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Radial distribution of ions in pores with a surface charge

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Abstract

A sorption model applicable to calculate the radial equilibrium concentrations of ions in the pores of ion-selective membranes with a pore structure is developed. The model is called the radial uptake model. Because the model is applied to a Nafion sulfonic layer with very small pores and the radial uptake model is based on the assumption that continuum equations are applicable, the model is used near its limits of fundamental validity. However, the results indicate that the calculated profiles with the radial uptake model are realistic and similar to literature results (e.g. [J.R. Bontha, P.N. Pintauro, J. Phys. Chem. 96 (1992) 7778; J.R. Bontha, P.N. Pintauro, Chem. Eng. Sci. 49 (1994) 3835]). The membrane microstructure parameters (surface charge density and pore diameter) have been determined by fitting the sorption of sodium as predicted by the radial uptake model to the sorption of sodium as predicted by the so-called modified Pitzer model [J.H.G. Van der Stegen, A.J. van der Veen, H. Weerdenburg, J.A. Hogendoorn, G.F. Versteeg, Fluid Phase Equilibria 157 (1999a) 181]. This modified Pitzer model has proven to be able to predict volume averaged sorption of ions in a sulfonic membrane layer. Via the introduction of a component dependent correction factor in the radial uptake model, the sorption of ions other than sodium could also be fitted to the volume averaged sorption data as predicted by the modified Pitzer model. The correction factors were in the order of magnitude of 0.05–10, and dependent on the concentration of sodium. The necessity of the application of correction factors for the ions other than sodium may have been induced by the assumption that:

- the applicability of continuum equations in the model is justified and/or;
- the activity coefficients in the radial uptake model are equal to unity.

It was observed that due to the preferential sorption of iron near the pore wall, the pore surface charge could be shielded, resulting in a decrease of the preferential selectivity of the membrane for sodium. However, such a phenomenon does not occur in the operating range of the chloralkali process, where the sorption of iron inside the membrane is proportional to its external concentration. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Pitzer model; Radial distribution; Surface charge; Nafion membrane

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Nomenclature

A	hydration constant ($J\,mol^{-1}$)
C	concentration ($mol\,m^{-3}$)
CE	current efficiency (%)
D	diffusion coefficient ($m^2\,s^{-1}$)
e_w	water uptake ($m^3\,m^{-3}$)
EW	equivalent weight ($kg\,eq^{-1}$)
F	Faraday's constant ($mol\,eq^{-1}$)
$\Delta_{vac}G$	hydration Gibbs free energy ($J\,mol^{-1}$)
L	length of pore (m)
m	molality ($kg\,kg^{-1}$)
n	refractive index
N_c	number of components
N_p	number of pores
r	radial coordinate (m)
r_p	pore radius (m)
R	universal gas constant ($J\,mol^{-1}\,K^{-1}$)
T	temperature (K)
X	fixed charge concentration ($mol\,m^{-3}$)
z_i	ionic charge of component i

Greek letters

α	water dipole moment ($C\,m^{-1}$)
β	constant in relation for electric permittivity
ϵ	dielectric permittivity ($F\,m^{-1}$)
ϵ^*	dielectric permittivity of vacuum ($F\,m^{-1}$)
γ	activity coefficient
Γ	sorption correction factor
φ	potential (V)
κ	Boltzmann constant ($J\,K^{-1}$)
μ	electrochemical potential ($J\,mol^{-1}$)
μ_0	standard electrochemical potential ($J\,mol^{-1}$)
ρ	density ($kg\,m^{-3}$)
ρ_e	charge density ($C\,m^{-3}$)
σ	surface charge density ($C\,m^{-2}$)

Superscripts

b	bulk
m	membrane phase

Subscripts

i	component index
p	pore
r	radial
w	water

1. Introduction

Ion exchange membranes are used in a number of electrochemical devices including batteries, fuel cells and electrochemical reactors. They have also found applications in the desalination of brackish water and in heavy metal removal from wastewater. Despite their widespread use, only very little is known about the molecular-level processes that control ion uptake and transport in these membranes. In a previous paper [3] the uptake of ions in a sulfonic membrane layer (which is present in the Nafion membranes as used in the chloralkali electrolysis process) was described by applying a modified Pitzer model which is an extension of a traditional liquid phase equilibrium model. Although the model was able to describe the sorption data satisfactorily, one of the basic assumptions is that the ions are homogeneously distributed in the membrane. However, it has been shown that for the sulfonic layer of the Nafion membrane such a homogeneous distribution of ions in the membrane is an oversimplification. For the sulfonic layer the presence of what is called a cluster-network configuration has successfully been demonstrated to exist [4,5]. This means that the uptake of ionic species is governed by inhomogeneous molecular level interactions in the pore between the solute, the solvent and the membrane polymer matrix.

In order to create better understanding about these topics, this paper will describe a model that is able to predict the radial distribution of ions in a pore with a surface charge.

2. The membrane

The most frequently used membrane types in the chloralkali electrolysis process are perfluorinated ionomer membranes with sulfonic and carboxylic

base polymers. These names are derived from the type of charged groups inside the membrane, that is $-SO_3^-$ (sulfonic) or $-COO^-$ (carboxylic), respectively. Due to the negative charge of the fixed groups the membranes will be cation selective, which is the main goal of the application of such a membrane in the chloralkali electrolysis process [6,7]. The perfluorinated ionomer membranes with sulfonic groups or carboxylic groups (e.g. the Flemion membranes of Asahi Glass Company or the Nafion membranes of Du Pont de Nemours) expose these properties and therefore are used in many electrochemical applications such as the chloralkali electrolysis.

In case of a carboxylic base membrane, the membrane is supposed to be a (pseudo)-homogeneous phase and the description of the equilibrium at the interfaces and the mass transfer process is mainly modeled on a macroscopic basis [8]. This implies that uniform properties are assumed and that a one-dimensional transport model can be applied.

