

# Developing Kedem-Katchalsky equations of the transmembrane transport for binary nonhomogeneous non-electrolyte solutions

ANDRZEJ ŚLĘZAK<sup>1</sup>, MARIA JARZYŃSKA<sup>2</sup>

<sup>1</sup>Department of Biology and Biophysics, Częstochowa University of Technology

<sup>2</sup>Vocational Secondary School of Environment Modeling, Piotrków Trybunalski

---

## Summary

The paper presents developing Kedem-Katchalsky equations for binary non-homogeneous non-electrolyte solutions. The obtained equation describes the volume flux ( $J_v$ ) depending on parameters of a membrane (reflection,  $\sigma$ , hydraulic permeability,  $L_p$ , and solute permeability,  $\omega$  coefficients), solution parameters (concentration,  $C_k$ , density,  $\rho$ , kinematic viscosity,  $\nu$  and diffusion coefficient,  $D$ ) and concentration Rayleigh number ( $R_C$ ). In order to verify of the elaborated equation of  $J_v$  for the single-membrane system, there were made the calculations of the dependence:  $J_v = f(\Delta C)_{R_C, \zeta_s = const}$ ,  $J_v = f(R_C)_{\Delta C, \zeta_s = const}$ , and  $J_v = f(\zeta_s)_{R_C, \Delta C = const}$ , for aqueous glucose solutions and the membrane made of bacterial cellulose.

**Key words:** membrane transport, Kedem-Katchalsky equations, concentration boundary layers, concentration Rayleigh number

---

# Rozwinięcie równań Kedem-Katchalsky'ego transportu membranowego dla binarnych niejednorodnych roztworów nieelektrolitów

## Streszczenie

W pracy przedstawiono rozwinięcie równań Kedem-Katchalsky'ego dla binarnych niejednorodnych roztworów nieelektrolitów. Otrzymane równanie opisuje strumień objętościowy ( $J_v$ ) w zależności od parametrów membrany (współczynników: odbicia,  $\sigma$ , przepuszczalności hydraulicznej,  $L_p$  oraz przepuszczalności solutu,  $\omega$ ) oraz stężeniowej liczby Rayleigha ( $R_C$ ). W celu weryfikacji wyprowadzonego równania na  $J_v$  dla układu jednomembranowego wykonano obliczenia zależności  $J_v = f(\Delta C)_{R_C, \zeta_s = const}$ ,  $J_v = f(R_C)_{\Delta C, \zeta_s = const}$  oraz  $J_v = f(\zeta_s)_{R_C, \Delta C = const}$ , dla wodnych roztworów glukozy i membrany wykonanej z celulozy bakteryjnej.

**Słowa kluczowe:** transport membranowy, równania Kedem-Katchalsky'ego, stężeniowe warstwy graniczne, stężeniowa liczba Rayleigha

---

## INTRODUCTION

In years 1958-65, O. Kedem and A. Katchalsky elaborated equations describing the transmembrane transport of homogeneous solutions on the basis of linear thermodynamics of irreversible processes [1]. Homogeneity of solutions can be reached by intensive mechanical stirring of solutions. Lack of such stirring causes formation of concentration boundary layers on both sides of the membrane, directly adjacent to the membrane surface. Thickness of the layers depends on concentration, density, viscosity and temperature of used solutions, on diffusive permeability coefficients of the membrane and layers, and Rayleigh number. It means that thicknesses have direct influence on the concentration's volume flux  $J_v$  value passing across the membrane [2].

In order to test the obtained in the paper equation for the volume flux of the solution ( $J_v$ ), there were made the calculations of the flux value for different values of the concentration difference ( $\Delta C$ ), concentration Rayleigh number ( $R_c$ ) and concentration polarisation coefficient ( $\zeta_s$ ).

