Description of electrolyte sorption into ion-exchange membranes
in terms of local Donnan equilibria

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Abstract

The following approaches to an ion-exchange membrane with respect to the electrolyte sorption have been compared: 1) the internal solution filling the pores is an equipotential phase (Donnan equation), 2) the internal solution fills two regions of pores – selective (Donnan equation) and non-selective ones, 3) the pores are represented by a capillary with charged walls (Poisson-Boltzmann equation). The models have been tested on various ion-exchange membrane|electrolyte systems. It has been found that the best description of experimental data gives the second approach. It is based, however, on one fitting parameter. The capillary model, based on the pore radius calculated from the transport experiment, yields only slightly better results than the first approach.

Introduction

The concentration of ions inside an ion-exchange membrane apart from their mobility is the basic factor determining their flow across the membrane. Thus, for the simulation of membrane processes it is still important to know which model describes most adequately the sorption of electrolyte.

In this work the following approaches to the membrane pores, based on the Boltzmann equation, will be compared:

1) the internal solution filling the pores is an equipotential phase, described by the ideal Donnan equation,

2) the internal solution fills two regions of pores – selective (Donnan equation) and non-selective ones,

3) the pores are represented by a capillary with charged walls (Poisson-Boltzmann equation).

The above described models will be tested on various ion-exchange membrane|electrolyte systems (membranes: Nafion, MRF, Neosepta, electrolytes: NaCl, NaOH, H_2SO_4, HCl).

Theory

If the internal solution filling the membrane pores is equipotential, then the Boltzmann equation:

$$\overline{c}_i = c_i \exp(- z_i F \overline{\psi} / RT) \tag{1}$$

where $\overline{\psi}$ is the electric potential relative to the potential of the solution bathing a membrane, leads to the ideal Donnan equation (binary electrolyte, $z_1 = -z_2 = 1$):

$$\overline{c}_1 \overline{c}_2 = (\overline{c}_2 - X_m)\overline{c}_2 = c_s^2 \tag{2}$$

where $X_m = z_m \overline{c}_m$ is the density of fixed charges.

It is a well documented fact that eq.(2) fails in the description of the equilibrium sorption of electrolytes in ion-exchange membranes. As it was pointed out by Glueckauf [i], the main reason should be the non-uniform distribution of ion-exchange groups, whereas the effect of different activity coefficients of ions inside and outside the membrane should be of minor importance. He proposed the equation based on two parameters k_0 and z:

$$dx_{Vp} / d\overline{m}_m = k_0 \overline{m}_m^{-z} \tag{3}$$

describing the distribution of $\overline{m}_m$ - the molality of ion-exchange groups; x_{Vp} is the volume fraction of pores of $\overline{m}_m \in \langle \overline{m}_{m,\min}, \overline{m}_m \rangle$, x_{Vp} changes from 0 to 1. These parameters can be expressed in terms of the mean and maximum values of $\overline{m}_m$. Applying the Donnan equation locally Glueckauf derived the following equation for electrolyte uptake $\hat{m}_2$:

$$\hat{m}_2 = km^{2-z} \tag{4}$$

where k and z have to be determined experimentally. Eq.(4) in the linearized logarithmic form is frequently used for the description of electrolyte sorption into ion-exchange membranes, however as it was shown in [ii] the linear relation between $\ln \hat{m}_2$ and $\ln m$ is not always fulfilled.

The simplest distribution of X_m is a 2-value function (0, X_m), i.e. the solution inside the membrane is divided into two parts – the Donnan region ($\overline{c}_i$ is given by eq.(2)) and the non-selective one which is filled with the external solution (c_s) [ii]:

$$\hat{c}_i = x_{Vp,D}\overline{c}_i + (1 - x_{Vp,D})c_s \quad i=1,2 \tag{5}$$

This model is, similarly as Glueckauf's one, also determined by two parameters – the mean concentration of fixed charges and the volume fraction of the selective region, $x_{Vp,D}$.

