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Comparison of different approaches to the description of the detection limit of ion-selective electrodes

Jerzy J. Jasielec[a], Tomasz Sokalski[a], Robert Filipek[b], Andrzej Lewenstam[a,b,*]

[a] *Process Chemistry Centre, c/o Centre for Process Analytical Chemistry and Sensor Technology (ProSens), Åbo Akademi University, Biskopsgatan 8, 20500 Åbo-Turku, Finland*
[b] *AGH - University of Science and Technology, Faculty of Material Science and Ceramics, Al. Mickiewicza 30, 30059 Cracow, Poland*

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ABSTRACT

The Nernst–Planck–Poisson (NPP) model is a general approach to the description of the electro-diffusion processes which lead to the formation of the membrane potential. It takes into consideration several parameters of ion-selective electrodes (ISEs) which are ignored in simpler models. This paper presents a critical comparison between the NPP model and simpler models. The influence of different parameters on the detection limit of ISEs is discussed. This is achieved by comparing direct predictions of the models and, in contrast to any earlier treatment, by inverse modelling. This makes it possible to simultaneously find out which set of physical parameters of the system will produce the desired detection limit.

1. Introduction

The formation of the membrane potential of ion-selective electrodes (ISEs) depends on the thermodynamic and kinetic properties of the membrane|solution system, and it is strongly time dependent. Selectivity (K_{IJ}) and detection limit (DL) are constitutive parameters of all ion-selective electrodes.

There is an ongoing and vigorous debate in the ISE literature concerning models describing ISE behaviour in general, and K_{IJ} and DL in particular. There are two main schools of thought. The first one opts for simplicity while the other one stresses generality [1]. The argument that simpler is better applies only if the simpler and the more complicated models are equally general (Ockham's razor).

Advocates of the simple model stipulate that it should be restricted in the following ways: (1) the diffusion coefficients in the membrane should be assumed to be equal for all participating ions, (2) the migration of ions should be disregarded, (3) only two (or, at the most, three) ions should be considered, (4) frequently only ions of the same charge should be taken into account and (5) the model should be restricted to steady-state conditions.

Sometimes proponents of the simple model assume the presence of only two ions of the same charge and time dependence, and sometimes of ions of different charges and steady-state (no time dependence), and from these two cases draw the conclusion that the model (simultaneously) encompasses both different charges and time dependence. This, however, is not true since the assumptions, which have to be made when we consider ions of different charges, are made at the cost of time dependence and vice versa.

The more general (NPP) model takes into account both diffusion (each ion having its own diffusion coefficient both in water and in the membrane), migration, an unlimited number of ions of any charge and time dependence (Table 1).

The ISE models can be roughly divided into three categories: phase boundary models, diffusion layer models, and models including migration. They might also be divided into time-dependent and time-independent (equilibrium and steady-state) models [1].

The debate about the merits of different models has been mostly verbal, and a critical comparison between existing models is lacking so far. In this paper, we compare three models which represent the three main categories: the time-dependent NPP model (NPP), the time-dependent diffusion model (TDM) and the steady-state diffusion model (SDM). We use a dedicated virtual experiment and experimental data to validate competing models.

We hope that the comparison of different models, used for the description of the same well known examples, can exemplify and clarify the basic merits and weaknesses of the different approaches.

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* Corresponding author at: Process Chemistry Centre, c/o Centre for Process Analytical Chemistry and Sensor Technology (ProSens), Åbo Akademi University, Biskopsgatan 8, 20500 Åbo-Turku, Finland.
E-mail addresses: alewenst@abo.fi, andrzej.lewenstam@gmail.com (A. Lewenstam).

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Table 1
Comparison of the dynamic models presented in this paper.

NPP model	Diffusion models	
	Time-dependent models	Steady-state models
Diffusion, migration (convection)	Diffusion	Diffusion
Exchange and coextraction described by heterogeneous rate constants	Exchange and coextraction described by equilibrium constants	Exchange and coextraction described by equilibrium constants
Potential calculated from electrical field profile	Potential calculated from the phase boundary equation	Potential calculated from the phase boundary equation
Fluxes in all layers are co-dependent (concentrations-potential feedback)	Fluxes in both layers are independent	Fluxes are co-dependent (linear concentration profiles and mass balance)
Ions of any charge	Monovalent ions only	Monovalent ions only
Site distribution depends on electrical field distribution	Sites distribution constant	Sites distribution constant

Note: There is a plethora of models describing ISE behaviour. In this contribution we limit the comparison strictly to models which are directly relevant to the description of low detection limit phenomena. Therefore, some approaches (interesting from the numerical point of view) are not discussed here, e.g. [2].

