Separation of Pd(II) and Pt(IV) ions using polymer inclusion membranes doped with alkylimidazoles

Elzbieta Radzyminska-Lenarcik, Małgorzata Ulewicz, Artur Kościuszko

Abstract

Polymer cellulose triacetate membranes doped with hydrophobic 1-alkylimidazoles as a carrier were applied for the investigation of the transport of palladium(II), and platinum(IV) ions from an aqueous chloride feed phase \((c_M = 0.001 \text{ M})\). The recovery of platinum and palladium was also carried out from the waste solution. The highest recovery coefficient of Pd(II) from the model solution was 92%, and from the waste solution – 87% using 1-hexylimidazole as carrier. The values characterizing the transport through the membrane (initial fluxes, separation coefficients, and diffusion coefficients) were calculated. The highest selectivity coefficient separation of Pd(II)/Pt(IV) (equal 4.26) was obtained using 1-hexylimidazole, while the lowest (3.27) using 1-decylimidazole. The influence of chloride ion concentration on the transport of Pd and Pt ions was also analyzed. The polymer membrane of CTA-o-NPPE with alkylimidazole were characterized by non-contact atomic force microscopy, and thermal analysis. The influence of membrane morphology on transport process was discussed.

Keywords: Polymer inclusion membrane; Separation process; Platinum and palladium; Waste solution

1. Introduction

Platinum and palladium, belonging to the platinum group metals (PGM) are shiny, silvery-white metals with similar chemical properties, high corrosion resistance even at high temperatures and high catalytic efficiency. The specific properties of these metals make them widely used in the automotive and chemical industries. These metals are also used in the production of jewelry and in medicine (dental restorative materials) [1,2]. The demand for these metals is much greater than primary production. The annual production of platinum in mines in 2019 was 186 metric tons, and palladium almost 227 metric tons. While the consumption of these metals was much greater. The world consumption of platinum in 2019 was 243 metric tons, of which 99.6 were used for exhaust treatment system, 68.0 for jewelry and 26.7 in the chemical industry. On the other hand, industrial palladium consumption was 357 tons, of which 294 tons were used in the automotive industry, 14.3 in chemistry industry, and 7.1 tons in jewelry [3,4]. As these metals are of strategic importance, the search for new methods of recovering and separating these metals from various waste materials is still a current problem.

The recovery and separation of platinum and palladium in the extraction process has been the subject of many studies [5–10]. Currently, a more promising method of separating these metals is membrane separation. Membrane techniques enabling simultaneous extraction and back
extraction of the target species at the membrane/feed and membrane/receiving solution interface, respectively. They are used for the separation of various metal ions, and their selectivity determines the type of carriers used [11–16]. This technique was also used to separate PGMs such as gold (Au), platinum (Pt), iridium (Ir), and palladium (Pd) [37–41]. There were also the first reports of the use of imidazole derivatives in the transport of these metal ions [35]. The PVA-g-(acrylic acid/N-vinyl imidazole) copolymer was used for the separation of zinc(II) and manganese(II) [26–36]. Moreover, the imidazole derivatives have also been used for transport of copper(II) ions across liquid membranes [36]. The imidazole azothiocrown derivatives were used for the separation of zinc(II), cadmium(II), and lead(II) ions [28]. Whereas for transport of palladium(II) ions from the chloride solutions in the process of transport through polymer inclusion membranes using calixarene derivatives as a carrier, the metals were removed from solutions in a series of selectivities: Au(III) > Pd(II) > Pt(IV) [25]. Considering that the demand for platinum and palladium exceeds their production from primary raw materials, the recovery of these metals from waste is a priority for the proper functioning of the economy.

