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Evaluation the reflection coefficient of polymeric membrane in concentration polarization conditions

Ocena współczynnika odbicia membrany polimerowej w warunkach polaryzacji stężeniowej

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Summary

Introduction. The reflection coefficient of the membrane (σ) is one of the basic parameters of the polymer membrane transport. Classical methods used to determine this parameter require intensive mixing of two solutions separated by a membrane to eliminate the effects of concentration polarization. In the real conditions, especially in biological systems, this requirement is challenging. Thus, concentration boundary layers, which are the essence of the phenomenon of concentration polarization, form on both sides of the membrane.

Purpose. The main aim of this paper is to determine whether the value of reflection coefficient in a concentration polarization conditions depend on the concentration of solutions and hydrodynamic state of concentration boundary layers.

Materials and methods. In this paper, we used the hemodialysis membrane of cellulose acetate (Nephrophan) and aqueous glucose solutions as the research materials. Formalism of nonequilibrium thermodynamics and Kedem-Katchalsky equations were our research tools.

Results. Derived mathematical equations describe the ratio of reflection coefficients in a concentration polarization conditions (σ_s) and in terms of homogeneity of the solutions (σ). This ratio was calculated for the configuration in which the membrane was oriented horizontally. It was shown that each of the curves has a bifurcation point. Above this point, the value of the reflection coefficients depended on the concentration of the solution, the configuration of the membrane system and the hydrodynamic concentration boundary layers. Below this point, the system did not distinguish the gravitational directions.

Conclusion. The value of reflection coefficient of the hemodialysis membrane in a concentration polarization condition (σ_s) is dependent on both the solutions concentration and the hydrodynamic state of the concentration boundary layers. The value of this coefficient is the largest in the state of forced convection, lower – in natural convection state and the lowest in diffusive state. Obtained equations may be relevant to the interpretation of membrane transport processes in conditions where the assumption of homogeneity of the solution is difficult to implement (**Polim. Med. 2013, 43, 1, 11–19**).

Key words: osmosis, reflection coefficient, concentration boundary layers, Kedem Katchalsky equations.

Streszczenie

Wprowadzenie. Współczynnik odbicia membrany (σ) należy do grupy podstawowych parametrów transportowych membrany polimerowej. Klasyczna metodyka określania tego parametru wymaga intensywnego mieszania roztworów rozdzielanych przez membranę, w celu eliminacji efektów polaryzacji stężeniowej. W warunkach rzeczywistych, a szczególnie w układach biologicznych, wymóg ten jest trudny do realizacji. W związku z tym po obydwu stronach membrany tworzą się stężeniowe warstwy graniczne, stanowiące istotę zjawiska polaryzacji stężeniowej.

Cel. Celem pracy jest sprawdzenie, czy wartość współczynnika odbicia wyznaczana w warunkach polaryzacji stężeniowej, zależy od stężenia roztworów i stanu hydrodynamicznego stężeniowych warstw granicznych.

Materiał i metody. Materiałem badawczym była membrana hemodializacyjna z octanu celulozy (Nephrophan) i wodne roztwory glukozy. Narzędziem badawczym jest formalizm termodynamiki nierównowagowej oraz równania Kedem-Katchalsky'ego.

Wyniki. Wyprowadzono równania matematyczne opisujące stosunek współczynników odbicia w warunkach polaryzacji stężeniowej (σ_s) i w warunkach jednorodności roztworów (σ). Wykonano obliczenia tego stosunku dla konfiguracji, w których membrana była zorientowana horyzontalnie i wykazano, że każda z krzywych posiada punkt bifurkacyjny. Powyżej tego punktu, wartość stosunku współczynników odbicia zależy zarówno od stężenia roztworów, konfiguracji układu membranowego oraz stanu hydrodynamicznego stężeniowych warstw granicznych. Poniżej tego punktu, układ nie rozróżnia kierunków grawitacyjnych.

Wniosek. Wartość współczynnika odbicia hemodializacyjnej membrany polimerowej w warunkach polaryzacji stężeniowej (σ_s), jest zależna od stężenia roztworów i od stanu hydrodynamicznego stężeniowych warstw granicznych. Wartość tego współczynnika jest największa w stanie konwekcji wymuszonej, mniejsza – w stanie konwekcji swobodnej, a najmniejsza – w stanie dyfuzyjnym. Otrzymane równania mogą mieć znaczenie dla interpretacji procesów transportu membranowego w warunkach, w których założenie o jednorodności roztworów jest trudne do realizacji (**Polim. Med.** 2013, 43, 1, 11–19).

Słowa kluczowe: osmoza, współczynnik odbicia, stężeniowe warstwy graniczne, równania Kedem Katchalsky'ego

Introduction

The reflection (σ), hydraulic permeability (L_p) and diffusive permeability (ω) coefficients are the triad of membrane transport coefficients resulting from the A. Katchalsky and O. Kedem thermodynamic formalism [1–3]. This formalism is based on the equations describing the volume (J_v) and solute (J_s) fluxes. For homogeneous solutions of nonelectrolytes, these equations can be written as

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

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

where L_p – hydraulic permeability coefficient, σ – the coefficient of reflection, $\Delta P = P_h - P_l$ – hydrostatic pressure difference, $\Delta \pi = RT(C_h - C_l)$ – osmotic pressure difference, RT – product of gas constant and thermodynamic temperature, C_h and C_l – solutions concentrations in the chambers separated by a membrane, ω – solute permeability coefficient,

$\bar{C} = (C_h - C_l) [\ln(C_h C_l^{-1})]^{-1} \approx 0.5(C_h + C_l)$ – the average concentration of the solution in a membrane.