The 3rd approach is the approximation of membrane pores by a charged capillary (other geometries are not excluded) in which the sorption is obtained by solving the Poisson-Boltzmann equation ($z_1 = -z_2 = 1$) for the electric potential:

$$\frac{1}{r}\frac{\partial}{\partial r}\left(\varepsilon_r r \frac{\partial \overline{\psi}}{\partial r}\right) = -\frac{F}{\varepsilon_0}\left(z_1 \overline{c}_1 + z_2 \overline{c}_2\right) = \frac{F}{\varepsilon_0} c_s \sinh\left(\overline{\psi}F/RT\right) \tag{6}$$

in the appropriate boundary conditions (see e.g. [iii, iv]), and then calculating the mean concentration of ions in the pore solution from:

$$\hat{c}_i = \int_0^{R_c} 2\pi r \overline{c}_i \, dr / \pi R_c^2 \tag{7}$$

In that model two parameters have to be known – the radius of capillary, R_c, and the mean concentration of fixed charges. As the Boltzmann equation is equivalent to the ideal Donnan equation, the segment $2\pi r dr$ of a given electric potential $\overline{\psi}(r)$ inside the capillary corresponds to the region of a given hypothetical $X_m(r)$. The calculations show that the distribution of such $X_m(r)$ can be described by a function similar to the Glueckauf's one:

$$dx_{Vp}(r)/dX_m(r) = k(X_m(r)+a)^{-z} \tag{8}$$

with a good accuracy (Fig.1). In eq.(8) $x_{Vp}(r) = \pi r^2 / \pi R_c^2$, k and a are constants.

Membranes

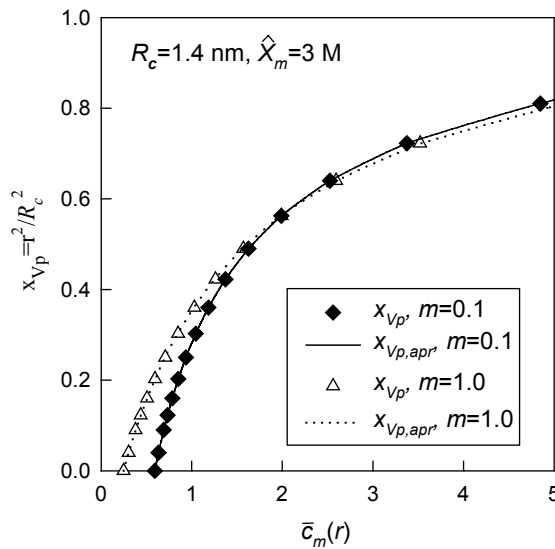The basic properties of ion-exchange membranes are listed in Table 1.

Fig. 1. Distribution of hypothetical $X_m(r)$ inside the capillary of radius R_c=1.4 nm and the mean concentration of fixed charges $\hat{X}_m$=3 M, calculated for two external concentrations (m=0.1 and 1.0) according to Boltzmann equation (symbols), the lines represent the fitted eq.(8).

Table 1. Characteristics of ion-exchange membranes [iv].

membrane	chemical composition	ionic form	V_p	$\overline{c}_m$, [mol fixed charge/dm^3 pore sol.]
Nafion 120	saponified copolymer of sulphonyl fluoride vinyl ether and tetrafluoroethylene	Na$^+$	0.39	3.1
Neosepta CM2	strongly acidic cation-exchange membrane prepared by paste method [v]	Na$^+$ H$^+$	0.33 0.27	5.4 7.3
Neosepta AM1	strongly basic anion-exchange membrane prepared by paste method [v]	Cl$^-$	0.27	6.4

