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Research Article

Zinc and Copper Separation through an Emulsion Liquid Membrane Containing Di-(2-Ethylhexyl) Phosphoric Acid as a Carrier

The separation of zinc and copper ions from sulfuric acid solutions by an emulsion liquid membrane (ELM), using di-(2-ethylhexyl) phosphoric acid (D2EHPA) as a carrier, has been investigated. The batch extraction of zinc and copper was carried out while varying a selection of experimental conditions, i.e., stirring speed, treatment ratio, concentrations of metal ions in the feed phase, carrier and Span 80 concentration in the membrane, and internal phase concentration. The results obtained demonstrate the effectiveness of D2EHPA as a carrier for the separation of zinc and copper from sulfuric acid media using an ELM. An increase of the D2EHPA concentration beyond 2 vol.-% does not result in the improved extraction of zinc because the viscosities of the membrane and emulsion have a trend to increase for higher carrier concentrations. It was found that the extraction rate of copper was affected by the carrier concentration in the liquid membrane and by the pH and metal content in the external phase. A 3 vol.-% concentration of surfactant in the organic phase was required to stabilize the emulsion. The number of stages required for the extraction of zinc and copper by an ELM was determined from McCabe-Thiele plots.

1 Introduction

Major industrial wastewaters worldwide include mine water, photo etching wastewater, electroplating rinse liquor and pickling solutions contain Cd, Cu, Cr, Hg, and Zn. Zinc and copper are the major components of these effluents. The concentrations of zinc and copper in the rinse solutions of the plating industry varies from 39–350 mg/L and from 6–535 mg/L, respectively [1]. Recently, hydrometallurgical processes have been widely applied to produce metals and their compounds from low-grade ores. In particular, the selective recovery of these metals from such solutions is required for economic/environmental reasons and has a high-priority status in many governmental and industrial sites. The development of technologies for the selective removal of these contaminants continues to be a major challenge. Electrochemical metal recovery is a promising technique. However, waste streams often have metal contents that are too low and have poor plating efficien-

cies [2]. There is a growing need for the development of an effective and efficient method for the removal and recovery of such metals from dilute solutions.

The selective separation of copper and zinc using D2EHPA modified Amberlite XAD-4 resin could preferentially remove Zn from practical leachate solutions, leaving only Cu ions in the solution [3]. To date, there are numerous published works on copper and zinc separation by liquid-liquid systems from chloride media using different extractants such as 4-pyridine derivatives (Kelex 100), alkyl-8-hydroxyquinoline [4–9], supported liquid membranes [10, 11], and hollow fiber contactors [12–14]. Organic-inorganic hybrid membranes containing di-(2-ethylhexyl) phosphoric acid or di-(2-ethylhexyl) dithiophosphoric acid as a carrier have been used for Zn(II), Cd(II) and Cu(II) separation [15]. However, there are no reports in the literature of research activity concerning the application of emulsion liquid membranes (ELMs) to the separation of Cu and Zn from their mixed sulfate solutions.

ELMs exhibit several attractive features and were invented by Li et al. [16–18]. These include a large specific surface area for extraction, simultaneous extraction and re-extraction in a single stage, and the requirement only small quantities of an expensive carrier. In fact, ELMs remove the equilibrium limita-

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tions, thereby, achieving a reduction of metal concentrations in the feed stream to very low levels.

The ELM process contains a three-phase dispersion system, which consists of a stripping phase encapsulated by a membrane phase (organic phase), which in turn contains the extractant in an organic diluent, together with a surfactant to stabilize the emulsion droplet. This emulsion is further dispersed in the feed aqueous phase. Therefore, a thin film of oil is formed between the outer (feed aqueous phase) and inner (stripping) aqueous phase, which serves as a membrane through which the metal ions diffuse. The metallic element present in lean solution forms a complex with the extractant at the interface of the emulsion globule and the feed phase. The complex formed is then shuttled through the organic phase to the organic phase-stripping phase interface from where it is stripped into the bulk of the encapsulated stripping phase. The process is completed by the separation of the emulsions in two steps. In the first step, the purified aqueous phase is separated from the emulsion, while in the second step, the concentrated solution of the heavy metal is separated from the oil phase. The latter is then recycled.

