1. Introduction

Lead and cadmium are hazardous environmental contaminants of global concern [1]. Their compounds are emitted into the atmosphere as constituents of industrial dust. From the air, they enter soil and groundwater. Cadmium is a burdensome contaminant of phosphate fertilizers, from which it can enter the soil and, ultimately, groundwater [2]. It also occurs in effluents, wastewater, and waste products [3].

Lead is still widely used for automotive batteries, pigments, ammunition, thermoplastic-sheathed cables, lifting weights, drive belts, lead crystal glass, radiation protection, and some solders. It is often used to store corrosive liquids.

Lead and cadmium are classified by Cote [4] as strategic metals. Cadmium is classified by the U.S. Environmental Protection Agency as a probable human carcinogen, whereas lead can cause central nervous system damage [5]. Therefore, these toxic metals should be removed from, that is, wastewater to protect people and environment.

Separation methods based on traditional solvent extraction (SX) usually consume large amounts of reagents, solvents, and extractants. In order to reduce the amounts of reactants and energy needed for separations, and to decrease the environmental and economic impact of SX separations, several membrane-based separation techniques have been proposed over the past 30 y. Among those techniques, polymer inclusion membranes (PIMs) have been extensively tested since they offer high transport rates and good selectivity, hence they are a very interesting option to overcome the SX downsides [6]. Several authors have reported that PIMs show good long-term stabilities. PIM systems have
been successfully designed for metal extraction using different extractants [6,7], such as crown ethers [8–10], trioctylphosphine oxide (TOPO) [11,12], phosphonium cation-based ionic liquids (i.e., trihexyl(tetradecyl)phosphonium chloride (Cyphos®IL101) [13,14] and β-diketones [15,16].

Imidazole and its derivatives can also be used for the purpose of membrane extraction of such metals as cobalt(II), nickel(II), copper(II), zinc(II), and cadmium(II) [17–20].

The aim of this work was to learn the complex formation and extraction properties of hydrophobic alkylimidazoles (alkyl = hexyl, heptyl, octyl, and decyl) in relation to cadmium(II) and lead(II) ions, and to use these alkylimidazoles to separate cadmium(II) and lead(II) ions in transport across PIMs.

2. Experimental

2.1. Reagents

The inorganic chemicals, that is, potassium, cadmium(II), and lead(II) nitrates, nitric acid, tetramethylammonium hydroxide were of analytical grade and were purchased from POCh (Gliwice, Poland). The organic reagents, that is, cellulose triacetate (CTA), o-nitrophenyl pentyl ether (o-NPPE), and dichloromethane were also of analytical grade and were purchased from Fluka (Switzerland) and used without further purification. The 1-alkylimidazole (Fig. 1) were synthesized according to the procedure described in [21].

The pH-meter was calibrated using commercial buffer solutions (Radiometer) of pH 4.01 ± 0.01 and 7.00 ± 0.01. The pH was also checked against hydrochloric acid according to IUPAC recommendations [22].

2.2. Solvent extraction procedures

The extraction process was studied for single component solutions containing cadmium or lead ions.

The measurements were run at 25°C and at fixed ionic strength (0.5) maintained in the aqueous phase with KNO₃ + HNO₃. Before extraction, concentrations of the metal ions (cadmium(II), lead(II)), and nitric acid in the aqueous phase were constant (0.01, 0.01, and 0.15 mol/L, respectively) and the ligand (1-alkylimidazole) concentrations in organic phase were varied from 0.01 to 0.25 mol/L. Six cubic centimeters of the aqueous phase were placed in a graduated test tube and an equal volume of an 1-alkylimidazole (alkyl = hexyl, heptyl, octyl, and decyl) solution in dichloromethane was added. The test tubes were then shaken for 30 min. The equilibrium was established after a few minutes, however, no longer than 30 min. After that the difference in the phase volume was checked, the phases were separated, and the pH of the aqueous phase was measured, as well as the metal ion concentration by atomic absorption spectrophotometry method (AAS Spectrometer, Solaar 939, Unicam).

