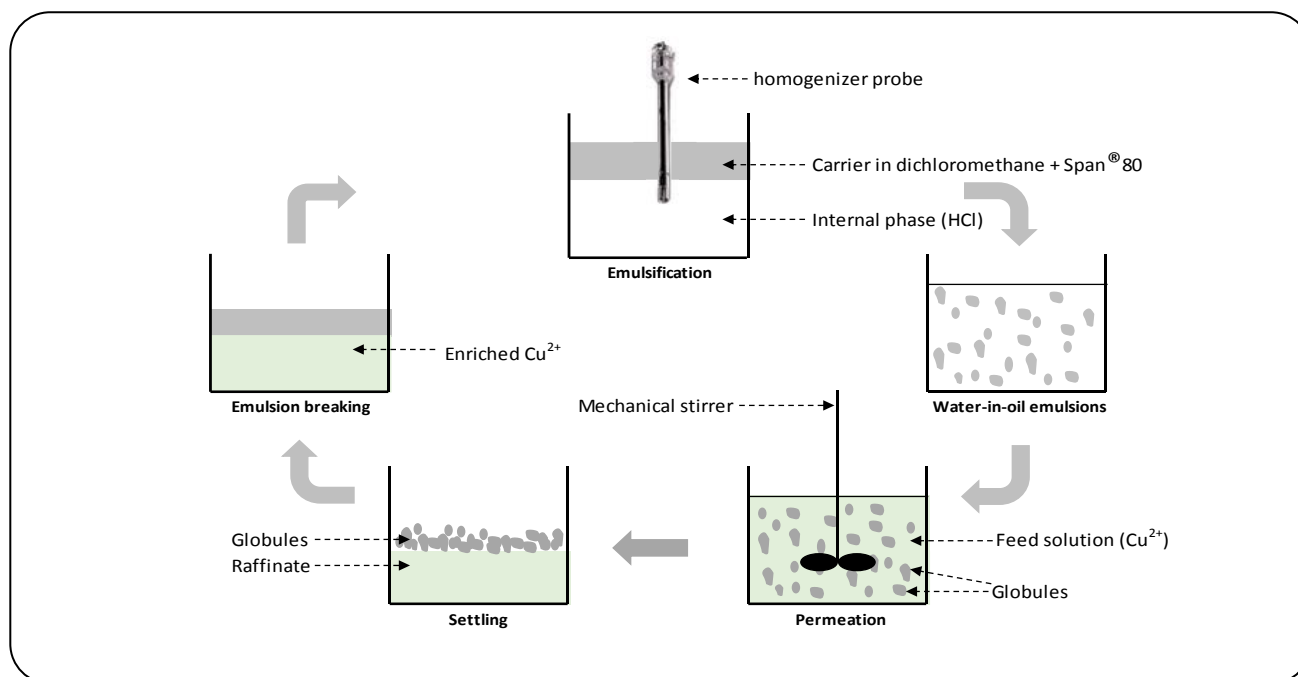
Fig. 1: Schematic diagram of the emulsion liquid membrane technique.

to a relatively considerable amount of organic solvents, which are usually expensive, toxic, and flammable. Furthermore, the extraction and back-extraction process cannot be performed simultaneously.

Liquid membranes have been invented to overcome some of the solvent extraction deficiencies [3]. They are designed in a variety of configurations [4]. Bulk Liquid Membranes (BLMs) [5] and Supported Liquid Membranes (SLMs) [6] are two of the most studied liquid membranes without phase dispersion which have been applied for the separation, removal, and purification of a number of chemical species. However, these liquid membranes themselves encounter some drawbacks. For instance, the small mass transfer area in BLMs prohibits achieving a reasonable transfer rate, and the weak capillary forces binding the liquid solution to the pores of the polymeric support used in SLMs cannot provide satisfying stability for such a technique.

Emulsion Liquid Membrane (ELM) is a phase dispersion technique [7]. The large mass transfer area involved in ELMs results in a very fast mass transfer rate for the solutes through the liquid membranes into receiving phase. "Water-in-oil" is a type of emulsion liquid membrane in which the receiving phase is entrapped and dispersed in globules formed by a surfactant or emulsifier dissolved in paraffin and a selective extractant (carrier)

in an organic diluent. Span® 80 (sorbitane monooleate), a nonionic surfactant is the most used emulsifier for the preparation of the emulsion liquid membranes. The globules are produced by mixing the membrane components (aqueous receiving phase, emulsifier, and carrier) with a homogenizer which can create a stable emulsion [8]. This step (step 1) is called "emulsification". The generated globules are then dispersed, by using a mechanical stirrer, with an aqueous feed phase containing the analyte (step 2, permeation). In most cases the relative volume of the feed aqueous phase to that of internal solution (receiving phase) is very large, and thus a concentration of analyte with a big concentration factor can be achieved.

