Published in final edited form as:

J Electroanal Chem (Lausanne Switz). 2010 March 15; 642(1-2): 45–56. doi:10.1016/j.jelechem.2010.01.001.

Theoretical Treatment and Numerical Simulation of Potential and Concentration Profiles in Extremely Thin Non-Electroneutral Membranes Used for Ion-Selective Electrodes

W. E. Morf^a, E. Pretsch^b, and N. F. De Rooij^a

^aInstitute of Microengineering (IMT), SAMLAB, Federal Institute of Technology (EPFL STI), CH-2000 Neuchâtel, Switzerland ^bInstitute of Biogeochemistry and Pollutant Dynamics, ETH Zürich, CH-8092 Zürich, Switzerland

Abstract

The applicability of extremely thin non-electroneutral membranes for ion-selective electrodes (ISEs) is investigated. A theoretical treatment of potential and concentration profiles in space-charge membranes of $\ll 1 \mu\text{m}$ thickness is presented. The theory is based on the Nernst-Planck equation for ion fluxes, which reduces to Boltzmann's formula at equilibrium, and on the Poisson relationship between space-charge density and electric field gradient. A general solution in integral form is obtained for the potential function and the corresponding ion profiles at equilibrium. A series of explicit sub-solutions is derived for particular cases. Membrane systems with up to three different ion species are discussed, including trapped ionic sites and co-extracted ions. Solid-contacted thin membranes (without formation of aqueous films at the inner interface) are shown to exhibit a sub-Nernstian response. The theoretical results are confirmed by numerical simulations using a simplified finite-difference procedure based on the Nernst-Planck-Poisson model, which are shown to be in excellent agreement.

Keywords

Ion-selective electrodes; Thin membranes; Space charge; Potential; Concentration profiles; Theory; Numerical simulation; Nernst-Planck-Poisson model

1. Introduction

The past decades have seen a continuous progress and a still growing interest in the field of ion-selective electrodes (ISEs). For example, various novel types, further improvements, and new applications of ISEs have been reported (for recent reviews, see [1, 2]). Considerable efforts have also been centered on the development of miniaturized sensors. Since their first appearance around 1970 [3, 4], microelectrodes based on glass-capillary-supported liquid membranes have been introduced for a wide range of useful applications in electrophysiology and biology [5-7]. Devices with inner tip diameters of down to about 50 nm were described [8, 9], and extremely fast responses within only a few milliseconds were

© 2009 Elsevier B.V. All rights reserved.

Publisher's Disclaimer: This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final citable form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

realized [10, 11]. More recently, solid-contact microelectrodes have also been described by several groups [12-15]. Solid-contact electrodes without redox reaction on the inner membrane side are conceivable with membranes having a capacitive inner contact [16-18].

Another way towards a miniaturization of ISEs is to reduce the thickness of the ion-sensing membrane, which is usually 100 to 200 μm for conventional devices. Lipid bilayers with dissolved ionophores have early been investigated as model systems for carrier-mediated ion transports [19-25]. The observed selectivity behavior was comparable to that of the respective macroelectrodes as long as no kinetic limitations come into play [25-27]. However, such lipid membranes with a thickness of only around 10 nm can obviously not be utilized as mechanically stable sensors. In contrast, solvent polymeric membranes of $< 1 \mu\text{m}$ thickness coated on suitable supports have been used as voltammetric ion sensors [28]. Further reductions in the membrane dimensions seem to be feasible, but the exact influence of such miniaturization steps on the sensor characteristics has not been studied so far.

The essential difference between the bulk membranes of conventional ISEs and extremely thin membranes is that the former behave as electroneutral phases (except for the boundary regions) whereas the latter are considered as distinct space-charge systems. Correspondingly, significant deviations should be found between the two cases when the ion distributions and the electric potential profiles within the membrane are compared. Another difference may arise from the fact that ion-selective bulk membranes are usually interposed between two aqueous phases, whereas very thin membranes have to be applied in an asymmetric arrangement with a solid contact on one side. Hence conventional ISEs exhibit a response that clearly depends on the trans-membrane potential difference [26, 27, 29]. In contrast, the response of devices with supported thin layers may be more influenced by the membrane-internal potential, which may result in new characteristics. It would therefore be an important task to thoroughly investigate the electrochemical properties of very thin ISE membranes.

In the past years, the potential response and the ion-transport behavior of ISE membranes were extensively studied by numerical simulation procedures introduced by Sandifer and Buck [30]. A series of such finite-difference procedures were based on a Nernst-Planck description of ion fluxes, assuming electroneutrality for membrane and aqueous phases [31-33]. These virtual ISE experiments are capable of modelling most of the observed phenomena including the effect of external current [34]. More universal approaches used a combined Nernst-Planck-Poisson formalism that also includes space-charge effects [1, 35-39]. Such extended treatments are especially suited for simulations of rapid or transient responses. Unfortunately, these investigations have so far been centered on bulk membrane systems. On the other hand, rigorous theoretical descriptions of lipid-bilayer membranes have been reported, but these are still restricted to symmetric systems with identical aqueous phases [20, 40, 41].

Here, we present a detailed analysis of potential and concentration profiles in ISE systems with extremely thin membranes. A theoretical treatment of the respective membrane characteristics at equilibrium is offered. The theory makes use of the Nernst-Planck equation for the ion fluxes, which leads to Boltzmann-type concentration distributions at zero fluxes, and of the Poisson relationship between space-charge density and electric field gradient. A general solution in integral form is presented for the potential function and the corresponding ion profiles, and a series of explicit sub-solutions is derived for particular cases with up to three different ionic species. Numerical simulations are performed in order to verify the theoretical results.

2. Theory

2.1. General derivation

The aim of this investigation is to demonstrate in detail the effect of space-charge regions in systems with ion-permeable membranes such as ISE membranes. To this end, a comprehensive theoretical treatment based on the Poisson-Boltzmann model is presented that permits the analysis of the concentration distribution of ions and the resulting potential profile. The approach is restricted to equilibrium conditions, but it can be applied for any type of membrane, that is for bulk and bilayer membranes with or without permanent ionic components (trapped ionic sites). Moreover, in contrast to earlier studies [20, 40, 41], the present theory is not restricted to symmetrical electrochemical cells where the membrane is interposed between two identical solutions.

The general system considered here is given by a membrane of thickness d ($0 \leq x \leq d$) that is in contact with two aqueous phases, namely a solution (') on the left side ($x = 0$), and a solution (") on the right side ($x = d$). All these subsystems are considered as phases that have uniform physical and chemical properties, except for concentration and potential profiles. The membrane is assumed to be free of chemically fixed charges or oriented dipolar structures at the surfaces. On the other hand, it may contain mobile lipophilic ions as well as selective ionophores to facilitate the extraction of specific ions from the external solutions. The aqueous phases may also contain background electrolytes that are insoluble in the membrane. For simplicity of the treatment, it is assumed that all cations and anions in the system are singly charged.

