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NUMERICAL SIMULATIONS OF DIFFUSION-MIGRATION PROCESSES IN THIN LAYERS

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Abstract - From the laboratory practice point of view one of the most important parameter strongly influencing the effectiveness of experiments is the dynamic of ion-selective electrode response and reaction time on main ion concentration changes in analysed solution. In this work a comparison between two analytical solutions, namely Lindner et al. and Morf et al. models, which are based on assumption of the existence of diffusion layer in analyte and numerical solution of Nernst-Planck-Poisson (NPP) system of equations for simple systems are presented. Obtained results show good agreement in potential-time response as well as in value of membrane potential in steady state for different scenarios of ionic species concentration changes. In contrast to analytical solutions, NPP model offers a description of diffusion and migration processes occurring in membrane layer as well as charge transfer kinetics at phase boundaries.

Résumé – Simulation numérique des processus de diffusion-migration dans des films minces. Du point des mesures expérimentales un des paramètres les plus importants d'une électrode sélective est la vitesse de sa réponse aux changements de concentration de l'ion cible en solution. Dans la présente étude nous avons comparé deux solutions analytiques, notamment celles de Lindner et Morf basées sur l'hypothèse de l'existence d'une couche de diffusion, avec la solution numérique du système d'équations de Nernst-Planck-Poisson (NPP). Ils montrent un bon accord dans les courbes temps-potentiel et dans les valeurs du potentiel de la membrane pour différents cas de changement de concentration des espèces ioniques. Contrairement aux solutions analytiques, le modèle NPP permet une description des processus de diffusion et de migration dans la membrane sélective ainsi que la prise en compte de la cinétique de transfert de charge aux interfaces.

1. INTRODUCTION

The formation of electric field across the layers such as passive films on metals or ion-selective membranes depends not only on thermodynamic properties of the layers but is also strongly influenced by kinetic parameters which affect the dynamic characteristic of the system and its response time. The factors as stirring rate, speed of flowing media and the direction of concentration change [1] have also strong impact on the precision of measurements in e.g. continuous monitoring systems [2].

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Several models describing the time evolution of membrane potential have been developed – most of which describe systems in which rapid change of concentration of main ion in sample solution occurs. In approaches introduced by Rechnitz and Hameka [3] as well as by Johansson and Norberg [4], the interface between the membrane and the solution is considered as an energetic barrier across which ions are transported, and additional layer possessing properties of capacitor is distinguished in the membrane phase. These fluxes depend on the concentration of ionic species and electric potential on both sides of barrier as well as on the nonelectric energy required to cross the barrier. At equilibrium, fluxes directed from and into the membrane are equal. When concentration in sample solution changes swiftly the fluxes and membrane potential also change in time until a new equilibrium is reached.

More recent models for time evolution of membrane potential (e.g. [5-7]) are based on the existence of a stagnant layer (Nernst layer [8]) between the bulk of the solution and the surface of solid phase. The species diffusing through the stagnant layer are assumed to be electroneutral. Hence, the diffusion is driven only by the concentration gradient between the bulk of the sample solution and the point in the vicinity of electrode surface (linear concentration profile within the stagnant layer are thus assumed) what, in turn, allows the form of Fick's first law to be employed and an exponential concentration (activity)-time relation to be derived. In each time step a membrane potential is calculated with the use of Nernst equation and the value of diffusing specie concentration (activity). In case of model developed by Lindner et al. [5-7] this relation is given by Equation (1).

$$\varphi(t)=\varphi_0+\Delta\varphi+\frac{RT}{z_iF}\ln\left(a_{iL}^{0}+\left(a_{iL}^{t_0}-a_{iL}^{0}\right)\left(1-\exp\left(\frac{-t}{\tau}\right)\right)\right);\quad \tau=\frac{4\delta^2}{\pi^2D_{i,aq}} \tag{1}$$

where: $\varphi(t)$, φ_0 and $\Delta\varphi$ denote the membrane potential, the standard potential of membrane cell assembly and liquid junction potential, respectively. Quantities a_{iL}^{0} and $a_{iL}^{t_0}$ are initial and final concentrations of diffusing specie carrying a charge z_i, respectively, $D_{i,aq}$ its diffusion coefficient, δ is a stagnant layer thickness. R, T and F have their usual meaning. τ is a time constant.