Homogeneity of solutions can be accomplished by their vigorous stirring with a mechanical stirrers placed in the solutions on both sides of the membrane. Such conditions can be ensured only in the macroscopic membrane systems [4]. In biological systems the homogeneity of the solutions is difficult to achieve [5–8]. Coefficient σ in the conditions of solutions homogeneity can be defined by the following expression resulting from Eq. (1)

$$\sigma = \left(\frac{\Delta P}{\Delta \pi} \right)_{J_v=0} \quad (3)$$

Values of this coefficient are in the following range $0 \leq \sigma \leq 1$. If $\sigma = 0$, then the membrane is indiscriminate. The fulfillment of condition $\sigma = 1$ is required for the semi-permeable membrane [2]. Eqs. (1) and (2) can be applied for both a membrane considered as black box and a porous membrane. For porous membrane the reflection coefficient it referred to individual pore of membrane and equals 1 or 0 [9].

In case of non-homogeneous solutions, i.e. without

mechanical stirring, concentration boundary layer (l_h , l_l) are created on both sides of the membrane (M), and treated as liquid membranes [10–17]. The thickness of these layers in the steady-state equals to δ_h and δ_l . Importantly, concentrations boundary layers (l_l , l_h) are components of the complex $l_l/M/l_h$ and therefore they do not appear as separate objects. Creation of these layers and their time-space evolution is a manifestation of concentration polarization effect. For layers l_h and l_l as well as for complex $l_h/M/l_l$, certain transport properties can be assigned according to Kedem-Katchalsky thermodynamic formalism. This means that the Kedem-Katchalsky equations can be used for the analysis of transport in the concentration polarization conditions.

Similar to previous paper [18] we consider single-membrane system shown in Fig. 1. This figure illustrates a membrane system with concentration boundary layers (l_h , l_l) created on both sides of the membrane. The membrane, which is an integral part of this system, is electroneutral and selective for dissolved substances. Membrane is mounted in the horizontal plane and separates compartments (h) and (l) filled with diluted and mechanically unstirred solutions of the same substances with concentrations of C_h and C_l ($C_h > C_l$) at the initial moment. Only at the initial moment ($t = 0$), these solutions are homogeneous throughout the solutions and at the membrane interface. Therefore, in steady-state concentration of solutions on the contacts l_h/M and M/l_l change according to the values of C_i and C_e ($C_h > C_i > C_e$, $C_i > C_e > C_l$).

In steady-state, the volume and solute fluxes through the membrane are denoted as the J_{vm} and J_{sm} , respectively. For the situation shown in Fig. 1, the fluxes J_{vm} ($J_{vm} = J_{vs} < J_v$) and J_{sm} ($J_{sm} = J_{ss} < J_s$) can be described using Eqs. (1) and (2) [13,14]. These equations can be written as

$$J_{vm} = L_p \Delta P_s - L_p \sigma RT (C_i - C_e) \quad (4)$$

$$J_{sm} = \omega_m RT (C_i - C_e) + \frac{1}{2} J_{vm} (1 - \sigma) (C_i + C_e) \quad (5)$$

Transport properties of layers l_l and l_h are characterized by the coefficients of: reflection fulfilling the condition $\sigma_l = \sigma_h = 0$, the coefficients of diffusion

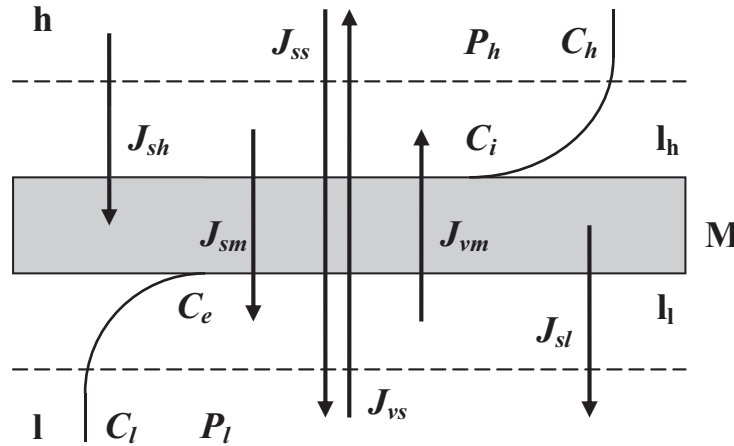


Fig. 1. A single-membrane system: M – membrane; l_l and l_h – the concentration boundary layers; P_h and P_l – mechanical pressures; C_l and C_h – concentrations of solutions outside the boundaries; C_e and C_i – the concentrations of solutions at boundaries l_l/M and M/l_h ; J_{vm} – the volume fluxes through membrane M; J_{vs} – the volume flux through complex $l_l/M/l_h$; J_{sb} , J_{sh} and J_{sm} – the solute fluxes through layers l_l , l_h and membrane; J_{ss} – the solute fluxes through a complex $l_l/M/l_h$ [19]

