

Membrane transport of the non-homogeneous ternary solutions: mathematical model of thicknesses of the concentration boundary layers

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Summary

We have presented the mathematical model, which can be the basis of determination of a numerical algorithm for the thickness of concentration boundary layers calculation for ternary nonelectrolyte solutions. This model is based on Rayleigh equation and second Kedem-Katchalsky equation for ternary solutions.

In proposed model, the thickness of concentration boundary layers is controlled by concentration Rayleigh number.

Key words: membrane transport, concentration boundary layers, concentration Rayleigh number, diffusion

Transport membranowy niejednorodnych roztworów ternarnych: model matematyczny grubości stężeniowych warstw granicznych

Streszczenie

Przedstawiono model matematyczny, który stanowi podstawę do opracowania algorytmu numerycznego obliczania grubości stężeniowych warstw granicznych dla ternarnych roztworów nieelektrolitów. Ten model oparty jest na równaniu Rayleigha i drugim równaniu Kedem-Katchalsky'ego dla roztworów ternarnych.

W związku z tym, w proponowanym modelu grubość stężeniowej warstwy granicznej jest sterowana przez stężeniową liczbę Rayleigha.

Słowa kluczowe: transport membranowy, stężeniowe warstwy graniczne, stężeniowa liczba Rayleigha, dyfuzja

INTRODUCTION

Concentration polarization (CP) is a well-known phenomenon arising at the interface between an ion-exchange membrane and an electrolyte solution when an electric current passes through the system [1]. CP occurs also when natural membrane divides nonelectrolyte solutions and the membrane transport is osmotic-diffusive [2-5]. Concentration boundary layers (CBL), created on the both sides of the membrane, limit the membrane transport because of a membrane concentration gradient decrease. It means that CBLs near membranes play the role of additional kinetics barriers in transport processes of rapidly permeating substances through natural and artificial membranes [6,7]. If solutions divided by the membrane mounted in a horizontal plane have layer characters, than for Rayleigh number's values lesser than critical value layer configuration is stable and membrane transport has only osmotic-diffusive character [8, 9]. On the other hand, for Rayleigh number's values greater than critical value the cell structure of the liquid, that is the indication of self-organization, can be observed [10].

In our papers each CBLs is treated as a quasi-membrane [4, 11-14]. It means that we can attribute transport coefficients to each CBLs the same as to real membrane. In this connection, mathematical description of the membrane transport in conditions where concentration boundary layers are on the both sides of the membrane may be done by classical methods like Nernst-Planck-Poisson [15,16], Fick [8, 17, 18] or Kedem-Katchalsky equations [4, 11, 13, 19-21]. The last way is the simplest one because of the assumption that concentration gradient in concentration boundary layers area is linear. Moreover, the Kedem-Katchalsky equations do not describe membrane structure. Rayleigh equations which introduce definition of concentration Rayleigh number may also contain linear concentration gradient [5, 9].

That is why in this paper we are presenting the mathematical model, which can be the basis of determination of a numerical algorithm for the thickness of CBLs calculation for ternary nonelectrolyte solutions. This model is based on the Rayleigh equation and the second Kedem-Katchalsky equation for multicomponent solutions. In this connection, in the proposed model the thickness of the concentration boundary layer is controlled by concentration Rayleigh number.

MATHEMATICAL MODEL OF CONCENTRATION BOUNDARY LAYERS IN TERNARY SOLUTIONS

In previous paper [22] it was shown that for linear gradient of concentration through CBLs, the Rayleigh equation for ternary solutions can be written in two forms

$$R_{Cl} = g \left[\frac{\partial \rho}{\partial C_1} (C_{e1} - C_{i1}) + \frac{\partial \rho}{\partial C_2} (C_{e2} - C_{i2}) \right] \delta_l^3 (D_l \rho_l \nu_l)^{-1} \quad (1)$$

$$R_{Ch} = g \left[\frac{\partial \rho}{\partial C_1} (C_{h1} - C_{i1}) + \frac{\partial \rho}{\partial C_2} (C_{h2} - C_{i2}) \right] \delta_h^3 (D_h \rho_h \nu_h)^{-1} \quad (2)$$

where D_l and D_h are the solute diffusion coefficients in layers l_l and l_h , C_e and C_i are the densities of solutions at interfaces: membrane/concentration boundary layers, ρ_l and ρ_h are the densities of solutions, ν_l and ν_h are the kinematic viscosity coefficients.

