Model equations of the volume transport of multicomponent and heterogeneous non-ionic solutions in double-membrane systems

A. ŚLĘZAK

Institute of Physics, Pedagogical University, ul. Armia Krajowa 13/15, PL 42-201 Częstochowa, Poland

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Abstract. The volume flows model equation for a double-membrane system, in which two membranes separate three compartments (l, m, r) containing the heterogeneous, non-ionic n -component solutions is elaborated. In this system the solution concentrations fulfill the condition $C_k^l > C_k^m > C_k^r$. The inter-membrane compartment (m) consists of the infinitesimal layer of solution. The volume of compartment m and external compartments (l and r) fulfill the conditions $V_m \rightarrow 0$ and $V_l = V_r \rightarrow \infty$ respectively. The linear dependences of the volume flux on concentration differences in binary solutions and nonlinear – in ternary solutions, were obtained. This model for binary and ternary non-electrolyte solutions is discussed. It is shown, that the double-membrane system has rectifying and amplifying properties for osmotic transport and mechanical pressure.

Key words: Membrane transport, Gravitation force, Kedem-Katchalsky equations, Boundary layers

1. Introduction

Kedem and Katchalsky [1] ascertained that as a result of a suitable thermodynamic force such as a gradient, e.g., osmotic pressure (π), electric potential (ψ), hydrostatic pressure (P) and/or temperature (T), a sequential double-membrane systems composed of two different membranes containing a 2-component electrolytic solution in the intermembranous phase with infinitesimal thickness, permits accumulation or depletion of the dissolved substance. The consequence of these processes are, among other things, electric [1–5], osmotic and diffusion [6] and hydraulic [7] rectifying properties of the double-membrane systems. The aforementioned processes are also the basis of the double-membrane osmotic pump [8].

In previous papers [9, 10] we ascertained that the processes of accumulation and depletion occur in the inter-membrane phase in a double-membrane system in which transport of multicomponent, heterogeneous non-ionic solutions is caused by an osmotic pressure gradient. In the present paper a thermodynamic model of volume flow of heterogeneous and non-ionic multicomponent solutions in a double-membrane system is presented. Two membranes and three solutions con-

Figure 1. The double-membrane system (M_l, M_r – membranes; l, m, r – compartments; C_k^l, C_k^m, C_k^r – solution concentrations; J_v^* – volume flux; J_s^* – solute flux; bl – diffusion boundary layers).

stitute this system. In this paper two cases will be considered. In the first case, the infinitesimal layer of solution is a part of inter-membrane compartments of sufficiently small volume. The volumes of the external compartments are identical and sufficiently large to maintain constant concentration. In the second case, the volumes of the all compartments are identical and sufficiently large. The present experiments provide an example of a concentration-driven Rayleigh-Taylor process in a double-membrane system.

2. Membrane system

Let us consider the double-membrane system represented schematically in Figure 1. In this system the compartments (l), (m) and (r), containing diluted and heterogeneous (not mechanically stirred) n -component solutions of the same non-electrolyte at concentrations C_k^l, C_k^m and C_k^r ($k = 1, 2, \dots, n$) are separated by isotropic and symmetrical membranes M_l and M_r of thickness d . In this system water and the dissolved substance diffusing across the membranes will lead to the formation of boundary layers. The membranes are characterized by hydraulic permeability (L_p), reflection (σ) and diffusive permeability (ω) coefficients. The reflection and diffusive permeability coefficients of complexes: boundary layer/membrane/boundary layer (bl/M/bl) are denoted by σ^* and Ω respec-

tively. The solutions contain $k = 1, 2, \dots, n$ substances dissolved in solvent w . The concentration of these solutions are denoted by $C_1^l, \dots, C_n^l$; $C_1^m, \dots, C_n^m$; $C_1^r, \dots, C_n^r$. These concentrations fulfill the condition $C_k^l > C_k^m > C_k^r$. Two cases are considered. In the first case, the volumes of the external compartments (V_l, V_r) containing solutions at concentrations C_k^l and C_k^r fulfill respectively the condition $V_l = V_r \rightarrow \infty$. The intermembrane compartment (m) consists of an infinitesimally thin layer of solution at a concentration C_k^m . The volume of this compartment fulfills the condition $V_m \rightarrow 0$. In the second case, the volumes of all compartments (l, m, r) are identical and fulfill the condition $V_l = V_m = V_r \rightarrow \infty$. The following assumptions are made: (i) the transport processes are isothermal and stationary, (ii) no chemical reactions occur in solutions.

The analysis of transport processes in a double-membrane system represented in Figure 1, are based on the modified Kedem-Katchalsky-Zelman model equation [11], using the Katchalsky-Curran method [2].

3. The generalization of the Kedem-Katchalsky-Zelman model equation of transmembrane transport to multicomponent non-ionic solutions

Our starting point is the Kedem-Katchalsky-Zelman model of transmembrane transport in multicomponent, non-ionic and heterogeneous solutions [11]

$$J_v^* = \ell \left(\frac{1}{\det K} \sum_i \sigma_i \Sigma_k \Delta \Pi_k \det K_{ik} \pm \Delta P^* \right), \quad (1)$$

$$J_s^* = J_v^* (1 - \sigma_s^*) \tilde{C}_s + \sum_k \Omega_{sk} \Delta \Pi_k \quad (2)$$

where J_v^* and J_s^* are the volume and solute fluxes, σ_i and σ_s the reflection coefficients of the membrane for i -th and s -th substances, respectively, $\Delta \Pi_k$ the osmotic pressure difference for the k -th substance, ΔP^* the hydrostatic pressure difference, Σ_s^* the reflection coefficient of the complex: boundary layer/membrane/boundary layer (bl/M/bl), $\tilde{C}_s$ the average solute concentration for the s -th substance, ω_{ks} and Ω_{ks} the diffusive permeability coefficients of the s -th substance, which passes across the membrane and complex (bl/M/bl) respectively, under the influence of the gradient of the k -th substance osmotic pressure difference ($\omega_{ks} = \omega_{sk} \tilde{C}_s / \tilde{C}_k$, $\Omega_{ks} = \Omega_{sk} \tilde{C}_s / \tilde{C}_k$) and $s \neq k = 1, 2, \dots, n$; the $(n+1)$ -th component is the solvent for which $\sigma_{n+1} = 0$.

