

# **Membrane transport of the non-homogeneous non-electrolyte solutions: mathematical model based on the Kedem-Katchalsky and Rayleigh equations**

ANDRZEJ ŚLĘZAK

Department Biology and Biophysics, Częstochowa University of Technology

---

## **Summary**

Mathematical model of the volume and solute flows through artificial polymeric membrane under occurrence of the concentration boundary layers on both sides of this membrane is presented. This nonlinear model, based on the Kedem-Katchalsky and Rayleigh equations, describes the volume flux generated by osmotic and hydrostatic forces, thicknesses of the concentration boundary layers, concentrations and hydrostatic pressures on the membrane-concentrations boundary layers' borders. Besides, this model shows that the volume flows and individual forces causes the flows influences on the thickness of concentration boundary layers.

The nonlinear equations for volume flux, concentration and thickness of concentration boundary layers can be used to numerical calculation in linear regime of the hydrodynamical stability.

**Keywords:** membrane transport, Kedem-Katchalsky equations, concentration boundary layers, concentration Rayleigh number

---

## **Transport membranowy niejednorodnych roztworów nieelektrolitów: model matematyczny oparty na równaniach Kedem-Katchalsk'ego i Rayleigha**

### **Streszczenie**

Przedstawiono model matematyczny przepływów objętościowych i substancji rozpuszczonej przez sztuczną membranę polimerową, w warunkach istnienia po obydwu jej stronach stężeńowych warstw granicznych. Ów nieliniowy model, oparty na równaniach Kedem-Katchalsky'ego i Rayleigha, opisuje strumień objętościowy generowany przez

bodziec osmotyczny i hydrauliczny, grubości stężeniowych warstw granicznych, stężenia i ciśnienia mechaniczne na granicach membrana-stężeniowe warstwy graniczne. Ponadto ten model pokazuje, że przepływy objętościowe i poszczególne bodźce wywołujące te przepływy mają wpływ na grubość stężeniowych warstw granicznych.

Otrzymane nieliniowe równania nadają się do obliczeń numerycznych w liniowym reżimie stabilności hydrodynamicznej.

**Słowa kluczowe:** transport membranowy, równania Kedem-Katchalsky'ego, stężeniowe warstwy graniczne, stężeniowa liczba Rayleigha

---

## INTRODUCTION

The famous Kedem-Katchalsky equations, describing the passive membranes transport was published in 1958 [1]. In the following years O. Kedem i A. Katchalsky presented a version of equations describing the membrane transport of electrolyte solutions regarding electrical effects [2] and active transport [3]. The active membrane transport was studied also by other authors [4]. In these papers the concentrations boundary layers were not regarded. The few first of meaning papers, in which creation of these layers were regarded and published by Dainty [5] and Ginsburg and Katchalsky [6]. But not till the end of last century papers devoted to the modification of the Kedem-Katchalsky (KK) equations were published. In these papers the range of KK equations' applications to membrane systems containing the concentration boundary layers was expanded. Papers published by A. Ślęzak [7, 8], M. Kargol [9] and A. Kargol [10] had significant contribution in the study of this problem.

A membrane is an interphase between two adjacent homogeneous phases (solutions) acting as a selective barrier, regulating the transport of substances between the two compartments. Homogeneity of these phases can be achieved e.g. by mechanical devices (stirrers). In case of binary homogeneous and diluted solutions the transport can be described by the volume ( $J_v$ ) and solute ( $J_s$ ) fluxes. Relationships between the fluxes and the generating forces ( $\Delta P$  and/or  $\Delta\pi$ ) have been described by Kedem-Katchalsky equations [11]. The classical version of these equations is as follows

$$J_v = L_p (\Delta P - \sigma \Delta\pi) \quad (1)$$

$$J_s = \omega \Delta\pi + \bar{C} (1 - \sigma) J_v \quad (2)$$

where  $L_p$ ,  $\sigma$  and  $\omega$  are the hydraulic permeability, reflection and solute permeability coefficients;  $\Delta P = P_h - P_l$  is the mechanical pressure difference,  $\Delta\pi = RT(C_h - C_l)$  is the

osmotic pressure difference,  $RT$  – product of the gas constant and thermodynamic temperature,  $C_h$  and  $C_l$  – solutions concentration,  $\bar{C} = (C_h - C_l)[\ln(C_h C_l^{-1})]^{-1} \approx \frac{1}{2}(C_h + C_l)$  – the average solute concentration in membrane.

In most cases, spontaneously occurring transport processes in the external field such as the electric or gravitational field, lead to creation of local and/or global non-homogeneity in solutions that modify the membrane transport [12-14]. One of the reasons for forming this non-homogeneity is the concentration polarization leading to the temporal-spatial evolution of and thermodynamic flows and forces [8, 15, 16]. In case of ion-exchange membranes and electrolyte solutions, concentration polarization is a well-known phenomenon arising at the interface between an ion-exchange membrane and electrolyte solution when an electric current passes through the system [17, 18]. In its prominent form, concentration polarization is observed by the fact that the transmembrane flux does not increase with increasing of driving force and reaches a limiting flux [19-21]. The theoretical modelling of the concentration polarization phenomenon is based on the Nernst-Planck, Poisson [22-24], Fick [15, 25, 26] and Kedem-Katchalsky [27-29] equations.

In the case of the nonelectrolyte solutions transport through a neutral membrane, the concentration polarization consists in formation of the concentration boundary layers (CBL) at both sides of this membrane [np. 7-10, 12-16]. The layers can be treated as a liquid membrane with suitable transport properties [8, 14]. One of the effects of the temporal-spatial evolution of the concentration boundary layers is the evolution of the concentrations field. This evolution causes that solutions concentrations at interfaces: membrane/solution in the stationary state ( $C_i, C_e$ ), are crucially different from concentrations in the initial moment ( $C_h, C_l$ ). These concentrations fulfil conditions  $C_i < C_h$  and  $C_e > C_l$  [15, 30]. Usually the width of the CBLs is estimated by flux measurements [e.g. 7, 8, 14, 31]. Alternatively, microelectrodes placed near the membrane surface can be used to determine thickness from the time-course of near membrane concentration changes [16,20,21,32,33-35]. Concentration profiles may be also registered with optical methods [14, 15, 25, 36, 37]. It means that these layers, by reducing the concentration gradient across the membrane, limit both the osmotic and diffusive flows. Kinetics of these flows, on the phenomenological level, is controlled by the concentration Rayleigh number [14, 37]:

$$R_c = g\alpha_c\beta_c d^4 (D\nu)^{-1} \quad (3)$$

where  $g$  is the gravitational acceleration,  $d$  – the fluid depth along the gravitational ( $z$ ) direction,  $\alpha_c = (\partial\rho/\partial C)/\rho$  – the variation of density with concentration,  $\beta_c = \partial C/\partial z$  – the concentration gradient,  $D$  – the solute diffusion coefficient and  $\nu$  – kinematic viscosity.

Near-membrane concentrations boundary layers play role of additional kinetics barriers in transport processes of rapidly permeating substances through natural and artificial membranes [38-43]. The rate and effectiveness of chemical transformations within the CBLs are affected by the availability of the reactants. Near-membrane boundary layers are the source of an inaccurate Michaelis constant in membrane transport [42]. The size of CBLs seems to have regulatory functions. Variations in epithelial function or luminal stirring can for example readily influence the absorption of small molecules [40, 41]. In terrestrial conditions, the concentration boundary layers can be destroyed by natural convection and sedimentation [44].

In the present paper the mathematical model of the volume and solute flows through artificial polymeric membrane under occurrence of the concentration boundary layers on both sides of this membrane is presented. This nonlinear model, based on the Kedem-Katchalsky and Rayleigh equations, describes the volume flux generated by osmotic and hydrostatic forces, thicknesses of the concentration boundary layers, concentrations and hydrostatic pressures on the membrane-concentrations boundary layers' borders. Besides, this model shows that the volume flows and individual forces causes the flows influences on the thickness of concentration boundary layers. The nonlinear equations for volume flux, concentration and thickness of concentration boundary layers can be used to numerical calculation in linear regime of the hydrodynamical stability.

