Study of the Solute Flows of Multicomponent and Heterogeneous Non-Ionic Solutions in Double-Membrane System

ANDRZEJ ŚLĘZAK

Institute of Physics, Pedagogical University, Armii Krajowej 13/15, 42-201 Częstochowa, Poland

Abstract. The solute flows were studied in a double-membrane osmotic-diffusive cell, in which two membranes mounted in horizontal planes separate three compartments (l, m, r) containing the non-homogeneous, non-electrolytic binary and ternary solutions. The volume of inter-membrane compartment (m), which is the infinitesimally layer of solution, and volume of external compartments (l and r) fulfill the conditions $V_m \rightarrow 0$ and $V_l = V_r \rightarrow \infty$, respectively. In an initial moment, the solution concentrations satisfy the condition $(C_s^o)_l > (C_s^o)_m > (C_s^o)_r$. The double-membrane osmotic-diffusive cell is composed of two complexes: boundary layer/membrane/boundary layer, mounted in horizontal planes. In the cell, solute flux was measured as a function of concentration and gravitational configuration. The linear dependencies of the solute flux on concentration difference in binary solutions and nonlinear – in ternary solutions were obtained. It was shown that the double-membrane osmotic-diffusive cell has rectifying and amplifying properties of solute flows.

Key words: Membrane transport, Kedem-Katchalsky equations, gravitation force, concentration boundary layers

1. Introduction

In previous papers [1, 2] 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 concentration. The Ω_{ik} factor, which determines the influence of concentration boundary layers on transmembrane transport, was introduced. For a vertically [1] and horizontally [2] mounted membrane and for binary and ternary solutions the modified KKZ-model was verified. On basis of the modified KKZ-model, the volume flows model equation for a double-membrane osmotic-diffusive cell (double-membrane system), in which two membranes separate three compartments (l, m, r) containing the heterogeneous, non-ionic n -component solutions was elaborated [3, 4]. 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 cell the solution concentrations satisfy the con-

Figure 1. A model of a concentration distribution for configurations A and B of the double-membrane osmotic-diffusive cell: M_l , M_r – membranes; l , m , r – compartments; $(C_s^o)_l$, $(C_s^o)_m$, $(C_s^o)_r$ – the total solution concentrations; $(C_s^A)_l$, $(C_s^B)_l$, $(C_s^A)_{mu}$, $(C_s^A)_{md}$, $(C_s^B)_{mu}$, $(C_s^B)_{md}$, $(C_s^A)_r$, $(C_s^B)_r$ – the local solution concentrations at the boundary; a membrane – boundary layer in configuration A and B, respectively; J_v^A and J_s^A – volume and solute fluxes, respectively in configuration A; J_v^B and J_s^B – volume and solute fluxes, respectively in configuration B; P_l^A , P_m^A , P_r^A – hydrostatic pressure in configuration A; P_l^B , P_m^B , P_r^B – hydrostatic pressure in configuration B; $(b.l.)_{lu}^A$, $(b.l.)_{ld}^A$, $(b.l.)_{ru}^A$, $(b.l.)_{rd}^A$ – concentration boundary layers in configuration A; $(b.l.)_{lu}^B$, $(b.l.)_{ld}^B$, $(b.l.)_{ru}^B$, $(b.l.)_{rd}^B$ – concentration boundary layers in configuration B.

dition $(C_s^o)_l > (C_s^o)_m > (C_s^o)_r$. It was shown that the double-membrane system has rectifying and amplifying properties of osmotic transport and mechanical pressure. This system should have similar properties with reference to solute transport.

In the present paper, the results of the experimental study upon solute flows in a double-membrane osmotic-diffusive cell were presented. In this cell, two membranes mounted in horizontal planes, separate three compartments (l , m , r) containing the non-homogeneous, non-electrolytic binary and ternary solutions. It will have been shown that the double-membrane osmotic-diffusive cell has rectifying and amplifying properties of solute transport.

2. Double-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 non-homogeneous (not mechanically stirred) multicomponent solutions of the same non-electrolyte with concentrations equal $(C_s^o)_l$, $(C_s^o)_m$ and $(C_s^o)_r$ ($s = 1, 2$) are

separated by isotropic, symmetrical, selective and electroneutral membranes M_l and M_r . These concentrations satisfy the condition $(C_s^o)_l > (C_s^o)_m > (C_s^o)_r$. In this system water and the dissolved substance diffusing across the membranes will lead to the formation of concentration boundary layers (bl). These layers can be treated as pseudomembranes. The membranes in the double-membrane osmotic-diffusive cell are characterized by hydraulic permeability (L_p), reflection (σ_s) and diffusive permeability (ω_{sk}) coefficients. The reflection and diffusive permeability coefficients of complexes: boundary layer/membrane/boundary layer ($bl/M/bl$) are denoted by σ_s^i and Ω_{sk}^i respectively. The solution contains s ($s = 1, 2$) uninteractional substances dissolved in solvent w . The concentrations of these solutions are denoted by $(C_1^o)_l, (C_2^o)_l, (C_1^o)_m, (C_1^o)_r$ and $(C_2^o)_r$. The volumes of the external compartments (V_l, V_r) containing solutions with concentrations $(C_s^o)_l$ and $(C_s^o)_r$ satisfy the condition $V_l = V_r \rightarrow \infty$. The intermembrane compartment (m) consists of an infinitesimally thin layer of solution at a concentration $(C_s^o)_m$. The volume of this compartment satisfy the condition $V_m \rightarrow 0$. The transport processes are isothermal and stationary, and no chemical reactions occur in the solutions. The analysis of transport processes in a double-membrane system represented in Figure 1, is based on the Kedem-Katchalsky-Zelman model equation of transmembrane transport in multicomponent, non-electrolytic and non-homogeneous solution [1], using the oneself Katchalsky-Curran method [4]. For this cell stationary solute flows across the membranes M_l and M_r we will describe using following equations [3]

