Study of the Transport of Chromium, Manganese and Zinc through Bulk Liquid Membrane Using D2EHPA and Cyanex 301 as a Carrier

CRISTIANA OLTEANU[1], PIOTR SZCZEPANSKI[2], CRISTINA ORBECI[1], CARMEN GEORGIANA LICA[1], LORETA COSTACHE[1], IOANA DIACONU[1*]

[1]University Politehnica of Bucharest, Department of Analytical Chemistry and Environmental Protection, 1-3 Gh. Polizu Str., 011061, Bucharest, Romania

[2]Nicolaus Copernicus University, Faculty of Chemistry, 7 Gagarin St., 87-100 Torun, Poland

This paper presents experimental results obtained at the transport of metal cations, such as Cr (III), Mn (II) and Zn (II), through a kerosene liquid membrane in the presence of D2EHPA and Cyanex 301. The influence of the metal cation concentration in the feed phase and the molar ratio Cyanex 301: D2EHPA on the system efficiency was studied. The transport process assay was done by calculating the efficiency (E%) and recovery factor (RF%) of mentioned cations. Thus it has been revealed the possibility of separation and recovery of Zn (II) cations in the presence of Mn (II) with efficiency of 96% when used as a carrier a mixture of Cyanex 301 and D2EHPA at a molar ratio 0.01 : 0.09. The recovery factor had a high value even in conditions of a low yield as a result of metal cations accumulation in the membrane phase.

Keywords: Bulk liquid membrane, D_2EHPA, Cyanex 301, chromium, manganese, zinc

Metal pollution is a subject, whose importance is growing due to developing industries such as paper industry, dyestuffs industry, fertilizers and fungicides or pesticides industry, glassware industry, plating facilities and lining or steelworks [1]. Therefore heavy metal pollution is encountered especially in developing countries. Heavy metals have an increased risk on the environment because, unlike organic pollutants, these are not biodegradable. Thus appears an accumulation of heavy metals in the ecosystem causing disorder and various diseases because of the carcinogenic potential of heavy metals. [2].

Chromium is a metal with a high toxic potential. It can be found in nature in two oxidation states Cr (VI) and Cr (III). Chromium can cause a series of diseases and even cancer. Cr (III) has not a toxic potential as high as Cr (VI). However the ingestion of this metal by humans in large quantities can cause liver and kidney malfunction [3-5]. Cr (III) has an increased risk on the environment by being able to oxidize to Cr (VI) in the environment. Permitted limits for Cr (III), as recommended by the Guidelines for Drinking Water United States Environmental Protection Agengy (USEPA) are 100 μg / L [6-7].

Manganese is also a heavy metal that is found in several oxidation states in nature from +2 to +7. According to the studies Mn [8] (II) has serious health effects and mutagenic effects. Thus according to the studies [8] performed on mice after exposure to Mn (II) chromosomal and micronuclei in bone narrow abnormalities were observed. There are no animal studies showing the carcinogenic potential of Mn (II), but there have been studies according that Mn (II) can develop tumors. So after administration of Mn (II) in injection form of some doses on mice for 22 weeks showed the increase number of pulmonary edemas [9]. Permitted limits for Mn (II) as recommended by the Guidelines for Drinking Water United States Environmental Protection Agengy (USEPA) are 0.5mg / L [6].

Zinc, a frequently encountered heavy metal, in high concentration presents serious effects on health such as: muscular stiffness, appetite loss, nauseous and weakening of immune system [10-12] Permitted limits for Zn (II) as recommended by the Guidelines for Drinking Water United States Environmental Protection Agengy (USEPA) are 0.5mg / L [6].

There are several ways of removing these heavy metals such as: removal by hydroxide precipitation or sulfide precipitation, heavy metal chelating precipitation, adsorption on activated carbon adsorbents, e.g. carbon nanotubes adsorbents or zeolite, solvent extraction, membrane filtration or ion exchange [1,7].

