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Concentration dependencies of the P_{ij} Peusner coefficient for the non-electrolyte ternary solutions

STĘŻENIOWE ZALEŻNOŚCI WSPÓŁCZYNNIKÓW PEUSNERA P_{ij} DLA TERNARNYCH ROZTWORÓW NIEELEKTROLITÓW

Streszczenie: Termodynamika sieciowa Peusnera należy do grupy termodynamiki współczesnej. Stanowi ona wygodne ramy badawcze transportów membranowych. Jednym z wielu narzędzi badawczych transportu membranowego są równania Kedem - Katchalsky'ego. Sieciowe postaci hybrydowych równań Kedem-Katchalsky'ego (K-K) dla ternarnych roztworów nieelektrolitowych mogą zawierać jeden z sześciu współczynników Peusnera: H_{ij} , W_{ij} , N_{ij} , K_{ij} , S_{ij} lub P_{ij} ($i, j \in \{1, 2, 3\}$), tworzących macierze trzeciego stopnia współczynników Peusnera $[H]$, $[W]$, $[N]$, $[K]$, $[S]$ lub $[P]$. Celem pracy było obliczenie rodziny zależności współczynników Peusnera P_{ij} ($i, j \in \{1, 2, 3\}$), od średniego stężenia jednego składnika jednorodnego roztworu w membranie (\bar{C}_1) dla kilku różnych, ustalonych wartości drugiego składnika (\bar{C}_2). Analizowano transport wodnych roztworów glukozy i etanolu przez membranę o parametrach transportowych L_p , σ i ω , przy pomocy sieciowych równań K-K dla ternarnych roztworów nieelektrolitów, zawierających współczynnik Peusnera P_{ij} . Stwierdzono, że współczynniki P_{ij} są nieliniowo (hiperbolicznie) zależne od stężeń \bar{C}_1 i \bar{C}_2 . Nieliniowość owych współczynników wynika z właściwości równań matematycznych

Abstract. Peusner's Network Thermodynamics belongs to a group of modern thermodynamics. It provides a convenient research framework for membrane transports. One of the many research tools to study membrane transport are Kedem-Katchalsky equations. A network forms of hybrid Kedem-Katchalsky equations (K-K) for ternary non-electrolyte solutions may contain one of the six Peusner coefficients i.e. H_{ij} , W_{ij} , N_{ij} , K_{ij} , S_{ij} or P_{ij} ($i, j \in \{1, 2, 3\}$) that form third-order matrices of the Peusner coefficients i.e. $[H]$, $[W]$, $[N]$, $[K]$, $[S]$ or $[P]$. Aim of this study was to calculation of family of dependencies of Peusner coefficients P_{ij} ($i, j \in \{1, 2, 3\}$) on average concentration of a homogeneous solution of one component in a membrane (\bar{C}_1) for several different values of the second component (\bar{C}_2). Calculations were made for aqueous glucose and ethanol solutions and membrane with transport parameters L_p , σ and ω on the basis of network K-K equations for ternary solutions of non-electrolytes that contain the coefficient P_{ij} . It has been shown that the P_{ij} are non-linearly (hyperbolic) dependent on solutions concentrations \bar{C}_1 and \bar{C}_2 . Non-linearity of coefficients P_{ij} results from the properties of mathematical

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opisujących współczynniki P_j .

equations describing them.

Słowa kluczowe: termodynamika sieciowa, transport membranowy, dyfuzja

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INTRODUCTION

Membrane transport processes are of interest in many fields of science, technology and medicine [Katchalsky, Curran, 1965; Baker, 2012]. Kedem-Katchalsky formalism, developed on the basis of non-equilibrium thermodynamics, is one of the most important methods to analyze membrane transport of both homogenous and non-homogenous solutions [Katchalsky & Curran, 1965; Kargol & Kargol, 2011]. Non-homogeneity is a typical feature of physicochemical systems. It is manifested on various levels of matter organization by formations such as equilibrium or dissipative structures that may undergo at least partial destruction in certain conditions [Ślęzak 1989; Kondepudi & Prigogine, 2006]. In contrast, homogeneity is an idealized state that is demonstrated only under laboratory conditions. Thus, homogeneity state of solutions separated by a membrane can be nearly accomplished by mechanical stirring of the solutions. Stirring destroys both equilibrium and dissipative structures that are formed on the membrane-solution contact surface [Ślęzak, 1989; Dworecki et al., 2005].

