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Membrane Extraction of Iron(III) by Diphenylthiocarbamide in the Presence of Palladium(II)

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Abstract: **The process of iron(III) and palladium(II) extraction from binary mixtures containing $8.1\cdot10^{-2}$ M $FeCl_3$ and $6.7\cdot10^{-3}$ M H_2PdCl_4 in 3.0 M HCl by diphenylthiocarbamide − 1,2-dichloroethane liquid membranes is studied at galvanostatic electrodialysis. It is demonstrated that the liquid membranes ensure a profound one-stage separation of iron(III) from palladium(II) at the stage of stripping (separation factor $\beta_{Fe/Pd} > 100$). Transport of $FeCl_4^-$ ions through the liquid membrane is supposed to occur in the form of ionic associates with cationic palladium(II) complex $PdL_4Cl\cdot FeCl_4$. The effects of the current density as well as of composition of the liquid membrane and of aqueous solutions on the rate of metal transport are determined. It is found out that the iron(III) extraction degree into the strip solution increases as the current density (0 − 5.6 mA/cm^2) and the duration of electrodialysis (0 − 80 min) increase. The increase of DPTC concentration in the organic phase as well as of composition of the stripping solution do not exert a considerable influence on the rate and selectivity of iron(III) and palladium(II) membrane extraction.**

Keywords: **liquid membrane, diphenylthiocarbamide, electro-dialysis, iron(III), palladium(II)**

I. Introduction

Organic derivatives of thiocarbamide are known as selective extractants of platinum metals [1]. Membrane extraction is a promising technique for removal and separation of valuable and toxic 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]. The process of $PdCl_4^{2-}$ and $PtCl_6^{2-}$ separation by bulk liquid membranes containing diphenylthiocarbamide and di-*o*-tolylthiocarbamide has been studied by the author previously [4, 5].

It has been demonstrated that the liquid membranes ensure an effective separation of Pt(IV) from Pd(II) when extracted from binary hydrochloric mixtures at galvanostatic electrodialysis. Transport of platinum(IV) is supposed to occur in the form of mixed palladium-platinum-carrier complex $(PdL_4Cl)_2PtCl_6$. The aim of the present work is to study the membrane extraction of iron(III) and palladium(II) from hydrochloric acid solutions by bulk liquid membranes containing diphenylthiocarbamide (DPTC) in 1,2-dichloroethane under the conditions of galvanostatic electrodialysis.

II. Experimental

The experiments were carried out in a five-compartment Teflon electrodialysis cell in the system:

(−) Pt, H_2SO_4	$FeCl_3$ H_2PdCl_4	DPTC 1,2-dichloroethane	HCl	H_2SO_4, Pt (+)

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. The films were soaked in water 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 from the electrode compartments by the solid cation-exchange membranes MK-40. The direct electric current was supplied to the plane platinum electrodes.

The solutions of DPTC in 1,2-dichloroethane were used as the liquid membranes. Reagents of pro-analysis grade were used without further purification. The feed solution containing as a rule $8{,}1\cdot10^{-2}$ M iron(III) and $6{,}7\cdot10^{-3}$ M palladium(II) was prepared by dissolving $PdCl_2$ and $FeCl_3\cdot6H_2O$ in 3.0 M hydrochloric acid solution. The solution of 1.0 M hydrochloric acid was used usually as a strip solution. The concentrations of iron(III) and palladium(II) in the aqueous solutions were determined by spectrophotometry using sulphosalicylic acid [6] and $SnCl_2$ [7], respectively.

III. Results and discussion

Palladium(II) exists in the form of anionic chlorocomplex $PdCl_4^{2-}$ in hydrochloric solutions [7] and can be extracted by DPTC forming neutral coordination complex:

$$PdCl_4^{2-}{}_{(aq)} + 2L_{(o)} \leftrightarrow PdL_2Cl_{2(o)} + 2Cl^-{}_{(aq)} \qquad (1)$$

where: L – DPTC, aq – aqueous phase; o – organic phase.