Ryc. 1. Układ jedno-membranowy: M – membrana; l_l i l_h – stężeniowe warstwy graniczne; P_h and P_l – ciśnienia mechaniczne; C_l i C_h – stężenia roztworów na zewnątrz warstw; C_e i C_i – stężenia roztworów na granicach l_l/M i M/l_h ; J_{vm} – strumień objętościowy przez membranę M; J_{vs} – strumień objętościowy przez kompleks $l_l/M/l_h$; J_{sb} , J_{sh} i J_{sm} – strumienie substancji rozpuszczonej przez warstwy l_l , l_h i membranę; J_{ss} – strumień substancji rozpuszczonej przez kompleks $l_l/M/l_h$ [19]

D_l and D_h and coefficients of solute permeability ω_l and ω_h , respectively. Coefficients ω_h and ω_l are associated with thicknesses δ_h and δ_l and diffusion coefficients D_l and D_h , by expression $\omega_h = D_h(RT\delta_h)^{-1}$ and $\omega_l = D_l(RT\delta_l)^{-1}$ [20]. Solute fluxes through the layers l_l and l_h are indicated by J_{sl} and J_{sh} , respectively. It can be described by using Eq. (2) [13,14]

$$J_{sl} = \omega_l RT(C_e - C_l) + \frac{1}{2} J_{vl}(C_e + C_l) \quad (6)$$

$$J_{sh} = \omega_h RT(C_h - C_i) + \frac{1}{2} J_{vh}(C_h + C_i) \quad (7)$$

Volume and solute fluxes through complex $l_l/M/l_h$, denoted by J_{vs} and J_{ss} , respectively, can be represented by using the following expressions [12]

$$J_{vs} = L_p \Delta P_s - L_p \sigma_s RT(C_h - C_h) \quad (8)$$

$$J_{ss} = \omega_s RT(C_h - C_h) + \frac{1}{2} J_{vs}(1 - \sigma_s)(C_h + C_h) \quad (9)$$

The reflection (σ_s) and solute permeability (ω_s) coefficients describe the transport properties of the complex $l_l/M/l_h$. In addition, coefficients σ_s and ω_s , that appear in Eqs. (8) and (9), can be defined by the following expressions resulting from Eqs. (8) and (9) [12]

$$\sigma_s = \left(\frac{\Delta P_s}{\Delta \pi} \right)_{J_{vs}=0} \quad (10)$$

$$\omega_s = \left(\frac{J_{ss}}{\Delta \pi} \right)_{J_{vs}=0} \quad (11)$$

In steady-state, the following relations $J_{sl} = J_{sm} = J_{sh} = J_{ss}$ and $J_{vm} = J_{vs}$ are fulfilled. The coefficients ω_s , ω_m , ω_l and ω_h for binary solutions, in con-

dition of diffusion ($J_{vs} = 0$), are related with following expression $\omega_s = \omega_l \omega_h (\omega_h \omega_l + \omega \omega_l + \omega \omega_h)^{-1}$ [2]. This expression can also be written as $\omega_s = \omega D_l D_h [D_h D_l + RT\omega(D_l \delta_h + D_h \delta_l)]^{-1}$ [2,20]. The ratio of coefficients ω_s and ω , defines a dimensionless diffusion coefficient of concentration polarization (ζ_s) [21]

$$\zeta_s = \frac{D_h D_l}{D_h D_l + \omega RT(D_l \delta_h + D_h \delta_l)} \quad (12)$$

The values of this coefficient fulfill the relation: $(\zeta_s)_{\min} \leq \zeta_s \leq 1$. This means that the concentration polarization is maximal when $\zeta_s \rightarrow (\zeta_s)_{\min}$ and minimal when $\zeta_s \rightarrow 1$.

By algebraic transforming of Eqs. (5) – (7), in the steady state, expressions for the concentrations C_i and C_e can be derived [13–15]. Considering these expressions in Eq. (5), we obtain

$$J_{vm}^3 + \lambda_1 J_{vm}^2 + \lambda_2 J_{vm} + \lambda_3 = 0 \quad (13)$$

where

$$\lambda_1 = \beta_1 - L_p[\beta_2 \Delta P_s - \sigma RT(\alpha_2 - \chi_2)]$$

$$\lambda_2 = \beta_0 - L_p[\beta_1 \Delta P_s - \sigma RT(\alpha_1 - \chi_1)]$$

$$\lambda_3 = -L_p[\beta_0 \Delta P_s - \sigma RT(\alpha_0 - \chi_0)]$$

$$\alpha_0 = C_l D_l \delta_l^{-1} \omega RT + C_h D_h \delta_h^{-1} (\omega RT + D_l \delta_l^{-1})$$

