

Network Hybrid Form of the Kedem–Katchalsky Equations for Non-homogenous Binary Non-electrolyte Solutions: Evaluation of P_{ij}^* Peusner's Tensor Coefficients

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Abstract Methods of Peusner's network of thermodynamics enable the symmetric or hybrid transformation of classic Kedem–Katchalsky (K–K) equations into a network form. In the case of binary non-electrolyte solutions (homogenous and non-homogenous ones), two symmetric and two hybrid forms of the K–K equations may be obtained, containing relatively symmetric (R_{ij}^* , R_{ij} , L_{ij}^* or L_{ij}), or hybrid (P_{ij}^* , P_{ij} , H_{ij}^* or H_{ij}) Peusner's coefficients. In the following paper, the network form of the K–K equations was obtained, containing the Peusner's coefficients P_{ij}^* ($i, j \in \{1, 2\}$), and creating matrix of the second row of the Peusner's coefficients [P^*]. The equations were used to study transport of aqueous glucose solutions through a Nephrophan membrane oriented horizontally as well as configurations A and B of a membrane system. The configuration A involves a solution with a higher concentration placed under the membrane, whereas a solution with a lower concentration is placed above the membrane. In the configuration B, the solutions are swapped with places. Dependences of the Peusner's coefficients P_{ij}^* and P_{ij} ($i, j \in \{1, 2\}$) for non-homogenous (P_{ij}^*) and homogenous (P_{ij}) solutions upon the average concentration of glucose in the membrane (\bar{C}) were calculated. The transport properties of membrane are characterized by coefficients determined experimentally: the coefficient of reflection (σ), hydraulic permeability (L_p), and solution permeability (ω) for aqueous glucose or ethanol solutions. The calculations show that values of coefficients P_{11}^* , P_{12}^* , P_{21}^* , and P_{22}^* depend non-linearly on both the membrane \bar{C} and the configuration of the membrane system. The values of the coefficients are different from the values of the coefficients P_{11} , P_{12} , P_{21} and P_{22} . Moreover, the coefficients P_{11} , P_{12} , P_{21} and P_{22} do not depend on the configuration of the membrane

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system. It was shown that there is a threshold value of concentration above which relations P_{11}^*/P_{11} , P_{12}^*/P_{12} and P_{22}^*/P_{22} depend on the configuration of the membrane system.

Keywords Membrane transport · Peusner's network thermodynamics · Kedem–Katchalsky equations · Concentration polarization · Peusner's coefficient

List of Symbols

R_{ij}, L_{ij}	Symmetric Peusner's coefficients for homogeneous solutions
P_{ij}	Hybrid Peusner's coefficients for homogeneous solutions
X_i	Thermodynamic forces in homogeneous conditions
J_i	Thermodynamic fluxes in homogeneous conditions
R_{ij}^*, L_{ij}^*	Symmetric Peusner's coefficients for non-homogeneous solutions
P_{ij}^*	Hybrid Peusner's coefficients for non-homogeneous solutions
X_i^*	Thermodynamic forces in non-homogeneous conditions
J_i^*	Thermodynamic fluxes in non-homogeneous conditions
L_p	Hydraulic permeability coefficient
J_v	Volume flux in homogeneous conditions
J_{vs}	Volume flux in non-homogeneous conditions
σ	Reflection coefficient
ω	Solute permeability coefficient
ν	Kinematic viscosity
ρ	Mass density of solution
δ_d, δ_k	Thickness of concentration boundary layers in diffusive (d) and convective (k) states
P_h, P_l	Hydrostatic pressure (h higher and l lower value)
$\Delta\pi$	Osmotic pressure difference
ΔP	Hydrostatic pressure difference
C_h, C_l	Solute concentrations in chambers of the membrane system
\bar{C}	Mean solute concentration in the membrane
R	Gas constant
R_C	Concentration Rayleigh number
T	Thermodynamic temperature
D_d, D_k	Diffusion coefficient in diffusive (d) and convective (k) states
ζ_p	Hydraulic concentration polarization coefficient
ζ_v	Osmotic concentration polarization coefficient
ζ_s	Diffusive concentration polarization coefficient
ζ_a	Advective concentration polarization coefficient
κ_{ij}	Asymmetry factor between configurations A and B

1 Introduction

Network thermodynamics (NT), created by Leonardo Peusner (Peusner 1970, 1986a) and George Oster, Alan Perelson, and Aharon Katchalsky (Oster et al. 1971; Perelson 1975) have introduced mathematical formalisms constituting one of many tools for analogical modeling of properties of complex systems functioning in different disciplines of science, technology, and medicine (Alhama et al. 2012; Bristow and Kennedy 2013; Imai 1996, 2003; Mikulecky

1990, 2005; Moya and Horno 2001, 2004; Peusner 1983a, b, 1985a, b, 1988, 2002; Peusner et al. 1985; Jamnik and Maier 2001; López-García et al. 1996). A version of NT worked out by Oster, Perelson and Katchalsky uses symbols of connectivity graphs (Oster et al. 1971), whereas the NT version worked out by Peusner (PNT) uses non-equilibrium thermodynamics and theory of electric circuits (Peusner 1970, 1986a). Despite different symbols, the both of versions are of equal importance (Peusner 1986a). One of the PNT use is the mathematical modeling of membrane transport (Batko et al. 2013a, b, c; Horno et al. 1989, 1990, 1992; Imai 1989, 1996, 2003; Imai et al. 1989; Horno and Castilla 1994; Szczepański et al. 2012; Szczepański and Wódzki 2013; Ślęzak et al. 2012; Wódzki et al. 2004) and micro-flows (Biscombe et al. 2014).

The original papers of Peusner (1983a, b, 1985a, b, 1986a) as well as papers of followers of his idea (Ślęzak et al. 2012; Batko et al. 2013a, b, c) show that PNT enables the symmetric or hybrid transformation of the membrane transport Kedem–Katchalsky (K–K) equations from the classic form into the network form. The network form of the equations includes new types of coefficients, called the Peusner’s tensor coefficients (Ślęzak et al. 2012; Batko et al. 2013a, b, c, 2014). The coefficients may be calculated by means of transport parameters determined experimentally, i.e., the coefficients of hydraulic permeability (L_p), solution permeability (ω), and reflection (σ) (Ślęzak et al. 2012; Batko et al. 2013a, 2014). In the case of binary non-electrolyte solutions, the transformation results in two symmetric and two hybrid forms of the K–K equations (Peusner 1983a, 1985a, 1986a). Under conditions of concentration polarization involving creation of concentration boundary layers (CBLs) at the both sides of the membrane (Barry and Diamond 1984; Kargol 1999, 2000; Ślęzak 1989), the symmetric network forms of the K–K equations contain the Peusner’s tensor coefficients R_{ij}^* or L_{ij}^* , whereas the hybrid network forms contain the Peusner’s tensor coefficients H_{ij}^* or P_{ij}^* ($i, j \in \{1, 2\}$) (Ślęzak et al. 2012; Batko et al. 2014). The network form of the K–K equations containing the Peusner’s coefficients R_{ij}^* ($i, j \in \{1, 2\}$) may be written in the following way (Ślęzak et al. 2012):

$$\begin{bmatrix} \Delta P - \Delta\pi \\ \frac{\Delta\pi}{\bar{C}} \end{bmatrix} = \begin{bmatrix} R_{11}^* & R_{12}^* \\ R_{21}^* & R_{22}^* \end{bmatrix} \begin{bmatrix} J_{vs} \\ J_{ss} \end{bmatrix} = [R^*] \begin{bmatrix} J_{vs} \\ J_{ss} \end{bmatrix}, \tag{1}$$

where $[R^*]$ is the matrix of Peusner’s coefficients R_{ij}^* ($i, j \in \{1, 2\}$) given by

$$[R^*] = \begin{bmatrix} \frac{\zeta_s\omega + \zeta_p L_p \bar{C} (1 - \zeta_v\sigma)(1 - \zeta_a\sigma)}{\zeta_p L_p \zeta_s \omega} & -\frac{1}{\zeta_s \omega} (1 - \zeta_v\sigma) \\ -\frac{1}{\zeta_s \omega} (1 - \zeta_a\sigma) & \frac{1}{\bar{C} \zeta_s \omega} \end{bmatrix}, \tag{1a}$$

where $\Delta P - \Delta\pi$, $\Delta\pi/\bar{C}$ are thermodynamic forces, $\Delta P = P_h - P_l$ is the hydrostatic pressure difference (P_h , P_l is the higher and lower value of hydrostatic pressure), $\Delta\pi = RT\Delta C$ is the osmotic pressure difference generated by the concentration difference $\Delta C = C_h - C_l$ (C_h , C_l are the higher and the lower value of concentration), J_v is the volume flux, J_{ss} is the dissolved substance flux, RT is the product of gas constant and absolute temperature, σ is the reflection coefficient, ω is the solution permeability coefficient, $\bar{C} = (C_h - C_l)[\ln(C_h C_l^{-1})]^{-1}$ is the average solution concentration in the membrane, J_{vs} and J_{ss} are the volume and solution fluxes, ζ_p , ζ_v , ζ_s , and ζ_a are, respectively, coefficients of hydraulic, osmotic, diffusive, and advective concentration polarization (Table 1).

