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The application of membrane extraction in the separation of zinc and cadmium ions

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ABSTRACT

The study involved the transport of cadmium(II) and zinc(II) ions from acidic aqueous solutions using alkyl imidazole derivatives as ion carriers. The polymer inclusion membranes consisted of cellulose triacetate as a support, *o*-nitrophenyl pentyl ether as a plasticizer, 1-decyl-2-methylimidazole (**1**), 1-decyl-4-methylimidazole (**2**) or 1-decyl-2,4-dimethylimidazole (**3**) as ion carriers were used. The membranes were characterized by means of atomic force microscopy. The initial fluxes were much higher for Zn(II) than for Cd(II) for all investigated carriers. Their values depended on the carrier used and increased in the following order: **2** < **1** < **3** for both transported metal ions. An increase in the carrier concentration in the membrane increased the zinc separation. The highest separation coefficient Zn(II)/Cd(II) (24.7) was obtained using **3** as a carrier. The highest recovery coefficient values were obtained for Zn(II) (87%, 83% and 94% for carriers **1**, **2** and **3**, respectively). The values of the recovery factor for Cd(II) ions decreased in the following order: **1** > **2** > **3**.

Keywords: Polymer inclusion membrane; Zinc; Cadmium; Metal separation; Imidazole derivatives

1. Introduction

Due to their wide application, zinc and cadmium are classified as strategic metals [1]. Both zinc and cadmium are one of the most useful among all metals in various industries. The wide industrial use of zinc and cadmium causes the generation of metal-bearing wastes in the form of sewage, dust, sludge, waste heap, etc. Due to its threat to the environment and human health, all wastes should be properly managed or treated towards these toxic metals [2,3].

Liquid–liquid extraction plays an important role in the development of processes of recovering metals from various sources [3–7]. This technique has frequently been used in the extraction of Zn(II) and Cd(II) [8–17]. An increasing demand for metal production has led to search of more efficient and economical methods required by the industry for purification of wastes. Membrane technologies have become an important alternative to conventional processes employed for wastewater treatment, separation and recovery of target metals [4]. The selective transport of metal ions has been widely studied with supported liquid membrane (SLM) and polymer inclusion liquid membrane [3,18–20]. Their high selectivity, high diffusion rates and the possibility to concentrate ions have made them particularly useful [18,19].

A properly selected carrier is an important component of all liquid membranes (LMs). It determines the efficiency of the transport process and the separating properties of the membrane. Metal separation is achieved by an appropriate differentiation of properties and structures of metal-carrier complexes. Metal-ion carriers used in transport across LMs are usually the same hydrophobic compounds as those used in solvent extraction processes.

Imidazole and its derivatives can also be used for the purpose of membrane extraction of such metals as Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) [21–26]. For instance, an *N*-vinylimidazole derivative enables the separation of Cu(II) and Fe(III) [27], while imidazole aza- and thioazacrown

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ethers are 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 transport across polymer inclusion membranes (PIMs) [28]. Recently, Ulewicz and Radzymińska-Lenarcik [29–34] have reported on the selective transport of Cu(II) or Zn(II) ions in the presence of nonferrous cations (Zn(II), Co(II), and Ni(II)) from chloride and nitrate solutions across PIMs doped with 1,2-dialkylimidazoles. It has been proven that with the elongation of the substituent chain in position 1 in the imidazole ring, the initial flux of the ions increases, but the separation coefficient decreases. The steric effect of the substituent in position 2 in the carrier's molecules decreases the transport of all ions except for Cu(II).

Also, Zn(II) ions could effectively be separated from Co(II) and Ni(II) ions across PIMs doped with alkylimidazoles [6,35–37]. The use of 1-hexyl-4-methylimidazole enables the separation of 98.5% of Zn(II) from a unary solution and 96.9% from a quaternary solution of Zn(II)-Cd(II)-Co(II)-Ni(II) after running the process for 24 h [36]. The recovery of zinc from galvanic waste using the membrane extraction method of 1-octyl-4-methylimidazole was used [6]. 96% and 84% of zinc were recovered from chloride and sulphate waste solutions, respectively.