The equilibrium between four-coordinated neutral and five-coordinated ionic Pd(II) complexes was reported in [8] for solutions of some derivatives of thiocarbamide:

$$PdL_2Cl_{2(o)} + 2\,L_{(o)} \leftrightarrow PdL_4\,Cl^+{}_{(o)} + Cl^-{}_{(o)} \qquad (2)$$

Iron(III) exists mainly as cationic and neutral complexes $FeCl(H_2O)_5^{2+}$, $FeCl_2(H_2O)_4^{+}$, $FeCl_3(H_2O)_3$ in hydrochloric solutions at $C_{HCl} < 7$ M [9] but anionic chlorocomplex $FeCl_4^-$ permeates across the liquid membrane into the strip anodic solution.

It was found that less than 0.03 % of iron(III) is transported from individual $FeCl_3$ solution across the liquid membrane containing 0.1 M DPTC within 1 hour without electric field application. When the binary hydrochloric mixtures are used, about 20 % of palladium(II) is extracted by the liquid membrane and 0.7 % of iron(III) is transferred into the strip solution. Application of an electric field significantly intensifies the transport of $FeCl_4^-$ ions through the liquid membrane. Iron(III) ions are found to be extracted selectively over palladium(II) ions. The extraction degree of palladium(II) into the strip solution is less than 0.1 % per hour of electrodialysis. The extracted compound, presumably $PdL_4Cl{\cdot}FeCl_4$, is transferred by electromigration across the liquid membrane layer and decomposes at the interface liquid membrane / strip solution due to the action of an electric field. Without electric field application the transport of iron(III) through the liquid membranes practically is not observed, as the stripping solution of 1.0 M HCl does not ensure $FeCl_4^-$ back extraction from the organic phase under conditions of dialysis. The transfer of iron(III) through the liquid membrane is accompanied by cotransport of the chloride ions.

The influence of current density on the metal transport rate was studied using the liquid membranes containing 0.1 M DPTC. The increase of the current density from 0 to 5.6 mA/cm^2 leads to a rise of iron(III) flux (Fig. 1). The current efficiency for $FeCl_4^-$ transport decreases when the current density comes up from 22 to 8 % within 1 hour of electrodialysis. The current is transferred through the liquid membranes mainly by chloride ions of the feed solution. The increase of the current efficiency can be achieved using more concentrated iron(III) solutions. Palladium(II) existing mainly in cationic part of the complex does not pass into the strip anodic solution. Therefore, a deep separation of Fe(III) and Pd(II) takes place at the stage of stripping during electrodialysis (separation factor $\beta_{Fe/Pd} > 100$).

Solutions of DPTC have a low electrical conductivity. During the electrodialysis process the Ohmic resistance of the membrane and the voltage can change considerably depending on the conditions of the experiment (Fig. 2). An increase of voltage in the beginning of process in some cases is followed by a gradual or sharp decrease. In the beginning of electrodialysis, when there is an excess of the carrier in the organic phase, the equilibrium (2) is shifted to the right, and the predominant form of coordination complex is PdL_4Cl^+. When the organic phase becomes saturated with Pd(II), the equilibrium (2) shifts to the left, the non-dissociated complex PdL_2Cl_2 predominates, and a rise in voltage is observed. The voltage decrease is determined by water accumulation in the liquid membrane. A jump-type abrupt decrease of voltage − electrical breakdown occurs at high current density (Fig. 2, curve 3). The water accumulation in the liquid membrane phase is due to the transfer in the composition of the ions hydration − solvation sheath as well as to electroosmosis [10]. The drops of water can form the through channels in the organic phase. When the electrical breakdown occurs, the membrane loses its selectivity.