$$\alpha_1 = 0.5[(\omega RT + D_l \delta_l^{-1})(C_h - C_l) + \sigma(C_h D_h \delta_h^{-1} + C_l D_l \delta_l^{-1})]$$

$$\alpha_2 = 0.25[C_l + \sigma(C_h - C_l)]$$

$$\beta_0 = D_l \delta_l^{-1} \omega RT + D_h \delta_h^{-1} (\omega RT + D_l \delta_l^{-1})$$

$$\beta_1 = 0.5\sigma(D_h \delta_h^{-1} - D_l \delta_l^{-1})$$

$$\beta_2 = 0.25(1 - 2\sigma)$$

$$\chi_0 = C_h D_h \delta_h^{-1} \omega RT + C_l D_l \delta_l^{-1} (\omega RT + D_h \delta_h^{-1})$$

$$\chi_1 = 0.5[(\omega RT + D_h \delta_h^{-1})(C_h - C_l) - \sigma(C_h D_h \delta_h^{-1} + C_l D_l \delta_l^{-1})]$$

$$\chi_2 = 0.25[C_h - \sigma(C_h - C_l)]$$

In previous papers [13–15] we showed that Eq. (13) described the solution volume flux in condition of concentration polarization. This equation can be used to determine the effect of concentration polarization on the value of reflection coefficient of the membrane. In this paper, suitable expressions were derived for the reflection coefficient of the membrane, under diffusive and diffusive-convective conditions for $J_{vm} = 0$. These expressions showed that the value of reflection coefficient of the membrane determined under conditions of concentration polarization is dependent, among others, on a thickness of concentration boundary layers (δ), concentration of solutions (C_h , C_l) and hydrodynamic state of concentration boundary layers controlled by the concentration Rayleigh number (R_C). As an example, the obtained equations were applied for cellulose membrane and aqueous glucose solutions. The study was carried out for the membrane transport processes under conditions in which homogeneity of the solutions is difficult or even impossible to achieve.

Expressions for Ratio of Reflection Coefficients

For $J_{vm} = 0$ in Eq. (13) and upon simple algebraic transformations, we obtain

$$\left(\frac{\Delta P_S}{\Delta \pi}\right)_{J_{vm}=0} = \sigma \frac{D_h D_l}{D_h D_l + \omega RT(D_l \sigma_h + D_h \sigma_l)} = \sigma_S \quad (14)$$

In this equation, σ_S is the reflection coefficient of $I_l/M/I_h$ complex. This coefficient was determined experimentally in the macroscopic membrane systems. It should be noted that even an intense stirring of solutions with a mechanical stirrer did not fully eliminate the concentration boundary layers. Therefore, a calculated value ΔP_S (for $J_{vm} = 0$), under conditions of concentration polarization, was lower than a value of ΔP (for $J_{vm} = 0$) determined in a homogeneous solution conditions. In microscopic systems, such as biological systems, where the use of stirring of solutions separated by the membrane is difficult or even impossible, the coefficient σ_S instead of σ , is appointed. By transforming Eq. (15), we obtain an expression that enables the evaluation of the impact of concentration polarization on a value of reflection coefficient of a membrane in diffusive ($i = d$) and diffusive-convective ($i = k$) states.

$$\left(\frac{\sigma_S}{\sigma}\right)_i = \frac{1}{1 + \omega RT \left(\frac{\sigma_{ih}}{D_{ih}} + \frac{\sigma_{il}}{D_{il}} \right)} \quad (15)$$

Thicknesses δ_{ih} and δ_{il} presented in the above equation can be determined by optical methods [22–24] or

by volume flux measurement method [4,17]. When the concentrations boundary layers are symmetrical, and the diffusion coefficients (D_{dh} , D_{dl}) are independent of the concentration of solutions separated by the membrane, then conditions $\delta_{dh} = \delta_{dl} = \delta_d$ and $D_{dh} = D_{dl} = D_d$ are fulfilled. Therefore for the state of diffusion (non-convective), Eq. (15) can be written as

$$\left(\frac{\sigma_S}{\sigma}\right)_d = \frac{1}{1 + 2\omega RT \left(\frac{\sigma_d}{D_d} \right)} \quad (16)$$

In the diffusive-convective state acceptance of constant value of these coefficients is large approximation. Therefore, in order to describe the diffusion coefficients under diffusive-convective condition (D_{kh} , D_{kl}), the expressions presented in a previous paper [4] can be used

$$D_{kh} = \frac{g\alpha_{Ch}\delta_{kh}^3}{2\nu_h R_{Ch}} [(C_h - C_l) - (C_i - C_e)] \quad (17)$$

$$D_{kl} = \frac{g\alpha_{Cl}\delta_{kl}^3}{2\nu_l R_{Cl}} [(C_h - C_l) - (C_i - C_e)] \quad (18)$$

The difference $C_i - C_e$ can be calculated, taking into account Eq. (5) and (9) in condition when $J_{vm} = J_{vm} = 0$. As a result of relatively simple transformations, we can write

$$C_i - C_e = \xi_{sk}(C_h - C_l) \quad (19)$$

where $\xi_{sk} = \omega_S/\omega$.

