



**ZINC(II) SELECTIVE REMOVAL FROM OTHER TRANSITION
METAL IONS BY SOLVENT EXTRACTION AND TRANSPORT
THROUGH POLYMER INCLUSION MEMBRANES
WITH D2EHPA**

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ABSTRACT

An experimental investigation concerns zinc(II), cobalt(II), nickel(II), copper(II) and cadmium(II) ions separation from aqueous chloride solutions by solvent extraction and transport through polymer inclusion membrane (PIM) processes. The selective transport of metal ions from the aqueous chloride source phase through PIM containing cellulose triacetate (support), *o*-nitrophenyl pentyl ether (plasticizer) and di(2-ethylhexyl)phosphoric acid (ion carrier) is shown. Zn(II) can be effectively removed from dilute aqueous chloride solutions by its transport through PIMs with di(2-ethylhexyl)phosphoric acid as the ionic carriers into 1.0 M HCl as the receiving phase. The transport selectivity of Zn(II) over Co(II), Ni(II), Cu(II) and Cd(II) decreases while the pH of the solution increases in the source phase. Also, by solvent extraction, Zn(II) can be selectively removed from dilute aqueous chloride solutions.

Keywords: Polymer inclusion membrane; Solvent extraction; Zinc(II); Cobalt(II); Nickel(II); Copper(II); Cadmium(II)

INTRODUCTION

In recent years a remarkable increase in the application of liquid membranes for separation processes has been noticed [1, 2]. The use of liquid membranes containing ion carriers is suggested as an alternative to solvent extraction for a selective removal and concentration of metal ions from the source aqueous phase in which the concentration of metal ionic species is above 1×10^{-4} M. There exists a variety of types of liquid membranes i.e., bulk (BLM), emulsion (ELM), supported (SLM), and polymer inclusion membranes (PIM) [3, 4]. PIMs are formed by casting cellulose triacetate (CTA) from an organic solution to form a thin film. The casting solution also contains an ion exchange carrier and a membrane plasticizer.

There are numerous papers which deal with metal ions removal and separation applying solvent extraction and transport through liquid membranes. Binghua et. al [5] reported the following solvent extraction order for D2EHPA: Fe(III) > Zn(II) > Mn(II) > Cd(II) > Cu(II) > Mg(II) > Co(II) > Ni(II). The separation of Co(II) and Ni(II) by supported and hybrid liquid membranes using D2EHPA, Cyanex 272, Cyanex 301, and Cyanex 302 was presented by Walkowiak et al. [6, 7], whereas Gill et. al. [8] studied the separation of Cu(II), Ni(II), and Fe(III). Zinc(II) ions were effectively transported through the multimembrane hybrid system with D2EHPA [9-11]. Polymer inclusion membranes were used for the removal of cadmium(II) from chloride aqueous solutions [12, 13] and for the separation of cadmium(II) and zinc(II) [14, 15]. Recently the polymer inclusion membranes containing macrocyclic components such as crown ethers, cryptands and calixarenes have been used for the removal of metal ions [16-22].

We now present the results of the competitive transport of zinc(II), cadmium(II), copper(II), cobalt(II), and nickel(II) cations from dilute aqueous solutions ($c_{Me} = 0.01$ M) by polymer inclusion membranes using di(2-ethylhexyl)phosphoric acid (D2EHPA) as the ion carrier. Also the competitive solvent extraction of these metal ions is studied.

EXPERIMENTAL

The initial aqueous solutions were prepared from twice distilled water and the CdCl₂, ZnCl₂, CuCl₂, CoCl₂, NiCl₂, HCl salts (POCh, Gliwice, analytical grade). The organic chemicals, i.e. cellulose triacetate (Fluka), di(2-ethylhexyl)phosphoric acid, o-nitrophenyl pentyl ether (Fluka), and dichloromethane (POCh) were also of analytical reagent grade.

The competitive solvent extraction of Zn(II), Cu(II), Co(II), Cd(II), and Ni(II) ions has been studied with di(2-ethylhexyl)phosphoric acid (D2EHPA) in kerosene (POCh). The equal volumes (5 cm^3) of the both phases were contacted for 30 minutes at constant temperature (25 ± 2 °C). The metals content in the aqueous phase has been determined by means of a AAS Solaar 939 (Unicam) spectrophotometer while the pH value has been

measured with a CX-731 (Elmetron) pH-meter. The concentration of metals in the organic phase was calculated from the mass balance. The extraction percentage was determined as equal to:

$$\% E = \frac{D}{D+1} \cdot 100\% \quad (1)$$

where distribution ratio D was calculated as the ratio of concentrations:

$$D = \frac{[Me]_{org}}{[Me]_{aq}} \quad (2)$$

Solutions of cellulose triacetate (as the support), di(2-ethylhexyl)phosphoric acid (as the ion carrier), and o-nitrophenyl pentyl ether (as the plasticizer) in dichloromethane were prepared. A portion of that organic solution was poured into a membrane mold composed of a glass ring attached to a plate glass with cellulose triacetate-dichloromethane glue. Dichloromethane, as an organic solvent, was allowed to evaporate slowly overnight and the resultant polymer inclusion membrane was separated from the glass plate by immersion in water. The membrane was stored in water. The concentration of D2EHPA in the membrane was 1.50 M based on plasticizer; the membrane contained of 2.50 cm³ ONPPE/1.0 g CTA. The membrane thickness was 35 μm. New membranes were used in each experiment.

