The Selective Transport of Copper Ion through Supported Liquid Membrane

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The selective transport of copper (II) from an aqueous solution containing zinc, cadmium, nickel and cobalt through supported liquid membrane, using LIX 984 dissolved as a mobile carrier, was studied. The effects of components of organic and feed phases on the transport were investigated. The components of organic phase were given as; diluents: n-heptan, n-octan and kerosene, and polymeric membrane support materials: hydrophobic synthetic polymer membrane (Gorotex Teflon), poly (vinylidine difluoride) (Durapore HVHP). The component of feed phase is given as pH. The transport order for diluents and support observed as the feed phase pH increases is: n-heptan > n-octan > kerosene and teflon > durapore. Also, the results showed that Cd^{+2}, Zn^{+2}, Co^{+2} and Ni^{+2} ions were not transported at the pH range of feed phase studied, and 85.3 % of copper ions in the feed phase were transported.

Key words:
Supported liquid membrane, selective transport, copper ion, LIX 984

Introduction

The selective transport of metal ions from solution is involved in many process for industrial clean production and resource recovery.[1] Liquid membranes have been recently proposed as a new technology for the selective separation, purification and concentration of metals in aqueous solutions, organic acid, bioproduct, and gases in gas mixtures. Liquid membranes have also received considerable attention due to characteristics such as ease of operation, low energy consumption, operation cost, high selectivity and rapid extraction capacity factors. Because of these factors, liquid membranes have been proposed as an alternative to liquid-liquid extraction, chromatography, and ion exchange for separation and purification.[2–11] But, in spite of the mentioned technical advantages of liquid membranes, there are no major industrial applications of liquid membranes. This is largely due to the stability problems that cause a gradual loss of membrane phase (carrier and diluent).[8,12,13]

In general, a membrane may be regarded as a semi permeable barrier. When liquid membrane placed between feed and stripping phases, chemical species can move through the membrane from a region of high solute concentration into a region of low solute concentration by means of a purely diffusional process. However, it has long been observed that species can also be transported across the liquid membrane against their own concentration gradient as a consequence of an existing concentration gradient of a second species present in the system. Liquid membrane, containing a carrier, may be divided into two categories: non-supported liquid membrane (emulsion and bulk) and supported liquid membrane (flat and hollow fiber). A supported liquid membrane (SLM) which uses a porous membrane support, impregnated with complexing carriers to separate the feed and stripping phases, represents one of the feasible types of liquid membranes.[3,12]

In this paper, the selectively transport of copper ions from feed solution containing copper, zinc, cadmium, nickel and cobalt ions through SLM containing LIX 984 as a carrier was investigated at various operation parameters.

Material and methods

The membrane module consists of aqueous phases and an organic phase which contains the carrier, diluent, and support. The membrane serves, both, as a support for the organic phase and as a uniform barrier between two aqueous phases. This results in two aqueous-organic interfaces with well-defined transfer areas. The relationships between the copper ion and the carrier in the membrane interface are governed by the equilibrium:

$$Cu^{2+}_{(aq)} + 2RH_{(org)} \rightleftharpoons R_2Cu_{(org)} + 2H^{+}_{(aq)} \quad (1)$$

The transport of the metals ion through the supported liquid membrane system is considered to

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be composed of many elementary steps. These steps are expressed as follows.[13–19]

– Diffusion of metal ions from the bulk of feed phase to the aqueous stagnant layer in the feed-membrane side

– Chelating reaction between metal ion and carrier at the feed-membrane interface.

– Diffusion of hydrogen ions from the feed-membrane interface to the bulk of feed phase

– Diffusion of carrier-metal complex from the feed-membrane interface to the stripping-membrane interface

– Diffusion of hydrogen ions from the bulk of stripping to the aqueous stagnant layer in the stripping-membrane side

– Decomplexation reaction of carrier-metal complex with hydrogen ion at the stripping-membrane interface

– Diffusion of the regenerated carrier back to the feed-membrane interface.

