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Application of polymer inclusion and membranes supported with 1-alkyl-2-methylimidazoles for separation of selected transition metal ions

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ABSTRACT

Supported liquid membranes (SLMs) and polymer cellulose triacetate inclusion membranes (PIMs) doped with 1-alkyl-2-methylimidazole (alkyl = hexyl, octyl, decyl) as fixed carriers were applied for the investigation of the facilitated transport of Cu(II), Zn(II), Co(II), and Ni(II) ions from an aqueous nitrate source phase (c_M = 1 mmol dm^{-3}). Membranes were characterized by non-contact atomic force microscopy (AFM). The results showed that Cu(II) could be separated very effectively from other cations such as Zn(II), Co(II), and Ni(II), from different equimolar mixtures of those ions. The highest initial flux of Cu(II) was found for PIMs (1.98–2.42 μmol m^{-2}·s), while lower values were observed for SLMs. The recovery coefficient of Cu(II) ions from different mixtures of cations after 24 h was above 95% and 92% during transport across PIMs and SLMs, respectively. The highest separation ratios for Cu(II)/Zn(II), Cu(II)/Co(II), and Cu(II)/Ni(II) were obtained using 1-hexyl-2-methylimidazole as a carrier (for PIMs: 7.9, 24.8, and 99.0, respectively, and for SLMs: 6.0, 17.0, and 59.5, respectively). PIMs containing 1-decyl-2-methylimidazole were stable for 120 h.

Keywords: Polymer inclusion membrane (PIM); Supported liquid membrane (SLM); Separation of transition metal ions; Imidazole derivatives

1. Introduction

Membrane processes are distinguished by the fact that there exists the ion carrier (extractant) in the organic phase (membrane), while compared with conventional extraction systems. The proper selection of the carrier is crucial to the effective performance of the liquid membrane. High separation selectivity factors are achieved for the chosen carrier, which reveal high affinities to one of the components of the feed solution. The same organic substances as ones used in extraction processes are employed as metal ion carriers in the membrane processes. Classical and new types of carriers are used for the separation of nonferrous ions in the liquid membrane transport process [1–3].

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, which enable the selective separation of metal ions from aqueous solutions, are sought.

Recently, macrocyclic compounds such as crown ethers, calixarenes and cyclodextrins have successfully been used as carriers of nonferrous metal ions [4,5]. Other organic compounds, e.g., imidazole and its derivatives, can also be used for this purpose in the solvent extraction of metals such as Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) [6–9]. For instance, an *N*-vinylimidazole derivative enables the separation of Cu(II) and Fe(III) [10], while imidazoles containing azo- and thioazo-crown ethers have been used for the separation of Pb(II) ions from solutions containing Zn(II), Cu(II), Cd(II), Ni(II), and Co(II) ions in the process with polymeric

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inclusion membranes (PIMs). Selectivity of transportation across PIMs with azocrown imidazole decreases in the following series: Pb(II) > Zn(II) > Cu(II) > Co(II) > Ni(II) > Cd(II) [11–13]. Pyrrole-azocrown ethers also enable the preferential transportation of lead(II) from equimolar mixtures of Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ag^{+}, and Pb^{2+} ions across bulk membrane systems [14]. Results of the authors' investigation on the separation of nonferrous metal ions using alkyl imidazole derivatives as ion carriers in polymer inclusion membrane were presented in previous works [15–21].

In this work, the authors present results of their investigation of the competitive transport of nonferrous metal ions such as copper(II), zinc(II), cobalt(II), and nickel(II) ions across supported and polymer inclusion membranes containing 1-alkyl-2-methylimidazoles (alkyl = hexyl, octyl, decyl) from dilute nitrate solutions.

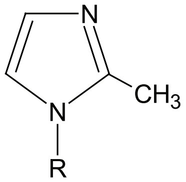
2. Experimental

Inorganic chemicals: copper(II), zinc(II), cobalt(II), and nickel(II) nitrates and tetramethylammonium hydroxide were of analytical grade and were supplied by POCh (Gliwice, Poland). Aqueous solutions were prepared with double distilled water (conductivity of 5 μS m^{-1}). Organic reagents, i.e., cellulose triacetate (CTA), *o*-nitrophenyl pentyl ether (*o*-NPPE), and dichloromethane (all from Fluka) were of analytical grade and were used without further purification. 1-Alkyl-2-methylimidazoles 1-3 (Fig. 1) were synthesized as described elsewhere [22].