Transport experiments were carried out in a permeation cell in which the membrane film (at the surface area of 4.9 cm²) was tightly clamped between two cell compartments. Both, the source and receiving aqueous phases (45 cm³ each), were mechanically stirred at 600 rpm. The receiving phase was 1.0 M aqueous solution of hydrochloric acid. The source phase was solutions containing Zn(II), Cu(II), Co(II), Cd(II), and Ni(II) ions at the concentration of 0.01 M for each metals. The PIM transport experiments were carried out at 20 ± 0.2 °C. Small samples (0.1 cm³ each) of the aqueous receiving phase were removed periodically via a sampling port with a syringe and analyzed to determine zinc and cadmium concentrations by the atomic absorption spectroscopy method. The source aqueous phase acidity was controlled by a pH-meter (CX-731 Elmetron, with a combined pH electrode, ERH-136, Hydromet, Poland) and the pH was kept constant by adding periodically small amounts of 1.0 M NaOH aqueous solution.

The kinetics of the PIM transport was described by a first order transport rate equation in metal ion concentration:

$$\ln\left(\frac{c}{c_i}\right) = -kt \quad (3)$$

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

To calculate the k values, plots of $\ln(c/c_i)$ versus time were drawn. The rate constant value for the duplicate transport experiment was averaged and a standard deviation was calculated. As it results from Fig. 1, the relationship of $\ln(c/c_i)$ vs. time is linear, which is confirmed by high values of the determination coefficient (r^2), i.e. from 0.9456 to 0.9955.

The initial flux (J_i) was determined as equal to:

$$J_i = \frac{V}{A} \cdot k \cdot c_i. \quad (4)$$

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

The selectivity coefficient S was defined as the ratio of the initial fluxes for $M1$ and $M2$ metal ions respectively:

$$S = J_{i,M1} / J_{i,M2} \quad (5)$$

The removal (R) of metal ions from the source phase into receiving phase was calculated as:

$$R = \frac{c_i - c}{c_i} \cdot 100\% \quad (6)$$

RESULTS AND DISCUSSION

The competitive transport of zinc(II), cadmium(II), copper(II), cobalt(II) and nickel(II) ions from the aqueous source phase ($c_{Me} = 0.01$ M) through the polymer inclusion membranes containing 1.5 M di(2-ethylhexyl)phosphoric acid as the ionic carrier into the receiving aqueous phase was investigated. The transport kinetic of metal ions is shown in Fig.1. The kinetics parameters and selectivity orders of the metal ions transport through PIM from the aqueous source phase containing an equimolar mixture of all the metal ions are shown in Tab. 1. The initial fluxes of all the investigated cations increase with the increasing feed phase pH, as it was expected [5, 6]. For the feed phase, with the pH lower than 3.0 the selectivity order was as follows: Zn(II) > Cu(II) > Co(II) > Ni(II) > Cd(II). At the higher pH value higher transport of Cd(II) was observed and the selectivity order was changed to the following one: Zn(II) > Cu(II) > Co(II) > Cd(II) > Ni(II). The highest selectivity coefficients values for Zn(II) over other metal ions were obtained for the pH equal 2.0 excluding the selectivity coefficient for Zn(II) over Cd(II), which was the highest at the pH equal 3.0 (Tab. 1). In Fig.2., the removal of metal ions after 24 hours of the membrane transport is shown. According to this figure, the removal

of zinc(II) is much higher in comparison with copper(II), cobalt(II), nickel(II), and cadmium(II) ions. The highest removal of zinc(II) was received at the pH equal to 5.0, i.e. 96.14 %.