Step 3 involves the separation of emulsions from the feed phase and ultimately the breakage of globules. The internal aqueous phase is then analyzed by an appropriate analytical technique to determine the amount of the transported analyte into the receiving phase. The recovered organic phase may be reused for a further emulsification step. A schematic representation of the designed ELM in the present study is given in Fig. 1.

The success in ion separation based on carrier-mediated liquid membranes, including emulsion liquid membranes, depends intensively on the binding ability and selectivity of the selected extractant. A variety of acidic extractants [9],

anion exchange compounds [10] and neutral molecules [11] have been incorporated in emulsion liquid membranes for the separation of various metal ions.

Schiff base ligands are a group of chemical compounds containing the azomethene moieties (-C=N-R), which are prepared by the condensation reaction of an amine and a carbonyl function containing molecule. These compounds are the potential to bind a variety of metal ions. This ability has been considered by a great number of research groups, and it has been applied widely for analytical purposes [12, 13]. Although these applications are extended to the incorporation of Schiff base molecules in bulk liquid membranes, particularly for the transport of copper ions [14-16], to the best of the authors' knowledge of the application of these compounds as the carrier in ELMs has not been previously reported.

Following our previously reported studies on the abilities of various Schiff base ligands towards copper ions [17-20] and the potential of ELMs in the separation of different chemical species [21-23], this paper reports on the carrier properties of a N_3O_2-type Schiff base extractant (shown in Scheme 1) called bis(1'-hydroxy-2'-acetonaphthone)-2,2'-diiminodiethylamine (**L**) in an emulsion liquid membrane for the transport of copper(II) ions. This Schiff-based has been synthesized and characterized previously in our laboratory [24] and its potential as a carrier for the transport of copper ions through a bulk liquid membrane has been assessed [18].

EXPERIMENTAL SECTION
Chemical and reagents

Bis(1'-hydroxy-2'-acetonaphthone) -2,2'-diiminodiethylamine (**L**) was synthesized and characterized according to the procedure reported previously [18]. Hydrochloric acid (37%, Merck, Germany), nitric acid (65%, Dr. Mojallali, Iran), acetic acid (GR, Dr. Mojallali, Iran), sodium hydroxide (≥95.0%, Dr. Mojallali, Iran), dichloromethane (GC grade, Dr. Mojallali, Iran), liquid paraffin (Merck, Germany), non-ionic surfactant Span® 80 (Sigma-Aldrich, USA), copper(II) nitrate trihydrate (≥99.5% Merck, Germany), cadmium(II) nitrate tetrahydrate (≥98.0%, Merck, Germany), lead(II) nitrate (>99%, Fluka, Switzerland), nickel(II) nitrate hexahydrate (≥98.0%, Fluka, Switzerland), zinc(II) nitrate hexahydrate (≥98.0% Merck, Germany), cobalt(II) nitrate hexahydrate (>99%, Merck, Germany),
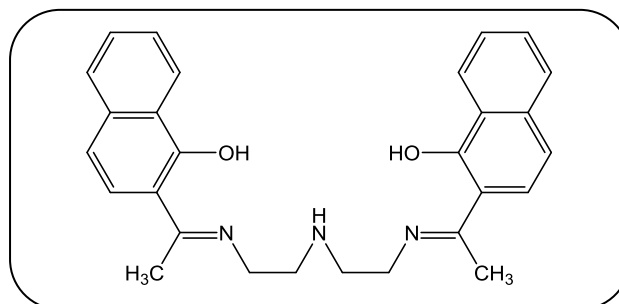
Scheme 1: bis(1'-hydroxy-2'-acetonaphthone)-2,2'-diiminodiethylamine (L)

chromium(III) nitrate nonahydrate (>98%, Merck, Germany), and iron(II) sulfate heptahydrate (>99%, Sigma-Aldrich, USA) were the chemicals used in this study. Glacial acetic acid (Neutron, Iran) was used for the preparation of buffer solutions. Deionized water (resistivity ≥ 18.2 MΩ cm) was used for the preparation of all aqueous phase solutions.

Instrumentation

The transport experiments were performed in a cylindrical glass vessel. Its height and diameter were 90 and 65 mm, respectively, and it was equipped with four round glass baffles (6 mm diameter). A homogenizer IKA (model UltraTurrax T-18) with the dispersing element S18N-10G (Germany) was used for the emulsification step. A stainless steel probe bearing four pitched blades (45° angle, 25 mm length, and 9 mm wide), attached to a mechanical mixer (Heidolph RZR-2021) with a variable speed 40–2000 rpm, was used for the extraction experiments. Separation of the phases was performed by a Heraeus centrifuge (Labofuge 300). A Zolalan deionizer (model m-UV-3+, Iran) was employed for the production of deionized water. The pH of aqueous solutions was adjusted by using a pH electrode (Metrohm, Switzerland) connected to a Metrohm analyzer (780 Herisau, Switzerland). A Flame Atomic Absorption Spectrophotometer (FAAS) (SpecrAA 220, Varian, Australia) served for the analysis of metals.