$$K \equiv \begin{bmatrix} \omega_{11} & \omega_{21} & \cdots & \omega_{n1} \\ \cdot & \cdot & \cdots & \cdot \\ \omega_{1n} & \omega_{2n} & \cdots & \omega_{nn} \end{bmatrix}, \quad \ell = \left[1 \mp (\det K)^{-1} L_p \sum_i \sigma_i \det M_i \right]^{-1},$$

$$K_{ik} \equiv \begin{bmatrix} \omega_{11} & \cdots & \omega_{i-1,1} & \Omega_{k1} & \omega_{i+1,1} & \cdots & \omega_{n1} \\ \cdot & \cdots & \cdot & \cdot & \cdot & \cdots & \cdot \\ \omega_{1n} & \cdots & \omega_{i-1,n} & \Omega_{kn} & \omega_{i+1,n} & \cdots & \omega_{nn} \end{bmatrix},$$

$$M_i \equiv \begin{bmatrix} \omega_{11} & \cdots & \omega_{i-1,1} & [(1 - \sigma_1^*)\tilde{C}_1 - (1 - \sigma_1)\tilde{c}_1] & \omega_{i+1,1} & \cdots & \omega_{n1} \\ \cdot & \cdots & \cdot & \cdot & \cdot & \cdots & \cdot \\ \omega_{1n} & \cdots & \omega_{i-1,n} & [(1 - \sigma_n^*)\tilde{C}_n - (1 - \sigma_n)\tilde{c}_n] & \omega_{i+1,n} & \cdots & \omega_{nn} \end{bmatrix}.$$

The interpretation of the phenomenological parameters of membrane transport for binary and ternary non-electrolyte solutions ($L_p, \sigma, \sigma_i^*, \omega, \Omega$) was presented in [11, 14]. In these papers it was shown that the values of coefficients σ_i^* and Ω_{ik} for binary and ternary solutions may be a function of the configuration of the membrane system and the values of Ω_{ik} for ternary solutions is a function of the concentration of the solutions.

4. Model equations of the volume flow of multicomponent, non-ionic and heterogeneous solutions for double-membrane systems

In order to describe, mathematically, stationary osmotic volume flows in a double-membrane system, we consider Equation 1. The equations for membrane M_l and M_r are written in the form

$$J_v^l = \ell_l \left[(\det K^l)^{-1} RT \sum_i \sigma_i^l \sum_k (C_k^l - C_k^m) \det K_{ik}^l + (P_l^* - P_m^*) \right], \quad (3)$$

$$J_v^r = \ell_r \left[(\det K^r)^{-1} RT \sum_i \sigma_i^r \sum_k (C_k^m - C_k^r) \det K_{ik}^r + (P_m^* - P_r^*) \right]. \quad (4)$$

Since in a mathematically stationary state $J_v^l = J_v^r = J_v^* = \text{const.}$ and $P_l^* = P_r^* = P_o = \text{const.}$, then

$$P_m^* = \frac{RT}{\ell_l + \ell_r} \left\{ \sum_k [\ell_l C_k^l (\sigma_k^l)^* + \ell_r C_k^r (\sigma_k^r)^*] - \sum_k \zeta C_k^m \right\} + P_o, \quad (5)$$

$$J_v^* = \frac{\ell_l \ell_r}{\ell_l + \ell_r} RT \left\{ \sum_k [\sum_i [C_k^l (\sigma_k^l)^* - C_k^r (\sigma_k^r)^*] + \sum_k \xi C_k^m] \right\}, \quad (6)$$

where

$$(\sigma_k^l)^* = \sum_i \sigma_i^l \frac{\det K_{ik}^l}{\det K^l}, \quad (\sigma_k^r)^* = \sum_i \sigma_i^r \frac{\det K_{ik}^r}{\det K^r},$$

$$\xi = (\sigma_k^r)^* - (\sigma_k^l)^*, \quad \zeta = \ell_l (\sigma_k^l)^* + \ell_r (\sigma_k^r)^*.$$

Equation 5 describes the hydrostatic pressure in the intermembrane compartment of a double-membrane system (P_m^*), and Equation 6, describes the volume flux across a double-membrane system. The above equations are valid for the case in

which the volume of the intermembrane compartment, (like the external compartments), is sufficiently large ($V_m \rightarrow \infty$).

Let us assume that the volume of the intermembrane compartment is infinitely small, i.e., the intermembrane compartment is an infinitesimal layer of solution. Also, the concentration of solution in the intermembrane compartment is different in steady and initial states. This concentration can be calculated using Equation 2. The double-membrane system represented in Figure 1 can be written

$$J_k^l = J_v^*[1 - (\sigma_k^l)^*]\tilde{C}_k^l + RT \sum_s \Omega_{sk}^l (C_s^l - C_s^m), \quad (7)$$

$$J_k^r = J_v^*[1 - (\sigma_k^r)^*]\tilde{C}_k^r + RT \sum_s \Omega_{sk}^r (C_s^m - C_s^r), \quad (8)$$

where $\tilde{C}_k^l = \frac{1}{2}(C_k^m + C_k^l)$, $\tilde{C}_k^r = \frac{1}{2}(C_k^m + C_k^r)$.

Since in the steady state $J_k^l = J_k^r = J_k^* = \text{const.}$, then

$$C_k^m = \frac{\gamma + \frac{1}{2}J_v^*\vartheta - \varphi}{\kappa - \frac{1}{2}J_v^*\xi} \quad (9)$$

where $\gamma = RT(\Omega_{kk}^l C_k^l + \Omega_{kk}^r C_k^r)$, $\vartheta = [1 - (\sigma_k^l)^*]C_k^l - [1 - (\sigma_k^r)^*]C_k^r$, $\kappa = RT(\Omega_{kk}^l + \Omega_{kk}^r)$, $\varphi = \sum_s \Omega_{sk}^r \Delta \Pi_s^r - \sum_s \Omega_{sk}^l \Delta \Pi_s^l$. Discussion of these equations leads to the following conclusions:

1. For $k = 2$ (ternary solution), Equations (5), (6) and (9) can be written in following forms

$$P_m^* = \frac{RT}{\ell_l + \ell_r} (\ell_l A + \ell_r B - C_1^m \zeta_1^1 - C_2^m \zeta_2^1) + P_o, \quad (10)$$

$$J_v^* = \frac{\ell_l \ell_r}{\ell_l + \ell_r} RT (\Gamma + \Theta + C_1^m \xi_1^1 + C_2^m \xi_2^1), \quad (11)$$

$$C_1^m = \frac{\gamma_1^1 + \frac{1}{2}J_v^*\vartheta_1^1 - \frac{v_1(\gamma_2^1 + \frac{1}{2}J_v^*\vartheta_2^1)}{\kappa_2^1 - \frac{1}{2}J_v^*\xi_2^1}}{\kappa_1^1 - \frac{1}{2}J_v^*\xi_1^1 - \frac{v_1 v_2}{\kappa_2^1 \frac{1}{2}J_v^*\xi_2^1}}, \quad (12)$$

$$C_2^m = \frac{\gamma_2^1 + \frac{1}{2}J_v^*\vartheta_2^1 - \frac{v_2(\gamma_1^1 + \frac{1}{2}J_v^*\vartheta_1^1)}{\kappa_1^1 - \frac{1}{2}J_v^*\xi_1^1}}{\kappa_2^1 - \frac{1}{2}J_v^*\xi_2^1 - \frac{v_1 v_2}{\kappa_1^1 \frac{1}{2}J_v^*\xi_1^1}}, \quad (13)$$

where $A = C_1^l(\sigma_1^l) + C_2^l(\sigma_2^l)^*$, $B = C_1^r(\sigma_1^r)^* + C_2^r(\sigma_2^r)^*$, $\vartheta_1^1 = [1 - (\sigma_1^l)^*]C_1^l - [1 - (\sigma_1^r)^*]C_1^r$, $\vartheta_2^1 = [1 - (\sigma_2^l)^*]C_2^l - [1 - (\sigma_2^r)^*]C_2^r$, $\zeta_1^1 = \ell_1(\sigma_1^l)^* + \ell_r(\sigma_1^r)^*$, $\zeta_2^1 = \ell_1(\sigma_2^l)^* + \ell_r(\sigma_2^r)^*$, $\gamma_1^1 = RT(\Omega_{11}^l C_1^l + \Omega_{11}^r C_1^r + \Omega_{21}^l C_2^l + \Omega_{21}^r C_2^r)$, $\gamma_2^1 = RT(\Omega_{22}^l C_2^l + \Omega_{22}^r C_2^r + \Omega_{12}^l C_1^l + \Omega_{12}^r C_1^r)$, $\xi_1^1 = (\sigma_1^r)^* - (\sigma_1^l)^*$, $\xi_2^1 = (\sigma_2^r)^* - (\sigma_2^l)^*$, $v_1 = RT(\Omega_{21}^l + \Omega_{21}^r)$, $v_2 = RT(\Omega_{12}^l + \Omega_{12}^r)$, $\Gamma = C_1^l(\sigma_1^l)^* - C_1^r(\sigma_1^r)^*$, $\Theta = C_2^l(\sigma_2^l)^* - C_2^r(\sigma_2^r)^*$, $\kappa_1^1 = RT(\Omega_{11}^l + \Omega_{11}^r)$, $\kappa_2^1 = RT(\Omega_{22}^l + \Omega_{22}^r)$.

2. For $k = 1$ (binary solution), Equations (5), (6) and (9) can be expressed in the form

$$P_m^* = \frac{RT}{\ell_l + \ell_r} \{ \ell_l C_1^l (\sigma_1^l)^* + \ell_r C_1^r (\sigma_1^r)^* \} - C_1^m \zeta_1^1 \} + P_o, \quad (14)$$

$$J_v^* = \frac{\ell_l \ell_r}{\ell_l + \ell_r} RT \{ C_1^l (\sigma_1^l)^* - C_1^r (\sigma_1^r)^* \} + C_1^m \xi_1^1, \quad (15)$$

$$C_1^m = \frac{\gamma_o + \frac{1}{2} J_v^* \vartheta_1^1}{\kappa_1^1 - \frac{1}{2} J_v^* \xi_1^1}, \quad (16)$$

where $\gamma_o = RT(\Omega_{11}^l C_1^l + \Omega_{11}^r C_1^r)$, $(\sigma_1^l)^* = \frac{\Omega_{11}^l}{\omega_{11}^l} \sigma_1^l$, $(\sigma_1^r)^* = \frac{\Omega_{11}^r}{\omega_{11}^r} \sigma_1^r$.

4. If we assume that $J_v^* \rightarrow 0$ in Equation (16) we obtain

$$C_l^m = \frac{\Omega_{11}^l C_1^l + \Omega_{11}^r C_1^r}{\Omega_{11}^l + \Omega_{11}^r}. \quad (17)$$

A similar equation was obtained by Kedem and Katchalsky [1] for the double-membrane system containing homogeneous solutions.

5. Let us consider the case in which $C_1^r > 0$, $C_1^m = 0.5C_1^r$ and $C_1^l = 0$. If in the double membrane system $\Omega_{11}^l > \Omega_{11}^r$ and $\sigma_1^l < \sigma_1^r$, then in the steady state $C_1^m < 0.5C_1^r$. Therefore, the intermembranous compartment permits depletion of the dissolved substance. If we change of sequence arrangement of membranes we obtain $\Omega_{11}^l < \Omega_{11}^r$, $\sigma_1^l > \sigma_1^r$ and $C_1^m > 0.5C_1^r$. In this case, the intermembranous compartment permits accumulation of the dissolved substance.

