Bulk Liquid Membrane Separation of Different Cations Using D2EHPA and Cyanex 302 as Carriers

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A bulk liquid membrane (BLM) system containing (D2EHPA) bis-2-ethylhexyl phosphoric acid and Cyanex 302 – bis-(2,4,4-trimethylpentyl) monothiophosphinic acid as a carriers and kerosene as solvent was studied for the separation of metal cations as Cr (III), Mn (II) and Zn (II) from aqueous solutions. The influence of the metal cation concentration in the feed phase and the molar ratio Cyanex 302: D2EHPA on the system efficiency were studied. The transport process assay was done by calculating the efficiency (E%) and recovery factor (RF%) of mentioned cations.

Keywords: Bulk liquid membrane, D2EHPA, Cyanex 302, 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].

Zinc is the most important nonferrous metal after copper and aluminum [2]. In the world, zinc is generally produced from primary sulphide ores or secondary materials. Solvent extraction of zinc is one of the most popular hydrometallurgical ventures. Zinc is used mainly for galvanizing iron. More than half of the metallic zinc goes into galvanizing steel, but is also an important material for the preparation of certain alloys. It is also used for the negative plates in some electric batteries, for roofing and gutters in buildings construction. The technique is expected to gain more popularity with the latest trends in the recovery of zinc from various low grade ores and industrial wastes [3].

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) does not have 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 [4-6].

Manganese is associated with nickel laterite waste effluents [7] and is used in many industries such as chemicals, fertilizers, ceramics, glass and paints. In the steel industry, manganese has special properties compared to other metals with respect to hardness, corrosive resistance, etc [8]. For the quantitative recovery of manganese and co-recovery of other metal ions present with it, solvent extraction offers the cheapest and most suitable technique.

Metallic ion solvent extraction is an important operation used in hydrometallurgical and chemical industries. Due to the growing demand for high purity metals and also to concerns over environmental issues and continuous depletion of high grade ores (which has resulted in the treatment of ores of lower grade and greater complexity), the solvent extraction has become an important hydrometallurgical tool [9, 10]. Materials like spent batteries, spent catalysts, mostly containing zinc, chrome and manganese could be recovered from aqueous media by solvent extraction [11, 12].

A combined SLM/strip dispersion process [13] was firstly reported for the removal and recovery of target species from a feed solution. This is a new liquid membrane process, which has several advantages: increased stability of the membrane, reduced costs, increased simplicity of operation, extremely efficient stripping of the target species from the organic phase to obtain high flux and a high concentration of the recovered target species in the aqueous strip solution. The liquid membrane is an organic solvent layer separating two aqueous solutions. The compounds that facilitate the transport of substances between the aqueous phases are dissolved in the organic phase. Some of the advantages of this technique are low capital, low operating costs, high selectivity and fluxes, continuous and easy operation, small amounts o extractants, increasing transport against concentration gradients. The principle of liquid membrane separation (or "liquid petraction") is very simple: the two miscible and homogeneous liquid, also known as the feed phase or the donor solution and the stripping phase or the acceptor solution are separated by the liquid membrane, the third liquid, which is immiscible and insoluble in the other two liquids. In most cases the donor and the acceptor solutions are aqueous solution. [14].

Most of the studies have been made using liquid membrane for the transport and concentration of zinc(II) ions in wastewater [15–22]. A great number of studies have been reported on the extraction of zinc from different aqueous media by organophosphorus extractants. The system of zinc sulphate/di (2-ethylhexyl) phosphoric acid (D2EHPA) has been used at commercial scale, mainly as

a method for recovering zinc from waste streams and secondary materials [23-25]. Because of low selectivity of D2EHPA for zinc and manganese separation at low pHs, employing secondary extractant as synergist is necessary [26]. The term synergism is used to describe cases where the extractive capability of a mixture of extractants is greater than the sum of their individual extractive capabilities [27]. Cyanex 302 (bis-(2,4,4-trimethylpentyl) monothiophosphinic acid) has been successfully used as the synergist for different metal separation [28-30].