Among the methods of removing heavy metals from wastewater, an important place is occupied by liquid membranes. Advantages such as simplicity of operation, low cost, low energy consumption and high efficiency makes this technique extensively studied [13-19]. So has been studied the removal of Mn (II) from acidic solutions by liquid membrane [20-24]. Thus using hybrid liquid membrane the total removal of Mn (II) from the feed phase was realized, and managed to achieve 88% recovery. The membrane system used here consists in a liquid membrane containing di (2-ethylhexyl) phosphoric acid and tri-n-octylamine in 1,2-dichloroethane with solid anion-exchange membranes [20]. Cr (III) was also removed by liquid membranes [25-29]. Cr (III) was removed using supported liquid membranes [28]. In this system the optimal transport conditions were the concentration of 5.26 mol / L triethanolamine membrane liquid in the microporous polypropylene film and 1.5 mol/dm3 H_2SO_4 concentrations in the stripping phase. Another study using pseudo-emulsion based hollow fiber strip dispersion (PEHFSD) technology and the Quaternary ammonium salt trioctyl methylammonium chloride (TOMACl) dissolved in n-decane as mobile carrier [29]. The process was assessed by determining of the overall permeation coefficient obtained under experimental standard conditions (4.0×10^{-4} cm s^{-1}).

Liquid membranes were also used in the removal of zinc. Thus Zn was recovered and separated from copper using a hybrid rotating film pertractor [30] with discs made

* *email.: diaconuioana12@yahoo.com*

of cation-exchange polymers (perfluorosulfonated polymer, sulfonated poly(ether ether ketone), and sulfonated polysulfon). The liquid membrane consisted in this case from of di(2-ethylhexyl) phosphoric acid dissolved in kerosene. A simultaneous recovery of copper and zinc was also achieved using a double multimembrane hybrid system (d-MHS) composed of: stripping solution (1) | MHS(1) | feed solution | MHS(2) | stripping solution (2) [31]. Supported liquid membranes were used to transport and separate Zn from copper [32].

The efficiency and selectivity of membrane processes are greatly enhanced by the use of carriers. When using the liquid membrane technique we can enumerate several carriers: di-2-ethylhexyl phosphoric acid (D2EHPA), di-2,4,4-trimethylpentyl phosphinic acid (Cyanex 272), di-2,4,4-trimethylpentyl dithiophosphinic acid (Cyanex 301), tri-octylmethylammonium chloride (Aliquat 336), tri-n-butylphosphate (TBP), Tri-n-octyl phosphine oxide (TOPO), calixarenes and calixarenes derivatives, cyclodextrins.

In this paper the transport of chromium (III) and separation of manganese (II) and zinc (II) ions from synthetic solutions using bulk liquid membrane was studied. In the study as selective carriers D2EHPA, Cyanex 301 and the mixtures of them were applied.

Experimental part

Reagents

$Cr_2(SO4)_3$, $MnSO_4$ $ZnSO_4$, HCl and H_2SO_4 (pure p.a) were purchased from POCh, Poland, Gliwice. Kerosene used as memmbranar solvent was supplied by CHMES Poland. The carriers of chromium and manganese cations used for the preparation of liquid membranes, di-(2-ethylhexyl) phosphoric acid (D2EHPA, 95%) and di-2,4,4-trimethyl-pentyl dithiophosphinic acid (Cyanex 301, 95%), were suplied by Alfa Aesar, Fluka respectively.

Experimental procedure

The transport experiments were performed in glass beaker-in-a-beaker type cell presented in figure 1.

The transport cell was termostated. The water in the thermostated vessel was maintained at constant temperature of 25°C by circulating water from bath through the jacket. The organic phase was agitated with a mechanical stirrer at 375 rpm. The stirring speed of the feed and stripping solutions (two Teflon-coated magnetic bars) was maintained at 200 rpm. The volume of the feed phase was 105 mL, the volume of the stripping phase - 25 mL and the volume of the liquid membrane - 25 mL. The pH of the feed source was of *p*H=5.07 adjusted with Hcland measured with a glass electrode using Elmetron 721. The concentration of the metal cations was determined using an atomic absorption spectrometer, Varian SpectrAA – 20 ABQ. The membrane content in metal cations was determined using material mass balance of the three phases of the membrane system.

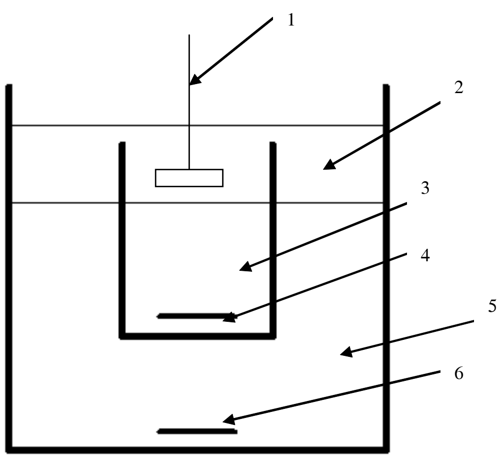

Fig. 1.Experimental device. 1 – mechanical stirrer, 2 –bulk liquid membrane, 3 –strip solution, 4 – magnetic stirrer, 5 – feed solution, 6 - magnetic stirrer

Two types of studies were performed.

