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Separation of Palladium(II) and Platinum(IV) by Bulk Liquid Membranes during Electrodialysis

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Abstract: The process of $PdCl_4^{2-}$ and $PtCl_6^{2-}$ separation extracting from binary hydrochloric mixtures as well as palladium(II) extraction from individual solutions by bulk liquid membranes containing diphenylthiourea and di-o-tolylthiourea in 1,2-dichloroethane is studied at galvanostatic electrodialysis. The effects of the current density, the composition of the liquid membrane and of aqueous solutions on the rate of the metal transport are determined. It is shown that an effective separation of Pt(IV) from Pd(II) is achieved in the presence of an excess of the carrier. Maximum separation factor $\beta_{Pt/Pd}$ of 380 is obtained in 1 hour of electrodialysis under optimal conditions. The transport of platinum(IV) is supposed to occur in the form of ionic associates $(PdL_4Cl)_2PtCl_6$. Platinum(IV) concentration and composition of the strip solution do not exert a considerable influence on the separation factor.

Keywords: Liquid membrane, electrodialysis, platinum metals, diphenylthiourea, di-o-tolylthiourea, separation

INTRODUCTION

A liquid membrane is determined as a layer of an organic solvent separating two aqueous solutions. Compounds, promoting the transport of substances from one aqueous solution to another may be dissolved in the organic phase (1). Membrane extraction is a promising technique for removal and separation

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of valuable metal ions from diluted acid solutions (2). Application of a direct electric field significantly intensifies the transport of ions through the bulk liquid membranes and facilitates the stripping of metals from the organic phase (3, 4). Data on electrodialysis of liquid membranes are rather low in comparison with those of membrane extraction. A theoretical model for the description of the transport of cations through thick neutral carrier membranes at electrodialysis is developed in (5, 6). Electrodialysis through liquid membranes containing aliphatic amines was used to extract Pd(II) and Pt(IV) from hydrochloric solutions (7, 8). An effective Cu(II) removal from sulfuric acid solutions by di(2-ethylhexyl)phosphoric acid–based bulk liquid membranes at electrodialysis has been demonstrated (9). Electroassisted Ni(II) transfer from a mixture with Cr(III), Fe(II), Co(II) using supported liquid membranes has been studied (10).

Platinum metals are widely used in electronics, radio engineering, instrument-making, in jewelry, medicine and as automotive and industrial catalysts (11). The resources of noble metals are limited, and their worth has increased in recent years. Thus, there is a growing need for novel separation techniques, which selectively extract platinum metals from dilute solutions. Significant difficulties arise in analytical chemistry and the technology of platinum metals in the course of their separation, particularly, Pt(IV) and Pd(II) separation. Existing methods for platinum metals separation are, as a rule, multistage and laborious. Dialkylsulfides are produced commercially for the separation of palladium from platinum. However, the slow extraction of metals is their disadvantage (12). In recent years, extraction by different phosphorus-, sulphur-, and nitrogen-containing reagents has been used for the separation of palladium and platinum in hydrochloric solutions (13–17). The processes are characterized by partial or complete irreversibility. Supported liquid membranes based on tri-isobutylphosphine sulphide, used for extracting palladium from the binary mixture Pd-Pt, are described in (18). The authors (19) used a derivative of 8-quinolinol for the separation of platinum from palladium by a supported liquid membrane. The application of emulsion liquid membranes for this purpose is reported in (20). Bulk liquid membranes have not been applied for platinum metals separation. At the same time, the electrodialysis of liquid membranes is a promising method in hydrometallurgy. It can be applied to the extraction of platinum metals from solutions at processing copper or nickel ores and at secondary raw materials recycling, in particular, of spent automotive catalysts and waste waters.

Organic derivatives of thiourea are known as selective extractants of platinum metals (21). The extractable species of palladium(II) with diphenylthiourea (DPTU) and di-o-tolylthiourea (DOTTU) are produced rapidly at room temperature, whereas platinum(IV) complexes require heating or the use of a catalyst, such as stannous chloride (22). Different reaction abilities of platinum metal chlorocomplexes are considered at their separation by extraction with DOTTU (23). However, the stripping of metals from the organic phase is troublesome because of the formation of stable compounds. The aim of the present work is to study the membrane extraction of Pt(IV) and Pd(II) from hydrochloric acid solution by bulk liquid membrane containing DOTTU or DPTU in 1,2-dichloroethane during galvanostatic electrodialysis and to find out optimal conditions for metal separation.

