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EFFECTS OF CONCENTRATION BOUNDARY LAYERS IN A DIFFUSIVE FLOWS OF ELECTROLYTE SOLUTIONS THROUGH HORIZONTAL MOUNTED POLYMERIC MEMBRANE

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The results of an experimental study of diffusive transmembrane transport in a single-membrane system with horizontally mounted membrane are presented. This system contains microporous and symmetrical flat polymeric membrane, which separate water and binary or ternary electrolyte solution. As binary solution the aqueous potassium chloride solutions were used. Then, as ternary solutions the potassium chloride in 0.25 and 0.5 mol·l⁻¹ aqueous ammonia solution were used. The configurations A and B of single-membrane osmotic-diffusive cell in a gravitational field were studied. In configuration A water was placed in a vessel above the membrane and the solution was below the membrane. In configuration B the arrangement of water and solution was reversed. In the cell, solute flux was measured as a function of concentration and gravitational configuration. The linear dependencies of the solute flux on concentration difference in binary solutions and nonlinear – in ternary solutions were obtained. It was shown that the single-membrane system has rectifying and amplification properties of solute flows. Besides, the model equations of the solute flux, asymmetry and amplification effects were developed. The results of calculations were interpreted in convectional instability category.

Ключові слова: membrane transport; gravitational effect; concentration boundary layers; Kedem–Katchalsky model-equations.

The membrane transport across a biological [1–4] as well as across an artificial membranes [5–8] separating solutions of different concentration and composition leads to the formation of concentration boundary layers (CBLs). CBLs are regions in the external solutions, adjacent to the membrane interfaces, where concentrations gradient are maintained under steady-state conditions and act as pseudo-membranes in series with

the physical membrane. Consequently, they can cause substantial reductions in the osmotic and diffusion fluxes [9]. Under terrestrial conditions, the gravitational force has an influence on the thickness of these layers and decreases value and change distributions of solution concentrations, which occur in them [6–8]. They explained this observation in terms of natural convection instability that reduced CBL thickness. These layers are thick and respectively high decreases of solution concentration occur on them. It is different in the case of layers on which the gravitational force has a destructive influence [5, 8]. These layers are relatively thin, and decreases of solution concentration are relatively small [6]. Intensive mechanical stirring of the external solutions minimises the CBL thickness and reduction of the osmotic and diffusion fluxes [9].

The directly observed effects of CBL creation in different configurations of a single-membrane system are: bending of interference stripes in the area near the membrane on received on interferograms by means of the Mach–Zehnder interferometer [6, 8], decrease in the volume and solute fluxes [9] and decrease in the diffusive membrane potential [10]. The influence of the gravitational field on the transmembrane flow can be demonstrated by measurements in a steady state of thermodynamical fluxes or forces when the solutions are well stirred and when the solutions are unstirred. The influence of the gravitational force on the passive transmembrane transport (due to the graviosmotic (flux and force), gravidiffusive (flux and force) and gravielectric (flux and force) effects [11]).

In the present paper, the results of the experimental and calculated results of a solute flux study in two different configurations (A and B) of single-membrane system containing a horizontally mounted membrane, under conditions of mechanical stirring and without mechanical stirring of binary or ternary electrolyte solutions were presented. A flat polymer membrane and aqueous solutions of potassium chloride and/or ammonia were used. The model equation of the solute flux for a single-membrane system was developed. In order to test this model, the results of experimental and calculation results for solute flux in a single-membrane osmotic-diffusive cell containing binary and ternary electrolyte solutions are presented. The effects of rectification and amplification of the solute flows of electrolyte solutions in a single-membrane osmotic-diffusive cell are described.

Let us consider the configurations A and B of the single-membrane system represented in fig. 1. We assume that this membrane system in both configurations contains three-component, non-ionic and heterogeneous (not mechanically stirred) solutions, separated by an isotropic and symmetric membrane (M) of thickness δ_m . In both configurations the membrane has horizontally oriented planes and the respective concentration gradients are antiparallel and parallel to the gravitational force. The transport processes are isothermal and stationary and no chemical reactions occur in the solutions. In this single-membrane system water and the dissolved substance diffusing across the membrane will lead to the formation of concentration boundary layers (CBL).

In this steady state system, the layers l_l^i and l_h^i of thickness δ_l^i and δ_h^i (superscript $i=A, B$ pertain to configurations A and B) are formed on both sides of the membrane. These layers can be treated as pseudo-membranes. The implication from the above is that the concentrations of solutions at the membrane-layers interfaces are different from those in the outside (in the bulk solutions) the layers.

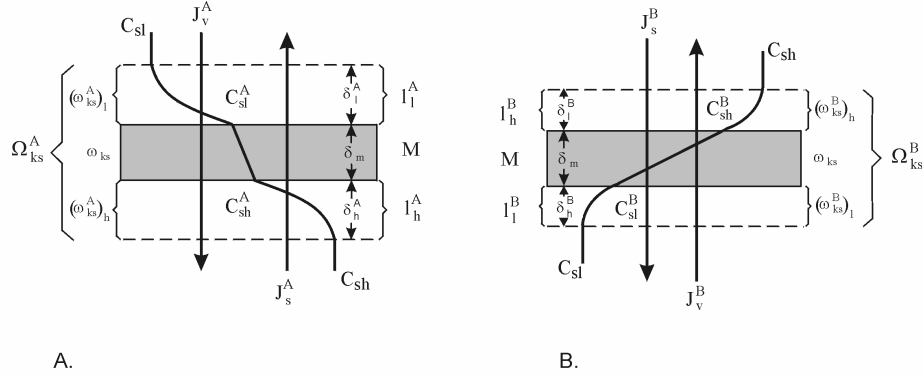


Fig. 1. Graphic illustration of the configurations A and B of single-membrane system with concentration profile. M, membrane; δ_m – thickness of membrane; l_l^A , l_h^A , l_l^B and l_h^B , concentration boundary layers in configurations A and B; δ_l^A , δ_h^A , δ_l^B and δ_h^B , thickness of CBL; C_{sl} and C_{sh} , global solution concentrations; C_{sl}^A , C_{sh}^A , C_{sl}^B and C_{sh}^B , local solution concentration in configurations A and B; J_v^A , J_s^A , J_v^B and J_s^B , volume and solute fluxes across the complex $l_l^i/M/l_h^i$ ($i=A, B$) in configurations A and B, respectively; J_{sm}^A , J_{sl}^A , J_{sh}^A , J_{sm}^B , J_{sl}^B and J_{sh}^B , solute fluxes across the membrane (M) and layers l_l^A , l_h^A , l_l^B and l_h^B , in configurations A and B, respectively; ω_{ks} , Ω_{ks}^A and Ω_{ks}^B , diffusive permeability coefficients of membrane and complex: boundary layer/membrane/ boundary layer; $(\omega_{ks}^A)_l$, $(\omega_{ks}^A)_h$, $(\omega_{ks}^B)_l$ and $(\omega_{ks}^B)_h$, diffusive permeability coefficients of layers l_l^A , l_h^A , l_l^B and l_h^B in configurations A and B, respectively.