The first type of study was the competitive transport of manganese and zinc. The experimental conditions were: 0.1 mol/L $MnSO_4$ and 0.1 mol/L $ZnSO_4$ in feed phase, for the membrane were used various molar ratio Cyanex 301:D2EHPA= 0.1:0, 0.09:0.01, 0.07:0.03, 0.05:0.05, 0.03:0.07, 0.01:0.09, 0:0.1 in kerosen and for the receiving phase 1 mol/L H_2SO_4 was used.

The second study consisted in the transport of chromium cations recovery when we used only D2EHPA as extractant In this case the experimental conditions were: variouse concentrations of $Cr_2(SO_4)_3$ in feed source 0.005, 0.1, the same concentration of carrier in kerosen in all the experiments 0.1 mol/L and for the receiving phase H_2SO_4 1 mol/L.

Results and discussions

In this paper are presented the experimental data obtained at the transport of metal cations chromium (III), manganese (II), zinc (II) in the presence of two carriers, commercially available, D2EHPA and Cyanex 301 whose structure is shown in figure 2.

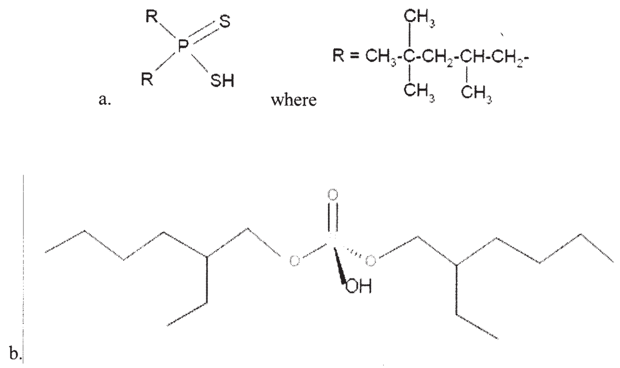

Fig. 2. Chemical Structure of a.CYANEX 301 and b.D2EHPA

In general, metal cations can pass through an organic membrane from an aqueous phase source in an aqueous receiving phase in the presence of adequate carriers. The carrier dissolved in the organic membrane has the role to complex the metal cations at the interface of feed phase/ membrane enabling its solubility in the membrane. The solute recovery in the receiving phase is done by decomposing the complex at the interface membrane / receiving phase. So at the interface of the extraction feed phase/membrane, the metallic cation M^{z+} in the presence of acids carriers RH (D2EHPA, Cyanex 301) the equilibrium occurs:

$$(M^{z+})_{f.p.} + z(HR)_m \rightleftharpoons (MR_z)_m + (zH^+)_{f.p.} \quad (1)$$

where is noted:

$M^{z+} = Cr^{3+}, Zn^{2+}, Mn^{2+}$

f.p.. = feed phase

m = membrane

r.p. = receiving phase

After the convective transport of the complex (MR_Z) through the membrane at the stripping interface the equilibrium occurs:

$$(MR_z)_m + (zH^+)_{r.p..} \rightleftharpoons (M^{z+})_{r.p..} + z(HR)_m \quad (2)$$

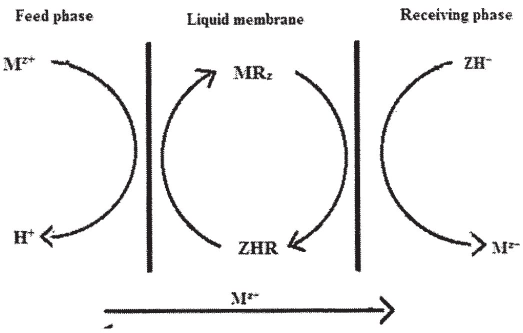

Fig. 3. Transport mechanism for metallic cations M^{z+}(Cr^{2+}, Zn^{2+}, Mn^{2+}) in the presence of carriers R (D2EHPA and Cyanex 301)

