Thermodynamic Model Equations for Heterogeneous Multicomponent Non-Ionic Solution Transport in a Multimembrane System

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Abstract. Non-equilibrium thermodynamic model equations for non-ionic and heterogeneous n -component solution transport in a m -membrane system are presented. This model is based on two equations. The first one describes the volume transport of the solution and the second the transport of the solute. Definitions of the hydraulic permeability, reflection and diffusive permeability coefficients of the m -membrane system and relations between the coefficients of the m -membrane system and the respective membranes of the system are also given. The validity of this model for binary and ternary solutions was verified, using a double-membrane cell with a horizontally mounted membrane. In the cell, volume and solute fluxes were measured as a function of concentration and gravitational configuration.

Key words: Concentration boundary layers, gravity effects, Kedem Katchalsky equations, membrane transport

1. Introduction

In most cases studied, multicomponent solution transport across biological and synthetic membranes is interpreted in terms of the generalized Kedem-Katchalsky model equation (K-K *model*) derived from irreversible thermodynamics of membrane processes (ITMP). The usefulness of the KK-model for interpretation of membrane processes has been confirmed [1–7]. Nevertheless, its application is limited to homogeneous membrane systems with diluted and homogeneous (well stirred) solutions [8, 9]. As a result of diffusion and osmosis on both sides of the membrane, separating two unstirred solutions, different concentration boundary layers (CBL) are created. The boundary layers are the areas immediately adjacent to the membrane surface area and can be treated as a pseudomembrane [10]. The liquid in the CBL area does not change its location and is adjacent to the laminar movement area, in which free convection does not cause substantial mixing of the solution. Thickness of CBL depends on: type of membrane and solutions used,

temperature gradient, concentration and density, velocity of mechanical stirring of solutions, geometry and orientation of membrane and measurement cells with solutions in the gravitational field. Most of the spontaneously occurring membrane processes, in physicochemical and biological systems in particular, proceed in the presence of the CBL on both sides of the membrane [8–16]. The paper by Barry and Diamond [17] reviews the effects of boundary layers on membrane phenomena. The modifications and generalizations of this KK-model have expanded the range of their application to non-diluted and weakly stirred and unstirred solutions. Now, the Kedem-Katchalsky model equations with later modifications and generalizations introduced by Zelman [18], Richardson *et al.* [19], Del Castillo and Mason [20] and Ślęzak *et al.* [8, 9, 21] have given rise to the full model equations of transmembrane transport.

Membranes composed of different elements arranged in a series-array (the membrane is a sandwich of several different selective components separated by homogeneous solutions) are of special interest since they frequently occur in living systems and also because of their remarkable physical properties, which are not exhibited by single elements. Multimembrane systems have rectification properties similar to those of biological membranes [22–25]. The direction of rectification is determined by the polarity of the membrane systems, not by concentrations in the bathing solutions. In a fundamental paper on the permeability of composite membranes, Kedem and Katchalsky [6] derived the overall practical parameters for membranes in series array. They proved that the transport parameters of membranes, composed of a series-array of elements for non-electrolytes (hydraulic permeability, L_p , diffusive permeability, ω and reflection, σ coefficients) are evaluated from the coefficients of the membrane elements: $L_p^{-1} = L_p^{a-1} + L_p^{b-1}$, $\omega^{-1} = \omega_a^{-1} + \omega_b^{-1}$ and $\sigma = \omega(\sigma_a\omega_a^{-1} + \sigma_b\omega_b^{-1})$.

In previous papers [8, 9], the Kedem-Katchalsky-Zelman model equations (KKZ-model) of the volume and solute flows across an isotropic membrane were modified for cases in which the membrane separated two multicomponent, non-ionic and non-homogeneous phases at different concentrations. The Ω_{ik} factor, which determines the influence of concentration boundary layers on transmembrane transport was introduced. For a vertically [8] and horizontally [9] mounted membrane and for binary and ternary solutions the modified KKZ-model was verified. On the basis of the modified KKZ-model, 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 was elaborated [26]. 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. In this system the solution concentration $C_k^l > C_k^m > C_k^r$. It was shown that the double-membrane system has rectifying and amplifying properties of osmotic transport and mechanical pressure.

The aim of this theoretical study is to generalize the Kedem-Katchalsky-Zelman (KKZ-model) model equations for m -membrane systems containing multicompon-

Figure 1. The m -membrane system (M – membrane, C – concentration of solution, J_v , J_s – volume and solute fluxes, respectively, b.l. – boundary layers).

ent, non-ionic and heterogeneous solutions. Definitions of the hydraulic permeability, reflection and diffusive permeability coefficients of the m -membrane system and the respective membranes of the system are given. In order to test the formalism, the results of experimental studies on osmotic and diffusive transport in a double-membrane system containing binary and ternary solutions are presented.

