

Non-equilibrium potentiometry—the very essence

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Abstract In most interpretations of potentiometric ion sensor responses with glass, solid, or liquid/polymer membranes, a model assuming electrochemical equilibrium between the aqueous sample and the membrane is used. This model is often called a phase boundary model to emphasize the importance of ion-exchange processes at the interface. The essence of the phase boundary model is that it accepts electroneutrality and thermodynamic equilibrium, and thus ignores electrochemical migration and the time-dependent effects. For this reason, this model is in conflict with many experimental reports on ion sensors in which both kinetic (time-dependent) discrimination of ions to improve selectivity and non-equilibrium transmembrane ion transport for lowering the detection limits are deliberately used. To respond to the experimental challenges in the author's groups, we elevated the potentiometric modeling by using the Nernst–Planck–Poisson (NPP) equations system to model the non-equilibrium response. In the NPP model, electroneutrality and steady-state/equilibrium assumptions are abandoned, and thus we access the space and time domain. This approach describes the concentration changes of ions participating in the ion-exchange and transport processes, as well as the electrical potential evolution over space and time, and allows in particular, the inspection of the equilibrium set by the phase boundary models as a special “stationary” case after infinite

time. Additionally, directly predicting the selectivity and the low detection limit variability over time and the influence of other parameters, e.g., ion diffusibility, is possible. As a coherent and non-arbitrary model, the NPP system facilitates solving the inverse problem, i.e., to optimize the sensor properties and measurement conditions in a customized way via desired target functions and hierarchical genetical strategy modeling. In this way the NPP allows setting the conditions under which the experimentally measured selectivity coefficients are true (unbiased) and the detection limits are optimized.

Keywords Membrane potential · Phase boundary potential · Nernst-Planck-Poisson model · Electroneutrality paradox · Potentiometric sensors · Thermodynamic detection limit

Introduction

The main purpose of this paper is to highlight the principles of non-equilibrium potentiometry and the new frontiers that it opens.

For this reason, the paper deliberately starts with a description of equilibrium potentiometry and critical discussion of its deficiencies. In this context, the place for non-equilibrium potentiometry is established, and the model is described and discussed.

Equilibrium potential models

Electrode potential formation of potentiometric electrodes mainly depends on the thermodynamic and kinetic processes at the electroactive material (membrane, film) and bathing solution interface. These processes are strongly time depen-

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dent, as are the constitutive parameters for all electrodes: the selectivity and the detection limit, and to a lesser extent, the standard potential and slope. Unfortunately, including dynamic aspects in any modeling is known to be not an easy task. For this reason, in order to model potentiometric ion/electron responses, the thermodynamic approach is used, which assumes the electrochemical equilibrium at the membrane–solution interface for potential-determining ions and electrons. The equilibrium is the result of a fast and reversible charge transfer process.

This process results in characteristic and quantitative compensation of electric potential drop (Galvani potential) at the interface by the chemical potential drop of all species involved in forming the equilibrium (for more details see [1, 2]):

$$\Delta\varphi = \frac{\Delta\mu_i}{z_i F} \quad (1)$$

where $\Delta\mu_i$ is the chemical potential drop of the i th ion and $\Delta\varphi$ the electrical potential drop at the membrane–solution interface, z_i the main ion valency, and F is the Faraday constant.

The intuition here (Eq. 1) refers to the energy conservation principle. In potentiometry, it was originally used by Nernst [3] and then formally set by Guggenheim [4, 5], who introduced electrochemical potential of the i th ion in a phase as an algebraic sum of two independent terms, the electrical (inner) potential of the phase and the chemical potential of the i th ion in the phase.

By rearranging Eq. 1, one obtains the characteristic potential drop at the membrane interface (phase boundary, PB) and the equation pivotal for all phase boundary potential models:

$$E_M = E_{PB} = \frac{RT}{z_i F} \ln k_i + \frac{RT}{z_i F} \ln \frac{c_i}{\bar{c}_i} \quad (2)$$

where E_M is a sensor PB potential, c_i denotes the concentration of the main ion i in the solution (in mole per deci cubic centimeter) and the barred symbol, \bar{c}_i the concentration of the main ion in the membrane/film phase, k_i is an ion-partition constant defined as $k_i = \exp\{(\mu_i^0 - \bar{\mu}_i^0)/RT\}$, where μ_i^0 is a standard chemical potential of ion i in the solution, $\bar{\mu}_i^0$ is a standard chemical potential of ion i in the membrane, and R , T , and F are the universal gas constants and the absolute temperature. For simplicity, single i th ionic activity is substituted by concentration.

