BOND-GRAPH DESCRIPTION AND SIMULATION OF MEMBRANE PROCESSES.
4. NON-EXCHANGE SORPTION OF 1-1 ELECTROLYTE INTO ION-EXCHANGE POLYMER MEMBRANE

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Abstract

The bond-graph description of transport processes was applied to analyse all the phenomena related to the sorption of free electrolytes into the internal solution of a polymeric cation-exchange membrane (no cation exchange reaction in the system). The kinetic constants for Nafion 120 and KNO_3 solution were determined.

1. INTRODUCTION

The problem of high non-exchange sorption of electrolytes (NESE) into the internal solution ion-exchange membranes was intensively studied in the context of its quantitative discrepancy with the classic Donnan equilibrium principle [1,2]. It was concluded that high NESE results from non-ideality of a membrane leading to the sorption of co-ions higher than that theoretically predicted. In practice, the membranes are of heterogeneous structure, i.e. they are composed of an inert backbone and an ion exchanging hydrogel dispersed therein (Fig.1).

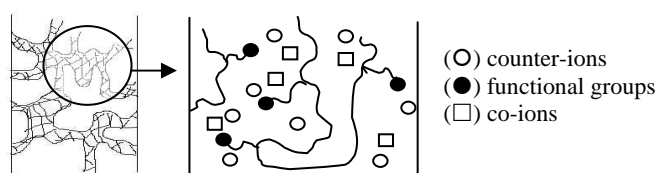
(O) counter-ions
(●) functional groups
(□) co-ions

Fig. 1. Scheme of ion-exchange polymer membrane structure

Additionally, a specific spatial distribution of the ion-exchange sites can be non-uniform which causes substantial deviation from the classic Donnan law for NESE. The equilibrium sorption was a subject of studies as

a fundamental property of the system membrane|electrolyte solution, and the corresponding sorption isotherms were proposed. On the other hand, the kinetics of this process and its detailed mechanism was not satisfactorily described. The electrolyte, when sorbed from an external medium, permeates the electrolyte|membrane interface and diffuses in the membrane with a diffusion coefficient markedly reduced by tortuosity of diffusion pathways. Thus, these two factors should be taken into account for constructing a phenomenological and mathematical description of the kinetics of the electrolyte sorption.

2. THEORY

The most general theory that describes the permeation across any heterogeneous medium is the theory of percolation [3] which suggests that the dependence between the diffusion coefficient in the membrane (D_{eff}) is related to the common diffusion coefficients in the membrane internal solution (D_o) by the following equation:

$$D_{eff} = D_0 \times (V_a - V_c)^\tau \qquad (1)$$

In Eq. (1), V_a, and V_c denote the accessible and critical volume fraction of the internal electrolyte, respectively; τ is the universal critical exponent.

Non-exchange sorption of the electrolyte into a heterogeneous membrane with non-uniform distribution of ion-exchanging sites can be described by the isotherm proposed by Glueckauf [2]:

$$\overline{C_A} = k_G \times C_A^{(2-z)} \qquad (2)$$

where $\overline{C_A}$, C_A are molal concentrations of co-ions (free electrolyte) in the internal membrane solution and external solution, respectively; k_G – constant, z – the non-uniformity parameter characteristic for a membrane. According to Eq.(2) the distribution coefficient of co-ions is represented by:

$$\alpha_{A(w)}^{f|m} = \overline{C_A} / C_A = k_G \times C_A^{(1-z)} \qquad (3)$$

2.1. COMPARTMENTAL AND NETWORK MODEL

The compartmental model of the external electrolyte (f) | cation exchange membrane (m) with a possible concentration profile of the sorbed and diffusing species S is presented in Fig.2. According to the scheme, the interfacial diffusion layer of the electrolyte of L^f thickness was divided into n^f sub-layers, and the membrane of L^m thickness into n^m sub-layers. The index b denotes the bulk solution, i.e. this part of the external electrolyte which is intensively agitated (convective transport only).
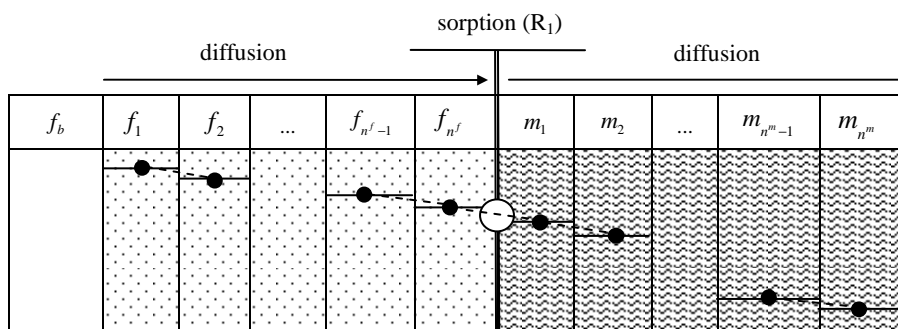
Fig. 2. Compartmental model for external electrolyte – cation exchange membrane system