2. Basic Assumptions

In order to receive the irreversible thermodynamic model equations of the trans-membrane transport of non-ionic and heterogeneous n -component solutions in a m -membrane system, let us consider the membrane system represented in Figure 1. In order to characterize this membrane system we make the following assumption:

1. The m -membrane system consists of m complexes: boundary layer/Membrane/boundary layer (b.l./ M /b.l.) (M_r , $r = 1, 2, \dots, m$) separating diluted n -components, non-ionic and heterogeneous solutions. There are m membranes and $2m$ concentration boundary layers in this system.
2. Each membrane of thickness d is isotropic, symmetric, selective and electroneutral.
3. The solutions contain $s = 1, 2, \dots, n$ non-interacting substances dissolved in solvent w . Their concentrations are denoted by C_r^s , where $r = 1, 2, \dots, m$; $C_m^s > C_{m-1}^s > \dots > C_2^s > C_1^s$.
4. In the m -membrane system water and the dissolved substance diffusing across the membranes will lead to the formation of concentration boundary layers

- (b.l.). Each membrane with two concentration boundary layers is composed of the complex: boundary layer/Membrane/boundary layers (bl/ M_a /bl).
5. The transport processes are isothermal and stationary; no chemical reactions occur in solution.
 6. Two configurations (A and B) of m -membrane system will be considered. In these configurations, the membranes are oriented in horizontal planes, the respective concentration gradients being antiparallel and parallel to the gravitational vector.

3. The Generalization of the Kedem Katchalsky Zelman Model Equations of the Transmembrane Transport for Multicomponent Nonelectrolyte Solutions

The starting point for our consideration is generalization of the Kedem-Katchalsky-Zelman model equations for transmembrane transport in multicomponent, non-ionic and heterogeneous solution [8]

$$J_v^j = \frac{L_p}{1 \pm L_p \sum_i \sigma_i \frac{\det M_i^j}{\det K}} \left[\sum_k \Delta \Pi_k \frac{\det K_{ik}^j}{\det K} \mp \Delta P^j \right], \quad (1)$$

$$J_s^j = J_v^j (1 - \sigma_s^j) \tilde{C}_s + \sum_i \Omega_{is}^j \Delta \Pi_i, \quad (2)$$

where indices $j = A, B$ pertain to configurations A and B , respectively, J_v^j and J_s^j 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^j the hydrostatic pressure difference, σ_s^j the reflection coefficient of the complex: boundary layer/membrane/boundary layer (bl/ M /bl), $\tilde{C}_s$ the average solute concentration for s -th substance, ω_{ks} and Ω_{ks}^j 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 ($\omega_{ks} = \omega_{sk} \tilde{C}_s / \tilde{C}_k$, $\Omega_{ks}^j = \Omega_{sk}^j \tilde{C}_s / \tilde{C}_k$) and $s \neq k = 1, 2, \dots, n$; the $(n+1)$ -th component is the solvent for which $\sigma_{n+1} = 0$

$$K = \begin{bmatrix} \omega_{11} & \omega_{21} & \cdots & \omega_{n1} \\ \cdot & \cdot & \cdots & \cdot \\ \omega_{1n} & \omega_{2n} & \cdots & \omega_{nn} \end{bmatrix}, \quad K_{ik}^j = \begin{bmatrix} \omega_{11} & \cdots & \omega_{i-1,1} & \Omega_{k1}^j & \omega_{i+1,1} & \cdots & \omega_{n1} \\ \cdot & \cdots & \cdot & \cdot & \cdot & \cdots & \cdot \\ \omega_{1n} & \cdots & \omega_{i-1,n} & \Omega_{kn}^j & \omega_{i+1,n} & \cdots & \omega_{nn} \end{bmatrix},$$

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

The interpretation of the phenomenological parameters of membrane transport for binary and ternary non-electrolyte solutions ($L_p, \sigma, \sigma_s^j, \omega_{sk}, \Omega_{sk}^j$) was presented in [9]. In this paper it was proved that the values of coefficients $\sigma_i^j, \Omega_{sk}^j$ and for binary and ternary solutions can be functions of the configuration of membrane system, and the values of Ω_{sk}^j for ternary solutions are functions of solute concentrations. The equations (1)–(2) for the respective membrane read:

$$(\det K)^{-1} \sum_i \omega_{is} \det M_i = (1 - \sigma_s^*) \tilde{C}_s - (1 - \sigma_s) \tilde{C}_s, \quad (3)$$

$$(\det K)^{-1} \sum_i \omega_{is} \sum_k \Delta \Pi_k \det K_{ik} = \sum_i \Omega_{is} \Delta \Pi_i. \quad (4)$$

