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Facilitated transport of copper through bulk liquid membrane containing di-2ethylhexyl phosphoric acid

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ABSTRACT

An experimental study is presented on facilitated transport of copper (II) cations through a bulk liquid membrane containing di(2-ethylhexyl) phosphoric acid (D2EHPA) in dichloromethane. The effects of different parameters on copper transport through the membrane such as the carrier concentration, pH of the product and feed phases, stirring speed and temperature were investigated. It was found that copper transport was greatly affected by stirring speed and the pH of both aqueous phases, while temperature influenced weakly the copper transport. The extraction of copper from ammoniacal solution was very fast reaching 100% after just 1 h while only 2% of copper remained into the membrane at the end of the operation.

Keywords: Facilitated transport; Bulk liquid membrane; D2EHPA; Ammoniacal solution of copper

1. Introduction

Extraction techniques for the removal and recovery of heavy metals are of increasing interest because of the growing importance given to environmental protection problems. A variety of industries are responsible for the release of heavy metals into the environment through their waste waters generated from hydrometallurgy, electroplating rinse liquors, petrochemical, refinery, fertilizer, etc. [1]. There is also an economic interest in their recycle for the recovery of the valuable metals. According to World Health Organization [2] the metals of most immediate concern are copper, chromium, zinc, iron, mercury and lead. Copper is widely used in many products such as in electrical equipment, construction (roofing and plumbing), industrial machinery (heat exchangers) and alloys. It is also used as catalyst [3–7]. Long-term exposure to copper can cause irritation of the nose, mouth and eyes and it causes headaches, stomachaches, dizziness, vomiting and diarrhea. Intentionally high uptakes of copper may cause liver and kidney damage and even death [8,9].

Separations by membranes have drawn maximum attention in recent years. Generally there are three basic types of liquid membrane, the bulk liquid membrane (BLM), the emulsion liquid membrane (ELM), and the supported liquid membrane (SLM). The latter two types of liquid membrane have been studied extensively from both fundamental and technological points of view. The main drawback of these two liquid membrane processes is the limited membrane stability. BLMs appear to be the most easily operated because of their simple configuration and data reproducibility.

In BLM, the extraction chemistry is basically the same as that found in liquid-liquid extraction, but the transport is governed by kinetic rather than

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equilibrium parameters, that is, it is governed by a non-equilibrium mass transfer.

Ion extraction by liquid membranes is normally facilitated by carrier mediated transport, in which an ion exchange reagent is incorporated into the membrane phase in order to carry the diffusing species across the membrane to the product phase. Several authors have described the use of liquid membranes for separating or recovering different positive and negative ions and a great number of exchange reagents have been used [10–13].

One of the most well known solvent extraction reagent for a variety of heavy metals like Ni^{2+}, Cd^{2+}, Zn^{2+} and Cu^{2+} is D2EHPA [14–22].

It is chemically stable, has good kinetics of extraction, good loading and stripping characteristics, low solubility in the aqueous phase and availability in commercial quantities.

The present work reports the facilitated transport of copper ions through BLM constituted by di(2-ethylhexyl) phosphoric acid (D2EPHA) in dichloromethane. Copper diffusion occurs from the bulk membrane phase to the feed membrane interface where the metal ions are exchanged for protons. The ion carrier complex formed diffuses through the membrane to the membrane product interface, where, by reversing the process, protons are exchanged for copper ions which are released into the product phase. The carrier is regenerated, thus initiating a new separation cycle. The transport mechanism is therefore a facilitated counter-transport mechanism, with Cu^{2+} and H^+ travelling in opposite directions.

Extraction of copper from aqueous solution using D2EHPA can be described by the following chemical equation:

$$Cu^{2+}_{(aq)} + 2HR_{(org)} \rightarrow CuR_{2(org)} + 2H^{+}_{(aq)} \qquad (1)$$

where HR represents the carrier, aq. and org. are aqueous and organic phases. The reaction that takes place at the interface of the membrane/product phase is described by:

$$CuR_{2(org)} + 2H^{+}_{(aq)} \rightarrow Cu^{2+}_{(aq)} + 2HR_{(org)} \qquad (2)$$

The effect of several variables such as the carrier concentration, pH of the product and feed phases, stirring and temperature was studied.

2. Experimental equipment and procedure

Reagent grade dichloromethane (99.5%, Carlo Erba) and chloroform (99.6%, Normapur) were used as organic solvents. The carrier D2EHPA (95%, Fluka) was used as received. Stock solutions of copper cations were prepared by dissolving $CuSO_4.5H_2O$ (99%, Merck) in distilled water. H_2SO_4 (97%, Organics) was used to acidify the product phase and a mixture of NH_4OH (33%, Riedel-de Haën) and $(NH_4)_2SO_4$ (99.95%, Alfa Aesar) was used to increase the pH of the feed phase. Distilled water was used throughout the experiments.