EXPERIMENTAL

The five-compartment electrodialysis cell was made of Teflon (Fig. 1). The liquid membrane (thickness 0.2 cm, volume 2 cm^3, surface area 7.1 cm^2) was separated from the aqueous solutions by two vertical cellophane films. Such films allow to create a reproducible hydrodynamic situation at the interface and serve as an aqueous phase continuation (4). The films had a thickness of 20–30 μm and a surface area of pores of $1 \cdot 10^{-3}$ cm^2 per 1 cm^2. The films were soaked in water for more than 24 hours before use. The electrode compartments (volume 17 cm^3) were filled with solutions of 0.15 M H_2SO_4. The compartments of feed and stripping solutions were separated by the solid cation-exchange membranes MK-40. The direct electric current was supplied to the plane platinum electrodes. Potentiostat P-5848 (Russia) was used as a current source. The voltage was measured by digital voltmeter. The electric conductivity was measured by means of ac bridge P-568 at a frequency of 1000 Hz using a cell with platinum electrodes (cell constant $3.9 \cdot 10^{-4}$ m^{-1}).

The solutions of DOTTU and DPTU in 1,2-dichloroethane were used as the liquid membranes. Reagents of pro-analysis grade were used without further purification. 1,2-dichloroethane was purified according to the procedure given in ref. (24), and the fraction with boiling point 83.4-83.5° C was used. The feed solution was prepared by dissolving $H_2PtCl_6 \cdot 6H_2O$ and/or $PdCl_2$ in 1.0 M hydrochloric acid solution. The solution of 1.0 M hydrochloric acid was used usually as a strip solution. The concentrations

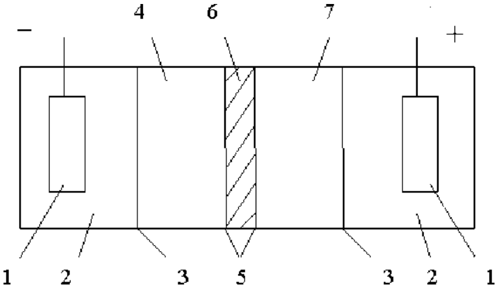


Figure 1. Electrodialysis cell (1 - platinum electrodes; 2 – sulfuric acid solutions; 3 – solid cation-exchange membranes; 4 – feed solution; 5 – cellophane films; 6 – liquid membrane; 7 – strip solution.

of platinum(IV) and palladium(II) in the aqueous solutions were determined by spectrophotometry using $SnCl_2$ (11) and α-furildioxime (25), respectively. Spectrophotometer SF-46 (LOMO, Russia) was used for the analysis of metal ions. Voltammograms of the liquid membranes were registered by the setup described in (26). Rate of potential sweep was 6 V/s.

RESULTS AND DISCUSSION

Stripping of Palladium(II)

It was found that the application of an electric field allows to strip Pd(II) from the liquid membrane, containing palladium extract with DOTTU, into an aqueous anodic solution of 1 M HCl (reaction 1):

$$\mathrm{Pd\ L_2Cl_{2(o)}} + 2\ \mathrm{Cl^-_{(a)}} \iff \mathrm{PdCl^{2-}_{4\,(a)}} + 2\ \mathrm{L_{(o)}} \qquad (1)$$

where: L – DOTTU; a – aqueous phase; o – organic phase.

The increase of the current density to 4 mA · cm^{-2} leads to a proportional rise of palladium flux (Fig. 2). The reduction of stripping rate at higher current densities is caused by the electric breakdown of the liquid membrane. It is characterized by a jump-type abrupt decrease of the ohmic resistance of the membrane system, and is caused by water accumulation in the organic phase (3).

The increase of the extractant concentration in the liquid membrane leads to an abrupt reduction of the palladium(II) flux. Stripping of Pd(II) from the

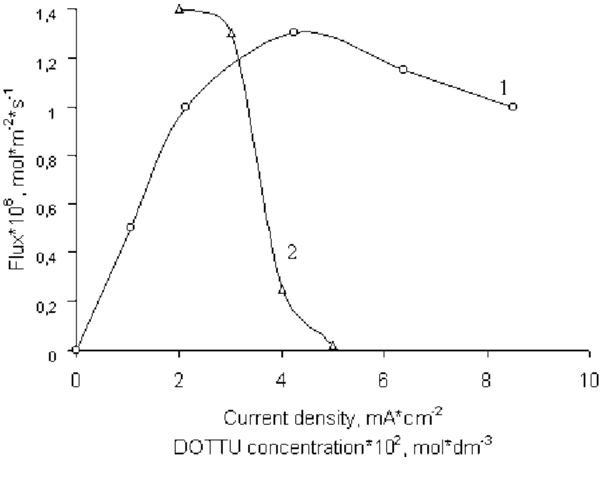


Figure 2. Effect of current density (1) and DOTTU concentration (2) on palladium back-extraction rate ($C_{Pd} = 1.1 \cdot 10^{-2}$ mol · dm^{-3}; i = 8.5 mA · cm^{-2}; t = 60 min; $C_{DOTTU} = 0.03$ mol · dm^{-3} (1); i = 4.2 mA · cm^{-2} (2)).

organic phase occurs within a rather narrow DOTTU concentration range of 0.02–0.03 M. The palladium(II) flux ($\sim 10^{-6}\,\mathrm{mol \cdot m^{-2} \cdot s^{-1}}$) is approximately one order of magnitude lower than the flux in systems with tertiary amine salts and quaternary onium base salts under the same experimental conditions (7, 8). The reason of low metal flux is a higher stability of the coordination Pd(II) complex with DOTTU compared with ionic associates.