In recent years, imidazole and its derivatives have been used to separate metal ions in transport processes across polymer inclusion membranes [26–36]. The imidazole azo-crown and imidazole azothiocrown derivatives were used to separate zinc(II), cobalt(II), and lead(II) ions from dilute solutions [26,27]. Also, pyrrolyl azocrown ethers in ordinary bulk membrane systems were also found to preferentially transport lead(II) from equimolar mixtures of Co(II), Ni(II), Cu(II), Zn(II), Ag(I), Cd(II), and Pb(II) ions [28]. Whereas for separation of non-ferrous metals, for example, Zn(II), Cd(II), Co(II), Ni(II), Cu(II) were used 1-alkylimidazoles [29–33] and 1-octyl-4-methylimidazole [34]. The 1-alkylimidazolium was also used for separation of zinc(II) and manganese(II) [35]. The PVA-g-(acrylic acid/N-vinyl imidazole) was used also for transport of copper(II) ions across liquid membranes [36]. Moreover, the imidazole derivatives have also been used for transport of Pt, Ir, and Pd ions in the solvent extraction process [37–41]. There were also the first reports on the use of imidazole derivatives in transport of metal ions across liquid membranes. Yoshida et al. [41] investigated the SLM system for the selective separation of Pt(IV) from palladium(II) using imidazolium-based IL 1-octyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide. The initial flux and separation factor of Pt(IV) from Pd(II) were found to significantly depend on the composition of the receiving solution. This carrier allows 93% of the Pt(IV) to be transported to the receiving solution, while most of the Pd(II) remains in the feed solution.

The aim of this work was to check the possibility of separation and recovery of Pd(II) from equimolar chloride mixtures of Pd(II)-Pt(IV) ions from aqueous solutions using PIMs doped with hydrophobic 1-alkyl-imidazoles (alkyl = 1-hexyl, 1-octyl, 1-decyl). This metals (Pd(II)-Pt(IV)) was selected because it is present in diesel oxidation catalyzed and catalyzed diesel particulate filter as well as in catalytic converters used in the chemical industry (isomerization and hydrogenation reactions). The effects of chloride ions concentration in feed phase upon the efficiency and selectivity Pd(II) ions transport is reported. Another aim was to determine the impact of the dependence of the physical properties of membranes on efficiency in the separation of Pd(II) and Pt(IV) ions.

2. Experimental

2.1. Reagents and apparatus

Platinum chloride PdCl₂ and platinum chloride PtCl₄ (both 99% pure, Pol-Aura, Zabrze, Poland), manganese sulfate MnSO₄·H₂O, chromium chloride CrCl₃·6H₂O, nickel chloride NiCl₂·6H₂O, iron chloride FeCl₃, hydrochloric acid HCl, thiourea, and sodium chloride NaCl (analytically pure, 35%, Chempur, Piekary Slaskie, Poland), were used to prepare the solutions. The 1-alkylimidazolide (Fig. 1) was synthesized by A. Skrzypczak (Poznan University of Technology, Poznan, Poland). Cellulose triacetate (CTA), o-nitrophenyl pentyl ether (o-NPPE), and methylene chloride (all analytically pure, Fluka, Busch, Switzerland) were used without further purification. The pH-meter (PHM 250 Radiometer, Copenhagen, Denmark)) and atomic absorption spectrometer AAS 240FS (Agilent, Santa Clara, CA, USA) were used to measure the pH value and the metal ions concentrations, respectively. Measurements were made for the following emission lines of the analyzed elements Pd 247.6 nm and Pt 265.9 nm. The pH-meter was calibrated using commercial buffer solutions (Radiometer, Copenhagen, Denmark) having a pH of 4.01 ± 0.01 and 7.00 ± 0.01, respectively.

2.2. Polymer inclusion membrane preparation

Polymer inclusion membranes were prepared as reported in the earlier paper [30,31]. A solution of cellulose triacetate as the support, o-nitrophenyl pentyl ether as the plasticizer, and 1-alkylimidazole 1 – 3 as the ion carriers in dichloromethane as the organic solution was prepared. A specified portion of this organic solution was poured into a membrane mold comprised of a 9.0 cm glass ring attached to a plate glass with cellulose triacetate – dichloromethane glue. After evaporation of the solvent overnight at room temperature the resulting membrane was peeled off.

![Fig. 1. The carrier (1-alkylimidazolide) molecule.](image-url)
from the glass plate by immersion in cold water. Then the membrane was soaked for 12 h in distilled water to ensure its homogeneity. The density of plasticizer, that is, \(\text{o-nitrophenyl pentyl ether} \) was 1.085 g/cm\(^3\). The aqueous solutions were prepared with double distillation water, which conductivity was 0.1 \(\mu\)S/m. The membrane film (surface area of 4.9 cm\(^2\)) was tightly clamped between two cell compartments. The membrane composition: 16% CTA, 42% 1-alkylimidazole \(1-3\) and 42% plasticizer.

