

**BOND-GRAPH DESCRIPTION AND SIMULATION
OF MEMBRANE PROCESSES.
3. DIFFUSION PHENOMENA IN A COMPARTMENTAL
SYSTEM**

Romuald WÓDZKI, Piotr SZCZEPAŃSKI, Radosław PAWŁOWSKI

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

Abstract

The calculations were carried out to estimate the degree of diaphragm reticulation as sufficient for quantitative modeling of stationary diffusion through a homogenous diaphragm.

1. INTRODUCTION

The network thermodynamic analysis [1-3] can be used for the interpretation, prediction, and general modeling of various diffusion systems [4,5]. The bond graph method used for this purpose is based on a conceptual division of the diaphragm into sub-layers (lumps, slices, sub-compartments) and their characterization as the storage (capacitor) and dissipation (diffusion) elements. However, since the amount of computations increases greatly with an increase in the diaphragm reticulation, it is of primary interest to determine the minimum of sub-layers (in each of the diffusion regions of the system) sufficient for the quantitative description of a diffusion system. Therefore, the number of volume elements that are used in a diaphragm (membrane) model should be established on a reasonable level. It should be noted here that the diffusion characteristics described by differential equations for homogeneous systems can be achieved only when the thickness of each sub-layer approaches zero. To evaluate the number of diaphragm sub-layers necessary to achieve results of modeling close to the analytical solution, the process ending with stationary diffusion was chosen. In such a case, the time-lags from modeling data can be compared with these calculated from Eq. (1).

Part 1: see ref. [4], Part 2: see ref [5]

$$\tau_L = \frac{(L^p)^2}{6D_S^p} \quad (1)$$

In Eq.(1) D_S^p is the diffusion coefficient of S substance in the diaphragm (p), L^p – diaphragm thickness [cm]. Consequently, the practical goal of this study was to evaluate the number of sub-layers in the diaphragm (n^p) of thickness and diffusivity corresponding with the membrane systems studied in our laboratory (liquid and polymer membranes).

2. MODEL AND MATHEMATICAL DESCRIPTION

The model deals with a closed system composed of a homogeneous diaphragm (p) of thickness L^p and area A , which separates two solutions, i.e. the feed (f) and stripping solution (s) of the volume V_f and V_s , respectively. The feed solution contains S substance which is able to permeate the diaphragm with the diffusion coefficient equal to D_S^p . In the system, the substance is transported according to the solution-diffusion mechanism. To simplify the calculations, it was additionally assumed that the distribution coefficient $\alpha = [S]^p / [S]^{i=f,s}$ is always equal to 1. Moreover, it was assumed that in the solutions adjacent to the diaphragm the existence of interfacial diffusion layers can be ignored.

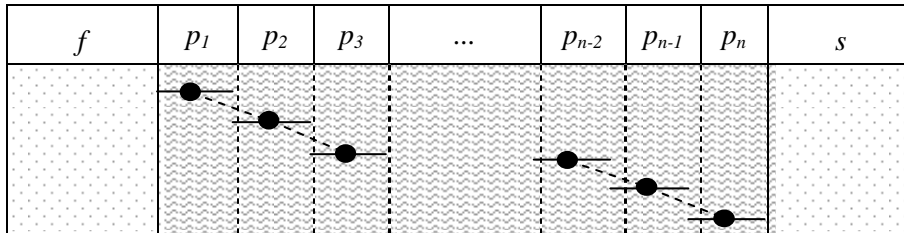
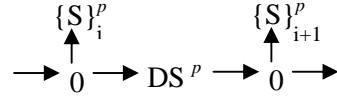


Fig. 1. Compartmental model of simple diffusion through a diaphragm

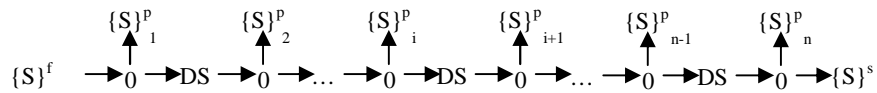
According to network modeling, the diaphragm is divided into n^p sub-layers (Fig.1). Each of them acts as a capacitor which stores S diffusing from i to $i+1$ layer. In the transient and unsteady state phase of transport, the local capacitances $\{S\}$ are dependent on time. After achieving the steady state conditions, the capacitance flows are zero valued and the S substance permeates the diaphragm with a constant flux which is experimentally verified by a linear increase of S content in the stripping solution.

