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APPLICATION OF SUPPORTED AND POLYMER MEMBRANE WITH 1 DECYL-2-METHYLIMIDAZOLE FOR SEPARATION OF TRANSITION METAL IONS

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Abstract. The facilitated transport of Cu(II), Zn(II), Co(II), and Ni(II) ions from different aqueous nitrate source phases (c_{Me} = 0.001M, pH 6.0) across polymer inclusion membranes (PIMs) consisting of cellulose triacetate (support) and 2-nitrophenylpentyl ether (plasticizer) doped with 1-decyl-2-methylimidazol as ion carrier was reported. The membrane is characterised by atomic force microscopy (AFM) and thermal analysis (DTA and TG) techniques. The results show that Cu^{2+} can be separated very effectively from other transition metal cations as Zn^{2+}, Co^{2+}, and Ni^{2+} from different equimolar mixtures of these ions. The recovery factor of Cu^{2+} ions during transport across PIM from different mixture is equal to 92-95.1%. The comparative transport of Cu(II), Zn(II), Co(II), and Ni(II) ions from aqueous nitrate source phase across supported (SLMs) containing 1-decyl-2-methylimidazol as ion carrier was reported.

keywords: polymer inclusion membrane (PIM), supported liquid membrane (SLM), separation ions, copper(II), zinc(II), nickel(II), cobalt(II), imidazole derivatives

1. Introduction

Liquid membrane techniques are slowly though continuously becoming a very important and promising alternative to solvent extraction for metal ions recovery and separation from aqueous solutions. In recent years a remarkable increase in the application of emulsion membranes for zinc(II) recovery from spent solutions after the production of cellulose fibres has been observed. Moreover, pilot plants for Zn(II) recovery from the zinc production process and for the recovery of metals (including zinc, copper, cobalt cadmium and lead) from spent water generated in municipal waste incineration plants was activated. The wider use of liquid membranes in practice is considerably limited by their low durability and instability of operation, resulting mainly from their structures and compositions. It is important now to enhance the stability of liquid membranes and extend the time of their operation, so that they could be used in practice, because, as has been demonstrated by numerous studies (Kislik, 2010; Nghiem et al., 2006), separation of many metals is possible in the process of transport through liquid membranes.

As metal ion carriers in the membrane processes, the same organic substances as those used in extraction processes are employed (Walkowiak et al., 2002). For the separation of nonferrous ions in the liquid membrane transport process both classical and new types of carriers are used (Nghiem et al., 2006). Commercial carriers of metal cations commonly used in the membrane technique enable the effective separation of ions but their selectivity is rather poor. Therefore, new complexing reagents are searched which selectively separate metal ions from aqueous solutions.

Gherrou et al. (2002) reported on the selective proton-driven transport of silver(I) ions in presence of nonferrous cations (Cu^{2+}, Zn^{2+}) across supported membranes with DB18C6. The transport selectivity of SLM was as follows: $Ag^{+} > Cu^{2+} > Zn^{2+}$. Gherrou et al. (2005) also obtained optimal compositions of the polymer membrane for copper(II) transported using DB18C6. Selective facilitated transport of Cu^{2+} across PLM with 1, 10-didecyl-1,10diaza-18-crown-6 or 1,7-diaza-15-crown-5 as ion carrier was studied by Parthasarathy and Buffle (1991) as well as Dadfarnia and Shamsipur (1992). The competitive transport of Cu^{2+} from solutions containing Mn^{2+}, Co^{2+}, Cd^{2+}, Ni^{2+}, and Pb^{2+} ions across bulk liquid membrane doped with DA18C6 was observed by Cho et al. (1988). Ulewicz et al. (2004) examined the competitive transport of Cd^{2+} from solutions containing Zn^{2+} and Cu^{2+} ions from aqueous chloride source phase through polymer inclusion membranes containing side-armed lariat ether-type derivatives of diphosphaza-16-crown-6 as ion carrier. The initial fluxes of all investigated cations increase with the acidity of the feed phase and the selectivity order was as follows: Cd(II) > Zn(II) > Cu(II).

