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Model equation of relative solute permeability coefficient of membrane-concentration boundary layers complex

Summary — Considering non-homogeneity of non-electrolyte solutions, the membrane transport is different than the transport of homogeneous solutions described by Kedem-Katchalsky equations, as a result of the concentration polarization phenomenon and concentration boundary layers formed up near the membrane. These layers have a significant influence on the volume and solution flows. The model equation for the relative permeability coefficient ζ_s of the system: the membrane and concentration boundary layers is presented, and dependence of this coefficient on the solution concentration, concentration Rayleigh number, and gravity acceleration is studied. The experimental tests were performed by a chamber system method in the membrane system with the membrane mounted horizontally. The test results show a good compliance with theoretical calculations and indicate that the relative solute permeability coefficient of the membrane-concentration boundary layers system decreases in time and seems to be independent on the initial concentration of the solution.

Key words: membrane transport, solute permeability coefficient, concentration boundary layers.

MODEL OPISUJĄCY WZGLĘDNY WSPÓŁCZYNNIK PRZEPUSZCZALNOŚCI W UKŁADZIE MEMBRANA-STĘŻENIOWE WARSTWY GRANICZNE

Streszczenie — Szerokie zastosowanie membran polimerowych w technologii i naukach medycznych, niesie ze sobą konieczność ich szczegółowego badania pod kątem właściwości transportowych. Ze względu na niejednorodność roztworów nieelektrolitów, ich transport membranowy różni się od transportu roztworów jednorodnych (opisanych równaniami Kedem-Katchalsky'ego) na skutek zjawiska polaryzacji stężeniowej i tworzenia się przy membranie stężeniowych warstw granicznych. Warstwy te mają znaczący wpływ na przepływy objętościowe i przepływy solutu. Przedstawiono model opisujący względny współczynnik przepuszczalności (ζ_s) w układzie membrana-stężeniowe warstwy graniczne oraz zbadano zależności tego współczynnika od stężenia roztworu, stężeniowej liczby Rayleigha i przyspieszenia grawitacyjnego. Poprawność modelu zbadano eksperymentalnie używając poziomo ustawionej membrany (*Nephrophan* wykorzystywanej w hemodializerze zwojowym) rozdzielającej przestrzeń układu membranowego. Wyniki badań są zgodne z obliczeniami teoretycznymi i wskazują, że względny współczynnik przepuszczalności solutu w układzie membrana-stężeniowe warstwy graniczne zmniejsza się w czasie i wydaje się być niezależny od początkowego stężenia roztworu.

Słowa kluczowe: transport membranowy, współczynnik przepuszczalności solutu, stężeniowe warstwy graniczne.

Due to a wide applications of polymeric membranes in technology and medicine science [1], it is necessary to examine them in detail in terms of their transport properties.

It is well known that transport phenomena across artificial (also polymeric) or biological membranes are strongly influenced by the concentration boundary layers (CBLs) that are adjacent to the membrane surfaces [2–9].

In some cases, these layers can form effective barriers like the membrane itself. CBLs (unstirred or diffusive) play an important role in the membrane transport as well as they accompany transformation processes due to the existence of differences between the solute concentrations near the membrane and concentrations in the bulk [3]. The CBLs operate as pseudo-membranes in series with the physical membrane and therefore the permeability coefficient of the system: membrane-concentration and boundary layers (ω_s) is smaller than the permeability coefficient of the membrane itself (ω_m) [10]. The consequence is a substantial reduction in the volume and solute flows [5, 7]. The thicknesses of the CBLs depend on the type of used solutions, their compositions, concentrations and densities as well as on the orientation of the membrane and the mea-

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surement chamber containing the solution relative to the vector of gravity [5, 11, 12]. When the denser liquid is below the membrane in a horizontally placed electrochemical cell, then the CBLs are thick and as a result a considerable decrease in volume and solute fluxes [5, 11], membrane potential [12] and ionic current [6, 8, 9] can be observed. In particular they play an important role in some physiological processes, such as coupling of the water transport to the active solute transport in the lateral intercellular spaces of epithelia, or the conservation of solutes transiently leaving a cell during a potential action [3, 13–16].