This model was first used in 1937 by Nikolskii [6] giving today's paradigmatic equation describing the potentiometric response of a pH-sensitive glass membrane electrode and the effect of interference by sodium ions (“thermodynamic ion-exchange theory”). The important feature of Nikolskii's model is that it provides the thermodynamic interpretation of, what is today known as, a selectivity coefficient, as the thermodynamic ion-

exchange constant, which is well defined for the separate solutions of the main ion ($i=H^+$) and interfering ($j=Na^+$) ions. Additionally, the model explains the influence of interfering ions on pH-sensitive glass and offers a way of *approximate* formal description by postulating that:

$$\bar{c}_i + \bar{c}_j \cong \text{const} \quad (3)$$

The above is a very important approximation but often goes unremarked. It is only recently that it has been made especially clear by Scholz [7].

From Eqs. 2 and 3 one obtains Nikolskii's equation for mixed ion response for the monovalent main and interfering ions:

$$\begin{aligned} E_M = E_{PB} &= \frac{RT}{F} \ln k_i + \frac{RT}{F} \ln \frac{c_i}{\bar{c}_i} \\ &= \frac{RT}{F} \ln k_i + \frac{RT}{F} \ln \left(\frac{c_i(\bar{c}_i + \bar{c}_j)}{\bar{c}_i(\bar{c}_i + \bar{c}_j)} \right) \\ &= \frac{RT}{F} \ln k_i + \frac{RT}{F} \ln \left(\frac{c_i + \frac{c_i \bar{c}_j}{\bar{c}_i}}{\bar{c}_i + \bar{c}_j} \right) \\ &= \text{const}' + \frac{RT}{F} \ln \left(\frac{c_i + K_{ij} c_j}{\bar{c}_i + \bar{c}_j} \right) \end{aligned} \quad (4)$$

Nikolskii's approach has been extensively applied for all other ion-sensitive membrane electrodes to semi-empirically characterize their responses. In all these cases, the phase boundary Eq. 2 is used as a tool to couple the ion equilibria in the electroneutral phases of the solution and membrane. In other words, c_i and \bar{c}_i are calculated similarly for the solution and membrane ion equilibria by using equations for complex formation constants, mass, and proton conservation, and the electroneutrality condition, all inserted into Eq. 2.

The elegant and simple but extremely idealized approach of Nikolskii is uncritically used by some authors who apply a strict electroneutrality condition in the membranes and seemingly ignore obvious inadequacy in this idealization, which is especially risky for plastic membranes (e.g., [8]). In such models, a phase boundary part belonging to the membrane is assumed non-electroneutral (as the place where charge separation takes place), but at the same time this membrane part is assumed to be electroneutral (the electroneutrality condition applies). Interestingly, the fathers of the phase boundary concept, Guggenheim and Nikolskii, were aware and deeply concerned about this *electroneutrality vs. non-electroneutrality* conflict (for more comments on this issue refer to [2]).

A fundamental extension of the thermodynamic model was proposed by De Battisti and Trasatti [9] who invited a “solvated electron” and formulated an open-circuit “dissolution potential theory” of metals. The authors were able to show that the mixed conductivity of a metal (treated as hypothetical $M^+ \cdot e^-$ salt) can result in positive Nernstian

slopes (cationic response) for excess of electroactive metal cation in the bathing solution and negative slopes (electron–redox response) in the case of controlled activity of electron, e.g., by redox pair or zero slope in the case of pure dissolution of the metal. The solubility equilibrium potential as such can be thus considered as a thermodynamic border line (*thermodynamic detection limit*) between the situations when the metal ion (M^+) can be regarded as the potential-determining ion (potential drop of the Nernst–Donnan type) and when the electron (e^-) can be considered as the potential-determining ion (potential drop of the Nernst type).