The cations Zn^{2+}, Pb^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+} and Cd^{2+} which are transported across PIMs containing azocrown and thioazocrown imidazole derivatives were investigated by Ulewicz et al. (2007, 2009). The linear decrease in the values of the initial metal ions transport fluxes was observed with the increase in the hydrophilic-hydrophobic balance (HLB) index of the imidazole crown ether derivatives. The transport selectivity of PIM with azocrown imidazole was as follows Pb(II) > Zn(II) > Cu(II) > Co(II) > Ni(II) > Cd(II). Recently, pyrrole azocrown ethers in ordinary bulk membrane systems were also found to preferentially transport lead(II) from equimolar mixture of Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ag^{+} and Pb^{2+} ions (Luboch et al., 2006).

The results of the authors' investigation of the separation of nonferrous metal ions using 1-alkylimidazoles as ion carriers are presented in their previous work (Ulewicz and Radzymińska-Lenarcik, 2011). In this work, the authors present the results of their investigation of the competitive transport of copper(II), zinc(II), cobalt(II), and nickel(II) ions across inclusion membranes containing 1-dodecyl-2-methylimidazoles from dilute nitrate solutions.

2. Experimental

2.1. Reagents

The inorganic chemicals, i.e. copper(II), zinc(II), nickel(II), and cobalt(II) nitrate were of analytical grade and were purchased from POCh (Gliwice, Poland). The organic reagents, i.e. cellulose triacetate (CTA), *o*-nitrophenylphentyl ether (*o*-NPPE) and dichloromethane were also of analytical grade and were purchased from Fluka and used without further purification. The 1-decyl-2-methylimidazol was synthesized according to a method reported in the literature (Pernak et al. 1987).

2.2. Supported and polymer membrane preparation and characterization

The polymer membranes were prepared according to the procedure reported in the previous paper (Ulewicz et al., 2007). A solution of cellulose triacetate as the support, plasticizer and 1-decyl-2-methylimidazol as ion carrier in dichloromethane was prepared. A specified portion of this solution was poured into a membrane mould comprised of a 9.0 cm in diameter glass ring placed on a glass plate with cellulose triacetate-dichloromethane glue. After slow solvent evaporation overnight the resulting membrane was peeled off from the glass plate by immersion in cold water. Then the membrane was soaked for 12 hours in distilled water to achieve their homogeneity. Microporous polypropylene membrane Celgard 2500 (Celgard, LLC) was used as the solid support. The membrane was soaked for 24 h in 1.0 M 1-decyl-2-methylimidazol in dichloromethane. Two samples of PIM and SLM membrane were cut from the same membrane film for duplicate transport experiments.

A surface characterization study of the membranes was performed by atomic force microscopy (AFM) according to the procedure described in our earlier paper (Ulewicz et al., 2010). The analysis of surface pore characteristics of polymer membrane was made using the AFM image processing program NanoScope v.5.12, which enabled the calculation of two parameters, roughness (R_q) and porosity (ε). The PIM's thermal analysis in nitrogen atmosphere (150 cm^3/min) were done using Netzsch TG 209 F3 Tarsus. Scanning speed was 15^{o}C/min.