For this purpose, the present study is concerned with the technical feasibility of the separation of zinc and copper by an emulsion liquid membrane process. The influence of various experimental parameters on the separation of binary Zn(II) and Cu(II) ions is investigated. Selective zinc/copper transport by di-(2-ethylhexyl) phosphoric acid (D2EHPA) as the carrier and Span 80 as the surfactant was chosen as a model system. The major parameters influencing the extent of extraction may include the speed of agitation in the external phase, acid concentration in the external phase, surfactant (Span 80) and extractant concentrations, feed concentration of Cu and Zn, and treatment ratio. Each of these parameters must be studied in order to have a better understanding of the dynamics of the ELM technique.

2   Experimental

Zinc and copper stock solutions were prepared by dissolving $ZnSO_4 \cdot 7\,H_2O$ and $CuSO_4 \cdot 5\,H_2O$ in deionized water. Zn and Cu ions were analyzed by a Hitachi Z8100 atomic absorption spectrophotometer. Zn and Cu feed solutions from a known amount of Zn and Cu stock solutions were diluted with deionized water to a given concentration. Internal aqueous standard solutions were prepared by taking the required amount of H_2SO_4 and diluting with deionized water to a known volume. The organic phase was prepared by dissolving D2EHPA in iso-dodecane and adding an appropriate amount of Span 80 as a surfactant. The emulsion was prepared by mixing the internal aqueous solution with the organic membrane phase using a rotor-stator type high-speed disperser (IKA Ultra Turrax T50) at 10000 rpm for a mixing time of 300 s. A predetermined volume ratio of 1:1 for the organic phase to the internal stripping phase was maintained. The viscosity of the emulsions was measured at different shear rates using a Brookfield DV-II+ programmable viscometer. Interfacial tension data were obtained with a LAUDA TVT1 tensiometer. A summary of the experimental conditions for the ELMs is presented in Tab. 1.

Table 1. Summary of experimental conditions for ELMs.

External Phase	
pH	3
Volume (mL)	100
Zn Conc. (ppm)	200
Cu Conc. (ppm)	200
Internal Phase	
Volume (mL)	10
$[H_2SO_4]$ (M)	1.5
Organic Solution	
Volume (mL)	10
Diluent	Iso-dodecane
[D2EHPA] (vol.-%)	4
Span 80 (vol.-%)	10
Mixer Speed (rpm)	300

The three-phase dispersion was stirred at 25 °C with a magnetic stirrer at 300 rpm (except when the effect of stirring speed was studied). The external phase solution was periodically sampled at various time intervals. The concentration of metal ions in the solutions was determined after separation of the emulsion phase.

3   Results and Discussion

The percent extraction, *E*, was determined from the mass balance of metals in the internal and external phases, Eq. (1) [19]:[1]

$$E = [1 - (C^e_{M,t}\,V^e/C^e_{M,t}\,V^e)] \times 100 \qquad (1)$$

and the separation factor for Zn and Cu is expressed as follows, Eq. (2):

$$\beta = R_{Zn}/R_{Cu} = [C^i_{Zn,t}/C^e_{Zn,0}]\,[C^e_{Cu,0}/C^i_{Cu,t}] \qquad (2)$$

The subscripts i and e denote the internal and external phases, while 0 and t indicate initial and feed concentration of metal ions at time *t*, respectively.

3.1   Effect of External Phase Acidity

The pH of the aqueous feed phase has a significant influence on the extraction behavior. The zinc and copper extraction from sulfuric acid media was studied using D2EHPA within an initial pH range of 1.0–5.5. The operating conditions used

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1)   List of symbols at the end of the paper.

