

**BOND-GRAPH DESCRIPTION AND SIMULATION  
OF MEMBRANE PROCESSES.  
5. PERMEATION OF 1-1 ELECTROLYTE  
ACROSS ION-EXCHANGE POLYMER MEMBRANE**

Grażyna SZCZEPAŃSKA, Piotr SZCZEPAŃSKI, Romuald WÓDZKI

Nicolaus Copernicus University, Faculty of Chemistry  
Gagarin Str. 7, 87-100 Toruń, Poland  
wodzki@chem.uni.torun.pl

*Abstract*

*Thermodynamic network analysis was applied to study the electrolyte permeation across a heterogeneous cation-exchange polymer membrane. The network of local flows and the mathematical description was used to evaluate the diffusion coefficient of  $KNO_3$  in the internal solution of Nafion membrane*

**1. INTRODUCTION**

The permeation of free electrolytes (electrolyte leakage) across a cation-exchange polymer membrane (CEM) is associated with similar physicochemical phenomena as the sorption of electrolyte described in the preceding Part 4. Additionally, some simplifying assumption could be made to formulate a simple model in the framework of network thermodynamic analysis [1]: (i) the cation exchange sites are fully loaded with the same counter-ion as the one present in the external feed solution ( $f$ ), (i.e. no ion-exchange reaction in the system), and (ii) osmotic transport of water between the feed ( $f$ ) and stripping solution ( $s$ ) across the membrane ( $m$ ) can be ignored. The model needs: (i) the reliable description of the membrane structure, (ii) description of local diffusion phenomena, (iii) description of non-exchange sorption and desorption of co-ions (electrolyte) at the  $f|m$  and  $m|s$  interface, respectively.

**2. THEORY**

The full description of electrolyte permeation in the system: feed solution |CEM| stripping solution can be achieved by a respective

modification of the model presented in the Part 4. The scheme of the corresponding compartmental model is presented in Fig.1, i.e. the feed solution contains the electrolyte  $K^+A^-$ , which can permeate to the stripping solution according to the following sequence of phenomena: diffusion at the  $f|m$  interface – sorption to the membrane internal solution – diffusion in the internal membrane solution – desorption from the membrane to the stripping solution – diffusion in the stripping solution at the  $m|s$  interface. To apply the network method of modeling, the diffusion layers in external solutions and the membrane were additionally divided into  $n^f$ ,  $n^s$  and  $n^m$  sub-layers.

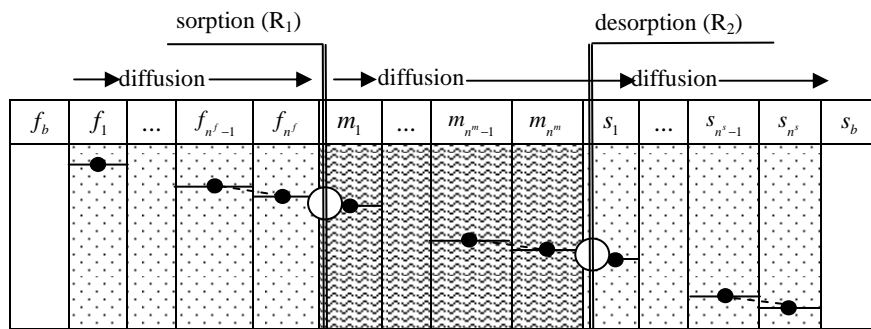


Fig. 1. Compartmental model for permeation of electrolyte in the system: feed solution | cation exchange membrane | stripping solution

The electrolyte  $K^+A^-$  permeates between the indicated sub-layers, and at the respective interfaces is sorbed ( $n^f|m_1$ ) or desorbed ( $n^m|s_1$ ) into or from the membrane phase. The overall permeation process can be represented by a series of the accumulation-diffusion graphs. Also, for a bond-graph description, it was assumed that the sorption and desorption processes can be represented by the graphs of uni-molecular reversible reactions:



Consequently, each local flow and accumulation of the electrolyte in the sub-layers is represented by the diffusion and sorption graphs connected by “0” junctions. The corresponding linear network of the electrolyte permeation from the feed to the stripping solution with mediating non-exchange sorption/desorption of the electrolyte is presented in Fig. 2.