In order to calculate $(C_{e1} - C_{i1})$, $(C_{e2} - C_{i2})$, $(C_{h1} - C_{i1})$ and $(C_{h2} - C_{i2})$ we will carry out the following considerations on the basis of the second Kedem-Katchalsky equation. In the case of diffusive membrane transport of ternary nonelectrolyte solutions this equation can be written as

$$J_s = RT \sum_{k=1}^2 \omega_{ks} \Delta C_k + J_v (1 - \sigma_k) \bar{C}_k \quad (3)$$

where RT is the product of the gas constant and thermodynamic temperature, ΔC_k is the concentration difference of the k -th substance and ω_{ks} is the solute permeability coefficient. The solute permeability coefficients of the l_l and l_h equal $(\omega_{ks})_l = (D_{ks})_l (RT \delta_l)^{-1}$ and $(\omega_{ks})_h = (D_{ks})_h (RT \delta_h)^{-1}$, where $(D_{ks})_l$ and $(D_{ks})_h$ are the solute diffusion coefficients in the layers l_l and l_h , J_v is the volume flux, σ_k is the reflection coefficient for k -th substance, \bar{C} is the mean concentration in solution in membrane. On the basis of Eq. (3) for membrane system presented in Fig. 1, taking into consideration the condition $RT \sum_k \omega_{ks} \Delta C_k \gg J_v (1 - \sigma_k) \bar{C}_k$, we can write

$$J_{sl} = \delta_l^{-1} \sum_{k=1}^2 (D_{ks})_l (C_{ek} - C_{lk}) \quad (4)$$

$$J_{sm} = RT \sum_{k=1}^2 \omega_{ks} (C_{ik} - C_{ek}) \quad (5)$$

$$J_{sh} = \delta_h^{-1} \sum_{k=1}^2 (D_{ks})_h (C_{hk} - C_{ik}) \quad (6)$$

In the steady state, the following condition is fulfilled

$$J_{sl} = J_{sm} = J_{sh} = J_s \quad (7)$$

In order to simplify the calculations we will take into consideration the conclusion resulted from experiments carried out previously[4], that the diagonal coefficients are greater than the non-diagonal coefficients by three orders of magnitude. Thus provides the basis of reduction of above equations accepting $(D_{12})_l = (D_{12})_h = (D_{21})_l = (D_{21})_h \approx 0$ and $\omega_{12} = \omega_{21} \approx 0$.

Regarding these conditions and equations (4) – (7) we get

$$D_{l1} \delta_l^{-1} (C_{e1} - C_{l1}) = \omega_1 RT (C_{i1} - C_{e1}) = D_{h1} \delta_h^{-1} (C_{h1} - C_{i1}) \quad (8)$$

$$D_{l2} \delta_l^{-1} (C_{e2} - C_{l2}) = \omega_2 RT (C_{i2} - C_{e2}) = D_{h2} \delta_h^{-1} (C_{h2} - C_{i2}) \quad (9)$$