Ali et al. [38] reported that 87% of Zn(II) could be selectively removed from aqueous solutions using SLMs doped with triethanolamine. Kozlowska [39] observed a higher transport rate for Pb(II) compared with Cd(II) and Zn(II), when the membrane contained Cyanex 301, and higher selectivity for Cd(II), when Cyanex 301 was replaced by Cyanex 302. For the separation of nonferrous metals, di(2-ethylhexyl) phosphoric acid [4,40], hydrophobic amines [4], macrocyclic ligands [41,42], β-diketone [43,44], pyridine derivatives [4], and quaternary ammonium salt [45,46] have also been used as carriers in PIMs, but their selectivity is low, especially for metal ions with similar physicochemical properties. Such metals include zinc and cadmium. Zinc and cadmium belong to the same subgroup of 10d electron metals. Their ionic radii are 1.12 and 1.15 pm for Zn and Cd, respectively. As a result, these both metals and their cations have similar properties, so the separation and extraction of these cations from aqueous solutions is difficult. Even in nature they appear side by side. Zinc ores contain small amounts of cadmium, which is difficult to be completely separated from zinc.

The aim of this work was to check the possibility of separation and recovery of Zn(II) from mixtures of Zn(II)-Cd(II) ions from aqueous solutions using PIMs. For this purpose, alkyl derivatives of imidazole with small alkyl groups in the vicinity of the donor nitrogen atom and a large alkyl substituent in position 1 ensuring the hydrophobicity of the molecule, were chosen as carriers in PIMs. Such carriers were 1-decyl-2-methylimidazole (1), 1-decyl-4-methylimidazole (2) and 1-decyl-2,4-dimethylimidazole (3). It was assumed that by differentiation of the complex formation of zinc and cadmium ions based on the above, it would be possible to diversify their properties, and in this way their separation would be enabled.

2. Experimental

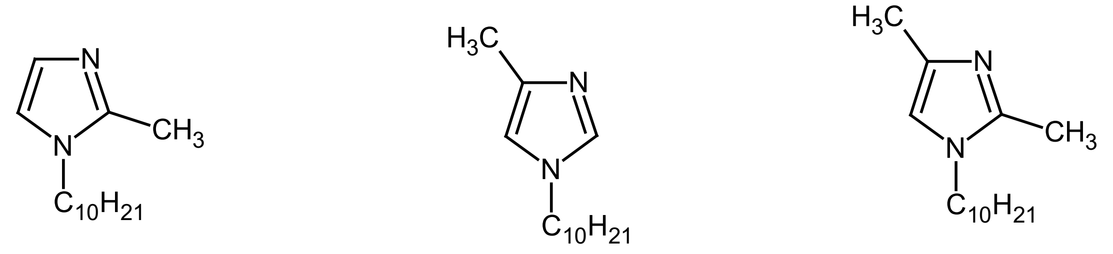
2.1. Reagents

Analytical grade chemical reagents: zinc(II) and cadmium(II) nitrates, hydrochloric acid, tetramethylammonium hydroxide and sodium acetate were purchased from (POCh, Gliwice, Poland). All aqueous solutions were prepared using analytical reagent grade chemicals and deionized water (conductivity – 0.10 μS/cm). Solutions of Zn(II) and Cd(II) were prepared by dissolving appropriate amounts of $Zn(NO_3)_2·6H_2O$ and $Cd(NO_3)_2·4H_2O$ in deionized water.

Analytical grade organic reagents, that is, cellulose triacetate (CTA), *o*-nitrophenyl pentyl ether (*o*-NPPE) and dichloromethane (all from Fluka, Munich, Germany) were used without further purification. 1-Decyl-2-methylimidazole (1) and 1-decyl-4-methylimidazole (2) (Fig. 1) were synthesized as described in Ref. [47]. 1-Decyl-2,4-dimethylimidazole (3) (Fig. 1) was synthesized by the alkylation of 2,4-dimethylimidazole (Sigma-Aldrich Company, Poland) in yields amounting to 63% according to the procedure described in Ref. [47].

The 1–3 structures were confirmed by ^1H NMR (400 MHz), ^{13}C NMR (100.6MHz) and ^{15}N NMR (40 MHz) spectroscopy (Bruker, Germany).

