Estimation of thickness of concentration boundary layers by osmotic volume flux determination

Jolanta S. Jasik-Ślęzak[1], Kornelia M. Olszówka[2] and Andrzej Ślęzak[1]

[1] *Department of Public Health, Częstochowa University of Technology, Armia Krajowa al. 36b, 42 200 Częstochowa, Poland*
[2] *Department of Informatics for Economics, University of Economics, Bogucicka 3B, 40 287 Katowice, Poland*

Abstract. The estimation method of the concentration boundary layers thicknesses (δ) in a single-membrane system containing non-electrolytic binary or ternary solutions was devised using the Kedem-Katchalsky formalism. A square equation used in this method contains membrane transport (L_p, σ, ω) and solution (D, C) parameters as well as a volume osmotic flux (J_v). These values can be determined in a series of independent experiments. Calculated values δ are nonlinearly dependent on the concentrations of investigated solutions and the membrane system configuration. These nonlinearities are the effect of a competition between spontaneously occurring diffusion and natural convection. The mathematical model based on Kedem-Katchalsky equations and a concentration Rayleigh number (R_C) was presented. On the basis of this model we introduce the dimensionless parameter, called by us a Katchalsky number (Ka), modifies R_C of membrane transport. The critical value of this number well describes a moment of transition from the state of diffusion into convective diffusion membrane transport.

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

Abbreviations: CBL, concentration boundary layers; J_v, osmotic volume flux; J_s, solute flux; Ka, Katchalsky number; K-K, Kedem-Katchalsky; R_C, concentration Rayleigh number.

Introduction

The creation of concentration boundary layers (CBL) is an important process occurring in model and biological systems (Barry and Diamond 1984; Levitt et al. 1989; Schlichting and Gersten 2004; Missner et al. 2008). These layers serve as additional kinetic barriers to the fast penetrating substances, both through natural and artificial membranes (Winne 1973; Ślęzak 1989; Dionne et al. 1996; Pohl et al. 1998; Peppenheimer 2001; Baumgartner and Montrose 2004; Loftsson et al. 2006; Knipfer and Steudle 2008). CBL are formed spontaneously on both sides of a membrane separating two solutions of different concentrations. The process involved in its creation is called diffusion. A process of CBL creation

is called the concentration polarization (Spiegler 1971). The basic parameter of CBL is its thickness (δ), which increases following to the equation $\delta = k \cdot t^a$, where k is a constant and t is time, for free diffusion a = 0.5. Diffusion may be accompanied by other processes of destructive nature, including free and forced convection (Rubinstein and Zaltzman 2000; Dworecki et al. 2005). The process of free convection creation is controlled by a dimensionless parameter called the concentration Rayleigh number (R_C) (Normand and Pomeau 1977; Ślęzak et al. 1984; Dworecki et al. 2005). This number that expresses the ratio of buoyancy forces to the dissipative forces of diffusion and viscosity is calculated on the basis of boundary layer thicknesses as a characteristic dimension. It characterizes the limit of stability, as

$$R_C = \frac{g\alpha_C\beta_C\delta^4}{Dv} \tag{1}$$

where: g is the gravitational acceleration, δ the thickness of the CBL, $\alpha_C = (\partial\rho/\partial C)/\rho$ the variation of density with

Correspondence to: Jolanta S. Jasik-Ślęzak, Department of Public Health, Częstochowa University of Technology, Armia Krajowa al. 36b, 42 200 Częstochowa, Poland
E-mail: ajslezak@zim.pcz.pl

the concentration, $\beta_C = \partial C/\partial z$ the concentration gradient through the CBL, ρ the mass density, D the diffusion coefficient of the solute and v is the kinematic viscosity of the fluid.

For the concentration Rayleigh number greater than its critical value, the hydrodynamic instability occurs to lead to natural convection which reduces the thickness of CBL and increases the value of concentration gradient of the membrane and consequently osmotic stimulus (Ślęzak 1989; Dworecki 2005). The existence of such a regulatory mechanism at the presence of an external field enables to explain an aim of the osmotic effects, such as the osmotic volume flux amplification (Kargol et al. 1979; Ślęzak 1989; Ślęzak et al. 2002). This effect occurs in the single-membrane system containing ternary solutions in conditions of concentration polarization (Ślęzak 1989), and occurs when the density gradient in CBL in surroundings of horizontally mounted membrane is anti-parallel to the vector of gravity. In the extreme case, the extensive movements throughout the solutions, which are caused in the model artificial systems usually by mechanical mixing, lead to homogeneity of these solutions. Thickness δ can be determined experimentally by the optical method (Dworecki 1995; Dworecki et al. 2003; Larchet et al. 2008; Fernández-Sempere et al. 2009). The thickness can also be estimated by measuring the osmotic volume flux (Helfferich 1962; Barry and Diamond 1984). The review of methods determining the thickness of CBL is presented in the papers as follows (Barry and Diamond 1984; Larchet et al. 2008).

In the previous paper (Ślęzak et al. 2010) it was presented that for binary solutions (aqueous glucose solutions), concentration polarization of the membrane in a horizontal plane depends both on diffusion and hydrodynamic instabilities at the membrane surface. The cause of such instabilities is asymmetry of membrane transport in the gravitational field. We state that this asymmetry was observed for the cases with R_C greater than a critical value. The mathematical model based on Kedem-Katchalsky (K-K) equations

and R_C number was presented. On the basis of this model and the dependence of volume flux through the membrane as a function of glucose concentration in the upper (Fig. 1, configuration B) and lower (Fig. 1, configuration A) chamber of the membrane system, the dependencies of thickness of CBL, R_C, and the introduced coefficient of asymmetry as a function of glucose concentration were presented for both configuration. The asymmetry of membrane transport is observed for $R_C > (R_C)_{crit}$ and $\Delta C > (\Delta C)_{crit}$.

In this paper we present a method for estimating the thickness of CBL (δ) in a single-membrane system that contains ternary nonionic solutions, i.e. glucose solution in 0.2 mol/l aqueous ethanol solution. This method, based on the K-K formalism for ternary solutions and an experimentally measured osmotic flux as a function of glucose concentration in aqueous ethanol solutions in the upper (Fig. 1, configuration B) and the lower (Fig. 1, configuration A) chamber of the membrane system with the membrane in a horizontal plane, is presented in this paper. We derive a mathematical formula, which contains the membrane (L_p, σ, ω), the solutions (D, C) transport parameters and the osmotic volume flux (J_v). Besides, we introduce a mathematical formula called by us the Katchalsky number (Ka), which contains the membrane (ω), solutions (v, C), thickness of CBLs (δ), α_C^{-1}, etc. The dependencies of Ka for the membrane system with Nephrophan hemodialyser membrane in the horizontal plane as a function of glucose concentration in binary and ternary solutions were also calculated.