4. Equation for Volume Flows

The equation describing the volume flux in a m -membrane system was derived on the basis of the following procedure. For this purpose the equation (3) was obtained. These equations were written down separately for each m -membrane system. This procedure leads to the system of m -equations:

$$(J_v^j)_1 = \frac{(L_p)_1}{1 \mp (L_p)_1 \sum_{i=1}^n (\sigma_i)_1 \frac{\det(M_i^j)_1}{\det K_1}} \left[\sum_{k=1}^n (\Delta \Pi_k)_1 \sum_{i=1}^n (\sigma_i)_1 \frac{\det(K_{ik})_1}{\det K_1} \pm \Delta P_1^j \right],$$

$$(J_v^j)_2 = \frac{(L_p)_2}{1 \mp (L_p)_2 \sum_{i=1}^n (\sigma_i)_2 \frac{\det(M_i^j)_2}{\det K_2}} \left[\sum_{k=1}^n (\Delta \Pi_k)_2 \sum_{i=1}^n (\sigma_i)_2 \frac{\det(K_{ik})_2}{\det K_2} \pm \Delta P_2^j \right],$$

$$\dots\dots\dots$$

$$(J_v^j)_m = \frac{(L_p)_m}{1 \mp (L_p)_m \sum_{i=1}^n (\sigma_i)_m \frac{\det(M_i^j)_m}{\det K_m}} \left[\sum_{k=1}^n (\Delta \Pi_k)_m \sum_{i=1}^n (\sigma_i)_m \frac{\det(K_{ik})_m}{\det K_m} \pm \Delta P_m^j \right]. \quad (5)$$

In the steady state, the following condition is fulfilled

$$(J_v^j)_1 = (J_v^j)_2 = \dots = (J_v^j)_m = J_v^j, \quad (6)$$

since

$$\sum_a \left[\sum_i (\sigma_i)_a \sum_k (\Delta \Pi_k)_a \frac{\det(K_{ik}^j)_a}{\det K_a} \right] = \sum_a \left[\sum_k (\Delta \Pi_k)_a \sum_i (\sigma_i)_a \frac{\det(K_{ik}^j)_a}{\det K_a} \right], \quad (7)$$

therefore

$$J_v^j = \frac{L_p}{1 \mp L_p \sum_a \sum_i (\sigma_i)_a \frac{\det(M_i^j)_a}{\det K_a}} \sum_k \sigma_k^j \Delta \Pi_k \pm \Delta P^j, \quad (9)$$

where

$$\sum_a \sum_k (\sigma_k^j)_a (\Delta \Pi_k)_a = \sum_k \sigma_k^j \Delta \Pi_k, \quad (8a)$$

$$(\sigma_k^j)_a = \sum_i (\sigma_i)_a \frac{\det(K_{ik}^j)_a}{\det K_a}, \quad (8b)$$

$$\frac{1}{L_p} = \sum_a \frac{1}{(L_p)_a}. \quad (8c)$$

J_v^j is the volume flux across m -membrane system; L_p , σ_k^j hydraulic permeability and reflection coefficients of the m -membrane system, respectively; $\Delta \Pi_k$, ΔP^j ($\Delta P^j = \sum_k \Delta P_a$, $a = 1, 2, \dots, m$) the osmotic and hydrostatic pressure difference of the m -membrane system, respectively. The above equation represents the equation for volume flux in a m -membrane system; indices $j = A, B$ pertain to configurations A and B , respectively.

The hydraulic permeability coefficient (L_p) and reflection coefficient (σ_k^j) of the m -membrane system can be defined by the following expressions

$$L_p = \left(\frac{J_v}{\Delta P} \right)_{\Delta \Pi_k=0}, \quad (9)$$

$$\sigma_k^j = \left(\frac{\Delta P^j}{\Delta \Pi_k} \right)_{J_v=0, \Delta \Pi_k=0, k \neq i}. \quad (10)$$

5. Equation for Solute Flows

The global flux of the dissolved substances (J_s^j) in the m -membrane system presented in Figure 1 is the sum of the diffusion flux (J_{sD}^j) and convection flux (J_{sK}^j). The equation for diffusion flux (J_{sD}^j) may be obtained by applying analogical algorithm, as in the case of the volume flux (J_v^j). It is necessary for this purpose in Equation (2), assume the condition $J_v = 0$. Moreover it is necessary to write down equation (2) for each membrane separately and to use stationarity condition: $(J_s^j)_1 = (J_s^j)_2 = \dots = (J_s^j)_m = J_s^j$. In this way the equation describing the diffusion flux may be written in the form:

$$J_{sD}^j = \sum_l \Omega_{ls}^j \Delta \Pi_l, \quad (11)$$

where

$$\Omega_{ls}^j = \left(\frac{J_{sD}^j}{\Delta \Pi_l} \right)_{J_v^j=0, \Delta \Pi=0, \Delta \Pi_k^a=0, l \neq k}, \quad (12)$$

is the definition of diffusive permeability coefficient of the m -membrane system.