1: ^1H NMR, $CDCl_3$, δ (ppm): 0.881 (t, 3H, $C–CH_3$), 1.293 (m, 8H, $C–(CH_2)_4–C$), 1.742 (m, 6H, $C–(CH_2)_3–C$), 3.249 (qw, 2H, $C–CH_2–C$), 3.889 (t, 3H, $CH_2 – N^1$), 2.408 (s, 3H, $^2C–CH_3$), 6.738 (s, 1H, ^5CH), 8.114 (s, 1H, ^4CH); ^{13}C NMR, $CDCl_3$, δ (ppm): 12.297, 12.649, 13.712, 22.399, 26.405, 28.793, 28.874,



1
1-decyl-2-methylimidazole
b.p. 110-112°C/12mmHg

2
1-decyl-4-methylimidazole
b.p. 104-106°C/8mmHg

3
1-decyl-2,4-dimethylimidazole
b.p. 233°C/733mmHg

Fig. 1. The chemical formulas of applied carriers.

29.215, 29.208, 30.847, 32.025, 118.375, 127.623, 136.661 and ^{15}N NMR $CDCl_3$, δ (ppm): 252.31, 169.52.

2: ^{1}H NMR, $CDCl_3$, δ (ppm): 0.898 (t, 3H, C–CH_3), 1.302 (m, 8H, C–$(CH_2)_4$–C), 1.714 (m, 6H, C–$(CH_2)_3$–C), 3.192 (qw, 2H, C–CH_2–C), 3.875 (t, 3H, CH_2 – N^1), 2.597 (s, 3H, ^{4}C–CH_3), 6.757 (s, 1H, ^{5}CH), 7.294 (s, 1H, ^{2}CH); ^{13}C NMR, $CDCl_3$, δ (ppm): 12.305, 12.682, 13.764, 22.397, 26.399, 28.806, 28.904, 29.182, 29.211, 30.821, 46.598, 118.423, 128.539, 136.695 and ^{15}N NMR, $CDCl_3$, δ (ppm): 253.46, 172.18.

3: ^{1}H NMR, $CDCl_3$, δ (ppm): 0.879 (t, 3H, C–CH_3), 1.278 (m, 8H, C–$(CH_2)_4$–C), 1.773 (m, 6H, C–$(CH_2)_3$–C), 3.288 (qw, 2H, C–CH_2–C), 3.916 (t, 3H, CH_2 – N^1), 2.369 (s, 3H, ^{2}C–CH_3), 2.408 (s, 3H, ^{4}C–CH_3), 6.890 (s, 1H, ^{5}CH); ^{13}C NMR, $CDCl_3$, δ (ppm): 12.310, 12.754, 13.808, 22.391, 26.392, 28.801, 28.999, 29.171, 29.215, 30.825, 31.599, 46.676, 118.459, 128.993, 136.719 and ^{15}N NMR, $CDCl_3$, δ (ppm): 255.86, 173.45.

2.2. The preparation and characteristics of PIMs

The polymer membranes were prepared according to the procedure reported in our previous papers [32,35]. Organic solutions of the support (CTA), the ion carrier (**1**, **2** or **3**) and the plasticizer (*o*-nitrophenyloctyl ether) solutions in dichloromethane were prepared. A portion of such a solution was poured into a membrane mould comprised of a 6.0 cm glass ring attached to a glass plate with CTA – dichloromethane glue. The organic solvent was allowed to evaporate overnight and the resulting membrane was separated from the glass plate by immersion in cold water.

The thickness of the PIM samples was measured using a digital micrometer (Panametrics® Magna-Mike® 8500 (San Diego, CA, USA)) with an accuracy of 0.1 µm. The thickness of a membrane was measured 10 times for each case and shown as the average value of these measurements, with the standard deviation below 1%. The thickness of membranes before and after transport was found to be the same. The average PIMs thickness varied in the range 28–32 µm.

Each experiential point was repeated four times, that is, membrane formed by immobilization, thickness measured and transport parameters calculated. Experimental reproducibility was high with standard deviation below 1% of the measured values.

