Nonequilibrium Properties of Weak Ion Exchange Membranes

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(Z. Naturforsch. **32 a**, 1344 – 1352 [1977]; received August 1, 1977)

The behaviour of a membrane with a low concentration of fixed charges in a constant external electric field is considered. The stationary flows, the concentration curves and the electric field are calculated for a system which has different concentrations on both sides of the membrane. The starting point of the calculation are the generalized Nernst-Planck equations which are deduced microscopically. Using a perturbation approach a solution to these equations is given. With this result the influence of fixed charges, of friction between the ions and the membrane and of the difference in concentrations can be discussed.

1. Problem

Flows in one-dimensional model of a membrane are considered in the steady state. The membrane extends in $y-z$ direction. This extension is much larger than the thickness of the membrane. The properties of the membrane do not depend on the x, y and z coordinates. The system consists of a membrane (phase $*$), two diffusion layers [phase $(')$ and $('')$] and two large homogeneous phases (see Figure 1). The thickness of the membrane is $2\,\delta$ and the thickness of a diffusion layer is $\mathrm{d}-\delta$. In the following calculations this thickness can be chosen independantly so that it can be matched to the experimental values. In the large homogeneous phases there are electrodes which can produce an external field. We only consider binary electrolytes of low concentration. There can be a difference of concentration between the two external phases. The membrane can have fixed charges so that there are different interactions.

There are electrical interactions between ions and fixed charges. Furthermore we have friction between ions and water (or another solvent) and friction between ions and the membrane. In the diffusion layers there is only friction between ions and solvent. These interactions produce the characteristic concentration curves and the electric field in the membrane.

The system is mathematically described by the generalized Nernst-Planck equations as deduced microscopically by Schröter[1] and West[1, 2]. They can be solved for this simple model of membrane.

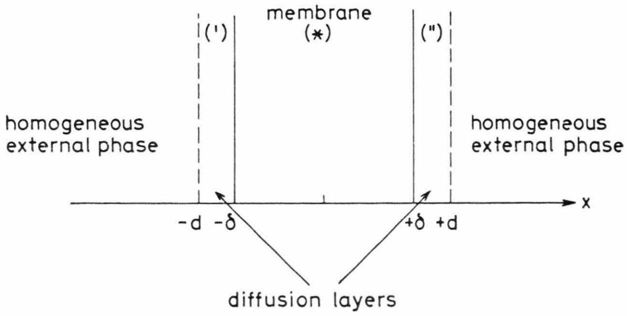

Fig. 1. Scheme of the whole system.

An approximate nonequilibrium solution has been obtained for the special case of constant field and equal concentrations on both sides of the membrane[3]. Here the equations are solved for the case of a difference in concentration. Furthermore, we calculate the electric field which is formed in the system. With the curves of the electric field and the concentration we can interpret the flows completely.

2. Calculation of the Concentration Curves

2.1. The Generalized Nernst-Planck Equations

The generalized Nernst-Planck equations consist of one and two particle equations. For a one dimensional membrane model the one particle equations read

$$\partial_t w_\alpha + \partial_x (k\,T\,m_\alpha{}^{-1}\,n_\alpha - n_\alpha\,u^2 + 2\,w_\alpha\,u) - m_\alpha{}^{-1}\,e_\alpha\,n_\alpha\,E - m_\alpha{}^{-1} \sum_{\delta=1}^{M+1} \int n_{\alpha\delta}\,K^{\mathrm{x}}_{\alpha\delta}\,\mathrm{d}^3 r_\delta = \sum_{\delta=0}^{M+2} S_{\alpha\delta} \qquad (1)$$

with:

$\alpha = 1, \dots, M$ indicates the ions $1, \dots, M$,
$\alpha = 0$ indicates the solvent,

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$\alpha = M+1$	indicates the fixed charges of the membrane,
n_α	density of particle α,
$n_{\alpha\beta}$	two-particle density,
u_α	average velocity of particle α,
u	average velocity,
E	external field,
$K^x_{\alpha\delta} = -\partial_x \psi_{\alpha\delta}$	x-component of the interaction of α and δ-particle,
$\varkappa_{\alpha\delta}$	friction coefficient for friction between an α-particle and a δ-particle,
$w_\alpha = n_\alpha u_\alpha$	flow of particle α,

$S_{\alpha\delta} = \varkappa_{\alpha\delta}\, m_\delta\, (n_\alpha w_\delta - n_\delta w_\alpha)$.

For the calculation of $n_{\alpha\delta}$ we need the two-particle equation which is not written down here because $n_{\alpha\delta}$ enters (1) in a very simple way if the following perturbation approach is used.

2.2. The Perturbation Approach

In [3] the one-particle equations were solved using a perturbation approach. The following restrictions were made:

1. We only consider stationary flows.
2. We only consider a binary symmetric electrolyte.
3. The concentration of electrolyte is low.
4. We only consider Coulomb-interactions.
5. The interactions between moving particles and the membrane are low, i. e. the concentrations of the fixed charges and of the other membrane particles are low.
6. The dielectric constant is constant in the whole system (this follows from 3 and 5).
7. The temperature is constant in the whole system and there is no pressure gradient.

The zeroth approach describes the homogeneous electrolyte. Then the first approach describes the influence of fixed charges, friction between ions and membrane and the correlations between positive and negative ions (see [3]).

The zeroth approach gives:

$$n_1{}^0 = n_2{}^0, \quad u_\alpha{}^0 = \frac{e_\alpha E}{m_\alpha m_0 n_0{}^0 \varkappa_{\alpha 0}},$$

e_α is the charge of particle α. The upper index indicates the order of the approach.

