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TRANSPORT OF METAL IONS ACROSS POLYMER INCLUSION MEMBRANE WITH 1-ALKYLIMIDAZOLE

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The facilitated transport of copper(II), zinc(II), cobalt(II), and nickel(II) ions across polymer inclusion membranes (PIMs), which consist of cellulose triacetate as polymeric support, *o*-nitrophenyl pentyl ether as plasticizer and 1-alkylimidazole as ion carrier was reported. PIM was characterized by using atomic force microscopy (AFM) technique. The results show that Cu²⁺ can be separated very effectively from others heavy and transition metal cations as Zn²⁺, Co²⁺, and Ni²⁺ (at concentration of 10⁻³ M each). Alkyl substituents in position 1 of imidazole ring have an effect on hydrophobic properties and the initial flux of the transported metal ions. Also, the influence of the chloride ions concentration on the separation process was investigated. To explain the mechanism of membrane transport the diffusion of metal ions complexes with 1-alkylimidazole was also measured.

key words: polymer inclusion membrane (PIM), ions separation, copper(II), zinc(II), nickel(II), cobalt(II), 1-alkylimidazole

1. INTRODUCTION

Presently, for separation of nonferrous metals from water solutions and industrial waste water on laboratory scale, membrane techniques are more and more often used. A liquid membrane constitutes a distinct organic phase that separates two other water phases. In terms of their construction, membranes are divided into: bulk liquid

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membranes (BLM), supported liquid membranes (SLM), emulsion liquid membranes (ELM), and polymer inclusion membranes (PIM).

Membrane processes are distinguished by a better use of the ion carrier (extractant) existing in the organic phase (membrane), compared to the traditional extraction system. The proper selection of the carrier is decisive for the effectiveness of the liquid membrane. High separation selectivity factors are achieved, when a chosen carrier shows high affinity with respect to one of the components of the feeding solution. As metal ion carriers in the membrane processes, the same organic substances as those used in extraction processes are employed in the membrane processes (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). The review on application of macrocyclic compound as ion carriers in a liquid membranes were presented by Ulewicz (2008) as well as Walkowiak and Kozłowski (2009).

Hayashi et al. (2003) reported on the selective proton-driven transport of lead(II) ions in presence of nonferrous cations (Cu^{2+} , Cd^{2+} , Zn^{2+} , Ni^{2+}) across polymer inclusion membranes with proton diionizable polyethers bearing different alkyl chain lengths (from $-\text{C}_7\text{H}_{15}$ to $-\text{C}_{16}\text{H}_{33}$). The transport selectivity of PIM with polyether bearing $-\text{C}_8\text{H}_{17}$ alkyl chain was as follows: $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+}$. Ulewicz et al. (2004) investigated competitive transport of Zn(II), Cu(II), and Cd(II) 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. It was found that the initial fluxes of all investigated cations increase with acidity of the feed phase and the selectivity order was as follows: $\text{Cd(II)} > \text{Zn(II)} > \text{Cu(II)}$.

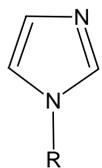
The cations: Zn^{2+} , Pb^{2+} , Cu^{2+} , Ni^{2+} , Co^{2+} and Cd^{2+} are transported across PIMs containing azocrown and thioazocrown imidazole derivatives were investigated by Ulewicz et al. (2007, 2009). A linear decrease in the values of the initial metal ions transport fluxes was observed with 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: $\text{Pb(II)} > \text{Zn(II)} > \text{Cu(II)} > \text{Co(II)} > \text{Ni(II)} > \text{Cd(II)}$. Recently, pyrrole azocrown ethers in ordinary bulk membrane system 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 present article deals with a competitive transport of copper(II), zinc(II), cobalt(II), and nickel(II) ions from a dilute aqueous solutions using PIM doped with 1-alkylimidazoles. The initial fluxes and selectivity coefficients of copper(II), zinc(II), cobalt(II) and nickel(II) ions transport across PIM doped with 1-alkylimidazole from aqueous source phase containing equimolar mixture of all metals are investigated too. The effects of chloride ions concentration in source phase upon the efficiency and selectivity Cu(II) ions transport is reported.

