Bilayer membranes for ion-selective electrodes

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ABSTRACT

In most cases described so far a potentiometric ion-selective membrane is made of one polymer (or one copolymer) used with ion-exchanger, ionophore and with a plasticizer of choice. In this work a concept of potentiometric bilayer membranes is introduced and their benefits from both theoretical and practical point of view are presented. They are related to response mechanism interpretation and to detection limit lowering of ion-selective electrodes.

The novel structurized bilayer potentiometric membranes represent a sequence of polyacrylate polymers with ion-exchangers (the same or different), the polymers applied were either poly(hexyl acrylate) or poly(lauryl acrylate) characterized by different ionic mobilities. It was shown that tailoring of the polymer material for the component layers, kind of ion-exchanger and the layer thickness can result in significantly improved analytical performance represented by wide linear response range and low detection limit, as shown in example of potassium-selective electrode. This effect was achieved due to controlled compensation of spontaneous ion fluxes in bilayer system. The experimental data were supplemented by digital simulation results explaining the role of the thickness of the internal layer on the ion fluxes and thus on the detection limit.

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1. Introduction

Potentiometric ion-selective electrodes are sensitive to the analyte activity changes in the solution layer adjacent to the ion-selective membrane phase. Stable, reproducible results are obtained in case of thermodynamic equilibrium at all interfaces, involving "saturated" ion-selective membrane, where the total charge of primary ions is equal to that of ion-exchange sites [1]. Therefore performance and analytical parameters of ion-selective electrodes are highly dependent on the membrane composition and concentration of ionic components within it.

Very often, ion-selective membranes, directly after preparation, contain no primary ions for which they are sensitive, e.g. because appropriate ion-exchangers available are mostly those with K^+ or Na^+ cations, thus the necessary process prior to sensor application is exchange of primary ions with membrane during conditioning and/or use of the sensor, e.g. [2]. Moreover, in course of the measurement, difference in concentration of ions in the sample solution and in the sensor components (membrane, internal solution or solid contact) can generate non-equilibrium conditions resulting in ion fluxes between the membrane and solution or the membrane and internal solution (solid contact). This not only affects analytical parameters, as detection limit, slope of the calibration plot and selectivity, but also results in composition changes of the membrane/solid contact and appearance of diffusion potentials.

Therefore, it is obvious that careful tailoring of ion fluxes through the membrane is essential to improve the sensor performance, e.g. [2,3]. These issues have been discussed in many papers in last twenty years. The gradients within the membrane were created through tailoring composition of the solution contacting the membrane, e.g. [2–4] or applying galvanostatic polarization, e.g. [5–7]. Some attempts were focused on membrane material to affect the membrane bulk properties, for example change of characteristics of the membrane material (different polymers, different plasticizers, variable proportion of plasticizer to the polymer, affecting ionic mobility), e.g. [4,8,9], or significantly changing membrane thickness [4,10]. On the example of calcium-selective polyacrylate membrane electrode it has been shown that full saturation of the membrane by primary ions resulted in elevated detection limit, while purposely established ratio of primary/interferent ion amount gives extended linear response range [11]. However, all these works were still using one define material (or one define composition) as a membrane.

The traditional approach — one material applied as a receptor layer — has significant limitations related to the membrane performance, determined mainly by diffusion coefficients of mobile components and membrane composition. For instance, relatively high diffusion coefficients characterizing poly(vinyl chloride) ion-selective membranes

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(typically of order of 10^{-8} cm^2 s^{-1} [12,13]), result in usually less favorable analytical parameters [13] of the electrodes, compared to sensors with polyacrylate membranes, where diffusion coefficients of mobile ions are around 10^{-11} cm^2 s^{-1} [12]. On the other hand, saturation of the polyacrylate membrane with primary ions in course of conditioning would require extremely long time, thus incorporation of primary ions in course of membrane preparation is advantageous [11].

Possibilities of membrane parameters tailoring can be extended by using a concept of multi-layer membranes, described in our preliminary paper [14]. In this approach polymer layers with gradually changing diffusion coefficients of primary ions were used, enabling additional control of ion fluxes and analytical parameters improvement, as shown on example of copper-selective electrode. A gradual change of diffusion coefficient — e.g. higher value of diffusion coefficient at the sample/solution interface region and lower within the membrane bulk, in principle can not only prevent accumulation of ions in the outer membrane surface but also can help to improve the membrane performance. This approach can be successful in case of good adhesion of component layers and similar physico-chemical properties. Materials which meet these requirements are polyacrylate polymers. Due to availability of different monomers belonging to this group, polymers of different properties could be easily prepared, e.g. [8,15,16].

