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Membrane potential and Donnan potential

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The Nernst-Planck-Poisson equations for the potential profile across a membrane are exactly solved without recourse to the assumption of constant field within the membrane. It is assumed that the membrane core of thickness d_c is covered by a surface layer of thickness d_s in which the membrane-fixed charges are distributed at a uniform density N. The membrane boundary potentials as well as the diffusion potentials contribute to the membrane potential. It is shown that for $d_s \gtrsim 1/\kappa$, κ being the Debye-Hückel parameter, the potential in the membrane surface layer except in the region very near the membrane/solution boundary is effectively equal to the Donnan potential and that its contribution to the membrane potential becomes dominant as N increases. For low N, on the other hand, the membrane potential arises mostly from the diffusion potential.

1. Introduction

A potential difference is generally established between two electrolyte solutions at different concentrations separated by an ion-permeable membrane. This potential difference, called the membrane potential, plays an important role in electrochemical phenomena observed in various biomembrane systems. As is well known, in the stationary state the membrane potential arises both from the diffusion potential [1,2] and from the membrane boundary potential [3–6].

In order to calculate the membrane potential one must simultaneously solve the Nernst-Planck equation and the Poisson equation. Because of the mathematical difficulty involved in these equations, both being nonlinear, an analytic formula for the membrane potential can be derived only if the electric field within the membrane is assumed to be constant [1,2]. In this paper we remove this constant-field assumption and numerically solve the above-mentioned nonlinear equations to calculate the membrane potential.

We use a model for the potential distribution which assumes that each side of the membrane core is covered by a surface charge layer [7–9]. This model shows that the potential diffuses over a distance of the order of $1/\kappa$ on both sides of the surface charge layer/solution boundary and that the potential far inside the surface charge layer is in practice equal to the Donnan potential, provided that the surface layer thickness $\gtrsim 1/\kappa$. In this paper we take into account the above-mentioned diffusive structure of the potential distribution across a membrane and examine how these membrane boundary potentials contribute to the membrane potential and are related to each other.

2. Theory

Imagine the stationary flow of electrolyte ions across a membrane separating two solutions I and

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II which contain a uni-univalent symmetrical electrolyte at different concentrations n_{I} and n_{II}, respectively. We employ a membrane model [7,9] in which each side of the membrane core of thickness d_c is covered by a surface charge layer of thickness d_s. In this layer membrane-fixed negative charges are assumed to be distributed at a uniform density N. We take the x-axis perpendicular to the membrane with its origin at the boundary between the left surface charge layer and the membrane core (fig. 1). The potential in the bulk phase of solution II is put equal to zero. The potential in bulk solution I is thus equal to the membrane potential, which we denote by E_{m}.

Consider first the regions $x < 0$ and $x > d_c$. We assume that the distribution of electrolyte ions in the surface charge layer and in solutions I and II is scarcely affected by ionic flows so that it is in practice at thermodynamic equilibrium. Accordingly, the potential $\psi(x)$ in these regions is given by the Poisson-Boltzmann equations, viz.,

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = \frac{2en_{\mathrm{I}}}{\epsilon_r\epsilon_0}\sinh\frac{e(\psi - E_{\mathrm{m}})}{kT},\quad x < -d_s, \tag{1}$$

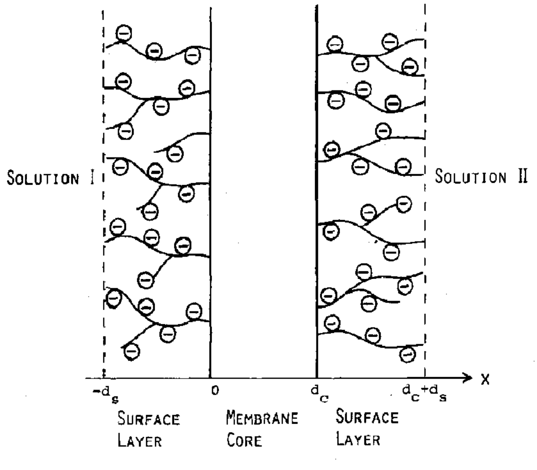

Fig. 1. Model for a charged membrane. The membrane core (of thickness d_c) is covered by a surface charge layer (of thickness d_s). The membrane-fixed charges are assumed to be negative and are encircled.