## DEVELOPING KEDEM-KATCHALSKY EQUATION

The starting point for elaborated in the paper considerations and calculations are Kedem-Katchalsky equations for the volume flux ( $J_v$ ) and solute flux ( $J_s$ ) [1]

$$J_v = L_p [\Delta P - RT\sigma(C_h - C_l)] \quad (1)$$

$$J_s = \omega RT(C_h - C_l) + J_v(1 - \sigma)\bar{C} \quad (2)$$

where:  $J_v$  and  $J_s$  are respectively volume and solute fluxes;  $L_p$ ,  $\sigma$  and  $\omega$  – respectively, hydraulic permeability, solute reflection, solute permeability coefficients,  $\Delta P$  – mechanic pressure difference,  $R$  – gas constant,  $T$  – thermodynamic temperature,  $\bar{C}$  – average concentration of solutions placed at both sides of the membrane ( $C_h, C_l$ ) was calculated on the basis of the following equation

$$\bar{C} = \frac{C_h - C_l}{\ln(C_h C_l^{-1})} \approx \frac{1}{2} (C_h + C_l) \quad (3)$$

Kedem-Katchalsky equation for the volume flux ( $J_v$ ) of the transmembrane transport for binary nonhomogeneous non-electrolyte solutions for a osmotic-diffusive cell, with the assumption that  $\Delta P = 0$ , takes the following form

$$J_v = L_p \sigma RT(C_h - C_l) \quad (4)$$

Taking into account Equations (1) and (2), the volume flux ( $J_v$ ) and solute fluxes  $J_l$ ,  $J_h$  and  $J_s$  in the single-membrane system, presented in Figure 1, according to Kedem-Katchalsky formalism reach the following values

$$J_v = L_p \sigma RT(C_i - C_e) \quad (5)$$

$$J_{sh} = \omega_h RT(C_h - C_i) + \frac{1}{2} (C_h + C_i) (1 - \sigma_h) L_p \sigma_h RT(C_h - C_i) \quad (6)$$

$$J_{sl} = \omega_l RT(C_e - C_l) + \frac{1}{2} (C_e + C_l) (1 - \sigma_l) L_p \sigma_l RT(C_e - C_l) \quad (7)$$

$$J_s = \zeta_s \omega RT (C_h - C_l) + \frac{1}{2} (C_h + C_l) (1 - \zeta_s \sigma) L_p \zeta_s \sigma RT (C_h - C_l) \quad (8)$$

where  $\omega_h = D_h (RT \delta_h)^{-1}$ ,  $\omega_l = D_l (RT \delta_l)^{-1}$ ,  $\omega_s = \zeta_s \omega$ ,  $\sigma_s = \zeta_s \sigma$ ,  $\zeta_s$  – concentration polarization coefficient,  $\delta_h$  and  $\delta_l$  are thicknesses of formed concentration boundary layers  $l_h$  and  $l_l$ , respectively. In the steady state

$$J_{sh} = J_{sl} = J_s \quad (9)$$

If we assume that  $\sigma_h = \sigma_l = 0$ , the Equations (6) and (7) can be presented in the form

$$J_{sh} = \frac{D_h}{\delta_h} (C_h - C_i) \quad (10)$$

$$J_{sl} = \frac{D_l}{\delta_l} (C_e - C_l) \quad (11)$$

where  $\delta_h$  and  $\delta_l$  are thicknesses of formed concentration boundary layers  $l_h$  and  $l_l$ , which are derived from the equations [2]

$$\delta_h = (R_C)^{\frac{1}{4}} \left\{ D_h^2 \nu_h \rho_h \left[ g RT \omega \zeta_s \left( \frac{\partial \rho}{\partial C} \right) (C_h - C_l) \right]^{-1} \right\}^{\frac{1}{4}} \quad (12)$$

$$\delta_l = (R_C)^{\frac{1}{4}} \left\{ D_l^2 \nu_l \rho_l \left[ g RT \omega \zeta_s \left( \frac{\partial \rho}{\partial C} \right) (C_h - C_l) \right]^{-1} \right\}^{\frac{1}{4}} \quad (13)$$

where  $R_C$  is the concentration Rayleigh number,  $D_h$  and  $D_l$  are the diffusion coefficients in layers  $l_h$  and  $l_l$ , respectively,  $\nu_h$  and  $\nu_l$  are the kinematic viscosity coefficients,  $\rho_h$  and  $\rho_l$  are the density of solutions,  $g$  is the gravity acceleration,  $RT$  is the product of gas constant and thermodynamic temperature,  $\partial \rho / \partial C$  change in solution density falling on change in its concentration.