Palladium(II) Transfer

Figure 3 illustrates the possibility of palladium(II) transport across the liquid membranes with DOTTU into a solution of 1 M HCl, when applying an electric field. Pd(II) extraction into the strip solution begins after saturation of the organic phase by metal (loading degree n ~ 1) and is accompanied by an increase of voltage. The precipitation on cellophane films at the liquid membrane/strip solution interface is observed during electrodialysis. It should be mentioned that the complexes with Pd: DOTTU ratio 1 : 1 along with the generally known (22) complexes with ratio Pd: DOTTU = 1 : 2 can be formed at Pd(II) interacting with the carrier. The experimental data on solvent extraction indicate the existence of such compounds in saturated extracts of 0.05 M DOTTU (Table 1).

The dependencies of Pd(II) fluxes through the interfaces feed solution/liquid membrane and liquid membrane/strip solution on its initial concentration are presented in Fig. 4. The palladium(II) flux into the liquid membrane increases ten times, as the metal concentration rises one order of magnitude, whereas the Pd(II) transfer rate into the strip solution increases

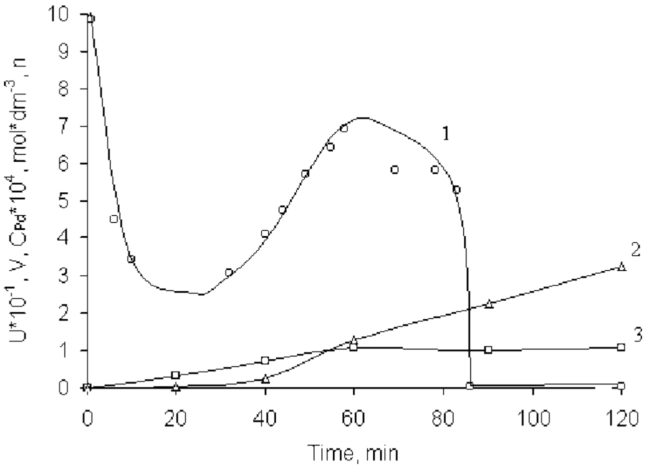


Figure 3. Change in voltage (1), kinetics of palladium accumulation in the strip solition (2) and change in loading degree of the liquid membrane (3) during electrodialysis ($C_{Pd} = 1.1 \cdot 10^{-2}\,\mathrm{mol \cdot dm^{-3}}$; $C_{DOTTU} = 0.03\,\mathrm{mol \cdot dm^{-3}}$; $i = 4.2\,\mathrm{mA \cdot cm^{-2}}$).

Table 1. Solvent extraction of palladium(II) by DOTTU at excess of H_2PdCl_4 ($C_{HCl} = 1$ mol · dm^{-3}; t = 2 min)

C_{Pd}, mol · dm^{-3}	C_{DOTTU}, mol · dm^{-3}	V_{aq}:V_{org}	$C_{Pd\ (o)}$, mol · dm^{-3}	C_{DOTTU}: C_{Pd}
0.01	0.02	2	0.01	2.0
0.01	0.03	2	0.014	2.1
0.08	0.05	1	0.032	1.56

approximately in 300 times. It can be interpreted as the absence of kinetic limitations at the stage of metal extraction into the organic phase. Rapid achieving of equilibrium in the solvent extraction of Pd(II) by DOTTU confirms diffusional control of the stage of metal transfer into the liquid membrane (23). At high electric current densities the transport of ions through the organic layer takes place due to electromigration. Thus, the most probable stage, limiting the rate of palladium(II) transfer through the membrane, is back extraction into the strip solution of the anode compartment (reaction 1). This process does not occur without the electric field applied to the present system.

It should be mentioned that the transfer of palladium(II) into the strip solution is accompanied usually by a significant rise in voltage, which increases from ~20 to 290 V at the maximum Pd(II) concentration (0.08 mol · dm^{-3}).

Separation of Platinum(IV) and Palladium(II) by DOTTU

Binary hydrochloric mixtures, containing equal amounts of Pt(IV) and Pd(II) of $1 \cdot 10^{-2}$ M in 1 M HCl, were used for platinum metal separation. It is found