Making suitable transformations of the above equations, we can write

$$C_{e1} - C_{l1} = \omega_1 RT D_{h1} \delta_l (C_{h1} - C_{l1}) [D_{l1} D_{h1} + \omega_1 RT (D_{l1} \delta_h + D_{h1} \delta_l)]^{-1} \quad (10)$$

$$C_{e2} - C_{l2} = \omega_2 RT D_{h2} \delta_l (C_{h2} - C_{l2}) [D_{l2} D_{h2} + \omega_2 RT (D_{l2} \delta_h + D_{h2} \delta_l)]^{-1} \quad (11)$$

$$C_{h1} - C_{i1} = \omega_1 RT D_{l1} \delta_h (C_{h1} - C_{l1}) [D_{l1} D_{h1} + \omega_1 RT (D_{l1} \delta_h + D_{h1} \delta_l)]^{-1} \quad (12)$$

$$C_{h2} - C_{i2} = \omega_2 RT D_{l2} \delta_h (C_{h2} - C_{l2}) [D_{h2} D_{l2} + \omega_2 RT (D_{l2} \delta_h + D_{h2} \delta_l)]^{-1} \quad (13)$$

Combining Eqs. (1), (2) and (10) – (13) we obtain

$$\delta_l^5 + (\gamma_1 + \gamma_2 \delta_h) \delta_l^4 - \gamma_3 \delta_l^2 - \gamma_4 \delta_h^2 - \gamma_5 \delta_l \delta_h - \gamma_6 \delta_l - \gamma_7 \delta_h - \gamma_8 = 0 \quad (14)$$

$$\delta_h^5 + (\chi_1 + \chi_2 \delta_l) \delta_h^4 - \chi_3 \delta_h^2 - \chi_4 \delta_l^2 - \chi_5 \delta_l \delta_h - \chi_6 \delta_h - \chi_7 \delta_l - \chi_8 = 0 \quad (15)$$

where: $\gamma_1 = [\omega_1 D_{l2} \frac{\partial \rho}{\partial C_1} (C_{h1} - C_{l1}) + \omega_2 D_{l1} \frac{\partial \rho}{\partial C_2} (C_{h2} - C_{l2})] (\omega_1 \omega_2 \xi)^{-1}$,

$$\chi_1 = [\omega_1 D_{h2} \frac{\partial \rho}{\partial C_1} (C_{h1} - C_{l1}) + \omega_2 D_{h1} \frac{\partial \rho}{\partial C_2} (C_{h2} - C_{l2})] (\omega_1 \omega_2 \xi)^{-1},$$

$$\gamma_2 = [D_{h1} D_{l2} \frac{\partial \rho}{\partial C_1} (C_{h1} - C_{l1}) + D_{l1} D_{h2} \frac{\partial \rho}{\partial C_2} (C_{h2} - C_{l2})] (D_{h1} D_{h2} \xi)^{-1},$$

$$\chi_2 = [D_{l1} D_{h2} \frac{\partial \rho}{\partial C_1} (C_{h1} - C_{l1}) + D_{l2} D_{h1} \frac{\partial \rho}{\partial C_2} (C_{h2} - C_{l2})] (D_{l1} D_{l2} \xi)^{-1},$$

$$\gamma_3 = R_{Cl} D_{l1} \rho_l \nu_l (g \xi)^{-1}, \quad \chi_3 = R_{Ch} D_{h1} \rho_h \nu_h (g \xi)^{-1}, \quad \gamma_4 = R_{Cl} D_{l1}^2 D_{l2} \rho_l \nu_l (g D_{h1} D_{h2} \xi)^{-1},$$

$$\chi_4 = R_{Cl} D_{h1}^2 D_{h2} \rho_h \nu_h (g D_{l1} D_{l2} \xi)^{-1}, \quad \gamma_5 = R_{Cl} \rho_l \nu_l D_{l1} (D_{l1} D_{h2} + D_{h1} D_{l2}) (g D_{h1} D_{h2} \xi)^{-1},$$

$$\chi_5 = R_{Ch} \rho_h \nu_h D_{h1} (D_{l1} D_{h2} + D_{h1} D_{l2}) (g D_{l1} D_{l2} \xi)^{-1},$$