In order to define the convection flux J_{sK}^j it is necessary take into consideration equation (2) with regard to the condition $\Delta \Pi_k = 0$. In the result we obtain the following system of the equations

$$\begin{aligned} (\tilde{C}_s)_1 &= \frac{(J_{sK}^j)_1}{J_v^j [1 - (\sigma_s^j)_1]}, \\ (\tilde{C}_s)_2 &= \frac{(J_{sK}^j)_2}{J_v^j [1 - (\sigma_s^j)_2]}, \\ &\dots\dots\dots \end{aligned} \quad (13)$$

$$(\tilde{C}_s)_m = \frac{(J_{sK}^j)_m}{J_v^j [1 - (\sigma_s^j)_m]}.$$

In the stationary state the convection fluxes through each membrane are equal: $(J_{sK}^j)_1 = (J_{sK}^j)_2 = \dots = (J_{sK}^j)_m = J_{sK}^j$, so after summation of (13) the equation for the convection flux is obtained:

$$J_{sK}^j = \frac{J_v^j \tilde{C}_s}{\sum_a [1 - (\sigma_s^j)_a]^{-1}}. \quad (14)$$

In this equation $\tilde{C}_s$ is represented by the following expression:

$$\tilde{C}_s = \sum_a (\tilde{C}_s)_a = \tilde{C}_s^u + \sum_{a=2}^{m-1} (\tilde{C}_s)_a, \quad (15)$$

where $\tilde{C}_s^u = \frac{1}{2}(C_s^1 + C_s^m)$ is the arithmetic mean of the concentrations of solution in the first and the last compartment of the m -membrane system. Combining Equations (11) and (12), we obtain the transport equation for dissolved substances in a m -membrane system:

$$J_s^j = J_{sK}^j + J_{sD}^j = J_v^j \tilde{C}_s \left(\sum_a \frac{1}{1 - (\sigma_s^j)_a} \right)^{-1} + \sum_i \Omega_{ls}^j \Delta \Pi_l. \quad (16)$$

6. The Expressions Binding the Global Reflection, Diffusive Permeability Coefficients of the m -Membrane System and the Individual Membranes of the m -Membrane System

The following expressions binding the diffusive permeability, reflection and hydraulic permeability coefficients of the m -membrane system and individual membranes of this system are obtained:

$$\frac{1}{\Omega^j} = \sum_a \frac{1}{\Omega_a^j}, \quad (17)$$

$$\sigma = \sum_a \sigma^a \frac{\Omega^j}{\Omega_a^j}, \quad (18)$$

where $\sigma = [\sigma_1 \sigma_2 \dots \sigma_n]$, $\sigma^a = [\sigma_1^a \sigma_2^a \dots \sigma_n^a]$ are the reflection coefficient tensors of the m -membrane system and of individual membranes respectively, whereas

$$\Omega^j = \begin{bmatrix} \Omega_{11}^j & \dots & \Omega_{n1}^j \\ \vdots & \dots & \vdots \\ \Omega_{1n}^j & \dots & \Omega_{nn}^j \end{bmatrix}, \quad \Omega_a^j = \begin{bmatrix} (\Omega_{11}^j)_a & \dots & (\Omega_{n1}^j)_a \\ \vdots & \dots & \vdots \\ (\Omega_{1n}^j)_a & \dots & (\Omega_{nn}^j)_a \end{bmatrix},$$

are the diffusive permeability coefficient tensors of m -membrane system and individual membranes, respectively.

The expression (17) relates the global permeability coefficient of the m -membrane system (Ω_{ls}^j) and the individual membrane permeability coefficients (Ω_{ls}^j) of the m -membrane system. The diffusive permeability and reflection coefficients of the m -membrane system and the individual membrane of this system are related by expression (18). The relation between the global hydraulic permeability coefficients of the m -membrane system (L_p) and the hydraulic permeability coefficients of the individual membrane of this system (L_p^a) is presented by expression (8c). The calculations of relations (17) and (18) are presented in the appendix. Similar expressions were obtained by O. Kedem and A. Katchalsky [6] for double-membrane, in which the homogeneous solutions were separated by two membranes.

If we omit the non-diagonal terms in Equations (8a), (8b), (17) and (18), for diagonal cases we obtain

$$\frac{1}{\Omega_{ll}^j} = \sum_a \frac{1}{(\Omega_{ll}^j)_a} = \sum_a \left(\sum_i (\omega_{il})_a \frac{\det (K_{il}^j)_a}{\det K_a} \right)^{-1}, \quad (20)$$

$$\sigma_l^j = \Omega_{ll}^j \sum_a (\sigma_l^j)_a \frac{1}{(\Omega_{ll}^j)_a} = \Omega_{ll}^j \sum_a \left[\frac{\sum_i (\sigma_l)_a \frac{\det (K_{il}^j)_a}{\det K_a}}{\sum_i (\omega_{il})_a \frac{\det (K_{il}^j)_a}{\det K_a}} \right], \quad (21)$$

where [19]

$$\frac{1}{(\Omega_{ll}^j)_a} = \frac{1}{(\omega_{ll})_a} + \frac{RT}{D_{ll}} \sum_{k=1}^2 (\delta_k^j)_a, \quad (22)$$

$$(\delta_k^j)_a = \left\{ \left[\frac{g}{R_C^j D_{ll} \nu \rho_o} \right] [(\rho - \rho_o)_k^j]_a \right\}^{-\frac{1}{3}}, \quad (23)$$

where $(\Omega_{ik}^j)_a$ and $(\omega_{ll})_a$ denotes the permeability coefficients of i -th substance of complex b.l./M/b.l. and membrane, respectively, D_{ik} the diffusion coefficient in a solution (coefficient D_{ik} is not depending on the concentration and gravity direction), $(\delta_k^j)_a$ the thickness of boundary layers, RT the product of gas constant and temperature, R_C^j the critical value of the concentration Rayleigh number, ν the kinematic viscosity, g the gravitational acceleration, ρ and ρ_o the density of solution and solvent, respectively.

