Ion and Water Transport through Ion Exchange Membranes

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An ion exchange membrane system is considered in which the concentration of the membrane particles is low. With the help of a perturbation procedure the transport equations for ions and solvent, the so called generalized Nernst-Planck equations can be solved up to the first order. Prescribing concentration differences for the ions, a pressure difference and an electrical field as external conditions, the fluxes and densities of ions and solvent, and the pressure within the system are calculated.

1. The Problem

In two previous papers [1, 2] we treated a simple membrane system (cf. Fig. 1) with the help of the generalized Nernst-Planck equations derived by Schröter [3] and West [3, 4]. This treatment was characterized by a perturbation technique up to the first order and by restriction to external conditions where no water flow occurs.

In this paper the latter restriction is abandoned, i.e. we study the most general case of the simple membrane model within the framework of a perturbation approach. It turns out that our problem can be reduced to a certain extend to the problems of the previous papers [1, 2].

To be more specific, we restate here briefly the essential features of our model. The system consists of a membrane (phase $*$), too diffusion layers (phase $'$ and $''$), and two large homogeneous phases (see Figure 1). The system is assumed to extend largely in the direction of y and z, so that the properties of the inner phases depend only on x. The fluid part of the system is an electrolyte. The solid membrane may contain fixed charges.

The interaction between the charged particles of the system is a Coulomb force modified by a short range interaction. The other particles are assumed to interact by short range forces only. Besides these forces we have friction between ions, solvent (e.g. water) and membrane (cf. [3, 4]).

The external conditions are given by an electrical field produced by electrodes in the homogeneous phases and by diffrences of the pressure and the ion-concentrations between the homogeneous phases. Assuming the properties of the membrane to be given quantities, the interactions of the membrane with the other parts of the system can be regarded as external conditions.

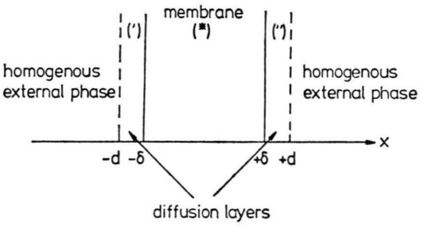

Fig. 1. Scheme of the whole system.

The aim of this paper is to calculate the fluxes of solvent and ions, and the spatial distributions of the pressure and the densities of ions. In order to do so, we treat the generalized Nernst-Planck equations for ions and solvent using again a perturbation approach similar to that of [1, 2].

2. The Generalized Nernst-Planck Equations

2.1. *Introduction of the Partial Pressures*

The generalized Nernst-Planck equations consist of one and two particle momentum equations. They form together with the continuity equations a complete set of equations for calculating the densities and the fluxes.

For a one dimensional membrane model the one particle equations read

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

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with

$\alpha = 1, \ldots, M$	indicating the ions $1, \ldots, M$,
$\alpha = 0$	indicating the water,
$\alpha = M + 1$	indicating the fixed charges of the membrane,
$\alpha = M + 2$	indicating the uncharged membrane particles,
n_α	density of particle α,
$n_{\alpha\beta} = n_\alpha n_\beta (1 + g_{\alpha\beta})$	two particle density,
$g_{\alpha\beta}$	correlation function,
u_α	average velocity of particle α,
u	barycentric velocity,
E	external field,
$K^x_{\alpha\delta}$	x-component of the interaction of α and δ-particle,
$\varkappa_{\alpha\delta}$	friction coefficient for friction between α-particle and δ-particle,
$w_\alpha = n_\alpha u_\alpha$	flow of particle α,
$S_{\alpha\delta} = \varkappa_{\alpha\delta} m_\delta (n_\alpha w_\delta - n_\delta w_\alpha)$.	

The one particle equations do not form a closed set. In order to calculate $n_{\alpha\delta}$ we need the two particle equations. Let us abbreviate the term which contains the correlation function $g_{\alpha\beta}$ by $J_{\alpha\beta}$, i.e.

$$J_{\alpha\beta} = \int n_\alpha n_\beta g_{\alpha\beta} K^x_{\alpha\beta} \, \mathrm{d}^3 r_\beta \, .$$

In the approximation used in this paper (see 3.1.) the $J_{\alpha\beta}$ do not depend on x. Thus we are left with the problem of solving the one particle momentum equations, the Nernst-Planck equations in the classical sense, and the continuity equations by a perturbation approach.