– Diffusion of metal ions from the stripping-membrane interface to the bulk of stripping phase.

Hydrophobic synthetic polimer membrane (GoroTex Teflon) and poly (vinylidine difluoride) (Durapore HVHP) (Millipore Corp) were used as a solid support for the liquid membrane. In Table 1 some characteristics of the support materials are shown. LIX 984 (Henkel Corp) was selected as a carrier. It is known that LIX 984, a mixed aldoxime (5-dodecylsalicylaldoxime) and ketoxime (2-hydroxy-5-nonylactophenone oxime) reagent, is a good reagent for the copper. Kerosene, n-heptan and n-octan (Fluka) were used as organic diluent. Liquid membrane solution was prepared by diluting LIX 984 with different diluents. The solid support was filled with about 2 – 2.5 mL membrane solution by capillarity. The feed phase was an aqueous solution that contain Cu^{+2} ($CuSO_4 \cdot 5H_2O$), Zn^{+2} ($ZnSO_4 \cdot 7H_2O$), Co^{+2} ($CoSO_4 \cdot 7H_2O$), Cd^{+2} ($3CdSO_4 \cdot 8H_2O$) and Ni^{+2} ($NiSO_4 \cdot 6H_2O$), (20 g m^{-3} Cu^{+2}, 20 g m^{-3} Zn^{+2}, 20 g m^{-3} Co^{+2}, 20 g m^{-3} Cd^{+2} and 20 g m^{-3} Ni^{+2}). The stripping phase was an aqueous solution containing H_2SO_4 (2.30 mol L^{-1}).

The supported liquid membrane module used in this study is given in Figure 1. SLM module has two cells, made by transparent fiberglass, one of which relating to feed solution, another to stripping solution. Porous membrane ($44 \cdot 10^{-6}$ m (Teflon) and $125 \cdot 10^{-6}$ m (Durapore) × 0.23 m × 0.09 m) was placed between the two cells. System temperature was controlled by a thermostat. After the system reached the desired temperature, the feed and stripping solutions were pumped to the membrane module. The concentration of metal ions (Cu^{+2}, Zn^{+2}, Co^{+2}, Cd^{+2} and Ni^{+2}), in the feed and stripping solutions, was determined by Atomic Absorption Spectrophotometer (Shmadzu AA–670), after the samples were taken at specific time periods. Experimental parameters and their levels to be studied were determined by preliminary tests and given in Table 2.

Table 1 – *Characteristics of support materials*

	Porosity ε / %	Pore diameter *d* / μm	Thickness δ / μm
Gorotex teflon	87.5	1	44
Durapore HVHP	75	0.45	125

Table 2 – *Parameters and their levels to be studied*

	Levels of parameters						
pH of feed phase	1	1.5	2	2.5	3	4	5
Porous support materals	Gorotex teflon				Durapore (HVHP)		
Diluent	n-heptan			n-octan		kerosene	

