

Separation properties of polymer inclusion membranes with tetrabutylammonium bromide in selective transport and recovery of gold

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Presented at
MEMSEP & PERMEA 2025
15th International Conference
on Membrane and Separation
Processes & 10th Membrane
Conference of Visegrad Countries
24–26.06.2025, Chorzów, Poland.
Guest Editor: Maciej Szwast.

Article info:

Received: 23 May 2025
Revised: 30 June 2025
Accepted: 16 July 2025

Abstract

Polymer inclusion membranes (PIMs) with tetrabutylammonium bromide (TBAB) as the ion carrier and cellulose triacetate (CTA) as the polymer support were used for selective transport of gold(III) from hydrochloric acid solutions containing Pd(II) and Pt(IV). TBAB is a novel ionic liquid (IL) with very good extraction properties for selected precious metals. The transport rate of Au(III) was higher than that of Pt(IV) and Pd(II). The obtained selectivity order was as follows: Au(III) > Pd(II) > Pt(IV). The selectivity coefficients were: $S_{Au/Pd} = 2.5$ and $S_{Au/Pt} = 3.2$. The results show that the application of PIM composed of 55% w/w CTA, 25% w/w NPOE and 20% w/w TBAB can be used as an effective method of recovering Au(III) from leach liquor of electronic-waste.

Keywords

gold(III), tetrabutylammonium bromide, polymer inclusion membrane

1. INTRODUCTION

Recently, ionic liquids (ILs) are widely used as extractants/ion carriers as well as solvents due to their interesting physico-chemical properties, including very good ability to selectively extract many metals, including precious metals, from aqueous solutions. Moreover, these compounds have many other valuable physicochemical properties, such as low vapour pressure, non-flammability, etc. They are classified as “green solvents” used in extraction methods for various metal ions.

Gold has always been an expensive and valuable metal used not only in jewellery. The metal belongs to the group of precious metals, like platinum and palladium, and has a number of applications in many industries, such as the production of corrosion-resistant materials and chemical catalysts (Nguyen et al., 2017).

Ore deposits contain usually very low concentrations of gold (less than 1 g/t). On the other hand, e-waste contains higher concentrations of gold from 10 to 10,000 grams of gold per ton (Fleischman, 2025). Therefore nowadays, it is extremely important to recover valuable metals from waste materials. This is crucial from the economic and ecological point of view. In fact, there is a growing amount of electronic waste (e-waste) that should be recycled. The recovery of gold from e-waste is of great importance for sustainability because the concentration of gold in e-waste can be higher than in primary gold deposits (Do et al., 2023). Hydrometallurgical technology has been successful in recovering gold from e-waste, but develop-

ing an optimal technology is still challenging due to the diverse composition of e-waste and low content of gold (Nguyen et al., 2017; Do et al., 2023). E-waste contains precious metals such as Au, Ag, Pd and other valuable metals (i.e. Cu, Al, Fe). Table 1 shows typical e-waste composition (Do et al., 2023). Recovery and management of waste is an effective method to save natural resources of precious metals and at the same time reduce the amount of metal waste. Pyrometallurgical and hydrometallurgical technologies are used to recover metals from secondary raw materials. Hydrometallurgical methods such as leaching with inorganic acids (i.e. aqua regia: mixture of HCl and HNO₃ in a ratio of 3:1; nitric acid, hydrochloric acid, sodium thiosulfate solutions, etc.) produce an aqueous solu-

Table 1. Typical e-waste composition (Do et al., 2023).

Metals	Contents, %
Copper, Cu	6–20
Iron, Fe	1.2–8
Tin, Sn	4.0
Nickel, Ni	0.3–5.4
Lead, Pb	1.0–4.2
Zinc, Zn	0.2–2.2
Silver, Ag	0.01–0.45
Gold, Au	0.02–0.2
Palladium, Pd	0.005–0.4



tion containing a mixture of different metal ions. The metals from the aqueous solution must be effectively separated to obtain pure metallic products (Saternus and Fornalczyk, 2013).

Several separation methods have been used to recover Au(III) from aqueous solutions, including ion exchange, liquid-liquid extraction, membrane processes and precipitation methods (Banik et al., 2020; Baczyńska et al., 2018; Bonggotgetsakul et al., 2010). The methods of metal ion separation are very important in hydrometallurgical technology for the recovery of important components. It can be observed that many studies report the separation of platinum(IV) and palladium(II), while there are few works on the separation of gold(III) from a solution containing these metal ions. It is worth knowing that the leach liquor of spent electronic waste usually contains many metal ions, such as Au(III), Pd(II), Pt(IV), Fe(III), Cu(II) and Cr(III) (Nguyen et al., 2017). Separating them is not an easy process and requires the use of appropriate methods. Hydrochloric acid is most commonly used to leach precious metals from waste raw materials. The separation of metals from chloride solutions in which they occur in the form of anionic complexes with a similar structure is a major technological challenge. Various commercial extractants have been used in solvent extraction to recover platinum group metals (PGMs) from aqueous chloride solutions. Amines and neutral extractants have usually been used for PGM extraction (Génand-Pinaz et al., 2013; Sun et al., 2011a; Sun et al., 2011b).

