Transport of non-electrolyte solutions through membrane with concentration polarization

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Abstract. Mathematical model of the volume fluxes through neutral membrane with concentration boundary layers on both sides of this membrane is presented. This model, based on the Kedem-Katchalsky equations, describes the volume flux generated by osmotic and hydrostatic forces for non-homogeneous and non-electrolyte solutions. Nonlinear equation for volume flux was used for numerical calculation in linear regime of hydrodynamic stability. In the steady state of non-homogeneous solutions the dependence of volume flux on pressure difference is shifted with regard to this dependence for homogeneous solution, while the volume flux as a function of osmotic pressure between chambers is characterized by different angle of inclination for homogeneous and non-homogeneous solutions.

Key words: Membrane transport — Kedem-Katchalsky equations — Concentration boundary layers

Introduction

The Kedem-Katchalsky equations (KK equations) describing passive membrane transport were published in 1958 (Kedem and Katchalsky 1958). In the case of binary homogeneous and diluted solutions the transport can be described by volume (J_v) and solute (J_s) fluxes. Relationships between the fluxes and generating forces (ΔP and/or $\Delta\pi$) in the classic version of KK equations (Katchalsky and Curran 1965) are as follows:

$$J_v = L_p(\Delta P - \sigma\Delta\pi) \tag{1}$$

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

where: L_p, σ and ω 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 is product of the gas constant and thermodynamic temperature; C_h and C_l are solute concentrations in chambers)

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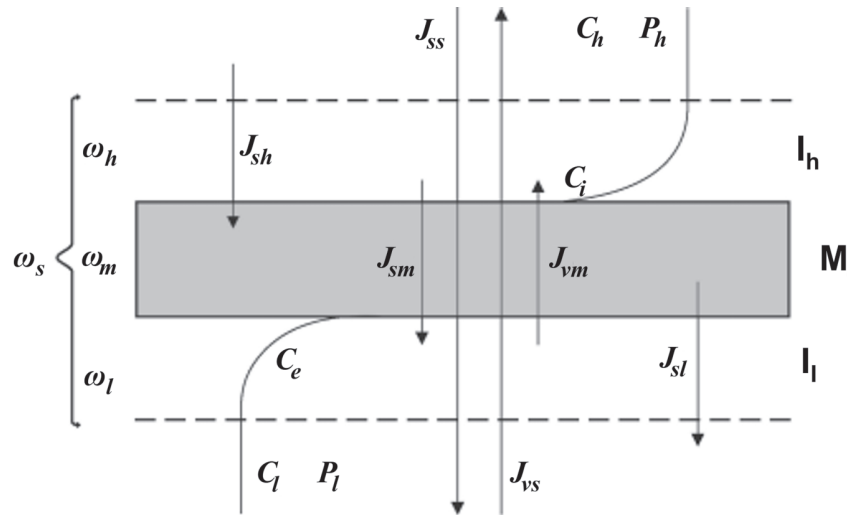E-mail: grzegorczyn@sum.edu.pl

$\overline{C} = (C_h - C_l)[\ln(C_h C_l^{-1})]^{-1} \approx 0.5 (C_h + C_l)$ represents the average solute concentration in membrane. As has been proved, KK equations are convenient exploratory tools of membrane transport (Katchalsky and Kedem 1962; Kedem and Katchalsky 1963; Axel 1976; Bresler and Groome 1981; Kiyosawa and Ogata 1987; Hempling and Katz 1989; Ślęzak 1989; Kargol and Kargol 2003; Liao at al. 2003; Dreher et al. 2006; Sun et al. 2007).

Spontaneously occurring transport processes lead to creation of local non-homogeneity in solutions called concentration polarization and are the cause of temporal evolution of thermodynamic fluxes and forces (Pedley 1983; Barry and Diamond 1984; Ślęzak et al. 1985; Kiyosawa and Ogata 1987; Ślęzak et al. 2006). In the case of transport of nonelectrolyte solutions through a neutral membrane, the concentration polarization consists in formation of the concentration boundary layers (CBLs) at both sides of this membrane (Pedley 1983; Barry and Diamond 1984; Ślęzak et al. 1985; Kiyosawa and Ogata 1987; Pohl et al. 1998; Dworecki et al. 2003; Ślęzak et al. 2006), which can be treated as a pseudomembrane (Barry and Diamond 1984; Ślęzak et al. 1985; Pohl et al. 1998). One of the effects of the temporal-spatial evolution of the concentration boundary layers is the evolution of the concentrations field, which

