APPLICATION OF D2EHPA FOR MANGANESE(II) AND NICKEL(II) SEPARATION BY SOLVENT EXTRACTION AND POLYMER INCLUSION MEMBRANES

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ABSTRACT

The separation of manganese(II) and nickel(II) from chloride solution with di-(2-ethylhexyl) phosphoric acid (D2EHPA) was studied. The metal ions were separated using solvent extraction and transport through polymer inclusion membranes (PIMs) with D2EHPA as the extractant/ion carrier. The aqueous solutions consisted of 0.010 M manganese(II) and nickel(II) chlorides. The influence of aqueous phase pH on the separation of Mn(II) and Ni(II) has been investigated. Mn(II) can be selectively removed from chloride solution at equilibrium pH equal to 2.90. From the organic phase, Mn(II) was stripped with 0.1-2.0 M aqueous solutions of HCl, H_2SO_4 and HNO_3. The competitive transport of Mn(II) and Ni(II) through PIMs was studied as a function of the ion carrier and plasticizer concentration in the membrane.

Keywords: Manganese(II); Nickel(II); D2EHPA; Solvent extraction, Polymer inclusion membranes

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INTRODUCTION

Nickel and manganese are important metals with several industrial applications such as steel, non − ferrous alloys, and batteries production. Technological importance of these elements has focused researchers attention on possible exploitation of manganese and nickel ores, eg. appearing in the form of sea nodules [1]. In hydrometallurgical processing of manganese sea nodules, the leach acidic liquor contains many valuable metals such as copper(II), nickel(II), cobalt(II) and zinc(II) and others [2]. In the separation of these metals ions, solvent extraction plays an important role. Nickel(II) and manganese(II) can be extracted from sulphate and chloride solutions using various reagents: di-(2-ethylhexyl) phosphoric acid (D2EHPA) and its sodium salts [3, 4], di-(2-ethylhexyl)phosphonic acid (PC 88 A) [5,6], and bis-(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272) [7].

The applications of liquid membranes offer a potentially attractive alternative to solvent extraction processes and combine the process of extraction and stripping in a single unit operation.

Liquid membranes containing D2EHPA as the ion carrier have been used for separation of many metal ions by several researchers. Moreno et al. [8] studied the mechanism of transport of lanthanide ions through supported liquid membranes containing D2EHPA as carrier. The transport kinetics of Fe(III) across *n*-decanol supported liquid membrane facilitated by D2EHPA was described by Zhang et al. [9]. Silver and copper ions removal from acidic solutions by supported liquid membranes containing D2EHPA was presented by Gherrou et al. [10]. Moreover, many applications of the hybrid liquid membranes with D2EHPA as the extractant/ion carrier have been described. Zinc(II) ions were effectively transported through a multimembrane hybrid system with D2EHPA [11-13].

A study of Co(II) and Ni(II) transport through supported and hybrid liquid membranes containing D2EHPA, Cyanex 272, 301, and 302 as the ion carriers was carried out by Gega et al. In hybrid liquid membrane processes, metal ion fluxes observed were lower than in supported liquid membrane processes. On the other hand, higher separation coefficients for Co(II)/Ni(II) were found for hybrid than liquid membrane processes [14].

Recently, a new type of liquid membrane system, called polymer inclusion membrane (PIM) has been developed. The PIMs are formed as thin stable films by casting cellulose triacetate (CTA) from an organic solution. This solution contains also an ion carrier and a membrane plasticizer (mostly *o*-nitrophenyl alkyl ethers). A number of researchers applied CTA membranes for carrier-mediated transport of metal ions [15-22].

The solvent extraction and transport of Zn(II), Cd(II), Cu(II), Co(II), and Ni(II) cations from chloride solutions by polymer inclusion membranes with D2EHPA as the extractant/ion carrier were studied by Ulewicz et al.

They reported the following selectivity order: Zn(II) > Cu(II) > Co(II) > Ni(II) > Cd(II) [23].