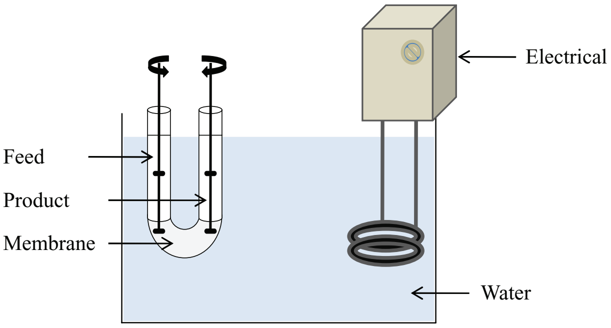

Fig. 1. Experimental setup.

Transport measurements were performed in a U-tube glass cell (Fig. 1) placed in a thermostated water bath (25 ± 1°C). The membrane is constituted by D2EHPA in dichloromethane. 0.5 mol/m^3 of aqueous solution of Cu^{2+} was used as feed phase and placed in one limb of the U-tube. Distilled water and distilled water acidified with sulfuric acid were used as product phases and placed in the other limb of the U-tube. The volumes of feed, membrane and product phases were 6×10^{-5} m^3 each. The internal diameter of the U tube is 0.025 m corresponding to an interface area of 4.9×10^{-4} m^2. The two aqueous phases, i.e. feed and product phases floating on the organic membrane phase, respectively in the two limbs of the U-tube. The three phases were constantly stirred using two mechanical stirrers. The feed and product phases were sampled and analyzed for the corresponding copper ion concentration by titration with EDTA using murexide as an indicator. Each experiment was repeated at least three times. For practical reasons, dimensionless reduced concentrations in percentage of copper ions in the feed (R_f), membrane (R_m) and product phases (R_p) were used: $R_f = (C_f/C_0) \times 100$, $R_m = (C_m/C_0) \times 100$ and $R_p = (C_p/C_0) \times 100$, where C_0 is the initial concentration of feed phase, C_f, C_m and C_p are the concentrations of copper at time t in feed, membrane and product phases, respectively, and the sum of $R_f + R_m + R_p$ obviously being a hundred.

The effect of process parameters can be also evaluated by the change in the fluxes calculated by:

$$J_{f/m} = \frac{(C_0 - C_f) \times V}{A \times t}, \qquad (3)$$

$$J_{\mathrm{m/p}} = \frac{C_{\mathrm{p}} \times V}{A \times t}, \tag{4}$$

where $J_{\mathrm{f/m}}$ and $J_{\mathrm{m/p}}$ are the fluxes across the feed/membrane and membrane/product interfaces, respectively, mol/m^2.s; $(C_0 - C_{\mathrm{f}})$ is the concentration of copper extracted from the feed phase, mol/m^3; V is the volume of the three phases, m^3; A is the effective area of the interface between feed/membrane and membrane/product phases, m^2; and t is time, s.

3. Results and discussion

The performance of the transport depends on the influence of various operational parameters as detailed below.

3.1. Carrier concentration

In preliminary studies, experiments were carried out at 25°C and 300 rpm using different concentrations of carrier in the membrane (3%, 10%, 20%, 25% and 35%) v/v and the product phase was formed by distilled water without acidification (pH = 6.7). The feed phase was formed by 0.5 mol/m^3 of Cu^{2+}, its pH was 4.8. Variation with time of the reduced concentrations of copper ions in the feed, membrane and product phases are shown in Fig. 2.

Increasing carrier concentration enhanced copper extraction. This enhancement was not proportional to carrier concentration since around sevenfold increase of D2EHPA concentration in the membrane phase from 3% to 20% resulted in an increase of copper concentration in the product phase from 7% to about 21% after 8 h, while further increase of D2EHPA up to 35% increased slightly copper concentration in the product phase reaching 28% after the same period of time. Copper concentration increased in membrane phase with increasing D2EHPA up to 20% and stabilized thereafter at ~60%. This may be due to the saturation of adsorptive layers formed at the interfaces involved indicating the existence of optimal D2EHPA concentration for this system. The flux of copper extracted from the feed phase after 3 h with 3% D2EHPA was 1.3×10^{-6} mol/m^2 s (Table 1). It increased up to 4.13×10^{-6} mol/m^2 s with 20% D2EHPA and reached slightly 4.64×10^{-6} mol/m^2 s with 35% D2EHPA. The values of fluxes of copper stripped in the product phase were lower than those calculated for the extraction since only 0.2×10^{-6} mol/m^2 s were stripped with 3% D2EHPA after 3 h and reached 1.24×10^{-6} mol/m^2 s with 35% D2EHPA after the same period of time. Increasing D2EHPA concentration leads to accelerate at the initial stage the transport of Cu^{2+} removed from the feed phase into the membrane phase. At 20% and up to 35% of D2EHPA, the extraction stabilized. The behavior of copper transported in this case may be explained as follows:

At the beginning of the operation there was no loading for the membrane liquid phase, so the copper could be transferred quickly from the feed into the membrane phase. Subsequently, the increase in loading of the membrane phase and decrease in copper concentration in the feed phase caused a decrease in copper transfer rate. Despite the increase in carrier amount, the stripping was not efficient because no H^+ ions were available to remove copper from the membrane which was consequently loaded with copper ions.

