



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

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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 ($c_M = 0.001$ 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 alkyylimidazole 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

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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 metals [16–25] in laboratory. Currently, PIMs are only used on a laboratory scale for the separation of different metal ions. Platinum(IV) ions were transported through PIM when using as ion carriers the tricaprilmethylammonium chloride (Aliquat 336) [17,18], di(2-ethylhexyl)phosphoric acid (D2EHPA) with tri-*n*-octylamine (TOA) [19]. On the other hand, palladium(II) ions from the hydrochloric acid solution were transported through polymer membranes containing Cyanex 471X, tricaprilmethylammonium thiosalicylate as well as trihexyl(tetradecyl)phosphonium chloride and bromide (CYPHOS IL 101 and 102) and trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate [20–23]. While, for selective transport of platinum(IV) and palladium(II) across a supported liquid membrane (SLM) we use as carrier alkylated derivative of 8-quinolinol – LIX 26 (alkyl substituted 8-hydroxyquinoline) [24]. This carrier caused the Pt(IV) to be completely removed from the weakly acidic solutions, but the Pd(II) to be completely retained in the organic phase. Also, Au(III), Pt(IV), Pd(II) ions were separated 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 process across polymer inclusion membrane [26–36]. The imidazole azocrown and imidazole azothiocrown derivatives were used to separate of Zn(II), Cd(II), and Pb(II) ions from dilute solutions [26,27]. Also pyrrole azocrown ethers in ordinary bulk membrane system were also found to preferentially transport lead(II) from equimolar mixture of Co(II), Ni(II), Cu(II), Zn(II), Ag(I), Cd(II), and Pb(II) ions [28]. Whereas for separation non-ferrous metal, for example, Zn(II), Cd(II), Co(II), Ni(II), Cu(II) were use 1-alkylimidazoles [29–33] and 1-octyl-4-methylimidazole [34]. The 1-alkylimidazole was also used for separation of zinc(II) and manganese(II) [35]. The PVA-g-(acrylic acid/*N*-vinyl imidazole) was use also for transport of Cu(II) ions across liquid membrane [36]. Moreover the imidazole derivatives have also been used for Pt, Ir and Pd ion separation in the solvent extraction process [37–41]. There were also the first reports on the use of imidazole derivatives in the transport PGM metals across liquid membrane. Yoshida et al. [41] investigated the SLM system for the selective separation of platinum(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 catalyst 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

Palladium 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-alkylimidazole (Fig. 1) were 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

No.	R-	
1	–C ₆ H ₁₃	1-hexylimidazole
2	–C ₈ H ₁₇	1-octylimidazole
3	–C ₁₀ H ₂₁	1-decylimidazole

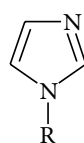


Fig. 1. The carrier (1-alkylimidazole) molecule.

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, *o*-nitrophenyl pentyl ether was 1.085 g/cm³. The aqueous solutions were prepared with double distillation water, which conductivity was 0.1 μS/m. The membrane film (surface area of 4.9 cm²) 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® Magna-Mike® 8500, San Diego, CA, USA) with an accuracy of 0.1 μm. 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 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 ± 0.2°C. The feed phase was an aqueous solution of Pd(II) and Pt(IV) ions with a concentration of $c_{0,M} = 0.001$ 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 cm²) was tightly clamped between two cell compartments. Both, that is, the source and receiving aqueous phases (45 cm³ each) were mechanically stirred at 600 rpm. Metal concentration was determined by withdrawing small samples (0.1 cm³ 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:

$$\ln \frac{c}{c_i} = -kt \quad (1)$$

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), $\ln(c_{0,M}/c_M)$ vs. time (t) was plotted.

The initial flux (J_0) is defined as:

$$J_0 = -\frac{V}{A} \cdot k \cdot c_i \quad (2)$$

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

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

$$S_{M_1/M_2} = \frac{J_{M_1}}{J_{M_2}} \quad (3)$$

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

$$\text{RF} = \frac{c_i - c}{c_i} \times 100\% \quad (4)$$

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

3. Results and discussion

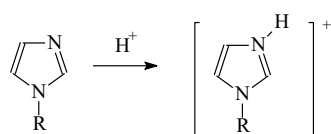
3.1. Pd(II) and Pt(IV) ions transport across PIMs doped **1**–**3**