Basic foundations, laws and rules of the Network Thermodynamics (NT) as well as its possible applications were formulated in *the nineteen-seventies* [Peusner, 1970; Oster, Perelson & Katchalsky, 1971; Peusner, 1986]. One of the important areas of NT applications is membrane transport [Imai, 1996; Moya & Horno 2004; Szczepański & Wódzki, 2013; Bristow & Kennedy, 2013]. Peusner showed that NT enables transformation of Kedem-Katchalsky equations (K-K) for binary homogenous solutions by symmetrical or hybrid transformation of thermodynamic networks [Peusner, 1986]. Based on Peusner idea, Ślęzak and collaborations presented network form of K-K equations for binary non-homogenous non-electrolyte solutions [Ślęzak et al., 2013; Batko et al., 2014a; 2014b; 2015].

Network Kedem-Katchalsky equations (K-K) contain Peusner coefficients that can be calculated based on experimentally determined transport

parameters i.e. hydraulic permeability (L_p), solute permeability (ω) and reflection (σ) coefficients [Peusner 1986; Ślęzak et al. 2013; Batko et al. 2014a; 2014b; 2015]. For binary homogenous non-electrolyte solutions, we have two symmetrical and two hybrid forms of network K-K equations. Symmetrical forms of network K-K equations for binary solutions contain Peusner coefficients R_{ij} or L_{ij} , whereas hybrid forms contain Peusner coefficients H_{ij} and P_{ij} [Peusner 1986; Ślęzak et al. 2013; Batko *et al.*, 2014a; 2014b; 2015]. We have two symmetrical and six hybrid forms of network K-K equations for ternary and homogenous non-electrolyte solutions [Jasik-Ślęzak et al., 2014]. Similar to binary solutions, symmetrical forms of K-K equations contain Peusner coefficients R_{ij} and L_{ij} , whereas hybrid forms contain Peusner coefficients H_{ij} , W_{ij} , N_{ij} , K_{ij} , S_{ij} and P_{ij} .

In series of our recent papers we presented network forms of K-K equations for homogeneous ternary non-electrolyte solutions containing Peusner coefficients R_{ij} , L_{ij} , H_{ij} , W_{ij} , S_{ij} , N_{ij} , K_{ij} and P_{ij} ($i, j \in \{1, 2, 3\}$) that are elements of the third-order matrix $[R]$, $[L]$, $[H]$, $[W]$, $[N]$, $[K]$, $[S]$ or $[P]$, respectively [Batko et al. 2014b; Jasik-Ślęzak et al., 2014]. Dependencies of these coefficients on average concentration of one component of the solution in the membrane (\bar{C}_1) were calculated for established value of the second one (\bar{C}_2), values of these coefficients were also compared (Batko et al. 2014b; Jasik-Ślęzak *et al.*, 2014). To expand scope of the calculations, in this paper we show dependencies $P_{ij}=f(\bar{C}_1, \bar{C}_2=\text{const.})$ ($i, j \in \{1, 2, 3\}$) calculated for six established \bar{C}_2 values. Coefficients were calculated based on mathematical model presented in Batko and colleagues paper (Batko *et al.*, 2014b).

$$\begin{bmatrix} J_v \\ \frac{\Delta\pi_1}{\bar{c}} \\ \frac{\Delta\pi_2}{\bar{c}} \end{bmatrix} = \begin{bmatrix} P_{11} & P_{12} & P_{13} \\ P_{21} & P_{22} & P_{23} \\ P_{31} & P_{32} & P_{33} \end{bmatrix} \begin{bmatrix} \Delta\phi \\ J_{s1} \\ J_{s2} \end{bmatrix} \quad (1)$$

where:

$$P_{11} = L_p A \xi^{-1} \quad (2), \quad P_{12} = L_p [(1 - \sigma_2)\omega_{21} - (1 - \sigma_1)\omega_{22}] \xi^{-1} \quad (3)$$

$$P_{13} = L_p [(1 - \sigma_1)\omega_{12} - (1 - \sigma_2)\omega_{11}] \bar{C}_1^{-1} \xi^{-1} \quad (4)$$