According to the network analysis [2], the local step of permeation of

S between p_i and p_{i+1} sub-layer is represented by the following bond-graph element:



Thus, applying the „0” junctions for building the full network one can synthesize the following linear network representing the permeation of S through the diaphragm (p):



According to the above assumptions and permeation network, the general mathematical model can be formulated as the set of equations describing all the local diffusion and capacitance flows (Tab.1).

Tab. 1. Mathematical descriptions of nonexchange sorption of 1-1 electrolyte into ion-exchange polymer membrane.

Local flows (N) [mol/s]	
Feed solution diaphragm interface ($f p$)	$N_S^{f \rightarrow p_i} = 2P_S^p \left([S^f] - [S_i^p] \right)$
Diaphragm (p)	$N_S^{p_i \rightarrow p_{i+1}} = P_S^p \left([S_i^p] - [S_{i+1}^p] \right) \quad i = 1 \dots n^p - 1$
Stripping solution diaphragm interface ($p s$)	$N_S^{p_n \rightarrow s} = 2P_S^p \left([S_{n^p}^p] - [S^s] \right)$
Capacitance fluxes [mol/cm ³ s]	
Feed solution (f)	$\frac{d[S]^f}{dt} = -N_S^{f \rightarrow p_i} / V^f$
Diaphragm (p)	$\frac{d[S]_1^p}{dt} = (N_S^{f \rightarrow p_i} - N_S^{p_i \rightarrow p_2}) / V_i^p$ $\frac{d[S]_i^p}{dt} = (N_S^{p_{i-1} \rightarrow p_i} - N_S^{p_i \rightarrow p_{i+1}}) / V_i^p; \quad i = 2 \dots n^p - 1$ $\frac{d[S]_n^p}{dt} = (N_S^{p_{n-1} \rightarrow p_n} - N_S^{p_n \rightarrow s}) / V_i^p$
Stripping solution (s)	$\frac{d[S]^s}{dt} = N_S^{p_n \rightarrow s} / V^s$

P - permeability coefficient: $P_S^p = D_S^p \times A / L_i^p$; A - contact area between the diaphragm and external solutions, [cm²]; D_S^p - diffusion coefficient of S in the diaphragm [cm²/s]; L_i^f , $L_i^p = L^p / n^p$ - the way of S diffusion between the adjacent sub-layers, [cm]; V_i^p - volume of i diaphragm sublayer [cm³].

The model was reduced to the form that guarantees achievement of the stationary conditions by assuming in calculations: (i) constant

concentration of S in the feed solution, i.e. $[S]^f = \text{const}$, (ii) independency of $N_S^{p_n \rightarrow s}$ flow of concentration of S in the stripping solution, i.e.: $N_S^{p_n \rightarrow s} = 2P_S^p [S_n^p]$.

3. CALCULATIONS AND RESULTS

The calculations were carried out using the program PRODYF exploiting the Runge-Kutta IV method as a solver of ordinary differential equations (listed in Tab.1). Stationary fluxes of S and corresponding time-lags were calculated as dependent on D_S^p , n^p and L^p . For calculations, three characteristic values of diffusion coefficient were selected, i.e. $D_S^p = 1 \times 10^{-7}$, 1×10^{-6} , 1×10^{-5} cm²/s. For these coefficients, the calculations were carried out with L^p varied in the range: 1×10^{-3} - 0.1 cm. Each calculation series was repeated (for a given value of D_S^p and L^p) with n^p changed from 3 to 1000. It was assumed that the diaphragm area (A) is 1 cm², and the concentration of S in the feed solution is constant and equal to 1×10^{-4} mol/cm³.

Stationary flux of S as equal to $N_{S,st}^{p \rightarrow s}$ was immediately calculated by the program and the respective time lag was evaluated from the simulated cumulation curve $[S]^s = f(t)$, as schematically presented in Fig. 2.