It is worth to mention that in the treatments in question, diffusion in the electrode phase is regarded as not to be rate-determining process and, hence, is omitted. It is also assumed that the diffusion through the stagnant layer does not change its potential, therefore does not contribute to overall membrane potential and the resulting potential evolution is purely due to concentration change in stagnant layer.

When diffusion processes within the membrane phase play an important role in signal formation and sample solution contains main and interfering ions, the potential evolution becomes dependent not only on the diffusion coefficients of species in the stagnant layer D_{aq} but also on the diffusion coefficients in the membrane phase D_{mem} as well as on selectivity coefficient of the electrode K_{ij} [1,2], Equation (2). This expression was derived by Morf et. al. [1,2] for neutral carrier membrane electrodes such as potassium selective valinomycin based PVC membrane.

$$\begin{gathered}\varphi(t)=\varphi(0)+\frac{RT}{z_iF}\log\left(A-(A-1)\exp\left(-\frac{t}{\tau'}\right)-\frac{B}{\sqrt{t/\tau}}\right)\\ A=\frac{a_i+K_{ij}a_j}{a_i(0)+K_{ij}a_j(0)};\quad B=\frac{1-K_{ij}}{a_i(0)+K_{ij}a_j(0)}\left(\frac{a_i}{a_i+K_{ij}a_j}-\frac{a_i(0)}{a_i(0)+K_{ij}a_j(0)}\right)\end{gathered} \tag{2}$$

where: $\tau=\dfrac{D_{mem}c_{R^-}{}^2\delta^2}{\pi z_{R^-}{}^2D_{aq}{}^2}$, $D_{mem}=D_{i,mem}=D_{j,mem}$; $\tau'=\dfrac{4\delta^2}{\pi^2D_{aq}}$, $D_{aq}=D_{i,aq}=D_{j,aq}$.

Presented paper is devoted to comparison between analytical models introduced by Lindner et al. [1,5-7] and Morf et al. [1,7,9], and the model based on Nernst-Planck-Poisson (NPP) system of equations given by Brumleve and Buck [10].

2. THE NERNST-PLANCK-POISSON MODEL

Since the work of Brumleve and Buck [10] several modifications have been introduced to NPP model such as method of lines (MOL), new integration scheme, namely Rosenbrock [11-14] or RADAU IIA [15] methods, extension to systems with arbitrary number of layers [15,16] and inverse method in simulations of impedance spectra for ion-selective electrodes [14,16].

The Nernst-Planck-Poisson problem (NPP) is known as the initial-boundary value problem that for one dimension is given by the set of equations briefly described below.

The ionic fluxes J_i in all phases are expressed by the Nernst-Planck equation:

$$J_i(t,x) = -D_i\left[\frac{\partial c_i(t,x)}{\partial x} - z_i c_i(t,x)\frac{F}{RT}E(t,x)\right] \tag{3}$$

where: D_i is constant diffusion coefficient of i-th specie, c_i and z_i denote their concentrations and charge numbers, F, R, T are Faraday constant, gas constant and temperature, respectively. E denotes electric field strength.

The evolution of electric field is represented by the Poisson equation, which for constant dielectric permittivity ε reads:

$$\frac{\partial E(t,x)}{\partial x} = \frac{\rho(t,x)}{\varepsilon}; \quad \rho(t,x) = F\sum_i z_i c_i(t,x) \tag{4}$$

where: ρ is charge density.

The mass conservation law in general form describes the evolution of concentration due to the presence of fluxes as well as bulk and/or interfacial reactions [16]:

$$\frac{\partial c_i(t,x)}{\partial t} = -\frac{\partial J_i(t,x)}{\partial x} + \Psi \tag{5}$$

where: Ψ denotes reaction term.