$$(J_s^i)_l = J_v^i [1 - (\sigma_s^i)_l] (\tilde{C}_s^i)_l + RT \sum_{k=1}^n (\Omega_{sk}^i)_l [(C_s^o)_l - (C_s^i)_m] \quad (1)$$

$$(J_s^i)_r = J_v^i [1 - (\sigma_s^i)_r] (\tilde{C}_s^i)_r + RT \sum_{k=1}^n (\Omega_{sk}^i)_r [(C_s^o)_m - (C_s^i)_r] \quad (2)$$

where $(\tilde{C}_s^i)_l = \frac{1}{2}[(C_s^i)_m + (C_s^o)_l]$ and $(\tilde{C}_s^i)_r = \frac{1}{2}[(C_s^i)_m + (C_s^o)_r]$ the average solute concentrations for s -th substance; $(C_s^i)_l, (C_s^i)_m$ and $(C_s^i)_r$ the solution concentrations; RT the product of gas constant and thermodynamic temperature; J_v^i and J_s^i are the volume and solute fluxes; $(\sigma_s^i)_j$ the reflection coefficient of the complex: boundary layer/membrane/boundary layer ($bl/M/bl$); $(\Omega_{sk}^i)_j$ the diffusive permeability coefficient of the s -th substance, which passes across the complex ($bl/M/bl$) under the influence of the gradient of the k -th substance osmotic pressure difference ($\Omega_{ks}^i = \Omega_{sk}^i \tilde{C}_s \cdot \tilde{C}_k^{-1}$) and $s \neq k = 1, 2, \dots, n$; the $(n+1)$ -th component is the solvent for which $\sigma_{n+1} = 0$; $j = k, l$ and $i = A, B$.

Since in steady state $(J_s^i)_l = (J_s^i)_r = J_s^i = \text{const.}$, thus

$$(C_s^i)_m = \frac{\gamma_s^i + \frac{1}{2} J_v^i \vartheta_s^i - \varphi_k^i}{\kappa_s^i - \frac{1}{2} J_v^i \xi_s^i} \quad (3)$$

where $\gamma_s^i = RT[(\Omega_{ss}^i)_l (C_s^o)_l + (\Omega_{ss}^i)_r (C_s^o)_r]$, $\kappa_s^i = RT[(\Omega_{ss}^i)_l + (\Omega_{ss}^i)_r]$, $\xi_s^i = (\sigma_s^i)_r - (\sigma_s^i)_l$, $\varphi_k^i = \sum_{k=1}^n (\Omega_{sk}^i)_r (\Delta \Pi_s^o)_r - \sum_{k=1}^n (\Omega_{sk}^i)_l (\Delta \Pi_s^o)_l$, $\vartheta_s^i = [1 - (\sigma_s^i)_l] (C_s^o)_l -$

$[1 - (\sigma_s^i)_r](C_s^o)_r$, $s = 1, 2$. For ternary solutions, if we assume that $J_v^i \rightarrow 0$ and taking into consideration Equation (3) in Equations (1) and (2) we obtain

$$J_1^i = RT\{\phi_1^i[(C_1^o)_l - (C_1^o)_r] - \varphi_1^i(C_2^o)_l - \psi_1^i(C_2^o)_r + \\ + \theta_1^i[(C_2^o)_l - (C_2^o)_r] - \varsigma_1^i(C_1^o)_l - \lambda_1^i(C_1^o)_r\} \quad (4)$$

$$J_2^i = RT\{\phi_2^i[(C_2^o)_l - (C_2^o)_r] - \varphi_2^i(C_1^o)_l - \psi_2^i(C_1^o)_r + \\ + \theta_2^i[(C_1^o)_l - (C_1^o)_r] - \varsigma_2^i(C_2^o)_l - \lambda_2^i(C_2^o)_r\} \quad (5)$$

where

$$\phi_1^i = \frac{(\Omega_{11}^i)_l \cdot (\Omega_{11}^i)_r}{(\Omega_{11}^i)_l + (\Omega_{11}^i)_r}, \quad \varphi_1^i = \frac{(\Omega_{11}^i)_l \cdot (\Omega_{12}^i)_l}{(\Omega_{11}^i)_l + (\Omega_{11}^i)_r}, \quad \psi_1^i = \frac{(\Omega_{11}^i)_l \cdot (\Omega_{12}^i)_r}{(\Omega_{11}^i)_l + (\Omega_{11}^i)_r}, \\ \phi_1^i = \frac{(\Omega_{12}^i)_l \cdot (\Omega_{22}^i)_r}{(\Omega_{22}^i)_r + (\Omega_{22}^i)_r}, \quad \varsigma_1^i = \frac{(\Omega_{12}^i)_l \cdot (\Omega_{21}^i)_l}{(\Omega_{22}^i)_l + (\Omega_{22}^i)_r}, \quad \lambda_1^i = \frac{(\Omega_{12}^i)_l \cdot (\Omega_{21}^i)_r}{(\Omega_{22}^i)_l + (\Omega_{22}^i)_r}, \\ \phi_2^i = \frac{(\Omega_{22}^i)_l \cdot (\Omega_{22}^i)_r}{(\Omega_{22}^i)_l + (\Omega_{22}^i)_r}, \quad \varphi_2^i = \frac{(\Omega_{12}^i)_l \cdot (\Omega_{21}^i)_l}{(\Omega_{22}^i)_l + (\Omega_{22}^i)_r}, \quad \psi_2^i = \frac{(\Omega_{22}^i)_l \cdot (\Omega_{21}^i)_r}{(\Omega_{22}^i)_l + (\Omega_{22}^i)_r}, \\ \theta_2^i = \frac{(\Omega_{21}^i)_l \cdot (\Omega_{11}^i)_r}{(\Omega_{11}^i)_l + (\Omega_{11}^i)_r}, \quad \varsigma_2^i = \frac{(\Omega_{21}^i)_l \cdot (\Omega_{12}^i)_l}{(\Omega_{11}^i)_l + (\Omega_{11}^i)_r}, \quad \lambda_2^i = \frac{(\Omega_{21}^i)_l \cdot (\Omega_{12}^i)_r}{(\Omega_{11}^i)_l + (\Omega_{11}^i)_r}.$$

