

Liquid Membrane System for Extraction and Electrodeposition of Cobalt(II)

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Abstract. The process of Co^{2+} ion extraction from sulphuric acid solutions by bulk liquid membranes, containing di(2-ethylhexyl)phosphoric acid and tri-*n*-octylamine, accompanied with cobalt electrodeposition from diluted solutions of some acids is studied at galvanostatic electrodialysis. The effects of the current density as well as of composition of the liquid membrane and aqueous solutions on the rate of cobalt(II) transport and electrodeposition are determined. It is demonstrated that a practically complete removal of Co(II) from the feed solution containing 0.01 M CoSO_4 is achieved during 0.5 – 3.0 h of electrodialysis. Maximum stripping degree of 77% and electrodeposition degree of 45% are obtained under optimal conditions. Sound adherent cobalt coatings have been deposited on platinum and copper cathodes.

Keywords: electrodialysis, cobalt, liquid membrane, Di(2-ethylhexyl)phosphoric acid, electrodeposition

I. INTRODUCTION

Membrane extraction is a promising technique for removal of metal ions from diluted solutions [1]. A liquid membrane is 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. Di(2-ethylhexyl)phosphoric acid (D2EHPA) is an important acidic extractant in hydrometallurgy. D2EHPA has been used commercially for the extraction of cobalt, zinc and rare earth metals [2]. Solutions of di(2-ethylhexyl)phosphoric acid in organic solvents are widely used as liquid membranes for the extraction of metals [1]. Cobalt is widely used in different branches of industry. The transport of cobalt(II) from weakly acidic solutions using D2EHPA-based supported, emulsion and bulk liquid membranes is reported in the literature [3–8]. To concentrate and to accelerate the transfer of ions through liquid ion-exchange membranes, an electric current may be used [9]. The electric field gradient is a driving force of the membrane extraction process during electrodialysis. It has been previously demonstrated by the author that the D2EHPA-based liquid membranes ensure an effective copper(II) and manganese(II) extraction from diluted sulphuric acid solutions [10,11], separation of copper(II) from palladium(II) and platinum(IV) extracted from hydrochloric mixtures [12], as well as silver(I) transport from nitric acid solutions accompanied by electrodeposition of metal during electrodialysis [13]. The aim of the present work is to study the membrane extraction of cobalt(II) from sulphuric acid solutions by D2EHPA-based bulk liquid membranes with electrodeposition of metal in the cathodic solution.

II. EXPERIMENTAL WORK

A. Instrumentation

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

(+)Pt	H_2SO_4	CoSO_4 H_2SO_4	D2EHPA TOA	Cathodic solution	Pt(–)
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The liquid membrane (average thickness 0.28 cm, volume 2 cm^3 , surface area 7.1 cm^2) was separated from the aqueous solutions by two vertical cellophane films. The anodic solution (volume 17 cm^3) was separated by the solid anion exchange membrane MA-40 from the feed solution (volume 13 cm^3). The cellophane films and the solid membranes were soaked in water for more than 24 h before use. The direct electric current was supplied to the plane platinum electrodes (surface area 7.1 cm^2). Some experiments were carried out with a copper cathode. Potentiostat II-5827M was used as a current source. Voltage was measured by digital voltmeter. The concentration of cobalt(II) in the aqueous solutions was determined by spectrophotometry using KSCN [14]. UV-Vis spectrophotometer CФ-46 was used for the analysis of metal ions. The properties of cobalt deposits were studied with a scanning electron microscope SEC Mini-SEM (Korea). The measurements were carried out at room temperature. The solutions were not agitated.

B. Reagents and materials

The solutions of D2EHPA (technical grade, contents of the main substance ~ 63%) with the admixtures of tri-*n*-octylamine (TOA, pure grade) in 1,2-dichloroethane were used as the liquid membranes. They contained usually 20 or 32 vol.% D2EHPA and 0.1 M TOA. The feed solution was prepared by dissolving $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ in the sulphuric acid solution. It contained as a rule 0.01 M CoSO_4 in 0.01 M H_2SO_4 . Reagents of pro-analysis grade were used without further purification.