CBLs are a great nuisance in experimental studies of membranes. They cause that measured values of particular membrane parameters are considerably different from the values that would be obtained in case of lack of CBLs. The thickness of the CBLs was usually estimated by volume and solute fluxes measurements [11, 15]. Alternatively, microelectrodes placed near the membrane surface were used to determine the thickness of CBLs by studying the time-course of near membrane concentration changes [6, 8, 9, 12, 17, 18]. Concentration profiles were recorded using optical methods, too [4, 7, 19]. The thicknesses of CBLs are governed by a complex combination of solute properties, membrane properties and hydrodynamics [20]. The theoretical modelling of CBLs creation/destruction (concentration polarization phenomenon) is based on the Nernst-Planck, Poisson, Stokes [6, 20, 21], Fick [2, 7, 9, 22] and/or Kedem-Katchalsky [18, 22, 23] equations. In 1963, Ginzburg and Katchalsky [24] introduced a relation among apparent coefficients for binary solutions such as permeability coefficient ω_s (solute permeability coefficient of the system CBL_h/membrane/CBL_l: $l_h / M / l_l$), true permeability coefficient ω_m (solute permeability coefficient of membrane), and solute permeability coefficient ω_h and ω_l of CBLs (l_h and l_l). These coefficients are bound by the following relation

$$\omega_s^{-1} = \omega_m^{-1} + \omega_h^{-1} + \omega_l^{-1} \quad (1)$$

where: $\omega_h = D_h(RT\delta_h)^{-1}$, $\omega_l = D_l(RT\delta_l)^{-1}$ are the solute permeability coefficients of l_h and l_l layers (D_h and D_l are the diffusion coefficients in l_h and l_l layers, respectively), and RT – product of the gas constant and thermodynamic temperature).

In the present paper, we introduce the relative permeability coefficient model equations derived within the scope of Kedem-Katchalsky's formalism for solute permeability coefficients of binary non-electrolyte solutions and the system: flat polymeric membrane-concentration boundary layers. The nonlinear expression of the coefficient ζ_s presenting its dependence on the concentration gradient, concentration Rayleigh number, the solute permeability coefficient of the membrane, etc. is derived. Having solved this equation we have estimated the values of ζ_s on the basis of experimental data, considering the transport parameters of the membrane and physicochemical parameters of solution.

THEORY

Let us consider the single-membrane system presented in Figure 1. We assume that this membrane system contains heterogeneous (not mechanically stirred) aqueous ethanol solutions (or other solutions which density decreases with an increase in concentration), separated by an isotropic and symmetric membrane (M). The membrane is placed in a horizontal plane and the respective concentration gradients are anti-parallel or parallel to the gravitational force. The transport processes are isothermal and a steady state and no chemical reactions occur in the solutions. In this single-membrane system, water and dissolved substance diffusing across the membrane will lead to the formation of CBLs. In the steady state, the l_h and l_l layers with the thicknesses δ_h and δ_l are formed at both sides of the membrane. These layers cause the concentration polarization of the membrane. The implication is that the concentrations of solutions at the membrane-layers surfaces are different from concentrations in the bulk.