In addition, a blank experiment was performed with no present carrier in the membrane. No detectable movement of Cu^{2+} ions through the membrane was found, suggesting that the transport of Cu^{2+} ions through the liquid membrane is fulfilled by the carrier. 20% D2EHPA was used to investigate the effect of the other parameters.

3.2. pH of product phase

In order to assess the effect of the H^+ concentration on the copper transport through BLM, water of the product phase was acidified by H_2SO_4 at different pH values (3.5, 2.5 and 1). The experiments were performed at 25°C, 20% D2EHPA in CH_2Cl_2 and 300 rpm. The results (Fig. 3) indicate that increasing the acidity of the product phase below 3.5 leads to considerable increase in the copper extraction rates. Stripping was improved with increasing the acidity of the product phase below 3.5, which has lowered copper accumulation and facilitated the regeneration of the membrane.

At pH 3.5 the effectiveness of copper transport was weak and the accumulation into the membrane was important. On the contrary, fast and effective transport of copper into the product phase was observed at pH 1. At this pH value R_{f} decreased monoexponentially with time, while R_{p} followed an increasing sigmoided curve and R_{m} presented a maximum. The flux of copper stripped into the product phase was 0.68×10^{-6} mol/m^2 s at pH 3.5 after 3 h, it increased up to 3.85×10^{-6} mol/m^2 s at pH 1 after the same period of time (Table 1).

Thus, the driving force for the Cu^{2+} transport through the liquid membrane was the concentration gradient of both hydrogen and copper ions across the liquid membrane. pH 1 was used to investigate the effect of the other parameters.