In this work, the selectivity of Mn(II) and Ni(II) extraction from acidic chloride solution with D2EHPA was studied. The solvent extraction and transport of manganese(II) and nickel(II) through PIMs containing CTA as a support, *orto*-nitrophenyl pentyl ether as a plasticizer (ONPPE), and D2EHPA as the ion carrier was performed. The kinetic and efficiency parameters of transport through polymer inclusion membranes with D2EHPA were studied. The influence of the membrane and receiving phase composition of the transport properties was investigated.

EXPERIMENTAL
Reagents

Inorganic chemicals, i.e. manganese(II), nickel(II) chlorides were of analytical grade and were purchased from POCh (Gliwice, Poland). Organic reagents, i.e. cellulose triacetate (CTA), *o*-nitrophenyl pentyl ether (ONPPE), di(2-ethylheksyl)phosphoric acid (D2EHPA) and dichloromethane were also of analytical reagent grade and were purchased from Fluka and used without further purification. Distilled kerosene (Fluka) was used as the diluent in solvent extraction. The plasticizer density, i.e. ONPPE, was 1.085 g cm^{-3}. Aqueous solutions were prepared with twice distilled water, with 0.1 μSm^{-1} conductivity

Procedure
Solvent extraction

Solvent extraction was carried out using equal volumes of aqueous and organic phases (10 cm^3 each) which were mechanically shaken (200 min^{-1}) for 20 minutes at constant temperature (25 ± 2 °C). The metal ions content in the aqueous phase was determined by means of AAS Solaar 939 (Unicam) spectrophotometer, while the pH value was measured with a CX-731 (Elmetron) pH-meter. The concentration of metals in the organic phase was calculated from the mass balance. The distribution coefficient (D) and extraction percent (%E) were determined as equal to:

$$D = \frac{[Me]_{org}}{[Me]_{aq}} \tag{1}$$

$$\%E = \frac{D}{D+1} \cdot 100\% \tag{2}$$

where [Me]$_{org}$ and [Me]$_{aq}$ are concentrations of metal ions in an organic and aqueous phase, respectively.

The selectivity coefficient (**S**) was defined as a ratio of the distribution coefficients for *Me1* and *Me2* metal ions, respectively:

$$S = \frac{D_{Me1}}{D_{Me2}} \qquad (3)$$

Polymer inclusion membrane

A solution of cellulose triacetate (CTA), ion carrier (D2EHPA), and plasticizer (ONPPE) in dichloromethane were prepared. A portion of this solution was poured into a membrane mold comprising 6.0 cm glass ring attached to a glass plate with CTA-dichloromethane glue. The organic solvent was allowed to evaporate overnight and the resultant membrane was separated from the glass plate by immersion in cold water. The membrane was soaked in 0.1 M HCl aqueous solution for 12 hours and stored in distilled water.

Membrane transport experiments

Transport across PIMs was carried out in a permeation cell in which the membrane film was tightly clamped between two cell compartments. The effective membrane area which was exposed to both phases was 3.14 cm^2. Both, the source and the receiving aqueous phases (50 cm^3 each) were stirred at 600 rpm with synchronous motors. The receiving phase was distilled water or hydrochloric acid aqueous solutions. The PIM transport experiments were conducted at room temperature (22-25 °C). The permeation of manganese(II), and nickel(II) was monitored by periodical sampling (0.1 cm^3 each) of the source phase, and the samples were analyzed after appropriate dilution by an atomic absorption spectrophotometer. The source phase acidity was controlled by a pH-meter (CX-731 Elmetron, with a combined pH electrode, EFH-136, Hydromet, Poland). pH was kept constant by adding periodically aqueous solution of 1.0 M NaOH.

PIM transport kinetics was described by a first-order transport rate equation:

$$\ln\left(\frac{c}{c_i}\right) = -kt \qquad (4)$$

where c is metal ion concentration (M) in the source phase at some given time, c_i is the initial metal ion concentration in the source phase, k is the rate constant (s^{-1}), and t is the time of transport process (s).

