

# Study of the electromotive force of electrochemical cell with polymeric membrane oriented in horizontal plane

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## Summary

In order to characterize processes proceeded in concentration boundary layers (CBLs), divided by neutral and horizontally mounted membrane, the electromotive force (EMF) during and after turning off mechanical stirring of aqueous KCl solutions was measured. The EMF was measured by means of Ag|AgCl electrodes and electrometer connected with a microcomputer. Aqueous solutions of KCl with fixed and lower concentration  $C_1=10^{-5} \text{ mol}\cdot\text{l}^{-1}$  was over the membrane, while KCl concentration under the membrane  $C_h>C_1$  was changed. Such configuration of membrane system caused stable reconstruction of CBLs after turning off mechanical stirring of solutions in electrochemical cell.

On the basis of time dependencies of EMF the concentration dependencies were performed and it was stated that dependencies of  $\text{EMF} = f(C_h/C_1)$  are nonlinear. It was found that maximal value of EMF, equal to 175 mV, was observed during mechanical stirring of solutions for  $C_h/C_1 = 400$ .

In order to interpret experimental results, the model of EMF changes in time after turning off mechanical stirring was elaborated on the basis of Kedem-Katchalsky model equations for transport of electrolytes through the membrane. The transport number of  $\text{K}^+$  ions ( $t_+$ ), appointed for the membrane, depended nonlinearly on  $C_h/C_1$  and for  $C_h/C_1 = 50$  was maximal and amounted to  $t_{+\text{max}} = 0.7$ . Besides, concentration dependence of relaxation time of CBLs reconstruction after turning off mechanical stirring was appointed. For  $C_h/C_1 < 500$ , increase of  $C_h/C_1$  caused considerable decrease of relaxation time, while for  $C_h/C_1 > 500$  the relaxation time was small and did not change considerably with increase of  $C_h/C_1$  in this range.

**Key words:** membrane transport, diffusion, concentration boundary layers, thickness of concentration boundary layers, electromotive force, diffusion membrane potential

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## **Badanie siły elektromotorycznej w komórce elektrochemicznej z membraną polimerową zorientowanej horyzontalnie**

### **Streszczenie**

W celu scharakteryzowania procesów zachodzących w stężeniowych warstwach granicznych (CBL), rozdzielanych przez obojętną i horyzontalnie ustawioną membranę, zmierzono siłę elektromotoryczną (EMF) podczas i po wyłączeniu mieszania mechanicznego wodnych roztworów KCl. Siłę elektromotoryczną zmierzono przy pomocy elektrod Ag|AgCl połączonych z mikrokomputerem. Wodne roztwory KCl z ustalonym i niższym stężeniem  $C_l = 10^{-5} \text{ mol} \cdot \text{l}^{-1}$  były nad membraną, podczas gdy stężenia KCl pod membraną  $C_h > C_l$  zmieniano. Taka konfiguracja układu membranowego powodowała stabilną rekonstrukcję CBL po wyłączeniu mechanicznego mieszania roztworów w komórce elektrochemicznej.

Na podstawie czasowych zależności EMF sporządzono stężeniowe zależności i stwierdzono, że zależności  $\text{EMF} = f(C_h/C_l)$  są nieliniowe. Wykazano, że maksymalną wartość EMF równą 175 mV zaobserwowano podczas mieszania mechanicznego roztworów dla  $C_h/C_l = 400$ .

W celu interpretacji wyników doświadczalnych, opracowano na bazie równań Kedem-Katchalsky'ego dla roztworów elektrolitów, model czasowych zmian EMF po wyłączeniu mieszania mechanicznego roztworów. Liczba przenoszenia jonów  $\text{K}^+$  ( $t_+$ ), wyznaczona dla membrany jest nieliniowo zależna od  $C_h/C_l$  i dla  $C_h/C_l = 50$  jest maksymalna i wynosi  $t_{+\text{max}} = 0.7$ . Ponadto wyznaczono stężeniową zależność czasu relaksacji rekonstrukcji CBL po wyłączeniu mieszania mechanicznego roztworów. Dla  $C_h/C_l < 500$ , wzrost wartości  $C_h/C_l$  powoduje znaczące zmniejszenie czasu relaksacji, podczas gdy dla  $C_h/C_l > 500$  czas relaksacji był krótki i nie zmieniał się istotnie ze wzrostem  $C_h/C_l$  w badanym zakresie stężeń.