Materials and Methods

Let us consider a model shown in Fig. 1, in which a neutral, symmetric, isotropic and selective polymer membrane (M) separates two heterogeneous (mechanically unstirred) ternary non-electrolyte solutions with concentrations C_{kh} and C_{kl} (C_{kh} C_{kl}, $k = 1, 2$) at the initial moment ($t = 0$). In the configuration A, solution with concentration C_{kl} is located in
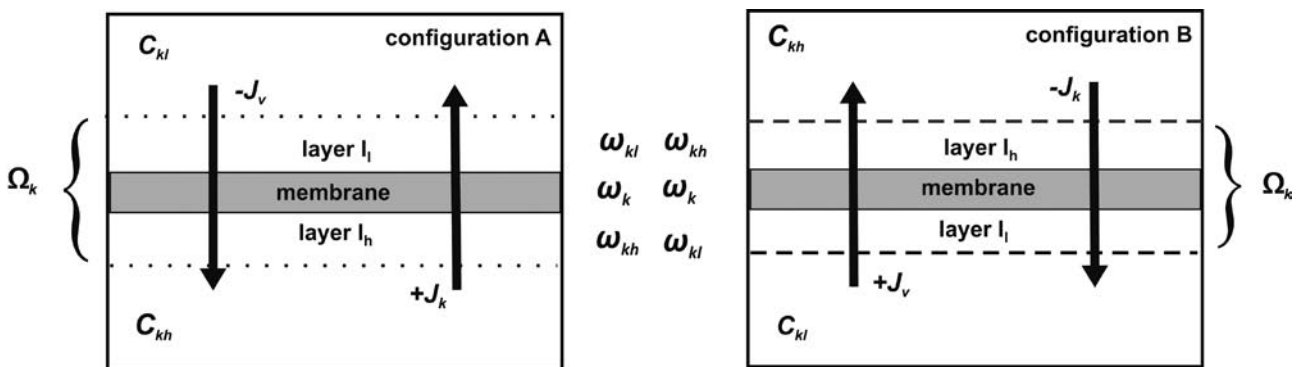

Figure 1. The model of single-membrane system (see the description in the text).

the compartment above the membrane, whereas a solution with concentration C_{kh} is located below the membrane. In the configuration B, the location of solutions with concentration of C_{kl} and C_{kh} is opposite.

Under these conditions, water and two dissolved substances ($k = 1, 2$) diffusing through the membrane form the CBL l_h and l_l on both sides of the membrane. The thicknesses of the layers l_h and l_l (δ_i and δ_e), respectively, are increased following the dependencies $\delta_I = K_i \cdot t^{0.5}$ and $\delta_e = K_e \cdot t^{0.5}$, where K_i and K_e are certain experimental constants (Dworecki et al. 2000, 2005). These layers cause that the concentration difference decreases from $C_{kh} - C_{kl}$ to $C_{ki} - C_{ke}$, where $C_{ki} > C_{ke}$, $C_{kh} > C_{ki}$ and $C_{ke} > C_{kl}$. When the solution of lower density is below the membrane, then the system $l_h/M/l_l$ loses stability and natural convection that has destructive properties may appear in the near-membrane areas. This process limits the growth in thickness of CBL and accelerates diffusion of substances outside the layers (Ślęzak 1989). Natural convection occurs when the hydrodynamic conditions cause that the CBL thickness δ_i and δ_e reach critical values $(\delta_i)_{crit}$ and $(\delta_e)_{crit}$, and R_C (R_{Ch}, R_{Cl}) that control the natural convection process reach their critical values. Then, the process of natural convection develops and in certain conditions can even lead to the liquid-type structure called "plum structure" (Puthenveettil and Arakeri 2008). The process of creation of concentration layers may be presented by optical methods (Dworecki 1995; Dworecki et al. 2005). Moreover, the characteristics $\delta_I = f(t)$, $\delta_e = f(t)$, $\Delta C_h = f(t)$ and $\Delta C_l = f(t)$ can be calculated using a proper set of measurement, the mathematical procedure presented in the papers Dworecki et al. (2003, 2005) and specialized software. In the special case, when the process of creation of the layers l_h and l_l is symmetrical, one can assume that $\delta_i = \delta_e = \delta$.

The process of creation of the CBL is accompanied by osmotic volume and solute flows, which are measured as the osmotic volume flux (J_v) and solute flux (J_s). We assume that J_v and J_s are positive when they are directed vertically upwards, and negative when directed downwards. In the initial moment, when solutions separated by the membrane are homogeneous, the flux J_v for the certain concentrations of solutions reaches the maximum value (Ślęzak and Dworecki 1984; Ślęzak et al. 2002). The formation of layers l_h and l_l reduces the difference in concentrations on the membrane, and thus reduces the value of the flux J_v (Ślęzak 1989). This flux can be determined using the procedure described in the paper Ślęzak and Dworecki (1984), or can be calculated using the K-K formalism (Grzegorczyn et al. 2008).

For osmotic volume flows of homogeneous (evenly stirred) solutions, the value of the osmotic volume flux does not depend on the configuration of the membrane cell. Therefore, to describe this volume flux the classic form of K-K equation is sufficient and can be written in the following form:

$$J_v = L_p \left(\sum_{k=1}^{2} \sigma_k \Delta \pi_k - \Delta P \right) \tag{2}$$

$$J_s = \sum_{k=1}^{2} \omega_{ks} \Delta \pi_k + J_v (1 - \sigma_s) \overline{C}_s \tag{3}$$

where J_v and J_s are volume and solute fluxes, respectively; L_p is the coefficient of hydraulic permeability; ΔP the hydrostatic pressure difference; σ_k and σ_s are the reflection coefficients of the membrane for the k-th and s-th substance, respectively, $\Delta \pi_k = RT(C_{kh} - C_{kl})$ is the osmotic pressure difference for k-th substance; RT the product of gas constant and thermodynamic temperature; C_{kh} and C_{kl} the concentration of homogeneous solutions; the subscript $k = 1, 2$ refers to the solute; indexes h and l signify higher (h) and lower (l) the concentration of "1" and "2" ternary solutions; $\overline{C}_s$ is an average solute concentration; $\overline{C}_s = 0.5(C_{sh} + C_{sl})$, ω_{ks} is the permeability of the s-th substance which passes across the membrane under the influence of a gradient of the k-th substance osmotic pressure difference ($\omega_{ks} = \omega_{sk} \overline{C}_s \overline{C}_k^{-1}$) and $s, k = 1, 2, s \neq k$. For $\Delta P = 0$, the following condition is fulfilled

$$\sum_{k=1}^{2} \omega_{ks} \Delta \pi_k \gg J_v (1 - \sigma_s) \overline{C}_s \tag{4}$$

