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Effective and selective Au(III) transport across plasticized membrane with resorcinarene derivatives

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ABSTRACT

The transport through polymer inclusion membranes (PIMs) was found to be the effective and selective method of Au(III) anions removal from chloride acidic aqueous solutions. The PIMs construction was as follows: cellulose triacetate as the support, resorcinarene derivatives as the ionic carrier, and *o*-nitrophenyl octyl ether as the plasticizer. The solution of KI + HCl could be used effectively, as receiving phase, for the presented system. The obtained results showed a linear decrease of initial flux values with HCl concentration increase in the source phase. The linear decrease of initial flux in log–log scale with Au(III) concentration increase was also observed. The value of the slope of this relationship indicated on a first order of Au(III) reaction with resorcinarene at the membrane/aqueous source interface. Au(III) transport was satisfactorily accomplished with an excellent separation from Pd(II), Pt(IV) in the resorcinarene-based system. Results of the transport mechanism suggested that cotransport of anions took place across plasticizer membranes.

Keywords: Polymer inclusion membranes; Resorcinarenes; Gold; Platinum; Palladium; Separation

1. Introduction

In recent decades, a large amount of research has been conducted on recovering metals from e-wastes, especially precious metals, using hydrometallurgical methods. In comparison with other pyrometallurgical methods, hydrometallurgical methods are more accurate and predictable. A hydrometallurgical process consists of a set of operations including acidic or alkaline dissolution (leaching) of solids. Several techniques for gold extraction from aqueous solutions have been invented, such as solvent extraction, carbon adsorption, or ion exchange. In the case of the conventional solvent extraction technique for the recovery of gold from hydrochloric acid solutions, several studies have been performed using various types of extractants, for example, basic extractants like amines, solvating extractants like neutral organophosphorus compounds, and other extractants containing S as the electron donor. Only several studies on the separation of gold ions by liquid membranes have been performed. Most of them have been done using the supported liquid membrane technique.

In recent years, a remarkable increase in the applications of polymer inclusion membranes (PIMs) for Au(III) separation from acid solutions is found [1–5]. It has been reported that PIMs offer advantages over traditional solvent extraction, as they mimic the latter's separation ability, but without the use of a large inventory of diluents, which are often highly volatile and flammable liquids [6–8]. PIMs consist of an extractant (often referred to as carrier) and a base polymer (commonly poly(vinyl chloride) (PVC) or cellulose triacetate (CTA)). In some cases, they may also contain a plasticizer or a modifier. The extractant is usually a liquid complexing agent or an ion exchanger, responsible for binding the target species and transporting it across the PIM; plasticizers improve the compatibility between the extractant and the base polymer, thus, making the membrane homogeneous

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and flexible, while modifiers enhance the solubility of the adduct of the extractant and the target species in the membrane liquid phase [7]. Several ion carriers have been used in Au(III) recovery from acidic solutions, such as Aliquat 336 [1,5], Kelex 100 [2], ω-thiocaprolactam [4], and thiacalix[4] arenes [3]. These studies have shown successful extraction of Au(III) from hydrochloric acid solutions, with good selectivity over other metal ions. However, difficulties with the efficient stripping of Au(III) from the proposed PIMs have been encountered, that is, in the case of the Kelex 100-based PIM, stripping of up to 85% of Au(III) could be achieved [2], while up to 65% of Au(III) could be transported across a thiacalix[4] arene-based PIM [3]. Argiropoulos et al. [1] have reported on the high selectivity of a PIM composed of PVC and Aliquat 336 as the carrier for Au(III) extraction from hydrochloric acid solutions, even in the presence of a 500-fold higher concentration of Cu(II). However, they encountered difficulties in stripping Au(III) from the receiving solution during transport experiments, and observed some instabilities of the membrane.

We have started working on the extraction of gold by plasticizer membranes with macrocyclic carrier. In this study, the modeling of gold transport by PIM was investigated. A novel resorcinarene carriers selective to gold ions were used for the first time for the preparation of PIMs. This work concerned the transport of Au(III) from aqueous solutions through PIMs that contained CTA as a support, *o*-nitrophenyl octyl ether (2-NPOE) as a plasticizer and calixresorcin[4] arene derivatives as ion carriers immobilized onto polymeric membrane. The several parameters such as the concentration of the carrier, the effect of hydrochloric acid solutions in the source phase, and the separation of Au(III), Pt(IV), and Pd(II) in these membrane systems were tested.