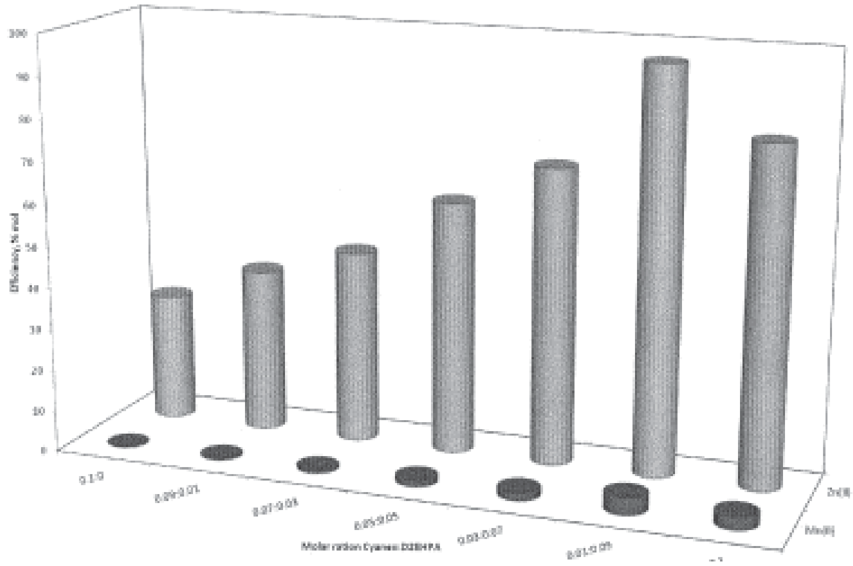

Fig. 4 . Transport efficiency of zinc and manganese depending on the molar ratio Cynex 301: D2EHPA Feed Phase: $MnSO_4$ 0.01M, $ZnSO_4$ 0.01M; Membrane: different molar ratio of Cynex 301: D2EHPA in kerosene; Receiving phase H_2SO_4 1M

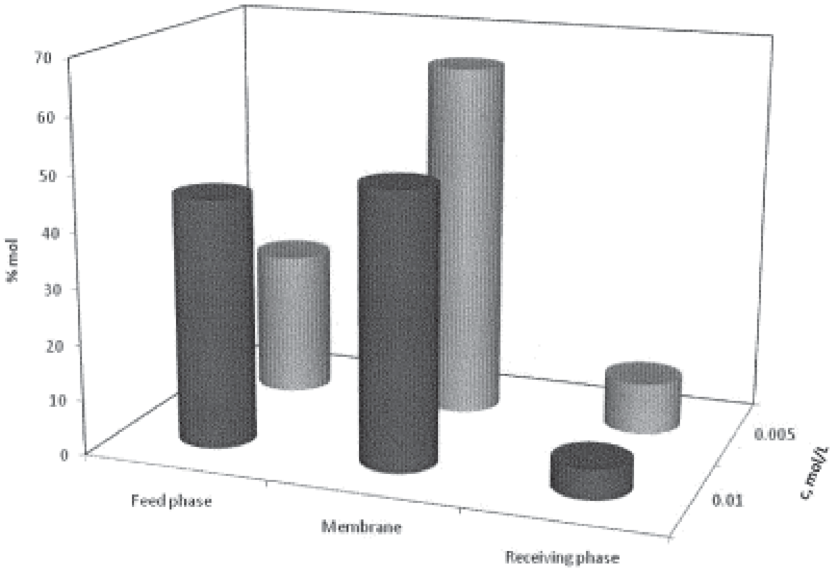

Fig. 5 Chromium phase distribution at the end of the transport Feed Phase: $Cr_2(SO_4)_3$ 0.01-0.005M, $ZnSO_4$ 0.01M; Membrane: D2EHPA 0.01M in kerosene; Receiving phase H_2SO_4 1M

The transport mechanism diagram is shown in figure 3.

As a first step was assessed the transport process of the studied cations by calculating the transport efficiency with the relation (3):

$$E\% = \frac{V_{r.p.} \cdot C_{r.p.}}{V_{f.p.} \cdot C_{f.p_0}} \qquad (3)$$

where :

E% - the transport efficiency
$V_{r,p}$ - the receiving phase volume[mL]
$C_{r,p}$ - the receiving phase concentration [mol/L]
$V_{f,p}$ - the feed phase volume[mL]
$C_{f,po}$ - the initial the feed phase concentration[mol/L]

The experimental results obtained have shown that the transport of the cations chromium and manganese using the studied system take place with low yields that do not exceed 10% for chromium ions and 5% for manganese ions. The highest efficiencies of 96 % are obtained only for the transport of zinc cations according to the figure 4.