The momentum equations can be brought in a more appropriate form by the following considerations. The interaction term of Eq. (1) can be written in the form $K_{\alpha\delta} = k^{\mathrm{s}}_{\alpha\delta} + k^{\mathrm{c}}_{\alpha\delta}$, where $k^{\mathrm{s}}_{\alpha\delta}$ are short range forces. We suppose that the long range parts $k^{\mathrm{c}}_{\alpha\delta}$ are Coulomb forces. Their potentials are denoted by $\psi_{\alpha\delta}$. It can be shown that the sum of the interaction-integrals of the short range forces is the divergence of a symmetrical tensor $\boldsymbol{P}_\alpha{}^{\mathrm{s}}$ (see [4], page 95):

$$\sum_{\delta=0}^{M+2} \int n_{\alpha\delta} k^{\mathrm{s}}_{\alpha\beta} \, \mathrm{d}^3 r_\delta = - \partial_r \cdot \boldsymbol{P}_\alpha{}^{\mathrm{s}} \, . \tag{2}$$

A similar result holds for the Coulomb forces. However it is more adequate from a physical point of view not to write internal electrical fields as pressure tensors. Thus we define the partial pressure tensor $\boldsymbol{P}_\alpha$ by the short range interactions $\boldsymbol{P}_\alpha{}^{\mathrm{s}}$ and the kinetic term $kT \, n_\alpha \mathbf{1}$, i.e.

$$\boldsymbol{P}_\alpha = \boldsymbol{P}_\alpha{}^{\mathrm{s}} + kT \, n_\alpha \mathbf{1} \, . \tag{3}$$

In what follows, it is assumed that $\boldsymbol{P}_\alpha$ is diagonal: $\boldsymbol{P}_\alpha = p_\alpha \mathbf{1}$. The momentum equations, i.e. Eqs. (1) now read:

$$\begin{aligned} &\partial_t m_\alpha w_\alpha + \partial_x p_\alpha + \partial_x m_\alpha (2 w_\alpha u - n_\alpha u^2) \\ &- e_\alpha n_\alpha E + \sum_{\delta=1}^{M+1} \int n_{\alpha\delta} \, \partial_x \psi_{\alpha\delta} \, \mathrm{d}^3 r_\delta = m_\alpha \sum_{\delta=0}^{M+2} S_{\alpha\delta} \, . \end{aligned} \tag{4}$$

In this paper we limit our interest to steady state solutions. Solving the one dimensional continuity equation we obtain $w_\alpha = \mathrm{const.}$

2.2. The Equation of the Barycentric Velocity

Adding up the equations of the particles $0, 1, \ldots, M$ we get an equation of the barycentric momentum. For this purpose we introduce the following abbreviations

$\sigma = \sum_{\alpha=1}^{M} e_\alpha n_\alpha$	resulting charge of the moving ions,
$u = \frac{1}{\varrho} \sum_{\alpha=0}^{M} \varrho_\alpha u_\alpha$	barycentric velocity,
$\varrho_\alpha = m_\alpha n_\alpha$	mass density of particle α,
$\varrho = \sum_{\alpha=0}^{M} \varrho_\alpha$	total mass density of the moving particles,
$p = \sum_{\alpha=0}^{M} p_\alpha$	pressure,

$$\psi_{\alpha\delta} = e_\alpha e_\delta \tilde{\psi}, \qquad \xi_{\alpha\delta} = n_\delta m_\delta \varkappa_{\alpha\delta}, \quad \xi_\alpha{}^* = \sum_{\delta=M+1}^{M+2} \xi_{\alpha\delta} .$$

Then we obtain the barycentric momentum equation:

$$\begin{aligned} \partial_t \varrho u + \partial_x p + \partial_x (\varrho u^2) - \sigma E & \\ + \sigma \int (\sigma + e_3 n_3) \, \partial_x \tilde{\psi} \, \mathrm{d}^3 r' & \\ + \sum_{\alpha=1}^{M} \sum_{\delta=1}^{M+1} e_\alpha e_\delta \int n_\alpha n_\delta g_{\alpha\delta} \, \partial_x \psi \, \mathrm{d}^3 r' & \\ = - \sum_{\alpha=0}^{M} \xi_\alpha{}^* m_\alpha w_\alpha \, . & \end{aligned} \tag{5}$$

In the same way the continuity equation for ϱ can be derived, the stationary solution of which is: $\varrho u = \mathrm{const.}$

3. The Perturbation Procedure

3.1. The Equations of the 0th and the 1st Approximation

Since the Eqs. (4) and (5) cannot be solved exactly some assumptions are imposed which allow the application of a perturbation approach. These assumptions are stated as follows:

1. Only binary symmetric electrolytes are considered ($e_1 = -e_2$) which are globally electroneutral, and in steady state.
2. The concentration of electrolyte is low compared with the one of the solvent.
3. The interactions between moving particles and the membrane are weak, i.e. the concentration of the membrane particles is low compared with the concentration of the electrolyte.
4. The dielectric constant does not depend on x (this follows from 2. and 3.).
5. The temperature is constant.
6. Only small differences of concentrations and of pressure are considered.