The thickness of the PIM was measured using a digital micrometer (Panametrics\textsuperscript{a} Magna-Mike\textsuperscript{a} 8500, San Diego, CA, USA) with an accuracy of 0.1 \(\mu\)m. A surface characterization study of the polymer inclusion membranes was performed by atomic force microscopy (AFM) using Atomic-Force MultiMode Scanning Probe Microscope IIIa (Digital Instruments, Veeco Metrology Group, Santa Barbara, CA, USA). Membrane spectrophotometric studies were performed using a Bruker Invenio R Infrared Spectrophotometer (Ettlingen, Germany) equipped with a broadband BeamSplitter and the ATR Quest attachment by Specac (Orpington, Great Britain). The research was carried out in the wavenumber range from 3,750 to 300 cm\(^{-1}\). The research was carried out in the wavenumber range from 3,750 to 300 cm\(^{-1}\). The Netzsch TG 209 F1 Libra thermogravimetric analyzer (Selb, Germany) was used in thermogravimetric studies.

2.3. Transport studies

Transport experiments were carried out in the system described precisely in earlier papers \([30,31]\) at 20°C \(\pm 0.2\)°C. The feed phase was an aqueous solution of Pd(II) and Pt(IV) ions with a concentration of \(c_{0,\text{M}} = 0.001\) M each. The feed phase pH was kept constant (pH = 2.0) except in the experiments when the effect of the chloride concentration was investigated (paragraph 3.2). The receiving phase was 0.1 M thiourea in 0.1 M HCl. At the receiving phase, metal ions concentrations were measured. A well-known disadvantage of the tested system is the high consumption of thiourea during the process due to its oxidation. This is a big problem due to the high cost of thiourea. However, Zhang et al. \([42]\) report that a mixture of thiourea, thiocyanate and iron sulfate reduces the consumption of thiourea and hence the cost of the process with a similar comparable process efficiency. Therefore, we assume that in the case of an effective separation process of the investigated metal ions, modifying the receiving phase may be the next step.

The membrane film (at surface area of 4.9 cm\(^2\)) was tightly clamped between two cell compartments. Both, that is, the source and receiving aqueous phases (45 cm\(^3\) each) were mechanically stirred at 600 rpm. Metal concentration was determined by withdrawing small samples (0.1 cm\(^3\) each) of the aqueous receiving and feed phase at different time intervals and analyzing by an atomic absorption spectroscopy method (AAS Spectrometer, Solaar 939, Unicam).

2.4. Parameters characterizing the transport process

The kinetics of metal ions transport across membranes was described by equation:

\[
\ln \frac{c}{c_i} = -kt
\]

(1)

where \(c\) and \(c_i\) are the metal ions concentration (M) in the feed phase at a given time, and the initial metal ions concentration, respectively; \(k\) is the first-order rate constants (s\(^{-1}\)). \(t\) is the time of transport (s) \([43,44]\).

In order to calculate the value of the rate constants \(k\), \(\ln(c_{\text{t},\text{M}}/c_{\text{i},\text{M}})\) vs. time \(t\) was plotted.

The initial flux \(J_0\) is defined as:

\[
J_0 = \frac{V}{A} \cdot c_i
\]

(2)

where \(V\) is the volume of the aqueous feed phase (m\(^3\)) and \(A\) is an effective area of the membrane (m\(^2\)).

The selectivity coefficient \(S_{M1,M2}\) was defined as the ratio of initial fluxes for \(M_1\) and \(M_2\) metal ions, respectively:

\[
S_{M1,M2} = \frac{J_{M1}}{J_{M2}}
\]

(3)

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

\[
\text{RF} = \frac{c_i - c}{c_i} \times 100\%
\]

(4)

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

3. Results and discussion

3.1. Pd(II) and Pt(IV) ions transport across PIMs doped \(1-3\)

Flat sheet PIMs doped with alkylimidazoles \((1-3)\) were used to investigated transport of Pd(II) and Pt(IV) ions. Because in preliminary experiments, no metal ion transport (for more than 24 h of continuous process run) was observed when using a membrane containing only a support (CTA) and a plasticizer (o-NPPE). Based on our previous research \([30-34]\), in this experiment used membranes containing 42% 1-alkylimidazole, 16% CTA and 42% of plasticizer.

