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Development of sensors based on synthetic receptors:
factors affecting the selectivity and the detection limit

Ph. D. thesis

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SUMMARY

Chemical sensors are easy to use integrated analytical tools for the selective recognition and determination of ions and molecules. Their main application fields are clinical chemistry, physiology, process control and environmental analysis. Chemical sensors contain two basic functional units: a receptor and a transducer part. The sensing element (receptor) that recognizes the target species from the environment can be isolated enzyme, antibody, inorganic salt or synthetic organic ligand. The transduction of the recognition reaction can be potentiometric, voltametric, optical or microgravimetric.

In the field of the ion-selective electrode (ISE) research a breakthrough result was recently reported, the detection limit (DL) of solvent polymeric membrane based ISEs could be extended to the lower picomolar range. The research has proved, that in certain analyte concentration ranges minor ionic fluxes across ionselective membranes have an important role in determining the potentiometric response. At micromolar and submicromolar sample activities, even minor ion transport significantly alters the analyte concentration in the solution phase adhering the membrane; e.g., leaching ions perturb ionic concentrations in the immediate vicinity of the sensing surface. Since surface concentrations control the phase boundary potentials, these altered concentrations determine the electrode calibration slopes and the lower detection limits.

Scanning electrochemical microscopy (SECM) supplemented with potentiometric measurements was used to follow the time-dependent buildup of a steady-state diffusion layer at the aqueous-phase boundary of lead ion-selective electrodes. Differential pulse voltammetry is adapted to SECM for probing the local concentration profiles at the sample side of solvent polymeric membranes. Major factors affecting the membrane transport-related surface concentrations were identified from SECM data and the potentiometric transients obtained under different experimental conditions (inner filling solution composition, membrane thickness, surface pretreatment). The determined surface analyte concentrations correlated well with the lower detection limits of the lead ion-selective electrodes.

The disturbing effect of analyte ion leaching or uptake by the sensor membrane can be decreased by passing nanoampere-level direct current across the membrane. In this work, we demonstrated that reproducible, Nernstian response down to 10^{-10} M can be achieved without apparent super-Nernstian response when there is no net primary ion flux across the membrane; i.e., the ion fluxes are balanced by external current.

The second part of the thesis describes the use of calix[4]resorcinarene derivative as recognition element in electrochemical sensors. The modification of glassy carbon electrode with calix[4]resorcinarene derivative was found to improve the selectivity of the electrode towards dopamine against ascorbic acid and uric acid. The interaction between the ionophore and dopamine was also used to improve the analytical properties of bilayer lipid membrane (BLM) based sensors. Calix[4]resorcinarene derivative modified piezoelectric sensor was found to be sensitive for chlorinated organic gases.

ACHIEVEMENTS

1. A new scanning electrochemical microscopic method was elaborated for the determination of the concentration profile at the membrane- sample solution interface of solvent polymeric membrane based ion-selective electrodes (ISE). A lead selective ionophore based ISE was used as a model. The small lead concentration difference in the solution phase could be determined by scanning electrochemical microscopy operating in the differential pulse voltammetric mode.
2. Evidences were provided for the theory of ionic fluxes across ion-selective membranes with independent analytical method. The ion-fluxes influencing the selectivity and detection limit of solvent polymeric membranes were presumed from the potentiometrical results. The membrane and experimental parameters, which can be crucial for the development of ISEs with low detection limit, were determined.
3. The apparent super-Nernstian response of the ISEs with ion buffer inner filling solution was interpreted. We proved that the decreased primary ion activity in the liquid phase at the sample solution – ion-selective membrane interface could be compensated by adjusting the ion transport into the membrane surface. We could achieve 10^{-10} mol/dm³ detection limit selecting the experimental parameters.

5. Original synthetic receptor (calix[4]resorcinarene derivative) modified glassy carbon voltammetric electrode was studied. The modification improved the dopamine selectivity of the electrode against ascorbic acid and uric acid. The electrode modified with Nafion polymer incorporated receptor possessed the best selectivity

($\frac{I_{\text{ascorbic acid}}}{I_{\text{dopamine}}} = 4 \cdot 10^{-3}$, $\frac{I_{\text{uric acid}}}{I_{\text{dopamine}}} = 10^{-2}$) and the best sensitivity ($6.51 \cdot 10^{-3} \text{ A}/(\text{mol}/\text{dm}^3)$).

6. We could improve the analytical properties of lipid bilayer membrane based sensors by incorporating calix[4]resorcinarene derivative receptor molecule into the film. The ion current detection based sensor measured dopamine with the detection limit of $5 \cdot 10^{-7} \text{ mol}/\text{dm}^3$.

7. Preliminary studies on organic solvent vapor sensing characteristics of different calix[4]resorcinarene derivatives modified piezoelectric sensor showed, that all three calix[4]resorcinarene derivatives modified sensor have the best selectivity for 1,2-dichlorobenzene.

PUBLICATIONS

Articles:

Robert E. Gyurcsányi, Éva Pergel, Renáta Nagy, Imre Kapui, Bui Thi Thu Lan, Klára Tóth, István Bitter, Ernő Lindner: Mapping of the aqueous diffusion layer of ionophore-based membrane electrodes: a scanning electrochemical microscopic study. *Anal. Chem.* 2001, 73, 2104-2111

Éva Pergel, Robert E. Gyurcsányi, Klára Tóth, Ernő Lindner: Picomolar detection limits with current polarized Pb^{++} ion-selective membranes. *Anal. Chem.* 2001, 73 4249-4253

Syrago – Styliani E. Petropoulou, Dimitrios P. Nikolelis, Éva Pergel, Klára Toth, István Bitter: One-shot minisensor for the rapid detection of dopamine using bilayer lipid membranes with incorporated calix[4]resorcinarene receptor. *Electroanalysis* 2002, 14, 783-789

Lectures:

Pergel Éva, Tóth Klára, Bitter István, Lindner Ernő: Ólom-ion szelektív elektród mérési alsóhatárának vizsgálata; Vegyészkonferencia (Július 5-7, 2000, Debrecen)

Pergel Éva: Ionszelektív elektródok analitikai jellemzőinek vizsgálata; IV Doktori Kémiai Iskola, (Május 20-22, 2001, Mátraháza)

Pergel Éva: Lipid kettősréteg alapú kémiai szenzorok; Kémiai Szenzorok Kutatásának Eredményei Workshop; Pécs, 2001. november 22-23.

Poster:

Imre Kapui, **Éva Pergel**, Bui Thi Thu Lan, Klara Tóth: Application of electrochemical microscopy in the study of detection limit of ISEs; poszter, Mátrafüred'98 International Symposium on Electrochemical and Biosensors (Október 14-17, 1998, Mátrafüred)

Coauthor in lectures:

Ernő Lindner, Éva Pergel, Robert E. Gyurcsányi, Bradford Pendley, Michael R. Neuman Current polarized ion-selective membranes. Steady state galvanostatic control and chronoamperometric transients; The Pittsburgh Conference 2000 (Március 12-17, 2000, New Orleans)

Klára Tóth, Éva Pergel, Bui Thi Thu Lan, István Bitter Imaging Ion-Permeation Across Solvent Polymeric Membrane Electrodes The Pittsburgh Conference 2001 (Március 4-9, 2001, New Orleans)