In order to solve the system of equations with the use of method of lines and employ integration schemes for ordinary differential equations (e.g. Rosenbrock scheme), the Poisson equation is replaced by its equivalent form, the total current equation [10,17], which introduces a time derivative of electric field strength ($\partial E(t,x)/\partial t$) – the displacement current:

$$I(t) = F\sum_i z_i J_i(t,x) + \varepsilon\frac{\partial E(t,x)}{\partial t} \tag{6}$$

The system of equations must be completed by a set of boundary and initial conditions. Chang-Jaffe [18] boundary conditions were employed in this work, which define fluxes at boundaries of all layers in the system. In case of ion-selective membrane they read:

$$\begin{aligned} J_i(t,0) &= \vec{k}_i^L c_{i,L} - \overleftarrow{k}_i^L c_i(t,0) \\ J_i(t,d) &= \vec{k}_i^R c_i(t,d) - \overleftarrow{k}_i^R c_{i,R} \end{aligned} \tag{7}$$

where: $\vec{k}_i^L, \overleftarrow{k}_i^L, \vec{k}_i^R, \overleftarrow{k}_i^R$ are rate constants for transport of species across the interface, superscripts R and L indicate the side of the membrane, arrows – directions of i-th specie permeation.

Initial conditions define concentration and electric field strength profiles for $t=0$ in all considered layers. Following Macdonald [19,20], flat band initial conditions were used and initial values of concentrations chosen to satisfy electroneutrality condition $\sum_i z_i c_i(0,x)=0$ what eliminates the presence of space charge at this time point. Consequently, the electric field strength in all layers is zero: $c_i(0,x)=c_i^0, E(0,x)=0$ for $x\in[0,d]$.

The membrane potential V is calculated for the entire system and is not divided arbitrarily into boundary and diffusion parts [10]:

$$V(t) = -\int_0^d E(t,x)\,dx \tag{8}$$

3. SIMULATION RESULTS

Let us consider the system of flat and homogeneous ion-selective membrane of thickness d separating two aqueous solutions – internal reference solution on the right hand side of the membrane and the sample solution on the opposite side of the membrane. An additional layer of constant thickness δ, the stagnant layer (Nernst layer [14]), is distinguished in the left bathing solution, *figure 1*.

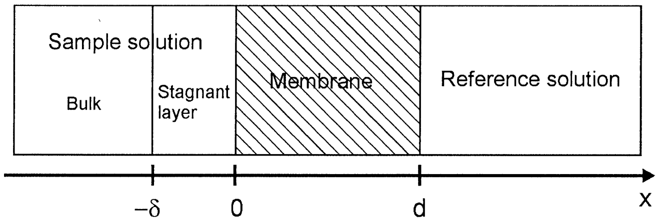

Figure 1. The system considered in model by Lindner et al. is restricted to only bulk and stagnant layers while in NPP model all layers are taken into account.

It is assumed that for time $t=0$ concentrations of ions in the sample solution and stagnant layer are constant $c_{iL}(0,x)=c_{iL}^0$. For times $0\le t<t_0$ a virtual potentiometric experiment is conducted which results in new concentration profiles in the stagnant layer. At $t=t_0$ a rapid change of concentrations of both ionic species in the bulk of sample solution occurs. For the range $t_0<t\le t_{end}$ the concentration profiles of ionic species in the stagnant layer change and the membrane potential is registered as a function of time. In contrast to the NPP model in the case of Lindner model, concentration profiles are assumed to be linear within the stagnant layer.

Table I. Initial conditions for simulations. Heterogeneous rate constants for all ions and both directions are equal $\vec{k}_i^L = \overleftarrow{k}_i^L = \vec{k}_i^R = \overleftarrow{k}_i^R = k_i$. Dielectric constants for stagnant layer and membrane are 79 and 4, respectively.