Flat sheet PIMs doped with alkylimidazoles (**1**–**3**) were used to investigate 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 chloro-complexes of the general formula $[MCl_n]^{n-}$, 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 $[PdCl_4]^{2-}$, while Pt(IV) ions form 6-coordinate octahedral complexes ($[PtCl_6]^{2-}$) (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:

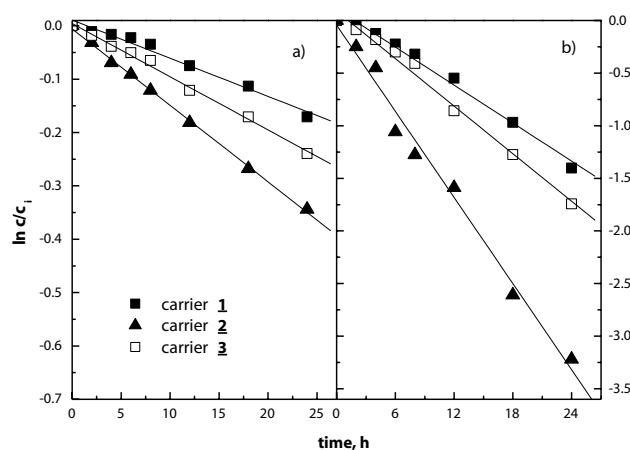
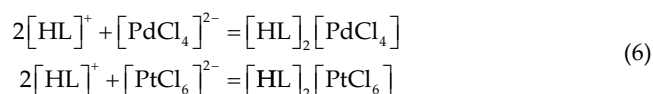


Fig. 2. Kinetic curves for metal ions transport of Pt(IV) ions (a) and Pd(II) ions (b) from equimolar mixture of metal ions across PIMs with 1-hexylimidazole (**1**), 1-octylimidazole (**2**), and 1-decylimidazole (**3**); $c_M = 0.001$ M each, $\text{pH} = 2.0$.

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 $\mathbf{1} < \mathbf{2} < \mathbf{3}$. 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 $9.8 \cdot 10^{-6}$ mol/m²s (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 $\mathbf{1} > \mathbf{2} > \mathbf{3}$. 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.

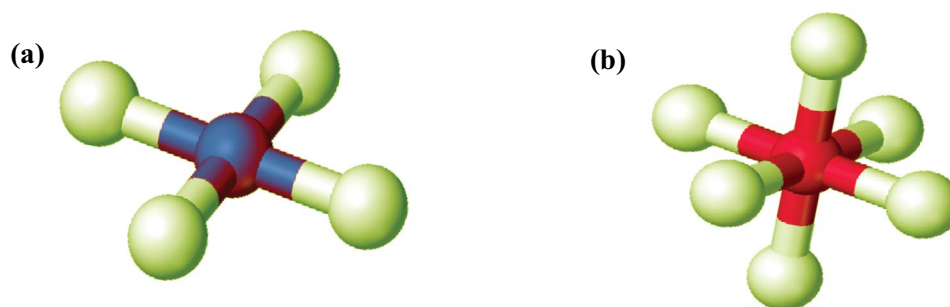


Fig. 3. Structure of the Pd(II) (a) and Pt(IV) (b) chloro-complexes.

Table 1

Initial fluxes, selectivity order and selectivity coefficients for competitive transport of Pd(II) and Pt(IV) ions across PIMs doped with 1-alkylimidazole (**1** – **3**); feed phase: 0.001 M each metal ion, receiving phase: 0.1 M thiourea in 0.1 M HCl

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

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 insignificant 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 crystallise 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 v.5.12 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]:

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

Concentration of NaCl, M	Metal ions	Initial flux $J_0 \times 10^6$, mol/m ² ×s	Selectivity coefficient $S_{Pd(II)/Pt(IV)}$
–	Pd(II)	9.8	4.26
	Pt(IV)	2.3	
0.5	Pd(II)	10.5	3.96
	Pt(IV)	2.6	
1.0	Pd(II)	10.9	4.04
	Pt(IV)	2.7	
1.5	Pd(II)	10.8	4.15
	Pt(IV)	2.6	

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

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 indicated 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