Results

The experimental results on the electrolyte uptake (taken from [vi,vii,viii,ix]), and their approximation by the Glueckauf eq.(4) transformed to $\log(\hat{m}_2) = \log(k) + (2 - z)\log(m)$, is shown in Fig. 2.
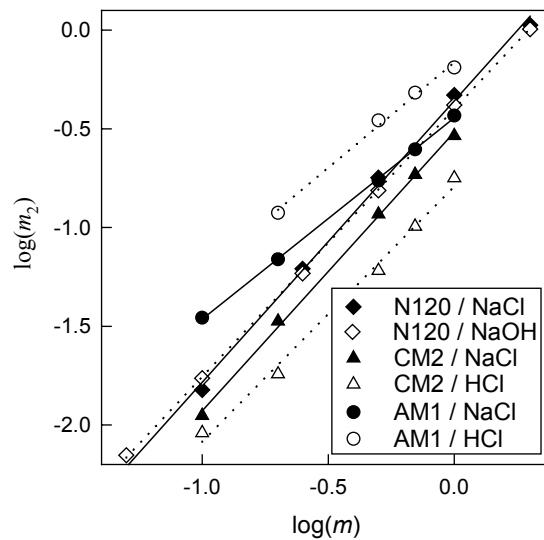

Fig. 2. Sorption of electrolyte, $\log(\hat{m}_2)$ vs. log(m), symbols – experimental values [vi,vii,viii,ix], lines – Glueckauf eq.(4).

To estimate adequacy of the two-value distribution function of fixed charges (0, X_m) the selective volume fraction of pores, $x_{Vp,D}$ has been calculated from the formula (8) obtained from eqs.(2), (5).

$$x_{Vp,D} = \frac{\left(\hat{c}_1 / c_s - 1\right)\left(\hat{c}_2 / c_s - 1\right)}{2 - (\hat{c}_1 + \hat{c}_2) / c_s} \tag{9}$$

The dependence of $x_{Vp,D}$ on the molality of external solution should inform us about the correctness of that approach. The results (Fig.3a) show that $x_{Vp,D}$ does not change substantially with the molality indicating that this distribution function is a reasonable approximation. With increase of external molality one should expect the decrease of the selective domain – it is observed for Nafion 120 (NaCl and NaOH) and AM1/NaCl. The smaller selective fraction of Nafion pores than that of CM2

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can result from the differences in the distribution of fixed charges in those membranes. According to cluster network model of Nafion one can distinguish two regions differing in the concentration of ionic groups, whereas in the case of CM2 the distribution of ionic groups can be more regular. A characteristic feature is observed in the case of the anion-exchange membrane AM1 – here $x_{Vp,D}$ for HCl is much lower than for NaCl. It clearly demonstrates higher sorption of HCl due to specific interactions of the H^+ coion with the membrane matrix. The mean values of $x_{Vp,D}$ in the whole concentration range, obtained by fitting $\log(\hat{m}_2)$ by the least squares method (Fig.3b), are:
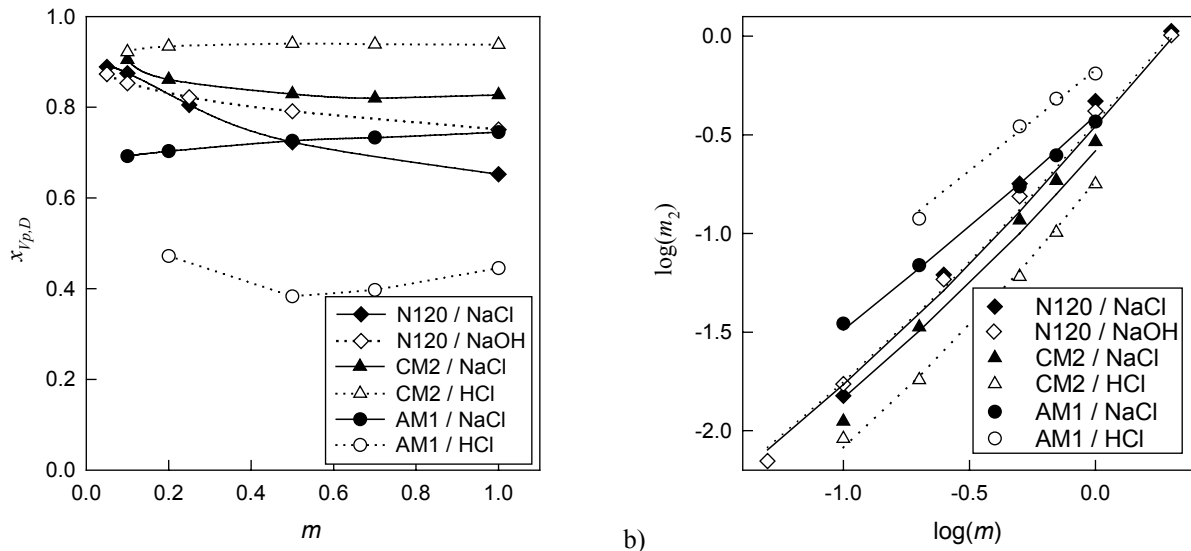