The paper is organized as follows. We characterize the model of membrane system in section 2. In section 3 we present the mathematical model of volume and solute flows of non-homogeneous non-electrolyte solutions based on the Kedem-Katchalsky equations. In this section we obtain two alternative third order equations for volume flux. The coefficients, that appear in these equations, depend on transport parameters of complex concentration boundary layers-membrane or membrane, difference of the mechanical and/or osmotic pressures and thicknesses of the concentration boundary layers. These thicknesses can be calculated on the basis on Rayleigh equation. In section 4 the mathematical model of the thicknesses of concentration boundary layers is presented. We obtain two fourth order equations in which the coefficients are dependent on transport parameters of complex membrane-concentration boundary layers or membrane, difference of the osmotic and/or mechanical pressures and

other parameters, which can be experimentally determined in series of independent experiments [8, 37].

## MEMBRANE SYSTEM

Let us consider the single-membrane system presented schematically in Fig.1. In this system the compartments (*l*) and (*h*), containing diluted and heterogeneous (not mechanically stirred) binary solutions of the same non-electrolyte are separated by isotropic, symmetrical, selective and electroneutral membrane *M*. In this system water and a dissolved substance diffused through the membrane will lead to formation of concentration boundary layers (CBLs)  $l_l$  and  $l_h$ . These layers can be treated as pseudomembranes [8,14]. The transport processes are isothermal and stationary and no chemical reactions occur in the solutions. We denote the concentrations of solutions at boundaries  $l_l/M$  and  $M/l_h$  by  $C_e$  and  $C_i$  respectively, while the concentrations of solutions outside the boundaries are denoted by  $C_l$  and  $C_h$ . The concentrations satisfy the conditions  $C_h > C_l$ ,  $C_i > C_e$ ,  $C_e > C_l$  and  $C_h > C_i$ . We denote the mechanical pressure at boundaries  $l_l/M$  and  $M/l_h$  by  $P_e$  and  $P_i$  respectively, while the mechanical pressures outside the boundaries are denoted by  $P_l$  and  $P_h$ . The pressures satisfy the conditions  $P_h > P_l$ ,  $P_i > P_e$ ,  $P_e > P_l$  and  $P_h > P_i$ . The membrane (*M*) is characterized by the hydraulic permeability ( $L_p = L_{pm}$ ), reflection ( $\sigma = \sigma_m$ ) and solute permeability ( $\omega = \omega_m$ ) coefficients. The layers ( $l_l$ ) and ( $l_h$ ) are characterized by the hydraulic permeability ( $L_{pl}$ ,  $L_{ph}$ ), reflection ( $\sigma_l = 0$ ,  $\sigma_h = 0$ ) and solute permeability ( $\omega_l$ ,  $\omega_h$ ) coefficients, respectively. The hydraulic permeability, reflection and solute permeability coefficients of complex  $l_l/M/l_h$  are denoted by  $L_{ps}$ ,  $\sigma_s$  and  $\omega_s$ , respectively. The parameters  $L_{pl}$ ,  $L_{ph}$ ,  $L_{pm}$ ,  $L_{ps}$ ,  $\sigma_l$ ,  $\sigma_h$ ,  $\sigma_m$ ,  $\sigma_s$ ,  $\omega_l$ ,  $\omega_h$ ,  $\omega_m$  and  $\omega_s$  are defined by the expressions listed in table 1. The volume fluxes through the layers  $l_l$ ,  $l_h$ , membrane *M* and complex  $l_l/M/l_h$  are denoted by  $J_{vl}$ ,  $J_{vh}$ ,  $J_{vm}$  and  $J_{vs}$ , respectively.

## DESCRIPTION OF THE MEMBRANE TRANSPORT OF NON-HOMOGENEOUS SOLUTIONS BASED ON KEDEM-KATCHALSKY EQUATIONS

The starting point of our description are equations (1) and (2). On the basis of equation 1 we can write:

$$J_{vh} = L_{ph}\Delta P_h = L_{ph}(P_h - P_i) \quad (4)$$

$$J_{vm} = L_{pm}\Delta P_m - L_{pm}\sigma_m\Delta\pi_m = L_{pm}(P_i - P_e) - L_{pm}\sigma_m RT(C_i - C_e) \quad (5)$$

$$J_{vl} = L_{pl}\Delta P_l = L_{pl}(P_e - P_l) \quad (6)$$

$$J_{vs} = L_{ps}(\Delta P - \sigma_s\Delta\pi) \quad (7)$$

At steady state, the following condition is fulfilled

$$J_{sh} = J_{vm} = J_{vl} = J_{vs} \quad (8)$$

Combining eqs. (4)-(6) we obtain

$$P_i = \frac{L_p\{L_{pl}[P_l + \sigma RT(C_i - C_e)] + L_{ph}P_h\} + L_{pl}L_{ph}P_h}{L_{pl}L_{ph} + L_p(L_{pl} + L_{ph})} \quad (9)$$

$$P_e = \frac{L_p\{L_{ph}[P_h - \sigma RT(C_i - C_e)] + L_{pl}P_l\} + L_{pl}L_{ph}P_l}{L_{pl}L_{ph} + L_p(L_{pl} + L_{ph})} \quad (10)$$

Subtraction equations (9) and (10) leads to expression

$$P_i - P_e = \frac{L_{pl}L_{ph}\Delta P + L_p\sigma RT(L_{pl} + L_{ph})(C_i - C_e)}{L_{pl}L_{ph} + L_p(L_{pl} + L_{ph})} \quad (11)$$

For coefficients  $L_{ps}$ ,  $L_p$ ,  $L_{pl}$  and  $L_{ph}$  the next relation applies

$$L_{ps}^{-1} = L_p^{-1} + L_{pl}^{-1} + L_{ph}^{-1} \quad (12)$$

From above relation results that, if  $L_{pl} \rightarrow \infty$  and  $L_{ph} \rightarrow \infty$ , we obtain  $L_{ps} \rightarrow L_p$ . Combining equations (4), (5) and (7) we obtain other versions of the equations (9) and (10)

$$P_i = P_h - L_{ps}L_{ph}^{-1}(\Delta P - \sigma_s\Delta\pi) \quad (13)$$

$$P_e = L_{ps}L_{pl}(\Delta P - \sigma_s\Delta\pi) + P_l \quad (14)$$

Combining equations (9), (10) and (12) or eqs. (13) and (14), the equation (11) can be written as

$$P_i - P_e = L_p^{-1}[L_{ps}\Delta P + \sigma RT(L_p - L_{ps})(C_i - C_e)] \quad (15)$$

Besides, combining equations (4), (6) - (8) we can write

$$L_{pl}(P_e - P_l) = L_{ps}(\Delta P - \sigma_s\Delta\pi) = L_{ph}(P_h - P_i) \quad (16)$$

Taking into consideration equation (15) in equation (5) we obtain

$$J_{vm} = L_{ps}[\Delta P - \sigma_m RT(C_i - C_e)] \quad (17)$$

Occurrence of the concentrations  $C_i$  and  $C_e$  in above equation can be determined by optical methods [15,25]. These concentrations can be calculated on the basis of equation (2) [27-29]. In order to calculate these concentrations the following considerations will be made.

The solute fluxes through the layers  $l_l$ ,  $l_h$ , membrane M and complex  $l_l/M/l_h$  are denoted by  $J_{sl}$ ,  $J_{sh}$ ,  $J_{sm}$  and  $J_{ss}$ , respectively. Besides, permeability coefficients of solute layers  $l_l$  and  $l_h$  can be written as  $\omega_l = D_l(RT\delta_l)^{-1}$  and  $\omega_h = D_h(RT\delta_h)^{-1}$  [6].