Figure 1. The membrane system: M – membrane; l$_l$ and l$_h$ – the concentration boundary layers (CBLs); ω_s, ω_l, ω_m and ω_h – the solute permeability coefficients; P_l and P_h – the mechanical pressures; 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_{vm} and J_{vs} – the volume fluxes through the membrane M and complex l$_l$/M/l$_h$, respectively; J_{sl}, J_{sh}, J_{sm} and J_{ss} – the solute fluxes through the layers l$_l$, l$_h$, membrane M and complex l$_l$/M/l$_h$, respectively.

causes that in the stationary state solute concentrations at interfaces membrane/solution (C_i, C_e) are crucially different from concentrations at the beginning (C_h, C_l). These concentrations fulfil conditions $C_l < C_e < C_i < C_h$ (Ślęzak et al. 1985; Kargol 2000). It means that these layers, by reducing the concentration gradient across the membrane, limit both the volume and solute fluxes. Concentration profiles in CBLs may be registered with optical methods (Barry and Diamond 1984; Ślęzak et al. 1985; Fischbarg et al. 1993; Dworecki 1995; Dworecki et al. 2003, 2005a). The modified form of KK equations for membrane system with CBLs (CBL/M/CBL) were elaborated by A. Kargol (Kargol 2000) on the basis of differential form of KK equations (Spiegler-Kedem equations). After integrating of these equations the complex form of equations on J_v and J_s were received and after Taylor series expansion the direct form of J_v and J_s as functions of membrane parameters (L_p, σ, ω) and CBL thickness (δ) were got.

In this paper, the mathematical model of the volume flux through neutral membrane under occurrence of the CBLs on both sides of that membrane is presented. We have developed this mathematical model by introducing a diffusion concentration polarization coefficient (ζ_{sD}). We introduced two forms of equations on osmotic flux through the membrane J_v, equivalent for the sake of ζ_{sD}. Moreover, we have used these nonlinear equations for volume flux in order to calculate volume flux as a function of mechanical or osmotic pressure in a linear regime of hydrodynamic stability.

The paper is organized as follows: we characterize the model of the membrane system and next we present the mathematical model of volume flux of non-homogeneous

non-electrolyte solutions based on the KK equations. As a result of these considerations, the third order equation for volume flux is obtained and solutions of that equation are discused. The coefficients, that appear in these equations, depend on concentration polarization coefficient, membrane parameters, difference of the mechanical and/or osmotic pressures and CBLs thicknesses.

Materials and Methods

Let us consider the single-membrane system presented in Fig. 1 whereby the compartments l and h, containing diluted and non-homogeneous (not mechanically stirred) binary solutions of the same non-electrolyte are separated by a porous, symmetrical, selective and electroneutral membrane M.

In this system water and dissolved substance diffusing through the membrane lead to formation of CBLs signed by l$_l$ and l$_h$, which can be treated as pseudomembranes (Barry and Diamond 1984; Kiyosawa and Ogata 1987). The thicknesses of these layers were denoted by δ_l and δ_h. 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 solute concentrations outside the boundaries are denoted by C_l and C_h. We denote the mechanical pressure by P_l and P_h ($P_h > P_l$). For unstirred solutions

$$\Delta\pi_m = RT(C_i - C_e) \qquad (3)$$

The membrane M is characterized by the hydraulic permeability (L_p), reflection (σ_m) and solute permeability (ω_m) coefficients. The layers l_l and l_h are characterized by the solute permeability coefficients ω_l and ω_h, respectively. The reflection and solute permeability coefficients of complex $l_l/M/l_h$ are denoted by σ_s and ω_s, respectively. The diffusion coefficients in layers l_l and l_h we denote by D_l and D_h, respectively. The following relation between coefficients ω_l, ω_h, ω_m and ω_s is fulfilled (Katchalsky and Curran 1965)

$$\omega_s^{-1} = \omega_m^{-1} + \omega_l^{-1} + \omega_h^{-1} \qquad (4)$$

where: $\omega_l = D_l (RT\delta_l)^{-1}$, $\omega_h = D_h (RT\delta_h)^{-1}$. The parameters L_p, σ_m, σ_s, ω_l, ω_h, ω_m and ω_s are defined by the expressions listed in previous papers (Katchalsky and Curran 1965; Schlichting and Gersten 2000).