In case of a sulfonic type membrane layer, Gierke et al. [4,5] have shown that the membrane structure is heterogeneous. This structure was derived from investigations on ion-exchange membranes with the help of X-ray scattering and neutron scattering techniques. In Fig. 1a the experimentally found structure according to Koh and Silverman [9] is shown schematically for the sulfonic base polymer. With this apparent microstructure both the equilibrium model applicable to the phase transitions and the transport model should account for the radial direction. As the exact pore structure is unknown assumptions and simplifications have to be made. According to Verbrugge and Pintauro [10], the experimentally found membrane structure can be represented by an array of parallel cylindrical capillaries, with a uniform charge density on the pore wall of the ion-exchange membrane (see Fig. 1b). Koh and Silverman [9] support this view because they report that ionic transport is mainly controlled by the dimensions of the channels connecting the clusters and surface charge densities, and that the role played by other structural characteristics, such as, e.g. the cluster dimensions, are less important. Therefore, in the present study, the sulfonic membrane was regarded as a matrix composed of straight parallel cylinders with a radius in the order of the channel radius (± 1 nm) and a pore length of about the thickness of the membrane [10].

In the present study attention will be paid to the thermodynamic equilibrium at the anolyte-sulfonic phase transition. The choice for this phase transition is obvious, as the sulfonic layer is always contacted with the anolyte. The equilibrium model should be able to predict the radial concentrations of the various components inside the pore. A model suitable for this is the so-called one-dimensional submodel, developed by Bontha and Pintauro [2]. Because parameters like the pore radius and the surface charge density are unknown these have to be determined from experimental volume averaged sorption data and/or from the theoretical volume averaged sorption data as predicted by the modified Pitzer model [3].

3. The radial uptake model

3.1. Introduction

A model will be presented, which can describe equilibrium sorption of ions in an ion-selective membrane with a pore structure. This can be applied to a membrane like the sulfonic membrane, which is supposed to have such a pore structure (see e.g. Fig. 1a and b). This model cannot only be used to predict membrane microstructure parameters and radial concentration profiles in the sulfonic layer at a phase transition, but also contribute to an improved understanding of the sorption process. Pintauro and Yang [11] first presented the complete model for the description of the sorption of ions in membranes with a pore structure. They combined the multicomponent partition coefficient theory described by Bontha and Pintauro [2] and the single-component transport theory developed by Guzman-Garcia et al. [12]. The model considers pore-water orientation by the strong radial electric field generated by the ion-exchange sites at the pore wall and variations in ion hydration forces due to the low water dielectric constant near the pore wall. One of the major assumptions in the application of the model is that equations for continuum models (such as the Poisson and Booth equation) are also applicable to the description of the interaction of the pore wall with the solutes. This, however, may not be true in the present situation, as the dimensions of the pores usually are in the same order of magnitude as the ions.
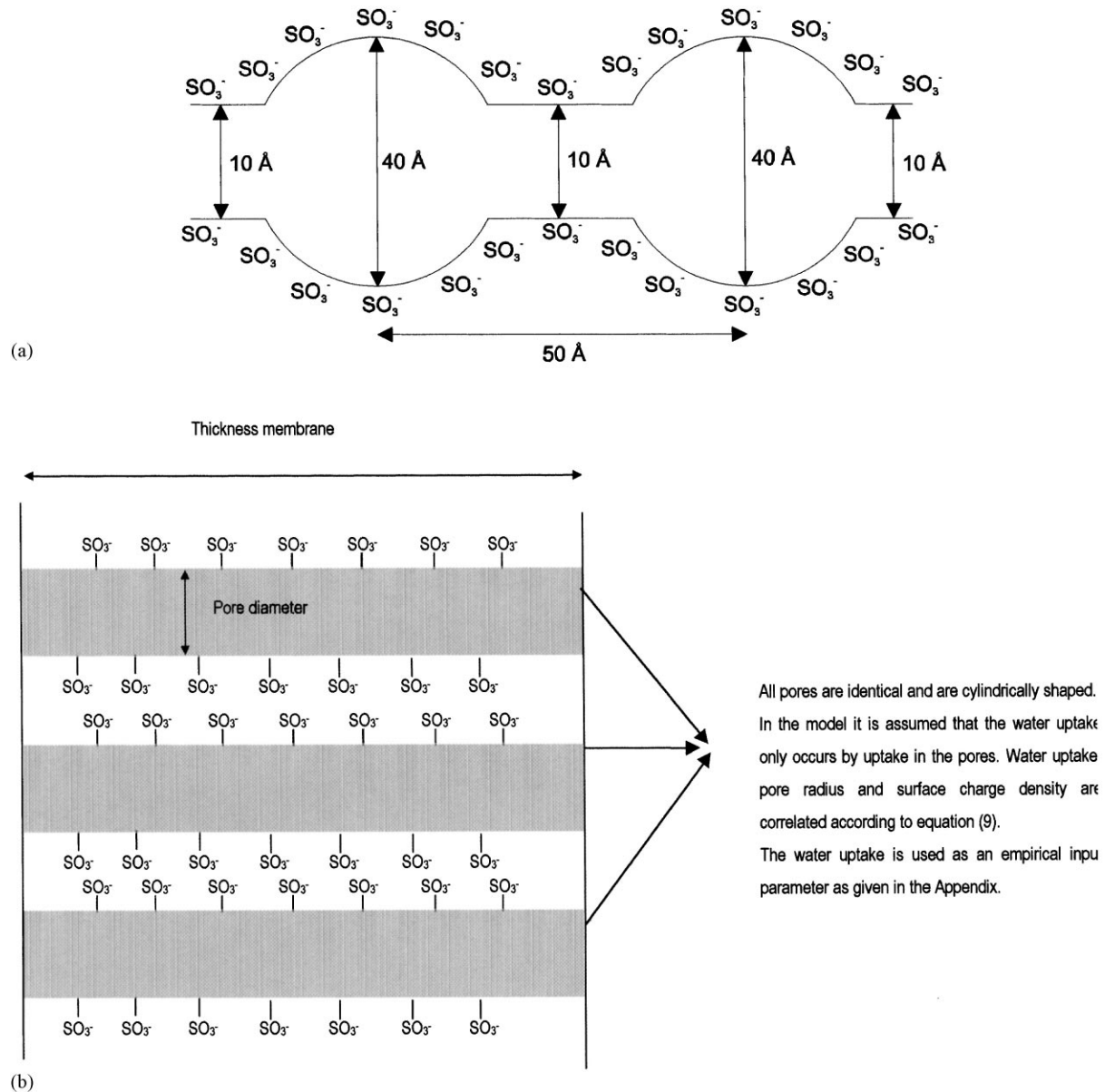
Fig. 1. (a) Experimentally found structure of an ion-exchange membrane with an sulfonic base polymer according to Koh and Silverman [9]; (b) schematic representation of simplified membrane structure as used in the present contribution. The gray area represents the pores.