### 3. CALCULATIONS

The mathematical model for permeation of the electrolyte according to the network in Fig.2 is presented in Tab.1. The model is composed of a set of differential equations describing the capacitance fluxes as dependent on the local input and output diffusion fluxes. The model can be used for simulation of the process when all the physicochemical constants (diffusion coefficients, interfacial permeability coefficients), membrane structural parameters ( $z$ ,  $t$ ,  $k_G$ ,  $V_k$ ), boundary and initial conditions for all the variables appearing in the model, and operational conditions (volume, thickness, etc.) are known. For such data, the model can be solved and it can generate the quantities which are commonly observed in this type of experiments.

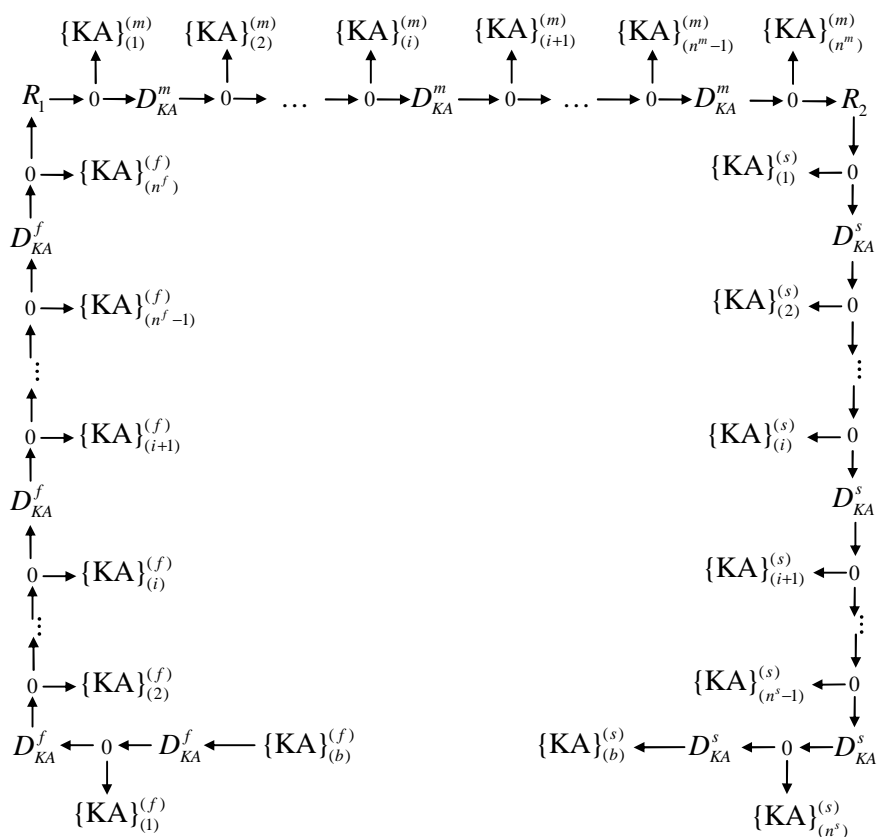


Fig. 2. Network model for permeation of electrolyte  $K^+A^-$  across a cation-exchange membrane

Tab. 1. Mathematical descriptions of permeation of 1-1 electrolyte across ion-exchange polymer membrane