Cr (III) was also removed by liquid membranes [31-35]. The Cr (III) was removed using supported liquid membranes [34].

Solvent extraction of manganese using various organo-phosphorous extractants such as D2EHPA and tri-n-butyl phosphate has been reported [36, 37] . Whilst extraction of Mn(II) with Cyanex 302 (*bis*(2,4,4-trimethyl-pentyl-) mono-thio-phosphinic acid) in toluene has been reported [38]. The extracted species was proposed to be [R2P(S)O] Mn and the extraction of Mn(II) became quantitative in the pH range 6–8. Extraction of Mn(II) using D2EHPA (di-2-(ethyl-hexyl)-phosphoric acid) from sulphate, nitrate and acetate media has been investigated by Wood and Roscoe (1970) [39]. A more detailed study with D2EHPA on the separation of divalent metal ions from a synthetic nickel laterite leach solution containing Zn, Ca, Mn, Cu, Ni, Co and Mg was reported by Cheng (2000) [40].

Di-(2-ethylhexyl) phosphoric acid (DEHPA or HDEHP) is used in the solvent extraction of uranium as well as of the rare earth metals [41]. DEHPA is a highly effective extractant commercially used to recover uranium, vanadium, beryllium, cobalt, zinc, rare earths and other valuble metals. DEHPA, could be used alone or in combination with other synergetic reactants including tioctylphophine oxide, trubutyl phosphate and dibutyl butyl phosphanate. This hydrophobic anion can chelate a cation from an aqueous phase, the chelate being soluble in the organic phase. Several studies have suggested that chelation by the DEHPA anion is assisted by coordination with the non-deprotonated species. The extraction of Zn^{2+} is a typical exemple of DEHPA chelation and coordination. The liquid membrane contained di-(2-ethylhexyl)-phosphoric acid (DEHPA) as mobile carrier dissolved in kerosene [42].

D2EHPA – bis-2-ethylhexyl phosphoric acid and Cyanex 302 – bis-(2,4,4-trimethylpentyl) monothiophosphinic acid have been used with success as extactants for various metal ions, including manganese from sulphate solutions. When this mixture of extractans (Cyanex 302 and D2EHPA) is used to separate Zn^{2+} from Mn^{2+} the synergism effect causes a better separation for zinc and manganese (higher zinc and lower manganese extraction) [10].

Continuing the previously studies of our group on liquid membranes [43-45], in the present work, it was studied the extraction of zinc [II] and manganese [II] and the transport of chromium [III] using D2EHPA and Cyanex 302 as co-extractants.

Experimental part

The reagents of magnesium sulphate, zinc sulphate, sulphuric acid, chromium sulphate and hydrochloric acid were purchased from, Poland, the cations carriers bis-2-ethylhexyl phosphoric acid (Alfa Aser), di-2,4,4,-trimethylpentyl mono-thio-phosphinic acid(Fluka) and the membranar solvent kerosen (Poland) were used as were bought from manufacturer without further purification.

Phase composition

The feed phase consists in solutions of $MnSO_4$ and/or $ZnSO_4$ of different concentrations made with double distilled water with a feed phase volume of 130 mL whith a *p*H of the feed source of 5.07 which was adjusted with HCl and measured with a glass electrode using Elmetron 721.

The stripping phase consists in solutions of H_2SO_4 of different concentrations, which were prepared from double distilled water and a stripping phase volume of 30 mL.

Membrane phase – for the liquid membrane were used the transporters bis-2-ethylhexyl phosphoric acid (D2EHPA) and di-2,4,4,-trimethylpentyl mono-thio-phosphinic acid (Cyanex 302) which were mixed in different proportions in kerosene, which was used as solvent, and the liquid membrane volume was 50 mL.