The transport of Pd(II) and Pt(IV) ions into the receiving phase across PIMs with 1-alkylimidazole \((1-3)\) was carried out. Generally, the content of metal ions in the feed phase decreases, while it increases in the receiving phase. Fig. 2 shows the changes in Pd(II) and Pt(IV) concentration over time in the feed phase.

As shown in Fig. 2, for all carriers used the concentration of Pd(II) ions in the feed phase decrease faster than Pt(IV). Both Pd(II) and Pt(IV) ions in the aqueous phase in the presence of chloride ions form a series of anionic chloring-complexes of the general formula \([\text{MCl}_n]^n-\), where \(n\) changes from 1 to \(N\) (\(N = \) maximum coordination number). At the pH = 2, Pd(II) ions form 4-coordinate, flat-square complexes of the formula \([\text{PdCl}_4]^2-\), while Pt(IV) ions form 6-coordination octahedral complexes (\([\text{PtCl}_6]^2-\)) (Fig. 3) \([45,46]\).

In an acidic medium, the carrier molecules (L-alkylimidazoles) show basic properties to attach a proton according to the equation:
The protonated form of the carrier (HL) can form salts with the Pd(II) or Pt(IV) chloro-complexes:

\[ L + H^+ = [HL]^+ \]  

(5)

The initial fluxes and selectivity coefficients of Pd(II) ions transport across PIMs doped with 1-alkylimidazole (1–3) from aqueous feed phase containing equimolar mixture of Pd(II)-Pt(IV) ions is shown in Table 1.

As seen from Table 1, the palladium(II) ions were transported with a highest rate which can be explained by the simpler structure of their chloro-complexes. The initial flux values of metal ions transport also depend on the type of carrier used and decreases in the order 1 < 2 < 3. The observed trend decreases with an increase in the hydrophobicity of the carrier (with an increase in the length of the –R groups in the carrier molecule). The maximum value of the initial flux for Pd(II) ions was equal to 9.8·10^{-6} mol/m^2s (for 1). The flat-square Pd(II) chloro-complexes are more easily transported by PIMs doped alkylimidazole than the octahedral Pt(IV) complexes. The initial fluxes of metal ions transport are very low, which means that membranes of this type have no chance for industrial application, but they can be successfully used in laboratory tests of metal ion separation with the use of new carriers.

As the hydrophobicity of the carrier increases, the separation coefficients \( S_{\text{Pd(II)/Pt(IV)}} \) decrease from 4.26 for carrier 1 to 3.27 for 3. The Pd(II) and Pt(IV) recovery coefficients decrease with the increase of the hydrophobicity of the carrier molecule in the series 1 > 2 > 3. The highest values of the Pd and Pt recovery coefficients were obtained in the case of 1 as the carrier in PIMs, they are 92% and 21%, respectively.

### Table 1

<table>
<thead>
<tr>
<th>Carrier</th>
<th>Metal ions</th>
<th>Initial flux ( J_0 \times 10^6 ), mol/m^2s</th>
<th>Selectivity coefficient ( S_{\text{Pd(II)/Pt(IV)}} )</th>
<th>Recovery coefficient after 24 h transport, RF, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pd(II)</td>
<td>9.8</td>
<td>4.26</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td>Pt(IV)</td>
<td>2.3</td>
<td></td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>Pd(II)</td>
<td>5.4</td>
<td>3.86</td>
<td>87</td>
</tr>
<tr>
<td>2</td>
<td>Pt(IV)</td>
<td>1.7</td>
<td></td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>Pd(II)</td>
<td>3.6</td>
<td></td>
<td>81</td>
</tr>
<tr>
<td>3</td>
<td>Pt(IV)</td>
<td>1.1</td>
<td>3.27</td>
<td>15</td>
</tr>
</tbody>
</table>

![Fig. 2. Kinetic curves for metal ions transport of Pt(IV) ions (a) and Pd(II) ions (b) from equimolar mixture of metal ions across PIMs with 1-hexylimidazole (1), 1-octylimidazole (2), and 1-decylimidazole (3); \( c_M = 0.001 \) M each, pH = 2.0.](image)

![Fig. 3. Structure of the Pd(II) (a) and Pt(IV) (b) chloro-complexes.](image)
The highest values of the separation and recovery coefficients were obtained when 1-hexylimidazole was used as a carrier in the membrane, therefore membranes with 1 as a carrier were used for further research.