2. EXPERIMENTAL

2.1. REAGENTS

The inorganic chemicals, i.e. copper(II), zinc(II), nickel(II), and cobalt(II) chlorides were of analytical grade and were purchased from POCh (Gliwice, Poland). The organic reagents, i.e. cellulose triacetate (CTA), *o*-nitrophenyl phenyl ether (*o*-NPPE) and dichloromethane were also of analytical grade and were purchased from Fluka and used without further purification. The 1-alkylimidazole were synthesized by Skrzypczak according to the procedure described in (Pernak et al. 1987).

	No	R-	pKa
	<u>1</u>	-C ₆ H ₁₃	7.30
	<u>2</u>	-C ₇ H ₁₅	7.32
	<u>3</u>	-C ₈ H ₁₇	7.34
	<u>4</u>	-C ₉ H ₁₉	7.39
	<u>5</u>	-C ₁₀ H ₂₁	7.43

2.2. POLYMER INCLUSION MEMBRANE PREPARATION

The 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-alkylimidazole 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 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. Two samples of membrane were cut from the same membrane film for duplicate transport experiments.

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 (surface area of 4.9 cm³) was tightly clamped between two cell compartments. Both, i.e. the source and receiving aqueous phases (45 cm³ each) were mechanically stirred at 600 rpm. The receiving phase was deionized water. The PIM transport experiments were carried out

at the temperature of $20 \pm 0.2^\circ \text{C}$. Small samples (0.1 cm^3 each) of the aqueous receiving phase were removed periodically via a sampling port with a syringe and analyzed to determine cation concentrations by atomic absorption spectroscopy method (AAS Spectrometer, Solaar 939, Unicam). The source phase pH was kept constant ($\text{pH} = 6.0$) 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 polymer membranes was described by the following equation (Danesi, 1984-85):

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

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:

$$J_i = P \cdot c_i. \quad (2)$$

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

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

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

3. RESULT AND DISCUSSION

The most significant factor determining metal ions transport across a liquid membrane are the properties of an ion carrier and its acidity or basicity strength. The imidazole ring is a stable molecule that according to Pearson's HSAB principle is ranged among 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 (Schaeckers et al., 2004). Alkyl substituents at position 1 of the imidazole ring distinctly affect hydrophobic properties of the molecule and weakly strengthen its basicity (Lenarcik and Ojczenasz, 2002) ($\text{pK}_a = 7,165 + n \cdot 0.0222$). Hence, 1-alkylimidazoles have been used as extractants of a number of metal ions, in particular those classified as intermediate HSAB acids (Cuprey, 1974).

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-alkylimidazole; membrane: 2.6 cm³ *o*-NPPE /1g CTA and 1.0 M carriers calculated on plasticizer

Carrier	Metal ions	J, $\mu\text{mol}/\text{m}^2\cdot\text{s}$	$S_{\text{Cu(II)/Me(II)}}$
<u>1</u>	Cu(II)	4.28	Cu(II) > Zn(II) > Co(II) > Ni(II) 3.7 17.8 35.7
	Zn(II)	1.17	
	Co(II)	0.24	
	Ni(II)	0.12	
<u>2</u>	Cu(II)	4.48	Cu(II) > Zn(II) > Co(II) > Ni(II) 3.6 9.0 26.4
	Zn(II)	1.26	
	Co(II)	0.25	
	Ni(II)	0.17	
<u>3</u>	Cu(II)	5.41	Cu(II) > Zn(II) > Co(II), Ni(II) 3.2 21.6
	Zn(II)	1.70	
	Co(II)	0.25	
	Ni(II)	0.25	
<u>4</u>	Cu(II)	5.74	Cu(II) > Zn(II) > Ni(II), Co(II) 3.1 19.8
	Zn(II)	1.88	
	Co(II)	0.29	
	Ni(II)	0.29	
<u>5</u>	Cu(II)	6.36	Cu(II) > Zn(II) > Ni(II) \geq Co(II) 3.0 14.8 15.5
	Zn(II)	2.15	
	Co(II)	0.36	
	Ni(II)	0.41	