Lack of mechanical mixing enables a spontaneous creation of CBL. In this case, K-K equation should be written in a different form, presented in the paper Ślęzak et al. (1989). For ternary non-electrolyte solutions in conditions $\Delta P = 0$, the equation describing the osmotic volume flux can be written in the following form:

$$J_v = L_p RT [\sigma_1 \zeta_1 (C_{1h} - C_{1l}) + \sigma_2 \zeta_2 (C_{2h} - C_{2l})] \tag{5}$$

where: ζ_1 and ζ_2 are coefficients of concentration polarization for substances "1" and "2", respectively, in ternary solution.

In the previous paper (Ślęzak et al. 2005) it was shown that coefficients ζ_1 and ζ_2 for the case where $\delta_i = \delta_e = \delta$ can be written as

$$\zeta_1 = \Omega_1 \omega_1^{-1} = D_1 (D_1 + 2RT\omega_1\delta)^{-1} \tag{6}$$

$$\zeta_2 = \Omega_2 \omega_2^{-1} = D_2 (D_2 + 2RT\omega_2\delta)^{-1} \tag{7}$$

where: Ω_1 and Ω_2 are permeability coefficients of the complex $l_h/M/l_l$ of the substance "1" and "2", D_1 and D_2 are coefficients of diffusion in solutions for substances "1" and "2", ω_1 and ω_2 are coefficients of permeability of substances through the membrane for substances "1" and "2", δ is average thickness of concentration boundary layer.

Taking into consideration Eqs. (6) and (7) in Eq. (5) and applying necessary transformations, we obtain the square equation for δ

$$\delta^2 + \psi\delta + \chi = 0 \tag{8}$$

where: $\psi = \alpha[\beta - L_p(\kappa_1\Delta C_1 + \kappa_2\Delta C_2)J_v^{-1}]$; $\chi = \gamma[1 - L_pRT(\sigma_1\Delta C_1 + \sigma_2\Delta C_2)J_v^{-1}]$; $\alpha = (2\omega_1\omega_2)^{-1}$; $\beta = (D_1\omega_2 + D_2\omega_1)(RT)^{-1}$; $\kappa_1 = \sigma_1D_1\omega_2$; $\kappa_2 = \sigma_2D_2\omega_1$; $\gamma = 0.25D_1D_2(RT)^{-2}(\omega_1\omega_2)^{-1}$; $\Delta C_1 = C_{1h} - C_{1l}$, $\Delta C_2 = C_{2h} - C_{2l}$

Solving Eq. (8), using the typical procedure for solving a square equation, we obtain the average δ that is dependent on the individual components of ternary solutions. For binary non-electrolytic solutions, Eq. (8) can be simplified to the form:

$$\delta = \tfrac{1}{2}D\omega^{-1}[L_p\sigma J_{vi}^{-1}(C_h - C_l) - (RT)^{-1}] \tag{9}$$

For the CBL l_l and l_h, using the following relations $\alpha_e\beta_e = (\rho_e - \rho_l)(\rho_l\delta_e)^{-1}$ and $\alpha_i\beta_i = (\rho_h - \rho_i)(\rho_h\delta_i)^{-1}$, Eq. (1) can be written in the following forms (Ślęzak et al. 1984; Guyon et al. 2001; Dworecki et al 2005):

$$(R_C)_e = \frac{\rho_e - \rho_l}{\rho_l}\frac{g\delta_e^3}{D_e\nu_l} \tag{10}$$

$$(R_C)_i = \frac{\rho_h - \rho_i}{\rho_h}\frac{g\delta_i^3}{D_i\nu_h} \tag{11}$$

where D_e and D_i are the solute diffusion coefficients in the layers l_l and l_h, ν_l and ν_h are the kinematic viscosity coefficients, ρ_e and ρ_i are the densities of solutions at the interfaces: membrane/CBLs, and ρ_l, ρ_h are the solutions densities outside the layers. In order to estimate $(\rho_e - \rho_l)$ and $(\rho_h - \rho_i)$ in the steady state, we will make the following consideration. For small glucose (index 1) and ethanol (index 2) concentrations the density is linear, so

$$\rho_e - \rho_l = \sum_{k=1}^{2}\frac{\partial\rho}{\partial C_k}(C_{ke} - C_{kl}) \tag{12}$$

$$\rho_h - \rho_i = \sum_{k=1}^{2}\frac{\partial\rho}{\partial C_k}(C_{kh} - C_{ki}) \tag{13}$$

In order to calculate differences of solutions $(C_{ke} - C_{kl})$ and $(C_{kh} - C_{ki})$ ($k = 1, 2$) for the stationary state, the following considerations will be carried out. In the case of membrane transport of ternary non-electrolyte solutions, on the basis of Eqs. (3) and (4) for the membrane system presented in Fig. 1, we can write

$$J_{sl} = \frac{1}{\delta_e}\sum_{k=1}^{2}D_{ks}(C_{ke} - C_{kl}) \tag{14}$$

$$J_{sm} = RT\sum_{k=1}^{2}\omega_{ks}(C_{ki} - C_{ke}) \tag{15}$$

$$J_{sh} = \frac{1}{\delta_i}\sum_{k=1}^{2}D_{ks}(C_{kh} - C_{ki}) \tag{16}$$

If fluxes of dissolved substances permeating through layer l_h, membrane M and layer l_h stand for J_{sl}, J_{sm} and J_{sh}, respectively, in the stationary state, they fulfill condition $J_{sl} = J_{sm} = J_{sh}$. Using Eqs. (14)–(16) we get

$$\frac{1}{\delta_e}\sum_{k=1}^{2}D_{ks}(C_{ke} - C_{kl}) = RT\sum_{k=1}^{2}\omega_{ks}(C_{ki} - C_{ke}) =$$
$$= \frac{1}{\delta_i}\sum_{k=1}^{2}D_{ks}(C_{kh} - C_{ki}) \tag{17}$$