In order to calculate  $C_i$  i  $C_e$ , equation 2 can be written as

$$J_h = D_h \delta_h^{-1} (C_h - C_i) + \frac{1}{2} (C_h + C_i) J_{vh} \quad (18)$$

$$J_m = \omega_m RT (C_i - C_e) + \frac{1}{2} J_{vm} (C_i + C_e) (1 - \sigma_m) \quad (19)$$

$$J_l = D_l \delta_l^{-1} (C_e - C_l) + \frac{1}{2} (C_e + C_l) J_{vl} \quad (20)$$

$$J_{ss} = \omega_s \Delta \pi + J_{vs} \bar{C} (1 - \sigma_s) \quad (21)$$

At steady state, the following conditions are fulfilled

$$J_{sh} = J_{sm} = J_{sl} = J_{ss} \quad (22)$$

From equations (18)-(22) it appears that two expressions for both  $C_i$  and  $C_e$  can be written. Two methods of obtaining these expressions will be presented below. The first method leads to equations, in which the coefficients  $\omega_s$  and  $\sigma_s$  (transport coefficients refers to complex  $l_l/M/l_h$ ) occur. The second method leads to equations, in which the coefficients  $\omega$  and  $\sigma$  (transport coefficients refers to membrane) occur.

The first method is a consequence of the following considerations. Combining equations (18), (20)-(22) we obtain

$$C_i = [D_h C_h - \omega_s \delta_h \Delta \pi + J_v \delta_h (\sigma_s \bar{C} - \frac{1}{2} C_l)] (D_h - \frac{1}{2} J_v \delta_h)^{-1} \quad (23)$$

$$C_e = [D_l C_l + \omega_s \delta_l \Delta \pi + J_v \delta_l (\frac{1}{2} C_h - \sigma_s \bar{C})] (D_l + \frac{1}{2} J_v \delta_l)^{-1} \quad (24)$$

where  $\omega_s = \zeta_s \omega_m$ ,  $\sigma_s = \zeta_s \sigma_m$  and  $0 \leq \zeta_s \leq 1$ .

If we assume that  $\delta_l = \delta_h = 0$  we obtain  $C_i = C_h$  and  $C_e = C_l$ . For  $J_v = 0$ , equations (23) and (24) reduced to form

$$C_i = C_h - \omega_s D_h^{-1} \delta_h \Delta \pi \quad (23a)$$

$$C_e = C_l + \omega_s D_l^{-1} \delta_l \Delta \pi \quad (24a)$$

Taking into consideration equations (23) and (24) in equation (17) we obtain

$$\gamma_1 J_{vm}^3 + \gamma_2 J_{vm}^2 + \gamma_3 J_{vm} + \gamma_4 = 0 \quad (25)$$

where

$$\gamma_1 = \frac{1}{2} \delta_l \delta_h \quad (26)$$

$$\gamma_2 = -\frac{1}{2} [(D_h \delta_l - D_l \delta_h) + L_{ps} \delta_h \delta_l (\Delta P + \frac{1}{2} \sigma_m \Delta \pi)] \quad (27)$$

$$\gamma_3 = -D_h D_l + L_{ps} [\frac{1}{2} \Delta P (D_h \delta_l - D_l \delta_h) - \sigma_m RT \bar{C} \sigma_s (D_l \delta_h + D_h \delta_l)] \quad (28)$$

$$\gamma_4 = L_{ps} \{D_h D_l \Delta P - \sigma_m \Delta \pi [D_h D_l - \omega_s RT (D_l \delta_h + D_h \delta_l)]\} \quad (29)$$

Here are main conclusions appearing from equation (25):

1. For  $\Delta P=0$  eqs. (27)-(29) reduced to the form  $\gamma_2 = -\frac{1}{2}[(D_h \delta_l - D_l \delta_h) + \frac{1}{2} L_{ps} \delta_h \delta_l \sigma_m \Delta \pi]$ ,

$$\gamma_3 = -D_h D_l - L_{ps} \{\sigma_m RT [\bar{C} \sigma_s (D_l \delta_h + D_h \delta_l)]\} \text{ and}$$

$$\gamma_4 = -L_{ps} \{\sigma_m \Delta \pi [D_h D_l - \omega_s RT (D_l \delta_h + D_h \delta_l)]\}.$$

2. The condition  $C_h=C_l \neq 0$  reduces only equations (27) and (29) to form

$$\gamma_2 = -\frac{1}{2}[(D_h \delta_l - D_l \delta_h) + L_{ps} \delta_h \delta_l \Delta P] \text{ and } \gamma_4 = L_{ps} \{D_h D_l \Delta P [D_h D_l - \omega_s RT (D_l \delta_h + D_h \delta_l)]\}.$$

3. For non selective membrane ( $\sigma=\sigma_s=0$ ) we obtain:  $\gamma_2 = -\frac{1}{2}[(D_h \delta_l - D_l \delta_h) + L_{ps} \delta_h \delta_l \Delta P]$ ,

$$\gamma_3 = -D_h D_l + \frac{1}{2} L_{ps} [\Delta P (D_h \delta_l - D_l \delta_h)], \gamma_4 = L_{ps} D_h D_l \Delta P.$$

4. If  $D_l=D_h=D$  and  $\delta_l=\delta_h=\delta$  we obtain the following form of equations (26)-(29):

$$\gamma_1 = \frac{1}{2} \delta^2, \gamma_2 = -\frac{1}{2} [L_{ps} \delta^2 (\Delta P + \frac{1}{2} \sigma_m \Delta \pi)], \gamma_3 = -D^2 + L_{ps} \{2 \Delta P \sigma_m RT \bar{C} \sigma_s D \delta\} \text{ and}$$

$$\gamma_4 = L_{ps} D [D \Delta P - \sigma_m \Delta \pi (D - 2 \omega_s RT \delta)].$$

5. Taking into account the condition  $\delta_l=\delta_h=0$ , we can write the eqsutions (26)-(29) in

following forms  $\gamma_1 = 0$ ,  $\gamma_2 = 0$ ,  $\gamma_3 = -D_h D_l$  and  $\gamma_4 = L_{ps} D_h D_l (\Delta P - \sigma_m \Delta \pi)$ . These conditions and expression (12) enable transformation of the equation (25) to equation (1).

The second method is a consequence of the following considerations. Combining equations (18) - (20) and (22) we obtain the following forms of equations for  $C_i$  and  $C_e$

$$C_i = \frac{C_h [D_h D_l + \omega RT D_h \delta_l - \frac{1}{2} J_{vm} (\sigma D_h \delta_l + D_l \delta_h + \omega RT \delta_l \delta_h) + \frac{1}{4} J_{vm}^2 \sigma \delta_l \delta_h]}{D_h D_l + (D_h \delta_l + D_l \delta_h) \omega RT + \frac{1}{2} J_{vm} (D_h \delta_l - D_l \delta_h) + \frac{1}{4} J_{vm}^2 (1 - 2\sigma) \delta_l \delta_h} + \frac{C_l \{ \omega RT D_l \delta_h - \frac{1}{2} J_{vm} \delta_h [\omega RT \delta_l + (1 - \sigma) D_l] + \frac{1}{4} J_{vm}^2 (1 - \sigma) \} \delta_l \delta_h}{D_h D_l + (D_h \delta_l + D_l \delta_h) \omega RT + \frac{1}{2} J_{vm} (D_h \delta_l - D_l \delta_h) + \frac{1}{4} J_{vm}^2 (1 - 2\sigma) \delta_l \delta_h} \quad (30)$$



$$C_e = \frac{C_l[D_h D_l + \omega RT D_l \delta_h - \frac{1}{2} J_{vm}(\sigma D_l \delta_h + D_h \delta_l + \omega RT \delta_l \delta_h) + \frac{1}{4} J_{vm}^2 \sigma \delta_l \delta_h] + C_h \{\omega RT D_h \delta_l + \frac{1}{2} J_{vm} \delta_l [\omega RT \delta_h + (1 - \sigma) D_h] + \frac{1}{4} J_{vm}^2 (1 - \sigma) \delta_l \delta_h\}}{D_h D_l + (D_h \delta_l + D_l \delta_h) \omega RT + \frac{1}{2} J_{vm} (D_h \delta_l - D_l \delta_h) + \frac{1}{4} J_{vm}^2 (1 - 2\sigma) \delta_l \delta_h} \quad (31)$$

