PHYSICAL CHEMISTRY

Electrokinetic Properties of
Nafion 117 in NaCl + KCl Solutions

by S. Koter

Faculty of Chemistry, Nicolaus Copernicus University, 7 Gagarin Street, 87-100 Toruń, Poland
e-mail: skoter@chem.uni.torun.pl

The applicability of the extended Nernst-Planck equation with the homogeneous distribution of ions and the capillary model (the Boltzmann distribution of ions) to the description of electrokinetic phenomena in the system Nafion 117|0.1 M mixture of NaCl and KCl has been discussed. It has been found that only the capillary model can reasonably describe those phenomena, simultaneously preserving the Onsager reciprocity relation. The extended Nernst-Planck equation gives unsatisfactory results by either strongly breaking the reciprocity relation or, assuming the reciprocity relation (α_i must be 1), leading to large discrepancies between the hydrodynamic permeability and the electrical conductivity. The interpretation of α_i in terms of the capillary model has been given. $\alpha_i <$ 1 for counterions and $\alpha_i > 1$ for coions result from the radial concentration profiles of those ions and of the convective velocity. The dependence of α_i on the kind of acting force has been proved.

Key words: capillary model, extended Nernst-Planck equation, ion-exchange membrane, electrokinetic coefficients

For the description of transport through ion-exchange membranes various approaches can be applied, like the extended Nernst-Planck equation (ENPE), the capillary model (CM) or irreversible thermodynamics (IT), depending on the problem to be solved. The most general system of equations offers the IT, however, it contains a large number of coefficients, even if the Onsager reciprocal relation (ORR) is taken into account. The use of the ENPE or CM makes it possible to estimate the transport coefficients from those referring to the free electrolyte solutions and from the parameters of a membrane like its ion-exchange capacity and swelling. Such approach reduces the number of transport coefficients to be determined, however, it should be verified. Results of such verification will inform to what extend the assumed model of transport is correct and whether other phenomena take place, which should be included into the model.

In this work the ENPE (with the homogeneous distribution of ions in the cross-section of membrane pores) and CM (with the nonhomogeneous distribution of ions) will be examined on the base of electrokinetic phenomena in the system cation-exchange membrane Nafion 117|0.1 M mixture of NaCl and KCl. The choice of Nafion has been motivated by its thoroughly investigated structure. After many investigations based on various methods (*e.g.* small angle X-ray scattering, transmission electron microscopy, Mössbauer spectroscopy, see references in [1]) it has been

found that in that membrane the fixed charges form clusters of diameter *ca*. 4–5 nm, which are connected by the channels *ca*. 1 nm in diameter [2]. In order to check the influence of counterions on the predictions of both models, the small concentration 0.1 M of mixture of the external solution has been chosen to eliminate the influence of coions. Three basic electrokinetic coefficients will be determined – the electrical conductivity, κ_m, the electroosmotic volume transport number, $\bar{t}_v$, and the hydrodynamic permeability coefficient, $L_p^{(m)}$. $\bar{t}_v$ will be used for the determination of the hydrodynamic permeability at the zero electric potential gradient d_h (ENPE) and of the equivalent radius of pores R (CM). κ_m and $L_p^{(m)}$ will be used for the verification of both approaches. Additionally, the transport number of cations, needed for the calculation of the convective coupling coefficient α_i, will be experimentally determined. The interpretation of α_i in terms of the CM will be given.

THEORY

The extended Nernst-Planck equation (ENPE): Below all the quantities refer to the pore solution of a membrane, unless stated otherwise. Subscript 0 denotes solvent, 1, .., n – ions (or generally solutes). The ENPE is given by [3–6]:

$$J_i = -\bar{u}_i \bar{c}_i (RT \nabla \ln \bar{c}_i + z_i F \nabla \bar{\psi}) + \alpha_i \bar{c}_i \nu \tag{1}$$

where $\bar{u}_i, \bar{c}_i, z_i, \alpha_i$ are the mobility, concentration, valency, the coupling convective coefficient of ion i, respectively. ν is the velocity of the centre of mass, however, usually ν is regarded as the velocity of the centre of volume. In this work it has been checked that the results obtained with these two velocities differ very slightly and, for simplicity of formulas, ν is regarded as the volume flux. From now on it will be denoted by J_v. Thus $\bar{u}_i$ denotes the mobility in that frame of reference. J_v depends on the gradients of electric potential, $\nabla \bar{\psi}$, and pressure, $\nabla \bar{p}$:

$$\nu = J_v = -d_h(-z_m \bar{c}_m F \nabla \bar{\psi} + \nabla \bar{p}) \tag{2}$$

In (2) d_h is the hydrodynamic permeability coefficient at $\nabla \bar{\psi} = 0$. Subscript m denotes the fixed charges of membrane. (1) and (2) can be transformed to the form:

$$J_i = -\bar{u}_i \bar{c}_i \nabla \tilde{\mu}_i + \alpha_i \bar{c}_i J_v \qquad i = 1,2, .., n \qquad (3); \qquad J_v = -d_h \sum_{k=0}^{n} \bar{c}_k \nabla \tilde{\mu}_k \tag{4}$$

by 1) substituting the first term in J_i by the more general term $\bar{u}_i \bar{c}_i \nabla \overline{\tilde{\mu}}_i$, 2) applying the relation:

$$\sum_{k=0}^{n} \overline{c}_k \nabla \overline{\widetilde{\mu}}_k = -z_m \overline{c}_m F \nabla \overline{\psi} + \nabla \overline{p} \tag{5}$$

and 3) assuming that $\overline{\overline{\mu}}_i = \widetilde{\mu}_i$, where $\widetilde{\mu}_i$ denotes electrochemical potential of ions as well as chemical potential of solvent in a hypothetical external solution being in equilibrium with the pore solution at a given point of the pore. A comment should be done on α_i. Transforming (3) and (4) into the form of those of non-equilibrium thermodynamics (13) yields the following expression for L_{ik}:

$$L_{ik} = \overline{c}_i(\delta_{ik}\overline{u}_i + d_h\alpha_i\overline{c}_k) \qquad i,k = 1, .., n \tag{6}$$

where δ_{ik} is the Kronecker δ. One can see that the equality $L_{ik} = L_{ki}$ (ORR) will be fulfilled, if all α_i are the same. From the additional symmetry relation for the electrokinetic transport [7]:

$$-Fd_h z_m \overline{c}_m = \left(\frac{J_v}{-\nabla\psi}\right)_{\Delta c, \Delta p=0}^{ORR} \left(\frac{I}{-\nabla p}\right)_{\Delta c, \Delta\psi=0} = Fd_h \sum_{i=1}^{n} \alpha_i z_i \overline{c}_i \tag{7}$$

it can be concluded that all α_i have to be exactly 1. As it will be shown later on the basis of the capillary model, α_i is a function of the radial profiles of concentration and of the convective velocity inside the pores. For the homogeneous distribution of ions α_i is exactly one.