In order to calculate the volume flux  $J_{vs}$ , it is necessary to find solutions concentrations  $C_i$  and  $C_e$  on the boundary of the membrane and concentration boundary layers. From calculated solutions, and taking into account Equations (8) – (13) we obtain

$$C_e = \frac{D_l C_l + \zeta_s \delta_l \omega RT (C_h - C_l) + \frac{1}{2} J_{vs} \delta_l (C_h + C_l) (1 - \zeta_s \sigma)}{D_l} \quad (14)$$

$$C_i = \frac{D_h C_h - \zeta_s \delta_h \omega RT (C_h - C_l) - \frac{1}{2} J_{vs} (C_h + C_l) (1 - \zeta_s \sigma)}{D_h} \quad (15)$$

Including Equations (14) and (15), the final solution of the formula (5), for the searched in the paper volume flux ( $J_{vs}$ ) passing across complex  $l_h/M/l_l$ , is described by the following equation

$$J_v = \frac{L_p \sigma RT (C_h - C_l) \left[ 1 - \frac{\zeta_s \omega (D_h \delta_l + D_l \delta_h)}{D_l D_h} \right]}{1 + \frac{L_p \sigma (C_h + C_l) (1 - \zeta_s \sigma) (D_h \delta_l + D_l \delta_h)}{2 D_l D_h}} \quad (16)$$

Discussion of this equation leads to the following conclusions:

1. If we assume that  $\zeta_s \omega (D_h \delta_l + D_l \delta_h) (D_l D_h)^{-1} = 0$  and  $\zeta_s \sigma = 1$  or  $\delta_h = \delta_l = 0$  in Equation (16) we obtain

$$J_v = L_p \sigma RT (C_h - C_l) \quad (17)$$

2. For  $\zeta_s = 0$ , Equation (16) can be written in following forms

$$J_v = \frac{L_p \sigma RT (C_h - C_l)}{1 + \frac{L_p \sigma (C_h + C_l) (D_h \delta_l + D_l \delta_h)}{2 D_l D_h}} \quad (18)$$

3. For  $\zeta_s = 1$ , Equation (16) can be written in following forms

$$J_v = \frac{L_p \sigma RT (C_h - C_l) \left[ 1 - \frac{\omega (D_h \delta_l + D_l \delta_h)}{D_l D_h} \right]}{1 + \frac{L_p \sigma (C_h + C_l) (1 - \sigma) (D_h \delta_l + D_l \delta_h)}{2 D_l D_h}} \quad (19)$$

## CALCULATION RESULTS AND DISCUSSION

For calculations there were used the parameters of the membrane made of bacterial cellulose. Values of the membrane parameters, i.e. coefficients of: hydraulic permeability  $L_p$ , reflection ( $\sigma$ ) and solute permeability ( $\omega$ ) and remain values for the whole system are: respectively,  $L_p = 5 \times 10^{-12} \text{ m}^3 (\text{Ns})^{-1}$ ,  $\sigma = 0.068$ ,  $\omega = 8 \times 10^{-10} \text{ mol} (\text{Ns})^{-1}$ ,  $R = 8.31 \text{ J} (\text{mol} \cdot \text{K})^{-1}$ ,  $\Delta C = C_h - C_l$  solutions concentration difference at both sides of the membrane causing the volume transport