III. RESULTS AND DISCUSSION

In D2EHPA organic solutions in the presence of TOA an ion pair is formed, which consists of an organic cation and an organic anion [15]:



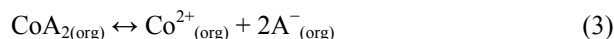
where HA is the di(2-ethylhexyl)phosphoric acid; R_3N is the tri-*n*-octylamine.

Cobalt(II) is extracted by D2EHPA due to the interfacial cation-exchange mechanism:



where subscripts aq and org represent aqueous and organic species.

The extraction complex can dissociate in polar solvent [16]:



Co^{2+} cations are transferred by diffusion to the interface feed solution / liquid membrane and interact with the carrier forming a complex. The transported compound is transferred across the liquid membrane layer and decomposes at the interface liquid membrane / cathodic solution due to the action of an electric field. The transfer of cobalt(II) through the liquid membrane is accompanied by cotransport of the hydrogen cations when the electric field is applied. Therefore, high acidity of the strip solution and correction of pH value of the feed solution are not necessary at electrodialysis in contrast to traditional membrane extraction. Anions from the cathodic solution are transported across the organic layer in the opposite direction interacting with amine salt:



Without electric field application the transport of cobalt(II) through the liquid membranes practically is not observed. The imposition of an electric field allows extracting Co^{2+} cations through the liquid membranes and obtaining cathodic cobalt coatings from solutions of sulphuric and perchloric acids.

Table 1 illustrates the influence of current density on the rates of cobalt(II) transport and electrodeposition. The increase of the current density up to 4.2 mA/cm² results in a proportional rise of cobalt flux through the liquid membrane. A practically complete (> 98 %) removal of Co(II) from the feed solution containing 0.01 M CoSO₄ can be achieved at a current density $i \geq 2.1$ mA/cm². The duration of electrodialysis is 40 – 175 min depending on the current density. At a low current density, about 77% of cobalt was removed into cathodic solution after 3.0 hours of experiment and about 45% of cobalt(II) was electrodeposited on the cathode.

TABLE 1

EFFECT OF CURRENT DENSITY UPON THE Co(II) EXTRACTION DEGREE E, STRIPPING DEGREE S, ELECTRODEPOSITION DEGREE D AND FLUX J ($C_{\text{D2EHPA}} = 20$ vol.%; cathodic solution – $2.5 \cdot 10^{-2}$ M HClO₄)

i (mA/cm ²)	t (min)	E	S	D	J·10 ⁵ (mol/m ² s)
		%			
2.1	175	99.7	32	45	1.3
2.8	98	99.7	41	27	2.1
4.2	55	99.0	36	6	2.4
5.7	40	98.4	30	2	2.4

The current efficiency for Co^{2+} ions is less than 10%. The current is transferred through the liquid membrane mainly by hydrogen ions from the feed solution and ClO_4^{-} or SO_4^{2-} anions from the cathodic solution. The increase in the current efficiency can be achieved using more concentrated cobalt(II) solutions.

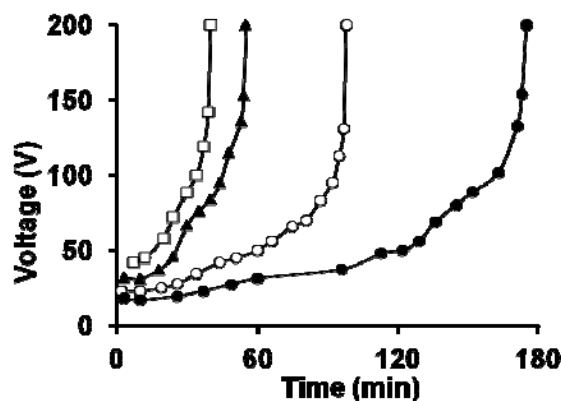


Fig. 1. Change in voltage during electrodialysis at various current densities (cathodic solution – $2.5 \cdot 10^{-2}$ M HClO₄; $C_{\text{D2EHPA}} = 20$ vol.%; i (mA/cm²): □ – 5.7; ▲ – 4.2; ○ – 2.8; ● – 2.1)

The duration of electrodialysis is limited as a rule by an abrupt increase of voltage in the membrane system within 40 – 180 min, depending on the current density (Fig. 1). It was found out that the decrease of the electrical conductivity corresponded to 98 – 99% extraction of cobalt(II) from the feed solution. Thus, the shape of the voltage and time dependence can be used for evaluating the removal completeness. The voltage increase is connected with desalination of the feed solution as a result of Co^{2+} and hydrogen ion extraction into the liquid membrane and SO_4^{2-} ion transfer through the solid anion-exchange membrane into the anodic solution.