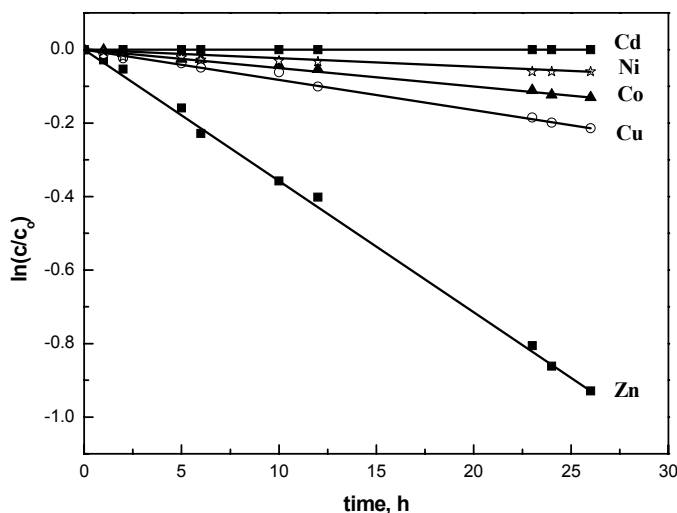


Fig. 1. Kinetics of Zn(II), Cu(II), Co(II), Ni(II), and Cd(II) transport through PIMs containing 1.5 M D2EHPA. Source phase: $c_{Me} = 1.0 \cdot 10^{-2}$ M, pH = 3.0; receiving phase: 1.0 M HCl; membrane: 2.50 cm³ ONPPE / 1.0 g CTA, 1.50 M D2EHPA

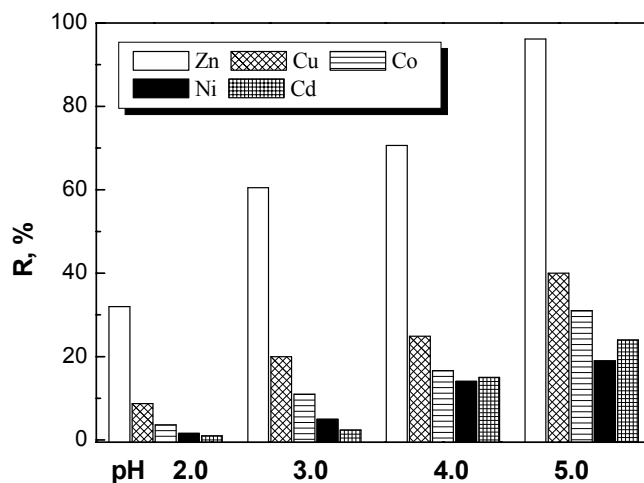
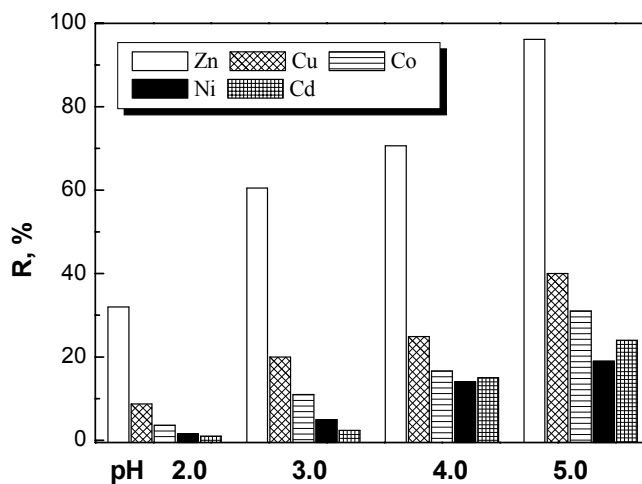


Fig. 2. Removal (%) of metal ions from chloride aqueous solutions in PIM transport at different pH after 24 hours. Source phase: $c_{Me} = 1.0 \cdot 10^{-2}$ M, pH = 3.0; Receiving phase: 1.0 M HCl, Membrane: 2.50 cm³ ONPPE / 1.0 g CTA, 1.50 M D2EHPA

Tab. 1. The values of initial fluxes, and selectivity orders for competitive transport of Zn(II), Cu(II), Co(II), Ni(II), and Cd(II) through PIM. Conditions as in Fig. 1

pH	Metal ions	Initial flux, ($\mu\text{mol}/\text{m}^2\text{s}$)	$k \times 10^6$ (s^{-1})	Selectivity orders and selectivity coefficient of Zn to other metals
2.0	Zn(II)	4.64	5.05	Zn(II) > Cu(II) > Co(II) > Ni(II) > Cd(II) 4.3 9.9 24.4 464.0
	Cu(II)	1.07	1.16	
	Co(II)	0.47	0.51	
	Ni(II)	0.19	0.21	
	Cd(II)	0.01	0.01	
3.0	Zn(II)	8.79	9.57	Zn(II) > Cu(II) > Co(II) > Ni(II) > Cd(II) 4.2 7.0 13.3 879.0
	Cu(II)	2.09	2.28	
	Co(II)	1.26	1.37	
	Ni(II)	0.66	0.72	
	Cd(II)	0.01	0.01	
4.0	Zn(II)	10.7	11.6	Zn(II) > Cu(II) > Co(II) > Cd(II) > Ni(II) 3.4 5.5 6.2 6.0
	Cu(II)	3.17	3.45	
	Co(II)	1.87	2.04	
	Ni(II)	1.72	1.84	
	Cd(II)	1.79	1.95	
5.0	Zn(II)	37.1	40.4	Zn(II) > Cu(II) > Co(II) > Cd(II) > Ni(II) 6.5 8.3 9.3 10.0
	Cu(II)	5.72	6.23	
	Co(II)	4.43	4.82	
	Ni(II)	3.70	4.03	
	Cd(II)	4.01	4.37	