Trasatti's concept was a basis for a generalized theory of potentiometric response. The concept was dedicated to modeling the potentiometric responses of all the electroactive materials (membranes, films) exhibiting mixed conductivity, such as conducting polymers, in electrochemical equilibrium with mixed solutions, containing cations, anions, and/or redox pairs [10]. According to this theory, cationic, anionic, or redox sensitivity is possible (even) for the same membrane, and the theory predicts how particular sensitivity can be induced and stabilized in the multi-component solution and membrane system. The theory was a milestone in sensor technology, opening an avenue to all-solid-state ion sensors, e.g., with conducting polymers as the solid contact or electroactive element and eliminating the internal solution [11–23]. All-solid-state sensors can be easily miniaturized, sterilized, made maintenance-free, and self- and remotely controlled.

The concept of the ionic responses under equilibrium for different ion-selective membrane electrodes developed by Buck for solid-state membranes [24] and Wuhrmann et al. [25] for liquid-state membranes (today known as plastic) is excellently presented in the classical book by Morf [1]. In an ingenious way, Morf showed how it applies to different types of membranes and when the ion-sensitive electrodes respond with Nernstian slope.

The characteristic formal feature of the thermodynamic equilibrium approach is a common Nernstian type of equation that it generates for all types of ion-sensitive membrane electrodes in mixed solutions [26].

$$E_M = \text{const} + s \log \left(c_i + K_{i,j}^{\text{pot}} \frac{z_i}{z_j} c_j + L \right) \quad (5)$$

where *const* is the standard potential, *s*—slope, $K_{i,j}^{\text{pot}}$ —selectivity coefficient and *L*—detection limit measured; z_j —charge of the interfering ion.

For $L \ll c_i + K_{i,j}^{\text{pot}} \frac{z_i}{z_j} c_j$, the equation is known as the Nikolskii–Eisenman equation.

By applying these approach parameters constitutive for ion sensor, i.e., standard potential, the slope, selectivity, and detection limit were interpreted. Undoubtedly, the

interpretation is thermodynamically correct for pure solutions containing either the main or interfering ions or a pure solvent. It was applied to calculate the standard potentials [10, 27, 28], slopes [29, 30], selectivity coefficients [31–34], and detection limits [35–37] of the ion-selective electrodes first with solid-state membranes and subsequently with plastic membranes [38–46]; however, in strict electrochemical theorizing on ion-sensitive sensors, applying the strategy of phase boundary potential (especially to describe the response in mixed solutions) bears a high cost, which historically was first emphasized by Baucke for glass membrane electrodes [47].

The reasons for this are outlined in the following short list (for more details see [2]): (1) assuming “sharp phase boundary” as the only place of charge separation means ignoring the ion mobilities, migrational effects, and diffusion potential; (2) assuming “infinite” ion transfer rates ignore the charge transfer kinetics; (3) assuming “time independence” deprives the model of the time domain and thus the direct possibility to interpret the transient effects and equilibration processes (time has to be added ad hoc); (4) assuming “independence over space” really makes occurring non-linear redistribution of ions over distance invisible; (5) assuming “equality of the bulk and interfacial concentrations” of ions ignores the model transport processes in the membrane and in the diffusion layers.

In consequence of the above and other assumptions [2], one obtains a theoretical description of electrochemical sensor responses that is simple, perhaps over-trivialized, but one which may not be true and valid.

Methodologically, to reproduce theoretically the form of the Nikolskii–Eisenman equation is a formidable task. This can be seen by repeated trials by numerous authors, saturated with numerous arbitral (ad hoc) assumptions, a growing complexity of equations used that in the end cannot be analytically solved and require computer simulation, etc., and finally, by merely verbal comments made in order to strengthen the phase boundary approach by overemphasizing the difficulties of more advanced models. Nevertheless, a theoretician should remember that even in the case of 1:1, one should be careful with the validity of this approach, as Nikolskii was himself (see [7]).

I urge for the better style of modern theorizing by avoiding verbal claims of the type, e.g., “by the end of the 1980s it started to become clear that subtle effects of ionic mobilities in ion selective electrodes (ISE) membranes may be typically ignored without a significant loss in accuracy” [48] or “it is now established that the importance of diffusion potential was overestimated in the early days of ion-selective electrodes” [8], and to inspect the processes of membrane potential formation using a quantitative model.