7. Materials and Methods

Studies on quasi-stationary volume and solute flows across a double-membrane system were carried out by means of methods of measurement that have been described in detail in a previous paper [26]. The apparatus consisted of three compartments (l, m, r) separated by two membranes (M_l, M_r) at equal active surfaces. The vessel (l) contained the investigated solution at concentration C_k^l , whereas vessel (r) in all the experiments – pure water. The vessel (m), initially, contained the solution at a concentration equal to the arithmetical mean of the solution concentrations from external compartments.

The volume flux J_v^j and solute flux J_s^j ($j = A, B$) ($j = A, B$) was measured for configurations A and B of the measuring system. In configuration A the vessel (l) containing pure water, was the upper compartment of double-membrane system, whereas the vessel containing investigated solution – lower compartment. In configuration B the upper compartment contained investigated solution, whereas the lower compartment – pure water. Two series of experiments were performed. In the first series the membrane M_l separated solutions C_k^l and C_k^m , whereas the membrane M_r – solutions C_k^m and C_k^r . In the second series of experiment the sequence arrangement of membranes was exchanged. The same procedure was followed for each configuration. The first step involved measurement of J_v^j or J_s^j , in the double-membrane system with mechanical stirring of the solution at 500 rpm. After achieving the initial steady state during which J_v^j or J_s^j were constant, stirring of the solutions was stopped, and subsequently the evolution of volume and solute fluxes were monitored up to the second steady state, when these fluxes remain fixed. We used an aqueous glucose and/or ethanol solution in experiments. Volume flux, J_v^j , was determined from

$$J_v^j = \frac{(\Delta V)^j}{S \cdot \Delta t}, \quad (25)$$

where S is the membrane surface area and ΔV is the volume change occurring in time Δt , indices $j = A, B$ pertain to configurations A and B , respectively.

Evaluation of the global concentration exchanges in the studied solution was performed by the standard isotope method. The measured value of the global concentration exchanges (dC) was used to calculate the solute flux (J_v^j) on the basis of following equation

$$J_s^j = \frac{(dC)^j \cdot V_v}{S \cdot \Delta t}, \quad (26)$$

where V_v is the volume of the measuring vessel, indices $j = A, B$ pertain to configurations A and B , respectively.

Measurements were taken at $T = (295 \pm 0.1)$ K. Each series of measurements was repeated five times. A typical plot of the time dependence for J_v^j and for J_s^j in configurations A and B of the double-membrane system in the case of a 0.1 mole l^{-1} aqueous glucose solution is presented in Figure 2. On the basis of stationary values of J_v^j or J_s^j the coefficients L_p , σ_s , σ_s^j , ω and Ω_{sk}^j were determined. To represent membrane M_l we used Nephrophane flat dialyzer membrane, whereas as membrane M_r – Cellulose IMP-1 flat dialyzer membrane. The membranes were positioned in horizontal planes. The values of membranes parameters for aqueous glucose or ethanol solutions, i.e. hydraulic permeability (L_p), reflection (σ_s) and diffusive permeability (ω_{sk}) coefficients of the membranes and the reflection (σ_s^j) and diffusive permeability (Ω_{sk}^j) coefficients of complexes (bl/M/bl) for configurations A and B were listed in Tables 1 and 2 in a previous paper [26]. The values of all these coefficients for diluted binary solutions do not depend on the solute concentrations, whereas the values of the coefficients Ω_{sk}^j for ternary solutions do, as shown in Reference [9].

8. Results and Discussion

The results of measurements of volume flux (J_v^j) and solute flux (J_s^j) are shown in Figures 3 and 4. In these figures are presented the dependences of $J_v^j = f(\Delta C_1^l)$ and $J_s^j = f(\Delta C_1^l)$ a solution of glucose in 0.75 mole l^{-1} aqueous ethanol solution. The graphs 1 and 2 presented in Figures 3 and 4 were obtained when the solutions were mechanically unstirred, whereas graphs 3 in these figures were obtained with the solutions being left mechanically stirred at 500 rpm. Graphs 1 and 2 show a non-linear dependence of J_v^j and J_s^j on the glucose concentration (ΔC_1^l) in configurations A and B , respectively. In contrast, in well stirred systems, both fluxes J_v^j and J_s^j are directly proportional to ΔC_1^l and independent of system configuration. The permeability parameters of double-membrane system were calculated on the basis of stationary values of J_v^j or J_s^j . Our investigations indicate that the values of the coefficients L_p , σ_s , σ_s^j , ω_{sk} and Ω_{sk}^j for diluted binary solutions do not depend on the solute concentrations. Their values for the Nephrophane-Cellulose IMP-1 membrane system and for aqueous glucose or ethanol solutions

Figure 2. Results on volume flux (J_v) and solute flux (J_s) as a function of time. Curves c were obtained for a system with mechanically stirred solutions; curves a and b for membrane system without mechanical stirring of the solutions.