2.1. Supported and polymer inclusion membrane preparation and characterization

A solution of cellulose triacetate, plasticizer, and 1-alkyl-2-methylimidazoles (1-3) as ion carriers in dichloromethane was prepared. A specified portion of the solution was poured into a membrane mould consisting of a 9.0 cm diameter glass ring fixed on a glass plate with cellulose triacetate-dichloromethane resin. After overnight evaporation of the solvent the resulting membrane was peeled off from the glass plate by immersion in cold water. Next, the PIM was soaked for 12 h in distilled water to ensure its homogeneity. Two discs were cut out from the same sample to duplicate transport experiments. The wet membrane contained 2.67 cm^3 *o*-NPPE/1 g CTA, and 0.25, 0.5, 1.0 or 1.5 mol dm^{-3} concentration of 1-alkyl-2-methylimidazoles based on plasticizer. The supported membrane was soaked for 12 h in 1.0 mol dm^{-3} 1-alkyl-2-methylimidazoles in dichloromethane.

Two samples of the PIM and SLM membranes were cut out from the same membrane film for the duplicate transport experiments. A surface characterization study of the polymer membranes was performed by atomic force microscopy (AFM) according to the procedure described in [11]. The analysis of surface pore characteristics 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). Parameter R_q is the standard deviation of the *z* values within the box cursor and is calculated as:



No	R-
1	$-C_6H_{13}$
2	$-C_8H_{17}$
3	$-C_{10}H_{21}$

Fig. 1. Chemical structure of investigated 1-alkyl-2-methylimidazole.

$$R_q = \sqrt{\frac{\sum (Z_i)^2}{n}} \tag{1}$$

2.2. Transport studies

Transport experiments were carried out in a permeation cell described in [11]. The membrane film (surface area 4.9 cm^2) was tightly clamped between two cell compartments. Both, the source and the receiving aqueous phases (45 cm^3 each) were mechanically stirred at 600 rpm. Metal nitrates were used as the source phase, whereas deionized water was the receiving phase. The PIM transport experiments were carried out at 20°C ± 0.2°C. Small samples of the aqueous receiving phase were taken periodically from the sampling port, equipped with a syringe, and analyzed by atomic absorption spectroscopy (AAS Spectrometer, Solar 939, Unicam) to determine zinc(II), cobalt(II), nickel(II), and copper(II) ions concentrations. The source phase pH = 5.5 was kept constant using tetramethylammonium hydroxide.

The kinetics of the transport across the PIMs was described as a first-order process with respect to the metal-ion concentration [23] expressed by Eq. (2):

$$In\left(\frac{c_t}{c_i}\right) = -kt \tag{2}$$

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

To calculate the value of k, a graph of $\ln(c_t/c_i)$ vs. time was plotted. The rate constant values for two independent transport experiments were averaged and standard deviation was calculated. The correlation between $\ln(c_t/c_i)$ and time was linear, what was confirmed by the high correlation coefficient (R^2) ranging from 0.9621 to 0.9995. The permeability coefficient (P) was calculated according to Eq. (3):

$$P = -\frac{V}{A}k \tag{3}$$

The initial flux (J_i) is equal to Eq. (4):

$$J_i = P \cdot c_i \tag{4}$$

The selectivity ratio (S) was defined as the ratio of initial fluxes of M_1 and M_2 metal ions, respectively, Eq. (5):

$$S = J_{i,M1} / J_{i,M2} \tag{5}$$

To describe the efficiency of metal removal from the source phase, the recovery factor (*RF*) was calculated according to Eq. (6):