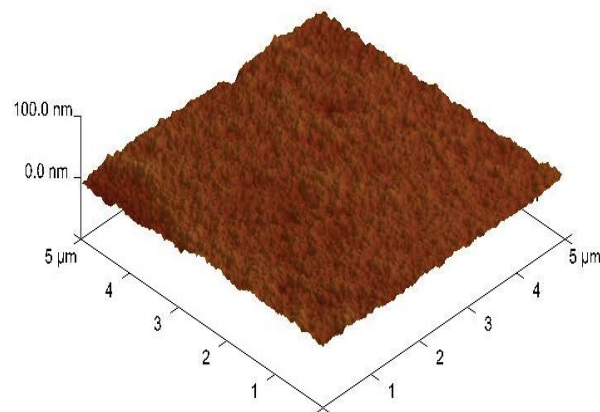


Fig. 4. Three-dimensional (3D) PIM image (CTA-*o*-NPPE – 1-hexylimidazole) from the atomic force microscope (AFM). Scanning area: 5 μm × 5 μm.

Table 3

AFM characterization parameters for PIM doped with 1-hexylimidazole

Average thickness, μm	Effective pore size, μm	Tortuosity	Roughness (R_q), nm
28	0.052 ± 0.002	2.27	5.68 ± 0.05

25°C to 800°C. Fig. 6 shows thermograms of CTA-*o*-NPPE membranes with and without 1-hexylimidazole (1) 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.

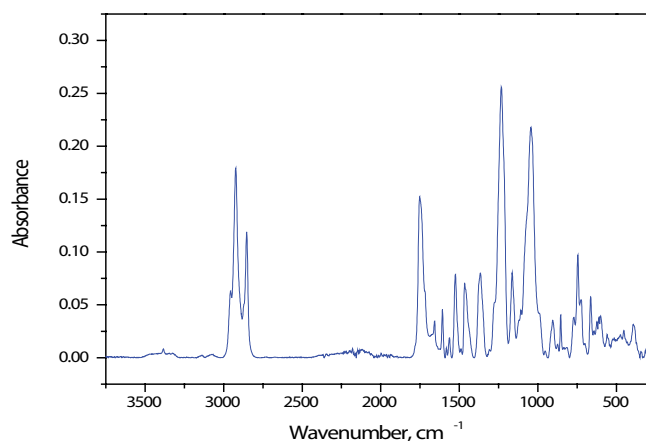


Fig. 5. FT-IR spectra of PIM doped 1-hexylimidazole after transport of Pd(II) and Pt(IV) ions.

Table 4
Indicated bonds in PIM doped 1-hexylimidazole

Range of wavenumbers, cm ⁻¹	Indicated bonds
2,925–2,750	C–H, N–H, O–H
1,755–1,450	C–C, C–O, C–N
1,660–1,490; 1,390–1,260	N–O
1,635–1,470	C=C, C=N (imidazole ring)
870–840	C–N
770–665	C–H
460–390	Chloride

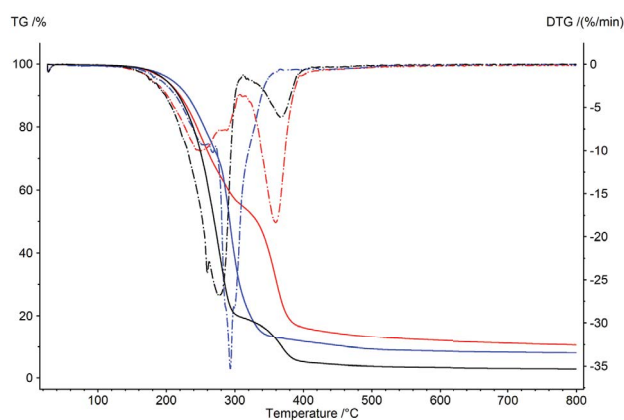


Fig. 6. Thermogravimetry/Differential thermal analysis (TG/DTA) curves for membranes CTA-*o*-NPPE (black line); CTA-*o*-NPPE with 1-hexylimidazole before process (blue line) and CTA-*o*-NPPE with 1-hexylimidazole after process (red line).

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 $[M^{2+}]_0 - [M^{2+}]_t$ vs. time of metal ions transport across PIM doped with 1-hexylimidazole is presented.

