

UNIVERSITY OF PÉCS

Doctoral School of Chemistry

**Investigation of the role of diffusion in analytical procedures by
electrochemical methods**

PhD thesis

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1. Introduction

The transport processes (such as diffusion, migration and convection) taking place in the sample and at the electrode's surface have significant role in electrochemical methods used for analytical measurements and detection. These processes strongly influence the power of the electroanalytical method of interest. The surface of the electrode in voltammetric and amperometric detection mode is often covered by artificial layer (for example size exclusion membrane) to improve its selectivity, however such a layer hinders the target molecules coming to the surface. In other cases (e.g. solid contact ion-selective electrodes or biosensors) the electrode surface is covered by an ion-selective polymeric film or biocatalytic layer containing enzyme, in which the rate of mass transport - because of the layer structure - varies from that is valid in homogeneous media. The mass transport inside the layers is diffusion; the determination of its optimal thickness is important with respect of its electroanalytical performances: thick layer results in higher analytical signal however also in prolonged response time.

By knowing the diffusion coefficient the chemical reactions, complex forming processes occurring in the layers can be modelled, the electroanalytical and sensor properties can be predicted and designed in advance. The effect of barriers present in the space (e.g. the insulating body sealing of the electrode) becomes more significant because of the small distance between the source and the detector, especially when using microelectrodes for the determination of diffusion coefficients and the so called time-of-flight method.

Similarly, in the so-called tortuous media (consisting of at least two phases) the diffusion is hindered, and the diffusion coefficient influences the magnitude of the measured signal when using voltammetric and/or amperometric techniques. Because of the barriers or wattles in the space, the measured diffusion coefficient of each material is apparently smaller than that in homogeneous solution. This makes difficult the analytical measurements carried out in such media, like soil samples and sediments. Namely the calibration is completed in homogeneous solutions usually, and this causes error in the direct determination.

The electric conductivity properties of the medium also influence the results of the electrochemical measurements. Highly resistive media do not contain additional supporting electrolyte, therefore significant ohmic potential drop appears. On the other hand, the polarity of medium also complicates the measurements. These cause large distortion in the measurements when using voltammetric and amperometric techniques. The lack of supporting electrolyte and the transport processes together influence the signal in a complicated way. By

measuring neutral electroactive compounds the mechanism of charge transfer process is an interesting question. If the species of interest is ionic in nature, the migration could have also contribution to the current intensity.

In my work studies have been carried out that are suitable for revealing the problems related to the different transport processes - primarily diffusion – in the electrochemical method's based analysis. It was necessary to find solutions for eliminating the emerging problems and their analytical concerns. During the studies micro-sized electrodes, conventionally sized electrodes were often applied or such an electrode arrangement was used where individual electrodes were separated by a tiny gap of some microns; the microelectrodes and cells have been designed and prepared by myself. The conclusions arising from the experimental data were confirmed by the analysis of real samples.

2. Aims of the thesis

- Studying the dependence of the electrochemical time-of-flight method on the electrode arrangement geometry and finding a suitable geometry.
- Studying tortuous media by using chronoamperometry and linear sweep voltammetry.
- Electrochemical investigation of neutral electroactive compounds in highly resistive media in the absence of supporting electrolyte.

3. Methods used

In the studies mainly chronoamperometric and voltammetric methods have been used; conventionally sized electrodes and in the highly resistive media microelectrodes have been applied. The microelectrodes, arrangements and measurement cells were designed and made by myself. The electrochemical measurements were carried out by potentiostats, pH meters and voltmeters.

4. Results

In my studies the performance of electrochemical time-of-flight method was investigated with multiple electrode arrangements using two model compounds triiodide ion and hexacyano-ferrate(III) ion. It was found that if the generating and detector electrodes were confined in planar arrangement, the results concerning the diffusion coefficient were not distorted. This geometry simplifies likely the determination of diffusion coefficients in polymer membranes, gels or any other tortuous media.

By continuing the above work, sand fractions have been used to model the tortuous systems in the experiments. The results showed that quantitative determination of a material is possible when using an electrode covered by a so called built-in diffusion layer in that the diffusion coefficient is smaller than the apparent diffusion coefficient in the tortuous medium.

In the further studies highly resistive *n*-heptane was chosen without any added supporting electrolyte as model system. The determinations of alcohols directly in hydrocarbon (petrol) have been successfully performed by using narrow-gap cells with microelectrodes in combination. Suggestions have been made both on the possible charge transfer materials and on the charge transfer mechanism concerning the high electric field gradient.

It was found in media containing no additional supporting electrolyte – in contrast to media generally used for electrochemical experiments – that stirring resulted in a decrease of the current intensity. Explanations have been made on the phenomenon.