3.2. Influence of chloride ions concentration in the feed phase on Pd(II) and Pt(IV) ions transport across PIM doped 1

In the next step, the influence of chloride ions concentration in the feed phase on the transport of metal ions across PIMs doped 1 was investigated. The parameters of Pd(II) ions transport across PIMs doped with 1-hexylimidazole (1) depending on the concentration of chloride ions in the feed phase are summarized in Table 2.

As seen from Table 2, the initial fluxes values of both ions insignificantly increase upon increasing chloride ion concentration in the feed phase. This increase is more evident in the case of palladium ions. However, the value of the Pd/Pt separation coefficient is highest in a solution containing no additional chloride ions and is 4.26.

3.3. PIMs doped 1-hexylimidazole 1 characterization

As demonstrated in a number of papers [31,32,47–50], the microstructure of the membrane has an impact on the transport process. For this reason, studies were carried out using an AFM. The thermal stability of the membrane was assessed. The studies concerned the CTA-o-NPPE membrane containing 1-hexylimidazole as a carrier. The Fourier transform infrared spectroscopy (FT-IR) spectrum was also discussed.

3.3.1. Microscopic research

The microscopic images of the CTA-o-NPPE – 1-hexylimidazole membrane is shown on Fig. 4. The membranes had dense and homogeneous structures. Moreover, the images showed visible roughness of film surfaces. Carrier could crystallize in the membrane. Its molecules migrated to the membrane surface, causing its roughness and porosity.

The roughness ($R_q$) and effective pore sizes of the membrane was calculated using the NanoScope v5.12 AFM image processing program from AFM images, and they are shown in Table 3 together with average thickness and the membrane’s tortuosity determined from the dependence developed by Wolf and Strieder [51]:

$$\tau = 1 - \ln \varepsilon \quad (7)$$

3.3.2. FT-IR analysis of the PIM doped 1-hexylimidazole

The membrane with 1-hexylimidazole after transport Pd(II) and Pt(IV) ions was analyzed using FT-IR spectroscopy. The spectra are presented in Fig. 5.

The interpretation of IR spectra was made using IRPal 2.0 program. Table 4 shows indicative bonds of signals recorded in Fig. 4.

3.3.2. Thermal stability of PIM doped 1-hexylimidazole

The CTA-o-NPPE membrane with 1-hexylimidazole was also tested for their thermal stability. About 20 mg of samples (two) were heated at 10°C/min under nitrogen from

**Table 2**

Initial fluxes, selectivity order and selectivity coefficients for competitive transport of Pd(II) and Pt(IV) ions across PIMs doped with 1-hexylimidazole (1); feed phase: 0.001 M each metal ion, receiving phase: 0.1 M thiourea in 0.1 M HCl

<table>
<thead>
<tr>
<th>Concentration of NaCl, M</th>
<th>Metal ions</th>
<th>Initial flux $J_x \times 10^6$, mol/m²×s</th>
<th>Selectivity coefficient $S_{Pd(II)/Pt(IV)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Pd(II)</td>
<td>9.8</td>
<td>4.26</td>
</tr>
<tr>
<td></td>
<td>Pt(IV)</td>
<td>2.3</td>
<td>3.96</td>
</tr>
<tr>
<td>0.5</td>
<td>Pd(II)</td>
<td>10.5</td>
<td>4.04</td>
</tr>
<tr>
<td></td>
<td>Pt(IV)</td>
<td>2.7</td>
<td>4.15</td>
</tr>
<tr>
<td>1.0</td>
<td>Pd(II)</td>
<td>10.8</td>
<td>4.15</td>
</tr>
<tr>
<td></td>
<td>Pt(IV)</td>
<td>2.6</td>
<td>3.96</td>
</tr>
<tr>
<td>1.5</td>
<td>Pd(II)</td>
<td>10.8</td>
<td>4.15</td>
</tr>
<tr>
<td></td>
<td>Pt(IV)</td>
<td>2.6</td>
<td>4.15</td>
</tr>
</tbody>
</table>
25°C to 800°C. Fig. 6 shows thermograms of CTA-o-NPPE membranes with and without 1-hexylimidazole (I) before and after ion transport.

