

# Facilitated transport of palladium(II) across polymer inclusion membrane with ammonium ionic liquid as effective carrier

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**Abstract** This work focuses on the application of polymer inclusion membrane (PIM) with tricaprilmethylammonium thiosalicylate, [A336][TS] (TOMATS), a thiol-containing task-specific ionic liquid for the transport of Pd(II) ions from aqueous solutions. 0.3 M thiourea in 0.1 M hydrochloric acid was found the most effective stripping phase in the transport of Pd(II) from membrane phase containing TOMATS. Separation of Pd(II) ions was also carried out from hydrochloric acid solution containing Pt(IV), Fe(III), Ni(II), and Mn(II). Pd(II) ions were preferably transported in the presence of these metal ions. The separation coefficients followed the order:  $S_{Pd/Pt} < S_{Pd/Fe} < S_{Pd/Ni} < S_{Pd/Mn}$ . [A336][TS] proved to be an excellent ion carrier for Pd(II) from hydrochloric acid solution. The results also showed that transport efficiency of the PIM was reproducible and it can be useful for the development of the simple and highly effective method of Pd(II) recovery from leach liquor of spent catalysts.

**Keywords** Palladium(II) · Methyltrioctylammonium thiosalicylate · Polymer inclusion membrane (PIM) · Ionic liquids

## Introduction

Ionic liquids (ILs) can be regarded as the alternative extractants/carriers of metal ions, inorganic acids, and organic compounds. These compounds show a number of important physicochemical properties such as negligible vapor pressure, thermal stability up to 300 °C, tunable viscosity, non-flammability, and excellent extractability for a variety of organic compounds and metal ions (Turgut et al. 2017; Mahandra et al. 2017; Rout et al. 2016; Baczynska et al. 2016; Rzelewska et al. 2016a, b; Pospiech and Kujawski 2015; Martak and Schlosser 2006). ILs are salts containing organic cation and anion (organic or inorganic) and their melting points are usually below 100 °C (Eyupoglu and Polat 2015). However, if the melting point is below room temperature, they are defined as room temperature ionic liquids (RTILs) (Turgut et al. 2017). Physicochemical properties of these compounds can be easily modified by changing an anion or a cation depending on aim of application (as solvent, extractant/carrier, reaction medium, etc.) (Turgut et al. 2017). This is very important property, and therefore, these ILs are of the great interest.

ILs can also be used in synthesis of polymer inclusion membranes (PIM) which are the type of the liquid membranes. Membrane processes are the important separation techniques and are used for removal of precious or hazardous metals from different sources (Eyupoglu and Kumbasar 2015). Transport of metal ions from aqueous solutions through polymer membrane containing the selective ion carrier is very attractive and economical compared to the solvent extraction with the high capital investment, higher organic solvent/extractant consumption, and two-step operation (extraction and stripping) (Eyupoglu et al. 2015). In the membrane process, substance is

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transferred from the source phase through PIM into the stripping phase within one-step operation. Moreover, the consumption of the chemicals is very low.

However, transport across PIM is not used in industry because of the limitations regarding the possibility of the loss of carrier from membrane phase into aqueous solutions during process. Adapting this type of liquids, membranes to the industrial conditions require many investigations. Studies in this range are very important and needed due to the possibility to obtain the high selectivity of transport at the very low cost. Therefore, the studies regarding stability of PIM and selectivity of the transport using membranes with different carriers are necessary. The results can be useful in the implementation of the transport through PIM in industry scale.