In this report, we extend possibilities of multi-layer system by changing not only membrane material and thus diffusion coefficient, but also purposely incorporated amount of primary/interferent ions to a classical potassium-selective membrane. To simplify the system and for easier quantitative interpretation of data we are testing electrodes with bilayer membranes composed of polyacrylates characterized either by the same or different diffusion coefficients, by using poly(hexyl acrylate) or poly(lauryl acrylate) with higher and lower diffusion coefficient, respectively [14]. Moreover, changing the amount of primary/interferent ion concentration in separate layers of the bilayer membrane system can induce advantageous ion fluxes and can be beneficial for analytical performance.

Some of experimental results, concerning mainly ion fluxes in the bilayer systems will be discussed theoretically basing on simple digital simulations using finite difference method.

2. Experimental

2.1. Apparatus

In the potentiometric experiments a multi-channel data acquisition setup and software, Lawson Labs. Inc. (3217 Phoenixville Pike, Malvern, PA 19355, USA) was used. The pump systems 700 Dosino and 711 Liquino (Metrohm, Herisau, Switzerland) were used to obtain sequential dilutions of calibrating solution.

The double junction silver/silver chloride reference electrode with 1 M lithium acetate in the outer sleeve (Möller Glasbläserei, Zürich, Switzerland) was used. The recorded potential values were corrected for the liquid junction potential calculated according to the Henderson approximation. As a support for all-solid-state ion-selective electrodes glassy carbon (GC) electrodes were used.

2.2. Reagents

Potassium-selective ionophore — valinomycin, sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB), potassium tetrakis(4-chlorophenyl)borate (KTChPB); 1,6-hexanedioldiacrylate (HDDA), 2,2-dimethoxy-2-diphenylacetophenone (DMPP) lauryl acrylate (La), hexyl acrylate (Hex), regioregular poly(3-octylthiophene-2,5-diyl) (POT), tetrahydrofuran (THF), chloroform were from Sigma-Aldrich (Germany).

Doubly distilled and freshly deionized water (resistance 18.2 MΩ cm, Milli-Qplus, Millipore, Austria) was used throughout this work. All salts used were of analytical grade and were obtained from POCh (Gliwice, Poland).

2.3. Indicator electrodes and solid contacts

Glassy carbon (GC) electrodes of surface area 0.07 cm^2 were used. The substrate electrodes were polished with Al$_2$O$_3$, 0.3 µm and rinsed well in water.

Ion-selective membranes were applied on the conducting polymer POT layer formed on top of the glassy carbon electrode placed in up-side down position. 2.5 mg ml^{-1} POT solution was prepared in chloroform. 10 µl of POT solution was applied on the top of the glassy carbon electrode placed in up-side down position and left for solvent evaporation, for 1 h in laboratory atmosphere.

2.4. Ion-selective membranes

Potassium-selective membrane cocktails contained (by weight): 1.5% of NaTFPB or KTChPB, 3.0% valinomycin, 0.1% HDDA, 1.2% DMPP and lauryl acrylate or hexyl acrylate. The component layers of bilayer membranes were prepared using either NaTFPB or KTChPB of the same concentrations.

One-layer membranes were obtained by application of 7 µl of the membrane cocktail on the surface of POT coated GC electrode, placed in upside down position, followed by photopolymerization carried out using an UV lamp (360 nm) for 5 min under argon atmosphere.

Bilayer membranes were obtained by consecutive application of 15 µl (inner layer) and 7 µl (outer layer, if not stated otherwise) of the chosen cocktail, followed by photopolymerization carried out using an UV lamp (360 nm) for 5 min under argon atmosphere. The thickness of the whole structured membrane was comparable to other potentiometric membranes tested/used and it was close to 250–300 µm.

The prepared sensors were conditioned before measurements in 10^{-3} M KCl solutions for 12 h. In-between measurements the electrodes were stored in the same solutions as used for conditioning.

The mean ion activities were calculated according to Debye–Hückel theory.

All experiments were performed at ambient temperature (23 °C).

2.4.1. Theoretical
Digital simulations concerning ion fluxes and concentration profiles in bilayer ion-selective membranes were based on Nernst–Planck equation concerning unidimensional mass transfer, in the absence of convection:

$$J_i(x,t) = -D_i \frac{\partial c_i}{\partial x} - z_i D_i c_i \frac{\partial \Psi}{\partial x} \qquad (1)$$

where J_i, D_i, c_i and z_i represent the flux of ions „i", the diffusion coefficient, concentration and charge, x is the distance from the internal layer/external layer interface, t is the time, Ψ is dimensionless potential function, i.e. the electrical potential multiplied by the constant (F/RT) (the Faraday's constant, the gas constant and the temperature).

Under zero-current conditions the sum of fluxes is equal to zero, and additionally the continuity expression holds:

$$\frac{\partial c_i}{\partial t} = -\frac{\partial J_i}{\partial x}. \qquad (2)$$

In digital simulations finite-difference method was applied, where the Nernst–Planck equation was discretized by representing the membrane by N thin segments, a protocol described by Morf et al. was used [17]. For this case the differentials can be replaced by differences