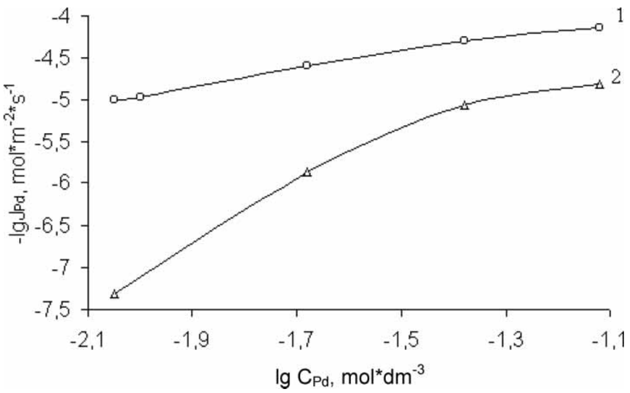


Figure 4. Dependence of palladium flux into the liquid membrane (1) and into the strip solution (2) on its initial concentration in the feed solution ($C_{DOTTU} = 0.05$ mol · dm^{-3}; i = 4.2 mA · cm^{-2}; t = 60 min).

that applying an electric field, both platinum(IV) and palladium(II) are extracted into the liquid membrane, with the Pt(IV) transport rate being essentially higher than that of Pd(II). In the absence of palladium(II), platinum(IV) does not transfer into the organic phase, as the interaction between Pt(IV) and DOTTU is hindered by kinetic inertness of $PtCl_6^{2-}$ and does not take place under ordinary conditions. The electric conductivity of the system with individual Pt(IV) solutions is very low.

The palladium(II) flux sharply decreases, when DOTTU concentration in the liquid membrane comes up, whereas the platinum(IV) transfer rate remains sufficiently high, and at an excess of the carrier an effective separation of metals is achieved (Fig. 5). The separation factor β is defined as:

$$\beta_{Pt/Pd} = \frac{C_{Pt} \cdot C^0_{Pd}}{C^0_{Pt} \cdot C_{Pd}}. \qquad (2)$$

where C_{Pt} and C_{Pd} - concentrations of platinum(IV) and palladium(II) in the strip solution, C^0_{Pt} and C^0_{Pd} - initial concentrations in the feed solution.

The obtained values of the Pt(IV) flux are typical of systems with ion-exchange carriers at electrodialysis (3, 8). Taking into account that platinum(IV) is not extracted by liquid membranes in the absence of palladium(II), one can conclude that Pd(II) is incorporated into the complex, transporting Pt(IV) across the liquid membrane.

The influence of metal concentrations in the feed solution upon the selectivity of Pd(II) and Pt(IV) separation is illustrated in Table 2. The increase of the platinum(IV) concentration up to 0.09 M, with the palladium(II) concentration being constant, does not exert significant influence on the separation factor, as the Pt(IV) flux is proportional to its concentration. Change in platinum(IV) concentration practically does not influence the

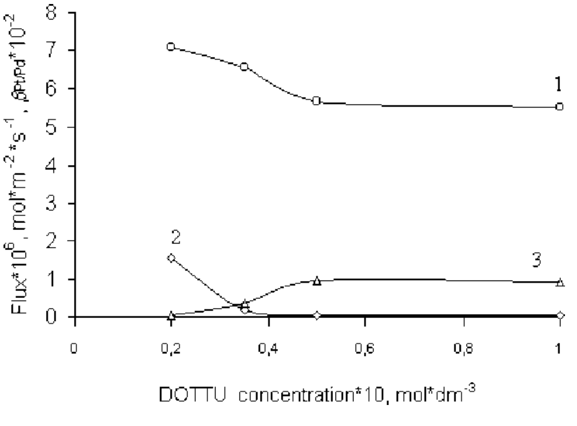


Figure 5. Effect of carrier concentration on platinum(IV) (1), palladium(II) (2) fluxes and separation factor (3) ($i = 4.2$ mA $\cdot$ cm^{-2}; $t = 60$ min).

Table 2. Effect of palladium(II) and platinum(IV) concentration in the feed solution upon the extraction degrees (E) and separation factor (β) ($C_{DOTTU} = 0.05\ mol \cdot dm^{-3}$; $i = 4.2\ mA \cdot cm^{-2}$; $t = 60$ min)

Feed solution				Strip solution		
C_{Pd}, $mol \cdot dm^{-3}$	C_{Pt}, $mol \cdot dm^{-3}$	E_{Pd}, %	E_{Pt}, %	C_{Pd}, $mol \cdot dm^{-3}$	C_{Pt}, $mol \cdot dm^{-3}$	$\beta_{Pt/Pd}$
0.009	0.01	0.11	11.3	$1.1 \cdot 10^{-5}$	$1.13 \cdot 10^{-3}$	103
0.009	0.09	0.1	12.6	$1.0 \cdot 10^{-5}$	$1.13 \cdot 10^{-2}$	126
0.025	0.01	1.36	10.9	$3.4 \cdot 10^{-4}$	$1.09 \cdot 10^{-3}$	8.0
0.05	0.01	3.65	13.4	$1.83 \cdot 10^{-3}$	$1.34 \cdot 10^{-3}$	3.7
0.075	0.01	3.92	14.4	$2.9 \cdot 10^{-3}$	$1.44 \cdot 10^{-3}$	3.7

shape of the voltage-time diagram either. At the same time, the increase of the palladium(II) concentration results in a sharp rise of the Pd(II) flux and in a decrease of the Pt(IV) transport selectivity. During the electrodialysis process the Ohmic resistance of the membrane and the voltage change considerably (Fig. 6). A sharp decrease of voltage in the beginning of process is followed by a noticeable rise, depending on the Pd(II) concentration in the feed solution. The initial increase of the electric conductivity can be explained by the rise of the concentration of ions in the liquid membrane