**Słowa kluczowe:** transport membranowy, dyfuzja, stężeniowe warstwy graniczne, grubość stężeniowych warstw granicznych, siła elektromotoryczna, dyfuzyjny potencjał membranowy

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## INTRODUCTION

Transport of ions through membranes, both neutral and ion-exchange, is dependent on solute concentrations at membrane-solution surface, structure of membrane and conditions on the membrane such as gradients of pressure or electrical potential [1,2]. One of the main physical phenomena connected with membrane transport and occurring in the area near membrane is concentration polarization, leading to formation at both sides of the membrane concentration boundary layers (CBLs) [3-7]. CBLs insert additional hydraulic and/or diffusion resistance, diminishing ions and water transport through the membrane [8,9], so CBLs can be treated as pseudomembranes connected with a real membrane in series [6]. In order to decrease the influence of concentration polarization on ions transport through the membrane mechanical stirring of solutions is used [10]. The rate of CBLs creation depends on different physical effects such as temperature, kinematic viscosity and type of solute, and external fields imposed on the membrane – electrical and/or gravitational. In the case of ion-exchange membranes, concentration polarization considerably manifests itself by achieving limiting values of both solute flux through the membrane during increase of electrochemical force on the membrane as well as ions current intensity through the membrane during increase of applied voltage [11].

The theoretical modeling of membrane transport is mainly based on the Nernst-Planck equations [11,12], while the processes proceeded in CBLs are described by equations of diffusion, mass and momentum balance. Solutions of those equations foresee phenomena generated in the layer of solution arranged in a specified manner in relation to gravitational field in conditions of gradients of temperature, solute concentration and electrical potential existence [13]. In the case of neutral membrane, volume, solute and current flows may be interpreted by the Kedem-Katchalsky model-

equations, related to stationary states and described by phenomenological coefficients of the membrane, such as: hydraulic permeability, reflection, diffusion permeability, electroosmotic, electrical conductance or transport number of ions [14].

Electrical phenomena in membrane systems has been studied by means of different methods, one of which is chronopotentiometry, often used to study electrical properties of ion-exchange membranes. This is an electrochemical method that allows the monitoring of time changes of electrode potential produced by a forced current through membrane with a fixed value, in other words in amperostatic conditions. This technique has frequently been used to investigate kinetic effects, such as adsorption and transport phenomena near electrode surface [15] and transport processes both through ion-exchange membrane as well through layers of solution to be in contact with membrane. The resultant potential-time data give important information regarding polarization phenomena, heterogeneity, the values of transference number of an ion-exchange membrane [16-18] and determination of pore size in membrane under investigation [19,20]. Compared to other methods, in chronopotentiometry more detailed information can be obtained because the dynamic voltage response in time can be analyzed, so this method is used to investigate transport processes in bipolar [21] and monopolar membranes [22].

One of the type of chronopotentiometry is the measurement of electromotive force in a single-membrane electrochemical cell (EMF), in conditions of free current flow caused by gradient of concentration or in condition without current flow:  $I=0$ . The measured values of: EMF, current through the membrane or membrane potential in a single-membrane electrochemical cell are dependent on physical properties of membranes, solutions used and CBLs arisen near membrane [23]. From the above it

results that time dependencies of EMF measured after turning off mechanical stirring are the reflection of concentration changes in CBLs.

As was earlier elaborated [8], the CBLs near membrane are important in describing the influence of gravitational field on transport of solutes and water through the membrane and on membrane potential. In the membrane system with membrane in horizontal plane, gradient of solute concentration (and density gradient) is created perpendicularly to the membrane [24,25]. The configuration of membrane system, with membrane in horizontal plane and with solution with lower density over the membrane, can be less sensitive to instability caused by gravity, because in that case gradient of density occurring in CBLs is directed as gravity vector [8,10]. So, in the configurations of the membrane system with membrane in horizontal plane, the case in which growing in time density gradient, parallel to gravity vector can cause, in some cases, stabilization of CBLs [24,26].

Reversible electrodes, which have been used to measure electrical properties of electrochemical membrane system, can be connected with solution by salt-bridges (electrodes in saturated KCl) or placed directly in solution. The measurements of EMF by means of Ag|AgCl electrodes in saturated KCl solutions, connected by bridges with solutions in electrolytic cell enable measuring membrane potential, weakly connected with concentration changes directly in CBLs. Location of electrodes reversible for  $\text{Cl}^-$  ions in CBLs at both sides of the membrane can allow to efficiently determine influence of concentration changes in CBLs on EMF generated in electrochemical cell, specially when oscillatory time changes of concentration in CBLs appear. So time dependencies of EMF are the reflection of processes occurring in CBLs. As an initial condition, the homogeneous distribution of solutions in chambers of electrolytic cell was assumed,

fulfilled in the case of mechanical stirring of solutions. Turning off mechanical stirring causes CBLs reconstruction in time, which is illustrated by EMF changes.