The kinetics of cobalt(II) transport and electrodeposition is presented in Fig. 2. Practically complete extraction of metal from the feed solution containing 0.01 M CoSO₄ in 0.01 M H₂SO₄ is achieved within 100 min of electrodialysis at the current density of 2.8 mA/cm², more than 65% of cobalt(II) is transported into the cathodic solution and more than 25% of metal is electrodeposited on the cathode. Metal concentration in the cathodic solution continuously increases during electrodialysis, whereas the cobalt(II) concentration in the liquid membrane has its maximum value at 80 min. The electrodeposition of metal on the platinum cathode is observed after 80 min of electrodialysis.

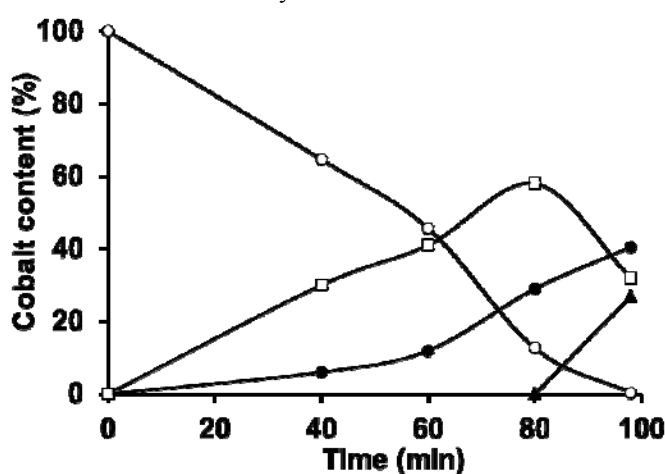


Fig. 2. Kinetics of cobalt(II) removal from the feed solution (○), accumulation in the liquid membrane (□) and cathodic solution (●), electrodeposition degree (▲) ($i = 2.8$ mA/cm²; $C_{\text{D2EHPA}} = 20$ vol.%; cathodic solution – $2.5 \cdot 10^{-2}$ M HClO₄)

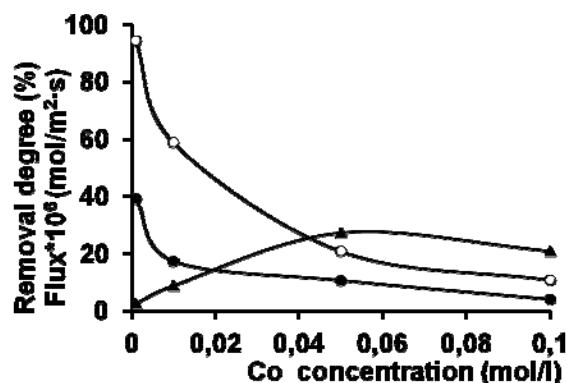


Fig. 3. Dependence of cobalt(II) flux (▲), removal degree into the liquid membrane (○) and into the cathodic solution (●) on CoSO_4 initial concentration ($i = 2.8 \text{ mA/cm}^2$; $t = 60 \text{ min}$; $C_{\text{D2EHPA}} = 32 \text{ vol.}\%$)

The increase in cobalt(II) content in the feed solution from $1 \cdot 10^{-3}$ to $5 \cdot 10^{-2} \text{ M}$ leads to rise in transport rate of the cobalt cations, whereas the extraction and stripping degrees reduce (Fig.3). The increase in the current efficiency is achieved using more concentrated cobalt(II) solutions. A maximum current efficiency of 24% is obtained for a system with $5 \cdot 10^{-2} \text{ M}$ CoSO_4 solution.