One interesting method of metal ion separation is transport across polymer inclusion membranes (PIMs) which are composed of a base polymer, a plasticizer and specific extractant (called ion carrier) (Carner et al., 2020; Croft et al., 2024). It is an alternative method to classical solvent extraction and has many advantages. The most important positive features of PIM are the following:

- reduction in the amount of volatile solvents and extractants,
- elimination of intermediate stages,
- high resistance to ion carrier leaching compared to other liquid membranes (Baczynska et al., 2016).

An extensive body of information about the synthesis of these membranes can be found in numerous scientific articles. It is a relatively simple and cheap process that does not require the use of complicated devices and reagents, which is a great advantage of this method (Fontàs et al., 2007; Makowka and Pospiech, 2019). A membrane is formed by the evaporation of a volatile solvent (e.g. dichloromethane, DCM, CH_2Cl_2) from a mixture containing a polymer matrix, a plasticizer, and an ion carrier. Cellulose triacetate (CTA) and poly(vinyl chloride) (PVC) mainly form the polymer matrix of these membranes. Nitrophenyl alkyl ethers and phthalates are often used as plasticizers, which play a crucial role in improving polymer flexibility. Cationic, anionic and neutral extractants as well as ionic liquids are used to synthesize membranes as selective metal ion carriers (Baczyńska et al., 2018; Carner et

al., 2020; Kogelnig et al., 2011). Ion carriers are usually acidic, basic, neutral and solvating in nature (Alcalde et al., 2024). Transport rate through a polymer membrane depends on:

- the kind of polymer used as the matrix,
- the concentration of the carrier and plasticizer in the membrane,
- the thickness of membranes,
- the kind of the receiving phase.

One of the most important factors determining the selectivity of metal ion transport is the appropriate carrier ion used for the synthesis of polymer membrane. Various extractants/ion carriers were investigated for the selective separation of gold(III). Table 2 lists the ion carriers used for the separation of gold(III) from aqueous solutions in the transport process through PIMs. de San Miguel et al. (2007; 2008) described the selective removal of Au(III) from hydrochloric acid solutions across PIM using Kelex 100 (7-(4-ethyl-1-methyloctyl)-8-hydroxyquinoline) as the carrier. Bonggotgetsakul et al. (2010) showed the application of Aliquat 336 (tricapryl methylammonium chloride) as the ion carrier of Au(III) using PIM containing: 20% of Aliquat 336, 10% of 1-dodecanol and 70% of PVC as the polymer matrix. Recently, ionic liquids are very often used as the extractants/ion carriers of gold(III). For instance, Alguacil (2017) reported that Cyphos IL 101 (triethyl(tetradecyl)phosphonium chloride) can be used as an efficient carrier of Au(III) from chloride solutions. On the other hand, Cyphos IL 104 (triethyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate) can also be used as the extractant of Au(III) from hydrochloric acid solutions (Bonggotgetsakul et al., 2015; 2016). Liu et al. (2021) reported a novel extractant synthesized by mixing tetraoctylphosphonium bromide and di(2-ethylhexyl)phosphoric acid (P204), which was used to recover gold(III) from HCl solutions. The resulting PIM composed of 70% PVDF (poly(vinylidene fluoride)), 5% NPOE (2-nitrophenyl octyl ether) and 25% ion carrier was characterized by high stability and reusability. The extraction efficiency of Au(III) was 92.4% after 5 transport experiments.

One of the many extractants is tetrabutylammonium bromide (TBAB) which belongs to the quaternary ammonium salts and can be used as an extractant in liquid-liquid extraction as well as an ion carrier of metal for the synthesis of PIMs (Banik et al., 2020; Hariharan et al., 2013; Kalidhasan and Rajesh, 2009; Muthuraman et al., 2005; Pospiech, 2024; Venkateswaran and Palanivelu, 2004). Moreover, TBAB behaves like an ionic liquid and can therefore be a promising alternative to organic solvents. However, the literature features only few works showing that this extractant/ion carrier is very effective in the selective separation of various metal ions from aqueous solutions, both in extraction processes and in membrane separation. For example, TBAB has been used as the ion carrier for the membrane separation of iron(III) from nickel(II), cobalt(II) and lithium(I) (Pospiech, 2023). The polymer inclusion membrane (PIM) used in the above study contained 35.5% w/w cellulose triacetate (CTA), 49.2% w/w

2-nitrophenyl octyl ether (NPOE) and 15.3% w/w TBAB and enabled the effective and selective removal of iron(III) from hydrochloric acid solutions into sulfuric acid. Another example of the use of TBAB as an efficient carrier of metals is the investigation of palladium transport from a solution containing platinum(IV) (Pospiech, 2024).