Fig. 2. Removal (%) of metal ions from chloride aqueous solutions in PIM transport at different pH after 24 hours. Source phase: $c_{\text{Me}} = 1.0 \cdot 10^{-2}$ M, pH = 3.0; Receiving phase: 1.0 M HCl, Membrane: 2.50 cm^3 ONPPE / 1.0 g CTA, 1.50 M D2EHPA

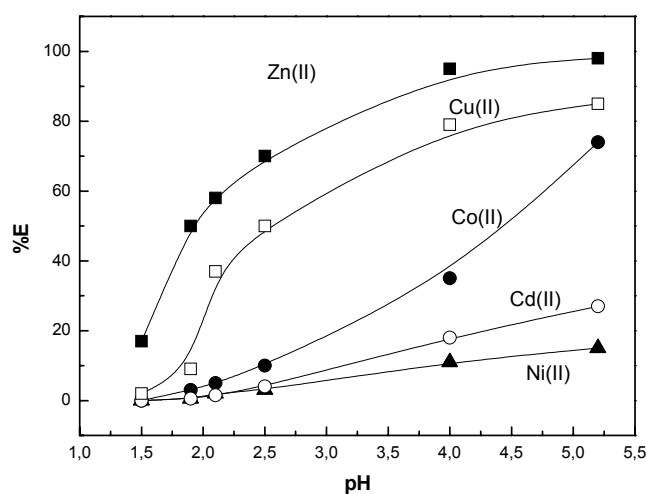


Fig.3. Plot of %E vs. equilibrium pH for Zn(II), Cu(II), Co(II), Ni(II) and Cd(II) extraction from chloride aqueous solution. The metal ions concentration 0.01M, D2EPHA concentration in kerosene: 0.1M

The results of the metals solvent extraction with 0.1 M solutions of D2EHPA in kerosene are shown in Fig.3. The results obtained for the solvent extraction are similar to those for the PIM transport. The extraction order is the same as the selectivity order obtained for transport at the pH higher than 3.0, i.e. Zn(II) > Cu(II) > Co(II) > Cd(II) > Ni(II). In extraction at pH of the aqueous phase lower than 2.5 percent, the extraction of Cd(II) and Ni(II) was very low, i.e. not higher than 4 % and 3 % for Cd(II) and Ni(II), respectively. In all the investigated pH ranges the most efficiently extracted ion was Zn(II), and the extraction selectivity was increased with an increase in the water phase pH (Tab. 2).

Tab. 2. Selectivity coefficients for solvent extraction (calculated as the ratio of distribution coefficients of appropriate metal ions). Conditions as in Fig. 3

Equilibrium pH	Separation coefficients			
	Zn(II)/Cu(II)	Zn(II)/Co(II)	Zn(II)/Cd(II)	Zn(II)/Ni(II)
1.5	1.52	N/D*	N/D*	N/D*
1.9	1.60	3.23	20.0	20.0
2.1	1.77	10.0	60.8	69.3
2.5	2.33	21.0	75.4	56.0
4.0	5.05	40.8	158	86.8
5.2	8.65	17.2	278	132

* N/D – concentration not detectable

CONCLUSION

Zinc(II) ions can be effectively separated from aqueous chloride solutions containing other metal ions, i.e. cadmium(II), copper(II), cobalt(II), and nickel(II) in hydrometallurgical processes of the solvent extraction and transport through the polymer inclusion membrane with di(2-ethylhexyl)phosphoric acid (D2EHPA) as the ion carrier. The best selectivity for Zn(II) over other metal ions was obtained for the $\text{pH} \leq 2.0$. The selectivity order was the same for the both processes. For the feed aqueous phase with the pH lower than 3.0, the initial fluxes decrease in the following order: $\text{Zn(II)} > \text{Cu(II)} > \text{Co(II)} > \text{Ni(II)} > \text{Cd(II)}$. At a higher pH the selectivity order was changed to: $\text{Zn(II)} > \text{Cu(II)} > \text{Co(II)} > \text{Cd(II)} > \text{Ni(II)}$. The highest selectivity coefficients for Zn(II)/Cd(II), Zn(II)/Ni(II), Zn(II)/Co(II), Zn(II)/Cu(II) were obtained as equal to 879, 24.4, 9.90, 6.50 for the polymer inclusion membrane transport and 278, 132, 17.2, 8.65 for solvent extraction processes.

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