$$P_{21} = L_p [(1 - \sigma_2)\bar{C}_2\omega_{12} - (1 - \sigma_1)\bar{C}_1\omega_{22}] \bar{C}_1^{-1} \xi^{-1} \quad (5)$$

$$P_{22} = [\omega_{22} - L_p \bar{C}_2 (1 - \sigma_1)^2] \bar{C}_1^{-1} \xi^{-1} \quad (6)$$

$$P_{23} = -[\omega_{22} - L_p \bar{C}_1 (1 - \sigma_1)(1 - \sigma_2)] \bar{C}_1^{-1} \xi^{-1} \quad (7)$$

$$P_{31} = L_p [(1 - \sigma_1) \bar{C}_1 \omega_{21} - (1 - \sigma_2) \bar{C}_2 \omega_{11}] \bar{C}_2^{-1} \xi^{-1} \quad (8)$$

$$P_{32} = -[\omega_{21} - L_p \bar{C}_2 (1 - \sigma_1)(1 - \sigma_2)] \bar{C}_2^{-1} \xi^{-1} \quad (9)$$

$$P_{33} = [\omega_{11} - L_p \bar{C}_1 (1 - \sigma_1)^2] \bar{C}_2^{-1} \xi^{-1} \quad (10)$$

$$\xi = A - L_p (\bar{C}_1 \alpha_1 + \bar{C}_2 \alpha_2) \quad (11)$$

where: J_v – volume flux, J_{s1} and J_{s2} – solute fluxes of substances “1” and “2” through the membrane in conditions of solution homogeneity, L_p – hydraulic permeability coefficient, σ_1 and σ_2 – reflection coefficients of substances “1” and “2”, respectively, ω_{11} and ω_{22} – solute permeability coefficients of substances “1” and “2” generated by forces with indexes “1” and “2”, ω_{12} and ω_{21} – cross solute permeability coefficient of substances “1” and “2” generated by forces with indexes “2” and “1”; $\Delta \phi = \Delta P + \Delta \pi_1 + \Delta \pi_2$, $\Delta P = P_h - P_l$ – hydrostatic pressures difference (P_h , P_l are higher and lower value of hydrostatic pressure); $\Delta \pi_k = RT(C_{kh} - C_{kl})$ is osmotic pressures difference (RT is a product of the gas constant and thermodynamic temperature, whereas C_h and C_l are solution concentrations, $k=1, 2$), $\bar{C}_k = (C_{kh} - C_{kl}) [\ln(C_{kh} C_{kl}^{-1})]^{-1}$ – average solute concentration; $\alpha_1 = (1 - \sigma_1) [\omega_{22}(1 - \sigma_1) + \omega_{21}(1 - \sigma_2)]$, $A = \omega_{11} \omega_{22} - \omega_{21} \omega_{12}$, $\alpha_2 = (1 - \sigma_2) [\omega_{11}(1 - \sigma_2) + \omega_{12}(1 - \sigma_1)]$.

Denominator of Eqs. (2)-(10) for certain \bar{C}_1 and \bar{C}_2 values may take positive values (for $\xi > 0$), negative (for $\xi < 0$) values or zero (for $\xi = 0$). Besides, for $\xi = 0$, Eqs. (2)-(10) have no solution in a real number set and

$$\bar{C}_1 = [A - L_p \bar{C}_2 (\omega_{11} \beta_1 + \omega_{12} \beta_2)] [L_p (\omega_{22} \beta_3 + \omega_{21} \beta_2)]^{-1} \quad (12)$$

where: $\beta_1 = (1 - \sigma_2)^2$, $\beta_2 = (1 - \sigma_1)(1 - \sigma_2)$, $\beta_3 = (1 - \sigma_1)^2$

RESULTS OF CALCULATIONS AND DISCUSSION

Applying an algorithm presented in the papers of Batko and colleagues, we calculate of family dependencies of Peusner's coefficients P_{ij} ($i, j \in \{1, 2, 3\}$) on average concentration of a homogeneous solution of one component in a membrane (\bar{C}_1) for several different values of the second component (\bar{C}_2) for Nephrophan hemodialyser membrane (Batko *et al.*, 2014b). Average concentration of components “1” and “2” in a membrane (\bar{C}_1, \bar{C}_2) was cal-

culated based on equations $\bar{C}_1 = (C_{1h} - C_{1l}) [\ln(C_{1h} C_{1l}^{-1})]^{-1}$ and $\bar{C}_2 = (C_{2h} - C_{2l}) [\ln(C_{2h} C_{2l}^{-1})]^{-1}$. The following assumptions were used for calculations:

- 1) Concentrations of a substance "1" in a compartment h varies in a range from $C_{1h} = 1 \text{ mol m}^{-3}$ to $C_{1h} = 2301 \text{ mol m}^{-3}$,
- 2) Concentrations of a substance "2" in a compartment h is constant and equals $C_{2h} = 6 \text{ mol m}^{-3}$ for the first series of calculations, for the second series – $C_{2h} = 11 \text{ mol m}^{-3}$, for the third one – $C_{2h} = 31 \text{ mol m}^{-3}$, for the fourth one – $C_{2h} = 201 \text{ mol m}^{-3}$, for the fifth one – $C_{2h} = 601 \text{ mol m}^{-3}$ and for the sixth one – $C_{2h} = 1051 \text{ mol m}^{-3}$,
- 3) Concentrations of substances "1" and "2" located in compartment l are constant and equal $C_{1l} = C_{2l} = 1 \text{ mol m}^{-3}$.

The calculations in Eqs. (2)-(10) were made for the following values of hydraulic permeability (L_p), reflection (σ_1, σ_2), diffusive permeability ($\omega_{11}, \omega_{22}, \omega_{21}, \omega_{12}$) coefficients: $L_p = 4.9 \times 10^{-12} \text{ m}^3 \text{ N}^{-1} \text{ s}^{-1}$, $\sigma_1 = 0.068$, $\sigma_2 = 0.025$, $\omega_{11} = 0.8 \times 10^{-9} \text{ mol N}^{-1} \text{ s}^{-1}$, $\omega_{12} = 0.81 \times 10^{-13} \text{ mol N}^{-1} \text{ s}^{-1}$ and $\omega_{22} = 1.43 \times 10^{-9} \text{ mol N}^{-1} \text{ s}^{-1}$ and $\omega_{21} = 1.63 \times 10^{-12} \text{ mol N}^{-1} \text{ s}^{-1}$ (for exemple Batko *et al.*, 2014b). These values were determined in our previous study (Ślęzak, 1989). Calculations of concentration dependencies of coefficients $P_{11}, P_{12}, P_{13}, P_{21}, P_{22}, P_{23}, P_{31}, P_{32}$ and P_{33} resulted in curves presented in Figs. 1 and 2.

Denominator of Eqs. (2)-(10) may take positive values, negative values or zero. Considering that \bar{C}_1 and \bar{C}_2 are always positive, ξ value determines sign of the denominator. Denominator is negative for $\xi < 0$, and positive for $\xi > 0$. Thus, it is important to calculate for which values of \bar{C}_1 and \bar{C}_2 condition $\xi = 0$ is fulfilled. Therefore, considering values of transport parameters for the Nephrophan hemodializer membrane in Eq. (12), we obtain the following values of \bar{C}_1 for the established values of \bar{C}_2 , $\bar{C}_1 = 186.05 \text{ mol m}^{-3}$ (for $\bar{C}_2 = 2.79 \text{ mol m}^{-3}$), $\bar{C}_1 = 185.21 \text{ mol m}^{-3}$ (for $\bar{C}_2 = 4.17 \text{ mol m}^{-3}$), $\bar{C}_1 = 182.41 \text{ mol m}^{-3}$ (for $\bar{C}_2 = 8.74 \text{ mol m}^{-3}$), $\bar{C}_1 = 164.69 \text{ mol m}^{-3}$ (for $\bar{C}_2 = 37.71 \text{ mol m}^{-3}$), $\bar{C}_1 = 130.40 \text{ mol m}^{-3}$ (for $\bar{C}_2 = 93.77 \text{ mol m}^{-3}$) and $\bar{C}_1 = 95.44 \text{ mol m}^{-3}$ (for $\bar{C}_2 = 150.92 \text{ mol m}^{-3}$).