Table 2. Examples of ion carriers used for the separation of gold(III) from aqueous solutions in the transport through PIMs.

Ion carrier	Ref.
Kelex 100	de San Miguel et al., 2007; 2008
Aliquat 336	Bonggotgetsakul et al., 2010
Cyphos 101	Alguacil, 2017
Cyphos 104	Bonggotgetsakul et al., 2015; 2016
P204	Liu et al., 2021

However, so far there have been no reports on the recovery of gold(III) ions using PIM with TBAB. Preliminary studies of Au(III) extraction from chloride solutions showed that this compound is a very good extractant of the ions of this metal. The results of these studies encourage the investigation of the selectivity of gold ion transport through PIM in the presence of other metals.

In this work, the experiments were carried out using a cellulose triacetate-based polymer membrane with a new ion carrier TBAB. The extraction properties of this ionic liquid with respect to gold(III) were tested through a series of conventional liquid-liquid extraction studies using $0.1 \text{ mol} \cdot \text{dm}^{-3}$ TBAB in toluene depending on the concentration of hydrochloric acid. In the next series of studies, the PIM with TBAB was synthesized. The membrane was used to transport gold(III) from aqueous solutions of hydrochloric acid. The result of the investigation made it possible to characterize the kinetics of the transport and the efficiency of extraction of this metal into the receiving phase. A mixture of thiourea and hydrochloric acid was used as the stripping phase. The crucial aspect of the experimental study was to determine the selectivity of gold(III) transport from the aqueous solutions containing Pt(IV) and Pd(II). This was a very important study from the practical point of view, as it allowed to determine the applicability of PIM for the separation of Au(III), Pd(II) and Pt(IV) from real solutions obtained as a result of leaching electronic waste.

2. MATERIALS AND METHODS

2.1. Reagents

2.1.1. Inorganic reagents

Chloride salts of precious metals, i.e. gold chloride(III) (purity = 99%), palladium(II) chloride, PdCl_2 (purity = 99%) as well as chloroplatinic acid, (30% H_2PtCl_6 , pure), were purchased from Sigma-Aldrich (St. Louis, USA). Hydrochloric acid (HCl, purity 37%) was supplied by POCh (Gliwice, Poland).

2.1.2. Organic reagents

Tetrabutylammonium bromide (TBAB; $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_4\text{N}(\text{Br})$ (ACROS, New Jersey, USA) (purity $\geq 99.0\%$); 2-nitrophenyl octyl ether (NPOE) (Sigma-Aldrich, St. Louis, USA), cellulose triacetate (CTA) (Sigma-Aldrich, St. Louis, USA), dichloromethane (P.P.H. STANLAB Sp. J., Lublin, Poland) and thiourea (POCh, Gliwice, Poland), were used directly without further purification.

2.2. Solvent extraction of Au(III)

In liquid-liquid extraction, equal volumes of aqueous and organic phases (O/A phase volume ratio = 1) were shaken for 20 min at $21 \pm 2^\circ\text{C}$. An HCl solution containing $0.001 \text{ mol} \cdot \text{dm}^{-3}$ Au(III) was used as the aqueous phase. The organic phase contained $0.1 \text{ mol} \cdot \text{dm}^{-3}$ TBAB in toluene. The volumes of the phases were equal and amounted to 10 ml. After shaking, when equilibrium was reached, the mixture was separated. The Au(III) concentration in the aqueous phase was analysed using a plasma emission spectrometer MP-AES 4200 (Agilent). Distribution ratio, D , and extraction efficiency, $\%E$, were calculated based on the following equations:

$$D = \frac{[\text{M}]_{\text{org}}}{[\text{M}]_{\text{aq}}} \quad (1)$$

$$\%E = \frac{D}{D+1} \cdot 100\% \quad (2)$$

where $[\text{M}]_{\text{org}}$ and $[\text{M}]_{\text{aq}}$ denote metal concentrations in the organic and aqueous phases, respectively.

2.3. Synthesis of polymer inclusion membranes (PIMs)

PIMs were prepared as previously described (Pospiech, 2023; 2024). A mixture containing CTA as a polymer matrix was dissolved in dichloromethane ($1.25 \text{ g}/100 \text{ cm}^3 \text{ CH}_2\text{Cl}_2$). The mixture also contained TBAB ($0.1 \text{ mol} \cdot \text{dm}^{-3}$) used as an ion carrier and NPOE (10% v/v) was prepared as a plasticizer. The resulting membrane consisted of 55% w/w CTA, 25% w/w NPOE and 20% w/w TBAB. The thickness of PIM was measured using a digital ultrameter (MG-401, Elmetron). The thickness of the membrane with TBAB was $75 \mu\text{m}$.