This is why in my group, the work was undertaken to elevate and generalize modeling to a “non-equilibrium level” form by which it is possible to address the equilibration processes and perceive models assuming electrochemical equilibrium as special cases.

Diffusion layer model

The model bridging “thermodynamic” phase boundary models discussed above and “kinetic” non-equilibrium models was initially formulated in the 70s as the so-called Diffusion Layer Model (DLM) [29, 31]. This model is characteristic of two assumptions which indicate departure from phase boundary formulation: (1) the potential is governed by the local equilibrium at the solution–membrane interface, depicted by local concentrations of ions, and the Nernst and/or Nikolskii–Eisenman equations rewritten in local form, and (2) only the Fickian diffusion is considered, i.e., the only source of ion fluxes is the concentration gradient (migration is ignored). This is a rough approximation since ions are charged, and therefore they both create and interact with an electrical field.

The DLM model assumes pure diffusion inside both the diffusion layer and the membrane. The concentration change of the i th ion inside the j th layer is given by the continuity equation and Fick’s law:

$$\begin{cases} \frac{\partial c_i^j}{\partial t}(x, t) = -\frac{\partial J_i^j}{\partial x}(x, t) = -D_i^j \frac{\partial^2 c_i^j}{\partial x^2}(x, t) \\ x \in]\lambda_{j-1}, \lambda_j[\text{ for each phase } j = 1, \dots, n; \\ t \in [0, t_{\text{END}}] \end{cases} \quad (6)$$

The solution of the diffusion problem given by Eq. 6, along with suitable initial and boundary conditions, belongs to the canon of diffusion and materials engineering. An important advantage of the DLM was the introduction of time as a model parameter [49, 50]. The DLM allowed interpretation of the variability of selectivity coefficients over time, first for ISEs with solid-state membranes [51] and later with plastic membranes [52]. It is used to interpret potential transients with ion-sensitive electrodes [50] and, recently, biomimetic ion-sensitive conducting polymers [53, 54]. Interestingly, already in early formulations of the DLM, the effect of lowering the detection limit as well as the detection limit dictated by an interference was calculated to be exactly the same as very recently calculated by Bakker (namely $R_T/2$) [8].

Non-equilibrium response model

The non-equilibrium response, i.e., the propagation of ionic concentrations and electrical field in space and time in the

“solution | ion-exchanging membrane” system as well as the influence of membrane components’ concentrations, membrane permittivity, transport parameters (diffusion coefficients), ion-partition processes, and charge transfer rates may be accessed by applying Nernst–Planck (NP) and Poisson (P) coupled equations, where the NP equation describes the transport of ions due to diffusion and migration and the P equation governs the electrical interaction of the species. These two equations and the continuity equation form a system of partial, non-linear differential equations that is solved numerically using proper boundary conditions by a finite difference or finite element method. This approach yields what we call the Nernst–Planck–Poisson (NPP) model.

The application of the NPP model to membrane electrochemistry was first offered in a seminal paper [55]. An approach, based upon this idea and dedicated to the general description of ISE behavior, was later developed [56–60]. General NPP scheme used in above publications is presented in Scheme 1 [60].

The NPP model describes a system consisting of n layers (phases), within which the concentration changes of r components (ions or uncharged chemical species) and a change of the electrical field in space and time takes place. The influence of diffusion and migration is expressed by the NP equation for the flux of the i th component inside the j th layer:

$$J_i^j(x, t) = -D_i^j \frac{\partial c_i^j}{\partial x}(x, t) - \frac{F}{RT} D_i^j z_i (c_i^j E^j)(x, t) \quad (7)$$