The coefficient ξ_{sk} is given by Eq. (5). This coefficient can be determined experimentally [25]. Inserting Eq. (19) in Eqs. (17) and (18), we obtain

$$D_{kh} = \frac{g\alpha_{Ch}\delta_{kh}^3 (1 - \xi_{sk})(C_h - C_l)}{2\nu_h R_{Ch}} \quad (20)$$

$$D_{kl} = \frac{g\alpha_{Cl}\delta_{kl}^3 (1 - \xi_{sk})(C_h - C_l)}{2\nu_l R_{Cl}} \quad (21)$$

where g – acceleration of gravity, $\alpha_{Ch} = (\partial\rho/\partial C)/\rho$ and $\alpha_{Cl} = (\partial\rho/\partial C)/\rho_l$ relative change in mass density (ρ_h , ρ_l) with the concentration, ν_h and ν_l – kinematic viscosity, R_{Cl} and R_{Ch} – concentration Rayleigh number. By introducing Eqs. (20) and (21), into the Eq. (15), we obtain

$$\left(\frac{\sigma_S}{\sigma}\right)_k = \frac{1}{1 + \frac{2\omega RT}{g(1 - \xi_{sk})(C_h - C_l)} \left(\frac{\nu_h R_{Ch}}{\alpha_{Ch}\delta_h^2} + \frac{\nu_l R_{Cl}}{\alpha_{Cl}\delta_l^2} \right)} \quad (22)$$

Assuming that in Eq. (22) conditions $\delta_{kh} = \delta_{kl} = \delta_k$, $\nu_h = \nu_l = \nu$, $\alpha_{Ch} = \alpha_{Cl} = \alpha_C$ and $R_{Ch} = R_{Cl} = R_C$ we get

$$\left(\frac{\sigma_S}{\sigma}\right)_k = \frac{1}{1 + \frac{4\omega RT\nu R_C}{g\alpha_C(1 - \xi_{sk})(C_h - C_l)\delta_k^2}} \quad (23)$$

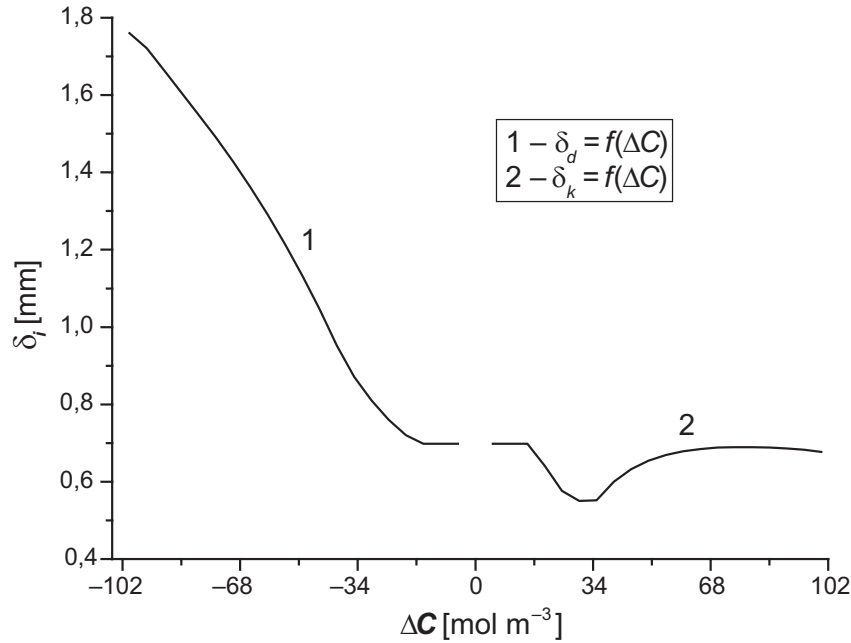


Fig. 2. Dependence of thickness of concentration boundary layers (δ_i) on the average concentration of glucose (ΔC) for the single-membrane system based on Ślęzak et al. paper [4]. Curve 1 illustrates a diffusive part ($i = d$), whereas curve 2 – a diffusive-convective part ($i = k$) of the characteristics $\delta_i = f(\Delta C)$

Ryc. 2. Zależność grubości stężeniowych warstw granicznych (δ_i) od różnicy stężeń glukozy (ΔC) dla układu jedno-membranowego opracowanie na podstawie pracy Ślęzak et al. [4]. Krzywa 1 ilustruje część dyfuzyjną ($i = d$) natomiast krzywa 2 – część dyfuzyjno-konwekcyjną ($i = k$) charakterystyki $\delta_i = f(\Delta C)$