Taking into consideration Eq. (3) in Eq. (1) we obtain

$$J_{vm} = L_p[\Delta P - \sigma_m RT(C_i - C_e)] \qquad (5)$$

The reflection coefficient of membrane is defined by the following equation

$$\sigma_m = \left[\frac{\Delta P_i}{RT(C_i - C_e)} \right]_{J_{vm}=0} \qquad (6)$$

The concentrations C_i and C_e can be calculated on the basis of Eq. (2) (Dworecki et al. 2005a; Ślęzak et al. 2005; Grzegorczyn and Ślęzak 2006) with assumptions that at steady state, the following conditions are fulfilled

$$J_{vm} = J_{vs} \qquad (7)$$

$$J_{sh} = J_{sm} = J_{sl} = J_{ss} \qquad (8)$$

In order to calculate these concentrations the following considerations will be made. For the membrane M, CBLs (l, h) and complex $l_l/M/l_h$ (s), Eq. (2) can be written in the forms

$$J_{sh} = D_h\delta_h^{-1}\Delta C_h + J_{vm}\overline{C}_h \qquad (9)$$

$$J_{sm} = \omega_m\Delta\pi_m + J_{vm}(1 - \sigma_m)\overline{C}_m \qquad (10)$$

$$J_{sl} = D_l\delta_l^{-1}\Delta C_l + J_{vm}\overline{C}_l \qquad (11)$$

$$J_{ss} = \omega_s\Delta\pi + J_{vm}\overline{C}(1 - \zeta_{sD}\sigma_m) \qquad (12)$$

where:

$\Delta C_h = C_h - C_i$	$\overline{C}_h = 0.5\,(C_h + C_i)$
$\overline{C}_h = 0.5(C_i + C_e)$	$\Delta C_l = C_e - C_l$
$\overline{C}_l = 0.5(C_e + C_l)$	$\omega_s = \zeta_{sD}\,\omega_m \,(0 \leq \zeta_{sD} \leq 1)$

and

$$\zeta_{sD} = D_l D_h [D_l D_h + RT\omega_m(D_h\delta_l + D_l\delta_h)]^{-1} \qquad (13)$$

Combining Eqs. (7)–(10) and (12) we obtain

$$C_i = [D_h C_h - \zeta_{sD}\omega_m\delta_h\Delta\pi + J_{vm}\delta_h(\zeta_{sD}\sigma_m\overline{C} - \tfrac{1}{2}C_l)] \\ (D_h - \tfrac{1}{2}J_{vm}\delta_h)^{-1} \qquad (14)$$

$$C_e = [D_l C_l + \zeta_{sD}\omega_m\delta_l\Delta\pi + J_{vm}\delta_l(\tfrac{1}{2}C_h - \zeta_{sD}\sigma_m\overline{C})] \\ (D_l + \tfrac{1}{2}J_{vm}\delta_l)^{-1} \qquad (15)$$

Taking into consideration Eqs. (14) and (15) in Eq. (5) we obtain

$$J_{vm}^{\,3} + \gamma_1 J_{vm}^{\,2} + \gamma_2 J_{vm} + \gamma_3 = 0 \qquad (16)$$

where:
$$\gamma_1 = -2\{(D_h\delta_l - D_l\delta_h) + \tfrac{1}{2}\zeta_{sL}L_p\delta_l\delta_h(\Delta P + \sigma_m\Delta\pi)]\} \\ (\delta_l\delta_h)^{-1} \qquad (16a)$$

$$\gamma_2 = 2\{L_p[\Delta P(D_h\delta_l - D_l\delta_h) - 2\sigma_m RT\overline{C}\zeta_{sD}\sigma_m \\ (D_l\delta_h + D_h\delta_l)] - 2D_l D_h\}(\delta_l\delta_h)^{-1} \qquad (16b)$$

$$\gamma_3 = 4L_p\{D_l D_h\Delta P - \sigma_m\Delta\pi[D_l D_h - \zeta_{sD}\omega_m RT \\ (D_l\delta_h + D_h\delta_l)]\}(\delta_l\delta_h)^{-1} \qquad (16c)$$