As seen from Fig. 5, the degradation of CTA-o-NPPE membrane with 1-hexylimidazole proceeds in two steps. The ranges of decomposition temperatures and the corresponding weight losses are summarized in Table 5.

PIM made of CTA-o-NPPE with 1-hexylimidazole shows high thermal stability (up to approx. 150°C) (Table 5). For these membranes, the first step of degradation occurs at 249.8°C–277.0°C, while the second one at 343.4°C–367.0°C. The corresponding weight losses are within ranges of 28.20%–80.61% and 3.02%–44.33%, respectively. The degradation of a CTA membrane occurs in two steps; the first one over a range of 292°C–320°C (main step) and the other one over a range of 450°C–476°C (the charring of products) [50,52,53].

3.4. Membrane diffusion coefficients of Pd(II) and Pt(IV) ions across PIM with 1-hexylimidazole

In Fig. 7, the correlation graphs [M 2+]0–[M2+]t vs. time of metal ions transport across PIM doped with 1-hexylimidazole is presented.

The diffusion coefficients of metal ions (Do, Do, n) were calculated from the equation:

\[
D_0 = \frac{d_0}{\Delta \alpha}
\]

where \(D_0\), \(D_{\alpha}\) – the diffusion coefficient and the normalized diffusion coefficient [48], respectively, \(d_0\) – the thickness of the membrane (0.0028 m), \(\epsilon\) – porosity and \(\tau\) – tortuosity, and \(\Delta\) could be evaluated by plotting \([M^{n+}]_0–[M^{n+}]_t\) vs. time.

Obtained values of diffusion coefficients are presented in Table 6.

Values of diffusion coefficient determined in this study are comparable with presented in literature data for different membranes are in the range from 10^{-12} to 10^{-6} cm^2/s and show that limiting step of the process is the transfer of metal-carrier compound across membrane barrier. The value of the diffusion coefficient of M-carrier salts (Table 6) is smaller than the value of 1.5·10^{-7} cm^2/s reported for the Pb(II) complex with the di(2-ethylhexyl)phosphoric acid (D2EHPA) in PIMs reported by Salazar-Alvarez et al. [47]. This may be due to the stiffness and inelasticity of the matrix. Taking into account the viscosity of the plasticizer used (o-NPPE; 7.3 cp), which was lower than that of the tris(2-butoxyethyl) phosphate (TBEP; 10.2 cp) used in the work [47], it can be assumed that the diffusion rate depends on the nature of the diffusing substances. Thus, the rate of transport of Pd(II) and Pt(IV) ions across PIMs doped with 1-hexylimidazole is determined by the diffusion rate of the M-carrier salts across the membrane.

3.5. Recovery of Pd(II) and Pt(IV) from model waste solution

Spent catalysts from automobile industry contain environmentally critical and economically valuable metals such as Pt, Pd, Fe, Ni, Mn, and Cr. The next step of our work was to investigate the possibility of selective separation and recovery of palladium (Pd) and platinum (Pt) from the model solution with the composition corresponding to the composition of the solution after leaching of the spent car catalyst. According to Reddy et al. [9], a typical solution after leaching of waste catalysts with hydrochloric acid contains (mg/L): Pd-150, Pt-550, Mn-500, Ni-1100, Fe-1500, Cr-100. For the next experiment, a solution diluted 1000 times...
with respect to the composition given in the literature [9] was prepared and the pH = 2 was adjusted with HCl. This solution was the feed phase. In order to investigate the possibility of Pd and Pt separation, a CTA membrane with 1-hexylimidazole as a carrier was used. The receiving phase was 0.1 M thiourea in 0.1 M HCl. Table 7 shows the recovery coefficient of metal ions from model e-waste solution after 24 h transport.

At pH 2 in the feed phase, Mn(II) ions oxidize to MnO$_4^-$, Fe(III) forms a complex [FeCl(H$_2$O)$_5$]$^+$ [54], Ni(II), and Cr(III) form Ni$^{2+}$, Cr$^{3+}$ cations [54], while Pd(II) and Pt(IV) form chloro-complexes with the formulas PdCl$_4^{2-}$ and PtCl$_6^{2-}$, respectively [45,46].

As can be seen from the data in Table 7, only Pd(II), Pt(IV) and Mn(II) ions are transported across this type of membrane. Fe(III), Ni(II) and Cr(III) ions remain in the feed phase.

