Short communication

Momentum Balance Equation for Ion Mediated Transport

Z. Gałdzicki, E. Strauchmann, M. Bartoszkiewicz and S. Miękisz

Department of Biophysics, Academy of Medicine, ul. Chalubinskiego 10, 50–368 Wrocław, Poland

The present work is a containuation of a previous paper by Gałdzicki and Miękisz (1984). The model presented in the latter work described permeation of nonelectrolytes. A more interesting case is developed here. This model is a continuous description of transport of ions through liquid membranes.

It is generally accepted that the transport of ions may be mediated by carriers or by channels. A carrier-like mechanism is operative when the transport site is not simultaneously exposed to both sides. For a channel the binding sites are accesible from both sides at the same time direct transport through biological membranes is practically impossible for hydrophylic molecules, such as sugars, amino acids or metal cations, due to the necessity of crossing the nonpolar hydrocarbon-like membrane interior from the high-dielectric constant aqueous phase. A carrier molecule or channel is used to reduce the energy barrier for the translocation of polar molecules (Parsegian 1969). Läuger (1980) showed that the channel and the carrier may be regarded as limiting cases of a more general mechanism of a channel with multiple conformational states.

The very distinct examples of a carrier are macrocyclic antibiotics, such as valinomycin, enniatin B, and macrotetrolides (neutral carriers), or nigericin, monensin, X-537 A, A 23187 (charged carriers). Incorporation of these substances into artificial or biological membranes results in a sharp increase in the permeability of the membrane for alkaline ions. X-357 A and A 23187 favour divalent cations against alkaline cations. Another big group of carrier-like molecules includes the crown ether type synthetic macrocyclic ligands. First experiments with this type of molecules were carried out by Pedersen in 1967 and Choy et al. in 1974. The third big group of the carrier-like molecules is represented by carriers of hydrogen ions.

The charged polar head groups of lipid molecules and peripherical proteins produce the electrostatic potential (Hladky 1979). At first approximation our model neglects this effect by neglecting the surface charge density of membrane molecules.

A typical system which models the behaviour of biological and artificial membranes must consist of a hydrophobic liquid phase which separates two hydrophylic liquid phases. Chemical species may pass from one phase through the

membrane to another phase provided they are to some degree soluble in the membrane.

The proposed description of the continuous model of carrier ion transport utilizes the approach and results presented in our previous paper (Gałdzicki and Miękisz 1984). The situation is considered in isothermal approximation. An ion A^+ permeating across the membrane participates in an association-dissociation reaction only inside the membrane. For the sake of simplicity, compartment I contains only solute A^+, and the contents of compartment II were not considered. The assumptions we accepted in the previous work are topical. The system is thermodynamically open and a steady state is maintained by a constant influx of A^+ $[J_A(0)]$. As a first step, the constant electric field approximation is made. This assumption means that the association-dissociation reaction does not disturb the homogeneity of the field.

For ions this influx is governed by the Goldman flux equation, and due to it this influx is dependent of the properties of the membrane, the gradient of the concentration of substance A and the strength of the electric field. The permeability of ion A is estimated according to the formulae in the friction picture (see Spiegler 1958):

$$P_A = \frac{D_A}{L} = \frac{1}{L} RT / \left(\sum_{j \neq A} \zeta_{Aj} c_j + f_{Am} \right)$$

where c_j denotes the concentration inside the membrane. (For the meaninng of other symbols, see Gałdzicki and Miękisz 1984).

Further considerations and the way of calculation is completely analogous to those presented in the work by Gałdzicki and Miękisz 1984. We used the full momentum balance equations with the term $c_i F z_i E$ which describes the action of the electric field. From these equations we obtained the detailed formulae for the expansion coefficients of concentrations of considered substances. The detailed equations for these coefficients have been presented in the work by Strauchmann (1984).

In the previous paper (Gałdzicki and Miękisz 1984) we presented the results as the plots of the degree of coupling between chemical reaction and diffusion versus the position inside the membrane. Here, we averaged the fluxes over the length of the membrane. The mean fluxes could be better compared with the experimental results. The influence of the electric field on the average flow of a complex of cation and carrier has been investigated for different values of parameters f_{im}, k_1, k_2.