	$c^0_{i,L}$ $[M]$	$c^{t_0}_{i,L}$ $[M]$	$c_{i,mem}$ $[M]$	$c_{i,R}$ $[M]$	$D_{i,aq}$ $[m^2s^{-1}]$	$D_{i,mem}$ $[m^2s^{-1}]$	$k_{i,aq/M1}$ $[ms^{-1}]$	k_i $[ms^{-1}]$
Lindner model								
M^+	$10^{-6} \div 1$	$b \times c^0_{i,L}$	-	-	10^{-9}	-	-	-
NPP model								
M^+	$10^{-6} \div 1$	$b \times c^0_{i,L}$	10^{-3}	1	10^{-9}	10^{-11}	100	100
X^-	$10^{-6} \div 1$	$b \times c^0_{i,L}$	0	1	10^{-9}	0	100	0
R^-	0	0	10^{-3}	0	0	10^{-11}	0	0

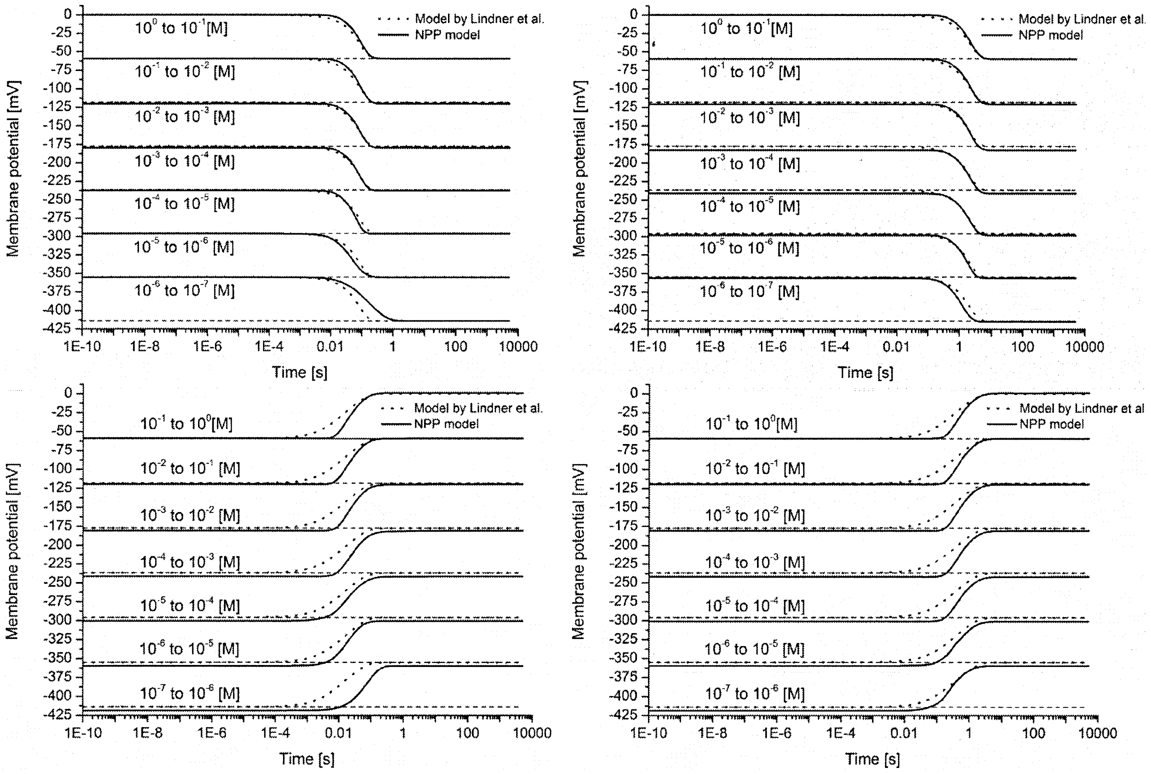

Figure 2. Simulation results for two values of the stagnant layer thickness: δ=10μm (left) and δ=50μm (right). Numbers below each curve indicate the direction of concentration change. Horizontal dashed lines indicate potential values calculated with the use of Nernst equation.