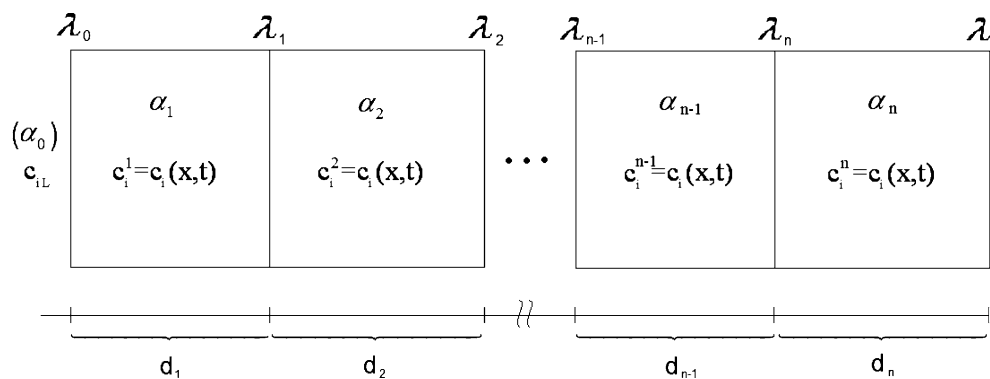
The continuity equation describes the change of the ion concentrations in time, and the Poisson equation describes the electrical changes caused by the interaction of the species. For convenience, the Poisson equation is replaced by the displacement current equation, as described earlier [57]. These equations form the following system of evolutionary non-linear partial differential equations (PDE) for r components in n phases:

$$\begin{cases} \frac{\partial c_i^j}{\partial t}(x, t) = -\frac{\partial J_i^j}{\partial x}(x, t) \text{ for } i = 1, \dots, r; \\ \frac{\partial E^j}{\partial t}(x, t) = \frac{1}{\varepsilon_j} I(t) - \frac{F}{\varepsilon_j} \sum_{i=1}^r z_i J_i^j(x, t); \\ x \in]\lambda_{j-1}, \lambda_j[\text{ for each phase } j = 1, \dots, n; \\ t \in [0, t_{\text{END}}] \end{cases} \quad (8)$$

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} :

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



Thus, the boundary conditions take a form similar to those described in [60]:

$$J_i^{\alpha_j}(\lambda_j, t) = J_i^{\alpha_{j+1}}(\lambda_j, t) = \overrightarrow{k_{i\lambda_j}} c_i^{\alpha_j}(\lambda_j, t) - \overleftarrow{k_{i\lambda_j}} c_i^{\alpha_{j+1}}(\lambda_j, t) \tag{9}$$

The ratio of the heterogenous constants relates explicitly to thermodynamic ion-partition coefficients and in consequence to the selectivity coefficients [57].

In simulations of the first point of a calibration curve, an arbitrary initial concentration profile (where the electroneutrality condition is fulfilled) is assumed. For the following calibration points, the initial concentration and the field profiles are based on the final values of the previous steps. This way of setting the initial values reflects the experimental procedure of ISE calibration, i.e., “the history of the ISE.”

There are several manifestations of the power of the NPP, which are in fact the answers to the above-listed inabilities of the phase boundary model.

The power of NPP

First of all, it is important to emphasize that the NPP facilitates calculating the potential change between the bulks of bathing solutions (representing the sample and internal contact solution) separated by the ion-exchanging membrane. In other words, it does not require an arbitral split of the membrane potential into the boundary and diffusion potentials, which is characteristic of electrochemical equilibrium models. In contrast to the phase boundary approach in the NPP, Nernstian equations are not starting points but limiting cases of the model. In other words, the NPP model and the phase boundary model are not equivalent. It is possible to reduce a more general model to a simpler one, but not to deduce a more complicated model from a simpler one.

To illustrate the power of the NPP, two very important advantages of the NPP are presented in Figs. 1 and 2.

One striking example is a space- and time-dependent concentration of anionic sites $R^-(x)$ confined to the membrane phase, as shown in Fig. 1. According to an idealized assumption of the phase boundary models, R^- is time- and space-independent, and its concentration is assumed to be constant in the membrane (R_T). The NPP shows a redistribution of R^- ion depending on the place in the membrane and time of equilibration, and other model parameters, with characteristically larger changes in the vicinity of the membrane surfaces. Similar non-linear redistributions were calculated for other ionic species [58]. Even more striking is a complementary simulation of the electric potential changes for the same system, as shown in Fig. 2. It discloses a contribution of the migrational effects to the potential of ion-selective membrane electrodes, which is ignored by the phase boundary interpretations even for transmembrane fluxes of ions with different charge/mobilities in plastic membranes. Interestingly, very close to the present NPP model was an early intuition of Morf, who said 30 years ago: “liquid (resp. plastic) membranes (...) in contrast to solid-state membranes (...) when equilibrated with electrolyte solutions, are subject to salt