Figure 3. Experimental volume flux, across the $M_l - M_r$ membrane system as a function of glucose concentration difference in 0.75 mole l^{-1} aqueous ethanol solution. Graph 3 (♦) was obtained for a $M_l - M_r$ membrane system with mechanical stirred solutions; graphs 1 (■) for configuration A and 2 (●) for configuration B without mechanical stirring of the solutions.

are listed in Table 1. The values of the coefficients Ω_{sk}^j and σ_s^j for ternary solutions depend on the solute concentrations, as shown in Figures 5–8.

Figure 5 presents the dependences of diffusive permeabilities Ω_{11}^j and Ω_{22}^j on glucose concentration, for solution of glucose in 0.75 mole l^{-1} aqueous ethanol solution in configurations A and B. Then Figure 6 presents the dependences of diffusive permeabilities Ω_{11}^j and Ω_{22}^j on ethanol concentration, for solution of ethanol in 0.1 mole l^{-1} aqueous glucose solution in configurations A and B. Solid lines in Figures 5 and 6 illustrate the $\Omega_{11}^j(C)$ and $\Omega_{22}^j(C)$ calculated on the basis of Equation 20 after taking into consideration $(\Omega_{11}^j)^l(C)$, $(\Omega_{11}^j)^r(C)$, $(\Omega_{22}^j)^l(C)$ and $(\Omega_{22}^j)^r(C)$ presented in a previous paper [26]. In Figures 7 and 8 the dependences of reflection coefficients $\sigma_1^j(C)$ and $\sigma_2^j(C)$ for solution of glucose in 0.75 mole l^{-1} aqueous ethanol solution (Figure 7) and in solution of ethanol in 0.1 mole l^{-1} aqueous glucose solution (Figure 8) in configurations A and B calculated on the basis of Equation 21. The measurement results presented in Figures 3–8 were

Figure 4. Experimental solute flux, across the $M_l - M_r$ membrane system as a function of glucose concentration difference in 0.75 mole l^{-1} aqueous ethanol solution. Graph 3 (◆) was obtained for a $M_l - M_r$ membrane system with mechanical stirred solutions; graphs 1 (■) for configuration A and 2 (●) for configuration B without mechanical stirring of the solutions.

Table I. Values of the double-membrane system (Nephropane and Celulose IMP-1) transport parameters for glucose (subscript 1) and ethanol (subscript 2)

Coefficient	Values of coefficient			
	Configuration A		Configuration B	
	Experimental	Calculated	Experimental	Calculated
$L_p \cdot 10^{12} (\text{m}^3/\text{N} \cdot \text{s})$	1.2 ± 0.04	1.21 ± 0.12	1.2 ± 0.04	1.21 ± 0.12
$\sigma_1 \cdot 10^2$	1.34 ± 0.06	1.33 ± 0.14	1.34 ± 0.06	1.33 ± 0.14
$\sigma_2 \cdot 10^2$	5.6 ± 0.1	5.6 ± 0.5	5.6 ± 0.1	5.6 ± 0.5
$\sigma_1^* \cdot 10^2$	0.6 ± 0.03	0.6 ± 0.1	7.2 ± 0.15	7.1 ± 0.65
$\sigma_2^* \cdot 10^2$	3.0 ± 0.1	2.9 ± 0.22	0.5 ± 0.02	0.5 ± 0.06
$\omega_{11} \cdot 10^{10} (\text{mole}/\text{N} \cdot \text{s})$	2.3 ± 0.2	2.34 ± 0.3	2.3 ± 0.1	2.34 ± 0.3
$\omega_{22} \cdot 10^{10} (\text{mole}/\text{N} \cdot \text{s})$	8.6 ± 0.3	8.57 ± 0.61	8.6 ± 0.3	8.57 ± 0.61
$\Omega_{11} \cdot 10^{10} (\text{mole}/\text{N} \cdot \text{s})$	0.1 ± 0.02	0.08 ± 0.03	1.1 ± 0.1	1.0 ± 0.2
$\Omega_{22} \cdot 10^{10} (\text{mole}/\text{N} \cdot \text{s})$	3.3 ± 0.1	3.4 ± 0.6	0.2 ± 0.03	0.2 ± 0.05

Figure 5. Glucose concentration dependences of Ω_{11}^j (upper panel) and Ω_{22}^j (lower panel) in 0.75 mole l^{-1} aqueous ethanol solution for $M_l - M_r$ membrane system. Curves A (■) and B (●) correspond to configurations A and B, respectively.

obtained for a case in which the membrane M_l separated solutions at concentrations C_k^l and C_k^m , whereas 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 do not change values Ω_{11}^j , Ω_{22}^j , σ_1^j and σ_2^j . The change of configuration of double-membrane system causes a change in Ω_{11}^j , Ω_{22}^j , σ_1^j and σ_2^j for all investigated ternary solutions.

