

**MEMBRANE EXTRACTION OF COPPER(II) DURING ELECTRODIALYSIS****VARA(II) MEMBRĀNEKSTRAKCIJA ELEKTRODIALĪZES APSTĀKĻOS**

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**Kopsavilkums**

Izpētītas šķidrū membrānu, kas satur tehnisko di(2-etilheksil)fosforskābi at tri-n-oktilamīna piedevām 1,2-dihloretānā, transportīpašības  $\text{Cu}^{2+}$  ekstrakcijas procesā. Noteikti strāvas blīvuma, šķidrās membrānas sastāva un vara jonu izejas koncentrācijas ietekme uz  $\text{Cu}^{2+}$  pārnese ātrumu. Atrasti optimālie apstākļi praktiski pilnīgai (>99%) vara izdalīšanai no atšķaidītiem  $\text{H}_2\text{SO}_4$  šķīdumiem.

Membrane extraction is a promising technique for removing non-ferrous metals from diluted acid solutions. Di(2-ethylhexyl)phosphoric acid (D2EHPA) is widely used as cation-exchange carrier in the processes of membrane extraction of copper by emulsion and supported liquid membranes [1]. The application of an electric field intensifies the transport of ions through the liquid membranes and facilitates the stripping of metals from the organic phase. The influence of some experimental factors on the copper transport rate through the liquid membranes containing pure D2EHPA had been studied by author previously [2]. The aim of the present work is to study the membrane extraction of copper by the D2EHPA (technical grade) –based bulk liquid membranes under the conditions of galvanostatic electrodialysis.

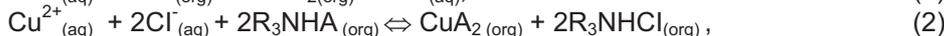
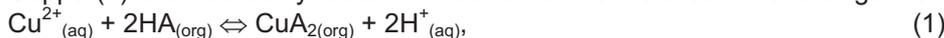
The experiments were carried out in a five-compartment electrolysytic cell in the system:

+Pt, $\text{H}_2\text{SO}_4$	$\text{CuSO}_4$	D2EHPA, TOA 1,2-dichloroethane	$\text{H}_2\text{SO}_4$	$\text{H}_2\text{SO}_4$ , Pt(-)
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The liquid membrane (thickness 0.2 cm, volume  $2 \text{ cm}^3$ , surface area  $7.1 \text{ cm}^2$ ) was separated from the aqueous solutions by two vertical cellophane films. The electrode compartments (volume  $17 \text{ cm}^3$ ) were filled with 0.05 M sulfuric acid solutions. The compartments of feed and stripping solutions were separated by the solid anion-exchange membranes MA-40. The direct electric current was supplied to the plane platinum electrodes. The electrodialysis was carried out under the galvanostatic conditions.

The solutions of D2EHPA (technical grade, contents of the main substance ~ 63%) with the admixtures of TOA (pure grade, contents of the main substance 95%) in 1,2-dichloroethane were used as the liquid membranes. The solution of  $3.2 \cdot 10^{-3} \text{ CuSO}_4$  in 0.01 M sulfuric acid was used usually as a feed solution and 0.1 M sulfuric acid was the strip solution. The concentration of copper(II) in the aqueous solutions was determined by spectrophotometry using rubeanic acid.

Copper(II) is extracted by D2EHPA due to the interfacial cation-exchange mechanism [1]:



where: HA – di(2-ethylhexyl)phosphoric acid,  $\text{R}_3\text{N}$  – tri-n-octylamine, aq – aqueous phase, org – organic phase.

The transfer of copper 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 dialysis.

The previous experiments have revealed that additions are to be introduced in D2EHPA solutions to increase their electric conductivity. Additions of 5% vol. TOA were used since the electrodialysis process is unstable when less amount of amine is introduced.

When the electric field is applied, electromigration is the only mechanism of copper transport through the liquid membrane. The diffusional flux of the metal is negligible ( $< 10^{-6} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ ). The rate of copper transport into the strip solution is as a rule proportional to the current density.

A practically complete (>99%) removal of copper from the feed solution can be achieved within 50-70 minutes of electrodialysis with the current density being 5-7  $\text{mA/cm}^2$ . Stripping of metal is strongly dependent on the carrier's concentration in the organic phase. Maximum (~67%) stripping was achieved in the studied system.

The duration of the electrodialysis is usually limited by an abrupt increase of ohmic resistance in the membrane system. It occurs in 30-70 minutes after the process begins and depends on the current density and composition of the phases. It has been found out that the decrease of electric conductivity of the membrane system due to the feed solution desalination corresponds to 98-99% extraction of copper by the liquid membrane (the remainder is  $\sim 10^{-5} \text{ mol/l CuSO}_4$ ). Thus, the shape of the voltage-time dependence can be used for evaluating the extraction completeness.

The increase of the current density leads to reduction of electrodialysis duration, and the decrease of the carrier's concentration results in increase of the process duration and in significant rise of the liquid membrane electric conductivity.

The copper flux through interface feed solution / liquid membrane increases as the carrier's concentration comes up to 25% vol., whereas the copper transfer rate through interface liquid membrane / strip solution decreases as the D2EHPA concentration varies from 15 to 65 % vol. The optimum composition of the liquid membrane is 20-25% vol. D2EHPA and 5% vol. TOA in 1,2-dichloroethane. The most probable rate-limiting stage of the process is stripping of copper from the organic phase into sulfuric acid solution.

The increase of copper concentration in the feed solution from  $3 \cdot 10^{-3}$  to  $3 \cdot 10^{-1}$  mol/l leads to a proportional rise of the metal fluxes through both interfaces. A similar dependence exists between copper concentration and current efficiency. Maximum current efficiency comprises 25% for 0.3 mol/l  $\text{CuSO}_4$ . It characterizes the copper cation transport selectivity.

The regularities of copper electrodialysis through D2EHPA-based liquid membranes studied in the present work can serve as a ground for development of the technology for effective one-stage copper removal from industrial solutions.

#### References

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