Procedure

Emulsions were prepared by slow and gradual addition of HCl aqueous solution (0.7 mol/L), as the internal phase, to a mixture of the studied Schiff base (0.001 mol/L) in dichloromethane and Span® 80 in paraffin (8 % v/v, 50 μL), while the mixture was homogenizing (13000 rpm).

The resulted mixture was homogenized for 10 min. The volume ratio of the internal aqueous phase (hydrochloric acid) to the organic phase was 1:3. Permeation was started by mechanically stirring (700 rpm) the freshly prepared emulsion in the external aqueous phase (5 mg/L Cu^{2+} in acetate buffer 0.1 mol/L, pH 5), with a volume ratio of 1:6. The experiments were done at room temperature 22±1 °C. Sampling from the feed phase was performed at given intervals with disposable sanitary syringes. The samples were centrifuged and the aqueous phase was used for the analysis of metal contents by FAAS. The experiments were done in triplicate and the maximum Relative Standard Deviations (RSD) are given in the figures caption.

Real samples preparation

The real samples were the Co and Ni-Cd filter cakes obtained from a zinc production plant in Zanjan Province (Iran). A mass of 3 g of the cobalt filter cake sample and 0.5 g of the nickel-cadmium filter cake were dissolved in 15 and 10 mL of a mixture of concentrated sulfuric acid and hydrochloric acid, respectively. The solutions were evaporated, to near dry, in order to reduce the acid contents. An aliquot of 150 mL of water was added to the samples. After 24 h, the solution was passed through a filter paper, and the solution was diluted to 200 mL with deionized water. After adjusting its pH to 5 by using sodium hydroxide solution, its final volume was increased to 200 mL by water. The obtained solutions were used for the ELM process.

RESULTS AND DISCUSSION

The extraction processes by emulsion liquid membranes involved three steps including the emulsification, the extraction (permeation), and the breaking of emulsions. The success in such processes depends on the parameters affecting these steps. The parameters influencing the emulsification step are (a) the homogenizer speed, (b) surfactant concentration, (c) extractant concentration, (e) internal aqueous phase composition, and the treat ratio (the organic to membrane volume ratio). The pH of the feed phase and the stirring rate of the feed phase with globules were the parameters affecting the extraction process. Ultimately, breaking the globules are required for recycling the organic phase and recovery of the analyte from the aqueous receiving phase. These parameters for the extraction of copper(II) by the emulsion liquid membrane containing bis(1'-hydroxy 2'-acetonaphton)-2,2-diaminoethylamine (**L**) were verified and the results are described in the following sections.
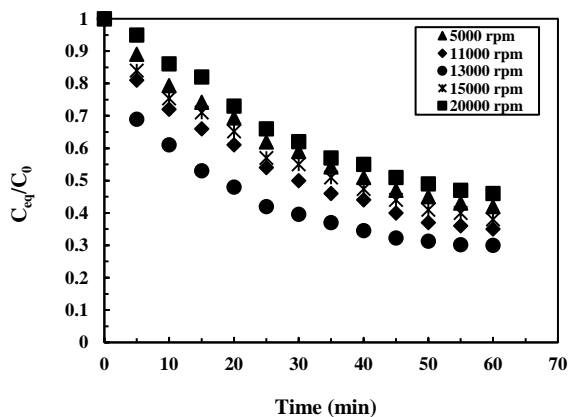
Emulsification speed

Emulsification is realized by using a homogenizer. The homogenizer speed affects directly the size and uniformity of the created globules. The size of globules defines the stability and the rate of solute uptake. In fact, the smaller size of the globules makes the production of a thinner membrane, and thus a higher extraction rate can be obtained. This may be provided by a higher emulsification speed. The advantage of thinner membrane thickness is compensated by the globules' stability [25]. Although the emulsion speed affects directly the size of globules and thus enlarges the surface contact area, beyond some emulsion speeds the instability of the globules may have occurred. Thus, the emulsion speed needs to be optimized for determining the appropriate size of the globules. To this end, a series of the extraction of Cu(II) into a nitric acid solution through the studied emulsion liquid membrane was performed. The results as a function of the emulsification rate (5000-20000 rpm) and time are shown in Fig. 2.

As was expected, an increase in the emulsification speed from 5000 to 13000 rpm increases the extraction rate and the extraction efficiency. This observation was attributed to the formation of the smaller globules and thus an increase in the mass transfer surface area and the formation of the globule with the thinner organic layer thickness. However, an increase of the homogenizer speed beyond 13000 rpm (i.e. 15000 and 20000 rpm), caused the formed emulsions are unstable and thus the extraction efficiency decreased. These results convinced us to select the emulsification speed of 13000 rpm, is the optimal emulsification speed for continuing the experiments.