The experiments were carried out in a separation cell presented in figure 1. The cell consists of two glass compartments. The experiments were carried out at 25° C for 30 h, the mixing speed was maintained at 200 rpm and the *p*H was 5. The organic phase was agitated with a mechanical stirrer at 375 rpm. The water in the thermostatic vessel was maintained at constant temperature of 25° C by circulating water from constant temperature bath through the jacket. Samples were taken at different time intervals for further analysis as follows: from the feed phase we took 0.2 mL and put it in a 50 mL flask and from the stripping phase we took 1 mL and put it in a 25 mL flask. After all samples were taken the flask were filled up to the mark with double distilled water. So that the samples should not exceed the limit of detection of the atomic absorption spectrometer they are diluted. Sometimes a second dilution is needed. The final concentration of metal ions in the aqueous solutions was determined using an atomic absorption spectrometer, SpectrAA – 20.

Fig. 1 Liquid membrane installation batch (general view)

The transport experiments have the following objectives:
- determination of the transport efficiency and recovery factor of Chromium (III) using as extractant D2EHPA. The experimental conditions were: constant concentrations of $Cr_2(SO_4)_3$ in feed 0.1 mol/L, the same concentration of carrier in kerosen in all the experiments 0.1 mol/L and for the receiving phase H_2SO_4 various concentrations 0.1, 0.5 and 1 mol/L;
- determination of the transport efficiency and recovery factor of Zinc(II) using as extractant D2EHPA. The experimental conditions were: a) 0.1 mol/L $ZnSO_4$ in feed phase and for the receiving phase 0.1, 0.3, 0.5,1 and 2 mol/L H_2SO_4 was used; b) 0.0005, 0.005, 0.001, 0.01 mol/L $ZnSO_4$ in feed phase and for the receiving phase 1 mol/L H_2SO_4;

- determination of the transport efficiency and recovery factor of Zinc (II) and Manganese (II) using as extractant D2EHPA. The experimental conditions were: 0.0005, 0.005, 0.001 and 0.01 mol/L MnSO$_4$ and ZnSO$_4$ in feed phase and for the receiving phase 1 mol/L H$_2$SO$_4$;

- determination of the transport efficiency and recovery factor of Zinc (II) and Manganese (II) using as extractant D2EHPA and CYANEX 302, by following the competitive transport of manganese and zinc. The experimental conditions were: and 0.01 mol/L ZnSO$_4$ and MnSO$_4$ in feed phase, for the membrane were used various molar ratio Cyanex 302: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$_2$SO$_4$ was used.

We characterized the separation of Cr^{3+}, Zn^{2+}, Mn^{2+} cations by calculating the following parameters:

a) transport efficiency - a first step of the transport process of the studied cations was calculated with the relation (1):

$$E\% = \frac{V_{r.p.} \cdot C_{r.p.}}{V_{f.p.} \cdot C_{f.p.0.}} \qquad (1)$$

where :

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

b) Another parameter often used for evaluating of the efficiency of transport process through liquid membranes is the recovery factor (RF%) calculated with equation (2):

$$R.F.\% = \frac{C_{f.p.0} - C_{f.p.f}}{C_{f.p.0}} \times 100 \qquad (2)$$

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]

Results and discussions

On the feed side interface of the BLM, the extraction of metal cations (M^{z+}) such as Zn(II), Cr(III) and Mn(II) from aqueous solutions with D2EHPA (HR) in kerosene could be expressed as

$$M_f^{z+} + z(HR)_{2, org} \leftrightarrow MR_z(HR)_{2, org} + zH_f^+ \qquad (3)$$

where *org* and *f* stand for organic phase and feed solution, respectively; (HR)$_2$ indicates that the D2EHPA in low-polarity kerosene mainly exists as a dimer and M^{z+} = Cr^{3+}, Zn^{2+}, Mn^{2+}

The stripping reaction on the other side of the LM is written as follows:

$$MR_z(HR)_{2, org} + zH_s^+ \ M_s^{z+} + zHR)_{2, org} \qquad (4)$$

where s represents the strip phase.