$$RF = \frac{c_i - c}{c_i} \cdot 100\% \tag{6}$$

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

3. Results and discussion

Imidazole, owing to the presence of a pyridinic nitrogen atom at position 3, is ranged among medium-strong bases according to Pearson's classification of acids and bases ($pK_a = 7.14$) and forms stable complexes with medium-range and soft Lewis bases owing to the contribution of $\pi_{M\rightarrow L}$ back-bonding during coordination. An alkyl substituent at position 1 only slightly strengthens the basicity of the pyridinic nitrogen atom of 1-alkylimidazole, contributing to an enhanced stability of its metal complexes. An additional alkyl substituent at position 2 of imidazole ring was found to increase basicity by one order of magnitude as compared with that of 1-alkylimidazoles, but at the same time the stability of the 1-alkyl-2-methylimidazole complexes declined due to the effect of $\pi_{M\rightarrow L}$ back-bonding and the steric effect. In particular, the latter hinders the formation of octahedral species, e.g., those of Ni(II), but has much less influence on the formation of tetrahedral species, for instance, those of Zn(II) and Co(II) [6,24,25]. On the other hand, Cu(II) ions are much less sensitive to the steric effect, because the coordination sphere of Cu(II) is much more flexible, i.e., more readily deformable [26]. Cu(II) ion can also form 4-coordination complexes [27]. Ion carriers embedded in the membrane interact with metal ions in the diffusion-controlled water phase to form complexes. These form electrically neutral ion pairs with anions, which penetrate the membrane in the co-transportation process Eq. (7):

$$\begin{aligned} &[M(H_2O)_6]^{2+} + L + 2A^- \leftrightarrow [M(H_2O)_5L]A_2 + H_2O \\ &[M(H_2O)_6]^{2+} + L + 2A^- \leftrightarrow [M(H_2O)_3L]A_2 + 3H_2O \end{aligned} \tag{7}$$

where M^{2+} is the metal ion, *L* is the carrier, and A^- is the co-transported anion (NO_3^-).

At increased ligand concentration, higher complexes can be formed, e.g., ML_2:

$$\begin{aligned} &[M(H_2O)_6]^{2+} + 2L + 2A^- \leftrightarrow [œ(-_2O)_4L_2]A_2 + 2H_2O \\ &[M(H_2O)_6]^{2+} + 2L + 2A^- \leftrightarrow [œ(-_2O)_2L_2]A_2 + 4H_2O \end{aligned} \tag{8}$$

Their stability constants, β_2, are higher than those of the corresponding ML_1 complexes Table 1.

3.1. Effect of carrier concentration in the membrane

In preliminary experiments, metal ion transport across a liquid membrane containing only the support (CTA) and plasticizer (*o*-NPPE), i.e., at the absence of any ion carrier was not observed. Then, the influence of the carrier concentration in the membrane on separation efficiency of the Cu(II), Zn(II), Co(II), and Ni(II) ions from their equimolar mixture was determined. Fig. 2 shows investigated metal ions recovery coefficient (RF) values of vs. concentration of 1-hexyl-2-methylimidazole (1) in PIMs.

With increasing carrier concentrations in the membrane, recovery coefficient of each metal ions increased compared with ones of the remaining ions. The highest RF of Cu(II) ions was found at the 1.0 mol dm^{-3} carrier concentration. For this and higher concentrations, recovery coefficient increased, especially those for Co(II) ions, which formed two types of

Table 1
Stability constants (log β_n) of Cu(II), Zn(II), and Co(II) complexes with 1-alkyl-2-methylimidazoles in aqueous solutions at 25°C, ionic strength 0.5 mol dm^{-3} K(H)NO$_3$

Ligand	Metal ions	log β_1	log β_2	log β_3	log β_4
1-hexyl-2-methylimidazole	Co(II) [25]	1.96	2.18	3.02	5.61
	Cu(II) [27]	3.52	6.63	8.98	
	Zn(II) [6]	3.48	5.80	8.30	10.10
1-octyl-2-methylimidazole	Co(II) [25]	1.94	2.14	3.06	5.70
	Cu(II) [27]	3.53	6.65	9.65	
	Zn(II) [6]	4.45	6.80	9.10	
1-decyl-2-methylimidazole	Co(II) [25]	1.95	2.21	3.16	5.76
	Cu(II) [27]	3.54	6.68	9.44	
	Zn(II) [6]	5.10	7.75	9.90	

