



## **TRANSPORT OF TRANSITION METAL IONS THROUGH POLYMER INCLUSION MEMBRANES WITH CYANEX 301**

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### **ABSTRACT**

The selective transport of zinc(II) and cadmium(II) ions from aqueous chloride or sulfate source phase through polymer inclusion membranes (PIM) containing cellulose triacetate (support), *o*-nitrophenyl pentyl ether (plasticizer) and di(2,4,4-trimethylpentyl)dithiophosphinic acid - Cyanex 301 (ion carrier) is shown. Zn(II) and Cd(II) ions can be effectively removed from dilute chloride and sulfate aqueous solutions into 1.0 M HCl or H<sub>2</sub>SO<sub>4</sub> as the receiving phase. The separation coefficients were practically constant for acid concentrations in the receiving phase ranging from 0.01 to 1.0 M

Copper(II), zinc(II), cadmium(II), cobalt(II), and nickel(II) ions removal from aqueous chloride solutions in transport through PIMs is also shown. These metal ions can be effectively removed from dilute aqueous chloride solutions in transport through PIMs with di(2,4,4-trimethylpentyl)dithiophosphinic acid as the ionic carriers into 1.0 M HCl. The selectivity coefficients of Cu(II) over Zn(II), Cd(II), Co(II) and Ni(II) were low and decreased with an increase in the pH of source aqueous phase.

Keywords: polymer inclusion membrane, zinc(II), cadmium(II), copper(II), cobalt(II), nickel(II), Cyanex 301

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### **INTRODUCTION**

The removal of toxic metal ions from aqueous solutions is an important process for both industry and environment. In recent years a remarkable increase in the application of liquid membranes for separation

processes has been noticed [1-4]. The use of liquid membranes containing ion carriers is offered as an alternative to solvent extraction. The membrane can be used for selective removal and concentration of metal ions from source aqueous phase, in which the concentration of metal ionic species is above  $1 \times 10^{-4}$  M. A variety of types of liquid membranes exists, i.e. bulk (BLM), emulsion (ELM), supported (SLM), and polymer inclusion membranes (PIM). Polymer inclusion membranes (PIMs) are formed as thin films by casting cellulose triacetate (CTA) from an organic solution. 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 Cyanex 301:  $\text{Cu(II)} > \text{Zn(II)} > \text{Fe(III)} > \text{Co(II)} \sim \text{Ni(II)}$ . The separation of Co(II) and Ni(II) by supported and hybrid liquid membranes with Cyanex 301, Cyanex 302, Cyanex 272, and D2EHPA, was presented by Gega et al. [6,7], whereas Ulewicz et al. [8-10] studied separation of Zn(II), Cd(II), Cu(II), Co(II), and Ni(II) by polymer liquid membranes with D2EHPA and Cyanex 272. Zinc(II) ions were effectively transported through the multimembrane hybrid system with D2EHPA [11-13]. Polymer inclusion membranes were used for cadmium(II) removal from chloride aqueous solutions [14, 15] and for cadmium(II) and zinc(II) [16, 17] separation. Recently, for the removal of metal ions the polymer inclusion membranes containing macrocyclic components such as crown ethers and calixarenes have been used [18-24].

In this paper the results of the competitive transport of copper(II), zinc(II), cadmium(II), cobalt(II), and nickel(II) cations from dilute aqueous chloride solutions ( $c_M = 0.01$  M) by polymer inclusion membranes containing di(2,4,4-trimethylpentyl) dithiophosphinic acid (Cyanex 301) as the ion carrier are reported. The competitive transport of Zn(II) and Cd(II) ions from dilute aqueous chloride and sulfate solutions was also studied. The influence of pH in the receiving phase was studied.