To calculate the value of k, a plot of $\ln(c/c_i)$ vs. time was prepared. The rate constant values for two transport experiments were check then averaged and standard deviation was calculated. Examples of such plots are given in Fig. 3. This figure shows a linear relationship of $\ln(c/c_i)$ vs. time, confirmed by high values of the determination coefficient (r^2)), i.e. from 0.978 to 0.991. The permeability coefficient (P) was calculated as follows:

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$$P = -\frac{V}{A}k \qquad (5)$$

where V is the volume of aqueous source phase, and A is the area of a membrane.

The initial flux (J_i) was determined as:

$$J_i = Pc_i \qquad (6)$$

RESULTS AND DISCUSSION
Solvent extraction of Mn(II) and Ni(II) from aqueous chloride solutions

The first series of experiments has been carried out to study the competitive extraction of Mn(II) and Ni(II) from aqueous chloride solutions containing 0.010 M Mn(II) and Ni(II) with 0.10 M D2EHPA in kerosene as the solvent. The effect of aqueous phase pH has been studied (Fig. 1). With an increase in the aqueous phase pH, the selectivity coefficients of Mn/Ni decrease. The obtained results indicate that separation of Mn(II) over Ni(II) is possible at pH 2.90. The use of 0.10 M D2EHPA enables to extract 68.75 % of Mn(II) and 4.30 % of Ni(II).
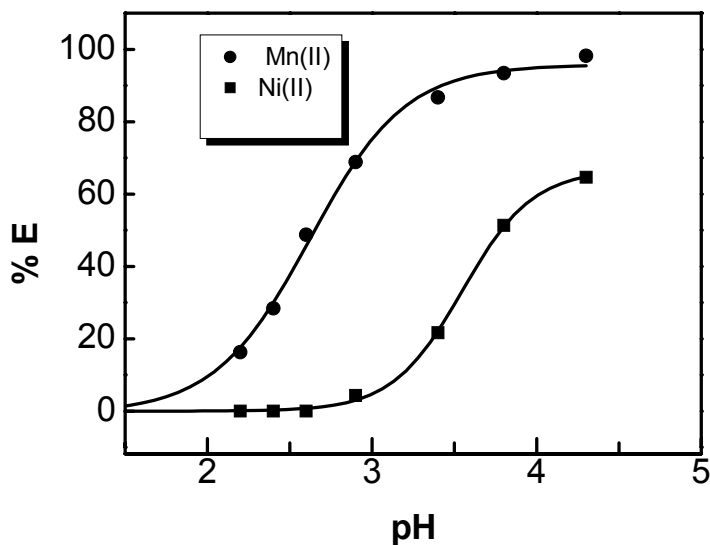

Fig. 1. Effect of pH on the extraction of Mn(II) and Ni(II) from chloride aqueous solutions with 0.10 M D2EHPA in kerosene. [Mn(II)] = 0.010 M, [Ni(II)] = 0.010 M.

The values of selectivity and distribution coefficients are presented in Table 1. The distributions coefficients of Mn(II) and Ni(II) increase with an

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increase in pH. The solvent extraction with D2EHPA as the extractant the results of which are presented in this study, makes the separation of manganese(II) and nickel(II) possible.

Table 1. The distribution and selectivity coefficients of Mn(II) over Ni(II) at different pH (conditions as in Fig. 1.)

pH	$D_{Mn(II)}$	$D_{Ni(II)}$	$S_{Mn(II)/Ni(II)}$
2.9	2.20	0.045	48.9
3.4	6.55	0.27	24.3
3.8	14.15	1.05	13.5
4.3	54.86	2.11	26.0

Mn(II) was stripped from the organic phase with various inorganic acids. The stripping of Mn(II) was observed to be quantitative with 2.0 M HCl, H_2SO_4 and HNO_3. The results are presented in Table 2. Among these inorganic acids, HCl was preferred as a stripping agent. The stripping of Mn(II) with 1.5 M HCl was equal to 99.50%.

Table 2. Stripping of Mn(II) from organic phase with HCl.