The diffusion coefficients of metal ions ($D_o, D_{o,n}$) were calculated from the equation:

$$D_o = \frac{d_o}{\Delta_o} \quad D_{o,n} = D_o \cdot \left(\frac{\varepsilon}{\tau} \right) \quad (8)$$

where $D_o, D_{o,n}$ – the diffusion coefficient and the normalized diffusion coefficient [48], respectively, d_o – the thickness of the membrane (0.0028 m), ε – porosity and τ – tortuosity, and Δ_o could be evaluated by plotting $[M^{2+}]_0 - [M^{2+}]_t$ 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} cm²/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 $1.5 \cdot 10^{-7}$ cm²/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-1000, Fe-1500, Cr-100. For the next experiment, a solution diluted 1000 times

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

Composition of membrane	First-step		Second-step		Residual mass, %
	Temp., °C	Weight loss, %	Temp., °C	Weight loss, %	
CTA- <i>o</i> -NPPE	277.0	80.61	367.8	16.37	3.02
CTA- <i>o</i> -NPPE 1-hexylimidazole before process	268.0	28.20	343.4	44.33	8.13
CTA- <i>o</i> -NPPE 1-hexylimidazole after process	249.8	44.91	359.6	44.33	10.70

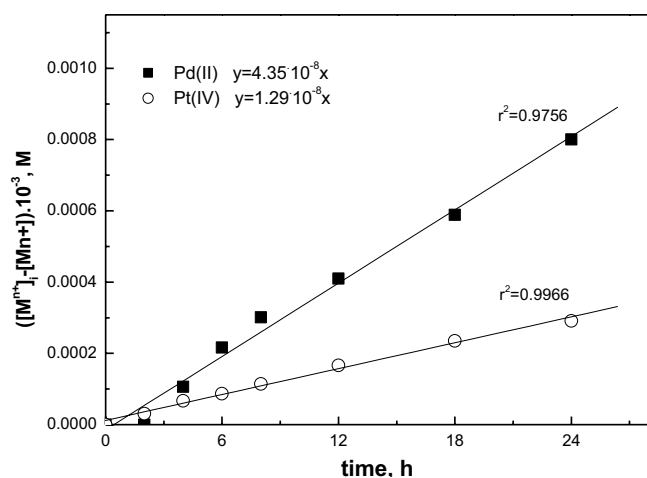


Fig. 7. Relation of $[M^{n+}]_t - [M^{n+}]_0$ plotted vs. time for Pd(II) and Pt(IV) ions, transport across PIMs doped 1-hexylimidazole.

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

Metal ion	Δ_{σ} , s/m	D_{σ} , cm ² /s	$D_{\sigma, \sigma'}$, cm ² /s
Pd(II)	10 ^{8.15}	5.027·10 ⁻⁰⁸	2.64·10 ⁻⁰⁹
Pt(IV)	10 ^{6.42}	4.582·10 ⁻¹⁰	3.71·10 ⁻¹¹

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 MnO₄⁻, Fe(III) forms a complex [FeCl(H₂O)₅]⁺ [54], Ni(II), and Cr(III) form Ni²⁺, Cr³⁺ cations [54], while Pd(II) and Pt(IV) form chloro-complexes with the formulas PdCl₄²⁻ and PtCl₆²⁻, 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

Table 7
Recovery coefficient (RF) of metal ions from model e-waste solution after 24 h transport across PIMs doped with 1-hexylimidazole (1); 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

Metals	RF, %
Pd(II)	76
Pt(IV)	15
Mn(II)	30
Ni(II)	–
Fe(III)	–
Cr(III)	–

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 5.027·10⁻⁸ and 4.582·10⁻¹⁰ for Pd(II) and Pt(II), respectively. These values are comparable with presented in literature data for different membranes.