These assumptions allow a perturbation approach up to the first order. We therefore make the ansatz

$$n_\alpha = n_\alpha{}^0 + \lambda\, n_\alpha{}^1, \quad w_\alpha = w_\alpha{}^0 + \lambda\, w_\alpha{}^1, \quad u = u^0 + \lambda\, u^1 \tag{6}$$

where λ is a parameter which indicates the order of magnitude. In the zeroth order, there is no need to consider the concentration of fixed charges ($n_3 \to \lambda n_3$) and the membrane friction ($\xi_\alpha{}^* \to \lambda\, \xi_\alpha{}^*$). Due to restriction 2. the correlations do not occur in the zeroth order ($n_{\alpha\beta} = n_\alpha n_\beta (1 + \lambda g_{\alpha\beta})$). Up to the zeroth order (indicated by the upper index 0), Eqs. (4) and (5) now read:

$$\begin{aligned}\partial_x p_\alpha^0 &+ \partial_x m_\alpha (2 w_\alpha{}^0 u^0 - n_\alpha{}^0 (u^0)^2) \\ &- e_\alpha n_\alpha{}^0 E + n_\alpha{}^0 \sum_{\delta=1}^{2} \int n_\delta{}^0\, \partial_x \psi_{\alpha\delta}\, \mathrm{d}^3 r_\delta \\ &= \sum_{\delta=0}^{2} m_\alpha m_\delta (n_\alpha{}^0 w_\delta{}^0 - n_\delta{}^0 w_\alpha{}^0)\, \varkappa_{\alpha\delta};\end{aligned} \tag{4a}$$

$$\begin{aligned}\partial_x p^0 &+ \partial_x (\varrho^0 (u^0)^2) - \sigma^0 E \\ &+ \sigma^0 \int \sigma^0\, \partial_x \psi\, \mathrm{d}^3 r' = 0\,.\end{aligned} \tag{5a}$$

These equations are to be solved under the boundary condition that there is no difference of the pressure and of the concentrations between the outer homogeneous phases. Furtheron, it is natural to assume global electroneutrality of the electrolyte. Consequently the solution of Eqs. (4a) and (5a) is given by

$$\begin{aligned}&p^0 = \text{const}, \quad p_\alpha = \text{const}, \\ &n_1{}^0 = n_2{}^0 = \text{const}, \\ &n_0{}^0 = \text{const}, \quad u^0 = \text{const}.\end{aligned}$$

This result means that the electrolyte is homogeneous and locally electroneutral, i.e.

$$e_1 n_1{}^0 + e_2 n_2{}^0 = \sigma^0 = 0\,.$$

Furthermore, from (4a) it follows that

$$\begin{aligned}u_1{}^0 - u_0{}^0 &= \frac{e_1 E}{m_1 \varkappa_{10}} \Big(m_0 n_0{}^0 + m_1 n_1{}^0 \frac{\varkappa_{12}}{\varkappa_{20}} \\ &\quad + m_2 n_1{}^0 \frac{\varkappa_{12}}{\varkappa_{10}} \Big)^{-1} \approx \frac{e_1 E}{m_1 \varkappa_{10} m_0 n_0{}^0}, \\ u_2{}^0 - u_0{}^0 &= \frac{-e_1 E}{m_2 \varkappa_{20}} \Big(m_0 n_0{}^0 + m_1 n_1{}^0 \frac{\varkappa_{12}}{\varkappa_{20}} \\ &\quad + m_2 n_1{}^0 \frac{\varkappa_{12}}{\varkappa_{10}} \Big)^{-1} \approx \frac{-e_1 E}{m_2 \varkappa_{20} m_0 n_0{}^0}.\end{aligned} \tag{7}$$

The zeroth order does not allow to calculate the flow of water $w_0{}^0$. This flow remains indefinite, i.e. every barycentric flow is possible. This is obvious because there is no friction of the ions and the water with the external system, and hence there is no exchange of momentum. The friction between the moving particles and the membrane is taken into account in the first order. So the calculation of the first order gives us the flow of water $w_0{}^0$ as well.

The first order of the perturbation approach of (4) and (5) reads:

$$\begin{aligned}\partial_x kT n_\alpha{}^1 &+ \partial_x p_\alpha{}^{s1} - e_\alpha n_\alpha{}^1 E \\ &+ n_\alpha{}^0 \int \sum_{\delta=1}^{2} (n_\delta{}^1 + n_\delta{}^0 g_{\alpha\delta}^0)\, \partial_x \psi_{\alpha\delta}\, \mathrm{d}^3 r_\delta \\ &+ n_\alpha{}^0 \int n_3\, \partial_x \psi_{\alpha 3}\, \mathrm{d}^3 r_3 \\ &+ m_\alpha\, \partial_x (2 w_\alpha{}^0 u^1 - n_\alpha{}^1 (u^0)^2 - 2 n_\alpha{}^0 u^0 u^1) \\ &= \sum_{\delta=0}^{2} m_\alpha m_\delta \varkappa_{\alpha\delta} (n_\alpha{}^1 w_\delta{}^0 + n_\alpha{}^0 w_\delta{}^1 - n_\delta{}^1 w_\alpha{}^0 \\ &\quad - n_\delta{}^0 w_\alpha{}^1) - m_\alpha \xi_\alpha{}^* w_\alpha{}^0;\end{aligned} \tag{4b}$$