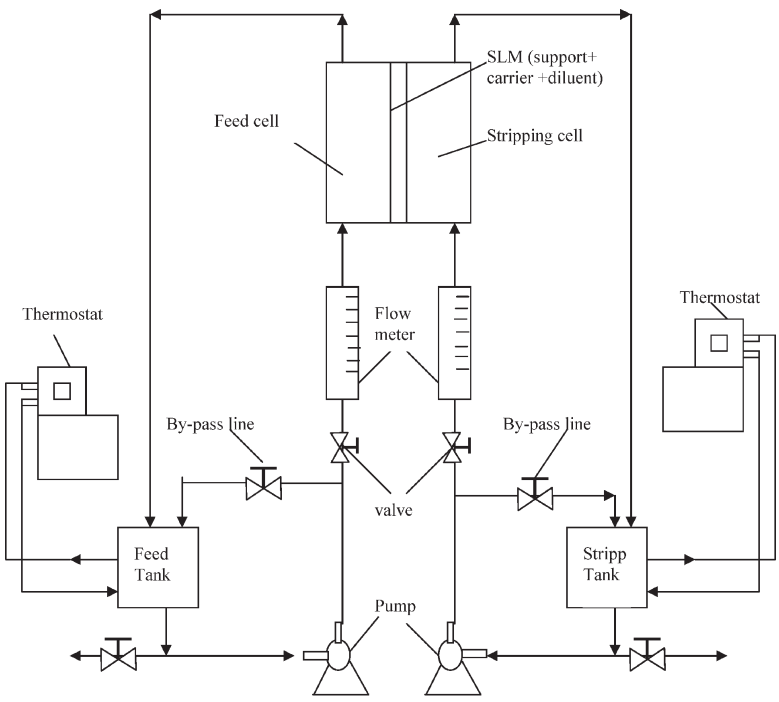


Fig. 1 – *Apparatus used for transport of metal ions through supported liquid membrane*

Results and discussion

The experiments were performed in the pH range of 1–5 to investigate the effect of pH of feed phase on transport by keeping hydrogen ion concentration of stripping phase, temperature, feed and stripping flow rates, carrier concentration constant at 2.3 mol L^{-1} H_2SO_4, 303 K, 2 L · min^{-1} and 10 %, respectively. The effect of pH of feed phase on the

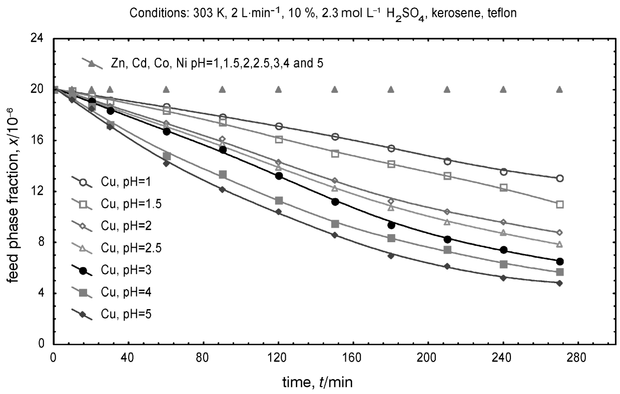


Fig. 2a – *Variation of molar fraction of metal ions in the feed phase at different pH with time*

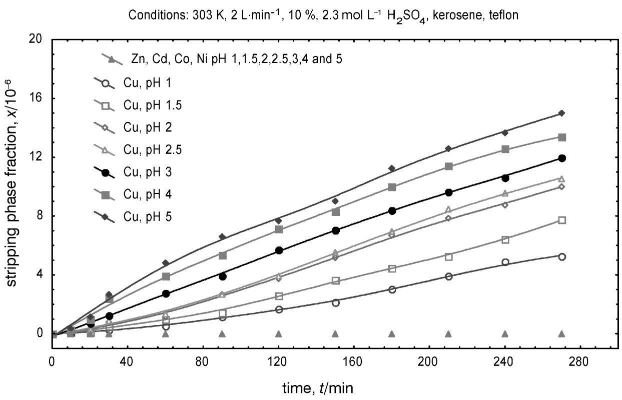


Fig. 2b – *Variation of molar fraction of metal ions in the stripping hase at different pH with time*

