

High Diffusion Permeability of Anion Exchange Membranes for Ammonium Chloride: Experiment and Modeling

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Supplementary materials

Determination of input parameters

The diffusion boundary layer thickness in the experimental cell is calculated using the Leveque equation [1]

$$\delta = 1.02 \left(\frac{LDh}{\bar{V}} \right)^{1/3} \quad (S1)$$

here L is the channel length, D is the electrolyte diffusion coefficient, h is the distance between the studied membrane and the cell wall, \bar{V} is the linear flow velocity.

Reaction rate constants. According to Simons [2], the rate constants k_{-1} and k_{-2} of recombination reactions (9) and (10) (such numbering hereinafter refers to the equations from the main text of the article) free solution have high values of the order of $10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The rate constants k_1 and k_2 of direct reactions (9) and (10) (considered as pseudomonomolecular) can be estimated using the following relations [23]:

$$k_1 = k_{-1} 10^{-(14-pK_a)}, \quad k_2 = k_{-2} 10^{-pK_a} \quad (S2)$$

The calculation using equation (S2) gives $k_1 \approx 10^6 \text{ s}^{-1}$, $k_2 \approx 10 \text{ s}^{-1}$. Thus, the rate limiting stage of protonation-deprotonation reactions (9) and (10) is the NH_4^+ deprotonation reaction. However, the value of the rate constant of this reaction (k_2) is quite high. It is almost 6 orders of magnitude higher than the rate constant of water dissociation in free solution ($2 \times 10^{-5} \text{ s}^{-1}$), 4 orders of magnitude higher than in the case of sulfonic groups, $3 \times 10^{-3} \text{ s}^{-1}$ [3] (the CMX membrane) and 2 orders of magnitude higher than in the case of secondary and tertiary amino groups, 10^{-1} s^{-1} [3] (the AMX membrane). Thus, $\text{NH}_4^+/\text{NH}_3$ couple may be considered as a catalyst for the reaction of H^+ and OH^- ions generation. The latter is important for electrodialysis of ammonium-containing solutions, where water splitting reactions are of great impact.

Diffusion coefficients. The model assumes that the membrane is a quasi-homogeneous medium. The diffusion coefficients may be estimated from the equation system, describing the conductivity, κ , and differential diffusion permeability, \bar{P} , of the membrane [4]:

$$\bar{P} = \bar{t}_1 \left(1 - \frac{z_2}{z_1} \right) \frac{\bar{D}_2 \bar{c}_2}{c_2} \quad (S3)$$

$$\kappa = \frac{F^2}{RT} (z_1^2 \bar{D}_1 \bar{c}_1 + z_2^2 \bar{D}_2 \bar{c}_2) \quad (S4)$$

$$\bar{t}_i = \frac{z_i^2 \bar{D}_i \bar{c}_i}{z_1^2 \bar{D}_1 \bar{c}_1 + z_2^2 \bar{D}_2 \bar{c}_2} \quad (S5)$$

where subscript 1 and 2 refer to the counterion and coion, respectively, \bar{t}_i is the transport number of ion i in the membrane.

Since \bar{t}_1 is close to 1, it can be seen from Equation (S3) that \bar{P} is mainly determined by the product $\bar{D}_2 \bar{c}_2$ at a given concentration of the external solution, c_2 . As $\bar{D}_2 \bar{c}_2 \ll \bar{D}_1 \bar{c}_1$, the membrane conductivity is controlled by the product $\bar{D}_1 \bar{c}_1$, Equation (S4). At a given concentration of the external solution and known values of κ and \bar{P} , it is possible to calculate \bar{D}_1 and \bar{D}_2 :

$$\bar{D}_2 = \frac{c_2 \bar{P}}{\bar{t}_1 \bar{c}_2 (1 - z_2 / z_1)} \quad (S6)$$

$$\bar{D}_1 = \frac{\kappa RT / F^2 - z_2^2 \bar{D}_2 \bar{c}_2}{z_1 Q - z_1 z_2 \bar{c}_2} \quad (S7)$$

the Donnan constant, K_D , is needed to relate the coion concentrations in the solution and membrane; in its approximate form, the Donnan equation reads [4,5]: $\bar{c}_2 = \frac{K_D}{Q} c_2^2$; \bar{c}_1

can be found using the local electroneutrality condition ($z_1 \bar{c}_1 + z_2 \bar{c}_2 = Q$).

Note that \bar{P} is the differential diffusion permeability, while the experiment gives the integral diffusion permeability, P . It is possible to convert the concentration dependence of $P(c)$ into $\bar{P}(c)$ [4]:

$$\bar{P}(c) = P(c) + d \lg P / d \lg c \quad (S8)$$

and then calculate \bar{D}_1 and \bar{D}_2 .

The comparison of experimental and simulated concentration dependencies of κ and P is shown in Figure 5 (see the main text of the article). Since the value of κ is very close for the AMX in KCl and NH_4Cl solutions, the Cl^- diffusion coefficient, \bar{D}_1 , in the membrane was taken the same for both cases, $\bar{D}_{\text{Cl}^-} = 2.7 \times 10^{-11} \text{ m}^2/\text{s}$ (Table 1). Since in the solution the diffusion coefficients of NH_4^+ and Cl^- are nearly identical, we assume the equality of these coefficients in the membrane: $\bar{D}_{\text{K}^+} = \bar{D}_{\text{NH}_4^+} = 2.7 \times 10^{-11} \text{ m}^2/\text{s}$ (Table 1).

The concentration of fixed groups in the pore solution of the AMX membrane is calculated from the value of the exchange capacity of this membrane в Cl^- form by dividing the latter by the membrane porosity $p=0.3$; the obtained value is $Q = 7.6 \pm 1.0 \text{ mol/dm}^3 \text{ H}_2\text{O}$ [6], Table 1. The value of ε is taken as 80 in solution [7] and 30 in the membrane [8].

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