## EXPERIMENTAL

The initial aqueous solutions were prepared with twice distilled water and the inorganic compounds such as  $\text{CdCl}_2$ ,  $\text{ZnCl}_2$ ,  $\text{CuCl}_2$ ,  $\text{CoCl}_2$ ,  $\text{NiCl}_2$ , HCl,  $\text{H}_2\text{SO}_4$  (all from POCh, Gliwice, reagents of analytical grade). The organic chemicals, i.e. cellulose triacetate (Fluka), o-nitrophenyl pentyl ether (ONPOE, Fluka), di(2,4,4-trimethyl-pentyl)dithiophosphinic acid (Cytec<sup>®</sup>, Canada), and dichloromethane (POCh) were also of analytical reagent grade. Solutions of cellulose triacetate (as the support), di(2,4,4-trimethylpentyl)dithiophosphinic acid (as the ion carrier), and o-nitrophenyl pentyl ether (as the plasticizer) in dichloromethane were prepared. A portion of this organic solution was poured into a membrane mold comprising a glass ring attached to a plate glass with cellulose triacetate -dichloromethane

glue. Dichloromethane, as the organic solvent, was allowed to evaporate overnight and the resulting polymer inclusion membrane was separated from the glass plate by immersion in water. The synthesized membrane was stored in water. The concentration of Cyanex 301 in the membrane was 1.0 M based on plasticizer; the membrane contained of 2.5cm<sup>3</sup> ONPOE / 1g CTA. The membrane thickness was 37 μm. The fresh membranes were used in each experiment.

Transport experiments were conducted in a permeation cell in which the membrane film (at the surface area of 4.9 cm<sup>2</sup>) was tightly clamped between two cell compartments. Both, i.e. the source and receiving aqueous phases (45 cm<sup>3</sup> each) were mechanically stirred at 600 rpm. The receiving phase was 1.0 M aqueous solution of hydrochloric or sulfuric acid. The source phase contained Zn(II) and Cd(II) at concentration of each metals equal to 0.01 M or solution containing Zn(II), Cu(II), Co(II), Cd(II) and Ni(II) ions at 0.01 M concentration for each metal. The PIM transport experiments were carried out at 20±0.2 °C. Small samples (0.1 cm<sup>3</sup> each) of the aqueous receiving phase were removed periodically via a sampling port with a syringe and analyzed to determine zinc, cadmium, copper, cobalt and nickel concentrations by atomic absorption spectroscopy method (AAS Spectrometer, Solaar 939, Unicam). The source phase acidity was controlled by a pH meter (pH meter, CX-731 Elmetron, with a combine pH electrode, ERH-136, Hydromet, Poland) and pH was kept constant by adding periodically small amounts of 1.0 M NaOH aqueous solution.

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

$$\ln\left(\frac{c}{c_i}\right) = -kt \quad (1)$$

where  $c$  is the metal ions concentration (M) in the source phase at some given time,  $c_i$  is the initial metal ions concentration in the source phase,  $k$  is the rate constant (s<sup>-1</sup>), and  $t$  is the time of transport.

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

$$J_i = \frac{V}{A} \cdot k \cdot c_i \quad (2)$$

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

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

$$S = J_{i,M1} / J_{i,M2} \quad (3)$$

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

$$R = \frac{c_i - c}{c_i} \cdot 100\% \quad (4)$$

### RESULTS AND DISCUSSION

The competitive transport of zinc(II) and cadmium(II) ions from the aqueous source phase ( $c_M = 0.01$  M) through polymer inclusion membranes containing 1.0 M di(2,4,4-trimethylpentyl)dithiophosphinic acid (Cyanex 301) as the ionic carrier into receiving aqueous phase was investigated. The transport kinetics of metal ions from chloride and sulfate source phase containing an equimolar mixture of both metals is shown in Fig.1., According to Fig.1 the rate of Zn(II) and Cd(II) transport decreases in the sequence: chloride > sulfate. Zinc(II) and cadmium(II) from sulfate aqueous solutions are removed slower than from chloride solutions. The amount (5) of Zn(II) and Cd(II) removed from chloride and sulfate solutions after 24 hours were 97.5; 96.7 and 89.2; 85.8 %, respectively.