3.2. Model description

When equilibrium is achieved between a membrane and its surroundings the electrochemical potential of each species inside the liquid in the membrane is equal to its electrochemical potential in the external solution [13]

$$\mu_{i,0}^{m} + RT \ln(\gamma_i^{m} c_i^{m}(r)) + \Delta_{vac}^{m} G_i(r) + z_i F \varphi$$
$$= \mu_{i,0}^{b} + RT \ln(\gamma_i^{b} c_i^{b}) + \Delta_{vac}^{b} G_i + z_i F \varphi^{b} \qquad (1)$$

in which m, b and i refer to membrane fluid, bulk fluid and component i, respectively. The $\Delta_{\text{vac}} G$ terms define the hydration (solvation) Gibbs free energy change associated with the transfer of an ion from vacuum to the given phase. These free energy terms account for the ion-solvent interaction energy contribution to the electrochemical potential because of the solvent dipole alignment in a pore. This interaction occurs due to the strong radially directed electric field generated by fixed-charge sites along the pore wall.

Bontha and Pintauro [1] have developed a model for the prediction of free energies of ionic solvation. They proposed a function that describes a hydration constant A_i, which is dependent on the free Gibbs solvation energies and the dielectric constant of the solvent (ε)

$$A_i = \frac{\Delta_{\text{vac}} G_i|_{\varepsilon=n^2} - \Delta_{\text{vac}} G_i|_{\varepsilon=\varepsilon_{\text{b}}}}{1/\varepsilon|_{\varepsilon=n^2} - (1/\varepsilon)|_{\varepsilon=\varepsilon_{\text{b}}}} \tag{2}$$

with n the refractive index of the solvent. The term A_i is called the hydration constant for species i and the expression was derived by using a two-point boundary approximation, because, according to the authors, the free Gibbs energy change seems to be a linear function of the reciprocal dielectric constant of the solvent. The minimum value of the dielectric constant is n^2 at infinite large potential gradients, while the other asymptote is given for zero potential gradient, ε_{b}.

The hydration constant for a species, as defined by Eq. (2), is a function of the charge of the ion and the hard sphere radius of the ion. The free Gibbs energies, pore radii and hydration constants for several components are tabulated in the Appendix A. For hydroxide it is in fact erroneous to define a hydration constant, because it is not an ordinary ion and has special properties in water. However, in order to implement hydroxide into the model, in this study the hydroxide is assumed to be similar to an ordinary ion. To realize this, the unknown hydration constant for hydroxide was taken equal to the value for Cl⁻. Although the model in this study is applied to both catholyte and anolyte, the model only has practical significance for situations in which the sulfonic layer is contacted with the anolyte (as in the chloralkali electrolysis process). This means that the aforementioned simplification seems to be acceptable because of the fact that the concentration of hydroxide in the anolyte is very low (pH $\sim$ 2–5). This means that even if the radial distribution of hydroxide in the pore is unreliable, this only has minor consequences with respect to the behaviour of other components in the pore for practical conditions.

If the standard state chemical potentials are presumed to be equal in both fluid phases and assuming the ion activity coefficients to be unity the following modified Boltzmann equation can be derived by rewriting Eqs. (1) and (2).

$$c_i^{\text{m}}(r) = c_i^{\text{b}} \exp\left\{\frac{z_i F}{RT}(\varphi^{\text{b}} - \varphi(r)) + \frac{A_i}{RT}\left(\frac{1}{\varepsilon^{\text{b}}} - \frac{1}{\varepsilon(r)}\right)\right\} \tag{3}$$

In order to use Eqs. (1) and (3) to compute the radial dependent equilibrium concentration of one or more ions inside a membrane pore, the dependency of the electrostatic potential and solvent dielectric constant on the radial pore position must be determined. This is accomplished by solving Poisson's equation with a nonuniform dielectric constant for n mobile ion species.

$$\nabla[\varepsilon(r)\nabla\varphi(r)] = -\frac{F}{\varepsilon^*}\sum_{i=1}^{N_{\text{s}}} z_i c_i^{\text{m}}(r) \tag{4}$$

in which ε^* is the permittivity of vacuum. An expression to relate the dielectric constant to the electric field strength in a membrane pore is given by Booth's equation [17].

$$\varepsilon(r) = n^2 + \frac{3(\varepsilon_{\text{b}} - n^2)}{\beta\nabla\varphi(r)} \times \left[\frac{1}{\tan h\{\beta\nabla\varphi(r)\}} - \frac{1}{\beta\nabla\varphi(r)}\right] \tag{5}$$

with

$$\beta = \left(\frac{5\alpha}{2\kappa T}\right)(n^2 + 2) \tag{6}$$

In Eq. (6) κ is the Boltzmann constant and α the dipole moment of the bulk solvent. The model is completed with the definition of boundary conditions for Eq. (4). On the centerline of the membrane ($r = 0$) symmetry of the potential field is assumed and at the pore wall ($r = r_{\text{p}}$) Gauss's law is applied.