Experimental observations suggest, that the time necessary for the system to reach the steady state depends strongly on the direction of concentration change [1,5-9,21]. This effect is observed also on potential-time curves calculated with the use of relation (1) and NPP model on the basis of data presented in *Table I* for decrease ($b = 0.1$) as well as for increase ($b = 10$) of the concentration of fully dissociated salt MX, *Figure 2.* A good agreement is observed in terms of steady state potential values as well in time after which system reaches steady state and this time increases with stagnant layer thickness. However, a slight delay on potential signals calculated with the use of NPP system of equations is observed in case of gradually increasing concentration for both values of stagnant layer thickness, which is caused presumably by diffusion-migration processes occurring in the membrane phase as well as in the stagnant layer or by ion transport across the solution-membrane boundary since all stipulated processes are omitted in analytical model.

The influence of the direction of concentration change on the shape of potential-time curves is even more pronounced for changing values of coefficient b, lower row of *Figure 3.*

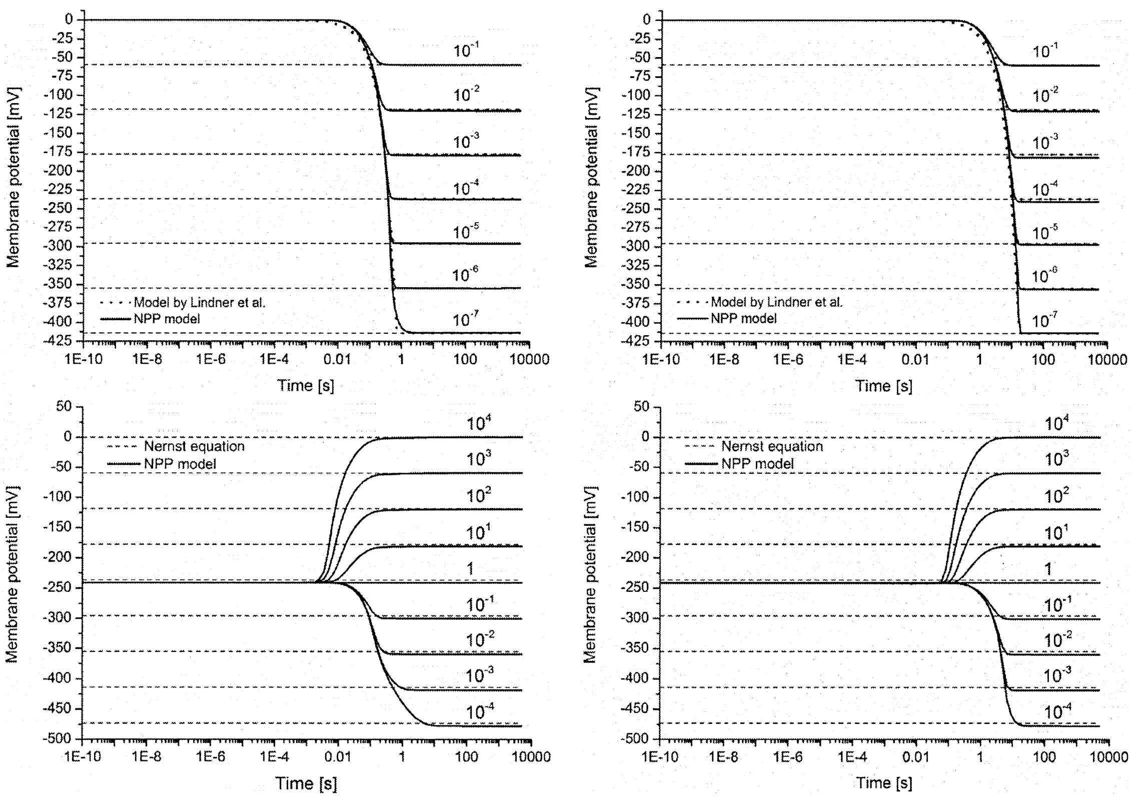

Figure 3. Simulation results for changing value of coefficient b and for two values of the stagnant layer thickness: $\delta=10\mu m$ (left) and $\delta=50\mu m$ (right). Numbers above each curve indicate the values of coefficient b. Horizontal dashed lines indicate membrane potential values calculated with the use of Nernst equation.