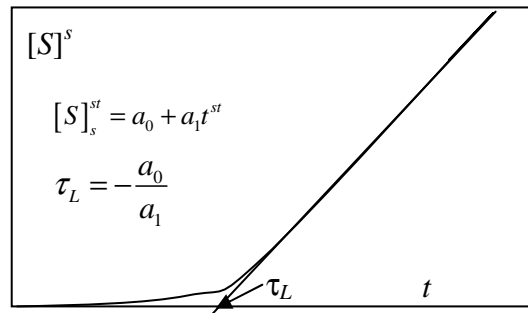


Fig. 2. Calculation of time-lag from simulation data

The results of calculations are presented in Fig.3a-c, as the plots of $\Delta \tau_L$ vs. n^p and L^p . From the presented plots and numerical data it can be concluded that for a typical polymeric membrane of the thickness 0.02 cm, the number of sub-layers $n^p=10$ (independently of D_S^p) is sufficient to obtain results of 0.5 % accuracy with respect to a theoretical value of time lag. In the case of a typical interfacial diffusion layer ($2-5 \times 10^{-3}$ cm), this

number remains the same. One can also conclude that the diffusion coefficient influences the value of time lag, however, it has no influence on the number of sub-layers necessary to achieve required result ($\Delta \tau_L$, %).

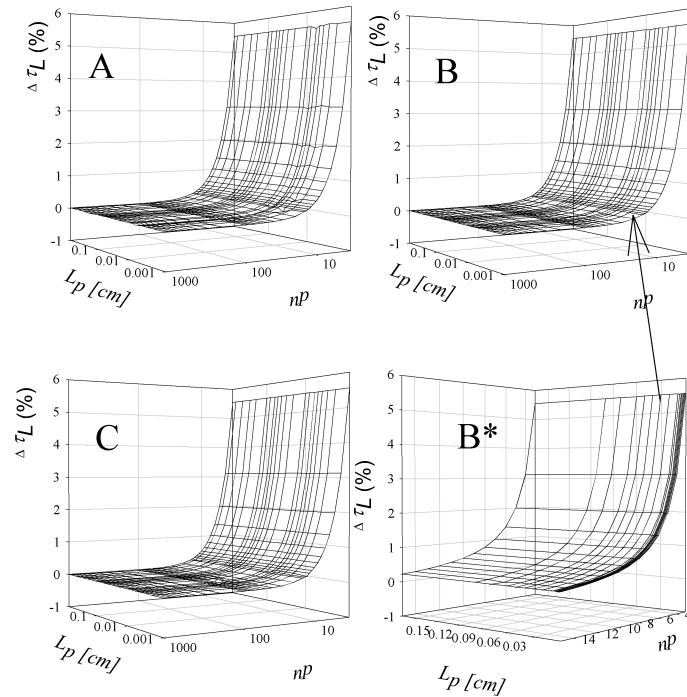


Fig. 3. Dependence of difference in calculated and theoretical time lag ($\Delta \tau_L$, %) on diaphragm thickness (L^p) and number of sub-layers (n^p): system with $D_s^p = 1 \times 10^{-5}$ (A), 1×10^{-6} (B), 1×10^{-7} cm²/s (C),.

REFERENCES

- [1] G.F. Oster, A.S. Perelson, A. Katchalsky, *Quart. Rev. Biophys.*, 1973, 6, 1
- [2] J. Schnakenberg, *Thermodynamic Network Analysis of Biological Systems*, Springer Verlag, Berlin, 1977
- [3] R. Wódzki, G. Szczepańska, P. Szczepański, *Sep. Purif. Technol.*, 2004, 36, 1
- [4] R. Wódzki, G. Szczepańska, Bond-graph description and simulation of membrane processes. 1. Donnan dialysis, *Mat. XXII Int. Symp. Physicochemical Meth. Sep., Ars Separatoria*, Szklarska Poręba 2007, 195-196.
- [5] R. Wódzki, G. Szczepańska, Bond-graph description and simulation of membrane processes. 2. Membrane extraction, *Mat. XXII Int. Symp. Physicochemical Meth. Sep., Ars Separatoria*, Szklarska Poręba 2007, 197-198.