With the solution of the two-particle equation the first approach of the one-particle equation is (see [3]):

$$\begin{aligned}(e_\alpha E + m_\alpha \xi_\alpha u_0{}^0)\, n_\alpha{}^1 - k T\, \partial_x n_\alpha{}^1 &\\ - n_\alpha{}^0 e_\alpha \Big[\int n_3{}^1 e_3\, \partial_x \tilde{\psi}\, \mathrm{d}^3 r_3 + \sum_{\delta=1,2} \int n_\delta{}^1 e_\delta\, \partial_x \tilde{\psi}\, \mathrm{d}^3 r_\delta\Big] &\\ = m_\alpha \xi_\alpha w_\alpha{}^1 + m_\alpha \mu_\alpha E + \sum_{\delta=3,4} m_\alpha \xi_{\alpha\delta} w_\alpha{}^0 & \qquad (2)\end{aligned}$$

with

$\alpha = 3$	fixed charge particles of membrane,
$\alpha = 4$	membrane particles without charges,
$\xi_\alpha = m_0 n_0{}^0 \varkappa_{\alpha 0}$	
$\xi_{\alpha\delta} = m_\delta n_\delta{}^1 \varkappa_{\alpha\delta}$	
ε	dielectric constant,
$\mu_\alpha = \dfrac{e_\alpha{}^3 n_\alpha{}^0 \varkappa}{24 \pi \varepsilon m_\alpha k T (1 + \sqrt{1/2})}$	correlation coefficient (see [3]),
$\varkappa^2 = \dfrac{2 e_\alpha{}^2 n_\alpha{}^0}{\varepsilon k T}$	where $\varkappa^{-1}$ is the Debye length,
$\psi_{\alpha\delta} = e_\alpha e_\delta \tilde{\psi}$.	

2.3. The Differential Equations and their Solution

The differentiated form of (2) gives a system of differential equations. With

$$a = \frac{e_1 E}{k T},$$

$$b = \frac{1}{\varepsilon k T} n_1{}^0 e_1{}^2 = \tfrac{1}{2} \varkappa^2,$$

$$c = \frac{1}{\varepsilon k T} n_1{}^0 e_1 e_3 n_3{}^1(0),$$

$$\sigma(x) = \begin{cases} 1 & x \in [-\delta, \delta] \\ 0 & x \notin [-\delta, \delta], \end{cases}$$

the differentiation of (2) gives:

$$\begin{aligned} a\, \partial_x n_1{}^1 - \Delta n_1{}^1 + c\, \sigma + b\, (n_1{}^1 - n_2{}^1) &= 0, \\ - a\, \partial_x n_2{}^1 - \Delta n_2{}^1 - c\, \sigma - b\, (n_1{}^1 - n_2{}^1) &= 0. \qquad 2\text{ a)} \end{aligned}$$

Let be

$$\lambda^2 = a^2 + 2 b,$$

$$B_1 = A_1 \left(\frac{a \lambda}{b} - \frac{\lambda^2}{b} + 1 \right),$$

$$B_2 = A_2 \left(- \frac{a \lambda}{b} - \frac{\lambda^2}{b} + 1 \right),$$

$$B_3 = \frac{a}{b} A_4 + A_3 + \frac{c}{b},$$

then the solution of (2 a) has the form:

$$\begin{aligned} n_1{}^1(x) &= A_1 e^{\lambda x} + A_2 e^{-\lambda x} + A_3 + A_4 x, \\ n_2{}^1(x) &= B_1 e^{\lambda x} + B_2 e^{-\lambda x} + B_3 + A_4 x \qquad (3) \end{aligned}$$

where in the diffusion layers the constant c has to be replaced by zero.

We assume that the large outer phases are homogeneous (stirred phases). Also there is no difference of concentration between positive and negative ions. Then we get the boundary conditions

$$\begin{aligned} n_1{}^1(+d) &= n_2{}^1(+d) = \Theta'' , \\ n_1{}^1(-d) &= n_2{}^1(-d) = \Theta' . \end{aligned} \tag{4}$$

The mathematical problem is now to calculate the 12 constants A_i', A_i^*, A_i'' and the flows w_1 and w_2. Equations (4) give 4 equations. The concentration is continuous at the edges of the membrane (see [3]), so that we get 4 equations too (see [3]).

If we put the solution (3) into the original differential equation (2), we get two more equations for each phase. With $\Theta' - \Theta'' = 2f$ we get:

$$\begin{aligned} A_4{}^* &= -\frac{b}{\lambda^2}(C_1{}^* + C_2{}^*) - \frac{a\,c}{\lambda^2} - \frac{\gamma}{d} f , \\ A_4' = A_4'' &= -\frac{b}{\lambda^2}(C_1 + C_2) - \frac{\gamma}{d} f , \end{aligned} \tag{5}$$

$$\begin{aligned} a A_3' - A_4' - a\,\delta(A_4' - A_4{}^*) &- \frac{\lambda - a}{2} \\ \cdot [A_1'(e^{-\lambda d} + e^{-\lambda\delta}) &+ A_1{}^*(e^{\lambda\delta} - e^{-\lambda\delta}) \\ + A_1''(e^{\lambda d} - e^{\lambda\delta})] &+ \frac{\lambda + a}{2}[A_2'(e^{\lambda d} + e^{\lambda\delta}) \\ + A_2{}^*(e^{-\lambda\delta} - e^{\lambda\delta}) &+ A_2''(e^{-\lambda d} - e^{-\lambda\delta})] = C_1 , \end{aligned}$$