Chromium (III) liquid membrane separation

The preliminary results obtained in evaluating the efficiency of the transport process of chromium in the stripping phase for different concentrations with D2EHPA in the organic solvent (kerosene) are presented in figure 2. The transport experiments were realised at different stripping phase concentrations: 0.1; 0.5 and 1.0 mol/L, respectively. In all experiments, the stripping phase consisted in solutions of H$_2$SO$_4$. D2EHPA was mixed in kerosene, while the same concentration of carrier in kerosen was used in all the experiments, equivalent to 0.1 mol/L. It can be seen that the best recovery factor (about 70%) was obtained when the stripping phase concentration was 0.5 mol/L.

The effect of the phase composition on the transport of chromium is shown in figure 3. Experiments were conducted in the same conditions as mentioned previously, varying the internal phase concentrations (0.1; 0.5 and 1.0 M of H$_2$SO$_4$) and using the D2EHPA 0.1 M, extraction reagent. The effect of the sulfuric acid on chromium phase distribution is different, depending on the phase compositions (feed phase, membrane phase and stripping phase) as follows: i) in the feed phase, the transport efficiency does not seem to change significantly under the influence of the sulfuric acid concentration; ii) in the membrane phase, the efficiency is strongly influenced by the sulfuric acid concentration ; when the H$_2$SO$_4$ concentrations increases, the stability of the emulsion decreases; this may be due to the reactions between H$_2$SO$_4$ and the surfactant that involves a reduction in the properties of the surfactant that consequently led to a destabilization of the emulsion; iii) in the stripping phase, increasing the concentration of the sulfuric acid lowers the efficiency of the transport. This different behaviour could be attributed to the fact that the transport of chromium and its separation from the solution are made dependent on the phase composition.

Determination of the transport efficiency and recovery factor of Zinc(II) using as extractant D2EHPA

The results obtained in the evaluation of the transport efficiency of zinc in the stripping phase for different concentrations of the sulfuric acid, equivalent to 0.3; 0.5; 1.0 and 2.0 mol/L , respectively, are presented in figure 4. In all experiments, D2EHPA was mixed in kerosene; the concentration was equivalent to 0.1 mol/L. From the analysis of the data presented in figure 4 it is observed that increasing the sulfuric acid concentration in the solution decreases the capacity of zinc recovery. It can be seen that the best recovery factor (more than 80%) was obtained for H$_2$SO$_4$ concentration in 0.3 mol/L solution.

The effect of the phase composition on the transport of zinc is shown in figure 5. It shows the profile of zinc distribution at the end of the process. Experiments were performed in the previously mentioned conditions, varying the concentrations of the internal phase (0.3; 0.5; 1.0 and 2.0 M of H$_2$SO$_4$) using the D2EHPA 0.1 M as extraction reagent. In accordance with the previous comments referring to the fact that the best zinc recovery factor was obtained for H$_2$SO$_4$ concentration in solution equal to 0.3 mol/L, now it can be noticed that the transport efficiency increases depending on the composition phase: feed phase < membrane phase << receiving phase. For concentrations equivalent to 0.5 and 2.0 mol/L H$_2$SO$_4$, the order of importance of the phase composition is: membrane phase < feed phase << receiving phase. If the concentration of H$_2$SO$_4$ is equivalent to 1.0 mol/L, then the order of importance changes as: feed phase >> membrane phase ~ receiving phase. Therefore, zinc is more preferably extracted into the feed phase in the 1 mol/L H$_2$SO$_4$ solution.