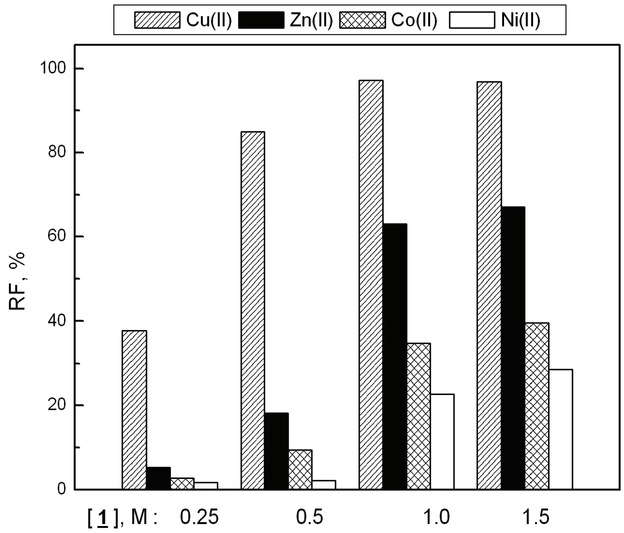


Fig. 2. Recovery coefficient of Cu(II), Zn(II), Co(II), and Ni(II) ions after 24 h transport depending on the concentration of the carrier (1-hexyl-2-methylimidazole (1)) in the membrane; membrane: 2.6 cm^3 *o*-NPPE/1 g CTA; source phase: [M^{2+}] = 0.001 mol dm^{-3} each, receiving phase: deionized water, pH = 5.5.

complexes at higher concentrations of the carrier (ligand) (Eq. 9).

$$
\begin{aligned}
&[\mathrm{Co(H_2O)_6}]^{2+} + 4\mathrm{L} + 2\mathrm{A}^{-} \leftrightarrow [\mathrm{M(H_2O)_2L_4}]\mathrm{A_2} + 4\mathrm{H_2O} \\
&[\mathrm{Co(H_2O)_6}]^{2+} + 4\mathrm{L} + 2\mathrm{A}^{-} \leftrightarrow [\mathrm{ML_4}]\mathrm{A_2} + 6\mathrm{H_2O}
\end{aligned}
\tag{9}
$$

Since the difference between RF values for the carrier concentrations of 0.5 and 1.0 mol dm^{-3} was small, while the selectivity ratios for copper recovery were better, the studies were continued using the concentration of 0.5 mol dm^{-3}. Thus, the ion carrier consumption was limited and a comparison of the obtained results with other studied carriers—imidazole derivatives was enabled [15–21].

In Fig. 3, the correlation graphs $[M^{2+}]_i$–$[M^{2+}]_t$ vs. time of metal ions transport from different mixture solutions across PIM doped with carrier <u>1</u> are presented. In the next step, the diffusion coefficient (D_o) of the metal-complex across the membrane doped with 1-hexyl-2-methylimidazole (<u>1</u>) was calculated according to the procedure reported in [15]. The diffusion coefficient of M(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 $[M^{2+}]_i$–$[M^{2+}]_t$ vs. time. The obtained values of diffusion coefficients are presented in Table 2.

Also, the corrected (normalized) membrane diffusion coefficient $D_{o,n}$, which considers the morphological features inside the membrane (ε – porosity and τ – tortuosity), as calculated from the equation described by Visser et al. [28]: $D_{o,n} = D_o \cdot (\varepsilon / \tau)$ is also presented in Table 3.

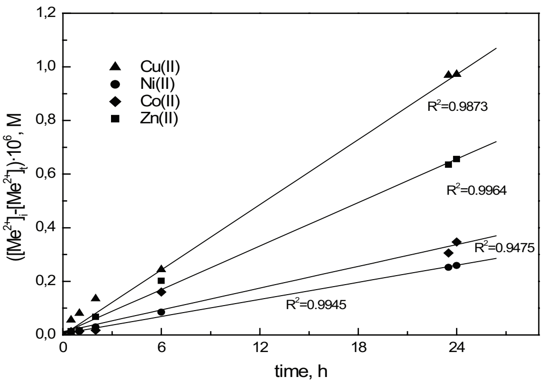


Fig. 3. $[M^{2+}]_i$–$[M^{2+}]_t$ vs. time for Cu(II), Zn(II), Co(II), Ni(II) transport across PIM with 0.5 mol dm^{-3} carrier <u>1</u> (1-hexyl-2-metylimidazole).

Table 2
Values of permeability coefficient - diffusion coefficient normalized for competitive transport of Cu(II), Zn(II), Co(II), and Ni(II) ions through PIM with <u>1</u> (1-hexyl-2-metylimidazole)

Cations	P (m s^{-1})	Δ_o (s m^{-1})	D$_o$ (cm^2 s^{-1})	D$_{o,n}$ (cm^2 s^{-1})
Cu^{2+}	3.86×10^{-3}	$10^{6.91}$	3.02×10^{-11}	1.75×10^{-12}
Zn^{2+}	1.10×10^{-3}	$10^{7.11}$	1.94×10^{-11}	1.12×10^{-12}
Co^{2+}	4.04×10^{-4}	$10^{7.51}$	1.01×10^{-11}	5.86×10^{-13}
Ni^{2+}	3.08×10^{-4}	$10^{6.91}$	7.70×10^{-12}	4.43×10^{-13}