$$\begin{aligned} a A_3'' - A_4' + a\,\delta(A_4' - A_4{}^*) &+ \frac{\lambda - a}{2} \\ \cdot [A_1'(e^{-\lambda\delta} - e^{-\lambda d}) &+ A_1{}^*(e^{\lambda\delta} - e^{-\lambda\delta}) \\ - A_1''(e^{\lambda\delta} + e^{\lambda d})] &- \frac{\lambda + a}{2}[A_2'(e^{\lambda\delta} - e^{\lambda d}) \\ + A_2{}^*(e^{-\lambda\delta} - e^{\lambda\delta}) &- A_2''(e^{-\lambda\delta} + e^{-\lambda d})] = C_1 , \end{aligned}$$

$$\begin{aligned} a A_3{}^* - A_4{}^* &- \frac{\lambda - a}{2}[A_1'(e^{-\lambda d} - e^{-\lambda\delta}) \\ &+ A_1{}^*(e^{-\lambda\delta} + e^{\lambda\delta}) + A_1''(e^{\lambda d} - e^{\lambda\delta})] + \frac{\lambda + a}{2} \\ &\cdot [A_2'(e^{\lambda d} - e^{\lambda\delta}) + A_2{}^*(e^{\lambda\delta} + e^{-\lambda\delta}) \\ &+ A_2''(e^{-\lambda d} - e^{-\lambda\delta})] = C_1 + \Delta_1 , \end{aligned} \tag{6}$$

with:

$$C_\alpha = \frac{1}{kT}(m_\alpha \xi_\alpha w_\alpha{}^1 + m_\alpha \mu_\alpha E) , \quad C_\alpha{}^* = C_\alpha + \Delta_\alpha ,$$

$$\Delta_\alpha = \frac{m_\alpha \xi_\alpha{}^* w_\alpha{}^0}{kT} , \quad \text{where} \quad \xi_\alpha{}^* = \sum_{\delta=3}^{4} \xi_{\alpha\delta} .$$

We can now calculate the A_i', A_i'', A_i^*. With these coefficients we can calculate the concentration curves [from Eq. (3)] and the flows [from Eq. (2)].

2.4. Calculation of the Concentration Curves

We make a restriction about the thickness of the membrane δ and the diffusion layers $d - \delta$:

$$e^{\lambda d} \gg e^{\lambda\delta} \gg e^{-\lambda\delta} \gg e^{-\lambda d} .$$

For the considered concentrations and ion exchange membranes this is a very weak restriction, because λ^{-1} is always smaller than the Debye length $\varkappa^{-1}$ ($\varkappa^{-1}$ ca. 10^{-8} m for $n_1{}^0 = 1\ \text{mol m}^{-3}$).

In [3] the calculation has been done for the special case $\Theta' = \Theta'' = 0$, i. e. the case of equal concentration on both sides of the membrane. Here the calculation has been done for the case of a difference in concentration.

We then get:

$$\begin{aligned} A_1' e^{-\lambda\delta} &= +\frac{\lambda + a}{2\lambda^2}\Delta_1 - \frac{c}{2\lambda^2} - \frac{1}{2\lambda} C_3 , \\ A_2' e^{\lambda d} &= \frac{\lambda - a}{2a}\left(\frac{a}{\lambda^2} C_1 + \delta(1-\gamma) C_3\right) + \frac{\delta}{2\lambda d} C_3 \gamma \\ &\quad - \frac{\lambda - a}{2a} f\left(1 - \gamma - \frac{a}{2db}\gamma\right) - \frac{\gamma}{2\lambda d} f , \\ A_1'' e^{\lambda d} &= -\frac{\lambda + a}{2a}\left(\frac{a}{\lambda^2} C_1 - \delta(1-\gamma) C_3\right) - \frac{\delta}{2\lambda d} C_3 \gamma \\ &\quad - \frac{\lambda + a}{2a} f\left(1 - \gamma + \frac{a}{2db}\gamma\right) + \frac{\gamma}{2\lambda d} f , \\ A_2'' e^{-\lambda\delta} &= -\frac{\lambda - a}{2\lambda^2}\Delta_1 - \frac{c}{2\lambda^2} + \frac{1}{2\lambda} C_3 , \\ A_1{}^* e^{\lambda\delta} &= +\frac{\lambda + a}{2a}\left(\frac{c}{\lambda^2} - \frac{a}{\lambda^2}\Delta_1\right) + \frac{1}{2\lambda}\left(C_3 - \frac{c}{a}\right) , \\ A_2{}^* e^{\lambda\delta} &= -\frac{\lambda - a}{2a}\left(\frac{c}{\lambda^2} - \frac{a}{\lambda^2}\Delta_1\right) - \frac{1}{2\lambda}\left(C_3 - \frac{c}{a}\right) , \\ A_3' &= \frac{a}{\lambda^2} C_1 + \delta C_3 + \frac{a\gamma}{2db} f , \\ A_3'' &= \frac{a}{\lambda^2} C_1 - \delta C_3 + \frac{a\gamma}{2db} f , \\ A_3{}^* &= \frac{a}{\lambda^2} C_1 - \frac{c}{\lambda^2} + \frac{a}{\lambda^2}\Delta_1 + \frac{a\gamma}{2db} f , \\ A_4' &= \frac{\delta}{d} C_3 \gamma - \frac{\gamma}{d} f , \\ A_4{}^* &= \frac{\delta}{d} C_3 \gamma - C_3 - \frac{\gamma}{d} f , \end{aligned} \tag{7}$$