The individual dependencies $P_{ij}=f(\bar{C}_1, \bar{C}_2 = \text{const.})$ for $i, j \in \{1, 2, 3\}$ obtained on the base of Eqs. (2)-(5) and (7)-(9) result in pairs of coupled hyperboles (Figs. 1A and 1B). One of the curves is located in the first and the other in the fourth quadrant of a coordinate system. Thus, values of P_{ij} coefficients that form curves located in the first quadrant are positive, and values of P_{ij} coefficients that form curves located in the fourth quadrant are negative. In contrast, results of calculations obtained based on Eq. (6) and illustrated by graphs presented in Fig. 3 show that dependencies $P_{ij}=f(\bar{C}_1, \bar{C}_2 = \text{const.})$ for $i, j \in \{1, 2, 3\}$ form three hyperbolic curves. Two of these curves are paired and one is not, since conditions $\bar{C}_1 > 0$ and $\bar{C}_2 > 0$ are always fulfilled. Two of the curves are located in the first quadrant of a coordinate system and one in the fourth quadrant of a coordinate system. Coefficients P_{ij} for $i, j \in \{1, 2, 3\}$ from the first quadrant of a coordinate system are positive, and from fourth are negative.

Curves presented in Fig. 1A illustrate dependence $P_{11}=f(\bar{C}_1, \bar{C}_2 = \text{const.})$ calculated based on Eq. (2). If $\xi > 0$ then curves 1, 2, 3 and 4 located in the first quadrant of a coordinate system are solutions of Eq. (2). In contrast, if $\xi < 0$ then curves 1', 2', 3' and 4' located in the fourth quadrant of a coordinate system are solutions of Eq. (2). Adequate pair of curves (1 and 1', 2 and 2', 3 and 3', 4 and 4') form pair of symmetrical hyperboles. Course of the curves presented in this figure indicate that curves illustrating dependence $P_{11}=f(\bar{C}_1, \bar{C}_2 = \text{const.})$ move in direction of descending \bar{C}_1 values with increasing \bar{C}_2 values. Additionally, curves 1-4 are located in the first quadrant of a coordinate system if $\bar{C}_1 < 186.05 \text{ mol m}^{-3}$ (for curve 1), $\bar{C}_1 < 164.69 \text{ mol m}^{-3}$ (for curve 2), $\bar{C}_1 < 130.40 \text{ mol m}^{-3}$ (for curve 3) and $\bar{C}_1 < 95.44 \text{ mol m}^{-3}$ (for curve 4). This indicates that curves 1'-4' are located in the fourth quadrant of a coordinate system, since $\bar{C}_1 > 186.05 \text{ mol m}^{-3}$ (for curve 1'), $\bar{C}_1 > 164.69 \text{ mol m}^{-3}$ (for curve 2'), $\bar{C}_1 > 130.40 \text{ mol m}^{-3}$ (for curve 3') and $\bar{C}_1 > 95.44 \text{ mol m}^{-3}$ (for curve 4').

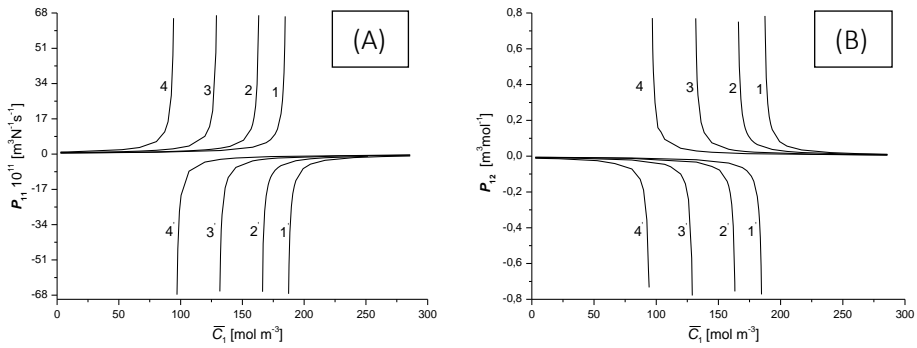


Fig. 1. Graphic illustration of dependence $P_{11}=f(\bar{C}_1, \bar{C}_2=\text{const.})$ calculated based on Eq. (2) (A) and dependence $P_{12}=f(\bar{C}_1, \bar{C}_2=\text{const.})$ calculated based on Eq. (3) (B) for solutions consisting of a solvent and two dissolved substances denoted with indexes "1" and "2". The average substance concentration indicated by the subscript "2" was constant and equaled: $\bar{C}_2=2.79 \text{ mol m}^{-3}$ (curves 1 and 1'), $\bar{C}_2=37.71 \text{ mol m}^{-3}$ (curves 2 and 2'), $\bar{C}_2=93.77 \text{ mol m}^{-3}$ (curves 3 and 3') and $\bar{C}_2=150.92 \text{ mol m}^{-3}$ (curves 4 and 4').