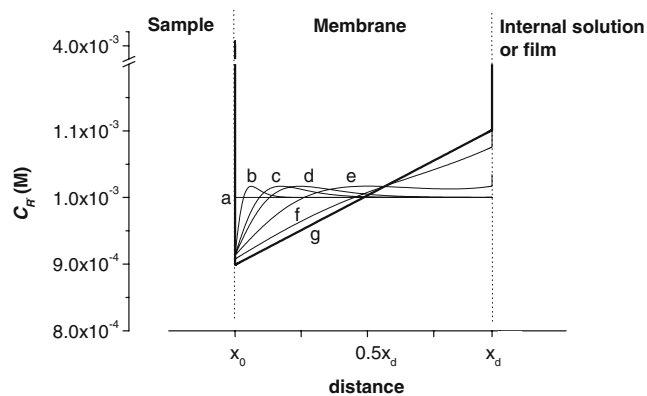


Fig. 1 Time-dependent concentration profiles for site R^- modeled by the NPP [57]. ($c_i = 10^{-4}$, $c_j = 10^{-3}$, $\frac{D_i}{D_j} = 0.5$, $K_{ij} = 0.1$ and $\overline{R}_{TOTAL} = 10^{-3}$). Curves a–g show profiles after: a $4 \cdot 10^{-4}$, b 1.64, c 13.1, d 26.2, e 104.8, f 420, and g 13 440 s (steady state)

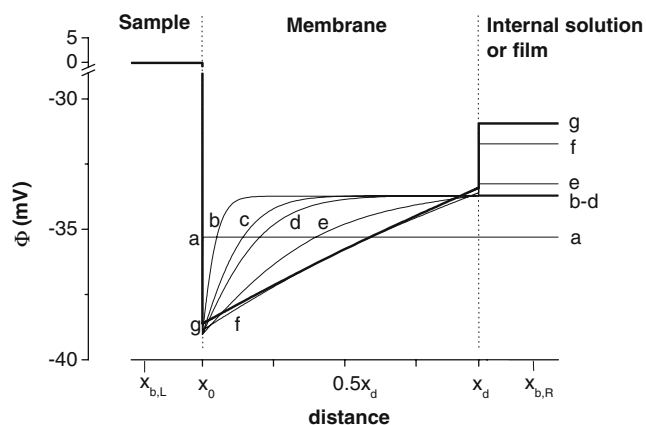


Fig. 2 Time-dependent and distance-dependent potential profiles, calculated as $\phi(x, t) = \int E(x, t) dx$ using the NPP equations system. Total membrane potential is: $E_M(x, t) = \int_{x_{b,L}}^{x_{b,R}} E(x, t) dx$, where $x_{b,L}$ and $x_{b,R}$ are the points in the bulk of bathing sample solution (on the left side of the membrane, L) and internal solution/film (on the right side of the membrane, R); x_0 and x_d denotes the left and right membrane–solution interface. Curves a–g show profiles after: **a** $4 \cdot 10^{-4}$, **b** 1.64, **c** 13.1, **d** 26.2, **e** 104.8, **f** 420, and **g** 13,440 s (steady state) [57, 70]

extraction and ion-exchange reactions at the surfaces. This leads to inhomogeneities in the interior of the membrane which normally give rise to a diffusion potential” [1].

The theoretical power of the NPP is transparently shown in Table 1 where, in accordance with the strategy of this paper, the NPP is compared with the equilibrium model, this time on the assumption level.

Non-equilibrium modeling—practical applications and new frontiers

As a logical consequence of the NPP, its power in helping to resolve the challenges related to application of the ISEs can be shown as well.