Results and Discussion

We calculated the ratio $(\sigma_s/\sigma)_{i=d,k}$ for the Nephrophan membrane and aqueous glucose solutions under isothermal conditions ($T = 295$ K), using Eqs. (16) and (23), for the diffusive and diffusive-convective conditions. Diffusive conditions occur when the membrane system is oriented in configuration A for $\Delta C > 0$ and in configuration B for $\Delta C \leq 15$ mol m⁻³. Convective-diffusive conditions occur when the membrane system is oriented in configuration B and $\Delta C > 15$ mol m⁻³. The membrane transport parameters, i.e. hydraulic permeability (L_p), reflection (σ) and solute permeability (ω) coefficients, presented in a previous paper [12]. Their values are: $L_p = 5 \times 10^{-12}$ m³ N⁻¹s⁻¹, $\sigma = 0.068$ and $\omega = 0.8 \times 10^{-9}$ mol N⁻¹s⁻¹. We previously showed dependencies of $\delta_i = f(\Delta C)$ for configurations A and B [4]. Here we modified these dependences (see. Fig. 2) assuming that following conditions were fulfilled: $\Delta C < 0$ (configuration A) and $\Delta C > 0$ (configuration B). To calculate $(\sigma_s/\sigma_m)_{i=d}$ (for diffusion conditions), we used Eq. (17) and the constant values of glucose diffusion coefficient in an aqueous solution of glucose (D_d) and the universal gas constant (R): $D_d = 0.69 \times 10^{-9}$ m²s⁻¹ and $R = 8.31$ J mol⁻¹K⁻¹.

To estimate $(\sigma_s/\sigma)_{i=k}$ (for the diffusive-convective conditions), we used Eq. (23) and the following data $\rho_h = \rho_l(1 + \alpha_C C_h)$, $\nu_h = \nu_l(1 + \gamma_h C_h)$, where $\alpha_C = \rho_h^{-1} \partial \rho / \partial C = 6.01 \times 10^{-5}$ m³ mol⁻¹ and $\gamma_h = \nu_h^{-1}$

$^1 \partial \nu / \partial C = 3.95 \times 10^{-4}$ m³mol⁻¹, ($\rho_l = 998$ kg m⁻³, $\nu_l = 1.012 \times 10^{-6}$ m² s⁻¹). Values ζ_{sk} derived from the dependencies $\zeta_{si} = f(\Delta C)$ were presented in a previous paper [25]. The critical value of concentration Rayleigh number $(R_C)_{cr} = 1709.3$ was used previously [4]. Relations $(\sigma_s/\sigma)_{i=d,k} = f(\Delta C)$ calculated based Eqs. (16) and (23) were shown by solid line in Fig. 4.

To calculate the ratio σ_s/σ , let us consider Eqs. (1) and (8), assuming the condition $J_v = J_{vs} = 0$. Dividing both sides of these equations, we can write

$$\left(\frac{\sigma_s}{\sigma} \right)_{J_v = J_{vs} = 0} = \frac{\Delta P_s}{\Delta P} \quad (24)$$

From the above expression, it results that to determine the ratio σ_s/σ for membranes oriented in a horizontal plane, it is sufficient to designate the following dependences $\Delta P_s = f(\Delta C)$ for $J_{vs} = 0$ and $\Delta P = f(\Delta C)$ for $J_v = 0$, for either negative or positive ΔC in a series of independent experiments. To fulfill the condition $\Delta C < 0$, solution at a concentration of C_l filled compartment above the membrane and solution with a concentration of C_h – compartment below the membrane. This configuration of the membrane system is denoted by A. When $\Delta C > 0$, a solution with a concentration of C_l filled a compartment below the membrane, a solution with a concentration of C_h filled a compartment above the membrane (configuration B). Ratio σ_s/σ , calculated on the basis of the dependences $\Delta P_s = f(\Delta C)$ and

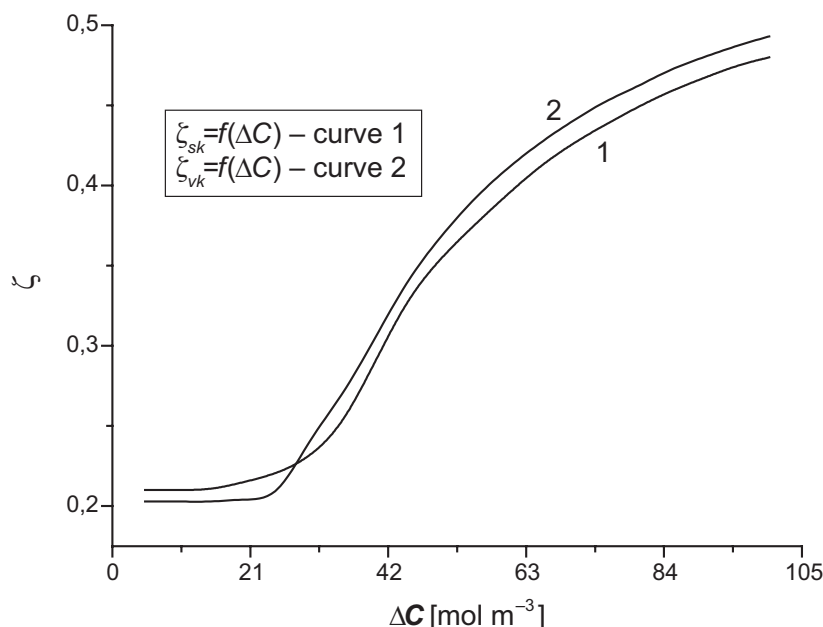


Fig. 3. Dependence of a diffusive-convective part (k) of the concentration polarization coefficient (ζ) on an average glucose solution concentration (ΔC) for the single-membrane system. Curve 1 illustrates the relation $\zeta_{sk} = f(\Delta C)$ for the diffusion concentration polarization coefficient (ζ_{sk}) and curve 2 illustrates the relation $\zeta_{vk} = f(\Delta C)$ for osmotic concentration polarization coefficient (ζ_{vk})