Amount of the emulsifier

In the absence of a suitable emulsifier (surfactant), the emulsions formed by the homogenization of the internal aqueous solution and the carrier solution are not stable. However, the amount of the surfactant needs to be optimized for the preparation of stable emulsions. This stability increases by the amount of surfactant. In contrast, an increase in surfactant concentration may result in a higher viscosity of the organic phase and thus the mass transfer rate is decreased [26].

Fig. 2: Variation of the relative copper concentration after extraction to its initial concentration in the feed phase as a function of time by the emulsions prepared at different emulsification speeds. Emulsion preparation conditions: 4 %v/v Span® 80 in paraffin, 0.001 mol/L Schiff base L in dichloromethane 50 μL, relative membrane phase volume to the internal aqueous phase (O/A) was 3, internal phase HNO₃ 0.5 mol/L. Extraction experiments conditions: initial copper concentration 5 mg/L, pH of the feed phase 5 (acetate buffer solution 0.1 mol/L), emulsion to feed phase volume (TR) was 0.1, stirring rate 700 rpm, at 22±1 °C. The calculated RSD for the data (n = 3) ≤ 3.5%.
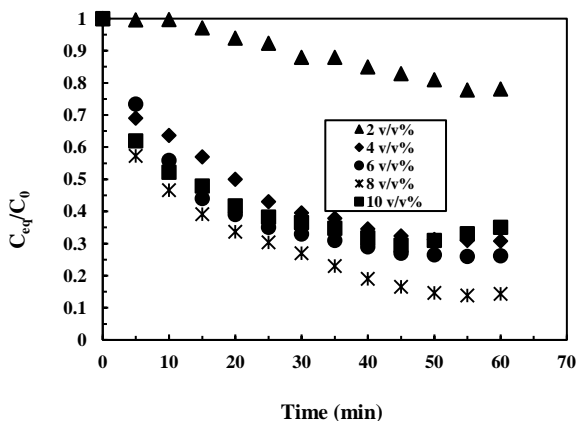
Fig. 3: Variation of the relative copper concentration after extraction to its initial concentration in the feed phase as a function of time by the emulsions prepared using different amounts of Span® 80. Experimental conditions as those presented in Fig. 3 except for the amount of Span® 80 in paraffin (2-10 %v/v) and emulsification speed (13000 rpm). The calculated RSD for the data (n = 3) ≤ 3.4%.

Span® 80 is a conventional emulsion stabilizer used in the emulsion liquid membrane preparation. In order to prepare the stable emulsions, a series of extraction experiments of copper(II) by the emulsions including the different amounts of Span® 80 in paraffin (2 – 10 % v/v) was realized. The plots of variation of the amount of extracted copper to its initial concentration as a function of time by the prepared emulsions are shown in Fig. 3.

As it is seen, the emulsions prepared by using 2 % v/v of Span® 80 are stable, and thus the extraction efficiency is not significant by the emulsions prepared in such conditions. The extraction efficiency was increased by increasing the Span® 80 concentration from 2 to 8 % v/v. The emulsions prepared based on 10 % v/v of the emulsion stabilizer showed a lower extraction efficiency. This was attributed to the higher viscosity of the membrane and mass transfer limitation of copper ions through the membrane prepared by this amount of the surfactant. However, the decrease in the extraction efficiency after 45 min observed the latter emulsions was explained by considering the swelling of the viscose globules due to the created osmotic pressure and the entrance of the feed aqueous phase to the globules which results in breakage of the globules [22, 27]. The results conduct us to use a concentration of 8 % v/v of Span® 80 in paraffin for preparation of the emulsions following the experiments.

Effect of the feed phase pH

It is known that the complexation of copper ions by Salen type Schiff base ligands has occurred *via* an ion-exchange mechanism, in which the Schiff base acts as an acidic ligand [18].

To assess the effect of the aqueous feed pH on the extraction of copper by the emulsions liquid membrane prepared under conditions mentioned in Fig. 3 (by using 8 % v/v Span® 80 in paraffin), a series of the extraction experiments by adjusting the aqueous feed phase pH to 4, 5 and 6 (acetate buffer 0.1 mol/L) was realized (Fig. 4).

The feed phase pH dependency of the process signifies that the proton exchange is involved in the extraction reaction. Keep in mind such a mechanism for the extraction of Cu(II) by the studied Schiff base, the structure of the extracted species may be proposed as it is shown in Scheme 2.