Table 1 Comparison of the assumptions of the NPP and phase boundary models

Phase boundary model	NPP model
Diffusion and migration ignored	Diffusion and migration allowed
Electroneutrality assumed	Electroneutrality not assumed
Potential calculated from the phase boundary equation	Potential calculated from electrical field profile
Ions of the same charge	Ions of any charge
Site distribution constant	Site distribution depends on electrical field distribution
Fluxes are not defined, assumed to be infinitely high	Fluxes in all layers are co-dependent (concentration-potential feedback)
Equal diffusion coefficients in the membrane	Any diffusion coefficients in the membrane

Let us start with time-dependent selectivity. The NPP provided important evidence that the validity of a so-called unbiased selectivity method is restricted by measurement time and can be unproductive when too long a measurement time is used [57, 58, 60]. Additionally, for a short measurement time, the NPP confirmed characteristic non-discrimination in sensitivity, manifested with convergence of the selectivity coefficient $K^{\text{pot}} \rightarrow 1$ for short readout times, the result known from the DLM model. This means additional support for the effect of *kinetic ion discrimination (apparent selectivity)* [61] which is of great analytical advantage if an ISE is applied in the presence of strongly interfering ions. This effect is already used in high-throughput clinical analyzers to minimize interferences on chloride ISE (e.g., by salicylates, bromides, or iodides) [62]. It is deliberately applied for measurement of strongly interfering heparin ions with chloride ISE because the chloride electrode does not discriminate between the main and interfering ion [63]. It is, as well, a base of the main code for the first ever automatic method of measurement of ionized magnesium in human blood [64–66].

Very recently, by using the NPP for plastic membranes, we showed that the detection limit could also be dependent on time [59]. The value of the NPP in this case is not only in the direct prediction of the response patterns, but in the possibility of inverse simulation (*inverse problem*). In the inverse problem, the NPP, as a closed and mathematically rigorous model in contrast to arbitral and open conventional models, can answer analytical demand given by a *target function*, e.g., request for optimal conditions in which the effect of the lowering of the detection limit would possibly

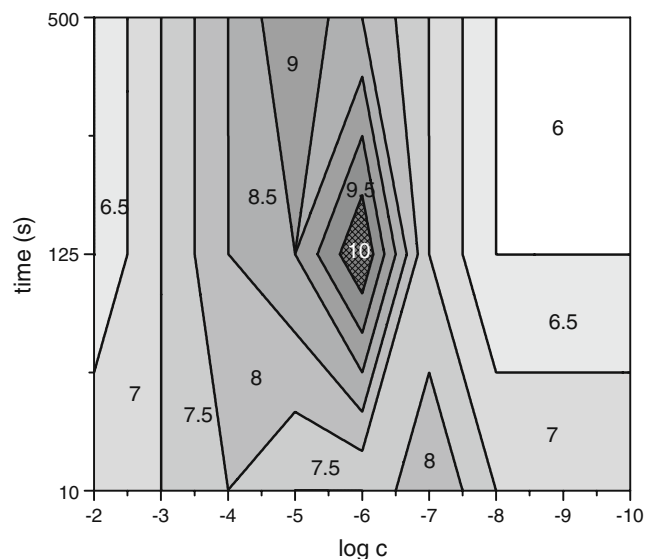


Fig. 3 Dependence of the detection limit on the inner filling solution concentration and the measurement time. The darker the shade of gray, the lower the detection limit (represented also by the numbers on the plot) [59]

be most stable. In this case, inverse numerical simulation of the NPP facilitates finding optimal values for the measurement time and internal solution concentration. The graph of this simulation is shown in Fig. 3. The same strategy was very recently used to validate different models in potentiometry. For the first time, quantitative response maps were presented to compare the NPP with simpler models used for the same conditions [60].

The NPP was also successfully applied for predicting electrochemical impedance spectra (EIS), which means omitting equivalent electrical circuits and binding the EIS spectra directly to the physicochemical properties of the membrane [67].

Because both ISE potentiometric and EIS responses can be interpreted by the NPP, we concluded that the NPP is a platform (*umbrella*) which allows finding *interdependence* between the EIS and potentiometric characteristics. Such possibility opens an avenue to self-diagnostics of the potentiometric ion sensors and automatic decision permitting their potentiometric application based on the EIS characteristics [68, 69].

Conclusions

The NPP model is more rigorous, complete, and more general than previous models. The NPP directly facilitates predicting the potentiometric responses over space and time, propagation of selectivity, and detection limit over time or solving inverse problems with a requested target function. The target can be a potentiometric response curve or electrochemical impedance spectra or their interdependence.

In particular, the NPP is an appropriate platform for dealing with the theory of ion-selective membrane electrodes for analytical applications, in particular when the advantages of time-dependent selectivity and/or detection limit are to be exploited or the disadvantages of poor response diagnosed and avoided.

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