2.4. Transport of metal ions

The transport experiments have been described by earlier researchers (Pospiech, 2023; 2024). The PIM separated the aqueous source containing metal ions in hydrochloric acid from the aqueous receiving phase. The receiving phase was $0.3 \text{ mol} \cdot \text{dm}^{-3}$ thiourea in $0.1 \text{ mol} \cdot \text{dm}^{-3}$ hydrochloric acid. Both aqueous phases (100 cm^3 each) were mixed with magnetic stirrers and pumped with a peristaltic pump (PP1B-05A, Zalimp, Poland). The source phase contained $0.001 \text{ mol} \cdot \text{dm}^{-3}$

Au(III) in the hydrochloric acid solution. The concentration of metal ions in the source phase and in the receiving phase was analysed hourly using a plasma emission spectrometer MP-AES 4200 (Agilent). Fig. 1 shows the research scheme. The kinetics of PIM transport process is described by a first-order reaction in metal ion concentration:

$$\ln\left(\frac{c}{c_i}\right) = -kt \quad (3)$$

where: k – observed rate constant [s^{-1}], t – time [s], c – gold(III) concentration [$mol \cdot dm^{-3}$] in the source phase at a given time, c_i – gold(III) ion concentration in the source phase [$mol \cdot dm^{-3}$].

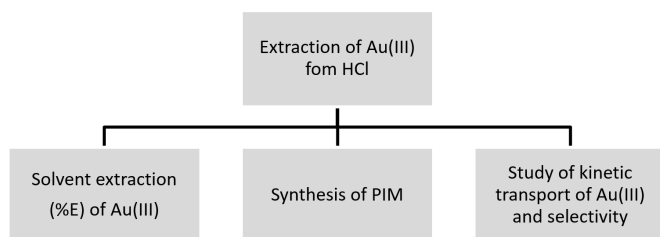


Figure 1. The research scheme.

To calculate the k (the rate constant), a plot of $\ln(c/c_i)$ vs. time was made. The permeability coefficient, P , was determined as:

$$P = \frac{V}{A}k \quad (4)$$

where: V – volume of the aqueous source phase, A – area of the membrane.

The initial flux, J_i , was calculated as follows:

$$J_i = P \cdot c_i \quad (5)$$

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

$$S = \frac{J_{i,M_1}}{J_{i,M_2}} \quad (6)$$

The recovery factor, RF , was calculated as:

$$RF = \frac{c_i - c}{c_i} \cdot 100\% \quad (7)$$

3. RESULTS AND DISCUSSION

3.1. Liquid-liquid extraction of Au(III) by TBAB in toluene

One can find several studies on the extraction of gold(III) from aqueous chloride solutions containing various metal ions. Mainly anionic and neutral extractants were used as the extractants/ion carriers of Au(III), for example: Kelex 100 (de San

Miguel et al., 2007; 2008), Aliquat 336 (Bonggotgetsakul et al., 2010), Cyphos 101 (Alguacil, 2017), Cyphos 104 (Bonggotgetsakul et al., 2015; 2016) as well as Alamine 336 (mixture of trioctyl/decyl amine) (Nguyen et al., 2017), Cyanex 471X (triisobutyl phosphine sulfide) (Nguyen et al., 2017), TBP (tributyl phosphate), MIBK (methyl isobutylketone) (Nguyen et al., 2017), Cyanex 923 (a mixture of tetra trialkylphosphine oxides) (Nguyen et al., 2017) and a series of tridentate thioethers as the selective extractants of Au(III) from Pd(II) (Huang et al., 2024). Nevertheless, the literature review has shown that to date there have been no reports on the extraction of gold(III) using TBAB as an extractant or ion carrier. Therefore, at the beginning, preliminary studies of the conventional solvent extraction of gold(III) ions using $0.1 \text{ mol} \cdot \text{dm}^{-3}$ TBAB in toluene were performed to check whether TBAB would be a suitable ion carrier of Au(III) during transport through a polymer membrane containing this compound.

Therefore, the liquid-liquid extraction of Au(III) from HCl solutions was carried out. The concentration of hydrochloric acid varied from 0.5 to $5 \text{ mol} \cdot \text{dm}^{-3}$. Fig. 2 shows the dependence of the extraction efficiency (%E) of Au(III) with $0.1 \text{ mol} \cdot \text{dm}^{-3}$ TBAB in toluene on the HCl concentration in the aqueous phase. As can be observed, the %E of Au(III) initially increased with the concentration of hydrochloric acid, and above $1 \text{ mol} \cdot \text{dm}^{-3}$ HCl the %E remains at the same level. The extraction efficiency was very high and reached a maximum of 99.5% at $3 \text{ mol} \cdot \text{dm}^{-3}$ HCl. Bonggotgetsakul et al. (2015; 2016) reported that gold(III) formed tri- and tetrachloro complexes at high chloride ions concentration in the solution, and that the main complexes of Au(III) in a chloride medium at high chloride ion concentration were $AuCl_4$. According to the review of literature "Most of gold(III) exists as $AuCl_4$, when the concentration of chloride ion is higher than 0.1 M." (Xing et al., 2018). Therefore, it can