2. Experimental part

2.1. Reagents

Materials and chemicals. Organic compounds, such as CTA (M_n = 72.000 − 74.000), 2-NPOE, and dichloromethane, were purchased from Fluka Chemie GmbH, Germany, and used without further purification. Inorganic compounds, such as sodium thiosulfate, hydrochloric acid, potassium iodide, were purchased from Merck KGaA, Germany, and used without further purification. The standards of 1,025 mg/dm^3 Au(III), 1,005 mg/dm^3 Pd(II), and 980 mg/dm^3 Pt(IV) in 5% HCl (Sigma Aldrich Co., USA) were used in proper dilutions. The carriers were synthesized in our laboratory. The calixresorcin[4]arene derivatives were prepared according to literature [9] and were used as a carrier. The structures and abbreviations of the carriers used in this study are shown in Fig. 1.

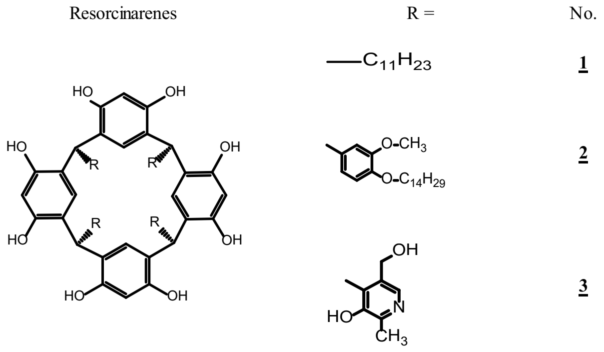

Fig. 1. The structures of resorcinarene derivatives used as ion carriers.

2.2. Transport studies

Transport experiments were carried out in a permeation module cell described in our previous paper [10]. Transport experiments were carried out in a permeation cell that consisted of two identical cylindrical compartments (half-cell volume 50 mL). An aqueous solution of 1 × 10^{-4} mol/dm^3 metal ions (Au, Pt, and Pd) in 0.25 mol/dm^3 HCl was used as a source phase. Equal volumes (50 mL) of the source and receiving phase were placed in the respective compartments of the cell that were separated by the prepared PIM. The resulting membrane contained 18 wt % CTA, 75 wt % 2-NPOE, and 7 wt % calixresorcin[4]arene derivative. In each experiment, the stirring of both phases was equal and kept at a constant rate of 600 rpm throughout the experiment. All tests were performed at room temperature 20°C ± 0.2°C. Samples were taken periodically from both cells with a micropipette. The analysis of metal ions content in the aqueous phase was carried out by flame atomic absorption spectrophotometry using a Solaar 939, Unicam Atomic Absorption Spectrometer. Instrumental conditions employed were those recommended by the operation manual. A Metrohm 620 pH meter with a combination glass electrode assembly was used for pH measurements.

The permeability coefficient (*P*) was calculated as in Eq. (1) according to the mass transfer model described by Danesi [11]:

$$\frac{dC}{dt} = -\frac{A}{V}PC \tag{1}$$

The mass balance could be derived by integration of Eq. (1) as follows:

$$\ln\frac{C}{C_i} = -\frac{AP}{V}t \tag{2}$$

where C is the metal ion concentration (kmol/m^3) in the source phase at a given time, C_i is the initial metal concentration in the source phase, t is the transport time (s), V is the volume of the aqueous in the source phase, and A is the area of the membrane. To calculate the P values, we prepared a plot of ln(C/C_i) versus time. The relationship of ln(C/C_i) versus time was linear, which was confirmed by the high values of the determination coefficient (R^2) 0.9538–0.9996.