The aim of this article is to study time evolution of EMF after disturbing solution homogeneity in electrochemical cell by CBLs creation. The chamber over the membrane in horizontal plane contained aqueous KCl solution with fixed concentration  $C_l$ , and the chamber under the membrane KCl concentration  $C_h$ , greater than  $C_l$ . The measurements of EMF were carried out by means of Ag|AgCl electrodes, located directly in CBLs area. In order to ensure homogeneity of solute concentration both solutions were intensively stirred. The investigation of time evolution of EMF was performed in two stages. During the first stage of EMF measurement, solutions were stirred until steady state was reached. During the second stage, time characteristics of EMF after turning off mechanical stirring were measured. In order to characterize processes proceeded in CBLs the relaxation time was defined and determined on the basis of temporal characteristics of EMF, received in condition of lack of mechanical stirring of solutions. Besides, on the grounds of the Kedem-Katchalsky model equations for neutral membrane, the model of EMF changes after turning off mechanical stirring has been elaborated and fitted to experimental data.

## **THEORY**

Turning off stirring of solutions (aqueous KCl solutions) in the membrane system causes thickness of CBLs to increase in time and the flows of solutes and water through the membrane and CBLs decrease in time [11]. The change of solute concentrations at the surface of the membrane can be observed. The main factors influencing the rate of

change of concentrations in the membrane system are: difference of concentration of solutes at the membrane surfaces, membrane orientation versus gravitational field and the kind of solutes and membrane in the membrane system. The electrodes Ag|AgCl are placed near membrane, so the electromotive force of electrolytic cell (EMF) can be measured. This EMF depends on thicknesses of CBLs, concentrations of solute at the surfaces of the membrane and near electrodes. The EMF for diluted solutions can be written as [23]

$$\Delta\psi_M = \frac{2RT}{F} \int_1^2 t_+ d \ln(C_s) \quad (1)$$

where  $\Delta\psi_M$  is the electromotive force,  $RT$  is the product of gas constant and thermodynamic temperature,  $F$  is the Faraday constant,  $t_+$  is the apparent transport number of  $K^+$  ions,  $C_s$  is the solute concentration, borders of integration 1 and 2 are near electrodes. Stirring of solutions causes borders of integration to be connected with the membrane surface, because the solutions in chambers are homogeneous. Assuming that transport number connected with the membrane  $\bar{t}_+$  is constant and solutions are stirred, the equation 1 describing EMF can be presented in the form

$$\Delta\psi_M^o = \frac{2RT}{F} \bar{t}_+ \ln\left(\frac{C_h}{C_l}\right) \quad (2)$$

where  $\Delta\psi_M^o$  is the EMF,  $C_l$  and  $C_h$  are the concentrations in chambers, indexes  $l$  and  $h$  are suitable for lower and higher concentrations of solute,  $\bar{t}_+$  is the apparent transport number of  $K^+$  ions in the membrane. Different mobility of ions in the membrane causes that the diffusion membrane potential appears. It can be written as [1]

$$\Delta\psi_D = -\frac{RT}{F} \sum_j \frac{\bar{t}_j}{z_j} \ln\left(\frac{C_i}{C_e}\right)$$

(3)

where  $\Delta\psi_D$  is the diffusion membrane potential,  $C_i$  and  $C_e$  are concentrations near membrane surfaces. Assuming that during stirring of binary solutions, concentrations near membrane are  $C_i=C_l$  and  $C_e=C_h$  and connecting equations (2) and (3) and  $t_+ + t_- = 1$  we arrive at

$$\Delta\psi_D^o = -\Delta\psi_M^o + \frac{RT}{F} \ln\left(\frac{C_h}{C_l}\right)$$

(4)

Where  $\Delta\psi_D^o$  is the diffusion membrane potential during stirring of solutions. In the case when stirring is turned off the CBLs appear and (equation 1) for EMF can be written in the form

$$\Delta\psi_M = \frac{2RT}{F} \left[ \int_{CBL_l} t_+ d \ln(C_j) + \int_M \bar{t}_+ d \ln(C_j) + \int_{CBL_h} t_+ d \ln(C_j) \right] \quad (5)$$