with

$$C_1 = -\frac{\delta\lambda^2}{2db} C_3 \gamma ,$$

$$C_3 = \frac{b}{\lambda^2}\,(\Delta_1 + \Delta_2) + \frac{a\,c}{\lambda^2} \equiv A_4{}' - A_4{}^* \,,$$

$$\gamma = \frac{1}{1 + a^2/2\,\lambda\,d\,b}\,.$$

The calculation for the flows gives:

$$\begin{aligned} w_1 = w_1{}^0 &- \frac{\delta}{2\,d}\,\frac{e_1\,\gamma}{m_1\,\xi_1\,b}\,c\,E - \frac{\mu_1}{\xi_1}\,E - \frac{\delta}{2\,d}\,\frac{\gamma}{m_1\,\xi_1} \\ &\cdot (m_1\,\xi_1{}^*\,w_1{}^0 + m_2\,\xi_2{}^*\,w_2{}^0) + \frac{k\,T}{m_1\,\xi_1}\,\frac{f}{d}\,\frac{\gamma}{1 + a^2/\lambda^2}\,, \\ w_2 = w_2{}^0 &- \frac{\delta}{2\,d}\,\frac{e_1\,\gamma}{m_2\,\xi_2\,b}\,c\,E - \frac{\mu_2}{\xi_2}\,E - \frac{\delta}{2\,d}\,\frac{\gamma}{m_2\,\xi_2} \\ &\cdot (m_1\,\xi_1{}^*\,w_1{}^0 + m_2\,\xi_2{}^*\,w_2{}^0) + \frac{k\,T}{m_2\,\xi_2}\,\frac{f}{d}\,\frac{\gamma}{1 + a^2/\lambda^2}\,. \end{aligned} \tag{8}$$

3. Calculation of the Electric Field in the Membrane and in the Diffusion Layers

In addition to the constant outer field we have electric fields in the membrane and in the diffusion layers. We can calculate this field knowing the difference between the concentrations of the negative and positive charges:

$$\begin{aligned} E_i(x) &= e \int\limits_{-d}^{+d} \int\limits_{-\infty}^{+\infty} \left(n_1(x') - n_2(x') + \frac{e_3}{e}\, n_3\, \sigma(x') \right) \\ &\quad \cdot \partial_x\, \tilde{\psi}\, \mathrm{d}^3 r' \\ &= \frac{e}{2\,\varepsilon} \int\limits_{-d}^{+d} \left(n_1(x') - n_2(x') + \frac{e_3}{e}\, n_3\, \sigma(x') \right) \\ &\quad \cdot \operatorname{sgn}(x' - x)\, \mathrm{d}x'\,. \end{aligned} \tag{9}$$

By integrating we obtain (under the restriction of 2.4.):

in phase (′) (für $-\delta > x > -d$)

$$\begin{aligned} \frac{2\,\varepsilon\,b}{e}\,E_i(x) &= A_2{}'(\lambda + a)\,(e^{\lambda d} - 2\,e^{-\lambda x}) \\ &\quad + 2\,A_1{}'(\lambda - a)\,e^{\lambda x} - 2\,a\,A_4{}'(\delta + x) \\ &\quad + 2\,a\,A_4{}^*\,\delta - A_1{}''(\lambda - a)\,e^{\lambda d} \end{aligned}$$

in the membrane (für $+\delta \geqq x \geqq -\delta$)

$$\begin{aligned} \frac{2\,\varepsilon\,b}{e}\,E_i(x) &= A_2{}'(\lambda + a)\,e^{\lambda d} + 2\,A_1{}^*(\lambda - a)\,e^{\lambda x} \\ &\quad - 2\,A_2{}^*(\lambda + a)\,e^{-\lambda x} - 2\,a\,A_4{}^*\,x - \frac{2\,b}{\lambda^2}\,(\Delta_2 - \Delta_1) \\ &\quad - A_1{}''(\lambda - a)\,e^{\lambda d} \end{aligned}$$

in phase (″) (für $d > x > \delta$)

$$\begin{aligned} \frac{2\,\varepsilon\,b}{e}\,E_i(x) &= + A_2{}'(\lambda + a)\,e^{\lambda d} - 2\,a\,\delta\,A_4{}^* \\ &\quad - A_1{}''(\lambda - a)\,(e^{\lambda d} - 2\,e^{\lambda x}) - 2\,A_2{}''(\lambda + a)\,e^{-\lambda x} \\ &\quad + 2\,a\,A_4{}'(\delta - x)\,. \end{aligned} \tag{10}$$

An interpretation of the electric field is only useful if we regard the curves of concentration as well. This interpretation is made in the next chapter. Here we consider only the influence of the linear term in (10).

If the field is constant the flows are proportional to the number of ions. In the linear regions of concentration a constant field would give a different flow at every point x. If we have stationary flows the linear regions of concentration cannot be electrically neutral. We see this in Equation (3).

If we are in a diffusion layer c is equal to zero. In a linear region of concentration only the factors A_3 or A_4 can make a difference of concentration. We see that here the gradients of $n_1{}^1$ and $n_1{}^2$ are the same. But there is always a small constant difference of concentration $(a/b)\,A_4$. The resulting charges produce an electric field (see Figure 2). This linear field makes stationary flows possible.