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were [D2EHPA] = 4 vol.-% and with an aqueous/emulsion phase ratio of 5:1 at room temperature. The level of extraction increases with the decrease in H$^+$ concentration in the aqueous phase, Fig. 1. By inspection of Fig. 1, it is observed that zinc was extracted at a lower pH value than copper. In the pH range of 1.0–3.0, the percent metal extraction increased from 19 to 90 % and from 18 to 26 % for zinc and copper, respectively. Beyond pH 3 for zinc and pH 4 for copper, the pH had no effect on the level of metal extraction. This could be explained by the fact that in the pH range of 1.0–3.0, the extraction is governed by the cation exchange reaction in which the protons are released, whereas beyond this range of values, an increase in the pH leads to the formation of other species that are less extractable by D2EHPA [20]. The observed difference in extraction percentage shows the opportunity for possible separation of zinc from copper at pH 3. For this goal, a separation factor was calculated according to Eq. (2) and is also presented in Fig. 1. In the pH region 3–4, the separation factor was high since the co-permeation of Cu with Zn was low in this region. After pH 4, copper co-permeates with Zn, and therefore, the separation factor decreased slightly.
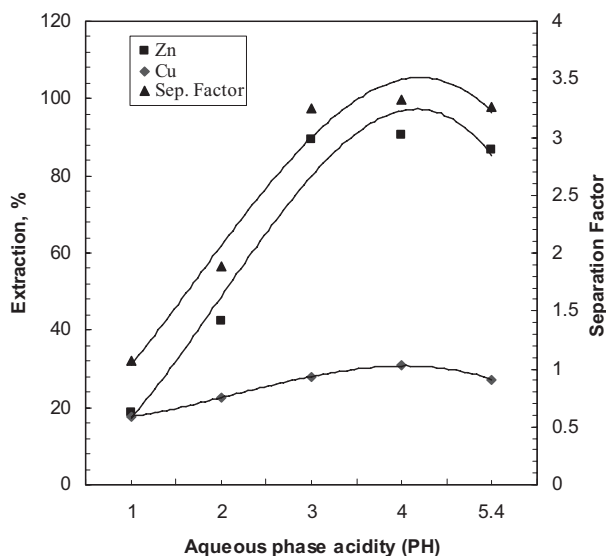

Figure 1. Effect of pH on the extraction of zinc and copper by an emulsion liquid membrane.

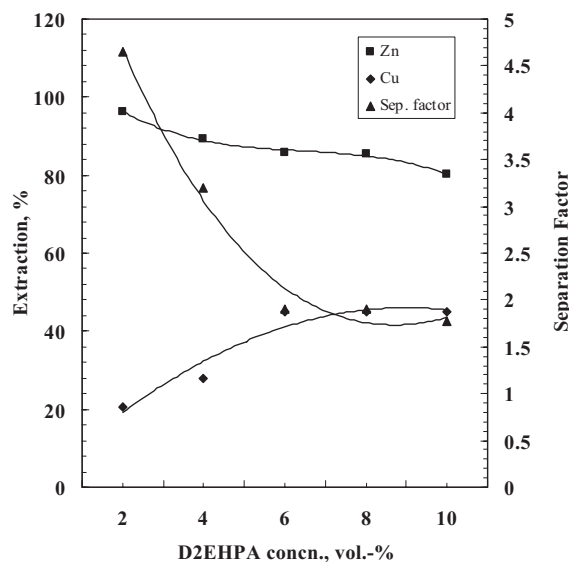## 3.2 Effect of D2EHPA Concentration in the Emulsion

The concentration of D2EHPA was varied in the range from 2–10 vol.-% to determine the effect of the organic-phase composition on the extraction of copper and zinc. The extraction of zinc ions is represented by Eq. (3) [21]:

$$Zn^{2+} + 3/2\,(HR)_2 \rightleftharpoons ZnR_2(HR) + 2\,H^+ \qquad (3)$$
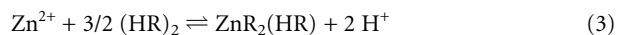
In addition, the extraction of copper ions may be represented by Eq. (4) as follows [22]:

$$Cu^{2+} + 2\,H_2R_2 \rightleftharpoons CuR_2 \cdot 2\,HR + 2H^+ \qquad (4)$$
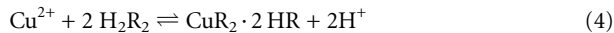
Based on Eqs. (3) and (4), it seems clear that the extraction dependence of Cu ions on [(HR)$_2$] is higher than that of zinc. Therefore, increases in the [(HR)$_2$] concentration result in greater extraction of copper. This is clear from the data presented in Fig. 2. It is observed that by increasing D2EHPA concentration, the zinc extraction decreased from 96 % at 2 vol.-% to 80 % at 10 vol.-% whereas copper extraction increased sharply from 19.5 % at 2 vol.-% to 46 % at 6 vol.-%. The extraction of copper did not increase further at higher concentrations of D2EHPA.

