

MEMBRANE EXTRACTION OF COPPER(II) BY DI(2-ETHYLHEXYL)PHOSPHORIC ACID IN THE PRESENCE OF PLATINUM METALS**VARA(II) MEMBRĀNEKSTRAKCIJA AR DI(2-ETILHEKSIL)FOSFORSKĀBI PLATĪNA METĀLU KLĀTBŪTNĒ**

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Summary

The process of Cu^{2+} , PdCl_4^{2-} and PtCl_6^{2-} separation extracting from binary hydrochloric mixtures by bulk liquid membranes containing di(2-ethylhexyl)phosphoric acid with admixtures of tri-n-octylamine is studied at galvanostatic electro dialysis. The effects of the current density as well as of composition of the liquid membrane and aqueous solutions on the rate and selectivity of the copper(II) transport are determined. An effective separation of Cu(II) from platinum metals is achieved.

Membrane extraction is a promising technique for removal and separation of valuable and toxic metal ions [1]. Di(2-ethylhexyl)phosphoric acid (D2EHPA) is widely used for copper(II) removal from weakly acidic solutions by liquid membranes. Application of a direct electric field significantly intensifies the transport of ions through the liquid membranes [2]. The aim of the present work is to study the membrane extraction of copper(II) from binary hydrochloric mixtures with palladium(II) and platinum(IV) by bulk liquid membranes of D2EHPA – dichloroethane with tri-n-octylamine (TOA) admixtures and to find out optimal conditions for metal separation.

The experiments were carried out in a five-compartment electro dialysis cell:

(+) Pt, H_2SO_4	CuSO_4 , H_2PdCl_4 or H_2PtCl_6	D2EHPA, TOA 1,2-dichloroethane	HCl	H_2SO_4 , Pt (-)
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The liquid membrane (thickness 0.2 cm, volume 2 cm³, surface area 7.1 cm²) was separated from the aqueous solutions by two vertical cellophane films. The electrode compartments were filled with 0.15 M H_2SO_4 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 electro dialysis was carried out under the galvanostatic conditions.

The solutions of D2EHPA (technical grade, contents of the main substance ~ 63%) with the admixtures of TOA in 1,2-dichloroethane were used as the liquid membranes. Binary mixtures contained, as a rule, 0.028 M Cu(II) and 0.016 M Pd(II) or 0.04 M Cu(II) and 0.018 M Pt(IV) in 0.01 M HCl. 0.1 M hydrochloric acid was used usually as the strip solution.

The copper(II) flux is directly proportional to the current density up to 6-10 mA*cm⁻² depending on the feed solution composition. The current efficiency for copper(II) is 12 –14 % for the studied systems. The current is transferred through the liquid membranes mainly by hydrogen ions and chloride ions of the strip solution.

The extraction degree of palladium(II) into the strip solution poorly depends on the current density and comprises 0.1 - 0.2 % per hour of electro dialysis and the extraction of platinum(IV) is, as a rule, less than 0.1%. The copper(II) extraction process is characterized by high selectivity. Separation factor of 430 is obtained for a system containing palladium(II) at the current density of 8.5 mA*cm⁻².

About 90% of copper(II) is extracted by the liquid membrane from the feed solution, containing palladium(II), more than 70% of copper(II) is transported into the strip solution within three hours of electro dialysis. The maximum separation factor for copper(II) and palladium(II) reaches 720 within two hours of electro dialysis and about 500 for copper(II) and platinum(IV). When extract copper(II) from the solutions, containing equal amounts of copper(II) and palladium(II) of $2.7 \cdot 10^{-2}$ M, the separation factor $\beta_{\text{Cu/Pd}}$ exceeds $1 \cdot 10^3$ under optimal experimental conditions.

The increase of the carrier's concentration from 10 to 30 vol.% results in a decrease of both metal fluxes and in an increase of Cu^{2+} transport selectivity. Negative effect of D2EHPA excess on copper ions transfer may be connected with an increase in the viscosity of the organic phase.

Solutions of technical D2EHPA contain significant amounts of admixtures of strongly associated monoalkylphosphoric acid and have a low electrical conductivity. To use them for the electro dialysis with liquid membranes, admixtures, for example, TOA have to be introduced. The increase of TOA concentration in the liquid membrane up to 0.1 M, with the D2EHPA concentration being constant, leads to a reduction of the copper(II) flux, and the platinum(IV) flux increases at $C_{\text{TOA}} > 0.2$ M. It is presumed to occur due to the chloride ions flux intensification from the strip solution through the liquid membrane, resulting in the current efficiency decrease for Cu^{2+} . The separation factor $\beta_{\text{Cu/Pt}}$ in the system, containing 0.05 M TOA in the liquid membrane, reaches its maximum value of more than 900 and sharply decreases as the TOA concentration rises..

The increase of hydrochloric acid concentration in the feed solution from 0.01 to 0.1 M sharply decreases

the copper(II) flux from the solution containing palladium(II). It is caused by a decrease of D2EHPA extraction ability at the aqueous phase acidity rise. The optimal acidity of the feed solution for copper(II) and palladium(II) separation is 0.01 M HCl.

The influence of copper(II) content in the feed solution on the Cu^{2+} transport rate was studied using individual CuCl_2 solutions in water. The copper(II) extraction degree is constant (approximately 65%) for concentrations ranging 0.02 - 0.04 M, while the Cu^{2+} flux and the current efficiency proportionally increase. Reduction of the copper cations transport rate at higher initial concentrations can be explained by the increase of the Cu^{2+} extraction degree by TOA, forming a complex $(\text{R}_3\text{NH})_2\text{CuCl}_4$, where copper(II) exists as anions and can be extracted back into the feed solution by the electric field.

As a rule, nature of acid in the strip solution does not exert significant influence on the transport of extracted components through the liquid membranes at electro dialysis. The transport of copper(II) proceeds with an approximately equal rate into the solutions of hydrochloric, sulfuric, nitric, perchloride acids and water. When nitric acid is used, the extraction of platinum(IV) increases, resulting in the separation factor decrease. Separation of copper(II) and platinum(IV) proceeds effectively in all others cases.

References

- [1]. S.Yu. Ivakhno, E.V.Yurtov, Membrane Extraction, VINITI, Moscow, 1990
- [2]. B.A.Purin, The Influence of an Electric Field on the Membrane Extraction of Substances, in Proceed. Intern. Solvent Extraction Symposium, Moscow, 1998, pp. 234-241.

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