According to the Poisson equation, Eq. (1), the electric potential ϕ is related to the space-charge density ρ at distance x , and hence to the local concentrations c_i of all ions i (assumed to have charge numbers $z_i = +1$ or -1):

$$\frac{d^2\phi}{dx^2} = -\frac{1}{\epsilon\epsilon_o}\rho(x) = -\frac{F}{\epsilon\epsilon_o}\sum_i z_i c_i(x) \quad (1)$$

where ϵ is the dielectric constant of the studied phase, ϵ_o is the permittivity of free space, and F is the Faraday constant. A second relationship between potential and ion concentrations is given by the Boltzmann equation, Eq. (2a,b), which describes the equilibrium distribution of cations (subscript m) and anions (subscript x), respectively:

$$c_m(x) = c_m(x_o) e^{-(\Psi(x) - \Psi(x_o))}; \quad c_x(x) = c_x(x_o) e^{+(\Psi(x) - \Psi(x_o))} \quad (2a,b)$$

$$\Psi(x) = \frac{F}{RT}\phi(x) \quad (3)$$

where Ψ is a dimensionless potential function, x_o is a reference position that may be chosen arbitrarily, R is the gas constant, and T is the absolute temperature. Eqs. (1)-(3) are combined into Eq. (4):

$$\frac{d^2\Psi}{dx^2} = -\frac{\kappa_m^2}{2}e^{-(\Psi(x) - \Psi(x_o))} + \frac{\kappa_x^2}{2}e^{+(\Psi(x) - \Psi(x_o))} \quad (4)$$

$$\kappa_m^2 = \frac{2F^2}{RT\epsilon\epsilon_o} \sum_m c_m(x_o) \quad ; \quad \kappa_x^2 = \frac{2F^2}{RT\epsilon\epsilon_o} \sum_x c_x(x_o) \quad (5a,b)$$

where κ_m and κ_x is the reciprocal Debye length defined for cations and anions, respectively. Eq. (4) can be integrated to yield the expression:

$$\left(\frac{d\Psi}{dx}\right)_x^2 = \left(\frac{d\Psi}{dx}\right)_{x_0}^2 + \kappa_m^2 \left\{ e^{-(\Psi(x) - \Psi(x_0))} - 1 \right\} + \kappa_x^2 \left\{ e^{+(\Psi(x) - \Psi(x_0))} - 1 \right\} \quad (6)$$

which may be rewritten in a simplified form:

$$\frac{dy}{dx} = \pm \frac{\kappa_m}{2} \sqrt{\delta\Psi^2 y^2 + (1 - y^2)(1 - k^2 y^2)} \quad (7)$$

where the following definitions are used:

$$y(x) = e^{\frac{1}{2}(\Psi(x) - \Psi(x_0))} \quad ; \quad y(x_0) = 1 \quad (8)$$

$$k^2 = \frac{\kappa_x^2}{\kappa_m^2} = \frac{\sum_x c_x(x_0)}{\sum_m c_m(x_0)} \quad (9)$$

$$\delta\Psi = \frac{1}{\kappa_m} \left(\frac{d\Psi}{dx} \right)_{x_0} \quad (10)$$

The sign in Eq. (7) evidently corresponds to that of the potential gradient at x . Finally, the potential profile is obtained from Eq. (8) after integration of Eq. (7):

$$\Psi(x) = \Psi(x_0) + 2 \ln y(x) \quad (11)$$

$$\int_{y(x_0)}^{y(x)} \frac{dy}{\sqrt{\delta\Psi^2 y^2 + (1 - y^2)(1 - k^2 y^2)}} = \pm \frac{\kappa_m}{2} (x - x_0) \quad (12)$$

and the concentration distributions are given by:

$$c_m(x) = c_m(x_0) \frac{1}{y^2(x)} \quad ; \quad c_x(x) = c_x(x_0) y^2(x) \quad (13a,b)$$

These results offer the basis for several explicit descriptions of the potential function and the concentration profiles, which apply for different boundary conditions and ranges of the parameters $\delta\Psi$ and k . A series of limiting cases will be treated below.

2.2. Aqueous phases

The aqueous solutions (‘) and (‘‘) in contact with the membrane at $x = 0$ and $x = d$, respectively, are assumed to be bulk phases. Accordingly, they can be considered as electroneutral systems at distances $x \ll 0$ and $x \gg d$:

$$\sum_m c_{m,aq}(x \ll 0) = \sum_x c_{x,aq}(x \ll 0) = c'_{aq,tot} \quad (14a)$$

$$\sum_m c_{m,aq}(x \gg d) = \sum_x c_{x,aq}(x \gg d) = c''_{aq,tot} \quad (14b)$$

$$\kappa'_{aq} = \frac{2F^2}{RT \varepsilon_{aq} \varepsilon_o} c'_{aq,tot} \quad ; \quad \kappa''_{aq} = \frac{2F^2}{RT \varepsilon_{aq} \varepsilon_o} c''_{aq,tot} \quad (15a,b)$$

$$\Psi(x \ll 0) = \Psi' \quad ; \quad \Psi(x \gg d) = \Psi'' \quad (16a,b)$$

In this case Eq. (12) with $k = 1$ and $\delta\Psi = 0$ can be applied if the reference position x_o is chosen to be sufficiently far from the respective membrane-solution interface. After solving the integral in Eq. (12) one obtains the results for the two aqueous phases:

$$y(x) = \frac{1 + \tanh[0.25(\Psi(0) - \Psi')]}{1 - \tanh[0.25(\Psi(0) - \Psi')]} \frac{e^{\kappa'_{aq} x}}{e^{\kappa'_{aq} x}} \quad (x \leq 0) \quad (17)$$

$$y(x) = \frac{1 + \tanh[0.25(\Psi(d) - \Psi'')]}{1 - \tanh[0.25(\Psi(d) - \Psi'')]} \frac{e^{-\kappa''_{aq}(x-d)}}{e^{-\kappa''_{aq}(x-d)}} \quad (x \geq d) \quad (18)$$

$$\Psi'' = \Psi' + \Delta\Psi_M \quad (19)$$

where $\Delta\Psi_M$ is the dimensionless value of the total membrane potential. Eqs. (17) and (18) agree with the Gouy-Chapman description of diffuse double layers (surface-charge layers) that generally arise in electrolyte solutions near electrode surfaces [42-45]. Due to the exponential terms, the potential-determining function $y(x)$ to be inserted in Eq. (11) approximates the bulk value of 1 within only a few Debye lengths $1/\kappa'_{aq}$ or $1/\kappa''_{aq}$. Space charge in the aqueous phases is therefore restricted to the interfacial regions.