A surface characterization study of the polymer membranes was performed using an Atomic-force MultiMode Scanning Probe Microscope IIIa (AFM) (Digital Instruments Veeco Metrology Group, Santa Barbara, CA, USA) according to the procedure described in other papers [30–32,34,36,37]. Pores characterization was performed using the AFM image processing program NanoScope v.5.12, which enabled the calculation of two parameters: roughness (R_q) and porosity (ε). The R_q parameter is the standard deviation of the *z* values within the box cursor and is calculated as follows:

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

2.3. Transport studies

Transport experiments were carried out in a permeation cell described in earlier papers [6,30–32,34–37]. The membrane film (surface area 4.9 cm^2) was tightly clamped between two cell compartments. Both, the source phase and the receiving aqueous phase (45 cm^3 each) were mechanically stirred at 600 rpm. Metal nitrates were used in the source phase, whereas the receiving phase was 0.5 M solution of sodium acetate CH_3COONa. 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 analysed by atomic absorption spectroscopy (AAS 240FS Spectrometer, Agilent, Santa Clara, CA, USA) to determine zinc(II) and cadmium(II) concentrations. The pH of the source phase equal to 4.5 was kept constant using tetramethylammonium hydroxide.

The kinetics of transport across PIMs was described as a first-order process with respect to the metal-ion concentration [48] expressed by Eq. (2) as follows:

$$\ln\left(\frac{c}{c_0}\right) = -kt \tag{2}$$

In order to calculate the value of *k*, $\ln(c/c_0)$ versus time was plotted. The rate constant values for two independent transport experiments were averaged and the standard deviation was calculated. The permeability coefficient (*P*) was calculated according to Eq. (3) as follows:

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

The initial flux (J_0) was calculated as follows:

$$J_0 = P \times c_0 \tag{4}$$

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

$$S = \frac{J_{0,M1}}{J_{0,M2}} \tag{5}$$

In order to describe the efficiency of metal removal from the source phase, the recovery coefficient (RF) was calculated as follows:

$$RF = \frac{c_0 - c}{c_0} \times 100\% \tag{6}$$

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

3. Results and discussion

3.1. Membranes characterization

An AFM image of the PIM doped with 1-decyl-2,4-dimethylimidazole (**3**) in two- and three-dimensional forms in a 5.0 × 5.0 µm format is shown in Fig. 2.

The porosity (ε), roughness (R_q) and effective pore sizes of the membrane doped with **3** were calculated using AFM characterization, and they are shown in Table 1 along with the data of membranes doped with **1** [31] and **2** [37].

The distribution of the carrier in the investigated membrane after the evaporation of dichloromethane was homogeneous on the entire surface. The membrane's tortuosity was

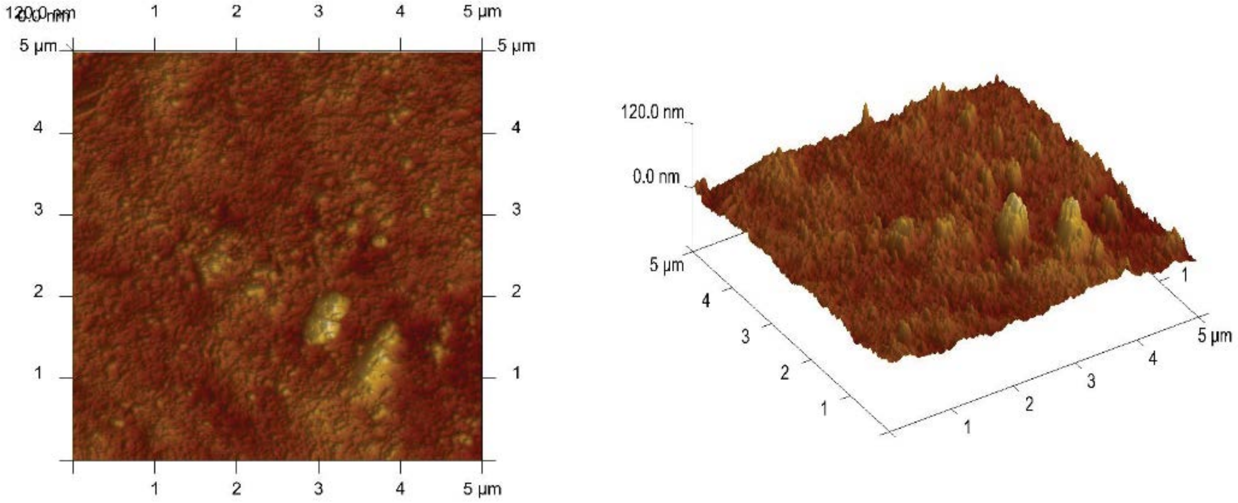


Fig. 2. 2D and 3D atomic force microscopy images of the PIM with 1-decyl-2,4-dimethylimidazole (**3**), scan area 5 × 5 µm.