The initial fluxes and selectivity coefficients of copper(II), zinc(II), cobalt(II) and nickel(II) ions transport across PIM doped with 1-alkylimidazole from aqueous source phase containing equimolar mixture of all metals is shown in Table 1. The copper(II) ions were transported with a highest rate, and the selectivity order for carrier 1 and 2 was as follows: Cu(II) > Zn(II) > Co(II) > Ni(II), whereas for 3 - 5 Cu(II) > Zn(II) > Ni(II), Co(II). The initial flux of copper(II) transport increases in the order 1 < 2 < 3 < 4 < 5. The observed trend is in accordance with increasing size of the -R groups on ring imidazole structure. The maximum value of the initial flux for Cu(II) ions was equal to 6.36 $\mu\text{mol}/\text{m}^2\cdot\text{s}$ (for 5).

The stability constants of all the 1-alkylimidazole complexes with Cu(II) are constant and independent of the alkyl chain length and $\text{p}K_a$ of the 1-alkylimidazole base (Radzaminska-Lenarcik, 2007). Stabilities of the Co(II), Zn(II), and Ni(II) complexes have been found to increase with increasing alkyl chain length of 1-alkylimidazoles (Lenarcik and Ojczenasz, 2004; Lenarcik and Kierzkowska, 2004; Lenarcik and Rauckyte, 2004). These dependences are lineal. Straight line parameters illustrating the dependence of the $\log \beta_n$ of Co(II), Ni(II), and the Zn(II) complexes

with 1-alkylimidazoles as a function of the carbon atoms (n) in the group of alkyl chain in 1-alkylimidazole are presented in the Table 2.

Table 2. Comparison of the stability constants β_n of Co(II), Ni(II), Cu(II), and Zn(II) complexes with 1-alkylimidazoles

$\log \beta_n$	Co(II)	Ni(II)	Cu(II)	Zn(II)
$\log \beta_1$	$y = 0.302n + 1.653$	$y = 0.161n + 2.631$	4.15	$y = 0.229n + 1.986$
$\log \beta_2$	$y = 0.342n + 3.592$	$y = 0.164n + 5.290$	7.57	$y = 0.229n + 4.500$
$\log \beta_3$	$y = 0.377n + 4.881$	$y = 0.164n + 7.233$	-	$y = 0.229n + 6.700$
$\log \beta_4$	$y = 0.434n + 5.780$	$y = 0.166n + 8.653$	-	-

Stability constants of the Cu(II) complexes are considerably higher than those of Co(II), Ni(II), and Zn(II). This may be explained in terms of a larger contribution of the $\pi_{M \rightarrow L}$ back donation to interaction of Cu(II) with the imidazole ring (Radzymińska-Lenarcik, 2008). The 1-alkyl substituent does not significantly affect either polarization of the imidazole ring or the energy of its antibonding π orbitals (Sundberg and Martin, 1974). It can thus be assumed that the contribution of the $\pi_{M \rightarrow L}$ bonding is invariable in the Cu(II) complexes with all the 1-alkylimidazoles. The initial fluxes of Zn(II) ions increase more rapidly than Co(II) and Ni(II) ions with increase of pK_a carriers. The values of the diffusion coefficient of metal complex in the membrane as well as the constant rate of reaction are the factors showing whether the given process is controlled by diffusion in the membrane or by indirect (mixed) kinetics, i.e. the state, in which the rates of diffusion process and chemical reaction are comparable. In this way in the next step, the diffusion coefficient (D_o) of the metal-complex across the membrane doped with 1-hexylimidazole was calculated according to the procedure reported in the previous paper (Ulewicz et al., 2010). In Fig. 1, the correlation graphs $[Me^{2+}]_i - [Me^{2+}]_t$ versus time of metal ions transport from different mixture solutions across PIM doped with carrier **1** is presented. The diffusion coefficient of Me(II) was calculated, substituting $D_o = d_o / \Delta_o$, where d_o is the thickness of the membrane (0.0025 cm) and Δ_o could be evaluated by plotting $[Me^{2+}]_i - [Me^{2+}]_t$ vs. time. Obtained values of diffusion coefficients are presented in Table 3. Also, the corrected (normalized) membrane diffusion coefficient $D_{o,n}$, which considers the morphological features inside the membrane (ε - porosity and τ - tortuosity), calculated from equation described by Salazar-Alvarez et al. (2005): $D_{o,n} = D_o \cdot (\varepsilon / \tau)$, are presented in this Table. The porosity (ε) as well as roughness (R_q) of the membrane were calculated using atomic force microscopy (AFM). Figure 2 shows an AFM image of PIM's with carrier **1** in three-dimensional form with format of 1.0 x 1.0 μm and example histogram for measurement. The distribution of the carrier in the