ILs were used as carriers in the synthesis of PIM by many researchers (Regel-Rosocka et al. 2015). Aliquat 336, [A336][Cl] (tricaprylmethylammonium chloride) is very popular and well-known compound widely used in the synthesis of PIM (Kolev et al. 2000; Blith-Raith et al. 2007; Gizli et al. 2012). Kolev et al. (2000) studied extraction of Pd(II) through PIM with Aliquat 336 as the ion carrier. In this work, the extraction of metal ions from the hydrochloric acid solutions into poly(vinyl chloride) (PVC)-based membranes containing Aliquat 336 chloride as both the extractant and the plasticizer was experimentally studied. The rate of extraction into membrane phase was considerably faster than observed previously for other metals, i.e., Au(III). The same compound was also used for separation of Ni(II) and Co(II) from 7 mol/dm<sup>3</sup> hydrochloric acid solution through PIM (Blith-Raith et al. 2007). Regel-Rosocka and Wisniewski (2011), Regel-Rosocka et al. (2015) and Nowak et al. (2010) studied phosphonium and ammonium quaternary salts as the extractants as well as the ion carriers of Zn(II) and Fe(II)/Fe(III). Kogelnig et al. (2011) reported application of phosphonium salt [Cyphos IL 101—trihexyl(tetradecyl)phosphonium chloride] as the carrier of Zn(II) from 5 mol/dm<sup>3</sup> hydrochloric acid into 1 mol/dm<sup>3</sup> sulfuric acid as the receiving phase. Guo et al. (2011) showed that Cyphos IL 104 [trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate] can be used as the carrier of Cr(VI) from hydrochloric acid into sodium hydroxide solution.

Kogelnig et al. (2008) synthesized task-specific ionic liquid (TSIL) containing thiol—tricaprylmethylammonium thiosalicylate [A336][TS]. TSILs contain functional groups appended to the cation and can extract metal ions without the ion exchange. The literature review shows that this TSIL is the excellent extractant of heavy metal ions, such as Hg(II), Cu(II), Ag(I), Fe(III), Cd(II), and Pb(II) from aqueous solutions (Kogelnig et al. 2008; Egorov et al. 2010; Fisher et al. 2011).

Spent catalysts and electronic scraps are potential source of palladium (Cieszynska and Wisniewski 2012; Saternus and Fornalczyk 2013; Lee et al. 2010). Palladium is usually present in aqueous solutions along with various metals, particularly present in the leach liquor of metallic waste. The transfer of metallic species from the source solution into the receiving phase depends on the nature of the species present in the aqueous solutions. The leach solutions containing Pd(II) and Pt(IV) as well as other metal ions are very often generated during the processing of various spent materials, i.e., spent catalysts (Sarioglan 2013). Selective separation of the precious metal ions from chloride leach liquors is difficult, because these metal ions exist usually as the anionic chlorocomplexes and show similar physicochemical properties (Jha et al. 2014). Chloride leach liquors of spent automobile catalysts contain usually mixture of various metal ions such as Pd(II), Pt(IV), Fe(III), Ni(II), and Mn(II) (Lee et al. 2010). Therefore, development of a simple, efficient, economical, and environmentally friendly process for the selective separation and recovery of palladium(II) ions from acidic chloride solutions is very important. Table 1 shows examples of PIM application for Pd(II) transport from hydrochloric acid solutions across membrane with various ion carriers (including ILs) reported in the literature.

The aim of this work was to study the facilitated transport of Pd(II) ions from hydrochloric acid solutions across PIM with [A336][TS]. It is worth highlighting that plasticizer is very important component of PIM which playing a role of solvent for the carrier within the membrane phase. Moreover, plasticizer improves flexibility of membrane and permeability of metal ions (Pospiech 2014). In this work, the competitive transport of Pd(II), Pt(IV), Fe(III), Ni(II), and Mn(II) from aqueous solutions has also been investigated.

## Experimental

### Reagents

*Inorganic chemicals*, i.e., palladium(II) chloride anhydrous, (PdCl<sub>2</sub>, purity = 99%), chloroplatinic acid, (30% H<sub>2</sub>PtCl<sub>6</sub>, pure), manganese(II) chloride tetrahydrate (MnCl<sub>2</sub>·4H<sub>2</sub>O, purity = 99%), nickel(II) chloride hexahydrate (NiCl<sub>2</sub>·6H<sub>2</sub>O, purity = 99%), iron(III) chloride (FeCl<sub>3</sub>, purity = 98%), and hydrochloric acid (HCl), were of analytical grade and were purchased from POCh (Gliwice, Poland). Aqueous solutions were prepared with deionized water.