References

- [1] Y. Seo, S. Morimoto, Analyzing platinum and palladium consumption and demand forecast in Japan, *Resources*, 6 (2017) 61, doi: 10.3390/resources6040061.
- [2] Platinum Metals Review, A Quarterly Journal of Research on the Platinum Group Metals and Developments in their Application in Industry, Johnson Matthey Plc, London, UK, 2012. Available at: <http://www.platinummetalsreview.com/>
- [3] <https://www.statista.com/statistics/693866/platinum-consumption-worldwide-by-industry/>
- [4] <https://www.statista.com/statistics/1170691/mine-production-of-platinum-worldwide/>
- [5] M.K. Jha, D. Gupta, J.-c. Lee, V. Kumar, J. Jeong, Solvent extraction of platinum using amine based extractants in different solutions: a review, *Hydrometallurgy*, 142 (2014) 60–69.
- [6] P. Yu, K. Huang, C. Zhang, K. Xie, X. He, H. Liu, One-step separation of platinum, palladium, and rhodium: a three-liquid-phase extraction approach, *Ind. Eng. Chem. Res.*, 50 (2011) 9368–9376.
- [7] H. Tateno, K.C. Park, T. Tsukahara, Direct extraction of platinum group metals from nitric acid solution using the phase transition of poly(*N*-isopropylacrylamide), *Chem. Lett.*, 47 (2018) 318–321.
- [8] J.S. Preston, A.C. du Preez, Solvent extraction of platinum-group metals from hydrochloric acid solutions by dialkyl sulphoxides, *Solvent Extr. Ion Exch.*, 20 (2002) 359–374.
- [9] B. Ramachandra Reddy, B. Raju, J.Y. Lee, H.K. Park, Process for the separation and recovery of palladium and platinum from spent automobile catalyst leach liquor using LIX 84I and Alamine 336, *J. Hazard. Mater.*, 180 (2010) 253–258.
- [10] R. Panda, M.K. Jha, D.D. Pathak, Commercial Processes for the Extraction of Platinum Group Metals (PGMs), H. Kim, B. Westrom, S. Alam, T. Ouchi, G. Azimi, N.R. Neelameggham, S. Wang, X. Guan, Eds., *Rare Metal Technology* 2018. TMS 2018, The Minerals, Metals & Materials Series. Springer, Cham, 2018.
- [11] L.D. Nghiem, P. Mornane, I.D. Potter, J.M. Perera, R.W. Cattrall, S.D. Kolev, Extraction and transport of metal ions and small organic compounds using polymer inclusion membranes (PIMs), *J. Membr. Sci.*, 281 (2006) 7–41.
- [12] M. Inês G.S. Almeida, R.W. Cattrall, S.D. Kolev, Polymer inclusion membranes (PIMs) in chemical analysis – a review, *Anal. Chim. Acta*, 987 (2017) 1–14.
- [13] R. Jha, M.D. Rao, A. Meshram, H.R. Verma, K.K. Singh, Potential of polymer inclusion membrane process for selective recovery of metal values from waste printed circuit boards: a review, *J. Cleaner Prod.*, 265 (2020) 121621, doi: 10.1016/j.jclepro.2020.121621.
- [14] A.F. Shaaban, M.M. Azab, A.A. Mahmoud, A.A. Khalil, A.M. Metwally, Selective transport of Cu(II), Co(II), Cd(II) and Ni(II) ions through polymer inclusion membranes (PIMs) based on some amide derivatives of 4-amino-1,5-dimethyl-2-phenylpyrazolidin-3-one, *Desal. Water Treat.*, 70 (2017) 190–200.
- [15] M. Ulewicz, E. Radzimska-Lenarcik, Application of polymer inclusion membranes doped with 1-hexyl-4-methylimidazole for pertraction of zinc(II) and other transition metal ions, *Physicochem. Probl. Miner. Process.*, 51 (2015) 447–460.
- [16] G. Arslan, A. Yilmaz, A. Tor, M. Ersoz, Preparation of polymer inclusion membrane with sodium diethyldithiocarbamate as a carrier reagent for selective transport of zinc ions, *Desal. Water Treat.*, 75 (2017) 348–356.
- [17] C. Fontàs, R. Tayeb, S. Tingry, M. Hidalgo, P. Seta, Transport of platinum(IV) through supported liquid membrane (SLM) and polymeric plasticized membrane (PPM), *J. Membr. Sci.*, 263 (2005) 96–102.
- [18] S.D. Kolev, Y. Sakai, R.W. Cattrall, R. Paimin, I.D. Potter, Theoretical and experimental study of palladium(II) extraction from hydrochloric acid solutions into Aliquat 336/PVC membranes, *Anal. Chim. Acta*, 413 (2000) 241–246.
- [19] T.Zh. Sadyrbaeva, Separation of copper(II) from palladium(II) and platinum(IV) by di(2-ethylhexyl)phosphoric acid-based liquid membranes during electrodialysis, *J. Membr. Sci.*, 275 (2006) 195–201.
- [20] B. Pospiech, Highly efficient facilitated membrane transport of palladium(II) ions from hydrochloric acid solutions through plasticizer membranes with Cyanex 471X, *Physicochem. Probl. Miner. Process.*, 51 (2015) 281–291.