The highest extraction efficiency was obtained by adjusting the feed phase to pH 5. The results also showed that the extraction of copper at pH 6 within 5 min of the early time of the process is taken place more efficiently than the two other examined pHs. However, the progress the process the extraction efficiency is decreased which
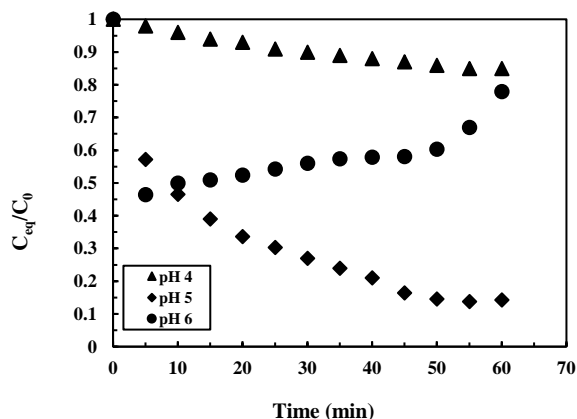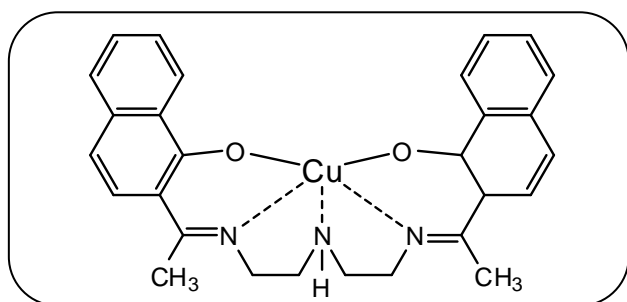
Fig. 4: Variation of the relative copper concentration after extraction to its initial concentration in the feed phase, adjusted by the acetate buffer solution 0.1 mol/L to different pH (4, 5, and 6) as a function of time. The emulsions were prepared by 8 %v/v of the surfactant. Other experimental conditions are given in Fig. 3. The calculated RSD for the data (n = 3) ≤ 2.8%.

Scheme 2: Suggested structure of the extracted copper(II) complex by the studied Schiff base.
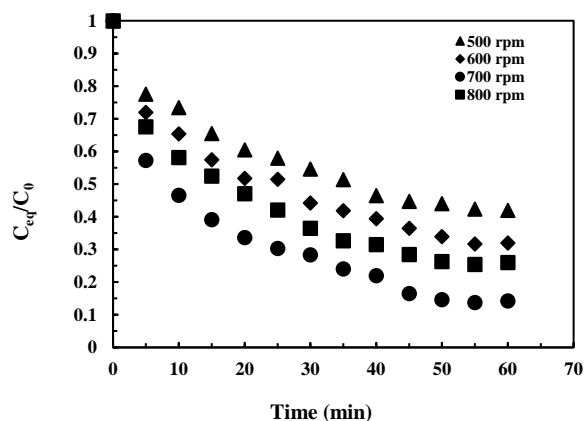

Fig. 5: Variation of the relative copper concentration after extraction to its initial concentration in the feed phase, using different feed phase/emulsion stirring rates. The feed phase was adjusted to pH 5. Other experimental conditions are given in Fig. 4. The calculated RSD for the data (n = 3) ≤ 3.5%.

can be attributed to the instability and breakage of the emulsions. This may be attributed to the possible hydrolysis of the emulsion stabilizer at pH 6 [28].

Effect of emulsions/feed phase stirring rate

The stirring rate in the extraction step affects the contact quality of the feed phase and emulsions. In fact, it allows the unfolding of the emulsions and thus a higher dispersion of them in the feed phase. Consequently, the contact surface area increases by augmentation of the stirring rate and an enhancement in the extraction is expected. However, by increasing the stirring rate beyond some optimized value, the breakage of emulsions due to the very high intensive collisions may be the cause of the reduction of the extraction efficiency.

The effect of this parameter has been appraised by performing a series of extraction experiments by applying the different stirring rates in the range 500-800 rpm at the extraction step (Fig. 5). It is seen that the extraction efficiency is increased with a stirring rate in the range 500-700 rpm. A further rise in the stirring rate to 800 rpm results in a reduction of the extraction efficiency due to the breakage of the emulsion, as it is discussed above. Therefore, a stirring rate of 700 rpm was selected as the optimal value.

Effect of carrier concentration in the membrane

In a carrier-mediated transport process, the carrier plays the role of a phase transfer catalyst and thus its concentration affects directly the extraction rate and extraction efficiency. In order to evaluate the effect of carrier concentration on the extraction rate and determine its optimum value the extraction process of copper ions by using the emulsions prepared by different amounts of the studied Schiff base (**L**) as a function of time was pursued. The results are demonstrated in Fig. 6. It is worthy of mention that the amount of the extracted copper in the absence of a carrier was not detectable.