For the case $\alpha_i = 1$ (ORR is satisfied) the combination of the equations for L_p, κ, and $\overline{t}_v$ (Table 1) yields the following relation between L_p, κ, and $\overline{t}_v$:

$$\frac{L_p}{\kappa} = \frac{\overline{t}_v}{-F^2 z_m \overline{c}_m} (1 + z_m \overline{c}_m \overline{t}_v) \tag{8}$$

The ratio L_p/κ refers to the pore solution. The assumption that it is the same as the experimentally observable ratio $L_p^{(m)}/\kappa_m$:

$$\frac{L_p}{\kappa} = \frac{L_p^{(m)}}{\kappa_m} \tag{9}$$

enables the verification of (8). (9) is justified by (10) relating the transport coefficient referring to the pore solution, L, with that for the whole membrane, $L^{(m)}$:

$$L = L^{(m)} \frac{\theta^2}{V_p} \qquad \text{for} \quad L = L_p, \kappa, L_{ik} \tag{10}$$

where V_p is the volume fraction of pores, θ^2 – the tortuosity factor of pores.

In the second case ($\alpha_i \neq 1$), α_i is calculated from the experimental transport coefficients, *i.e.* the ENPE fits those experimental data, however, the ORR is lost. The combination of the formulas listed in Table 1 gives the following expression for α_i:

$$\alpha_i = \frac{1}{z_i \bar{c}_i \bar{t}_v} \left(\bar{t}_i + \frac{F^2 z_m \bar{c}_m L_p / \kappa}{\bar{t}_v \sum_{k=1}^{n} \bar{c}_k z_k^2 \bar{u}_k / z_i^2 \bar{c}_i \bar{u}_i} \right) \quad i = 1, .., n \tag{11}$$

In (11) L_p/κ can be approximated by (9) and $\bar{u}_k/\bar{u}_i$ by the corresponding ratio for the free solution. If only one kind of counterions is present in the membrane and the concentration of coions is negligible, then the term with $\bar{u}_i$ disappears and α_i is the function of the measurable quantities only. According to (7), the deviation from the ORR can be expressed as:

$$\frac{(I/\nabla p)_{\Delta c, \Delta\psi=0}}{(J_v/\nabla\psi)_{\Delta c, \Delta p=0}} \overset{eqs.\,(7,11)}{=} \frac{1}{-z_m \bar{c}_m \bar{t}_v} \left(1 + \frac{F^2 z_m \bar{c}_m}{\bar{t}_v} \frac{L_p}{\kappa} \right) \tag{12}$$

Table 1. Electric conductivity, κ, transport number of ion i, $\bar{t}_i$, electroosmotic volume transport number, $\bar{t}_v$, and hydrodynamic permeability coefficient, L_p, according to the ENPE and the capillary model based on irreversible thermodynamics (IT).

Transport coefficient	ENPE (all the quantities refer to the pore solution)	capillary model/IT
$\kappa = \left(\dfrac{I}{\nabla\psi} \right)_{\Delta c, \Delta p=0}$	$F^2 \sum_{k=1}^{n} z_k \bar{c}_k (z_k \bar{u}_k - \alpha_k z_m \bar{c}_m d_h)$	$F^2 \left(\sum_{k=1}^{n} z_k^2 L_{kk} + 2 \sum_{k \neq j=1}^{n} z_j z_k L_{jk} \right)$
$\bar{t}_i = \left(\dfrac{F z_i J_i}{I} \right)_{\Delta c, \Delta p=0}$	$\dfrac{z_i \bar{c}_i (z_i \bar{u}_i - \alpha_i z_m \bar{c}_m d_h)}{\kappa/F^2}$	$\dfrac{z_i \sum_{k=1}^{n} z_k L_{ik}}{\kappa/F^2}$
$\bar{t}_v = \left(\dfrac{F J_v}{I} \right)_{\Delta c, \Delta p=0}$	$\dfrac{-z_m \bar{c}_m d_h}{\kappa/F^2}$	$\bar{v}_0 \bar{t}_0 + \sum_{k=1}^{n} \bar{v}_k \bar{t}_k / z_k$
$L_p = \left(\dfrac{J_v}{-\nabla p} \right)_{I, \Delta c=0}$	$d_h \dfrac{\sum_{k=1}^{n} z_k^2 \bar{c}_k \bar{u}_k}{\kappa/F^2}$	$\sum_{i,k=0}^{n} \bar{v}_i \bar{v}_k L_{ik} - \bar{t}_v^2 \kappa / F^2$

The capillary model (CM): Usually the transport equations of the CM are based on the extended Nernst-Planck and Navier-Stokes equations [8–10]. In this work the transport equations of the CM are the same as those of linear irreversible thermodynamics:

$$J_i = \sum_{k=0}^{n} L_{ik} X_k \qquad i = 0, 1, .., n \tag{13}$$

where J_i is the flux of species i, X_i – the thermodynamic force – the negative gradient of (electro)chemical potential of species i. As it was shown in [11], the transport coefficients, L_{ik}, are the sum of convective, B_{ik}, and diffusive, $\bar{l}_{ik}$, contributions:

$$L_{ik} = B_{ik} + \bar{l}_{ik} \qquad i,k = 0,1, .., n \tag{14}$$

For the capillary of radius R the convective part, B_{ik}, is given by:

$$B_{ik} = \frac{2}{R^2} \int_0^R \bar{c}_{i,r} r \int_r^R \frac{1}{\bar{\eta}_r r} \int_0^r \bar{c}_{k,r} r dr^3 \tag{15}$$

where $\bar{\eta}_r$ is the viscosity of pore solution, $\bar{c}_{i,r}$ – concentration of species i at r. The second term in (14), $\bar{l}_{ik}$, describes the transport with respect to the center of mass of pore solution. All the coefficients B_{ik}, $\bar{l}_{ik}$, and thus L_{ik} are symmetrical. The methods of estimating $\bar{l}_{ik}$ and $\bar{\eta}_r$ are described in the Appendix.