The recovery factor of zinc in the feed phase for different concentrations of ZnSO$_4$ (0.0005; 0.005; 0.001 and 0.01 mol/L) and 1 mol/L H$_2$SO$_4$ shows non-uniform variations (fig. 6). As seen from the figure, increasing the feed phase concentration from 0.0005 to 0.001 mol/L, the percentage
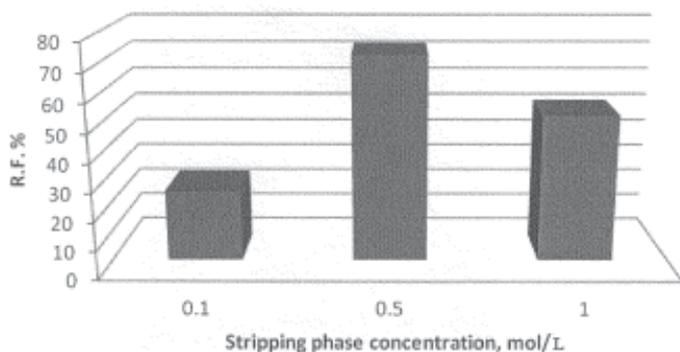
Fig.2 Profile of recovery factor for chromium with stripping phase concentrations
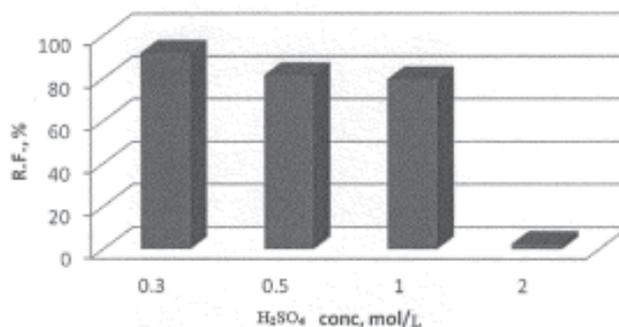
Fig.4. Profile of recovery factor for zinc with stripping phase concentrations
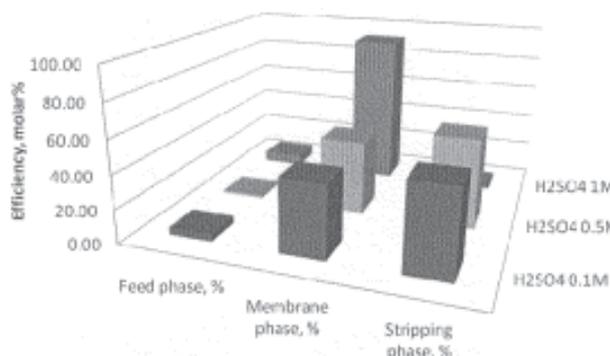
Fig.3 Chromium phase distribution at the end of the transport
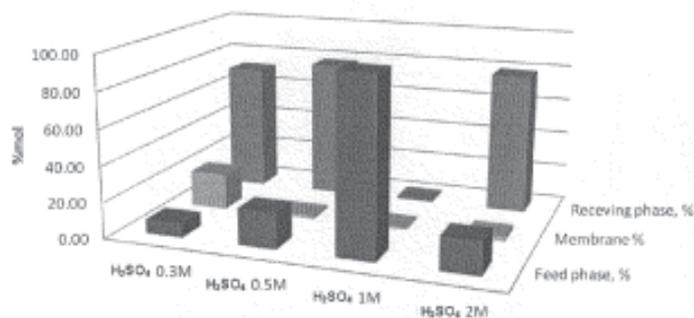
Fig.5. Zinc phase distribution at the end of the transport

of zinc extraction finally increases, while for a substantial increase in the feed phase to 0.01 mol/L, the percentage of zinc recovery is very low.

The effect of the phase composition on the transport of zinc is shown in figure 7. Experiments were conducted in the same conditions as mentioned previously, using the extraction reagent D2EHPA in kerosene, equivalent to 0.1 mol/L and 1 mol/L sulfuric acid concentration. The liquid membrane phase is composed of a surfactant, an extractant, and a diluent. As can be seen from figure 7a, the best results for to the extraction of metal were obtained in the receiving phase for 0.005 mol/L $ZnSO_4$ (about 80%) and from figure 7b the best recovery for zinc was observed for membrane phase (about 60%).