The initial flux (J_i) was determined as shown in Eq. (3)

$$J_i = PC_i \tag{3}$$

To describe the efficiency of metal ions removal from the source phase, we calculated the recovery factor (RF) with Eq. (4)

$$RF = \frac{C_i - C}{C_i} \times 100\% \tag{4}$$

3. Results and discussion

3.1. Modification of source phase content

Studies on the effect of the composition of the source phase, that is, the concentration of chloride ions (HCl solutions) and the Au(III) ions concentration on the parameters of transport of this metal by PIMs were also carried out. Resorcinarenes 1, 2, and 3 were used as ion carriers in the membrane. First, the effect of HCl concentration in the source phase in the range of 0.001–0.5 M HCl on the transport of Au(III) ions by PIMs was investigated. Fig. 2 shows the dependence of the initial Au(III) fluxes on the HCl concentration value in the source phase containing 1.0×10^{-4} M Au(III) through PIM into a receiving phase containing 0.01 M $Na_2S_2O_3$ solution.

The initial flux values of Au(III) ion transport increased with the increase of Cl^- from 10^{-3} to 0.1 M. For $Cl^- = 0.5$ M the maximum initial flux of Au(III) transport (from the aqueous source phase containing 1.0×10^{-4} M metal) across PIM with 1, 2, and 3 was 2.2, 9.9, and 5.5 μmol/m^2 s, respectively. In the concentration range of 0.001–0.5 M HCl, the transport flux stabilized its value, and the parameters did not change their values as seen in the case of nonionizable resorcinarene 1 (Fig. 2). The highest increase of Au(III) transport rate was observed for resorcinarene 2. However, above 0.1 M Cl^- concentration, the deprotonation fraction of the carrier molecule was smaller, which resulted in small changes in the value of J_i for measurements above 0.1 M HCl. This proves the common mechanism of transport, however, with a significant participation in the formation of complexes by fitting $AuCl_4^-$ to the cavity 2. The change in transport rate versus the concentration (acidity) for 2 was therefore typical for cotransport and neutralization of complex molecules in the membrane rather than for the reaction mechanism $R - H^+ + AuCl_4^- = \left(RH - AuCl_4\right)_{mem}$, where R was a resorcinarene molecule.

The influence of Au(III) initial concentration in the source phase on PIM transport rate was also investigated. In order to determine the kinetics of the PIM process due to the concentration of Au(III) ions in the source phase four gold solutions in 0.1 M HCl containing 19.7, 49.25, 98.5, and 197 ppm Au(III) were prepared and used as the source phase. The receiving phase was 0.01 M $Na_2S_2O_3$ solution. The dependence $\ln(C/C_i)$, since the Au(III) ion transport by PIM, allowed to determine the values of ion fluxes as a function of Au(III) concentration in the source phase. Fig. 3 presents the obtained linear dependences of the J_i value versus the Au(III) concentration in the log–log system.

The changes in Au(III) initial flux values as a function of the metal concentration in the source phase (C_i) in the logarithmic system were linear, so the complexing reaction equation took place in the membrane phase. The tangents of the angle values for the straight line (Fig. 3) determined for the carriers 1, 2, and 3 were 0.99, 0.98, and 1.20, respectively. The obtained values of the slope indicated that $AuCl_4^-$, was involved in reactions occurring at the interface between the source phase and the membrane, so this reaction, due to the metal phase, was described by the first-order equation. This suggests that limiting mass transfer across PIM, is predominated by $AuCl_4^-$. Logarithmic dependencies of the flux on the concentration of metal and carriers aimed to demonstrate the stoichiometry of the complex composite and to optimize the transport process.

3.2. Modification of receiving phase

To determine the effect of the composition of the receiving phase on the transport rate at the interface of the membrane/receiving phase, two solutions of 0.01 M KI as well as 0.01 M KI + 0.01 M HCl solutions at pH = 2.0 were used. Fig. 4 presents the dependence of the recovery coefficient (RF) on the time of Au(III) ion transport by PIM containing carrier 2.