$$\begin{aligned}
\gamma_6 &= R_{Cl} \rho_l \nu_l D_{l1} (D_{l1} \omega_2 + D_{l2} \omega_1) (gRT \omega_1 \omega_2 \xi)^{-1}, \quad \chi_6 = R_{Ch} \rho_h \nu_h D_{h1} (D_{h1} \omega_2 + D_{h2} \omega_1) (gRT \omega_1 \omega_2 \xi)^{-1} \\
\gamma_7 &= R_{Cl} D_{l1}^2 \rho_l \nu_l D_{l2} (D_{h1} \omega_2 + D_{h2} \omega_1) (gRT D_{h1} D_{h2} \omega_1 \omega_2 \xi)^{-1}, \\
\chi_7 &= R_{Ch} D_{h1}^2 \rho_h \nu_h D_{h2} (D_{l1} \omega_2 + D_{l2} \omega_1) (gRT D_{h1} D_{h2} \omega_1 \omega_2 \xi)^{-1}, \\
\gamma_8 &= R_{Cl} D_{l1}^2 D_{l2} \rho_l \nu_l [g(RT)^2 \omega_1 \omega_2 \xi]^{-1}, \quad \chi_8 = R_{Ch} D_{h1}^2 D_{h2} \rho_h \nu_h [g(RT)^2 \omega_1 \omega_2 \xi]^{-1}, \\
\xi &= \frac{\partial \rho}{\partial C_1} (C_{h1} - C_{l1}) + \frac{\partial \rho}{\partial C_2} (C_{h2} - C_{l2}).
\end{aligned}$$

The (15) and (16) are fifth order equations and contain components, in which l and h mixed indicators occur. That is why they can only be calculated numerically by Mathematica program. If we assume that $R_{Cl} = R_{Ch} = R_C$, $D_{l1} = D_{h1} = D_1$, $D_{l2} = D_{h2} = D_2$, $\rho_l = \rho_h = \rho$ and $\nu_l = \nu_h = \nu$, we obtain $\delta_l = \delta_h = \delta$, $\gamma_1 = \chi_1$, $\gamma_2 = \chi_2$, $\gamma_3 = \chi_3$, $\gamma_4 = \chi_4$, $\gamma_5 = \chi_5$, $\gamma_6 = \chi_6$, $\gamma_7 = \chi_7$ and $\gamma_8 = \chi_8$. In result, Eqs. (14) and (15) can be rewritten in form

$$\delta^5 + \alpha_1 \delta^4 - \alpha_2 \delta^2 - \alpha_3 \delta - \alpha_4 = 0 \quad (16)$$

where $\alpha_1 = [\omega_1 D_2 \frac{\partial \rho}{\partial C_1} (C_{h1} - C_{l1}) + \omega_2 D_1 \frac{\partial \rho}{\partial C_2} (C_{h2} - C_{l2})] (2\omega_1 \omega_2 \xi)^{-1}$, $\alpha_2 = 2R_C D_1 \rho \nu (g\xi)^{-1}$,

$$\alpha_3 = R_C \rho \nu D_1 (D_1 \omega_2 + D_2 \omega_1) (gRT \omega_1 \omega_2 \xi)^{-1}, \quad \alpha_4 = R_C D_1^2 D_2 \rho \nu [2g(RT)^2 \omega_1 \omega_2 \xi]^{-1}.$$

The formalism described above, that we propose to calculate concentration boundary layers, is correct with regard to way of calculating the concentration difference, states a little far from stable hydrodynamic state [10]. Similarly like for binary solutions, the thickness of concentration boundary layers may be determined with Mach-Zehnder interferometer equipped with proper software [23].