*Organic reagents*, i.e., cellulose triacetate (CTA) (Fluka), thiourea (POCh, Gliwice, Poland), dichloromethane (POCh, Gliwice, Poland), *o*-nitrophenyl octyl

**Table 1** Examples of Pd(II) transport from hydrochloric acid solutions across PIM with various carriers reported in the literature

| Ion carrier   | Source phase                | Receiving phase              | Recovery factor RF (%) | References                  |
|---------------|-----------------------------|------------------------------|------------------------|-----------------------------|
| Cyanex 471X   | 0.001 M Pd(II) in 1 M HCl   | 0.5 M KSCN                   | 81.7% after 8 h        | (Pospiech 2015a, b)         |
| Cyphos IL 101 | 0.005 M Pd(II) in 0.1 M HCl | 0.1 M thiourea and 0.5 M HCl | 25% after 90 h         | (Regel-Rosocka et al. 2015) |
| Cyphos IL 102 | 0.005 M Pd(II) in 0.1 M HCl | 3 M HCl                      | 60% after 90 h         | (Regel-Rosocka et al. 2015) |
| Cyphos IL 104 | 0.005 M Pd(II) in 0.1 M HCl | 3 M HCl                      | 60 after 90 h          | (Regel-Rosocka et al. 2015) |

ether (ONPOE) (Fluka), tricaprylmethylammonium thiosalicylate, and [A336][TS] ( $\geq 95\%$ ), were supplied as reagent grade products by Sigma-Aldrich and used without further purification. The chemical structure of [A336][TS] ionic liquid is presented in Fig. 1.

### Polymer inclusion membrane

The membranes were prepared as described in detail elsewhere (Pospiech 2015a, b). Solutions of cellulose triacetate (CTA), ion carrier ([A336][TS], TOMATS), and plasticizer, i.e., nitrophenyl octyl ether (ONPOE) in dichloromethane, were prepared. A portion of this solution was poured on a flat-bottom glass Petri dish which was kept on a leveled surface. Organic solvent was allowed to evaporate over a period of 12 h. The obtained membrane was peeled off of the Petri dish, and subsequently, it was washed with water and conditioned in distilled water before the use. The thickness of PIMs was measured using the digital ultrameter (MG-401, Elmetron).

In the preliminary experiment, the membrane containing only CTA (40 wt%) as the polymer support and ONPOE (60 wt%) as the plasticizer was prepared (PIM 1). In the next experiments, the membrane containing CTA, ONPOE, and TOMATS as the carrier was prepared and used for the investigation (PIM 2). Table 2 shows the composition of the used PIMs.

### Transport experiments

Transport measurements were carried out in the experimental rig described and presented in detail elsewhere (Pospiech 2015a, b). The volumes of source and receiving phases were both equal to 100 cm<sup>3</sup>. During experiments, membrane samples with an effective membrane area of 12.56 cm<sup>2</sup> were used. The source and receiving aqueous

phases were stirred using magnetic stirrers. Aqueous phases were pumped through the membrane module at the flow rate of 50 cm<sup>3</sup> min<sup>-1</sup>, using a multichannel peristaltic pump (PP1B-05A type, Zalimp, Poland). The permeation rate of Pd(II) ions was determined by sampling of the source phase. Samples were subsequently analyzed using an atomic absorption spectrophotometer (Solaar 939, Unicam). The source phase contained 0.001 M PdCl<sub>2</sub> in solution. To study the influence of the hydrochloric acid concentration in the source phase on palladium transport, a series of experiments was carried out at various hydrochloric acid concentrations. The single Pd(II) transport across PIM at 0.001 M metal ion concentration from aqueous source phase at varying hydrochloric acid concentrations was studied using 0.1 M HCl and 0.3 M thiourea as the receiving phase. Time of the transport process was 24 h. Table 3 shows the conditions of the respective experiments.