2.3. Solvent extraction studies

The extraction process was characterized by inspecting dependence between distribution ratio \(D_M\) and pH. The free ligand molar concentration in the aqueous phase \([L]\) was calculated from the pH values using Eq. (1):

\[
[L] = \frac{K_a [HL]^+}{[H_3O^+]^+}
\]

where \(K_a\) is the dissociation constant of the protonated ligand (1-alkylimidazole) over a particular concentration range, and [HL] is the concentration of protonated ligand, equal to the analytical concentration of nitric acid in the aqueous phase. The dissociation constant of the protonated ligand of the 1-alkylimidazoles were taken from literature [23] and listed in Fig. 1.

Distribution ratio \(D_M\) of metal ion (cadmium(II) or lead(II)) in the systems studied was calculated on the basis of the metal ions concentrations in the aqueous phase before and after attaining equilibrium from the following equation:

\[
D_M = \frac{C_{M(\text{org})}}{C_{M(\text{aq})}} = \frac{C_{M0} - C_M}{C_M}
\]

where \(C_{M0}\) and \(C_M\) denote analytical cadmium(II) or lead(II) concentrations in the aqueous phase before and after attaining partition equilibrium, respectively.

The magnitude of variable \(D_M\) depends on the alkylimidazole concentration in both phases, and consequently on the pH.

2.4. PIM preparation

The membranes were prepared according to the procedure reported in the previous paper [19,20,24–29]. A solution of CTA as the support, plasticizer, and alkylimidazole (1 or 2) as ion carrier in dichloromethane was prepared. A specified portion of this solution was poured into a membrane mould consisting of a 9.0 cm diameter glass ring fixed on a glass plate by means of CTA – 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 h in distilled water to achieve its homogeneity. Two samples of the PIM membranes (containing 2.6 cm³ o-NPPE/1 g CTA and 1.0 mol/L carriers calculated on plasticizer) were cut from the same membrane film for duplicate transport experiments.

2.5. Characteristic of PIMs

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.
A surface characterization study of the PIMs was performed by atomic force microscopy (AFM) according to the procedure described in our earlier paper [10,20,24]. The analysis of surface pore characteristics of the polymer membrane was made using the NanoScope v.5.12 AFM image processing program.

2.6. Transport studies across PIMs

Transport experiments were carried out in a permeation module cell described in our earlier paper [19,20,24–29]. The membrane film (at surface area of 4.9 cm²) was tightly clamped between two cell compartments. Both, that is, the feed and receiving aqueous phases (45 cm³ each) were mechanically stirred at 600 rpm. The receiving phase was kept constant (pH = 6.5) and controlled with a pH meter (CX-731 Elmetron, with combined pH electrode, ERH-126, Hydromet, Poland).

The kinetics of the transport across the PIMs was described as a first-order process with respect to the examined metal-ion concentration [30] expressed by Eq. (3):

\[ \ln \left( \frac{C}{C_0} \right) = -kt \]  

where \( C \) is the metal ions concentration (mol/L) in the feed aqueous phase at a given time (mol/L), \( C_0 \) is the initial metal ions concentration in the feed phase (mol/L), \( k \) is the rate constant (s⁻¹), and \( t \) is the time of transport (s) [31].

The permeability coefficient \( (P) \) was calculated according to Eq. (4):

\[ P = \frac{V}{A} \cdot k \]  

where \( V \) is the volume of the aqueous feed phase (m³), \( k \) is the rate constant, and \( A \) is an effective area of the membrane (m²).

The initial flux \( (J_0) \) is equal to:

\[ J_0 = P \cdot C_0 \]  

The selectivity coefficient \( (S) \) was defined as the ratio of initial fluxes for \( M_i \) and \( M_j \) metal ions, respectively:

\[ S = \frac{J_{0,M_i}}{J_{0,M_j}} \]  

To describe the efficiency of metal removal from the feed phase, the recovery coefficient \( (RF) \) was calculated:

\[ RF = \left( \frac{C_0 - C}{C_0} \right) \cdot 100\% \]

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

3. Results and discussion

3.1. Solvent extraction studies

Solvent extraction (SX) of cadmium(II) and lead(II) was performed in order to evaluate the best conditions for operation of the membrane separation systems.

The results of the extraction experiments are presented as plots of the logarithm of the distribution ratio \( \log(D_{M}) \) of cadmium(II) and lead(II) as a function of \( \text{pH} \) of the aqueous phase, separately for cadmium(II) (Fig. 2a) and lead(II) (Fig. 2b).

