

SYNERGETIC ADSORPTION IN ELECTROCHEMICAL DETERMINATION OF METAL IONS IN SEAWATER

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To enable a simple and convenient electrochemical determination of metal-ion concentrations in natural waters it is necessary to find a system of ligands which can complex them and form a highly hydrophobic species strongly adsorbed at the mercury drop electrode surface. In that way the enhancement of metal-ion concentration occurs in the adsorption layer at the electrode surface then in the bulk of the solution. Such an approach is interesting because metal-ions in natural waters are present in a very low concentrations and as complexes with various organic substances. Due to that they are specifically adsorbed at different surfaces (sediments or particles in seawater and fresh waters).

So-called synergetic adsorption of few metal ions (uranyl-ion, copper(II)) at the mercury drop electrode surface was studied. The method is compared with the simple anion-induced adsorption (MLAKAR *et al.*, 1990). Synergetic adsorptive accumulation is based on the principles of synergetic solvent extraction that is from the aqueous to the organic phase. The phenomenon of synergism is described as a manifold enhancement of the metal-ion extraction from the aqueous solution to the organic by the system of two ligands which form a hydrophobic complex species with the metal-ion. Basic conditions which must be fulfilled are :

- (i) the neutralization of the charge at the central metal-ion by forming a chelate complex;
- (ii) the second ligand, so-called synergist, which is not soluble in the water solutions and therefore is very hydrophobic, reacts with the chelate complex and substitutes all remained water molecules from the coordination sphere in the central metal-ion;
- (iii) the convenient spatial arrangement of ligands around the central metal-ion;
- (iv) the accomplishment of maximum coordination number of the central metal-ion. Such complexes become extremely hydrophobic and they are formed only in the organic phase.

As the adsorption layer at the mercury drop electrode surface can be very good replacement for the organic phase, due to its highly hydrophobic behaviour, it can serve as a good replacement for the organic phase. Therefore, the hydrophobic mixed ligand complex will be formed only in the adsorption layer at the electrode surface (MLAKAR and BRANICA, 1988). In that way the concentration of the metal-ion at the electrode surface will be manifold enhanced and it will be possible to measure very low concentration levels of metal-ions present in natural water systems. In the adsorbed state the metal-ion remains to be electroactive with the increased overpotential and it responds well to various voltammetric excitation signals.

In this study it will be presented a synergetic adsorption of uranyl-ion mixed ligand complex with 2-thenoyltrifluoroacetone and tributylphosphate and copper(II)-ion mixed ligand complex with 1,10-phenanthroline and tributylphosphate.

The effect of synergetic adsorption in the system UO_2^{2+} -TTA-TBP was obtained at pH about 3.6. After the accumulation at -0.15 V very sharp and pronounced peak was registered at about -0.5 V vs. Ag/AgCl. By this system of ligands the lowest detection limit by linear sweep voltammetry after the accumulation of 10 minutes at -0.15 V was found to be $(1.1 \pm 0.2) \cdot 10^{-10}$ mol/l. The results of uranyl ion measurements in natural water samples of saline and fresh waters will be presented.

By the system Cu(II)-Phen-TBP (CULJAK *et al.*, 1994) the situation was more complicated. The mixed ligand complex with copper(II)-ion and the synergetic adsorption were obtained in narrow pH range between 9.5 and 10. In spite that the phenanthroline molecules chelate copper(II)-ion in a broad range, they do not neutralize the charge of the Cu-chelate complex. The charge of Cu^{2+} -phen₂ complex is neutralized by two hydroxide ions in pH range between 9 and 10.5, in accordance with the calculated distribution curves of Cu(II)-ion. After that step TBP molecules in the adsorption layer form a mixed ligand complex $Cu(OH)_2Phen_2TBP$. The reduction peak was registered after the accumulation at -0.3 V at the potential about -0.6 V. A detection limit of Cu(II)-ion by square-wave voltammetry (after the accumulation of 10 minutes at -0.3) was found to be $(1.2 \pm 0.2) \cdot 10^{-10}$. The concentration of copper(II)-ion was detected in fresh and saline water samples from the Rasa Bay and Rasa River.

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