6. Taking into consideration Equation (9) in (14) and (15) we obtain

$$P_m^* = \frac{1}{\ell_l + \ell_r} \frac{\Omega_{11}^l \Omega_{11}^r}{\Omega_{11}^l + \Omega_{11}^r} \frac{(\ell_l \omega_{11}^l \omega_{11}^r - \ell_r \sigma_1^r \omega_{11}^l) RT (C_1^l - C_1^r)}{\omega_{11}^l \omega_{11}^r}, \quad (18)$$

$$J_v^* = \frac{\ell_l \ell_r}{\ell_r + \ell_r} \frac{\Omega_{11}^l \Omega_{11}^r}{\Omega_{11}^l + \Omega_{11}^r} \frac{(\sigma_1^l \omega_{11}^r + \sigma_1^r \omega_{11}^l) RT (C_1^l - C_1^r)}{\omega_{11}^l \omega_{11}^r}. \quad (19)$$

7. Taking into consideration Equation (16) in Equations (14) and (15) we obtain

$$P_m^* = \frac{RT}{\alpha(\ell_l + \ell_r)} [\mathfrak{S}_1 - J_v^* \mathfrak{S}_2] (C_1^l - C_1^r) + J_v^* (C_1^l \mathfrak{S}_3 - C_1^r \mathfrak{S}_4) + P_o, \quad (20)$$

$$\frac{1}{2} (J_v^*)^2 + \wp J_v^* - \Re = 0 \quad (21)$$

where

$$\alpha = RT(\Omega_{11}^l + \Omega_{11}^r) + \frac{1}{2} J_v^* [(\sigma_1^l)^* - (\sigma_1^r)^*],$$

$$\mathfrak{S}_1 = RT[\ell_l \Omega_{11}^r (\sigma_1^l)^* - \ell_r \Omega_{11}^l (\sigma_1^r)^*],$$

$$\mathfrak{S}_2 = \frac{1}{2} [\ell_l (\sigma_1^l)^* + \ell_r (\sigma_1^r)^*], \quad \mathfrak{S}_3 = \ell_l [(\sigma_1^l)^*]^2 + \frac{1}{2} (\sigma_1^r)^* (\sigma_1^l)^* (\ell_r - \ell_l),$$

$$\begin{aligned}\mathfrak{S}_4 &= \ell_r [(\sigma_1^r)^*]^2 + \frac{1}{2} (\sigma_1^r)^* (\sigma_1^l)^* (\ell_l - \ell_r), \\ \wp &= - \frac{RT \left\{ \Omega_{11}^l + \Omega_{11}^r - \frac{\ell_l \ell_r}{\ell_l + \ell_r} \left[\frac{1}{2} \xi_1^1 (C_1^l - C_1^r) - C_1^r \tau_1 - C_1^l \tau_2 \right] \right\}}{\xi_1^1}, \\ \mathfrak{R} &= - \frac{\ell_l \ell_r}{\ell_l + \ell_r} \frac{(RT)^2 (C_1^l - C_1^r) [\Omega_{11}^r (\sigma_1^l)^* + \Omega_{11}^l (\sigma_1^r)^*]}{\xi_1^1}, \\ \tau_1 &= [(\sigma_1^r)^*]^2 - (\sigma_1^l)^* (\sigma_1^r)^*, \quad \tau_2 = [(\sigma_1^l)^*]^2 - (\sigma_1^r)^* (\sigma_1^l)^*, \quad \xi_1^1 \neq 0.\end{aligned}$$

The calculations of J_v^* , on the basis of Equation (21), were presented in [16].

8. Gravitational effects on transmembrane volume and solute fluxes and transmembrane potential were reported in a previous papers [12, 14, 15]. Solution-membrane-water membrane cells were examined both with solutions less dense and with solution more dense, than water. Horizontally mounted membrane volume and solute fluxes of each solution-water combination were measured in two different configurations: first, with water above and substantially larger with the denser liquid (solution or water) above the membrane. This observation was examined in terms of the gravitational stability or instability of boundary layers at the membrane-liquid interfaces. Through an extension of Rayleigh-Taylor stability analysis density gradients were linked to a concentration gradient Rayleigh number R_C

$$R_C = \frac{g \alpha_c \beta_c d^4}{D_c v}, \quad (22)$$

where g is the gravitational acceleration, $\alpha_c = [(\partial \rho / \partial c) / \rho]$ the variation of density with concentration, $\beta_c = (\partial C / \partial z)$ the concentration gradient, d the fluid depth along the gravitational (z) direction (the boundary layer thickness), D_c is a solute diffusion coefficient, v is the kinematic viscosity. When $\alpha_c \beta_c$ is negative, i.e., the boundary layer is denser than the liquid beneath it, convective instability occurs when R_C exceeds a critical value. This convection reduces boundary layers dimensions, thereby increasing transmembrane flux. A concentration-gradient Rayleigh number was used in a mathematical model for gravitationally sensitive volume flux [12]. Using the relation $\alpha_c \beta_c = (\rho - \rho_o) / (\rho_o d)$, this becomes

$$R_c = \frac{g(\rho - \rho_o)d^3}{D_c v \rho_o}, \quad (23)$$

where ρ and ρ_o are the density of solution and solvent, respectively.

Our previous investigations [11, 14] indicate that the values of the coefficients Ω_{ik} for ternary solutions do depend on the solute concentrations and on the gravitational configuration of the single-membrane system. Regarding the expression

Figure 2. Glucose concentration dependences of Ω_{11}/ω_{11} in 0.4 mole l^{-1} aqueous ethanol solution for configuration A and B. Solid lines illustrate the term Ω_{11}/ω_{11} calculated on the basis of Equation 26.

$$\frac{1}{\Omega_{ik}^j} = \frac{1}{\omega_{ik}^j} + \frac{RT}{D_{ik}^o} \sum_{k=1}^2 \delta_k^j \quad (24)$$

in which ω_{ik}^j and Ω_{ik}^j are the diffusion permeability coefficients of the membrane and complex bl/M/bl, respectively, D_{ik}^o is the diffusion coefficient of substances in solution, RT the product of the gas constant and temperature, δ_k^j the thickness of the boundary layers, $i \neq j = 1, 2$; $j = l, r$ number the membrane. It is assumed that δ_k^j varies with the gravitational stability, or instability, of density gradients produced during volume flow. δ_k is identified with d , the characteristic length appearing in Equation (22) and (23). Thus

$$\delta_k^j \approx d = \left[\frac{g(\rho - \rho_o)}{R_C^* D_{ik}^o \rho_o} \right]^{-\frac{1}{3}}. \quad (25)$$

If we assume that the boundary layer are symmetrical ($\delta_1^j = \delta_2^j = \delta_o^j$) and the coefficient D_{ik}^o does not depend on the solution concentrations and on the gravitational direction, the Ω_{ik}^j coefficient can be written as [14, 15]

$$\Omega_{ik}^j = \frac{\omega_{ik}^j}{1 + 2RT\omega_{ik}^j \left[\frac{R_C^* v}{(D_{ik}^o)^2 g(\rho - \rho_o)} \right]^{\frac{1}{3}}}. \quad (26)$$

Figure 3. The double-membrane measuring system (M_l, M_r – membranes; l, m, r – measuring vessels; C_k^l, C_k^m, C_k^r – solution concentrations; P_l, P_m, P_r – hydrostatic pressure; MA – manometer; N – external reservoir; K – calibrated pipette).