The acidity of the feed solution has been found to influence the cobalt extraction efficiency. The increase in sulphuric acid concentration in the feed solution from $1 \cdot 10^{-3}$ to 0.1 M results in the decrease of the cobalt(II) flux into the cathodic solution, extraction degree and stripping degree (Fig. 4). It is caused by the decrease of D2EHPA extraction ability at the aqueous phase acidity rise [2]. The increase in sulphuric acid concentration leads to rise in the hydrogen ion flux through the organic layer, resulting in the current efficiency decrease for Co^{2+} cations. The optimal acidity of the feed solution is $1 \cdot 10^{-3} - 1 \cdot 10^{-2} \text{ M}$ H_2SO_4 . A practically complete extraction of Co(II) from the feed solution and stripping degree of 70 – 75% are achieved in this system.

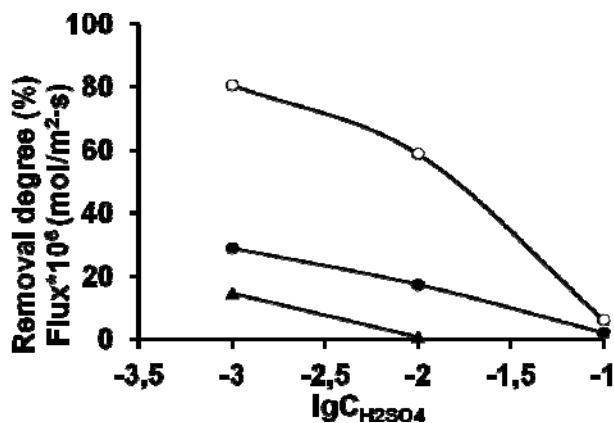


Fig. 4. Dependence of cobalt(II) flux (▲), removal degree into the liquid membrane (○) and into the cathodic solution (●) on H_2SO_4 concentration in the feed solution ($i = 2.8 \text{ mA/cm}^2$; $t = 60 \text{ min}$; $C_{\text{D2EHPA}} = 32 \text{ vol.}\%$)

The effects of D2EHPA and TOA concentrations in the liquid membranes on the rates of cobalt(II) extraction and stripping are illustrated in Table 2. The increase in the carrier's concentration from 5 to 50 vol%, with the TOA concentration being constant, does not exert significant

influence on the Co^{2+} extraction degree into the organic phase and transfer rate into the cathodic solution. The increase in TOA concentration in the liquid membrane from 0.05 to 0.4 M , with the D2EHPA concentration being constant, leads to some reduction of cobalt(II) transfer rate into the strip solution. It is presumed to occur due to the perchlorate anion transfer intensification from the strip solution through the liquid membrane resulting in the current efficiency decrease for Co^{2+} ions.

TABLE 2

EFFECT OF LIQUID MEMBRANE COMPOSITION UPON THE COBALT(II) TRANSPORT AND ELECTRODEPOSITION
($i = 2.8 \text{ mA/cm}^2$; $t = 60 \text{ min}$; cathodic solution – $2.5 \cdot 10^{-2} \text{ M}$ HClO_4)

C_{D2EHPA} (vol.%)	C_{TOA} (M)	E (%)	S (%)	Flux $\cdot 10^5$ (mol/m ² ·s)
5	0.1	68	17	0.9
20	0.1	54	14	0.7
32	0.1	59	17	0.9
50	0.1	69	15	0.8
32	0.05	65	17	0.9
32	0.2	59	13	0.7
32	0.4	61	14	0.7

The influence of strip solution composition on the Co^{2+} permeation and electrodeposition rates is illustrated in Table 3. The transfer of cobalt(II) proceeds with an approximately equal rate into 0.01 M solutions of perchloric, hydrochloric, sulphuric and nitric acids. The maximum electrodeposition rate was obtained in the system containing HClO_4 . When the concentration of acid is lower ($1 \cdot 10^{-3} \text{ M}$), the organic cations begin to participate in the electricity transfer through the liquid membrane/ cathodic solution interface, and the organic phase appears in the aqueous solution. The increase in HClO_4 concentration from $1 \cdot 10^{-2}$ to $2.5 \cdot 10^{-2} \text{ M}$ leads to the decrease in the cobalt (II) extraction degree, whereas electrodeposition is not observed during 1 h of electrodialysis. This effect of pH value of the cathodic solution differs from traditional membrane extraction by D2EHPA, where high acidity of the strip solution is necessary. The increase in HClO_4 concentration leads to the rise in the perchlorate ion flux from the cathodic solution through the organic layer, resulting in the current efficiency decrease for Co^{2+} .