Let us consider gravitational configurations A and B of this double-membrane system. In both configurations, the membranes M_l and M_r are mounted in horizontal planes with corresponding concentration gradients being antiparallel and parallel to the gravitational vector. In configuration A, because of natural convection, thicknesses of the boundary layers continually increase. Therefore, the process of layers formation finishes when a thermodynamic equilibrium state is reached. This is well founded by the inverted density gradient in a solution. In this case, the concentrations at membrane interfaces M_1 and M_2 are in stationary state of membrane transport: $(C_s^B)_l$, $(C_s^B)_{mu}$, $(C_s^B)_{md}$ and $(C_k^r)_B$ but $(C_s^B)_l < (C_s^o)_l$, $(C_o^B)_{mu} > (C_s^o)_m$, $(C_s^B)_{md} < (C_s^o)_m$, $(C_k^r)_B < C_k^r$. In configuration B, the process of boundary layers formation is terminated at the moment of appearance of natural convection and when the stationary state is attained by the double-membrane system. Then the thicknesses of these layers are maintained, since extension of layer thickness is limited by natural convection. In this connection the solution concentration at the membrane interfaces M_1 – increases from $(C_s^o)_r$ to $(C_s^A)_r$ whereas concentration $(C_s^o)_m$ reduces to $(C_s^A)_{mu}$. The concentration of solution at membrane interfaces M_r increases from $(C_s^o)_m$ to $(C_s^A)_r$ whereas concentration $(C_s^o)_r$ reduces to $(C_s^A)_r$. For the configurations A and B, the following relations hold: $(C_s^A)_r > (C_s^B)_l$, $(C_s^A)_{mu} < (C_s^B)_{md}$, $(C_s^A)_{md} < (C_s^B)_{mu}$ and $(C_s^A)_l < (C_s^B)_r$.

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

Coefficient	Value of coefficient	
	Configuration A ($i = A$)	Configuration B ($i = B$)
$L_p \cdot 10^{12} \text{ (m}^3 \text{ N}^{-1} \text{ s}^{-1}\text{)}$	5.0 ± 0.2	5.0 ± 0.2
$\sigma_1 \cdot 10^2$	6.8 ± 0.2	6.8 ± 0.2
$\sigma_2 \cdot 10^2$	2.5 ± 0.1	2.5 ± 0.1
$\sigma_1^i \cdot 10^2$	0.24 ± 0.01	3.4 ± 0.1
$\sigma_2^i \cdot 10^2$	1.0 ± 0.04	0.1 ± 0.01
$\omega_{11} \cdot 10^{10} \text{ (mole N}^{-1} \text{ s}^{-1}\text{)}$	8.0 ± 0.3	8.0 ± 0.3
$\omega_{22} \cdot 10^{10} \text{ (mole N}^{-1} \text{ s}^{-1}\text{)}$	2.0 ± 0.08	2.0 ± 0.08
$\omega_{12} \cdot 10^{13} \text{ (mole N}^{-1} \text{ s}^{-1}\text{)}$	8.1 ± 3.5	8.1 ± 3.5
$\omega_{21} \cdot 10^{12} \text{ (mole N}^{-1} \text{ s}^{-1}\text{)}$	1.6 ± 0.6	1.6 ± 0.6
$\Omega_{11}^i \cdot 10^{10} \text{ (mole N}^{-1} \text{ s}^{-1}\text{)}$	0.3 ± 0.04	4.0 ± 0.2
$\Omega_{22}^i \cdot 10^{10} \text{ (mole N}^{-1} \text{ s}^{-1}\text{)}$	1.0 ± 0.06	0.06 ± 0.02
$\Omega_{12}^i \cdot 10^{13} \text{ (mole N}^{-1} \text{ s}^{-1}\text{)}$	0.85 ± 0.3	0.07 ± 0.05
$\Omega_{21}^i \cdot 10^{12} \text{ (mole N}^{-1} \text{ s}^{-1}\text{)}$	0.4 ± 0.3	4.0 ± 0.8

are satisfied, although $[(C_s^A)_{mu} - (C_s^A)_r] < [(C_s^B)_r]$ and $[(C_s^A)_l - (C_s^A)_{md}] < [(C_s^B)_l - (C_s^B)_{mu}]$. Therefore, it appears that $J_v^A < J_v^B$, $J_s^A < J_s^B$, $\Omega_{11}^A < \Omega_{11}^B$, $\sigma_1^A < \sigma_1^B$, $\Omega_{22}^A > \Omega_{22}^B$ and $\sigma_2^A > \sigma_2^B$.