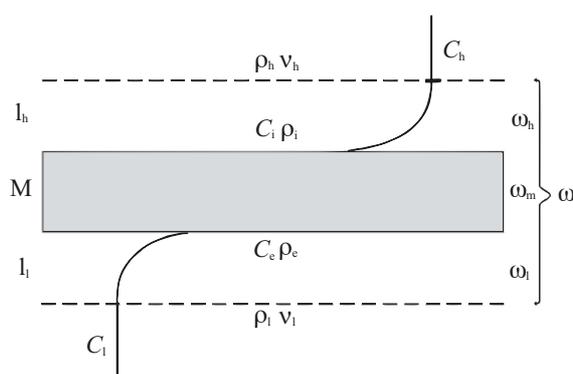


Fig. 1. Membrane system for non-homogeneous solutions with formation of concentration boundary layers (CBL)

We are denoting the concentrations as C_i , C_e and the densities of solution at surfaces l_h/M and M/l_l as ρ_i and ρ_e , respectively. The concentrations of solution outside the CBLs (the bulk solutions) are denoted as C_h and C_l (subscripts h and l denote higher and lower concentration, respectively). The densities and kinetic viscosities of these solutions are denoted as ρ_h , ρ_l , v_h and v_l , respectively. For any solutions which densities decrease with an increase in solute concentration, the following relations are fulfilled:

$$\begin{aligned} C_h &> C_i > C_e > C_l \\ \rho_h &< \rho_l < \rho_e < \rho_l \\ v_h &> v_l \end{aligned}$$

When the upper compartment of this system is filled with the aqueous ethanol solution of concentration C_l , and the lower one with the solution of concentration C_h ($C_h > C_l$), the layers of higher density are over the layers of lower density. This configuration of the single-membrane system is stable when the concentration gradient is relatively small [25, 26]. In that case the viscosity forces

counteract the vertical fluid motion, so the solute is transported only by diffusion. In this state all concentration fluctuations and fluid density fluctuations are damped. The transformation from stable into the unstable state occurs when the buoyancy forces are greater than viscosity forces. At this moment, except diffusion, the convective instability occurs. It is caused by the density (concentration) differences. With the appropriate relations between concentrations, due to the gravitation there the convection phenomena take place limiting CBLs' thicknesses [5, 10, 25]. When the upper compartment is filled with the aqueous solution of concentration C_h , only the diffusive transport occurs and this configuration is gravitationally stable [5, 10, 25]. Kinetics of the formation and evolution of the CBLs (l_h and l_l) is controlled, both on the phenomenological and molecular levels, by the dimensionless parameter known as the concentration Rayleigh number (R_{Cl} , R_{Ch}) [5, 25]

$$R_{Ch} = g \left(\frac{\partial \rho}{\partial C} \right) (C_h - C_i) \delta_h^3 (D_h \rho_h \nu_h)^{-1} \quad (2)$$

$$R_{Cl} = g \left(\frac{\partial \rho}{\partial C} \right) (C_e - C_l) \delta_l^3 (D_l \rho_l \nu_l)^{-1} \quad (3)$$

where: g — the gravitational acceleration.

On the basis of the modified Kedem-Katchalsky model [11, 26], we can calculate

$$C_h - C_i = RT \zeta_s \omega_m \delta_h D_h^{-1} (C_h - C_l) \quad (4)$$

$$C_e - C_l = RT \zeta_s \omega_m \delta_l D_l^{-1} (C_h - C_l) \quad (5)$$

where: $\zeta_s = \omega_s \omega_m^{-1}$ ($0 \leq \zeta_s \leq 1$) — relative solute permeability coefficient for the membrane-concentration boundary layers.

The coefficient ζ_s is also called the concentration polarization coefficient [10]. For the steady state we obtain the following formula [10]

$$\zeta_s = [1 + RT \omega_m (\delta_h D_h^{-1} + \delta_l D_l^{-1})]^{-1} \quad (6)$$

Combining eqs. 2 and 3, we obtain equations describing thicknesses δ_l and δ_h of the layers l_h and l_l , respectively, for the isothermal membrane transport [22]

$$\delta_h = R_{Ch}^{0.25} \left\{ D_h^2 \nu_h \rho_h \left[g RT \omega_m \zeta_s \left(\frac{\partial \rho}{\partial C} \right) (C_h - C_l) \right]^{-1} \right\}^{0.25} \quad (7)$$

$$\delta_l = R_{Cl}^{0.25} \left\{ D_l^2 \nu_l \rho_l \left[g RT \omega_m \zeta_s \left(\frac{\partial \rho}{\partial C} \right) (C_h - C_l) \right]^{-1} \right\}^{0.25} \quad (8)$$

where: $\partial \rho / \partial C$ — the variation of solution density with concentration.