of the solution across complex  $l_h/M/l_l$ ,  $R_C$  – concentration Rayleigh number: elementary dimensionless value characterizing convection of flow of viscose incompressible liquid,  $D_h=D_l=D=0.69\times10^{-9} \text{ m}^2\text{s}^{-1}$  are diffusive coefficients describing motion of a molecular diffusing in layers  $l_h$  and  $l_l$ ,  $\nu_l=1.012\times10^{-6} \text{ m}^2\text{s}^{-1}$  kinematic viscosity coefficient, values  $\nu_h$  in layer  $l_h$  in the dependence on solution density are: respectively,  $\nu_{h(n)} = \nu_{h(0)} + n\Delta\nu$ ,  $\Delta\nu=4\times10^{-11} \text{ m}^2\text{s}^{-1}$ ,  $\nu_{h(0)}=1.012\times10^{-6} \text{ m}^2\text{s}^{-1}$ ,  $\rho_l=998.000 \text{ kg}\cdot\text{m}^{-3}$  and  $\rho_{h(n)} = \rho_{h(0)} + n\Delta\rho$ , where  $\Delta\rho=0.006 \text{ kg}\cdot\text{m}^{-3}$ ,  $\rho_{h(0)}=998.000 \text{ kg}\cdot\text{m}^{-3}$ ,  $g=9.81 \text{ m}\cdot\text{s}^{-2}$ ,  $T=295 \text{ K}$ ,  $\omega_s=0.3\times10^{-10} \text{ mol}(\text{Ns})^{-1}$ ,  $\zeta_s=\omega_s\omega^{-1}=0.0375$ ,  $\partial\rho/\partial C=0.06 \text{ kg}(\text{mol})^{-1}$ . Calculations were made using Mathcad 2001 professional software. Calculations results are presented graphically in Figures 2, 3 and 4.

Figure 2 presents calculations results of the concentration dependence of the volume flux  $J_v = f(\Delta C)_{R_C, \zeta_s=\text{const}}$ . Calculations were made for different  $R_C$ , for the single-membrane system, using aqueous glucose solution at  $\zeta_s=\text{const}$ . The  $J_v$  was calculated for different concentrations values present in compartment 'h'. Calculations results are demonstrated by lines in Figure 2. The lines are sloping at different angles to the axis containing independent variable  $\Delta C$ , in the dependence on Rayleigh number value  $R_C$ . This is because convection flows are driven by dimensionless parameter called concentration Rayleigh number.

Figure 3 presents graphs of the dependence  $J_v = f(R_C)_{\zeta_s=0,0375}$  for different values  $\Delta C$  for the single-membrane system. The value of  $J_v$  is decreasing with increasing parameter  $R_C$ , because increase of this parameter leads also to increase in thickness of concentration boundary layers which are being formed at both sides of the membrane. Concentration boundary layers thickness is proportional to  $\sqrt[4]{R_C}$ . Increase causes that permeability coefficient of layers is decreasing, thus  $J_v$  is also decreasing.

Figure 4 presents graphs of the dependence  $J_v = f(\zeta_s)_{\Delta C=\text{const}}$  for different Rayleigh numbers, each for  $\Delta C=100 \text{ mol}\cdot\text{m}^{-3}$ . The dependence is demonstrated by lines which sloppiness to the axis  $\zeta_s$  depends on the number  $R_C$  value. With increasing concentration polarization coefficient  $\zeta_s$ , the model and number  $R_C$  the volume flux  $J_v$  is decreasing. The bigger value of concentration Rayleigh number  $R_C$ , the bigger decrease in the volume flux; that confirms the destructive influence of Rayleigh number value on volume fluxes

values running across the membrane in the system. Considering flows in the system of fluxes  $J_v$  under the constant concentrations gradient for different Rayleigh numbers, the attention was also paid that flows of the flux  $J_v$  in a given system are limited by the value of concentration polarization coefficient  $\zeta_s$ , complex  $l_h/M/l_l$  and value of  $R_C$  number.

The single-membrane system, which is considered in the paper, may be treated as an osmotic-diffusive cell, whose membrane separates the solution into two compartments with different concentrations causing particular osmotic and diffusive fluxes. The solution concentration in these compartments may be indicated by solutions concentrations in external and internal compartment of the cell under the conditions of lack of mechanical stirring of solutions. Therefore this system may be treated as a part of a simple model of functioning of a biological cell. In the event of lack of mechanical stirring, as it is known, concentration boundary layers are formed at both sides of the membrane. Such situation takes place in biological systems. The process of concentration layers forming is finished at the moment of reaching the stationary state by the cell. In given conditions of the cell, thickness of layers has a constant value. Calculations have shown that the value of modified volume flux of the solution passing across the membrane depends on: concentrations gradient  $\Delta C$  of solutions at both sides of the membrane, Rayleigh number  $R_C$  which value has direct influence on thickness of boundary layers, and on the value of diffusive conductivity quotient of complex  $l_h/M/l_l$  to diffusive conductivity  $\omega$  of the membrane, presented by particular graphs.