The course of curves illustrating dependence $P_{23}=f(\bar{C}_1, \bar{C}_2=\text{const.})$ and $P_{32}=f(\bar{C}_1, \bar{C}_2=\text{const.})$ obtained based on Eqs. (7) and (9) is very similar to the course of curves presented in Fig. 1. It should be indicated that coefficients P_{23} and P_{32} are measured in the same units ($\text{N}\cdot\text{s}\cdot\text{mol}^{-1}$) and slightly differ for the same \bar{C}_1 and \bar{C}_2 , whereas coefficient P_{11} is measured in different unit than coefficients P_{23} and P_{32} and it is also several ranges lower for the same \bar{C}_1 and \bar{C}_2 .

Curves shown in Fig. 1B illustrate dependence $P_{12}=f(\bar{C}_1, \bar{C}_2=\text{const.})$ calculated based on Eq. (3) for different \bar{C}_2 values. In contrast to curves shown in Fig.1, for $\xi>0$, curves 1'-4' located in the fourth quadrant of a coordinate system are a solution of Eq. (3). If $\xi<0$, curves 1-4 located in the first quadrant of a coordinate system are a solution of Eq. (3). Corresponding pairs of these curves (1 and 1', 2 and 2', 3 and 3', 4 and 4') form pairs of symmetrical hyperboles. It may be noticed that pairs of hyperboles illustrating dependence $P_{12}=f(\bar{C}_1, \bar{C}_2=\text{const.})$ are reversed compared to hyperboles illustrating dependence $P_{11}=f(\bar{C}_1, \bar{C}_2=\text{const.})$ for the same \bar{C}_2 values. The course of curves presented in this figure indicates that curves illustrating dependence

$P_{12}=f(\bar{C}_1, \bar{C}_2 = \text{const.})$ move in direction of descending \bar{C}_1 values with increasing \bar{C}_2 values. Moreover, curves 1-4 are located in the first quadrant of a coordinate system if $\bar{C}_1 > 186.05 \text{ mol m}^{-3}$ (for curve 1), $\bar{C}_1 > 164.69 \text{ mol m}^{-3}$ (for curve 2), $\bar{C}_1 > 130.40 \text{ mol m}^{-3}$ (for curve 3) and $\bar{C}_1 > 95.44 \text{ mol m}^{-3}$ (for curve 4). In contrast, curves 1'-4' are located in the fourth quadrant of a coordinate system, since $\bar{C}_1 < 186.05 \text{ mol m}^{-3}$ (for curve 1'), $\bar{C}_1 < 164.69 \text{ mol m}^{-3}$ (for curve 2'), $\bar{C}_1 < 130.40 \text{ mol m}^{-3}$ (for curve 3') and $\bar{C}_1 < 95.44 \text{ mol m}^{-3}$ (for curve 4').

Families of curves 1-4, 1'-4' and 1''-4'' presented in Fig. 2A illustrate dependence $P_{22}=f(\bar{C}_1, \bar{C}_2 = \text{const.})$ that is calculated based on Eq. (6). If $\xi > 0$, then hyperbolic curves 1-4 and 1''-4'' located in the first quadrant of a coordinate system are a solution of Eq. (6).

If $\xi < 0$, then hyperbolic curves 1'-4' located in the fourth quadrant of a coordinate system are solution of Eq. (6). It should be mentioned that curves 1 and 1', 2 and 2', 3 and 3', 4 and 4' form pair of symmetrical hyperboles. The course of curves presented in this figure indicates that curves illustrating dependence $P_{22}=f(\bar{C}_1, \bar{C}_2 = \text{const.})$ move in direction of descending \bar{C}_1 values with increasing \bar{C}_2 values. Moreover, curves 1-4 are located in the first quadrant of a coordinate system if $\bar{C}_1 < 186.05 \text{ mol m}^{-3}$ (for curve 1), $\bar{C}_1 < 164.69 \text{ mol m}^{-3}$ (for curve 2), $\bar{C}_1 < 130.40 \text{ mol m}^{-3}$ (for curve 3) and $\bar{C}_1 < 95.44 \text{ mol m}^{-3}$ (for curve 4).