The K^+A^- species can permeate between the sub-layers and can be accumulated (or exhausted) in dependence on the local capacitance. Sorption of K^+A^- occurs at the interface, i.e. between the sub-layers marked as n^f and m_1. By applying the graphs of diffusion and reaction [4] one can construct the linear network of the overall process presented in Fig.3. The construction is based on the properties of "0" junction which obeys Kirchhoff Current Law.
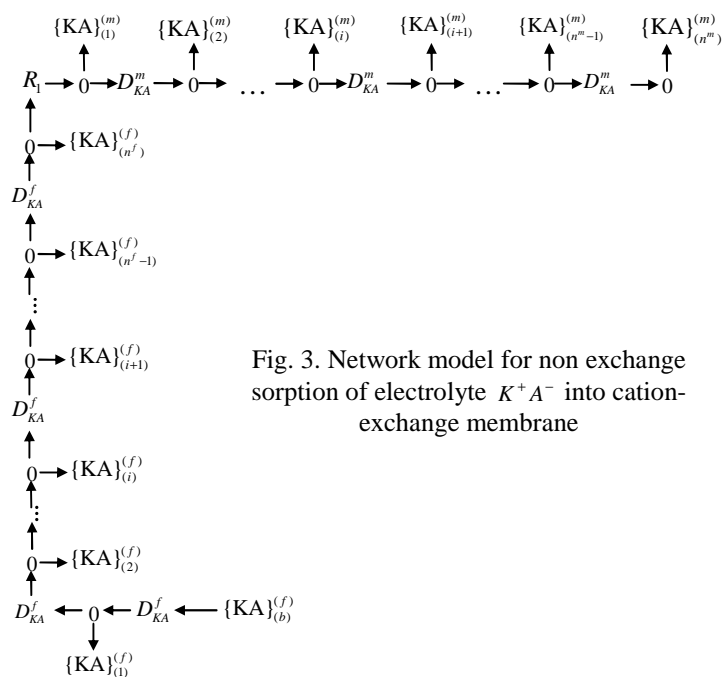

Fig. 3. Network model for non exchange sorption of electrolyte K^+A^- into cation-exchange membrane

3. CALCULATIONS

The network model in Fig.3 is equivalently represented by a set of ordinary differential equations describing the state of each capacitance as dependent on local flows (Tab. 1). The model can be solved numerically (Berkeley Madonna ver. 8.01) for a given set of operational, initial and boundary conditions.

Tab. 1. Mathematical descriptions of nonexchange sorption of 1-1 electrolyte into cation-exchange (CE) polymer membrane.

Local flows (N) [mol/s]	
External solution (f)	$N_{KA}^{f_b \to f_1} = D_{KA}^f \times 2 \times A / L_i^f \times \left([KA]_b^f - [KA]_1^f \right)$
	$N_{KA}^{f_i \to f_{i+1}} = D_{KA}^f \times A / L_i^f \times \left([KA]_i^f - [KA]_{i+1}^f \right)$
External solution | membrane interface ($f\|m$)	$N_{KA}^{n_f \to m_1} = k_{KA, eff}^{n_f \to m_1} \times A \times \left([KA]_{n_f}^f - [KA]_1^m / \alpha_{A(w)}^{m_1|n_f} \right)$
CE polymer membrane (m)	$N_{KA}^{m_i \to m_{i+1}} = D_{KA}^m \times A / L_i^m \times \left([KA]_i^m - [KA]_{i+1}^m \right)$

Capacitance fluxes [mol/cm³s]	
External solution (f)	$d[KA]_b^f / dt = -N_{KA}^{f_b \to f_1} / V_b^f$
	$d[KA]_1^f / dt = \left(N_{KA}^{f_b \to f_1} - N_{KA}^{f_1 \to f_2} \right) / V_i^f$
	$d[KA]_i^f / dt = \left(N_{KA}^{f_{i-1} \to f_i} - N_{KA}^{f_i \to f_{i+1}} \right) / V_i^f$
	$d[KA]_{n_f}^f / dt = \left(N_{KA}^{n_f-1 \to n_f} - N_{KA}^{n_f \to m_1} \right) / V_i^f$
CE polymer membrane (m)	$d[KA]_1^m / dt = \left(N_{KA}^{n_f \to m_1} - N_{KA}^{m_1 \to m_2} \right) / V_i^m$
	$d[KA]_i^m / dt = \left(N_{KA}^{m_{i-1} \to m_i} - N_{KA}^{m_i \to m_{i+1}} \right) / V_i^m$
	$d[KA]_{n_m}^m / dt = N_{KA}^{n_m-1 \to n_m} / V_i^m$

A - contact area between the membrane and electrolyte, [cm²]; $k_{KA, eff}^{n_f \to m_1}$ - the effective permeability coefficient (mas transfer constant) of $K^+ A^-$ at the $f|m$ interface, [cm/s]; $\alpha_{A(w)}^{m_1/n_f}$ - the distribution coefficient of A^- co-ions between the membrane internal solution (sub-layer m_1) and the external electrolyte solution (sub-layer n_f); D_{KA}^f, D_{KA}^m - the diffusion coefficient of $K^+ A^-$ in the external electrolyte and membrane [cm²/s]; L_i^f, L_i^m - the way of $K^+ A^-$ diffusion between the adjacent sub-layers in the external electrolyte and membrane, [cm]; V_i^f, V_i^m - volume of i sub-layer of the external electrolyte and membrane, [cm³].