The first and third components of equation (5) are connected with  $CBL_k$  ( $k=l, h$ ) the second with the membrane (M). The first and third components of equation (5) can be neglected during mechanical stirring, which ensure homogeneous solutions in chambers. If we assume the constant values of transport numbers in the membrane  $\bar{t}_+$  and in solution  $t_+$ , integration of equation (5) gives

$$\Delta\psi_M = \frac{2RT}{F} \left[ (\bar{t}_+ - t_+) \ln\left(\frac{C_i}{C_e}\right) + t_+ \ln\left(\frac{C_i^*}{C_e^*}\right) \right] \quad (6)$$

where  $t_+$  is the transport number of  $K^+$  ions in the solute,  $C_i$  and  $C_e$  are concentrations of solutes near membrane surfaces,  $C_i^*$  and  $C_e^*$  are concentrations of solutes near electrodes and fulfill condition  $C_h > C_i^* > C_i > C_e > C_e^* > C_l$ . Equation (6) connects EMF with quotient of concentrations at the surface of the membrane. The transport number of



ions  $K^+$  for the membrane ( $\bar{t}_+$ ) as a function of quotient of concentrations near membrane can be calculated from equation (2).

In order to calculate the quotient of concentrations  $C_i/C_e$  and  $C_i^*/C_e^*$ , the following considerations will be taken into account. Transport of solutes through the membrane and diffusion of solute near membrane causes appearance of gradient of solute concentration near membrane (CBL). Stirring homogenizes solutions in the chambers and thickness of CBL is small during stirring. Turning off stirring of solutions causes that the thickness of CBLs increase in time. Thickness of CBL ( $\delta_i$ ) depends on transport processes of ions in membrane and near membrane. It can be assumed that after turning off mechanical stirring of solutions the thickness of CBL increases in time in agreement with formula [11]

$$\delta_i = A_i \times t^{0.5} + \delta_{io} \quad (7)$$

where  $t$  is time after turning off mechanical stirring of solutions,  $A_i = (\pi D)^{0.5}$  is the parameter determining the rate of CBL thickness increase, subscript  $i = h$  or  $l$ . We assume that during stirring the CBLs thickness  $\delta_{io} \neq 0$ . Besides, the parameter  $A_i$  in reality can be different from  $(\pi D)^{0.5}$  [3].

In the case of high resistance of electrometer we can assume that electrical current through the membrane equals zero. Assuming also that for low concentration differences between external phases and no applied pressure difference, the volume flux across the membrane can be neglected. Therefore diffusion fluxes through the CBL over the membrane, through the membrane M and through CBL under the membrane are suitably denoted as  $J_{sl}(t)$ ,  $J_{sm}(t)$ ,  $J_{sh}(t)$ . Taking into consideration condition  $J_{sl}(t) = J_{sm}(t) = J_{sh}(t)$  fulfilled in a steady-state, and second Kedem-Katchalsky equation we can write [14]

$$\frac{D_l}{\delta_l}(C_e - C_l) = RT\omega(C_i - C_e) = \frac{D_h}{\delta_h}(C_h - C_i) \quad (8)$$

where  $\omega$  – solute permeability coefficient of the membrane,  $D_l$ ,  $D_h$  – diffusion coefficients in CBLs. Assuming that  $D_h = D_l = D$  and taking into consideration Eq. (8) we get conditions on concentrations near membrane surfaces

$$C_i = [RT\omega(\delta_l C_h + \delta_h C_l) + DC_h][D + (\delta_l + \delta_h)RT\omega]^{-1} \quad (9a)$$

$$C_e = \frac{\delta_l}{\delta_h}C_h + C_l - \frac{\delta_l}{\delta_h}C_i \quad (9b)$$

Equations (9a) and (9b) allow to count time changes of quotient of solute concentrations near membrane  $C_i C_e^{-1}$  and can be used for calculation of EMF by means of equation (6) in the case when the electrodes are far away from the membrane ( $C_i^* = C_h$  and  $C_e^* = C_l$ ). When the electrodes are near membrane, in the area of CBLs, the concentrations  $C_i^*$  and  $C_e^*$  in equation (4) also depend on time. Let us assume that solute concentrations near electrodes  $C_i^*$  and  $C_e^*$  are changing in time similarly to concentrations  $C_e$  and  $C_i$  and fulfill these same equations. This can be done because the points at membrane surface and suitable electrode are in these same CBLs. The modification for concentrations  $C_i^*$  and  $C_e^*$  can be done by parameter connected with thickness of CBL. There has to be taken into consideration the fact that the initial moment of change of concentrations  $C_i^*$  and  $C_e^*$  is not at the moment of turning off mechanical stirring but is shifted in time by  $t_o$ , which is schematically shown in Figure 1. Time after turning off mechanical stirring for graph 1 is lower than for graph 2, so it causes that thickness of CBL after time  $t_l$  ( $\delta_l(t_l)$ ) is lower than thickness of CBL after

