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Bernadeta GAJDA*, Andrzej SKRZYPCZAK**, Mariusz B. BOGACKI***

SEPARATION OF COBALT(II), NICKEL(II), ZINC(II) AND CADMIUM(II) IONS FROM CHLORIDE SOLUTION

Selective distribution of cobalt(II), nickel(II), zinc(II) and cadmium(II) ions from chloride solutions through polymer inclusion membranes (PIM) has been studied. The carrier was 1-decylimidazole. The effect of chloride ion concentration on the ion permeation was analysed. The results suggest that some of metal ions change for the worse selectivity of separation process. Especially zinc(II) and cadmium(II) ions decreased five-fold selectivity of ion separation process.

keywords: zinc(II), cobalt(II), nickel(II) cadmium(II); polymer inclusion membranes; solvent extraction; 1-decylimidazole

1. INTRODUCTION

Cobalt, nickel, zinc and cadmium are important elements known as industry useful metals. Main sources of them are sulfide and oxide ores. Other source of them is ocean in which many metal ions are dissolved or present in the concrete form. That source will be very useful in the future when traditional ores of many metals are exhausted (Gajda and Bogacki, 2010).

Also many industrial processes produce liquid or solid wastes containing metal

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* Department of Metal Extraction and Recirculation, Częstochowa University of Technology, Armii Krajowej 19, 42-200 Częstochowa, Poland
** Division of Organic Technology, Poznań University of Technology, Pl. M. Skłodowskiej–Curie 2, 60-965 Poznań
*** Division of Process Engineering, Poznań University of Technology, Pl. M. Skłodowskiej – Curie 2, 60-965 Poznań. e-mail: Mariusz.Bogacki@put.poznan.pl

ions. That kind of wastes are produced in chemical metallurgy, industrial metallurgy and industrial electronics. A next potential source of heavy metal waste is battery and accumulator recycling (Rudnik and Nikiel, 2007). Ecological and economical regulations caused recycling of all wastes, especially containing cadmium, nickel and even cobalt ions.

Today the most important processes to obtain such metals as cobalt, nick, zinc and cadmium are: ion-exchange, hydrometallurgy, especially solvent extraction and liquid membrane ion transportation.

During the last two decades we observe growing interest in application polymer inclusive membranes (PIM) for metal ion separation. The PIM membranes have better mechanical strength and chemical resistance than liquid membranes. Plasticizing additive in polymer membrane causes their good or even very good flexibility. Membrane containing plasticizers has also good ability to miscible ion carrier in polymer. Today several ion carriers are used as metal extractants such as phosphoric acids (Reddy et al., 2005; Aouad et al., 1998; Ulewicz and Walkowiak, 2005; Kozłowski et al., 2002), trioctyloamine (Pośpiech and Walkowiak, 2007), and coronene ethers (Walkowiak et al., 2000).

In the last ten years some imidazolium derivatives were also used for ion separation (Radzymińska-Lenarcik, 2008; du Preez et al., 2001; Radzymińska-Lenarcik, 2007). Imidazolium compounds have two nitrogen atoms in the aromatic ring. One nitrogen atom has a free electron pair, efficient for a coordinate bond and we observe reactions of complex formation of imidazolium compounds with metal chlorides MCl_2.

The aim of the work is to study selective separation process of Ni(II), Co(II), Zn(II) and Cd(II) ions from chloride solutions using 1-decylimidazole.

2. EXPERIMENTAL

1-Decyloimidazole was synthesized in the reaction of imidazole and 1-bromodecane in the solution of sodium methylate in methanol – Fig. 1.
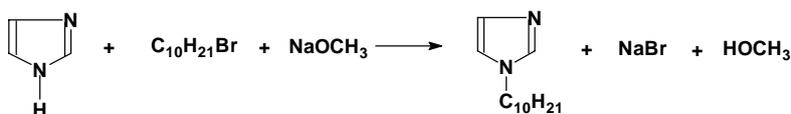

Fig. 1. 1-decylimidazole synthesis

After dissolving all substrates, the mixture was stirred and heated under reflux for 2 hours. After cooling the solution to room temperature, the crude product was separated from the solid sodium bromide, extracted with hexane and dried in vacuum. 1-decylimidazole was twicely distilled under reduced pressure. The yield of the reaction was 91%.