The kinetics of Pd(II) ions transport through the PIM can be modeled with the following equation (Pospiech 2015a, b):

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

where  $c$  is the metal ion concentration (M) in the source phase at a given time,  $c_i$  is the initial metal ion concentration in the source phase,  $k$  is the rate constant (s<sup>-1</sup>), and  $t$  is the time of transport (s).

The value of rate constant ( $k$ ) was calculated from the plot of  $\ln(c/c_i)$  vs. time—Eq. (1). Experiments were run in duplicates and the rate constant value is an average from the both experiments. The value of the permeability coefficient ( $P$ ) was subsequently calculated using

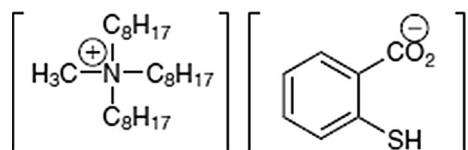
$$P = \frac{V}{A}k, \quad (2)$$

where  $V$  is volume of the aqueous source phase, and  $A$  is the effective area of the membrane.

The initial flux value ( $J_i$ ) was subsequently calculated using

$$J_i = P \times c_i. \quad (3)$$

In addition, the recovery factor (RF) was determined using



**Fig. 1** Structure of TOMATS ([www.sigmaaldrich.com/technical-documents](http://www.sigmaaldrich.com/technical-documents))

**Table 2** Composition of PIMs

| PIM   | Polymer support<br>CTA, wt% | Plasticizer<br>ONPOE, wt% | Ion carrier<br>[A336][TS] (TOMATS), wt% |
|-------|-----------------------------|---------------------------|---|
| PIM 1 | 40.0                        | 60.0                      | –                                       |
| PIM 2 | 40.0                        | 38.0                      | 22.0                                    |

**Table 3** Conditions of the respective experiments

| Experiment   | PIM            | Source phase  | Receiving phase                      | Time (h) |
|--|----------------|---|--------------------------------------|----------|
| Kinetic of transport   | PIM 1<br>PIM 2 | 0.001 M Pd(II) in 1 M HCl                                     | Mixture: 0.3 M thiourea in 0.1 M HCl | 24       |
| Influence of hydrochloric acid concentration in the source phase     | PIM 2          | 0.001 M Pd(II) in 1–5 M HCl                                   | Mixture: 0.3 M thiourea in 0.1 M HCl | 24       |
| Effect of thiourea concentration in 0.1 M HCl as the receiving phase | PIM 2          | 0.001 M Pd(II) in 1 M HCl                                     | 0.0–0.5 M thiourea in 0.1 M HCl      | 24       |
| Selectivity studies  | PIM 2          | 0.001 M Pd(II), Pt(IV), Fe(III), Ni(II) and Mn(II) in 1 M HCl | Mixture: 0.3 M thiourea in 0.1 M HCl | 24       |
| Stability of PIM   | PIM 2          | 0.001 M Pd(II) in 1 M HCl                                     | Mixture: 0.3 M thiourea in 0.1 M HCl | 24       |

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

The selectivity coefficient ( $S$ ) was defined as the ratio of initial fluxes for  $M_1$  and  $M_2$  metal ions, respectively (Pospiech 2015a):

$$S = \frac{J_{i,M_1}}{J_{i,M_2}}. \quad (5)$$

### Stability of PIM

The stability of the PIM containing 40 wt% CTA, 38 wt% ONPOE, and 22 wt% TOMATS was evaluated on the basis of the initial flux values obtained from four sequential experiments in which the membrane was used under the following experimental conditions: 1 M HCl as the source phase, concentration of Pd(II) ions 0.001 M, and the receiving phase: 0.3 M thiourea in 0.1 M HCl.