Two types of driving forces may be applied to the system considered, the electric field and the gradient of concentration. It has been shown that for f_{im} above $\sim 10^{15}$ the friction between the membrane and the permeating species changes the dependence of J_{AB}^{mean} on Δc and E in a similar way (see Fig. 1). The plot 1 shows

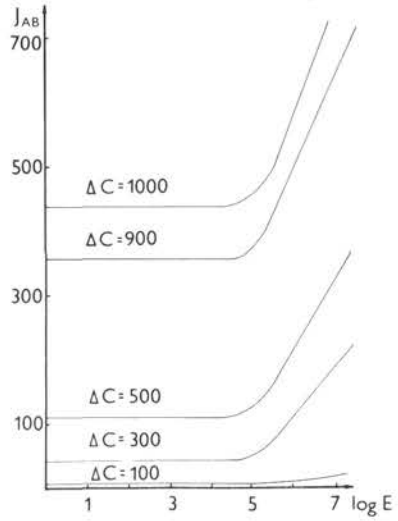

Fig. 1. The mean flux of complex AB versus the logarithm of the electric field strength for various gradients Δc [mol/m^3] of ion A concentration. $f_{Am} = 3 \times 10^{17}$ kg/smol, $f_{Bm} = 10^{15}$ kg/s mol, $k_1 = 3 \times 10^2$ m^3/mol s, $k_2 = 2 \times 10^5$ 1/s.

that for $\Delta c \neq 0$ (here, Δc is changed from 100 to 1000 mol/m^3) there is a threshold value of the electric field strength close to $E = 10^5$ V/m, above which the electric field raises significantly the mean value of the J_{AB} flux. This threshold value is determined by the rate constants of the chemical reaction and this may be the reason why the electric field is so high under physiological conditions.

Additional calculations which have not been shown on the plots (Strauchmann 1984) have shown an only slight influence of the partial viscosity tensor on the degree of coupling between diffusion and complex formation (in contrast to nonelectrolytes). The flux J_{AB} is enhanced slightly, by about 1%. Viscosity is predominantly shown as a friction force.

Rate constants of association and dissociation reaction for k_1 above 3×10^2 and k_2 below 1.5×10^5 sharply raised the flux J_{AB} (see Fig. 2).

Values of the electric field strength as high as they are met in biological systems (up to 10^7 V/m, 100 mV for a 10 nm thick membrane), in the light of our model, are necessary for an efficient control of physiological processes.

In our previous paper (Gałdzicki and Miękisz 1984) attention has already been turned to the contradictory effects of the viscosity action, i.e. the friction and the influence on the accesibility of the carrier (according to Shinitzky et al. 1980). Similar results have also been obtained in experiments carried out e.g. by Graham and Green (1970) and Aithal et al. (1976). The inhibition of ion transport due to

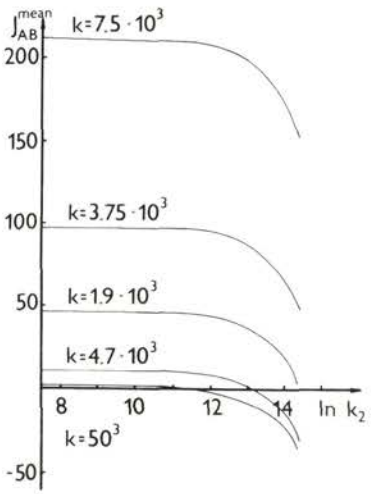

Fig. 2. The mean flux versus the logarithm of dissociation constant for various association constants. $E = 10^5$ V/m, for values of f_m see legend to Fig. 1.

an increase in viscosity appears as a pure frictional effect. The increase of transport rate is due to an increase in the accesibility of the active transport site.

According to our above results, the effect of partial viscosity on carrier ion transport could be neglected for the discussed values of chemical reaction rate constants.

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