investigated membrane after evaporation of the dichloromethane is homogeneous on the entire surface. The porosity and roughness for PIM doped with **1** is 24.2% and 3.9 nm, respectively. This value of roughness is comparable with that found for polymer membrane with thioazocrown derivative imidazole (R_q equal 3.3-5.3) reported by Ulewicz et al. (2009) and for membrane with D2EHPA prepared by Salazar-Alvarez et al. (2005), which is equal to 4.6 nm. The membrane tortuosity was determined from the relationship developed by Wolf and Strieder (1990): $\tau = 1 - \ln \varepsilon$ and was equal to 2.42 (for $\varepsilon = 0.242$). Values of diffusion coefficient determined in this study (Table 3) are comparable with presented in literature data for different membranes and are in the range 10^{-6} to 10^{-12} cm^2/s showing that the limiting step of the process is transfer of metal complex across membrane barrier.

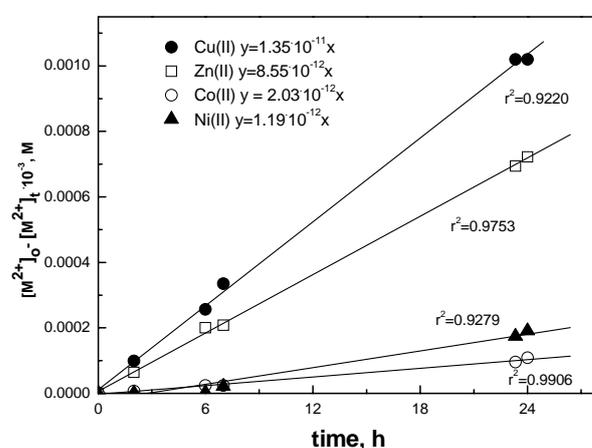


Fig. 1. Relation of $[\text{Me}^{2+}]_i - [\text{Me}^{2+}]_t$ plotted vs. time for Cu^{2+} , Zn^{2+} , Co^{2+} and Ni^{2+} transport across PIM membrane doped with 1.0 M carrier **1**. Conditions of experiment as in Table 1

Table 3. Permeability and diffusion coefficients normalized for competitive transport of $\text{Cu}(\text{II})$, $\text{Zn}(\text{II})$, $\text{Co}(\text{II})$, and $\text{Ni}(\text{II})$ ions through PIM with **1**

Cations	P , m/s	Δ_o , s/m	D_o , cm^2/s	$D_{o,n}$, cm^2/s
Cu^{2+}	$4.28 \cdot 10^{-3}$	$10^{6.86}$	$3.44 \cdot 10^{-11}$	$4.17 \cdot 10^{-10}$
Zn^{2+}	$1.17 \cdot 10^{-3}$	$10^{7.06}$	$2.18 \cdot 10^{-11}$	$2.64 \cdot 10^{-10}$
Co^{2+}	$0.24 \cdot 10^{-3}$	$10^{7.69}$	$5.17 \cdot 10^{-12}$	$6.26 \cdot 10^{-11}$
Ni^{2+}	$0.12 \cdot 10^{-3}$	$10^{7.92}$	$3.03 \cdot 10^{-12}$	$3.67 \cdot 10^{-11}$