2.3. Bulk membrane

Plasticized polymeric ISE membranes of around 0.1 mm thickness are to a large extent electroneutral and can be described in analogy to the aqueous phases:

$$y(x) = \frac{1 + \tanh[0.25(\Psi(0) - \Psi(x_o))]}{1 - \tanh[0.25(\Psi(0) - \Psi(x_o))]} \frac{e^{-\kappa x}}{e^{-\kappa x}} \quad (0 \leq x \leq x_o) \quad (20)$$

$$y(x) = \frac{1 + \tanh[0.25(\Psi(d) - \Psi(x_o))]}{1 - \tanh[0.25(\Psi(d) - \Psi(x_o))]} \frac{e^{\kappa(x-d)}}{e^{\kappa(x-d)}} \quad (x_o \leq x \leq d) \quad (21)$$

$$\kappa^2 = \frac{2F^2}{RT \varepsilon \varepsilon_o} c_{tot} \quad \text{with} \quad c_{tot} = \sum_m c_m(x_o) = \sum_x c_x(x_o) \quad (22)$$

where the symbols refer to the membrane and the reference point x_o is preferably set at $d/2$. The potential value $\Psi(x_o)$ in the center of the membrane is related to the external values Ψ' and Ψ'' by the boundary conditions that must be fulfilled at the interfaces:

$$c_i(0) = K_i c_{i,aq}(0) \quad ; \quad c_i(d) = K_i c_{i,aq}(d) \quad (23a,b)$$

$$\varepsilon \left(\frac{d\Psi}{dx} \right) = \varepsilon_{aq} \left(\frac{d\Psi_{aq}}{dx} \right) \quad (\text{for } x=0 \text{ and } x=d) \quad (24)$$

where K_i is the overall distribution coefficient of an ion i between the aqueous solution and the membrane, including possible contributions from complex formation with ionophores [26, 27, 29]. Eq. (23) holds only for ions that are present in all phases and cannot be applied for insoluble ions and trapped ionic sites. It should be mentioned that an equilibrium distribution of different species, without any formation of ion fluxes, is possible only in symmetrical systems at zero current. In cases where the membrane is placed between non-identical solutions, ideal permeability selectivity for one species is required to fulfill the equilibrium condition. According to Eqs. (13), (20), and (21), the concentration profiles in such bulk membranes are almost flat except for the two interfacial regions.

2.4. Very thin symmetrical membrane without ionic sites (space-charge membrane)

The present membrane is much thinner than $1 \mu\text{m}$, as for a lipid bilayer, and does not contain permanent ionic components. For simplicity, it is assumed that this membrane is placed between two identical aqueous solutions, and that only one sort of cations is soluble in the membrane. In this case the potential profile shows a maximum in the center of the membrane, that is at $x_0 = d/2$. Hence, Eq. (12) is solved with $k = 0$ and $\delta\Psi = 0$ to yield:

$$y(x) = \cos [0.5\kappa_m (x - d/2)] \quad (25)$$

$$\kappa_m^2 = \frac{2F^2}{RT\varepsilon\varepsilon_o} c_m(d/2) \quad (26)$$

which leads to the potential profile with Eq. (11) [20]. The corresponding concentration profile is given by:

$$c_m(x) = \frac{c_m(d/2)}{\cos^2 [0.5\kappa_m (x - d/2)]} \quad (27)$$

$$c_m(d/2) = K_m c'_m e^{-(\Psi(d/2) - \Psi')} \quad (28)$$

The potential difference between the membrane center and the bulk aqueous phases is determined from the Gauss theorem, Eq. (24).

A limiting case is found when Eq. (25) or (27) would be applied to a bulk membrane. Obviously, it must hold that $0.5 \kappa_m d/2 < \pi/2$, which sets an upper limit to $c_m(d/2)$:

$$c_m(d/2) < \frac{2\pi^2 RT\varepsilon\varepsilon_o}{F^2 d^2} \quad (29)$$

For a $200 \mu\text{m}$ thick membrane of very low dielectric constant ($\varepsilon = 2.5$) the resulting concentration would be as low as 2.9 pM , and the resulting membrane resistance would exceed 10^{13} ohm cm^2 [41].

It should be added that the potential and concentration profiles in a membrane with anions instead of cations would be described by the expressions:

$$y(x) = \frac{1}{\cos[0.5\kappa_x(x-d/2)]} \quad (30)$$

$$c_x(x) = \frac{c_x(d/2)}{\cos^2[0.5\kappa_x(x-d/2)]} \quad (31)$$

where κ_x and $c_x(d/2)$ are defined in analogy to Eqs. (26) and (28).

2.5. Very thin site-free space-charge membrane in asymmetric arrangements

The same membrane of $< 1 \mu\text{m}$ thickness with only one sort of cations is considered, but now it is in contact with different solutions on both sides. In this case two possible solutions are derived from Eq. (12) with $k = 0$, depending on the degree of asymmetry of the studied system. If the concentration difference between the boundaries of the membrane is relatively small, we always get $\delta\psi^2 < 1$, and a maximum exists for the potential function. The location x_0 of this maximum (where $\delta\psi=0$) is preferably chosen as reference position, which finally results in potential and concentration profiles analogous to the former ones:

$$y(x) = \cos[0.5\kappa_m(x-x_0)] \quad (32)$$

$$c_m(x) = \frac{c_m(x_0)}{\cos^2[0.5\kappa_m(x-x_0)]} \quad (33)$$

$$\kappa_m^2 = \frac{2F^2}{RT\varepsilon\varepsilon_0} c_m(x_0) = \frac{2F^2}{RT\varepsilon\varepsilon_0} K_m c'_m e^{-(\psi(x_0)-\psi')} \quad (34)$$

Obviously, the present description also includes the symmetrical case with $x_0=d/2$. For asymmetric systems, the position x_0 can be on either side of the membrane center. The formal maximum of the potential function may even be far from the membrane and thus not really observable in the actual potential profile. As limiting case for $x_0 \rightarrow \infty$ and $0.5\kappa_m x_0 \rightarrow \pi/2$, expansion of Eq. (32) into a series yields a simple linear function of x between 0 and d . The same result may be obtained directly from Eq. (12) with $k = 0$ and $\delta\psi^2 = 1$.

A completely different solution is found for strongly asymmetric arrangements where Eq. (12) applies with $\delta\psi^2 > 1$ throughout and hence no potential maximum exists. The simplest version of the result is obtained when the reference position x_0 is set at the distance where exactly $\delta\psi^2 = 2$ holds:

$$y(x) = \sinh[b \pm 0.5\kappa_m(x-x_0)] \quad \text{with} \quad b = \sinh^{-1} 1 \quad (35)$$

$$c_m(x) = \frac{c_m(x_0)}{\sinh^2[b \pm 0.5\kappa_m(x-x_0)]} \quad (36)$$

All the parameters needed in Eqs. (32)-(36) can be determined from the boundary conditions, given by Eqs. (23a), (23b), and (37):

$$\varepsilon_{aq} \left(\frac{d\Psi_{aq}}{dx} \right)_0 - \varepsilon_{aq} \left(\frac{d\Psi_{aq}}{dx} \right)_d = \varepsilon \left(\frac{d\Psi}{dx} \right)_0 - \varepsilon \left(\frac{d\Psi}{dx} \right)_d \quad (37)$$

which is the general form of the Gauss theorem for asymmetric cases. A fourth condition to be fulfilled is a minimum for the total charge separation, which corresponds to the lowest possible absolute value for both sides in Eq. (37). In the end, the evaluation of the best-fitting parameters turns out to be relatively involved.