Under the conditions of homogeneity of solutions separated by the membrane, i.e., when the condition $\zeta_p = \zeta_v = \zeta_s = \zeta_a = 1$ is fulfilled, Eqs. (1) and (1a) are simplified to the following expression (Peusner 1985a, 1986a)

$$\begin{bmatrix} \Delta P - \Delta\pi \\ \frac{\Delta\pi}{C} \end{bmatrix} = \begin{bmatrix} R_{11} & R_{12} \\ R_{21} & R_{22} \end{bmatrix} \begin{bmatrix} J_v \\ J_s \end{bmatrix} = [R] \begin{bmatrix} J_v \\ J_s \end{bmatrix}, \quad (2)$$

where $[R]$ is the matrix of Peusner's coefficients R_{ij} ($i, j \in \{1, 2\}$) given by

$$[R] = \begin{bmatrix} \frac{\omega + L_p \bar{C}(1-\sigma)^2}{L_p \omega} & -\frac{1}{\omega}(1-\sigma) \\ -\frac{1}{\omega}(1-\sigma) & \frac{1}{\bar{C}\omega} \end{bmatrix}. \quad (2a)$$

In Eq. (3), J_v ($J_v > J_{vs}$) and J_s ($J_s > J_{ss}$) stand for respectively the volume flux and the solution flux through the membrane under the conditions of homogeneity of solutions separated by the membrane. Determinants of the square matrix of Peusner's coefficients R_{ij}^* and R_{ij} are equal to $\det [R^*] = (\bar{C}\zeta_p\zeta_s L_p \omega)^{-1}$ and $\det [R] = (\bar{C}L_p \omega)^{-1}$, whereas the quotient of the determinants is equal to $\det [R^*]/\det [R] = (\zeta_p\zeta_s)^{-1}$.

Transforming Eq. (1) we get (Batko et al. 2014)

$$\begin{bmatrix} J_{vs} \\ J_{ss} \end{bmatrix} = \begin{bmatrix} L_{11}^* & L_{12}^* \\ L_{21}^* & L_{22}^* \end{bmatrix} \begin{bmatrix} \Delta P - \Delta\pi \\ \frac{\Delta\pi}{C} \end{bmatrix} = [L^*] \begin{bmatrix} \Delta P - \Delta\pi \\ \frac{\Delta\pi}{C} \end{bmatrix}, \quad (3)$$

where $[L^*]$ is the matrix of Peusner's coefficients L_{ij}^* ($i, j \in \{1, 2\}$) given by

$$[L^*] = \begin{bmatrix} \zeta_p L_p & \bar{C}(1-\zeta_v\sigma)\zeta_p L_p \\ \bar{C}(1-\zeta_a\sigma)\zeta_p L_p & \bar{C}[\zeta_s\omega + \bar{C}(1-\zeta_a\sigma)(1-\zeta_v\sigma)\zeta_p L_p] \end{bmatrix}. \quad (3a)$$

If the condition $\zeta_p = \zeta_v = \zeta_s = \zeta_a = 1$ is fulfilled, then Eqs. (3) and (3a) are simplified to the following expression (Peusner 1985a, 1986a)

$$\begin{bmatrix} J_v \\ J_s \end{bmatrix} = \begin{bmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{bmatrix} \begin{bmatrix} \Delta P - \Delta\pi \\ \frac{\Delta\pi}{C} \end{bmatrix} = [L] \begin{bmatrix} \Delta P - \Delta\pi \\ \frac{\Delta\pi}{C} \end{bmatrix}, \quad (4)$$

where $[L]$ is the matrix of Peusner's coefficients L_{ij} ($i, j \in \{1, 2\}$) given by

$$[L] = \begin{bmatrix} L_p & \bar{C}(1-\sigma)L_p \\ \bar{C}(1-\sigma)L_p & \bar{C}[\omega + \bar{C}(1-\sigma)^2 L_p] \end{bmatrix}. \quad (4a)$$

Determinants of the square matrix of Peusner's coefficients L_{ij}^* and L_{ij} are equal to $\det [L^*] = \bar{C}\zeta_p\zeta_s L_p \omega$ and $\det [L] = \bar{C}L_p \omega$ (Peusner 1985a, 1986a; Batko et al. 2014), whereas the quotient of the determinants is equal to $\det [L^*]/\det [L] = \zeta_p\zeta_s$.

Equations (1)–(4) may be derived by the symmetric transformation of the classic K–K equations using the methods of PNT (Peusner 1983a, 1985a, 1986a). In the case of homogenous non-electrolyte solutions, PNT implements four tensor coefficients into the study of membrane transport: L_{ij} , R_{ij} , P_{ij} and H_{ij} (Peusner 1983a, 1985a, 1986a). For non-homogenous solutions, the tensor coefficients are as follows: L_{ij}^* , R_{ij}^* , P_{ij}^* and H_{ij}^* . The coefficients P_{ij}^* are derived when in Eq. (1) places of $\Delta P - \Delta\pi$ and J_v are swapped, whereas the coefficients H_{ij}^* are derived when places of $\Delta\pi/\bar{C}$ and J_{ss} are swapped.

It results from Eqs. (1a) and (2a) that for the tensor Peusner's coefficients of the second degree R_{ij}^* and R_{ij} ($i, j \in \{1, 2\}$) we have $R_{12}^* = -(1-\zeta_v\sigma)\zeta_s^{-1}\omega^{-1} \neq R_{21}^* = -(1-\zeta_a\sigma)\zeta_s^{-1}\omega^{-1}$, $R_{12} = -(1-\sigma)\omega^{-1} \neq R_{21}$ (Ślęzak et al. 2012). By contrast, Eqs. (3a) and (4a) show that for the tensor Peusner's coefficients L_{ij}^* and L_{ij} ($i, j \in \{1, 2\}$) we have $L_{12}^* = \bar{C}(1-\zeta_v\sigma)\zeta_p L_p \neq L_{21}^* = \bar{C}(1-\zeta_a\sigma)\zeta_p L_p$, $L_{12} = \bar{C}(1-\sigma)L_p = L_{21}$ (Batko et al. 2014).

In the previous papers (Ślęzak et al. 2012; Batko et al. 2014), using the symmetric transformation of the classic K–K equations, the network form of the K–K equations was derived. The

network equations contain the tensor coefficients R_{ij}^* or L_{ij}^* , constituting the combination of the practical transport coefficients of membrane (L_p, σ, ω) and the average concentration of solutions in the membrane (\bar{C}). The equations were used to describe the membrane transport of aqueous glucose solution through a hemodialysis Nephrophan membrane under conditions of diffusion, and diffusion and convection simultaneously. The latter study includes the Rayleigh concentration number (R_C) used in equations describing the coefficients R_{ij}^* and L_{ij}^* . In the following paper, we are presenting the further network form of the K–K equations which were derived by the hybrid transformation of the classic K–K equations. The transformations were made by the methods of PNT. The equations derived contain the tensor coefficients P_{ij}^* ($i, j \in \{1, 2\}$). Similar to previous experiments, the derived equations are used for the study of the membrane transport of aqueous glucose solutions through the polymeric membrane under the conditions of diffusion, and diffusion and convection simultaneously. The coefficients $P_{11}^*, P_{12}^*, P_{21}^*$ and P_{22}^* are calculated for aqueous glucose solutions and for the hemodialysis Nephrophan membrane. Values of the coefficients are compared to values of the coefficients P_{11}, P_{12}, P_{21} and P_{22} calculated for the conditions of solution homogeneity and the same solution concentration but different configurations of the membrane system. The concentration dependence of the determinant of matrix quotient $[P^*]$ and $[P]$ is calculated.

2 Theory

The source of coefficients P_{ij}^* ($i, j \in \{1, 2\}$) under the conditions of concentration polarization, for a two-directional two-port of PNT with a single input for the flux J_1^* and the flux-coupled force X_1 , as well as a single input for the flux J_2^* and the flux-coupled force X_2 , is a hybrid equation (Ślęzak 2011a, 2011b)

$$\begin{bmatrix} J_1^* \\ X_2 \end{bmatrix} = \begin{bmatrix} P_{11}^* & P_{12}^* \\ P_{21}^* & P_{22}^* \end{bmatrix} \begin{bmatrix} X_1 \\ J_2^* \end{bmatrix}. \tag{5}$$

For the conditions of homogeneity of solutions separated by the membrane, the above equation is written as follows (Peusner 1983a, 1985a, 1986a)

$$\begin{bmatrix} J_1 \\ X_2 \end{bmatrix} = \begin{bmatrix} P_{11} & P_{12} \\ P_{21} & P_{22} \end{bmatrix} \begin{bmatrix} X_1 \\ J_2 \end{bmatrix}. \tag{6}$$

For the conditions of concentration polarization, the K–K equations may be written in the following way (Ślęzak et al. 2012)

$$J_{vs} = \zeta_p L_p \Delta P - \zeta_p L_p \zeta_v \sigma \Delta \pi, \tag{7}$$

$$J_{ss} = L_p \zeta_p (1 - \zeta_a \sigma) \bar{C} \Delta P + [\zeta_s \omega - L_p \zeta_p \sigma \zeta_v (1 - \sigma \zeta_a)] \Delta \pi. \tag{8}$$

In the above equations J_{vs} is the volume flux, and J_{ss} is the solution flux under the conditions of concentration polarization. By contrast, $\zeta_p, \zeta_v, \zeta_a$ and ζ_s are respectively hydraulic, osmotic, advective and diffusive coefficient of Katchalsky (Ślęzak et al. 2012).