It should be mentioned that in order to calculate coefficients of permeability  $\omega_h$  and  $\omega_l$  as well as thicknesses  $\delta_h$  and  $\delta_l$  of concentration boundary layers that are needed in order to calculate the value of the solution volume flux for the dependence  $J_v = f(\Delta C)$ , there were used Equations (6) and (7) only for Rayleigh number  $R_C=1$ . Calculations of values  $\omega_h$  and  $\omega_l$  as well as  $\delta_h$  and  $\delta_l$  for remaining numbers:  $R_C=50$ ,  $R_C=500$ ,  $R_C=1255$  and  $R_C=2000$  were conducted on the basis of the following relations found in the paper

$$(\omega_{h,l})_{R_C} = (\omega_{h,l})_{R_C=1} (R_C)^{-\frac{1}{4}} \quad (20)$$

and

$$(\delta_{h,l})_{R_C} = (\delta_{h,l})_{R_C=1} (R_C)^{\frac{1}{4}} \quad (21)$$

Similarly it was done while calculating the dependence  $J_v = f(R_C)$ . Calculations of values  $\omega_h$  and  $\omega_l$  as well as  $\delta_h$  and  $\delta_l$  for:  $\Delta C = 10 \text{ mol} \cdot \text{m}^{-3}$ ,  $\Delta C = 50 \text{ mol} \cdot \text{m}^{-3}$ ,  $\Delta C = 100 \text{ mol} \cdot \text{m}^{-3}$ ,

$\Delta C = 150 \text{ mol} \cdot \text{m}^{-3}$  and  $\Delta C = 300 \text{ mol} \cdot \text{m}^{-3}$ , except  $\Delta C = 1 \text{ mol} \cdot \text{m}^{-3}$ , were also conducted from the following own relations :

$$(\omega_{h,l})_{R_C} = (\omega_{h,l})_{R_C, \Delta C=1} (\Delta C)^{\frac{1}{4}} \quad (22)$$

$$(\delta_{h,l})_{R_C} = (\delta_{h,l})_{R_C, \Delta C=1} (\Delta C)^{\frac{1}{4}} \quad (23)$$

Finally, it should be emphasize that KK equations hold wide application in the world, particularly in research work concerning a substance transport across different biological membranes, especially cell membranes. However, application of the equations is limited to homogenous membranes, whereas cell membranes are non-homogenous in terms of transport, because pores, which they posses, have differentiated dimensions [3].

## LITERATURE

- [1] KATCHALSKY A, CURRAN P.F.: Nonequilibrium thermodynamic in biophysics, Harvard University Press, Cambridge MA, 1965.
- [2] ŚLĘZAK A., DWORECKI K., JASIK-ŚLĘZAK J., WĄSIK J.: Method to determine the critical concentration Rayleigh number in isothermal passive membrane transport processes. Desalination (2004), 168, 397-412.
- [3] KARGOL M., KARGOL A.: Mechanistic formalism for membrane transport generated by osmotic and mechanical pressure. Gen. Physiol. Biophys. (2003), 22, 51-68.