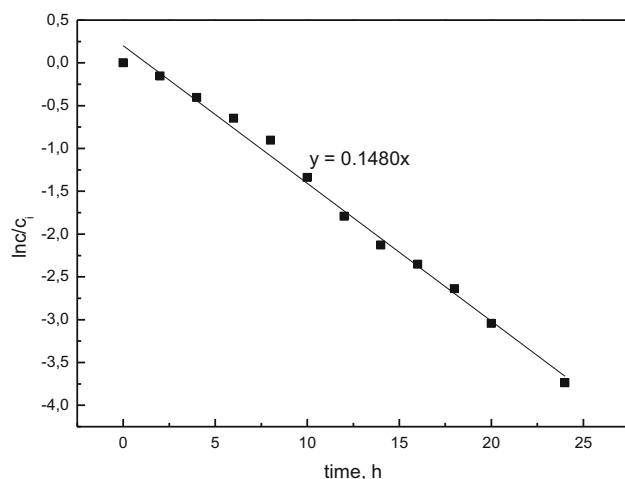
## Results and discussion

### Kinetic of transport

The physicochemical properties of the ion carrier (e.g., density, viscosity), the cation and anion combination, as well as the presence of the sulfur in the functional group of ionic liquid are essential factors strongly influencing the extraction efficiency and transfer of metal ions from the aqueous solutions (Fisher et al. 2011). Therefore, the study of the transport of Pd(II) through PIM with TOMATS can

provide important knowledge concerning the efficiency and selectivity of the separation process applying this IL as the ion carrier. Considering strong complexing properties of this ammonium ionic liquid, the high values of the recovery factor (% RF), the initial flux ( $J_i$ ), and the permeability coefficient ( $P$ ) should be expected.

Initially, the transport of Pd(II) ions was investigated using PIM without the ion carrier (membrane PIM1—Table 2). The results of this experiment showed that Pd(II) ions were not transported through membrane into the receiving phase. The conditions used to perform this process are shown in Table 3. In the subsequent experiments, PIM 2 membrane (Table 2) with TOMATS as the ion carrier was prepared and used. Pd(II) ions were transported from 1 M HCl solution into 0.3 M thiourea in 0.1 M HCl as the receiving phase. To calculate the  $k$  value (rate constant), a plot of  $\ln(c/c_i)$  vs. time was prepared. Figure 2 shows the kinetics dependence of  $\ln(c/c_i)$  vs. time for the transport of Pd(II) through the studied membrane. The results show that the ion carrier is necessary in the synthesis of the membrane. The relationship of  $\ln(c/c_i)$  vs. time is linear. The rate constant of this transport process was  $0.148 \text{ h}^{-1}$ . The recovery factor (RF) of Pd(II) after 24 h amounted to 97.6%. The results of this experiment show that the transport rate of Pd(II) is high. For instant, the rate constant of the transport of Pd(II) through PIM containing 19.9 wt% CTA, 55.2 wt% ONPOE, and 24.9 wt% Cyanex 471X was  $0.138 \text{ h}^{-1}$  in the similar conditions (Pospiech 2015b). As it can be seen, transport of Pd(II) across PIM with [A336][TS]—TOMATS is effective and the obtained results can be recognized as the promising ones.

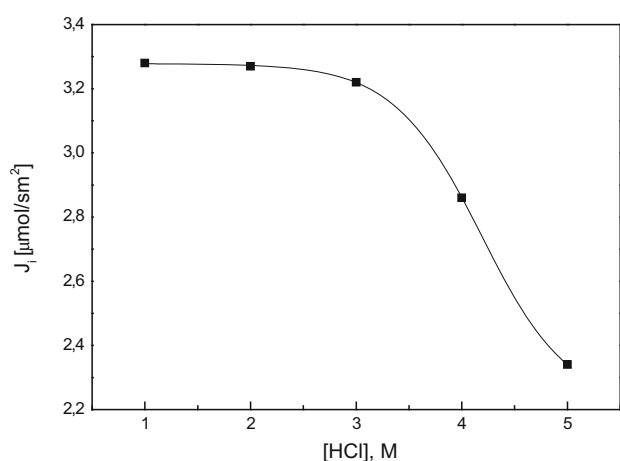


**Fig. 2** Relationship of  $\ln(c/c_i)$  vs. time for Pd(II) transport across PIM2 with TOMATS. The source phase: 0.001 M Pd(II) in 1 M HCl; the receiving phase: 0.3 M thiourea in 0.1 M HCl

### Influence of hydrochloric acid concentration in the source phase

The single Pd(II) transport across PIM at 0.001 M metal ion concentration from aqueous source phases of varying hydrochloric acid concentrations was studied. Figure 3 shows the influence of HCl concentration in the source phase on the value of the initial flux ( $J_i$ ). Kinetic parameters of this transport of Pd(II) are gathered in Table 4.