Employing simple algebra, Eqs. (7) and (8) may be transformed into the following ones:

$$J_{vs} = \frac{L_p \zeta_{ps}}{\omega \zeta_s + L_p \zeta_p (1 - \sigma \zeta_v) (1 - \sigma \zeta_a) \bar{C}} [\omega \zeta_s (\Delta P - \Delta \pi) + (1 - \sigma \zeta_s) J_{ss}], \tag{9}$$

$$\frac{\Delta \pi}{\bar{C}} = \frac{1}{\omega \zeta_s + L_p \zeta_p (1 - \sigma \zeta_v) (1 - \sigma \zeta_a) \bar{C}} \left[-L_p \zeta_p (1 - \sigma \zeta_v) (\Delta P - \Delta \pi) + \frac{1}{\bar{C}} J_{ss} \right]. \tag{10}$$

The above system of equations is the further version (hybrid version) of the K–K transformed equations for the conditions of concentration polarization, which may be written in a form of matrix equation

$$\begin{bmatrix} J_{vs} \\ \frac{\Delta\pi}{C} \end{bmatrix} = \begin{bmatrix} P_{11}^* & P_{12}^* \\ P_{21}^* & P_{22}^* \end{bmatrix} \begin{bmatrix} \Delta P - \Delta\pi \\ J_{ss} \end{bmatrix} = [P^*] \begin{bmatrix} \Delta P - \Delta\pi \\ J_{ss} \end{bmatrix}, \quad (11)$$

where $[P^*]$ is the matrix of Peusner's coefficients P_{ij}^* ($i, j \in \{1, 2\}$) given by

$$[P^*] = \begin{bmatrix} \frac{L_p \zeta_p \omega \zeta_s}{\xi} & \frac{L_p \zeta_p (1 - \sigma \zeta_v)}{\xi} \\ -\frac{L_p \zeta_p (1 - \sigma \zeta_v)}{\xi} & \frac{1}{C \xi} \end{bmatrix}, \quad (11a)$$

where $\xi = [\omega \zeta_s + L_p \zeta_p (1 - \zeta_v \sigma)(1 - \zeta_a \sigma) \bar{C}]$.

It results from Eq. (11a) that for non-diagonal coefficients $P_{12}^* \neq P_{21}^*$ and $P_{12}^*/P_{21}^* = (\zeta_v \sigma - 1)/(1 - \zeta_a \sigma)$. Moreover, the matrix determinant $[P^*]$ is equal to

$$\det[P^*] = P_{11}^* P_{22}^* - P_{12}^* P_{21}^* = \frac{\zeta_p L_p}{\bar{C}[\zeta_s \omega + \bar{C} \zeta_p L_p (1 - \zeta_v \sigma)(1 - \zeta_a \sigma)]}. \quad (12)$$

For the conditions of homogeneity of solutions separated by a selective membrane, i.e., when the condition $\zeta_p = \zeta_v = \zeta_s = \zeta_a = 1$ is fulfilled, Eq. (4) is taking the following form (Peusner 1983a, 1985a, 1986a)

$$\begin{bmatrix} J_v \\ \frac{\Delta\pi}{C} \end{bmatrix} = \begin{bmatrix} P_{11} & P_{12} \\ P_{21} & P_{22} \end{bmatrix} \begin{bmatrix} \Delta P - \Delta\pi \\ J_s \end{bmatrix} = [P] \begin{bmatrix} \Delta P - \Delta\pi \\ J_s \end{bmatrix}, \quad (13)$$

where $[P]$ is the matrix of Peusner's coefficients P_{ij} ($i, j \in \{1, 2\}$) given by (Peusner 1983a, 1985a, 1986a)

$$[P] = \begin{bmatrix} \frac{L_p \omega \zeta_s}{\omega + L_p (1 - \sigma)^2 \bar{C}} & \frac{L_p (1 - \sigma)}{\omega + L_p (1 - \sigma)^2 \bar{C}} \\ -\frac{L_p (1 - \sigma)}{\omega + L_p (1 - \sigma)^2 \bar{C}} & \frac{1}{\bar{C}[\omega + L_p (1 - \sigma)^2 \bar{C}]} \end{bmatrix}. \quad (13a)$$

The determinant of the matrix $[P]$ is equal to

$$\det[P] = P_{11} P_{22} - P_{12} P_{21} = \frac{L_p}{\bar{C}[\omega + \bar{C} L_p (1 - \sigma)^2]}. \quad (14)$$

Considering Eqs. (11a) and (13a), we are deriving the following expression for the selective membrane

$$\frac{P_{11}^*}{P_{11}} = \frac{\zeta_p \zeta_s [\omega + \bar{C} (1 - \sigma)^2 L_p]}{\zeta_s \omega + \bar{C} \zeta_p L_p (1 - \zeta_v \sigma)(1 - \zeta_a \sigma)}, \quad (15)$$

$$\frac{P_{12}^*}{P_{12}} = \frac{\zeta_p L_p (1 - \zeta_v \sigma) [\omega + \bar{C} (1 - \sigma)^2 L_p]}{(1 - \sigma) [\zeta_s \omega + \bar{C} \zeta_p L_p (1 - \zeta_v \sigma)(1 - \zeta_a \sigma)]}, \quad (16)$$

$$\frac{P_{21}^*}{P_{21}} = \frac{\zeta_p L_p (1 - \zeta_a \sigma) [\omega + \bar{C} (1 - \sigma)^2 L_p]}{(1 - \sigma) [\zeta_s \omega + \bar{C} \zeta_p L_p (1 - \zeta_v \sigma)(1 - \zeta_a \sigma)]}, \quad (17)$$

$$\frac{P_{22}^*}{P_{22}} = \frac{\omega + \bar{C} (1 - \sigma)^2 L_p}{\zeta_s \omega + \bar{C} \zeta_p L_p (1 - \zeta_v \sigma)(1 - \zeta_a \sigma)}. \quad (18)$$

For a non-selective membrane ($L_p = L_{pmax}$, $\sigma = 0$ and $\omega = \omega_{max}$), Eqs. (15)–(18) are written in the following forms

$$\frac{P_{11}^*}{P_{11}} = \frac{\zeta_p \zeta_s [\omega_{max} + \bar{C} L_{pmax}]}{\zeta_s \omega_{max} + \bar{C} \zeta_p L_{pmax}}, \tag{15a}$$

$$\frac{P_{12}^*}{P_{12}} = \frac{\zeta_p L_{pmax} [\omega_{max} + \bar{C} L_{pmax}]}{\zeta_s \omega_{max} + \bar{C} \zeta_p L_{pmax}} = \frac{P_{12}^*}{P_{12}}, \tag{16a}$$

$$\frac{P_{22}^*}{P_{22}} = \frac{\omega_{max} + \bar{C} L_{pmax}}{\zeta_s \omega_{max} + \bar{C} \zeta_p L_{pmax}}. \tag{18a}$$

This results in $P_{11}^*/P_{11} = \zeta_s P_{12}^*/L_{pmax} P_{12}$, $P_{11}^*/P_{11} = \zeta_p \zeta_s P_{22}^*/P_{22}$ and $P_{12}^*/P_{12} = \zeta_p L_{pmax} P_{22}^*/P_{22}$. By contrast, for a partially selective membrane ($L_p > 0$, $\sigma = 1$ and $\omega = 0$) we have $P_{11}^*/P_{11} = P_{22}^*/P_{22} \rightarrow 0$ and $P_{12}^*/P_{12} = P_{21}^*/P_{21} \rightarrow +\infty$.

In order to make Eqs. (6)–(9) sensitive to hydrodynamic conditions, we may implement into them the Rayleigh concentration number (R_C). The number controls the processes of turning from diffusive state into convective state in the membrane systems (Ślęzak et al. 1985, 2010): when the number value is becoming critical, then turning from diffusive (stable) state into convective (non-stable) state is noticed. In the previous paper (Ślęzak et al. 2010) it was shown that the critical value of R_C is reached at a bifurcation point of the coordinates: $\bar{C} = 5.41 \text{ mol m}^{-3}$, $(R_C)_{crit.} = 1, 709.3$. To implement R_C into Eqs. (6)–(9), we are using procedure presented in a previous paper (Ślęzak et al. 2012). The paper showed that with a sufficient approximation, we may write as follows

$$\zeta_p = \zeta_a = 1, \tag{19}$$

$$\zeta_v = \zeta_p = \zeta_i. \tag{20}$$

By contrast, the coefficient ζ_i may be written with the equation (Katchalsky and Curran 1965; Ślęzak et al. 2012)

$$\zeta_i = D_i (D_i + 2RT\omega\delta_i)^{-1}, \tag{21}$$

where D_i is the diffusion coefficient, RT is the product of gas constant and thermodynamic temperature, δ_i is the thickness of CBL. For the diffusive conditions $i = d$, whereas for the convective conditions $i = k$.