The transport of Au(III) ions across PIM containing resorcinarene 2, where the receiving phase was 0.01 M KI and 0.01 M KI + 0.01 M HCl, was very fast. After 4 h of transport, the removal of Au(III) ions was above 90%, whereas when

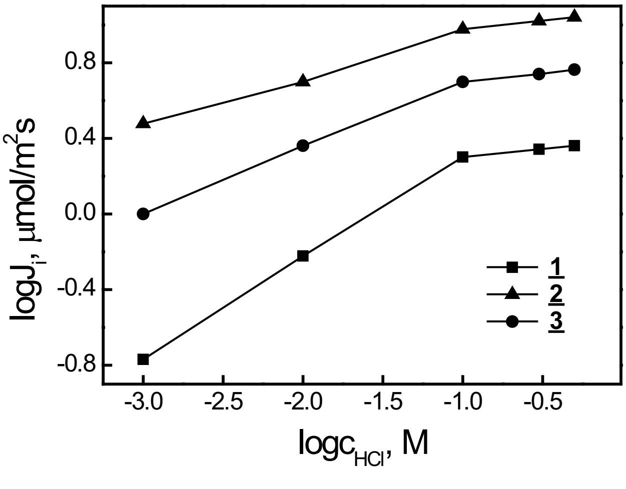

Fig. 2. The effect of HCl concentration in the source phase on the initial flux for transport of Au(III) through PIMs. Source phase: 1.0×10^{-4} M Au(III); membrane: 4.0 cm^3 o-NPOE/1.0 g CTA, 0.25 M 1, 2, 3; receiving phase: 0.01 M $Na_2S_2O_3$.

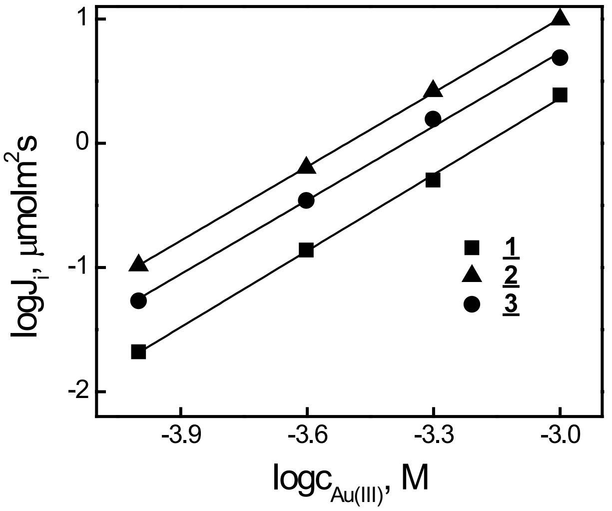

Fig. 3. The plot of an initial flux versus Au(III) concentration in the source phase. Membrane: 4.0 cm^3 o-NPOE/1.0 g CTA, 0.25 M 1, 2, 3; receiving phase: 0.01 M $Na_2S_2O_3$.

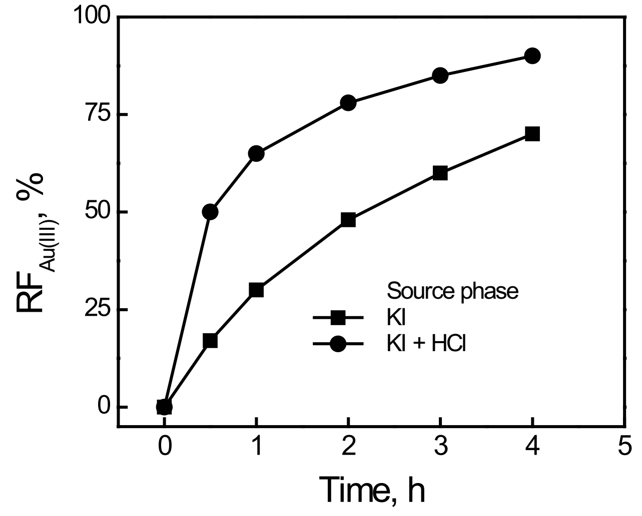

Fig. 4. The dependence of the recovery coefficient (RF) on the time of Au(III) transport across PIM. Source phase: 1.0×10^{-4} M Au(III); membrane: 4.0 cm^3 *o*-NPOE/1.0 g CTA, 0.25 M 2; receiving phase: 0.01 M KI; 0.01 M KI + 0.01 M HCl.