Figure 2. Effect of D2EHPA concentration on the extraction of zinc and copper by an ELM.

Interfacial tension measurements between the emulsion and 0.5 M H$_2$SO$_4$ solutions are presented in Fig. 3 to study the effect of varying D2EHPA concentration on the behavior of zinc and copper extraction. Fig. 3 shows that the interfacial tension sharply decreased with increasing D2EHPA concentration. Increasing the D2EHPA concentration would not result in an improvement in the extraction of zinc because the viscosities of both the membrane and emulsion have a tendency to increase for higher carrier concentrations. Larger globules would then be produced and the diffusivity of the complex would be lowered under such conditions, as is noted by other authors [23]. From these data, it is concluded that the zinc extraction is diffusion controlled, but copper extraction is controlled by the interfacial reactions.

The separation factor is calculated as a function of D2EHPA concentration and is also indicated in Fig. 2. Therefore, increasing the D2EHPA concentration is seen to enhance greater extraction of copper such that the separation factor is expected to decrease. However, the results show that the separation factor is higher at lower D2EHPA concentrations, i.e., 2 vol.-%.
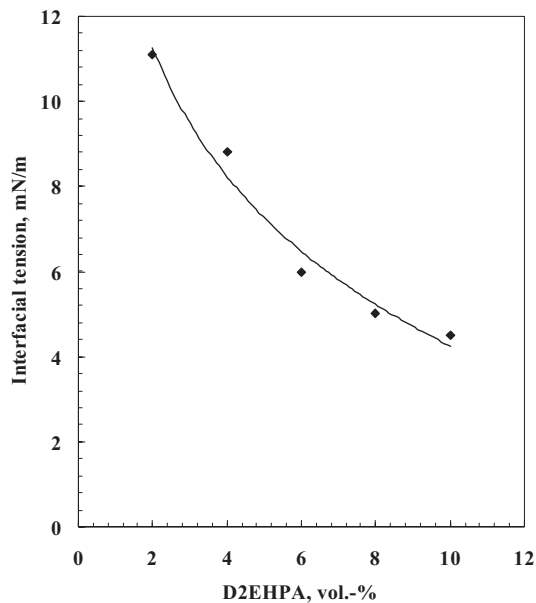
Figure 3. Effect of D2EHPA on the interfacial tension between the emulsion and 0.5 M sulfuric acid solution.
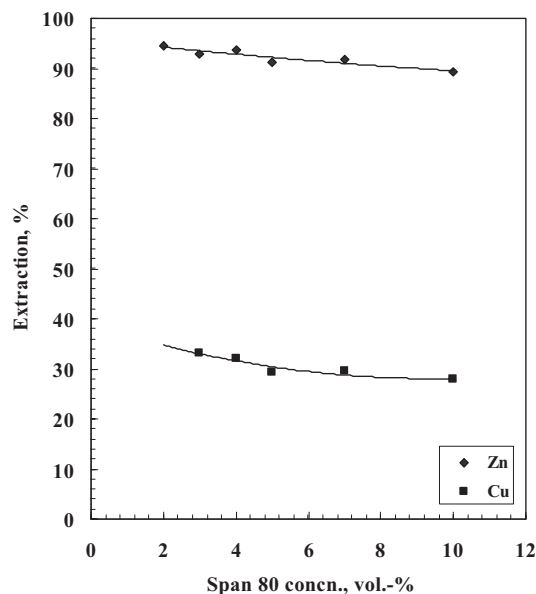
3.3 Effect of Span 80 Concentration