Including Eq. (21) into Eqs. (15)–(18), we are deriving

$$\frac{P_{11}^*}{P_{11}} = \left(1 + \frac{2RT L_p \omega \bar{C} (1 - \sigma) \delta_i}{D_i [\omega + \bar{C} (1 - \sigma)^2 L_p]} \right)^{-1}, \tag{22}$$

$$\frac{P_{12}^*}{P_{12}} = \left(1 + \frac{2RT \omega \delta_i}{D_i (1 - \sigma)} \right) \left(1 + \frac{2RT L_p (1 - \sigma) \omega \bar{C} \delta_i}{D_i [\omega + \bar{C} (1 - \sigma)^2 L_p]} \right)^{-1}, \tag{23}$$

$$\frac{P_{21}^*}{P_{21}} = \left(1 + \frac{2RT \omega \delta_i}{D_i} \right) \left(1 + \frac{2RT L_p (1 - \sigma) \omega \bar{C} \delta_i}{D_i [\omega + \bar{C} (1 - \sigma)^2 L_p]} \right)^{-1} = \frac{P_{22}^*}{P_{22}}. \tag{24}$$

To derive Eqs. (16)–(18) for the diffusive conditions, the equations may be written assuming that $i = d$. Under non-convective (diffusive) conditions, the thickness of CBLs (δ_d) for $\bar{C} > (\bar{C})_{crit.}$ is larger than that one under the convective conditions (δ_k) and it depends on the

solution concentration (Ślęzak et al. 2012). The diffusion coefficient value under the diffusive conditions (D_d) is approximately constant, i.e., it does not depend on the concentration of non-electrolyte solutions diluted and is lower than the diffusion coefficient value under the convective conditions (D_k). Moreover, D_k depends on the solution concentration. The equation for the diffusion coefficient under convective conditions (D_k) may be written as follows (Ślęzak et al. 2012)

$$D_k = \frac{g\alpha_C \delta_k^3 (J_v - J_{vs})}{2L_p \sigma RT \nu RC}. \quad (25)$$

Including Eq. (25) in Eqs. (22)–(24), we are deriving

$$\frac{P_{11}^*}{P_{11}} = \left(1 + \frac{4(RT)^2 L_p^2 \omega \sigma (1 - \sigma) \bar{C} \nu RC}{g\alpha_C \delta_k^2 (J_v - J_{vs}) [\omega + \bar{C}(1 - \sigma)^2 L_p]} \right)^{-1}, \quad (26)$$

$$\frac{P_{12}^*}{P_{12}} = \left(1 + \frac{4(RT)^2 L_p \sigma \omega \nu RC}{g\alpha_C (1 - \sigma) \delta_k^2 (J_v - J_{vs})} \right) \left(1 + \frac{(RT)^2 L_p^2 \sigma \omega \bar{C} (1 - \sigma) \nu RC}{g\alpha_C \delta_k^2 (J_v - J_{vs}) [\omega + \bar{C}(1 - \sigma)^2 L_p]} \right)^{-1}, \quad (27)$$

$$\frac{P_{21}^*}{P_{21}} = \left(1 + \frac{4(RT)^2 L_p \sigma \omega \nu RC}{g\alpha_C \delta_k^2 (J_v - J_{vs})} \right) \left(1 + \frac{4(RT)^2 L_p^2 \sigma \omega \bar{C} (1 - \sigma) \nu RC}{g\alpha_C \delta_k^2 (J_v - J_{vs}) [\omega + \bar{C}(1 - \sigma)^2 L_p]} \right)^{-1} = \frac{P_{22}^*}{P_{22}}. \quad (28)$$

The equation for the diffusion coefficient under convective conditions (D_k) may also be written in the following form

$$D_k = \frac{g\alpha_C \delta_k^3 (J_s - J_{ss})}{2\omega RT \nu RC}. \quad (29)$$

Including Eq. (29) in Eqs. (22)–(24), we are deriving

$$\frac{P_{11}^*}{P_{11}} = \left(1 + \frac{4(RT)^2 L_p \omega^2 (1 - \sigma) \bar{C} \nu RC}{g\alpha_C \delta_k^2 (J_s - J_{sm}) [\omega + \bar{C}(1 - \sigma) L_p]} \right)^{-1}, \quad (30)$$

$$\frac{P_{12}^*}{P_{12}} = \frac{[g\alpha_C (1 - \sigma) (J_s - J_{sm}) \delta_k^2 + 4(RT)^2 \omega^2 \nu RC] [\omega + \bar{C}(1 - \sigma)^2 L_p]}{(1 - \sigma) \{g\alpha_C \delta_k^2 (J_s - J_{sm}) [\omega + \bar{C}(1 - \sigma) L_p] + 4(RT)^2 \omega^2 L_p \bar{C} (1 - \sigma) \nu RC\}}, \quad (31)$$

$$\frac{P_{21}^*}{P_{21}} = \frac{P_{22}^*}{P_{22}} = \frac{[g\alpha_C \delta_k^2 (J_s - J_{sm}) + 4(RT)^2 \omega^2 \nu RC] [\omega + \bar{C}(1 - \sigma)^2 L_p]}{g\alpha_C \delta_k^2 (J_s - J_{sm}) [\omega + \bar{C}(RT)^2 L_p] + 4(RT)^2 \omega^2 L_p \bar{C} \nu RC}. \quad (32)$$

Equations for δ_d and δ_k may be calculated using the equations below (Ślęzak et al. 2012)

$$\delta_d = -\frac{D_d}{2RT \omega_m} \left(1 - \frac{J_v}{J_{vs}} \right), \quad (33)$$

$$\delta_k = \frac{RT}{2(J_v - J_{vm})} \left(\frac{L_p \sigma \omega \nu RC}{g\alpha_C} \right)^{0.5}, \quad (34)$$

or

$$\delta_d = -\frac{D_d}{2RT \omega_m} \left(1 - \frac{J_s}{J_{ss}} \right), \quad (35)$$

$$\delta_k = \frac{\omega RT}{2(J_s - J_{sm})} \left(\frac{\nu RC}{g\alpha_C} \right)^{0.5}. \quad (36)$$

In the equations above J_v , J_{vs} ($J_v > J_{vs}$), J_s , J_{ss} ($J_s > J_{ss}$) may be determined in a series of independent experiments (Ślęzak et al. 2012). By contrast, the values δ_d and δ_k may be determined by optical methods (Dworecki et al. 2003; Dworecki et al. 2005). The Peusner’s coefficients P_{ij}^* and P_{ij} in the matrixes $[P^*]$ and $[P]$ may be linked by the determinant of matrix quotient, which may be written in the following way

$$\frac{\det[P^*]}{\det[P]} = \det \frac{[P^*]}{[P]} = \frac{P_{11}^* P_{22}^* - P_{12}^* P_{21}^*}{P_{11} P_{22} - P_{12} P_{21}} = \frac{\zeta_p[\omega + \bar{C}L_p(1 - \sigma)^2]}{\zeta_s\omega + \bar{C}\zeta_p L_p(1 - \zeta_v\sigma)(1 - \zeta_a\sigma)}. \tag{37}$$

Assuming that $\zeta_p = \zeta_a = 1$ and $\zeta_v = \zeta_s = \zeta$, and including Eqs. (21) and (25), then Eq. (37) can be written for the diffusive and convective state, respectively

$$\left(\det \frac{[P^*]}{[P]}\right)_d = \frac{[\omega + \bar{C}L_p(1 - \sigma)^2][D_d + 2RT\omega\delta_d]}{D_d[\omega + \bar{C}L_p(1 - \sigma)^2] + 2RT\bar{C}L_p\omega(1 - \sigma)\delta_d}, \tag{38}$$

$$\det \left(\frac{[P^*]}{[P]}\right)_k = \left[1 + \frac{4(RT)^2 L_p \sigma \omega \nu R_C}{g\alpha_C \delta_k^2 (J_v - J_{vs})}\right] \left[1 + \frac{4\bar{C}(RT)^2 L_p^2 \sigma \omega \nu (1 - \sigma) R_C}{g\alpha_C \delta_k^2 (J_v - J_{vs})[\omega + \bar{C}L_p(1 - \sigma)^2]}\right]^{-1}. \tag{39}$$

3 Calculations Results and Discussion

In order to calculate the coefficients P_{11}^* , P_{12}^* , P_{21}^* , P_{22}^* , P_{11} , $P_{12} = P_{21}$, P_{22} , P_{11}^*/P_{11} , P_{12}^*/P_{12} , P_{21}^*/P_{21} , P_{22}^*/P_{22} , as well as $\det([P^*]/[P])$ we are using the following data: $L_p = 4.9 \times 10^{-12} \text{ m}^3 \text{ N}^{-1} \text{ s}^{-1}$, $\sigma = 0.068$, $\omega = 0.8 \times 10^{-9} \text{ mol N}^{-1} \text{ s}^{-1}$, $C_h = 2.6 \text{ mol m}^{-3}$ do $C_h = 101 \text{ mol m}^{-3}$, $C_l = 2.6 \text{ mol m}^{-3}$, $D_d = 0.69 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, $\alpha_C = \rho_1^{-1} \partial \rho / \partial C = 6.01 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$, $\nu_h = \nu_l(1 + \gamma_1 C_h)$ when coefficients $\gamma_1 = \nu_1^{-1} \partial \nu / \partial C = 3.95 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1}$, $\nu_l = 1.012 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ and $(R_C)_{\text{crit.}} = 1, 709.3$ (Ślęzak et al. 2010; Ślęzak et al. 2012). The coefficient values L_p , σ and ω were determined under conditions of intensive stirring of solutions (Katchalsky and Curran 1965; Ślęzak 1989). Therefore, their values are independent of the membrane configuration, i.e., setup of the membrane and solutions separated by the membrane relative to a gravitation vector. According to Fig. 1, in the case of single-membrane system in which the membrane is placed horizontally, two configurations are distinguished, namely A and B (Ślęzak 1989). In the configuration A, the solution with the concentration C_l is in a compartment above the membrane, and with the concentration C_h —under the membrane. The diverse placement of solutions towards the membrane mounted horizontally is provided in the configuration B.