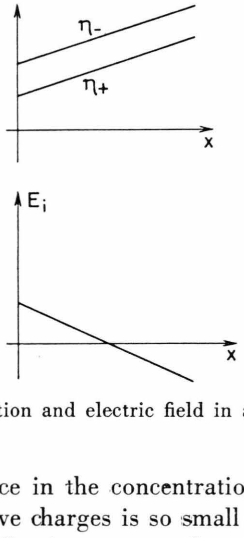

Fig. 2. Concentration and electric field in a linear region of concentration.

The difference in the concentrations of the positive and negative charges is so small that we cannot see it in the following curves of concentration, but it is big enough to produce an important electric field.

4. Discussion

The calculation of the coefficients A_i $(i = 1, \ldots, 4)$ shows that we can divide the results into 3 special cases, because these coefficients are linear in c, Δ_a,

f. So we can consider the following cases:

1. $c \neq 0, \quad \Delta_a = 0, \quad f = 0.$
   This case describes the influence of fixed charges.
2. $c = 0, \quad \Delta_a \neq 0, \quad f = 0.$
   This case describes the influence of friction between membrane and moving particles.
3. $c = 0, \quad \Delta_a = 0, \quad f \neq 0.$
   This case describes the influence of the difference of concentration.

The addition of these 3 cases is a solution for $c \neq 0$, $\Delta_a \neq 0$, $f \neq 0$.

4.1. Influence of Fixed Charges

We can compare the first case ($c \neq 0$, $\Delta_a = 0$, $f = 0$) with a membrane with fixed charges, but negligible friction between ions and membrane. In [3] this case has been discussed in detail, but without discussing the influence of the inner electric field E_i. Figure 3 shows the curves of electric field and concentration. We can calculate the electric field in the membrane from Eq. (10):

$$\frac{2\,\varepsilon\, b}{e}\, E_i(x) = +2\,A_1^*\,(\lambda - a)\, e^{\lambda x} - 2\,A_2^*\,(\lambda + a)\, e^{-\lambda x} - 2\,a\,A_4^*\,x\,. \qquad (11)$$

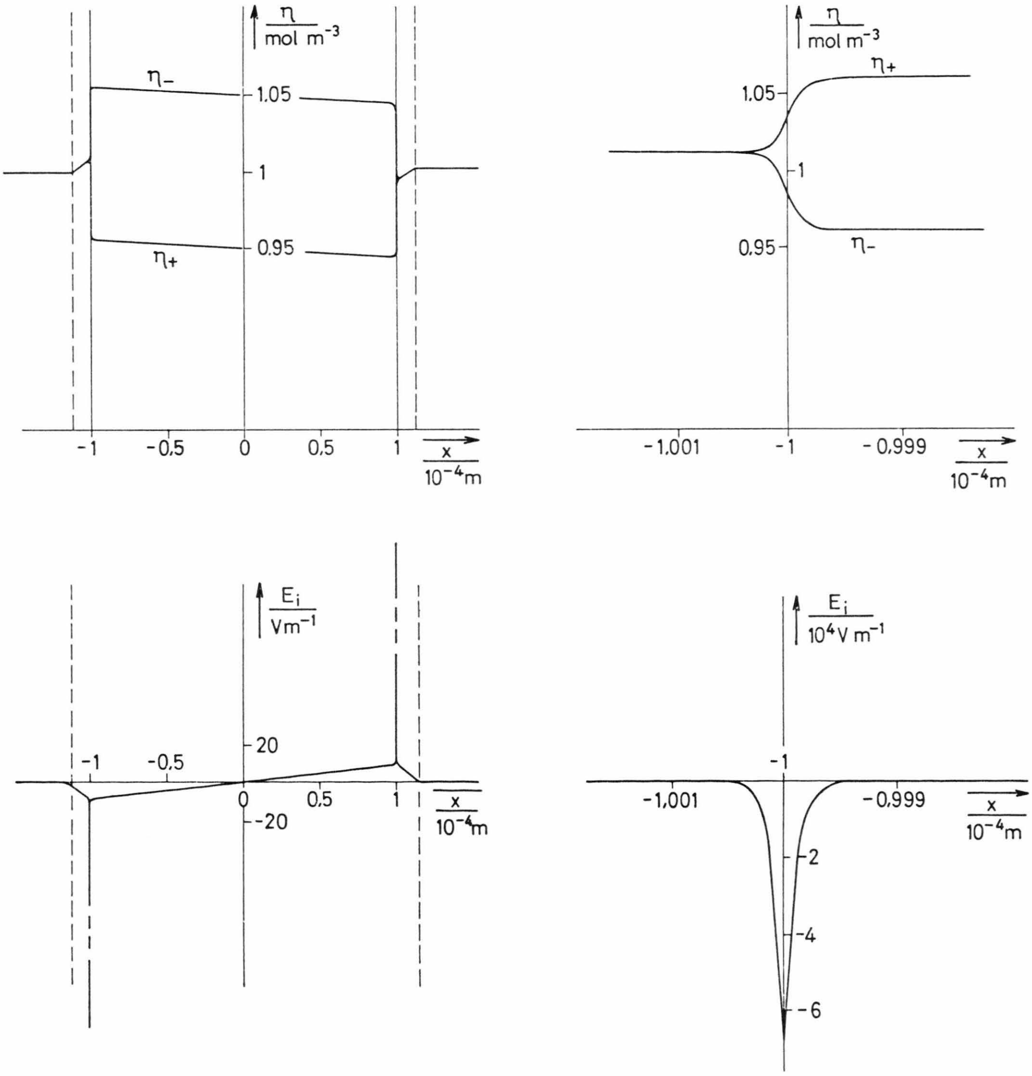

Fig. 3. Influence of fixed charges (0.1 mol/m³) on the concentration and on the electric field in a membrane system (thickness of the membrane: $2 \cdot 10^{-4}$ m, thickness of the diffusion layers: $2 \cdot 10^{-5}$ m). External field ca. 500 V/m. a) The whole system, b) the left edge of the membrane.