Address of the authors:

Częstochowa University of Technology

Department of Biology and Biophysics

19B Armia Krajowa Al., 42-200 Częstochowa

e-mail: [ajslezak@zim.pcz.czest.pl](mailto:ajslezak@zim.pcz.czest.pl)



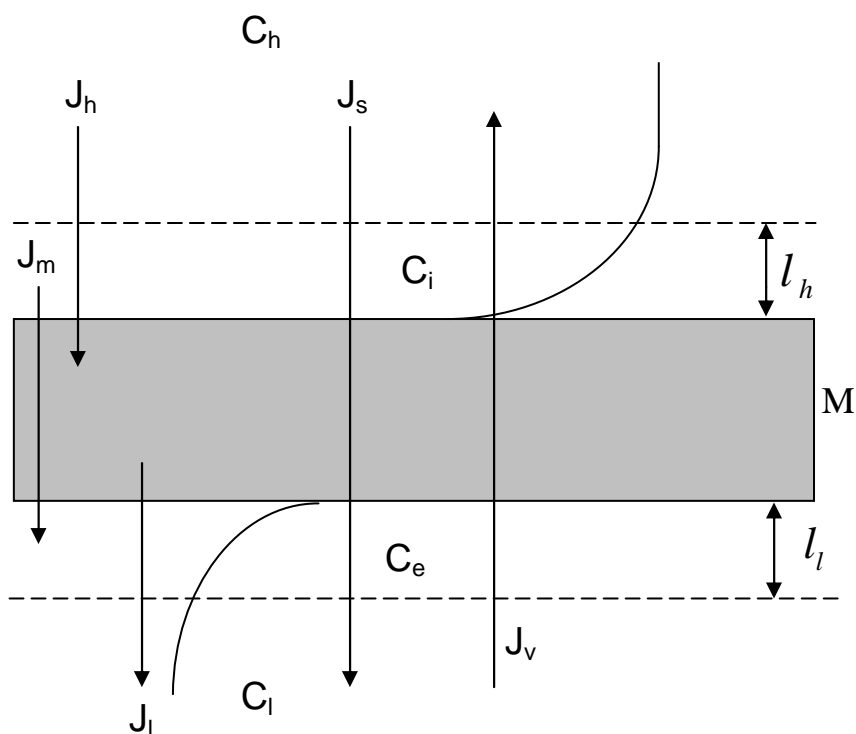


Fig. 1. Single-membrane system: M – membrane,  $\delta_h$  and  $\delta_l$  – thicknesses of concentration boundary layers;  $C_h$  and  $C_l$  – solutions concentrations in compartments separated by the membrane;  $C_i$  and  $C_e$  – solutions concentrations of boundary layers;  $J_m$ ,  $J_h$ ,  $J_l$  and  $J_s$  – solute fluxes through: the membrane, boundary layers  $l_h$  and  $l_l$  and complex  $l_h/M/l_l$ ;  $J_v$  – the solution volume flux through complex  $l_h/M/l_l$ .

Ryc. 1. Model układu 1-membranowego: M – membrana,  $\delta_h$  i  $\delta_l$  – grubości warstw granicznych,  $C_h$  i  $C_l$  – stężenia roztworów w przedziałach rozdzielonych membraną,  $C_i$  i  $C_e$  – stężenia roztworów warstw granicznych,  $J_m$ ,  $J_h$ ,  $J_l$  oraz  $J_s$  – strumienie substancji przez: membranę, stężeniowe warstwy graniczne  $l_h$  i  $l_l$ , kompleks  $l_h/M/l_l$ ;  $J_v$  – strumień objętościowy roztworu transportowany przez kompleks  $l_h/M/l_l$ .