time  $t_2$  ( $\delta_i(t_2)$ ). If  $t_1 < t_o < t_2$  then  $\delta_i(t_1) < d < \delta_i(t_2)$ , where  $d$  is the distance of the electrode ( $E_i$ ) from the surface of the membrane. The proposed modification has the form: if  $t < t_o$  then  $C_i^* = C_h$  and  $C_e^* = C_l$  and for  $t > t_o$   $C_i^*$  and  $C_e^*$  fulfill equations (9a) and (9b) with modified parameter connected with thickness of CBL

$$\delta_i^{el} = A_i^{el} \cdot (t - t_o)^k \quad \text{if } t \geq t_o$$

(10)

where  $A_i^{el}$  and  $k$  are the parameters determining the rate of change of concentrations near electrodes,  $i = h$  or  $l$ ,  $t_o$  is the time after turning off mechanical stirring, when the concentrations near electrodes begin to change – the CBL reaches the area near electrode.

## EXPERIMENTAL SYSTEM

Studies of the EMF in single-membrane electrochemical cell were carried out by means of an experimental setup presented in Figure 2. Experiments were performed with a flat-sheet neutral cellulose membrane, which thickness was 800 $\mu$ m and hydraulic membrane permeability  $L_p = 0.85 \times 10^{-12} \text{ m}^3(\text{N}\cdot\text{s})^{-1}$  [8]. The membrane was housed between two Plexiglas vessels ( $l$  and  $h$ ), each a volume 200 ml, with  $7.1 \pm 0.2 \text{ cm}^2$  of available membrane area. Vessel  $l$  of the membrane system in all experiments contained aqueous KCl solution with fixed concentration  $C_l = 10^{-5} \text{ mol}\cdot\text{l}^{-1}$ . Vessel  $h$  contained aqueous KCl solutions at various concentrations ( $C_h$ ) in the range from  $2.5 \times 10^{-5}$  to  $10^{-1} \text{ mol}\cdot\text{l}^{-1}$ . The cell was thermostated and enclosed in a Faraday cage to minimize electrical interference.

In order to measure the EMF, electrodes Ag|AgCl were used. Electrodes  $E_l$  and  $E_h$  were placed on both sides of the membrane, 2 mm from the membrane surface. The electrodes were selected so that membrane voltage for those same concentrations in the chambers was lower than 5 mV. The difference of potentials between electrodes was measured by means of electrometer connected with a computer. The accuracy of electrometer was  $\pm 0.1$  mV. The temperature of solutions was  $295 \pm 0.1$  K. At the beginning of each experiment the chambers of the membrane system were filled with solutions with given concentrations of solutes. Solutions were stirred by magnetic stirrers in order to lower the thickness of CBLs near membrane. Stirring of solutions lasted as long as the EMF was settled – no longer than 3÷4 minutes. The rate of solution stirring was 500 rpm. After turning off stirring of solutions the EMF was measured every 4 seconds during six hours after turning off mechanical stirring and next was monitoring through 24 hours.

## RESULTS AND DISCUSSION

The EMF was measured in the membrane system with horizontally oriented membrane and with solutions of KCl with greater concentration (and greater density) under the membrane. The highest EMF in the membrane system were observed during stirring of solutions, while turning off mechanical stirring caused decrease of EMF, connected with arising of CBLs near membrane. The concentration characteristic of EMF determined during stirring of solutions is presented in Figure 3. As results from Figure 3 the increase of concentration up to concentration  $(2.5 \div 5) \times 10^{-3} \text{ mol} \cdot \text{l}^{-1}$  in the chamber under the membrane causes increase of  $\Delta \psi_M^o$  to maximal value of about 175 mV and next decrease of EMF with increase of solute concentration. Using data presented in

Figure 3 and equation (2) the transport number  $t_+$  in the membrane was calculated. The transport number for  $K^+$  ions as a function of  $C_h / C_l$  is presented in Figure 4. As results from Figure 4 increase of KCl concentration in the chamber under the membrane up to  $7.5 \times 10^{-4} \text{ mol} \cdot \text{l}^{-1}$  causes that the transport number of  $K^+$  ions increases and reaches maximal value 0.7. Further increase of concentration in the upper chamber causes that transport number for  $K^+$  ions decreases. The transport number in the membrane as a function of quotient of concentrations on the membrane ( $C_i C_e^{-1}$ ), calculated from experimental data can be written as

$$\begin{aligned} \bar{t}_+ = & 0.00064 [\ln (C_i C_e^{-1})]^4 - 0.010394 [\ln (C_i C_e^{-1})]^3 + 0.02712 [\ln (C_i C_e^{-1})]^2 \\ & + 0.138403 \ln (C_i C_e^{-1}) + 0.195383 \end{aligned}$$