Ryc. 3. Zależność części dyfuzyjno-konwekcyjnej (k) współczynnika polaryzacji stężeniowej (ζ) od różnicy stężeń glukozy (ΔC) dla układu jedno-membranowego. Krzywa 1 ilustruje zależność $\zeta_{sk} = f(\Delta C)$ dla współczynnika dyfuzyjnego współczynnika polaryzacji stężeniowej (ζ_{sk}). Krzywa 2 ilustruje zależność $\zeta_{vk} = f(\Delta C)$ dla współczynnika osmotycznego współczynnika polaryzacji stężeniowej (ζ_{vk}).

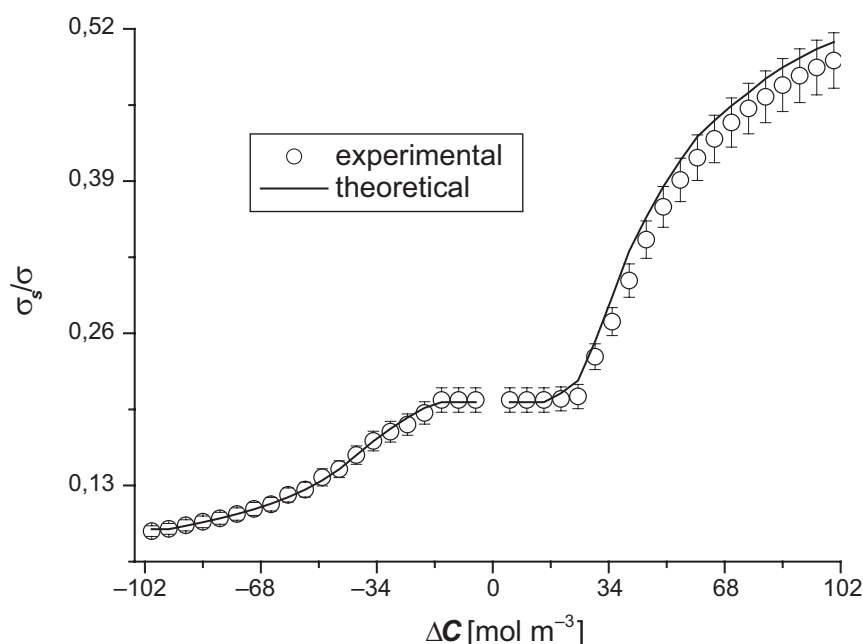


Fig. 4. Dependence of a ratio of reflection coefficients in conditions of concentration polarization (σ_s) and solution homogeneity (σ) on difference in glucose concentration (ΔC) in the single-membrane system, calculated from Eqs. (16) for $\Delta C \leq 0.15 \text{ mol m}^{-3}$ and (23) – for $\Delta C > 0.15 \text{ mol m}^{-3}$

Ryc. 4. Zależność stosunku współczynnika odbicia w warunkach polaryzacji stężeniowej (σ_s) i w warunkach jednorodności roztworów (σ) od różnicy stężeń glukozy (ΔC) dla układu jedno-membranowego, obliczone na podstawie równania (16) dla $\Delta C \leq 0.15 \text{ mol m}^{-3}$ i równania (23) – dla $\Delta C > 0.15 \text{ mol m}^{-3}$

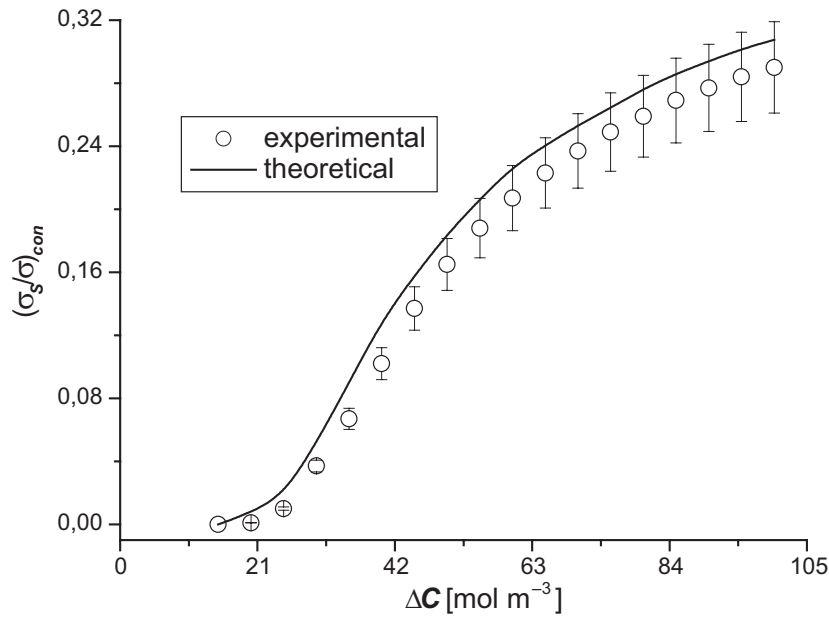


Fig. 5. Dependence of a convection part of reflection coefficients on the difference in glucose concentration (ΔC). In the single-membrane system, the reflection coefficient σ_S is calculated in conditions of concentration polarization and the reflection coefficient σ is calculated in conditions of homogeneity of solutions. Dependences were calculated from Eqs. (25) ($\circ$) and (26) (solid line) for $\Delta C > 0.15 \text{ mol m}^{-3}$