Combining Eqs. (7)–(11) we obtain other forms of concentrations C_i and C_e

$$C_i = \frac{\alpha_o + \alpha_1 J_{vm} + \alpha_2 J_{vm}^{\,2}}{\beta_o + \beta_1 J_{vm} + \beta_2 J_{vm}^{\,2}} \qquad (17)$$

$$C_e = \frac{\chi_o + \chi_1 J_{vm} + \chi_2 J_{vm}^{\,2}}{\beta_o + \beta_1 J_{vm} + \beta_2 J_{vm}^{\,2}} \qquad (18)$$

where:
$\alpha_0 = C_l D_l\delta_l^{-1}\omega_m RT + C_h D_h\delta_h^{-1}(\omega_m RT + D_l\delta_l)$
$\alpha_1 = 0.5\,[(\omega_m RT + D_l\delta_l^{-1})(C_h - C_l) + \sigma_m(C_h D_h\delta_h^{-1} + $
$\qquad + C_l D_l\delta_l^{-1})]$
$\alpha_2 = 0.25[C_l + \sigma_m(C_h - C_l)]$
$\beta_0 = \omega_m RT D_l\delta_l^{-1} + D_h\delta_h^{-1}(\omega_m RT + D_l\delta_l^{-1})$
$\beta_1 = 0.5\sigma_m(D_h\delta_h^{-1} - D_l\delta_l^{-1})$
$\beta_2 = 0.25(1 - 2\sigma_m)$
$\chi_0 = C_h D_h\delta_h^{-1}\omega_m RT + C_l D_l\delta_l^{-1}(\omega_m RT + D_h\delta_h^{-1})$
$\chi_1 = 0.5[(\omega_m RT + D_h\delta_h^{-1})(C_h - C_l) - \sigma_m(C_h D_h\delta_h^{-1} + $
$\qquad + C_l D_l\delta_l^{-1})]$
$\chi_2 = 0.25[C_h - \sigma_m(C_h - C_l)]$

Taking into consideration Eqs. (17) and (18) in Eq. (5) we obtain

$$J_{vm}^{\,3} + \xi_1 J_{vm}^{\,2} + \xi_2 J_{vm} + \xi_3 = 0 \qquad (19)$$

where:

$$\xi_1 = \{\beta_1 - L_p[\beta_2\Delta P - \sigma_m RT(\alpha_2 - \chi_2)]\}\beta_2^{-1} \qquad (19a)$$

$$\xi_2 = \{\beta_o - L_p[\beta_1\Delta P - \sigma_m RT(\alpha_1 - \chi_1)]\}\beta_2^{-1} \qquad (19b)$$

$$\xi_3 = -L_p[\beta_o\Delta P - \sigma_m RT(\alpha_o - \chi_o)]\beta_2^{-1} \qquad (19c)$$

The forms of Eqs. (16) and (19) are equivalent for the sake of Eq. (13).

Using Eqs. (14) and (15) in Eq. (6) we get

$$\sigma_m = \frac{D_l D_h}{D_l D_h - RT\zeta_{sD}\omega_m(D_l\delta_h + D_h\delta_l)}\left(\frac{\Delta P_i}{\Delta\pi}\right)_{J_{vm}=0} \qquad (20)$$

If we assume that for complex $l_l/M/l_h$, in steady state, $D_l = D_h = D$ we can write on the basis of Eqs. (13) and (20)

$$\sigma_m = \left[1 + \frac{RT\omega_m(\delta_l + \delta_h)}{D}\right]\sigma_s \qquad (21)$$

where $\sigma_s = (\Delta P_i/\Delta\pi)_{J_{vm}=0}$. Eq. (21) allows to count the reflection coefficient of the membrane (σ_m) in the case when the assurance of homogeneity of solutions divided by the membrane or determination of concentration gradient on the membrane ($C_i - C_e$) is impossible.