It is very important to ascertain the effect of surfactant concentration on the emulsion properties, i.e., viscosity, interfacial tension between emulsion and external aqueous phase, which affect the behavior of zinc and copper extraction by an ELM. The data on emulsion viscosity with varying surfactant concentration using 4 vol.-% D2EHPA dissolved in iso-dodecane as diluent, are presented in Fig. 4. The emulsion viscosity increased from 19 to 81 mPa s when the Span 80 concentration increased from 2 to 10 vol.-%. On the other hand, the interfacial tension decreased sharply with increasing surfactant concentration, Fig. 4. The effect of changing these properties on the Zn and Cu separation is indicated in Fig. 5. It is observed that increasing Span 80 concentration from 1 to 10 vol.-% decreases the extraction levels of both zinc and copper. In this range, the viscosity increased by ca. four times at 10 vol.-% Span 80 and at values above 2 vol.-%, a reduction of diffusivity of the metal complex in the emulsion and adverse affects on mass transfer were observed. Therefore, in order to obtain better overall mass transfer, it was decided to maintain 3 vol.-% surfactant concentration in all other experiments.

3.4 Effect of Zinc and Copper Concentration in the External Aqueous Phase

The effect of metal ion concentration on the metal extraction was studied in the range of 200–1000 ppm of Zn and Cu. The Zn and Cu ratio was varied from 1:5 to 5:1. The pH of the feed solution was kept constant at 3.0. The results are represented in Tab. 2. The separation factor decreased from 8.94 to 3.32 by keeping the copper concentration constant in the feed solution
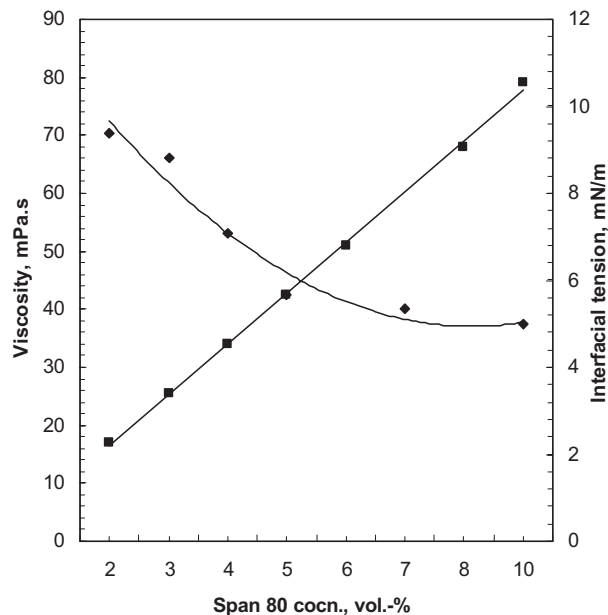
Figure 4. Effect of Span 80 concentration on the emulsion viscosity and interfacial tension between the emulsion and 0.5 M H$_2$SO$_4$.

Figure 5. Effect of Span 80 concentration on the extraction of zinc and copper by an ELM.

at 200 ppm and increasing the zinc concentration from 200 to 1000 ppm. The separation factor slightly decreased from 8.94 to 6.82 by keeping the zinc concentration constant at 200 ppm and increasing the copper concentration from 200 to 500 ppm, and with further increases of copper concentration up to 1000 ppm, it decreased to 4.75. Prolongation of the mixing time results in a significant decrease in the separation fac-

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Table 2. Effect of zinc/copper concentration on the separation factor.

Time (min)	Zn /Cu Separation Factor				
	Zn (ppm)/Cu (ppm)				
	200/500	200/1000	500/200	1000/200	200/200
2	6.82	4.75	6.56	3.32	8.94
5	4.91	4.43	4.86	3.48	4.73
7	4.11	4.84	3.67	3.34	3.78
10	3.42	4.36	3.41	3.12	3.20
20	2.46	3.21	2.68	2.01	2.82
30	2.21	2.06	1.93	1.07	2.44
40	1.72	1.41	1.46	0.27	2.25

tor. This is may be due to emulsion breaking. From these data, it is found that 2 min of mixing time at 700 rpm are the optimum conditions.