$$r = 0, \qquad \frac{\partial\varphi(r)}{\partial r} = 0,$$

$$r = r_{\text{p}}, \qquad \frac{\partial\varphi(r)}{\partial r} = -\frac{\sigma}{\varepsilon^*\varepsilon(r_{\text{p}})} \tag{7}$$

where σ is the surface charge density of ion exchange sites on the pore wall. The resulting concentrations from Eq. (3) can be transformed to volume averaged concentrations by

$$C_{i,\,\text{average, pore}} = \frac{\int_0^{r_p} 2\pi r C_i(r)\,dr}{\pi r_p^2}$$
$$= \frac{C_{i,\,\text{average, membrane}}}{e_w} \tag{8}$$

in which e_w is the volume averaged water uptake of the membrane.

In order to calculate radial ion distributions across the pore, membrane microstructure parameters must be known. On the other hand, if the pore radius and the surface charge density are unknown they can be estimated by fitting the calculated volume-averaged concentrations (Eq. (8)) to experimental data or results derived from an appropriate theoretical equilibrium model, like the modified Pitzer model [3]. The latter approach was followed in the present study. This means that there is only one degree of freedom remains because the surface charge density and the pore radius are also correlated to each other as shown below.

predictions of the modified Pitzer model can be regarded as smoothed experimental data (see Fig. 2 for a schematic representation). Sodium was chosen as key component, because this is the main component present in the negatively charged membranes as used in the chloralkali electrolysis process. In the optimization procedure for the determination of the pore radius the counter ions chloride and/or hydroxide also play a role via Eq. (4). Because for a given surface charge density (see relation 9) there is only one degree of freedom (i.e. pore radius) to fit the sodium sorption data, two extra degrees of freedom are required to be able to fit the measured or predicted chloride and hydroxide sorption data. Therefore, a correction or fit parameter Γ_i is introduced in Eq. (3) to obtain the correct averaged sorption data of components other than Na$^+$ (of course for Na$^+$ the introduction of a correction factor is not necessary, effectively this means that there is one degree of freedom per component).

$$c_i^m(r) = c_i^b \Gamma_i \exp\left\{ \frac{z_i F}{RT}(\varphi^b - \varphi(r)) \right.$$
$$\left. + \frac{A_i}{RT}\left(\frac{1}{\varepsilon^b} - \frac{1}{\varepsilon(r)} \right) \right\} \tag{10}$$

Total charge inside the membrane per cubic meter of membrane	total charge $= ((1 - e_w)\rho_{\text{membrane}} F)/\text{EW}$
Total amount of pore surface per cubic meter of membrane	total surface $= 2 N_p \pi r_p L_p$
Total pore volume per cubic meter of membrane	$e_w = \pi r_p^2 L_p N_p$
Surface charge density	$\sigma = $ total charge/total surface area $= (e_w/(1 - e_w))(\rho_m F)/(2\text{EW})r_p$

$$\frac{e_w}{(1 - e_w)} = 1000 \frac{\rho_{\text{polymer}} F}{2\text{EW}} \frac{r_p}{\sigma} \tag{9}$$

The water uptake in Eq. (9) can be calculated by, e.g. the empirical relations of Van der Stegen [18] (see Appendix A).

In this report the pore radius was fitted to the sodium volume averaged concentration as predicted by the modified Pitzer model which has shown to be able to reliably predict volume averaged sorption data [3]. The modified Pitzer model was used to generate theoretical sorption data, however, it was used in the same concentration range as the Pitzer model parameters were derived from experiments. This means that the

The model equations were solved simultaneously, using a standard finite difference numerical algorithm with variable mesh point spacing. Numerical integration of the resulting radial ion concentration profiles across the membrane pore (Eq. (8)) was performed to obtain the average ion concentration in the solvent in the membrane. Of course, the sorption data of all components obtained in this way should equal the sorption data as predicted by the modified Pitzer model of van der Stegen et al. [3].

The optimization (or minimization of the difference) was performed by a downhill simplex method described by Nelder and Mead [19]. The method is described more extensively by Press et al. [20].
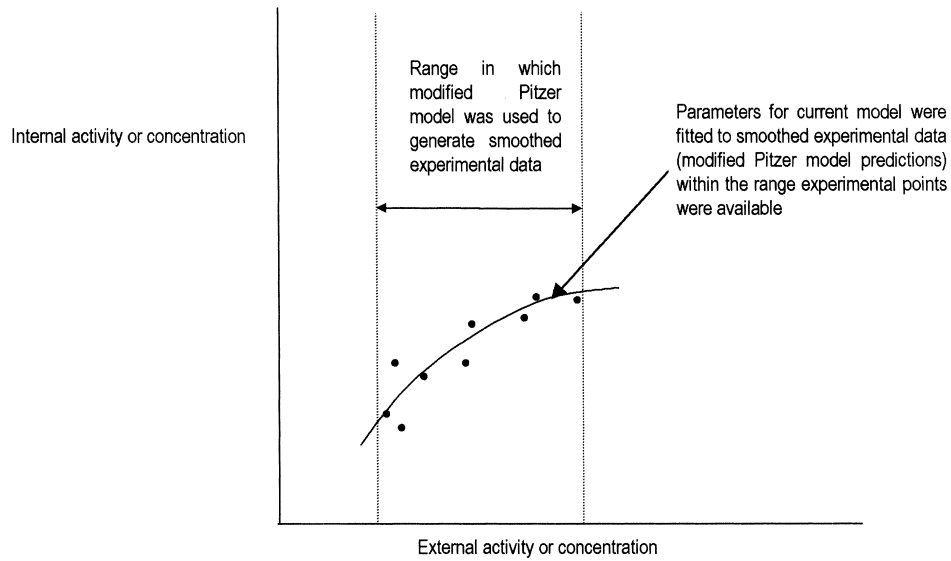
Fig. 2. Schematic representation of how the modified Pitzer model predictions [3] can be regarded as smoothed experimental points which were used to fit several parameters (r_p, σ, Γ_i) for the current model.