TABLE 3

EFFECT OF CATHODIC SOLUTION COMPOSITION UPON THE COBALT(II) TRANSPORT AND ELECTRODEPOSITION
($C_{\text{D2EHPA}} = 20 \text{ vol.}\%$; $i = 2.8 \text{ mA/cm}^2$; $t = 45 \text{ min}$)

Cathodic solution ($C = 1 \cdot 10^{-2} \text{ M}$)	Cobalt content (%)			Flux $\cdot 10^5$ (mol/m ² ·s)
	Feed solution	Cathodic solution	Cathode	
HClO_4	48	3	7	0.7
HCl	43	12	3	1.0
H_2SO_4	41	15	—	1.0
HNO_3	42	10	—	0.7

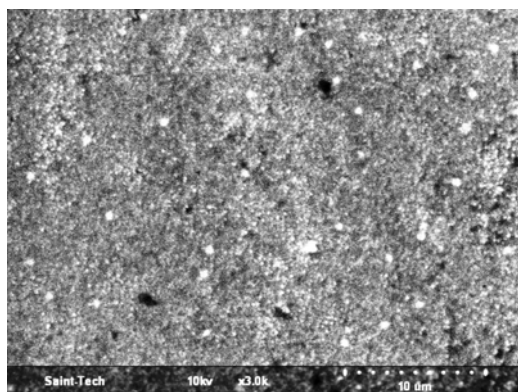


Fig. 5. Scanning electron microscopy image of cobalt coating deposited on copper cathode ($i = 6.0 \text{ mA/cm}^2$; cathodic solution – $2.5 \cdot 10^{-2} \text{ M HClO}_4$)

The surface morphology of cobalt electrodeposits was studied by scanning electron microscopy. Cobalt coatings were deposited on the platinum and copper cathodes at various current densities. The deposits were of dark color, dense and adherent in all cases. It can be seen from Fig.5 that cobalt coating obtained from 0.025 M perchloric acid solution at moderate current density has a fine-grained poreless structure.

IV. CONCLUSIONS

The liquid membranes containing di(2-ethylhexyl)phosphoric acid and tri-*n*-octylamine in 1,2-dichloroethane ensure the transport of Co^{2+} from sulphuric acid solutions into diluted solutions of HClO_4 , H_2SO_4 , HCl and HNO_3 accompanied by cathodic electrodeposition of cobalt. Dense, dark, adherent deposits of cobalt with fine-grained structure are obtained in all studied systems. Increasing the current density and Co^{2+} initial concentration in the feed solution results in the increase of cobalt(II) transport and electrodeposition rates. The increase in H_2SO_4 concentration in the feed solution and in HClO_4 concentration in the cathodic solution, as well as in TOA content in the liquid membrane negatively effects the cobalt(II) transport and electrodeposition rates. Change in D2EHPA concentration in the organic phase poorly affects the cobalt(II) extraction and electrodeposition degrees.

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Tatjana Sadirbajeva. Sistēma ar šķidrām membrānām kobalta(II) ekstrakcijai un elektroizgulsēšanai.