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = \frac{2en_{\mathrm{I}}}{\epsilon_r\epsilon_0}\sinh\frac{e(\psi - E_{\mathrm{m}})}{kT} + \frac{eN}{\epsilon_r\epsilon_0},\quad -d_s < x < 0, \tag{2}$$

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = \frac{2en_{\mathrm{II}}}{\epsilon_r\epsilon_0}\sinh\frac{e\psi}{kT} + \frac{eN}{\epsilon_r\epsilon_0},\quad d_c > x > d_c + d_s, \tag{3}$$

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = \frac{2en_{\mathrm{II}}}{\epsilon_r\epsilon_0}\sinh\frac{e\psi}{kT},\quad x > d_c + d_s, \tag{4}$$

where ϵ_r is the relative permittivity of solutions I and II, ϵ_0 the permittivity of a vacuum, e the elementary electric charge, k Boltzmann's constant, and T the absolute temperature.

Consider next the region $0 < x < d_c$ (i.e., the membrane core). We regard this region as a different phase from the surrounding solution phase and introduce the ionic partition coefficients between the membrane core and the solution phase. We denote by b_+ and b_-, respectively, the partition coefficients for cations and anions. The electric potential $\psi(x)$ in this region is given by the following Poisson equation:

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -\frac{e}{\epsilon_r'\epsilon_0}\{n_+(x) - n_-(x)\},\quad 0 < x < d_c, \tag{5}$$

where $n_+(x)$ and $n_-(x)$ are the respective concentrations of cations and anions at position x $(0 < x < d_c)$ and ϵ_r' the relative permittivity of the membrane core. The flows of cations and anions, denoted by J_+ and J_-, respectively, can be expressed as

$$J_\pm = -D_\pm\left[\frac{\mathrm{d}n_\pm}{\mathrm{d}x} \pm \frac{n_\pm e}{kT}\frac{\mathrm{d}\psi}{\mathrm{d}x}\right], \tag{6}$$

where D_+ and D_- are the diffusion coefficients of cations and anions, respectively, in the membrane core. In the stationary state, $\operatorname{div} J_\pm = \mathrm{d}J_\pm/\mathrm{d}x = 0$ and the net electric current must be zero in the absence of external field so that

$$J_+ = J_- = \text{constant (independent of } x\text{)}. \tag{7}$$

The boundary conditions for $\psi(x)$ are

$$\psi(x) \xrightarrow[x \to +\infty]{} 0, \tag{8}$$

$$\psi(x)\xrightarrow[x\to-\infty]{}E_{\mathrm{m}}, \tag{9}$$

$$\psi(-d_{\mathrm{s}}-0)=\psi(-d_{\mathrm{s}}+0), \tag{10}$$

$$\psi(-0)=\psi(+0), \tag{11}$$

$$\psi(d_{\mathrm{c}}-0)=\psi(d_{\mathrm{c}}+0), \tag{12}$$

$$\psi(d_{\mathrm{c}}+d_{\mathrm{s}}-0)=\psi(d_{\mathrm{c}}+d_{\mathrm{s}}+0), \tag{13}$$

$$\left.\frac{\mathrm{d}\psi}{\mathrm{d}x}\right|_{-d_{\mathrm{s}}-0}=\left.\frac{\mathrm{d}\psi}{\mathrm{d}x}\right|_{-d_{\mathrm{s}}+0}, \tag{14}$$

$$\epsilon_{\mathrm{r}}\left.\frac{\mathrm{d}\psi}{\mathrm{d}x}\right|_{-0}=\epsilon'_{\mathrm{r}}\left.\frac{\mathrm{d}\psi}{\mathrm{d}x}\right|_{+0}, \tag{15}$$

$$\epsilon'_{\mathrm{r}}\left.\frac{\mathrm{d}\psi}{\mathrm{d}x}\right|_{d_{\mathrm{c}}-0}=\epsilon_{\mathrm{r}}\left.\frac{\mathrm{d}\psi}{\mathrm{d}x}\right|_{d_{\mathrm{c}}+0}, \tag{16}$$

$$\left.\frac{\mathrm{d}\psi}{\mathrm{d}x}\right|_{d_{\mathrm{c}}+d_{\mathrm{s}}-0}=\left.\frac{\mathrm{d}\psi}{\mathrm{d}x}\right|_{d_{\mathrm{c}}+d_{\mathrm{s}}+0}. \tag{17}$$

The boundary conditions for $n_+(x)$ and $n_-(x)$ are

$$n_\pm(+0)=b_\pm n_\pm(-0), \tag{18}$$

$$n_\pm(d_{\mathrm{c}}-0)=b_\pm n_\pm(d_{\mathrm{c}}+0), \tag{19}$$

where $n_\pm(-0)$ and $n_\pm(d_{\mathrm{c}}+0)$ are given by

$$n_\pm(-0)=n_{\mathrm{I}}\exp(\mp e\{\psi(-0)-E_{\mathrm{m}}\}/kT), \tag{20}$$

$$n_\pm(d_{\mathrm{c}}+0)=n_{\mathrm{II}}\exp(\mp e\psi(d_{\mathrm{c}}+0)/kT). \tag{21}$$

The solution of coupled equations, eqs. 1–7, subject to the boundary conditions, eqs. 8–19, determines the whole potential profile across a membrane.