We denote respectively by C_{sl}^A , C_{sh}^A (in configuration A) and by C_{sl}^B and C_{sh}^B (in configuration B), the concentrations of solutions at interfaces: membrane/near membrane layers, while the concentrations of solutions outside the layers are denoted by C_{sl} and C_{sh} ($C_{sh} > C_{sl}$), ($s=1, 2$). For configurations A and B and for any solutions whose density is proportional or inversely proportional to their concentration, the following relations hold

$$C_{sh} > C_{sh}^B > C_{sh}^A > C_{sl}^A > C_{sl}^B > C_{sl} . \quad (1)$$

The thicknesses (δ_l^i , δ_h^i) of the layers (l_l^i , l_h^i) are defined in terms of the concentration gradient at the membrane-water and membrane-solutions interfaces, respectively [1,2]

$$\frac{|C_{sl}^i - C_{sl}|}{\delta_l^i} = \frac{\partial C_{sl}}{\partial x} \Big|_{x=0} ; \quad (2)$$

$$\left. \frac{C_{sh}^i - C_{sl}^i}{h} \right|_{x=0} = \frac{\partial C_{sh}^i}{\partial x} \Big|_{x=0}, \quad (3)$$

where x is the distance from the membrane, C_{sh} and C_{sl} denotes the solute concentrations in the compartment h and l respectively, C_{sh}^i and C_{sl}^i denotes the solute concentrations at the interfaces respectively, index $i=A, B$ pertain to configuration A and B respectively $s=1, 2$.

The membrane is characterised by the hydraulic permeability (L_p), reflection (σ_s) and solute permeability (ω_{ks}) coefficients. The solute fluxes across membrane are denoted by J_{sm}^A and J_{sm}^B . The reflection and solute permeability coefficients of the complexes: near membrane layer/membrane/near membrane layer ($l_l^A/M/l_h^A$ and $l_l^B/M/l_h^B$) are denoted by σ_s^A , σ_s^B , Ω_{ks}^A and Ω_{ks}^B , respectively. The solute fluxes across the complexes $l_l^A/M/l_h^A$ and $l_l^B/M/l_h^B$ are denoted by J_s^A and J_s^B , respectively. The layers l_l^A , l_l^B , l_h^A and l_h^B are characterised by solute permeability coefficients: $(\omega_{ks}^A)_l$, $(\omega_{ks}^B)_l$, $(\omega_{ks}^A)_h$ and $(\omega_{ks}^B)_h$ respectively. The solute fluxes across layers l_l^A , l_l^B , l_h^A and l_h^B are denoted by J_{sl}^A , J_{sl}^B , J_{sh}^A and J_{sh}^B , respectively. The solute permeability coefficients $(\omega_{ks}^i)_l$, ω_{ks} and $(\omega_{ks}^i)_h$, can be rewritten as [12]

$$(\omega_{ks}^i)_l = \frac{(D_{ks}^i)_l}{RT(\delta_s^i)_l}; \quad (4)$$

$$\omega_{ks} = \frac{D_{ks}}{RT(\delta_s)_m}; \quad (5)$$

$$(\omega_{ks}^i)_h = \frac{(D_{ks}^i)_h}{RT(\delta_s^i)_h}, \quad (6)$$

where $(D_{ks}^i)_l$, D_{ks} and $(D_{ks}^i)_h$ are the coefficients of solute diffusion in the layer l_l^i , in the membrane M and in the layer l_h^i , respectively; RT is the product of the gas constant and thermodynamic temperature.

For coefficients Ω_{ks}^i , ω_{ks} , $(\omega_{ks}^i)_l$ and $(\omega_{ks}^i)_h$ the relation is valid [12]

$$\frac{1}{\Omega_{ks}^i} = \frac{1}{\omega_{ks}} + \frac{1}{(\omega_{ks}^i)_l} + \frac{1}{(\omega_{ks}^i)_h}. \quad (7)$$

The basic manner of description of membrane transport processes of non-homogeneous electrolyte solutions, originated from non-equilibrium thermodynamics of irreversible processes, is the classical [12] and modified Kedem–Katchalsky model equations [13]. In the case of osmotic membrane transport of ternary electrolyte solutions this model consists of equation

$$J_s = RT \sum_{k=1}^2 \zeta_s \omega_{ks} (C_{sh} - C_{sl}) + J_v (1 - \sigma_s) \bar{C}_s; \quad (8)$$

$$J_s^i = RT \sum_{k=1}^2 \zeta_s \Omega_{ks}^i (C_{sh} - C_{sl}) + J_v^i (1 - \sigma_s^i) \bar{C}_s^i; \quad (9)$$

$$J_v = L_p \left(RT \sum_{s=1}^2 \sigma_s \zeta_s (C_{sh} - C_{sl}) \pm \Delta P \right); \quad (10)$$

$$J_v^i = \xi_v^i \left((\det K)^{-1} RT \sum_{s=1}^2 \zeta_s \gamma_s^i (C_{sh} - C_{sl}) \pm \Delta P \right), \quad (11)$$

where J_s , J_s^i , J_v and J_v^i are the solute and volume fluxes, respectively; RT is the product of the gas constant and thermodynamic temperature; ζ_s is the Van't Hoff coefficient ($1 \leq \zeta_s \leq 2$, for non-electrolyte solutions $\zeta_s=1$); C_{sh} and C_{sl} (with $C_{sh} > C_{sl}$) are higher (superscript h) and lower (superscript l) the bulk solution concentrations; L_p , σ_s and ω_{ks} are the hydraulic permeability, reflection and diffusion permeability coefficients, respectively; σ_s^i and Ω_{ks}^i are the reflection and diffusion permeability coefficient of the complex CBL/M/CBL for s -th substance, which passes across membrane and complex (CBL/M/CBL) respectively, under the influence of gradient of the k -th substance osmotic pressure difference ($\omega_{ks} = \omega_{sk} \bar{C}_s \cdot \bar{C}_k^{-1}$, $\Omega_{ks}^i = \Omega_{sk}^i \bar{C}_s^i \cdot \bar{C}_k^{i-1}$) and $s \neq k=1, 2, \dots, n$; L_p is the hydraulic permeability coefficient of the membrane, ΔP is the hydrostatic pressure difference,

$$\xi_v^i = L_p \left[1 + (\det K)^{-1} L_p \left(\sum_{s=1}^2 \sigma_s \det M_s^i \right) \right]^{-1}, \quad \det K = \omega_{11} \omega_{22} - \omega_{21} \omega_{12},$$

$$\det M_1^i = \omega_{22} [\bar{C}_1^i (1 - \sigma_1^i) - (1 - \sigma_1) \bar{C}_1] - \omega_{21} [\bar{C}_2^i (1 - \sigma_2^i) - (1 - \sigma_2) \bar{C}_2^i],$$

$$\det M_2^i = \omega_{11} [\bar{C}_2^i (1 - \sigma_2^i) - (1 - \sigma_2) \bar{C}_2] - \omega_{12} [\bar{C}_1^i (1 - \sigma_1^i) - (1 - \sigma_1) \bar{C}_1^i],$$