Izpētīts kobalta(II) ekstrakcijas process no atšķaidītiem sērskābiem šķīdumiem ar šķidrām membrānām uz di(2-etilheksil)fosforskābes pamata ar tri-*n*-oktilamīna piedevām galvanostatiskās elektrodialīzes apstākļos ar metāla elektroizgulsēšanu uztvērējšķīdumā. Noteikts, ka šķidrās membrānas īsteno kobalta(II) jonu pārneš atšķaidītos sērskābes, perhlorskābes, sāļsskābes un slāpekļskābes šķīdumos. Parādīts, ka praktiski pilnīga metāla izdalīšana no izejas šķīduma, kas satur 0.01 M CoSO_4 $0.01 \text{ M H}_2\text{SO}_4$ šķīdumā, tiek sasniegta pēc $0,5 - 3,0$ stundām elektrodialīzē. Optimālajos apstākļos kobalta(II) reekstrācija uztvērējšķīdumā sasniedz 77% , un $\sim 45 \%$ metāla izgulsnējās uz katoda. Konstatēts, ka izturīgas, sīkkristālisks kobalta nogulsnes, kas labi turās uz katoda, izdalās visās izpētītajās sistēmās. Parādīts, ka hronopotenciogrammu forma var kalpot par kritēriju kobalta(II) jonu izdalīšanas pilnīgumam no izejas šķīduma. Krasa sprieguma paaugstināšanās ir saistīta ar izejšķīduma atsāļošānu un atbilst $\geq 98\%$ metāla izdalīšanai. Noteikts, ka palielinot strāvas blīvumu intervālā $0 - 5.7 \text{ mA/cm}^2$ un paaugstinot kobalta saturu izejas šķīdumā ($1 \cdot 10^{-3} - 5 \cdot 10^{-2} \text{ M}$), notiek jonu plūsmas un katoda nogulšņu masas palielināšanās. Parādīts, ka sērskābes koncentrācijas palielināšana izejas šķīdumā ($1 \cdot 10^{-3} - 0,1 \text{ M}$) un perhlorskābes koncentrācijas palielināšana katoda šķīdumā ($1 \cdot 10^{-2} - 2.5 \cdot 10^{-2} \text{ M}$) negatīvi ietekmē kobalta jonu pārnešes un elektroizgulsēšanas ātrumu. Konstatēts, ka D2EHFS daudzuma izmaiņa ($5 - 50 \text{ tilp.}\%$) un TOA koncentrācijas izmaiņa ($0,05 - 0,4 \text{ M}$) organiskajā fāzē fāzē maz ietekmē kobalta jonu transmembrānās pārnešes un elektroizgulsēšanas ātrumu.

Татьяна Садырбаева. Система с жидкими мембранами для извлечения и электроосаждения кобальта(II).

Исследован процесс мембранной экстракции ионов кобальта(II) из сернокислых растворов, содержащих 0.01 М CoSO_4 в 0.01 М H_2SO_4 , растворами технической ди(2-этилгексил)фосфорной кислоты (Д2ЭГФК) с добавками три-н-октиламина (ТОА) в 1,2-дихлорэтаноле в условиях гальваностатического электролиза с электроосаждением металла из принимающего раствора. Установлено, что перенос ионов Co^{2+} протекает примерно с одинаковой скоростью в $1 \cdot 10^{-2}$ М растворы хлорной, серной, соляной и азотной кислот. Показано, что процесс электролиза обычно заканчивается резким подъемом напряжения в системе, соответствующим полному ($\geq 98\%$) извлечению кобальта(II) в жидкую мембрану. Установлено, что скорости трансмембранного переноса и электроосаждения катионов Co^{2+} повышаются при увеличении плотности тока электролиза в интервале $0 - 5,7 \text{ мА/см}^2$, концентрации ионов кобальта(II) ($1 \cdot 10^{-3} - 5 \cdot 10^{-2}$ М) в исходном растворе и мало зависят от содержания Д2ЭГФК (5 - 50 об.%) и ТОА (0,05 - 0,4 М) в органической фазе. Показано, что повышение концентрации серной кислоты ($1 \cdot 10^{-3} - 0,1$ М) в исходном растворе и хлорной кислоты в катодном растворе ($1 \cdot 10^{-2} - 2,5 \cdot 10^{-2}$ М) приводит к снижению степеней извлечения и электроосаждения ионов кобальта(II). В оптимальных условиях достигается практически полное извлечение кобальта(II) из исходного раствора, при этом около 77% кобальта(II) транспортируется через жидкую мембрану и $\sim 45\%$ металла осаждается на катоде. Получены катодные осадки кобальта в виде темных мелкокристаллических покрытий, прочно сцепленных с электродом.