This means that curves 1'-4' are located in the fourth quadrant of a coordinate system, since $\bar{C}_1 > 186.05 \text{ mol m}^{-3}$ (for curve 1'), $\bar{C}_1 > 164.69 \text{ mol m}^{-3}$ (for curve 2'), $\bar{C}_1 > 130.40 \text{ mol m}^{-3}$ (for curve 3') and $\bar{C}_1 > 95.44 \text{ mol m}^{-3}$ (for curve 4'). In contrast, based on analysis of the course of curves 1''-4'', we can state that curves illustrating dependence $P_{22}=f(\bar{C}_1, \bar{C}_2 = \text{const.})$ move in direction of ascending \bar{C}_1 values with increasing \bar{C}_2 values and that curves 1''-4'' nearly overlap.

Families of curves 1-6 and 1'-6' presented in Fig. 2B graphically illustrate dependence $P_{33}=f(\bar{C}_1, \bar{C}_2 = \text{const.})$ calculated based on Eq. (10). If $\xi > 0$, curves

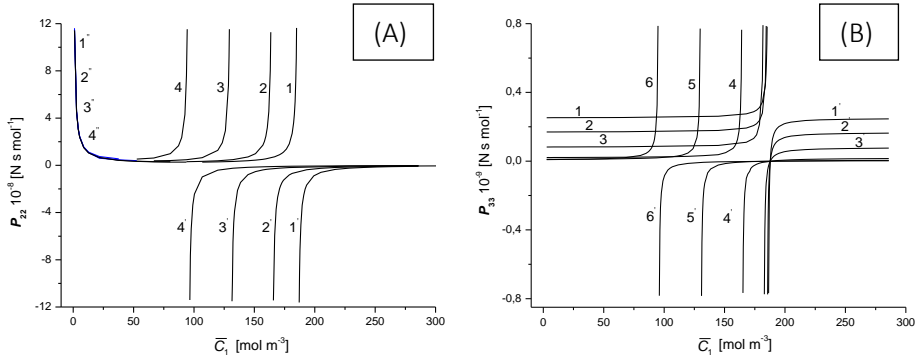


Fig. 2. Graphic illustration of dependence $P_{22}=f(\bar{C}_1, \bar{C}_2=\text{const.})$ calculated based on equation (6) (2A) and dependence $P_{33}=f(\bar{C}_1, \bar{C}_2=\text{const.})$ calculated based on Eq. (10) (2B) for solutions consisting of a solvent and two dissolved substances denoted with indexes "1" and "2".

The average substance concentration indicated by the subscript "2" in Fig. 2A was constant and equaled: $\bar{C}_2=2.79$ mol m⁻³ (curves 1 and 1'), $\bar{C}_2=37.71$ mol m⁻³ (curves 2 and 2'), $\bar{C}_2=93.77$ mol m⁻³ (curves 3 and 3') and $\bar{C}_2=150.92$ mol m⁻³ (curves 4 and 4'). The average substance concentration indicated with the subscript "2" in Fig. 2B was constant and equaled: $\bar{C}_2=2.79$ mol m⁻³ (curves 1 and 1'), $\bar{C}_2=4.17$ mol m⁻³ (curves 2 and 2'), $\bar{C}_2=8.74$ mol m⁻³ (curves 3 and 3'), $\bar{C}_2=37.71$ mol m⁻³ (curves 4 and 4'), $\bar{C}_2=93.77$ mol m⁻³ (curves 5 and 5') and $\bar{C}_2=150.92$ mol m⁻³ (curves 6 and 6').