If in the double-membrane system $(\Omega_{sk}^i)_l > (\Omega_{sk}^i)_r$ and $(\sigma_s^i)_l < (\sigma_s^i)_r$, then in the steady state $(C_s^i)_m < (C_s^o)_m$. Therefore, the intermembranous compartment permits depletion of the dissolved substances. If we exchange of the sequence arrangement of membranes we obtain $(\Omega_{sk}^i)_l < (\Omega_{sk}^i)_r$, $(\sigma_s^i)_l > (\sigma_s^i)_r$, and $(C_s^i)_m > (C_s^o)_m$. In this case, the intermembranous compartment permits accumulation of the dissolved substance.

3. Materials and methods

Studies upon quasi-stationary solute flows across double-membrane osmotic-diffusive cell were carried out by means of methods of measurements that have been described in detail in previous paper [3]. The apparatus consisted of three compartments (l, m, r) separated by two membranes (M_l, M_r) of equal active surface areas of $S_l = S_r = 3.36 \text{ cm}^2$. Volumes of the external compartments (l, r) were identical and equal to $V_l = V_r = 350 \text{ cm}^3$, whereas a central compartment volume was equal to $V_m = 2.1 \text{ cm}^3$. The vessel (l) contained an investigated solution with concentration $(C_s^o)_l$, whereas the vessel (r) was filled with pure water in all the experiments. The vessel (m) contained the solution with a concentration equal to

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

Coefficient	Value of coefficient	
	Configuration A ($i = A$)	Configuration B ($i = B$)
$L_p \cdot 10^{12} \text{ (m}^3 \text{ N}^{-1} \text{ s}^{-1}\text{)}$	1.6 ± 0.1	1.6 ± 0.1
$\sigma_1 \cdot 10^2$	16.0 ± 0.5	16.0 ± 0.5
$\sigma_2 \cdot 10^2$	7.9 ± 0.1	7.9 ± 0.1
$\sigma_1^i \cdot 10^2$	0.7 ± 0.02	8.4 ± 0.2
$\sigma_2^i \cdot 10^2$	3.9 ± 0.1	0.8 ± 0.02
$\omega_{11} \cdot 10^{10} \text{ (mole N}^{-1} \text{ s}^{-1}\text{)}$	3.3 ± 0.1	3.3 ± 0.1
$\omega_{22} \cdot 10^{10} \text{ (mole N}^{-1} \text{ s}^{-1}\text{)}$	1.5 ± 0.06	1.5 ± 0.06
$\omega_{12} \cdot 10^{13} \text{ (mole N}^{-1} \text{ s}^{-1}\text{)}$	2.8 ± 0.1	2.8 ± 0.1
$\omega_{21} \cdot 10^{13} \text{ (mole N}^{-1} \text{ s}^{-1}\text{)}$	2.0 ± 0.1	2.0 ± 0.1
$\Omega_{11}^i \cdot 10^{10} \text{ (mole N}^{-1} \text{ s}^{-1}\text{)}$	0.1 ± 0.01	1.4 ± 0.03
$\Omega_{22}^i \cdot 10^{10} \text{ (mole N}^{-1} \text{ s}^{-1}\text{)}$	0.5 ± 0.01	0.04 ± 0.01
$\Omega_{12}^i \cdot 10^{13} \text{ (mole N}^{-1} \text{ s}^{-1}\text{)}$	0.2 ± 0.01	2.0 ± 0.1
$\Omega_{21}^i \cdot 10^{13} \text{ (mole N}^{-1} \text{ s}^{-1}\text{)}$	0.4 ± 0.02	0.03 ± 0.01

mean value of the solution concentrations of the external compartments. The vessel (l) was coupled with a calibrated pipette (K), while the vessel (r) was connected to an external reservoir of pure water at the same height as the pipette. A *Nephrophane* flat dialyzer membrane was used as membrane M_l , whereas a *Celulose IMP-1* flat dialyzer served as the membrane M_r . The membranes were mounted in horizontal planes. Parameters of the membranes, i.e. hydraulic permeability (L_p), reflection (σ_s) and diffusive permeability (ω_{sk}) coefficients of the membranes and the reflection (σ_s^i) and diffusive permeability (Ω_{sk}^i) coefficients of the complexes ($bl/M/bl$) have been determined for configurations A and B in accordance with methods described in [2, 4]. Their values for the *Nephrophane* and *Celulose IMP-1* and for the aqueous glucose or ethanol solutions are listed in Tables I and II. The values of all these coefficients do not depend on the solution concentrations for binary solutions, whereas values of the coefficients Ω_{sk}^i and σ_s^i for ternary solutions do, as is shown in previous paper [3].

The solute flux J_s^i was measured for configurations A and B of the measuring system (indices $i = A, B$ pertain to configurations A and B, respectively). In configuration A, the vessel (l) (containing pure water) was the upper compartment of the double-membrane osmotic-diffusive cell, whereas the vessel containing the investigated solution served as the lower compartment. In configuration B, the upper compartment contained the solution, whereas the lower compartment was filled with pure water. Two series of such experiments have been performed. In

the first series, the membrane M_l separated solutions $(C_s^o)_l$ and $(C_s^o)_m$, whereas the membrane M_r separated solutions $(C_s^o)_m$ and $(C_s^o)_r$. In the second series of the experiments the sequence arrangement of membranes was exchanged. The same procedure was repeated for each configuration. Measurements of J_s^i were performed according to the following procedure. The first step consisted in measurements of the solute flux (J_s^i) in the double-membrane osmotic-diffusive cell with a mechanical stirring of the solution at 500 rpm. After achieving the initial steady state with constant $J_s^i = J_s^o$, the stirring of the solutions was stopped and the evolution of solute flux has been measured until the second steady state, when the J_s^i remain constant. We have used aqueous glucose and/or ethanol solutions in the experiments. The evaluation of the global concentration exchanges has been performed by a standard isotope method. The measured value of the concentration exchange (dC/dt) was used to calculate the solute flux J_s^i based on the following equation

$$J_s^i = \frac{V_c}{S} \left(\frac{dC}{dt} \right)_{J_v^i=0}^i \quad (6)$$

where S is a membrane surface area and V_c is a volume of the measuring vessel.