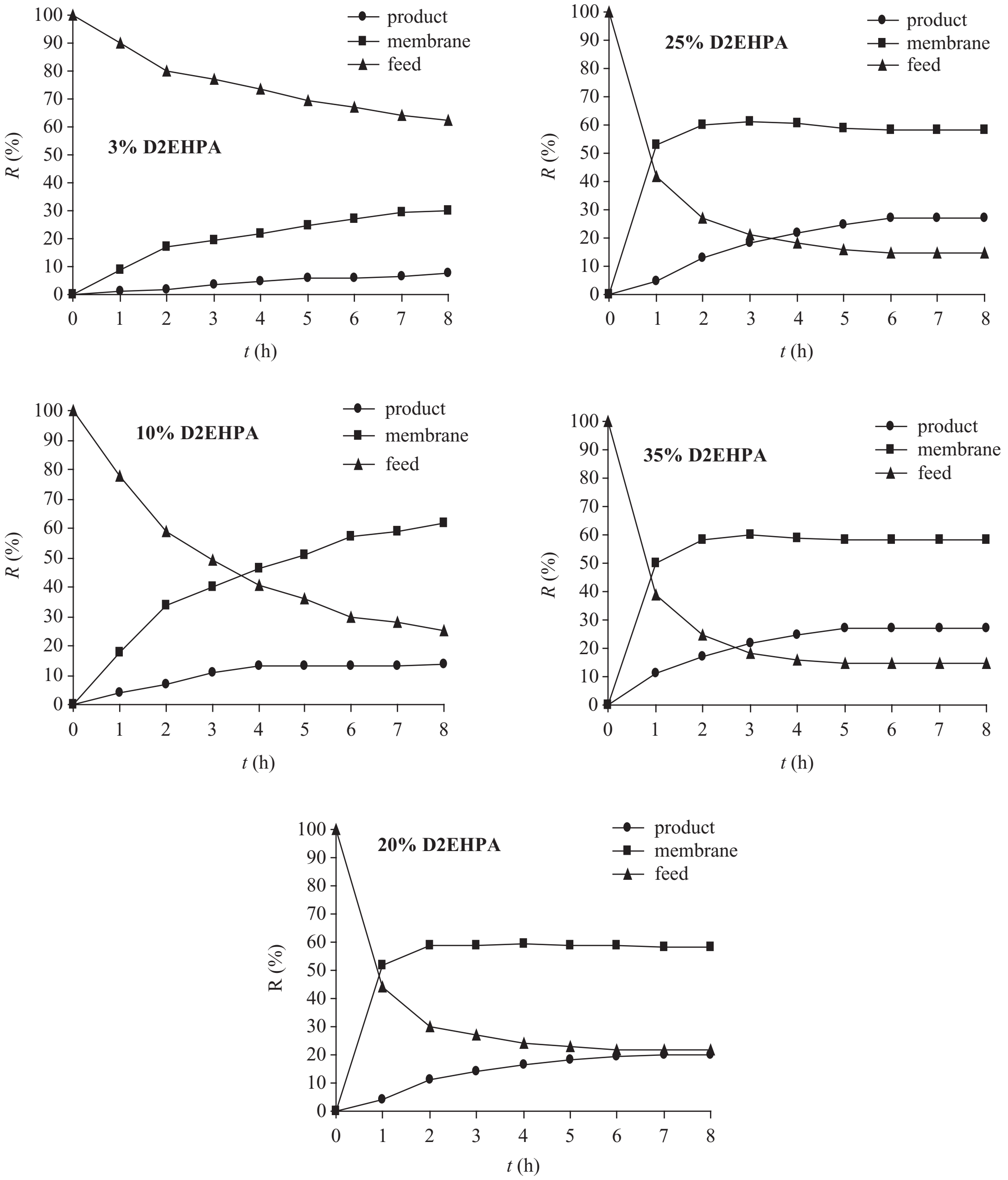

Fig. 2. Effect of carrier concentration on *R* in product, membrane and feed phases.

3.3. Stirring speed

The effects of hydrodynamic conditions on Cu^{2+} transport were determined for the system studied at varying speeds (100, 200 and 300 rpm) at 25°C and pH of the product phase equal to 1 when the carrier concentration was 20% in CH_2Cl_2. In this study all phases were stirred.

The results presented in Fig. 4 indicate that the stirring affected the transport rate of Cu^{2+} through the liquid membrane. With 100 and 200 rpm the slopes of the transport curves for the feed and product phases were almost constant from 1 to 6 h and the content of the membrane was not changed within this period of time. This indicates that during this period the copper transport reached steady or at least quasi-steady state. After 3 h of transport, 2.43×10^{-6} and 3.22×10^{-6} mol/m^2 s of copper were extracted at 100 and 200 rpm, respectively (Table 1).

At 300 rpm, a remarkable increase in extraction and stripping was observed. The bulk membrane registered

Table 1
Flux of copper extracted and stripped after 3h of transport through the membrane formed by D2EHPA in Dichloromethane

	Flux (mol/m^2 s)																			
	D2EHPA amount (%)					pH of the product phase				Agitation speed (rpm)			Temperature (°C)			pH of the feed phase				
	Conditions: 25°C, 300 rpm, $pH_f = 4.8$, $pH_p = 6.7$					Conditions: 25°C, 300 rpm, $pH_f = 4.8$, 20%D2EHPA				Conditions: 25°C, $pH_f = 4.8$, $pH_p = 1$, 20%D2EHPA			Conditions: 300 rpm, $pH_f = 4.8$, $pH_p = 1$, 20%D2EHPA			Conditions: 30°C, 300 rpm, $pH_p = 1$, 20%D2EHPA				
	3	***10***	***20***	***25***	***35***	***3.5***	***2.5***	***1.5***	***1***	***100***	***200***	***300***	***25***	***30***	***35***	***8***	***9***	***10***	***11***	***12***
$J_{Extraction} \times 10^6$	1.3	2.88	4.13	4.47	4.64	4.02	4.3	4.64	4.75	2.43	3.22	4.75	4.75	4.81	4.92	4.86	13.7	16.97	15.27	5.32
$J_{Stripping} \times 10^6$	0.2	0.62	0.79	1.02	1.24	0.68	1.47	2.26	3.85	1.53	2.37	3.85	3.85	4.27	4.41	4.41	5.09	5.37	3.45	3.11

a max of copper accumulation of about 39% at 1 h. This maximum registered in the membrane phase was probably due to the high convective flux of copper through feed–membrane interface generated at 300 rpm and as a result the concentration of copper in the membrane phase grows rapidly at the beginning and then falls due to consecutive permeation of copper into the receiving phase. Higher values of copper fluxes were obtained with 300 rpm since the extraction of copper from the feed phase attained 4.75×10^{-6} and 3.85×10^{-6} mol/m^2 s were stripped after 3 h (Table 1).