The more challenging test for NPP model is the system defined by the set of initial conditions and parameters presented in *Table II*, which represents an ion-selective electrode immersed in the solution containing both main ion J^{2+} and interfering ion I^{+}. The latter is partially blocked at the interfaces of the membrane since the selectivity in NPP model is represented by heterogeneous rate constants. R^{-} are mobile ionic sites restricted only to the membrane phase (e.g. anions of dissociated hydrophobic salt potassium tetrakis(4-chlorophenyl) borate), X^{-} represents a counterion blocked at both solution-membrane interfaces.

Table II. Initial conditions for polymeric ion-selective membrane – "bi-ionic case". Thickness of polymeric membrane d=200μm and δ=10μm for stagnant layer. Dielectric constants for stagnant layer and membrane are 79 and 4, respectively.

	$c_{i,L}$ $[M]$	$c_{i,M1}$ $[M]$	$c_{i,M2}$ $[M]$	$c_{i,R}$ $[M]$	$D_{i,M1}$ $\left[m^2s^{-1}\right]$	$D_{i,M2}$ $\left[m^2s^{-1}\right]$
J^{2+}	$10^{-13}\div 1$	b)	5×10^{-4} or b)	1	10^{-9}	10^{-11}
I^+	0.15	0.15 or b)	0 or b)	0	10^{-9}	10^{-11}
R^-	0	0	10^{-3} or b)	0	10^{-9}	10^{-11}
X^-	a)	a) or b)	0	1	10^{-9}	10^{-11}
	$\vec{k}_{i,aq/M1}$ $\left[ms^{-1}\right]$	$\overleftarrow{k}_{i,aq/M1}$ $\left[ms^{-1}\right]$	$\vec{k}_{i,M1/M2}$ $\left[ms^{-1}\right]$	$\overleftarrow{k}_{i,M1/M2}$ $\left[ms^{-1}\right]$	$\vec{k}_{i,M2/aq}$ $\left[ms^{-1}\right]$	$\overleftarrow{k}_{i,M2/aq}$ $\left[ms^{-1}\right]$
J^{2+}	100	100	10^{-3}	10^{-3}	10^{-3}	10^{-3}
I^+	100	100	4.472×10^{-7}	10^{-3}	10^{-3}	4.472×10^{-7}
R^-	0	0	0	0	0	0
X^-	100	100	0	0	0	0

a) $2c_{J^{2+},L}+c_{I^+,L}$ b) Input concentration profiles from previous simulation step.

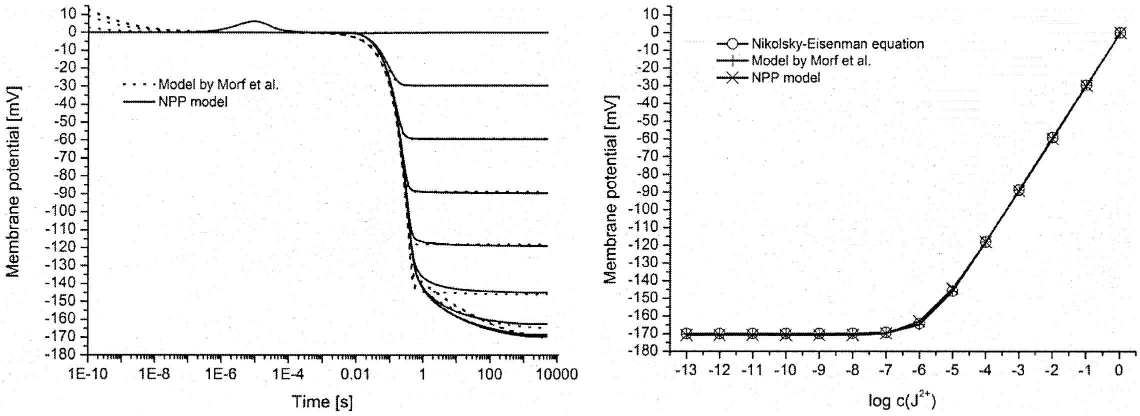

Figure 4. A comparison between model by Morf et al. and NPP model (left image) and the resulting calibration curve (right image). The value of selectivity coefficient $K_{ij}=10^{-5}$.