In the membrane the interpretation is easy because the charges of the phase (′) are compensated by the charges of the phase (″). Thus we have to discuss only three terms.

The first is non-negligible only at the right edge of the membrane. Here the electric field is exponential. This makes stationary flows possible in spite of the gradient of concentration. The second term of (11) does the same at the left edge of the membrane. Several Debye-length away from the edges of the membrane we can neglect the influence of the exponential terms in (11). We have only to consider the linear term. As mentioned above, this linear field is necessary for stationary flows. Without this the constant field E would produce different flows at each point x because the concentration of ions is not constant.

In Fig. 3 we can also see that the electric field E_i is very strong at the edges of the membrane. Here the field is similar to that in equilibrium, i. e. no outer field (see [4]).

4.2. Influence of Friction Between Membrane and Moving Particles

If we consider only the friction between the membrane and the moving ions we can calculate the

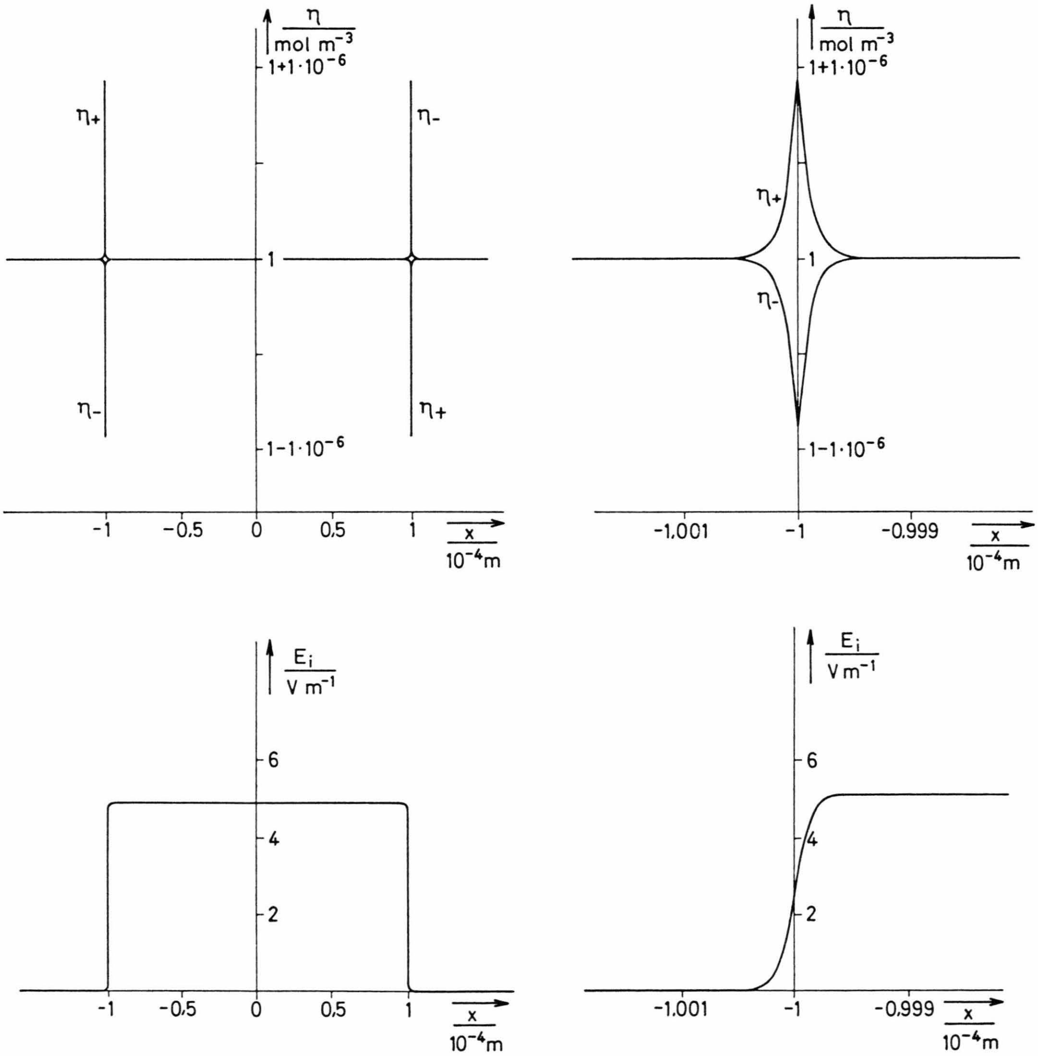

Fig. 4. Influence of friction between ions and membrane on the concentration and on the electric field. External field ca. 500 V/m; $\xi_1^*/\xi_1=\xi_2^*/\xi_2$. a) The whole system, b) the left edge of the membrane.

curves of concentration if we know the friction coefficients. But it is sufficient to know the quotients ξ_1^*/ξ_1 and ξ_2^*/ξ_2. So we have only to know the relation between the ion-water and the ion-membrane friction. First we consider the special case

$$\xi_1/\xi_1^* = \xi_2/\xi_2^* .$$

It follows that only the coefficients A_1', A_2'', A_1^*, A_2^* are not zero [see (7)]. If, in this case, we consider the electric field the interpretation is easy. There is a resulting charge at the edge of the membrane so that we have an electric field in the membrane. But the resulting charge of the left edge of the membrane compensates for the charge of the right edge so that there is no field in the diffusion layers. The electric field in the membrane supports the constant external field so that the ions can move as fast as they do in the diffusion layers in spite of the additional friction in the membrane.