3. Results and discussion

An example of the numerical calculation for several values of N (expressed in M) is given in figs. 2 and 3. We have used the following typical numerical values: $n_{\mathrm{I}}=0.01$ M, $n_{\mathrm{II}}=0.1$ M, $\epsilon_{\mathrm{r}}=78.5$, $\epsilon'_{\mathrm{r}}=2$, $d_{\mathrm{c}}=d_{\mathrm{s}}=50$ Å, $D_+/D_-=2$, $b_\pm=10^{-3}$ and $T=298$ K.

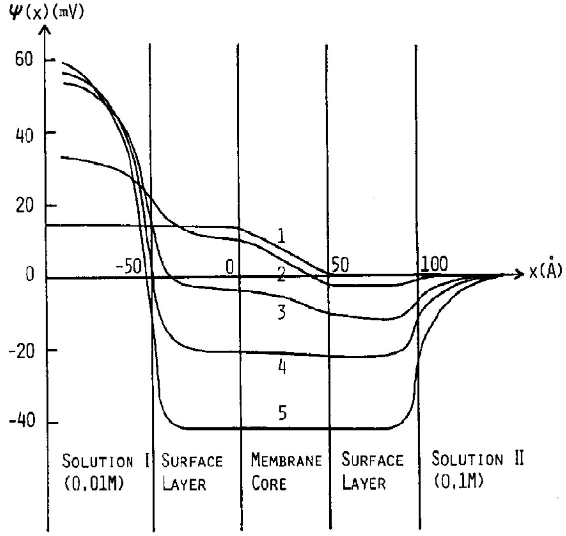

Fig. 2. Potential distribution $\psi(x)$ across a membrane in the stationary state for several values of the density of the membrane-fixed charges N. Curve: (1) $N=0.0005$ M, (2) $N=0.02$ M, (3) $N=0.1$ M, (4) $N=0.2$ M, (5) $N=0.5$ M. Calculated when $n_{\mathrm{I}}=0.01$ M, $n_{\mathrm{II}}=0.1$ M, $d_{\mathrm{s}}=d_{\mathrm{c}}=50$ Å, $b_\pm=0.001$, $\epsilon_{\mathrm{r}}=78.5$, $\epsilon'_{\mathrm{r}}=2$ and $T=298$ K.

As fig. 2 shows, the potential diffuses at the boundaries $x=-d_{\mathrm{s}}$, $x=0$, $x=d_{\mathrm{c}}$ and $x=d_{\mathrm{c}}+d_{\mathrm{s}}$. Note that the potential at the boundary between the surface charge layer and the solution (i.e., $\psi(-d_{\mathrm{s}})$ and $\psi(d_{\mathrm{c}}+d_{\mathrm{s}})$) is different from that far inside the surface charge layers. It follows from eqs. 2 and 3 that when $d_{\mathrm{s}}\gtrsim 1/\kappa_{\mathrm{I}}$, $1/\kappa_{\mathrm{II}}$, where $\kappa_{\mathrm{I}}=(2n_{\mathrm{I}}e^2/\epsilon_{\mathrm{r}}\epsilon_0 kT)^{1/2}$ and $\kappa_{\mathrm{II}}=(2n_{\mathrm{II}}e^2/\epsilon_{\mathrm{r}}\epsilon_0 kT)^{1/2}$ are the Debye-Hückel parameters of solutions I and II, respectively ($1/\kappa_{\mathrm{I}}\approx 30$ Å and $1/\kappa_{\mathrm{II}}\approx 10$ Å for $n_{\mathrm{I}}=0.01$ M and $n_{\mathrm{II}}=0.1$ M), the potential at points far away from the boundaries in the surface charge layer (where $\mathrm{d}^2\psi/\mathrm{d}x^2\approx 0$) relative to the bulk solution phase is effectively equal to the Donnan potential, which is, for the region $-d_{\mathrm{s}}<x<0$,

$$\psi^{\mathrm{I}}_{\mathrm{DON}}=-\frac{kT}{e}\operatorname{arcsinh}\left(\frac{N}{2n_{\mathrm{I}}}\right), \tag{22}$$

and for the region $d_{\mathrm{c}}<x<d_{\mathrm{c}}+d_{\mathrm{s}}$

$$\psi^{\mathrm{II}}_{\mathrm{DON}}=-\frac{kT}{e}\operatorname{arcsinh}\left(\frac{N}{2n_{\mathrm{II}}}\right). \tag{23}$$