Table 1
AFM characterization parameters for PIMs doped with 1-decyl-2-methylimidazole (**1**), 1-decyl-4-methylimidazole (**2**) and 1-decyl-2,4-dimethylimidazole (**3**). Scan areas 25 µm^2

Membrane	Effective pore size (µm)	Tortuosity	Roughness (R_q) (nm)	Porosity (ε) (%)	Reference
PIM with **1**	0.057	2.81	7.2	18.1	[31]
PIM with **2**	0.060	2.85	6.7	16.0	[37]
PIM with **3**	0.065	2.45	5.8	23.7	This work

determined from the dependence developed by Wolf and Strieder [49] as follows:

$$\tau = 1 - \ln \varepsilon \tag{7}$$

As demonstrated in a number of papers [6,29–37,43,50], the microstructure of a membrane has an impact on its transport process. CTA membranes have porous structures with nearly uniform pores distribution (porosity 50%) [49,51]. The pores in a CTA matrix were filled with a plasticizer (*o*-NPPE) and the carrier. The carrier crystallized inside the membrane, with the texture of the surface being relatively homogeneous, but with different porosities and roughness. The roughness of a CTA membrane obtained by Tor et al. [51] equalled 14 nm.

*3.2. The effect of plasticizer content on the transport of Zn(II) across PIMs with **1**, **2** and **3***

Initially, the study involved the transport of zinc(II) ions through PIMs containing **1**, **2** and **3** as ionic carriers and with various plasticizer contents. Blank experiments, in the absence of carrier, yielded no significant flux across a PIM containing only the support and the plasticizer. In order to understand the influence of the plasticizer on the transport of zinc ions through the PIM, membranes with different *o*-NPPE contents were prepared and tested at a temperature of 20°C.

Based on the data presented in Fig. 3, membranes containing 5% of the plasticizer were selected and prepared for further investigation.

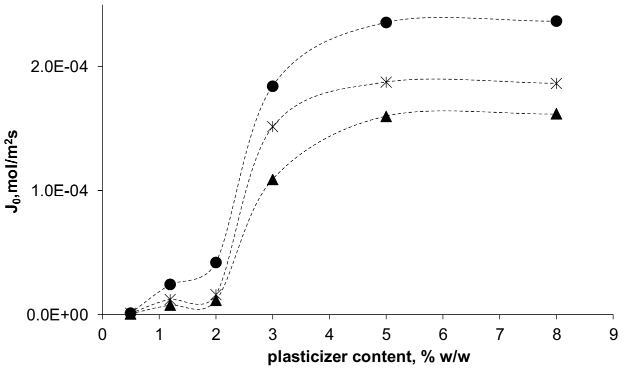


Fig. 3. The relationship between initial fluxes and plasticizer contents in the membrane support in regard to the transport of zinc(II) with **1** (*), **2** (▲) and **3** (●) as ion carriers.

*3.3. The effect of carrier concentration on the transport of Zn(II) and Cd(II) across PIMs with 1-decyl-2,4-dimethylimidazole (**3**)*

The influence of carrier concentration in the membrane on the efficiency of separating Zn(II) and Cd(II) ions from their equimolar mixture was determined. The values of initial fluxes for competitive transport of Zn(II) and Cd(II) across PIM versus the percentage of carrier (**3**) concentration in the PIMs are shown in Table 2.

The fluxes of both metal ions rapidly increased with an increase in the carrier content up to 60% in the membrane. The separation coefficient ($S_{Zn(II)/Cd(II)}$) also increased. The

Table 2
Initial fluxes (J_0) for competitive transport of Zn(II) and Cd(II) ions across PIMs doped with 1-decyl-2,4-dimethylimidazole (**3**), the recovery (RF) and separation (*S*) coefficients after 24 h; membrane: *x*% **3**, 5% *o*-NPPE, (100-5-*x*)% CTA; source phase: $[M^{2+}] = 0.001$ M each metal ion, receiving phase: 0.5 M CH_3COONa

Percentage of carrier (%)	Metal ions	Initial flux, J_0 (μmol/m² s)	RF after 24 h (%)	$S_{Zn(II)/Cd(II)}$
30	Zn(II)	0.78	25	3.00
	Cd(II)	0.26	11	
40	Zn(II)	1.25	48	3.68
	Cd(II)	0.34	12	
50	Zn(II)	3.68	62	4.66
	Cd(II)	0.79	14	
55	Zn(II)	9.85	90	11.45
	Cd(II)	0.86	16	
60	Zn(II)	25.44	94	24.70
	Cd(II)	1.03	14	

higher concentration of carrier promoted the separation of Zn(II) from Cd(II). It was not possible to obtain a membrane containing more than 60% of the carrier. During further testing, membranes with the following composition were used: 35% of CTA, 5% of *o*-NPPE and 60% of the carrier (**1**, **2** or **3**).