If we assume that $D_1 \gg D_{21}$, $D_2 \gg D_{12}$, $\omega_1 \gg \omega_{21}$ and $\omega_2 \gg \omega_{12}$ on the basis of above equation, we obtain

$$C_{1e} - C_{1l} = \frac{RT\omega_1\delta_e D_{1i}(C_{1h} - C_{1l})}{RT\omega_1(D_{1i}\delta_e + D_{1e}\delta_i) + D_{1e}D_{1i}} \tag{18}$$

$$C_{2e} - C_{2l} = \frac{RT\omega_2\delta_e D_{2i}(C_{2h} - C_{2l})}{RT\omega_2(D_{2i}\delta_e + D_{2e}\delta_i) + D_{2e}D_{2i}} \tag{19}$$

$$C_{1h} - C_{1i} = \frac{RT\omega_1\delta_i D_{1e}(C_{1h} - C_{1l})}{RT\omega_1(D_{1e}\delta_i + D_{1i}\delta_e) + D_{1e}D_{1i}} \tag{20}$$

$$C_{2h} - C_{2i} = \frac{RT\omega_2\delta_i D_{2l}(C_{2h} - C_{2l})}{RT\omega_2(D_{2e}\delta_i + D_{2i}\delta_e) + D_{2e}D_{2i}} \tag{21}$$

Combining Eqs. (10)–(13) and (18)–(21), we obtain equations describing concentration Rayleigh numbers R_{Cl} and R_{Ch} for the isothermal membrane transport

$$R_{Cl} = \frac{gRT\delta_e^4}{\rho_l\nu_lD_{1e}}\left\{\frac{\partial\rho}{\partial C_1}\eta_1(C_{1h} - C_{1l}) + \right.$$
$$\left. + \frac{\partial\rho}{\partial C_2}\eta_2(C_{2h} - C_{2l})\right\} \tag{22}$$

$$R_{Ch} = \frac{gRT\delta_i^4}{\rho_h\nu_hD_{1i}}\left\{\frac{\partial\rho}{\partial C_1}\lambda_1(C_{1h} - C_{1l}) + \right.$$
$$\left. + \frac{\partial\rho}{\partial C_2}\lambda_2(C_{2h} - C_{2l})\right\} \tag{23}$$

where

$\eta_1 = \omega_1D_{1i}[RT\omega_1(D_{1i}\delta_e + D_{1e}\delta_i) + D_{1e}D_{1i}]^{-1}$
$\eta_2 = \omega_2D_{2i}[RT\omega_2(D_{2i}\delta_e + D_{2e}\delta_i) + D_{2e}D_{2i}]^{-1}$
$\lambda_1 = \omega_1D_{1e}[RT\omega_1(D_{1i}\delta_e + D_{1e}\delta_i) + D_{1e}D_{1i}]^{-1}$
$\lambda_2 = \omega_2D_{2e}[RT\omega_2(D_{2i}\delta_e + D_{2e}\delta_i) + D_{2e}D_{2i}]^{-1}$

$\partial\rho/C_1$ and $\partial\rho/C_2$ are the variation of solution density with concentration of glucose (subscript 1) and ethanol (subscript 2), D_{1e} and D_{1i} the coefficients of solute diffusion in the layers l_l and l_h, respectively, and δ_e and δ_i are the

thicknesses of the layers l_l and l_h, respectively. One anticipates the onset of large-scale natural convection when the experimental R_C exceeds some critical value.

Assuming that for the complex $l_l/M/l_h$, in steady state, $\delta_e = \delta_i = \delta$, $D_{1e} = D_{1i} = D_1$, $D_{2e} = D_{2i} = D_2$, and for small glucose and ethanol concentration $v_l\rho_l = v_h\rho_h = v_o\rho_o$, we can write on the basis of above equation

$$R_{Cl} = R_{Ch} = R_C = \frac{gRT\delta^4}{\rho_o v_o D_1}\left\{\frac{\partial\rho}{\partial C_1}\left[\frac{\omega_1(C_{1h} - C_{1l})}{2RT\omega_1\delta + D_1}\right] + \right.$$
$$\left. + \frac{\partial\rho}{\partial C_2}\left[\frac{\omega_2(C_{2h} - C_{2l})}{2RT\omega_2\delta + D_2}\right]\right\} \qquad (24)$$

We have obtained the equation describing the R_C for isothermal passive trans-membrane transport processes. If we find the critical value of $\delta = \delta_{crit}$, on the basis of that equation we can calculate the critical value of R_C. The remaining parameters: ρ_o, v_o, ω_1, ω_2, D_1, D_2, $\partial\rho/C_1$, $\partial\rho/\partial C_2$ needed to calculate $(R_C)_{crit}$ value on the basis of Eq. (24) were determined experimentally.

Eqs. (6) and (7) can be transformed to the following form

$$D_1 = \frac{2\zeta_1 RT\omega_1\delta}{1 - \zeta_1} \qquad (25)$$

$$D_2 = \frac{2\zeta_2 RT\omega_2\delta}{1 - \zeta_2} \qquad (26)$$

Inserting Eqs. (25) and (26) into Eq. (24), we get

$$R_C = \frac{g\delta^2(1 - \zeta_1)}{4RT\rho_o v_o\omega_1\zeta_1}\left[\frac{\partial\rho}{\partial C_1}(1 - \zeta_1)(C_{1h} - C_{1l}) + \right.$$
$$\left. + \frac{\partial\rho}{\partial C_2}(1 - \zeta_2)(C_{2h} - C_{2l})\right] \qquad (27)$$

We have obtained the equation describing the modified R_C for isothermal passive trans-membrane transport processes.