- [21] C. Fontàs, V. Salvadó, M. Hidalgo, Selective enrichment of palladium from spent automotive catalysts by using a liquid membrane system, *J. Membr. Sci.*, 223 (2003) 39–48.
- [22] B. Pospiech, Facilitated transport of palladium(II) across polymer inclusion membrane with ammonium ionic liquid as effective carrier, *Chem. Pap.*, 72 (2018) 301–308.
- [23] M. Regel-Rosocka, M. Rzelewska, M. Baczynska, M. Janus, M. Wisniewski, Removal of palladium(II) from chloride solutions with cyphos phosphonium ionic liquids as metal ion carriers for liquid-liquid extraction and transport across polymer inclusion membranes, *Physicochem. Probl. Miner. Process.*, 51 (2015) 621–631.
- [24] J.S. Fu, S. Nakamura, K. Akiba, Selective transport of platinum(IV) from a palladium(II) mixture across a liquid membrane impregnated with an 8-quinolinol derivative, *J. Membr. Sci.*, 107 (1995) 283–288.
- [25] C. Fontàs, E. Anticó, F. Vocanson, R. Lamartine, P. Seta, Efficient thiacalix[4]arenes for the extraction and separation of Au(III), Pd(II) and Pt(IV) metal ions from acidic media incorporated in membranes and solid phases, *Sep. Purif. Technol.*, 54 (2007) 322–328.
- [26] M. Ulewicz, K. Sadowska, J.F. Biernat, Transport of Zn(II), Cd(II) and Pb(II) across polymer inclusion membranes doped with imidazole azocrown ethers, *Desalination*, 214 (2007) 352–364.
- [27] M. Ulewicz, J. Szczygelska-Tao, J.F. Biernat, Selectivity of Pb(II) transport across polymer inclusion membranes doped with imidazole azothiacrown ethers, *J. Membr. Sci.*, 344 (2009) 32–38.
- [28] E. Luboch, E. Wagner-Wysiecka, M. Fainerman-Melnikova, L.F. Lindoy, J.F. Biernat, Pyrrole azocrown ethers. Synthesis, complexation, selective lead transport and ion-selective membrane electrode studies, *Supramol. Chem.*, 18 (2006) 593–601.
- [29] M. Ulewicz, E. Radzimska-Lenarcik, Transport of metal ions across polymer inclusion membrane with 1-alkylimidazole, *Physicochem. Probl. Miner. Process.*, 46 (2011) 119–130.
- [30] E. Radzimska-Lenarcik, M. Ulewicz, M., Polymer inclusion membranes (PIMs) doped with alkylimidazole and their application in the separation of non-ferrous metal ions, *Polymers (Basel)*, 11 (2019) 1780, doi: 10.3390/polym11111780.
- [31] E. Radzimska-Lenarcik, M. Ulewicz, Selective transport of Cu(II) across a polymer inclusion membrane with 1-alkylimidazole from nitrate solutions, *Sep. Sci. Technol.*, 47 (2012) 1113–1118.
- [32] E. Radzimska-Lenarcik, M. Ulewicz, The use of 1-alkylimidazoles for selective separation of zinc ions in the transport process across a polymeric inclusion membrane, *Physicochem. Probl. Miner. Process.*, 50 (2014) 131–142.
- [33] E. Radzimska-Lenarcik, M. Ulewicz, The use of the steric effect of the carrier molecule in the polymer inclusion membranes for the separation of cobalt(II), nickel(II), copper(II), and zinc(II) ions, *Pol. J. Chem. Technol.*, 17 (2015) 51–56.
- [34] E. Radzimska-Lenarcik, R. Ulewicz, M. Ulewicz, Zinc recovery from model and waste solutions using polymer inclusion membranes (PIMs) with 1-octyl-4-methylimidazole, *Desal. Water Treat.*, 102 (2018) 211–219.
- [35] E. Radzimska-Lenarcik, M. Ulewicz, The application of polymer inclusion membranes based on CTA with 1-alkylimidazole for the separation of zinc(II) and manganese(II) ions from aqueous solutions, *Polymers*, 11 (2019) 242, doi: 10.3390/polym11020242.
- [36] Z. Aji, A.M. Ali, Separation of copper ions from iron ions using PVA-g-(acrylic acid/*N*-vinyl imidazole) membranes prepared by radiation-induced grafting, *J. Hazard. Mater.*, 173 (2010) 71–74.
- [37] M.L. Firmansyah, W. Yoshida, T. Hanada, M. Gota, Application of ionic liquids in solvent extraction of platinum group metals, *Solvent Extr. Res. Dev., Jpn.*, 27 (2020) 1–24.
- [38] N. Papaiconomou, L. Svecova, C. Bonnaud, L. Cathelin, I. Billard, E. Chainet, Possibilities and limitations in separating Pt(IV) from Pd(II) combining imidazolium and phosphonium ionic liquids, *Dalton Trans.*, 46 (2015) 20131–20138.