To calculate the transport coefficients, the distribution function of ions has to be assumed. Taking the classical Boltzmann equation, one can notice that it does not take into account individual properties of ions, *i.e.* the ratio of concentrations of ions of the same charge in the membrane will be the same as in the equilibrating solution. In literature one can find some modifications of the Boltzmann equation. One of them, made by Gur *et al*. [12], takes into account the character of ions by introducing the dielectric constant dependent on the electric field, $\varepsilon_{r,r}$, and the hydration constant of ions, A_i:

$$\bar{c}_{i,r} = c_{i,ext} \exp\left(-z_i \frac{F}{RT} \bar{\varphi} - \frac{A_i}{RT} \left(\frac{1}{\varepsilon_{r,r}} - \frac{1}{\varepsilon_{r,\text{ext}}} \right) \right) \tag{16}$$

$\bar{\varphi}$ is the potential measured against that of the external solution. The dependence of $\varepsilon_{r,r}$ on the electric field describes the Booth equation [9,10]. The radial profile of $\bar{\varphi}$ is obtained by solving the Poisson-Boltzmann equation written in cylindrical coordinates:

$$\frac{1}{r} \frac{\partial}{\partial r} \left(r \varepsilon_{r,r} \frac{\partial \bar{\varphi}}{\partial r} \right) = -\frac{F}{\varepsilon_0} \sum_{i=1}^n z_i \bar{c}_{i,r} \tag{17}$$

The boundary conditions are as follows:

$$\left(\frac{\partial \bar{\varphi}}{\partial r} \right)_{r=0} = 0 \qquad (18) \qquad \text{and} \qquad \left(\frac{\partial \bar{\varphi}}{\partial r} \right)_{r=R} = -\frac{\pi R^2 F \sum_{i=1}^n z_i \bar{c}_i}{2\pi R \varepsilon_{r,R} \varepsilon_0} = \frac{RF z_m \bar{c}_m}{2\varepsilon_{r,R} \varepsilon_0} \tag{19}$$

The first one results from the symmetry, the second one – from the Gauss law and the electroneutrality condition:

$$\sum_{i=1}^{n} z_i \bar{c}_i + z_m \bar{c}_m = 0 \tag{20}$$

In (19) and (20) $\bar{c}_i$ ($i = 1, .., n$) denotes the concentration of ion i, averaged over the cross-section of the capillary:

$$\bar{c}_i = \frac{2}{R^2} \int_0^R \bar{c}_{i,r} r dr \qquad i = 1, .., n \tag{21}$$

The values of A_i (16), calculated by Gur *et al.* [12] and by Bontha and Pintauro [13], are listed in Table 2. For $A_i = 0$ (16) reduces to the classical Boltzmann equation. The formulas for κ, $\bar{t}_i$, $\bar{t}_v$, and L_p in terms of L_{ik} are listed in Table 1.

Table 2. The hydration constant A_i of the modified Boltzmann eq. (16) (T = 298 K).

ion:	Na$^+$	K$^+$	Cl$^-$
A_i/RT (Gur *et al.* [12])	174	144	120
A_i/RT (Bontha & Pintauro [13])	84	80	111

The convective coupling coefficient α_i according to the capillary model: In order to express the convective coupling coefficient α_i in terms of the CM let's write the transport equations (13) in the form similar to the ENPE:

$$J_i = \sum_{k=0}^{n} (B_{ik} + \bar{l}_{ik}) X_k = \alpha_i' \bar{c}_i \nu + \sum_{k=0}^{n} \bar{l}_{ik} X_k \tag{22}$$

In (22) α_i' is the convective coupling coefficient corresponding to that from (1), ν is the averaged over cross-section of capillary velocity of mass centre of pore solution, given by [11]:

$$\nu = \sum_{k=0}^{n} B_k X_k \tag{23}, \qquad \text{where} \qquad B_k = \frac{2}{R^2} \int_0^R r \int_r^R \frac{1}{\eta_r r} \int_0^r \bar{c}_{k,r} r dr^3 \tag{24}$$

From (22) and (23) it results that:

$$\alpha_i' = \frac{\sum_{k=0}^{n} B_{ik} X_k}{\bar{c}_i \nu} = \frac{\sum_{k=0}^{n} B_{ik} X_k}{\bar{c}_i \sum_{k=0}^{n} B_k X_k} \tag{25}$$

As $\sum_{k=0}^{n} B_{ik} X_k$ denotes the product of $\overline{c}_{i,r}$ and v_r averaged over the cross-section of capillary $\langle \overline{c}_{i,r} v_r \rangle$ [11], α_i' can be simply expressed as:

$$\alpha_i' = \frac{\langle \overline{c}_{i,r} v_r \rangle}{\overline{c}_i v} \tag{25a}$$

From that formula it results that if v_r for each r has the same sign, then α_i' is always positive. (25) quantitatively describes the remark of Dresner [4] that the convective coupling coefficient of coions and counterions could be different because of different profiles of their concentrations and of the velocity of solvent inside the membrane pores. According to (25), α_i' depends on the magnitude of forces, if more than one force acts. Regarding the electrokinetic phenomena, α_i' is given by:

1) for $\Delta\psi \neq 0$ ($\Delta c, \Delta p = 0$): $(\alpha_i)_{\Delta c, \Delta p=0} = \dfrac{\sum_{k=1}^{n} z_k B_{ik}}{\overline{c}_i \sum_{k=1}^{n} z_k \langle B_k \rangle}$ \hfill (25b)