For the membrane system shown in Fig. 1, in which an artificial membrane mounted horizontally separates two aqueous ethanol solutions with concentrations $C_l = 0$ mol·m^{-3} (pure water) and C_h in the range from 0 to 800 mol·m^{-3}, numerical solutions of Eqs. (16) and (21) are presented. The calculations were performed by Mathcad 14.0 for isothermal conditions, $T = 295$ K. For numerical calculations, the following dependencies of the density and kinematic viscosity on the ethanol concentration were used: $\rho_h = (998.2 - 0.009\,C_h)$ kg·m^{-3} and $\nu_h = (1006.80 + 0.26\,C_h) \times 10^{-9}$ m^2·s^{-1} (Dworecki et al. 2005b). Because the diffusion coefficient of ethanol in the aqueous ethanol solution within the tested concentrations does not depend on concentration, the constant value of $D_l = D_h = D = 1.074 \times 10^{-9}$ m^2·s^{-1} (Dworecki et al. 2005b) was assumed for calculations. The transport properties of flat neutral membrane (membrane Nephrophan) are characterised by the coefficients: $\omega_m = 14.3 \times 10^{-10}$ mol·N^{-1}·s^{-1}, $\sigma_m = 0.025$ and $L_p = 5 \times 10^{-12}$ m^3·N^{-1}·s^{-1} (Ślęzak 1989; Dworecki et al. 2003).

Results and Discussion

The results of calculations of the volume flux (J_{vm}) in the dependence on parameters ΔP and $\Delta\pi$, respectively, were presented in Figs. 2 and 3. In the case of a stationary state of the membrane system with membrane in a horizontal plane, which divides two ethanol solutions with higher
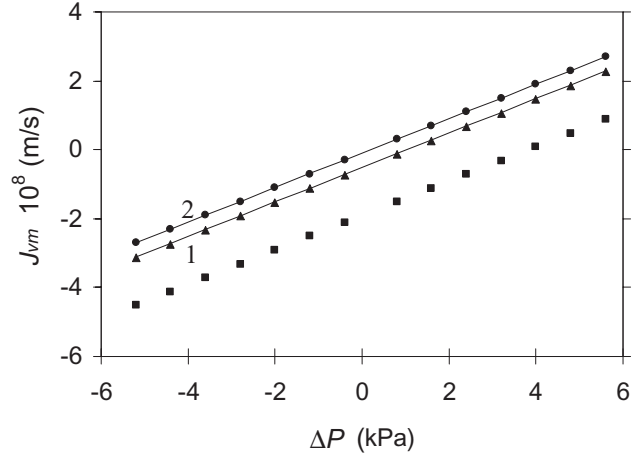

Figure 2. Graphic illustration of dependencies $J_{vm} = f(\Delta P)$ counted on the basis of Eq. (16) (lines 1 and 2) and from experiment (■, ▲, ●); for membrane system without CBLs (■), for membrane system with CBLs and with lower ethanol concentrations over the membrane (line 1 and ▲) and with higher ethanol concentrations over the membrane (line 2 and ●) for membrane Nephrophan ($\omega_m = 14.3 \times 10^{-10}$ mol·N^{-1}·s^{-1}, $\sigma_m = 0.025$ and $L_p = 5 \times 1^{-12}$ m^3·N^{-1}·s^{-1}) and fixed parameters: $\Delta\pi = 0.153$ MPa, $\zeta_{sD} = 0.28$ (line 1) and $\zeta_{sD} = 0.05$ (line 2).

concentration (lower density) over the membrane $(\zeta_{sD})_{stab} \approx 0.05$ and with lower concentration (higher density) over the membrane $(\zeta_{sD})_{unstab} \approx 0.28$ (Ślęzak 1989). For the case of diffusive states both δ_l and δ_h increase in time and in steady states CBLs thicknesses and volume fluxes reach stationary values (Dworecki et al. 2003). In this stationary state for aqueous ethanol solutions the CBLs thicknesses can be assumed as: $(\delta_l)_{stab} \approx (\delta_h)_{stab} = 2.9 \times 10^{-3}$ m in the case with higher ethanol concentration over the membrane, while in the case of diffusive-convective states (with lower ethanol concentration over the membrane) $(\delta_l)_{unstab} \approx (\delta_h)_{unstab} = 0.4 \times 10^{-3}$ m (Dworecki et al. 2005b).

In Fig. 2 the dependencies $J_{vm} = f(\Delta P)$ for membrane system with higher ethanol concentrations under the membrane (line 1 and ▲) and with higher ethanol concentrations over the membrane (line 2 and ●) are presented. These dependencies were counted on the basis of Eq. (16) (lines 1 and 2) and experimentally measured for the membrane system without CBLs (■), with CBLs (▲ and ●). Thicknesses of CBLs and ζ_{sD} in the model were assumed as $\delta_l = \delta_h = 0.0004$ m, $\zeta_{sD} = 0.28$ (graph 1) and $\delta_l = \delta_h = 0.0029$ m, $\zeta_{sD} = 0.05$ (graph 2), respectively. Besides the parameters: $\omega_m = 14.3 \times 10^{-10}$ mol·N^{-1}·s^{-1}, $\sigma_m = 0.025$, $L_p = 5 \times 10^{-12}$ m^3·N^{-1}·s^{-1} (for membrane Nephrophan) (Ślęzak 1989; Dworecki et al. 2003) and the osmotic pressure in the membrane system $\Delta\pi = 0.153$ MPa were used.