If we assume that $\zeta_1 = \zeta_2 = \zeta$, we can write on the basis of above equation

$$\frac{4R_C\rho_o v_o RT\omega_1}{g\delta^2}\left[\frac{\partial\rho}{\partial C_1}(C_{1h} - C_{1l}) + \frac{\partial\rho}{\partial C_2}(C_{2h} - C_{2l})\right]^{-1}$$
$$= \frac{(1 - \zeta)^2}{\zeta} = Ka \qquad (28)$$

Such a modified form of R_C we will call the Katchalsky number (Ka). The above expression can be used to describe the transition from the state of diffusion to convective diffu-

sion in the membrane system. On the basis of Eqs. (1), (24), or (28) the critical values of the density gradient $(\partial\rho/\partial z)_{crit}$ were obtained, in which the diffusive-convective transport appears as well

$$\frac{\partial\rho}{\partial z} = RT\left[\left(\frac{\partial\rho}{\partial C_1}\right)\frac{\omega_1(C_{1h} - C_{1l})}{D_1 + 2RT\omega_1\delta} + \left(\frac{\partial\rho}{\partial C_2}\right)\frac{\omega_2(C_{2h} - C_{2l})}{D_2 + 2RT\omega_2\delta}\right] \qquad (29)$$

or

$$\frac{\partial\rho}{\partial z} = \frac{D_1 Ka}{4RT\omega_1\delta^2}\left[\left(\frac{\partial\rho}{\partial C_1}\right)(C_{1h} - C_{1l}) + \left(\frac{\partial\rho}{\partial C_2}\right)(C_{2h} - C_{2l})\right] \qquad (30)$$

Experimental studies of osmotic volume flows were carried out by means of the measurement set-up that was described in detail in a previous paper (Ślęzak and Dworecki 1984). The set-up consisted of two Plexiglas vessels (l, h) separated by a membrane (M) with an equal active surface area of 3.36 ± 0.2 cm^2. The membrane was mounted in a horizontal plane. The experiments were performed with the flat sheet Nephrophan membrane. Parameters of the membrane, i.e. hydraulic permeability (L_p), reflection (σ_k) and solute permeability (ω_k) coefficients were determined in accordance with methods described in previous papers (Katchalsky and Curran 1965). Their values for the Nephrophan membrane and for binary aqueous glucose solutions are as follows: $L_p = 4.9 \times 10^{-12}$ m^3 N^{-1}s^{-1}, $\sigma_1 = 0.068$, $\sigma_2 = 0.025$, $\omega_1 = 0.8 \times 10^{-9}$ mol N^{-1}s^{-1} and $\omega_2 = 1.43 \times 10^{-9}$ mol N^{-1}s^{-1}. The diffusion of each individual component in solution is characterized by the following coefficients: $D_1 = 0.69 \times 10^{-9}$ m^2/s and $D_1 = 1.074 \times 10^{-9}$ m^2/s. Volumes of the vessels (l, h) were the same and equal to 200 cm^3. For small glucose and ethanol concentration: $\rho_h = \rho_l(1 + \alpha_1 C_{1h} + \alpha_2 C_{2h})$, $v_h = v_l(1 + \gamma_1 C_{1h} + \gamma_2 C_{2h})$ where coefficients $\alpha_1 = \rho_l^{-1}\partial\rho/\partial C_1 = 6.01 \times 10^{-5}$ m^3/mol, $\gamma_1 = v_l^{-1}\partial v/\partial C_1 = 3.95 \times 10^{-4}$ m^3/mol, $\alpha_2 = \rho_l^{-1}\partial\rho/\partial C_2 = -9.02 \times 10^{-6}$ m^3/mol and $\gamma_2 = v_l^{-1}\partial v/\partial C_2 = 1.82 \times 10^{-5}$ m^3/mol ($\rho_l = 998$ kg/m, $v_l = 1.012 \times 10^{-6}$ m^2/s). The vessel (h) contained aqueous glucose or glucose in 0.2 mol/l aqueous ethanol solution, whereas the vessel (l) contained pure water in all experiments at the initial moment. The vessel (h) was coupled with a calibrated pipette, while the vessel (l) was connected to an external reservoir of pure water at the same height as the pipette. The volume flux, J_v, was determined from $J_v = \Delta V/S\Delta t$, where S is the membranes surface area and $\Delta V/\Delta t$ is the volume change (V) occuring in the time (t). All experiments were carried out at temperature $T = 295$ K.

Results and Discussion

Values of the osmotic volume flow for configurations A and B of the single-membrane system were determined experimen-

tally, as shown in Fig. 2. This figure shows that dependencies $J_v = f(\Delta C_1)$ for the binary solutions and for configurations A and B are linear outside the range of concentrations $5 \text{ mol/m}^3 \le \Delta C_1 \le 25 \text{ mol/m}^3$. Whereas for ternary solutions, these characteristics are nonlinear, but contain ranges ΔC_1, where the tangent of the angle between the tangent to the curve and the axis of ΔC_1 is a constant value. The figure also shows that the flux of binary solutions J_v in the configuration B of the membrane system is significantly greater than in the configuration A of the membrane system. The curves presented in Fig. 2 show that J_v for ΔC_1 fulfilled the conditions $5 \text{ mol/m}^3 \le \Delta C_1 \le 25 \text{ mol/m}^3$ (for binary solutions and configurations A and B), $0 \text{ mol/m}^3 \le \Delta C_1 < 0.0325 \text{ mol/m}^3$ (for ternary solutions and configurations B) $-25 \text{ mol/m}^3 \le \Delta C_1 \le -5 \text{ mol/m}^3$ (for binary solutions and configuration A) and to $-60 \text{ mol/m}^3 \le \Delta C_1 \le -40 \text{ mol/m}^3$ (for binary and ternary solutions and configuration A) and is approximately equal. Moreover, for $0 \text{ mol/m}^3 \le \Delta C_1 < 32.5 \text{ mol/m}^3$, the fluxes J_v for ternary solutions in the configuration B and the same values ΔC_1 are lower than the fluxes J_v in the configuration A. For $\Delta C_1 > 32.5 \text{ mol/m}^3$, fluxes J_v for ternary solutions in the configuration B are higher than the fluxes in the configuration A for the same values of ΔC_1. Relatively large increase in the value of the volume flow is due to the emergence of additional osmotic pressure gradients caused by hydrodynamic instabilities of CBL (Dworecki et al. 2005; Ślęzak et al. 2005). These instabilities are caused by sufficiently large gradients of solutions density in the CBLs areas with the opposite direction to the gravity vector. They are the cause of change in the nature of the solute transport
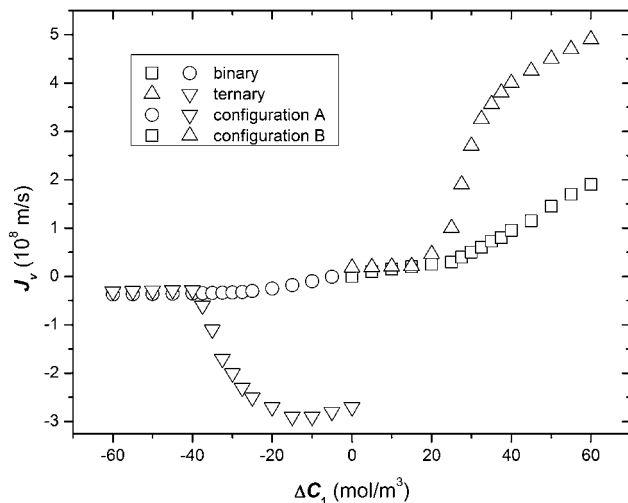