The polymeric inclusive membranes (PIM) were prepared mixing solutions: 1.25 g

of cellulose triacetate (CTA) in 100 cm^3 dichloromethane, 10% solution of o-nitrophenyloctyl ether (ONPOE, Fluka) in dichloromethane and 0.1M of ion carrier (1-decylimidazole) also in dichloromethane. After careful stirring, the solution was poured into 4 cm diameter glass ring, placed on a glass horizontal plate. After 12 h, dichloromethane has evaporated the membrane was ready and immediately dipped for next 12 h into distilled water. The working membrane contained 8.0 cm^3 ONPOE/1.0 g CTA and 1.0 M carrier. Molar concentration of ion carrier in the membrane was calculate for the volume of the plasticizer

The measurement vessel for membrane test contained two 50 cm^3 in volume cells separated by 4.9 cm^2 surface membrane (Fig. 2).
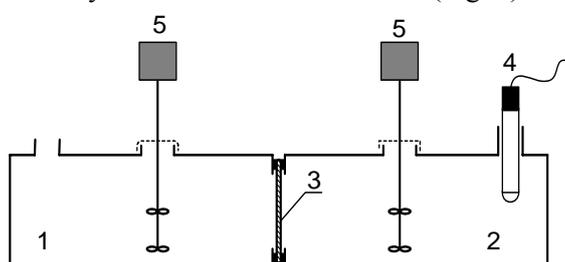

Fig. 2. Measurement system for PIM membrane metallic ion transportation 1– receiver solution, 2– feed solution, 3– membrane, 4– pH electrode, 5– stirrer

The feeding phase was 10^{-2} M chloride solution of appropriate Co(II), Ni(II), Zn(II) and 5·10^{-3} M chloride solution of Cd(II) ions. To have 2 M solution of chloride anions, NaCl was added. Four chloride solutions of metal ions were tested: 1) Co(II) – Ni(II); 2) Co(II) – Ni(II)) – Zn(II); 3) Co(II) – Ni(II) – Cd(II); 4) Co(II) – Zn(II) – Cd(II); 4) Co(II) – Ni(II) – Zn(II) – Cd(II).

The receiver solution was distilled water. Prepared solutions were stirred by a 600 rpm rotating mixer. During transportation process 0.20 cm^3 samples were taken from the feed and receiver solutions. After dilution, samples were quantitative analyzed for ion metallic concentration using atomic absorbing spectrophotometer (ASA, Solar 939, Unicam).

The kinetics of transport across the PIMs was described as first–order process in relation to the metal ion concentration:

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

where c – metal ions concentration, c_i – initial metal ions concentration in source phase, k – rate coefficient, $1/s$, and t – time of transport, s. The initial flux, J_i (mol·m^{-2}s^{-1}) is equal to:

$$J_i = \frac{V}{A}kc_i, \qquad (2)$$

where V – volume of aqueous source phase, m^3; A – effective area of membrane, m^2. The permeability coefficient , P, (m/s) was calculated according to equation:

$$P = \frac{V}{A} k \,.$$

(3)

The selectivity coefficient was defined as a ratio of initial fluxes for to the metal ions:

$$S_{M_I / M_{II}} = \frac{J_{M_I}}{J_{M_{II}}} \,.$$

(4)

3. RESULTS AND DISCUSSION

An exemplary relationship between $\ln(c/c_i)$ and time for Co(II), Zn(II), Ni(II) and Cd(II) ions transport across the PIM membranes are shown in Figs 3 and 4.

Looking at Figs 3 and 4 we can state that there is big difference between tested ion transportation coefficients for appropriate metal ions. From Table 1 we can see that the values of feeding phase for starting streams of metal ions differ even three order of magnitude from $6.13 \cdot 10^{-7}$ for nickel ions in solution of Co – Ni – Zn and $1.31 \cdot 10^{-4}$ for cobalt ions in solution of Co – Ni.
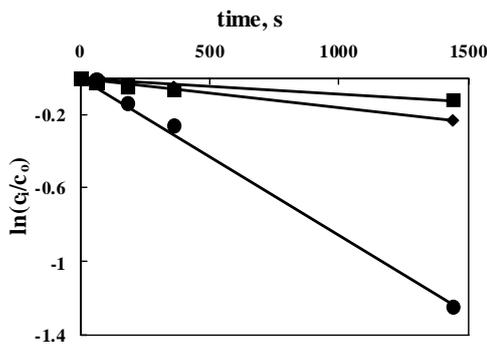
Fig. 3. Ion concentration change as a function of time in the feeding phase ♦– Co(II), ■– Ni(II) ●– Cd(II). Ion carrier 1-decyloimidazol. Chloride concentration in feeding phase– 2 M. Receiver solution – distilled water. Starting ion concentration: Co, Ni – 10^{-2} M, Cd – $5 \cdot 10^{-3}$ M