2) for $\Delta p \neq 0$ ($\Delta c, I = 0$): $(\alpha_i)_{\Delta c, I=0} = \dfrac{\sum_{k=0}^{n} B_{ik} (\overline{v}_k - z_k \overline{t}_v)}{\overline{c}_i \sum_{k=0}^{n} B_k (\overline{v}_k - z_k \overline{t}_v)}$ \hfill (25c)

Thus, α_i' depends on the kind of acting force, whereas α_i from the ENPE should remain the same. For the homogeneous distribution of species ($\overline{c}_{i,r} = \overline{c}_i$) or if the convective velocity $v_r = \text{const}$, α_i' reduces to 1. For $\overline{c}_{i,r} = \overline{c}_i$ and $\overline{\eta}_r = \overline{\eta}$, (15) and (24) take the forms:

$$B_{ik} = \frac{R^2}{8\overline{\eta}} \overline{c}_i \overline{c}_k \qquad (15a), \qquad\qquad B_k = \frac{R^2}{8\overline{\eta}} \overline{c}_k \qquad (24a)$$

Substituting these expressions into (25) gives $\alpha_i' = 1$.

EXPERIMENTAL

The measurements were performed for the mixtures of NaCl and KCl solutions of the total concentration $c_s = 0.1$ M and the molar fraction of KCl equal to $x_{KCl} = 0, 0.25, 0.5, 0.75,$ and 1, at 298 K. The ion-exchange capacity, swelling, sorption were determined using the standard methods described *e.g.* in [14]. The electroosmotic coefficient was determined by the volume method using the experimental setup described in [15]. The electric conductance was determined by the ac method [16] using the RLC bridge Meratronik Type E318. The transport number of counterions were determined by the Hittorf method. The membrane separated two compartments, each filled with 150 cm^3 of the solution. The effective area of membrane was 10 cm^2, the current density – 2 mA/cm^2. The Ag/AgCl electrodes were used. For a given

concentration 3 runs were performed. Each run lasted at least 1 h. From the concentration and mass changes of solutions the transport number was calculated:

$$\bar{t}_i = F \frac{c_{i,t}m_t - c_{i,0}m_0}{\rho t I} \tag{26}$$

where $c_{i,0}$, $c_{i,t}$, m_0, m_t are the concentration of ion i, mass of the solution before and after passing the current I during time t, respectively. The density of solution, ρ, was assumed to be the same as that at $t = 0$. As the transport number of coions Cl⁻ in Nafion equilibrated with 0.1 M solution can be neglected, and the transport numbers of Na⁺ and K⁺ are related by $\bar{t}_1 + \bar{t}_2 = 1$, the best estimates of $\bar{t}_i, \hat{t}_i$ ($i = 1,2$), were calculated from the following formulas [17]:

$$\hat{\bar{t}}_1 = \frac{1}{2}(\bar{t}_{1,\exp} + 1 - \bar{t}_{2,\exp}); \qquad \hat{\bar{t}}_2 = 1 - \hat{\bar{t}}_1 \tag{27a,b}$$

The concentrations of potassium and sodium ions were determined by the AAS method. The hydrodynamic permeability coefficient, L_p, was determined using the Sartorius setup (the thermostated dead-end cell).

RESULTS AND DISCUSSION

Experimental results: The basic, non-equilibrium parameters of the system in the function of molar fraction of KCl are presented in Table 3. It is seen that with the increase of the KCl content, the swelling of membrane, expressed as a volume pore fraction, decreases. The selectivity coefficient, defined as the ratio of ratios of molar fractions of KCl and NaCl, inside the membrane, $\bar{x}_{K^+}/\bar{x}_{Na^+}$, and in the external solutions,

x_{K^+}/x_{Na^+}:

$$K_{Na^+}^{K^+} = \frac{\bar{x}_{K^+}/\bar{x}_{Na^+}}{x_{K^+}/x_{Na^+}} \tag{28}$$

is high, *ca.* 2.8–3.1 (similar to those obtained for Nafion 120 [18] and Nafion 417 [19]), which indicates the preference of Nafion towards the K⁺ ions. As the ionic radius of K⁺ is larger than that of Na⁺ ($r_{K^+} = 0.133$ nm, $r_{Na^+} = 0.095$ nm [20]),the hydration of K⁺ is lower, what enables a closer contact of K⁺ with the fixed charges. Another reason is that the electric field of ionic groups aligns the water molecules. Energetically it is more favourable, when the less hydrated K⁺ ions stay close to the fixed charges, where the electric field is high.

The transport properties – the electric conductivity, κ_m, electroosmotic volume transport number, $\bar{t}_v$, and the hydrodynamic permeability coefficient $L_p^{(m)}$ – are shown in Fig. 1. Their dependence on the content of KCl and the swelling of membrane is similar – all the coefficients decrease with the decrease of swelling or the increase of KCl content. The decreasing of the conductivity with x_{KCl} seems to be rather astonishing, remembering that the mobility of K⁺ in a free solution is higher than that of Na⁺

(in 0.1 M solution the mobility ratio $u_{K^+}/u_{Na^+} = 1.27$). Again it can be concluded that the reduction of the mobility of the K^+ ions is caused by their higher concentration in the vicinity of the fixed charges than that of the Na^+ ions.

