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Generalization of the Spiegler–Kedem–Katchalsky frictional model equations of the transmembrane transport for multicomponent non-electrolyte solutions

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Abstract

The Spiegler–Kedem–Katchalsky frictional model equations of the transmembrane transport for systems containing n-component, non-ionic solutions is presented. The frictional interpretation of the phenomenological coefficients of membrane and the expressions connecting the practical coefficients (L_p, σ_i, ω_{ij}) with frictional coefficients (f_{ij}) are presented.

Keywords: Transmembrane transport; Spiegler–Kedem–Katchalsky friction model; Multicomponent non-electrolyte systems

1. Introduction

The idea of describing steady-state transport processes in a membrane as balances between the gross thermodynamic forces acting on the system and frictional interactions between the components of the system, was advanced by Lord Rayleigh in 1873 [1]. In 1954 the term molecular friction coefficient has been applied to the coefficient which relates the frictional force between two components to the difference between their velocities [2]. This approach has been used to describe transmembrane transport by several authors, especially by Spiegler [3]. The Spiegler friction model equations [3] were used by Kedem and Katchalsky [4] to give a physical interpretation of the phenomenological coefficients of membranes (L_p, σ, ω), and by Meares et al. [5] to give a mechanistical interpretation of the molecular interaction by using the macroscopic friction coefficient (R_{ij}). Spiegler's frictional model equations describing transport processes in membrane use the friction coefficients (f_{ik}) which represent the interactions of a particular pair of flows.

In this paper, the aim of this theoretical study is to generalize the Spiegler–Kedem–Katchalsky frictional model equations (SKK model) for membrane systems containing multicomponent, nonionic and homogeneous solutions.

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2. Basic assumptions

The starting point for our considerations, similarly to those of Spiegler [3], Kedem and Katchalsky [4], and Meares et al. [5], is that in steady flow the thermodynamic forces ($\boldsymbol{X}_k$) are counterbalanced by the sum of mechanical frictional forces ($\boldsymbol{F}_k$) acting at each molecule

$$X_k + F_k = 0, \qquad k = w, 1, 2, \cdots, n \tag{1}$$

where X_k is the thermodynamic force, $\boldsymbol{F}_k = \sum_{j \neq k} F_{kj}$, $j \neq k = w, m, 1, 2, \cdots, n$ is the frictional force acting on the kth molecule and is equal to the sum of interactions forces between the kth and jth species, index "w" meaning water and "m"–membrane.

The frictional character of intermolecular interactions is illustrated by the following expression

$$F_{kj} = -f_{kj}(\boldsymbol{v}_k - \boldsymbol{v}_j), \tag{2}$$

where f_{ij} is the friction coefficient between the kth and jth molecules, $\boldsymbol{v}_k$ and $\boldsymbol{v}_j$ are the velocities of the kth and jth molecules, respectively, the minus sign means, that the frictional force has opposite sense with respect to the velocity of the moving molecule. In order to simplify the treatment, we will consider the one-dimensional case only. That is why we will not write the index vector.

The flux of the kth substance passing perpendicularly to the unit of the surface of the membrane at point "x" is expressed by the following expression

$$J_k(x) = \frac{\mathrm{d}n_k}{S\,\mathrm{d}t}(x) = \tilde{C}(x) v_k(x), \quad k = s, w \tag{3}$$

where n_k is the number of molecules of the kth species, S is the effective surface of the membrane, $\tilde{C}_k(x)$ and $v_k(x)$ are concentration and velocity, respectively, of the kth substance at point "x".

3. Generalization of SKK model equations

In steady state J_k is independent of "x" and equal to the macroscopic flow. From expressions (1)–(3) we obtain an equation connecting the thermodynamic forces (X_w, X_s) and fluxes (J_w, J_s) by means of the friction tensor **R**

$$\begin{bmatrix} X_\mathrm{w} \\ X_\mathrm{s} \end{bmatrix} = \mathbf{R} \begin{bmatrix} J_\mathrm{w}/\tilde{C}_\mathrm{w} \\ J_\mathrm{s}/\tilde{C}_\mathrm{s} \end{bmatrix}, \quad s = 1, 2, \cdots, n \tag{4}$$

where the friction tensor **R** is defined by the following expression

$$\mathbf{R} \equiv \begin{bmatrix} \sum_{s-1}^{n} (f_{\mathrm{w}s} + f_{\mathrm{w}m}) & -f_{\mathrm{w}1} & \cdots & -f_{\mathrm{w}n} \\ -f_{1\mathrm{w}} & \sum_{k \neq 1}^{n} (f_{1k} + f_{1m}) & \cdots & -f_{1n} \\ -f_{n\mathrm{w}} & -f_{n1} & \cdots & \sum_{k \neq n} (f_{nk} + f_{nm}) \end{bmatrix} \tag{5}$$

J_w is the water flux, J_s is the molecular flux of the kth substance.