Local flows ( $N$ ) [mol/s]	
Feed solution ( $f$ )	$N_{KA}^{f_b \rightarrow f_1} = D_{KA}^f \times 2 \times A / L_i^f \times [KA]_b^f - [KA]_1^f$
	$N_{KA}^{f_i \rightarrow f_{i+1}} = D_{KA}^f \times A / L_i^f \times ([KA]_i^f - [KA]_{i+1}^f)$
Feed solution   membrane interface ( $f m$ )	$N_{KA}^{n^f \rightarrow m_1} = k_{KA,eff}^{n^f \rightarrow m_1} \times A \times ([KA]_{n^f}^f - [KA]_1^m / \alpha_{A(w)}^{m_1 n^f})$
CEM ( $m$ )	$N_{KA}^{m_i \rightarrow m_{i+1}} = D_{KA}^m \times A / L_i^m \times ([KA]_i^m - [KA]_{i+1}^m)$
Membrane   strip solution interface ( $m s$ )	$N_{KA}^{n^m \rightarrow s_1} = k_{KA,eff}^{s_1 \rightarrow n^m} \times A \times ([KA]_{n^m}^m / \alpha_{A(w)}^{n^m s_1} - [KA]_1^s)$
Stripping solution ( $s$ )	$N_{KA}^{s_i \rightarrow s_{i+1}} = D_{KA}^s \times A / L_i^s \times ([KA]_i^s - [KA]_{i+1}^s)$
	$N_{KA}^{n^s \rightarrow s_b} = D_{KA}^s \times 2 \times A / L_i^s \times ([KA]_{n^s}^s - [KA]_b^s)$
Capacitance fluxes [mol/cm <sup>3</sup> s]	
Feed solution ( $f$ )	$d[KA]_b^f / dt = -N_{KA}^{f_b \rightarrow f_1} / V_b^f$
	$d[KA]_1^f / dt = (N_{KA}^{f_b \rightarrow f_1} - N_{KA}^{f_i \rightarrow f_2}) / V_i^f$
	$d[KA]_i^f / dt = (N_{KA}^{f_{i-1} \rightarrow f_i} - N_{KA}^{f_i \rightarrow f_{i+1}}) / V_i^f$
	$d[KA]_{n^f}^f / dt = (N_{KA}^{n^f-1 \rightarrow n^f} - N_{KA}^{n^f \rightarrow m_1}) / V_i^f$
CEM ( $m$ )	$d[KA]_1^m / dt = (N_{KA}^{n^f \rightarrow m_1} - N_{KA}^{m_1 \rightarrow m_2}) / V_i^m$
	$d[KA]_i^m / dt = N_{KA}^{m_{i-1} \rightarrow m_i} - N_{KA}^{m_i \rightarrow m_{i+1}} / V_i^m$
	$d[KA]_{n^m}^m / dt = N_{KA}^{n^m-1 \rightarrow n^m} - N_{KA}^{n^m \rightarrow s_1} / V_i^m$
Stripping solution ( $s$ )	$d[KA]_1^s / dt = (N_{KA}^{n^m \rightarrow s_1} - N_{KA}^{s_1 \rightarrow s_2}) / V_i^s$
	$d[KA]_i^s / dt = (N_{KA}^{s_{i-1} \rightarrow s_i} - N_{KA}^{s_i \rightarrow s_{i+1}}) / V_i^s$
	$d[KA]_{n^s}^s / dt = (N_{KA}^{n^s-1 \rightarrow n^s} - N_{KA}^{n^s \rightarrow s_b}) / V_i^s$
	$d[KA]_b^s / dt = -N_{KA}^{n^s \rightarrow s_b} / V_b^s$

$A$  - contact area between membrane and electrolyte, [cm<sup>2</sup>];  $k_{KA,eff}^{n^f \rightarrow m_1}$  and  $k_{KA,eff}^{n^m \rightarrow s_1}$  - the effective permeability coefficient (mass transfer constant) of  $K^+A^-$  at the  $f|m$  and  $m|s$  interface respectively, [cm/s];  $\alpha_{A(w)}^{m_1|n^f}$  and  $\alpha_{A(w)}^{n^m|s_1}$  - the distribution coefficient of  $A^-$  co-ions at the  $n^f|m_1$  and  $n^m|s_1$  interface, respectively;  $D_{KA}^f$ ,  $D_{KA}^s$ ,  $D_{KA}^m$  - the diffusion coefficient of  $K^+A^-$  in the feed, stripping solution and membrane [cm<sup>2</sup>/s];  $L_i^f$ ,  $L_i^s$ ,  $L_i^m$  - distance for  $K^+A^-$  diffusion between the adjacent sub-layers in the feed, stripping solution and membrane, [cm];  $V_i^f$ ,  $V_i^s$ ,  $V_i^m$  - volume of  $i$  sublayer of the feed, stripping solution and membrane, [cm<sup>3</sup>].