Fig. 4. Ion concentration change as a function of time in the feeding phase ♦– Co(II)), ▲– Zn(II) and ●– Cd(II). Ion carrier 1-decyloimidazol. Chloride concentration in feeding phase – 2 M. Receiver solution – distilled water. Starting ion concentration: Co, Zn – 10^{-2} M, Cd – $5 \cdot 10^{-3}$ M
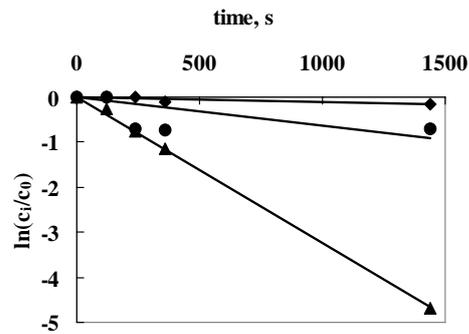
As we can see from Tables 1 and 2 the highest value of rate the ion transport is for zinc(II) ion. Measured values (10^{-4}) of starting stream do not depend on feeding phases. Also the rate ion transportat for zinc(II) ion does not depend on the feeding phase composition. But the ion rate transportat for Ni(II) and Co(II) depends on the feeding phase composition because Zn(II) and Cd(II) in tested composition highly lowered their ion transportation rate.

Presented in Table 2 selectivity coefficients show that presence of Zn(II) or Cd(II) ions in the tested solutions lowered selectivity of ion partition coefficient of Ni(II) and Co(II) ions. For instance, the selectivity coefficient for solution contained only Ni(II)

and Co(II) ions is 8.1. When Zn(II) and Cd(II) ions were added, selectivity coefficient lowered 4-5 times. We observed similar behavior for other ion pairs. The selectivity coefficient for solution containing only Zn(II) and Co(II) ions also was lowered when Cd(II) ions were added. In that case selectivity coefficient was lowered 5 times.

Table 1. Starting stream of metal ions (J_i, mol/(m^{2}s)) for three different solutions of feeding phase. Ion carrier – 1-decylimidazole. Chloride concentration in feeding phase – 2 M. Receiver solution – distilled water. Metal ion concentration: Co, Ni, Zn – 10^{-2} M, Cd – $5 \cdot 10^{-3}$ M

Ion	Feeding phase				
	Co – Ni	Co – Ni – Zn	Co – Ni – Cd	Co – Zn – Cd	Co – Ni – Zn – Cd
Co	$1.31 \cdot 10^{-4}$	$1.19 \cdot 10^{-6}$	$1.50 \cdot 19^{-5}$	$1.24 \cdot 10^{-5}$	$8.33 \cdot 10^{-6}$
Ni	$1.63 \cdot 10^{-5}$	$6.13 \cdot 10^{-7}$	$9.14 \cdot 10^{-6}$	-	$1.17 \cdot 10^{-5}$
Zn	-	$1.32 \cdot 10^{-4}$	-	$2.78 \cdot 10^{-4}$	$1.12 \cdot 10^{-4}$
Cd	-	-	$4.59 \cdot 10^{-5}$	$3.64 \cdot 10^{-5}$	$8.03 \cdot 10^{-6}$

Table 2. Selectivity coefficient of metal ions ($S_{MI/MII}$) for different solutions of feeding phase. * indicates the reverse value ($S_{MII/MII}$). Ion carrier – 1-decyloimidazole. Chloride concentration in feeding phase – 2 M. Receiver solution– distilled water. Metal ions concentration: Co, Ni, Zn – 10^{-2} M, Cd – $5 \cdot 10^{-3}$ M

Ion	Feeding phase				
	Co – Ni	Co – Ni – Zn	Co – Ni – Cd	Co – Zn – Cd	Co – Ni – Zn – Cd
Co/Ni	8.10	1.94	1.64	-	1.41*
Co/Zn	-	9.05*	-	2.24*	1.35*
Co/Cd	-	-	3.07*	2.94*	1.04
Ni/Zn	-	2.15*	-	-	9.59*
Ni/Cd	-	-	5.03*	-	6.86
Zn/Cd	-	-	-	1.31	1.40

4. CONCLUSION

Many industrial processes produce wastes containing polymetallic ion solutions. Our measurements proved that metal ions – especially zinc(II) and cadmium(II) ions - present in the feeding phase, can improve or sometimes lower the efficiency of ion separation.

ACKNOWLEDGMENTS

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W pracy przedstawiono wyniki badań selektywnego rozdziału jonów kobaltu(II), niklu(II), cynku(II) i kadmu(II) z roztworów chlorkowych w procesie selektywnego ich rozdziału w procesie membranowym przez polimerowe membrany inkluzyjne (PIM). Jako przenośnik zastosowano 1-decyloimidazol. Uzyskane wyniki wskazują, że obecność jonów niektórych metali pogarszać może selektywność rozdziału. Szczególne znaczenie mają tutaj jony cynku(II) oraz kadmu(II), które prawie 5-krotnie pogarszają selektywność rozdziału jonów niklu(II) od kobaltu(II).

słowa kluczowe: nikiel(II), kobalt(II), cynk(II), kadm(II), ekstrakcja rozpuszczalnikowa, polimerowe membrany inkluzyjne, 1-decylimidazol