A condition  $\delta_l = \delta_h = 0$  reduces equations (30) and (31), analogously as in case of equations (23) and (24), to forms  $C_i = C_h$  and  $C_e = C_l$ . Next, the condition  $J_v = 0$ , reduces equations (30) and (31) to following forms

$$C_i = [C_h(D_h D_l + \omega RT D_h \delta_l) + C_l \omega RT D_l \delta_h] D_h D_l + (D_h \delta_l + D_l \delta_h) \omega RT]^{-1} \quad (30a)$$

$$C_e = \{C_l[D_h D_l + \omega RT D_l \delta_h] + C_h \omega RT D_h \delta_l\} [D_h D_l + (D_h \delta_l + D_l \delta_h) \omega RT]^{-1} \quad (31a)$$

Taking into consideration equations (3), (8) and (9) we obtain

$$\chi_1 J_{vm}^3 + \chi_2 J_{vm}^2 + \chi_3 J_{vm} + \chi_4 = 0 \quad (32)$$

where

$$\chi_1 = \frac{1}{4} (1 - 2\sigma) \delta_l \delta_h \quad (33)$$

$$\chi_2 = \frac{1}{2} [\sigma (D_h \delta_l - D_l \delta_h) - \frac{1}{2} L_p (1 - 2\sigma) \delta_l \delta_h (\Delta P + \sigma \Delta \pi)] \quad (34)$$

$$\chi_3 = D_h D_l + (D_h \delta_l + D_l \delta_h) \omega RT - \frac{1}{2} L_p \sigma \Delta P (D_h \delta_l - D_l \delta_h) + \frac{1}{2} L_p \sigma RT \{C_h [D_l \delta_h - D_h \delta_l (1 - 2\sigma)] - C_l [D_l \delta_h (1 - 2\sigma) - D_h \delta_l]\} \quad (35)$$

$$\chi_4 = -L_p [D_h D_l (\Delta P - \sigma \Delta \pi) + \Delta P \omega RT (D_h \delta_l + D_l \delta_h)] \quad (36)$$

Discussion of these equations leads to the following conclusions:

1. If we assume that  $\Delta P = 0$ , in equations (12) and (13) we obtain

$$\chi_2 = \frac{1}{2} [\sigma (D_h \delta_l - D_l \delta_h) - \frac{1}{2} L_p (1 - 2\sigma) \delta_l \delta_h \sigma \Delta \pi]$$

$$\chi_3 = D_h D_l + (D_h \delta_l + D_l \delta_h) \omega RT - \frac{1}{2} L_p \sigma (D_h \delta_l - D_l \delta_h) + \frac{1}{2} L_p \sigma RT \{C_h [D_l \delta_h - D_h \delta_l (1 - 2\sigma)] - C_l [D_l \delta_h (1 - 2\sigma) - D_h \delta_l]\}$$

$$\chi_4 = L_p [D_h D_l \sigma \Delta \pi - \omega RT (D_h \delta_l + D_l \delta_h)]$$

2. If we assume that  $C_h = C_l \neq 0$ , in equations (12) and (14) we obtain

$$\chi_2 = \frac{1}{2} [\sigma (D_h \delta_l - D_l \delta_h) - \frac{1}{2} L_p (1 - 2\sigma) \delta_l \delta_h \Delta P]$$

$$\chi_3 = D_h D_l + (D_h \delta_l + D_l \delta_h) \omega RT - \frac{1}{2} L_p \sigma \Delta P (D_h \delta_l - D_l \delta_h) + \frac{1}{2} L_p \sigma RT \{C_h [D_l \delta_h - D_h \delta_l (1 - 2\sigma)] - C_l [D_l \delta_h (1 - 2\sigma) - D_h \delta_l]\}$$

$$\chi_4 = -L_p \Delta P \{D_h D_l + \omega RT (D_h \delta_l + D_l \delta_h)\}$$

3. For non selective membrane ( $\sigma=0$ ),  $\chi_1 = \frac{1}{4} \delta_l \delta_h$ ,  $\chi_2 = -\frac{1}{4} L_p \delta_l \delta_h \Delta P$ ,

$$\chi_3 = D_h D_l + (D_h \delta_l + D_l \delta_h) \omega RT, \chi_4 = -L_p \Delta P [D_h D_l + \omega RT (D_h \delta_l + D_l \delta_h)].$$

4. For  $D_l = D_h = D$  and  $\delta_l = \delta_h = \delta$ , equations (33)-(36), are simplified to forms

$$\chi_1 = \frac{1}{4} (1 - 2\sigma) \delta^2, \chi_2 = -\frac{1}{4} L_{ps} (1 - 2\sigma) \delta^2 (\Delta P + \sigma \Delta \pi), \chi_3 = D [D + RT (2\delta \omega + 2L_p \sigma^2 \bar{C})]$$

$$\text{and } \chi_4 = -L_{ps} D [D (\Delta P - \sigma \Delta \pi) + 2\omega \delta RT \Delta P].$$

5. For permselective membrane ( $\sigma=1$ ) we obtain

$$\chi_1 = -\frac{1}{4} \delta_l \delta_h$$

$$\chi_2 = \frac{1}{2} [(D_h \delta_l - D_l \delta_h) + \frac{1}{2} L_{ps} \delta_l \delta_h (\Delta P + \Delta \pi)]$$

$$\chi_3 = D_h D_l + (D_h \delta_l + D_l \delta_h) \omega RT - L_{ps} [\frac{1}{2} \Delta P (D_h \delta_l - D_l \delta_h) - \bar{C} RT (D_l \delta_h + D_h \delta_l)]$$

$$\chi_4 = -L_{ps} [D_h D_l (\Delta P - \Delta \pi) + \Delta P \omega RT (D_h \delta_l + D_l \delta_h)]$$

6. For  $\sigma=0.5$ , equations (33)-(36) can be written in following forms

$$\chi_1 = 0 \tag{33a}$$

$$\chi_2 = \frac{1}{4} (D_h \delta_l - D_l \delta_h) \tag{34a}$$

$$\chi_3 = D_h D_l + RT [(D_h \delta_l + D_l \delta_h) \omega + \frac{1}{4} L_p (C_h D_l \delta_h + C_l D_h \delta_l)] - \frac{1}{4} L_p \Delta P (D_h \delta_l - D_l \delta_h) \tag{35a}$$

$$\chi_4 = -L_p [D_h D_l (\Delta P - \frac{1}{2} \Delta \pi) + \Delta P \omega RT (D_h \delta_l + D_l \delta_h)] \tag{36a}$$

Taking into account the condition  $\chi_1 = 0$ , the equation (32) reduces to following form

$$\chi_2 J_{vm}^2 + \chi_3 J_{vm} + \chi_4 = 0$$

In above equation the coefficients  $\chi_1$ ,  $\chi_2$ ,  $\chi_3$  and  $\chi_4$  are illustrated by expressions (34a)-(36a).

7. The condition  $\delta_l = \delta_h = 0$  enable to write the expressions (33)-(36) in forms

$\chi_1 = 0$ ,  $\chi_2 = 0$ ,  $\chi_3 = D_h D_l$  and  $\chi_4 = -L_p D_h D_l (\Delta P - \sigma \Delta \pi)$ . These conditions and expression (12) transform equation (32) to equation (1).