1–6 located in the first quadrant of a coordinate system are a solution of Eq. (10). In contrast, if $\xi < 0$, curves 1'–6' located in the first and fourth quadrant of a coordinate system are a solution of Eq. (10). This figure shows that pairs of these curves 1 and 1', 2 and 2', 3 and 3', 4 and 4', 5 and 5', 6 and 6' form pairs of symmetrical hyperboles. Courses of the curves presented in this figure indicate that curves illustrating dependence $P_{33}=f(\bar{C}_1, \bar{C}_2=\text{const.})$ move in direction of descending \bar{C}_1 values with increasing \bar{C}_2 values. Moreover, it may be noticed that curves 1-6 are located in the first quadrant of a coordinate system if $\bar{C}_1 < 186.05$ mol m⁻³ (for curve 1), $\bar{C}_1 < 185.21$ mol m⁻³ (for curve 2), $\bar{C}_1 < 182.41$ mol m⁻³ (for curve 3), $\bar{C}_1 < 164.69$ mol m⁻³ (for curve 4), $\bar{C}_1 < 130.40$ mol m⁻³ (for curve 5) and $\bar{C}_1 < 95.44$ mol m⁻³ (for curve 6). This means that curves 1'–6' are located in the first and fourth quadrant of a coordinate system, since $\bar{C}_1 > 186.05$ mol m⁻³ (for curve 1), $\bar{C}_1 > 185.21$

mol m⁻³ (for curve 2), $\bar{C}_1 > 182.41$ mol m⁻³ (for curve 3), $\bar{C}_1 > 164.69$ mol m⁻³ (for curve 4), $\bar{C}_1 > 130.40$ mol m⁻³ (for curve 5) and $\bar{C}_1 > 95.44$ mol m⁻³ (for curve 6).

Curves 1'–6' pass from fourth to the first quadrant through a point where $P_{33}=0$ (Batko *et al.*, 2014b). Using Eq. (10) we can show that for this point $\bar{C}_1 = \omega_{11} [L_p(1-\sigma_1)^2]^{-1}$. Considering data in this equation, we obtain $\bar{C}_1 = 187.96$ mol m⁻³. This means that curve 1 is located in the fourth quadrant of a coordinate system for 186.05 mol m⁻³ < \bar{C}_1 < 187.96 mol m⁻³, curve 2 – for 185.21 mol m⁻³ < \bar{C}_1 < 187.96 mol m⁻³, curve 3 – for 182.41 mol m⁻³ < \bar{C}_1 < 187.96 mol m⁻³, curve 4 for 164.69 mol m⁻³ < \bar{C}_1 < 187.96 mol m⁻³, curve 5 – for 130.40 mol m⁻³ < \bar{C}_1 < 187.96 mol m⁻³ and curve 6 – for 95.44 mol m⁻³ < \bar{C}_1 < 187.96 mol m⁻³. For $\bar{C}_1 > 187.96$ mol m⁻³ curves 1'–6' are located in the first quadrant of a coordinate system.

CONCLUSIONS

The Peusner coefficients P_{ij} ($i, j \in \{1, 2, 3\}$) are non-linearly dependent on solutions concentrations \bar{C}_1 and \bar{C}_2 . Non-linearity of these coefficients results from the properties of mathematical equations describing coefficients P_{ij} . Equations describing dependence $P_{ij}=f(\bar{C}_1, \bar{C}_2=\text{const.})$ for coefficients P_{11} , P_{12} , P_{13} , P_{21} , P_{23} , P_{31} and P_{32} and different \bar{C}_2 values have solutions that form pairs of coupled hyperbolic curves located in the first and fourth quadrant of a coordinate system. In turn, for coefficient P_{22} , have solutions that form a family of coupled symmetrical hyperbolic curves located in the first and fourth quadrant of a coordinate system and a family of unpaired hyperbolic curves located in the first quadrant of a coordinate system. While for coefficient P_{33} has solutions forms families of coupled symmetrical hyperbolic curves. Top part of the family of curve pairs is located the first, whereas bottom part in the fourth and first quadrant of a coordinate system. Coefficient P_{33} changes from negative to positive upon passing through a point with the following coordinates ($P_{33}=0$, $\bar{C}_1=187.96$ mol m⁻³). Besides the network form of K-K equations containing Peusner coefficients P_{ij} ($i, j \in \{1, 2, 3\}$) is a convenient tool suitable for the examination of the membrane transport. The presented calculations showed that the values of coefficients P_{ij} are sensi-

tive to the composition and concentration of the solutions separated by a membrane.

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