3.2. Membranes characterization

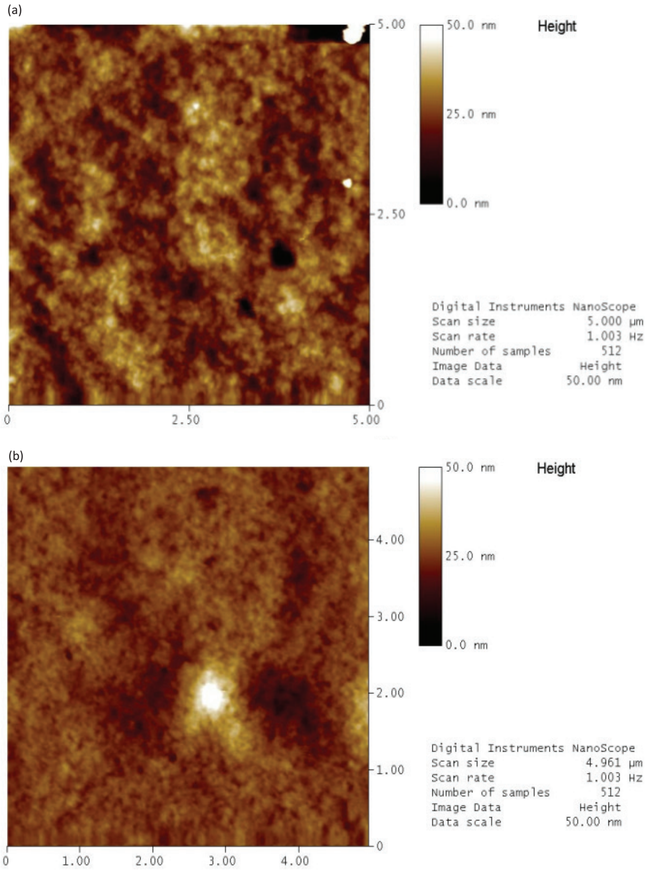
Membrane's porosity (ε) and roughness (R_q) were calculated using AFM and are shown in Table 3.

The AFM image of PIMs with carrier <u>1</u> and <u>3</u> in a two-dimensional form with the format 5.0 × 5.0 μm and representative histograms for the measurement made after experiments are shown in Figs. 4(a) and (b). The membrane's tortuosity was determined from the relationship developed by Wolf and Strieder [29]: τ = 1 – ln ε and it was equal to

Table 3
AFM characterization parameters for PIMs with <u>1</u> (1-hexyl-2-metylimidazole) and <u>3</u> (1-decyl-2-metylimidazole)

Membrane	Roughness *(Rq)*, nm	Porosity (ε), %
PIM with 1-hexylimidazol	3.90 [16]	21.1 [16]
PIM with <u>1</u>	3.56	16.3
PIM with <u>3</u>	7.15	18.1

Note: Scan areas 25 mm^2.