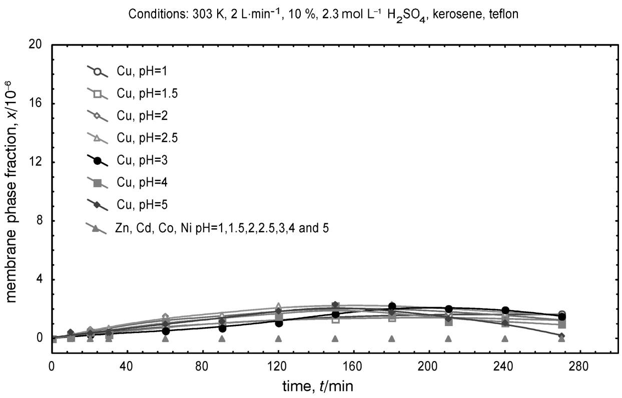
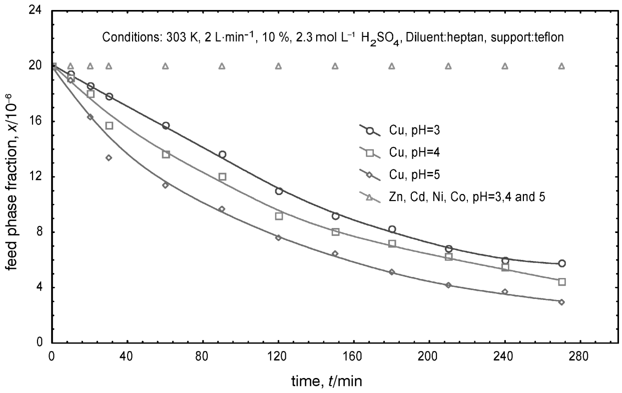


Fig. 2c – *Variation of molar fraction of metal ions in the membrane phase at different pH with time*

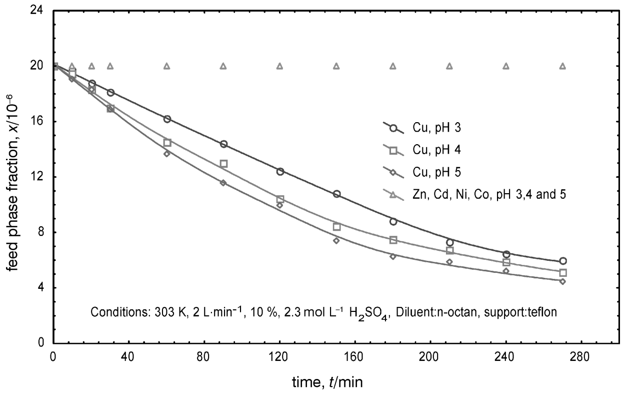
transport of copper ions through supported liquid membrane is an important parameter because of the equilibrium limitations of extraction reaction (equation 1), and also, the transport driving force for acidic extractants is a pH gradient between the feed and stripping phases. The effect of pH of feed phase on the transport of metal ions through SLM, containing LIX 984 (carrier), kerosene (diluent) and support material (Teflon membrane), is given in Figures 2a, 2b and 2c. It was observed from Figures 2a-c that Cd^{+2}, Co^{+2}, Zn^{+2} and Ni^{+2} ions were not transported at pH range of 1 – 5. Also, as it can be seen from figures 2a-c that 34.50 % of copper ions in the feed phase were transported at pH of 1 and at pH of 5, 75.75 % of copper ions in the feed phase were transported.

The effect of diluents on the metal ions transport was investigated. Experiments were performed in the pH range of 3 – 5 by keeping hydrogen ion concentration of stripping phase, temperature, feed and stripping flow rates, carrier concentration constant at 2.3 mol L^{-1} H_2SO_4, 303 K, 2 L · min^{-1} and 10 %, respectively. Diluents used to dilute carrier have an effect on the mass transfer in the porous support materials. With decreasing molecular– mass of diluents increases maas transfer rate in the porous support materials. The effect of diluents (n-heptan, n– octan and kerosene) on the transport of metal ions through SLM is given in Figures 3a-c, 4a-c and 5a-c, respectively. It can be seen from Figures 3a-c, 4a-c and 5a-c that the transport of copper ions transport increases with decreasing molecular mass of diluents. For n-heptan, n-octan and kerosene, the transport efficiencies of copper ion through SLM containing LIX 984 as a carrier at the conditions of feed phase pH of 5, 303 K temperature, φ = 10 % carrier concentration, 2.3 mol L^{-1} H_2SO_4 stripping phase concentration and 2 L · min^{-1} flow rate of feed and stripping phases are 85.3 %, 77.75 % and 75.75 %, respectively. The transport order for diluents observed as the feed phase pH increases is n-heptan > n-octan > kerosene.