3.3. Results of the equilibrium sorption calculations for the main components with the radial uptake model

The model was applied to two sulfonic membranes which are also present in the sulfonic layer of two Nafion membranes: the Nafion 117 (with an equivalent weight of $1100 \, \mathrm{g \, mol^{-1}}$) and Nafion 152 (with an equivalent weight of $1500 \, \mathrm{g \, mol^{-1}}$). In the calculations the bulk electrolyte strength was varied from

1 to $5 \, \mathrm{M}$ sodium chloride and from 1 to $12 \, \mathrm{M}$ sodium hydroxide. The pore radius was fitted on the volume averaged sodium concentrations as predicted by the modified Pitzer model [3]. The results for the calculations are shown in Figs. 3 and 4. From these figures it becomes clear that the surface charge decreases with an increase of the water activity. As the water activity decreases with increasing sodium concentration, this means that the surface charge density increases with
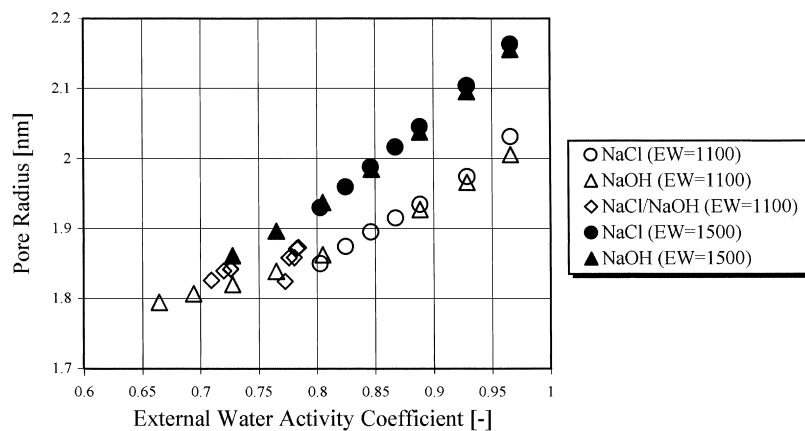

Fig. 3. The results of the model calculation on the membrane microstructure parameters for the Nafion 117 membrane, i.e. the fitted pore radii. The fit was performed on the smoothed sorption data, calculated by the modified Pitzer model [3].
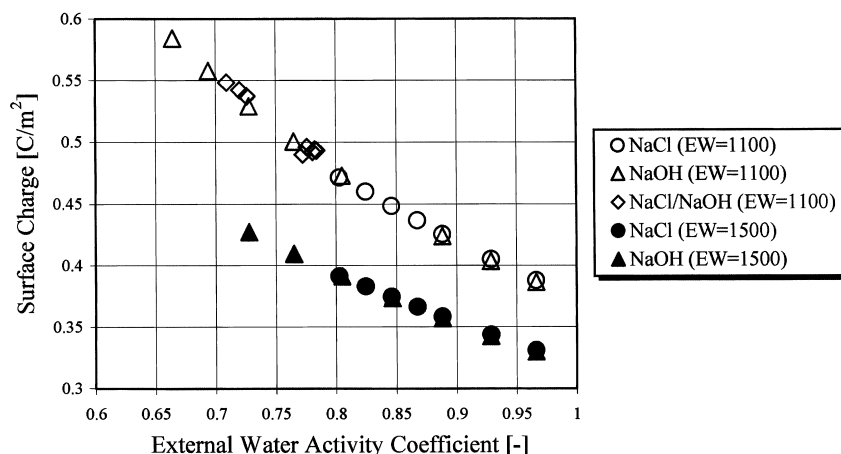
Fig. 4. The results of the model calculation on the membrane microstructure parameters for the Nafion 117 membrane, i.e. the calculated surface charges. The fit was performed on the smoothed sorption data, calculated by the modified Pitzer model [3].

an increase in the sodium concentration. This means that according to the model the pore radius decreases with an increase in the salt concentration, which is also found experimentally [4,5]. The reason for a shrinking membrane pore with an increasing salt concentration is a higher shielding effect provided by the more concentrated electrolyte solution. It can be seen that Nafion 152 shows smaller surface charge densities and larger pore radii than Nafion 117. This is because of the larger equivalent weights for this membrane type.

From Van der Stegen [18] it is clear that the membrane pores are smaller for a caustic soda bulk solution than for a NaCl bulk solution. However, in Fig. 3 the calculated pore radii for caustic soda and sodium chloride seem to be identical. The reason for this is simple. Because no data for the hydration coefficient of hydroxide were available in literature (see Appendix A) the hydration coefficient for hydroxide was assumed to be equal to the hydration coefficient of chloride. Therefore, the radial uptake model is not able to discriminate between hydroxide and chloride and thus no differences in pore radii and surface charge densities were found between a caustic and sodium chloride solution contrary to the experimental results of van der Stegen [18].