$$\gamma_1^i = \sigma_1 \det K_{11}^i + \sigma_2 \det K_{21}^i, \quad \gamma_2^i = \sigma_1 \det K_{21}^i + \sigma_2 \det K_{22}^i,$$

$$\det K_{12}^i = \omega_{22} \Omega_{21}^i - \omega_{21} \Omega_{22}^i,$$

$$\det K_{21}^i = \omega_{11} \Omega_{12}^i - \Omega_{11}^i \omega_{12}, \quad \det K_{11}^i = \Omega_{11}^i \omega_{22} - \omega_{21} \Omega_{12}^i, \quad \det K_{22}^i = \omega_{11} \Omega_{22}^i - \Omega_{21}^i \omega_{12},$$

$$\bar{C}_s^i = [(C_{sh})^i - (C_{sl})^i] \{ \ln [(C_{sh})^i / (C_{sl})^i] \} \approx 0.5 [(C_{sh})^i + (C_{sl})^i],$$

$$\bar{C}_s = (C_{sh} - C_{sl}) \{ \ln(C_{sh} / C_{sl}) \} \approx 0.5(C_{sh} + C_{sl})$$

are the average concentration of solution for the s -th substance; $(n+1)$ -th component is a solvent, for which $\sigma_{n+1} = 0$.

The definitions and interpretation of the phenomenological coefficients of the membrane transport for ternary solutions (L_p , σ_s , σ_s^i , ω_{ks} , Ω_{ks}^i) were presented previous paper [9]. In these papers it was shown that the values of coefficients σ_{ks}^i and Ω_{ks}^i for binary and ternary solutions may be a function of the configuration of the single-membrane system and the values of σ_s^i and Ω_{ks}^i for ternary solutions is a function of the concentration of the solutions.

Studies upon stationary solute flows across single-membrane system were carried out by means of an experimental setup presented in previous paper [14]. Experiments were performed with flat sheet *Nephrophane* dialyzer membrane mounted in horizontal plane. The membrane was housed between two Plexigals cylindrical vessels (U and D), each with a volume of 200 cm³, with 3.36±0.2 cm² of available membrane 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 approximately 500 rpm using independently controlled stirrer motors (r). The vessel U of the single-membrane osmotic-diffusive cell contained aqueous potassium chloride and/or ammonia solution at varied concentration. This vessel was attached to a calibrated pipette (K), which allowed volume to be measured with accuracy $\pm 0.5 \text{ mm}^3$. The vessel D in all experiments contained pure water. This vessel was contacted to an external reservoir (N). Parameters of the membrane, i.e. hydraulic permeability (L_p), reflection (σ_s) and diffusive permeability (Ω_{ks}^i) coefficients of membrane and the reflection (σ_s^i) and diffusive permeability (Ω_{ks}^i) coefficients of the complex CBL/M/CBL have been determined in accordance with methods described in [9]. Their values for the aqueous potassium chloride or ammonia solutions are listed in table 1. The values of all these coefficients do not depend on the solution concentrations for binary solutions, whereas values of the coefficients σ_s^i and Ω_{ks}^i for ternary solutions do. Suitable values of the density (ρ) and kinematic viscosity (ν) of binary (aqueous potassium chloride solutions) and ternary (potassium chloride in 0.25 and 0.5 mol·l⁻¹ aqueous ammonia solution) are listed in table 2.

Each experiment was performed for two gravitational configurations of the single-membrane system: first, with water in the vessel above the membrane and the solution below (configuration A); second, with these positions reversed (configuration B). The aqueous potassium chloride solutions have higher density than pure water. In contrast, water is denser than aqueous ammonia solutions. In contrast to binary solutions, the density of ternary solutions, composed of water, potassium chloride and ammonia, may be lower, equal to or greater than that of the water. Consequently, the solute flux was greater when the upper vessel contained the denser solution. The osmotic pressure gradient generated a solute flux directed from the solution towards the water in every case, irrespective of the gravitational configuration. The same procedure was repeated for each configuration.

Measurements of $J_s^i(t)$ were performed according to the following procedure. The first step consisted in measurements of the solute flux (J_s^i) in the single-membrane osmotic-diffusive cell with mechanical stirring of the solutions at 500 rpm. After achieving the initial steady state with constant $J_s^i = J_s^o$, the stirring of the solutions was stopped and the evolution of solute flux has been measured until the second steady state, when the J_s^i (i=A, B) remain constant.

The evaluation of the global concentration exchanges (dC_s) of KCl in binary and ternary solutions has been performed by a total reflection X-ray fluorescence (TRXRF) method described in [15] in the series of independent experiments. Detection limit of this method is in the low ppb range (10^{-9} g/g) in direct analysis and in the ppt (10^{-12} g/g), when special pre concentration techniques are applied. The procedure of determining dC_s was following: after time $t_1, t_2, t_3, \dots, t_n$ the average solution concentration were measured in vessel D, until receiving the steady state, getting values $C_1, C_2, C_3, \dots, C_n$. Next, we calculated increments $dC_1 = C_1 - C_0, dC_2 = C_2 - C_1, dC_3 = C_3 - C_2, \dots, dC_n = C_n - C_{n-1}$ in time $dt_1, dt_2, dt_3, \dots, dt_n$. Taking under consideration increment dC_k in steady state, we calculated dC_s as an arithmetic average of concentration increments in steady state.

Table 1

The values of transport parameters for membrane *Nephrophane* for aqueous solutions of potassium chloride (index 1) and ammonia (index 2)

Coefficient	Values of membrane coefficients	
	Configuration A	Configuration B
$L_p \cdot 10^{12} [\text{m}^3 \cdot \text{N}^{-1} \cdot \text{s}^{-1}]$	5.0±0.2	5.0±0.20
$\sigma_1 \cdot 10^2$	4.0±0.1	4.0±0.2
$\sigma_2 \cdot 10^2$	1.00±0.02	1.00±0.02
$\sigma_1^i \cdot 10^3$	0.50±0.01	9.6±0.1
$\sigma_2^i \cdot 10^3$	2.90±0.02	0.04±0.01
$\omega_1 \cdot 10^9 [\text{mol} \cdot \text{N}^{-1} \cdot \text{s}^{-1}]$	2.5±0.1	2,5±0.1
$\omega_2 \cdot 10^9 [\text{mol} \cdot \text{N}^{-1} \cdot \text{s}^{-1}]$	2.68±0.02	2.68±0.02
$\Omega_1^i \cdot 10^9 [\text{mol} \cdot \text{N}^{-1} \cdot \text{s}^{-1}]$	0.03±0.01	0.6±0.2
$\Omega_2^i \cdot 10^9 [\text{mol} \cdot \text{N}^{-1} \cdot \text{s}^{-1}]$	0.78±0.06	0.01±0.01

Table 2

Values of the density (ρ_1) and kinematic viscosity (v_1) of binary (water-NaCl) and ternary (water-KCl-ammonia) solutions for various concentrations of KCl (C_1) and constant ammonia content (C_2)