The RF of Zn(II) ions from source phase after 24 h increased with an increase in the carrier content of the membrane from 25% to 94%, while the recovery of Cd(II) ions was low (ca. 10%–15%) and independent of the composition of the membrane. Practically, Cd(II) ions were not transferred across the membrane and remained in the source phase.

3.4. Separation of Zn(II) and Cd(II) from their equimolar solution across PIMs

The investigation involved the transport of Zn(II) and Cd(II) ions from an equimolar nitrate mixture of two metal ions, each with a concentration of 0.001 M, across PIMs doped with imidazole **1**, **2** and **3** into 0.5 M receiving solution of CH_3COONa. The relationship between $\ln(c/c_0)$ and time for the transport of Zn(II) and Cd(II) across PIM containing **1**–**3** imidazole derivatives is shown in Fig. 4.

The correlation between $\ln(c/c_0)$ and time was linear, which was confirmed by the high correlation coefficient (R^2) ranging from 0.9908 to 0.9986. For blank experiment, no transport was detected for more than 24 h of continuous process run.

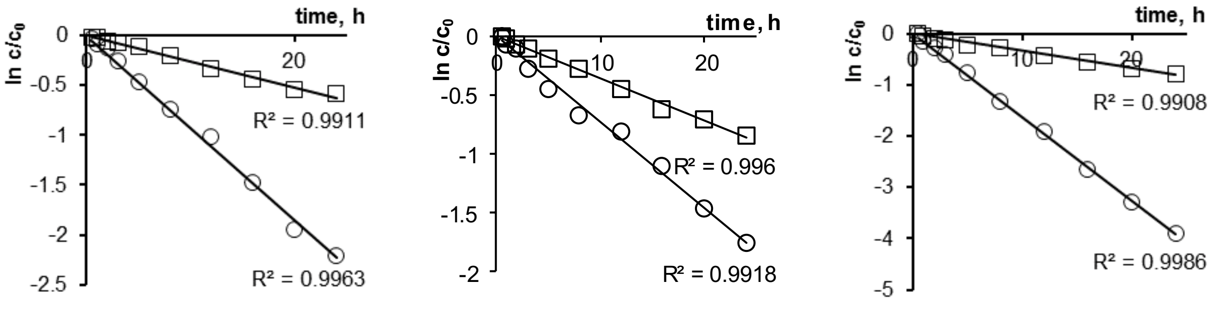
As shown in Fig. 4, the transport of metal ions across PIMs with imidazole derivatives could be described by first-order kinetics in metal ion concentration in accordance with changes. It is in agreement with the mathematical model proposed by Danesi [48]. Initial fluxes and selectivity ratios are summarized in Table 3.

The initial fluxes were much higher for Zn(II) than for Cd(II) for all investigated carriers (Table 3). Their values depended on the carrier used and they increased in the following order: **2** < **1** < **3** for both transported metal ions. This was caused by differences in both, the basicity of the carriers and their stability constants with metal ions.

The total stability constants of Zn(II) and Cd(II) ions complexes with 1-decyl-2,4-dimethylimidazole (**3**), are summarized in Table 4, and compared with the data available in the literature for 1,2-dimethylimidazole [21] and 1,4-dimethylimidazole [22].

The methyl substituent at position 2 or 4 of the imidazole ring increased the basicity of the investigated carriers in comparison with that of 1-decylimidazole ($pK_a = 7.43$ [53]). 1-Decyl-2,4-dimethylimidazole (**3**) was the strongest base.