Analyzing the molar percentage distribution in the phases of membrane system we can make some observations. According to the data presented in figure 5 it is observed a chromium removal from the feed phase in a proportion of 74%, a percentage distributed between membrane and receiving phase. This result was obtained under the terms of use a phase source which contains $Cr_2(SO_4)_3$ in the concentration of 0.005 mol / L acidified with HCl at *p*H = 5.07.

From the figures 6-8 it is observed the separation of the Mn^{2+} from Zn^{2+} cations with the recovery of the Zn^{2+} ions. The best results in the separation of Mn^{2+} from Zn^{2+} ions

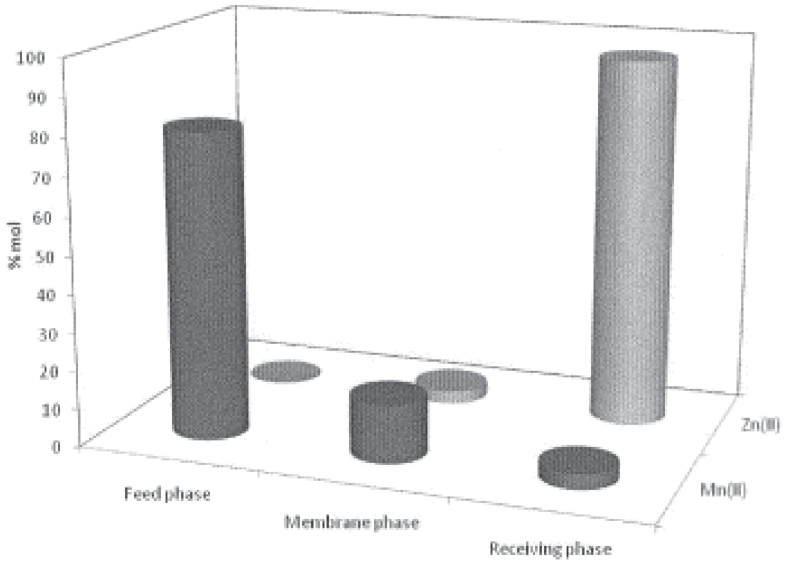

Fig. 6. Zinc and manganese phase distribution at the end of the transport when using a carier molar ratio Cyanex 301 :D2EHPA 0.01: 0.09 Feed Phase: $MnSO_4$ 0.01M, $ZnSO_4$ 0.01M; Membrane: diferent molar ratio of Cynex 301: D2EHPA 0.01: 0.09 in kerosene; Receiving phase H_2SO_4 1M

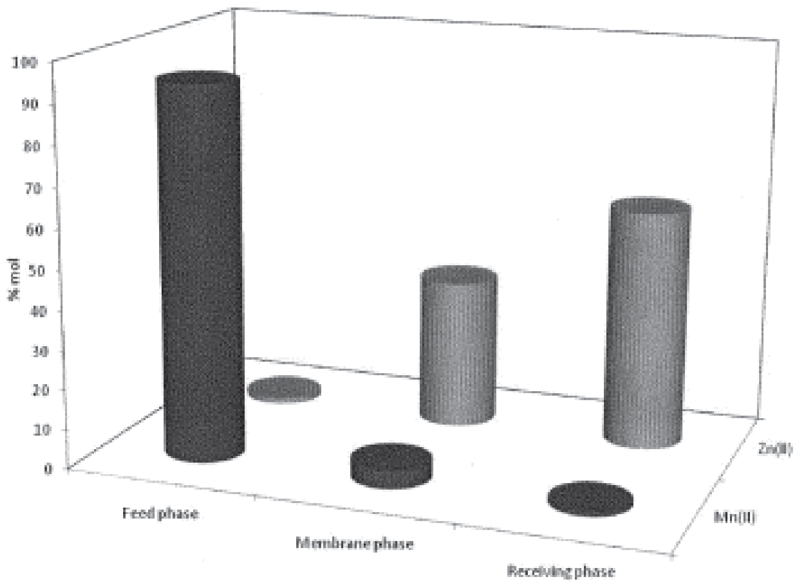

Fig. 7. Zinc and manganese phase distribution at the end of the transport when using a carier molar ratio Cyanex 301 :D2EHPA 0.05: 0.05 Feed Phase: $MnSO_4$ 0.01M, $ZnSO_4$ 0.01M; Membrane: diferent molar ratio of Cynex 301: D2EHPA 0.05: 0.05 in kerosene; Receiving phase H_2SO_4 1M