In Figure 2, for example, the experimental and calculated (on basis of equation 26) results for Ω_{ii}/ω_{ii} as a function of the glucose concentration in 0.4 mole l^{-1} aqueous ethanol solution were presented.

5. Materials and methods

Studies upon quasi-stationary volume flows across double-membrane systems (J_v^*) and mechanical pressure in an intermembrane compartment of this system, (P_m^*) were carried out by means of the experimental setup represented in Figure 3. The apparatus consisted of a three compartments (l, m, r) separated by two membranes (M_l, M_r) of equal active surface, $S_l = S_r = 3,36 \text{ cm}^2$. Two series of experiments were performed. In the first, the volume of the external compartments (l, r) were identical and equal ($V_l = V_r = 350 \text{ cm}^3$), whereas the central compartment ($-V_m = 2,1 \text{ cm}^3$). In the second series the volume of the all compartments (l, m, r) were identical and equal ($V_l = V_m = V_r = 350 \text{ cm}^3$). The vessel (l) contained the investigated solution at concentration C_k^l , whereas vessel (r) in all the experiments contained pure water. The vessel (m), initially had a solution at a concentration equal to the arithmetical means of the concentration solutions from the external compartments. The vessel (l) was coupled with a calibrated pipette

Table I. Values of Nephrophane flat dialyze membrane transport parameters for glucose (subscript 1) and ethanol (subscript 2)

Coefficient	Value of parameter	
	Configuration A	Configuration B
$L_p \cdot 10^{12} [\text{m}^3 \text{Ns}^{-1}]$	$5.0 \pm 0, 2$	$5.0 \pm 0, 2$
$\sigma_1 \cdot 10^2$	$6.8 \pm 0, 2$	$6.8 \pm 0, 2$
$\sigma_2 \cdot 10^2$	$2.5 \pm 0, 1$	$2.5 \pm 0, 2$
$\sigma_1^* \cdot 10^2$	$0.24 \pm 0, 01$	$3.4 \pm 0, 1$
$\sigma_2^* \cdot 10^2$	$1.0 \pm 0, 04$	$0.1 \pm 0, 01$
$\omega_{11} \cdot 10^{10} [\text{mole Ns}^{-1}]$	$8.0 \pm 0, 3$	$8.0 \pm 0, 3$
$\omega_{22} \cdot 10^{10} [\text{mole Ns}^{-1}]$	$2.0 \pm 0, 08$	$2.0 \pm 0, 08$
$\omega_{12} \cdot 10^{13} [\text{mole Ns}^{-1}]$	$8.1 \pm 3, 5$	$8.1 \pm 3, 5$
$\omega_{21} \cdot 10^{12} [\text{mole Ns}^{-1}]$	$1.63 \pm 0, 6$	$1.63 \pm 0, 6$
$\Omega_{11} \cdot 10^{10} [\text{mole Ns}^{-1}]$	$0.3 \pm 0, 04$	$4.0 \pm 0, 2$
$\Omega_{22} \cdot 10^{10} [\text{mole Ns}^{-1}]$	$1.0 \pm 0, 06$	$0.06 \pm 0, 02$
$\Omega_{12} \cdot 10^{13} [\text{mole Ns}^{-1}]$	$0.85 \pm 0, 3$	$0.07 \pm 0, 05$
$\Omega_{21} \cdot 10^{12} [\text{mole Ns}^{-1}]$	$0.4 \pm 0, 3$	$4.0 \pm 0, 8$

Table II. Values of Cellulose IMP-1 flat dialyze membrane transport parameters for glucose (subscript 1) and ethanol (subscript 2).

Coefficient	Value of parameter	
	Configuration A	Configuration B
$L_p \cdot 10^{12} [\text{m}^3 \text{Ns}^{-1}]$	$1.6 \pm 0, 1$	$1.6 \pm 0, 1$
$\sigma_1 \cdot 10^2$	$16.0 \pm 0, 5$	$16.0 \pm 0, 5$
$\sigma_2 \cdot 10^2$	$7.9 \pm 0, 1$	$7.9 \pm 0, 1$
$\sigma_1^* \cdot 10^2$	$0.7 \pm 0, 02$	$8.4 \pm 0, 2$
$\sigma_2^* \cdot 10^2$	$3.9 \pm 0, 1$	$0.8 \pm 0, 02$
$\omega_{11} \cdot 10^{10} [\text{mole Ns}^{-1}]$	$3.3 \pm 0, 1$	$3.3 \pm 0, 1$
$\omega_{22} \cdot 10^{10} [\text{mole Ns}^{-1}]$	$1.5 \pm 0, 06$	$1.5 \pm 0, 06$
$\omega_{12} \cdot 10^{13} [\text{mole Ns}^{-1}]$	$2.8 \pm 0, 1$	$2.8 \pm 0, 1$
$\omega_{21} \cdot 10^{13} [\text{mole Ns}^{-1}]$	$2.0 \pm 0, 1$	$2.0 \pm 0, 1$
$\Omega_{11} \cdot 10^{10} [\text{mole Ns}^{-1}]$	$0.1 \pm 0, 01$	$1.4 \pm 0, 03$
$\Omega_{22} \cdot 10^{10} [\text{mole Ns}^{-1}]$	$0.5 \pm 0, 01$	$0.04 \pm 0, 01$
$\Omega_{12} \cdot 10^{13} [\text{mole Ns}^{-1}]$	$0.2 \pm 0, 01$	$2.0 \pm 0, 1$
$\Omega_{21} \cdot 10^{13} [\text{mole Ns}^{-1}]$	$0.4 \pm 0, 02$	$0.03 \pm 0, 01$

(K), whereas the (r) was connected to an external reservoir with pure water at the same height as the pipette. The manometer (MA) serving to measure the pressure (P_m^*) was coupled with a vessel (m). No external mechanical stirring was used. These solutions were exchanged every 5 hours, until a steady state for J_v^* and P_m^* was attained in order to assure a constant value of the solution concentration in the external compartments. The solution in the central compartment was not exchanged. Membrane M_l was a Nephrothane flat dialyzer membrane; membrane M_r – was a Cellulose IMP-1 flat dialyzer membrane. The values of hydraulic permeability (L_p), reflection (σ) and diffusive permeability (ω) coefficients of the membranes and the reflection (σ^*) and diffusive permeability (Ω) coefficients of the complexes (bl/M/bl) for configurations A and B are listed in Tables 1 and 2. The membranes were positioned in horizontal planes.