The measurements have been carried out at temperature $T = (295 \pm 0.1)$ K. Typical plots of the time dependencies for J_s^i in the configurations A and B of the double-membrane osmotic-diffusive cell in case of a 0.1 mole l^{-1} aqueous glucose solution were presented in previous paper [5]. The concentration dependencies J_s^i was determined on the basis of time-dependent changes of J_s^i chosen by consideration of the values of J_s^i at steady state, for different solution concentrations of the same substance. Each series of measurements was repeated five times.

4. Results and discussion

4.1. CONCENTRATION DEPENDENCIES OF SOLUTE FLUX

Concentration dependencies of the solute flux (J_s^i) for mechanically unstirred binary solutions (aqueous glucose or ethanol solutions) and ternary solutions (aqueous glucose and ethanol solutions) for A and B configurations of membrane system are shown in Figures 2 and 4. The results presented in Figures 3 and 5 were obtained for case, in which the solutions separated by membranes M_l and M_r were mechanically stirred at 500 rpm.

In Figure 2, the dependencies of solute flux (J_s^i) on glucose concentration difference (ΔC_1) with fixed ethanol concentration difference (ΔC_2) were presented. Indices $i = A, B$ pertain to A and B configurations of the membrane system. The graphs 1A and 1B were obtained in the case where $\Delta C_2 = 0 \text{ mole l}^{-1}$ (binary solution), the graphs 2A and 2B – for $\Delta C_2 = 0.75 \text{ mole l}^{-1}$. From this figure it appears that in the case of binary solution J_s^i linearly depends on ΔC_1 and in configuration B the values of J_s^i are greater than in configuration A. Moreover the

Figure 2. The solute flux (J_1^i) across a double-membrane osmotic-diffusive cell as a function of the glucose concentration difference (ΔC_1) for configuration A (upper) and B (lower): plot 1 – no ethanol, 2 – $\Delta C_2 = 0.75 \text{ mole l}^{-1}$ ethanol. Plots 1 and 2 were obtained without any mechanical stirring.

Figure 3. The solute flux (J_1^0) across a double-membrane osmotic-diffusive cell as a function of the glucose concentration difference (ΔC_1) obtained under good stirring conditions by mechanical means.

values of J_s^i , are greater when the solution with greater density is in the chamber over the membrane M_l and water under the membrane M_r . Therefore it results that gravitational force caused stronger solute flow in configuration A than in configuration B. For ternary solutions, i.e. glucose solutions in 0.75 mole l⁻¹ aqueous ethanol solution (graphs 2A and 2B), the values of J_s^i are also greater when the solution with greater density in the chamber over the membrane M_l and water under the membrane M_r . From the course of the curve 2A it appears, that J_s^i reaches maximum in the point $J_1^A = 1.83 \cdot 10^{-5}$ mole m⁻² s⁻¹ and $\Delta C_1 = 0.1$ mole l⁻¹. In the case of graph 2A, for $\Delta C_1 > 0.15$ mole l⁻¹ the J_1^A is linearly dependent on ΔC_1 , with the same tangent of inclination angle as straight line 1A. In that case, the density of ternary solutions, being in the chamber under the membrane is lower than water density being over the membrane. Next from the course of curve 2B results, that for $\Delta C_1 < 0.1$ mole l⁻¹ the flux value in a small degree depends on concentration. In this case, the density of ternary solutions, being under the membrane M_l , is smaller than water density being in the chamber over the membrane M_r . For $\Delta C_1 > 0.1$ mole l⁻¹ the flux J_1^B is linearly dependent on ΔC_1 with the same tangent of inclination angle as straight line 1B. From experimental data presented in the Figure 2 it results that the lower value of J_s^i is the greater hampering influence of gravitational force on solute flow.

Figure 4. The solute flux (J_2^i) across a double-membrane osmotic-diffusive cell as a function of the glucose concentration difference (ΔC_2) for configuration A (upper) and B (lower): plot 1 – no glucose, 2 – $\Delta C_1 = 0.1 \text{ mole l}^{-1}$ glucose. Plots 1 and 2 were obtained without any mechanical stirring.

Figure 5. The solute flux (J_2^o) across a double-membrane osmotic-diffusive cell as a function of the ethanol concentration difference (ΔC_2) obtained under good stirring conditions by mechanical means.

In Figure 3, plot illustrated the dependence of glucose flux J_1^o on glucose concentration difference (ΔC_1) was obtained when the solutions were mechanically stirred at 500 rpm. The glucose flux (J_1^o) is not depending on ethanol concentration difference (ΔC_2).

In Figure 4, the dependencies of ethanol flux (J_2^i) on ethanol concentration difference (ΔC_2) and fixed concentration difference of glucose (ΔC_1) were presented. As previously, indices $i = A, B$ refer suitably to A and B configurations of double-membrane system. The graphs 1A and 1B were received for the case of $\Delta C_1 = 0$ mole l⁻¹ and the graphs 1A and 1B – for $\Delta C_1 = 0.1$ mole l⁻¹. From this figure it appears that in the case of binary solutions J_s^i is linearly dependent on ΔC_2 . In this case the value of J_s^i in configuration A is greater than in configuration B. This also means that the values of J_s^i is greater, when the solution with greater density is in the chamber over the membrane and water is under the membrane.