$$\begin{aligned}\partial_x (p^1 &+ 2 \varrho^0 u^0 u^1 + \varrho^1 (u^0)^2) - \sigma^1 E \\ &+ \sum_{\alpha=1}^{2} \sum_{\delta=1}^{2} n_\alpha{}^0 n_\delta{}^0 \int g_{\alpha\delta}^0\, \partial_x \psi_{\alpha\delta}\, \mathrm{d}^3 r_\delta \\ &= -\sum_{\alpha=0}^{2} \xi_\alpha{}^* m_\alpha w_\alpha{}^0.\end{aligned} \tag{5b}$$

In Eq. (5b) we have taken into account that there is no resulting charge in the zeroth order ($\sigma^0 = 0$).

Let us now consider the correlation term due to the Coulomb force

$$\sum_{\delta=1}^{2} n_\alpha{}^0\, n_\delta{}^0 \int g^0_{\alpha\delta}\, \partial_x\, \psi_{\alpha\delta}\, \mathrm{d}^3 r_\delta = a_\alpha{}^{\mathrm{c}}. \tag{8}$$

Since $g^0_{\alpha\delta}$ describes the homogeneous electrolyte in an external field E it depends only on $r_\alpha - r_\delta$. Thus, $a_\alpha{}^{\mathrm{c}}$ is independent of r_α. If we expand $g^0_{\alpha\delta}$ up to the first order of E we get $a_\alpha{}^{\mathrm{c}} = a^{\mathrm{c}}_{\alpha 0} + \gamma_\alpha{}^{\mathrm{c}} E$. The constant term $a^{\mathrm{c}}_{\alpha 0}$ is equal to zero because the functions $g^0_{\alpha\delta}$ depend only on the distance $|r_\alpha - r_\delta|$ for $E = 0$. Linear dependence on E is a very good approximation even for extremely high fields.

Similar arguments hold for the short range forces. Up to the first order, the pressure term (2) can be expressed as

$$\begin{aligned} \partial_x\, p_\alpha{}^{\mathrm{s}1} &= n_\alpha{}^0 \sum_{\delta=0}^{4} \int n_\delta{}^1\, k^{\mathrm{s}x}_{\alpha\delta}\, \mathrm{d}^3 r_\delta \\ &\quad + n_\delta{}^0 \sum_{\delta=0}^{2} n_\delta{}^0 \int g^0_{\alpha\delta}\, k^{\mathrm{s}x}_{\alpha\delta}\, \mathrm{d}^3 r_\delta . \end{aligned} \tag{9}$$

The second term on the right hand side is a constant $a_\alpha{}^{\mathrm{s}}$, which is proportional to E, i.e. $a_\alpha{}^{\mathrm{s}} = \gamma_\alpha{}^{\mathrm{s}} E$, where $\gamma_\alpha{}^{\mathrm{s}}$ depends on the concentrations of the homogeneous electrolyte.

Since we are not interested in the concentration dependence of $a_\alpha = a_\alpha{}^{\mathrm{s}} + a_\alpha{}^{\mathrm{c}}$ it is not necessary to calculate the correlation functions $g^0_{\alpha\delta}$.

Finally, let us consider the correlation term in (5b) which we abbreviate by a^{c}. Using the abbreviations introduced above we have: $a^{\mathrm{c}} = a_1{}^{\mathrm{c}} + a_2{}^{\mathrm{c}}$.

Now we want to show that the correlation term a^{c} vanishes. This can be seen as follows.

If $g^{00}_{\alpha\delta}$ is the equilibrium correlation function it is plausible from electrolyte theory (cf. [5, 6]) that $g^0_{\alpha\alpha} = g^{00}_{\alpha\alpha}$. Using the abbreviation $k^{\mathrm{c}x} = \partial_x \tilde{\psi}$ one finds

$$\begin{aligned} a_1{}^{\mathrm{c}} &= -\, e^2 (n_1{}^0)^2 \int g^0_{12}\, k^{\mathrm{c}x}\, \mathrm{d}^3 r' , \\ a_2{}^{\mathrm{c}} &= -\, e^2 (n_1{}^0)^2 \int g^0_{21}\, k^{\mathrm{c}x}\, \mathrm{d}^3 r' . \end{aligned}$$

The result follows immediately from the symmetry relation $g^0_{\alpha\delta}(r - r') = g^0_{\delta\alpha}(r' - r)$.