From Fig. 2 it results that volume flux through the membrane linearly depends on pressure difference on the mem-
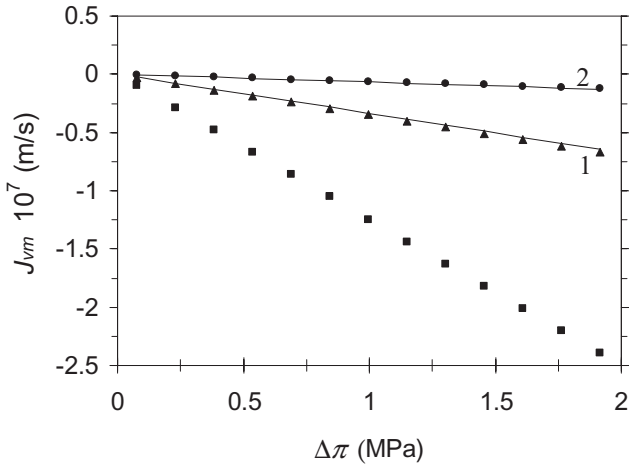
Figure 3. Graphic illustration of dependencies $J_{vm} = f(\Delta\pi)$ counted on the basis of Eq. (16) (lines 1 and 2) and from experiment (■, ▲, ●), for membrane system without CBLs (■), for membrane system with lower ethanol concentrations over the membrane (line 1 and ▲) and with higher ethanol concentrations over the membrane (line 2 and ●) for membrane Nephrophan ($\omega_m = 14.3 \times 10^{-10}$ mol·N^{-1}· s^{-1}, $\sigma_m = 0.025$ and $L_p = 5 \times 10^{-12}$ m^3·N^{-1}·s^{-1}) and fixed parameters: $\Delta P = 0$ Pa, $\zeta_{sD} = 0.05$ (line 2) and $\zeta_{sD} = 0.28$ (line 1).

brane for both homogeneous (■) and non-homogeneous solutions in stable (line 2 and ●) and unstable (line 1 and ▲) configurations. Non-homogeneity of solutions in near membrane areas caused by building up of CBLs is the cause of shifting of the dependence $J_{vm} = f(\Delta P)$ (without change of inclination coefficient) in comparison to $J_{vm} = f(\Delta P)$ for homogeneous solutions. Greater shift is observed for stable configuration. This is connected with greater changes of concentrations at membrane surfaces (C_i, C_e) during building up of CBLs in stable configuration than in unstable configuration. The experimental results for membrane Nephrophan (points 2 and 3) are in good agreement with prediction of the model (lines 1 and 2).

In Fig. 3 the dependencies $J_{vm} = f(\Delta\pi)$ for membrane system with higher ethanol concentrations under the membrane (line 1 and ▲) and with higher ethanol concentrations over the membrane (line 2 and ●) are presented. These dependencies were counted on the basis of Eq. (16) (lines 1 and 2) and experimentally measured for membrane system without CBLs (■) and for membrane system with CBLs (▲ and ●). In the model the values of CBLs thicknesses and ζ_{sD} were assumed respectively as $\delta_l = \delta_h = 0.0004$ m, $\zeta_{sD} = 0.28$ (line 1) $\delta_l = \delta_h = 0.0029$ m, $\zeta_{sD} = 0.05$ (line 2), for fixed parameters: $\omega_m = 14.3 \times 10^{-10}$ mol·N^{-1}·s^{-1}, $\sigma_m = 0.025$ and $L_p = 5 \times 10^{-12}$ m^3·N^{-1}·s^{-1} (Nephrophan membrane) (Ślęzak 1989; Dworecki et al. 2003) and $\Delta P = 0$ Pa.