From the course of curve 2A it results that for $\Delta C_2 < 0.65$ mole l⁻¹ (in the case of graph 2A) the value of J_s^i in a small degree depends on ΔC_2 and ΔC_1 . Therefore the density of ternary solutions, being in the chamber over the membrane is lower than the water density being in the chamber under the membrane. For $\Delta C_2 > 0.8$ mole l⁻¹ (in the case of curve 2A) the flux J_2^A is linearly dependent on ΔC_2 with

the same tangent of inclination angle as straight line 1A. In this case the density of ternary solutions being in the chamber over the membrane is greater than water density being in the chamber under the membrane. Then from the course of graph 2B it results that the flux J_2^B gains the maximum for $J_2^B = 3.2 \cdot 10^{-5} \text{ mole m}^{-2} \text{ s}^{-1}$ and $\Delta C_2 = 0.5 \text{ mole l}^{-1}$. In this case the density of ternary solutions, being in the chamber over the membrane is greater than water density in the chamber under the membrane. For $\Delta C_2 > 0.7 \text{ mole l}^{-1}$ in the case of curve 2A the flux is linearly dependent on ΔC_2 with this same tangent of inclination angle as straight line 1B. In this case the density of ternary solutions being in the chamber under the membrane is lower than water density being over the membrane. All the measurements results presented in Figures 2 and 3 were obtained for the situation, in which the membrane M_l separated solutions with concentrations $(C_k^o)_l$ and $(C_k^o)_m$, whereas the membrane M_r – solutions with concentrations $(C_k^o)_m$ and $(C_k^o)_r$. One should state that the change of sequence arrangement of the membranes does not change the value and of mark J_s^i . The change of configuration of the double-membrane system causes of change in J_s^i for all investigated binary and ternary solutions. The reason for changes of J_s^i is identical as changes of J_v^i and P_m^i described in previous paper [3].

In Figure 5, plot illustrated the dependence of solute flux J_2^o on ethanol concentration difference (ΔC_2), which was obtained when the solutions were mechanically stirred at 500 rpm. The ethanol flux (J_2^o) is not depending on glucose concentration difference (ΔC_1).

A possible origin of these changes can be explained as follows. In the double-membrane system, containing unstirred solutions, on both sides of each membrane the concentration boundary layers were formed. These layers were observed during an interferometric study of near-membrane phases for single and double-membrane systems [7, 8] and investigations of the volume and solute flows in a mixed and unmixed solutions [6]. The complex $(bl/M/bl)$ in the configuration A is stable, if density of the binary solution is directly proportional to its concentration. A change of the configuration from A to B, for the same solutions, causes the hydrodynamic instability, in which as a result a convection mixing of solutions take place. In the case of the binary solutions (where the density is inversely proportional to the concentration) the complex $(bl/M/bl)$ is unstable in the configuration A, whereas it is hydrodynamically stable in the configuration B. Therefore, it is assumed that the complex of two layers formed at both sides of each membrane of the examined double-membrane system is stable in the configuration A, containing the solution which density increases with increase of the concentration, whereas it is unstable in the configuration B. The complex of the boundary layers is stable in the double-membrane system in the configuration A, in which the solution density decreases with increase of the concentration, whereas is hydrodynamically stable in the configuration B. The dynamics of the boundary layers complex (i.e. their stability and instability) is mainly determined by size of the volume and solute fluxes. The values of these fluxes are several times smaller in the stable system than in the

unstable one [2, 3, 6]. For the stable configuration, the concentration Rayleigh number (R_C) was smaller than its critical value (R_C^*). For unstable configuration we found $R_C > R_C^*$ and a convective flow perpendicular to the membrane surface was observed in this case [9].

From curve 2A, in the upper panel of Figure 2, and from curve 2B, in the lower panel of Figure 4, we conclude that $\Delta C_1 < 0.12 \text{ mole l}^{-1}$ and $\Delta C_2 < 0.7 \text{ mole l}^{-1}$ complex ($bl/M/bl$) is unstable, whereas $\Delta C_1 > 0.12 \text{ mole l}^{-1}$ and $\Delta C_2 > 0.7 \text{ mole l}^{-1}$ – is hydrodynamically stable. The critical concentrations are $\Delta C_1 = 0.12 \text{ mole l}^{-1}$ and $\Delta C_2 = 0.7 \text{ mole l}^{-1}$ and after it has been exceeded we can observe a transition from the convection state to nonconvection one. Next, from curve 2B, in the lower panel of Figure 2, and from curve 2A, in the upper panel of Figure 4, it appears that $\Delta C_1 < 0.11 \text{ mole l}^{-1}$ and $\Delta C_2 < 0.65 \text{ mole l}^{-1}$ complex ($bl/M/bl$) is stable, whereas $\Delta C_1 > 0.11 \text{ mole l}^{-1}$ and $\Delta C_2 > 0.65 \text{ mole l}^{-1}$ – is hydrodynamically unstable. The critical concentrations are $\Delta C_1 = 0.11 \text{ mole l}^{-1}$ and $\Delta C_2 = 0.65 \text{ mole l}^{-1}$ and after it has been exceeded we can observe a transition from the nonconvection state to convection one.