8. For  $\sigma = \frac{1}{2}$ ,  $\delta_l = \delta_h = \delta$  and  $D_l = D_h = D$  equations (33a)-(36a) can be written in following forms  $\chi_1 = 0$ ,  $\chi_2 = 0$ ,  $\chi_3 = D[D + RT\delta(2\omega + L_p\bar{C})]$  and

$\chi_4 = -L_p D[D(\Delta P - \frac{1}{2}\Delta\pi) + 2\omega RT\delta\Delta P]$ . Besides, for  $\chi_1 = 0$  and  $\chi_2 = 0$ , the equation (32) can be written in following form [29]

$$J_v = L_p [(D + 2\omega RT\delta)\Delta P - \frac{1}{2} D\Delta\pi][D + RT(2\omega + L_p\bar{C})]^{-1}.$$

In order to calculate the mechanical pressure difference described by equation (15) analogical procedure can be used.

## EQUATIONS FOR THICKNESSES OF CONCENTRATION BOUNDARY LAYERS

In order to calculate  $\delta_l$  and  $\delta_h$  we will use the definition of concentration Rayleigh number, presented by equation (3) (Rayleigh equation). If we identify the thickness  $\delta_l$  and  $\delta_h$  of concentration boundary layers  $l_l$  and  $l_h$  with  $d$  [14], then using the relations  $\alpha_{cl}\beta_{cl} = g \frac{\partial \rho}{\partial C} (C_e - C_l)(\rho_l \delta_l)^{-1}$ ,  $\alpha_{ch}\beta_{ch} = g \frac{\partial \rho}{\partial C} (C_h - C_i)(\rho_h \delta_h)^{-1}$  equation. 3 can be written in the following forms

$$\delta_l^3 = R_{cl} D_l \rho_l \nu_l \left[ g \left( \frac{\partial \rho}{\partial C} \right) (C_e - C_l) \right]^{-1} \quad (37)$$

$$\delta_h^3 = R_{ch} D_h \rho_h \nu_h \left[ g \left( \frac{\partial \rho}{\partial C} \right) (C_h - C_i) \right]^{-1} \quad (38)$$

Taking into account equations (23) and (24) in equations (37) and (38), respectively, we obtain the following system of equations

$$\vartheta_1 \delta_l^4 - \vartheta_2 \delta_l - \vartheta_3 = 0 \quad (39)$$

$$\kappa_1 \delta_h^4 + \kappa_2 \delta_h - \kappa_3 = 0 \quad (40)$$

where

$$\vartheta_1 = g \left( \frac{\partial \rho}{\partial C} \right) \{ \omega_s \Delta\pi + \frac{1}{2} J_v [C_h(1 - \sigma_s) - C_l(1 + \sigma_s)] \} \quad (41)$$

$$\vartheta_2 = \frac{1}{2} J_v R_{cl} \rho_l \nu_l D_l \quad (42)$$

$$\vartheta_3 = R_{cl} \rho_l \nu_l D_l^2 \quad (43)$$

$$\kappa_1 = g \left( \frac{\partial \rho}{\partial C} \right) \{ \omega_s \Delta \pi + \frac{1}{2} J_v [C_l (1 - \sigma_s) - C_h (1 + \sigma_s)] \} \quad (44)$$

$$\kappa_2 = \frac{1}{2} J_v R_{Ch} \rho_h \nu_h D_h \quad (45)$$

$$\kappa_3 = R_{Ch} \rho_h \nu_h D_h^2 \quad (46)$$

If we assume that  $J_v = 0$  in equations (41)-(46), we obtain  $\vartheta_1 = g \left( \frac{\partial \rho}{\partial C} \right) \omega_s \Delta \pi$ ,  $\vartheta_2 = 0$

$\vartheta_3 = R_{Cl} \rho_l \nu_l D_l^2$ ,  $\kappa_1 = g \left( \frac{\partial \rho}{\partial C} \right) \omega_s \Delta \pi$ ,  $\kappa_2 = 0$  and  $\kappa_3 = R_{Ch} \rho_h \nu_h D_h^2$ . Then equations (39) and

(40) are reduced to following forms [28,29]

$$\delta_l = R_{Cl}^{0.25} \left\{ D_l^2 \nu_l \rho_l \left[ g \omega_s \left( \frac{\partial \rho}{\partial C} \right) \Delta \pi \right]^{-1} \right\}^{0.25} \quad (47)$$

$$\delta_h = R_{Ch}^{0.25} \left\{ D_h^2 \nu_h \rho_h \left[ g \omega_s \left( \frac{\partial \rho}{\partial C} \right) \Delta \pi \right]^{-1} \right\}^{0.25} \quad (48)$$

The basis of second method derivation of the equations for thicknesses of concentration boundary layers is regarding the equations (30) and (31) in equations (37) and (38), respectively. In results we obtain the following system of equations [45]

$$\begin{aligned} & (\beta_1 - \beta_2 \delta_l) (-\alpha_1 \delta_l^4 + \alpha_3 \delta_l - \alpha_6)^4 (\alpha_2 \delta_l^4 - \alpha_5 \delta_l - \alpha_4)^{-4} - \\ & (\beta_3 + \beta_5 \delta_h) (-\alpha_1 \delta_l^4 + \alpha_3 \delta_l + \alpha_6) (\alpha_2 \delta_l^4 - \alpha_5 \delta_l - \alpha_4)^{-1} - \beta_4 \delta_l - \beta_6 = 0 \end{aligned} \quad (49)$$

$$\begin{aligned} & (\alpha_1 + \alpha_2 \delta_h) (\beta_1 \delta_h^4 - \beta_3 \delta_h - \beta_6)^4 (\beta_2 \delta_h^4 + \beta_5 \delta_h + \beta_4)^{-4} - \\ & (\beta_3 + \alpha_5 \delta_h) (\beta_1 \delta_h^4 - \beta_3 \delta_h - \beta_6) (\beta_2 \delta_h^4 + \beta_5 \delta_h + \beta_4)^{-1} - \alpha_4 \delta_h - \alpha_6 = 0 \end{aligned} \quad (50)$$

where

$$\alpha_1 = g \left( \frac{\partial \rho}{\partial C} \right) \{ D_h \omega \Delta \pi + \frac{1}{2} J_{vm} D_h [C_h (1 - \sigma) - C_l (1 + \sigma)] \}, \quad (51)$$

$$\alpha_2 = g \left( \frac{\partial \rho}{\partial C} \right) \frac{1}{2} J_{vm} \{ \omega \Delta \pi + \frac{1}{2} J_{vm} [C_h (1 - \sigma) - C_l (1 - 3\sigma)] \}, \quad (52)$$

$$\alpha_3 = D_l D_h \rho_l \nu_l R_{Cl} (\omega RT + \frac{1}{2} J_{vm} \sigma), \quad \alpha_4 = D_l^2 R_{Cl} \rho_l \nu_l (\omega RT - \frac{1}{2} J_{vm} \sigma) \quad (53)$$

$$\alpha_5 = \frac{1}{4} J_{vm}^2 R_{Cl} D_l \rho_l \nu_l (1 - 2\sigma),$$

$$\alpha_6 = D_h D_l^2 R_{Cl} \rho_l \nu_l, \quad (54)$$

$$\beta_1 = g \left( \frac{\partial \rho}{\partial C} \right) \{ D_l \omega \Delta \pi - \frac{1}{2} J_{vm} D_l [C_h (1 + \sigma) - C_l (1 - \sigma)] \}, \quad (55)$$

$$\beta_2 = g \left( \frac{\partial \rho}{\partial C} \right) \frac{1}{2} J_{vm} \{ \omega \Delta \pi - \frac{1}{2} J_{vm} [C_h (1 - 3\sigma) + C_l (1 - \sigma)] \}, \quad (56)$$

$$\beta_3 = D_l D_h \rho_h \nu_h R_{Ch} (\omega RT - \frac{1}{2} J_{vm} \sigma), \quad (57)$$

$$\beta_4 = D_h^2 R_{Ch} \rho_h \nu_h (\omega RT + \frac{1}{2} J_{vm} \sigma) \quad (58)$$

$$\beta_5 = \frac{1}{4} J_{vm}^2 R_{Ch} D_h \rho_h \nu_h (1 - 2\sigma), \quad (59)$$

$$\beta_6 = D_l D_h^2 R_{Ch} \rho_h \nu_h. \quad (60)$$

Taking the following cases into considerations:

1. If we assume that  $J_v = 0$  in equations (43)-(54) we obtain

$$\alpha_1 = g \left( \frac{\partial \rho}{\partial C} \right) D_h \omega \Delta \pi, \quad \alpha_3 = D_l D_h \rho_l \nu_l R_{Cl} \omega RT, \quad \alpha_4 = D_l^2 R_{Cl} \rho_l \nu_l \omega RT, \quad \alpha_6 = D_h D_l^2 R_{Cl} \rho_l \nu_l,$$

$$\beta_1 = g \left( \frac{\partial \rho}{\partial C} \right) D_l \omega \Delta \pi, \quad \beta_3 = D_l D_h \rho_h \nu_h R_{Ch} \omega RT, \quad \beta_4 = D_h^2 R_{Ch} \rho_h \nu_h \omega RT, \quad \beta_6 = D_l D_h^2 R_{Ch} \rho_h \nu_h,$$

$$\alpha_2 = \alpha_5 = \beta_2 = \beta_5 = 0.$$

This causes the equations (43) and (44) reduction to forms

$$\beta_1 (-\alpha_1 \delta_l^4 + \alpha_3 \delta_l - \alpha_6)^4 (-\alpha_4)^{-4} - \beta_3 (-\alpha_1 \delta_l^4 + \alpha_3 \delta_l + \alpha_6) (-\alpha_4)^{-1} - \beta_4 \delta_l - \beta_6 = 0 \quad (61)$$

$$\alpha_1 (\beta_1 \delta_h^4 - \beta_3 \delta_h - \beta_6)^4 (\beta_4)^{-4} - \beta_3 (\beta_1 \delta_h^4 - \beta_3 \delta_h - \beta_6) (\beta_4)^{-1} - \alpha_4 \delta_h - \alpha_6 = 0 \quad (62)$$

This case was considered in previous paper [46].

2. If we assume that  $R_{Cl} = R_{Ch} = R_C$ ,  $D_l = D_h = D$ ,  $\rho_l = \rho_h = \rho$ ,  $\nu_l = \nu_h = \nu$  and  $\delta_l = \delta_h = \delta$  in equations (43)-(54) we obtain

$$\alpha_1 = g \left( \frac{\partial \rho}{\partial C} \right) D \{ \omega \Delta \pi + \frac{1}{2} J_{vm} [C_h (1 - \sigma) - C_l (1 + \sigma)] \},$$

$$\alpha_2 = g \left( \frac{\partial \rho}{\partial C} \right) \frac{1}{2} J_{vm} \{ \omega \Delta \pi + \frac{1}{2} J_{vm} [C_h (1 - \sigma) - C_l (1 - 3\sigma)] \},$$

$$\beta_1 = g \left( \frac{\partial \rho}{\partial C} \right) D \{ \omega \Delta \pi - \frac{1}{2} J_{vm} [C_h (1 + \sigma) - C_l (1 - \sigma)] \},$$

$$\beta_2 = g \left( \frac{\partial \rho}{\partial C} \right) \frac{1}{2} J_{vm} \{ \omega \Delta \pi - \frac{1}{2} J_{vm} [C_h (1 - 3\sigma) + C_l (1 - \sigma)] \}$$

$$\alpha_3 = D^2 \rho \nu R_C (\omega RT + \frac{1}{2} J_{vm} \sigma), \alpha_4 = D^2 R_C \rho \nu (\omega RT - \frac{1}{2} J_{vm} \sigma)$$

$$\beta_3 = D^2 \rho \nu R_C (\omega RT - \frac{1}{2} J_{vm} \sigma), \beta_4 = D^2 R_C \rho \nu (\omega RT + \frac{1}{2} J_{vm} \sigma)$$

$$\alpha_5 = \beta_5 = \frac{1}{4} J_{vm}^2 R_C D \rho \nu (1 - 2\sigma), \alpha_6 = \beta_6 = D^3 R_C \rho \nu.$$

The above conditions reduce the equations (43) and (44) to following form

$$\alpha_2 \delta^5 + \alpha_1 \delta^4 - \alpha_5 \delta^2 - (\alpha_3 + \alpha_4) \delta - \alpha_6 = 0 \quad (63)$$

$$\beta_2 \delta^5 - \beta_1 \delta^4 + \alpha_5 \delta^2 + (\beta_3 + \beta_4) \delta + \alpha_6 = 0 \quad (64)$$

3. If we introduce the conditions from point 2, to equations (47) and (48) we can write

$\alpha_1 = \beta_1 = \gamma_1$ ,  $\alpha_3 = \beta_3 = \alpha_4 = \beta_4 = \gamma_2$  and  $\alpha_6 = \beta_6 = \gamma_3$ . Reduction number of equations from two to one is a consequence of this conditions. Now, this equation can be written as

$$\gamma_1 \delta^4 - 2\gamma_2 \delta - \gamma_3 = 0 \quad (65)$$

where  $\gamma_1 = g \left( \frac{\partial \rho}{\partial C} \right) D \omega \Delta \pi$ ,  $\gamma_2 = D^2 \rho \nu R_C \omega RT$ ,  $\gamma_3 = D^3 R_C \rho \nu$ .

## CONCLUSIONS

In the paper we presented the mathematical model of the volume and solute flows through artificial polymeric membrane under occurrence of the concentration boundary layers on both sides of this membrane is presented. This nonlinear model, based on the Kedem-Katchalsky and Rayleigh equations, describes the volume flux generated by osmotic and hydrostatic forces, thicknesses of the concentration boundary layers, concentrations and hydrostatic pressures on the membrane-concentrations boundary layers' borders. Besides, this model shows that the volume flows and individual forces causes the flows influences on the thickness of concentration boundary layers.

The starting point of this model is an equation (5) which contains unknown concentrations ( $C_i$ ,  $C_e$ ) and pressures ( $P_i$ ,  $P_e$ ) in borders of concentration boundary layers-membrane. These concentrations and pressures can be calculated. The equation (15) which transforms equation (5) to equation (17) is a result of calculation. The methods of calculations of  $C_i$  and  $C_e$  proposed in the paper lead to pairs of equations: (23), (24) and (30), (31), alternatively. Regarding these equations in equation (17) leads to two third order equations for volume flux, in which coefficients occurring at  $J_v$  in the same power differ from each other (see eqs. 26-29 and 33-36). In equations (26)-(29) and (33)-(36) the thicknesses of

concentrations boundary layers occur. The equations (25)-(29) and (39)-(46), and (32)-(36) and (49)-(60) make two alternative mathematical models of membrane transport of non-homogenous solutions. The nonlinear equations for volume flux, concentration and thickness of concentration boundary layers can be used to numerical calculation in linear regime of the hydrodynamical stability.