Combining eqs. (6)—(8) we obtain the following formula

$$\zeta_s + a \zeta_s^{0.75} = 1 \quad (9)$$

where:

$$a = \left\{ (RT \omega_m)^3 \left[g \left(\frac{\partial \rho}{\partial C} \right) \right]^{-1} \right\}^{0.25} \left[\left(\frac{R_{Cl} \rho_l \nu_l}{D_l^2} \right)^{0.25} + \left(\frac{R_{Ch} \rho_h \nu_h}{D_h^2} \right)^{0.25} \right] (C_h - C_l)^{-0.25}$$

This equation allows us to calculate numerically the relative solute permeability coefficient for the membrane-concentration boundary layers (ζ_s) as parameters g , C_h , R_C are varied respectively, with other parameters fixed.

EXPERIMENTAL

Studies on the solute flows through the horizontally-mounted membrane were carried out by means of the measuring apparatus which the detailed description has been given in the previous paper [27]. Experiments were carried out with a flat sheet Nephrophane hemodialyzer membrane from cellulose acetate ([trio-acetate cel-(O-CO-CH₃)_n] after partial hydrolysis) presented in Figure 2. This is the microporous membrane of a spongy structure. The membrane was placed between two Plexiglas vessels (presented in Figure 3), each of volume 200 cm³, with 3.36±0.2 cm² of available area. An additional support consisting of a large mesh screen on each side of the membrane was used to prevent buckling or tearing of thin dialysis membrane. The stirring speed in each chamber was maintained at 0–500 rpm using stirrer motors controlled independently. One of vessels of

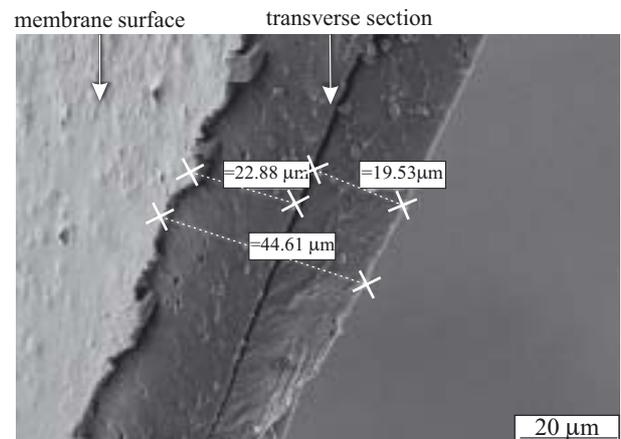


Fig. 2. Photography of Nephrophane polymeric membrane used in a hemodialyzer, made with high resolution scanning microscope Zeiss Supra 35