Figure 3. Dependencies of concentration boundary layer thickness (δ) on glucose concentration difference (ΔC_1) at constant ethanol concentration difference (ΔC_2) in binary ($\Delta C_2 = 0$) and ternary ($\Delta C_2 = 200 \text{ mol/m}^3$) for configurations A and B of the single-membrane system. Squares, experimental results (Ślęzak et al. 2005); lines, calculated from Eq. (8).

from diffusive to diffusion-convection (Rubinstein and Zaltzman 2000; Dworecki et al. 2005; Larchet et al. 2008; Puthenveettil and Arakeri 2008). Such a situation occurs in the case of binary solutions and configurations B of the membrane system for $\Delta C_1 < 15 \text{ mol/m}^3$. In the case of ternary solutions, hydrodynamic instability appears to $\Delta C_1 < 25 \text{ mol/m}^3$ (for configuration B of the membrane system) and $-40 \text{ mol/m}^3 \le \Delta C_1 \le 0 \text{ mol/m}^3$ (for the configuration A of the membrane system). Except for these ranges ΔC_1, transport in CBL areas is diffusion. Taking into consideration the experimentally determined transport parameters of the Nephrophan membrane, the experimental results of J_v shown in Fig. 2 and Eq. (7), the calculations of thicknesses δ were done for aqueous solutions of glucose and glucose in 200 mol/m³ aqueous ethanol solution for ΔC_1, that is in the range of $5 \text{ mol/m}^3 \le \Delta C_1 \le 60 \text{ mol/m}^3$ for configurations A and B of the membrane system.

The results of calculations of dependence $\delta = f(\Delta C_1)$ for the configurations A and B of the membrane system and binary solutions are represented by curves 1 and 2 in Fig. 3. The figure shows that this dependence for both tested configurations of the membrane system is non-linear. For $5 \text{ mol/ } \text{m}^3 \le \Delta C_1 \le 20 \text{ mol/m}^3$ and $-20 \text{ mol/m}^3 \le \Delta C_1 \le -5 \text{ mol/m}^3$, thickness of δ_i for both configurations is the same and the value is equal to 0.7 mm. However, for $\Delta C_1 > 20 \text{ mol/m}^3$ the value of δ in the configuration B decreases and for $\Delta C_1 = 60 \text{ mol/m}^3$ reaches 0.28 mm. In the configuration A, the value of δ decreases non-linearly for $\Delta C_1 < -20 \text{ mol/m}^3$ to about the value $\delta = 1.33 \text{ mm}$ for $\Delta C_1 = -60 \text{ mol/m}^3$.

Figure 2. Dependencies of the experimental volume osmotic flux (J_v) on glucose concentration difference (ΔC_1) at constant ethanol concentration difference (ΔC_2) in binary ($\Delta C_2 = 0 \text{ mol/m}^3$) and ternary ($\Delta C_2 = 200 \text{ mol/m}^3$) for configurations A and B of the single-membrane system.
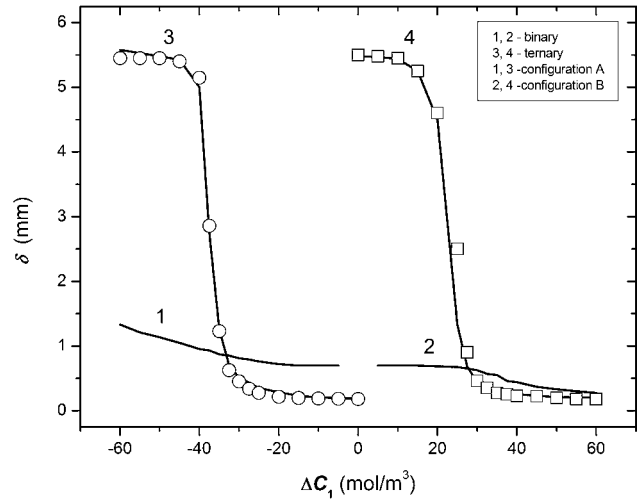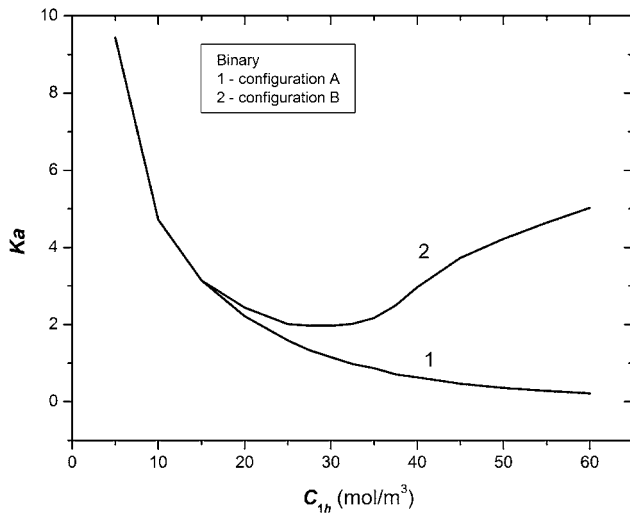
Figure 4. Dependencies of Katchalsky number (Ka) on glucose concentration (C_{1h}) in binary solutions for configurations A and B of the single-membrane system calculated on the basis of Eq. (28).