(11)

The equation (11) allows taking into consideration dependence of transport number in the membrane on quotient of solute concentrations at the membrane surfaces in the model for calculation of dynamic changes of EMF after turning off mechanical stirring of solutions. Using data from the concentration characteristic  $\Delta\psi_M^o(C_h / C_l)$  presented in Figure 3. and equation (4) the diffusion membrane potential during mechanical stirring of solutions ( $\Delta\psi_D^o$ ) was calculated and presented as a function of  $C_h / C_l$  in Figure 5. As results from Figure 5, for concentration  $7.5 \times 10^{-5} \text{ mol} \cdot \text{l}^{-1} < C_h < 7.5 \times 10^{-3} \text{ mol} \cdot \text{l}^{-1}$  the membrane potential is negative because  $\bar{t}_+ > \bar{t}_-$ , while for concentration  $C_h < 7.5 \times 10^{-5} \text{ mol} \cdot \text{l}^{-1}$  and  $C_h > 7.5 \times 10^{-3} \text{ mol} \cdot \text{l}^{-1}$  is positive ( $\bar{t}_+ < \bar{t}_-$ ). Using equation (6), describing EMF and equations (9a) and (9b) describing solute concentrations near membrane, and near electrodes with modification determined by equation (10) and taking into consideration the dependence of transport number of  $K^+$  ions in membrane on quotient of concentrations near membrane determined by equation (11), changes in

time of  $\Delta\psi_M$  after turning off mechanical stirring can be counted. For calculations we assume that:  $\omega=2.54\times10^{-10}\text{ mol}\cdot(\text{Ns})^{-1}$  for cellulose membrane;  $D=2.01\times10^{-9}\text{ m}^2\text{s}^{-1}$  and  $t_+=0.49$  for KCl solutions;  $C_l=10^{-5}\text{ mol}\cdot\text{l}^{-1}$ ;  $R=8.31\text{ J}(\text{mol}\cdot\text{K})^{-1}$ ;  $T=295\text{ K}$  and  $F=96500\text{ C}\cdot\text{mol}^{-1}$ . In order to fit curves counted on the basis of the model consisted of equations (6), (7), (9a,b), (10) and (11) to experimental data, the parameters presented in table 1 were admitted.

The electromotive force of electrolytic cell as a function of time after switching off mechanical stirring for different  $C_h/C_l$ , measured by means of Ag|AgCl electrodes, placed in CBLs (points) and counted from the model (solid lines) are presented in Figure 6. From this figure results that changes of  $\Delta\psi_M$  can be divided into two classes. For concentrations lower than  $2.5\times10^{-4}\text{ mol}\cdot\text{l}^{-1}$ , in the first few minutes after turning off mechanical stirring considerable decrease of  $\Delta\psi_M$  can be connected with concentration changes at membrane surfaces. Next there was stabilization of  $\Delta\psi_M$  during time greater than 200 minutes. After that time the  $\Delta\psi_M$  gradually decreased in time. Increase of KCl concentration in the chamber under the membrane resulted in decrease of  $\Delta\psi_M$  in the first few minutes after turning off mechanical stirring being greater. For low KCl concentration in the chamber under the membrane, changes of KCl concentrations near electrodes did not influence the EMF for a long time after turning off mechanical stirring. This was probably caused by small changes of concentrations near electrodes. For small concentrations of solutions under the membrane (lower than  $2.5\times10^{-3}\text{ mol}\cdot\text{l}^{-1}$ ) those changes were neglected in the model. For concentrations of solutions under the membrane greater than  $2.5\times10^{-3}\text{ mol}\cdot\text{l}^{-1}$  ( $C_h/C_l>250$ ) changes of concentration near electrodes cause that after great decrease of  $\Delta\psi_M$  in the first few

minutes, connected mainly with changes of concentrations near membrane surfaces, the  $\Delta\psi_M$  gradually and slowly decreases during time greater than 100 minutes. This is probably caused by the small distance of electrodes from the membrane surface and changes of KCl concentrations near electrodes proceeded with short time delay. Changes of concentrations near electrodes are lower in comparison with changes of concentrations near membrane surfaces, which was taken into consideration in the model.