The concentration is constant in the whole system except in the two regions of the edges of the membrane (see Figure 4).

We now consider another case which seems to be more interesting. In Fig. 5 we can see the concentra-

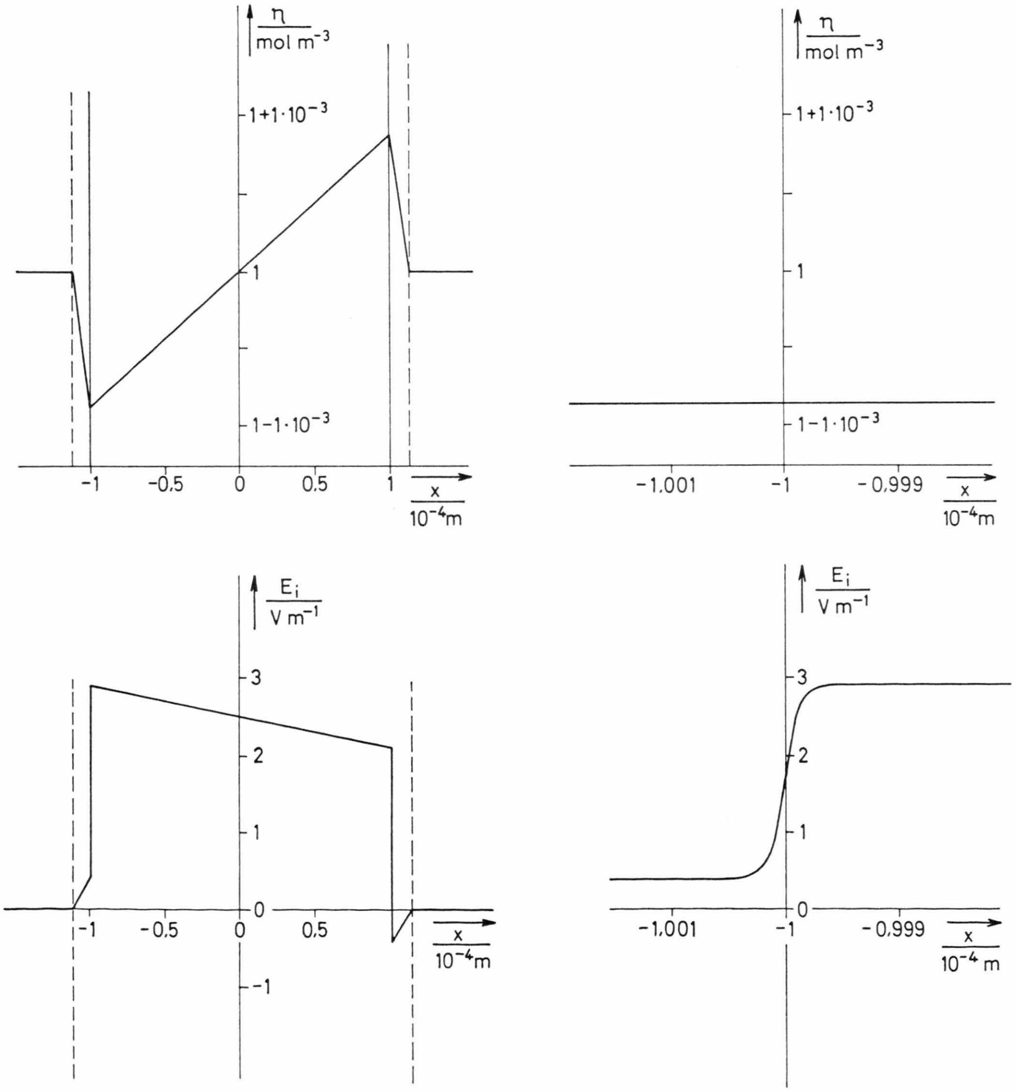

Fig. 5. Influence of friction between ions and membrane on the concentration and on the electric field. External field ca. 500 V/m; $\xi_1^*=0$, $\xi_2^*=0.01\,\xi_2$. a) The whole system, b) the left edge of the membrane.

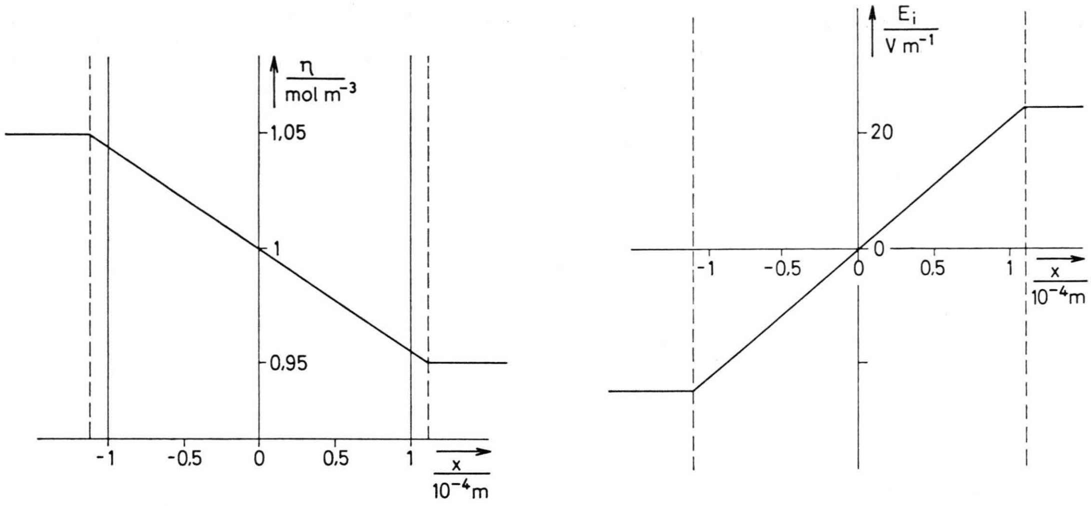

Fig. 6. Influence of the difference of concentration ($\Delta n = 0.1$ mol/m^3) on the concentration and on the electric field. External field ca. 500 V/m.