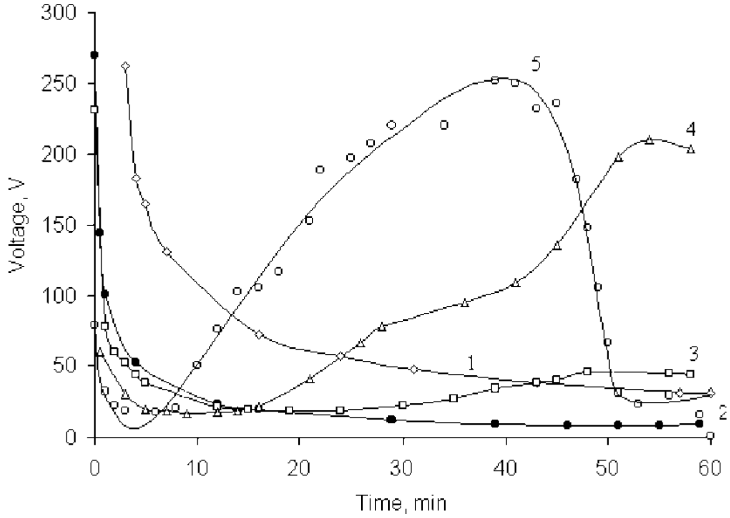


Figure 6. Change in voltage during electrodialysis for various palladium concentrations in the feed solution ($C_{DOTTU} = 0.05\ mol \cdot dm^{-3}$; $i = 4.2\ mA \cdot cm^{-2}$; $C_{Pt} = 0.01\ mol \cdot dm^{-3}$; C_{Pd} ($mol \cdot dm^{-3}$) $= 2.2 \cdot 10^{-3}$ (1); $9 \cdot 10^{-3}$ (2); $2.5 \cdot 10^{-2}$ (3); $5 \cdot 10^{-2}$ (4); $7.5 \cdot 10^{-2}$ (5)).

due to the extraction of Pd(II), accompanied by ion pairs formation. The electric conductivity decreases, when the organic phase saturates with palladium(II). At low Pd(II) concentrations the rise in voltage is not observed. Values of molar electric conductivity of saturated DOTTU extracts are presented in Table 3. The obtained data allow to evaluate the dissociation constant of ion pairs in the organic phase $K_{diss} \leq 10^{-6}$.

Visible-spectroscopic measurements confirm the change in composition of Pd(II) extracted compounds during saturation of the organic phase. There is a complex with maximum absorption at 410 nm in the presence of an excess of the reagent. However, saturated extracts show only monotonous lowering of absorption in the visible spectra.

Cyclic voltammetry with linear potential sweep was used for investigating the liquid membranes. Voltammograms in Fig. 7 show that the total concentration of ions in the organic phase increases in the course of electrodialysis, as a result of the interaction of Pd(II) with DOTTU. The electric conductivity of the liquid membrane is small in the absence of palladium(II) in the aqueous solution. If the feed solution contains only platinum(IV), the current-voltage dependence coincides with the voltammogram of the background electrolyte (Fig. 7, curve 2). In the presence of palladium(II), an increase of the electric conductivity of the liquid membrane is observed. It is the result of appearance of ion pairs in the organic phase. The run of the voltammograms is determined by the palladium(II) concentration in the feed solution. The DOTTU concentration poorly influences the current passing through the membrane. S-shaped voltammograms with the reverse current exceeding the forward current are determined by the increase of the total concentration of ions in the membrane after the reverse of voltage.

Saturated palladium(II) extract with DOTTU was used as a liquid membrane in some voltammetric experiments. The voltammograms in Fig. 8 illustrate the process of exchange of anions in the organic phase to perchlorate-ions of the aqueous solution of the catode compartment. Appearance of more lipophilic anions in the membrane leads to an increase in electric conductivity of the system.