Rewriting the friction tensor **R** in a form which allows to introduce the C_k concentration and using Onsager's reciprocal relations we obtain

$$f_{kj}/\tilde{C}_j = f_{jk}/\tilde{C}_k \tag{6}$$

Equation (4) has a solution in the form of the Kramer formulas

$$\frac{J_s}{\tilde{C}_s} = \frac{1}{\det \mathbf{R}} \Big[X_\mathrm{d} \det R_{\mathrm{w}s}(-1)^{s+2} + \sum_l \big(X_l \det R_{1s}(-1)^{l+s} \big) \Big] \tag{7}$$

$$\frac{J_\mathrm{w}}{\tilde{C}_\mathrm{w}} = \frac{1}{\det \mathbf{R}} \Big[X_\mathrm{w} \det R_\mathrm{ww} + \sum_l \big(X_l \det R_{l\mathrm{w}}(-1)^{l+2} \big) \Big] \tag{8}$$

where $s, l = 1, 2, \cdots, n$. Taking into consideration the definition of volume flux [6] ($J_\mathrm{v} = J_\mathrm{w}\overline{V}_\mathrm{w} + \sum_s (J_s \overline{V}_s)$ where $\overline{V}_s$, $\overline{V}_\mathrm{w}$ are the partial molar volumes of sth substance and water, respectively) and eqs. (7) and (8), we obtain

$$J_\mathrm{v} = \frac{1}{\det \mathbf{R}} \Big[X_\mathrm{w} A + \sum_l (X_l B) \Big] \tag{9}$$

where

$A = \phi_{\rm w} \det R_{\rm ww} + \Sigma_s((-1)^{s+2}\phi_s \det R_{{\rm w}s})$,

$B = \phi_{\rm w}(-1)^{l+2} \det R_{l{\rm w}}$
$\quad + \Sigma_s(\phi_s(-1)^{l+s} \det R_{ls})$

$\phi_s = \tilde{C}_s\bar{V}_s, \qquad \phi_{\rm w} = \tilde{C}_{\rm w}\bar{V}_{\rm w}$.

The thermodynamic forces existing in the system: solution I–membrane–solution II, are the result of the gradients of the chemical potentials. Thus the definitive thermodynamic forces acting on a water molecule (or on a solute molecule) at point "x" of membrane can be expressed by the differential of the hydrostatic pressure (dP) and by the differential of the osmotic pressure (dπ) in following way

$$X_w \cong -\frac{{\rm d}\mu_{\rm w}}{{\rm d}x} = -\bar{V}_{\rm w}\left[\frac{{\rm d}P}{{\rm d}x} - \sum_k\left(\frac{{\rm d}\pi_k}{{\rm d}x}\right)\right] \qquad (10)$$

$$X_s \cong -\frac{{\rm d}\mu_s}{{\rm d}x} = -\left(\bar{V}_s\frac{{\rm d}P}{{\rm d}x} + \frac{1}{\bar{c}_s}\frac{{\rm d}\pi_s}{{\rm d}x}\right) \qquad (11)$$

In eqs. (10) and (11), $P(x)$ and $\pi(x)$ are defined by quantities related to the solutions existing outside the membrane. In order to find relations between concentration outside of the membrane $\tilde{C}_s(x)$ and concentration in the membrane $\bar{c}_s(x)$ corresponding to "x", we have to introduce the distribution coefficient K_s [4] by the expression

$$K_s = \frac{\bar{c}_s(x)}{\tilde{C}_s(x)} \qquad (12)$$

In the first approximation, when $\bar{V}_s \ll 1/\bar{c}_s$, eq. (11) gives

$$X_s \cong -\frac{1}{\bar{c}_s}\frac{{\rm d}\pi_s}{{\rm d}x} = -\frac{1}{K_s\tilde{C}_s}\frac{{\rm d}\pi_s}{{\rm d}x} \qquad (13)$$

Now taking into consideration expressions (10) and (13) in eq. (9) we obtain

$$J_{\rm v} = \frac{1}{\det \mathbf{R}}\left[-A\bar{V}_{\rm w}\frac{{\rm d}P}{{\rm d}x} + \sum_l\left(A\bar{V}_{\rm w} - \frac{1}{\bar{c}_l}B_l\frac{{\rm d}\pi_l}{{\rm d}x}\right)\right] \qquad (14)$$