The increase in carrier concentration from 0.00001 to 0.001 mol/L in dichloromethane had an augmentation of the extraction efficiency, while a further increase (0.01 mol/L) caused the copper uptake to be drastically reduced. These results convinced us to select a concentration of 0.001 mol/L in dichloromethane as an optimal value of the carrier concentration.
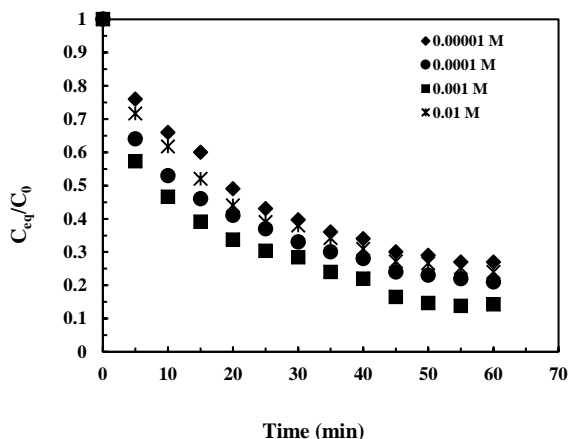
Fig. 6: Variation of the relative copper concentration after extraction to its initial concentration in the feed phase, using 50 μL different carrier concentrations. The feed phase/emulsions stirring rate 700 rpm. Other experimental conditions are given in Fig. 5. The calculated RSD for the data (n = 3) ≤ 3.3%.
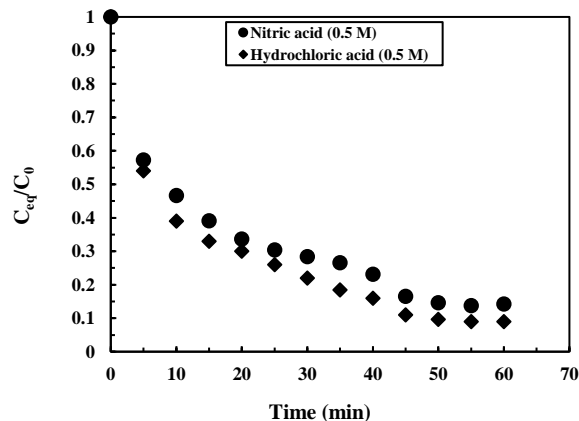

Fig. 7: Evaluation of the 0.5 mol/L nitric acid and hydrochloric acid solutions as stripping agents. Experimental conditions: see Fig. 6. The calculated RSD for the data (n = 3) ≤ 4.1%.

Although the interpretation of the enhancement of the extraction efficiency by the carrier concentration can be presented based on the carrier-mediated mechanism for the proposed transport system, the diminished extraction of copper by using a higher concentration than 0.001 mol/L, may be described by considering the higher viscosity of the emulsions prepared by using such concentration of carrier and thus the lowered mass transfer rate of copper complexes through the membrane phase.

Selection of the stripping reagent

A successful transport process needs not only a rapid, efficient, and selective extraction step at the first interface (feed/membrane), but also it depends on the stripping reagent with the ability to withdraw rapidly the analyte from the membrane. It was mentioned that the extraction reaction at the first interface is taken place *via* a cation exchange mechanism (see the section "effect of the feed phase pH"), in which the acidic proton of the carrier is replaced by copper cations. Based on this mechanism, an acid solution should be used as an appropriate stripping phase. Under such conditions, the copper complexes in the membrane are dissociated at the membrane/stripping phase interface, and the protons enter the membrane based on a counter-current transport mechanism.

To select an acid solution as the stripping reagent, the 0.5 mol/L solutions of nitric acid and hydrochloric acid were examined. The results of the transport of copper ions,

under experimental conditions given in Fig. 6 and by using 50 mL solution of 0.001 mol/L carriers for preparation of the emulsions, are presented in Fig. 7. The results revealed that hydrochloric acid may be considered a more suitable stripping. This may be interpreted by the possibility of the formation of copper chloro-complex in hydrochloric acid solutions [29].

In order to verify the hydrochloric acid concentration on the transport efficiency, a series of experiments were designed and realized by using different concentrations of this acid as a stripping reagent. The corresponding results are demonstrated in Fig. 8. The results state that an increase in the hydrochloric acid concentration from 0.1 to 0.5 mol/L augments the extraction efficiency. However, independency of the extraction efficiency to the acid concentration is observed beyond 0.5 mol/L. Based on these results a concentration of 0.7 mol/L of HCl was selected for following the experiments.