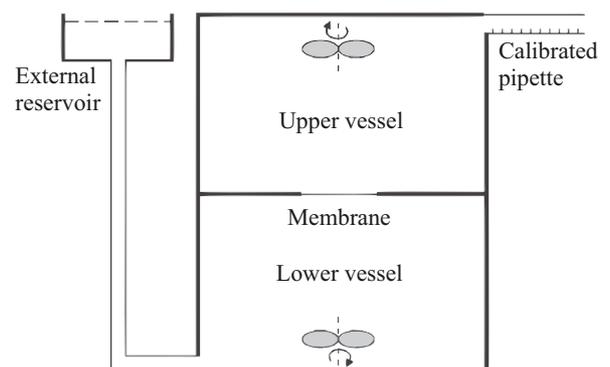


Fig. 3. Test equipment setup

the membrane system contained aqueous ethanol solution at varied concentrations. This vessel was attached to a calibrated pipette making possible to measure the volume with the accuracy of $\pm 0.5 \text{ mm}^3$. The second vessel in all experiments contained pure water ($C_l = 0$). This vessel was connected to an external reservoir with solution surface at the same level as the pipette. Transport parameters, *i.e.* hydraulic permeability (L_p), reflection (σ_m) and solute permeability (ω_m) coefficients of the membrane have been determined according to the method described in [26]. Their values for the Nephrothane membrane and for aqueous ethanol solution are equal to: $L_p = 5 \cdot 10^{12} \text{ m}^3/(\text{N} \cdot \text{s})$, $\sigma_m = 0.025$ and $\omega_m = 1.43 \cdot 10^{-9} \text{ mol}/(\text{N} \cdot \text{s})$. Each experiment was carried out for two gravitational configurations of the membrane system: first one with water in the vessel above the membrane and the solution below (configuration A); the other one with these positions reversed (configuration B). All experiments were carried out at a constant temperature of $T = 295 \text{ K}$.

Measurement of the total concentration changes in the solution was performed by an optical method using a refractometer. The measured value of the total concentration changes (dC/dt) was used to calculate the solute flux (J_s) on the basis of the following equation [11, 27]

$$J_s^i = \frac{1}{S} \left(\frac{dC}{dt} \right)_{J_v^i=0}^i \quad (10)$$

where: S — membrane surface area, superscript $i = A, B$ pertains to configurations A and B.

Measurements of J_s^i for both configurations were carried out according to the following procedure. The first step involved the measurement of the solute flux in the membrane system with solutions stirred mechanically at 500 rpm. After reaching the initial steady state during which J_s^0 was constant, stirring was stopped, and subsequently the evolution of the solute flux was measured up to the moment of reaching the steady state, for which the J_s^i remained fixed.

RESULTS AND DISCUSSION

Experimental results

A typical plots of the time dependence of the solute flux in configurations A and B of the membrane system in the cases of aqueous ethanol solution at various concentrations are shown in Figure 4. The graphs contain the experimental data for both configurations obtained for solutions with mechanical stirring at 500 rpm, and they show that J_s^0 is independent on the gravitational configuration of the membrane system. Plots 1A—4A and 1B—4B, obtained for configurations A and B, respectively, demonstrate that the J_s^i values for both configurations are different. After switching off the mechanical stirring of solutions (60 min), the fluxes J_s^A, J_s^B decrease and after 1—2 minutes they attain the constant values.