The results can be summarized as follows:

5. Thesis of the work

1. By using of a newly designed planar cell I showed that the geometry dependent parameter *C* in the Stokes-Einstein equation is independent on the distance. According with the theory, in case of spherical diffusion and cylindrical diffusion values close to 6 and 4 have been calculated, respectively. By using the planar arrangement results were not distorted by the wall effect, and it simplified the determination of diffusion coefficients in coherent systems such as gels.
2. By using triiodide ion as a model compound and chronoamperometry as method I showed that the measured current intensities are significantly smaller in sediment than in the bulk solution when the measurements were performed in tortuous system with a bare electrode.
3. Electrode covered by a built-in diffusion layer can be applied successfully for concentration determinations in tortuous systems. Feasibility of the new electrode for analytical purposes has been demonstrated by the direct determination of active chlorine in soils samples.

4. A combined CO₂ microelectrode has been developed for studies in gaseous phase; the reference electrode was deposited with a silver-plating onto the outer surface of a glass capillary that contained inside a pH sensitive antimony fibre. The potentiometric electrode fabricated this way was successfully used for determining the position of a gas source by scanning along a line above the target.

5. I applied narrow-gap cells for the amperometric studies of alcohols in highly resistive media. Copper sulphide modified copper electrodes were more suitable than bare copper electrodes because of the higher current intensities for alcohol determination in heptane. For practical applications carbon microelectrode showed better long-time stability performances over Cu or Cu/CuS electrodes. It was used for the direct quantification of ethanol in petrol sample.

6. First time on my knowledge I demonstrated in some solvents containing no supporting electrolyte and with two different model compounds that stirring resulted in current intensity drop comparing to quiescent solution, when using amperometry for the measurement of a neutral electroactive material. This result might be a proof for the existence of a local electrolyte zone which is forming during the electrochemical measurement.

6. Publications

Publications related to the thesis:

1. András Kiss, **László Kiss**, Barna Kovács, Géza Nagy: Air gap microcell for scanning electrochemical microscopic imaging of carbon dioxide output. Model calculation and gas phase SECM measurements for estimation of carbon dioxide producing activity of microbial sources. *Electroanalysis*, **2011**, 23, 2320-2326 (IF: **2,872**)

2. **László Kiss**, Géza Nagy, Barna Kovács: Amperometric response of alcohols dissolved in high resistance hydrocarbon media at microelectrodes without supporting electrolyte. *Electroanalysis*, **2012**, 11, 2117-2124 (IF: **2,817**)

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4. **László Kiss**, Géza Nagy, Barna Kovács: Direct chronoamperometric determination of free available chlorine in soil samples using in-built diffusion layer coated glassy carbon electrode. *Journal of Solid State Electrochemistry*, **2015**, 19, 261-267 (IF: **2,279**)

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2. Yin Li, Zsolt Csók, Péter Szuroczki, László Kollár, **László Kiss**, Sándor Kunsági-Máté: Fluorescence quenching studies on the interaction of a novel deepened cavitand towards some transition metal ions *Analytica Chimica Acta* **2013**, 799, 51-56 (IF: **4,387**)

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2. Kovács Barna, Tesanovic Damir, Csóka Balázs, **Kiss László**, Nagy Géza: A mérési elrendezés hatása a diffúziós együttható „time-of-flight” mérésére – modell számítások, *Centenárium Vegyészkonferencia*, **2007**, május 29. – június 1., Sopron

3. **Kiss László**, Tesanovic Damir, Nagy Géza, Kovács Barna: Vizsgálatok különböző elektród elrendezések mellett diffúziós együtthatók meghatározásához, *XXX. Kémiai Előadói Napok*, **2007**, október 29-31., Szeged

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8. **Kiss László**, Kovács Barna, Nagy Géza: Keskeny-rés cellák felhasználása nagy ellenállású közegekben, elektrokémiai vizsgálatokhoz, *Kémiai Szensorok Workshop IV.*, **2012**, április 26-27., Pécs
9. Óri Zsuzsanna, **Kiss László**, Nagy Livia, Nagy Géza: Diffúziós réteggel módosított munkaelektrod tortuózus közegben való analízisre, *Kémiai Szensorok Workshop V.*, **2013**, április 18-19., Pécs
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11. **László Kiss**, Zsuzsanna Óri, Livia Nagy, Géza Nagy: Modified, layer coated amperometric sensor for measuring in natural, porous matrices, *CECE 2013 10th International Interdisciplinary Meeting on Bioanalysis*, April 25-27, **2013**, Pécs, p. 35
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3. Y. Li, Zs. Csók, G. Matisz, **L. Kiss**, L. Kollár, S. Kunsági-Máté: A novel deepened cavitand fluorescent chemosensor for detection of Fe³⁺ and Cu²⁺, *Symposium on Weak Molecular Interactions*, March 5-6, **2013**, Pécs, Hungary, p. 74
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