2. ISE response models

2.1. General model

2.1.1. The Nernst–Planck–Poisson (NPP) model

2.1.1.1. History. The first numerical simulation procedure for the time-dependent NPP problem using an explicit method was developed in 1965 [3]. Later, in 1975, a mixed implicit method (for electric field) and an explicit method (for concentration) similar to [3] was presented [4]. However, due to the explicit nature of the concentration calculation, this method suffered from a very small time step of integration and therefore was very time-consuming.

2.1.1.2. Application of NPP to ISEs. The NPP model offers the most complete and universal description of membranes and related systems (for advanced analysis of the power and limitations of the NPP see [1]).

The application of the NPP model to membrane electrochemistry was presented in a seminal paper [5]. The authors developed an efficient finite difference scheme, totally implicit in time. The resulting set of non-linear algebraic equations was solved using the Newton–Raphson method.

An approach, based upon this idea and dedicated to the general description of ISE behaviour, was later developed [6–9].

The first extension of the NPP model for a two layer system was presented in [10]. The first NPP model implementation where the method of lines (MOL) [11] was used was presented in [12,13]. Later on, MOL extensions of the NPP model for an arbitrary number of layers were developed and implemented in C++ [14] or in MathCad [9] and Matlab [15] scripts.

2.1.1.3. NPP implementation used in this work. The NPP model describes a system consisting of *n*-layers (phases), inside of which concentration changes of *r* components (ions or uncharged chemical species) and a change of the electrical field in space and time take place (Scheme 1). The influence of diffusion and migration is expressed by the Nernst–Planck equation for the flux of the *i*th component inside the *j*th layer:

$$J_i^j(x,t) = -D_i^j \frac{\partial c_i^j}{\partial x}(x,t) - \frac{F}{RT} D_i^j z_i (c_i^j E^j)(x,t) \tag{1}$$

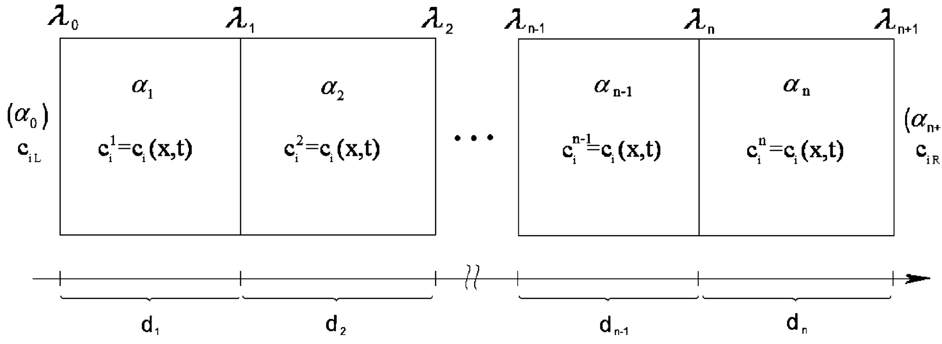
The continuity equation describes the change of the ion concentrations in time, and the Poisson equation describes the electrical changes caused by the interaction of the species. For convenience, the Poisson equation is replaced by the displacement current equation, as described in [3]. These equations form the following system of evolutionary non-linear partial differential equations (PDE) for *r* components in n phases:

$$\begin{cases} \dfrac{\partial c_i^j}{\partial t}(x,t) = -\dfrac{\partial J_i^j}{\partial x}(x,t) \quad \text{for } i = 1, \ldots, r; \\ \dfrac{\partial E^j}{\partial t}(x,t) = \dfrac{1}{\varepsilon_j} I(t) - \dfrac{F}{\varepsilon_j} \displaystyle\sum_{i=1}^{r} z_i J_i^j(x,t); \\ x \in [\lambda_{j-1}, \lambda_j] \quad \text{for each phase } j = 1, \ldots, n; \\ t \in [0, t_{\mathrm{END}}] \end{cases} \tag{2}$$

where λ_j is the interface between phases. The above system of PDE is accompanied by boundary and initial conditions.

The mass balance condition at the boundary is expressed by the equality of the fluxes in the boundary point in both phases, $J_i^{\alpha_j}(\lambda_j,t) = J_i^{\alpha_{j+1}}(\lambda_j,t)$. The heterogeneous first order rate constants are used to describe the interfacial kinetics at the interface λ_j between phases α_j and α_{j+1}: thus the boundary conditions take a form similar to these described in [16]:

$$J_i^{\alpha_j}(\lambda_j,t) = J_i^{\alpha_{j+1}}(\lambda_j,t) = \vec{k}_{i\lambda_j} c_i^{\alpha_j}(\lambda_j,t) - \overleftarrow{k}_{i\lambda_j} c_i^{\alpha_{j+1}}(\lambda_j,t) \tag{3}$$



Scheme 1. Scheme of the *n*-layer system between two solutions.