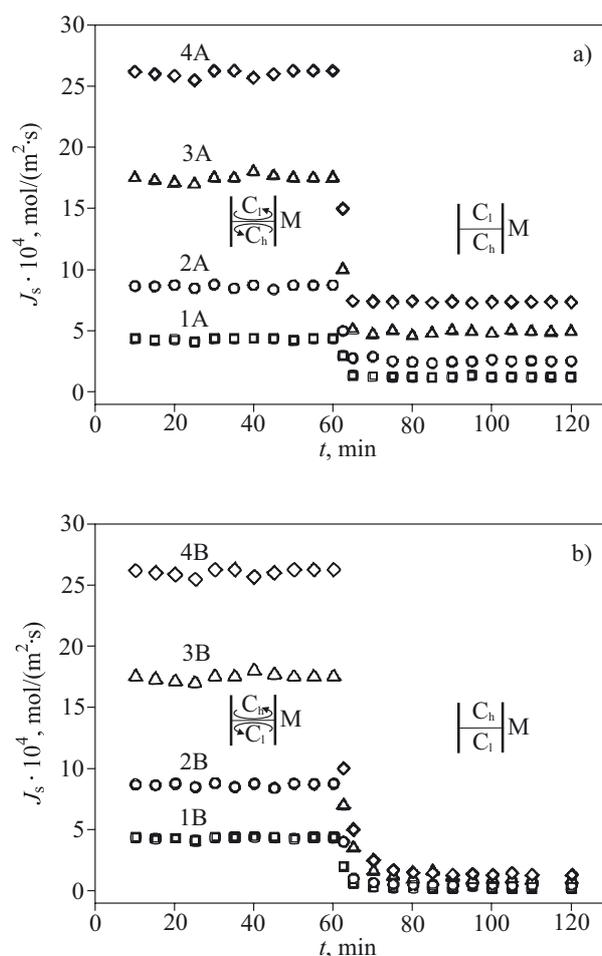


Fig. 4. Time dependence of the solute flux in the configuration A (a) and B (b) with and without mechanical stirring, for the following concentrations C_h : \square — 125 mol/dm^3 (1A, 1B), \circ — 250 mol/dm^3 (2A, 2B), \triangle — 500 mol/dm^3 (3A, 3B), \diamond — 750 mol/dm^3 (4A, 4B)

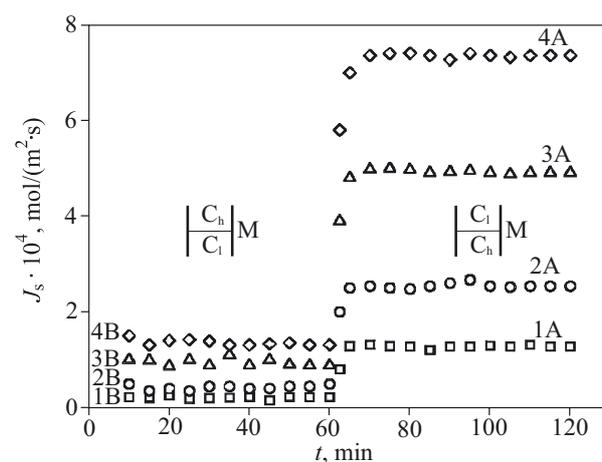


Fig. 5. Evolution of the solute flux (J_s^B) from the steady state in configuration B to the steady state of the solute flux in configuration A (J_s^A), after reorientation of the membrane system from configuration B (plots 1B—4B) to A (plots 1A—4A), for the following concentrations C_h : \square — 125 mol/dm^3 (1A, 1B), \circ — 250 mol/dm^3 (2A, 2B), \triangle — 500 mol/dm^3 (3A, 3B), \diamond — 750 mol/dm^3 (4A, 4B)

The evolution of J_s^o to J_s^B or J_s^A reflects the process of formation of CBLs at both sides of the membrane. Thus, we can state that $J_s^o > J_s^B$, $J_s^o > J_s^A$ and $J_s^B < J_s^A$. For the stable state, the following formulas present experimentally obtained dependence between the ethanol solute flux and aqueous ethanol solution concentration: $J_s^o = 3.505 \cdot 10^{-6} C_h \text{ mol}/(\text{m}^2\text{s})$, $J_s^A = 0.9816 \cdot 10^{-6} C_h \text{ mol}/(\text{m}^2\text{s})$ and $J_s^B = 0.1753 \cdot 10^{-6} C_h \text{ (mol}/\text{m}^2\text{s})$.

The experimental data presented in Figure 5 show the evolution of the solute flux (J_s) from the stationary state in configuration B into the stationary value of the solute flux in configuration A (J_s^A), after reorientation of the membrane system from configuration B (graphs 1B—4B) into A (graphs 1A—4A). Figure 5 implies that the flux J_s^A is visibly higher than the flux J_s^B .