As it can be seen from the data presented in Table 4, the rate constants and the permeability coefficients as well as the recovery factor of Pd(II) after 24 h are strongly dependent on the concentration of HCl in the source phase, especially at concentration of acid in the source phase above 3 M. To explain these transport experimental results, the contributions of formed chloride species of Pd(II) in the aqueous chloride solutions can be used. The percent molar

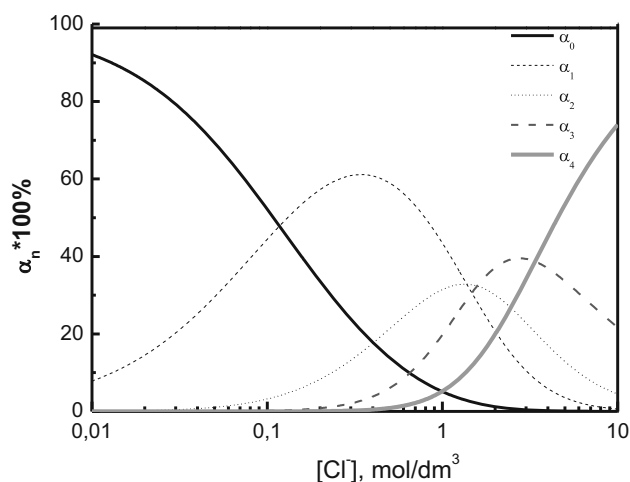


**Fig. 3** Effect of hydrochloric acid concentration in the source phase on the initial flux ( $J_i$ ) of Pd(II). Conditions as in Fig. 2

**Table 4** Kinetic parameters for Pd(II) transport across PIM depending on HCl concentration in the source phase

| [HCl], mol/dm <sup>3</sup> | Rate constant ( $k$ , h <sup>-1</sup> ) | Permeability coefficient ( $P$ ), (μm/s) | Recovery factor after 24 h RF (%) |
|----------------------------|---|--|-----------------------------------|
| 1.0                        | 0.148                                   | 3.28                                     | 97.6                              |
| 2.0                        | 0.142                                   | 3.15                                     | 96.4                              |
| 3.0                        | 0.132                                   | 2.92                                     | 95.7                              |
| 4.0                        | 0.129                                   | 2.86                                     | 95.2                              |
| 5.0                        | 0.106                                   | 2.34                                     | 90.5                              |

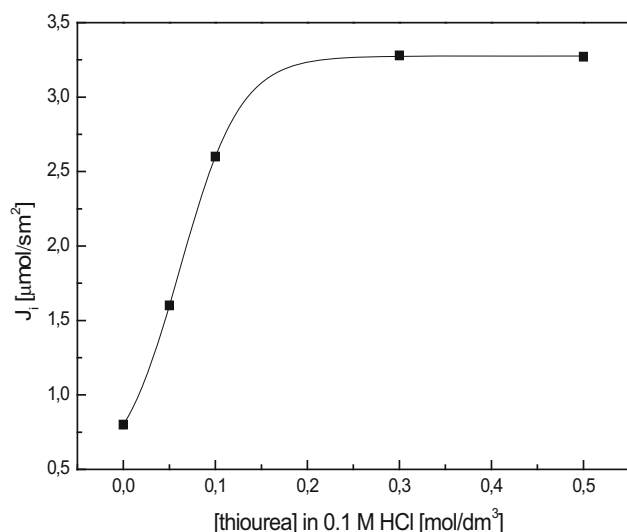
PIM: 40 wt% CTA, 38 wt% ONPOE and 22 wt%. The source phase: 0.001 M Pd(II) in 1 M HCl; the receiving phase: 0.3 M thiourea in 0.1 M HCl