The results of calculation of $\delta = f(\Delta C_1)$ for different concentration of glucose in 200 mol/m³ aqueous solutions of ethanol and the configurations A and B in the membrane system are presented as curves 3 and 4 in Fig. 3. Curves 3 and 4 show dependence $\delta = f(\Delta C_1)$ for configurations A and B in the single-membrane system. Points on this figure illustrate the experimental results of δ, obtained using methods of laser interferometry. These data were published in the previous paper (Ślęzak et al. 2005). We observe two different rates of increase (curve 3) and decrease (curve 4) in thickness δ accompanying the ΔC_1 increase. From Fig. 3 it results that for ternary solutions and the configuration A of the membrane system (curve 3) for -32.5 mol/m³ $\leq \Delta C_1 \leq 0$ mol/m³ and $\Delta C_1 < -40$ mol/m³, and for the configuration B and $0 \leq \Delta C_1 \leq 32.5$ mol/m³ and $\Delta C_1 > 40$ mol/m³, the value δ is weakly dependent on the value ΔC_1. For the curve 3 the sudden change in δ occurs for ΔC_1 in the range -40 mol/m³ $\leq \Delta C_1 \leq -35$ mol/m³, whereas for the curve 4 the sudden change in δ occurs for ΔC_1, satisfying the condition 15 mol/m³ $\leq \Delta C_1 \leq 30$ mol/m³. It should be noted, that for the curve 3 the value δ increases from $\delta = 0.4$ mm up to $\delta = 5.5$ mm, and for the curve 4 the value δ decreases from $\delta = 5.4$ mm to $\delta = 0.5$ mm. The changes of the δ value are associated with changes in the value of J_v. Jumping decreasing values δ are associated with transition from the non-convective to convective areas of CBL.

The results of calculations of δ obtained in this paper can be confronted with the results of δ measurements using a laser interferometer presented in other papers (Dworecki 1995; Dworecki et al. 2003, 2005; Ślęzak et al. 2005). In the stability state (the state of the system with diffusion) of CBL

the thickness of the layer is 4–6 mm, whereas in the instability state (the state of the membrane system with diffusion and gravitational convection), the average value calculations of δ is in the range between 0.2–0.4 mm. Therefore, the presented method is compatible with the method that uses a laser Mach-Zehnder Interferometer (Dworecki 1995; Dworecki et al. 2003). However, interferometric (Dworecki 1995; Dworecki et al. 2003) or holographic (Fernandez-Sempere et al. 2009) optical methods enable the visualization of the processes occurring in near-membrane areas.

The results of calculations presented in the paper Dworecki et al. (2005) indicate that in the diffusive state the dependence $\delta = K \cdot t^a$, for $a = 0.5$, is satisfied. For the convective state this dependence is incorrect, since the value of a calculated in the same way as for the diffusive state gives the value of $a \approx 0$. This means that δ interferometrically recorded or calculated on the basis of Eq. (8), is the thickness of the hydrodynamics layer, called the Prandtl layer (Schlichting and Gersten 2000). Its value in the convective state for binary and ternary solutions is constant (Dworecki et al. 2005; Ślęzak et al. 2005), which is reasonable in relation to the data published in Schlichting and Gersten (2000). Recently, it has been reported (Puthenveettil and Arakeri 2008) the registration of dendritic structure of solution under turbulence conditions for the case of Rayleigh-Benard natural convection with the use of optical methods. Recorded images show that the dendritic structure is a mark of fractal structure for large values of concentration Rayleigh number. In this situation, i.e. in the center of convection, super-diffusion occurs (Iomin and Baskin 2005).

Figs. 4 and 5 shows the dependence $Ka = f(C_{1h})$ for binary (Fig. 4) and ternary (Fig. 5) solutions. From the Fig. 4 it is seen that the shape of these curves is different. Let us consider the curves 1 and 2 in the Fig. 4. The curve 1 is a hyperbola, and the curve 2 is an asymmetrical parabola, of which the minimum has coordinates $Ka = 2$, $C_{1h} = 29$ mol/m³. Moreover, the point of coordinates of $Ka = 3.11$, $C_{1h} = 15$ mol/m³ is the last common point of curves 1 and 2. From the course of curves 1 and 2 results that $C_{1h} \leq 15$ mol/m³ transport of the solute has a nature of diffusion and the membrane system does not distinguish the direction of gravity. This means that the viscous forces prevail over the forces of buoyancy. Concentration of the solution $C_{1h} = 15$ mol/m³ is a critical concentration above which the nature of transport transforms from diffusive into diffusion-convection. For this concentration $Ka = 3.11$. It is worth mentioning that determined in the previous paper (Ślęzak et al. 2010) the critical value of concentration Rayleigh number $(R_c)_{crit.} = 1709.3$.

The courses of curves 1 and 2 in the Fig. 5 differ from each other. In the case of curve 1, for $0 \leq C_{1h} \leq 27.5$ mol/m³ Ka increases non-linearly up to the value about -22.63 for $C_{1h} = 0$ mol/m³ to a minimal value of $Ka = -48.8$ for $C_{1h} = 27.5$ mol/m³ ($C_{2h} = 200$ mol/m³). For $C_{1h} > 37.5$ mol/m³ Ka
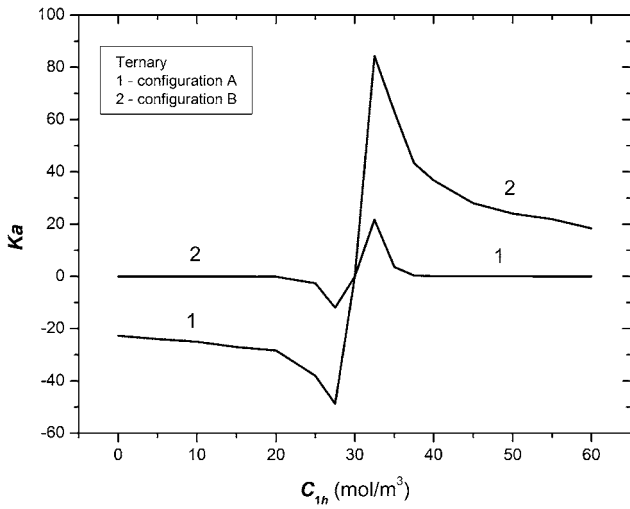
Figure 5. Dependencies of Katchalsky number (*Ka*) on glucose concentration (C_{1h}) at constant ethanol concentration (C_{2h}) in ternary solutions ($C_{2h} = 200$ mol/m^3) for configurations A and B of the single-membrane system calculated on the basis of Eq. (28).