Time dependence of the coefficient ζ_s^i calculated on the basis of experimental data included in Figs. 4 and 5 and the following formula

$$\zeta_s^i = \omega_s \omega_m^{-1} = J_s^i (J_s^o)^{-1} \quad (11)$$

are presented in Figure 6. The curves A and B in Fig. 6 show the time dependence of ζ_s^i calculated on the basis of experimental results presented in Figs. 4 and 5 for configuration A and B, respectively, for different concentrations. Then, the curve BA in Fig. 6 shows time de-

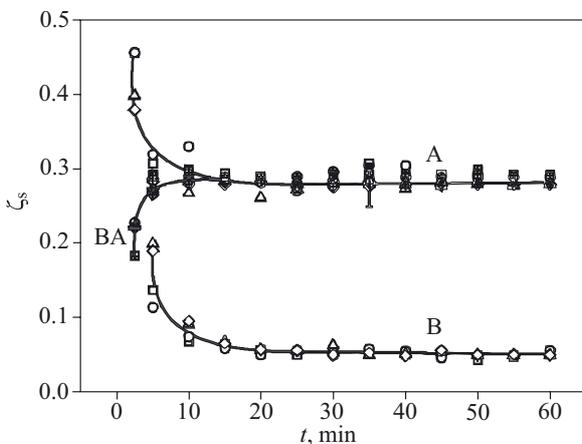


Fig. 6. Time dependence of the coefficient ζ_s^i calculated on the basis of the experimental data included in Fig. 4 (after stopping of mechanical stirring — configuration A and B) and Fig. 5 (after reorientation of the membrane system from the configuration B into A), and the eq. (11) for the following concentrations C_h : \square — 125 mol/dm³ (A, B, BA), \circ — 250 mol/dm³ (A, B, BA), Δ — 500 mol/dm³ (A, B, BA), \diamond — 750 mol/dm³ (A, B, BA)

pendence of ζ_s^i , calculated on the basis of experimental results presented in Fig. 5 and eq. (11), after reorientation of the membrane system from the configuration B into A. Instability and stability of the CBLs in the configuration A and B in the aqueous ethanol solution are presented in Fig. 7.

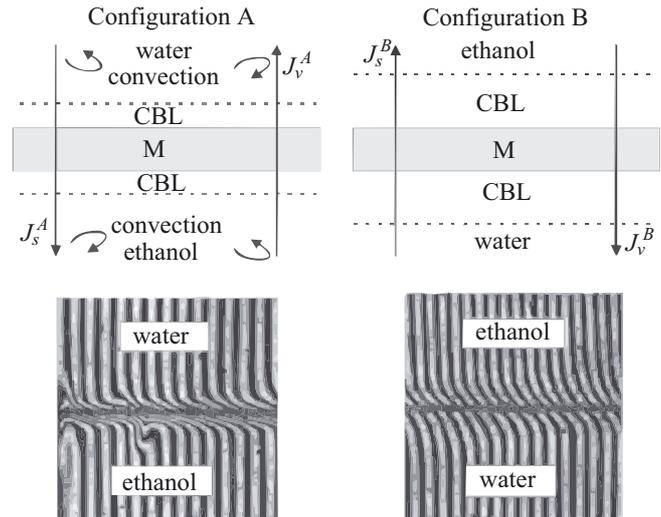


Fig. 7. Instability (configuration A) and stability (configuration B) of CBLs in the aqueous ethanol solution: J_s — solute flux, J_v — volume flux

Calculations results

The ζ_s coefficient values as functions of parameters C_h , R_c , g and/or ω_m were calculated for the membrane system presented in Fig. 1, with artificial membrane mounted in a horizontal plane and aqueous ethanol solutions. Solutions concentrations (C_h , C_l), densities (ρ_h , ρ_l), and kinematic viscosities (ν_h , ν_l), fulfill the correlations:

$$C_h = C_l + n\Delta C$$

$$\rho_h = \rho_l + \frac{\partial \rho}{\partial C} C_h$$

$$\nu_h = \nu_l + \frac{\partial \nu}{\partial C} C_h$$

where: n — number of steps.