2.6. Very thin symmetrical membrane with ionic sites and exchangeable ions

Here we focus on a membrane such as a lipid bilayer that contains anions trapped due to their high lipophilicity and cations extracted from the aqueous phase. It is assumed that the external solutions have identical compositions and contain only one species being soluble in the membrane. If the overall distribution coefficient of this cation is sufficiently high, and the average concentration of anionic sites is relatively low, Eq. (12) can be applied for the symmetrical case ($x_0 = d/2$) with $k < 1$ and $\delta\psi = 0$ to yield the result [41]:

$$F[k, y(x)] = F[k, 1] - \frac{\kappa_m}{2} |x - d/2| \quad (38)$$

$$F[k, y(x)] = \int_0^{y(x)} \frac{dy}{\sqrt{(1-y^2)(1-k^2y^2)}} \quad (39)$$

where κ_m is given by Eq. (34), and $F[k, y(x)]$ is an elliptic integral of the first kind that must be evaluated to get the potential-determining function $y(x)$. The potential profile is then obtained from Eq. (11), and the cation and site concentration profiles from Eq. (13a) and (13b), respectively. According to Eq. (38), a potential maximum appears at $x = d/2$, which corresponds to a minimum of the cation concentration and a maximum of the site concentration.

A complementary solution is derived for the case where the anionic sites predominate over the extracted cations, that is for $k > 1$. For such a system, Eq. (12) leads to:

$$F\left[\bar{k}, \bar{y}(x)\right] = F\left[\bar{k}, 1\right] - \frac{\kappa_v}{2} |x - d/2| \quad (40)$$

where $\bar{k}$ denotes $1/k$, and $\bar{y}$ is used for $1/y$. In this case, a potential minimum is found in the center of the membrane, and hence a maximum for the cation profile and a minimum for the site profile. The parameters required in Eqs. (38)-(40) can be determined by using the boundary conditions specified earlier. Another condition to be fulfilled is the conservation of the total amount of sites in the membrane. This makes the application of the theory for the evaluation of potential and concentration profiles rather laborious. It should be mentioned that Eqs. (38)-(40) also include the descriptions of bulk membranes and thin site-free membranes as the limiting cases for $k = \bar{k} = 1$ and $k = 0$ or $\bar{k} = 0$, respectively.

2.7. Very thin membrane with ionic sites in asymmetric arrangements

Again, a membrane with anionic sites and exchangeable cations is treated, but now the aqueous phases on both sides differ in their compositions. Two limiting cases are discerned for such asymmetric systems, which is analogous to the description of site-free membranes in Section 2.5. For moderately asymmetric arrangements, there always exists a position x_0 where the potential function reaches a maximum or minimum ($\delta\psi=0$). Obviously, the solution of Eq. (12) is then given by an extension of Eq. (38) and (40), respectively:

$$F[k, y(x)] = F[k, 1] - \frac{\kappa_m}{2} |x - x_o| \quad \text{for } k < 1 \quad (41)$$

$$F\left[\bar{k}, \bar{y}(x)\right] = F\left[\bar{k}, 1\right] - \frac{\kappa_x}{2} |x - x_o| \quad \text{for } k = \bar{k}^{-1} > 1 \quad (42)$$

with $\bar{y} = 1/y$. Since the reference distance x_o may be on either side and even very far from the membrane, the general application of these results for practical purposes seems to be difficult. Distinct examples using a given location x_o can nevertheless be evaluated from the theory.

In highly asymmetric systems, the anionic sites may predominate on one side of the membrane, and the extracted cations on the other side. Accordingly, the potential and concentration profiles do not show any maxima or minima. On the other hand, there always exists an electroneutral plane at distance x_o where both species have identical concentrations. This means that Eq. (12) applies with $k = 1$ and $\delta\psi^2 \gg 0$ (in contrast to bulk membranes with $\delta\psi^2 = 0$):

$$\int_{y(x_o)}^{y(x)} \frac{dy}{\sqrt{1 + (\delta\psi^2 - 2)y^2 + y^4}} = \pm \frac{\kappa}{2} (x - x_o) \quad (43)$$

where κ is the common reciprocal Debye length for cations and anions, and the sign on the right side is defined by that of the potential gradient.

In general cases the integral in Eq. (43) has to be solved numerically. A closed form of the solution can be found only in the special case with $\delta\psi^2 = 4$:

$$y(x) = \tan[0.5\kappa|x - x_o|] \quad (\text{for } x \geq x_o) \quad (44)$$

$$y(x) = \frac{1}{\tan[0.5\kappa|x - x_o|]} \quad (\text{for } x \leq x_o) \quad (45)$$

where the validity ranges hold for $\delta\psi > 0$, and have to be reversed for $\delta\psi < 0$. The potential profile obtained with Eq. (11) correctly shows an inflexion point at $x = x_o$, as is actually predicted from the Poisson equation, Eq. (1), for this electroneutral plane.

3. Numerical simulations and parameters used

To verify the theoretical calculations, and especially the optimal choice of the basic parameters, all results were compared with the respective data obtained from computer simulations. Finite-difference numerical simulations of ISE membranes and related systems were developed earlier and described in great detail [1, 30-39]. The group of Lewenstam and Sokalski [36-39] reported on a universal and highly sophisticated approach being based on a combined Nernst-Planck-Poisson model. However, a quite complex mathematical procedure is used for these calculations, which requires very long computing times [37, 38]. Therefore, a much simpler and fully transparent version of computer simulation running with conventional MS Excel software (Microsoft Inc.) was preferred in this work. To this end, the previously described numerical methods for simulating membranes with Nernst-Planck ion fluxes [31-33] were extended to also include Poisson-type space-charge terms.

The applied finite-difference formalisms for the Nernst-Planck flux equation, the continuity equation, and the Poisson equation are given in Eqs. (46), (47), and (48), respectively:

$$J_i(n, n+1) = D_i \frac{c_i(n) - c_i(n+1)}{\Delta x} + z_i D_i \frac{c_i(n) + c_i(n+1)}{2} \frac{\Psi(n) - \Psi(n+1)}{\Delta x} \quad (46)$$

$$\frac{\Delta c_i(n)}{\Delta t} = \frac{J_i(n-1, n) - J_i(n, n+1)}{\Delta x} \quad (47)$$

$$\frac{\Psi(n-1) - 2\Psi(n) + \Psi(n+1)}{(\Delta x)^2} = - \frac{F^2}{RT\epsilon\epsilon_o} \sum_i z_i c_i(n) \quad (48)$$

where $n-1$, n , and $n+1$ are the numbers of successive elements (slices) of the treated phases, Δx is the thickness of each element, $J_i(n, n+1)$ is the ion flux from element n to $n+1$, $c_i(n)$ is the concentration of ions i in element n , z_i is the charge and D_i the diffusion coefficient of ions i , $\Psi(n)$ is the dimensionless potential value in element n , $\Delta c_i(n)$ is the flux-induced change of $c_i(n)$ during a short time interval Δt , and the other symbols are the same as in Eq. (1). The boundary conditions to be considered have been specified in Section 2.