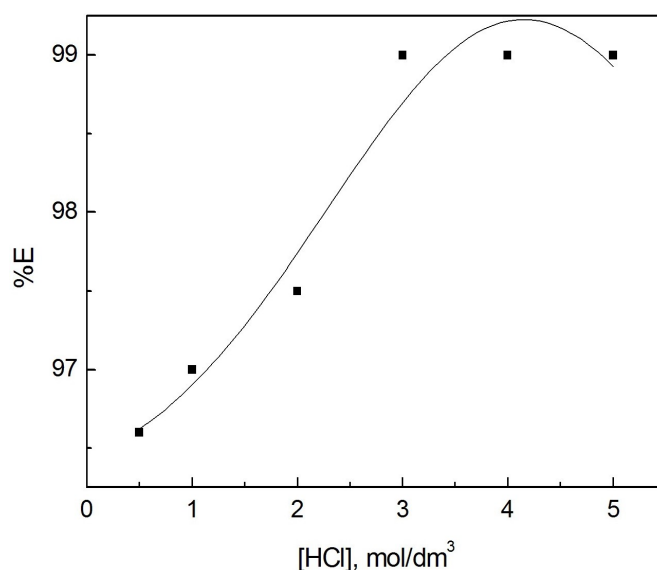
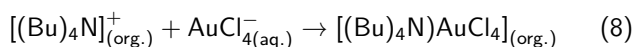


Figure 2. Relationship between the extraction efficiency of Au(III) with $0.1 \text{ mol} \cdot \text{dm}^{-3}$ TBAB in toluene on the hydrochloric acid concentration in the aqueous phase.

be concluded that in this case, the anionic chlorocomplexes of gold(III) are also extracted from the aqueous solution by means of an anion-exchange mechanism. This mechanism is illustrated by the following reaction equation:



3.2. Transport kinetics of Au(III) from hydrochloric acid solutions across PIM with TBAB

As can be seen from the results of the solvent extraction of Au(III), TBAB shows strong complexing properties for this metal. Therefore, this compound can be used as the ion carrier for the synthesis of a CTA-based polymer membrane. In this experiment, the composition of PIM was as follows: 55% w/w CTA, 25% w/w NPOE and 20% w/w TBAB (Fig. 1). The concentration of TBAB was $1 \text{ mol}\cdot\text{dm}^{-3}$ (based on the volume of plasticizer). Au(III) was transported from $3 \text{ mol}\cdot\text{dm}^{-3}$ HCl solution into $0.3 \text{ mol}\cdot\text{dm}^{-3}$ thiourea in $0.1 \text{ mol}\cdot\text{dm}^{-3}$ hydrochloric acid as the receiving phase.

To calculate the k value (observed rate constant), a plot of $\ln(c/c_i)$ vs. time was prepared. Fig. 3 shows a graph of the relationship between $\ln(c/c_i)$ and time for Au(III). As can be observed, the relationship between $\ln(c/c_i)$ and time is linear. On this basis, it can be concluded that the transport of Au(III) was described by a first-order reaction according to the following equation:

$$\ln\left(\frac{c}{c_i}\right) = -kt \quad (9)$$

Table 3 shows the kinetic parameters of Au(III) transport through PIM, such as the observed rate constant (k) and the permeability coefficient (P) which was calculated according to the following equation:

$$P = \frac{V}{A}k \quad (10)$$

The observed rate constant of this transport process was 0.165 h^{-1} . The recovery factor (RF) of Au(III) was 97%. As can be seen, the results of the transport of Au(III) across PIM with TBAB are very interesting and show that this method can be considered to be a selective and effective process. Bonggotgetsakul et al. (2010) also investigated the transport of Au(III) from hydrochloric acid solutions using poly(vinyl chloride) (PVC) based polymer inclusion membrane containing the commercial ion carrier Aliquat 336. Good transport effects were obtained only after the use of sonification. In the second work (Bonggotgetsakul et al., 2016), the authors found that better results were achieved using a ionic liquid Cyphos IL 104 as the ion carrier, which extracted both metal cations and anions. Unfortunately, it was therefore not selective. The use of TBAB seems to be a promising ion carrier. Further studies will focus on its selectivity.

Table 3. Kinetic parameters for transport of Au(III). Conditions as in Fig. 3.