Fig. 3. a) The volume fraction of selective region of membrane pores, $x_{Vp,D}$, fulfilling the condition $\hat{c}_2 = \hat{c}_{2,\exp}$, according to the two-value distribution function of fixed charges (eq.(9)), b) $\log(\hat{m}_2)$ vs. $\log(m)$, symbols – experimental values [vi,vii,viii,ix], lines – calculated on the base of eq.(9) with only one fitting parameter, $x_{Vp,D}$ in the whole concentration range
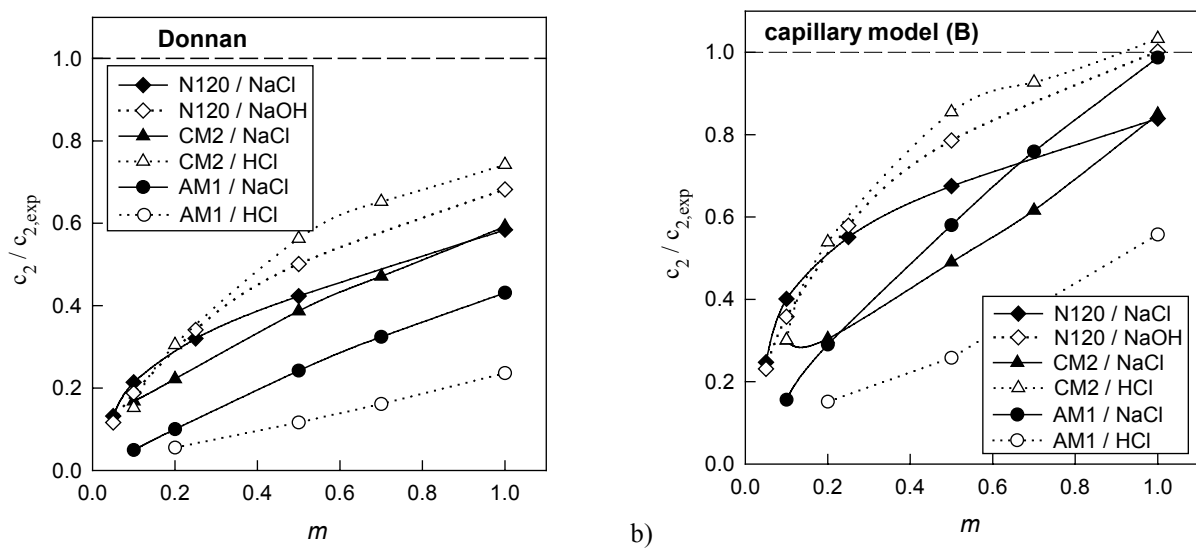

Fig. 4. The ratio of calculated to experimental electrolyte uptake, $\hat{c}_2 / \hat{c}_{2,\exp}$, vs. the molality of external solution, a) Donnan eq.(2), b) capillary model based on the Poisson-Boltzmann eq.(6) with the pore radius calculated from the electroosmotic transport (Fig.4a).

Nafion 120/NaCl – 0.853, Nafion 120/NaOH – 0.849, CM2/NaCl – 0.823, CM2/HCl – 0.931, AM1/NaCl – 0.715, AM1/HCl – 0.417.