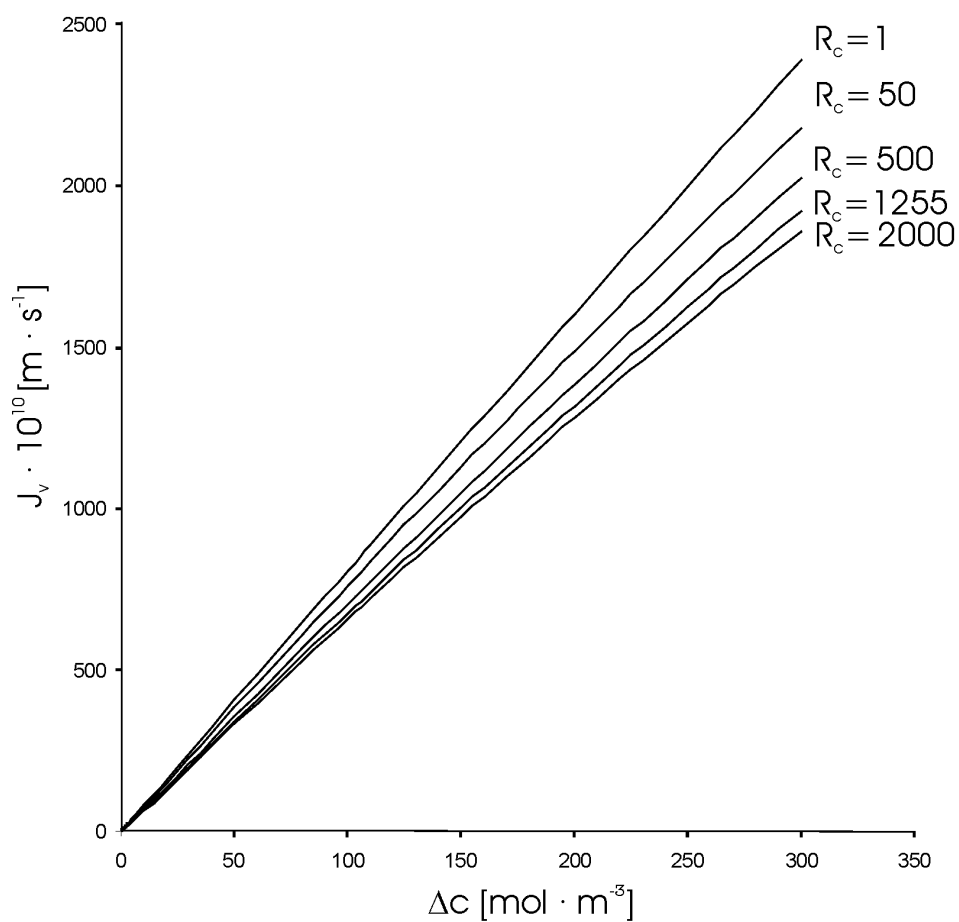


Fig. 2. Concentration dependencies of the volume flux ( $J_v$ ) in the conditions of lack of mechanical stirring of solutions of the single-membrane system for different Rayleigh numbers at the constant value  $\zeta_s$ .

Ryc. 2. Stężeniowe zależności strumienia objętościowego ( $J_v$ ) w warunkach braku mieszania mechanicznego roztworów w układzie 1-membranowym dla różnych liczb Rayleigha przy stałej wartości  $\zeta_s$ .