From Fig. 3 it results linear dependence of $J_{vm} = f(\Delta\pi)$ for both homogeneous (experimental data ■) and non-homogeneous solutions for stable (line 2 and ●) and unstable (line 1 and ▲) configuration. The greatest coefficient of inclination of $J_{vm} = f(\Delta\pi)$ is for homogeneous solutions while the smallest is for stable configuration with CBLs. Smaller influence of osmotic pressure ($\Delta\pi$) on the volume flux in the case of stable configuration with CBLs is caused by smaller difference of that pressure on the membrane ($\Delta\pi_m$) in steady state of that configuration.

The thicknesses of CBLs from experiment, dependent on configuration of the membrane system for Nephrophan membrane were assumed in the model. As results from earlier paper (Ślęzak et al. 2006) CBLs thicknesses can be counted using Raileigh number. In order to calculate δ_l and δ_h we use the definition of concentration Rayleigh number, presented by equation (Barry and Diamond 1984; Schlichting and Gersten 2000)

$$R_C = g\alpha_C\beta_C d^4 (D\nu)^{-1} \qquad (22)$$

Where: g is the gravitational acceleration, d is the fluid depth along the gravitational (z) direction, $\alpha_C = (\partial\rho/\partial C)\rho^{-1}$ is the variation of density with concentration, $\beta_C = \partial C/\partial z$ is the concentration gradient, D is the solute diffusion coefficient and ν is kinematic viscosity. If we identify the thicknesses δ_l and δ_h of concentration boundary layers with d (Ślęzak et al. 1985), then using the relations

$$\alpha_{Cl}\beta_{Cl} = (\partial\rho/\partial C)(C_e - C_l)(\rho_l\delta_l)^{-1}$$

and

$$\alpha_{Ch}\beta_{Ch} = (\partial\rho/\partial C)(C_h - C_i)(\rho_h\delta_h)^{-1}$$

Eq. (22) can be written in the following forms:

$$\delta_l^3 = R_{Cl}D_l\rho_l\nu_l\left[g\left(\frac{\partial\rho}{\partial C}\right)(C_e - C_l)\right]^{-1} \qquad (23)$$

$$\delta_h^3 = R_{Ch}D_h\rho_h\nu_h\left[g\left(\frac{\partial\rho}{\partial C}\right)(C_h - C_i)\right]^{-1} \qquad (24)$$

Taking into account Eqs. (14) and (15) in Eqs. (23) and (24), respectively, we obtain the following system of equations:

$$\vartheta_1\delta_l^4 - \vartheta_2\delta_l = 1 \qquad (25)$$

$$\kappa_1\delta_h^4 + \kappa_2\delta_h = 1 \qquad (26)$$

where:

$\theta_1 = g[\zeta_{sD}\Delta\pi(\omega_m - 0.5L_p\sigma_m\mu_1) + 0.5L_p\mu_1\Delta P](R_{Cl}\rho_l\nu_lD_l^2)^{-1}$ $(\partial\rho/\partial C)$

$\theta_2 = 0.5L_pD_l^{-1}(\Delta P - \zeta_{sD}\sigma_m\Delta\pi)$

$\kappa_1 = g[\zeta_{sD}\Delta\pi(\omega_m + 0.5L_p\sigma_m\mu_2) + 0.5L_p\mu_2\Delta P](R_{Ch}\rho_h\nu_h$ $D_h^2)^{-1}(\partial\rho/\partial C)$

$$\kappa_2 = 0.5 L_p D_h^{-1}(\Delta P - \zeta_{sD}\sigma_m\Delta\pi)$$
$$\mu_1 = (C_h - C_l) - 2\zeta_{sD}\sigma_m\overline{C}$$
$$\mu_2 = (C_h - C_l) + 2\zeta_{sD}\sigma_m\overline{C}$$

For steady states of volume and solute fluxes, the concentration Rayleigh number depends on the concentration of ethanol in chambers (Dworecki et al. 2005). Experimental study shows that the thickness of CBL in steady state for membrane Nephrophan and ethanol solutions does not depend on the initial ethanol concentrations in chambers (Dworecki et al. 2005). Using in Eqs. (25) and (26) transport parameters of the membrane and foreseen values of concentration Rayleigh number in steady states, thicknesses of CBLs in steady states can be counted. Assuming for calculation: transport coefficients for membrane Nephrophan, $\Delta P = 0$, $C_h = 600$ mol·m^{-3}, $C_l = 0$ mol·m^{-3} and suitably for stable configuration $(R_C)_{stab} = 5 \times 10^5$, $\zeta_{sD} = 0.05$ and unstable configuration $(R_C)_{crit} = 1708$, $\zeta_{sD} = 0.28$ (Ślęzak 1989), we get CBLs thicknesses suitably for stable configuration $(\delta)_{stab} = 2.8 \times 10^{-3}$ m and unstable configuration $(\delta)_{crit} = 0.44 \times 10^{-3}$ m.