Stirring seems to be an important factor in copper transport because it minimizes the diffusion layer at the interfaces and generates a convective flux inside the three phases as a result of their deformation and vibration. It should be noted that when the stirring speed was higher than 300 rpm, the hydrodynamic stability of the two interfaces was affected significantly

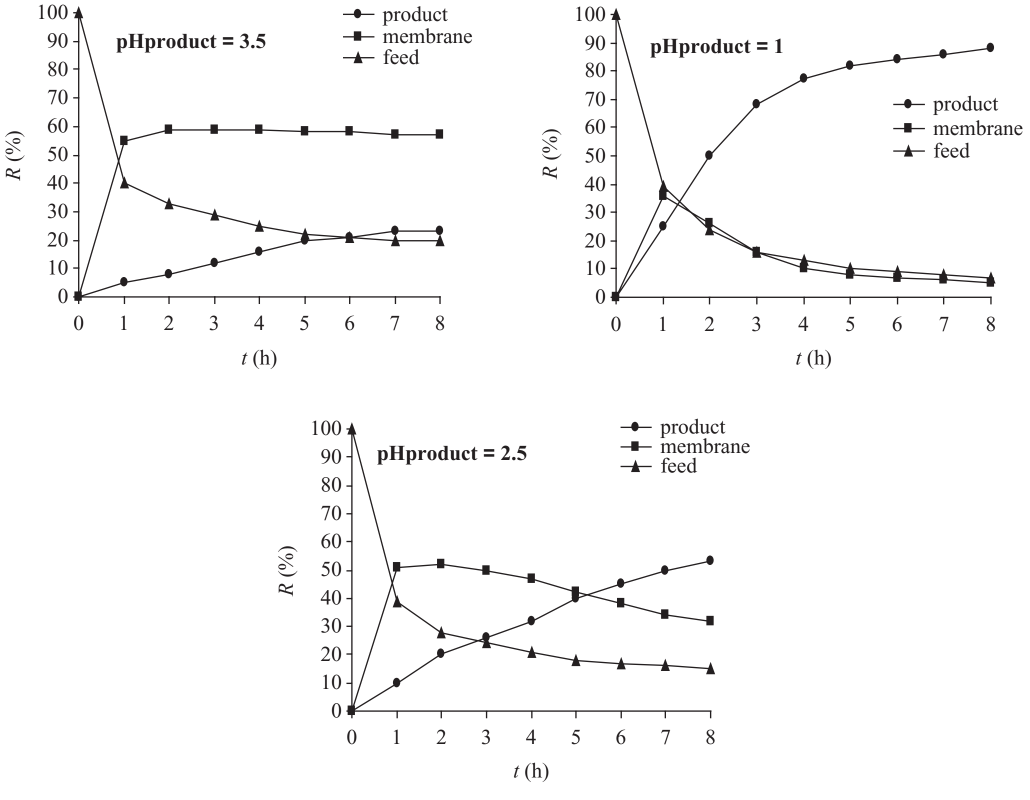

Fig. 3. Effect of pH of the product phase on R in product, membrane and feed phases.