3.2. *The Solution of the Ion Equations*

Thus far, Eq. (4b) together with the treatment of the correlation terms is completely exact within the framework of the perturbation approach. But in this form the equations cannot be solved. Therefore we have to impose further restrictions. It turns out that under reasonable physical conditions which are spezified below, three parts of (4b) can be neglected yielding the equations

$$\begin{aligned} & e_\alpha\, n_\alpha{}^1\, E - kT\, \partial_x\, n_\alpha{}^1 - u_\alpha{}^0\, e_\alpha \int n_3\, e_3\, \partial_x\, \tilde{\psi}\, \mathrm{d}^3 r_3 \\ &\qquad - n_\alpha{}^0\, e_\alpha \sum_{\delta=1}^{2} \int n_\delta{}^1\, e_\delta\, \partial_x\, \tilde{\psi}\, \mathrm{d}^3 r_\delta \qquad \text{(4c)} \\ &\qquad = m_\alpha\, \xi_{\alpha 0}\, w_\alpha{}^1 + m_\alpha\, \xi_\alpha{}^*\, w_\alpha{}^0 + \gamma_\alpha\, E, \\ &\qquad\qquad \alpha = 1, 2. \end{aligned}$$

They are identical with the ionic transport equations treated in [1, 2]. Therefore we obtain the same densities $n_\alpha{}^1$ and fluxes $w_\alpha{}^1$, $\alpha = 1, 2$ as derived in [1, 2].

For the explicite solution of (4c) and for the following derivation of (4c) from (4b) it is assumed that n_3 and n_4 are constant within the membrane. In order to bring this supposition in an appropriate mathematical form we introduce the function $\tilde{\sigma}$ with

$$\tilde{\sigma}(x) = \begin{cases} 1, & x \in [-\,\delta, \delta]\,, \\ 0, & x \notin [-\,\delta, \delta]\,. \end{cases} \tag{10}$$

Then one has $n_\delta(x) = \bar{n}_\delta\, \tilde{\sigma}(x)$, $\delta = 3, 4$. In what follows we use the abbreviations $\xi_\alpha{}^* = \sum_{3}^{4} m_\delta \bar{n}_\delta \varkappa_{\alpha\delta}$.

The derivation of (4c) from (4b) is now based on the following estimates.

As a first step, let us treat again the term $\partial_x p_\alpha{}^{\mathrm{s}1}$ given by (9). In section 3.1 it was shown that the correlation part of (9) is constant. The remaining part reads

$$n_\alpha{}^0 \sum_{\delta=0}^{4} \int n_\delta{}^1\, k^{\mathrm{s}x}_{\alpha\delta}\, \mathrm{d}^3 r_\delta\, . \tag{11}$$

The range of the short range forces is much smaller than the regions in which the functions $n_\delta{}^1$, $\delta = 0, 1, 2$ change in an appreciable way. Therefore in (11) the functions $n_\delta{}^1$, $\delta = 0, 1, 2$ can be taken outside the integral sign. Hence the term (11) vanishs. It can be shown that this approximation is internally consistent. The argument does not hold for $\delta = 3, 4$, because the $n_\delta{}^1 = n_\delta$, $\delta = 3, 4$ are step functions. The respective terms depend only on membrane properties. Their sum can intuitively be interpreted as the gradient of the swelling pressure. Thus, if we want to derive from (4b) the transport equations (2.1) of [1, 2], we have to assume in addition to assumption 1. to 6. assumption 7. The swelling pressure is negligible.

Considering the convective terms of (4b) one finds by a straight-forward calculation:

$$\partial_x u^1 = - u^0 \sum_{\alpha=0}^{2} m_\alpha \, \partial_x n_\alpha{}^1 \Big/ \sum_{\alpha=0}^{2} m_\alpha \, n_\alpha{}^0 .$$

Inserting this result in the convective terms, i.e. in

$$K_\alpha = 2 m_\alpha w_\alpha{}^0 \, \partial_x u^1 - m_\alpha (u^0)^2 \, \partial_x n_\alpha{}^1 - 2 m_\alpha n_\alpha{}^0 u^0 \, \partial_x u^1 ,$$

it follows that $K_\alpha \ll kT \partial_x n_\alpha{}^1$ if an addition to condition 5 the assumption 5a is valid:

5a) The thermal energy is much higher than the kinetic energy of all convective flows, and the gradients $\partial_x n_\alpha{}^1$, $\alpha = 0, 1, 2$ are all of the same order of magnitude.

Thus, assuming 5a we can neglect K_α. Assumption 5a is internally consistent.