Let us make an assumption that, $\omega_{12} = \omega_{21} = \Omega_{12} = \Omega_{21} \approx 0$ [2]. Then, $\varphi_1^i = \psi_1^i = \theta_1^i = \varsigma_1^i = \lambda_1^i = \varphi_2^i = \psi_2^i = \theta_2^i = \varsigma_2^i = \lambda_2^i \approx 0$ and Equations (4) and (5) we can write in the form

$$J_1^i = RT\phi_1^i[(C_1^o)_l - (C_1^o)_r] \quad (7)$$

$$J_2^i = RT\phi_2^i[(C_2^o)_l - (C_2^o)_r] \quad (8)$$

where

$$\phi_1^i = \frac{(\Omega_{11}^i)_l \cdot (\Omega_{11}^i)_r}{(\Omega_{11}^i)_l + (\Omega_{11}^i)_r}, \quad \phi_2^i = \frac{(\Omega_{22}^i)_l \cdot (\Omega_{22}^i)_r}{(\Omega_{22}^i)_l + (\Omega_{22}^i)_r}.$$

These equations can be used to calculations solute flux and analyses solute transport across horizontally mounted membranes in two gravitational configurations of a double-membrane system. Let us consider the results shown in Figures 2 and 4. From these data we see that all dependencies $J_s^i = f(\Delta C_s)$ for ternary solutions display non-linear behavior. In order to apply Equations 7 and 8 to a description of solute transport in ternary solutions, the assumption of the Ω_{sk}^i coefficients being dependent on the concentration and configuration is required. The pertinence of the above assumption is confirmed by the data on Ω_{11}^l , Ω_{11}^r , Ω_{22}^l and Ω_{22}^r in ternary solutions shown in previous paper [3].

Taking into consideration the concentration dependence of the coefficients Ω_{11}^l , Ω_{11}^r , Ω_{22}^l and Ω_{22}^r , demonstrated in papers [3], and the values for the membrane parameters listed in Tables I and II, the values of J_s^i as functions of the concentration differences ΔC_1 and ΔC_2 were calculated on basis of Equations 7 and 8. The solid lines in Figures 2 and 3 present the results calculated for J_s^i . One observes good agreement between the experimental data and the results of the calculation.

If we assume that J_s^i is the generalized flux and ΔC_s a generalized thermodynamic force, the regions where $[dJ_s^i/d(\Delta C_s)] < 0$ 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 [10], membranology [11] and biophysics [12].

The nonlinear characteristics $J_s^i = f(\Delta C_s)$ presented in the Figures 2 and 4 (graphs 2A and 2B) shows that the investigating double-membrane system which contain the ternary solutions determine the nonlinear element. In the case of the characteristic $J_1^A = f(\Delta C_1)$, for $0.1 \text{ mole l}^{-1} \leq \Delta C_1 \leq 0.125 \text{ mole l}^{-1}$, the condition $[\Delta J_1^A/\Delta(\Delta C_1)] < 0$ is fulfilled. If ΔC_1 accomplishes the relations $0 \text{ mole l}^{-1} \leq \Delta C_1 < 0.1 \text{ mole l}^{-1}$ and $\Delta C_1 > 0.125 \text{ mole l}^{-1}$, the condition $[\Delta J_1^A/\Delta(\Delta C_1)] \geq 0$ is fulfilled. In case of characteristic $J_1^B = f(\Delta C_1)$, for all values of ΔC_1 , we can write a condition $[\Delta J_1^B/\Delta(\Delta C_1)] \geq 0$. Similarly, in case of characteristic $J_2^A = f(\Delta C_2)$, for all values of ΔC_2 , the condition $[\Delta J_2^A/\Delta(\Delta C_2)] \geq 0$ is fulfilled. Then, in case of characteristic $J_2^B = f(\Delta C_2)$, for $0.5 \text{ mole l}^{-1} \leq \Delta C_2 < 0.75 \text{ mole l}^{-1}$, fulfil the condition $[\Delta J_2^B/\Delta(\Delta C_2)] < 0$. If ΔC_2 accomplishes the relations $0 \text{ mole l}^{-1} \leq \Delta C_2 < 0.5 \text{ mole l}^{-1}$ and $\Delta C_2 > 0.75 \text{ mole l}^{-1}$, the relation $[\Delta J_2^B/\Delta(\Delta C_2)] \geq 0$ is fulfilled.

If in the nonlinear element there is the negative resistance region, then in this element the generation of electrical and/or mechanical oscillation may be appeared. Examples of these behaviors: Teorell's membranous oscillator [13], semiconductor generator [14] and electrical oscillations in excitable tissues [12].

4.2. ASYMMETRY OF SOLUTE TRANSMEMBRANE FLOW

The results of investigations of J_s^i in double-membrane system show those values of solute flux obtained for the same ΔC_s in configurations A and B are different. It shows the rectifying property of the double-membrane system. The measure of these properties is the asymmetry coefficient solute flux (k_s) defined as quotients J_s^i in configurations B and A of a double-membrane system

$$k_s = \frac{J_s^B}{J_s^A} \cong \frac{\phi_s^B}{\phi_s^A} \quad (9)$$

where $s = 1, 2$.

For aqueous glucose solutions $k_s^{cal} = 13.8$ and $k_s^{ex} = 13.9$, then for aqueous ethanol solutions $k_s^{cal} = 0.013$ and $k_s^{ex} = 0.015$. For ternary solutions the values k_s depend on the solution concentration (see Figures 6 and 7).

4.3. AMPLIFICATION OF SOLUTE FLOW

In order to demonstrate an effect of solute flux (J_s^i) amplification let's take into consideration graphs 1 and 2 showed in the Figures 2 and 4. The graphs 1A and 1B show, that the same change of value of concentration differences $\Delta(\Delta C_1)$ or

Figure 6. The asymmetry coefficient solute flux (k_1) as a function of the glucose concentration difference (ΔC_1) in a binary (plot 1) and ternary solutions (glucose in 0.75 mole l^{-1} ethanol aqueous solutions) – plot 2).