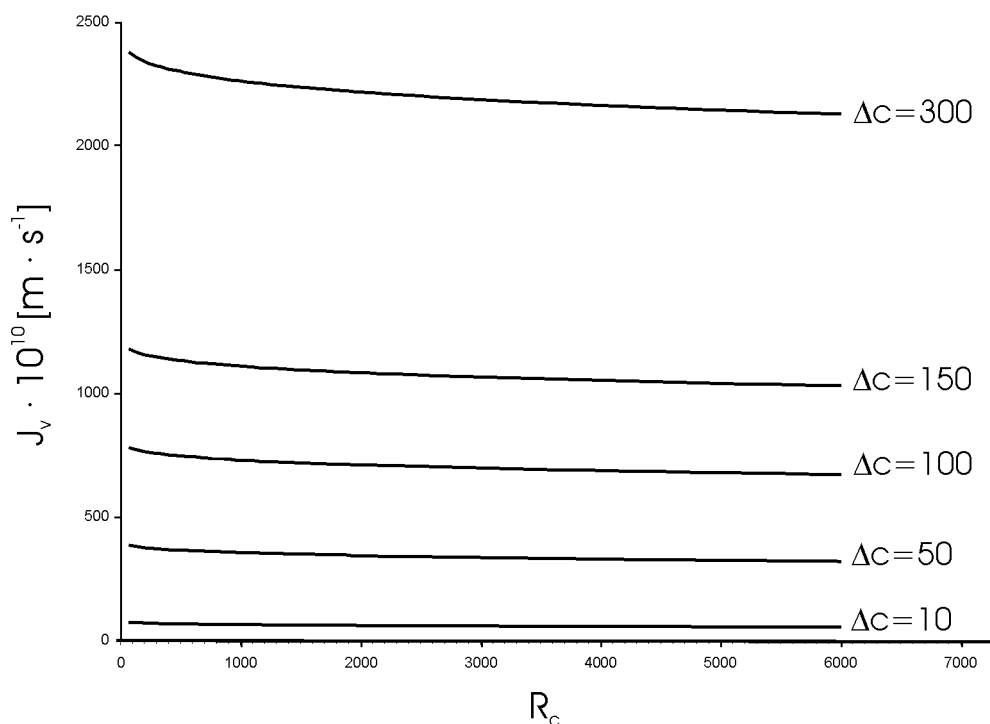


Fig. 3. Graphs of the volume flux dependence  $J_v = f(R_c)$  in the conditions of lack of mechanical stirring of solutions of the single-membrane system for different concentrations difference  $\Delta C$  present at both sides of the membrane.

Ryc. 3. Wykresy zależności strumienia objętościowego  $J_v = f(R_c)$  w warunkach braku mieszania mechanicznego roztworów w układzie 1-membranowym dla różnych gradientów stężeń  $\Delta C$  występujących po obydwu stronach membrany.

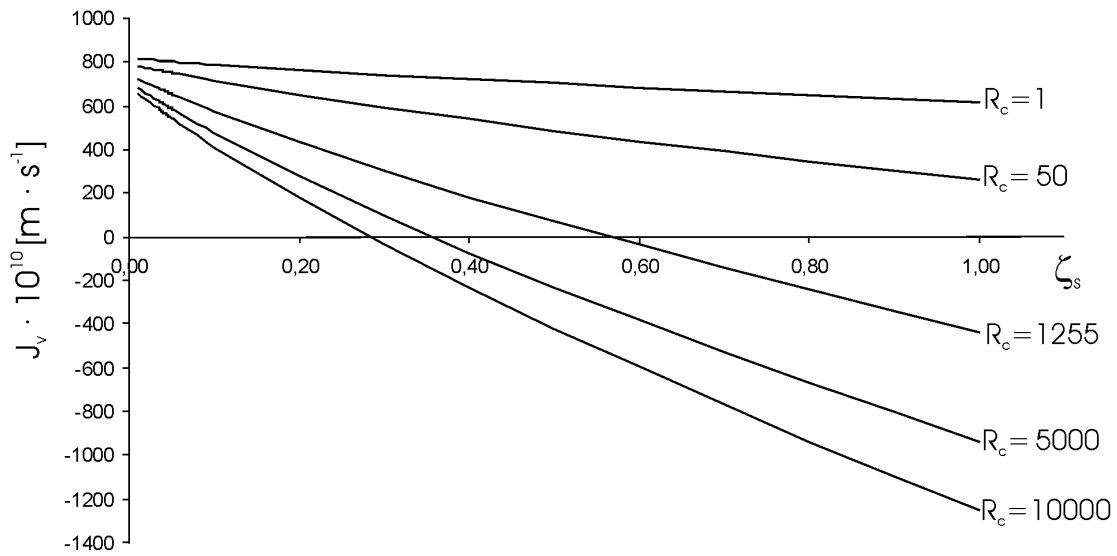


Fig. 4. The volume flux dependence  $J_v = f(\zeta_s)_{\Delta c = 100 \text{ mol} \cdot \text{m}^{-3}}$  on concentration polarization coefficient ( $\zeta_s$ ) in the conditions of lack of mechanical stirring of solutions of the single-membrane system for different Rayleigh numbers.

Ryc. 4. Zależność strumienia objętościowego  $J_v = f(\zeta_s)_{\Delta c = 100 \text{ mol} \cdot \text{m}^{-3}}$  od współczynnika polaryzacji stężeniowej ( $\zeta_s$ ) w warunkach braku mieszania mechanicznego roztworów w układzie 1-membranowym dla różnych liczb Rayleigha.