The obtained results allow to conclude that during the palladium(II) interaction with DOTTU a compound is formed, which transports

Table 3. Ohmic resistance (R), specific (κ) and molar (λ) electric conductivity of the saturated extracts of palladium(II) by DOTTU in dichloroethane

C_{DOTTU}, mol · dm^{-3}	R · 10^{-3}, Ω	$\kappa \cdot 10^{6}$, $\Omega^{-1} \cdot cm^{-1}$	λ, $cm^2 \cdot \Omega^{-1} \cdot mol^{-1}$
10^{-6}–10^{-3}	>100	—	—
$5 \cdot 10^{-3}$	46.2	0.83	0.17
$1 \cdot 10^{-2}$	17.2	2.23	0.22
$1 \cdot 10^{-1}$	1.9	20.6	0.21

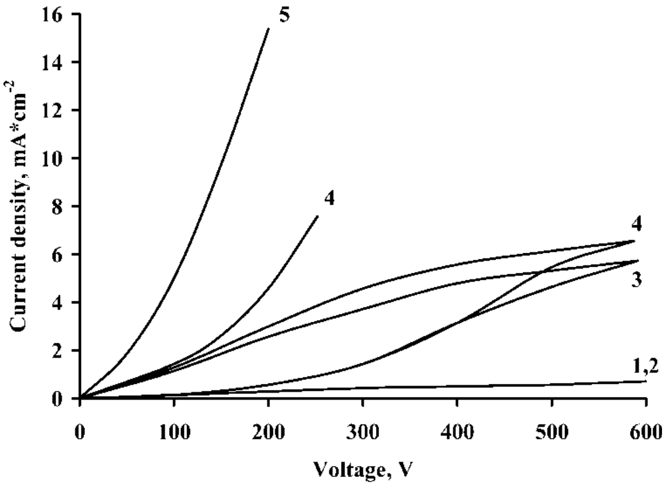
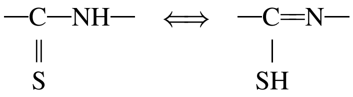


Figure 7. Voltammograms of the liquid membranes (C_{Pd} (mol · dm^{-3}) = $1 \cdot 10^{-3}$ (3, 4); $1 \cdot 10^{-2}$ (5); C_{DOTTU} (mol · dm^{-3})= $1 \cdot 10^{-2}$ (1, 2, 4); $2 \cdot 10^{-2}$ (3, 5); $C_{Pt} = 0.01$ mol · dm^{-3} (2)).

platinum(IV) across the liquid membrane due to the anion-exchange mechanism. In order to confirm the possibility to transfer some other metal chlorocomplexes in the studied system, binary mixtures of Pd(II) and Fe(III) were used (0.01 mol · dm^{-3} $H_2PdCl_4 + 0.1$ mol · dm^{-3} $FeCl_3$). It was demonstrated that the transport of $FeCl_4^-$ across the liquid membrane into the strip solution and effective separation of metals takes place under conditions optimal for Pd(II) and Pt(IV) separation ($\beta_{Fe/Pd} = 40$ at 0.05 mol · dm^{-3} DOTTU and 4.2 mA · cm^{-2}).

To discuss the composition of extracted Pd(II) complexes, it is necessary to consider data available in literature. Poor protonation ability of derivatives of thiourea (diphenylthiourea does not protonate up to 12.5 M HCl (27)) allows not to regard the extraction of anion complexes as the main extraction mechanism. The formation of chelate complexes is also highly improbable, since the tautomeic equilibrium (3) for these reagents in acidic and neutral solutions is shifted to the thione



$$\underset{\underset{S}{\|}}{—C}—NH— \Longleftrightarrow \underset{\underset{SH}{|}}{—C}{=}N— \qquad (3)$$

form (22). Thus, the formation of coordination compounds of formula (PdL_mCl_n), where ligands are bonded through their sulphur atom, is, obviously, the main extraction mechanism. Low values of the electric conductivity (Table 3) testify that Pd(II) mostly forms neutral PdL_2Cl_2 complex at saturation of the organic phase. The transport of platinum(IV), as well as of

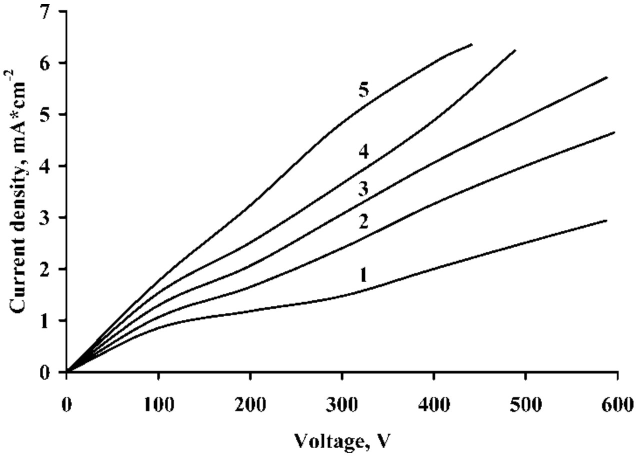


Figure 8. Voltammograms of the liquid membranes (organic phase: $C_{Pd} = 3 \cdot 10^{-3}$ mol $\cdot$ dm^{-3}; $C_{DOTTU} = 5 \cdot 10^{-3}$ mol $\cdot$ dm^{-3}; aqueous phase: $C_{HCl} = 1$ mol $\cdot$ dm^{-3}; $C_{HClO_4} = 0.01$ mol $\cdot$ dm^{-3}; 1–5 — potential sweep cycles).