The process of distribution of cadmium(II) and lead(II) complexes with 1-alkylimidazole bases takes place at different \( \text{pH} \) values for each of the bases investigated. Separate curves \( \log(D_{M}) \) vs. \( \text{pH} \) were obtained for each system studied. The curves are strongly shifted towards lower \( \text{pH} \) values with increasing 1-alkyl chain lengths. For most of the systems studied, the curve shape is similar so they indicate that one type of complexes is being extracted.

The values of stability constants for the investigated complexes were calculated using the Rydberg formula:

\[ D_M = \frac{P \cdot \beta_1 [L] + P_2 \cdot \beta_{11} [L]^2 + \ldots + P_n \cdot \beta_{1n} [L]^n}{\sum_{n=0}^{\infty} \beta_n [L]^n} \]  

where \( P_1, \beta_1, \) and \( [L] \) denote the partition constant, stability constant, and the free ligand concentration (mol/L) in the aqueous phase, respectively, and \( n \) is the number of ligand particles in the first metal complex which is hydrophobic enough to freely pass into the organic phase [32–34].

Stability constants, \( \beta_1 \), obtained in this way are collected in Table 1 for each metal ion and ligand.

In general, the complexation reaction consists in a statistical exchange of ligands according to the Bjerrum’s model [35]. Formation of an \( n \)-th complex can be described by the equation:

\[ [M(H\text{H}_2\text{O})_{N_{-n+1}}I_{n-1}]^{\alpha\sigma} + L \leftrightarrow [M(H\text{H}_2\text{O})_{N_{-n}}I_{n}]^{\alpha\sigma} + \text{H}_2\text{O} \]

where \( N \) is the maximum coordination number of the metal ion [35].

According to Table 1, the stability constants of cadmium(II) complexes with 1-alkylimidazoles have higher values at each stage of complexation when compared to analogous lead(II) complexes. The stability of both cadmium(II) and lead(II) complexes with 1-alkylimidazoles does not depend on the length of the alkyl group and thus does not depend on hydrophobicity of the ligand molecule. The same phenomenon was observed in the case of copper(II) complexes with 1-alkylimidazoles [36].

In aqueous solutions, cations of cadmium(II) and lead(II) exist in the form of octahedral aqua complexes \([\text{M(H}_2\text{O})_6]^{\text{z}+}\).

To establish the sequence of the formation of 1-alkylimidazole complexes with cadmium(II) and lead(II), the
Panthaleon van Eck’s formula \( \log K_n = fn - 1 \) [37] was employed. The formation constants, \( K_n \), were calculated from Eq. (10).

\[
K_n = \beta_n / \beta_{n-1}
\]

Generally, plots of the \( \log K_n = fn - 1 \) function are straight lines with a small slope. When the complexation process is accompanied by additional phenomena, such as for instance, a change in the shape of the coordination polyhedron of the metal complexes being formed, changes in the mode of binding of the ligands, and so on, the plot of the function assumes the shape of broken lines [37]. In Fig. 3, the shape of the function is shown for the formation of the cadmium(II) (Fig. 3a) and lead(II) (Fig. 3b) complexes with the 1-alkylimidazoles studied in aqueous solution.

Fig. 3b shows that lead(II) complexes are formed in accordance with an Eq. (9), as a result of the statistical exchange of \( H_{2}O \) molecules with 1-alkylimidazole (L) molecules, that is, according to the Bjerrum model [35].

In the case of lead(II) complexes, owing to the effect of ligands (L) (extractant, carrier), octahedral aqua complexes of certain cations tend to change their coordination number (c.n.) from 6 to 4, and they change their coordination sphere into a deformed tetrahedron. The process is illustrated by Eq. (11).

\[
\left[ \text{Cd}(H_{2}O)_{n-L} \right]^{2+} + nL \leftrightarrow \left[ \text{Cd}(H_{2}O)_{n+2}L \right]^{2+} + (n+2)H_{2}O \quad (11)
\]

In this case, both the stability constants \( \beta_n \) and the \( K_n \) values make up the sum of the stability constants of both structural isomers, the tetrahedral \( [\text{Cd}(H_{2}O)_{n-L}]^{2+} \) and the octahedral \( [\text{Cd}(H_{2}O)_{n+2}L]^{2+} \) ones. The contribution of the tetrahedral species is particularly evident at the 4th complexation step \((n = 4)\).