Treat ratio optimization

Treat Ratio (TR) is the ratio of emulsions to feed phase volumes. A lower TR value is desired because it provides a higher concentration factor. The limitation of using the lower TR comes from various sources. To find out the lowest TR possible, the extraction experiments of copper ions under the conditions determined in the previous sections, by using different TR values in the range 1:4 to 1:16 were run. The results (Fig. 9) confirm that a TR ratio of 1:6 can be applied for the quantitative extraction of
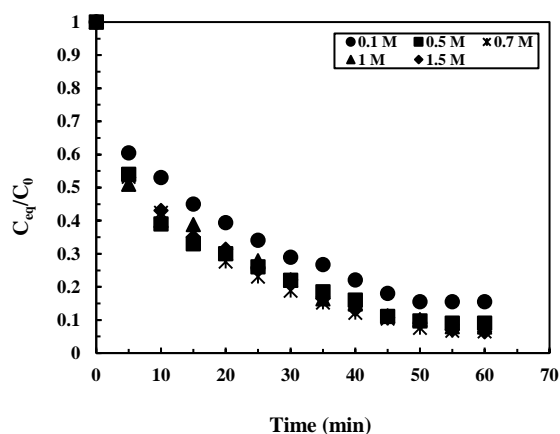
Fig. 8: Effect of the hydrochloric acid concentration used as stripping reagent on the extraction efficiency of copper by the proposed emulsion liquid membrane. Other experimental conditions: see the caption of Fig. 6. The calculated RSD for the data (n = 3) ≤ 3.4%.
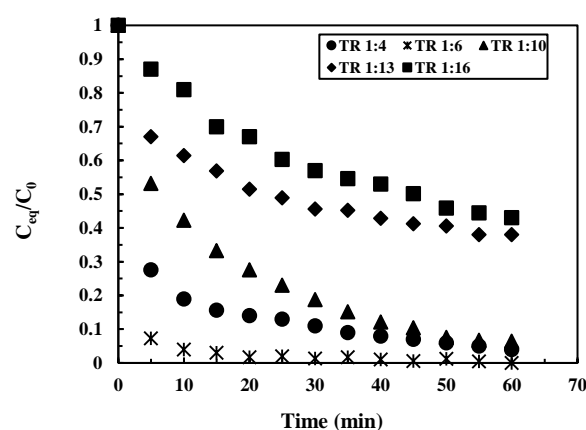

Fig. 9: Effect of the treat ratio on the extraction efficiency of copper by the proposed emulsion liquid membrane. The selected stripping solution was 0.7 mol/L hydrochloric acid. Other experimental conditions: see the caption of Fig. 6. The calculated RSD for the data (n = 3) ≤ 3%.

copper under selected experimental conditions. It is seen also that a quantitative extraction (>95%) can be achieved after 10 min.

Organic to aqueous phase ratio of the emulsions

The organic to aqueous volume ratio used for the preparation of emulsions affects the thickness of the organic membrane in the globules. In fact, this thickness influences the rate of copper transfer through the membrane. Although thinner membranes enhance the transfer rate, they may reduce the stability of emulsions. This parameter was optimized by the examination of four different organics to aqueous phase ratios. The results shown in Fig. 10, persuaded us to use an organic to aqueous phase ratio of 3 for the preparation of the emulsions.

Emulsions breakage

An ELM transport process is completed when the feed aqueous phase and the emulsions are separated and ultimately the separated emulsions are broken by a conventional method. This step is important because it allows to obtain the transported analyte and recover the organic phase. This latter may be used for a further extraction cycle. For breaking the globules, the loaded emulsions were put in a freezer (-14 °C), for 24 h. The volume expansion of the internal aqueous phase caused the breakdown of the emulsions. Ultimately, the organic and aqueous phases were separated by centrifugation, and the aqueous phase was used for copper content analysis.

Selectivity of the proposed ELM

In order to appraise the selectivity of the developed ELM, the competitive extraction of copper ions in the presence of some associated metal ions (cadmium(II), lead(II), nickel(II), zinc(II), cobalt(II), iron(II), and chromium(III)), under optimized experimental conditions, were run for 30 min. The concentration of all tested ions was 5 mg L^{-1}. This investigation was shown that except for lead ions, which have been co-extracted (~60%) with copper, the proposed ELM cannot extract other examined ions.

Application of the method

Analysis of the metal contains in the solutions obtained by the acid leaching of the cobalt and nickel-cadmium filter cakes of a zinc production plant and the percentage of the copper recovered from these solutions are given in Table 1. The transport experiments have been performed triplicate under optimized conditions. The results showed the potential of the proposed method for efficient copper recovery from the complex matrices.

### Comparison with some related studies

The recovery of Cu(II) from the wastewaters containing Pb(II), Cd(II), Zn(II), Co(II), Ni(II) and Mn(II) by applying two ELM systems employing LIX 84® (2-hydroxy-5-nonylacetophenone oxime) and LIX 622® (5-dodecylsalicylaldoxime) have been studied was studied by *Chakravarti et al.* [33]. This study showed that although

Table 1: The results of the application of the proposed method for the recovery of copper from cobalt and nickel-cadmium filter cakes of a zinc production plant.[a]

Metal ion	Concentration in the prepared solution (mg/L)		Recovered metal (%)	
	Co filter cake	Ni-Cd filter cake	Co filter cake	Ni-Cd filter cake
Cu(II)	4.5 (±0.2)	5.2 (±0.3)	91.3 (2.1)	90.4 (±1.6)
Mn(II)	1334.1 (±15.2)	4.7 (±0.6)	1.3 (±0.2)	ND[a]
Zn(II)	1648.1 (±17.6)	568.0 (±9.8)	1.7 (±0.8)	1.1 (±0.4)
Co(II)	157.3 (±7.1)	0.8 (±0.1)	3.4 (±0.8)	ND
Cd(II)	33.0 (±1.2)	309.1 (±11.2)	ND[a]	0.9 (±0.5)
Ni(II)	10.5 (±0.6)	85.1 (±3.3)	ND[a]	1.3 (±0.5)
Fe(II)	3.9 (±0.3)	0.2 (±0.1)	ND[a]	ND[a]