C_1 [mol·l ⁻¹]	$\rho_1 \cdot [10^{-3} \text{ kg} \cdot \text{m}^{-3}]$			$v_1 \cdot [10^7 \text{ m}^2 \cdot \text{s}^{-1}]$		
	$C_2=0$ mol·l ⁻¹	$C_2=0.25$ mol·l ⁻¹	$C_2=0.5$ Mol·l ⁻¹	$C_2=0$ mol·l ⁻¹	$C_2=0.25$ mol·l ⁻¹	$C_2=0.5$ mol·l ⁻¹
0.00	0.9980	0.9950	0.9920	9.148	10.128	10.110
0.05	1.0004	0.9974	0.9944	9.104	10.141	10.091
0.10	1.0028	0.9980	0.9968	9.053	10.150	10.072
0.15	1.0052	1.0022	0.9992	9.031	10.160	10.051
0.20	1.0076	1.0046	1.0016	8.975	10.170	10.032
0.25	1.0100	1.0070	1.0040	8.943	10.180	10.011
0.30	1.0124	1.0094	1.0064	8.920	10.190	9.981

The measured value of the concentration exchange (dC_s/dt) was used to calculate the solute flux J_s^i based on the following equation

$$J_s^i = \frac{V_c}{S} \left(\frac{dC_s}{dt} \right)_{J_v^i=0}^i, \quad (12)$$

where V_c is a volume of measuring vessel, S is a membrane surface area, J_v^i is the volume osmotic flux; superscript $i=A, B$ pertain to configurations A and B of the measuring system, respectively. The relative error of measurement J_s^i was estimated by the total differential method accepting $S=\text{const.}$, $V_c=\text{const.}$, $\rho=\text{const.}$, $g=\text{const.}$, the error of time measurement 5 s and the error of concentration measurement $10^{-6} \text{ mol} \cdot \text{l}^{-1}$. The measurements have been carried out at temperature $T=(295 \pm 0.1) \text{ K}$. The concentration dependencies J_s^i were determined on the basis of time-dependent changes of J_s^i chosen

by consideration of the values of J_s^i at steady state, for different solution concentrations of the same substance.

Temporal dependencies of solute flux. A typical plot of the time dependence of J_1^i in configuration A and B of the single-membrane system in the case of a $0.1 \text{ mol}\cdot\text{l}^{-1}$ aqueous potassium chloride solution and *Nephrophane* membrane is shown in fig. 2. Line 1 common for both configurations, contain the results obtained under conditions of thorough mechanical stirring, and show that J_1^o is independent of the gravitational configuration of the single-membrane system. Curves 1A and 1B, obtained for configurations A and B respectively, demonstrate that J_1^i values for both configurations differ. The evolution of J_1^o to J_1^A or J_1^B is a reflection of the process of concentration boundary layers formation on both sides of the membrane. This process stops once a steady state has been attained. Thus, we can write that $J_1^o > J_1^A$, $J_1^o > J_1^B$ and $J_1^B > J_1^A$. The concentration dependencies J_1^i at steady state, obtained for different solution concentrations of the same substance.

Concentration dependence of the solute flux. Concentration dependencies of solute flux (J_1^i) on concentration difference of potassium chloride (ΔC_1) with fixed concentration difference of ammonia (ΔC_2) for mechanically stirred and unstirred solutions were showed in fig. 3. Superscript $i=A, B$ refer suitably to the configurations A and B of the single-membrane system. The lines 1A and 1B were obtained for the case of $\Delta C_2 = 0 \text{ mol}\cdot\text{l}^{-1}$ (binary solutions), the curves 2A and 2B – for $\Delta C_2 = 0.25 \text{ mol}\cdot\text{l}^{-1}$ and curves 3A and 3B – for $\Delta C_2 = 0.5 \text{ mol}\cdot\text{l}^{-1}$ (ternary solutions). From this figure it results that in the case of binary solution, J_1^i linearly dependent on ΔC_1 and in this case the values of J_1^i in configuration B are greater than in configuration A. This also means that the values of J_1^i are greater, when the solution with greater density is in the chamber over the membrane and water is under the membrane. The lines 4 were obtained when the solutions were mechanically stirred at 500 rpm. In this case the flux J_1^o is linearly dependent on ΔC_1 and is non-dependent on ΔC_2 and gravitational configuration of single-membrane system.

From the course of curve 2A and 3A results, that solute flux J_1^i gains the maximum for: $J_1^A = 2.5 \cdot 10^{-4} \text{ mol}\cdot\text{m}^{-2} \text{ s}^{-1}$ and $\Delta C_1 = 0.05 \text{ mol}\cdot\text{l}^{-1}$ (curve 2A) and $J_1^B = 4.0 \cdot 10^{-4} \text{ mol}\cdot\text{m}^{-2} \text{ s}^{-1}$ and $\Delta C_1 = 0.1 \text{ mol}\cdot\text{l}^{-1}$ (curve 3A). In this case the density of ternary solutions, being in the chamber over the membrane is greater than water density in the chamber under the membrane.

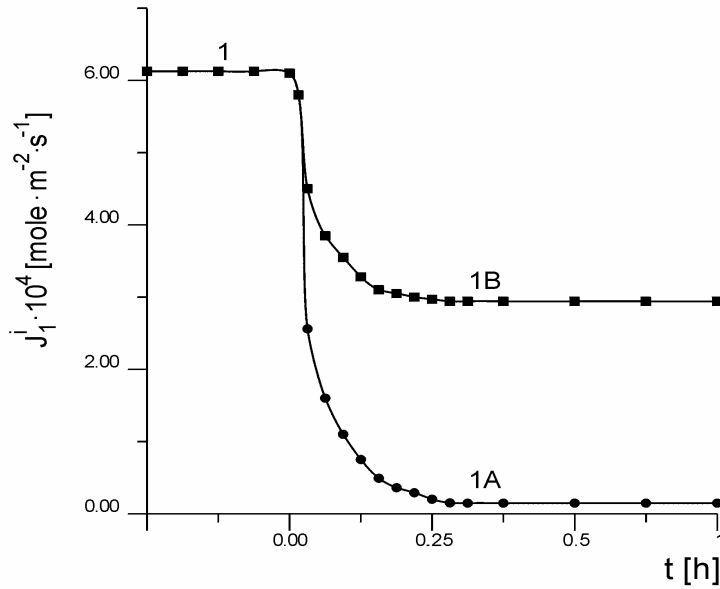


Fig. 2. Evolution of the solute flux (J_1^i) from J_1^o (line 1) to J_1^A and J_1^B in configuration A (curve 1A) and B (curve 1B) after turning off the mechanical stirrers.