2.3. Transport studies

Transport experiments were carried out in a permeation module cell described in our earlier paper (Ulewicz et al., 2007). The membrane film (at surface area of 4.9 cm^3) was tightly clamped between two cell compartments. Both, i.e. the source and receiving aqueous phases (45 cm^3 each) were mechanically stirred at 600 rpm. The receiving phase was deionized water. The SLM and PIM transport experiments were carried out at the temperature of 20 ± 0.2^o C. Metal concentration was determined by withdrawing small samples (0.1 cm^3 each) of the aqueous receiving phase at different time intervals and analysing by atomic absorption spectroscopy method (AAS Spectrometer, Solaar 939, Unicam). The source phase pH was kept constant (pH = 5.0) and controlled by pH meter (pH meter, CX-731 Elmetron, with combine pH electrode, ERH-126, Hydromet, Poland). The permeability coefficient (*P*, m/s) of metal ions across membranes was described by the following equation (Danesi, 1984-85):

$$\ln\left(\frac{c}{c_i}\right) = -\frac{A}{V}\cdot P\cdot t\,, \tag{1}$$

where c is the metal ions concentration (M) in the source aqueous phase at some given time, c_i is the initial metal ions concentration in the source phase, t is the time of transport (s), V is volume of the aqueous source phase (m^3), and A is an effective area of membrane (m^2).

A linear dependence of $\ln(c/c_i)$ in the source phase versus time was obtained and the permeability coefficient was calculated from the slope of the straight line that fits the experimental data. The initial flux (J_i) was determined as equal to:

$$J_i = P\cdot c_i\,. \tag{2}$$

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

$$S = J_{i,M1} / J_{i,M2}\,. \tag{3}$$

To describe the efficiency of metal removal from the source phase, the recovery factor (*RF*) was calculated:

$$RF = \frac{c_i - c}{c_i}\cdot 100\% \tag{4}$$

The reported values correspond to the average values of three replicates, with the standard deviation within 5%.

3. Results and discussion

The imidazole ring is a stable molecule that, according to Pearson’s HSAB principle, is ranged among the intermediate class of bases. Although its basicity is by an order of magnitude lower than that of ammonia, imidazole forms more stable complexes with metal ions belonging to the intermediate class of Pearson’s acids (Schaekers et al., 2004). Decyl substituents at position 1 of the imidazole ring distinctly affect the hydrophobic properties of the molecule and weakly strengthen its basicity (pK_a = 7.43) (Lenarcik and Ojczenasz, 2002). An additional methyl substituent at position 2 of the imidazole ring has been found to increase basicity by one order of magnitude, compared with that of 1-decylimidazoles (pK_a = 8.47), though at the same time the stability of the 1-decyl-2-methylimidazole complexes declined due to the effect of $\pi_{M\rightarrow L}$ back-bonding and the steric effect of the subsituent at position 2.

The initial flux transport of Cu^{2+}, Zn^{2+}, Co^{2+} and Ni^{2+} ions across the polymer inclusion membrane doped with 1-decyl-2-methylimidazole vs. 2-nitrophenyl pentyl ether concentration is shown in Fig. 1. As can be seen, 53.4% of the plasticizer in the membrane containing the imidazole derivative is an optimal concentration. Neither too low nor too high concentrations of the plasticizer in the membrane are desirable. Below this concentration an anti-softening effect occurs and the membrane becomes very brittle. Also, an excess of the plasticizer proved to be negative, because the plasticizer migrating into the aqueous phase formed at the interface of a barrier to the transfer of the metal ions. Furthermore, an increase in the plasticizer concentration resulted in an excessive increase in the thickness of the membrane, which also adversely affects the stream of ionic transfer. A similar phenomenon has also been reported by Gyves et al. (2006) during the transfer of Cu^{2+} across a membrane containing LIX 84 using tri-n-butoxyethyl phosphate (TBEP) as a plasticizer and by Gherrou et al. (2005) across a polymeric membrane containing DB18C6 using 2-nitrooctyl ether (oNPOE) as a plasticizer.