3.4. Correction factors for trace components

In the electrolysis process the exact role of trace components like iron is unknown, but from industrial experience it can be concluded that it is very important, because of the possibility of precipitation inside the membrane. Therefore the sorption and transport of these trace components has to be predicted accurately. The radial uptake model was extended to the application of aqueous solutions that contain more components than sodium, chloride and hydroxide. In the radial uptake model correction factors for other components than sodium had to be introduced to fit the sorption data, obtained from the modified Pitzer model [3]. Again the concentration range in which the current model was used was identical to the range in which the modified Pitzer model predicts reliable and verifiable results (also see Fig. 2). In order to fit the theoretical results of the present model to the smoothed experimental data (as represented by the predictions of the modified Pitzer model), Eq. (3) was modified again with a component specific correction factor Γ_i like was previously done for Cl^- and OH^- in Eq. (10) (this means that there is one degree of freedom per component).

$$c_i^m(r) = c_i^b \Gamma_i \exp\left\{ \frac{z_i F}{RT}(\varphi^b - \varphi(r)) + \frac{A_i}{RT}\left(\frac{1}{\varepsilon^b} - \frac{1}{\varepsilon(r)}\right) \right\} \tag{10}$$

Again for sodium a correction factor is superfluous as this component fits the sorption data predicted by the modified Pitzer model via the optimized

Table 1
Typical brine composition [18] and properties of the membrane type (Nafion 117)

Component	Brine composition	
	Concentration	Concentration (mol l^{-1})
Sodium chloride	180 g l^{-1}	3.08
Sulfate	6 g l^{-1}	0.063
Chlorate	2.3 g l^{-1}	0.028
Borate	1.5 g l^{-1}	0.026
Calcium	43 μg l^{-1}	1.07×10^{-6}
Magnesium	7 μg l^{-1}	2.88×10^{-7}
Iron	47 μg l^{-1}	8.4×10^{-7}
Potassium	11 g l^{-1}	0.281
Aluminum	180 μg l^{-1}	6.67×10^{-6}
Property	Membrane properties Nafion 117	
Equivalent weight	1100 (g mol^{-1})	
$\rho_{polymer}$	1640 (kg m^{-3})	

membrane microstructure parameters (pore radius and accompanying surface charge density) and thus $\Gamma_i = 1$. In order to determine the correction factors for components other than sodium, simulations with the radial uptake model were performed for several anolyte strengths. The typical anolyte concentrations for the trace components are shown in Table 1. In Fig. 5 the resulting correction factors (Γ_i) for various components are shown as a function of the external sodium chloride concentration. A correction factor larger than unity means that in case of absence of the correction factor the sorption predicted by the radial uptake model would be lower than indicated by the modified Pitzer model.

Fig. 5 shows that the correction factor for all components differs from one. From these results it can be concluded that the radial uptake model is not capable of predicting the sorption of ions other than sodium (which implicitly fits the sorption data using $\Gamma_i = 1$ because the surface charge density and pore diameter
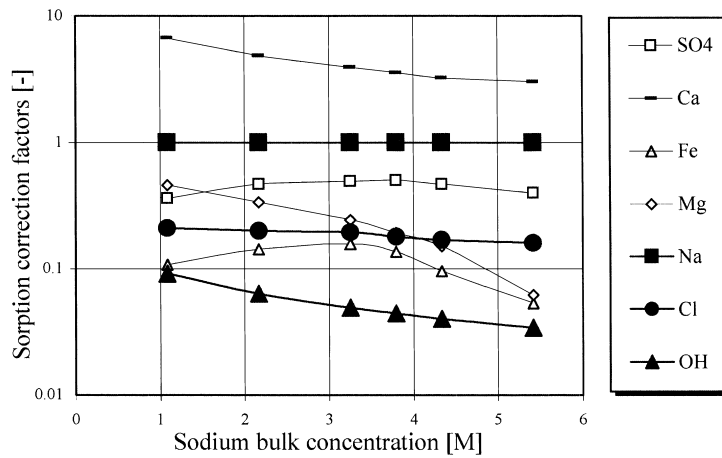

Fig. 5. Correction factors in Eq. (10) in the radial uptake model. The correction factor for sodium is at unity, because it fits the modified Pitzer model [3] via the membrane microstructure parameters. The simulations were performed for the sulfonic layer of the Nafion 117 sulfonic membrane.

were previously fitted to the sorption data of sodium) without the use of a correction factor. These correction factors have to be calibrated from either theoretical or experimental sorption data. With the implementation of correction factors it is possible to reliably predict the sorption of all components.

Bontha and Pintauro [1] obtained a similar result in a system of sodium and lead chloride. These authors also introduced a correction factor to fit experimental sorption data to the predictions of their radial uptake model, but they defined a correction factor acting on the effective surface charge. For higher valent cation (in their case lead) this resulted in a lower effective surface charge which was explained by the formation of bonds of these ions with the membrane sulfonic groups. With this procedure good agreement was achieved between experiments and calculations. Analysis with 207 Pb nuclear magnetic resonance spectroscopy of lead containing Nafion membranes was performed in an attempt to verify the formation of Pb(II)-sulfonate bonds. An amount of 50–90% of the sorped lead was bound to the membrane charged groups. This means that a large number of the sulfonic ion-exchange sites in Nafion membrane were thereby neutralized by Pb(II). The extent of binding increased with the surface charge density of the coabsorbed monovalent cation and decreased with increasing total external salt concentration. Remarkably, they did not alter the surface charge for sodium because otherwise incorrect sodium sorption data would be predicted. This means that with the method of Bontha and Pintauro [1], the radial uptake model must be fed with component and concentration dependent correction factors for the surface charge. This seems incorrect from a physical point of view. Therefore, the method with the correction factors Γ_i as shown in Eq. (10) was used in this study. The necessity of introducing the factor Γ_i may then be caused by neglecting non-ideality effects from Eq. (1) or Eq. (10). However, it seems very impractical to introduce non-idealities in relation (10), as this would certainly require radially dependent activity coefficients. Therefore, in this study we restricted ourselves to the use of an averaged correction factor.

The bonding of higher charged cat-ions to membrane charged groups is discussed in detail in the next section, because of its large influence on the decrease of the membrane selectivity and performance.