For $\Delta C_1 > 0.1 \text{ mol} \cdot \Gamma^{-1}$ (curve 2A) and $\Delta C_1 > 0.2 \text{ mol} \cdot \Gamma^{-1}$ (curve 3A) the flux J_1^A is linearly dependent on ΔC_1 , and is non-dependent on ΔC_2 . In that case the density of ternary solutions being in the chamber under the membrane is lower than water density being over the membrane. From the course of curves 2B and 3B results that for $\Delta C_1 < 0.07 \text{ mol} \cdot \Gamma^{-1}$ (curve 2B) and $\Delta C_1 < 0.14 \text{ mol} \cdot \Gamma^{-1}$ (curve 3B) the value of J_1^B in a small degree depends on ΔC_1 and ΔC_2 . Therefore the density of ternary solutions, being in the chamber under the membrane is smaller than the water density being in the chamber over the membrane. For $\Delta C_1 > 0.12 \text{ mol} \cdot \Gamma^{-1}$ (curve 2A) and for $\Delta C_1 > 0.22 \text{ mol} \cdot \Gamma^{-1}$ (curve 3B) the flux J_1^B is linearly dependent on ΔC_1 with the same tangent of inclination angle as straight line 1B. The linear segment of curves 2B and 3B shows, that the greater value of ΔC_2 , the smaller value of J_1^B . In this case, the density of ternary solutions is being in the chamber over the membrane than water density being in the chamber under the membrane.

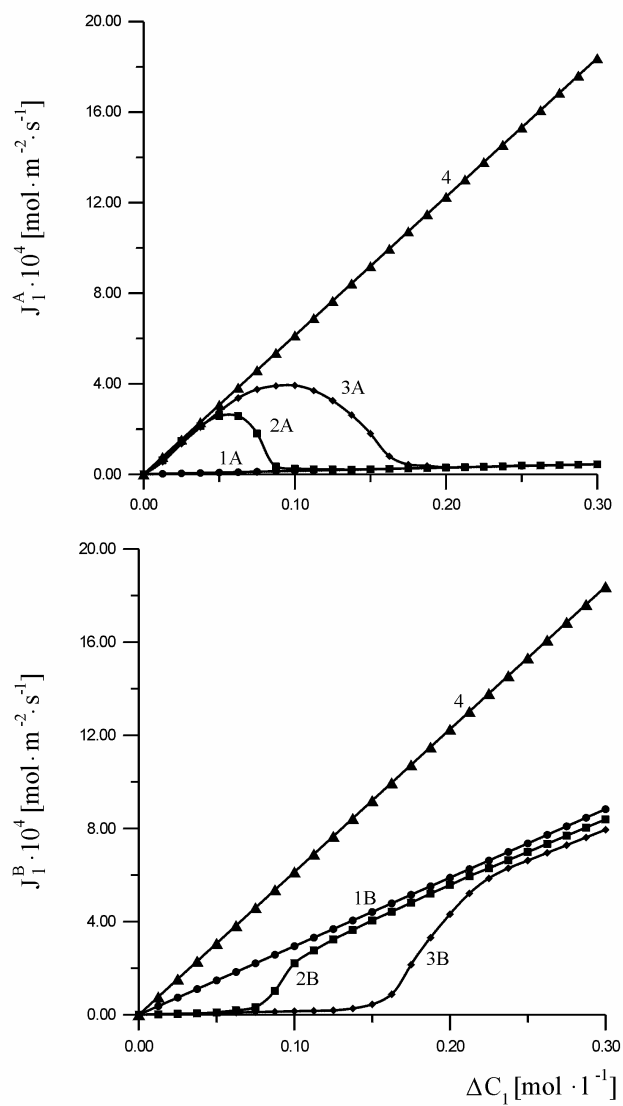


Fig. 3. Experimental solute flux (J_1^i) across a single-membrane system as a function of the potassium chloride difference (ΔC_1) obtained without any mechanical stirring: lines 1A and 1B – no ammonia, curves 2A and 2B – $\Delta C_2=0.25 \text{ mol}\cdot\text{l}^{-1}$ ammonia and curves 3A and 3B – $\Delta C_2=0.5 \text{ mol}\cdot\text{l}^{-1}$. The lines 4 were obtained under stirring conditions by mechanical means.

Concentration dependencies of coefficients Ω_{11}^i for ternary solutions. In the fig. 4 the dependencies of coefficients Ω_{11}^A (upper figure) and Ω_{11}^B (lower figure) on the

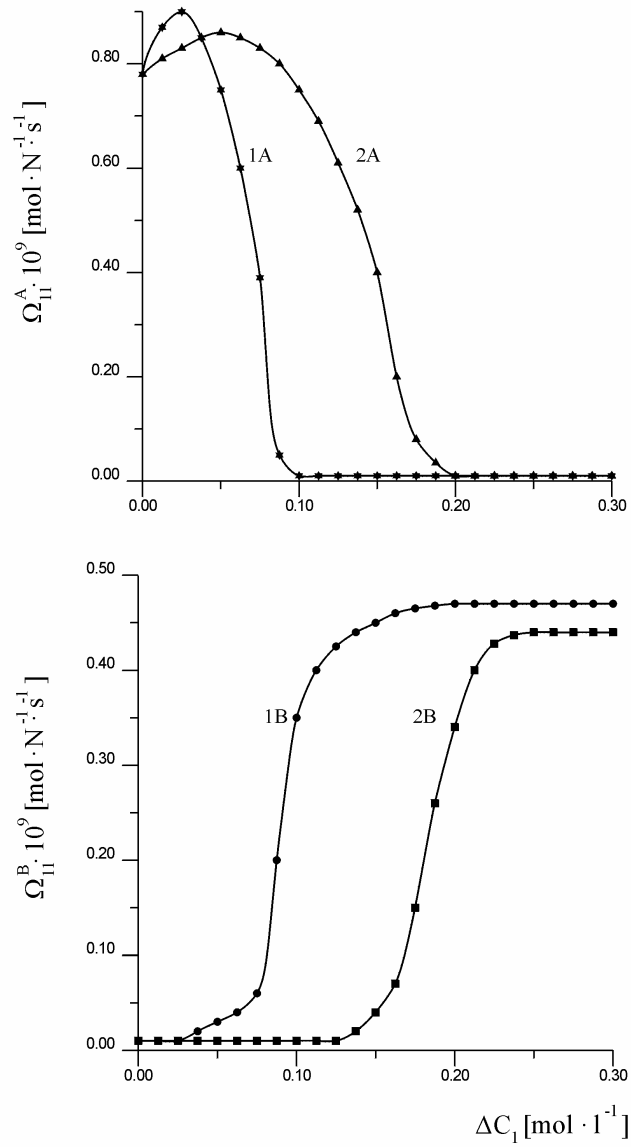


Fig. 4. Potassium chloride concentration dependencies of Ω_{11}^i in $0.25 \text{ mol} \cdot \text{l}^{-1}$ (curves 1A and 1B) and in $\Delta C_2 = 0.5 \text{ mol} \cdot \text{l}^{-1}$ (curves 2A and 2B) aqueous ammonia solutions for configuration A (curves 1A and 2A) and in configuration B (curves 1B and 2B).