The decrease of  $\Delta\psi_M$  after turning off mechanical stirring is connected with CBLs reconstruction during a long lasting experiment. The main processes influencing time changes of  $\Delta\psi_M$  after turning off mechanical stirring are: ions and water transport through the membrane and ions diffusion in the area of CBL. These processes are mutually connected and the shares of each are depended on concentrations of solute in the chambers of the membrane system. The ions and water transport through the membrane depends on concentrations of solute near membrane surfaces, while diffusion of solute in the CBL depends on the gradient of solute concentration in CBL. Both processes lead to diminishing of concentration differences on the membrane and in effect decrease of  $\Delta\psi_M$ , measured by means of electrodes Ag|AgCl placed near membrane.

When the gradient of density is parallel and in direction with vector of gravity field (solution with lower density is over the membrane), the gravitational instability does not appear. It causes reconstruction of stable CBLs after turning off mechanical stirring near membrane and increase of CBL thickness in time. Stable CBLs cause diminishing of membrane transport, differences of solution concentration on both sides of the membrane and influence on the  $\Delta\psi_M$ . The EMF as a function of quotient of solute concentrations on the membrane for steady-state ( $\Delta\psi_M^s$ ) is presented in Figure 7. As

results from Figure 7 the  $\Delta\psi_M^S$  as a function of quotient of solute concentration has maximum for concentration  $C_h=5\times10^{-4} \text{ mol}\cdot\text{l}^{-1}$  and amounts to about 60 mV. Increase of solute concentration  $C_h$  over  $10^{-3} \text{ mol}\cdot\text{l}^{-1}$  causes steep decrease of  $\Delta\psi_M^S$  to 20 mV at solute concentration  $C_h=2.5\times10^{-3} \text{ mol}\cdot\text{l}^{-1}$ . For solute concentration  $C_h$  greater than  $5\times10^{-3} \text{ mol}\cdot\text{l}^{-1}$   $\Delta\psi_M^S$  is the same. Let us define the relaxation time ( $\tau$ ) for the membrane system as a time from turning off mechanical stirring to the moment when  $\Delta\psi_M$  reaches the value determined by equation

$$\Delta\psi_M^r = \frac{\Delta\psi_M^o - \Delta\psi_M^S}{e} + \Delta\psi_M^S \quad (12)$$

where:  $\Delta\psi_M^o$  is the EMF during mechanical stirring in chambers,  $\Delta\psi_M^S$  is the EMF for the steady-state,  $e = 2.71$  is the base of natural logarithms. Short relaxation time indicate that the main changes of concentration proceed at the beginning after turning off mechanical stirring, while longer relaxation time indicate, that changes of concentrations in chambers, connected with transport properties of membrane and unstirred layers, are evenly distributed in time. The relaxation time as a function of quotient of solute concentrations is presented in Fig. 8. As results from Figure 8, for small solute concentration under the membrane relaxation time was great and amounts to about 400 minutes. Increase of solute concentration caused decrease of relaxation time. For solute concentrations under the membrane greater than  $5\times10^{-3} \text{ mol}\cdot\text{l}^{-1}$  the relaxation time was lower than 30 minutes. Only for concentration  $10^{-1} \text{ mol}\cdot\text{l}^{-1}$  relaxation time exceeded 50 minutes. For membrane system with smaller concentration under the membrane the main process proceeded in the membrane system is the CBLs creation by diffusion [11], so long relaxation time for lower concentrations indicates that CBLs arise slowly, while for higher concentrations relaxation time is short, which indicates that arising of CBLs proceeds quickly.



## CONCLUSIONS

Based on the investigations conducted above we can infer that:

1. The EMF in electrochemical cell during mechanical stirring depends on solute concentrations in chambers. The maximal value of EMF during mechanical stirring is for concentration  $4 \times 10^{-3} \text{ mol} \cdot \text{l}^{-1}$  and amounts to  $\Delta\psi_M^o = 175 \text{ mV}$ .
2. The transport number for  $\text{K}^+$  ions for neutral cellulose membrane also depends on solute concentration and has maximal value for concentration  $7,5 \times 10^{-3} \text{ mol} \cdot \text{l}^{-1}$  in the chamber under the membrane.
3. After turning off mechanical stirring, the EMF decreases in time, quickly at the initial moment; then for small concentrations in the chamber under the membrane do not change during time longer than 100 minutes and after that slowly decreases. For concentrations greater than  $2.5 \times 10^{-3} \text{ mol} \cdot \text{l}^{-1}$  the EMF evenly decreases with time longer than 100 min. This is probably caused by changes of solute concentrations near electrodes.
4. The relaxation time, which characterizes CBLs creation after turning off mechanical stirring, depends on concentrations in the chambers of the membrane system: increase of concentration causes decrease of relaxation time to minimal value for concentration  $5 \times 10^{-3} \text{ mol} \cdot \text{l}^{-1}$  and then a very small increase of relaxation time with increase of concentration.