Table 3. Characteristics of Nafion 117 in 0.1 M (NaCl + KCl) solutions.

| x_{KCl}	porosity V_p	$\bar{c}_m$ [mol/dm^3 pore sol.]	$K_{Na^+}^{K^+}$
0.00	0.328	3.63	
0.25	0.314	3.90	2.80
0.50	0.305	4.16	3.10
0.75	0.295	4.42	2.77
1.00	0.283	4.62	

The transport numbers of K^+ and Na^+ are presented in Fig. 2. As the transport number of an ion depends on its concentration in the external solution, the relative transport number, $t_{Na^+}^{K^+}$, defined as the ratio of the transport number ratio to the concentration ratio of K^+ and Na^+ in the solution bathing the membrane

$$t_{Na^+}^{K^+} = \frac{\bar{t}_{K^+}/\bar{t}_{Na^+}}{x_{KCl}/x_{NaCl}} \tag{29}$$

has been also calculated (Fig. 2). It amounts to about 2, *i.e.* the K^+ ions are favourable in the electrical transport, which results from the increased content of K^+ (high selectivity coefficient $K_{Na^+}^{K^+}$). Dividing $t_{Na^+}^{K^+}$ by $K_{Na^+}^{K^+}$ yields the ratio of their mobilities with respect to the membrane:
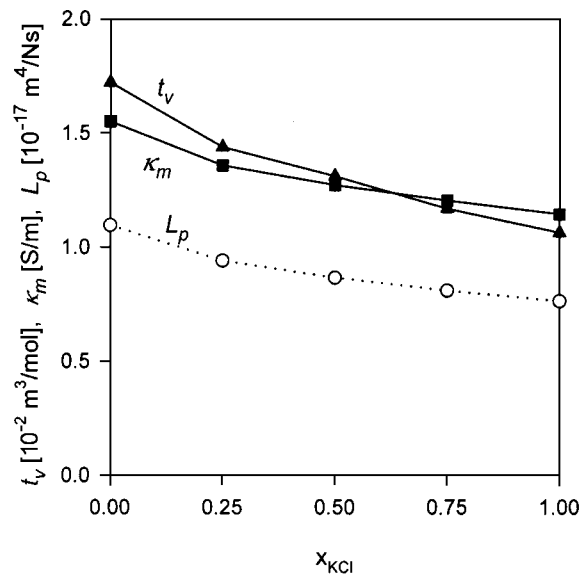
Figure 1. Dependence of electrical conductivity, κ_m, electroosmotic volume transport number, $\bar{t}_v$, and the hydrodynamic permeability coefficient, $L_p^{(m)}$, on the molar fraction of KCl; Nafion 117, c_s(NaCl + KCl) = 0.1 M, T = 298 K.
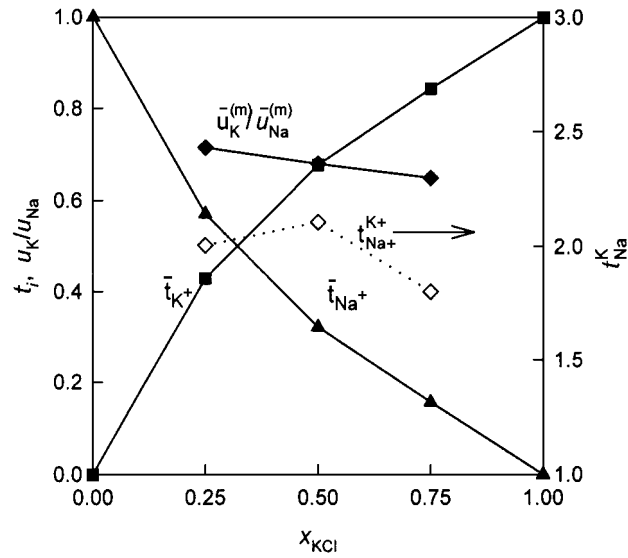
Figure 2. Dependence of $\bar{t}_{K^+}$ (squares), $\bar{t}_{Na^+}$ (triangles), relative transport number $t_{Na^+}^{K^+}$, and the ratio of mobilities $\bar{u}_{K^+}^{(m)}/\bar{u}_{Na^+}^{(m)}$ inside Nafion 117 on the molar fraction of KCl; c_s (NaCl + KCl) = 0.1 M, T = 298 K.

$$\frac{t_{Na^+}^{K^+}}{K_{Na^+}^{K^+}} = \frac{\bar{t}_{K^+}/\bar{t}_{Na^+}}{\bar{x}_{KCl}/\bar{x}_{NaCl}} = \frac{\bar{u}_{K^+}^{(m)}}{\bar{u}_{Na^+}^{(m)}} \tag{30}$$

It amounts to *ca*. 0.65–0.7 (Fig. 2), *i.e.* comparing to $u_{K^+}/u_{Na^+} = 1.27$ in the free solution the mobility of K^+ in the membrane is reduced, as it has been concluded from the conductivity results.

   Model calculations: The discussion of the model predictions will be started with the selectivity coefficient $K_{Na^+}^{K^+}$, which characterizes the ionic composition of membrane, influencing the transport phenomena.

   The selectivity coefficient $K_{Na^+}^{K^+}$ calculated on the base of the modified Boltzmann eq. (16) for two sets of the hydration constant A_i (G – Gur *et al*., BP - Bontha and Pintauro) is presented in Fig. 3. As the difference between A_{Na^+} (BP) and A_{K^+} (BP) is very small, it is not possible to obtain the agreement of calculated $K_{Na^+}^{K^+}$ with the experimental one for reasonable values of pore radius, *i.e.* not exceeding the radius of clusters, *ca*. 2–2.5 nm. On the other hand, if the Gur values of A_i are taken, then $K_{Na^+}^{K^+}$(calc.) $= K_{Na^+}^{K^+}$ (exper.) for $R = 1$ nm. This value of R is similar to the radius of channels, however, it is 2 times lower than that of clusters, which are the predominant constituent of pores in that membrane. Thus, A_i should be between A_i(BP) and A_i(G).
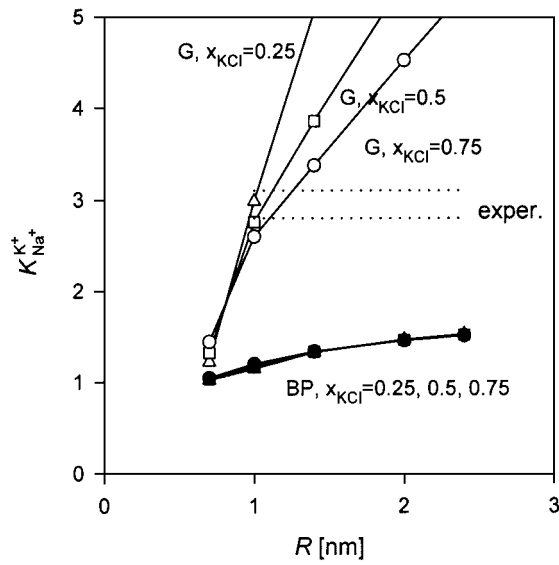
Figure 3. Selectivity coefficient $K_{Na^+}^{K^+}$ *vs.* capillary radius calculated from the modified Boltzmann eq. (17) assuming A_i as given by Gur *et al*. (G) and Bontha and Pintauro (BP), the experimental lower and upper values of $K_{Na^+}^{K^+}$ are denoted by dotted lines.
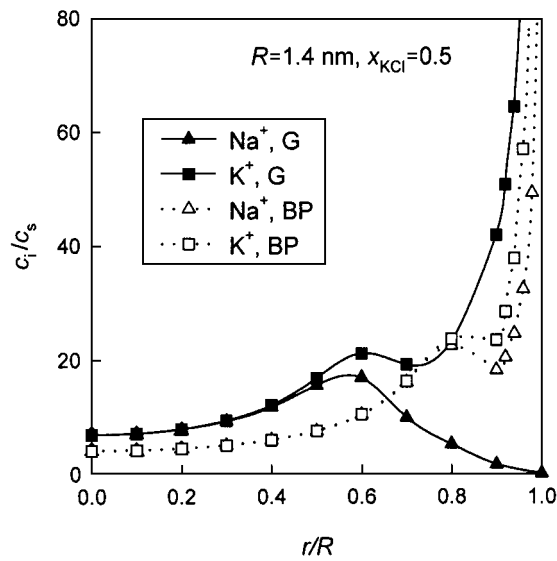
Figure 4. Radial concentration profiles of Na^+ (triangle) and K^+ (square) in the capillary of radius 1.4 nm according to the modified Boltzmann eq. (17), A_i taken from Gur *et al*. [11] – solid lines (G), from Bontha and Pintauro [12] – dotted lines (BP), $\bar{c}_m = 4.2$ M, $c_s = 0.1$ M, $x_{KCl} = 0.5$.