About 33 % of palladium(II) is extracted by the liquid membrane from the feed solution containing $8{,}1\cdot10^{-2}$ M iron(III) and $6{,}7\cdot10^{-3}$ M palladium(II) within 80 minutes of electrodialysis at current density of 4.2 mA/cm^2 (Fig. 3). The transfer of palladium(II) through the liquid membranes practically is not observed. The extraction degree of palladium(II) into the strip solution is less than 0.1 % per 80 minutes of electrodialysis and it does not vary during the process. About 15 % of iron(III) is extracted

from the feed solution and more than 11 % of metal is transported into the strip anodic solution. The kinetic curves show saturation in 1 hour of electrodialysis. It should be noted that iron(III) is partially absorbed by the solid cation-exchange membrane MK-40 in the feed solution.

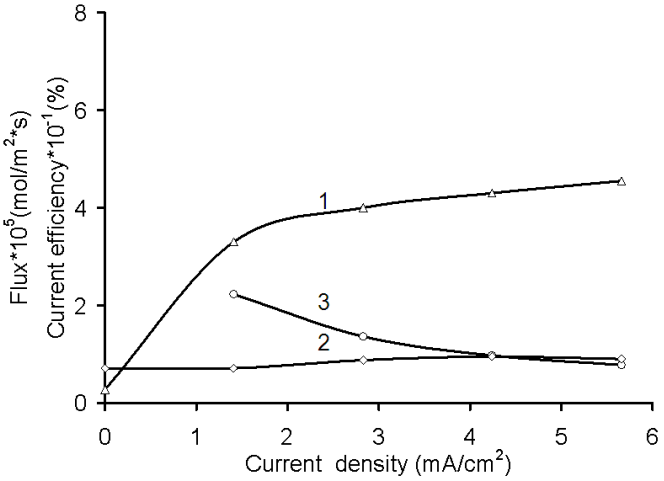

Fig. 1. Dependence of iron flux into the strip solution (1), palladium flux into the liquid membrane (2) and current efficiency (3) on current density (C_{DPTC} = 0.1 M; t = 60 min)

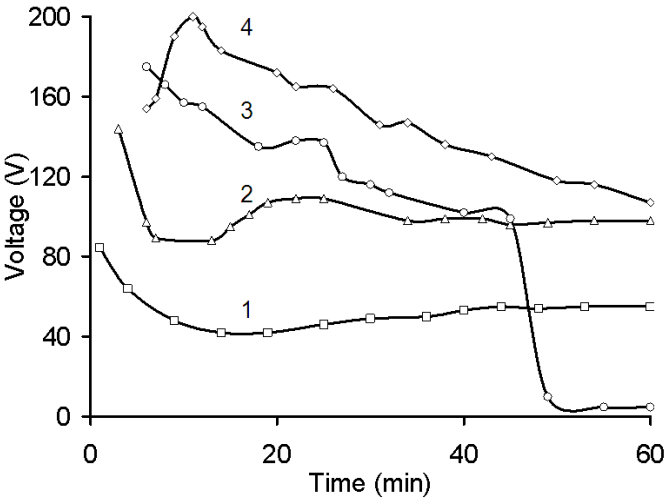

Fig. 2. Change in voltage during electrodialysis for different current densities and DPTC concentrations (i (mA/cm^2) = 1.4 (1); 2.8 (2); 5.7 (3); 4.2 (4); C_{DPTC} (M) = 0.1 (1 – 3); 0.05 (4)).

Fig. 4 illustrates the influence of DPTC concentration in the liquid membrane on the rates of iron(III) and palladium(II)

extraction. The increase of the carrier's concentration from 0.05 to 0.13 M insignificantly increases the palladium(II) flux into the liquid membrane, whereas the iron(III) ions flux through the liquid membrane somewhat decreases. The optimal composition of the liquid membrane is 0.05 M DPTC in 1.2-dichloroethane. The most probable rate-limiting stage of the process is stripping of iron(III) from the organic phase into hydrochloric acid solution.