The computation starts with an arbitrary choice of initial concentration and potential values for all elements, except for the given bulk regions of the two aqueous phases. Eq. (47) is used with Eq. (46) to predict the concentration changes after a time increment Δt . The new concentration values are then inserted in Eq. (48) to yield the actual potential profile. The same procedure is continued until a final equilibrium state is reached. This permits it, in principle, to analyze the time-dependent evolution of concentration and potential profiles in the system. In the present context, however, just the equilibrium profiles were determined from the computer simulations. Since the studied membranes were in most cases only 30 nm thick, the length Δx of the elements was chosen as 1 nm, and the time steps Δt were 0.5 or 20 ns, depending on the system. To reduce the computation times, first-order profiles inside the membrane were obtained with time steps of 20 ns, starting from approximate boundary concentrations. Then, these profiles were introduced in simulations of the whole system, including the aqueous solutions, using time steps of 0.5 ns. This artifice allowed it to complete the numerical analysis of a system within a few minutes, whereas simulations with the more complex mathematical procedure are much longer [38]. The diffusion coefficient in the membrane was taken as $10^{-8} \text{ cm}^2 \text{ s}^{-1}$ [46-49], but this value has no influence on the final shape of concentration and potential profiles being established at equilibrium. The dielectric constant ϵ of the membrane was assumed to be 2.5, which is typical for a very nonpolar medium. The overall distribution coefficient K_i of all extractable ions i was taken as 0.002 (with one exception), which value may be representative either for highly lipophilic ions or for species solubilized by specific ionophores in the membrane. For simplicity, all activity coefficients were set equal to unity. The agreement between simulated and theoretical concentration values was found to be excellent, the relative deviations being <1 % throughout.

4. Results and discussion

Extremely thin membranes can extract considerable concentrations of soluble ions, even in the absence of ionic components as membrane additives. Accordingly, these systems are far from electroneutrality, which is in contrast to the interior of bulk membranes. Figure 1 shows the ion distribution and the potential profile in a 30 nm thin space-charge membrane, being placed between two aqueous solutions of identical composition. For diluted sample

solutions, the concentration in the center of the membrane approximates the upper limit $K_m c_m(\text{aq})$ (see Figure 1a), but it drops well below this value at higher sample concentrations (see Figures 1b and 1c). This implies that the potential at $d/2$ gradually increases with increasing sample concentrations. The points in Figure 1 represent theoretical results according to Section 2, whereas the solid lines were obtained by computer simulation using the same parameters (see Section 3). The nearly perfect agreement between the two sets of data in Figure 1 is evident.

Figure 2 illustrates concentration and potential profiles for the same membrane when it is interposed between two different solutions. Obviously, the asymmetric arrangement also causes an asymmetry of the ion distribution within the membrane. With increasing concentration of solution ($'$) the reference position x_o is shifted from the center of the membrane, as in Figure 1, to the right boundary zone of the membrane (see Figure 2a), or even to a location quite far from the membrane (see Figures 2b and 2c). The corresponding concentration level $c_m(x_o)$ decreases at the same time. This is clearly indicated by a steeper concentration profile in the membrane. It should be mentioned that only the cases in Figures 1a, 2a, and 2b are directly comparable because they are of the cosine-function type treated in Section 2.5 (Eqs. (32) and (33)). The example shown in Figure 2c, on the other hand, follows a different formal description given in Eqs. (35) and (36). Again, theoretical and computer-simulated profiles are in excellent agreement.

Figure 3 shows results for a site-free membrane in a symmetric set-up when the membrane thickness is varied relative to the system specified in Figure 1a. An increase in d obviously leads to a drastic reduction of the ion concentration in the membrane interior. For very thick membranes the concentration at $d/2$ finally approximates the limiting value defined in Eq. (29). The respective upper limits would be given by 29.1 nM for the 2 μm thick membrane, and 2.91 pM for the 200 μm thick membrane. Accordingly, the potential at $d/2$ strongly increases from very thin to bulk membranes (see also below). It should be noted that such low cation concentrations are reached only for membranes that are free from any ionic sites and in which sample anions are completely insoluble.

Figure 4 summarizes all the details on ion concentrations and potentials at $d/2$, and on trans-membrane potential differences of site-free membranes. In Figure 4a, values of $\log c_m(d/2)$ and $\Delta\phi(d/2)$ are given as a function of $\log c_m(\text{aq})$. The results include a total of 13 symmetric and asymmetric cases (specific comments are found in the figure caption). The data illustrate that $c_m(d/2)$ is proportional to $c_m(\text{aq})$ for diluted samples, but approximates the dotted upper limit for extremely high sample concentrations. Correspondingly, the membrane-internal potential $\Delta\phi(d/2)$ is near zero for diluted samples, and gradually increases with a sub-Nernstian slope at higher concentrations. It is remarkable that the results from asymmetric systems are quite close to the curve established for symmetric cells. The potential difference $\Delta\phi(d/2)$ may be of relevance for highly miniaturized devices where a thin membrane is coated directly, that is without formation of an intermediate aqueous film, on the inert surface of a suitable substrate (e. g., with capacitive inner contact [16-18] or on the insulated gate of a field-effect transistor). For such a membrane of thickness $d/2$ (here 15 nm), the concentration and potential profiles would be comparable to those in a half-membrane of the type shown in Figure 1. Hence, the potential response would be determined by $\Delta\phi(d/2)$, provided that the detection could be realized without further interference. Figure 4a documents that the response of such a sensor with a site-free membrane does not meet at all the requirements for practical applications. This is in clear contrast to the behavior of conventional ISEs where the so-called boundary potential difference between sample solution and bulk membrane is considered to be the basis for a Nernstian response [26, 27, 29].

Figure 4b shows data for $\log c_m(d/2)$ and $\Delta\phi(d/2)$ as a function of the membrane thickness. The membrane-internal concentration $c_m(d/2)$ is evidently defined by $K_m c_m(aq)$ for extremely thin membranes, and converges on the dotted limiting line predicted by Eq. (29) for thick membranes. In complete analogy, the potential difference at $d/2$ increases with increasing d from zero towards the dotted limiting line. One may therefore conclude that a thick ($> 1 \mu\text{m}$) site-free membrane coated on a substrate surface would yield a sensor with a perfect Nernstian response. However, the resistance of such a membrane turns out to be extremely high, as mentioned before in Section 2.4. Figure 4c demonstrates on the other hand that even very thin membranes can exhibit an ideal response behavior. The basic requirement is that they have to be contacted with two aqueous phases between which the total trans-membrane potential difference is determined. Further important points are that an equilibrium distribution of the permeating ion must be fulfilled, and that species other than the primary ion are excluded from the membrane due to a very low solubility (see also below). The obvious drawback of this sensor type is the poor mechanical stability of membranes in the sub-micrometer range.