3.1. PROBLEM TO SOLVE

The main goal of calculations was to calibrate the interfacial $f|m$ permeability coefficient $k_{KA, eff}^{n_f \to m_1}$. This quantity cannot be measured

immediately by experiments. No information is accessible on its value for KNO$_3$ and the Nafion membrane as well. On the other hand, the value of $k_{KA,eff}^{n^f \to m_1}$ is also necessary for constructing a reliable model of sorption. For this purpose, the dependence between the overall permeability coefficient $k_{KA,eff}^{f|m}$ (which can be determined experimentally) and the local (interfacial) coefficient $k_{KA,eff}^{n^f \to m_1}$ should be recognized. The equation relating the respective experimental variables to the time of sorption is:

$$\frac{V_b^f \times \left([KA]_{b(t=0)}^f - [KA]_{b(t\to\infty)}^f\right)}{A \times [KA]_{b(t=0)}^f} \ln\left[\frac{[KA]_b^f - [KA]_{b(t\to\infty)}^f}{[KA]_{b(t=0)}^f - [KA]_{b(t\to\infty)}^f}\right] = -k_{KA,calc}^{f/m} \times t \qquad (4)$$

In Eq.(4) $[KA]_b^f$, $[KA]_{b(t=0)}^f$, $[KA]_{b(t\to\infty)}^f$ are the concentrations of electrolyte in the bulk phase of the external solution at time t, $t=0$, and $t \to \infty$, respectively.

The permeability coefficient $k_{KA,calc}^{f|m}$ can be calculated as a slope of the corresponding linear regression function. The value of $k_{KA,calc}^{f|m}$ calculated for the assumed series of $k_{KA,eff}^{n^f \to m_1}$ can be compared thereafter with the experimental value, and the proper interfacial permeability coefficient can be estimated. The following physicochemical, structural and experimental characteristics were used in calculations: the initial concentration of the external electrolyte $[KA]_{b(t=0)}^f = 1\times10^{-4}$ mol/cm^3; the volume of the external electrolyte, $V^f = 1000$ cm^3; the membrane area, $A= 9.2$ cm^2, and thickness $L^m = 0.0196$ cm; the thickness of the diffusion layer at the $f|m$ interface $L^f = 0.005$ cm, [5]; the critical exponent $\tau = 1.5$ [6]; the critical volume fraction of the internal membrane electrolyte $v_k = 0.10$ [6]; the constant $k_G = 0.91$ [7]; the membrane non-uniformity parameter $z = 0.73$ [7]; the volume fraction of the internal electrolyte in membrane $V_{(w)}^m = 0.33$. The diffusion coefficients of KNO$_3 \equiv K^+ A^-$ in the aqueous solution of 1×10^{-4} mol/cm^3 concentration was equal to $D_{KA}^f = 1.43\times10^{-5}$ cm^2/s value of which was evaluated using literature data [8]. Similarly, the value of the diffusion coefficient in the internal membrane solution was assumed as $D_{KA,0}^m = 1.17\times10^{-5}$ cm^2/s. After the iterative procedure, the following curve calibrating the dependence of $k_{KA,calc}^{f|m}$ vs. $k_{KA,eff}^{n^f \to m_1}$ was found (Fig. 4).

From the curve presented in Fig.4, one can conclude that the overall permeability coefficient $k_{KA,\,\exp}^{f|m}$ = $k_{KA,\,calc}^{f|m}$ = 4×10^{-5} found experimentally corresponds with the interfacial one $k_{KA,\,eff}^{n^f\to m_1}$ = 6.74×10^{-5} cm/s.
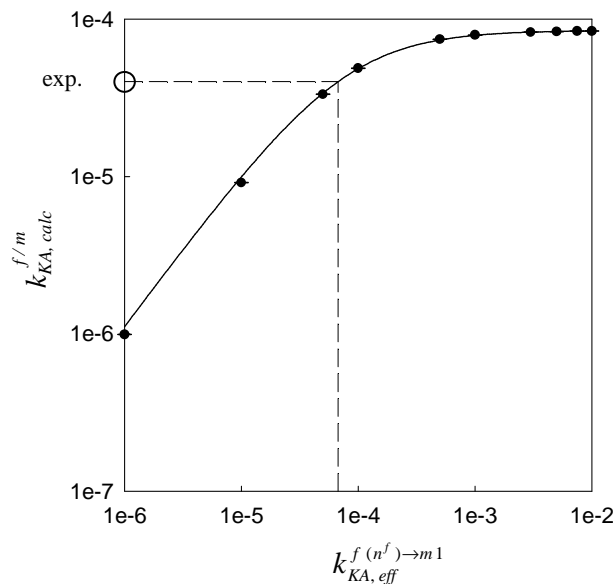

Fig. 4. The relationship between the overall $k_{KA,\,calc}^{f|m}$ and local $k_{KA,\,eff}^{n^f\to m_1}$ permeability coefficient of KNO$_3$.

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