A comparison between the approach by Morf et al. and NPP model shows good agreement in values of steady state membrane potentials as well as in shapes of potential-time curves, *Figure 4*. However, a large "bump" is observed on the curve for 1[M] solution of MX salt. The explanation of this behaviour can be found elsewhere [16]. Simulated steady state potential values allow to construct a calibration curve for such a virtual ion sensor, which reveals the existence of detection limit due to the presence of interfering ion I^+ in the sample solution.

4. CONCLUSION

It is shown that the NPP model can be useful tool in prediction of response time of ion sensors. Potential-time curves were simulated, they show good agreement with analytical models.

Steady state membrane potential values match those calculated with the use of Nernst or Nikolsky-Eisenman equations. The NPP model offers much more advanced description of diffusion-migration processes than analytical models and is free from restrictions such as linear concentration profiles in stagnant layer, limited number of layers or species. It also allows interfacial or bulk reactions to be considered [16]. Thanks to direct link between observed response of the system and its physical parameters, an analysis of impedance spectra is possible [14].

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5. REFERENCES

[1] W.E. Morf, E. Lindner, W. Simon, Anal. Chem., 47 (9) (1975) 1596-1601.
[2] W.E. Morf, The Principles of Ion-Selective Electrodes and of Membrane Transport, Akademiai Kiado, Budapest 1981.
[3] G.A. Rechnitz, H.F. Hameka, Z. Anal. Chem., 214 (1965) 252-257.
[4] G. Johansson, K. Norberg, J. Electroanal. Chem., 18 (1968) 239-252.
[5] E. Lindner, K. Toth, E. Pungor, Anal. Chem., 48 (7) (1976) 1071-1078.
[6] E. Lindner, K. Toth, E. Pungor, W.E. Morf, W. Simon, Anal. Chem., 50 (12) (1978) 1627-1631.
[7] E. Lindner, K. Toth, E. Pungor, Anal. Chem., 54 (1) (1982) 72-76.
[8] W. Nernst, Z. Phys. Chem., 47 (1904) 52-55.
[9] W.E. Morf, Anal. Chem., 55 (7) (1983) 1165-1168.
[10] T.R. Brumleve, R.P. Buck, J. Electroanal. Chem., 90 (1978) 1-31.
[11] T. Sokalski, P. Lingenfelter, A. Lewenstam, J. Phys. Chem. B, 107 (2003) 2443-2452.
[12] W. Kucza, M. Danielewski, A. Lewenstam, Electrochem. Comm., 8 (3) (2006) 416-420.
[13] B. Grysakowski, A. Lewenstam, M. Danielewski, Diffusion Fundamentals, 8 (2008) 4.1-4.7.
[14] B. Grysakowski, J.J. Jasielec, B. Wierzba, T. Sokalski, A. Lewenstam, M. Danielewski, J. Electroanal. Chem., 662 (2011) 143-149.
[15] J.J. Jasielec, T. Sokalski, R. Filipek, A. Lewenstam, Electrochim. Acta, 55 (2010), 6836-6848.
[16] B. Grysakowski, Zagadnienie odwrotne w symulacjach widm impedancyjnych elektrod jonoselektywnych, PhD Thesis (in Polish), AGH-UST, Krakow 2011.
(http://www.chemia.odlew.agh.edu.pl/o_katedrze/B.Grysakowski_PhD_Thesis.pdf)
[17] H. Cohen, W. Cooley, Biophys. J., 5 (1965) 145-162.
[18] H. Chang, G. Jaffe, J. Chem. Phys., 20 (1952) 1071-1077.
[19] J.R. Macdonald, J. Chem. Phys., 61 (1976) 1117-1123.
[20] J.R. Macdonald, J. Electroanal. Chem., 70 (1974) 1.
[21] A. Shatkay, Anal. Chem., 48 (7) (1976) 1039-1050.

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