The preliminary determination of the transport efficiency and recovery factor of Zinc (II) and Manganese (II) are shown in figure 8. The effect of different concentrations (0.01–0.0005 mol/L) of $MnSO_4$ and $ZnSO_4$ in liquid phase was examined. These results show that the maximum uptake percentage is recorded for 0.01 mol/L concentration, i.e. in the feed phase for manganese (~90%) and receiving phase for zinc (~70%) and there is a drastic decrease capacity of transport efficiency in the membrane phase.

The feed phase consists in $MnSO_4$ and $ZnSO_4$ solutions of different concentrations (from 0.0005 to 0.01 mol/L), examined in terms of the recovery of metal (fig. 9). Experimental data indicate high values of the recovery factors for zinc in the range 80-93% and lower values for manganese, with increasing uneven concentration variations in the solution. This study aimed at a competitive transport of manganese and zinc and the selectivity of transition metal ions.

Finally, the determination of the transport efficiency and recovery factor of Zinc (II) and Manganese (II) using as
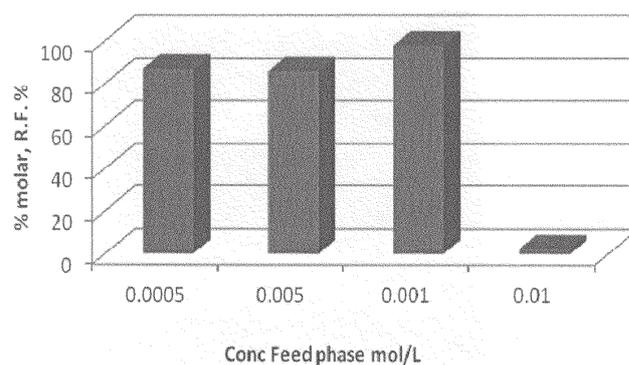
Fig.6. Zinc phase distribution in feed phase
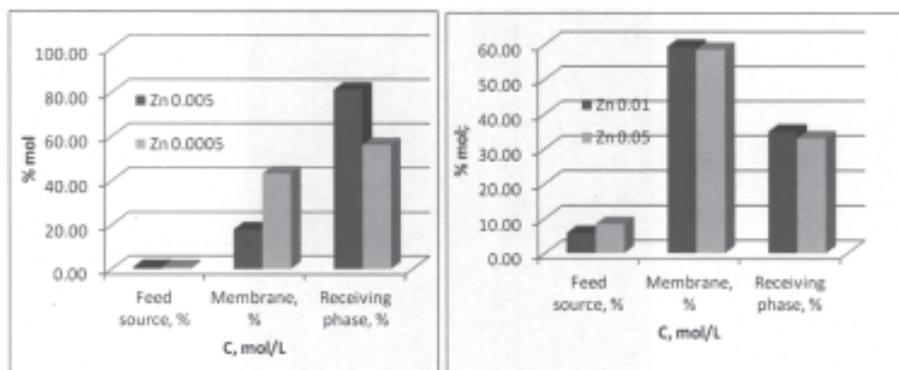