In the next step, the influence of chloride ions concentration in the source phase on the transport of metal ions was investigated. As seen from Table 4, the permeability coefficients of Cu(II) ions decrease only slightly upon increasing chloride-ion concentration in the source phase. Whereas the permeability coefficient of the Zn(II), Co(II), and Ni(II) ions increases with an increase of chloride ions concentration, in particular those of the Zn(II) ions. On the other hand, the selectivity coefficients of Cu(II)/Zn(II) decreases with Cl^- concentration increase in the source phase. The lowest value of the selectivity coefficient Cu(II)/Zn(II) was equal to 1.4 for 1.0 M of Cl^- in the source phase. For compound **1** the selectivity coefficients of Cu(II)/Co(II) and Cu(II)/Ni(II) were 11.4; 14.4; for 0.5 and 2.8 for 1.0 M Cl^- , respectively. Among all of the cations studied, only Cu(II) has the propensity for deformation of the coordination sphere owing to the Jahn-Teller effect (Bersuker, 1972; Gažo et al., 1976) (this being favourable for the process).

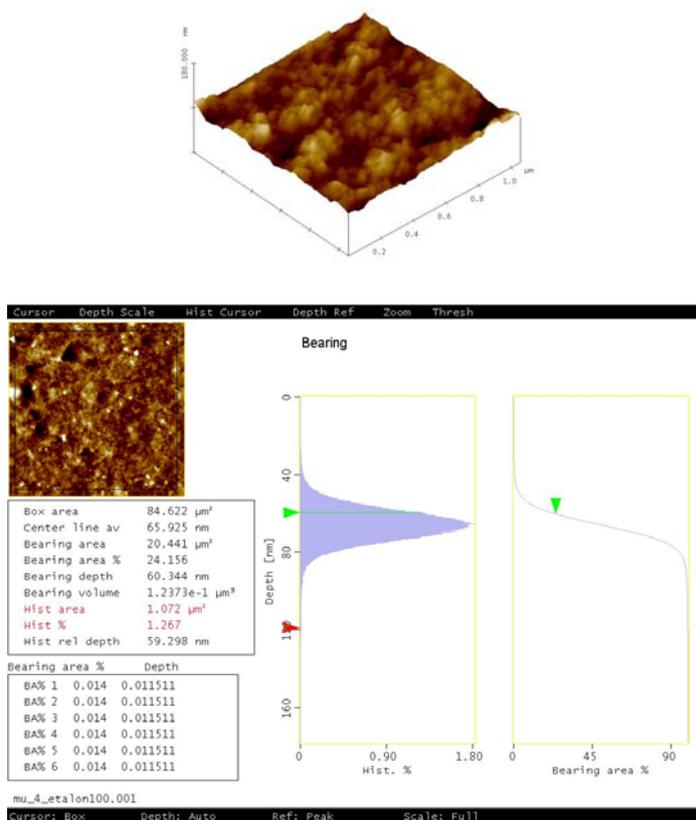


Fig. 2. 3D-view atomic force microscopy for PIM with carrier **1** and example histogram

A necessary condition for the transfer a metal ion through PIM is its complexation with 1-alkylimidazole. Permeability coefficients (P) of the cations are fairly compatible with stability constants of their 1-alkylimidazole complexes (Table 2 and 4). Elongation of the alkyl chain of the 1-alkylimidazole molecule results in the volume of the donor molecule thus increasing the probability of formation of the Zn(II) and Cu(II) complexes according to the equation:



The phenomenon increases the P value and at the same time suppresses selectivity coefficients of Cu(II)/Zn(II) and Cu(II)/Co(II). Addition of the chloride ions to the feeding phase enables formation of the MCl and MCl_2 complexes, especially with the Cu(II) and Zn(II) ions. Those complexes are more dissociableness. This phenomenon increases permeability coefficient P and suppresses selectivity coefficient.