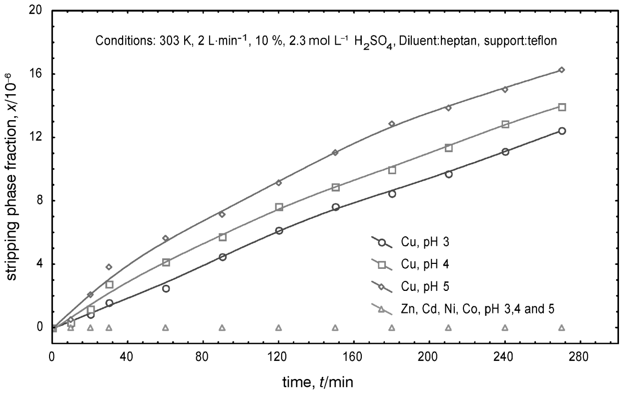
The physical composition of the porous support plays an important role in the transport of metal ions through SLM. Identical transport experiments were performed with Teflon and Durapore membrane. The effect of support materials (Teflon and Durapore membrane) on the transport of metal ions through SLM, using LIX 984 in kerosene as a carrier, is given in Figures 6a-c. As it can be seen from Figures 5a-c and 6a-c that for Gorotex Teflon and Durapore HVHP, the transport efficiencies of copper ions through SLM containing LIX 984 in kerosene at the conditions of feed phase pH of 5, 303 K temperature, φ = 10 % carrier fraction, 2.3 mol L^{-1} H_2SO_4 stripping phase



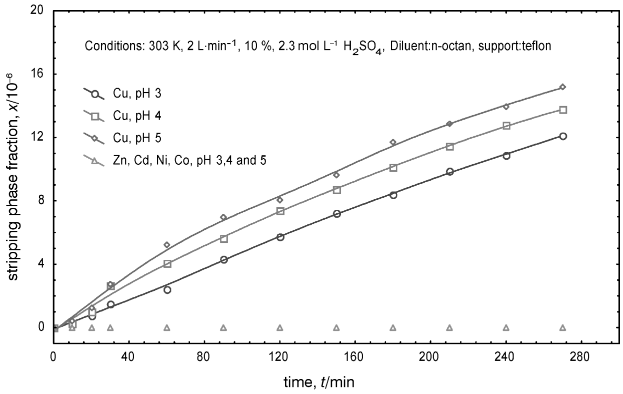
F i g . 3 a – *Variation of molar fraction of metal ions in the feed phase at different pH with time*



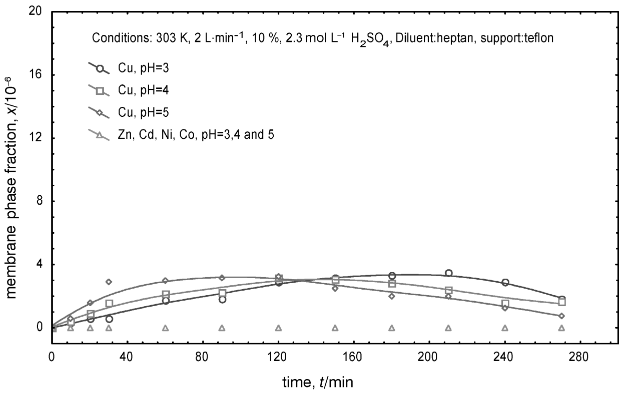
F i g . 4 a – *Variation of molar fraction of metal ions in the feed phase at different pH with time*