So far the discussion of results was restricted to thin membranes that do not permanently contain ions. This is in clear contrast to common ISE systems where plasticized polymer membranes with native or intentionally introduced ionic components are used [50]. The presence of such sites in bulk membranes generally induces a certain permeability selectivity for oppositely charged counter ions [26, 27]. However, it has never been demonstrated in the past that the same favourable effect would also result for extremely thin membranes in which space-charge regions are predominant. An exact theoretical solution for these systems has been offered in Section 2, but the practical evaluation of concentration and potential profiles turns out to be highly involved. The reason is that values for the relevant integrals have to be determined numerically or taken from mathematical tables. Accordingly, only a few examples are shown in the following.

Figure 5 illustrates the ion distributions and the potential profiles in 30 nm thin site membranes that are in contact with two identical solutions of increasing electrolyte concentration (from a to d). Figures 5a and 5b show examples with $c_m(x) < c_r(x)$ and $\bar{k} = 0.95$, whereas Figures 5c and 5d are cases with $c_m(x) > c_r(x)$ and $k = 0.95$ (see Section 2.6). An intermediate singular case with completely flat profiles ($c_m(x) = c_r(x) = K_m c_m(aq)$, $k = 1$) also exists but is not shown here. The membranes presented in Figure 5 are evidently quite different from electroneutral phases. The influence of extended space-charge domains leads to a strongly curved shape of the concentration profiles and to considerable potential changes. The sign of the potential differences relative to the aqueous phases is obviously governed by the charge of the predominant species in the membrane. Hence a concentration minimum is found for these ions at $d/2$, and a maximum for the oppositely charged species. Unfortunately, it was not possible to offer theoretical results for systems with one and the same average site concentration $c_{r,av}$. Thus appropriate corrections have to be made for a more profound interpretation (see below). For a proof, all the evaluated points in Figure 5 are compared with computer-simulated curves, which give an excellent fit to the theoretical data.

In Figure 6 three examples of 30 nm thin site membranes with asymmetric concentration and potential profiles are presented. Figure 6a shows a case with $c_m(x) < c_r(x)$ and $\bar{k} = 0.95$, whereas Figure 6c illustrates a complementary case with $c_m(x) > c_r(x)$ and $k = 0.95$ (see Section 2.6). An intermediate example is given in Figure 6b where an electroneutral zone appears in the membrane interior ($c_m(d/2) = c_r(d/2)$, $k = 1$). In Figures 6a and 6c, all profiles reach a maximum or minimum at a distance x_0 of 0 and 30 nm, respectively. Figure 6b on the other hand exhibits an inflexion point of the potential profile at 15 nm (see also Section 2.6). For all systems a clear predominance of space-charge regions is observed. The

theoretical data points in Figure 6 are again in nearly perfect and convincing agreement with computer-simulated curves.

Figure 7 summarizes the results for the cation concentrations and the potential values in the center of symmetric membranes with anionic sites, as well as data for the total trans-membrane potential differences in asymmetric arrangements. In Figure 7a logarithmic values for $c_m(d/2)$ are related to those for $c_m(aq)$, after the respective corrections for differing site concentrations $c_{r,av}$ have been made. Besides, the corresponding results for $\Delta\phi(d/2)$ are also shown. If the membranes were nearly electroneutral, as for bulk phases, one would expect a horizontal line at zero for the logarithmic concentration plot since then it holds that $c_m(d/2) = c_{r,av}$. At the same time the potential response would become Nernstian and yield a slope of unity. The curves found in Figure 7a are actually linear, but they clearly deviate from those predicted for bulk membranes. Only the zero point for the singular system with $k = 1$ conforms to the characteristics of an electroneutral membrane. Obviously, the concentrations in the center of the membrane are not independent of the sample concentration, and hence the potential response is in fact sub-Nernstian. Although these results may be surprising, they are a strict consequence of space-charge phenomena. It can be concluded that extremely thin membranes coated on substrates are not suited as perfect sensors, even when they contain ionic sites as additives. A contrasting behavior is again found for membranes that are placed between two aqueous phases. Figure 7b shows results for the trans-membrane potential difference as a function of the logarithm of the external concentration ratio. A Nernstian response is evidently achieved for the support-free 30 nm membrane, however, at the cost of a reduced stability.

Figure 8 illustrates results for membranes that contain anionic sites, cations as counter ions, and also soluble anions as co-ions. For simplicity, it was assumed that all extractable species have the same interfacial distribution coefficients. In Figure 8a concentration and potential profiles in a 30 nm thin membrane are shown. The traces for the cation concentration and the potential are identical to the corresponding profiles in Figure 5a, and hence the total anion concentration must also be the same. The relative population of anionic sites and co-ions in the membrane is determined by the respective boundary concentrations. For comparison, analogous profiles are presented in Figure 8b for a bulk membrane. Evidently the interior of the latter membrane is electroneutral, whereas the thin membrane is throughout a space-charge system. Nevertheless, the co-ion profile near the interface is very similar for both cases. It appears that the presence of anionic sites in the membrane generally results in an efficient exclusion of co-ions [26, 27, 29]. In fact, the concentrations of extracted anions in the center of the membrane are quite low, namely about 6 μM for the 30 nm membrane, and about 3 μM for the bulk membrane. It should be noted, however, that a failure of co-ion exclusion would occur at high sample concentrations and/or low site concentrations. This is demonstrated in Figure 9 where concentration and potential profiles are shown for 30 nm thin site-free membranes that are exposed to concentrated aqueous solutions. Evidently, a perfect exclusion of sample anions from the membrane is obtained only for $K_x \rightarrow 0$ (Figure 9a), whereas a significant co-extraction is found for sufficiently soluble anions although their average concentration remains well below the cation concentration (Figure 9b). For diluted samples, on the other hand, the anion interference effects in thin membranes would generally decrease since the corresponding concentration levels of cations and anions would be roughly proportional to the respective overall distribution coefficients. Hence, the membrane in Figure 9b would finally contain an anion/cation concentration ratio of only about 0.02. This is in clear contrast to site-free bulk membranes in which the concentrations of cations and anions are always nearly the same.

A final comment may elucidate the practical relevance of space-charge effects in bulk membranes as used for conventional ISE applications. In Figure 8b the space-charge region

of the membrane phase is obviously restricted to a depth of about 15 nm, which is only 0.01 % of the typical membrane thickness of 100 to 200 μm . The diffusion time for an ion crossing this zone would be around 10^{-4} s. The space-charge layer in the aqueous solution is about 10 nm thick, as can be inferred from the potential profile in Figure 8b. This would correspond to a diffusion time of only around 10^{-7} s. Evidently space-charge phenomena play a minor role in the case of steady-state potentiometric measurements on bulk membranes. Accordingly, classical ISE models [26, 27, 29] that treat the interfacial region as a 'sharp' boundary with step-like concentration and potential changes turn out to be a very reasonable and well acceptable approach to reality.

