

## Abstract

In the present thesis, both the published and the "ready-to-be-submitted" results concerning electrochemistry of calixarenes are summarized. The main focus is given to the detailed interpretation of experimental data, acquired during a systematic study of electroactive calixarene derivatives. The experiments were conducted under aprotic conditions (DMF) on mercury electrodes (mainly cyclic voltammetry and DC-polarography). It is demonstrated that electrochemistry should not serve only for redox characterization of studied compounds, but it offers a great number of other valuable information.

The subject matter of the study are the calix[4]arenes (prevalently in the *cone*-conformation) which bear one to four reducible or oxidizable substituents ("redox probes") at various positions in order to be electrochemically investigable. Nitro- and nitroso compounds together with aldehydes, ketones, nitriles, aldoximes, carboxylic acids and corresponding esters, sulphones and esters of sulphonic acids are the most discussed compound series. Their relationship between structure and electrochemical response is presented in new connections ("stereoelectrochemistry"), in other words, how the redox probe position on the benzene ring (*para-/meta-*), bridging groups, or adjacent *vs.* opposite aromatic units substitution is reflected in electrochemical data. It became apparent, how important factors are conformation of calix[4]arene, type of bridging units, symmetry of substitution on the upper/lower rim or absence/presence of acidic ionizable groups. From the electrochemical response it is even possible to learn about the dynamical properties of calixarenes in solutions.

Although many logical and systematic links between the structural properties of calixarenes and their electrochemical responses were observed and described in this work, it seems still impossible to derive from them, or to definitively predict information on rigidity / flexibility for a hypothetical compound because all the individual factors affect each other strongly. On the other hand, the observation of stereoelectrochemical nonequivalence of two adjacent, and, reversely, the equivalence of two opposite benzene rings is likely to be a common feature for vast majority of *cone*-calix[4]arenes.

Many discussed compounds contain more than one redox active group, thus the interpretation of their reduction mechanism needs previous analysis of mutual communication of the redox centers, of intramolecular electronic interactions and of electron delocalization. In addition to this, by means of voltammetry, it is possible to reveal also intermolecular interactions, namely formation of complexes, ion pairs or other adducts (e.g. "host-guest" interaction). Proposed hypotheses and interpretations of effects observed electrochemically are simultaneously (or subsequently) confronted with independent results taken from *in-situ* UV-Vis / EPR spectroscopy in combination with electrochemistry (spectroelectrochemistry), and correlated to quantum chemical calculations.