The volume flux J_v^* and hydrostatic pressure P_m^* was measured for a two configurations (A and B) measuring system. In configuration A the vessel (l) with pure water, was the upper compartment of the double-membrane system, whereas the solution vessel was the lower compartment. In configuration B, the upper compartment contained the solution. Two series of experiments were performed. In the first series the membrane M_l separated solutions C_k^l and C_k^m , while membrane M_r separated solutions C_k^m and C_k^r . In a second series of experiments, the sequence of membranes was reversed. We used aqueous glucose and/or ethanol solutions in the experiments. Measurements were taken at $T = (295 \pm 0.1)$ K. The concentration dependences J_v^* and P_m^* were determined on the basis of time-dependent changes of J_v^* and P_m^* chosen by consideration of the values of J_v^* and P_m^* at steady state, for different solution concentrations of the same substance. Each series of measurements was repeated five times.

6. Results and discussion

The measurements of volume flux J_v^* and hydrostatic pressure P_m^* are shown in Figures 4 and 5. In Figure 4 are presented the dependences of $J_v^* = f(\Delta C_1^l)$ for a solution of glucose in water (line 1) and in 0,75 mole l^{-1} aqueous ethanol solution (line 2). Similarly, dependences for P_m^* are presented in Figure 5. The experimental results of J_v^* and P_m^* as a function of ethanol concentration difference (ΔC_2^l) in binary (aqueous ethanol solutions) and ternary (ethanol-glucose-water solutions) were presented in [9].

All the measurement results presented in Figures 4 and 5 were obtained for the situation in which the membrane M_l separated solutions at concentrations C_k^l and C_k^m , and the membrane M_r – solutions at concentrations C_k^m and C_k^r . One should state that the change of sequence arrangement of the membranes does not change the value and of sign of J_v^* . However, it causes a change of sign of P_m^* . The change of configuration of the double-membrane system causes change in both J_v^* and P_m^* for all investigated binary and ternary solutions. The reason for these changes follow.

Figure 4. The volume flux (J_v^*) as a function of the glucose concentration difference (ΔC_1^l) in binary and ternary solutions.

Figure 5. The hydrostatic pressure (P_m^*) as a function of the glucose concentration difference (ΔC_1^*) in binary and ternary solutions.

The double-membrane system, with unstirred solutions, like the single-membrane system [11–15], produces diffusion boundary layers on both sides. These layers were observed using an interferometric study for single and double-membrane systems [17, 18] and investigations of J_v^* in solution stirred by application of suitable mechanical stirrers [13]. The complex (bl/M/bl) in configuration A is stable if the density of the binary solution is directly proportional to its concentration. A change of configuration from A to B, for the same solutions, produce hydrodynamical instability, which results in convective mixing of solutions. Also, in the case of binary solutions, the density is inversely proportional to concentration and the complex (bl/M/bl) is unstable in configuration A, whereas it is hydrodynamically stable in configuration B. Therefore, we may assume that the complex of two layers produced at both sides of each of the membranes of examined double-membrane systems, in configuration A and containing solutions in which density increases with the increase of concentration, is stable, whereas it is unstable in configuration B. Likewise, the complex of boundary layers in double-membrane systems, in configuration A and containing solutions in which the density decreases with the increase of concentration, is unstable, whereas the one being in configuration B is hydrodynamically stable. The dynamic character of the complex of boundary layers (stability and instability) is determine the quality of flows. The value of the volume flux is several times smaller in the stable system compared to the unstable one. From curve 2, in the upper panel of Figure 4, we conclude that $C_1^l < 0.1$ mole l^{-1} complex (bl/M/bl) is unstable, whereas $C_1^l > 0.1$ mole l^{-1} is hydrodynamically stable. The critical concentration is $C_1^l = 0.1$ mole l^{-1} and after it has been exceeded we observe a transition from the convection state to nonconvection one. The situation is reversed in configuration B (the Figure 2). The results of the measurements of P_m^* presented are for comparison in Figure 5. The results in Figures 4 and 5 were obtained for the case: $V_m \rightarrow 0$. The analogical studies of J_v^* and P_m^* were performed also for the case $V_m \rightarrow \infty$. On both cases similar curves $J_v^* = f(\Delta C_1)$ and $P_m^* = f(\Delta C_1)$ were obtained. Only, the values of J_v^* and P_m^* for the case $V_m \rightarrow \infty$ were 10% smaller than the values of J_v^* and P_m^* for the case $V_m \rightarrow 0$.

Let us make the assumptions, $\omega_{12} = \omega_{21} = \Omega_{12} = \Omega_{21} \approx 0$ and $C_1^m = (\Omega_{11}^r C_1^r + \Omega_{11}^l C_1^l)(\Omega_{11}^l + \Omega_{11}^r)^{-1}$ and $C_2^m = (\Omega_{22}^r C_2^r + \Omega_{22}^l C_2^l)(\Omega_{22}^l + \Omega_{22}^r)^{-1}$. Equations (10) and (11) can be written in the form

$$J_v^g = \frac{\ell_l \ell_r}{\ell_l + \ell_r} RT [\alpha_1^g \beta_1 (C_1^l - C_1^r) + \alpha_2^g \beta_2 (C_2^l - C_2^r)], \quad (27)$$

$$P_m^g = \frac{RT}{\ell_l + \ell_r} [\alpha_1^g \chi_1 (C_1^l - C_1^r) + \alpha_2^g \chi_2 (C_2^l - C_2^r)], \quad (28)$$

where

$$\alpha_1^g = \frac{\Omega_{11}^l \Omega_{11}^r}{\Omega_{11}^l + \Omega_{11}^r}, \quad \alpha_2^g = \frac{\Omega_{22}^l \Omega_{22}^r}{\Omega_{22}^l + \Omega_{22}^r},$$