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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            50.00 nm
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Digital Instruments NanoScope
Scan size                4.961 µm
Scan rate                1.003 Hz
Number of samples          512
Image Data              Height
Data scale            50.00 nm
```

Fig. 4. 2D-view atomic force micrographs of PIMs with <u>1</u> (1-hexyl-2-metylimidazole) (a) and <u>3</u> (1-decyl-2-metylimidazole) (b) at a 0.5 mol dm^{-3} carrier concentration after process. Scan areas 25 μm^2.

2.81 (for $\varepsilon = 0.163$). The values of the diffusion coefficient determined in this study, comparable with those reported in literature for different membranes, were in the range 10^{-11}–10^{-12} cm^2 s^{-1} and showed, that the metal complex transfer across the membrane barrier was the process limiting step.

As demonstrated in a number of papers [11, 30–33], membrane's microstructure has an impact on the transport process. CTA membranes have porous structures, and the pore distribution is nearly uniform (porosity 50%) [23]. The pores on a CTA matrix were filled with a plasticizer (*o*-NPPE) and the carrier. The carrier crystallized inside the membrane, the surface texture of which was relatively homogeneous, with different porosities and roughnesses. Roughness of CTA membrane obtained by Tor et al. [33] was equal to 14 nm.

The roughness of a membrane with 1-decyl-2-methylimidazole (**3**) was higher than that with 1-hexyl-2-methylimidazole (**1**), and it equaled to 7.15 and 3.56 nm, respectively.

Roughness, calculated according to the procedure reported in the previous paper [11], decreased with an increasing molar volume of the carrier. Elongation of the alkyl substituent from C_6H_{13} to $C_{10}H_{21}$ resulted in an increase in its molar volume. The molar volumes, V_x, of carriers **1** and **3** were 152.3 and 208.63 cm^3 mol^{-1}, respectively. This regularity was also confirmed by the results obtained previously for a PIM membrane with 1-hexylimidazole (V_x = 138.2 cm^3 mol^{-1}; Table 3). Moreover, the methyl substituent in the ionophore molecule upon inclusion into the membrane matrix reduced its roughness. This was in agreement with the results obtained for an imidazole azathiacrown ether [11], where an increase in the carrier molar volume V_x of the ionophore resulted in a lower roughness of the polymeric membrane. The roughness of the 1-alkyl-2-methylimidazole doped membranes was slightly lower than that of the membranes doped with an ether derivatives of imidazole (R_q equal to 3.3–5.3), as reported in [11] and for a D2EHPA membrane prepared by Salazar-Alvarez et al. [30], and it was equal to 4.6 nm.

3.3. Competitive transport of metal ions across liquid membranes (LMs)

In the next experiment, Cu(II), Zn(II), Co(II) and Ni(II) ions were transported into the receiving deionized water across LMs doped with carriers **1**-**3**. Values of initial fluxes, selectivity orders and selectivity ratios for the competitive transport of divalent metal ions from different equimolar mixtures across SLM and PIM doped with 1-decyl-4-methylimidazole are summarized in Table 4. Values of initial fluxes of each metal ions transport across PIM were higher than those for SLM. It was evident that, Cu(II) ions were the most efficiently transported ones for each carrier. This can be interpreted as to the result of high stability constants of Cu(II) ions complexes with applied carriers and due to the fact that the steric effect, caused by the presence of the substituent at position 2 of the imidazole ring, did not hinder the formation of Cu(II) complexes, compared with the same compounds in the case of other metals.

The initial fluxes of metal ions across PIMs doped with **1**-**2**, decreased in the order: Cu(II) > Zn(II) > Co(II) > Ni(II); whereas for **3** the rank order was: Cu(II) > Zn(II) > Co(II), Ni(II). The initial fluxes of metal ions transport across SLMs containing **1**-**3** decreased in the following order: Cu(II) > Zn(II) > Co(II) > Ni(II). A steric effect, which increases selectivity coefficients for Cu(II) in respect to Ni(II), though only in the case of carriers **1** and **2**, was observed. Conversely, this effect did not change the order of the respective cations in the series of selectivity ratios. With elongation of the 1-alkyl substituent of the imidazole ring from hexyl to decyl, selectivity ratios of Cu(II) decreased, as compared with those of the remaining metals. The highest separation ratios for Cu(II)/Zn(II), Cu(II)/Co(II) and Cu(II)/Ni(II) ions were obtained using 1-hexyl-2-methylimidazole (**1**) as carrier (for PIMs: 7.9, 24.8 and 99.0, respectively, and for SLMs: 6.0, 17.0, and 59.5, respectively).