5. Conclusions

The aim of this work was to analyze the behavior of extremely thin non-electroneutral membranes and their applicability for ion-selective electrodes. An extended theoretical treatment of steady-state potential and concentration profiles in space-charge membranes of $<< 1 \mu\text{m}$ thickness was presented. The theory was based on the Poisson equation and the Boltzmann equation, the latter being the equilibrium version of the Nernst-Planck flux equation. A general solution in integral form was developed, from which a series of explicit sub-solutions was derived for particular cases. Systems with up to three different ion species were discussed, including membranes with trapped ionic sites and co-extracted ions. It was shown that space-charge membranes exhibit a perfect Nernstian response only when they are contacted with aqueous solutions on both sides, which is at the cost of the mechanical stability of such sensors. Solid-contacted thin membranes, on the other hand, are much more robust but they respond with a clearly sub-Nernstian slope. The theoretical results were verified by numerical simulations based on the Nernst-Planck-Poisson model, as pioneered by the groups of Buck [35] and Lewenstam and Sokalski [36, 37, 39]. To this end, a simplified and fully transparent finite-difference procedure was developed by which steady-state profiles for the ion concentrations and the electric potential were obtained within only a few minutes. The relative deviations of the simulated data from the exact values were $<1\%$ throughout. It is here the first time that the enormous capability and the excellent reliability of these simulation techniques for ISEs could be demonstrated in a very direct comparison with true results.

Acknowledgments

EP gratefully acknowledges the financial support by the National Institutes of Health (R01-EB002189).

References

1. Bobacka J, Ivaska A, Lewenstam A. Chem. Rev. 2008; 108:329. [PubMed: 18189426]
2. Bakker E, Pretsch E. Angew. Chem., Int. Ed. Engl. 2007; 46:5660. [PubMed: 17457791]
3. Orme, FW. Glass Microelectrodes. Lavallée, M.; Schanne, O.; Hebert, NC., editors. Wiley; New York: 1969.
4. Walker JL Jr. Anal. Chem. 1971; 43:A89.
5. Ammann, D. Ion-Selective Microelectrodes. Springer-Verlag; Berlin: 1986.
6. Bakker E, Pretsch E. Trends Anal. Chem. 2008; 27:612.
7. Messerli MA, Collis LP, Smith PJS. Electroanalysis. 2009; 21:1906.
8. Yamaguchi H. Cell Calcium. 1986; 7:203. [PubMed: 3094959]
9. Simon W, Morf WE, Ammann D. Microchem. J. 1987; 36:3.
10. Manz A, Fröbe Z, Simon W. J. Chromatogr. Libr. 1985; 30:297.
11. Manz, A. PhD thesis. 1986.
12. Gyurcsányi RE, Nybäck AS, Tóth K, Nagy G, Ivaska A. Analyst. 1998; 123:1339.

13. Sundfors L, Bereczki R, Bobacka J, Tóth K, Ivaska A, Gyurcsányi RE. *Electroanalysis*. 2006; 18:1372.
14. Gyetvai G, Sundblom S, Nagy L, Ivaska A, Nagy G. *Electroanalysis*. 2007; 19:1116.
15. Shim JH, Kim J, Cha GS, Nam H, White RJ, White HS, Brown RB. *Anal. Chem.* 2007; 79:3568. [PubMed: 17411008]
16. Lai C, Fierke MA, Stein A, Bühlmann P. *Anal. Chem.* 2007; 79:4621. [PubMed: 17508716]
17. Crespo GA, Macho S, Rius FX. *Anal. Chem.* 2008; 80:1316. [PubMed: 18271511]
18. Crespo GA, Macho S, Bobacka J, Rius FX. *Anal. Chem.* 2009; 81:676. [PubMed: 19093752]
19. Läuger P. *Science*. 1972; 178:24. [PubMed: 5070513]
20. Läuger, P.; Neumcke, B. *Membranes, A Series of Advances*. Eisenman, G., editor. Vol. Vol. 2. Dekker; New York: 1973.
21. Läuger P, Stark G. *Biochem. Biophys. Acta*. 1970; 211:458. [PubMed: 5456977]
22. Ciani, SM.; Eisenman, G.; Laprade, R.; Szabo, G. *Membranes, A Series of Advances*. Eisenman, G., editor. Vol. Vol. 2. Dekker; New York: 1973.
23. Szabo, G.; Eisenman, G.; Laprade, R.; Ciani, S.; Krasne, S. *Membranes, A Series of Advances*. Eisenman, G., editor. Vol. Vol. 2. Dekker; New York: 1973.
24. Eisenman G, Krasne S, Ciani S. *Ann. N. Y. Acad. Sci.* 1975; 264:34. [PubMed: 1062960]
25. Minami H, Sato N, Sugawara M, Umezawa Y. *Anal. Sci.* 1991; 7:853.
26. Morf, WE. *The Principles of Ion-Selective Electrodes and of Membrane Transport*. Elsevier; New York: 1981.
27. Koryta, J.; Stulik, K. *Ion-Selective Electrodes*. Cambridge University Press; Cambridge, GB: 1983.
28. Si P, Bakker E. *Chem. Commun.* 2009:5260.
29. Morf WE, Badertscher M, Zwickl T, de Rooij NF, Pretsch E. *J. Phys. Chem. B*. 1999; 103:11346.
30. Sandifer JR, Buck RP. *J. Phys. Chem.* 1975; 79:384.
31. Morf WE, Pretsch E, de Rooij NF. *J. Electroanal Chem.* 2007; 602:43.
32. Morf WE, Pretsch E, de Rooij NF. *J. Electroanal. Chem.* 2008; 614:15.
33. Morf WE, Pretsch E, de Rooij NF. *J. Electroanal. Chem.* 2009; 633:137.
34. Höfler L, Bedlechowicz I, Vigassy T, Gyurcsányi RE, Bakker E, Pretsch E. *Anal. Chem.* 2009; 81:3592. [PubMed: 19338286]
35. Brumleve TR, Buck RP. *J. Electroanal. Chem.* 1978; 90:1.
36. Sokalski T, Lewenstam A. *Electrochem. Commun.* 2001; 3:107.
37. Sokalski T, Lingenfelter P, Lewenstam A. *J. Phys. Chem. B*. 2003; 107:2443.
38. Lingenfelter P, Bedlechowicz-Sliwakowska I, Sokalski T, Maj-Zurawska M, Lewenstam A. *Anal. Chem.* 2006; 78:6783. [PubMed: 17007497]
39. Sokalski T, Kucza W, Danielewski M, Lewenstam A. *Anal. Chem.* 2009; 81:5016. [PubMed: 19459654]
40. Ciani, SM.; Eisenman, G.; Laparde, R.; Szabo, G. *Membranes, A Series of Advances*. Eisenman, G., editor. Vol. Vol. 2. Dekker; New York: 1973.
41. Morf WE, Simon W. *Helv. Chim. Acta*. 1986; 69:1120.
42. Gouy G. *J. Physique*. 1910; 9:457.
43. Chapman DL. *Phil. Mag.* 1913; 25:475.
44. Kortüm, G. *Lehrbuch der Elektrochemie*. Verlag Chemie; Weinheim: 1972.
45. Bard, AJ.; Faulkner, LR. *Electrochemical Methods*. Wiley; New York: 2001.
46. Püntener M, Fibbioli M, Bakker E, Pretsch E. *Electroanalysis*. 2002; 14:1329.
47. Long R, Bakker E. *Anal. Chim. Acta*. 2004; 511:91.
48. Bodor S, Zook JM, Lindner E, Tóth K, Gyurcsányi RE. *Analyst*. 2008; 133:635. [PubMed: 18427685]
49. Bodor S, Zook JM, Lindner E, Tóth K, Gyurcsányi RE. *J. Solid State Electrochem.* 2009; 13:171.
50. Bakker E, Bühlmann P, Pretsch E. *Chem. Rev.* 1997; 97:3083. [PubMed: 11851486]

Fig. 1.