[a]*ND: not detectable.*
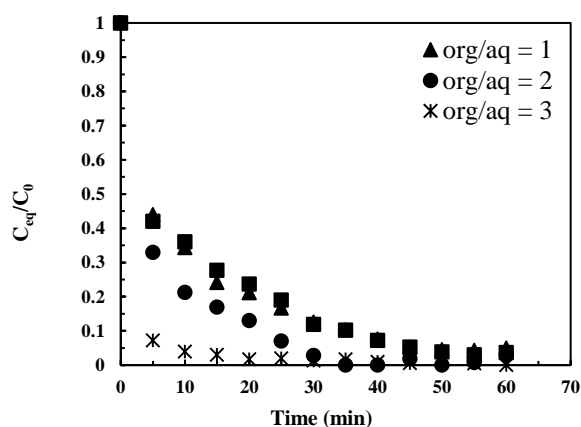
Fig. 10: The influence of the organic to aqueous phase ratio used during the emulsification process on the efficiency of the proposed transport system. The selected TR was 1:6. Other experimental conditions: see the caption of Fig. 9. The calculated RSD for the data (n = 3) ≤ 3.2%.

the copper ions from the acetate buffer solutions (pH 6) were transported quantitatively into a 2 mol/L solution of H_2SO_4 as the stripping phase within 20 min, all the other examined ions were also co-transporters and thus they were considered as interferences for the developed system. However, the copper transfer rate was also diminished in the presence of these interfering ions. The results in the present study demonstrate a comparable transport rate with the systems introduced by *Chakravarti et al.*. However, the application of a more dilute acid solution as the receiving phase (0.7 mol/L), and the absence of any interfering effect by the examined ions, except for lead ions, can be considered as the advantages of the method introduced in the present study.

Sengupta *et al.* [34] have studied an ELM containing the oxime LIX 98N-C® (a mixture of 5-nonylsalicylaldoxime and 2-hydroxy 5-nonylacetophenone oxime) as a carrier. The proposed system was able to transfer quantitatively copper ions from aqueous solutions adjusted to pH 2 into a 2 mol/L of sulfuric acid, after 30 min. The transport rate achieved by this membrane is comparable to that we found by using the ELM containing the investigated Schiff base. However, a harsher receiving phase (2 mol/L of H_2SO_4 vs. 0.7 mol/L HCl) has been used in the *Sengupa et. al.* report. On the other hand, they have not reported the selectivity towards copper ions with respect to the possible interfering ions. In 2007, this group studied the transport of copper ions from ammonium sulfate solution adjusted to pH 8.1 into a 1.5 mol/L solution of sulfuric acid as the receiving solution through an ELM membrane containing LIX 84 I® [35]. The transport was very rapid and it was completed within 2 min. However, this study lacks information concerning on the selectivity potential of the presented separation system.

One of the interesting aspects of the presented study is the excellent selectivity of the proposed method toward copper ions with respect to some other transition metals, including Zn(II). The separation of copper and zinc is an important topic in the field of the separation of metal ions. *Fouad* [36] has designed an emulsion liquid membrane containing bis(2-ethylhexyl)phosphoric acid for the separation of copper and zinc ions. The comparison of the selectivity of this strategy with the results obtained in the present study confirms the higher selectivity towards copper ions by the ELM developed in this study.

CONCLUSIONS

This is the first report on the application of a Schiff base, called bis(1'-hydroxy-2'-acetonaphthone)-2,2'-diiminodiethylamine, as the carrier for the transport of copper ions through an emulsion liquid membrane. The stable emulsions formed by the dichloromethane solution of the Schiff base, which surrounds the hydrochloric acid solution as the internal phase, have been used as a selective and efficient membrane for the transport of copper ions from feed phase aqueous solution (pH 5). The designed membrane provided a relatively fast transfer of copper. It extracts quantitatively copper ions (initial concentration of 5 mg L^{-1}) from the feed phase into the receiving phase, in less than 30 min. The optimal value of the treat ratio revealed that the copper can be concentrated in the receiving phase with a factor of >6. The membrane was highly selective towards copper ions with respect to Cd(II), Ni(II), Zn(II), Co(II), and Cr(III). However, a co-extraction of lead ions (~60%) is a plague for the system which prohibits using the investigated method for efficient recovery of copper from the samples containing lead ions. The method is able to be used for the recovery of copper from the real samples with the complex matrix.

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