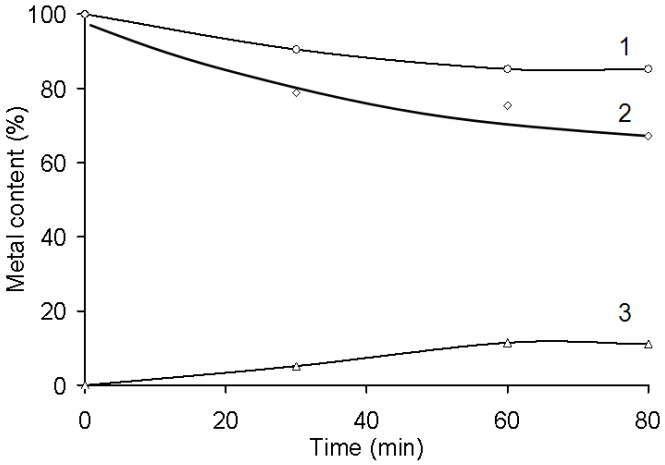

Fig. 3. Kinetics of iron (1) and palladium (2) extraction from the feed solution and iron accumulation in the strip solution (3) (i = 4.2 mA/cm^2; C_{DPTC} = 0.1M)

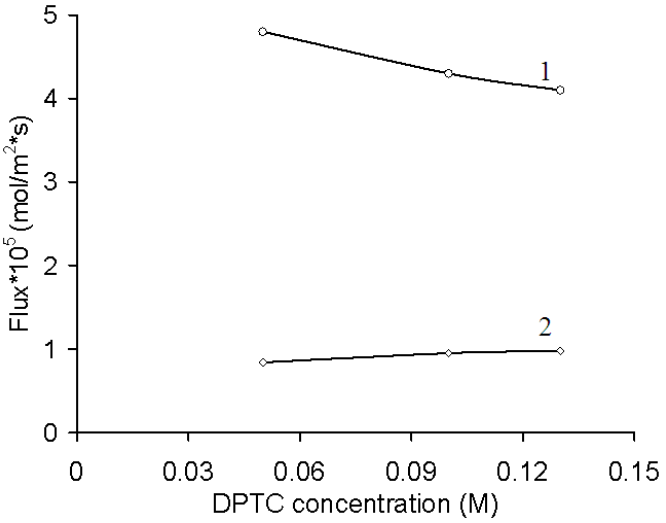

Fig. 4. Effect of carrier concentration on iron flux into the strip solution (1) and palladium flux into the liquid membrane (2) (i = 4.2 mA/cm^2; t = 60 min)

TABLE 1

EFFECT OF THE STRIPPING REAGENT UPON THE PD(II) EXTRACTION INTO THE LIQUID MEMBRANE AND FE(III) TRANSPORT INTO THE STRIP SOLUTION
(C_{Fe} = 8.1·10^{-2} M; C_{Pd} = 6,7·10^{-3} M; I = 4.2 mA/cm^2; T = 60 min)

Stripping solution	Flux $J_{Pd}\cdot10^5$	Flux $J_{Fe}\cdot10^5$	Extraction R_{Pd}	Extraction R_{Fe}
	mol/m^2·s		%	
0.1 M HCl	0.6	3.2	17.4	7.7
3.0 M HCl	0.6	3.6	17.6	8.6
1.0 M H_2SO_4	0.5	3.1	14.2	7.4

In contrast to traditional membrane extraction, the nature of mineral acid in the strip solution does not exert, as a rule, a considerable influence on the electrodialytic transport of metals. $FeCl_4^-$ anions transfer with an approximately equal rate into the solutions of hydrochloric and sulphuric acids (Table 1). Separation of iron(III) and palladium(II) proceeds effectively in all cases (separation factor $\beta_{Fe/Pd}$ > 100). It should be noted that the electrical breakdowns occur within 1 hour of electrodialysis when 1 M H_2SO_4 solution is used, resulting in the extraction rate decrease.