The presence of the substituent at position 2 or 4 of the imidazole ring hindered the formation of each metal complex (steric effect). The stability constants of Zn(II) and Cd(II) complexes with ligands presented in Table 4 increased in the following order: 1,4-dimethylimidazole < 1,2-dimethylimidazole < 1-decyl-2,4-dimethylimidazole (**3**). In aqueous solutions, cations of Zn(II) and Cd(II) exist in the form of octahedral aquacomplexes $[M(H_2O)_6]^{2+}$. Owing to the steric effect of ligands (extractants), octahedral aquacomplexes of certain cations tend to change their coordination number (c.n.) from 6 to 4 and they change their coordination sphere into



1 **2** **3**

Fig. 4. Kinetics of the transport of Zn(II) (○) and Cd(II) (□) ions across PIMs containing 1-decyl-2-methylimidazole (**1**), 1-decyl-4-methylimidazole (**2**) or 1-decyl-2,4-dimethylimidazole (**3**) from aqueous solutions. Source phase: $c_{Zn(II)} = c_{Cd(II)} = 0.001$ M; pH = 4.5; receiving phase: 0.5 M CH_3COONa; membrane: 60% **1**, **2** or **3**; 5% *o*-NPPE and 35% CTA.

Table 3
Initial fluxes and separation coefficients for competitive transport of Zn(II) and Cd(II) ions across PIMs doped with **1**, **2** or **3**. Source phase: $c_{Zn(II)} = c_{Cd(II)} = 0.001$ M; pH = 4.5; receiving phase: 0.5 M CH_3COONa; membrane: 60% **1**, **2** or **3**; 5% *o*-NPPE; 35% CTA

Carrier	Metal ions	Initial flux, J_0 (μmol/m^2 s)	$S_{Zn(II)/Cd(II)}$
1-Decyl-2-methylimidazole, **1**	Zn(II)	10.28	10.8
	Cd(II)	0.95	
1-Decyl-4-methylimidazole, **2**	Zn(II)	8.79	9.9
	Cd(II)	0.89	
1-Decyl-2,4-dimethylimidazole, **3**	Zn(II)	25.44	24.7
	Cd(II)	1.03	

Table 4
A comparison of basicity and the stability constants β_n of Zn(II) and Cd(II) complexes with imidazole derivatives at 25°C, ionic strength 0.5 M KNO_3

Ligand	pK_a	Metal ion	log β_1	log β_2	log β_3	log β_4	Reference
1-Decyl-2,4-dimethylimidazole **3**	8.62	Zn(II)	2.17	4.48	6.39	9.87	[52]
		Cd(II)	2.53	4.21	5.68	7.56	
1,2-Dimethylimidzole	8.21	Zn(II)	1.92	4.32	7.11	9.00	[21]
		Cd(II)	2.20	3.45	5.05	6.34	
1,4-Dimethylimidzole	7.72	Zn(II)	1.70	4.48	5.40	8.90	[22]
		Cd(II)	2.05	3.93	5.11	5.81	

tetrahedral or flat, depending on the structure of their d-electron layer. The process is illustrated by the equation:

$$\left[M(H_2O)_{6-n+1}L_{n-1}\right]^{2+} + L \leftrightarrow \left[M(H_2O)_{4-n}L_n\right]^{2+} + (n+2)H_2O \quad (8)$$

where L is the carrier molecule.

Therefore, tetrahedral complexes (c.n. = 4) are formed in the solution in addition to octahedral ones (c.n. = 6). Tetrahedral complexes are specific to Zn(II) and Cd(II). Changes in the coordination sphere lead to higher sums of complex stability constants ($\beta_n = \beta_n^t + \beta_n^o$) (the stability constants are the sum of stability constants for complexes with c.n. = 4 (β_n^t) and with c.n. = 6 (β_n^o)) and higher susceptibility to extraction in the liquid–liquid system, because complexes with c.n. = 4 are less hydrated, and thus they pass more readily into the organic phase.

The 4-coordination Zn(II) and Cd(II) complexes form in the second, third and fourth complexing stage (Table 4), especially in the case of Zn(II). Cd(II) complexes have lower stability than analogical Zn(II) complexes. [ZnL_4] complexes are the most stable. In the case of Cd(II), the third subsequent complex ([ML_3]) has the highest stability. Hence, a higher concentration of a carrier in the membrane is needed to create the conditions for the formation of tetrahedral Cd(II) complexes. A similar relationship was observed in the separation of a mixture of Cu(II), Zn(II) and Cd(II) ions by solvent extraction using **3** as the extractant. At higher pH values of the aqueous phase (pH > 6), the extraction curves of Zn(II) and Cd(II) complexes were approaching each other [52].