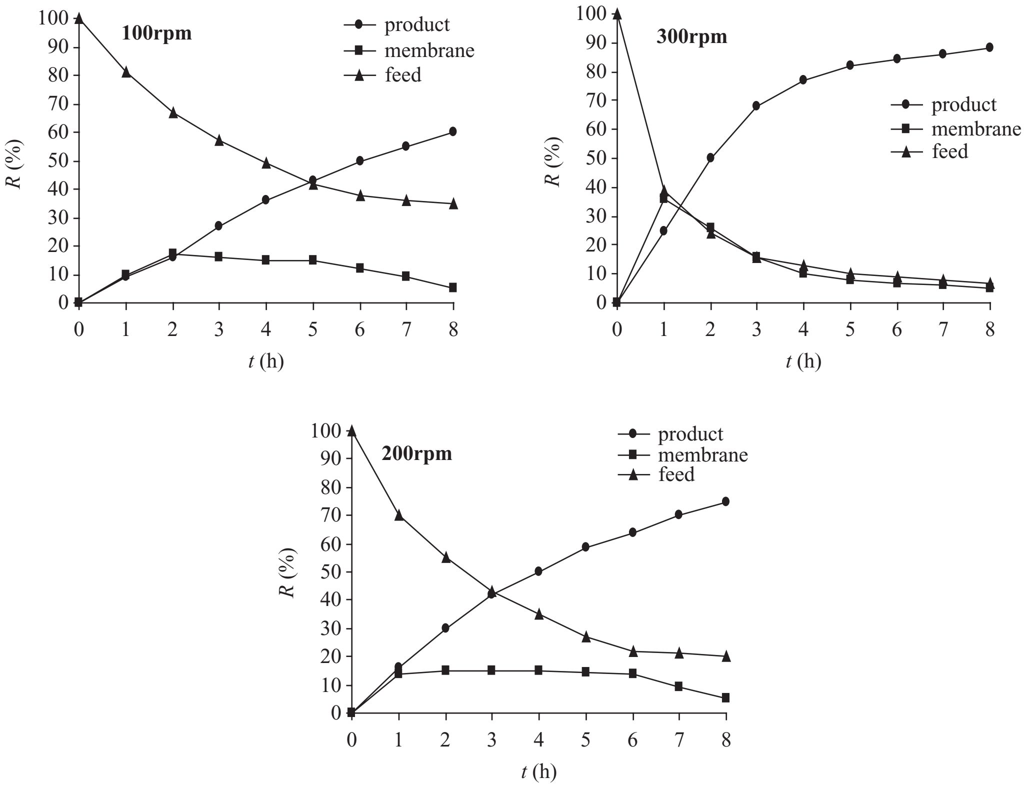

Fig. 4. Effect of stirring speed on R in product, membrane and feed phases.

and drops of the organic membrane were observed in both aqueous phases.

3.4. Temperature

The effect of temperature on the transport of Cu^{2+} ions through the liquid membrane containing 20%v/v of carrier in dichloromethane was examined at 25–30 and 35°C at pH of the product phase equal to 1 and 300 rpm.

Fig. 5 shows that the temperature has more significant effect on decreasing the copper accumulation into the organic membrane. In fact, the maximum of 39% accumulated at 25°C after 1 h was lowered to 20% at 30°C after the same period of time.

Stripping was also improved when the temperature was increased from 25 to 30°C but remains almost the same at 35°C. A temperature of 30°C was used to investigate the rest of the parameters.

3.5. Nature of solvent

The effect of solvent on the transport of Cu^{2+} ions through the liquid membrane containing 20% D2EHPA in dichloromethane and chloroform was examined (Fig. 6). CH_2Cl_2 and CH_3Cl were studied under the same operation conditions (30°C, 300 rpm, 20% D2EHPA and pH of the product phase equal to 1). Higher transport efficiency was observed with CH_2Cl_2. In fact, 92% of copper ions were extracted with CH_2Cl_2 against 79% with $CHCl_3$ after 8 h, and 87% were stripped with CH_2Cl_2 against 68% with $CHCl_3$ after the same period of time. The results are consistent with the literature [23] in which the efficiency of CH_2Cl_2 was higher than CH_3Cl because their viscosity values were in the reverse order. Thus, the characteristics of the membrane solvents are one of the main factors in establishing transport efficiency.

3.6. pH of feed phase

As shown in the previous experiments, pH gradient between the feed and product phases is the driving force for the transport of Cu^{2+} through the membrane phase. So, an acidic solution was needed for the stripping of Cu^{2+} ions from the liquid membrane. Increasing the pH gradient between the two aqueous phases by increasing the pH of the feed phase to caustic values may be an interesting way to improve the transport of Cu^{2+} through the membrane.

The ammoniacal leaching is an attractive approach to process concentrates since copper ion is easily