- [39] N. Papaiconomou, S. Génand-Pinaz, J.-M. Leveque, S. Guittonneau, Selective extraction of gold and platinum in water using ionic liquids. A simple two-step extraction process, *Dalton Trans.*, 6 (2013) 1979–1982.
- [40] F. Kubota, E. Shigyo, W. Yoshida, M. Goto, Extraction and separation of Pt and Pd by an imidazolium-based ionic liquid combined with phosphonium chloride, *Solvent Extr. Res. Dev., Jpn.*, 24 (2017) 97–104.
- [41] W. Yoshida, F. Kubota, R. Kono, M. Goto, Selective separation and recovery of Pt(IV) from Pd(II) through an imidazolium-ionic-liquid-based supported liquid membrane, *Anal. Sci.*, 35 (2019) 343–346.
- [42] J. Zhang, S. Shen, Y. Cheng, H. Lan, X. Hu, F. Wang, Dual lixiviant leaching process for extraction and recovery of gold from ores at room temperature, *Hydrometallurgy*, 144–145 (2014) 114–123.
- [43] P.R. Danesi, Separation of metal species by supported liquid membranes, *Sep. Sci. Technol.*, 19 (1984) 857–894.
- [44] A.M. St John, R.W. Cattrall, S.D. Kolev, Determination of the initial flux of polymer inclusion membranes, *Sep. Purif. Technol.*, 116 (2013) 41–45.
- [45] F.L. Bernardis, R.A. Grant, D.C. Sherrington, A review of methods of separation of the platinum-group metals through their chloro-complexes, *React. Funct. Polym.*, 65 (2005) 205–217.
- [46] J.J. Cruywagen, R.J. Kriek, Complexation of palladium(II) with chloride and hydroxide, *J. Coord. Chem.*, 60 (2007) 439–447.
- [47] G. Salazar-Alvarez, A.N. Bautista-Flores, E.R. de San Miguel, M. Muhammed, J. de Gyves, Transport characterization of a PIM system used for the extraction of Pb(II) using D2EHPA as carrier, *J. Membr. Sci.*, 250 (2005) 247–257.
- [48] A. Tor, G. Arslan, H. Muslu, A. Celikbas, Y. Cengeloglu, M. Ersoz, Facilitated transport of Cr(III) through polymer inclusion membrane with di(2-ethylhexyl)phosphoric acid (DEHPA), *J. Membr. Sci.*, 329 (2009) 169–174.
- [49] A. Gherrou, H. Kerdjoudj, R. Molinari, P. Seta, Preparation and characterization of polymeric plasticized membranes (PPM) embedding a crown ether carrier application to copper ions transport, *Mater. Sci. Eng., C*, 25 (2005) 436–443.
- [50] O. Arous, H. Kerdjoudj, P. Seta, Comparison of carrier-facilitated silver(I) and copper(II) ions transport mechanisms in a supported liquid membrane and in a plasticized cellulose triacetate membrane, *J. Membr. Sci.*, 241 (2004) 177–185.
- [51] J.R. Wolf, W. Strieder, Surface and void tortuosities for a random fiber bed: overlapping, parallel cylinders of several radii, *J. Membr. Sci.*, 49 (1990) 103–115.
- [52] A. Gherrou, H. Kerdjoudj, R. Molinari, P. Seta, E. Drioli, Fixed sites plasticized cellulose triacetate membranes containing crown ethers for silver(I), copper(II) and gold(III) ions transport, *J. Membr. Sci.*, 228 (2004) 149–157.
- [53] O. Arous, M. Amara, H. Kerdjoudj, Synthesis and characterization of cellulose triacetate and poly(ethylene imine) membranes containing a polyether macrobicyclic: their application to the separation of copper(II) and silver(I) ions, *J. Appl. Polym. Sci.*, 93 (2004) 1401–1410.
- [54] Chr. K. Jorgensen, *Inorganic Complexes*, Academic Press Inc., London and New York, 1963.