Fig.7 Effect of zinc concentration and the phase composition on the extraction of metal
(a. D2EHPA in kerosen is 0.1 mol/L and b. H_2SO_4 in the receiving phase is 1 mol/L)
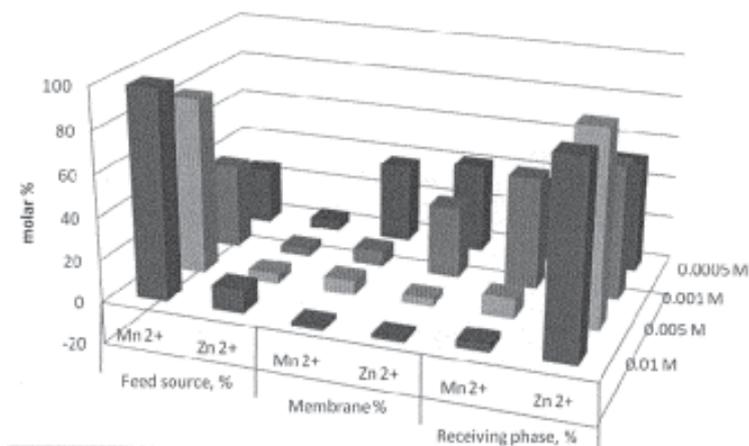
Fig.8. Profiles of zinc and manganese phase distribution (D2EHPA 0.01M in kerosene; Receiving phase H_2SO_4 1M)
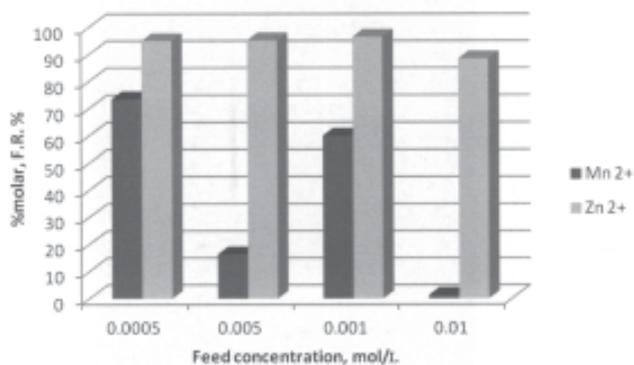
Fig.9 Zinc and manganese recovery factor (D2EHPA 0.01 mol/L in kerosene; Receiving phase H_2SO_4 1 mol/L)
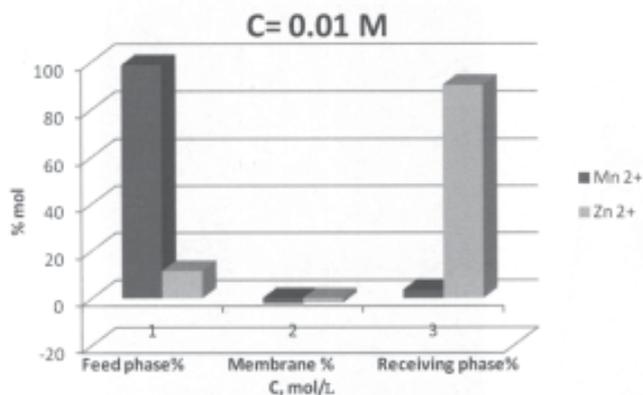
Fig. 10 Zinc and manganese phase distribution (D2EHPA 0.01 mol/L in kerosene; Receiving phase H_2SO_4 mol/L, Feed phase: $MnSO_4$ 0.01 mol/L, $ZnSO_4$ 0.01 mol/L)
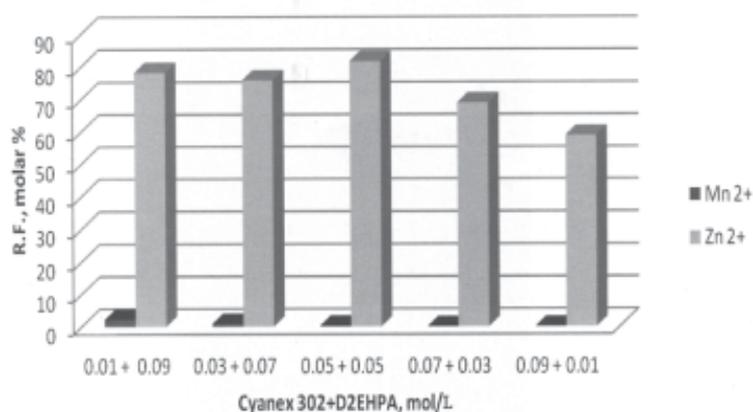
Fig.11. Recovery factor of zinc and manganese depending on the molar ratio Cynex 302: D2EHPA

extractant D2EHPA for 0.01 M concentration of $MnSO_4$ and $ZnSO_4$ in liquid phase and for the receiving phase 1 mol/L H_2SO_4 is presented in figure 10. The presence of extractant (D2EHPA) in the feed phase indicates the affinity for the manganese against the zinc transport; in the membrane phase no competition appears to transport ions, but in the receiving phase the affinity for the zinc is very high in comparison with the manganese transport.