Ryc. 5. Zależność konwekcyjnej części stosunku współczynnika odbicia w warunkach polaryzacji stężeniowej (σ_S) i w warunkach jednorodności roztworów (σ) od różnicy stężeń glukozy (ΔC) dla układu jedno-membranowego, obliczone na podstawie równań (25) ($\circ$) i na podstawie równania (26) (linia ciągła) dla $\Delta C > 0,15 \text{ mol m}^{-3}$

$\Delta P = f(\Delta C)$, was represented ($\circ$) in Fig. 4. This figure shows good correlation (within 6% measurement error range) between experimental ($\circ$) and theoretical (solid line) results. The graph also indicates that for the ΔC fulfilling the condition $-15 \text{ mol m}^{-3} \leq \Delta C \leq 15 \text{ mol m}^{-3}$, σ_S/σ does not depend on ΔC . For ΔC fulfilling the condition $\Delta C < -15 \text{ mol m}^{-3}$, σ_S/σ decreases linearly, and for $\Delta C > 15 \text{ mol m}^{-3}$, σ_S/σ – increases linearly with increase of ΔC the absolute value. Moreover, both the experimental and the theoretical dependence for $-15 \text{ mol m}^{-3} > \Delta C > 15 \text{ mol m}^{-3}$ is asymmetric to the axis of ordinates. In previous papers [24] we named the ratio σ_S/σ as the coefficient of the osmotic concentra-

tion polarization and we denoted the ratio by ζ_v . For comparison, Fig. 3 presents the results of calculations $\zeta_{vk} = \sigma_S/\sigma = f(\Delta C)$. This figure shows that $\zeta_{vk} = \zeta_{vs}$ within 10% estimation error.

Based on the findings presented in Fig. 4, under convective conditions ratio σ_S/σ can be calculated as a difference

$$\left(\frac{\sigma_S}{\sigma} \right)_{con} = \left(\frac{\sigma_S}{\sigma} \right)_k - \left(\frac{\sigma_S}{\sigma} \right)_d \quad (25)$$

Inserting Eqs (23) and (17) in Eq. (25), the following expression can be written as

$$\left(\frac{\sigma_S}{\sigma} \right)_{con} = \frac{2\omega RT[gRT\alpha_C(1-\xi_{sk})(C_h - C_l)\delta_k^2\delta_d - 2\nu D_d R_C]}{[g\alpha_C(1-\xi_{sk})(C_h - C_l)\delta_k^2 + 4\omega RT\nu R_C][D_d + 2\omega RT\delta_d]} \quad (26)$$

The dependencies $(\sigma_S/\sigma)_{con} = f(\Delta C)$, calculated on the basis of Eqs. (26) and (27) are shown in Fig. 5. In Fig. 5, the solid line illustrating the dependences $(\sigma_S/\sigma)_{con} = f(\Delta C)$ that were calculated from Eq. (26), and the symbols ($\circ$) illustrated the results obtained from Eq. (25). This figure shows that the results obtained by both methods are consistent within 10% error range of ratio $(\sigma_S/\sigma)_{con}$ estimation. Fig. 4. shows that a point with coordinates $(\sigma_S/\sigma)_{con} = 0$ and $\Delta C = 0.15 \text{ mol m}^{-3}$ serves as a bifurcation point. This bifurcation point is a border between diffusive-convective and diffusive state.

This is one of many examples of the role of structure-thermodynamic environment in thermodynamic systems [26].

Conclusions

Presented mathematical expressions illustrate the dependence of the ratio (σ_S/σ) on physicochemical parameters of the solutions (ρ , ν , D), membrane transport parameters (ω_m) and concentrations Rayleigh number

(R_C). These expressions were derived from nonlinear Eq. (13) where the flux rate in a concentration polarization was described. Taking into account the obtained expressions, the calculations of ratio σ_s/σ were performed for Nephrophan membrane and aqueous solutions of glucose. The calculated curves presented in Fig. 4 and 5 have a bifurcation point in which $R_C = (R_C)_{crit}$. Above this point, i.e. in convective area, σ_s/σ de-

pends both on solution concentration and the hydrodynamic state of concentration boundary layers. Below this point, the system is in the area of diffusion (non-convection) and σ_s/σ depends solely on the concentration of the solutions. In biological systems, obtained results may be applied for interpretation of membrane transport processes under conditions of concentration polarization [5–8, 27].

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