Figure 6. Dependencies of density gradient (*dρ/dz*) on glucose concentration difference (ΔC_1) at constant ethanol concentration difference (ΔC_2) in binary ($\Delta C_2 = 0$) and ternary ($\Delta C_2 = 200$ mol/m^3) for configurations A and B of the single-membrane system calculated on the basis of Eq. (29).

is approximately constant and equals $Ka \approx 0.02$. A maximal value of $Ka = 21.76$ was obtained for $C_{1h} = 32.5$ mol/m^3 and in the case of curve 2, Ka decreases non-linearly from the value of $Ka = -0.02$ for $C_{1h} = 0$ mol/m^3 ($C_{2h} = 200$ mol/m^3) to the minimal value of $Ka = -11.99$ for $C_{1h} = 27.5$ mol/m^3. A maximal value of $Ka = 84.43$ was obtained for $C_{1h} = 32.5$ mol/m^3. In addition, curves 1 and 2 meet at the point of coordinates $Ka = 0$ and $C_{1h} = 30$ mol/m^3. Results presented in Figs. 4 and 5 suggest that the critical value of Ka for the binary solutions is different than for the ternary solutions. Is that reasonable? To answer this question, we calculate the appropriate values for the density gradients ($\partial \rho / \partial z$) for binary (aqueous solutions of glucose) and ternary solutions (glucose solutions in 0.2 mol/l aqueous solutions of ethanol) using Eq. (29), results of δ shown in Fig. 2, and $\partial \rho / \partial C_1 = 0.06$ kg/mol and $\partial \rho / \partial C_2 = -0.009$ kg/mol. The calculation results are shown in Fig. 6. Curves 1 and 2 were obtained for binary solutions and the curves 3 and 4 – for ternary solutions. Curves 1 and 3 were obtained for the configuration A, and curves 2 and 4 – for the configuration B of the membrane system. From the figure it results, that for the configuration A the density gradient is consistent with the direction of the gravity vector, which means that $\partial \rho / \partial z < 0$. For the configuration B the density gradient has the reverse direction to the gravity vector, which means that $\partial \rho / \partial z > 0$. For ternary solutions, within one configuration depending on the value ΔC_1, the density gradient may fulfill one of the following conditions: $\partial \rho / \partial z < 0$, $\partial \rho / \partial z = 0$ or $\partial \rho / \partial z > 0$. For $\Delta C_1 < -29$ mol/m^3 and the configuration A and $\Delta C_1 > 29$ mol/m^3 and the configuration B of the membrane system, $\partial \rho / \partial z < 0$. On the other hand, for $\Delta C_1 = -29$ mol/m^3 and the configuration
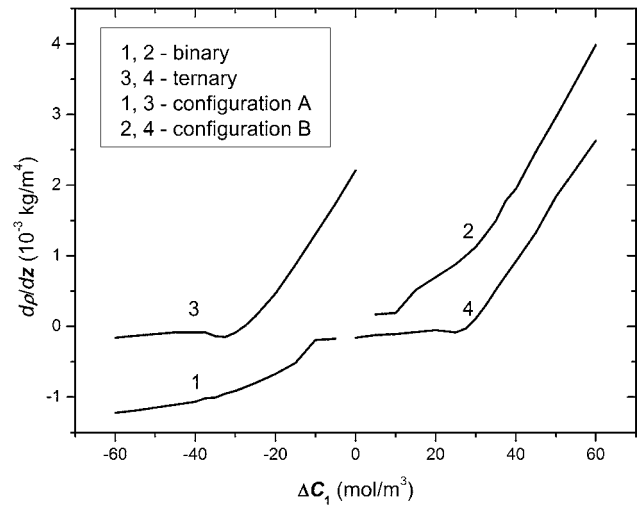
A and $\Delta C_1 = 29$ mol/m^3 and the configuration B, $\partial \rho / \partial z = 0$. And for $\Delta C_1 > -29$ mol/m^3 and the configuration A and $\Delta C_1 > 29$ mol/m^3 and B configuration of the membrane system, $\partial \rho / \partial z > 0$. Let us consider the case $\partial \rho / \partial z = 0$. The comparison of the test results for ternary solutions presented in Figs. 2–6 shows that for this case and the configuration A of the membrane system $J_v = -2.2 \times 10^{-8}$ m/s (Fig. 2), $\delta = 0.5$ mm (Fig. 3) and $Ka = 1.64$ (Fig. 4). Analogically, for the configuration B we obtain: $J_v = 2.25 \times 10^{-8}$ m/s (Fig. 2), $\delta = 0.66$ mm (Fig. 3) and $Ka = 1.64$ (Fig. 4). It is worth noticing that a minimum of curve 2 in Fig. 4 and the point of meet of curves 1 and 2 in Fig. 5 occur for the same glucose values, i.e. $C_{1h} = 30$ mol/m^3. The presented considerations show, that the critical value $\partial \rho / \partial z$ for $C_{1h} = 15$ mol/m^3 (in binary solution) is $\partial \rho / \partial z = 5.15 \times 10^2$ kg/m^4, while the critical value $\partial \rho / \partial z$ for $C_{1h} = 30$ mol/m^3 (in ternary solution) is much smaller because $\partial \rho / \partial z = 0$. It means that in such conditions buoyancy forces balance the viscous forces. The critical thickness values of CBLs for these concentrations are of the order of 0.5–0.7 mm. This means, that achieving the thickness δ_{crit} of CBLs is a necessary condition for the transition from diffusive into convective diffusion state. This process can be controlled by a modified concentration Rayleigh number, called by us the Katchalsky number.

Conclusions

1. The square equation, derived from the K-K thermodynamic formalism, is useful to estimate the thickness

of CBL (δ) in the single-membrane system, which contains non-electrolyte ternary solutions. This equation can be used if the transport parameters of the membrane (L_p, σ, ω), solutions (D, C) and osmotic volume flux (J_v) are known.

2. The value of average thickness δ is dependent upon the concentration of the solutions separated by the membrane and upon the orientation of a membrane in relation to the gravity field (the configuration of the membrane system).

3. Nonlinearity of characteristics $\delta = f(\Delta C_1)_{\Delta C_2 = const.}$ is the result of competition between spontaneously occurring processes of diffusion and the natural convection.

4. The process of transition from diffusive into convective diffusion state can be controlled by a modified R_C called by us the Katchalsky number (Ka)

$$Ka = \frac{4 R_C \rho \nu R T \omega}{g \delta^2} \left(\sum_k \frac{\partial \rho}{\partial C_k} \Delta C_k \right)^{-1}$$

5. Designated in the paper the critical value of Ka for aqueous glucose solutions is $Ka = 3.11$, and for glucose solutions in 200 mol/m^3 aqueous ethanol solution is $Ka = 1.64$.

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