The determination of the transport efficiency and recovery factor of Zinc(II) and Manganese(II) using as

extractant D2EHPA and CYANEX 302 was studied according to the data shown in figures 11 and 12. This study aimed to evaluate the competitive transport of manganese and zinc, in the following experimental conditions: 0.01 mol/L $ZnSO_4$ and $MnSO_4$ in the feed phase, various molar ratios used for the membrane Cyanex 302: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. Experimental data referring to the ions transport in the liquid membrane

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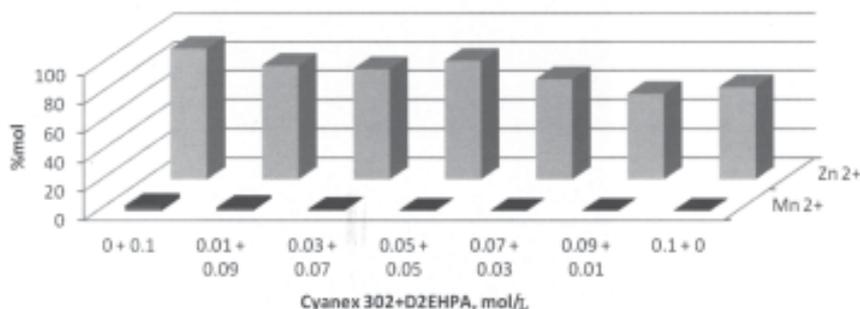
Fig.12. Transport efficiency of zinc and manganese depending on the molar ratio Cynex 302: D2EHPA

Transport conditions			Recovery factor
Feed source	Membrane	Receiving phase	R.F.%
MnSO$_4$ 0.01M ZnSO$_4$ 0.01M	D2EHPA 0,1 M	H$_2$SO$_4$, 1M	R.F.% (Zn)=88.5o% R.F.% (Mn)=1.23%
Cr$_2$(SO$_4$)$_3$, 0,001M	D2EHPA 0,1 M	H$_2$SO$_4$, 1M	52.00%
Cr$_2$(SO$_4$)$_3$, 0,001M	D2EHPA 0,1 M	H$_2$SO$_4$, 0.1M	25.00%

Table 1. The value of the recovery factor at the end of the transport process (the time of transport= 30 h)

were calculated by recovery factor (fig. 11) and transport efficiency (fig. 12) .

The carriers Cyanex 302 and D2EHPA both separately and in mixtures and as a solvent for the liquid membrane are competitors in the process studied. The separation of the cations under study using bulk liquid membranes can be performed; the optimum ratio of the Cyanex 302 : D2EHPA mixture is 0.05 +0.05 (mol/L) for the separation of Zn(II) and 0 + 0.1 (mol/L) for the separation of Mn(II).

In table 1 are presented comparative values   of the recovery factors obtained for the membrane systems studied. The separation of chromium, manganese and zinc from the solutions was appreciated according to the transport conditions and the efficiency of the transport process through the liquid membranes.

The working procedure for the separation of cations (chromium, manganese and zinc) through bulk liquid membrane revealed the importance of using D2EHPA and Cyanex 302 as carriers, quantified in terms of values of the recovery factor at the end of the transport process (table 1).

Conclusions

The purpose of the present paper was to study the behaviour of the cation transport through a system of bulk liquid membranes.

The experimental results of zinc and manganese extraction using D2EHPA, Cyanex 302 and their mixtures in kerosene was used to develop a model for extraction of chromium, zinc and manganese.

The system was studied for individual cations as chromium, zinc, manganese and for mixtures of zinc and manganese using as cation carriers Cyanex 302 and D2EHPA both separately and in mixtures and kerosene as a solvent for the liquid membrane.

From the experimental data obtained we concluded that the separation of the studied cations using bulk liquid membranes could be performed and the optimum ratio of the Cyanex 302 and D2EHPA mixture is 0.05 : 0.05 M for the separation of Zn(II) and 0 : 0.1 M for the separation of Mn(II).

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