Symmetric profiles of ion concentration and potential in 30 nm thin membranes without permanent ionic sites. The aqueous solutions contain 5 mM (a), 50 mM (b), and 500 mM (c) of extractable ions M⁺, respectively. Points: theoretical results from Eqs. (11) and (25)-(27) with values obtained for c_m(d/2) as 8.446 μM (a), 40.46 μM (b), and 85.01 μM (c), respectively. Solid lines: results obtained from computer simulations at equilibrium. All concentrations in the membrane are multiplied by 1/K_m.

Fig. 2. Asymmetric profiles of ion concentration and potential in 30 nm thin site-free membranes. Solution ('): 10 mM (a), 100 mM (b), and 500 mM (c) of ions M^+ , respectively; solution ("): 5 mM. Points predicted by theory are compared with computer-simulated curves. Calculations were based on Eqs. (11) and (32)-(36) with values x_0 of 27.09 nm (a), 71.5 (b), and 101.4 nm (c), and values $c_m(x_0)$ of 9.945 μM (a), 4.635 μM (b), and 0.8332 μM (c), respectively. Example (c) is a strongly asymmetric case, as treated in Section 2.

Fig. 3.

Ion-concentration and potential profiles in site-free membranes with a thickness of 200 nm (a), 2 μm (b), and 200 μm (c), respectively. The aqueous solutions contain 5 mM of extractable ions M⁺. In (c) only a small section of the membrane is shown. Calculations using the indicated values of c_m(d/2) were done as for Fig. 1 where the example of a 30 nm thin membrane is found for comparison. Note the different potential scales.

Fig. 4.

(a) Ion concentrations and potentials in the center of 30 nm thin site-free membranes. The influence of the external concentrations $c_m(\text{aq})$ on the values of $c_m(d/2)$ and $\Delta\phi(d/2) = \phi(d/2) - \phi(\text{aq})$ is illustrated. Filled points: results for symmetric cells (see Fig. 1); open points: results for asymmetric cells (see Fig. 2). In the latter case, $c_m(\text{aq})$ is defined as $(c'_m c''_m)$, and $\phi(\text{aq})$ as $(\phi' + \phi'')/2$. Examples not shown in Figs. 1 and 2 are included. Upper dotted line: maximum concentration according to Eq. (29); lower dotted line: corresponding potential function.

(b) Ion concentrations and potentials in the center of site-free membranes placed between two 5 mM aqueous solutions. The dependence of $c_m(d/2)$ and $\Delta\phi(d/2)$ on the membrane thickness d is shown (see Figs. 1a and 3). The dotted lines again indicate maximum concentrations and limiting potentials. (c) Total membrane potentials of 30 nm thin site-free membranes in asymmetric cells (see Fig. 2). The dependence of $\phi'' - \phi'$ on the logarithm of the concentration ratio between the aqueous solutions is shown. The dotted line corresponds to Nernstian behavior.

Fig. 5.

Symmetric profiles of concentrations and potential in 30 nm thin membranes with permanent ionic sites R^- . The aqueous solutions contain 17.4 mM (a), 34.3 mM (b), 164 mM (c), and 788 mM (d) of extractable ions M^+ , respectively. Points predicted by theory are compared with computer-simulated curves. Calculations were based on Eqs. (11), (13), and (38)–(40) with values $c_m(d/2)$ of 0.2256 mM (a), 0.1444 mM (b), 0.16 mM (c), and 0.25 mM (d), and with values $c_r(d/2)$ of 0.25 mM (a), 0.16 mM (b), 0.1444 mM (c), and 0.2256 mM (d), respectively. The average site concentrations are specified.

Fig. 6.

Asymmetric profiles of ion concentrations and potential in 30 nm thin membranes with sites R^- . Solution ('): 32.5 mM (a), 350 mM (b), and 681 mM (c); solution ("): 1.7 mM (a), 0.28 mM (b), and 36 mM (c), respectively. Points predicted by theory are compared with computer-simulated curves. Calculations were based on Eqs. (11), (13), and (41)–(45) with values x_0 of 0 nm (a), 15 nm (b), and 30 nm (c), values $c_m(x_0)$ of 0.065 mM (a), 0.02 mM (b), 0.072 mM (c), and values $c_r(x_0)$ of 0.072 mM (a), 0.02 mM (b), 0.065 mM (c), respectively. The average site concentrations are specified. Example (b) is a case with electroneutrality at $d/2$, as treated in Section 2.

Fig. 7.

(a) Cation concentrations and potentials in the center of 30 nm thin membranes with anionic sites R^- (see Fig. 5). The influence of the external concentrations $c_m(aq)$ on the values of $c_m(d/2)$ and $\Delta\phi(d/2)=\phi(d/2)-\phi'$ is illustrated. To account for differences in the average site levels, all concentrations are given in units of $c_{r,av}$. The linear regression slope is 0.306 for the logarithmic concentrations, and 0.648 for the reduced potentials.

(b) Total membrane potentials of 30 nm thin membranes with anionic sites R^- (see Fig. 6). The dependence of $\phi''-\phi'$ on the logarithm of the concentration ratio between the aqueous solutions is shown. The dotted line corresponds to Nernstian behavior.

Fig. 8.

Ion-concentration and potential profiles in membranes with sites R^- , counter ions M^+ , and co-extracted ions X^- . A 30 nm thin membrane is compared with a bulk membrane. The experimental conditions in Fig. 8a are the same as in Fig. 5a, except that sample anions are also extracted with a distribution coefficient of $K_x = 0.002$. Points predicted by theory are compared with computer-simulated curves. More details are given in the text.

Fig. 9.

Ion-concentration and potential profiles in 30 nm thin site-free membranes with cations M^+ and co-extracted anions X^- for 788 mM aqueous solutions. (a) Results from Eqs. (11) and (25)-(27) for insoluble anions with $K_x = 0$. (b) Results obtained in analogy to Fig. 5d for soluble anions with $K_x = K_m/44 = 0.00004545$, instead of anionic sites. The concentrations in the membrane are multiplied by $1/K_m$.