In this case, by integrating eqs. 1–4 once and

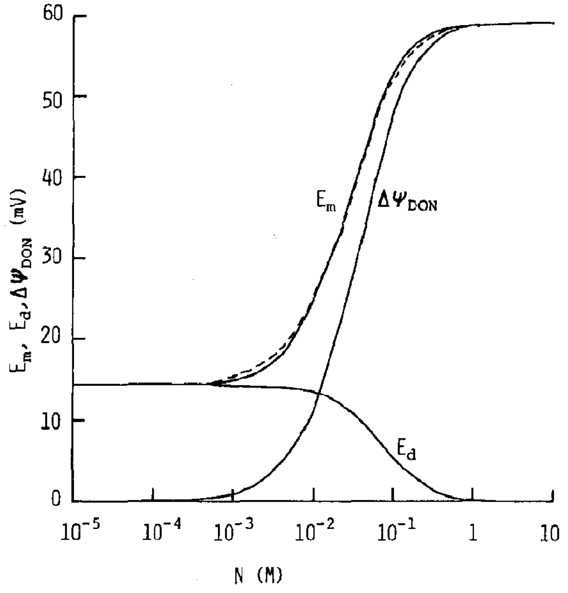

Fig. 3. Membrane potential E_m, contributions from the diffusion potential E_d and the Donnan potential difference $\Delta\psi_{DON} = \psi_{DON}^{II} - \psi_{DON}^{I}$ as functions of the density of membrane-fixed charges N. The values of the parameters used in the calculation are the same as those in fig. 2. The dashed line is the approximate result for E_m (eq. 29). As $N \to \infty$, E_m tends to the Nernst potential for cations (59 mV in the present case).

substituting the results into eqs. 14 and 17, we have

$$\psi(-d_s) = \psi_{DON}^{I} - \frac{kT}{e}\tanh\frac{e\psi_{DON}^{I}}{2kT} + E_m, \tag{24}$$

$$\psi(d_c + d_s) = \psi_{DON}^{II} - \frac{kT}{e}\tanh\frac{e\psi_{DON}^{II}}{2kT}, \tag{25}$$

which relate the membrane surface potentials $\psi(-d_s)$ and $\psi(d_c + d_s)$ to the Donnan potentials ψ_{DON}^{I} and ψ_{DON}^{II}. When the potential far inside the surface charge layer is effectively equal to the Donnan potential, the membrane potential can be expressed as

$$\begin{aligned} E_m = {} & [\psi(0) - \psi(d_c)] + [\psi_{DON}^{II} - \psi_{DON}^{I}] \\ & + [(\psi_{DON}^{I} + E_m - \psi(0)) \\ & - (\psi_{DON}^{II} - \psi(d_C))], \end{aligned} \tag{26}$$

where the first term enclosed by brackets on the right-hand side corresponds to the diffusion potential, the second to the contribution from the Donnan potentials in the surface charge layers, and the third to that from deviation in the boundary potentials at $x = 0$ and $x = d_c$ due to the ionic flows. The contribution from the third term is normally very small so that the diffusion potential E_m can practically be regarded as arising from the diffusion potential and the Donnan potential. Note that the Donnan potentials (eqs. 22 and 23) are independent of the surface layer thickness d_s and therefore the membrane potential depends little on d_s, provided that $d_s \gtrsim 1/\kappa_I$, $1/\kappa_{II}$.

Fig. 2 (in which the potential far inside the surface layer is almost equal to the Donnan potential) shows how the contributions from the diffusion potential and from the Donnan potential change with density N of the membrane-fixed charges. For very low N the potential in the surface charge layer differs little from that in the bulk solution phase (the Donnan potential itself is very small) and the membrane potential is due mostly to the potential gradient in the membrane core. In other words, the membrane potential is almost equal to the diffusion potential. As N is increased, however, the potential gradient in the membrane core becomes small, which means that the contribution from the diffusion potential decreases. Instead, the potential difference between the surface charge layer and the surrounding solution becomes appreciable and the membrane potential for very large N is determined almost solely by this potential difference in each surface charge layer. As stated before, this potential difference is in practice equal to the Donnan potential in each surface charge layer if $d_s \gtrsim 1/\kappa_I$, $1/\kappa_{II}$ so that the membrane potential E_m for large N is expressed as

$$\begin{aligned} E_m & \approx \psi_{DON}^{II} - \psi_{DON}^{I} \\ & = \frac{kT}{e}\ln\left[\frac{N/2n_I + \{(N/2n_I)^2 + 1\}^{1/2}}{N/2n_{II} + \{(N/2n_{II})^2 + 1\}^{1/2}}\right]. \end{aligned} \tag{27}$$

To illustrate more clearly the above-mentioned N dependence, we have displayed in fig. 3 the contributions from the diffusion and Donnan potentials to the membrane potential as a function of N.