IV. CONCLUSIONS

The liquid membranes containing diphenylthiocarbamide in 1,2-dichloroethane ensure the tansport of iron(III) into diluted solutions of some mineral acids accompanied by a profound separation from palladium(II) at the stage of stripping when extracted from binary hydrochloric mixtures at galvanostatic electrodialysis. Iron(III) is presumably extracted due to the anion-exchange mechanism, forming complex of composition $PdL_4Cl{\cdot}FeCl_4$ in the organic phase. The iron(III) extraction degree increases as the current density and process duration increase. DPTC concentration in the organic phase and composition of the stripping solution poorly effect $FeCl_4^-$ ions transport rate. The tansport of palladium(II) through the liquid membranes practically is not observed (the extraction degree is less than 0.1 %).

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Tatjana Sadirbajeva. Dzelzs(III) membrānekstrakcija ar difeniltiokarbamīdu pallādija(II) klātbūtnē

Izpētīts dzelzs(III) un pallādija(II) membrānekstrakcijas process no bināriem sālsskābiem šķīdumiem, kas satur $8{,}1\cdot10^{-2}$ M $FeCl_3$ un $6{,}7\cdot10^{-3}$ M H_2PdCl_4 ar šķidrām membrānam difeniltiokarbamīds−1,2-dihloretāns galvanostatiskās elektrodialīzes apstākļos. Parādīts, ka šķidrās membrānas nodrošina efektīvu dzelzs(III) atdalīšanu no pallādija(II) reekstrakcijas stadijā (metālu sadalīšanas koeficienti pārsniedz 100). Domājams, ka dzelzs(III) anjonu pārnese caur šķidrām membrānām noris jonu asociātu veidā ar katjonu, ko veido pallādija(II) koordinatīvi solvatēts komplekss ar difeniltiokarbamīdu $PdL_4Cl\cdot FeCl_4$. Noskaidrota uztvērējšķīduma un šķidrās membrānās sastāva, elektrodialīzes strāvas blīvuma ietekme uz dzelzs(III) pārneses ātrumu. Noteikts, ka paaugstinot strāvas blīvumu no 0 līdz 5,6 mA/cm^2 un palielinot membrānekstrakcijas procesa ilgumu līdz 80 minūtēm, pieaug dzelzs(III) jonu reekstrakcijas pakāpe uztvērējšķīdumā. Noteikts, ka difeniltiokarbamīda koncentrācijas palielināšana organiskājā fāzē no 0,05 līdz 0,13 M un skābes raksturs uztvērējšķīdumā maz ietekmē dzelzs(III) un pallādija(II) membrānekstrakcijas ātrumu un selektīvitāti.

Татьяна Садырбаева. Мембранная экстракция железа(III) дифенилтиокарбамидом в присутствии палладия(II)

Исследован процесс мембранной экстракции железа(III) и палладия(II) из бинарных растворов, содержащих $8{,}1\cdot10^{-2}$ M $FeCl_3$ и $6{,}7\cdot10^{-3}$ M H_2PdCl_4 в 3,0 M HCl, растворами дифенилтиокарбамида в 1,2-дихлорэтане в условиях гальваностатического электродиализа. Показано, что изученные жидкие мембраны обеспечивают глубокое одностадийное отделение анионов $FeCl^{4-}$ от $PdCl_4^{2-}$ на стадии реэкстракции; коэффициент разделения металлов $\beta_{Fe/Pd}$ превышает 100. Предполагается, что перенос железа(III) через жидкие мембраны происходит в виде ионных ассоциатов с катионной формой комплекса палладия(II) $PdL_4Cl\cdot FeCl_4$. Установлено, что степень извлечения железа(III) в принимающий раствор возрастает при повышении плотности тока электродиализа в интервале 0 – 5,6 $мА/см^2$ и увеличении продолжительности процесса до 80 мин. Изменение содержания переносчика (0,05 – 0,13 М) в жидкой мембране, а также природа и концентрация кислоты в принимающем растворе мало влияют на скорость и селективность мембранной экстракции железа(III) и палладия(II).