Let us write the generalized Kedem–Katchalsky equation for volume flux in a local form [7]

$$J_{\rm v} = L_{\rm p}\left[-\frac{{\rm d}P}{{\rm d}x} + \sum_l\left(\sigma_l\frac{{\rm d}\pi_l}{{\rm d}x}\right)\right] \qquad (15)$$

where $L_{\rm p}$ and $\sigma_{\rm l}$ are the local filtration and reflection coefficients respectively, $l = 1, 2, \cdots, n$. The coefficients $L_{\rm p}$ and $\sigma_{\rm l}$ are defined by the following expressions

$$L_{\rm p} = \left(\frac{J_{\rm v}}{{\rm d}P/{\rm d}x}\right)_{{\rm d}\pi/{\rm d}x=0} \qquad (16)$$

$$\sigma_{\rm l} = \left(\frac{{\rm d}P/{\rm d}x}{{\rm d}\pi/{\rm d}x}\right)_{J_{\rm v}=0} \qquad (17)$$

Combining eqs. (14) and (15) we obtain expressions for the local filtration and reflection coefficients, respectively

$$L_{\rm p} = \frac{A\bar{V}_{\rm w}}{\det \mathbf{R}} \qquad (18)$$

$$\sigma_l = 1 - \frac{B_l}{\bar{V}_{\rm w}\bar{c}_l} \qquad (19)$$

If we assume in eqs. (18) and (19) that $\bar{V}_s \propto 1/\bar{c}_s$ we find

$$L_{\rm p}^* = \frac{\bar{V}_{\rm w}A + \sum\limits_k(\bar{V}_kB_k)}{\det \mathbf{R}} \qquad (20)$$

$$\sigma_l^* = \frac{\sigma_l}{1 + \dfrac{1}{\bar{V}_{\rm w}}\sum\limits_l(\bar{V}_lB_l)} \qquad (21)$$

Combining eqs. (10), (11) and (8) we obtain

$$\frac{J_s}{\tilde{C}_s} = \frac{1}{\det \mathbf{R}}\left[E_s\frac{{\rm d}P}{{\rm d}x} + \sum_l\left(\Delta_l^s\frac{{\rm d}\pi_l}{{\rm d}x}\right)\right] \qquad (22)$$

where

$E_s = \bar{V}_{\rm w}(-1)^{s+3} \det R_{{\rm w}s}$
$\quad + \Sigma_l(\bar{V}_l(-1)^{l+s+1} \det R_{ls})$

$\Delta_l^s = \bar{V}_{\rm w}(-1)^{s+2} \det R_{{\rm w}s}$
$\quad + 1/\bar{c}_l\bar{V}_l(-1)^{l+s+1} \det R_{ls}$

Using in eq. (22) the differential pressure (dP/dx) calculated from eq. (15) we find the following expression

$$J_s = J_{\rm v}\tilde{C}_s(1 - \sigma_s) + \sum_l\left(\omega_{ls}\frac{{\rm d}\pi_l}{{\rm d}x}\right) \qquad (23)$$

where $\omega_{ls} = (E_s\sigma_l + \Delta_l^s\tilde{C}_s/\det \mathbf{R})$ is the permeability coefficient of membrane for sth substance passing under the influence of thermodynamic forces X_s and X_l.

However, the local equations are impractical for experimental verification. Therefore they should be integrated over the thickness of the membrane. This yields the following equation

$$J_v = L_p \left[\Delta P - \sum_l (\sigma_l \, \Delta\pi_l) \right] \tag{24}$$

where $L_p = \bar{V}_w A / \Delta x \det \mathbf{R}$, $\sigma_l = 1 - B_l / \tilde{c}_l \bar{V}_w$, $\Delta\pi = \pi_0 - \pi_{\Delta x}$, $\Delta P = P_0 - P_{\Delta x}$. Similarly, by integrating eq. (23) we obtain

$$J_s = J_v \tilde{C}_s (1 - \sigma_s) + \sum_k (\omega_{ks} \, \Delta\pi_k) \tag{25}$$

where $\omega_{ks} = (-\tilde{C}_s \, \Delta_k^s + \tilde{C}_s E_s \sigma_k)/\Delta x \det \mathbf{R}$. For $s = 1$ and $s = 2$ we obtain the Spiegler–Kedem–Katchalsky frictional model equations for binary and ternary solutions, respectively [8].

3. Conclusions

The quantitative application of the Spiegler frictional model to biological membrane systems is restricted by the difficulty of measuring or estimating values for the average or local concentrations of the permeating species in the membrane. These values are required for the calculation of the friction coefficients from the measured experimental parameters [6]. Thus, although values for sets of L_{ik} coefficients have been obtained for some biological systems, it has been possible to interpret these in terms of the friction coefficients in only a qualitative manner [5,9,10].

The Spiegler frictional model equation [3] was used for the interpretation of the phenomenological coefficients of the membrane (L_p, σ and ω) by Kedem and Katchalsky [4]. The field of application of this model called by us the Spiegler–Kedem–Katchalsky frictional model equations, is limited to binary solutions. Generalization of this model presented in this paper, for systems containing multicomponent, non-electrolyte solutes increases the field of applications, particularly to biosystems.

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