Under conditions of concentration polarization, i.e., when solutions separated by the membrane are not stirred mechanically, at the both sides of the membrane the CBLs are created limiting the volume and diffusive flows of the solution (Abu-Rjal et al. 2014; Barry and Diamond 1984; Jasik-Ślęzak et al. 2011; Kargol 1999, 2000; Ślęzak 1989; Wang et al. 2014). The CBLs are created as a result of molecular diffusion of a dissolved substance from the solution with the higher concentration into the solution with the lower concentration (Dworecki et al. 2003; Nikonenko et al. 2010; Wang et al. 2014). That fact may be included in equations introducing the additional/supporting coefficients ζ_p , ζ_v , ζ_s and ζ_a . For the haemodialysis Nephrophan membrane and aqueous glucose solutions, the coefficients ζ_v and ζ_s determined under the conditions of concentration polarization depend on the concentration of solutions separated by the membrane as well as on the configuration of membrane system (Ślęzak et al. 2012). By contrast, the coefficients ζ_p and ζ_a fulfill the condition $\zeta_p = \zeta_a = 1$ under conditions of solution homogeneity as well as conditions of concentration polarization

Table 1 Values of the volume fluxes of homogeneous solution (J_v), volume fluxes of non-homogeneous solution in diffusive–convective state (J_{vs}), osmotic (ζ_v) and diffusive (ζ_s) concentration polarization coefficient in configurations A (ζ_{vA} , ζ_{sA}) and B (ζ_{vB} , ζ_{sB}), and thicknesses of concentration boundary layers (δ_i) in diffusive (δ_d) and convective (δ_k) states for various mean concentrations of glucose (\bar{C} ; [Ślęzak et al. 2012](#))

\bar{C} (mol m ⁻³)	$J_v \times 10^8$ (m s ⁻¹)	$J_{vs} \times 10^8$ (m s ⁻¹)	ζ_v		ζ_s		$\delta_i \times 10^3$ (m)	
			ζ_{vA}	ζ_{vB}	ζ_{sA}	ζ_{sB}	δ_d	δ_k
2.7905	0.41	0.09	0.208	0.208	0.21	0.21	0.698	0.698
4.1703	0.80	0.17	0.208	0.208	0.21	0.21	0.698	0.698
5.4101	1.19	0.26	0.208	0.208	0.21	0.21	0.698	0.698
6.5692	1.61	0.34	0.200	0.209	0.205	0.215	0.720	0.641
7.6732	2.04	0.43	0.190	0.210	0.200	0.220	0.760	0.576
8.7362	2.41	0.55	0.176	0.220	0.183	0.230	0.810	0.550
9.7669	2.79	0.70	0.168	0.260	0.178	0.250	0.871	0.552
10.7713	3.21	0.95	0.155	0.285	0.164	0.290	0.952	0.600
11.7535	3.59	1.20	0.144	0.320	0.154	0.330	1.046	0.632
12.7167	4.02	1.45	0.134	0.348	0.141	0.355	1.133	0.654
13.6634	4.41	1.70	0.126	0.371	0.131	0.375	1.214	0.669
14.5954	4.79	1.95	0.120	0.390	0.122	0.388	1.291	0.679
15.5144	5.21	2.20	0.114	0.406	0.115	0.412	1.361	0.685
16.4216	5.60	2.45	0.110	0.420	0.109	0.422	1.428	0.688
17.3180	6.02	2.70	0.106	0.432	0.105	0.438	1.490	0.690
18.2048	6.41	2.95	0.102	0.442	0.100	0.447	1.549	0.689
19.0820	6.79	3.20	0.100	0.451	0.096	0.457	1.607	0.688
19.9518	7.21	3.45	0.096	0.459	0.092	0.467	1.664	0.686
20.8130	7.59	3.70	0.092	0.467	0.088	0.475	1.721	0.683
21.6679	8.02	3.94	0.088	0.473	0.084	0.480	1.760	0.677

([Ślęzak et al. 2012](#)). The dependences $\zeta_v = f(\bar{C})$ and $\zeta_s = f(\bar{C})$, $J_v = f(\bar{C})$, $J_{vs} = f(\bar{C})$, $\delta_d = f(\bar{C})$ and $\delta_k = f(\bar{C})$ were already presented ([Ślęzak et al. 2012](#)). The calculations results of the dependence $P_{11}^* = f(\bar{C})$, $P_{12}^* = f(\bar{C})$, $P_{21}^* = f(\bar{C})$, $P_{22}^* = f(\bar{C})$, $P_{11} = f(\bar{C})$, $P_{12} = P_{21} = f(\bar{C})$, $P_{22}^* = f(\bar{C})$, $P_{11}^*/P_{11} = f(\bar{C})$, $P_{12}^*/P_{12} = f(\bar{C})$, $P_{21}^*/P_{21} = f(\bar{C})$, $P_{22}^*/P_{22} = f(\bar{C})$ and $\det[P^*]/\det[P] = f(\bar{C})$ are presented in Figs. 2, 3, 4, 5, 6, 7, 8, and 9.

The calculations results of the coefficient dependence $P_{11}^* = f(\bar{C})$ and $P_{11} = f(\bar{C})$ for the configurations A and B of the membrane system within Eqs. (11) and (13) are depicted in Fig. 2. Figure shows that the values of coefficient P_{11} are decreasing linearly together with the increase in the value \bar{C} . By contrast, the values of coefficient P_{11}^* for \bar{C} fulfilling the condition $0 \leq \bar{C} \leq 5.41$ mol m⁻³ are decreasing linearly and do not depend on the configuration of the membrane system. For $\bar{C} > 5.41$ mol m⁻³, the value of coefficient P_{11}^* depends on both the value \bar{C} and the configuration of the membrane system. Moreover, from the comparison of the value P_{11}^* for the same values $\bar{C} > 5.41$ mol m⁻³ and the configurations A and B of the membrane system, it is resulting that $(P_{11}^*)_A < (P_{11}^*)_B$. Within the whole range of \bar{C} , the following condition $(P_{11}^*)_A < (P_{11}^*)_B < P_{11}$ is fulfilled.

The calculations results of the coefficient dependence $P_{12}^* = f(\bar{C})$ and $P_{12} = f(\bar{C})$ for the configurations A and B of the membrane system are depicted in Fig. 3. Figure shows that together with the increase in value \bar{C} , the values of coefficients P_{12} are decreasing linearly

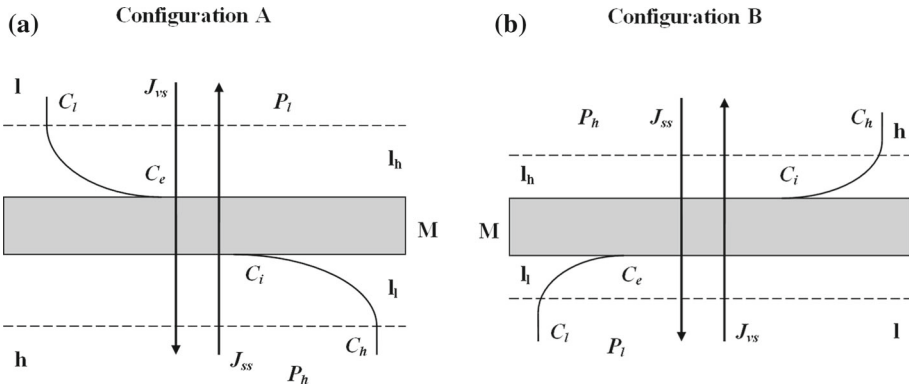


Fig. 1 Configurations A and B of a single-membrane system: M membrane, l_l and l_h the concentration boundary layers (CBLs), P_h and P_l mechanical pressures, C_l and C_h concentrations of solutions outside the boundaries, C_e and C_i the concentrations of solutions at boundaries l_l/M and M/l_h , J_{vm} the volume fluxes through membrane M , J_{vs} the volume fluxes through complex $l_l/M/l_h$, J_{sl} , J_{sh} and J_{sm} the solute fluxes through layers l_l , l_h and membrane, respectively, J_{ss} the solute fluxes through complex $l_l/M/l_h$ (Ślęzak et al. 2012)

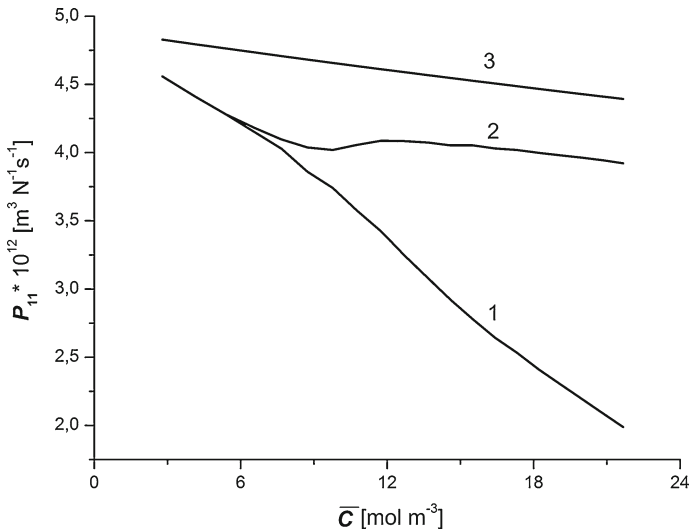


Fig. 2 The graphic illustration of dependence $P_{11}^* = f(\bar{C})$ for aqueous glucose solutions in a concentration polarization conditions for the configuration A (graph 1), and B (graph 2) of the membrane system. The graph 3 illustrates the dependence $P_{11} = f(\bar{C})$ in conditions of homogeneous solutions separated by the membrane. The values of the coefficients P_{11}^* and P_{11} were calculated on the basis of Eq. (11) and of Eq. (13), respectively

and are the same in the configurations A and B of the membrane system. By contrast, the values of coefficient P_{12}^* for $0 \leq \bar{C} \leq 5.41 \text{ mol m}^{-3}$ are decreasing approximately linearly. Similar to the coefficient P_{11}^* , the coefficient value P_{12}^* does not depend on the configuration of the membrane system. For $\bar{C} > 5.41 \text{ mol m}^{-3}$, the coefficient value P_{12}^* depends on both the value \bar{C} and the configuration of the membrane system. The comparison of values P_{12}^* for the same values $\bar{C} > 5.41 \text{ mol m}^{-3}$ and the configurations A and B of the membrane system showed that $(P_{12}^*)_A > (P_{12}^*)_B$. Within the whole range of \bar{C} , the following condition $(P_{12}^*)_A > (P_{12}^*)_B > P_{12}$ is fulfilled.