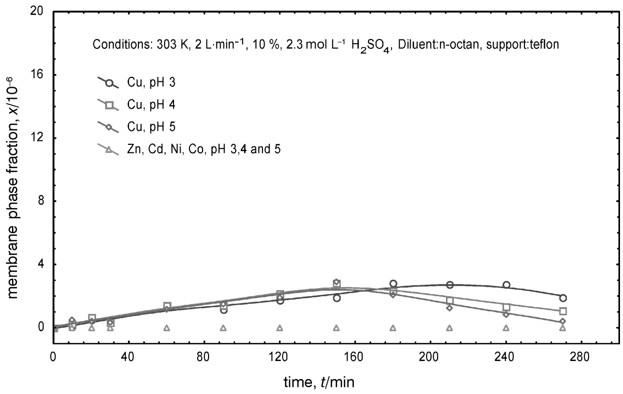
F i g . 3 b – *Variation of molar fraction of metal ions in the stripping phase at different pH with time*



F i g . 4 b – *Variation of molar fraction of metal ions in the stripping phase at different pH with time*



F i g . 3 c – *Variation of molar fraction of metal ions in the membrane phase at different pH with time*



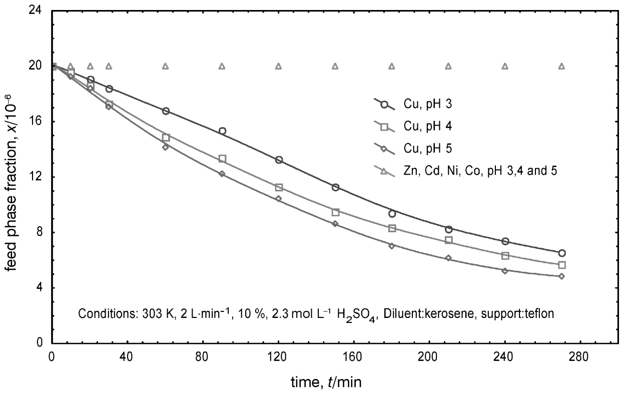
F i g . 4 c – *Variation of molar fraction of metal ions in the membrane phase at different pH with time*

concentration and 2 L · min^{-1} flow rate of feed and stripping phases are 75.75 % and 70.75 %, respectively.

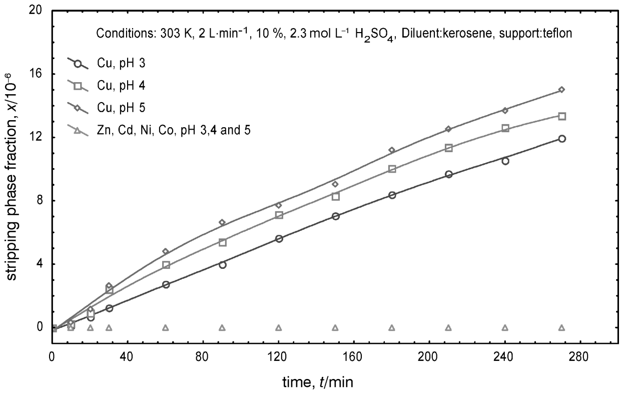
Conclusions

The transport of various metals such as copper, zinc, cobalt, nickel and cadmium ions through SLM containing LIX 984 as a carrier was studied. The effect of pH of feed phase, diluents and support materials on the transport of metal ions was investigated. The major conclusions derived from work as follows:

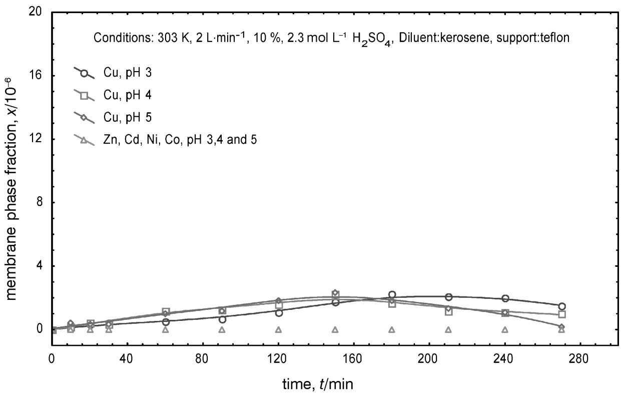
– It was observed that Cd^{+2}, Co^{+2}, Zn^{+2} and Ni^{+2} ions were not transported at pH range of feed phase studied.