Kinetic parameters	Values
The observed rate constant, k [h^{-1}]	0.165
The permeability coefficient, P [$\mu\text{mol}\cdot\text{s}^{-1}$]	3.640

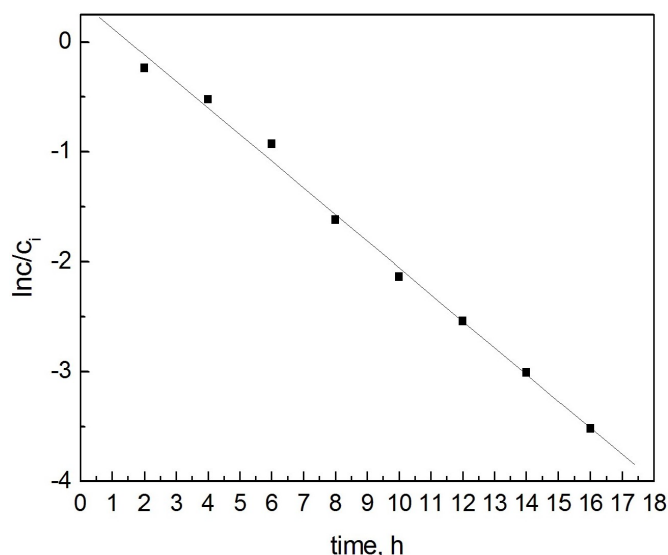


Figure 3. Relationship between $\ln(c/c_i)$ and time for Au(III) transport through PIM; source phase: $0.001 \text{ mol}\cdot\text{dm}^{-3}$ Au(III) in $3 \text{ mol}\cdot\text{dm}^{-3}$ HCl, receiving phase: $0.3 \text{ mol}\cdot\text{dm}^{-3}$ thiourea in $0.1 \text{ mol}\cdot\text{dm}^{-3}$ HCl.

Fig. 4 shows the recovery factor of Au(III) after 16 hours. This metal recovery rate (in%) can be calculated as follows:

$$RF = \frac{c_i - c}{c_i} \cdot 100\% \quad (11)$$

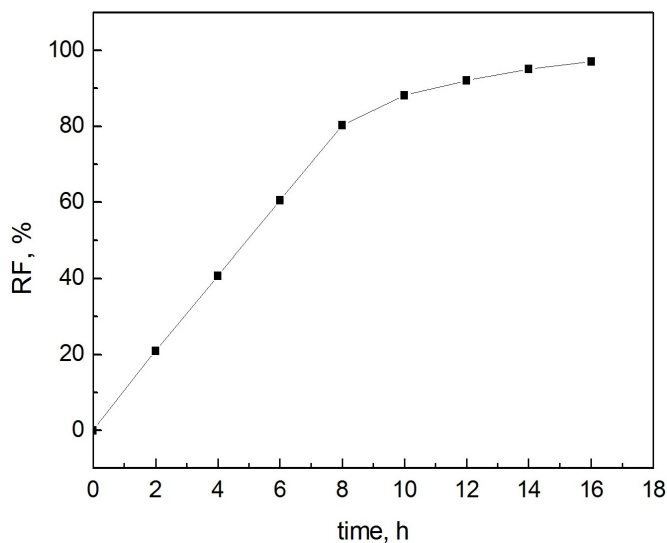


Figure 4. Recovery factor of Au(III). Conditions as in Fig. 3.

3.3. Application of a thiourea solution as the stripping phase in Au(III) transport

The literature review shows that various solutions have been investigated as a solution for stripping Au(III) from organic phases after solvent extraction. A mixture of thiourea with hydrochloric acid has very often been used for the stripping of precious metals. The aim of the next experiment was to study the effect of the thiourea concentration in $0.1 \text{ mol}\cdot\text{dm}^{-3}$ HCl on the transport rate of Au(III). The concentration varied from 0.1 to $0.5 \text{ mol}\cdot\text{dm}^{-3}$. As can be seen, the recovery factor of Au(III) increased with the increase in thiourea concentration in the aqueous phase. Figure 5 shows that the highest value was obtained for $0.3 \text{ mol}\cdot\text{dm}^{-3}$ thiourea in $0.1 \text{ mol}\cdot\text{dm}^{-3}$ HCl. The review of the literature shows that other solutions for gold re-extraction have also been studied in the past. For example, Bonggotgetsakul et al. (2016) used $0.5 \text{ Na}_2\text{SO}_3$ solution as the receiving phase and Kozłowski et al. (2018) applied $0.01 \text{ M KI} + 0.01 \text{ M HCl}$ for Au(III) re-extraction during transport of this metal ion from chloride acidic aqueous solutions through PIM with resorcinarene derivatives. According to another investigation (Xiong et al., 2010), aqueous mixtures of thiourea and hydrazine in combination with varying concentrations of HCl and NaOH can be used as the stripping phase of Au(III). On the other hand, Alguacil (2017) applied water or 0.1 M sodium borohydride solution in the stripping phase for Au(III) during transport across PIM with Cyphos IL 101.