concentration difference of potassium chloride (ΔC_1) we presented, with constant concentration difference of ammonia $\Delta C_2=0.25 \text{ mol}\cdot\text{l}^{-1}$ (curves 1A and 1B) and $\Delta C_2=0.5 \text{ mol}\cdot\text{l}^{-1}$ (curves 2A and 2B) for configuration A (graphs 1A and 2A) and configuration B (graphs 1B and 2B). From graphs 1A and 2A results, that value of coefficient Ω_{11}^A increases from value $\Omega_{11}^A=0.78\cdot 10^{-9} \text{ mol}\cdot\text{N}^{-1}\cdot\text{s}^{-1}$ to $\Omega_{11}^A=0.9\cdot 10^{-9} \text{ mol}\cdot\text{N}^{-1}\cdot\text{s}^{-1}$ (curve 1A) or to $\Omega_{11}^A=0.85\cdot 10^{-9} \text{ mol}\cdot\text{N}^{-1}\cdot\text{s}^{-1}$ (curve 2A) and next decreases nonmonotonically to $\Omega_{11}^A=0.03\cdot 10^{-9} \text{ mol}\cdot\text{N}^{-1}\cdot\text{s}^{-1}$, and for $\Delta C_1\geq 0.1 \text{ mol}\cdot\text{l}^{-1}$ (curve 1A), $\Delta C_1\geq 0.2 \text{ mol}\cdot\text{l}^{-1}$ (curve 2A) is independent on ΔC_1 and ΔC_2 . From graphs 1B and 2B results, that value of coefficient Ω_{11}^B is initially constant and amounts $\Omega_{11}^B=0.03\cdot 10^{-9} \text{ mol}\cdot\text{N}^{-1}\cdot\text{s}^{-1}$ and next from $\Delta C_1=0.0375 \text{ mol}\cdot\text{l}^{-1}$ (curve 1B) and from $\Delta C_1=0.125 \text{ mol}\cdot\text{l}^{-1}$ (curve 2B) increases to $\Omega_{11}^B=0.56\cdot 10^{-9} \text{ mol}\cdot\text{N}^{-1}\cdot\text{s}^{-1}$ (curve 1B) and to $\Omega_{11}^B=0.54\cdot 10^{-9} \text{ mol}\cdot\text{N}^{-1}\cdot\text{s}^{-1}$ (curve 2B). For $\Delta C_1\geq 0.15 \text{ mol}\cdot\text{l}^{-1}$ (curve 1B) and for $\Delta C_1\geq 0.2125 \text{ mol}\cdot\text{l}^{-1}$ (curve 2B), Ω_{11}^B is constant and independent on ΔC_1 . Besides for $\Delta C_1\geq 0.15 \text{ mol}\cdot\text{l}^{-1}$ and $\Delta C_2=0.25 \text{ mol}\cdot\text{l}^{-1}$ (curve 1B) the value of Ω_{11}^B is greater than for $\Delta C_1\geq 0.2125 \text{ mol}\cdot\text{l}^{-1}$ and $\Delta C_2=0.5 \text{ mol}\cdot\text{l}^{-1}$ (curve 2B).

Asymmetry of solute flux. The results of studies of J_1^i in single-membrane system show those values of solute flux obtained for the same ΔC_1 in configurations A and B are different. It shows the rectifying property of single-membrane system. The measure of this property is the asymmetry coefficient solute flux (k_1) defined as quotients J_1^i in configurations B and A of a single-membrane system [14]

$$k_1 = \frac{J_1^B}{J_1^A} \approx \frac{\Omega_{11}^B(C_1)}{\Omega_{11}^A(C_1)}. \quad (13)$$

In fig. 5 the dependencies of coefficient k_1 on concentration difference ΔC_1 were presented graphically. The line 1 was obtained for binary solutions and curves 2 and 3 – for ternary solutions. From line 1, shown in this figure results, that for binary solutions, k_1 is independent on ΔC_1 . Its value is $k_1 = 20$. For ternary solutions, the values of this coefficient are dependent on ΔC_1 and ΔC_2 (see curves 2 and 3). From curves 2 and 3 results, that for $\Delta C_1 < 0.075 \text{ mol}\cdot\text{l}^{-1}$ (curve 2) and $\Delta C_1 < 0.15 \text{ mol}\cdot\text{l}^{-1}$ (curve 3) with increase of value ΔC_1 and ΔC_2 the value of coefficient k_1 is independent on both on ΔC_1 and ΔC_2 . For $0.075 \text{ mol}\cdot\text{l}^{-1} \leq \Delta C_1 \leq 0.125 \text{ mol}\cdot\text{l}^{-1}$ (curve 2) and $0.1125 \text{ mol}\cdot\text{l}^{-1} \leq \Delta C_1 \leq 0.225 \text{ mol}\cdot\text{l}^{-1}$ (curve 3) the value of k_1 increases from minimal value $k_1=0.05$ to maximal values $k_1=17$ (for curve 2) and $k_1=15$ (for a curve 3). For $\Delta C_1 > 0.15 \text{ mol}\cdot\text{l}^{-1}$ and $\Delta C_1 > 0.225 \text{ mol}\cdot\text{l}^{-1}$ the value of coefficient k_1 is constant and independent on ΔC_1 . In this range ΔC_1 the greater value of ΔC_2 the smaller value of k_1 .

The amplification of solute flux. In order to demonstrate an effect of solute flux (J_1^i) amplification let us take into consideration the pairs of graphs 1 and 2 and 1 and 3 showed in fig. 3. The graphs 1A and 1B show, that the same change of value of concentrations differences $\Delta(\Delta C_1)$ in the case of binary solutions cause the same change of value ΔJ_1^i in the whole range of used concentrations difference ΔC_1 . In case of ternary solutions, illustrated in the graphs 2A, 2B, 3A and 3B on above mentioned

figure, the same change of concentration differences cause different in the value and sign value changes of ΔJ_1^i .

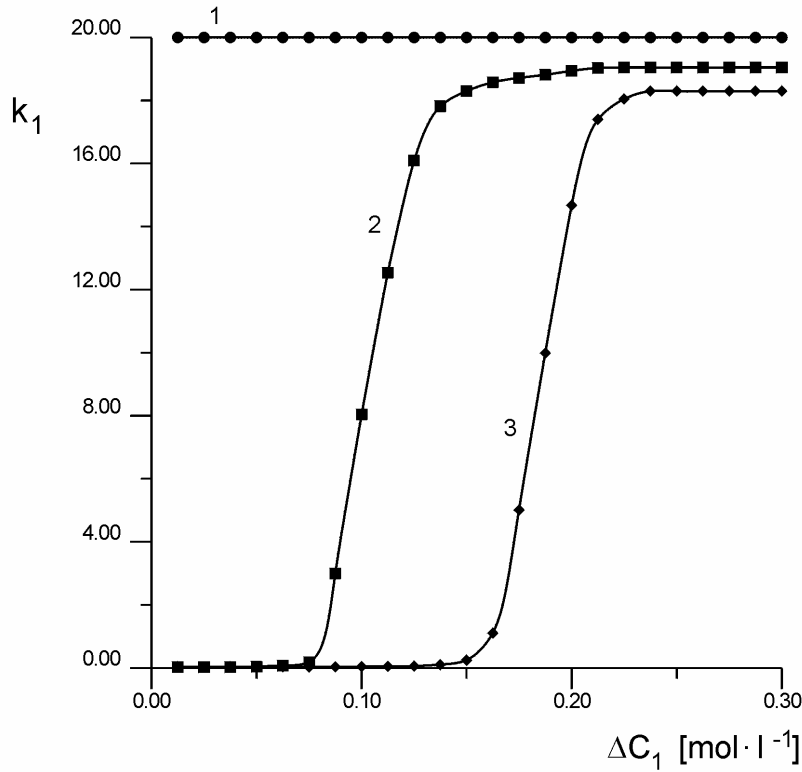


Fig. 5. The asymmetry coefficient solute flux (k_1) as a function of the potassium chloride concentration difference (ΔC_1) in a binary (line 1) and ternary solutions (potassium chloride in 0.25 mol·l⁻¹ – curve 2, and in 0.5 mol·l⁻¹ ammonia aqueous solutions – curve 3).