The calculated radial profiles of Na$^+$ and K$^+$ (Fig. 4) show that K$^+$ of smaller hydration constant are located close to the charge wall. The higher difference between A_{Na^+} and A_{K^+}, the stronger exclusion of Na$^+$ from the vicinity of the wall is observed.

Although it was possible to solve the Poisson and modified Boltzmann equations, it was not possible to calculate precisely the straight B_{ii} coefficients of counterions from the radial concentration profiles approximated by a polynomial. Another, more sophisticated method has to be elaborated. Therefore, from now on the classical Boltzmann equation will be discussed only.

As it was mentioned earlier, in Nafion the fixed charges are grouped into the clusters connected by narrow channels. Thus, the equivalent radius of Nafion pores, R, should range from that of channels to that of clusters. Instead of assuming some arbitrary average of those radii it has been determined from the electroosmotic volume flow by solving for R the equation:

$$\bar{t}_v(R) = \bar{t}_v(\text{exp.}) \tag{31}$$

The calculated in this way R (Table 4) changes from 1.2 to 1.4 nm, *i.e.* it lies in the range of the channel and cluster radii.

Table 4. The capillary model with the classical Boltzmann distribution of ions: the equivalent radius of pores estimated from eq. (31), the tortuosity factor θ^2 calculated from the model κ, L_p and the experimental κ_m, $L_p^{(m)}$ according to eq. (10).

x_{KCl}	R [nm]	$\theta^2(\kappa)$	$\theta^2(L_p)$	$\theta^2(L_p)/\theta^2(\kappa)$
0	1.32	3.3	3.8	1.14
0.25	1.40	5.3	5.8	1.10
0.5	1.38	6.6	6.7	1.01
0.75	1.30	7.5	6.5	0.87
1	1.24	8.2	6.3	0.77

To check the consistency of the model the tortuosities of the electric conductivity, $\theta^2(\kappa_m)$, and of the hydrodynamic transport, $\theta^2(L_p)$, have been calculated from (10). It is seen (Table 4) that the agreement is fairly good – the difference between them does not exceed 14% except for the pure solution of KCl ($x_{KCl} = 1$). The increase of $\theta^2(\kappa_m)$ with x_{KCl} and, consequently, decrease of $\theta^2(L_p)/\theta^2(\kappa_m)$ indicates that the mobility of K$^+$ comparing to Na$^+$ inside the membrane is overestimated. The main reason of that overestimation is the use of the Boltzmann equation, which yields the same radial profiles of both ions. In fact the K$^+$ ions stay closer to the fixed charges than the Na$^+$ ions (Fig. 4), which hampers the movement of K$^+$.

According to the capillary model, the convective coupling coefficients $\alpha_i^{'}$ (25) are high (> 1, Fig. 5) for those ions, whose concentration decreases towards the capillary wall (Fig. 6a), whereas if the concentration increases, then $\alpha_i^{'}$ of that ion falls below 1. $\alpha_i^{'}$ depends also on the kind of acting force (Fig. 5), which results from the different profiles of the convective velocity (Fig. 6b).
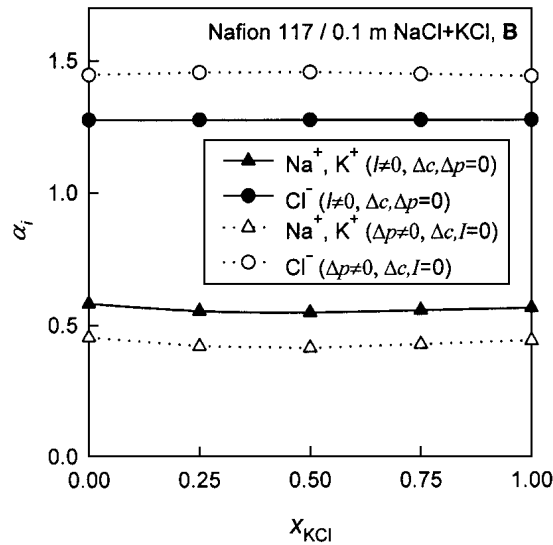
Figure 5. Convective coupling coefficient of counterions Na^+, K^+ (triangle) and coions Cl^- (circle) in the electric transport ($I \neq 0$, Δc, $\Delta p = 0$, solid lines) and of the hydrodynamic transport ($\Delta p \neq 0$, Δc, $I = 0$, dotted lines) for the system Nafion 117|0.1 M NaCl + KCl, according to the capillary model with the Boltzmann distribution of ions.