3.5. Calculated radial concentration profiles

In this section the radial concentration and potential profiles obtained with the radial uptake model are given for a base case. The input data for this base case are tabulated in Table 1. The data in Table 1 are based on the typical brine composition of the experimental set-up in Hengelo (the Netherlands) as described by Hoetjer [21]. The choice for a brine composition is obvious, because the sulfonic part of a commercially used membrane is always situated at the anode compartment (which contains the brine solution).

3.5.1. Concentration profiles

For the base case a calculation with the radial uptake model was performed. The resulting radial concentration profiles were transformed to dimensionless ones by dividing the local radial concentrations by their corresponding external bulk concentration. By doing this, radial partition coefficients are obtained, defined similar to Bontha and Pintauro [2]. The resulting profiles for several components are shown in Fig. 6. From Fig. 6 it can be seen that each species behaves in a different manner. This is the result of the different bulk concentrations and hydration coefficients (see Appendix A). Because of the negative surface charge in the membrane pore, a competition between cations takes place for occupying the desirable positions near the wall. The anions show the opposite behavior, since they are repelled from the pore wall and preferably are situated in the center of the pore. For both sodium and magnesium a local maximum is observed, which phenomenon was also reported by Bontha and Pintauro [2] and Guzman-Garcia et al. [12]. It is the result of the local domination of hydration forces over electrostatic forces and vice versa. These phenomena are neither observed for the other cations, nor for the anions. The first group has a (bulk) concentration too low to observe the phenomena, the latter group has induced forces in the same direction, i.e. towards the centerline. With increasing hydration constant the chance of showing the maximum as observed for sodium and magnesium decreases, because the hydration force is a reciprocal function of this hydration constant. For positively charged species with small hydration constants the partition near the wall will be at its maximum. This trend is shown for sodium, potassium and iron. Potassium and sodium have bulk concentrations
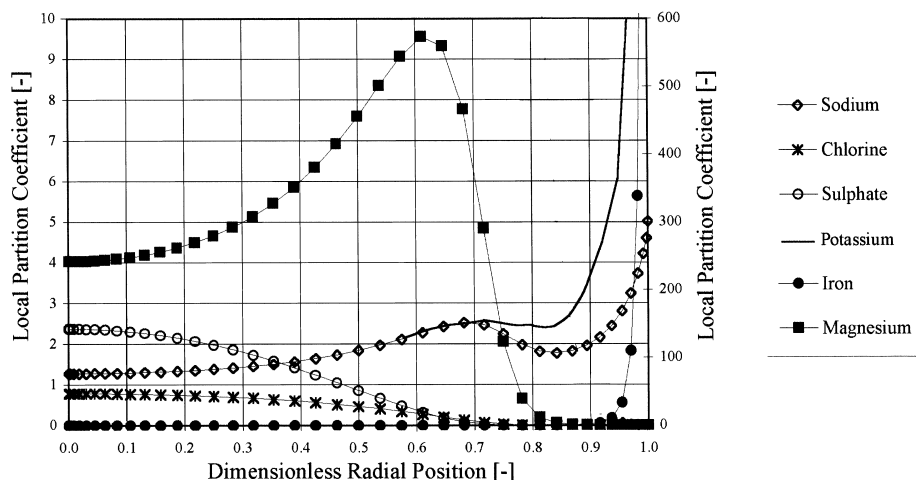
Fig. 6. Dimensionless concentration profiles as a function of the dimensionless radial position for some selected components. The resulting radial concentration profiles are transformed to dimensionless local partition coefficients by dividing the local dimensionless radial concentrations by their corresponding bulk concentration. Calculations are performed for the base case with a sodium ion concentration of 3.08 M (see Table 1). Components that are represented by closed symbols use the right axis. The dimensionless radial position of 0 represents the pore center while a position of 1 represents the pore wall.

in the same order of magnitude, but since potassium has the smallest hydration constant, its partition near the pore wall is larger than for sodium. Although iron has a larger hydration constant than potassium the partition coefficient of iron near the pore wall is even larger than the partition of potassium, because of its smaller bulk concentration and higher charge. From this it can be seen that only the iron cations are mainly located at the pore wall. Bontha and Pintauro [1] observed a similar phenomenon for lead. It is therefore likely that iron also forms bondings to the charged groups of the membrane phase, as lead does [1]. The effect of this possible bonding on the surface charge may be of importance in the transport process through the membrane.

The anions show an increasing partition coefficient on the pore centerline with increasing ion charge and decreasing hydration constant. The partition of anions near the pore wall is near zero for all anions. The potential profile for the base case calculation is shown in Fig. 7.

3.5.2. Selective uptake of iron

In industrial operation the precipitation of ironhydroxide just inside the sulfonic layer is a major problem leading to deterioration of the membrane. Not

only the precipitation of iron but also the very selective bonding of iron with the sulfonic groups could have dramatic effects on the performance and selectivity of the membrane by shielding off the charged groups of the membrane. This can reduce the effectiveness in repelling anions, resulting in an increase in transport of unfavorable anions and thus a decrease in current efficiency. To prevent or minimize this a minimum sorption of iron is desired. In the previous
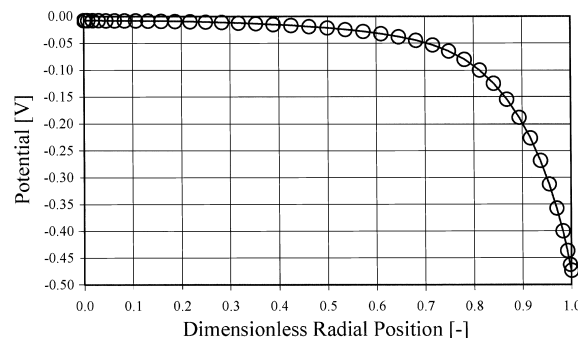