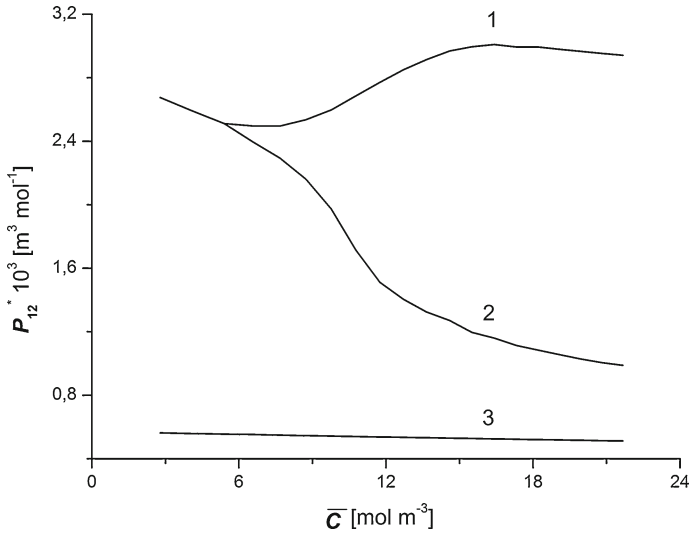


Fig. 3 The graphic illustration of dependence $P_{12}^* = f(\bar{C})$ for aqueous glucose solutions in a concentration polarization conditions for the configuration A (graph 1), and B (graph 2) of the membrane system. The graph 3 illustrates the dependence $P_{12} = f(\bar{C})$ in conditions of homogeneous solutions separated by the membrane. The values of the coefficients P_{12}^* and P_{12} were calculated on the basis of Eq. (11) and of Eq. (13), respectively,

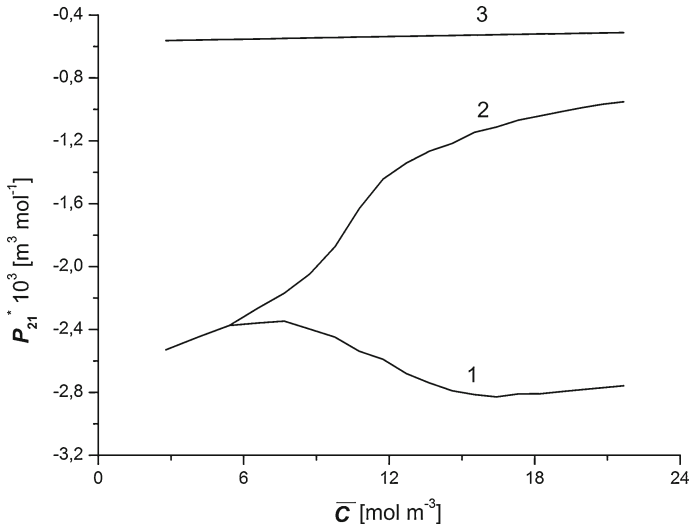


Fig. 4 The graphic illustration of dependence $P_{21}^* = f(\bar{C})$ for aqueous glucose solutions in a concentration polarization conditions for the configuration A (graph 1), and B (graph 2) of the membrane system. The graph 3 illustrates the dependence $P_{21} = f(\bar{C})$ in conditions of homogeneous solutions separated by the membrane. The values of the coefficients P_{12}^* and P_{12} were calculated on the basis of Eq. (11) and of Eq. (13), respectively,

The dependences $P_{21}^* = f(\bar{C})$ and $P_{21} = f(\bar{C})$ for the configurations A and B of the membrane system are presented in Fig. 4. Figure shows that together with the increase in value \bar{C} , the values of coefficient P_{21} are increasing linearly and are the same in both configurations

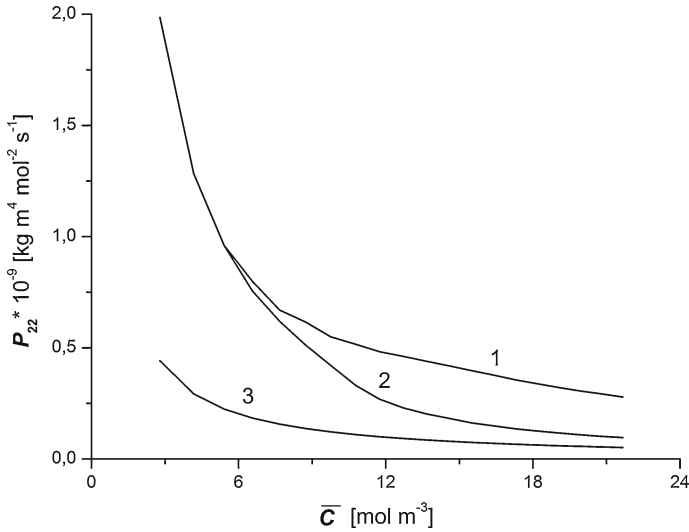


Fig. 5 The graphic illustration of dependence $P_{22}^* = f(\bar{C})$ for aqueous glucose solutions in a concentration polarization conditions for the configuration A (graph 1), and B (graph 2) of the membrane system. The graph 3 illustrates the dependence $P_{22} = f(\bar{C})$ in conditions of homogeneous solutions separated by the membrane. The values of the coefficients P_{22}^* and P_{22} were calculated on the basis of Eq. (11) and of Eq. (13), respectively

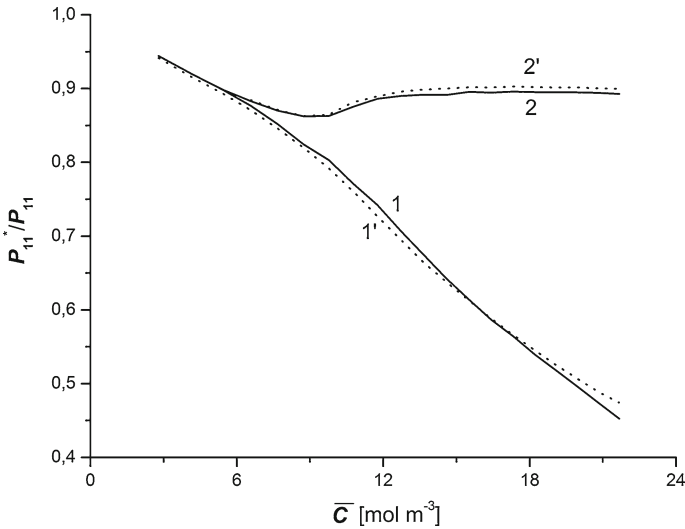


Fig. 6 The graphic illustration of dependence $P_{11}^*/P_{11} = f(\bar{C})$ for the configuration A (graphs 1 and 1') and B (graphs 2 and 2') of the membrane system. Graphs 1 and 2 were calculated on the basis of Eq. (15), graph 1' on the basis of Eq. (22), and graph 2' on the basis of Eq. (26)

of the membrane system. By contrast, the values of coefficient P_{21}^* for $0 \leq \bar{C} \leq 5.41 \text{ mol m}^{-3}$ are increasing linearly and are the same in the configurations A and B of the membrane system. For $\bar{C} > 5.41 \text{ mol m}^{-3}$, the coefficient value P_{21}^* depends on both the value \bar{C} and the configurations A and B of the membrane system. From the comparison of values P_{21}^* for the same values \bar{C} it is resulting that for $\bar{C} > 5.41 \text{ mol m}^{-3}$ and the configurations A and

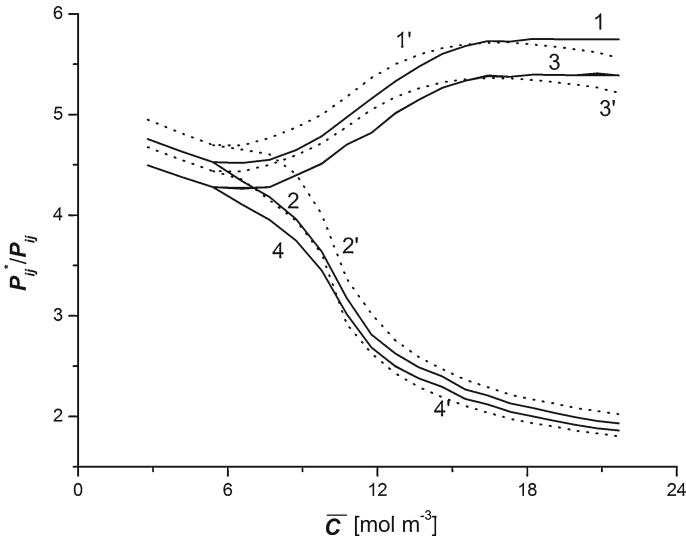


Fig. 7 The graphic illustration of dependence $P_{ij}^*/P_{ij} = f(\bar{C})$ ($i, j \in \{1, 2\}$) for aqueous glucose solutions in condition a concentration polarization for configuration A (graphs 1, 1', 3, 3') and B (graphs 2, 2', 4, 4') of the membrane system. The graphs 1, 1', 2 and 2' illustrates the dependence $P_{12}^*/P_{12} = f(\bar{C})$ and graphs 3, 3', 4 and 4'—the dependence $P_{21}^*/P_{21} = P_{22}^*/P_{22} = f(\bar{C})$. Graphs 1 and 2 were calculated on the basis of Eq. (16), graphs 3 and 4 on the basis of Eqs. (17) and (18), graph 1' on the basis of Eq. (23), and graph 2' on the basis of Eq. (27), graph 3' on the basis of Eq. (24) and graph 4' on the basis of Eq. (28)