Regarding the capillary model the problem is how to estimate the equivalent radius of membrane pores. It can be calculated using one of the transport properties, e.g. the electroosmotic transport number of water [x]. Using that radius (Fig.5a) the calculated uptake of electrolyte, although better than that given by the ideal Donnan equation (2), still it is too low at lower range of concentrations of external electrolyte (Fig.4).
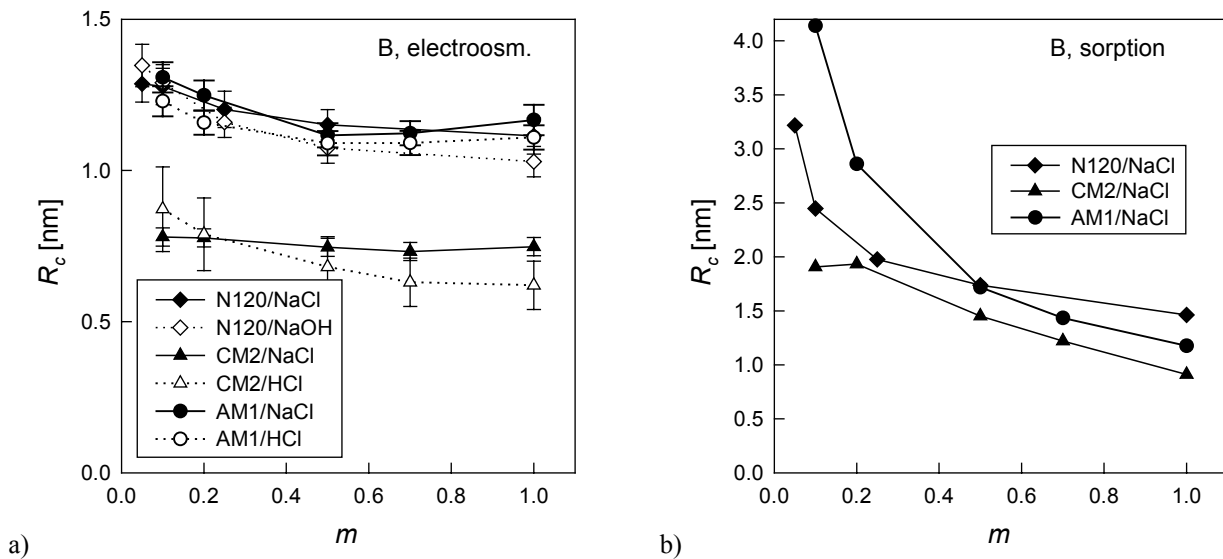

a)   b)

Fig. 5. The equivalent capillary radius calculated a) from the electroosmotic transport number of water ($\bar{t}_2(R_c) = \bar{t}_{2,\exp}$, [iv]), b) from the sorption ($\hat{c}_2(R_c) = \hat{c}_{2,\exp}$).

On the other hand, the equivalent radius of pore calculated from the sorption shows too strong concentration changes and too high values at low concentrations of external electrolyte (Fig.5b). When discussing the Boltzmann equation one should also mention its modifications. One of them is that including the change of solvation energy due to the change of dielectric constant of pore solution [xi,iii]:

$$\bar{c}_{i,r} = c_i \exp\left(- z_i F \bar{\psi} / RT - A_i \left(1/ \varepsilon_{r,r} - 1/ \varepsilon_{r,0}\right)/ RT\right) \qquad (10)$$

Because of strong radial electric field inside the charged capillary the dielectric constant at $r > 0$, $\varepsilon_{r,r}$, is lower than that at the centre of capillary, $\varepsilon_{r,0}$, and thus the solvation term in (10) repels the ions from the capillary. Consequently, the modified Boltzmann eq.(10) yields even smaller uptake than the classical one for the same pore radius.

Conclusions

The discussed approaches, which do not include any fitting parameter – the Donnan equation and the capillary model, do not describe the electrolyte uptake properly. In both cases the predicted concentration of sorbed electrolyte is too low. The discrepancy increases, as the concentration of external solution diminishes. This effect can result from many factors, e.g. nonhomogeneous distribution of fixed charges, differences in activity coefficients, association of ions. The most important seems to be the distribution of fixed charges, as confirmed by the results obtained for the approach dividing the membrane pores into the selective and non-selective domains.

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