

**„Electrode processes of selected redox probes at liquid-modified electrodes”**

**Wojciech Adamiak**

**Abstract**

The goal of this thesis was to investigate and understand selected electrode processes that occur at the liquid-modified electrodes.

An intrinsic property of such electrodes is an interface between a liquid deposited on the electrode and a liquid where the electrode is immersed. Under such conditions the electrode reactions are coupled to ion transfer across the liquid|liquid interface. Such electrodes can be applied to model biological membranes or to construct ion-selective amperometric sensors.

The electrodes were modified with a microliter volume of the redox probe solution in the water-immiscible solvent: 1,2-dichlorobenzene, toluene or hydrophobic ionic liquid. Then the electrode was immersed in the aqueous electrolyte solution. Decamethylferrocene (DMFc), fullerene C<sub>60</sub> or manganese(III) tetraphenylporphyrin (Mn(III)TPP) were used as redox probes. Cyclic voltammetry and differential pulse voltammetry were used for electrochemical measurements. UV-Vis spectroscopy was employed to investigate possible interactions between the ionic liquid and Mn(III)TPP. Mechanisms of the electrode processes were determined on the basis of Nernst equations.

The results obtained with DMFc indicated that the electrodes modified with organic solvents of low polarity are suitable for studying processes of ion transfer across liquid|liquid interface. It was found that in the presence of hydrophobic anions in the aqueous phase, oxidation of DMFc is coupled to anion transfer from the aqueous to the organic phase. Multiple electrode processes were observed when fullerene C<sub>60</sub> was used as the redox probe. It was found that depending on the composition of the water-immiscible phase, transfer of various ions can be driven, i.e. transfer of aqueous electrolyte cations and anions, or transfer of ionic liquid-constituting anions and cations. Studies of Mn(III)TPP and the hydrophobic ionic liquid (used as the supporting electrolyte in the organic phase) revealed that the ionic liquid affects the mechanism of the electrode process when the redox probe possesses coordination sites.

Conclusions drawn from this thesis further the knowledge about the electrode processes that occur at the liquid-modified electrodes. Understanding of the latter is a prerequisite for their effective application to chemistry or biology.