In the case of cadmium(II) ions, owing to the effect of ligands (L) (extractant, carrier), octahedral aqua complexes of certain cations tend to change their coordination number (c.n.) from 6 to 4, and they change their coordination sphere into a deformed tetrahedron. The process is illustrated by Eq. (11).

3.2. Characteristic of membranes

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 obtained values of average PIMs thicknesses are presented in Table 2. Experimental reproducibility was high with a standard deviation below 1% of the measured values.

An AFM image of the PIM with 1-hexylimidazole (1), 1-heptylimidazole (2), 1-octylimidazole (3), 1-decylimidazole (4) in two-dimensional forms is shown in Fig. 4. In the image of PIM samples (Fig. 4) there are clearly visible elongated pores, also called “cavity channels” (darker regions). Such morphology of the membrane surface can be related to the crystallinity of the CTA. A wide network
of pores 5–25 nm in size is likely to be responsible for the improved transport performance across membranes.

The roughness ($R_q$) and effective pore sizes of the membrane were calculated using AFM and they are shown in Table 2 together with the tortuosity ($\tau$) of the membrane, determined from the dependence developed by Wolf and Strieder [31]:

$$\tau = 1 - \ln \varepsilon$$

(12)

where $\varepsilon$ is the means porosity.

The values of all parameters, that is, roughness, effective pore size, tortuosity, and thickness (Table 2) for the tested membranes, depend on the carrier used and increase in the order: 1 > 2 > 3 > 4. As demonstrated in a number of papers [10,37–40], the microstructure of the membrane has an impact on the transport process. CTA membranes have porous structures, and the distribution of pores is nearly uniform (porosity of 50%) [31].

The pores in a CTA matrix were filled with a plasticizer (o-NPPE) and molecules of the carrier. The carrier crystalizes inside the membrane, with the texture of the surface being relatively homogeneous, with varying porosity and roughness. The roughness of a CTA membrane obtained by Tor et al. [41] equaled 14 nm.

### 3.3. Transport of cadmium(II) and lead(II) ions across PIMs

Findings on the transport of cadmium(II) and lead(II) ions from equimolar nitrate solutions across PIMs containing alkylimidazole (1, 2, 3, or 4) as an ion carrier are discussed below. The studies were carried out using two-component solutions containing metal ions, each with a concentration of 0.001 mol/L. The initial flux values and selectivity coefficients for the metal ion transport across the PIM’s are shown in Table 3.

As indicated by the data shown in Table 3, for all investigated PIMs, the initial flux value for the transport of cadmium(II) ions is higher than for lead(II) ions, and it increases with increasing hydrophobicity of the carrier molecule. This means that in the case of a PIM with 1-decylimidazole (4), the initial flux has the highest value. In the case of a PIM with 1-hexylimidazole (1), the Cd(II)/Pb(II) selectivity coefficient ($S$) has the highest value.

From Eq. (6), the permeability coefficient of both ions was calculated for each investigated membrane. Fig. 5 shows the dependence of membrane permeability coefficients ($P$) on the dissociation constant ($pK_a$) of the carrier molecules used in these membranes for cadmium(II) and lead(II) ions.

For both ions (Fig. 5), the permeability coefficients increase with an increase in the basicity of carrier molecules (increased $pK_a$ value); however, for lead(II) ions this increase is smaller.

The values of permeability coefficient ($P$) increase linearly with increasing basicity of the carrier. A similar linear correlation for 1-alkylimidazoles was obtained in the case of chloride [24] and sulfate [29] solutions; this is in agreement with literature reports.
Table 3