As a last step, we have to consider the first order term $S^1_{\alpha\delta}$ of the friction terms. Let $\alpha = 1$, then

$$\begin{aligned} &\sum_{\delta=0}^{4} S^1_{1\delta} + \gamma_1 E \\ &\quad = m_0 \varkappa_{10} (n_1{}^1 w_0{}^0 + n_1{}^0 w_0{}^1 - n_0{}^1 w_1{}^0 - n_0{}^0 w_1{}^1) \\ &\quad + m_2 \varkappa_{12} (n_1{}^1 w_2{}^0 + n_1{}^0 w_2{}^1 - n_2{}^1 w_1{}^0 - n_2{}^0 w_1{}^1) \\ &\quad - m_3 \varkappa_{13} n_3 w_1{}^0 - m_4 \varkappa_{14} n_4 w_1{}^0 + \gamma_1 E . \qquad (12) \end{aligned}$$

We want to give reasonable conditions so that all the terms except the fourth one and those of the last row of (12) can be neglected. For this purpose we specify the conditions 2., 3. and 6. as follows:

2a) The electrolyte is diluted: $n_0{}^0 \gg n_1{}^0$.

3a) The concentration of the fixed charges is small compared with the concentration of the other membrane particles: $\bar{n}_4 \gg \bar{n}_3$. This condition holds for "normal" ion exchange membranes.

6a) Let p' and p'' be the pressure at the left hand side of phase $'$ and at the right hand side of phase $''$. Then the external pressure is assumed to fulfil the condition: $|p' - p''| \leqq 2 \bar{n}_3 | e_3 E | \delta$.

In addition we assume the following condition to be valid

8. The coefficients $m_\beta \varkappa_{\alpha\beta}$ are all of the same order of magnitude.

With the help of these suppositions it can be shown that in (12) all terms except the first one, the foruth one and those of the last row of (12) can be neglected. In order to neglect the first one as well, we take advantage of a result which can be seen independently of these considerations in Section 3.3, namely: $|w_0{}^0|$ is of the same order of magnitude as $|w_1{}^0|$ or of the same order of magnitude as $\bar{n}_3 | e_3 E | / (\bar{\xi}_0{}^* m_0)$.

If we choose, e.g. $|w_0{}^0| \approx |w_1{}^0|$, $|n_1{}^1 w_0{}^0|$ is of the same order of magnitude as $|n_2{}^1 w_1{}^0|$. Hence it can be neglected. Similar estimates hold for the other cases.

Thus, if the above conditions are satisfied, Eq. (4c) is valid. It must be emphasized that some of the restrictions assumed here are not necessary. They are imposed only for mathematical convenience. What we really need is the vanishing of the convection terms and that of the friction term $n_0{}^1 w_1{}^0$. A better approximation of the pressure term is obtained by expanding $n_1{}^1$ and $n_2{}^1$ under the integral sign. Also the swelling pressure could be taken into account. But, though the resulting equations can be solved exactly and explicitely, the results are extremely complicated expressions which are completely useless for any intuitive interpretation.

3.3. The Solution of the Barycentric Momentum Equation

Analogously to Eq. (4b), the barycentric momentum equation (5b) can be simplified by neglecting the convective terms. Since the correlation terms vanish Eq. (5b) becomes

$$\partial_x p^1 - \sigma^1 E = - \sum_{\alpha=0}^{2} m_\alpha \, \xi_\alpha{}^* \, w_\alpha{}^0 . \qquad (5c)$$

The validity of this approximation can be seen by the following estimates.

The convective term reads:

$$\begin{aligned} &2 \varrho^0 n^0 \, \partial_x u^1 + (u^0)^2 \, \partial_x \varrho^1 \\ &\quad = - \sum_{\alpha=0}^{2} m_\alpha (u^0)^2 \, \partial_x n_\alpha{}^1 . \end{aligned}$$

With the help of assumption 5a, which implies $m_\alpha (u^0)^2 \ll kT$, the convective term can be neglected compared with the kinetic part of $\partial_x p^1$.

In order to solve Eq. (5c) we choose the following boundary conditions

$$p^1(-d) = p_1 , \quad p^1(d) = - p_1 .$$

Thus one finds for the pressure in the homogeneous phases

$$\begin{aligned} &p' = p^0 + p_1 , \quad p'' = p^0 - p_1 , \\ &\Delta p = p' - p'' = 2 p_1 \end{aligned}$$

where p^0 is the pressure of the zeroth approximation. Then the solution of (5c) is given by

$$p^1(x) = p_1 + E\int_{-d}^{x}\sigma^1(x')\,\mathrm{d}x' - \int_{-d}^{x}R(x')\,\mathrm{d}x' \qquad (13)$$

with $R = \sum_{\alpha=0}^{2}\xi_\alpha{}^* m_\alpha w_\alpha{}^0$. The quantities R and $\xi_\alpha{}^*$ are step functions which vanish outside the membrane. Their values are denoted by $\bar{R}$ and $\bar{\xi}_\alpha{}^*$. The system was supposed to be globally electroneutral, i.e.