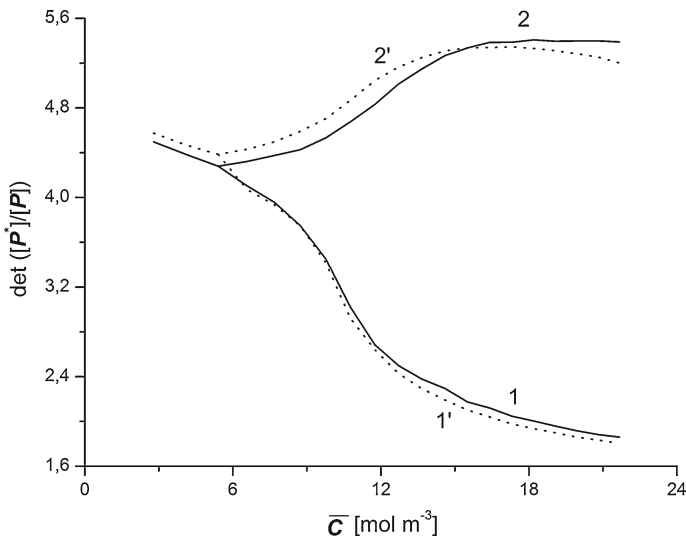


Fig. 8 The graphic illustration of dependence $\det([P^*]/[P]) = f(\bar{C})$ for aqueous glucose solutions in a concentration polarization conditions for the configuration A (graphs 1 and 1'), and B (graphs 2 and 2') of the membrane system. Graphs 1 and 2 were calculated on the basis of Eq. (37), graph 1' on the basis of Eq. (38), and graph 2' on the basis of Eq. (39)

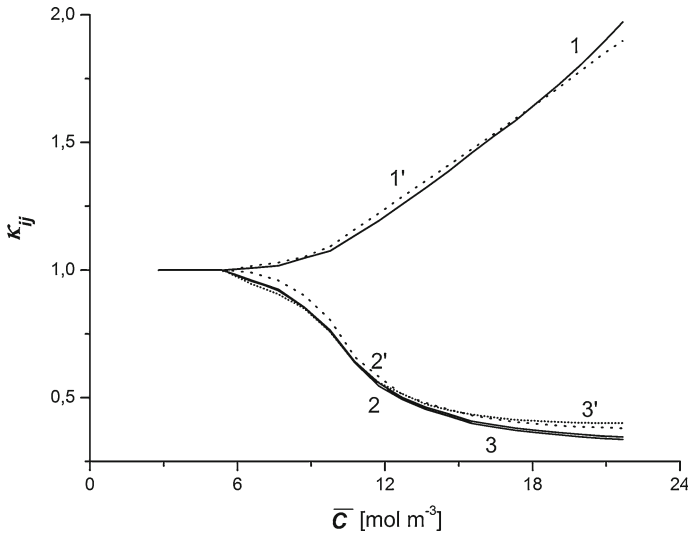


Fig. 9 The graphic illustration of dependence $\kappa_{ij} = f(\bar{C})$ ($i, j \in \{1, 2\}$) for aqueous glucose solutions in a concentration polarization conditions. *Graphs 1–3* were calculated on the basis of Eqs. (41)–(43), *graph 1'* on the basis of Eq. (44), *graph 2'* on the basis of Eq. (45) and *graph 3'* on the basis of Eq. (46)

B of the membrane system, the following condition $(P_{21}^*)_A < (P_{21}^*)_B$ is fulfilled. Moreover, within the whole range of \bar{C} the following condition $(P_{21}^*)_A < (P_{21}^*)_B < P_{21}$ is fulfilled.

The dependences depicted in Fig. 5 $P_{22}^* = f(\bar{C})$ and $P_{22} = f(\bar{C})$ are hyperbolas. The dependences $P_{22}^* = f(\bar{C})$ illustrated by a graph 1 (for configuration A) and a graph 2 (for configuration B) were obtained under conditions of concentration polarization. The comparison of the curves present that for $0 \leq \bar{C} \leq 5.41 \text{ mol m}^{-3}$ we have $(P_{22}^*)_A = (P_{22}^*)_B$, whereas for $\bar{C} > 5.41 \text{ mol m}^{-3}$ we have $(P_{22}^*)_A > (P_{22}^*)_B$. The dependence $P_{22} = f(\bar{C})$ on a graph 3 shows that under the conditions of homogeneity of solutions separated by the membrane, the values P_{22} are equal, i.e., $(P_{22})_A = (P_{22})_B$. Figure shows as well that for $\bar{C} > 5.41 \text{ mol m}^{-3}$ we have $(P_{22}^*)_A < (P_{22}^*)_B < P_{22}$.

Considering the results showed in Fig. 2, it is possible to spot particular quantity differences between the concentration dependences of coefficients P_{11}^* and P_{11} and the dependence of coefficient value P_{11}^* on the configuration of the membrane system. Therefore, Fig. 6 presents the dependence $P_{11}^*/P_{11} = f(\bar{C})$ for the configuration A (graph 1) and the configuration B (graph 2) of the membrane system. The dependences were calculated using Eqs. (15), (22), (26) and (30). Figure shows that P_{11}^*/P_{11} depend on \bar{C} , and for $\bar{C} > 5.41 \text{ mol m}^{-3}$ —they depend on the configuration of the membrane system, too. Moreover, from figure it results that for $\bar{C} > 5.41 \text{ mol m}^{-3}$ we have the following values of relation $(P_{11}^*/P_{11})_B > (P_{11}^*/P_{11})_A$. It may be noticed that the point with coordinates $P_{11}^*/P_{11} = 0.898$ and $\bar{C} = 5.41 \text{ mol m}^{-3}$ is a last joint point of the graphs 1 and 2. The point may be treated as the bifurcation point. It means that crossing the bifurcation point and reaching by P_{11}^* the value belonging to the graphs 1 or 2 are constituting the choice between convective state (B) and non-convective state (A) of the membrane system.

Data depicted in Figs. 3, 4 and 5 allow to make the quantity analysis of the concentration dependences P_{12}^* and P_{12} , P_{21}^* and P_{21} , P_{22}^* and P_{22} on the configuration of the membrane system. Therefore, Fig. 7 presents the dependences $P_{12}^*/P_{12} = f(\bar{C})$ and

$P_{21}^*/P_{21} = P_{22}^*/P_{22} = f(\bar{C})$ for the configuration A (graphs 1, 1', 3 and 3') and the configuration B (graphs 2, 2', 4 and 4') of the membrane system. The dependences were calculated using Eqs. (16)–(18), (23), (24), (27) and (28). The graphs depicted in Fig. 7 indicate that for $\bar{C} \leq 5.41 \text{ mol m}^{-3}$, the values P_{12}^*/P_{12} , P_{21}^*/P_{21} and P_{22}^*/P_{22} depend on \bar{C} but do not depend on the configuration of the membrane system. By contrast, for $\bar{C} > 5.41 \text{ mol m}^{-3}$ the values P_{12}^*/P_{12} , P_{21}^*/P_{21} and P_{22}^*/P_{22} depend on both \bar{C} and the configuration of the membrane system. Moreover, it may be noticed that points with the coordinates $P_{12}^*/P_{12} = 4.55$ (for graphs 1 and 2), $P_{12}^*/P_{12} = 4.7$ (for graphs 1' and 2'), $P_{21}^*/P_{21} = P_{22}^*/P_{22} = 4.27$ (for graphs 3 and 4), and $P_{21}^*/P_{21} = P_{22}^*/P_{22} = 4.42$ (for graphs 3' and 4') as well as $\bar{C} = 5.41 \text{ mol m}^{-3}$ are the last joint point of the graphs. The point has the properties of the bifurcation point. What is more, the graphs show that for $\bar{C} > 5.41 \text{ mol m}^{-3}$ we have $(P_{12}^*/P_{12})_B < (P_{12}^*/P_{12})_A$, $(P_{21}^*/P_{21})_B < (P_{21}^*/P_{21})_A$ and $(P_{22}^*/P_{22})_B < (P_{22}^*/P_{22})_A$. Figure shows as well that $(P_{12}^*/P_{12})_A > (P_{21}^*/P_{21})_A = (P_{22}^*/P_{22})_A$ and $(P_{12}^*/P_{12})_B > (P_{21}^*/P_{21})_B = (P_{22}^*/P_{22})_B$.