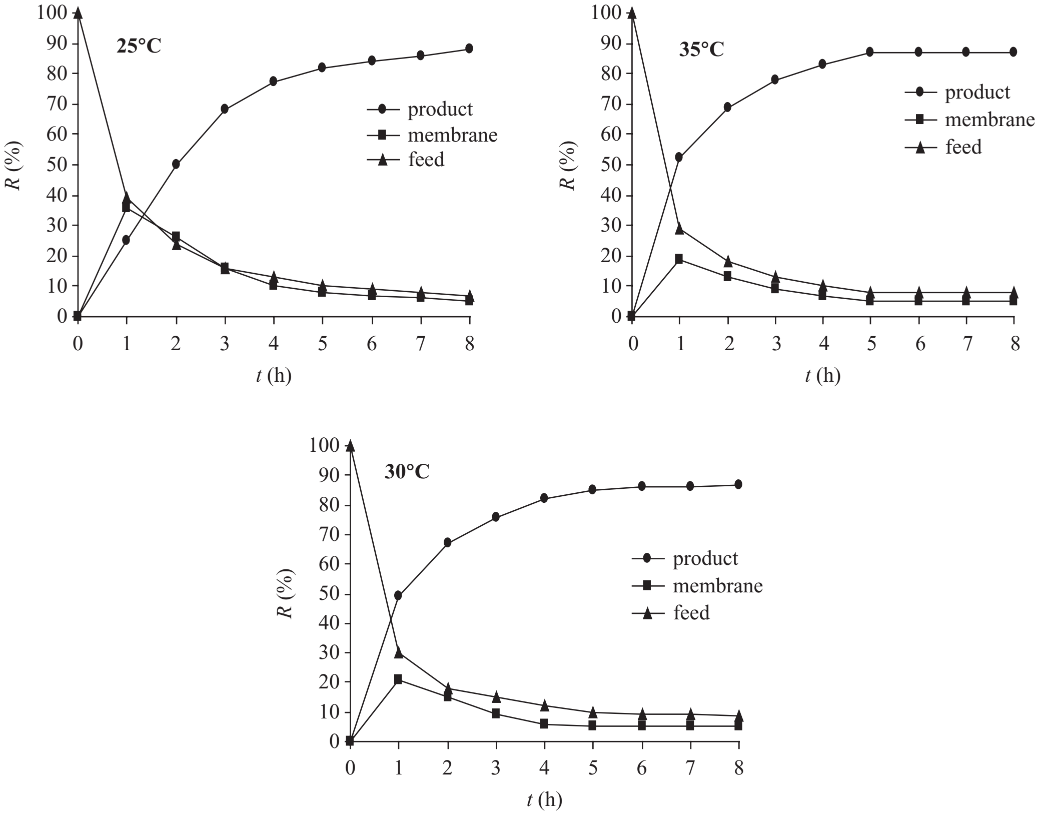

Fig. 5. Effect of the temperature on R in product, membrane and feed phases.

solubilized through the formation of ammine complexes [24–27].

In ammoniacal feed solution the predominant metallic specie of copper is the complex $Cu(NH_3)_4^{2+}$. The extraction reaction of the copper species is assumed to occur with the extractant HR according to the following equilibrium:

$$Cu(NH_3)_4^{2+}(aq) + 2HR_{(org)} \leftrightarrow CuR_{2(org)} + 2NH_{3(aq)} + 2NH_4^{+}(aq) \tag{5}$$

Feed solutions were prepared by dissolving $CuSO_4{\cdot}5H_2O$ and ammonium sulfate (50 g/l) in distilled water. The pH of the feed solution was adjusted

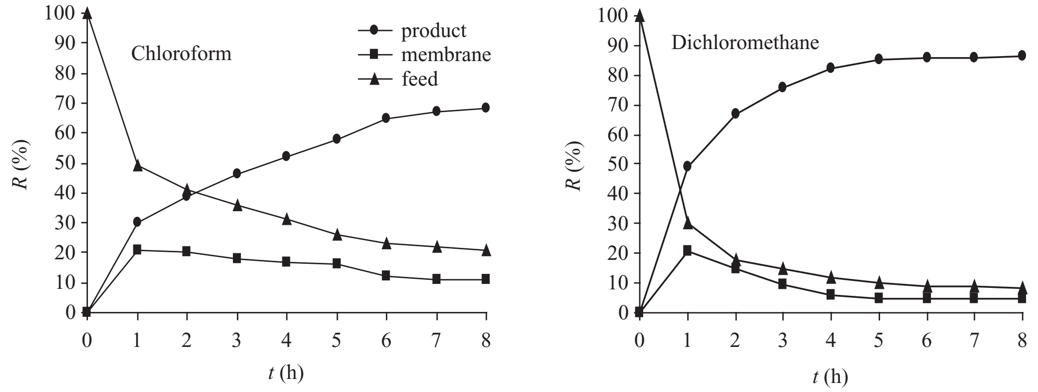

Fig. 6. Effect of the nature of solvent on R in product, membrane and feed phases.