3.5   Effect of Stirring Speed

Higher stirring rates lead to the formation of smaller sized globules, thereby increasing the interfacial area between the continuous phase and the membrane phase, leading to an increase in the rates of mass transfer. Higher stirring speeds can also lead to more swelling and globule rupture. The effect of stirring speed on the Zn and Cu concentrations in the feed aqueous phase is shown in Figs. 6 and 7. It was observed that in-
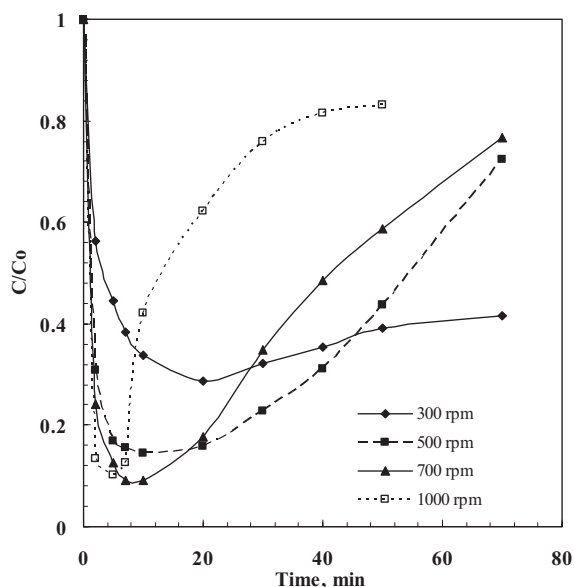
Figure 6. Effect of mixing speed on zinc concentrations in the feed aqueous phase by an ELM.
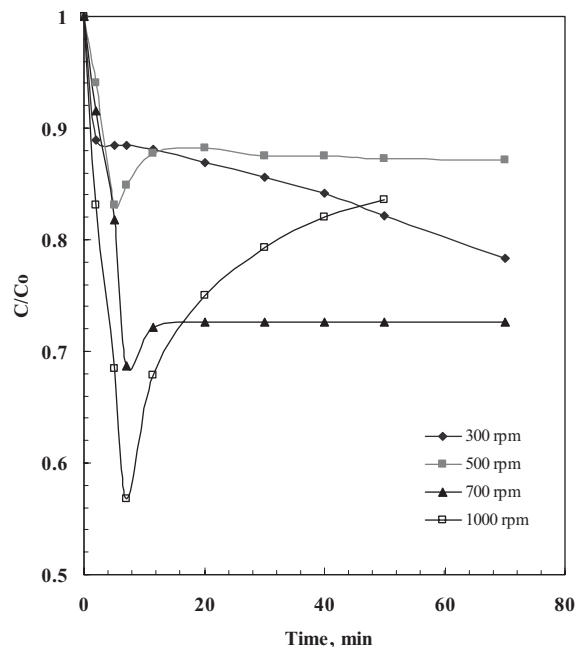
Figure 7. Effect of mixing speed on copper concentrations in the feed aqueous phase by an ELM.

creasing stirring speed from 300 to 700 rpm decreased the value of $C/C°$ from 0.38 to 0.08 and 0.89 to 0.57, for Zn and Cu, respectively during the first 7 min. This was due to an increase in the mass transfer coefficient in the aqueous feed phase (between the emulsion globules and the aqueous solution). However, further increases in stirring time resulted in a reduction of the extraction level. A further increase of the stirring speed to 1000 rpm did not have any effect on extraction, but the metal ion concentration in the external phase sharply increased and the value of $C/C°$ reached 0.44 for zinc after 12 min. This is due to the higher shear rates that resulted in a significant level of membrane rupture. Consequently, 700 rpm was recommended as the most appropriate stirring speed.

3.6   Effect of Internal Phase Concentration

A series of experiments was carried out in the range from 0.5–4 M to investigate the influence of internal sulfuric acid concentration on metal ion transfer. Fig. 8 shows the influence of the concentration of sulfuric acid as the internal stripping phase on the extent of zinc and copper extraction. It was found that the extraction increased when the concentration of sulfuric acid in the internal phase, increased from 0.5 to 1.5 M. However, further increases in the concentration did not affect the zinc extraction while the level of copper extraction was reduced. This is a result of the increases in the ionic strength difference between internal and external phases that resulted in an increase in swelling, which resulted in greater amounts of water to permeate through the membrane causing the internal droplets to swell and coalesce.