**Fig. 4** Percent molar contributions ( $\alpha_n \cdot 100\%$ ) of chloride complex species for Pd(II) vs. chloride concentration

contributions of chloride complex species for Pd(II) vs. chloride ions concentration are presented in Fig. 4.  $\alpha_0$  is the percent molar contribution of uncomplexed cations (i.e., Pd<sup>2+</sup>), and  $\alpha_1$ ,  $\alpha_2$ ,  $\alpha_3$ , and  $\alpha_4$  are percent molar contributions of complexed ions with 1, 2, 3, and 4 ligands, respectively (i.e., PdCl<sup>+</sup>, PdCl<sub>2</sub>, PdCl<sub>3</sub><sup>-</sup>, and PdCl<sub>4</sub><sup>2-</sup>). At high chloride ion concentration, the predominant species in solution is PdCl<sub>4</sub><sup>2-</sup>. Probably, the transport proceeds according to a coordination salvation mechanism. Further studies are necessary to describe the transport mechanism. It was found that the permeability of process decreases slightly with the increase in hydrochloric acid concentration up to 3 M.

The results indicated that Pd(II) ions transport decreased as the acid concentration in the source phase increased. This decrease can be explained in terms of competition between the PdCl<sub>4</sub><sup>2-</sup> complexes and HCl to react with [A336][TS]. The similar observations during transport of Cd(II) ions from hydrochloric acid solutions through PIM with TiOAC (tri-isooctylammonium chloride) were



**Fig. 5** Effect of thiourea concentration in 0.1 M HCl as the receiving phase on the initial flux ( $J_i$ ) of Pd(II). PIM: 40 wt% CTA, 38 wt% ONPOE, 22 wt% TOMATS; the source phase: 0.001 M Pd(II) in 1 M HCl

reported by Alguacil et al. (2016). This behavior can be explained by the co-transport of hydrochloric acid at high concentration of this acid in the source phase.

#### Effect of thiourea concentration in 0.1 M hydrochloric acid as the receiving phase

In the next series of the experiments, the influence of the thiourea concentration in the receiving phase on the transport and recovery factor of Pd(II) has been studied. The stripping reaction at the membrane/stripping interface is very important during transport of metal ions. To analyze the effect of thiourea concentration in 0.1 M hydrochloric acid as the receiving phase on the transport of Pd(II), the aqueous solutions of thiourea were prepared and the concentration of the solution varied in the range from 0.0 to 0.5 M. The initial flux of Pd(II) increases with increase of thiourea concentration in 0.1 M HCl the receiving phase up to 0.3 M (Fig. 5).

Transport of metal ions increased and the mass flux was practical constant beyond thiourea concentration of 0.3 M. The highest initial flux ( $J_i$ ) was for 0.3 M thiourea concentration in 0.1 M HCl as the receiving phase ( $J_i = 3.2 \mu\text{mol s}^{-1} \text{m}^{-2}$ ). This kind of the stripping phase was also used by other researchers in liquid–liquid extraction (Swain et al. 2010) as well as in membrane system (Regel-Rosocka et al. 2015). Swain et al. (2010) studied the stripping of Pd(II) from organic phase after extraction by Alamine 300 (trioctylamine). They reported that, in the case of chloride solutions, there metal ions are stripping by a coordination–substitution reaction between thiourea  $(\text{NH}_2)_2\text{CS}$  and chloride ions. Regel-Rosocka et al. (2015) reported that 0.1 M thiourea and 0.5 M HCl formed the effective receiving phase for the transport of Pd(II) from aqueous chloride solutions across PIM with Cyphos IL 101.

#### Selectivity studies

The effect of other metal ions, including Pd(II), Pt(IV), Mn(II), Ni(II), and Fe(III) ions on the transport of Pd(II) through PIM, was also investigated. Table 5 contains the results of this study, presenting values of the rate constants ( $k$ ), initial fluxes ( $J_i$ ), and the selectivity coefficient ( $S_{\text{Pd}/\text{metal}}$ ) obtained during the experiments.