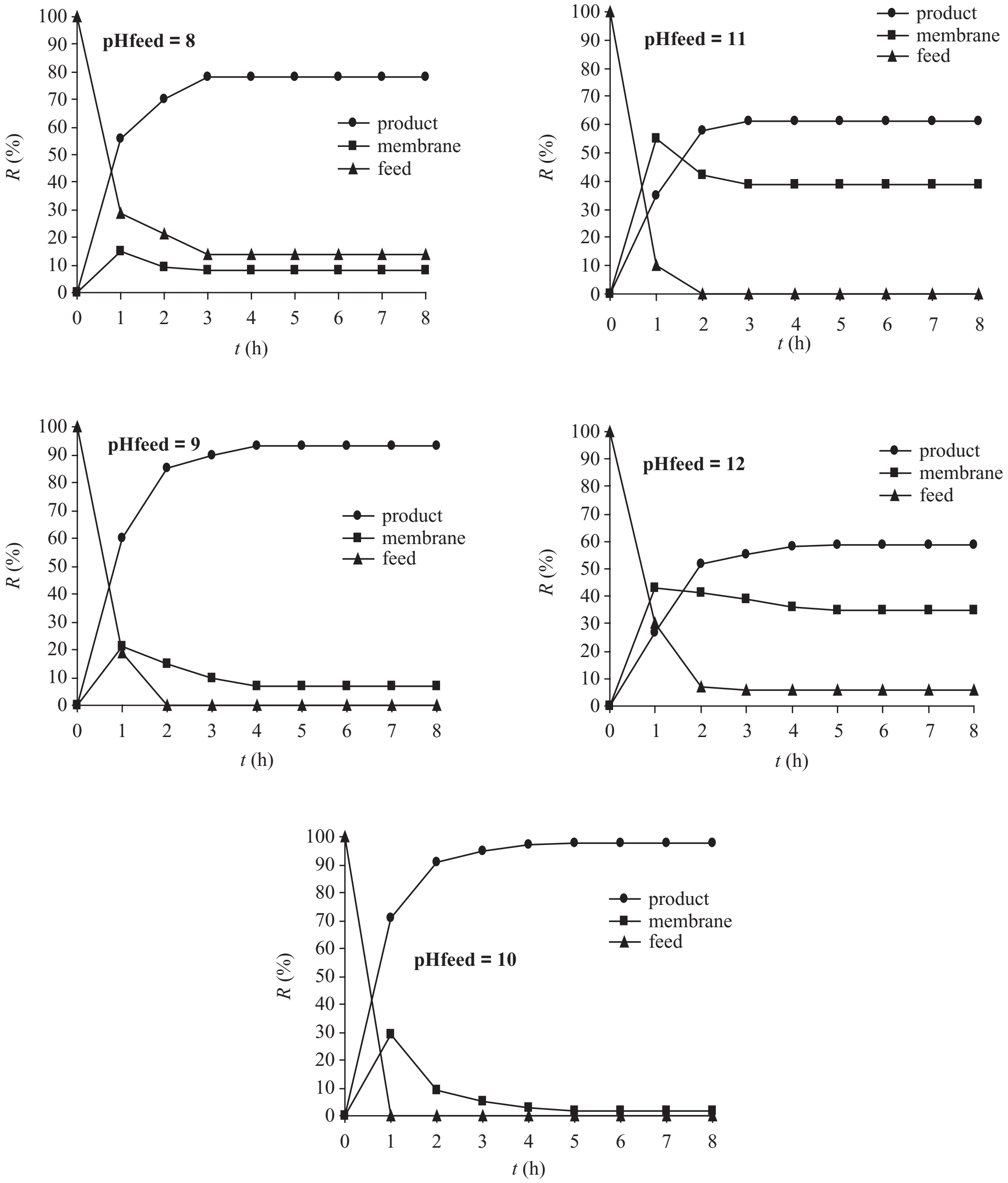

Fig. 7. Effect of the pH of the feed phase on R in product, membrane and feed phases.

to the desired value (8, 9, 10, 11 and 12) using ammonium hydroxide.

The experiments were then carried out at 30°C, 300 rpm and a pH of product phase equal to 1.

The results (Fig. 7) show that the extraction of Cu^{2+} from the aqueous phase into the organic membrane occurred very rapidly, so that the extraction was complete after just 1 h at pH 10. The highest value of the flux of copper extracted from the feed phase was obtained at pH 10 (16.97×10^{-6} mol/m^2 s) as shown in Table 1. The release of Cu^{2+} from the membrane into the product phase was about 95% attained after 3 h while 5% of Cu^{2+} remained in the membrane phase. A release of 98% was reached after 5 h.

At pH > 10, the percentage of copper extracted remained high and attained 100% at 2 h with pH 11 while the accumulation into membrane increased rapidly attaining 55% at 1 h and decreased thereafter to a plateau of about 40%. At pH 11 and 12 the product phases stripped lower amounts of copper than in case of pH 10.

It can be speculated that a stable complex was formed between the carrier and $Cu(NH_3)_4^{2+}$ that was difficult to dissociate at the membrane/product interface leading to decrease the efficiency of copper transport from the membrane. There is a lack of detailed knowledge about the mechanism of transport of $Cu(NH_3)_4^{2+}$ by D2EHPA and other experiments are needed to clarify such behavior.

4. Conclusion

From the results obtained in this study, it can be concluded that some parameters play an important role on copper transport through the organic membrane, while other parameters seem not to affect greatly the transport. In fact, extraction and stripping were greatly improved when the pH of the product and feed phases were adjusted to 1 and 10, respectively. Under these conditions, extraction was over in 1 h of contact with the membrane containing 20% D2EHPA. Stirring seems also to affect the transport efficiency. In fact, the agitation promotes the regeneration of the interfacial area leading to increase the amount of copper transported through the membrane.

On the other hand, it was observed that the transport of copper ions in the presence of dichloromethane was more efficient than that in the presence of chloroform, probably because of the lower viscosity of the former. However, temperature seems not to affect greatly the extraction of copper. In fact, only a slight improvement on the behavior of the organic membrane and stripping was observed when the temperature was increased from 25°C to 30°C.

Thus, the optimal conditions for an efficient transport of copper ions through the organic membrane are: 300 rpm, 30°C, 20% D2HPA in CH_2Cl_2, ammoniacal feed phase of copper at pH 10 and acidified product phase at pH 1.

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