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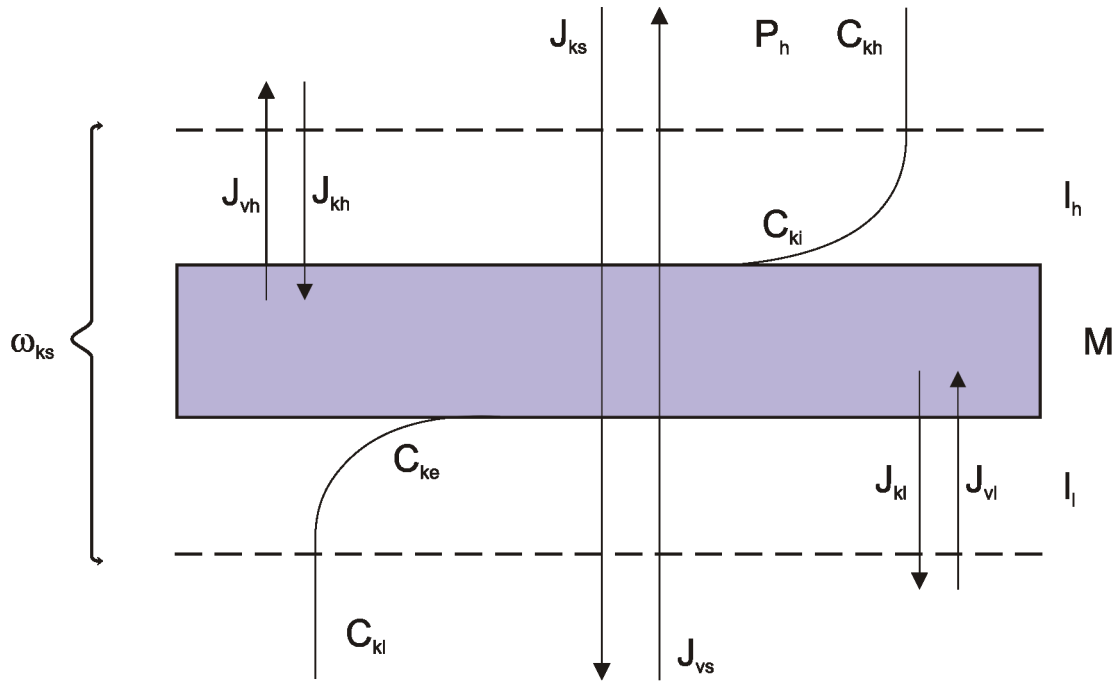


Fig. The membrane system: M – membrane; l_l , l_h – concentration boundary layers (CBLs); ω_{ks} – solute permeability coefficient; P_l , P_h – the mechanical pressures outside the boundaries; P_e , P_i – the mechanical pressure at boundaries l_l/M and M/l_h ; C_{kl} , C_{kh} – concentrations of solutions outside the boundaries; C_{ke} , C_{ki} – the concentrations of solutions at boundaries l_l/M and M/l_h ; J_{vl} , J_{vh} i J_{vs} – volume fluxes through the layers l_l and l_h , and complex $l_l/M/l_h$, respectively; J_{kl} , J_{kh} i J_{ks} – fluxes of k-th substance ($k=1, 2$) through the layers l_l and l_h , and complex $l_l/M/l_h$, respectively.

Ryc . Układ membranowy: M – membrana; l_l , l_h – stężeniowe warstwy graniczne (CBL); ω_{ks} – współczynnik przepuszczalności substancji rozpuszczonej; P_l , P_h – ciśnienia hydrostatyczne za zewnątrz warstw; P_e , P_i – ciśnienia mechaniczne na granicach l_l/M oraz M/l_h ; C_{kl} , C_{kh} – stężenia roztworów na zewnątrz warstw; C_{ke} , C_{ki} – stężenia roztworów na granicach l_l/M oraz M/l_h ; J_{vl} , J_{vh} i J_{vs} – strumienie objętościowe odpowiednio przez warstwy l_l i l_h oraz kompleks $l_l/M/l_h$; J_{kl} , J_{kh} i J_{ks} – strumienie k-tej ($k=1, 2$) substancji odpowiednio przez warstwy l_l i l_h oraz kompleks $l_l/M/l_h$.