The results show that the initial transport fluxes of Pd(II), Pt(IV), Ni(II), and Mn(II) ions across PIM with [A336][TS] decrease in the sequence: Pd(II) > Pt > Fe(III) > Ni(II) > Mn(II). Since the selectivity coefficient values are greater than 1, this system is able to separate palladium(II) from the examined base metals.

#### Stability of PIM in transport process of Pd(II)

There were four repeated membrane transport experiments which used the same membrane. This membrane was taken away from the cell and washed in deionized water. The permeability coefficient of Pd(II) varied slightly after four cycles of 24 h each. In Table 6, the variation of the initial

**Table 5** Initial fluxes, rate constants, selectivity order, and selectivity coefficients for competitive transport of Pd(II), Pt(IV), Fe(III), Ni(II), and Mn(II) across PIM with TOMATS

| Metal ions | Rate constant, ( $k$ , $\text{h}^{-1}$ ) | Initial flux, $J_i$ , ( $\mu\text{mol s}^{-1} \text{m}^{-2}$ ) | Selectivity order and selectivity coefficient                                  |
|------------|--|--|--|
| Pd(II)     | 0.148                                    | 3.28   | Pd(II) > Pt(IV) > Fe(III) > Ni(II) > Mn(II)                                    |
| Pt(IV)     | 0.125                                    | 2.76   | 1.2                      3.2                      5.6                      6.3 |
| Fe(III)    | 0.047                                    | 1.03   |  |
| Ni(II)     | 0.026                                    | 0.58   |  |
| Mn(II)     | 0.024                                    | 0.52   |  |

PIM: 40 wt% CTA, 38 wt% ONPOE and 22 wt% TOMATS. The source phase:  $[\text{Me}] = 0.001 \text{ M}$  in 1 M HCl; the receiving phase: 0.3 M thiourea in 0.1 M HCl

**Table 6** Effect of cycles' number for Pd(II) transport across PIMs on the initial flux ( $J_i$ )

| Cycle number | Initial flux, $J_i$ ( $\mu\text{ms}^{-1}$ ) |
|--------------|---|
| 1            | 3.28  |
| 2            | 3.20  |
| 3            | 3.12  |
| 4            | 3.05  |

PIM: 40 wt% CTA, 38 wt% ONPOE and 22 wt% TOMATS. The source phase: 0.001 M Pd(II) in 1 M HCl; the receiving phase: 0.3 M thiourea in 0.1 M HCl

flux of Pd(II) observed during all four experiments is shown.

As it can be seen, the value of the initial flux for Pd(II) decreased slightly from 3.28 to 3.05  $\mu\text{molm}^{-2}\text{s}^{-1}$ . This observation confirms low tendency to leach the ion carrier from membrane matrix like in the earlier studies (Pospiech 2015a, b). Membrane with TOMATS has good stability, because the decrease in the initial flux is very small. It confirms that the rate of loss of the carrier to the aqueous phases that the membrane is in contact is also very small. In view of the high stability of the PIM in these experimental conditions, the membrane can be used for the recovery and separation of Pd(II) from acidic solutions, i.e., from leach liquor of spent catalysts.

## Conclusions

Palladium(II) was recovered from hydrochloric acid solutions by transport through PIM containing 40 wt% CTA, 38 wt% ONPOE, and 22 wt% TOMATS as the ion carrier into 0.3 M thiourea in 0.1 M HCl as the receiving phase. It was found that the recovery factor (RF, %) of Pd(II) and kinetic parameters are dependent on hydrochloric acid concentration in the source phase. PIM with TOMATS was successfully used for the transport of Pd(II) ions from the aqueous solution containing Pt(IV), Fe(III), Ni(II), and Mn(II) ions. The studies proved that the application of 0.3 M thiourea in 0.1 M hydrochloric acid solution allows for an efficient transport of Pd(II). The results also revealed that the membrane separation process can be an alternative method for the selective recovery of palladium(II) from acidic chloride solutions, i.e., leach liquor of spent catalysts.

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