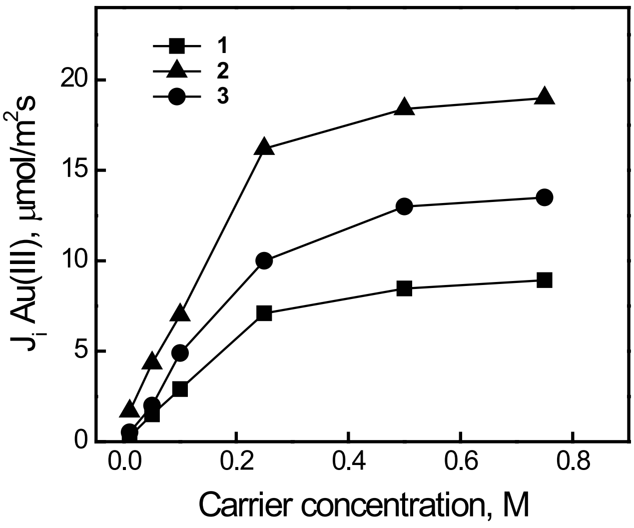

Fig. 5. The effect of carrier concentration upon the initial flux on Au(III) transport across PIMs with resorcinarenes 1, 2, and 3. Source phase: 1.0×10^{-4} M Au(III); membrane: 4.0 cm^3 *o*-NPOE/1.0 g CTA, 0.01–0.5 M 1, 2, 3; receiving phase: 0.01 M KI + 0.01 M HCl.

the receiving phase was only the KI solution, the efficiency of Au(III) extraction ions from the membrane was worse.

The transport process running in time approached the stationary state as the extraction extended to 100%. The ion transport proved to be fast despite the use of macrocyclic carriers. The application of the receiving phase 0.01 M KI + 0.01 M HCl significantly accelerated the transport of Au(III) across PIM. Our processes with resorcinarene 2 were more effective than those described in the literature [2], as process time was only 4–5 h for RF over 85%.

3.3. Modification of membrane phase

An important factor affecting the efficiency of the separation of metal ions by transport through PIMs is undoubtedly the composition of the membrane phase differing in the type and concentration of the ion carrier, plasticizer as well as the type of the polymer matrix used.

The analysis of the influence of the type and quantity of the extractants in PIM, selected from the resorcinarenes group, on the permeation of Au(III) ions was performed. As in previous studies, the source phase was a solution of 1.0×10^{-4} M Au(III) at pH = 2.0, and the receiving phase was 0.01 M KI + 0.01 M HCl solution. Membranes with a constant CTA (25 mg) and plasticizer (4 cm^3 *o*-NPOE/1.0 g CTA) content were prepared, whereas the concentration of the carrier in the membrane varied from 0.01 to 0.75 M. The experiments were carried out for 6 h. Membranes deprived of the ion carrier did not transport Au(III) ions, which indicated that its concentration had a key influence on the facilitated transport of metal ions by PIM.

The relationship of the Au(III) ion transport flux versus the ion carrier concentration in PIM is shown in Fig. 5; the curves were determined for resorcinarenes 1, 2, and 3.

The carrier concentration in the membrane equal to 0.25 M (based on volume plasticizer and carrier) resulted in the saturation of carrier in polymer membrane. The transport rates for this concentration were the maximum ones and for 1, 2, and 3 they were 8.85, 18.80, and 13.34 μmol/m^2 s, respectively.

Fig. 6 shows the dependence of the initial flux on the carrier concentration (in the log–log system) in the range from 0.01 to 0.25 M. Determination of the stoichiometry of the transported complex was enabled by the "*a*" parameter from the linear regression (tgα), determining the number of carrier molecules connected to the metal ion in the membrane phase.

From the dependence of the flux versus carrier concentration, it can be concluded at which concentration the saturation of the membrane occurs. The flux becomes stabilized and sometimes, in the case of macrocyclic carrier (crown ether), the crystallization of immobilized carrier in the liquid phase (carrier and plasticizer) occurs. On the basis of Fig. 6, the stoichiometry of the transported gold complex through the membrane was determined.

We were the first to use PIMs with resorcinarenes to transport Au(III) from hydrochloric aqueous solution. This transport proved to be very effective and selective. The results of the research presented in Figs. 5 and 6 were used to optimize the competitive transport of gold, platinum, and palladium ions.