<table>
<thead>
<tr>
<th>Carrier</th>
<th>Metal ions</th>
<th>Initial fluxes ($J_0$), µmol/m² s</th>
<th>Selectivity coefficients ($S_{Cd(II)/Pb(II)}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cd(II)</td>
<td>1.71 ± 0.01</td>
<td>Cd(II) &gt; Pb(II)</td>
</tr>
<tr>
<td></td>
<td>Pb(II)</td>
<td>0.58 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Cd(II)</td>
<td>1.79 ± 0.01</td>
<td>Cd(II) &gt; Pb(II)</td>
</tr>
<tr>
<td></td>
<td>Pb(II)</td>
<td>0.62 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Cd(II)</td>
<td>1.95 ± 0.01</td>
<td>Cd(II) &gt; Pb(II)</td>
</tr>
<tr>
<td></td>
<td>Pb(II)</td>
<td>0.96 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Cd(II)</td>
<td>2.24 ± 0.01</td>
<td>Cd(II) &gt; Pb(II)</td>
</tr>
<tr>
<td></td>
<td>Pb(II)</td>
<td>1.38 ± 0.01</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 4. 2D-view atomic force photomicrographs of PIMs with 1-alkylimidazole at a 1 mol/dm³ carrier concentration: 1-hexylimidazole (1), 1-heptylimidazole (2), 1-octylimidazole (3), and 1-decylimidazole (4).

Fig. 5. Dependence of the pKₐ 1-alkylimidazole molecules vs. permeability coefficients ($P$) for cadmium(II) and lead(II) ions transported across PIMs.
An AL with anions that penetrate the membrane in the co-transport: most effectively. These form electrically neutral ion pairs also has the highest effective pore size (Table 2). Given values of RF and %E carry 2% and 2.5% tolerance, respectively.

A PIM with 1-decylimidazole (4) is the most permeable for cadmium(II) and lead(II) ions. The membrane (4) also has the highest effective pore size (Table 2). In the case of cadmium(II) ions, the recovery factors and percent extraction are much higher than for lead(II) ions. The best result for cadmium(II) removal after 24 h was 95.5% for PIMs with 1-decyl-imidazole (4) and is the same as in the extraction.

4. Conclusions

Cadmium(II) ions can be effectively separated from equimolar aqueous solutions of lead(II) nitrates by using transport across PIMs with 1-alkylimidazoles (alkyl = hexyl, heptyl, octyl, and decyl) as well in solvent extraction in the water-methylene chloride system. The initial fluxes of cadmium(II) and lead(II) ions increase with an increase in the hydrophobicity of carrier molecules, so that the best membranes for Cd(II)–Pb(II) separation are PIMs with 1-decyl-imidazole, but for this carrier, the Cd(II)/Pb(II) separation coefficient is the lowest.

It can be assumed that more hydrophobic 1-alkylimidazoles (alkyl > hexyl) can be more effective in the separation of cadmium and lead ions in membrane techniques.

It can be expected that increasing the share of cadmium(II) tetrahedral complexes by shifting the balance of complex formation, for example, due to steric effect (e.g., by applying 1-alkyl-2-methylimidazoles) may increase the separation efficiency of Cd–Pb.

### Table 4

<table>
<thead>
<tr>
<th>Carrier/extractant</th>
<th>Metal ions</th>
<th>RF, %</th>
<th>%E, %</th>
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<tbody>
<tr>
<td>1</td>
<td>Cd(II)</td>
<td>88</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td>Pb(II)</td>
<td>46</td>
<td>71</td>
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<tr>
<td>2</td>
<td>Cd(II)</td>
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<td></td>
<td>Pb(II)</td>
<td>70</td>
<td>85</td>
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Symbols and abbreviations

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>RF, %</td>
<td>Percentage of metal ion removal, %</td>
</tr>
<tr>
<td>S, m</td>
<td>Separation coefficient</td>
</tr>
<tr>
<td>R, nm</td>
<td>Roughness, nm</td>
</tr>
<tr>
<td>E, %</td>
<td>Percentage of extraction, %</td>
</tr>
<tr>
<td>P, m/s</td>
<td>Permeability coefficient, m/s</td>
</tr>
<tr>
<td>SX, solvent extractions</td>
<td>Solvent extractions</td>
</tr>
<tr>
<td>TOPO, trioctylphosphate oxide</td>
<td></td>
</tr>
<tr>
<td>CTA, cellulose triacetate</td>
<td></td>
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<tr>
<td>CTX, atomic-force microscopy</td>
<td></td>
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<tr>
<td>AAS, atomic absorption spectroscopy</td>
<td></td>
</tr>
<tr>
<td>TCE, tri(2-chloroethyl) o-phenylenediamine</td>
<td></td>
</tr>
</tbody>
</table>

### References


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