Stripping agents, M	Stripping of Mn(II), %				
	0.1	0.5	1.0	1.5	2.0 M
HCl	59.4	91.2	97.7	99.5	99.9
H_2SO_4	47.7	84.7	73.2	93.7	99.7
HNO_3	61.2	93.5	98.3	96.3	99.9

Transport of Mn(II) and Ni(II) across polymer inclusion membranes from aqueous chloride solutions

The competitive transport of Mn(II) and Ni(II) from aqueous chloride solutions (c_{Me} = 0.010 M) at pH 2.90 through PIM containing D2EHPA as an ionic carrier into 1.0 M HCl as the receiving phase was investigated. The influence of the plasticizer concentration in the membranes on metals transport was studied. The polymer inclusion membranes contained constant amounts of the ion carrier and the support. The concentration of the plasticizer (ONPPE) was changed from 1.6 cm^3/1 g CTA to 2.4 cm^3/1 g CTA. The obtained results are presented in Fig. 2 and summarized in Table 3. As it can be seen from this figure, the separation and the initial fluxes of Mn(II) and Ni(II) depend strongly on the concentration of ONPPE in the polymer inclusion membranes.
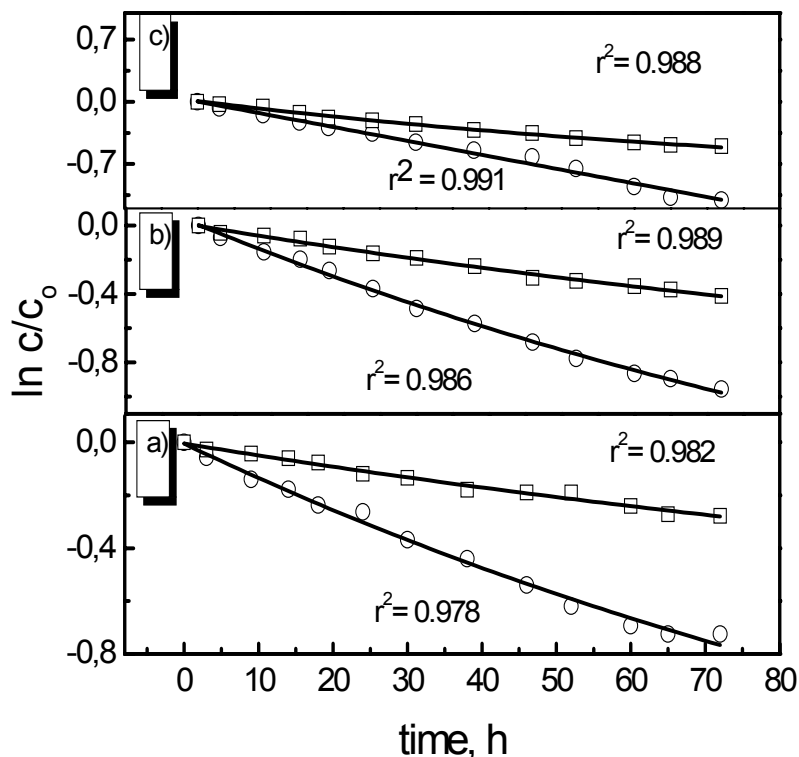
Fig. 2. Kinetics of Mn(II) and Ni(II) transport through PIM by D2EHPA. Source phase: c_{Me} = 0.010 M, pH = 2.90; receiving phase: 1.0 M HCl; PIM: 0.0625 g CTA, 0.0644 g D2EHPA; a) 1.60 cm^3 ONPPE/1 g CTA, b) 1.90 cm^3 ONPPE/1 g CTA, c) 2.4 cm^3 ONPPE/1 g CTA

The transport rate increases with an increase in the plasticizer concentration. The selectivity coeffient of Mn/Ni is higher when the PIM contains 1.6 cm^3 ONPPE/1 g CTA and is equal to 2.76. The resulting membrane contained 26.54 wt% CTA, 46.07 wt% ONPPE and 27.39 wt% D2EHPA. The content of the plasticizer is higher in comparison to PIMs used by other autors. For instance, PIMs used by Kozlowski and Walkowiak [21] contained 41 wt % CTA, 36 wt % ONPPE and 23 wt % tri-*n*-octylamine (TOA). An unusually low content of the plasticizer in PIM used in this study is due to good plasticizing properties of tertiary amines serving as the ion carriers. On the other hand, PIMs used by Nazarenko and Lamb [22] contained 76 wt% *orto*-nitrophenyl octyl ether (ONPOE).