From curves 1 and 2 in Figures 3 and 4 and curves A in Figures 5 and 7 and curves B in Figures 6 and 8 we conclude that $C_1^l < 0,1 \text{ mole l}^{-1}$ and $C_2^l <$

Figure 6. Ethanol concentration dependences of Ω_{11}^j (upper panel) and Ω_{22}^j (lower panel) in 0.1 mole l^{-1} aqueous glucose solution for $M_l - M_r$ membrane system. Curves A (■) and B (●) correspond to configurations A and B, respectively.

0.6 mole l^{-1} complex (bl/M/bl) is stable, whereas for $C_1^I > 0, 1$ mole l^{-1} and $C_2^I > 0.6$ mole l^{-1} is hydrodynamically unstable. The critical concentrations are $C_1^I \approx 0, 1$ mole l^{-1} and $C_2^I \approx 0.6$ mole l^{-1} and after it has been exceeded we can observe a transition from the non-convective state to the convective one. Then, from curves B in Figures 5 and 7 and curves A in 6 and 8 we conclude that $C_1^I < 0.125$ mole l^{-1} and $C_2^I < 0.74$ mole l^{-1} complex (bl/M/bl) is unstable, whereas $C_1^I > 0.125$ mole l^{-1} and $C_2^I > 0.74$ mole l^{-1} – is hydrodynamically stable. The critical concentrations are $C_1^I \approx 0.125$ mole l^{-1} and $C_2^I \approx 0.74$ mole

Figure 7. Glucose concentration dependences of σ_1^j (upper panel) and σ_2^j (lower panel) in 0.75 mole l^{-1} aqueous ethanol solution for $M_l - M_r$ membrane system. Curves A (■) and B (●) correspond to configurations A and B, respectively.

l^{-1} and after it has been exceeded we can observe a transition from the convection to non-convection state. Besides, in non-convection state $\Omega_{11}^A(C_1^l) = \Omega_{11}^B(C_1^l) = \Omega_{11}^A(C_2^l) = \Omega_{11}^B(C_2^l) = 8 \cdot 10^{-12} \text{ mole/N}\cdot\text{s}$, $\Omega_{22}^A(C_1^l) = \Omega_{22}^B(C_1^l) = \Omega_{22}^A(C_2^l) = \Omega_{22}^B(C_2^l) = 2.5 \cdot 10^{-11} \text{ moleN}\cdot\text{s}$, $\sigma_1^A(C_1^l) = \sigma_1^B(C_1^l) = \sigma_1^A(C_2^l) = \sigma_1^B(C_2^l) = 0.005$, $\sigma_2^A(C_1^l) = \sigma_2^B(C_1^l) = \sigma_2^A(C_2^l) = \sigma_2^B(C_2^l) = 0.02$, whereas in convection state $\Omega_{11}^A(C_1^l) = \Omega_{11}^B(C_1^l) = \Omega_{11}^A(C_2^l) = 1 \cdot 10^{-10} \text{ mole/N}\cdot\text{s}$, $\Omega_{22}^A(C_1^l) = \Omega_{22}^B(C_1^l) = \Omega_{22}^A(C_2^l) = 3.3 \cdot 10^{-10} \text{ mole/N}\cdot\text{s}$, $\Omega_{11}^B(C_2^l) = 8 \cdot 10^{-11} \text{ mole/N}\cdot\text{s}$, $\Omega_{22}^B(C_2^l) = 2.5 \cdot 10^{-10} \text{ mole/N}\cdot\text{s}$, $\sigma_1^A(C_1^l) = \sigma_1^B(C_1^l) = \sigma_1^A(C_2^l) = 0.058$, $\sigma_2^A(C_1^l) = \sigma_2^B(C_1^l) =$

Figure 8. Ethanol concentration dependences of σ_1^j (upper panel) and σ_2^j (lower panel) in 0.1 mole l^{-1} aqueous glucose solution for $M_l - M_r$ membrane system. Curves A (■) and B (●) correspond to configurations A and B, respectively.

$\sigma_2^A(C_2^I) = 0.22$, $\sigma_1^B(C_2^I) = 0.047$ and $\sigma_2^B(C_2^I) = 0.16$. The reason for these changes may be given as follows.

For solutions containing 0.75 mole l^{-1} ethanol, progressive glucose addition increases the density of solution from below to above that of water. In contrast to the preceding case, progressive addition of ethanol to 0.1 mole l^{-1} glucose lowers the density from above to below that of water. On account of the complex, (bl/ M_a /bl) in configuration A is stable. A change of configuration from A to B, for the same solutions, produces the hydrodynamic instability, the result of which

is convective mixing of solutions. Dynamic character of the complex (bl/ M_a /bl) (stability and instability) is adjoined with the quality of volume and solute flows and in this connection with the quality of diffusive permeability (Ω_{sk}^j) and reflection (σ_s^j) coefficients of this complex. The value of the volume and solute fluxes, diffusive permeability and reflection coefficients are several times smaller in a stable system than in an unstable one. If $1/\Omega_{sk}^j$ is regarded as a resistance of solute transport, then Equation (17) is an expression of the additivity of resistances across a series of complex (bl/ M_a /bl). However, for ternary solutions, Ω_{sk}^j is a function of concentration and configuration of the double membrane system.