The decrease of the contribution from the diffusion potential with increasing N can be explained as follows. For large N, i.e., for the case where the surface layers are highly negatively charged, co-ions (i.e., anions) are repelled by the membrane so that the membrane is in practice impermeable to co-ions and their flow within the membrane, J_-, decreases. Since the net electric current must be zero ($J_+ - J_- = 0$), the flow of counterions (i.e., cations), J_+, must decrease to the same extent as J_-. That is, all ionic flows decrease, resulting in a smaller diffusion potential. In the limit of $N \to \infty$, the membrane becomes fully impermeable to anions and an equilibrium is reached with respect to cations so that the membrane potential tends to the Nernst potential for cations, viz.,

$$E_\mathrm{m} \xrightarrow[N \to \infty]{} \frac{kT}{e} \ln\left(\frac{n_\mathrm{II}}{n_\mathrm{I}}\right), \tag{28}$$

which is obtained by taking the limit $N \to \infty$ in eq. 27. In this limit, the membrane behaves like a semipermeable membrane (permeable to cations only). Note that eq. 28 also holds when $b_- \to 0$, irrespective of the value of N.

As shown in fig. 2, the potential gradient in the membrane core is slightly concave (see curve 3, in particular). However, deviation from linearity is seen to be small in fig. 2. This means that the usual assumption of constant field within the membrane is not a bad approximation. If we employ this approximation, eq. 6 can easily be integrated in the following two limiting cases. When $d_\mathrm{s} \gtrsim 1/\kappa_\mathrm{I}$, $1/\kappa_\mathrm{II}$, in which case the potential far inside the membrane surface layer is in practice the Donnan potential, the constant-field assumption yields [3]

$$E_\mathrm{m} = \frac{kT}{e} \ln\left[\frac{P_+ n_\mathrm{II} e^{-e\psi^\mathrm{II}_\mathrm{DON}/kT} + P_- n_\mathrm{I} e^{e\psi^\mathrm{I}_\mathrm{DON}/kT}}{P_+ n_\mathrm{I} e^{-e\psi^\mathrm{I}_\mathrm{DON}/kT} + P_- n_\mathrm{II} e^{e\psi^\mathrm{II}_\mathrm{DON}/kT}}\right] + \psi^\mathrm{II}_\mathrm{DON} - \psi^\mathrm{I}_\mathrm{DON}, \tag{29}$$

with

$$P_\pm = b_\pm D_\pm / d_\mathrm{c}, \tag{30}$$

where P_+ and P_- are the permeabilities of cations and anions, respectively. The approximate result calculated from eq. 29 is plotted in fig. 3 in comparison with the exact numerical results. A good agreement is obtained; the relative error is less than a few percent. On the other hand, in the limit $d_\mathrm{s} \to 0$ with Nd_s kept constant, we can then obtain the following formula [5,6]:

$$E_\mathrm{m} = \frac{kT}{e} \ln\left[\frac{P_+ n_\mathrm{II} e^{-e\psi^\mathrm{II}_\mathrm{s}/kT} + P_- n_\mathrm{I} e^{e\psi^\mathrm{I}_\mathrm{s}/kT}}{P_+ n_\mathrm{I} e^{-e\psi^\mathrm{I}_\mathrm{s}/kT} + P_- n_\mathrm{II} e^{e\psi^\mathrm{II}_\mathrm{s}/kT}}\right] + \psi^\mathrm{II}_\mathrm{s} - \psi^\mathrm{I}_\mathrm{s}, \tag{31}$$

where

$$\psi^\mathrm{I}_\mathrm{s} = \frac{2kT}{e} \operatorname{arcsinh}\left[\frac{\sigma}{(8 n_\mathrm{I} \epsilon_\mathrm{r} \epsilon_0 kT)^{1/2}}\right], \tag{32}$$

$$\psi^\mathrm{II}_\mathrm{s} = \frac{2kT}{e} \operatorname{arcsinh}\left[\frac{\sigma}{(8 n_\mathrm{II} \epsilon_\mathrm{r} \epsilon_0 kT)^{1/2}}\right]. \tag{33}$$

Eqs. 32 and 33 are the familiar Gouy-Chapmann double-layer potential of the membrane surface with a surface charge density $\sigma = -eNd_\mathrm{s}$.

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