$$-\int_{-d}^{d}\sigma^1\,\mathrm{d}x' = e_3\int_{-d}^{\delta}\bar{n}_3\,\mathrm{d}x' = 2\,\delta\,e_3\,\bar{n}_3\,. \qquad (14)$$

Using the Eqs. (13), (14) and the boundary condition on the right hand side of the ″-phase, one immediately obtains the water flux up to the zeroth order

$$\bar{\xi}_0^*\,m_0\,w_0{}^0 = -\,\bar{\xi}_1{}^*\,m_1\,w_1{}^0 - \bar{\xi}_2{}^*\,m_2\,w_2{}^0 + (p_1/\delta) - e_3\,\bar{n}_3\,E\,. \qquad (15)$$

With the help of assumption 6a and of Eq. (15) it is possible to estimate the order of magnitude of $w_0{}^0$ obtaining the result used at the end of Section 3.2.

We introduce the step function θ by

$$\theta(x) = \begin{cases} 0, & x \leqq \delta\,,\\ 1, & x > \delta\,.\end{cases}$$

Then one can write Eq. (13) in the form

$$p^1(x) = p_1(1 - 2\,\theta(x) - (x/\delta + 1)\,\tilde{\sigma}(x)) + E\int_{-d}^{x}(\sigma^1(x') + e_3\,n_3(x'))\,\mathrm{d}x' \qquad (13\mathrm{a})$$

where $\tilde{\sigma}$ is defined by (10).

The charge density σ^1 is known from the ionic momentum Equations (4c). But the explicite form is a very complicate expression. Equation (13a) is the adequate form to discuss qualitatively the spatial variation of the pressure. The integral gives an appreciable value only in the neighbourhood of the membrane surface. Thus, the pressure is approximately constant outside the membrane, and depends nearly linear on x inside the membrane.

4. Discussion

4.1. The Pressure

The x-dependence of the pressure can be discussed using Eq. (5c) or Equation (13a). Since we assume that the system is under steady state conditions the flows of water and ions are constant throughout the system. Thus, the right hand side of Eq. (5c) is constant in each phase. In the diffusion layers this constant is equal to zero, within the membrane it is equal to

$$-\sum_{\alpha=0}^{2}\bar{\xi}_\alpha{}^*\,w_\alpha{}^0\,.$$

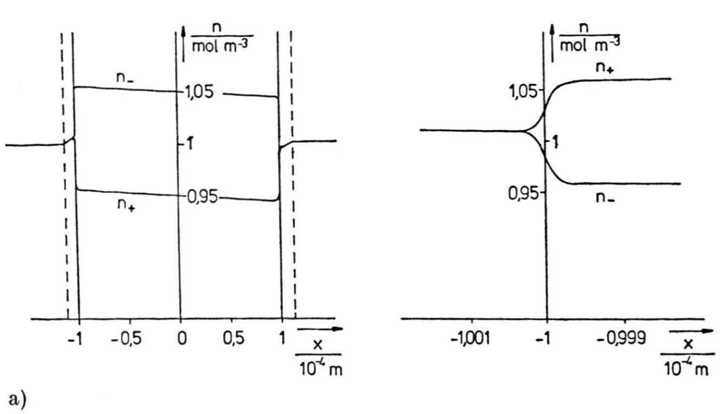
Thus, the pressure gradient follows the resulting charge σ^1. If σ^1 varies with respect to x this happens for the pressure gradient as well. This phenomenon can be understand by considering the steady state. The flow of water is influenced by the pressure gradient and by the force $\sigma^1 E$. In order to guarantee a steady state the pressure gradient must compensate the influence of the resulting charge. This is illustrated by a numerical example which was calculated using the results of [2] under the hypothesis that there is no concentration difference between the outer homogeneous phases. Figure 2a shows the concentration, Fig. 2b the resulting charge, and Fig. 2c the pressure versus the x-coordinate of the membrane.

The pressure p^1 is a sum of the kinetic part and the part produced by the short range forces (cf. (3)). In order to calculate these two parts separately it is necessary to know the concentration of water. For low ion-concentrations one can easily calculate the concentration of water by the assumption of incompressibility. Knowing all concentrations we can calculate the kinetic part of the pressure and therefore obtain the pressure which is produced by the short range forces.

4.2. The Water Flow

Knowing the flows of water and ions we can easily calculate the volume flow. This flow or the barycentric flow plays an important role in the Nernst-Planck equations (see [7, 8]) which have been used for the interpretation of various experiments. The volume flow, for example, plays an important role in the oscillatory phenomena at ion exchange membranes (see for example [9]).