Building up of CBLs is the spontaneous process with diffusive character, revealing itself particularly in microgravity conditions (Cogoli and Gmünder 1991). In terrestrial conditions thicknesses of CBLs can be limited by processes caused hydrodynamic instability, for example gravitational convection (Dworecki et al. 2005), so taking into consideration CBLs is very important during measurement of reflection (σ) and diffusion permeability (ω) coefficients (Ye et al. 2006). The results of experimental study show that value of reflection coefficient of complex l$_l$/M/l$_h$ – σ_s is considerably lower than reflection coefficient of membrane σ_m and depends on hydrodynamic state of CBLs. For the hemodialyses Nephrophan membrane (Ślęzak 1989) and aqueous solution of ethanol with concentration $C_h = 250$ mol·m^{-3}, reflection coefficient appointed experimentally amounts to $(\sigma_m)_{ex} = 0.025$, while the reflection coefficient σ_s determined experimentally in conditions without convection amounts to $(\sigma_s)_{ex} = 1.22 \times 10^{-3}$. The thickness of CBL estimated on the basis of interferograms in the chamber with lower concentration C_l ($C_l < C_h$) and in the state with condition $J_s =$ const., performed by means of Mach-Zehnder interferometer for ethanol concentration $C_h = 250$ mol·m^{-3}, amounts to $(\delta)_{ex} = 2.91 \times 10^{-3}$ m. Taking into consideration the above mentioned values in Eq. (18) this gives $(\sigma_m)_{cal} = (2.44 \pm 0.10) \times 10^{-2}$, which is in agreement with $(\sigma_m)_{ex} = 2.5 \times 10^{-2}$. The calculations were performed for Nephrophan membrane and ethanol solutions $(\omega_m = 1.43 \times 10^{-9}$ mol·N^{-1}·s^{-1}, $D = 1.074 \times 10^{-9}$·m^2·s$^{-1})$ with concentrations $C_l = 0$ and $C_h = 250$ mol·m^{-3}.

Conclusions

The above studies allow the following conclusions and statements:

1. The mathematical model of the volume fluxes through artificial polymeric membrane with CBLs on both sides of this membrane is presented. This nonlinear model, based on the KK equations, describes the volume flux generated by osmotic and hydrostatic forces, concentrations on the membrane-concentrations boundary layers' borders.

2. As results from the model and experiment the dependences of $J_{vm} = f(\Delta P)$ are linear for both homogeneous and non-homogeneous solutions in steady states. For stable configuration the osmotic fluxes for given pressure difference are lower than for unstable configuration.

3. The dependencies $J_{vm} = f(\Delta\pi)$ are linear. As results from experiment and model the influence of $\Delta\pi$ on J_{vm} is greater for the case of unstable configuration than in the case of stable configuration.

4. Two ways of description of membrane system with CBLs: on the basis on differential form of KK equations (Kargol 2000) and presented in this article give linear dependencies of $J_{vm}(\Delta P)$ and $J_{vm}(\Delta\pi)$ in steady states, in spite of nonlinear equations on J_v.

5. Near-membrane CBLs can be taken into consideration as additional kinetics barriers in transport processes of rapidly permeating substances through natural and artificial membranes (Winne 1973, 1981; McLaughin and Dilger 1980; Cotton and Reuss 1989; Levitt et al. 1992; Peppenheimer 2001). The rate and effectiveness of chemical transformations within the CBLs are affected by the availability of the reactants. Near-membrane CBLs are the source of an inaccurate of the Michaelis constant in membrane transport (Winne 1973). The size of CBL seems to have regulatory functions. Variations in epithelial function or luminal stirring can for example readily influence the absorption of small molecules (McLaughin and Dilger 1980; Cotton and Reuss 1989). In terrestrial conditions, the concentration boundary layers can be destroyed by natural convection and sedimentation (Cogoli and Gmünder 1991).

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