The values of α'_i, shown in Fig. 5, are similar to those determined by Meares [5] for the cation-exchange membrane ZeoKarb 315 and the NaBr solutions. It should be noted that the Meares' α_i were calculated from the conductivity, electroosmotic transport number of water, and the tracer diffusion coefficients, not from the hydrodynamic permeability coefficient, as it results from (11). Although ZeoKarb 315 is much more porous than Nafion 117 ($V_p = 0.75$ vs. 0.33 of Nafion) and its concentration of fixed charges is much smaller ($\bar{c}_m = 0.55$ M *vs.* 3.6 M of Nafion) [21], some preliminary calculations using the capillary model with such $\bar{c}_m$ show that for pores 3–5 nm $\alpha_{Na^+} = 0.64$–0.53, $\alpha_{Cl^-} = 1.24$–1.2, *i.e.* the agreement with the experimentally determined by Meares α_i is fairly good.

In the discussion of the ENPE two cases are presented – with and without the condition of the ORR (eq. (7)). The results are gathered in Table 5. As the expression for L_p is the same in both cases, the tortuosity of the hydrodynamic flow $\theta^2(L_p)$ is also the same. It is close to 2 and about 3 times smaller than that resulting from the capillary model (Table 4).

If the ORR condition (7) is not imposed, then $\theta^2(\kappa) = \theta^2(L_p)$, because the calculation of κ (through α_i) is based on that assumption. Regarding α_i, both α_{Na^+} and α_{K^+} are negative even in the pure solutions of NaCl ($x_{KCl} = 0$) and KCl ($x_{KCl} = 1$), for which the formula for α_i (11a) depends on the measurable quantities only. The negative α_i contradict the experimental fact that the electroosmotic volume flow is directed towards the movement of counterions and also the predictions of the capillary model. What is more the deviation from ORR, expressed by $(I/\nabla p)_{\Delta c, \Delta \psi = 0}/(J_v/\nabla \psi)_{\Delta c, \Delta p}$ (eq. (12)), is
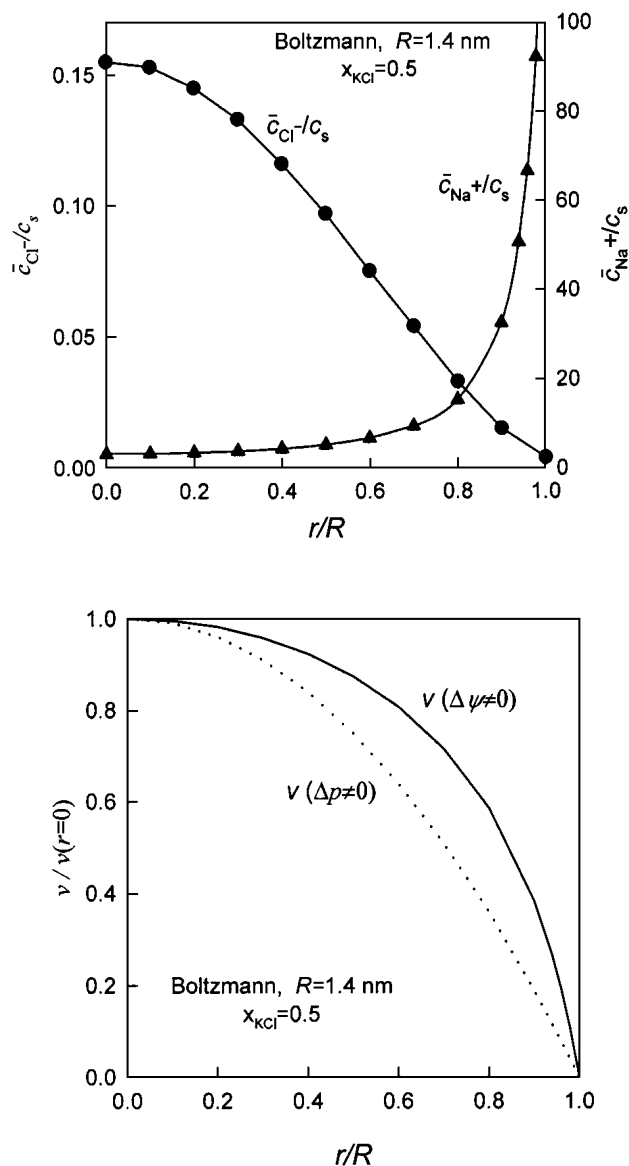
Figure 6. a) The radial profiles of the concentration of counterions (triangle) and coions (circle); b) the radial profile of the convective velocity for two force conditions: $\Delta\psi \neq 0$, Δp, $\Delta c_i = 0$ (solid line) and $\Delta p \neq 0$, I, $\Delta c_i = 0$ (dotted line); the Boltzmann equation, c_s(NaCl + KCl) = 0.1 M.

very large. It should be stressed that the calculated $(I/\nabla p)_{\Delta c, \Delta\psi = 0}/(J_v/\nabla\psi)_{\Delta c, \Delta p}$ does not depend on $\bar{u}_i$, which has to be assumed more or less arbitrarily, but on the experimental variables and the assumption $\theta^2(\kappa) = \theta^2(L_p)$ only.