iron(III) and perchlorate ions through the liquid membrane can be explained, in our opinion, by the equilibrium between four-coordinated neutral and five-coordinated ionic Pd(II) complexes with DOTTU, resulting in ion pair formation between $PtCl_6^{2-}$ and the ionic form of palladium(II) complex. Such equilibrium was reported in (28) for solutions of some derivatives of thiourea in weakly coordinating solvents:

$$\text{Pd L}_4\text{Cl}^+ + \text{Cl}^- \iff \text{Pd L}_2\text{Cl}_2 + 2\text{ L} \qquad (4)$$

Thus, in the beginning of electrodialysis, when there is an excess of the carrier in the organic phase, the equilibrium (4) shifts to the left, and the predominant form of coordination complex is PdL_4Cl^+. It extracts $PtCl_6^{2-}$ anions due to the interfacial anion-exchange mechanism:

$$\text{PdCl}_{4\,(a)}^{2-} + 4\text{ L}_{(o)} \iff [\text{PdL}_4\text{Cl}]^+\text{Cl}_{(o)}^- + 2\text{ Cl}_{(a)}^- \qquad (5)$$

$$\text{PtCl}_{6\,(a)}^{2-} + 2[\text{PdL}_4\text{Cl}]^+\text{Cl}_{(o)}^- \iff [\text{PdL}_4\text{Cl}]_2\text{PtCl}_{6(o)} + 2\text{ Cl}_{(a)}^- \qquad (6)$$

Figure 9 represents schematically the separation process during electrodialysis. The mixed palladium-platinum-carrier complex is transported through the liquid membrane, and $PtCl_6^{2-}$ is stripped into the aqueous HCl solution due to the action of an electric field. Palladium(II), existing mainly in cationic part of the complex, does not pass into the anodic solution. Therefore, a deep separation of Pd(II) and Pt(IV) takes place at the stage of stripping during electrodialysis. When the organic phase becomes saturated with Pd(II), the equilibrium (4) shifts to the right, the non-dissociated complex predominates, and a rise in voltage is observed. The shift of

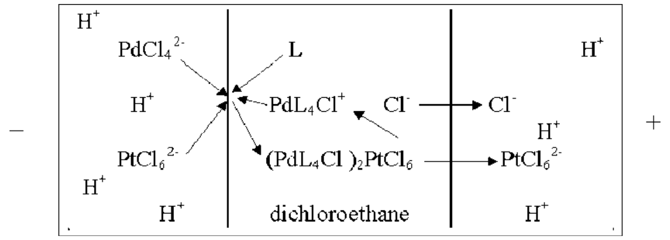


Figure 9. Scheme for palladium(II) and platinum(IV) extraction by a liquid membrane during electrodialysis.

equilibrium, accompanied by the change in palladium(II) coordination number, affects the appropriate absorption spectra of the organic phase.

It should be mentioned that the presence of other complexes of formula PdL_mCl_n in the liquid membrane phase is not impossible. The palladium(II) transport across the saturated organic membranes is connected, probably, to the existence of $PdCl_4^{2-}$ anions in solutions of DOTTU.

Separation of Pt(IV) and Pd(II) by DPTU

Binary hydrochloric mixture of palladium(II) and platinum(IV) containing $6.1 \cdot 10^{-3}$ M H_2PdCl_4 and $4.5 \cdot 10^{-3}$ M H_2PtCl_6 was used usually as a feed solution in the experiments. It has been demonstrated that the application of an electric field allows to extract platinum(IV) through the liquid

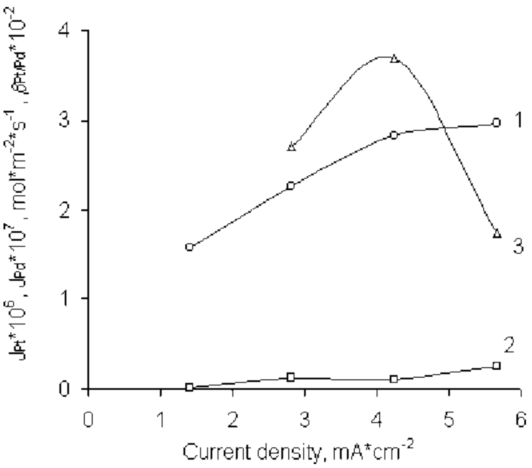


Figure 10. Effect of current density on platinum(IV) (1), palladium(II) (2) fluxes and separation factor (3) ($C_{DPTU} = 0.1$ mol $\cdot$ dm^{-3}; t = 60 min).