tion and electric field for $\xi_1^* = 0$; $\xi_2^* = 0.1\ \xi_2$. Between ion 1 and the membrane there is no friction and the friction of ion 2 with the membrane is high.

In the diffusion layers there is a concentration gradient which strengthens the flows of ion 1 and weakens the flow of ion 2. The concentrations of positive and negative ions are not equal so that an electric field is formed (see Chapter 4.1.). In the membrane there is a similar field because there is a concentration gradient. But there is also a constant field. This field and the concentration gradient speed up the ions 2. Combining these effects with the ion-membrane friction, we get a flow which is the same as in the diffusion layers. The effect of the electric field is stronger than the effect of the concentration gradient so that we get an amplified flow of ion 1. If we compare the flows with the case of no membrane friction we see that the flow of ion 2 gets smaller and the flow of ion 1 gets bigger due to the friction between the membrane and ion 2.

4.3. The Influence of Difference of Concentration

The difference of the concentration produces a constant concentration gradient in the membrane and in the diffusion layers (see Figure 6). As discussed in Chapter 4.1., there must be an electric field which is produced by different concentrations of negative and positive charges. This difference is so small (ca. 10^{-8} mol/m^3) that it cannot be seen in Figure 6. Here we can see the meaning of the coefficients A_2' and A_1''. The concentration of positive and negative ions are equal in the homogeneous regions. The exponential term in (3) cannot be neglected at the outer edges of the diffusion layers and this produces the small difference between the concentrations of the positive and negative ions.

4.4. Flow and Concentration without Electric Current

So far we have not considered the electric current. But, of course, there is always an electric current if the flows of positive and negative charges are not equal. There is a current in the system and through the electrodes and also in the outer system. Now we consider the case in which there is no electric current in the membrane. The flows must be equal, that is $w_1 = w_2$. Of course, there must be an outer electric field which produces this situation. We can calculate this field E_{D} by the condition $w_1 = w_2$:

$$E_{\mathrm{D}} = -\frac{f}{d}\,\frac{k\,T\,\dfrac{\gamma}{1+a^2/\lambda^2}\left(\dfrac{1}{m_1\,\xi_1}-\dfrac{1}{m_2\,\xi_2}\right)}{\left(\dfrac{1}{m_1\,\xi_1}+\dfrac{1}{m_2\,\xi_2}\right)(n_1^0\,e_1-m_1\,\mu_1)-\left(\dfrac{\delta e_1}{2\,d}\,\gamma\,n_1^0\left[\dfrac{\xi_1^*}{\xi_1}-\dfrac{\xi_2^*}{\xi_2}\right]+\dfrac{\delta}{2\,d}\,\dfrac{c\,e_1\,\gamma}{b}\right)\left(\dfrac{1}{m_1\,\xi_1}-\dfrac{1}{m_2\,\xi_2}\right)}\,. \tag{12}$$

We see that this condition is only possible if we have a difference of concentration. With the calculated E_D we now can calculate concentration curves by Eq. (7) and the flows by Equation (8).

The importance of this special case is that we can compare it with the case of no outer field. If we have a concentration difference and primarily no external field there will be produced an electric field by a flow of charges in the outer phases. A stationary state of the system is then only possible if the flows are equal, i. e. $w_1 = w_2$ (compare [5]). Only for this case can the outer field be constant. If the outer phases are large enough, the difference between the charge densities is very small so that the concentrations of positive and negative charges are nearly equal. In this case we can estimate the field by Equation (12).

4.5. Further Comments

In the preceding sections we did not ask the question: Which results can be proofed by experiments? Of course, it's nearly impossible to measure the curves of the concentration and the electric field in the membrane and especially at the edges of the membrane. So a possible proof of the theory can only be given by measuring the flows. By measuring the flows the friction coefficients $\xi_a{}^*$ can be determined. Knowing these coefficients a quantitative verification of Eqs. (8) is possible because the external field E and the difference of the concentration f can be varied independantly. Also the electric field E_D [Eq. (12)] can be measured easily and can be used as a quantitative verification of the theory. On the other hand, the main aim of this work was the calculation of the curves which are nearly impossible to measure. Only with these curves, i. e. the curves of the electric field and of the concentration, a complete interpretation of membrane-transport is possible.

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[1] G. West and J. Schröter, Ann. Physik. **32,** 19 [1975]; **32,** 33 [1975]; **32,** 227 [1975].

[2] G. West, Dissertation, Marburg 1974.

[3] J. Schröter and H.-P. Stormberg, Z. Naturforsch. **31 a,** 815 [1976].

[4] H.-P. Stormberg, Z Naturforsch. **31 a,** 1289 [1976].

[5] Schlögl, Stofftransport durch Membranen, Dr. Dietrich Steinkopff-Verlag, Darmstadt 1964.