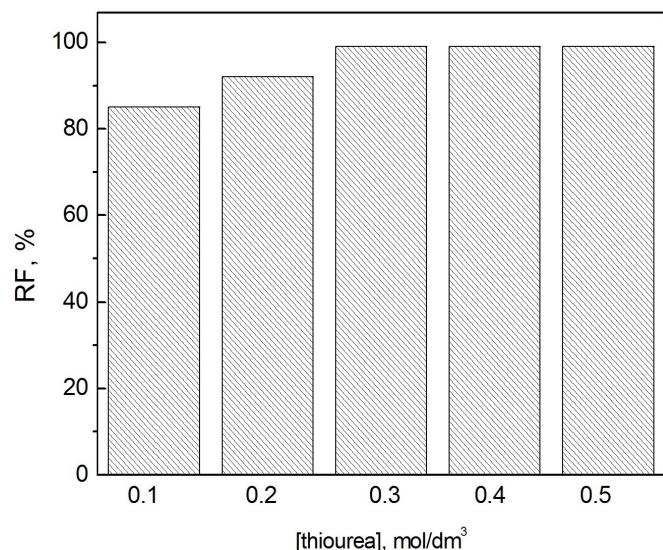


Figure 5. Dependence of thiourea concentration in 0.1 M HCl as the receiving phase on the recovery factor (RF). Source phase: $0.001 \text{ mol}\cdot\text{dm}^{-3}$ Au(III) in $3 \text{ mol}\cdot\text{dm}^{-3}$ HCl.

3.4. Selectivity study

The selectivity of gold(III) extraction from $3 \text{ mol}\cdot\text{dm}^{-3}$ HCl compared to platinum(IV) and palladium(II) was also investigated. Fig. 6 shows a plot of $\ln(c/c_i)$ vs. time for Au(III), Pt(IV) and Pd(II) across PIM with TBAB, with $0.3 \text{ mol}\cdot\text{dm}^{-3}$

thiourea in $0.1 \text{ mol}\cdot\text{dm}^{-3}$ HCl as the receiving phase. The values of the transport rate, initial flux, selectivity order and selectivity ratio for the competitive transport of the metal ions under study are summarized in Table 4. The results show that the rate constant of Au(III), Pd(II) and Pt(IV) through PIM with a TBAB decreases in the following sequence: Au(III) > Pd(II) > Pt(IV). The recovery factors (%) of Au(III), Pt(IV) and Pd(II) are shown in Fig. 7. The highest recovery factor was obtained for Au(III) and amounted to more than 90%. A similar observation was reported by Kozłowski et al. (2018). They showed that Au(III) transport was obtained with an excellent separation from Pd(II), Pt(IV) in the resorcinarene-based system, which was connected with the high affinity of resorcinarene molecules to anionic forms of Au(III) species. In this case, high values of selectivity coefficient of Au(III) in relation to Pt(IV) and Pd(II) can be connected with the high affinity of TBAB molecules to anionic form of Au(III) (AuCl_4^-). On the other hand, Xing et al. (2018) reported that in the solvent extraction, gold(III) was selectively extracted by Cyanex 272 in the hydrochloric acid concentration range from 0.5 to 9 M . Gold(III) was not completely extracted using 0.2 M Cyanex 272 when HCl concentration was less than 3 M . However, Pt(IV) and Pd(II) were not extracted by Cyanex 272 and thus complete separation of Au(III) from Pt(IV) and Pd(II) was possible. Therefore, the decisive factor influencing the selectivity of the process is probably the complex form of a given metal and its high affinity to the extractant molecules. A similar observation is possible during Au(III) extraction in the presence of Cu(II), Ni(II), and Fe(III, II).

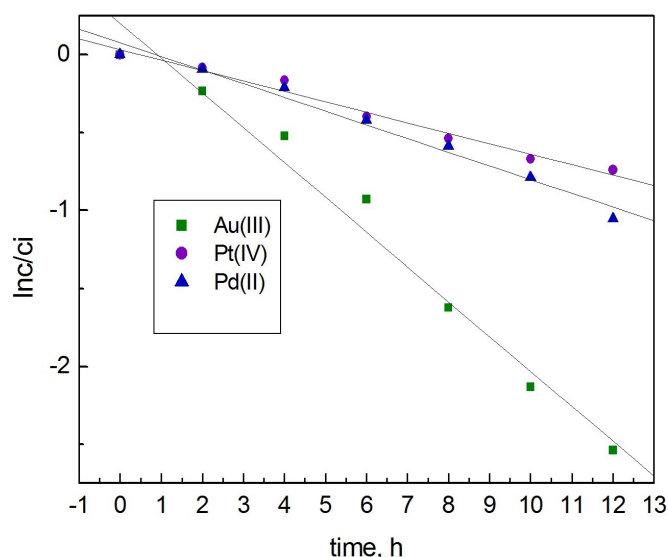


Figure 6. Relationship between $\ln(c/c_i)$ and time for Au(III), Pt(IV) and Pd(II) transport through PIM (composition of PIM as in Figure 1); source phase: Au(III) $0.001 \text{ mol}\cdot\text{dm}^{-3}$, $0.001 \text{ mol}\cdot\text{dm}^{-3}$ Pd(II) and $0.001 \text{ mol}\cdot\text{dm}^{-3}$ Pt(IV) in $3 \text{ mol}\cdot\text{dm}^{-3}$ HCl, receiving phase: $0.3 \text{ mol}\cdot\text{dm}^{-3}$ thiourea in $0.1 \text{ mol}\cdot\text{dm}^{-3}$ HCl.