The AFM image of PIM's consists of 53.4% plasticizer, 20% CTA and 26.6% 1-decyl-2-methylimidazol in a two-dimensional form with the format 5.0 x 5.0 μm shown in Fig.2. The porosity (ε) and roughness (R_q) of the polymer membrane were calculated using atomic force microscopy (AFM) and were equal to 17.2% and 6.8 nm, respectively. The effective pore size was 0.064μm. The distribution of the carrier in the investigated membrane after evaporation of dichloromethane is homogeneous on the entire surface. The membrane tortuosity was determined from the relationship developed by Wolf and Strieder (1990): $\tau = 1 - \ln \varepsilon$ and equal to 2.76 (for $\varepsilon = 0.172$). The values of initial fluxes, selectivity order and selectivity ratio for the competitive transport of divalent metal ions from different equimolar mixtures across PIM doped with 1-decyl-2-methylimidazol are summarised in Table 1. The values of initial fluxes of Cu(II) ions transport across PIM are higher than any of the components of the investigated equimolar mixtures. The selectivity order of metal ions transported from a mixture containing three metal ions decreases in the sequence: Cu(II) > Co(II) > Ni(II), whereas from the mixture containing four metal ions – in the sequence: Cu(II) > Zn(II) > Co(II), Ni(II). The stability constants ($\log\beta_1$) of Co(II), Ni(II), and the Zn(II) complexes with 1-decylimidazole and 1-decyl-2-methylimidazole are presented in Table 2 (Lenarcik and Ojczenasz, 2004; Lenarcik and Kierzkowska, 2004, 2006; Radzyminska-Lenarcik, 2007, 2008, 2011). The stability constants of the 1-decyl-2-methylimidazole complexes are lower, compared with those of 1-decylimidazole, except Zn(II) ion. The steric effect of the substituent at position 2 decreases the stability constants of octahedral complexes of all the metals studied though it does not hinder the formation of tetrahedral species. Therefore, the Co (II), Zn (II) and Cu (II) ions, which are able to form such compounds, have larger overall stability constants. The formation of tetrahedral complexes with 1-alkylimidazoles has been proven for the Co (II), Zn (II) and Cu (II) ions (Lenarcik and Ojczenasz, 2004; Lenarcik and Kierzkowska, 2004; Lenarcik and Rauckyte, 2004; Radzyminska-Lenarcik, 2007). It seems that the initial flux values correspond to those of the stability constants of the complexes.

The highest percentage removals Cu^{2+} was obtained from the source phase containing an equimolar mixture of three metal ions and was equal to 95.1%. Recovery factors for Ni(II) and Co(II) were not very high, they did not exceed 24%. The percentage removals of Cu^{2+} from the source phase containing an equimolar mixture Cu^{2+}-Zn^{2+}, and Cu^{2+}-Zn^{2+}-Co^{2+}-Ni^{2+} ions were above 92%.

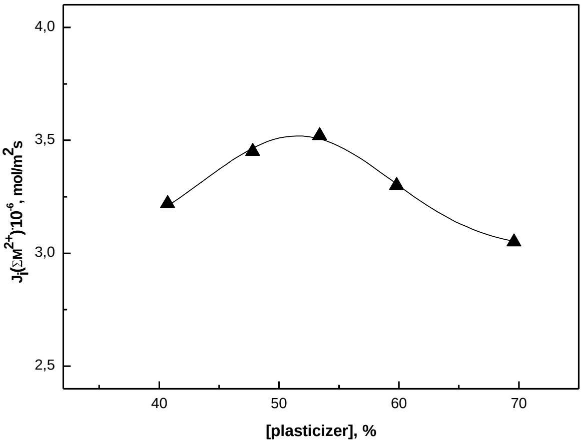


Fig. 1. Summary initial flux for competitive transport of Zn^{2+}, Co^{2+}, Cu^{2+}, and Ni^{2+} ions transport across PIM doped with 1-decyl-2-methylimidazol vs. of plasticizer concentration, membrane: 7.65 mg/cm^2 CTA and 2.26 mg /cm^2 1-decyl-2-methylimidazole