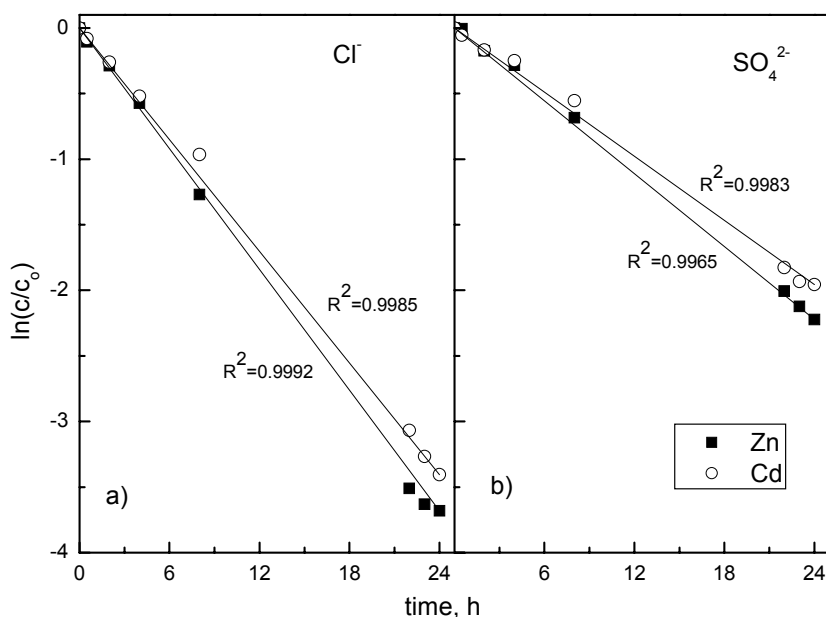


Fig. 1. Kinetics of zinc(II) and cadmium(II) transport through PIMs containing 1.0 M Cyanex 301 from a) chloride and b) sulfate source aqueous phase  
Source phase:  $c_M = 0.01$  M each metal; Receiving phase: 1.0 M HCl or 1.0 M  $H_2SO_4$ ; Membrane: 2.50  $cm^3$  ONPPE / 1.0 g CTA, 1.0 M Cyanex 301;  
 $R^2$  – squared linear correlation coefficient.

The dependence of the values of initial fluxes on the concentrations of receiving aqueous acid solutions is shown in Fig. 2. According to presented data, the initial fluxes of zinc(II) are higher than those of cadmium(II) ions for chloride as well as sulfate solutions. The initial fluxes of Zn(II) and Cd(II) increase with an increase in HCl and H<sub>2</sub>SO<sub>4</sub> concentration in receiving phase, but the selectivity coefficients Zn/Cd in both the studied solutions are comparable. For HCl or H<sub>2</sub>SO<sub>4</sub> concentration ranging between 0.01÷1.0 M the selectivity coefficients are equal to 1.1 ÷ 1.5. These results demonstrate poor selectivity for Zn(II)/Cd(II) in PIM transport with Cyanex 301.