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## Figures description

Fig. 1. The schematic representation of concentration distribution of solute near membrane areas. (CBL – concentration boundary layer area; M – membrane;  $C_h$ ,  $C_l$  – solutions concentrations in the bulk;  $C_b$ ,  $C_e$  – solution concentrations at the surface of the membrane,  $\delta_k$ ,  $\delta_h$  – thickness of CBLs;  $E_l$ ,  $E_h$  – electrodes Ag|AgCl). Graph 2 represents distribution of concentration of solute near membrane for longer time after turning off mechanical stirring than distribution of concentration presented by graph 1

Ryc. 1. Schematyczna ilustracja rozkładu stężenia roztworu w otoczeniu membrany. (CBL – obszar stężeniowych warstw granicznych; M – membrana;  $C_h$ ,  $C_l$  – stężenia roztworów w obszarze poza CBL;  $C_b$ ,  $C_e$  – stężenia roztworów na powierzchni membrany;  $\delta_k$ ,  $\delta_h$  – grubości CBL;  $E_l$ ,  $E_h$  – elektrody Ag|AgCl)

Fig. 2. The schematic representation of the membrane system:  $E_l$ ,  $E_h$  – Ag|AgCl electrodes; M – membrane; m – magnets; St – stirrers

Ryc. 2. Schematyczna ilustracja układu membranowego:  $E_l$ ,  $E_h$  – Ag|AgCl elektrody; M – membrana; m – magnesy; St – mieszadła

Fig. 3. The electromotive force during stirring of solutions ( $\Delta\psi_M^o$ ) as a function of  $C_h / C_l$ .

Ryc. 3. Siła elektromotoryczna podczas mieszania roztworów ( $\Delta\psi_M^o$ ) w funkcji  $C_h / C_l$

Fig. 4. The transport number of  $K^+$  ions ( $\bar{t}_+$ ) as a function of  $C_h / C_l$ . Solid line is for Eq. (11)

Ryc. 4. Liczba przenoszenia jonów  $K^+$  ( $\bar{t}_+$ ) w funkcji  $C_h / C_l$ . Linie ciągłe otrzymano dla równania (11)

Fig. 5. The diffusion membrane potential ( $\Delta\psi_D^o$ ) as a function of  $C_h / C_l$  during stirring of solutions

Ryc. 5. Dyfuzyjny potencjał membranowy ( $\Delta\psi_D^o$ ) w funkcji  $C_h / C_l$  podczas mieszania roztworów

Fig. 6. The electromotive force ( $\Delta\psi_M$ ) as a function of time ( $t$ ) after switching off mechanical stirring of solutions, for aqueous KCl solutions:  $C_h/C_l = 5$  (1),  $C_h/C_l = 10$  (2),  $C_h/C_l = 50$  (3),  $C_h/C_l = 250$  (4),  $C_h/C_l = 750$  (5). Solid lines were received from the mathematical model

Ryc. 6. Siła elektromotoryczna ( $\Delta\psi_M$ ) w funkcji czasu ( $t$ ) po wyłączeniu mieszania mechanicznego roztworów. Dla wodnych roztworów KCl:  $C_h/C_l = 5$  (1),  $C_h/C_l = 10$  (2),  $C_h/C_l = 50$  (3),  $C_h/C_l = 250$  (4),  $C_h/C_l = 750$  (5). Linie ciągłe otrzymano z modelu matematycznego

Fig. 7. The electromotive force for steady-state of membrane system ( $\Delta\psi_M^s$ ) as a function of  $C_h/C_l$

Ryc. 7. Siła elektromotoryczna dla stanu ustalonego układu membranowego ( $\Delta\psi_M^s$ ) w funkcji  $C_h/C_l$

Fig. 8. The relaxation time ( $\tau$ ) as a function of  $C_h/C_l$

Ryc. 8. Czas relaksacji ( $\tau$ ) w funkcji  $C_h/C_l$

Table. The values of parameters for the modeling curves in Figure 6

Tabela. Wartości parametrów dla modelowania krzywych na rycinie 6

$C_h/C_l$	$A_i \times 10^5 \text{ [m} \cdot \text{s}^{-1/2}]$	$\delta_o \text{ [}\mu\text{m]}$	$A_{el}$	s	$t_o \text{ [min]}$
5	0.29	5	0	-	-
10	0.85	5	0	-	-
50	1.7	10	0	-	-
250	5.7	60	$1,4 \times 10^{-12} \text{ m} \cdot \text{s}^{-2}$	2	8
750	5.7	80	$1,1 \times 10^{-7} \text{ m} \cdot \text{s}^{-1}$	1	3