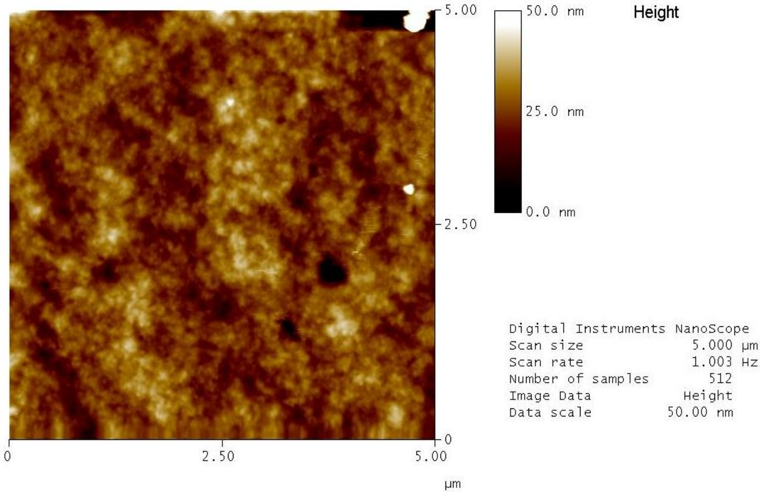


Fig. 2. 2D atomic force microscopy for PIM with 1-decyl-2-methylimidazole

Table 1. Initial fluxes, selectivity order and selectivity coefficients for competitive transport of Cu(II), Zn(II), Co(II), and Ni(II) ions across PIM doped with 1-decyl-2-methylimidazole; membrane: 53.4% plasticizer, 20% CTA and 26.6% 1-decyl-2-methylimidazole

Mixture	Metal ions	J, μmol/m^2·s	$S_{Cu(II)/Me(II)}$
1	Cu(II)	2.89	Cu(II) > Co(II) > Ni(II)
	Co(II)	0.28	10.3 13.8
	Ni(II)	0.21	
2	Cu(II)	2.36	Cu(II) > Zn(II)
	Zn(II)	0.92	2.6
3	Cu(II)	2.35	
	Zn(II)	0.81	Cu(II) > Zn(II) > Co(II), Ni(II)
	Co(II)	0.18	2.9 13.1
	Ni(II)	0.18	

Table 2. Comparison of the stability constants (log β_1) of Co(II), Ni(II), Cu(II), and Zn(II) complexes with 1-decylimidazole and 1-decyl-2-methylimidazole

	Co(II)	Ni(II)	Cu(II)	Zn(II)
1-decylimidazole	4.67	4.24	4.15	4.28
1-decyl-2-methylimidazole	3.32	2.68	3.54	5.1

The thermal stability of the polymeric membrane has also been examined (Fig. 3). In general, the thermal stability of polymeric membranes depends on the networking as well as on the presence of aromatic rings and degradable functional groups. Degradation of the CTA membrane proceeds in two steps. The first step extends over the temperature range of 292–320°C (the main step) and the other does over the range of 450–476°C (charring of dust) (Gharrou et al., 2004 and 2005, Arous et al., 2004). Other authors have reported a single degradation step only of a cellulose triacetate membrane at 300°C (Benosmane et al., 2009), although only *ca* 80% of CTA had been degraded at that temperature. Also a degradation tempeature of 350°C can be found for CTA in the literature (Resina et al., 2007). CTA-oNPE membranes containing 1-decyl-2-methylimidazole underwent degradation to an extent of 80.09% at 251.3°C and to 5.12% at 359.1°C. The onset of degradation of that membrane has also been recorded at 192.1°C (in 71.69%) and charring of the products at 361.2°C (with a 19.89% loss in weight).