## LITERATURE

- [1] KEDEM O., KATCHALSKY A.: Thermodynamics analysis of the permeability of biological membranes to non-electrolytes. *Biochem. Biophys. Acta* (1958), 27, 229-246.
- [2] KEDEM O., KATCHALSKY A.: Permeability of composite membranes. Part. I. Electric current, volume flow and flow of solute through membranes, *Trans. Faraday Soc.* (1963), 59, 1918-1928.
- [3] KATCHALSKY A.: Membrane permeability and the thermodynamics of irreversible processes. In: *Membrane transport and metabolism* A. Kleinzeller, A. Kotyk (eds.) Symposja CSAV, Prague, 1961, pp. 60-86
- [4] HOSHIKO T., LINDLEY B. D.: Phenomenological description of active transport of salt and water. *J. Gen. Physiol.* (1967), 50, 729-758.
- [5] DAINITY J.: Water relations of plant cells. *Adv. Bot. Res.* (1963), 1, 279-326.
- [6] GINZBURG B. Z., KATCHALSKY A.: The frictional coefficients of the flows of nonelectrolytes through artificial membranes. *J. Gen. Physiol.* (1963), 47, 403-418.
- [7] ŚLĘZAK A., TURCZYŃSKI B.: Modification of the Kedem-Katchalsky equations. *Biophys. Chem.* (1986), 24, 173-178.
- [8] ŚLĘZAK A.: Irreversible thermodynamic model equations of the transport across a horizontally mounted membrane. *Biophys. Chem.* (1989), 34, 91-102.
- [9] KARGOL M.: A more general form of Kedem and Katchalsky's practical equations. *J. Biol. Phys.* (1996), 2215-26.
- [10] KARGOL A.: Modified Kedem-Katchalsky equations and their applications. *J. Membrane. Sci.* (2000), 174, 43-53.
- [11] KATCHALSKY A., Curran P.F.: *Nonequilibrium thermodynamics in biophysics*, Harvard Univ. Press, Cambridge, 1965.
- [12] PEDLEY T. J.: Calculation of unstirred layer thickness in membrane transport experiments. *Quart. Rev. Biophys.* (1983), 16, 115-150.
- [13] BARRY P. H., DIAMOND J. M.: Effects of unstirred layers on membrane phenomena. *Physiol. Rev.* (1984), 64, 763-872.
- [14] ŚLĘZAK A., DWORECKI K., ANDERSON J. E.: Gravitational effects on transmembrane flux: the Rayleigh-Taylor convective instability. *J. Membr. Sci.* (1985), 23, 71-81.
- [15] DWORECKI K., ŚLĘZAK A., WĄSIK S.: Temporal and spatial structure of the concentration boundary layers in membrane system. *Physica A* (2003), 326, 360-369.
- [16] POHL P., SAPAROV S. M., ANTONENKO Y. N.: The size of the unstirred layer as a function of the solute diffusion coefficient. *Biophys. J.* (1998), 75, 1403-1409.
- [17] RUBINSTEIN I., STAUDE E., KEDEM O.: Role of the membrane surface in concentration polarization at ion-exchange membrane. *Desalination* (1988), 69, 101-114.
- [18] RUBINSTEIN I., ZALTZMAN B.: Electro-osmotically induced convection at a permselective membrane, *Phys. Rev. E* (2000), 62, 2238-2251.
- [19] SPIEGLER K. S.: Polarization at ion exchange membrane-solution inter-face. *Desalination* (1971), 9, 367-385.

- [20] RUBINSTEIN I., MALETZKI F.: Electroconvection at an electrically inhomogeneous permselective membrane surface. *J. Chem. Soc. Faraday Trans.* (1991), 87, 2079-2087.
- [21] VASIL'EVA V. I., GRIGORCHUK O. V., SHAPOSHNIK V. A.: Limiting current density in electromembrane systems with weak electrolytes. *Desalination* (2006), 192, 401-407.
- [22] MURHY W. D., MANZANARES J. A., MAFE S., REISS H.: A numerical study on the equilibrium and nonequilibrium diffuse double layer in electrochemical cells. *J. Phys. Chem.* (1992), 96, 9983-9991.
- [23] RUBINSTEIN I., SEGEL L.A.: Breakdown of a stationary solution to the Nernst-Planck-Poisson equations, *J. Chem. Soc. Faraday Trans.* (1979), 759, 36-940.
- [24] RUBINSTEIN I., ZALTZMAN B.: Electroosmotic slip of the second kind and instability in concentration polarisation at electrodialysis membranes. *Mathemat. Models Method. Appl. Sci.* (2001), 11, 263-300.
- [25] DWORECKI K.: Interferometric investigations of the near-membrane diffusion layers. *J. Biol. Phys.* (1995), 21, 37-49.
- [26] SCHLICHTING H., GERSTEN K.: *Boundary layer theory*, Springer, Berlin, 2000.
- [27] ŚLĘZAK A., ŚLĘZAK I. H., ZYSKA A., JASIK-ŚLĘZAK J., BRYLL A.: Mathematical model equation of the volume flows through polymeric membrane of heterogeneous non-ionic solutions. *Polym. Med.* (2005), 35, 13-18.
- [28] ŚLĘZAK A., ŚLĘZAK I.H., ŚLĘZAK K.: Influence of the concentration boundary layers on membrane potential in a single-membrane system. *Desalination* (2005), 184, 113-123.
- [29] JARZYŃSKA M.: The application of practical Kedem-Katchalsky equation in membrane transport. *Central Eur. J. Phys.* (2006), 4, 429-438.
- [30] DWORECKI K., ŚLĘZAK A., ORNAL-WĄSIK B., WĄSIK S.: Evolution of concentration field in a membrane system. *J. Biochem. Biophys. Methods* (2005), 62, 153-162.
- [31] FISCHBARG J., L.I. j., KUANG K., ECHEVARRIA M., ISEROVICH P.: Determination of volume and water permeability of platea cells from measurements of light scattering. *Am. J. Physiol.* (1993), 265, C1412-C1423.
- [32] GRZEGORCZYN S., ŚLĘZAK A.: Time characteristics of electromotive force in single-membrane cell for stable and unstable conditions of reconstructing of concentration boundary layers. *J. Membr. Sci.* (2006), 280, 485-493.
- [33] ANTONENKO Y. N., POHL P., ROSENFELD E.: Visualization of the reaction layer in the Immediate. *Archiv. Biochem. Biophys.* (1996), 333, 225-232.
- [34] SISTAT P., POURELLY G.: Chronopotentiometric response of an ion exchange membrane in the underlimiting current range. *Transport phenomena within the diffusion layers. J. Membr. Sci.* (1997), 123, 121-131.
- [35] KROL J.J., WESSLING M., STRATHMANN H.: Chronopotentiometry and overlimiting ion transport through monopolar ion exchange membranes. *J. Membr. Sci.* (1999), 162, 155-164.
- [36] FERNANDEZ-SEMPRE J., RUIZ-BEVIA F., SALCEDO-DIAZ R.: Measurements by holographic interferometry of concentration profiles in dead-end ultrafiltration of polyethylene glycol solutions. *J. Membr. Sci.* (2004), 229, 187-197.
- [37] DWORECKI K., ŚLĘZAK A., ORNAL-WĄSIK B., WĄSIK S.: Effect of hydrodynamic instabilities on solute transport in a membrane system. *J. Membr. Sci.* (2005), 265, 94-100.
- [38] WINNE D.: Unstirred layer as a diffusion barrier in vitro and in vivo. In: *Intestinal absorption and secretion*. F. Skadhause and K. Heintse (eds.) MTP-Press, Lancaster, 1981, 21-38.
- [39] LEVITT M. D., STROCCHI D., LEVITT G.: Human jejunum unstirred layer: evidence for extremely efficient luminal stirring. *Am. J. Physiol.* (1992), 262, 593-596.
- [40] COTTON C.U., REUSS L.: Measurement of the effective thickness of the mucosal unstirred layer in Necturus gallbladder epithelium. *J. Gen. Physiol.* (1989), 93, 631-647.
- [41] MCLAUGHIN S. G. A., DILGER J. P.: Transport of protons across membranes by weak acids, *Physiol. Rev.* (1980), 60, 825-863.
- [42] WINNE D.: Unstirred layer, source of biased Michaelis constant in membrane transport. *Biochim. Biophys. Acta* (1973), 298, 27-31.
- [43] PEPPENHEIMER J. R.: Role of pre-epithelial "unstirred" layers in a absorption of nutrients



- from the human jejunum. J. Membr. Biol. (2001), 179, 185-204.
- [44] COGOLI A., GMUNDER F. K.: Gravity effects on single cells: techniques, findings and theory. Adv. Space Biol. Med. (1991), 1, 183-248.
- [45] ŚLĘZAK A., BRYLL A.: Membrane transport of the non-homogeneous non-electrolyte solutions: a numerical study of the influence of volume flows in creation of concentration boundary layers in binary solutions. Polym. Med. (2006) in preparation.
- [46] ŚLĘZAK A., BRYLL A., GRZEGORCZYN S.: A numerical study of the hydrodynamic stable concentration boundary layers in a membrane system. J. Biol. Phys. (2006) in preparation.