### 3.1. PROBLEM TO SOLVE

A fundamental problem in the studies of membrane permeability is the information on the exact value of the diffusion coefficients in the internal membrane solution  $D_{KA,0}^m$ . Most frequently, this quantity is estimated as the diffusion coefficient in aqueous media additionally corrected with the use of the so called tortuosity factor. On the other hand, the experimental quantity commonly determined from the studies on “diaphragm permeability” is the permeability coefficient (effective diffusion coefficient, mass transfer coefficient)  $P_{KA}^{f|s}$ . Its value can be calculated from the time dependence of the concentration of permeating species in the feed and stripping solution:

$$-\left(\frac{A}{L^m} \times (1/V_b^f + 1/V_b^s)\right)^{-1} \times \ln \left( \frac{[KA]_b^f - [KA]_b^s}{[KA]_{b(t=0)}^f - [KA]_{b(t=0)}^s} \right) = P_{KA,calc}^{f|s} \times t \quad (3)$$

In Eq.(3):  $[KA]_b^f$ ,  $[KA]_b^s$ ,  $[KA]_{b(t=0)}^f$ ,  $[KA]_{b(t=0)}^s$  denote the concentrations of the electrolyte in the bulk phase of the feed (f) and stripping (s) solution at time  $t$  and  $t=0$ , respectively. The permeability coefficient  $P_{KA,calc}^{f|s}$  can be calculated as the slope of the corresponding linear regression function using simulated concentrations of  $K^+A^-$  - in the bulk external solutions. After a comparison of the  $P_{KA,calc}^{f|s}$  coefficients, as calculated for a series of assumed  $D_{KA,0}^m$  values, with the experimental  $P_{KA,exp}^{f|s}$  coefficient, the proper value of unknown  $D_{KA,0}^m$  can be evaluated by the standard analysis of  $P_{KA,calc}^{f|s} = f(D_{KA,0}^m)$  dependence. In this way, the values of  $D_{KA,0}^m$  can be adjusted to the real behavior of the system. To verify the model applicability, the calculations were carried out for the Nafion-120 membrane in contact with  $KNO_3$  solution as the feed phase. All other characteristics necessary for calculations (Berkeley Madonna v. 08) corresponding with the experimental system were the same as described in Part 4. Additionally, it was assumed that the effective permeability constants of  $KNO_3$  at the interfaces are  $k_{KNO_3,eff}^{n^f \rightarrow m_1} = k_{KNO_3,eff}^{s_1 \rightarrow n^m} = 6.74 \times 10^{-5}$  [cm/s] the value of which was evaluated after calculations of the electrolyte sorption according to the model described in Part 4.

The results of calculations are presented in Fig.3 as the plot of  $P_{KNO_3,calc}^{f|s}$  vs.  $D_{KNO_3,0}^m$ . As it is seen, the experimental value of the overall  $KNO_3$  permeability corresponds with  $D_{KA,0}^m$  value equal to  $7.98 \times 10^{-6}$  cm<sup>2</sup>/s.

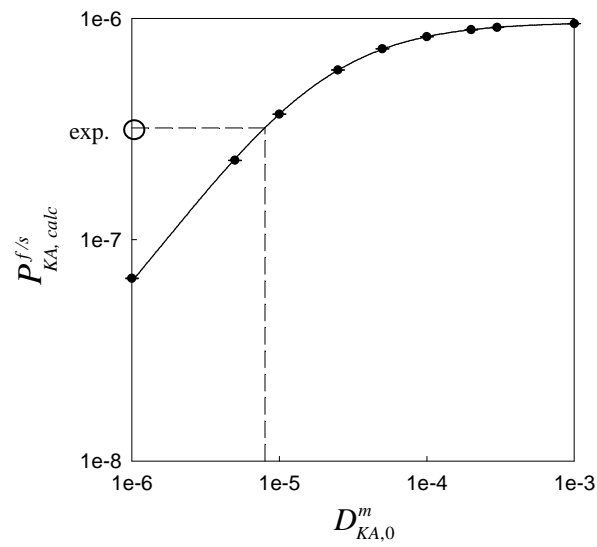


Fig. 3. Dependence between overall permeability coefficient  $P_{KA,calc}^{f/s}$  and the diffusion coefficient in the internal electrolyte of cation-exchange membrane ( $K^+ A^- \equiv KNO_3$ ).

#### REFERENCES

- [1] J. Schnakenberg, *Thermodynamic Network Analysis of Biological Systems*, Springer Verlag, Berlin-Heidelberg-New York, 1977