Then a comparative study was made of the separation of the d-electron metal ions during their transfer across Celgard-2500-based membranes. The AFM image of SLM in a two-dimensional form with the format 5.0x5.0 μm is shown in Fig.4. The membrane Celgard 2500 was characterized by porosity 0.55, thickness 25 μm, and effective pore size 0.209x0.054 μm. The SLM membrane tortuosity was determined also from the relationship developed by Wolf and Strieder (1990) and was found to be equal to 1.60 (for ε=0.550). The values of initial fluxes, selectivity order and selectivity ratio for the competitive transport of divalent metal ions from different equimolar mixtures across SLM containing 1-decyl-2-methylimidazol are summarised in Table 3. As it is seen from these Tables, the values of initial fluxes of Cu(II) ions are higher than that for any of the other components of the mixture. For a mixture of the fourth metal ion, the initial fluxes of metal ions transport across SLMs with 1-decyl-2-methylimidazole decreases in the sequence: Cu(II) > Zn(II) > Co(II) > Ni(II). The selectivity coefficient Cu^{2+} of other divalent metal ions during transport across SLM are lower than that across PIM. The percentage of removals of Cu^{2+} from the source phase after 24h obtained for this (1, 2 and 3) mixture are 82.7; 77.2 and 82.0%, respectively.

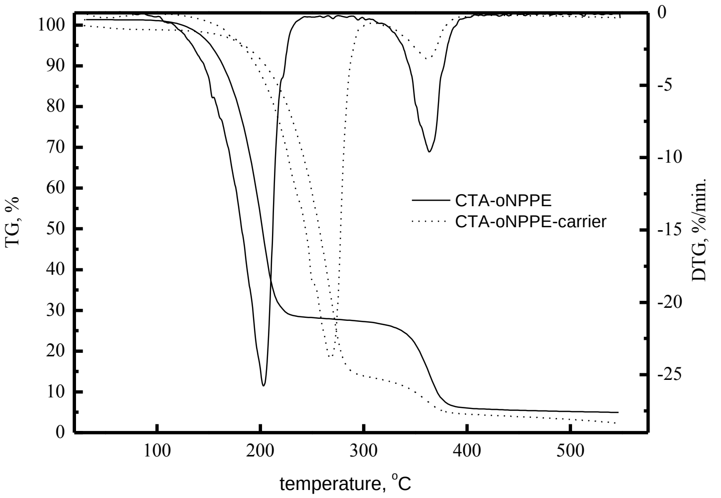
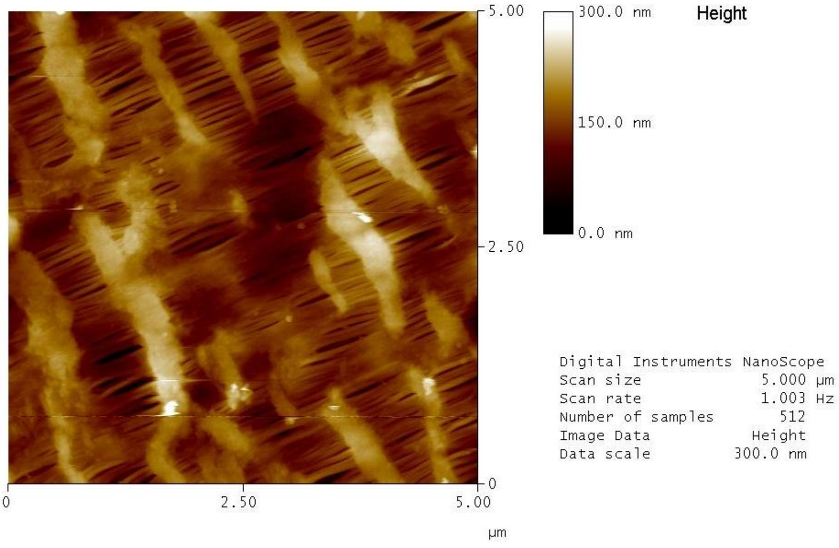