The volume flow due to an external electric field can be calculated by Equation (15). This interesting effect has been studied for example by Fisher [10]. In the following we don't want to discuss the approximate solution (15), but the original Eq. (5), which describes the flow of water in general. We want to compare this equation, which is deduced microscopically, with analogous equations which are deduced by thermodynamics. A frequently used



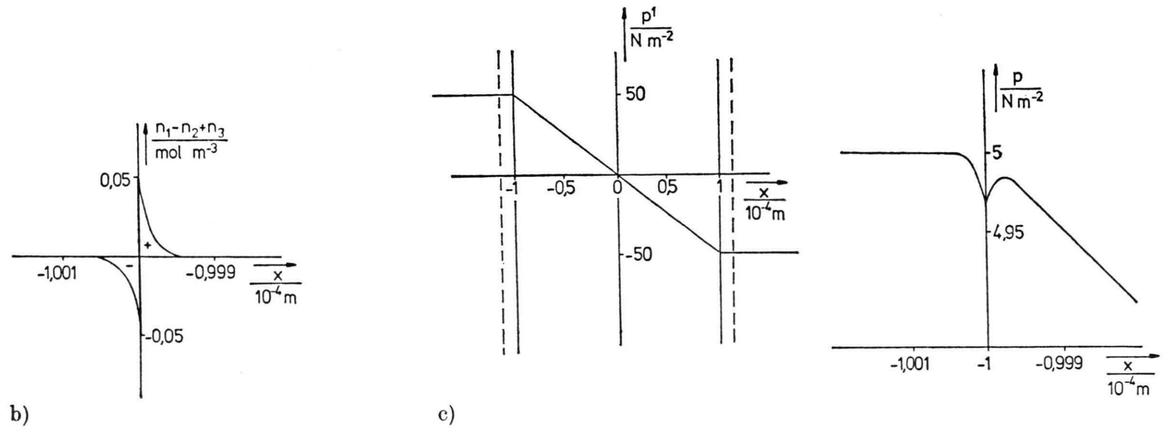


Fig. 2. Concentration and pressure for a membrane with fixed charges (0.1 mol/m³). Thickness of the membrane: $2 \cdot 10^{-4}$ m, thickness of the diffusion layers: $2 \cdot 10^{-5}$ m. External field: ca. 500 V/m. $\Delta p = 100$ N/m².

a) The concentration as a function of x.
b) The resulting charge at the left edge of the membrane as a function of x.
c) The pressure as a function of x.

formula for calculating the flow of water in an ion exchange membrane is an equation given by Schlögl [7]:

$$\partial_x p - \sigma \bar{E} = \frac{1}{d_{\mathrm{h}}} u_{\mathrm{V}} \tag{16}$$

where u_{V} is the flow of volume, d_{h} the permeability and $\bar{E}$ the total field in the membrane.

We want to compare Eq. (5) with Equation (16). In Eq. (5) three terms can be neglected. In Chapter 3.1 we have seen that for a weak ion exchange membrane the correlation term in Eq. (5) is equal to zero. For such a membrane the term $\partial_x(\underset{\sim}{\varrho} u^2)$ can also be neglected. Finally in a steady state $\partial_t \underset{\sim}{\varrho} u$ vanishes. Since the integral

$$-\int (\sigma + e_3 n_3)\, \partial_x \tilde{\psi}\, \mathrm{d}^3 r'$$

is the electric field produced by the ions and the fixed charges we obtain for the total electric field $\bar{E}$ in the membrane

$$\sigma \bar{E} = \sigma E - \sigma \int (\sigma + e_3 n_3)\, \partial_x \tilde{\psi}\, \mathrm{d}^3 r' .$$

But there remains one remarkable difference between (5) and (16). The right hand side of Eq. (5) cannot be expressed by the volume flow. The volume flow in Eq. (16) must be replaced by a term

$$\sum_{\alpha=0}^{2} \frac{1}{D_{\alpha\mathrm{M}}} w_\alpha ,$$

where $D_{\alpha\mathrm{M}}$ are augmented diffusion coefficients. Then we get an equation which has been deduced from thermodynamics by Mehta et al. [8]. Nevertheless, this phenomenological equation is still an approximate formula, for which the restrictions for the validity are unknown.

Another advantage of our treatment is that we can interpret our transport equations on microscopical grounds. For instance, Eq. (5) helps us to understand why a flow of water due to an electric field is possible for each ion exchange membrane. A complete interpretation would be possible for a membrane model, for which the Eqs. (4) and (5) could be solved exactly.

Up to now we have not taken into account the structure of membranes. The membranes for which Eqs. (4c) and (5c) are valid are membranes with constant concentrations of fixed charges and the other membrane particles all over the membrane. But in most cases real membranes have a different structure. Consequently, a quantitative comparison of experimental data and the equations given above is only possible for a very restricted class of membranes. The flow of water due to an electric field (electro-osmosis) should be high in membranes with high concentrations of fixed charges. But this effect has not been found for membranes with capillary systems (see for example [10]). So, at least for these membranes a theoretical calculation has to take into account the membrane structure.

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