Authors address:

Department of Biology and Biophysics  
Częstochowa University of Technology  
36b Armia Krajowa Al., PL-42200 Częstochowa, Poland  
tel. (034) 325 0395  
tel./fax (034)361 3876  
e-mail: [ajslezak@zim.pcz.czest.pl](mailto:ajslezak@zim.pcz.czest.pl)

Adres do korespondencji:

42-575 Strzyżowice  
ul. Podwale 23,  
e-mail: [ajslezak@zim.pcz.czest.pl](mailto:ajslezak@zim.pcz.czest.pl)

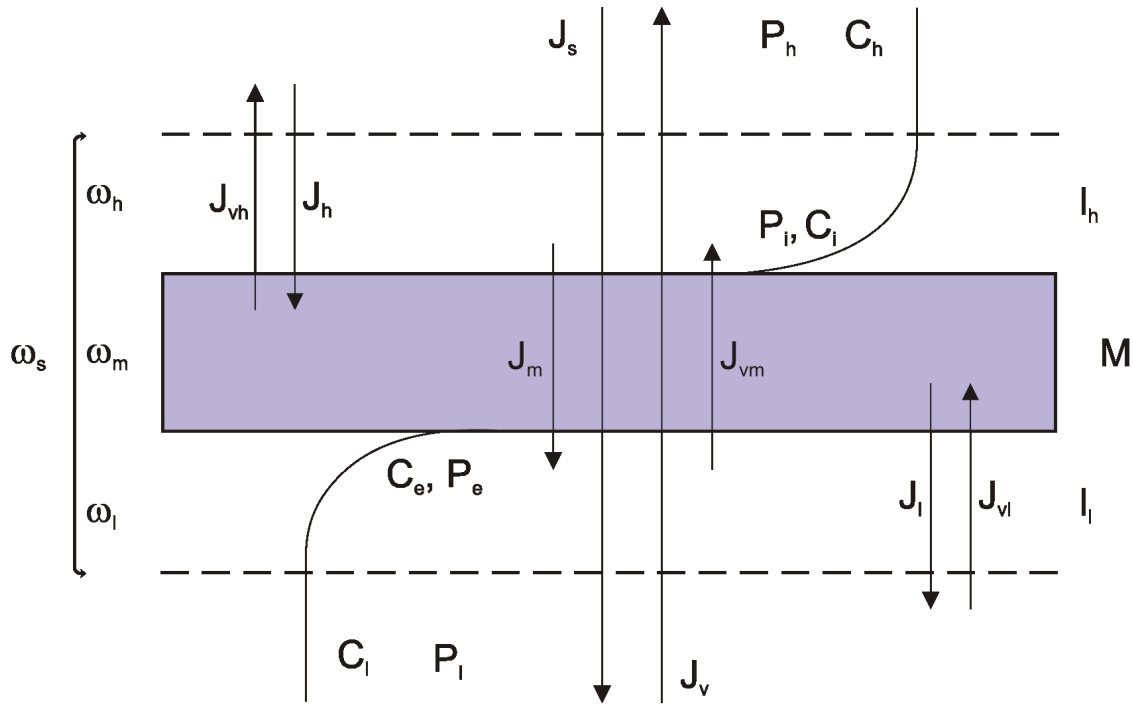


Fig. The membrane system: M – membrane;  $l_l$  and  $l_h$  – the concentration boundary layers (CBLs);  $\omega_s$ ,  $\omega_l$ ,  $\omega_m$  and  $\omega_h$  – the solute permeability coefficients;  $P_l$  and  $P_h$  – the mechanical pressures outside the boundaries;  $P_e$  and  $P_i$  – the mechanical pressure at boundaries  $l_l/M$  and  $M/l_h$ ;  $C_l$  and  $C_h$  – the concentrations of solutions outside the boundaries;  $C_e$  and  $C_i$  – the concentrations of solutions at boundaries  $l_l/M$  and  $M/l_h$ ;  $J_{vl}$ ,  $J_{vh}$ ,  $J_{vm}$  and  $J_v$  – the volume fluxes through the layers  $l_l$ ,  $l_h$ , membrane M and complex  $l_l/M/l_h$  respectively;  $J_l$ ,  $J_h$ ,  $J_m$  and  $J_s$  – the solute fluxes through the layers  $l_l$ ,  $l_h$ , membrane M and complex  $l_l/M/l_h$  respectively;

Rys 1. Układ membranowy: M – membrana;  $l_l$  i  $l_h$  – stężeniowe warstwy graniczne (CBLs);  $\omega_s$ ,  $\omega_l$ ,  $\omega_m$ ,  $\omega_h$  – współczynniki przepuszczalności substancji rozpuszczonej;  $P_l$  i  $P_h$  – ciśnienia hydrostatyczne za zewnątrz warstw;  $P_e$  i  $P_i$  – ciśnienia mechaniczne na granicach  $l_l/M$  oraz  $M/l_h$ ;  $C_l$  i  $C_h$  – stężenia roztworów na zewnątrz warstw;  $C_e$  i  $C_i$  – stężenia roztworów na granicach  $l_l/M$  oraz  $M/l_h$ ;  $J_{vl}$ ,  $J_{vh}$ ,  $J_{vm}$  i  $J_v$  – strumienie objętościowe odpowiednio przez warstwy  $l_l$  i  $l_h$ , membranę M oraz kompleks  $l_l/M/l_h$ ;  $J_l$ ,  $J_h$ ,  $J_m$  i  $J_s$  – strumienie substancji rozpuszczonej odpowiednio przez warstwy  $l_l$  i  $l_h$ , membranę M oraz kompleks  $l_l/M/l_h$ .

Table1. Interpretation of phenomenological coefficients

Tabela 1. Interpretacja współczynników fenomenologicznych

coefficient	definition				
	stirred solution	unstirred solutions			
	membrane (M)	layer (l <sub>l</sub> )	membrane (M)	layer (l <sub>h</sub> )	system (l <sub>l</sub> /M/l <sub>h</sub> )
hydraulic permeability	$L_p = \left( \frac{J_v}{\Delta P} \right)_{\Delta \pi = 0}$	$L_{pl} = \left( \frac{J_{vl}}{\Delta P_l} \right)_{\Delta \pi_l = 0}$	$L_{pm} = \left( \frac{J_{vm}}{\Delta P_m} \right)_{\Delta \pi_m = 0}$	$L_{ph} = \left( \frac{J_{vh}}{\Delta P_h} \right)_{\Delta \pi_h = 0}$	$L_{ps} = \left( \frac{J_{vs}}{\Delta P_s} \right)_{\Delta \pi_s = 0}$
reflection coefficient	$\sigma = \left( \frac{\Delta P}{\Delta \pi} \right)_{J_v = 0}$	$\sigma_l = \left( \frac{\Delta P_l}{\Delta \pi_l} \right)_{J_{vl} = 0}$	$\sigma_m = \left( \frac{\Delta P_m}{\Delta \pi_m} \right)_{J_{vm} = 0}$	$\sigma_h = \left( \frac{\Delta P_h}{\Delta \pi_h} \right)_{J_{vh} = 0}$	$\sigma_s = \left( \frac{\Delta P_s}{\Delta \pi_s} \right)_{J_{vs} = 0}$
solute permeability	$\omega = \left( \frac{J_s}{\Delta \pi} \right)_{J_v = 0}$	$\omega_l = \left( \frac{J_{sl}}{\Delta \pi_l} \right)_{J_{vl} = 0}$	$\omega_m = \left( \frac{J_{sm}}{\Delta \pi_m} \right)_{J_{vm} = 0}$	$\omega_h = \left( \frac{J_{sh}}{\Delta \pi_h} \right)_{J_{vh} = 0}$	$\omega_s = \left( \frac{J_{ss}}{\Delta \pi_s} \right)_{J_{vs} = 0}$