Fig. 3. Thermograms of CTA-oNPPE and CTA-oNPPE -1-decyl-2-methylimidazole



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Digital Instruments NanoScope
Scan size              5.000 μm
Scan rate              1.003 Hz
Number of samples       512
Image Data            Height
Data scale           300.0 nm
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Fig. 4. 2D atomic force microscopy for SLM with 1-decyl-2-methylimidazole

To compare the magnitude of the stream of ionic transfer across Celgard-2500-based membranes and polymeric ones, structural differences between them should be accounted for (Tayeb et al., 2005). Because the carrier concentrations in both membranes are equal, a standardized stream of the transfer across the membranes can be described by the following equation (Tayeb et al., 2005)

$$J_{N(PIM)} = J_{\exp(PIM)} \cdot \frac{d_{PIM}\tau_{PIM}}{\varepsilon_{PIM}} \cdot \frac{\varepsilon_{SLM}}{d_{SML}\tau_{SLM}}, \tag{5}$$

where d is the thickness of the membrane, ε denotes porosity and τ is tortuosity.

The normalized PIM flux calculated by Eq.(5) for Cu^{2+} from the mixture 1, 2 and 3 were 0.437; 0.357 and 0.355 μmol/m^2·s, respectively. Accordingly, the stream of the transfer of Cu^{2+} ions across Accurel-based membranes is larger than that across polymeric ones. The finding is compatible with that of Tayeb et al. (2005) reported for the transfer of Cd^{2+} ions across membranes with low concentrations of a *Lasalocid A* carrier. On the other hand, larger streams of the transfer of alkali metal ions across membranes with the DC18C6 ether than those across Celgard-2500-based membranes have been reported by Schow et al. (1996) and by Kim et al. (2000) who studied the transfer of Cs^{+} ions across membranes doped with a calix[4]-crown-6 derivative. However, the authors did not account for the structural features of the membranes. The advantage of the polymeric membranes over the carrier-based ones is their stable performance. From the latter, the carrier is washed off already during the first cycle of operation and its re-use is possible only after a repeated immobilization of the carrier in the pores of the polypropylene film. On the other hand, the polymeric membranes (PIM) can be re-used and the stream of the Cu^{2+} transfer does not diminish during another cycle of operation.

Table 3. Initial fluxes, selectivity order and selectivity coefficients for competitive transport of Cu(II), Zn(II), Co(II), and Ni(II) ions across SLM containing 0.5 M 1-decyl-2-methylimidazole

Mixture	Metal ions	J, μmol/m^2·s	$S_{Cu(II)/Me(II)}$
1	Cu(II)	1.75	Cu(II) >> Co(II) > Ni(II)
	Co(II)	0.51	3.4 4.5
	Ni(II)	0.39	
2	Cu(II)	1.54	Cu(II) > Zn(II)
	Zn(II)	0.91	1.7
3	Cu(II)	1.23	
	Zn(II)	0.74	Cu(II) > Zn(II) > Co(II) > Ni(II)
	Co(II)	0.15	1.6 8.2 8.8
	Ni(II)	0.14	

4. Conclusion

Copper(II) cations can be effectively removed from aqueous nitrate solutions in the hydrometallurgical process of supported and polymer inclusion membrane transport with 1-decyl-2-methylimidazol as ion carriers. The optimum composition of membranes is 53.4% plasticizer, 20% CTA and 26.6% 1-decyl-2-methylimidazole. The selectivity coefficients of Cu^{2+}/Zn^{2+}, Cu^{2+}/Co^{2+} and Cu^{2+}/Ni^{2+} obtained during transport across polymer membranes are higher then supported membranes containing a carrier at the same concentration.The percentage removals of Cu^{2+} from the source phase containing an equimolar mixture Cu^{2+}-Zn^{2+}, and Cu^{2+}-Zn^{2+}-Co^{2+}-Ni^{2+} ions were above 92%. Owing to the steric effect, 1-decyl-2-methylimidazole fairly well differentiates the properties of its complexes with Co(II), Ni(II), Cu(II) and Zn(II).

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