$\Delta(\Delta C_2)$ in the case of binary solutions cause the same change of value ΔJ_s^i in the whole range of used concentrations differences ΔC_1 or ΔC_2 . In the case of ternary solutions, illustrated in the graphs 2A and 2B on above mentioned figures, the same change of concentration differences cause different in the value and sign value changes of ΔJ_s^i . Quantitative measure of this effect is the coefficient of volume flux amplification (a_s^i) specified by the following equation

$$a_s^i = \frac{(\Delta J_s^i)_t}{(\Delta J_s^i)_b} \cong \frac{[\Delta \phi_s^i(C_s)]_t}{[\phi_s^i]_b} \quad (10)$$

where $(\Delta J_s^i)_t$ – change of flux J_s^i in ternary solutions, $(\Delta J_s^i)_b$ – change of the flux J_s^i in binary solutions, $i = A, B$; $s = 1, 2$.

In Figures 8 and 9 the dependencies of coefficients ($i = A, B$ relate suitably to A and B configurations of one membrane system) on mean concentration $\bar{C}_1$ and a_2^i on mean concentration $\bar{C}_2$ were presented graphically. The graphs 1A were obtained for configuration A, whereas graphs 1B – for configuration B of double-membrane system. The procedure of calculation of concentrations $\bar{C}_1$ or $\bar{C}_2$ was as follows. If, for example, $\Delta C_k = C_k - C_o$ (where $k = 1, 2, 3, \dots, n$) then $\bar{C}_1 = (C_1 + C_o)/2$, $\bar{C}_2 = (C_2 + C_o)/2$ and so on.

Figure 7. The asymmetry coefficient solute flux (k_2) as a function of the ethanol concentration difference (ΔC_2) in a binary (plot 1) and ternary solutions (ethanol in 0.1 mole l⁻¹ glucose aqueous solutions) – plot 2.

From graph 1A, shown in Figure 8 results, that with increase of value $\bar{C}_1$ the value of coefficient a_s^i decreases nonmonotonically from value $a_s^i = +120$ to minimal value $a_s^i = -130$ and next increases to constant value $a_s^i = 1.5$ for $\bar{C}_1 > 0.08$ mole l⁻¹, independent on $\bar{C}_1$. Minimal value of $a_s^i = -130$ was obtained for $\bar{C}_1 = 0.08$ mole l⁻¹. Next, the value of a_s^i coefficient, initially is independent on value of $\bar{C}_1$ and amounts $a_s^i = 0.05$ and next for $\bar{C}_1 > 0.025$ mole l⁻¹ increases to maximal value amounts $a_s^i = 4.5$. After exceeding maximal value, a_s^i decreases to value $a_s^i = 1$ independent on $\bar{C}_1$.

From graph 1A, shown in Figure 8 results, that value of coefficient a_s^i for $\bar{C}_2 < 0.5$ mole l⁻¹ is independent on value $\bar{C}_2$. For $\bar{C}_2 > 0.5$ mole l⁻¹ the value of coefficient a_s^i increases and for $\bar{C}_2 = 0.55$ mole l⁻¹ reaches value $a_s^i = 16$. For $\bar{C}_2 > 0.8$ mole l⁻¹ the value of a_s^i does not depend on $\bar{C}_2$ value and amounts $a_s^i = 3$. From the graph 1B results, that with increase of $\bar{C}_2$, value of coefficient a_s^i decreases nonmonotonically from value $a_s^i = +80$ to minimal value $a_s^i = -370$, and next increases to constant value $a_s^i = 0.05$ independent on $\bar{C}_2$. Minimal value of $a_s^i = -370$ was gained for $\bar{C}_2 = 0, 25$ mole l⁻¹.

Figure 8. The amplification coefficient solute flux (a_1^i) $i = A, B$ as a function of the mean glucose concentration ($\bar{C}_1$) in a binary (plot 1) and ternary solutions (glucose in 0.75 mole l^{-1} ethanol aqueous solutions – plot 2).

Figure 9. The amplification coefficient solute flux (a_2^i) $i = A, B$ as a function of the mean glucose concentration ($\bar{C}_2$) in a binary (plot 1) and ternary solutions (ethanol in 0.1 mole l^{-1} glucose aqueous solutions – plot 2).

5. Conclusions

Inferences the conducted investigations show that:

1. The irreversible thermodynamics model equations of solute transmembrane transport have been elaborated for non-ionic and heterogeneous multicomponent solutions in a double-membrane system. The proposed model expands the range of application of the Kedem-Katchalsky model equations to weakly stirred and unstirred multicomponent and double-membrane systems.
2. In the case of the weakly stirred (i.e., a convective mixing) or the unstirred solutions, usefulness of the Kedem-Katchalsky model equations is limited by values of the parameters σ_s and ω_s . The coefficients determined under such conditions do not refer to the membrane itself to the complex of a membrane and concentration boundary layers and they should be expressed by the pseudo-reflection coefficient (σ_s^i) and diffusive permeability coefficient (Ω_{ks}^i).
3. Double-membrane system, consisting of two membranes differs in permeability parameters. Rectification and amplification the solute flow characterizes it. These effects are the result of creation of gravitation and/or destruction of concentration boundary layers.
4. The effects of rectification and amplification solute flow are the indication of new diffusive properties in double-membrane system.
5. The effects of rectification and amplification of transmembrane transport are indications of natural convection 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 flows.

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