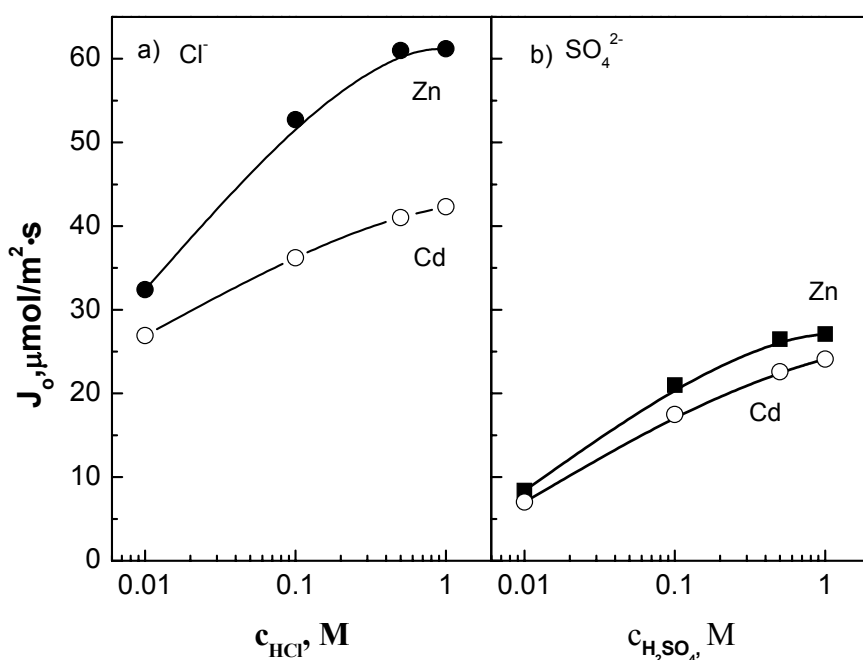


Fig. 2. Relationship of initial fluxes of zinc(II) and cadmium(II) transport through PIMs on concentration a) chloride and b) sulfate of receiving phase  
Source phase: chloride or sulfate solutions  $c_M = 0.01$  M each metal;  
Membrane: 2.50 cm<sup>3</sup> ONPPE / 1.0 g CTA, 1.0 M Cyanex 301

Also, the competitive transport of copper(II), zinc(II), cadmium(II), cobalt(II) and nickel(II) ions from the aqueous source phase ( $c_M = 0.01$  M each metal) through the polymer inclusion membranes containing 1.0 M Cyanex 301 as the ionic carrier into the receiving aqueous phase was investigated. The flux and selectivity orders of metal ions transport through PIM from the aqueous source phase containing an equimolar mixture of all

the metals is shown in Table 1. As it can be seen from the table, the initial fluxes decrease in the following order: Cu > Zn > Cd > Co > Ni. A similar order (Cu > Zn > Fe > Co, Ni) was obtained by Sole and Hiskey [25] for solvent extraction with Cyanex 301.

Table 1. Values of initial fluxes and selectivity orders for competitive transport of Zn(II), Cu(II), Co(II), Ni(II), and Cd(II) through PIM.

Source phase:  $c_M = 0.01$  M each metal; Receiving phase: 1.0 M HCl  
Membrane: 2.50 cm<sup>3</sup> ONPPE / 1.0 g CTA, 1.0 M Cyanex 301

pH	Metal ions	Initial flux, $J_0$ ( $\mu\text{mol}/\text{m}^2\text{s}$ )	Determination coefficient $R^2$	Selectivity order and selectivity ratios
2.0	Cu(II)	2.89	0.9913	Cu(II) > Zn(II) > Cd(II) > Co(II) > Ni(II) 1.5    1.7    2.1    2.7
	Zn(II)	1.92	0.9666	
	Cd(II)	1.70	0.9768	
	Co(II)	1.37	0.9456	
	Ni(II)	1.07	0.9721	
3.0	Cu(II)	3.32	0.9951	Cu(II) > Zn(II) > Cd(II) > Co(II) > Ni(II) 1.2    1.4    1.5    1.6
	Zn(II)	2.82	0.9762	
	Cd(II)	2.32	0.9698	
	Co(II)	2.18	0.9756	
	Ni(II)	2.11	0.9112	
4.0	Cu(II)	3.43	0.9871	Cu(II) > Zn(II) > Cd(II) > Co(II) > Ni(II) 1.1    1.3    1.5    1.6
	Zn(II)	3.11	0.9919	
	Cd(II)	2.64	0.9398	
	Co(II)	2.22	0.9814	
	Ni(II)	2.14	0.9207	
5.0	Cu(II)	3.68	0.9897	Cu(II) > Zn(II) > Cd(II) > Co(II) > Ni(II) 1.0    1.2    1.4    1.5
	Zn(II)	3.53	0.9699	
	Cd(II)	3.05	0.9793	
	Co(II)	2.70	0.9891	
	Ni(II)	2.44	0.8992	

The selectivity coefficients for Cu(II) over other metal cations decrease with an increase in source phase pH. The selectivity coefficients at lowest investigated pH, i.e. 2.0 for Cu/Zn, Cu/Cd, Cu/Co, Cu/Ni were 1.5, 1.7, 2.1, and 2.7, and at pH = 5.0 1.0; 1.2; 1.4 and 1.5, respectively. These results demonstrate very poor selectivity of PIM transport with Cyanex 301 as the ions carrier. The removal of metal ions (%) after 24 hours of experiment is shown in Fig. 3.