Fig. 7. Potential distribution in a pore as a function of the radial position for the base case. The dimensionless radial position of 0 represents the pore center while a position of 1 represents the pore wall.
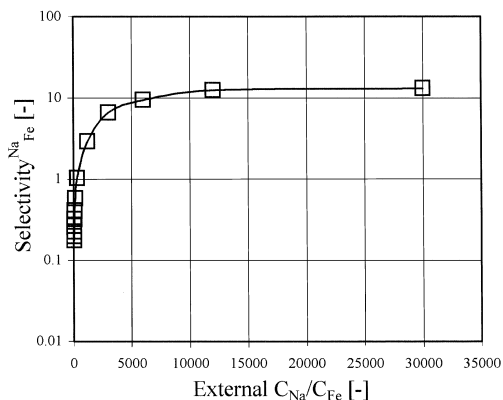
Fig. 8. Selectivity of the membrane sorption of a system, containing sodium and iron salts in varying ratios. It was assumed that the correction factor for iron were independent from the external concentration.

section it was shown that each component affects the sorption of any other component. In this section the uptake of iron will therefore be studied for various external iron salt concentration at a constant external sodium concentration.

The selectivity of the membrane for sodium can be defined as a ratio of average partition coefficients.

$$S_{Fe}^{Na} \frac{C_{Fe}^{b} \int_0^{r_p} C_{Na}^{m}(r) 2\pi r \, dr}{C_{Na}^{b} \int_0^{r_p} C_{Fe}^{m}(r) 2\pi r \, dr} \tag{11}$$

The selectivity of the uptake of sodium into the membrane is calculated for different compositions of the bulk, i.e. the total salt concentration was kept constant and the ratio of the sodium–iron concentrations was varied. The resulting data are shown in Fig. 8. If the iron forms bondings with the surface charged groups, then it is important that the amount of sorped iron cations is minimized in relation to the sorption of sodium. As can be seen in Fig. 8 a low external ratio of the sodium–iron concentrations causes a relatively large extent of trivalent ion bonding. In Fig. 8 it is also shown that the selectivity is almost constant for a sodium–iron ratio of 12,000 or larger. In practice the ratio is about 300 times this maximum, as can be derived from Table 1. This means that changing the bulk concentration of iron relative to the concentration of sodium for typical experimental conditions has a proportional effect on the iron concentration in the membrane.

4. Conclusions

The results of a sorption model applicable to calculate the concentrations in membrane sheets with a pore structure were shown. The model is called the radial uptake model. Because the model is specifically applied to a Nafion sulfonic layer with very small pore sizes and the radial uptake model is based on the assumption that the continuum equations are applicable, the model is operated at or beyond the limits of its fundamental validity. However, the results in this study indicate that the calculated profiles with the radial uptake model are realistic and similar to literature results (see, e.g. [1]). The membrane microstructure parameters also have been determined successfully by fitting the sorption of sodium as predicted by the radial uptake model to the sorption of sodium as predicted by the modified Pitzer model [3]. Via the introduction of a component dependent correction factor the sorption of other ions could also be matched to the data as predicted by the modified Pitzer model. These correction factors were in the order of magnitude of 0.05–10, and dependent on the concentration of sodium. The necessity of the application of correction factors for the ions other than sodium may have been induced by the assumption of (a) continuum equations in the model; (b) activity coefficients equal to unity in the radial uptake model.

It was observed that due to the preferential sorption of iron near the pore wall, the pore surface charge can be shielded, resulting in a decrease of the selectivity of the membrane for sodium. The sodium sorption selectivity of the membrane can be increased to a maximum for a sodium–iron system. The selectivity in practical situations has reached this maximum by far, meaning that the iron sorption is directly proportional to the iron content in the external solution.

Appendix A. Hydration constants for various species

Several values for the Gibbs free energy changes and hydration constants. Data are retrieved from [14–16] and used in the radial uptake model. Data for hydroxide are assumed to have the same values as chlorine.

Ion	Hard sphere radius (Å)	$\Delta_{vac}G_i$ at ε $= \varepsilon_b$ ($J\,mol^{-1}$)	$\Delta_{vac}G_i$ at ϵ $= n^2$ ($J\,mol^{-1}$)	A_i ($J\,mol^{-1}$)
Sodium	1.05	-4.11×10^5	-2.87×10^5	223839
Hydroxide	1.81	-3.18×10^5	-1.67×10^5	273902
Chloride	1.81	-3.18×10^5	-1.67×10^5	273902
Sulfate	2.30	-7.79×10^5	-5.25×10^5	460468
Chlorate	2.45	-1.96×10^5	-1.23×10^5	132592
Potassium	1.33	-3.37×10^5	-2.27×10^5	198862
Iron	0.76	-1.89×10^5	-1.59×10^5	542723
Magnesium	0.82	-1.90×10^5	-1.47×10^5	771275
Aluminum	0.50	-5.49×10^5	-5.43×10^5	919220
Calcium	0.99	-1.59×10^5	-1.22×10^5	663452
Borate	1.52	-4.53×10^5	-7.94×10^5	460153

A.1. Empirical water uptake functions

With the water activity of the external liquid and the equivalent weight of the used membrane the following empirical expression for the water uptake is determined on the basis of experiments by Van der Stegen [18]

$$e_{w,s} = 0.6455 + 0.6044\gamma_w + 0.112\gamma_w^2 - 0.935EW$$
$$+ 0.36EW^2 - 0.44151EW\gamma_w \qquad (A.1)$$

in which γ_w is the water activity coefficient and EW the equivalent weight of the membrane, defined as the reciprocal of the number of charged sites per kilogram of dry membrane. Note that in this equation water activity coefficients are used instead of water activities as in [18]. The relation holds for sulfonic based polymers. If carboxylic base polymers are used Eq. (10) changes to

$$e_{w,c} = 1.045 + 0.3272\gamma_w + 0.1343\gamma_w^2 - 1.496EW$$
$$+ 0.55EW^2 - 0.28922EW\gamma_w$$

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