

Abstract of the PhD dissertation: *Novel systems for ion-transfer studies*

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Abstract

The goal of this thesis was to develop novel, low-cost systems for liquid/liquid electrochemistry that are easier to handle than presently used methods. Transfer of ions across the interface between two immiscible electrolyte solutions (ITIES) is a very interesting and powerful technique enabling direct electrochemical detection of various ionic species, even these non-electroactive. Unfortunately, traditional setups used for this kind of measurement require a lot of experience and present difficulties in practical handling, making ion-transfer voltammetry available only to a small number of scientists specialized in the field of liquid/liquid electrochemistry and keeping it confined to the laboratory. To solve these issues, simpler alternative versions of classic 3- and 4-electrode systems were developed and described herein.

Instead of a droplet-based 3-electrode approach, a system with paper as a liquid phase reservoir can be applied to investigate electrochemically driven anion-transfer. The unique absorptive properties of the cellulose matrix allow keeping both aqueous and organic phase soaked on a paper sheet. Moreover, the paper support helps increase the mechanical stability of the interface leading to better control of the three-phase junction line and higher reproducibility of the results. Proper performance of the system was confirmed through the observation of two effects typical for setups with three-phase junction, namely, the effect of anion concentration on the peak position and shift of the signal with increasing hydrophobic properties of the anion.

In the case of facilitated cation transfer as an alternative can serve a 3-electrode system with pencil lead as a working electrode. Successful experiments using three different ionophores prove that it can be an excellent tool for comparing ionophores' selectivities. In contrast to ion-selective electrodes, usually used for that purpose, in the proposed system, the ionophore does not have to be immobilized in the membrane eliminating the influence of membrane components on the obtained results. Additionally, it was shown, for the first time, that fullerene C₆₀ can be applied as a redox probe for electrochemically driven cation transfer.

The last setup described in this thesis simplifies ion-transfer measurements using polarizable ITIES. To create a system amenable for scientists from different fields and applicable for on-site analysis, the organic phase was gelled in the pen-like device while the aqueous phase was supported in a paper platform. This electrochemical pen system was applied for the transfer of model organic cations, facilitated cation transfer and stripping analysis of proteins. Moreover, it was shown that thanks to the presence of sodium ions in the cellulose matrix, ion-transfer experiments can be performed without the addition of any supporting electrolyte. Importantly adsorptive properties of cellulose fibers allow a sample to be analysed simply by spotting it on the platform or collecting it by swabbing. Furthermore, the electrochemical pen setup was combined with the paper-based flow system to chromatographically separate ions and proteins or protein mixtures then detected by ion-transfer technique. An alternative, entirely paper-based version of the organogel/paper system is also presented, in which the organic phase is gelled directly on the paper platform. Although the described results are very preliminary, they can serve as a basis for the future development of a flat, low-cost, paper-based system for ion transfer measurements using polarizable ITIES.