The recovery coefficients of Cu(II), Zn(II), Co(II) and Ni(II) ions from the source phase containing an equimolar mixture of all metal ions by PIMs and SLMs doped with **1**-**3** after 24 h are shown in Table 5. The highest removal from the source phase was obtained for Cu(II) ions.

Table 4
Initial fluxes, selectivity order and selectivity coefficients for competitive transport of metal ions across PIMs and SLMs with carriers **1** (1-hexyl-2-metylimidazole), **2** (1-octyl-2-metylimidazole), and **3** (1-decyl-2-metylimidazole)

Carrier	Metal ion	Initial flux, J_0 μmol m^{-2}·s		Selectivity order and selectivity ratios
		PIM	SLM	
1	Cu(II)	1.98	1.19	for PIMs: Cu(II) > Zn(II) > Co(II) > Ni(II)
	Zn(II)	0.25	0.20	7.9 24.8 99.0
	Co(II)	0.08	0.07	for SLMs: Cu(II) > Zn(II) > Co(II) > Ni(II)
	Ni(II)	0.02	0.02	6.0 17.0 59.5
2	Cu(II)	2.18	1.25	for PIMs: Cu(II) > Zn(II) > Co(II) > Ni(II)
	Zn(II)	0.55	0.22	4.0 14.5 36.3
	Co(II)	0.15	0.09	for SLMs: Cu(II) > Zn(II) > Co(II) > Ni(II)
	Ni(II)	0.06	0.04	5.7 13.9 31.3
3	Cu(II)	2.42	2.29	for PIMs: Cu(II) > Zn(II) > Co(II),Ni(II)
	Zn(II)	0.85	0.81	2.8 12.1
	Co(II)	0.20	0.25	for SLMs: Cu(II) > Zn(II) > Co(II) >Ni(II)
	Ni(II)	0.20	0.23	2.8 9.2 10.0

Note: The membrane contained 2.67 cm^3 *o*-NPPE/1 g CTA, and 0.5 mol dm^{-3} carrier calculated on plasticizer volume, pH = 5.5.

Table 5
Recovery factors of Cu(II), Zn(II), Co(II), and Ni(II) ions from source phase after 24 h in transport across PIMs and SLMs doped with **1** (1-hexyl-2-metylimidazole), **2** (1-octyl-2-metylimidazole), and **3** (1-decyl-2-metylimidazole)

Carrier	Metal ion	RF, %	
		PIM	SLM
1	Cu(II)	83.2	76
	Zn(II)	18.7	16.5
	Co(II)	9	6.2
	Ni(II)	3	2.3
2	Cu(II)	86.5	78.6
	Zn(II)	35.4	32.3
	Co(II)	11.0	7.0
	Ni(II)	5.0	4.0
3	Cu(II)	94.5	91.8
	Zn(II)	58.0	48.3
	Co(II)	17	25.8
	Ni(II)	17	25.1

The best result for Cu(II) removal after 24 h was obtained for a membrane with carrier **3** (94.5% and 91.8% for PIMs and SLMs, respectively). On the other hand, for Zn(II) ions, there occurred a rapid increase of the RF parameter with the alkyl chain length increasing from C_6H_{13} to $C_{10}H_{21}$, what resulted in a 3-fold increase in degree of separation of Zn(II) ions amounting to 58% (PIMs) and 48% (SLMs) with carrier **3**. Recovery factors for Ni(II) and Co(II) ions were not very high and did not exceed 17% (for PIMs) and 25.8% (for SLMs) for carrier **3**.

4. Conclusions

Copper(II) ions can be effectively separated from equimolar aqueous solutions of copper, zinc, cobalt, and nickel nitrates by using transport across polymer inclusion membranes doped with 1-alkyl-2-methylimidazoles. The initial fluxes of metal ions transport across PIMs with the **1** and **2** decreased in the order: Cu(II) > Zn(II) > Co(II) > Ni(II), whereas for **3** they were following Cu(II) > Zn(II) > Co(II), Ni(II). The highest initial flux of Cu(II) ions (2.68 μmol m^{-2}·s) was found for PIM doped with the 1-decyl-2-methylimidazole (**3**), whereas the best selectivity was obtained for the 1-hexyl-2-methylimidazole (**1**) carrier. The best result for Cu(II) removal after 24 h was obtained for a membrane with carrier 1-decyl-2-methylimidazole (**3)** (94.5% and 91.8% for PIMs and SLMs, respectively).The highest separation ratios of Cu(II)/Zn(II), Cu(II)/Co(II), and Cu(II)/Ni(II) were obtained using 1-hexyl-2-methylimidazole (**1**) as a carrier (for PIMs: 7.9, 24.8, and 99.0, respectively, and for SLMs: 6.0, 17.0, and 59.5, respectively). The roughness of the polymer inclusion membrane with 1-alkyl-2-methylimidazole decreased with an increase in the molar intrinsic volumes of the carriers in the following order: **1** > **3**.

Symbols

R_q — Roughness
ε — Porosity
z_i — Current z-value
n — Number of points within the box cursors
c_t — Metal ions concentration in the source phase at a given time, mol dm^{-3}
c_i — Initial metal ions concentration in the source phase, mol dm^{-3}
k — Rate constant, s^{-1}
t — Time of transport, s
P — Permeability coefficient
V — Volume of the aqueous source phase, m^3
A — Effective area of the membrane, m^2
J_i — Initial flux
S — Selectivity ratios
RF — Recovery factor

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