Quantitative measure of this effect is the coefficient of solute flux amplification (a_1^i) specified by the following equation [14]

$$a_1^i = \frac{(\Delta J_1^i)_t}{(\Delta J_1^i)_b} \approx \frac{[\Omega_{11}^i(C_1)]_h(\Delta C_1)_h - [\Omega_{11}^i(C_1)]_l(\Delta C_1)_l}{\Omega_{11}^i[(\Delta C_1)_h - (\Delta C_1)_l]}, \quad (15)$$

where $(\Delta J_1^i)_t$ – change of the flux J_1^i in ternary solutions, $(\Delta J_1^i)_b$ – change of the flux J_1^i in binary solutions, $i=A, B$ relate suitably to A and B configurations of single-membrane system.

In fig. 6 the dependencies of coefficient a_1^i on mean concentration \bar{C}_1 were presented graphically. The curves 1A and 2A were obtained for configuration A, whereas curves 1B and 2B – for configuration B of single-membrane system.

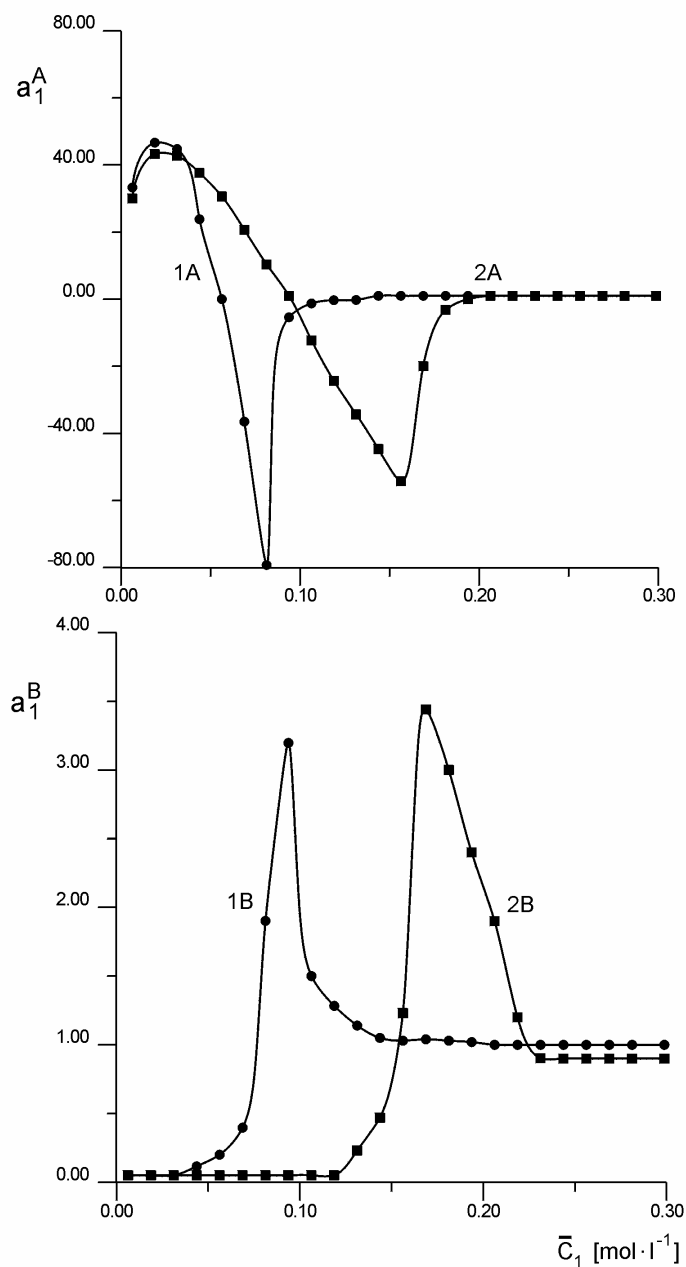


Fig. 6. The amplification coefficient solute flux (a_1^i) $i=A, B$ as a function of the mean potassium chloride concentration (\bar{C}_1) in $0.25 \text{ mol}\cdot\text{l}^{-1}$ and in $0.5 \text{ mol}\cdot\text{l}^{-1}$ aqueous ammonia solutions for configuration A (curves 1A and 2A) and configuration B (curves 1B and 2B).

The procedure of calculation of \bar{C}_1 was as follows. If, for example $\Delta C_k = C_k - C_0$ (where $k=1, 2, 3, \dots, n$) then $\bar{C}_1 = (C_1 + C_0)/2$, and so on. From curves 1A and 2A results, that with increase of value \bar{C}_1 the value of coefficient a_1^A initially increases and next decreases nonmonotonically from maximal value $a_1^A = 48$ to minimal value $a_1^A = -80$ (curve 1A) and $a_1^A = -60$ (curve 2A). Next, the value of a_1^A coefficient increases to constant value $a_1^A = 1.5$ for $\bar{C}_1 > 0.1 \text{ mol}\cdot\text{l}^{-1}$ (curve 1A) and $\bar{C}_1 > 0.16 \text{ mol}\cdot\text{l}^{-1}$ (curve 2A), independent on \bar{C}_1 and \bar{C}_2 . Minimal values of a_1^A were obtained for $\bar{C}_1 = 0.08 \text{ mol}\cdot\text{l}^{-1}$ (curve 1A) and $\bar{C}_1 = 0.16 \text{ mol}\cdot\text{l}^{-1}$ (curve 2A). From curves 1B and 2B, shown in fig. 9 results, that values of coefficient a_1^B , for $\bar{C}_1 < 0.05 \text{ mol}\cdot\text{l}^{-1}$ (curve 1B) and $\bar{C}_1 < 0.12 \text{ mol}\cdot\text{l}^{-1}$ (curve 2B) is independent on both \bar{C}_1 and \bar{C}_2 and amounts $a_1^B = 0.05$. For $\bar{C}_1 \geq 0.05 \text{ mol}\cdot\text{l}^{-1}$ (curve 1B) and $\bar{C}_1 \geq 0.12 \text{ mol}\cdot\text{l}^{-1}$ (curve 2B) the values of coefficient a_1^B increases and for $\bar{C}_1 = 0.09 \text{ mol}\cdot\text{l}^{-1}$ (curve 1B) and $\bar{C}_1 = 0.17 \text{ mol}\cdot\text{l}^{-1}$ (curve 2B) reaches values $a_1^B = 3.25$ (curve 1B) and $a_1^B = 3.5$ (curve 2B). For $\bar{C}_1 > 0.09 \text{ mol}\cdot\text{l}^{-1}$ (curve 1B) and $\bar{C}_1 \geq 0.17 \text{ mol}\cdot\text{l}^{-1}$ (curve 2B) values of coefficient a_1^B decreases and for $\bar{C}_1 > 0.14 \text{ mol}\cdot\text{l}^{-1}$ (curve 1B) and $\bar{C}_1 = 0.23 \text{ mol}\cdot\text{l}^{-1}$ (curve 2B) does not depend on both \bar{C}_1 and \bar{C}_2 and is $a_1^B \approx 1$.