Table 4. Kinetic parameters for transport of Au(III), Pt(IV) and Pd(II). Conditions as in Fig. 6.

Kinetic parameters	Au(III)	Pd(II)	Pt(IV)	Selectivity order and selectivity coefficient
Rate constant, k [h^{-1}]	0.20	0.08	0.06	$\text{Au(III)} > \text{Pd(II)} > \text{Pt(IV)}$
Initial flux, J_i [$\mu\text{mol} \cdot \text{s}^{-1} \cdot \text{m}^{-2}$]	4.4	1.8	1.4	$S_{\text{Au/Pd}} = 2.5$ $S_{\text{Au/Pt}} = 3.2$

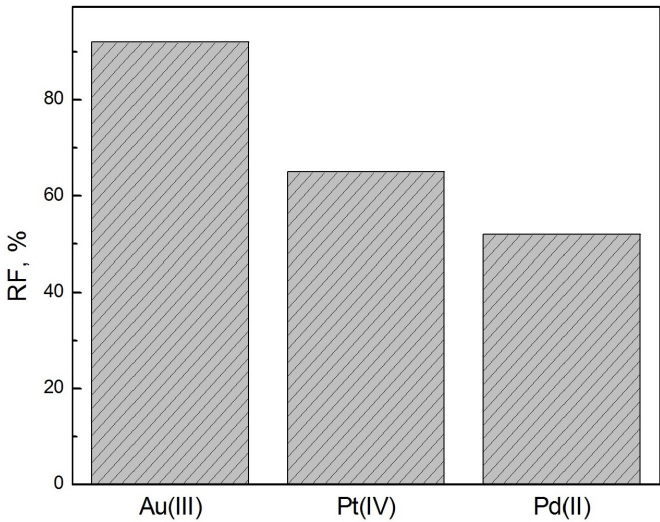


Figure 7. Recovery factor of Au(III), Pd(IV) and Pt(IV). Conditions as in Fig. 6.

3.5. Stability of PIM with TBAB

An important feature of the membrane is its resistance to the leaching of ion carrier from the polymer matrix. Therefore, the next stage of the research involved checking the stability of PIM operation during the separation of gold(III) ions from 3 mol·dm⁻³ hydrochloric acid solution. The composition of PIM is shown in Fig. 1. Au(III) transport studies were carried out 5 times using the same membrane, which was washed with distilled water after each transport cycle. Au(III) was extracted from 3 mol·dm⁻³ HCl into 0.3 mol·dm⁻³ thiourea in 0.1 mol·dm⁻³ HCl. As a result, a slight decrease in the initial gold(III) transport flux value was observed from 4.5 to 3.4 μmol·s⁻¹·m⁻². This is a relatively small loss and makes it possible to conclude that PIM is stable under these conditions. Therefore, there is a chance to use PIM with TBAB for the separation of gold(III) from real solutions obtained after the leaching of e-waste.

4. CONCLUSIONS

This paper described the use of PIM containing TBAB as an ion carrier for the recovery of Au(III) from 3 mol·dm⁻³ hydrochloric acid. Au(III) was successfully transported at both low and high concentrations of this acid into 0.3 mol·dm⁻³

Table 5. Effect of the number of Au(III) transport cycles through PIM on initial flux. Conditions as in Fig. 3.

Cycle number	Initial flux [$\mu\text{mol} \cdot \text{s}^{-1} \cdot \text{m}^{-2}$]
1	4.5
2	4.1
3	3.9
4	3.5
5	3.4

thiourea in 0.1 mol·dm⁻³ HCl as the stripping phase. This method can be considered to be useful for the recovery of Au(III) from aqueous acidic chloride solutions. The membrane extraction of Au(III) is faster and more efficient than that of Pd(II) and Pt(IV). The selectivity order obtained was as follows: Au(III) > Pd(II) > Pt(IV). The selectivity coefficients were: $S_{\text{Au/Pd}} = 2.5$ and $S_{\text{Au/Pt}} = 3.2$. Very high selectivity observed in this work is a particularly interesting result. Subsequent research should focus on the separation of precious metal ions and other metal ions (Fe, Cu, etc.) from real solutions obtained after the leaching of e-waste.

SYMBOLS

A	area of the effective membrane, m^2
J_i	the initial flux, $\mu\text{mol} \cdot \text{s}^{-1} \cdot \text{m}^{-2}$
k	rate constant, s^{-1}
c	concentration of metal ion, $\text{mol} \cdot \text{dm}^{-3}$ in the source phase at a given time
c_1	concentration of metal ion in the source phase, $\text{mol} \cdot \text{dm}^{-3}$
P	the permeability coefficient $\mu\text{mol} \cdot \text{s}^{-1}$
PIMs	polymer inclusion membranes
TBAB	tetrabutylammonium bromide
t	time, s
V	volume of the aqueous source phase, m^3

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