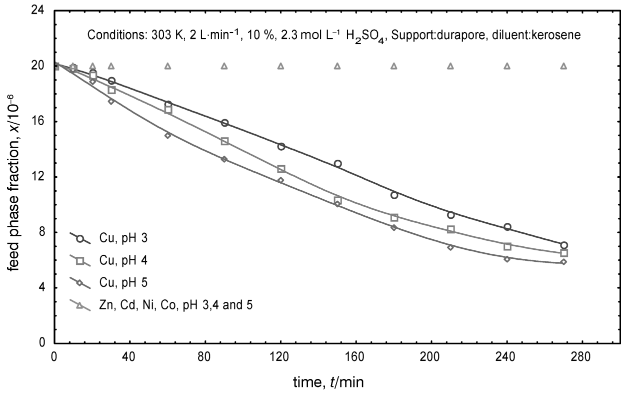
F i g . 5 a – *Variation of molar fraction of metal ions in the feed phase at different pH with time*



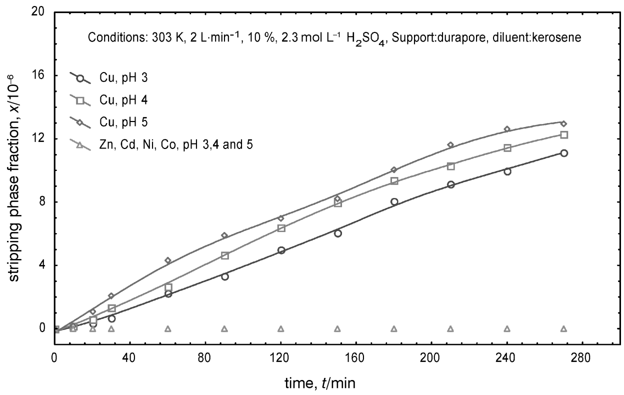
F i g . 5 b – *Variation of molar fraction of metal ions in the stripping phase at different pH with time*



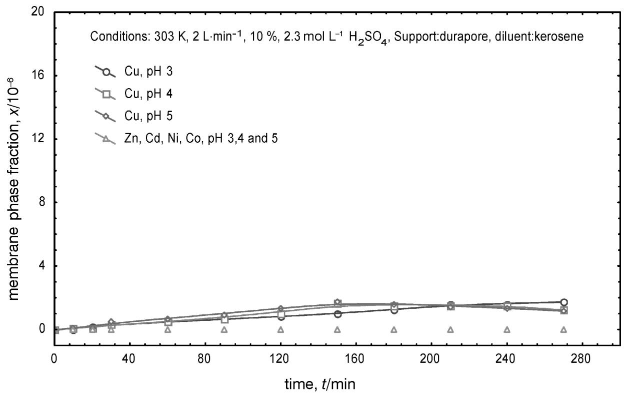
F i g . 5 c – *Variation of molar fraction of metal ions in the membrane phase at different pH with time*



F i g . 6 a – *Variation of molar fraction of metal ions in the feed phase at different pH with time*



F i g . 6 b – *Variation of molar fraction of metal ions in the stripping phase at different pH with time*



F i g . 6 c – *Variation of molar fraction of metal ions in the membrane phase at different pH with time*

– The transport order for diluents observed, as the feed phase pH increases, is n-heptan > n-octan > kerosene.

– The transport order for support observed, as the feed phase pH increases, is Gorotex teflon > durapore HVHP.

– Acording to the obtained data, it can be said that copper ions from feed phase containing copper, zinc, cadmium, cobalt and nickel were selectively transported through SLM containing LIX 984 as a carrier.

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