Figure 6. Glucose concentration dependences of Ω_{11}^l (upper) and Ω_{11}^r (lower) in 0.75 mole l^{-1} aqueous ethanol solution. Curves 1 correspond to configuration A; 2 to configuration B.

$$\beta_1 = \frac{\sigma_1^l \sigma_{11}^r + \sigma_1^r \omega_{11}^l}{\omega_{11}^l \omega_{11}^r}, \quad \beta_2 = \frac{\sigma_2^l \omega_{22}^r + \sigma_2^r \omega_{22}^l}{\omega_{22}^l \omega_{22}^r},$$

$$\chi_1 = \frac{\ell_1 \sigma_1^l \omega_{11}^r - \ell_r \sigma_1^r \omega_{11}^l}{\omega_{11}^l \omega_{11}^r}, \quad \chi_2 = \frac{\ell_1 \sigma_2^l \omega_{22}^r - \ell_r \sigma_2^r \omega_{22}^l}{\omega_{22}^l \omega_{22}^r}, \quad g = A, B.$$

We have obtained equations, including parameters (Ω) which refer to the boundary layers. The equations can be used to analyze transmembrane transport across horizontally mounted membranes in two gravitational configurations of a double-membrane system. Let us consider the results shown in Figures 4 and 5. From these data we see that all dependences $J_v^* = f(\Delta C)$ and $P_m^* = f(\Delta C)$ for ternary solutions display non-linear behavior. In order to apply Equations 27 and 28 to

Figure 7. Glucose concentration dependences of Ω_{22}^l (upper) and Ω_{22}^r (lower) in 0.75 mole l^{-1} aqueous ethanol solution. Curves 1 correspond to configuration A and curves 2 – B.

a description of transmembrane transport in ternary solutions, the assumption of the Ω coefficients being dependent on the concentration and configuration is required. The pertinence of the above assumption is confirmed by the data for Ω_{11}^l , Ω_{11}^r , Ω_{22}^l and Ω_{22}^r in ternary solutions shown in Figures 6 and 7. In these figures curves 1 represent the glucose concentration dependence of the coefficients Ω_{11}^l , Ω_{11}^r , Ω_{22}^l and Ω_{22}^r (at constant ethanol) for configuration A. In configuration B the patterns of glucose concentration dependence of Ω_{11}^l , Ω_{11}^r , Ω_{22}^l and Ω_{22}^r are inverted, as illustrated by curves 2. Both Ω_{11}^l , Ω_{11}^r , Ω_{22}^l and Ω_{22}^r depend on ethanol concentration [9]. Taking into consideration the concentration dependence of the coefficients Ω_{11}^l , Ω_{11}^r , Ω_{22}^l and Ω_{22}^r , demonstrated in Figures 6 and 7, and the values for the membrane parameters listed in Tables 1 and 2, the values of J_v^* and P_m^*

Figure 8. The asymmetry coefficients: volume flux (k_v) and hydrostatic pressure (k_p) as a function of the glucose concentration difference (ΔC_1^I) in ternary solutions.

as functions of the concentration differences ΔC_1 and ΔC_2 , were calculated on basis of Equations 27 and 28. The solid lines in Figures 4 and 5 present the results calculated for J_v^* and P_m^* . One observes good agreement between the experimental data and the results of the calculation. Therefore, Equations 27 and 28, after taking into consideration the concentration dependence of $\Omega(C)$, yield satisfactory curve fitting to the experimental results.

If we assume that J_v^g is the generalized flux and ΔC_1 a generalized thermodynamic force, the regions where (dJ_v^g/dC_1) is decreased (see Figure 4) can be classified as the negative differential resistance regions. The phenomenon of negative resistance appears in nature and constitutes a very important factor in the physics of semiconductors [19], membranology [20] and biophysics [21].

7. Gravitational effects of transport in a double-membrane system

Among the group of gravitational effects of transmembrane transport in membrane system examined in this paper, the following properties can be included: asymmetry and amplification of osmotic transport and mechanical pressure.

7.1. ASYMMETRY EFFECTS OF OSMOTIC TRANSPORT AND MECHANICAL PRESSURE

The results of investigations of J_v^s and P_m^s in double-membrane system show that values both for volume flux and for hydrostatic pressure obtained for the same ΔC_1^l in configurations A and B are different. They show the rectifying properties of the double-membrane system. The measure of these properties are the asymmetry coefficients: volume flux (k_v) and hydrostatic pressure (k_p) defined as quotients J_v^* or P_m^* in configurations B and A of a double-membrane system

$$k_v = \frac{J_v^B}{J_v^A} = \frac{\alpha_1^B \beta_1 (C_1^l - C_1^r) + \alpha_2^B \beta_2 (C_2^l - C_2^r)}{\alpha_1^A \beta_1 (C_1^l - C_1^r) + \alpha_2^A \beta_1 (C_2^l - C_2^r)}, \quad (29)$$

$$k_p = \frac{P_m^B}{P_m^A} = \frac{\alpha_1^B \chi_1 (C_1^l - C_1^r) + \alpha_2^B \beta_2 (C_2^l - C_2^r)}{\alpha_1^A \chi_1 (C_1^l - C_1^r) + \alpha_2^A \chi_2 (C_2^l - C_2^r)}. \quad (30)$$

For our experiments with binary solutions $k_v = k_p \approx 13$. For ternary solutions the values k_v and k_p depend on the concentration (see Figure 8). Combining Equations (25) and (26) we obtain

$$k_v = \frac{(k_p \alpha_1^A - \alpha_1^B) \alpha_2^B \chi_1 \beta_2 - (k_p \alpha_2^A - \alpha_2^B) \alpha_1^B \beta_1 \chi_2}{(k_p \alpha_1^A - \alpha_1^B) \alpha_2^B \chi_1 \beta_2 - (k_p \alpha_2^A - \alpha_2^B) \alpha_1^A \beta_1 \chi_2}. \quad (31)$$