For stable configuration, the concentration Rayleigh number (R_C^j) was smaller than its critical value ($(R_C^j)^*$). For unstable configuration, $R_C^j > (R_C^j)^*$ and in this respect convective flow perpendicular to the membrane surface was present. The thickness of the concentration boundary layers was determined on the basis of interferograms obtained for a 0.1 mole l⁻¹ aqueous glucose solution [10] and a 0.75 mole l⁻¹ aqueous ethanol solution [11]. The results were as follows: for stable configuration, $\delta_A \approx 550 \mu\text{m}$; unstable configuration $\delta_B \approx 180 \mu\text{m}$. In the previous paper [10] we determined the experimental R_C^j , marking the onset of convection. Choosing as reasonable values [28] $D_l = 0.69 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$, $g = 9.81 \text{ m s}^{-2}$, $\delta = 180 \mu\text{m}$, $(\rho - \rho_o) = 3 \cdot 10^{-1} \text{ kg m}^{-3}$, $\rho_o = 0.998 \cdot 10^3 \text{ kg m}^{-3}$, $\nu = 1.12 \cdot 10^{-6} \text{ m}^2 \text{ s}^{-1}$, we obtain $(R_C^j)^* = \{g\delta^3(\rho - \rho_o)\}/\{D_l\nu\rho_o\} \approx 22.2$. For $(\rho - \rho_o) = 2.1 \text{ kg m}^{-3}$, $\nu = 1.056 \cdot 10^{-6} \text{ m}^2 \text{ s}^{-1}$ (with all other parameters the same) we obtain $(R_C^j)^* = 154.4$.

9. Conclusion

Based on the investigations conducted above we can infer that:

1. Irreversible thermodynamic model equations of volume and solute flows of non-ionic and heterogeneous n -component solutions have been derived for a m -membrane system. This model consists of Equations (8), (15) and (17)–(18). The proposed model expands the range of application of the Kedem-Katchalsky model equations to weakly stirred and unstirred multicomponent and multimembrane systems.
2. The values of the hydraulic permeability, reflection and diffusive permeability coefficients both for individual membranes and for double-membrane systems do not depend on the binary solute concentrations, whereas those for ternary solutions do. The values of these coefficients depend on the gravitational configurations of both single-membrane and double-membrane systems. These effects are the result of influence of gravitation and/or destruction of concentration boundary layers.

Appendix

1. PROOF OF RELATION (17)

In the steady state, the following equations are fulfilled: $J = \Omega^j \cdot \Delta\Pi$ and $J_a = (\Omega^j)_a \cdot \Delta\Pi_a$, where

$$J = \begin{bmatrix} J_1^j \\ \vdots \\ J_n^j \end{bmatrix} = J_a, \quad \Omega^j = \begin{bmatrix} \Omega_{11}^j & \cdots & \Omega_{n1}^j \\ \vdots & \cdots & \vdots \\ \Omega_{1n}^j & \cdots & \Omega_{nn}^j \end{bmatrix}, \quad \Omega_a = \begin{bmatrix} (\Omega_{11}^j)_a & \cdots & (\Omega_{n1}^j)_a \\ \vdots & \cdots & \vdots \\ (\Omega_{1n}^j)_a & \cdots & (\Omega_{nn}^j)_a \end{bmatrix},$$

$$\Delta\Pi = \begin{bmatrix} \Delta\Pi_1 \\ \vdots \\ \Delta\Pi_n \end{bmatrix}, \quad \Delta\Pi_a = \begin{bmatrix} \Delta\Pi_1^a \\ \vdots \\ \Delta\Pi_n^a \end{bmatrix}.$$

Since $\Delta\Pi = \sum_a \Delta\Pi^a$ and $J = J_a$ therefore $1/\Omega^j = \sum_a 1/(\Omega^j)_a$.

PROOF OF RELATION (18)

In the steady state, $\Delta P^j = \sigma^j \cdot \Delta\Pi$ and $\Delta P_a^j = \sigma_a^j \cdot \Delta\Pi^a$, where

$$\sigma^j = [\sigma_1^j \cdots \sigma_n^j], \quad \sigma_a^j = [(\sigma_1^j)_a \cdots (\sigma_n^j)_a],$$

$$\Delta\Pi = \begin{bmatrix} \Delta\Pi_1 \\ \vdots \\ \Delta\Pi_n \end{bmatrix}, \quad \Delta\Pi^a = \begin{bmatrix} \Delta\Pi_1^a \\ \vdots \\ \Delta\Pi_n^a \end{bmatrix}.$$

Because $\Delta P = \sum_a \Delta P^a$ so $\sigma^j \cdot \Delta\Pi = \sum_a \sigma_a^j \cdot \Delta\Pi^a$. Taking into account the expression $\Omega^j \cdot \Delta\Pi = \Omega_a^j \cdot \Delta\Pi^a$ we obtain $\sigma^j = \sum_a \sigma_a^j (\Omega_a^j)^{-1} \Omega^j$.

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