Table 3. Kinetic parameters for Mn(II) and Ni(II) transport through PIM in depending on the plasticizer content. PIM: 0.0625 g CTA, 0.0644 g D2EHPA.

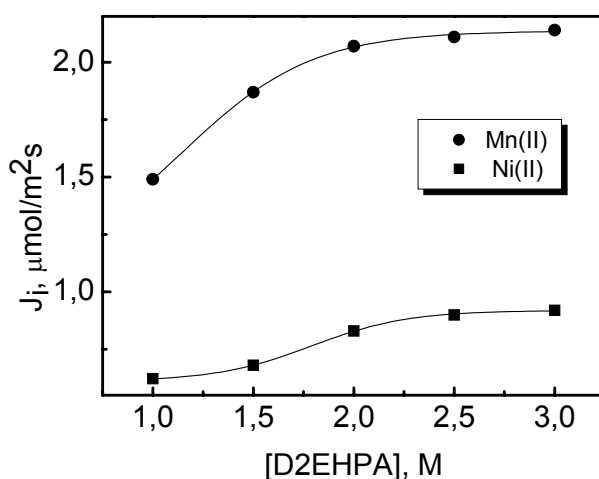| Concentration of ONPPE, (cm^3 / 1 g CTA)	Metal ions	Rate constant, k (h^{-1})	Permeability coefficient, P (μms^{-1})	Initial flux, J_i (μmolm^{-2}s^{-1})	Selectivity coefficient, $S_{Mn/Ni}$
1.6	Mn(II)	0.0112	0.196	1.96	2.76
	Ni(II)	0.0040	0.071	0.71	
1.9	Mn(II)	0.0140	0.248	2.48	2.36
	Ni(II)	0.0057	0.105	1.05	
2.4	Mn(II)	0.0151	0.267	2.67	2.00
	Ni(II)	0.0075	0.133	1.33	

Fig. 3. Effect of D2EHPA concentration upon initial flux for Mn(II) and Ni(II) transport through PIMs. Membrane phase: 0.0625 g CTA, 1.6 cm^3 ONPPE/1 g CTA.

Next, the influence of the ion carrier concentration (D2EHPA) on the kinetics of Mn(II) and Ni(II) transport through polymer inclusion membranes was performed. The polymer inclusion membranes contained constant amounts of the support (0.0625 g CTA) and plasticizer (1.6 cm^3 /1 g CTA). The concentration of D2EHPA was changed from 1.0 to 3.0 M (based on plasticizer). The obtained results are presented in Fig. 3.

For the both metal ions, the flux increases with an increase in D2EHPA concentration and finally reaches a plateau. This can be explained by increasing resistance to the diffusion of the carrier metal ion complexes.

For 3.0 M D2EHPA, the initial flux for Mn(II) and Ni(II) was equal to 2.14 and 0.92 $\mu molm^{-2}s^{-1}$, respectively.

CONCLUSION

The present investigations show that D2EHPA enables the selective extraction of Mn(II) and Ni(II) from chloride solution. The best selectivity was obtained at pH 2.90, and the selectivity coefficient for Mn/Ni was equal to 48.90.

The polymer inclusion membrane transport of Mn(II) and Ni(II) with D2EHPA as the ion carrier is an effective method of separation. The highest selectivity coefficient ($S_{Mn/Ni}$) was obtained for PIM containing 1.6 cm^3 ONPPE/1 g CTA, 0.0625 g CTA, and 2.0 M D2EHPA. The optimal membrane for the separation of Mn(II) and Ni(II) contained 26.54 wt % CTA, 46.07 wt % ONPPE and 27.39 wt % D2EHPA.

ACKNOWLEDGMENT

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