7.2. AMPLIFICATION EFFECT OF VOLUME FLUX

In order to discuss this effect we take into consideration curves 1 and 2 illustrating the dependence $J_v^* = f(\Delta C_1)$ for binary and ternary solutions, respectively, presented in Figure 4. From an analysis of the course of these variations in configuration B, it was determined that changes in J_v^* for binary solutions result from alterations in the glucose concentration $\Delta(\Delta C_1) = 0.01 \text{ mole l}^{-1}$ and are identical throughout the entire range of glucose concentrations: $(\Delta J_v^B)_1 = 0.28 \cdot 10^{-8} \text{ m s}^{-1}$. In the case of ternary solutions, the variations in $(\Delta J_v^B)_2$ due to identical changes in concentration are different for various concentration ranges. The largest change in volume flux is $(\Delta J_v^B)_2 = 2.1 \cdot 10^{-8} \text{ m s}^{-1}$, 7.5-fold greater than the value of $(\Delta J_v^B)_1$. In configuration A an identical change in glucose concentration in a binary solution was the result of changes of $(\Delta J_v^A)_1 = 0.3 \cdot 10^{-9} \text{ m s}^{-1}$ and the maximal change in J_v^A in ternary solutions was $(\Delta J_v^A)_2 = -2.4 \cdot 10^{-8} \text{ m s}^{-1}$, being 80-fold greater than the value $(\Delta J_v^A)_1$. The above means that the membrane system in both configurations is able to amplify flux, and the formula

$$\begin{aligned} a_v^s &= \frac{(\Delta J_v^s)_2}{(\Delta J_v^s)_1} = \frac{[\alpha_1^s(C_1)]_2 (C_1^l)_2 - [\alpha_1^s(C_1)]_1 (C_1^l)_1}{\alpha_1^s[(C_1^l)_2 - (C_1^l)_1]} \\ &+ \frac{\beta_2 C_2^l ([\alpha_2^s(C_1)]_2 - [\alpha_2^s(C_1)]_1)}{\beta_1 \alpha_1^s [(C_1^l)_2 - (C_1^l)_1]} \end{aligned} \quad (32)$$

expresses the amplification coefficient of osmotic transport. From the values quoted for $(\Delta J_v^g)_2$ and $(\Delta J_v^g)_1$, it can be determined that the double-membrane system in configuration B is characterized by a positive amplification coefficient, and in configuration A by a negative value. The values of the amplification coefficients calculated from these formula are as follows: for configuration A, $a_v \approx -65$ and for configuration B, $a_v \approx +7$.

7.3. AMPLIFICATION EFFECT OF MECHANICAL PRESSURE

In order to demonstrate this effect, let us now turn to a consideration of the dependence $P_m^* = f(\Delta C_1)$ for binary (curves 1) and ternary solutions (curves 2) depicted in Figure 5. Precisely as in the case of J_v^* in configuration B, changes in mechanical pressure for binary solutions are the consequence of variation in the glucose concentration $\Delta(\Delta C_l) = 0.01 \text{ mole l}^{-1}$ and are identical over the whole range of glucose concentrations: $(\Delta P_m^B) = 0.25 \text{ kPa}$. In the case of ternary solutions, changes in $(\Delta P_m^B)_2$ due to identical variations in glucose concentrations vary according to the concentration range. The maximal change in mechanical pressure amounts to $(\Delta P_m^B) = 2.1 \text{ kPa}$, being 8.4-times larger than the value $(\Delta P_m^B)_1$ for binary solutions. In configuration A an analogous alteration in $\Delta(\Delta C_1)$ for binary solutions gives rise to an identical change in $(\Delta P_m^A)_1$ over the entire range of glucose concentrations. In the case, $(\Delta P_m^A)_1 = 0.18 \text{ hPa}$. The maximal change in P_m^A in ternary solutions is now $(\Delta P_m^A) = -1.73 \text{ kPa}$, which is 96-fold greater than the value of $(\Delta P_m^A)_1$ for binary solutions. From the above, it is concluded that a double-membrane system in both gravitational configurations possesses the property of amplification of mechanical pressure. In turn, the following equation

$$a_p^g = \frac{(\Delta P_m^g)_2}{(\Delta P_m^g)_1} = \frac{[\alpha_1^g(C_1)]_2(C_1^l)_2 - [\alpha_1^g(C_1)]_1(C_1^l)_1}{\alpha_1^g[(C_1^l)_2 - (C_1^l)_1]} + \frac{\chi_2 C_2^l([\alpha_2^g(C_1)]_2 - [\alpha_2^g(C_1)]_1)}{\chi_1 \alpha_1^g[(C_1^l)_2 - (C_1^l)_1]} \quad (33)$$

defines the coefficient of amplification of mechanical pressure. Using appropriate values for $(\Delta P_m^g)_2$ and $(\Delta P_m^g)_1$, it can be shown that the double-membrane system is characterized by a positive amplification coefficient in configuration B, whereas it is negative for configuration A. The values of the amplification coefficients calculated from this formula are as follows: for configuration A, $a_p \approx -97$ and for configuration B, $a_p \approx +9$.

Taking the dependence (28) and (29) into account, as a result of simple transformation we obtain

$$a_v^g = a_p^g + \frac{C_2^l([\alpha_2^g(C_1)]_2 - [\alpha_2^g(C_1)]_1)}{\alpha_1^g[(C_1^l)_2 - (C_1^l)_1]} \left(\frac{\beta_2}{\beta_1} - \frac{\chi_2}{\chi_1} \right). \quad (34)$$

8. Conclusion

These investigations show that:

1. We have created a thermodynamic model of volume flows for n-component solutions in a double-membrane system. This model is illustrated by Equations (5), (6) and (9).
2. A double-membrane system, consisting of two membranes differs in permeability parameters. It is characterized by asymmetry and amplifies the volume flux and hydrostatic pressure. These effects are the result of the creation of gravitation and/or destruction of diffusion boundary layers.
3. The effects of asymmetry and amplification of the volume flux and mechanic pressure are indications of new osmotic and mechanical properties in double-membrane systems.
4. The effects of amplification and asymmetry of transmembrane transport are indications of natural convections appearing or disappearing in the membrane system. They may be subdivided into a group of regulatory effects, including phenomena such as rectification, amplification and oscillation of transmembrane fluxes.
5. One can make use of Equations (10)–(19) in numerical calculations. The possibility of application of these equations in modeling certain transport features of double-membrane systems has been schematically presented on Figure 1, and will be described in paper [16].

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