From the experimental and calculated data presented in this paper it results, that in the case of mechanically stirred binary and ternary electrolyte solutions solute flux is directly proportional to solution concentrations and does not depend on orientation of membrane and measurement chamber with solution, relative to vector of gravitational force. Similar results for non-electrolyte solutions were obtained [9]. In the case of mechanically unstirred binary electrolyte solutions solute flux is directly proportional to the solutions concentration, and is strongly dependent on the sequence of solutions relative to the horizontal membrane orientation. The values of this flux are higher when the solution with a higher density is in the chamber above the membrane. In the case of ternary electrolyte solutions solute flux depends not only on the concentration and solution orientation relative horizontally mounted membrane but also on solutions composition. Therefore, this flux is non-linear functions of one solute concentration in solvent when the other solute concentration is constant. These observations can be examined in terms of the gravitational stability or instability of CBL, controlled by the Rayleigh number [8,16].

If we assume that J_{vs}^i is the generalized flux and ΔC_s a generalized thermodynamical force, the regions where $[dJ_s^i / d(\Delta C_s)] < 0$ can be classified as the negative differential resistance regions. This phenomenon appears in nature and constitutes a very important factor in the physics of semiconductors [17], membranology [18] and biophysics [19]. If in the non-linear element there is negative resistance region, then in this element the generation of electrical and/or mechanical oscillation may be appeared. Examples of these behaviours: Teorell's membranous oscillator [20], semiconductor generator [21] and electrical oscillations in excitable tissues [19].

The non-linear characteristics $i_s(C_s)$ presented in the fig. 6 (graphs 2A, 2B, 3A and 3B) shows, that the investigating single-membrane system which contain the ternary ionic solutions, determine the non-linear element. In the case of the characteristic $J_1^A = f(\Delta C_1)$, for $0.05 \text{ mole}\cdot\Gamma^{-1} < \Delta C_1 < 0.1 \text{ mole}\cdot\Gamma^{-1}$ (curve 2A) and $0.1 \text{ mole}\cdot\Gamma^{-1} < \Delta C_1 < 0.2 \text{ mole}\cdot\Gamma^{-1}$, the condition $\Delta J_1^A / \Delta(\Delta C_1) < 0$ is fulfilled. In this region the amplification coefficient fulfil the condition $a_1^A < 0$. If ΔC_1 accomplishes the relation $0 \text{ mole}\cdot\Gamma^{-1} < \Delta C_1 < 0.05 \text{ mole}\cdot\Gamma^{-1}$, $\Delta C_1 > 0.1 \text{ mole}\cdot\Gamma^{-1}$ (for the curve 2A), and $0 \text{ mole}\cdot\Gamma^{-1} < \Delta C_1 < 0.1 \text{ mole}\cdot\Gamma^{-1}$, $\Delta C_1 > 0.2 \text{ mole}\cdot\Gamma^{-1}$ (for the curve 3A), the condition $\Delta J_1^A / \Delta(\Delta C_1) \geq 0$ is fulfilled. In this region the amplification coefficient fulfil the condition $a_1^A > 0$. In case of characteristic $J_1^B = f(\Delta C_1)$, for all values of ΔC_1 , we can write a condition $\Delta J_1^B / \Delta(\Delta C_1) \geq 0$.

Inferences the conducted investigations show that:

1. In case of the lack of mechanical stirring solutions, on both sides of the membrane, the concentration boundary layers are created. Only in the situation when sense of density gradient is opposite to gravitational force in the area near membrane the natural convection appears and causes weak solution stirring. Such situation could occur in biological systems, present in Earth gravitational field [22, 23]. The state without natural convection responds to the microgravity (hypogravity) conditions. This is the situation when the cell membrane is not proved with nutrients. This means, that in the close vicinity of cell membrane the concentration of nutrients is minimal.

2. Single-membrane system is characterised by rectification and amplification properties of the solute flows. These effects are the results of destruction by gravitation of concentration boundary layers. The effects of rectification and amplification of the solute flows is indication of new diffusion property in single-membrane system. It may be subdivided into a group of regulatory effects, including phenomena such as rectification, amplification and oscillation of transmembrane flows.

3. The interest of microgravity conditions influence on the biological systems function is connected with the crew space flights [22]. It's been shown, that long – term stay in the state of weightlessness influences for human organism behaviour also during the flight and after it. That's why the gravitational biology and space medicine belong to the most dynamically developing science disciplines. However the studies lead in a space are very expensive and accessible only for not many people. Some of those studies, specifically about the mechanism of creating the concentrational boundary layers can be leaded in the earth conditions on model systems. For this we can use the artificial electrochemical membrane cells.

4. The experimental results presented in this paper can be of importance for recognition of influence the mechanism of hypo- and hypergravity on the passive transmembrane transport in the biological systems.

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КОНЦЕНТРАЦІЙНІ ЕФЕКТИ В ГРАНИЧНИХ ШАРАХ ДИФУЗІЙНИХ ПОТОКІВ ЕЛЕКТРОЛІТИЧНИХ РОЗЧИНІВ ЧЕРЕЗ ГОРИЗОНТАЛЬНО РОЗТАШОВАНУ ПОЛІМЕРНУ МЕМБРАНУ

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Наведено результати експериментальних досліджень дифузного трансмембранного транспортування в одномембранних системах з горизонтально розташованою мембраною. Така система містить мікропористу та симетричну плоску полімерну мембрану, здатну розділяти воду та подвійні чи потрійні розчини. Як бінарний вибрано водний розчин хлориду калію. Потрійним розчином слугував водний розчин аміаку зі 0,25 і 0,5 моль л⁻¹ хлориду калію. Розглянуто А і В конфігурації одномембранної осмотично-дифузної комірки в гравітаційному полі. У випадку конфігурації А вода була в посудині над мембраною, а розчин – під нею, у випадку В – навпаки. Досліджено потік розчину в комірці залежно від концентрації та гравітаційної конфігурації. Для бінарних розчинів отримано лінійну, а для потрійних – нелінійну залежність потоку від концентрації. З'ясовано, що одномембранна система здатна випрямляти та підсилювати властивості потоку розчину. Запропоновано модель для опису ефектів асиметрії та підсилення потоку. Результати розрахунків проінтерпретовано в наближенні конвекційної нестабільності.

Ключові слова: мембранне транспортування, гравітаційний ефект, концентрація граничних шарів, модель Кедема–Качальського.

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