Figure 8 depicts the calculations results of the dependence $\det([P^*]/[P]) = f(\bar{C})$ for the configuration A (graphs 1 and 1') and the configuration B (graphs 2 and 2'). The graphs 1 and 2 were calculated on the basis of Eq. (37), graph 1' on the basis of Eq. (38), and graph 2' on the basis of Eq. (39). From the curves presented it results that for $\bar{C} \leq 5.41 \text{ mol m}^{-3}$, the values $\det([P^*]/[P])$ depend on \bar{C} but do not depend on the configuration of the membrane system. By contrast, for $\bar{C} > 5.41 \text{ mol m}^{-3}$ the values $\det([P^*]/[P])$ depend on both \bar{C} and the configuration of the membrane system. Moreover, it may be noticed that points with the coordinates $\det([P^*]/[P]) = 4.27$ (for graphs 1 and 2) and $\det([P^*]/[P]) = 4.41$ (for curves 1 and 2) as well as $\bar{C} = 5.41 \text{ mol m}^{-3}$ are the last joint point of the graphs. Similar to the cases discussed above, the point has the properties of the bifurcation point (Ślęzak et al. 2012). What is more, the graphs show that for $\bar{C} > 5.41 \text{ mol m}^{-3}$ we have $(\det[P^*]/[P])_A < (\det[P^*]/[P])_B$.

For coefficients P_{ij} and P_{ij}^* ($i, j \in \{1, 2\}$) with the same indices, units are the same and values differ; whereas for these coefficients with different indices, units are different and values differ even by several orders of magnitude. Quotients P_{ij}^*/P_{ij} are dimensionless and their values have, at least for a Nephrophan membrane and water glucose solutions, the same order of magnitude. This facilitates analysis of the results obtained under conditions of concentration polarization or homogeneity of solutions. Calculation of $\det([P^*]/[P])$ provides basis to reduce number of parameters needed to characterize transport properties of the membrane.

The experiments carried out previously indicate that if the coefficient values P_{11}^* , P_{12}^* , P_{21}^* and P_{22}^* do not depend on the configuration of the membrane system, then the CBLs setting is symmetric towards the horizontal surface in which the membrane is placed separating solutions with the concentrations C_1 and C_h . In order to show the relationship between the coefficients P_{11}^* , P_{12}^* , P_{21}^* and P_{22}^* in the configurations A and B of the membrane system, we are calculating the quotients $(P_{11}^*)_B/(P_{11}^*)_A$, $(P_{12}^*)_B/(P_{12}^*)_A$, $(P_{21}^*)_B/(P_{21}^*)_A$, $(P_{22}^*)_B/(P_{22}^*)_A$. The quotients may be generalized and the definition of asymmetry coefficient κ_{ij} ($i, j = 1, 2$) may be introduced as follows

$$\kappa_{ij} = \frac{(P_{ij}^*)_B}{(P_{ij}^*)_A}. \quad (40)$$

It results from the definition that the absence of asymmetry means $\kappa_{ij} = 1$, whereas the asymmetry $\kappa_{ij} > 1$ and $\kappa_{ij} < 1$.

The calculations results of the dependence $\kappa_{11} = f(\bar{C})$, $\kappa_{12} = f(\bar{C})$, $\kappa_{21} = f(\bar{C})$ and $\kappa_{22} = f(\bar{C})$ are point. For $\bar{C} > 5.41 \text{ mol m}^{-3}$ the values of coefficients κ_{11} , κ_{12} , κ_{21} and κ_{22} depend on the concentration of solutions separated by the membrane. Moreover, the graphs in Fig. 9 show that for $\bar{C} > 5.41$ the course of the graph $\kappa_{11} = f(\bar{C})$ differs from the course of graphs $\kappa_{12} \approx \kappa_{21} = \kappa_{22} = f(\bar{C})$. The latter graphs showing the dependence overlies. What is more, for $\bar{C} > 5.41$ the conditions $\kappa_{11} > 1$ and $\kappa_{12} \approx \kappa_{21} = \kappa_{22} < 1$ are fulfilled for each \bar{C} .

Using Eq. (11), then Eq. (40) for the coefficients κ_{11} , κ_{12} , κ_{21} and κ_{22} depicted in Fig. 9. The calculations were made using Eq. (31). Figure shows that for $\bar{C} \leq 5.41 \text{ mol m}^{-3}$ the values of coefficients κ_{11} , κ_{12} , κ_{21} and κ_{22} do not depend on the solution concentration. Their value, similar to the value of the last joint point of the graphs 1–3, is equal to $\kappa_{11} = \kappa_{12} = \kappa_{21} = \kappa_{22} = 1$. The point has the properties of the bifurcation may be written in the following way

$$\kappa_{11} = \frac{(P_{11})_B}{(P_{11})_A} = \frac{(\zeta_s)_B\{(\zeta_s)_A\omega + \bar{C}\zeta_p L_p[1 - (\zeta_v)_A\sigma](1 - \zeta_a\sigma)\}}{(\zeta_s)_A\{(\zeta_s)_B\omega + \bar{C}\zeta_p L_p[1 - (\zeta_v)_B\sigma](1 - \zeta_a\sigma)\}}, \tag{41}$$

$$\kappa_{12} = \frac{(P_{12})_B}{(P_{12})_A} = \frac{[1 - (\zeta_v)_B\sigma]\{(\zeta_s)_A\omega + \bar{C}\zeta_p L_p[1 - (\zeta_v)_A\sigma](1 - \zeta_a\sigma)\}}{[1 - (\zeta_s)_A\sigma]\{(\zeta_s)_B\omega + \bar{C}\zeta_p L_p[1 - (\zeta_v)_B\sigma](1 - \zeta_a\sigma)\}}, \tag{42}$$

$$\kappa_{21} = \frac{(P_{21})_B}{(P_{21})_A} = \frac{(\zeta_s)_A\omega + \bar{C}\zeta_p L_p[1 - (\zeta_v)_A\sigma](1 - \zeta_a\sigma)}{(\zeta_s)_B\omega + \bar{C}\zeta_p L_p[1 - (\zeta_v)_B\sigma](1 - \zeta_a\sigma)} = \kappa_{22}. \tag{43}$$

Using Eqs. (21), (25), (34) and (35), then Eqs. (41)–(43) may be written in the following way

$$\kappa_{11} = [1 + \bar{C}a_1(1 + a_2\delta_d)] \left[1 + \bar{C}a_1 \left(1 + \frac{a_3 R C}{\delta_k^2(J_v - J_{vs})} \right) \right]^{-1}, \tag{44}$$

$$\kappa_{12} = [1 + a_1(1 + a_2\delta_d)] \left(1 + \frac{a_3 R C}{\delta_k(J_v - J_{vs})} \right) \left[(1 + a_2\delta_d)(1 + a_1) \left(1 + \frac{a_4 R C \bar{C}}{\delta_k^2(J_v - J_{vs})} \right) \right]^{-1}, \tag{45}$$

$$\kappa_{21} = \frac{D_d[1 + a_1(1 + a_2\delta_d)]}{D_d + 2RT\omega\delta_d} \left(1 + \frac{a_3(1 - \sigma)RC}{\delta_d^2(J_v - J_{vs})} \right) \left[1 + a_1\bar{C} \left(1 + \frac{a_3 R C}{\delta_k^2(J_v - J_{vs})} \right) \right]^{-1} = \kappa_{22}, \tag{46}$$

where $a_1 = L_p(1 - \sigma)^2\omega^{-1}$, $a_2 = 2RT\omega[D_d(1 - \sigma)]^{-1}$, $a_3 = 4(RT)2L_p\sigma\omega\nu[g\alpha_C(1 - \sigma)]^{-1}$, $a_4 = a_3(1 - \sigma)^2L_p\omega^{-1}(1 + \bar{C}a_1)^{-1}$.

According to theory of functionally graded materials (Shen 2009; Woźniak et al. 2001; Woźniak 2007), contact of two objects, i.e., solutions with different concentrations and/or composition, causes conflicts. In the case of solutions, the conflict is eliminated quickly due to the transport processes such as diffusion or convection. The processes are generated by concentration gradients of substance. Therefore, the situation discussed is a non-conflict one when the concentrations and compositions of both solutions are homogenous within the space and time. By contrast, the membrane placement (as an additional object) between homogenous solutions is slowing down the transport processes due to extended in time retention of concentration gradients of particular solutions flowing across the membrane, and consequently it is defusing the conflict. It has to be emphasized that the homogeneity of solutions separated by the membrane may be provided solely by intensive mechanical stirring. Under real conditions (the absence of mechanical stirring), at the both sides of the

membrane the CBLs (diffusive ones) are created. They may be treated as two additional objects between the membrane and solutions, created spontaneously. The objects defuse the conflict by the reduction of concentration gradients and become units of functionally graded materials.

4 Conclusion

Considering the study above, we may conclude that:

- (1) The network form of the K–K equations introduced in the following paper, containing the Peusner's coefficients P_{ij}^* ($i, j \in \{1, 2\}$) creating the second degree matrix of the Peusner's coefficients [P^*], is the new tool in the study on the membrane transport under conditions of concentration polarization.
- (2) The calculated dependences of the Peusner's coefficients P_{ij}^* and P_{ij} ($i, j \in \{1, 2, 3\}$) and the quotients of the coefficients for the conditions of non-homogeneity (P_{ij}^*) and homogeneity (P_{ij}) of solutions depend on the average glucose concentration in the membrane (\bar{C}).
- (3) Above the threshold value $\bar{C} = 5.41 \text{ mol m}^{-3}$ we have the coefficients P_{11}^* , $P_{12}^* = -P_{21}^*$ and P_{22}^* , consequently the relations P_{11}^*/P_{11} , P_{12}^*/P_{12} and P_{22}^*/P_{22} depend as well on the configuration of the membrane system.
- (4) For the same values $\bar{C} > 5.41 \text{ mol m}^{-3}$, the coefficient value P_{11}^* in convective state is higher than in non-convective state, whereas the values of coefficients $P_{12}^* = -P_{21}^*$ and P_{22}^* in convective state are lower than in non-convective state.

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