Table 4. The permeability coefficients for transport of Cu(II), Zn(II), Co(II), and Ni(II) ions across PIM with **1** vs. the concentration of Cl^- in the source phase; membrane: 2.6 cm^3 *o*-NPPE /1g CTA and 1.0 M carriers **1** calculated on plasticizer

Metal ions	Permeability, P , m/s		
	-	0.5 M	1.0 M
Cu(II)	$4.28 \cdot 10^{-3}$	$3.75 \cdot 10^{-3}$	$2.94 \cdot 10^{-3}$
Zn(II)	$1.17 \cdot 10^{-3}$	$1.38 \cdot 10^{-3}$	$2.14 \cdot 10^{-3}$
Co(II)	$2.43 \cdot 10^{-4}$	$3.28 \cdot 10^{-4}$	$1.04 \cdot 10^{-3}$
Ni(II)	$1.19 \cdot 10^{-4}$	$2.61 \cdot 10^{-4}$	$1.28 \cdot 10^{-3}$

3. CONCLUSION

The 1-alkylimidazoles under study can be used for separation of the Cu(II) ions from an equimolar mixture of the Cu(II), Zn(II), Co(II) and Ni(II) ions in the transportation process across PIM. With elongation of the chain length of substituent - R in the imidazole ring, the initial flux of the ions increases, but the separation coefficients decrease. The highest flux of the Cu(II) ions was noticed for carrier **5**,

whereas the highest separation coefficient for compound **1**. It was also proved that an increase in chloride-ion concentration in the source phase resulted in the increase in the permeability coefficients which attained their top values at 1.0 M concentration of the chloride ions. The permeability coefficient of the Cu(II) ions from solutions with 1.0 M chloride-ion concentration was $2.94 \cdot 10^{-3}$ m/s. The rate limiting step in transport of Cu^{2+} across PIM doped with **1** can be the diffusion coefficient of the carrier-cation complex across the membrane. The studied PIM membrane exhibit good stability described with the Danesi thermodynamical model.

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Zbadano selektywność transportu jonów Cu(II), Zn(II), Co(II) i Ni(II) ($c_{Me}=0,001M$, każdy) przez polimerowe membrany inkluzyjne składające się z trójocianu celulozy (suportu), eteru o-nitrofenylooktylu (plastyfikatora) i przenośnika jonów (1 alkylimidazole). Polimerowa membrana została scharakteryzowana przy pomocy mikroskopii sił atomowych (AFM). Wykazano, że podstawnik alkilowy w pozycji 1 pierścienia imidazolu zmieniając własności hydrofobowe przenośnika wpływa na strumień początkowy transportu jonów metali. Wartości strumienia początkowego transportu jonów przy użyciu przenośnika **1** i **2** maleją w szeregu: Cu(II) > Zn(II) > Co(II) > Ni(II), natomiast dla **3** - **5** w szeregu: Cu(II) > Zn(II) > Ni(II), Co(II). Strumień transportu Cu(II) wzrasta w szeregu użytych przenośników: **1** < **2** < **3** < **4** < **5**, osiągając najwyższą wartość 6,36 $\mu\text{mol}/\text{m}^2\cdot\text{s}$ (dla **5**). Na selektywność

transportu wpływ również stężenie jonów chlorkowych w fazie zasilającej. Czynnikiem limitującym szybkości transportu Cu^{2+} przez PIM jest współczynnik dyfuzji kompleksu przenoszonego kationu przez membranę.

słowa kluczowe: polimerowa membrana inkluzyjna, separacja jonów, miedź(II), cynk(II), nikiel(II), kobalt(II), 1-alkilimidazol