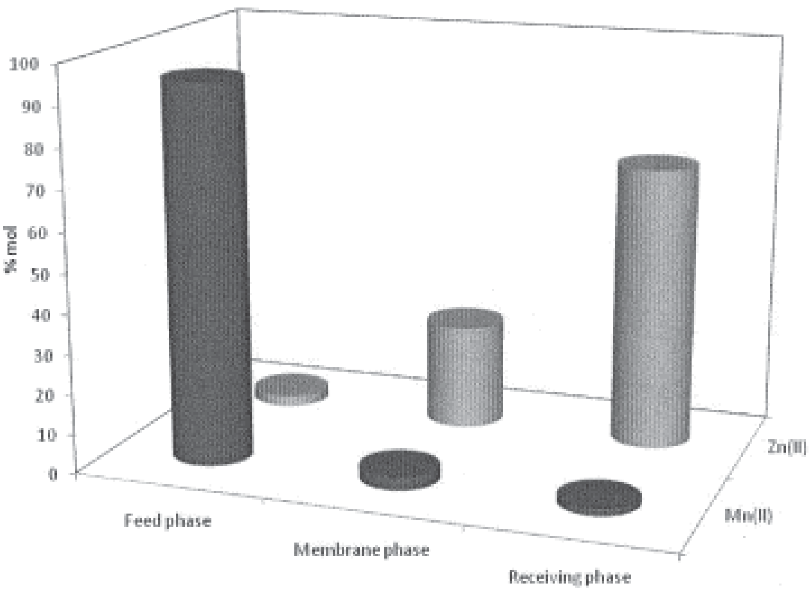

Fig. 8. Zinc and manganese phase distribution at the end of the transport when using a carier molar ratio Cyanex 301 :D2EHPA 0.03: 0.07 Feed Phase: $MnSO_4$ 0.01M, $ZnSO_4$ 0.01M; Membrane: diferent molar ratio of Cynex 301: D2EHPA 0.03: 0.07 in kerosene; Receiving phase H_2SO_4 1M

are obtained in the case of use a mixtures of Cyanex 301 and D2EHPA as carriers in the following molar ratios Cyanex 301 : D2EHPA : 0.05 : 0.05, 0.03 : 0.07; 0.01 : 0.09. The maximum separation yield is obtained in the case of molar ratio of the carriers Cyanex 301 : D2EHPA 0.01 : 0.09.

A parameter often used in appreciation of the efficiency of transport process through liquid membranes is the recovery factor (RF%) calculated with equation (4):

Transport conditions			Recovery factor
Feed phase	Membrane	Receiving phaser	R.F.%
$MnSO_4$ 0.01M $ZnSO_4$ 0.01M	D2EHPA 0,1 M	H_2SO_4, 1M	R.F.% (Zn)=86.65% R.F.% (Mn)=5.30%
$Cr_2(SO_4)_3$, 0,005M	D2EHPA 0,1 M	H_2SO_4, 1M	73.75 %
$Cr_2(SO_4)_3$, 0,01M	D2EHPA 0,1 M	H_2SO_4, 1M	55 %

Table 1
VALUE OF THE RECOVERY FACTOR AT THE END OF THE TRANSPORT PROCESS (THE TIME OF TRANSPORT = 27 h)

$$R.F.\% = \frac{C_{f.p.0} - C_{f.p.f}}{C_{f.p}} \times 100 \qquad (4)$$

where :

$C_{f.po}$ - the initial concentration in the feed phase [mol/L]

$C_{f.p.f}$ - the concentration at the end of the transport process in the feed phase[mol/L]

Some values of recovery factors obtained in the case of membrane systems studied in this work are presented in table 1.

It is observed that high values of recovery factors are encountered even when the transport yields are low, due to a phenomenon of acumulation in the membrane.

Conclusions

In the present paper was studied the behaviour at transport through bulk liquid membranes of metal cations (individual -chromium (III)) and mixed- Mn (II) and Zn (II)) in the presence of the carriers Cyanex 301 and D2EHPA dissolved in a kerosene membrane at different molar ratios.

The experimental results indicate the possibility of separation of Mn (II) from Zn (II) cations using bulk liquid membrane. The optimum molar ratio of Cyanex 301: D2EHPA for the separation of Zn (II) and Mn (II) was 0.01 : 0,09 and for the concentration of Mn (II) was 0 : 0.1.

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