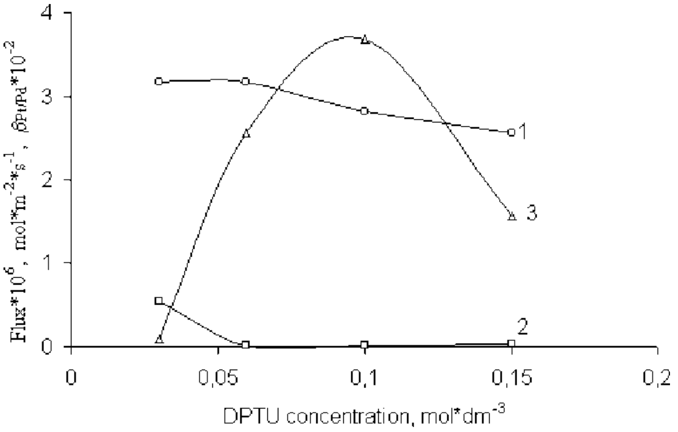


Figure 11. Dependence of platinum(IV) (1), palladium(II) (2) fluxes and separation factor (3) on DPTU concentration (i = 4.2 mA · cm^{-2}; t = 60 min).

membranes selectively over palladium(II). The extraction degree of Pd(II) is less than 0.1% in 1 hour of electrodialysis. The increase of the electric current density to 5.7 mA · cm^{-2} leads to a rise of the platinum(IV) flux (Fig. 10). The separation factor has its maximum value of 380 at 4.2 mA · cm^{-2}. The palladium(II) transport increases significantly at i $>$ 4.2 mA · cm^{-2}. It should be noted that electric breakdowns of the liquid membrane were observed at high current densities.

The influence of DPTU concentration on the metal permeation rates is illustrated in Fig. 11. The palladium(II) flux sharply reduces at C_{DPTU} being

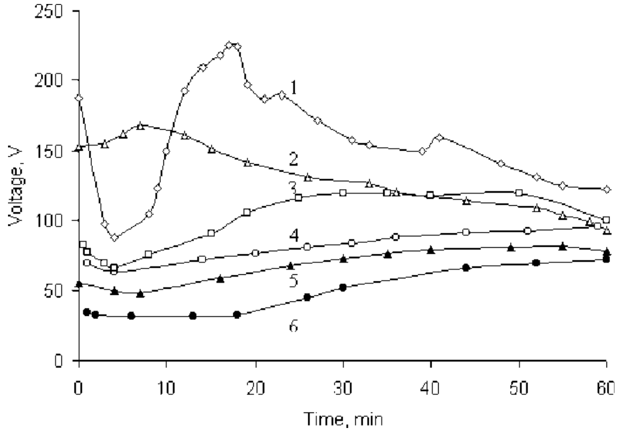


Figure 12. Change in voltage during electrodialysis for different DPTU concentrations and current densities (C_{DPTU} (mol · dm^{-3}) = 0.03 (1); 0.06 (2); 0.1 (3, 4, 6); 0.15 (5); i (mA · cm^{-2}) = 1.4 (6); 2.8 (4); 4.2 (1–3,5)).

Table 4. Effect of the stripping reagent upon the membrane extraction of metals ($C_{DPTU} = 0.06\ mol \cdot dm^{-3}$; $i = 4.2\ mA \cdot cm^{-2}$; $t = 60$ min)

Stripping solution	E_{Pd}, %	E_{Pt}, %	$\beta_{Pt/Pd}$
$1\ mol \cdot dm^{-3}$ HCl	0.054	13.8	256
$1\ mol \cdot dm^{-3}$ H_2SO_4	0.059	12.9	219

higher than 0.03 M. Maximum separation factor was obtained in a system with 0.1 M DPTU. The separation of Pd(II) and Pt(IV) by liquid membranes containing DPTU is more effective in comparison with DOTTU under conditions of experiments.

The Ohmic resistance of the liquid membrane and the voltage vary considerably during the process, depending on the current density and carrier's concentration in the organic phase (Fig. 12). The initial decrease of voltage changes to the gradual rise or maximum of voltage under different experimental conditions. The complicated shape of the voltage-time dependencies, as well as the selective transport of platinum(IV) through the DPTU-based liquid membranes can be explained similarly to the system with DOTTU from equilibrium (4) and equations (5, 6).

In contrast to traditional membrane extraction, the nature of mineral acid in the strip solution does not exert a considerable influence on the electrodialytic transport of metals (Table 4). It can be mentioned that the replacement of HCl for H_2SO_4 leads to an insignificant rise of the electric conductivity.

CONCLUSIONS

The liquid membranes containing DOTTU or DPTU in 1,2-dichloroethane ensure the transport of palladium(II) from individual solutions as well as an effective separation of Pt(IV) and Pd(II), when extracted from hydrochloric binary mixtures at electrodialysis. The separation factor $\beta_{Pt/Pd}$ depends on the carrier's concentration, current density, palladium(II) concentration in the feed solution, and poorly depends on the platinum(IV) concentration and composition of the strip solution. Maximum separation factor of 380 is obtained in the system with DPTU. Platinum(IV) is presumably extracted due to the anion-exchange mechanism, forming a complex of composition $(PdL_4Cl)_2PtCl_6$ in the organic phase.

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