As shown in Table 1, the determined slope values (*a*) from the regression equations were obtained at high values of determination coefficients (R^2), besides they were burdened with low errors of standard deviation, which proved its high level of statistical significance.

The logarithmic dependence of the initial flux on the concentration of the carrier in the membrane (c_{carrier}) enabled to determine the stoichiometry of the complexes formed during the transport of metal ions through the membrane. The values of the slope determined for 1, 2, and 3 suggested that the complex that was formed in the organic phase had

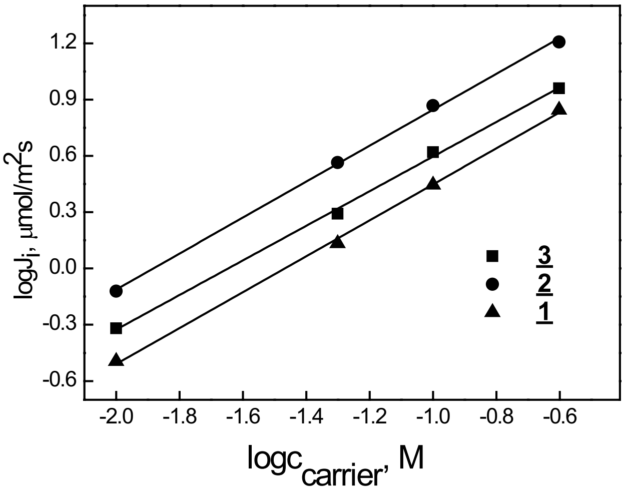

Fig. 6. The logarithmic dependence of the Au(III) initial fluxes versus the ion carrier concentration 1, 2, and 3. Source phase: 1.0 × 10^{-4} M Au(III); membrane: 4.0 cm^3 *o*-NPOE/1.0 g CTA, 0.01–0.75 M 1, 2, 3; receiving phase: 0.01 M KI + 0.01 M HCl.

Table 1
The parameters of linear regression log(J_i) versus log($c_{carrier}$) determined using the data from Fig. 6

Carriers	Slope (*a*): tgα = *a*	Determination coefficients, R^2
1	tgα = 0.9576 ± 0.02	0.9978
2	tgα = 0.9575 ± 0.02	0.9984
3	tgα = 0.9225 ± 0.025	0.9982

the composition M:L = 1:1; the values set out in Table 1 and Fig. 6 also supported this fact. Relationships obtained for the transport of Au(III) ions by membranes with a content of less than 0.75 M were linear. For higher concentrations, the crystallization of the carrier or complex caused that the transport rate did not differ, as evidenced by the formation of metal complexes with different stoichiometry. The efficiency of membrane transport with resorcinarenes as carriers, determined by Au(III) fluxes, decreased in the series 2 > 3 > 1. The high transport rate for 2 was certainly related to the presence of the ionized group and cooperative interaction with the metal ion at the pH of the receiving phase = 4.0. However, low values of the transport flux was observed for 1 suggested weak interactions of Au(III) ions with the cavity and donor centers of resorcinarenes. The carriers 2 and 3 had similar chemical structures of their active centers binding Au(III), but they differed in the substituents that could form complexes. It can be seen the difference in the value of fluxes depending on the type and concentration of the resorcinarenes in membranes.

The competitive transport of Au(III), Pt(IV), and Pd(II) ions from an equimolar mixture of 5.0 × 10^{-4} M across PIM containing 1, 2, and 3 was also investigated. The receiving phase was 0.01 M KI + 0.01M HCl. These metal ions were transported through the membranes for a period of 6 h. The change of RF versus time of the competitive transport of Au(III), Pt(IV), and Pd(II) is presented in Fig. 7.