An increase in a carrier concentration within the membrane increased Zn separation in relation to Cd (Table 2). The highest Zn(II)/Cd(II) separation coefficient (24.7) was obtained using 1-decyl-2,4-dimethylimidazole (**3**) as the carrier.

3.5. Zinc separation

Fig. 5 shows the dependence of the RF for zinc and cadmium ions from the source phase on the carrier type after 24 h during transport across PIMs doped with **1**, **2** or **3**.

The highest recovery values were obtained for Zn(II) and they amounted to 87%, 83% and 94% for carriers **1**, **2** and **3**, respectively. The values of RF for Cd(II) ions decreased in the following order: **1** > **2** > **3**. The steric effect of the investigated carrier hindered the transport of Cd(II) ions. Practically, Cd(II) ions remained in the source phase. For carriers **1**, **2** and **3** the percentage of cadmium ions remaining

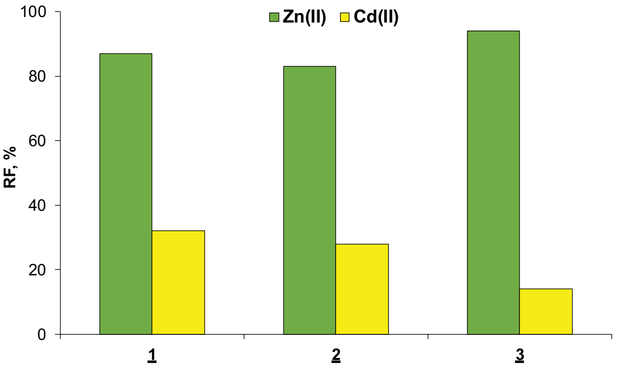


Fig. 5. The recovery coefficient (RF) of metal ions from the source phase after 24 h during transport across PIMs doped with 1-decyl-2-methylimidazole (**1**), 1-decyl-4-methylimidazole (**2**) and 1-decyl-2,4-dimethylimidazole (**3**).

in this phase was 68%, 72% and 86%, respectively. The use of **3** as a carrier in the PIMs promoted the transport of Zn(II) ions and significantly inhibited the transport of Cd(II) ions.

1-Decyl-2,4-dimethylimidazole (**3**) is the carrier that causes the highest steric effect. It proved to be the best carrier for the separation of Zn(II) from Cd(II).

4. Conclusions

Zinc(II) ions can be removed effectively from aqueous nitrate solutions of Zn(II) and Cd(II) in the membrane extraction with 1-decyl-2-methylimidazole (**1**), 1-decyl-4-methylimidazole (**2**) or 1-decyl-2,4-dimethylimidazole (**3**).

The initial fluxes are much higher for Zn(II) than for Cd(II) for all investigated carriers. Their values depend on the type of the carrier used and they increase in the following order: **2** < **1** < **3** for both transported metal ions. This is caused by differences in both, the basicity of carriers and stability constants of their complexes with metal ions.

An increase in a carrier concentration within the membrane increases the Zn separation in relation to Cd. The highest Zn(II)/Cd(II) separation coefficient (24.7) was obtained using 1-decyl-2,4-dimethylimidazole (**3**) as the carrier.

The highest RF values are obtained for Zn(II) (87%, 83% and 94% for carriers **1**, **2** and **3**, respectively). The values of RF for Cd(II) ions decrease in the following order: **1** > **2** > **3**. The steric effect of the investigated carriers hinders the transport of Cd(II) ions.

The application of hydrophobic alkyl imidazole derivatives with a high steric effect as carriers in PIMs enables the separation of Zn(II) from Cd(II) ions.

Symbols

δ — Chemical shift, ppm
R_q — Roughness, nm
ε — Porosity, %
z_i — Current z value
n — Number of points within the box cursors
τ — Tortuosity
c — Metal ions concentration in the feed phase at a given time, mol/dm^3
c_0 — Initial metal ions concentration in the source phase, mol/dm^3
k — Rate constant, s^{-1}
t — Time of transport, s
P — Permeability coefficient, m/s
V — Volume of the aqueous source phase, m^3
A — Effective area of the membrane, m^2
J_0 — Initial flux, mol/m^2 s
S — Separation coefficient
RF — Recovery coefficient, %
pK_a — Dissociation constant
β_n — Stability constant

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