Table 5. The ENPE: the convective coupling coefficients, α_i, calculated from eq. (11) assuming that $\bar{u}_i$ equals to the mobility in the 3 M solution $u_{Na^+} = 2.46 \times 10^{-13}$, $u_{K^+} = 5.19 \times 10^{-13}$ mol·m/N·s according to the data from [23].

x_{KCl}	$\theta^2(L_p)$	α_i (11), ORR (7) is not fulfilled $\theta^2(\kappa) = \theta^2(L_p)$			$\alpha_i = 1$ ORR (7) is fulfilled	
		α_{Na^+}	α_{K^+}	$\dfrac{(I/\nabla p)_{\Delta c, \Delta\psi=0}}{(J_v/\nabla\psi)_{\Delta c, \Delta p}}$	$\theta^2(\kappa)$	$\dfrac{\theta^2(L_p)}{\theta^2(\kappa)}$
0	1.3	−0.62	−	−0.6	4.7	0.27
0.25	1.8	−0.10	−2.8	−1.3	7.1	0.25
0.5	2.1	0.39	−2.6	−1.9	9.2	0.23
0.75	2.1	0.52	−3.0	−2.6	10.2	0.20
1	2.1	−	−3.4	−3.4	10.9	0.19

If the ORR (7) is imposed, then the ENPE yields the relation (8) between L_p/κ and $\bar{t}_v$. Its comparison with the experimental ratio $L_p^{(m)}/\kappa_m$, expressed by $\theta^2(L_p)/\theta^2(\kappa)$, shows that the agreement is very poor. The calculated L_p is about 4–5 times too small comparing to κ. It cannot be explained by such differences in the tortuosities of real paths of the hydrodynamic and electric transports.

All these observations lead to the conclusion that the ENPE with the homogeneous radial distribution of ions inside the membrane pores is not adequate for the description of the electrokinetic phenomena in the ion-exchange membranes.

CONCLUSIONS

The capillary model with the Boltzmann distribution of ions relatively well describes the electrokinetic phenomena in the cation-exchange membrane Nafion 117 in the mixed ionic form Na^+-K^+. As the classical Boltzmann equation does not distinguish the K^+ and Na^+ ions, whereas in the reality the affinity of K^+ to Nafion 117 is higher than that of Na^+, it is expected that the modified Boltzmann equation (16), taking into account the individual properties of K^+ and Na^+, could improve the agreement. However, the calculations of the straight convective coefficients B_{ii} with the adequate accuracy have failed.

The extended Nernst-Planck equation with the homogeneous distribution of ions in the cross-section of membrane pores and the coupling convective coefficients α_i equal to 1 is not fit for that description. On the other hand, the introduction of α_i, calculated from the experimental data, strongly violates the Onsager reciprocal relation. Thus, with a given set of α_i the extended Nernst-Planck equation can describe one kind of transport only.

Contrary to the ENPE the capillary model is able to explain α_i different from one ($\alpha_i > 1$ for coions and $\alpha_i < 1$ for counterions in accordance to those determined experimentally [5]), still retaining the Onsager reciprocal relation. This fact results from the different radial profiles of the ions concentrations and of the convective velocity. As the last profile depends on the kind of acting force, the α_i are different for the different forces. The general formula relating α_i with the forces is given.

Appendix

Calculation of $\bar{l}_{ik}$ and $\bar{\eta}$

Assuming that the movement of ions in frame of mass centre of pore solution is similar to that in a free solution, $\bar{l}_{ik}$ can be calculated from l_{ik} for the free solution from the relation:

$$\bar{l}_{ik} = l_{ik} \frac{2}{\sqrt{c_i c_k}} \int_0^1 \sqrt{\bar{c}_{i,r}\bar{c}_{k,r}}\, r\, dr \qquad i,k = 1,2, .., n \qquad (A1)$$

The $\bar{l}_{0k}$ coefficients, related to water, are given by the formula (A2), resulting from the dependence of flows in the frame of mass centre.

$$\bar{l}_{0k} = -\frac{1}{M_0} \sum_{i=1}^n M_i \bar{l}_{ik} \qquad k = 0,1, .., n \qquad (A2)$$

As the l_{ik} coefficients for the ternary mixture of NaCl and KCl are not available in literature, they have been estimated in the following way. At first the $l_{ik}^{(0)}$ coefficients (water as a frame of reference) for the ternary system have been estimated by the LNI approximation proposed by Miller [22] using the data from [23]. Then the l_{ik} coefficients in the frame of mass centre were calculated from:

$$L = AL^{(0)}A^T \qquad (A3)$$

where

$$a_{ik} = \delta_{ik} - c_i M_k/\rho \qquad (A3a)$$

$$L^{(0)} = \begin{bmatrix} l_{11}^{(0)} & l_{12}^{(0)} & l_{13}^{(0)} & 0 \\ l_{21}^{(0)} & l_{22}^{(0)} & l_{23}^{(0)} & 0 \\ l_{31}^{(0)} & l_{32}^{(0)} & l_{33}^{(0)} & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \qquad (A3b)$$

The subscripts *1,2,3* denote Na^+, K^+, and Cl^-, respectively.
As the concentration of Na^+ and K^+ in the pore solution is high (Table 1), the calculations were made for the highest electrolyte concentration (3 M), for which $l_{ik}^{(0)}$ are available.

Table A1. The $\bar{l}_{ik}$ coefficients in the frame of mass centre of pore solution calculated from eq. (A2) for the concentration of fixed charges and radius of pores listed in Tables 3, 4, respectively.

x_{KCl}	$\bar{x}_K$	$\bar{l}_{ik}$ [10^{-10} mol/m^2 Ns] 1-Na$^+$, 2-K$^+$, 3-Cl$^-$					
		$\bar{l}_{11}$	$\bar{l}_{22}$	$\bar{l}_{12}$	$\bar{l}_{33}$	$\bar{l}_{13}$	$\bar{l}_{23}$
0	0.00	10.23	0.00	0.00	0.025	0.0076	0.0000
0.25	0.48	11.01	6.05	−0.48	0.030	−0.0034	−0.0001
0.5	0.75	9.03	11.73	−0.56	0.031	−0.0034	−0.0006
0.75	0.89	5.12	17.74	−0.44	0.029	−0.0013	−0.0013
1	1.00	0.00	23.79	0.00	0.027	0.0000	−0.0025

The viscosity of pore solution, assumed to be the same in the cross-section of pores $\bar{\eta}_r = \bar{\eta}$, was estimated from the formula:

$$\bar{\eta} = (1 - x_{KCl})\eta_{NaCl} + x_{KCl}\eta_{KCl} \tag{A4}$$

where η_{NaCl} and η_{KCl} are the viscosities of the pure NaCl and KCl solutions. For 3 M solutions $\eta_{NaCl} = 0.00123$ and $\eta_{KCl} = 0.000919$ Ns/m^2.

Acknowledgments

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