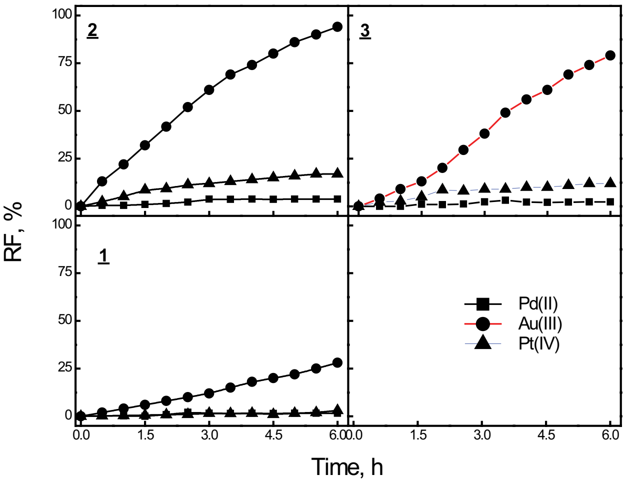

Fig. 7. The recovery factor (%) of Au(III), Pt(IV), and Pd(II) species from acidic aqueous solutions in PIM process. Source phase: 5.0 × 10^{-4} M Au(III), Pt(IV), Pd(II); membrane: 4.0 cm^3 *o*-NPOE/1.0 g CTA, 0.25 M 1, 2, 3; receiving phase: 0.01 M KI + 0.01 M HCl.

Effective separation of Au(III) ions was possible through membranes containing 2 and 3, for which the remaining metals were much worse separated from the aqueous phase, and their fluxes did not exceed 0.20 μmol/m^2 s. The transport rate of Au(III) ions by means of these membrane systems was determined by the series: 2 > 3 > 1. The values of Au(III) fluxes for membranes containing 1, 2, and 3 were 6.21, 26.9, and 15.8 μmol/m^2 s, respectively. High values of separation factors of Au(III) ion in relation to other metals indicated on the selectivity of these membranes were determined by the order Au(III) > Pt(IV) > Pd(II), which was connected with the high affinity of resorcinarene molecules to anionic forms of Au(III) species. The high selectivity of gold over palladium ($S_{Au/Pd}$ = 122), with the high Au(III) transport rate, was observed during transport with resorcinarene 2.

4. Conclusion

The PIMs containing resorcinarene derivative in plasticizer are promising for the removal of Au(III) from HCl solutions. The rate of the membrane transport of Au(III) anions, as a rule, increased with the increase of hydrochloric acid concentration in the source solution and significantly depended on the metal concentration in the source solution and on the carrier concentration in the liquid phase of membrane. Au(III) can be effectively removed from acidic chloride aqueous solutions by transport through PIMs with resorcinarenes 2 and 3 as an ion carriers into 0.01 M KI + 0.01 M HCl as a receiving phase. The membrane with a composition of 18 wt % of CTA as the support, 7 wt % of resorcinarene as the ion carrier, and 75 wt % of *o*-NPOE as the plasticizer showed the fastest rate of the extraction and the highest amount of Au(III) was extracted from solutions with HCl concentration of 0.5 M. The linear relationship between initial flux of Au(III) and HCl concentration of source aqueous phase was found. The linear relationship (in log–log scale) between initial metal flux and Au(III) concentration in the source aqueous phase is also observed. The slope values for investigated carriers were equal to 1.0, which indicates on a first order of $AuCl_4^-$ reaction with ionic carrier at the membrane/aqueous source phase boundary layer. A study of a number of back-extracting reagents for the back-extraction of Au(III) from Au(III)-loaded PIMs showed that the solution containing 0.01 M KI + 0.01 M HCl gave the highest initial back-extraction flux.

In conclusion, we demonstrated that the selectivity of functionalized resorcinarene derivatives toward Au(III), Pt(IV), and Pd(II) was greatly influenced by lower rim substituents. When the resorcinarene with ionizable group **2** was selected, the efficiency of gold transport was much higher than for other species and the recovery was almost complete.

Gold was selectively recovered from a mixture of Au, Pd, and Pt in a PIM system containing macrocycle **2**, whereas other metals were poorly transported through a PIM into 0.01 M KI + 0.01 M HCl solution used as a stripping agent. The good behavior of carriers **2** and **3** used in plasticizer membrane experiments was also an encouraging result. Hence, this new family of resorcinarene compounds in view of the analytical and hydrometallurgical applications should be further tested. Nevertheless, the newly developed PIM containing resorcinarenes could be potentially suitable for a single use process for efficient recovery of Au(III) from diluted aqua regia solutions from electronic scrap or jewelry recycle. The high price of gold financially justifies this approach.

Acknowledgments

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