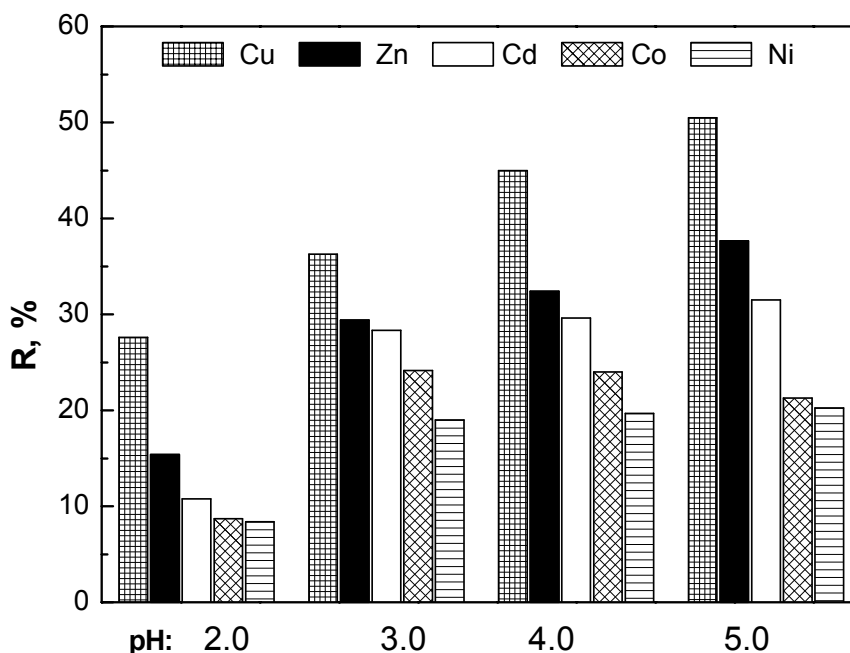


Fig. 3. Removal (%) of metal ions from chloride aqueous solutions in PIM transport at different pH after 24 hours. Source phase:  $c_M = 0.01$  M each metal; Receiving phase: 1.0 M HCl, Membrane:  $2.50 \text{ cm}^3$  ONPPE / 1.0 g CTA, 1.0 M Cyanex 301.

According to this figure, the removal of copper(II) is slightly higher than those of zinc(II), cadmium(II), cobalt(II) and nickel(II) ions. The removal of metal ions increases with increase in source phase pH. The highest removal of copper(II) was received at pH equal to 5.0, i.e. 50.5 % whereas Zn(II) and Cd(II) are removed in 37.7 and 31.5 %, respectively. The removal of Zn(II) and Cd(II) ions from a mixture of the both metal ions is threefold higher than from a mixture of five metal ions.

### CONCLUSION

Zinc(II) and cadmium(II) ions can be removed from aqueous sulfate and chloride solutions in transport through PIMs with Cyanex 301 as the ion carrier. Transport of these ions decreases in the sequence: chloride > sulfate. The initial fluxes of Zn(II) and Cd(II) increase with increasing HCl and  $\text{H}_2\text{SO}_4$  concentration in the receiving phase. An increase in acidity of the receiving phase causes an increase in the transport of Zn(II) and Cd(II) ions.

Also, copper(II), zinc(II), cadmium(II), cobalt(II) and nickel(II) ions can be removed from aqueous chloride solutions in transport through the polymer inclusion membrane with Cyanex 301 as the ion carrier. The initial fluxes decrease in the following order: Cu(II) > Zn(II) > Cd(II) > Co(II) > Ni(II). With an increase in pH, the transport of all metal ions increase and the selectivity of Cu(II) over other ions separation decreases. The values of

selectivity coefficients for Cu/Zn, Cu/Co, Cu/Ni, Cu/Cd at pH range 2.0 ÷ 5.0 were from 2.7 to 1.0.

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