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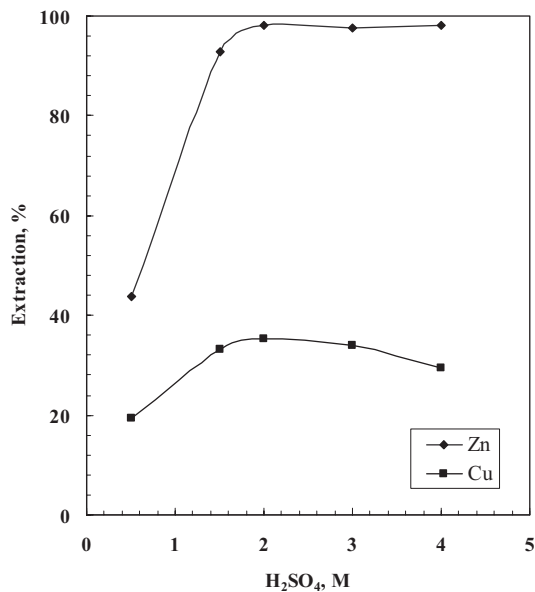
Figure 8. Effect of internal phase concentration on zinc and copper extraction by an ELM.

## 3.7 Effect of External to Emulsion Phase Volume Ratio

The treatment ratio, defined as the volume ratio of aqueous feed solution to the emulsion phase, plays an important role in determining the effectiveness of emulsion liquid membranes. Experiments were performed to study the effect of treatment ratio on the extraction rate of both zinc and copper. The treatment ratio was varied from 5:1 to 40:1. Fig. 9 shows the effect of treatment ratio on the extraction rates of Zn and Cu. As can
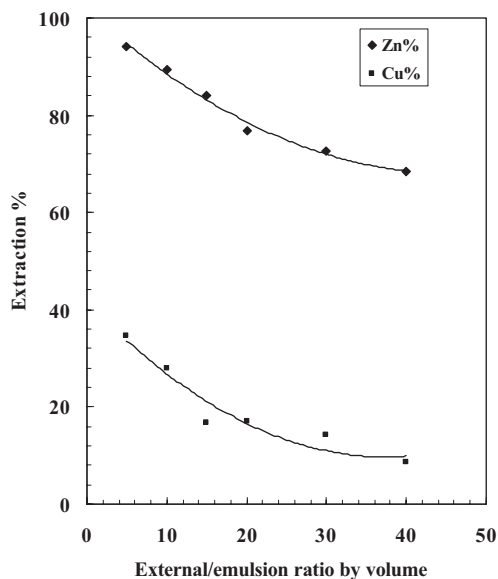
Figure 9. Effect of external/emulsion phase ratio on Zn and Cu extraction by D2EHPA.

be seen from Fig. 9, the extraction rate of both metal ions decreased with increasing phase ratio. For zinc, the extraction % decreased from 94 at a ratio of 5:1 to 68.5 at 40:1, while for copper, the extraction % decreased from 34.6 at 5:1 to 8.5 at 40:1. With a decrease in the treatment ratio, the volumes of both the carrier and the stripping agent, i.e., the volume of emulsion as a whole, increased towards the external aqueous phase. Therefore, the surface area for mass transfer increased due to the formation of a larger number of emulsion globules. As a result, a higher degree of extraction was obtained. The higher treatment ratio means less emulsion is required to extract the metal ions, which is desirable from a processing point of view to ensure maximum enrichment with respect to the feed phase.

Plots of McCabe-Thiele diagrams for the separation of zinc and copper were performed and are in Figs. 10 and 11. It is seen from Figs. 10 and 11 that by using D2EHPA as a carrier in the emulsion liquid membrane, complete extraction of zinc requires three stages and the extraction requires ten stages for copper. This means that D2EHPA favors the extraction of zinc ions rather than copper ions.
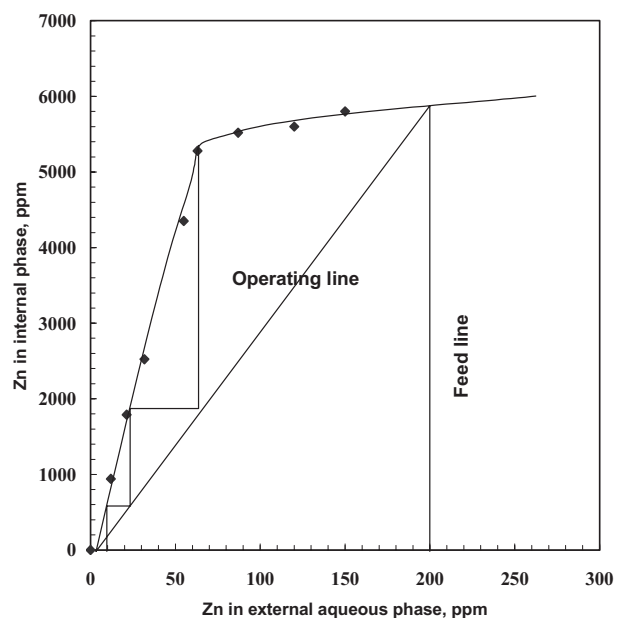
Figure 10. Mc-Cabe Thiele diagram for zinc extraction by an ELM.