This result confirms that at pH 2 of the feed phase, anions are transported through the PIM which form salts with the imidazole cation [Eqs. (5) and (6)]. Pd(II) ions are most easily transported. 1-Hexylimidazole as a carrier in PIMs can be used for the selective separation of noble metal ions from leach solutions of spent automotive catalysts, especially for palladium separation.

### 4. Conclusion

The recovery of platinum and palladium from waste is particularly important due to the fact that the demand for these metals exceeds their production from primary raw materials. Based on the conducted research, it was shown that the proposed hydrophobic alkyl imidazole derivatives could be successfully used for the separation of Pd(II) and Pt(IV) ions from the acidic solutions. Polymer inclusion membranes doped with 1-hexylimidazoles enable the recovery of palladium and platinum both from their mixtures in model solutions and from waste, for example, from spent car catalysts. The palladium recovery coefficient from Pd-Pt model solutions and from leach solutions of spent car catalysts is 92% and 87%, respectively; while platinum – 21% and 15%, respectively. The selectivity coefficient of Pd(II) to Pt(IV) decreases in a number of used carriers: 1-hexylimidazole > 1-octylimidazole > 1-decylimidazole. The highest value equal 4.26 was obtained by using 1-hexylimidazole.

The rate of transport of Pd(II) and Pt(IV) ions across PIMs doped with 1-hexylimidazole is determined by the diffusion rate of the M-carrier salts across the membrane. The value of the diffusion coefficient of M-carrier salts are $5.027 \times 10^{-8}$ and $4.582 \times 10^{-10}$ for Pd(II) and Pt(II), respectively. These values are comparable with presented in literature data for different membranes.

### Table 5
Degradation temperatures, weight losses and residual mass of investigated PIMs

<table>
<thead>
<tr>
<th>Composition of membrane</th>
<th>First-step</th>
<th>Second-step</th>
<th>Residual mass, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temp., °C</td>
<td>Weight loss, %</td>
<td>Temp., °C</td>
</tr>
<tr>
<td>CTA-o-NPPE</td>
<td>277.0</td>
<td>80.61</td>
<td>367.8</td>
</tr>
<tr>
<td>CTA-o-NPPE</td>
<td>268.0</td>
<td>28.20</td>
<td>343.4</td>
</tr>
<tr>
<td>1-hexylimidazole before process</td>
<td>249.8</td>
<td>44.91</td>
<td>359.6</td>
</tr>
</tbody>
</table>

### Table 6
Diffusion coefficients for competitive transport of Pd(II) and Pt(IV) ions through PIM doped with 1-hexylimidazole (I)

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>$\Delta r$, m</th>
<th>$D_0$, cm$^2$/s</th>
<th>$D_{\text{cm}}$, cm$^2$/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(II)</td>
<td>$10^{13}$</td>
<td>$5.027 \times 10^{-10}$</td>
<td>$2.64 \times 10^{-9}$</td>
</tr>
<tr>
<td>Pt(IV)</td>
<td>$10^{42}$</td>
<td>$4.582 \times 10^{-10}$</td>
<td>$3.71 \times 10^{-11}$</td>
</tr>
</tbody>
</table>

### Table 7
Recovery coefficient (RF) of metal ions from model e-waste solution after 24 h transport across PIMs doped with 1-hexylimidazole (I); feed phase: 0.15 mg/L Pd(II), 0.55 mg/L Pt(IV), 0.50 mg/L Mn, 1.0 mg/L Ni(II), 1.5 mg/L Fe(III), 0.10 mg/L Cr(III); receiving phase: 0.1 M thiourea in 0.1 M HCl

<table>
<thead>
<tr>
<th>Metals</th>
<th>RF, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(II)</td>
<td>76</td>
</tr>
<tr>
<td>Pt(IV)</td>
<td>15</td>
</tr>
<tr>
<td>Mn(II)</td>
<td>30</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>–</td>
</tr>
<tr>
<td>Fe(III)</td>
<td>–</td>
</tr>
<tr>
<td>Cr(III)</td>
<td>–</td>
</tr>
</tbody>
</table>

Fig. 7. Relation of $[M^{n+}] - [M^{n+}]$ plotted vs. time for Pd(II) and Pt(IV) ions, transport across PIMs doped 1-hexylimidazole.