For numerical calculations, the following values were taken: $C_l = 0$, $\Delta C = 0.125 \cdot 10^2 \text{ mol}/\text{dm}^3$, $n = 20$, $\rho_l = 998.2 \text{ kg}/\text{m}^3$, $\partial \rho / \partial C = 0.009 \text{ kg}/\text{mol}$, $\nu_l = 1006.8 \cdot 10^{-9} \text{ m}^2/\text{s}$,

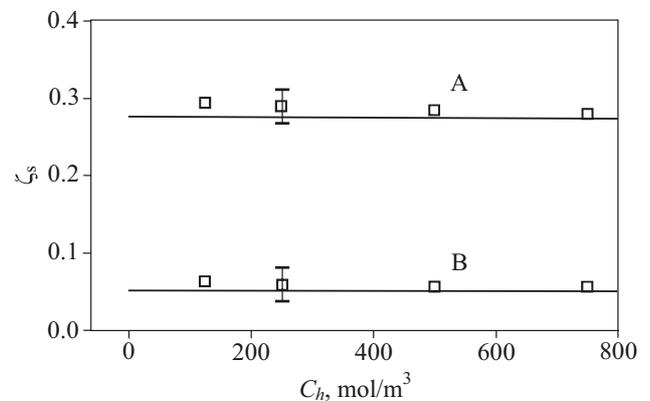


Fig. 8. Dependence of the concentration polarization coefficient ζ_s^i on C_h concentration calculated on the basis of eq. (9) for concentration Rayleigh number $R_c = 880 \cdot C_h$ (B) and $R_c = 1,893 \cdot C_h$ (A); the experimental points (squares) were derived from Fig. 5 for $t = 25 \text{ min}$

$\partial v/\partial C = 0.26 \cdot 10^{-9} \text{ m}^5/(\text{s} \cdot \text{mol})$, $T = 295 \text{ K}$, $R = 8.31 \text{ J}/(\text{mol} \cdot \text{K})$, $g_z = 9.81 \text{ m/s}^2$. The following formula presents experimentally obtained dependence between the critical value of concentration Rayleigh number $R_c = A \cdot C_h$, where $A = \text{const}$. For $\delta_l = \delta_h = 3.8 \cdot 10^{-3} \text{ m}$ we have $A = 880 \text{ m}^3/\text{mol}$, and for $(\delta_l)_{\text{crit}} \approx (\delta_h)_{\text{crit}} = 0.4 \cdot 10^{-3} \text{ m}$ we have $A = 1.893 \text{ m}^3/\text{mol}$ [25]. Due to the fact that the diffusion coefficient of the ethanol in the aqueous ethanol solution within tested concentrations range slightly depends on the concentration, therefore the constant value $D_l = D_h = 1.074 \cdot 10^{-9} \text{ m}^2/\text{s}$ was assumed for the calculations. For these calculations, the flat neutral membrane was used with the solute permeability coefficient for ethanol $\omega_m = 1.43 \cdot 10^{-9} \text{ mol N}^{-1}/\text{s}$. Numeric calculations of ζ_s on the basis of eq. (8) were carried out using a computer program Mathcad 2000. The calculations results of ζ_s are presented in Figure 8.

CONCLUSIONS

— The carried out tests confirm the strong influence of CBLs on the substance transport through the membranes. In the steady state of the unstable gravitationally configuration, the flux of the dissolved substance J_s is much larger than the one in the gravitationally stable configuration (Figs. 4 and 5). The change of the configuration from B into A causes the rapid increase in the solute flux because then the CBLs are smaller.

— When the solutions are stirred strongly enough, both gravitational configurations are equal because the stirring eliminates the effect (CBLs) of the concentration polarization phenomenon irrespective of the configuration.

— The permeability coefficient of the system CBL/M/CBL decreases with time, and within the examined concentrations, range it seems to be independent (or weakly dependent) on the initial concentration of the solution (Fig. 6).

— The time changes of the flux J_s show that the diffusive flow of the substance across the membrane dominates the free diffusion of the substance in the solution. There is an accumulation of the substance at one side of the membrane, while at another one — a depletion, which is the reason of the high concentration polarization of the membrane.

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