4 Conclusions

D2EHPA can be used to separate zinc from an aqueous solution containing copper in an ELM, with 96 % extraction for zinc and 25 % for copper. Zinc extraction started at pH 1.0 and increased up to pH 3.0, whereas copper extraction started at pH 1.0 and increased up to pH 4.0, but at a slower rate than for zinc. The maximum separation factor was obtained at pH 3.0. An extractant concentration of 2 vol.-% in the membrane phase and a concentration of H_2SO_4 of 1.5 M in the internal
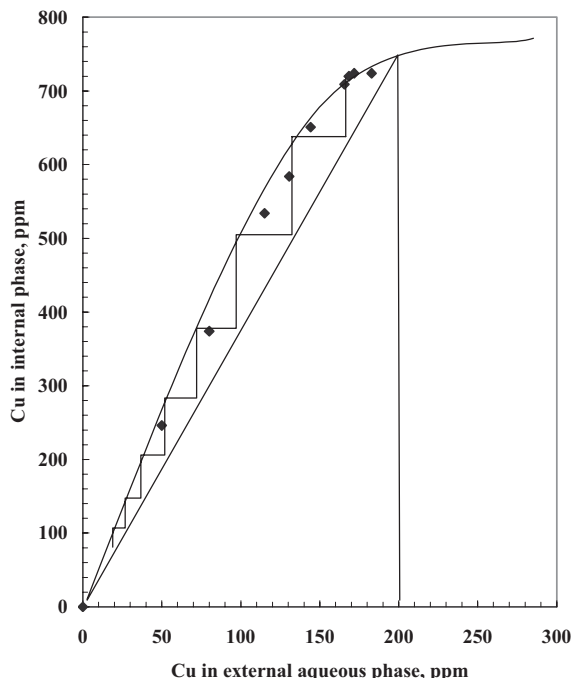
Figure 11. Mc-Cabe Thiele diagram for copper extraction by an ELM.

solution were found to be optimum conditions for obtaining a higher separation factor. It was found that 700 rpm can be recommended as the optimum stirring speed with a stirring time of 7 min. Span 80 was used as a surfactant and had a significant effect on the emulsion viscosity, since it hinders the mass transfer of metal ions. Increasing the D2EHPA concentration resulted in a decrease in interfacial tension, which had a significant effect on copper extraction. From the data obtained, it is concluded that the zinc extraction is diffusion controlled, but copper extraction is controlled by the interfacial reaction. From McCabe-Thiele plots, it is found that three stages are sufficient for complete zinc extraction.

Symbols used

C	[M]	concentration of metal ion
E	[%]	extraction efficiency
V	[mL]	volume of aqueous phase

Abbreviations

$CuR_2 \cdot 2HR$	copper-D2EHPA complex in membrane phase
HR	monomeric form of D2EHPA
H_2R_2	dimeric form of D2EHPA
R	ratio of metal ion transferred to the membrane phase
$ZnR_2(HR)$	zinc-D2EHPA complex in membrane phase

Subscripts

Cu,t	concentration of copper in external phase at time t
Cu,0	initial concentration of copper in external phase
M,t	concentration of species M in external phase at time t
M,0	initial concentration of species M in external phase
Zn,t	concentration of zinc in external phase at time t
Zn,0	initial concentration of zinc in external phase

Superscripts

e	external phase
i	internal phase

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