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MATHEMATICAL MODEL OF TWO-CHAMBER ELECTROLYSER DYNAMICS FOR STUDYING PROPERTIES OF ION EXCHANGE MEMBRANES BASED ON PROTON IONIC LIQUIDS

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A mathematical model of mass transfer processes in the electrolysis of one-component solutions of 1,1 symmetric strong electrolytes NaOH and NaCl in a two-chamber electrochemical reactor with mesh electrodes based on platinum titanium is formulated. Experimental modeling of processes is performed was carried out under conditions of continuous precise monitoring of the system (NaOH concentration and volume of solution in the chambers).The electrolysis system was designed to balance the flow of components through the membrane to study its properties and to determine five unknown parameters of mathematical modeling of the process. The mathematical model is a system of equations, which includes the unknown transfer numbers of counterions through the membrane, the electrolyte diffusion coefficient, the electroosmotic flux constant, and the empirical parameters of the approximating expressions.

Keywords: electrolysis, mathematical model, ion exchange membrane, transfer number, electroosmosis, diffusion.

INTRODUCTION. Ionic liquids are organic substances, mainly salts, which exist in liquid-phase form over a wide range of temperatures. Their characteristic properties are ionic electrical conductivity and low melting point, which in most cases does not exceed 100°C. We studied some Proton Ionic Liquids (PIL) based on ammonium oligoesters - chemical compounds with organic cations and inorganic anions (residues of sulfuric, orthophosphate and acetic acids), which were synthesized by neutralization of organic acids and inorganic bases[1]. The high interest in ionic liquids for ion exchange is due to the fact, that they have a clear ability to serve as effective cation exchange membranes with high selectivity.Due to such properties, the aim of many experiments with water-soluble ionic liquids has always been to measure their individual physicochemical properties (specific conductivity (κ), concentration of protons (pH), and their dependence on concentration and temperature).Thus, using the known laws of physicochemical processes (theory of electrical conductivity and electrolytic dissociation) it is possible to establish the parameters of the charge transfer process and the role of individual ions in the mechanism of electrical conductivity. The analysis of the revealed regularities made it possible to reveal correlations between the possible structure of ionic liquids and the physicochemical properties of their aqueous solutions.

Another way to study ion-exchange properties of electrochemical systems with PIL membranes is mathematical modeling.In [1] the method of computerresistometry [2] was used. The probability of the existence of dynamic processes far from equilibrium was also experimentally assessed. On the basis of

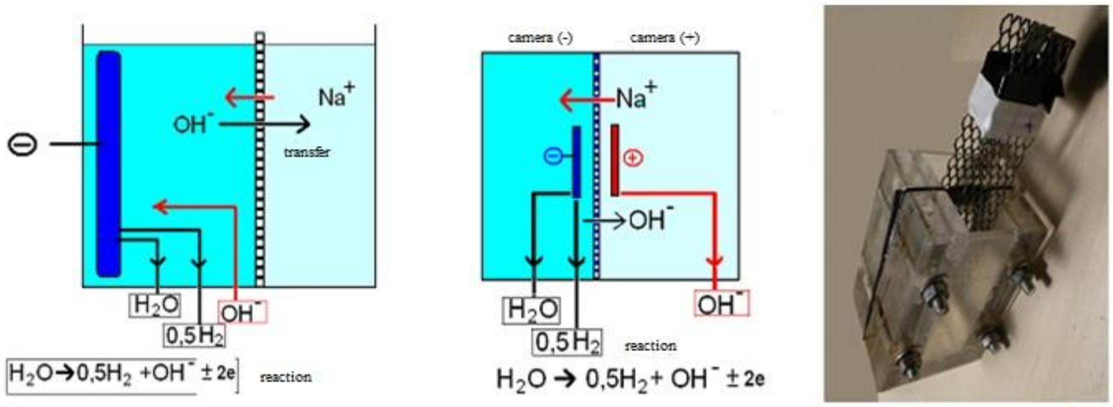

Fig.1. Principled scheme of the cathode chamber (a), two-chamberelectrolyzer-reactor (b) work, and a photo of there actor.

complex measurement results, correlations were established between the physicochemical properties of the studied aqueous-organic mixtures and the estimated possible parameters of the structure of organic components.

The aim of this study was to build a mathematical model of processes in a two-chamber reactor-electrolyzer using in experiments known types of industrial cation exchange (МФ-4СК, МА-40) membranes and anion exchange membrane MA-40.

EXPERIMENT AND DISCUSSION OF THE RESULTS. The experiment was performed in a two-chamber electrolyzer-reactor for electrolysis of theNaOH solutions with initial concentration of 0,004 mol/dm^3(fig. 1).Heterogeneous membranes of the MK and MA-40 series were used in the experiment.The calculations base on the following items.

The migratory flux of OH$^-$ions $g_{OH}{}^{M}$ and the molar flux of Na$^+$ ions equal to it are proportional to the charge flow $I\cdot\tau$ (A·min) and the number of n$^+$ cation transfers according to equation:

$$g_{OH}^{M} = I\cdot\tau\cdot\frac{1}{26,8}\cdot(n^{+}) \quad . \tag{1}$$

Diffusion flow is carried out through the membrane according:

$$g_{NaOH}^{D} = -D\cdot\frac{dC}{dx} \quad , \tag{2}$$

D –the effective diffusion coefficient of NaOH, δ– the membrane thickness, dC/dx = dC/δ – the gradient of NaOH concentration in the membrane. The concentration of C in (2) has a dimension of mol / cm^3.

The water is consumed in the electrochemical reaction at the cathode chamber (Fig. 1 a, b), and the speed of this process can be accurately calculated according to Faraday's law.

$$g_{H2O}^{R} = I\cdot\tau\cdot 0{,}891 \quad , \tag{3}$$

0,891 - water flow rate, g/minute (respectively 0,0495 mol/minute).

In parallel, a rather significant electroosmotic flow of water molecules (according to [3] to 5.1 molecules of water per mobile cation) is carried out through the membrane according to the equation:

$$g_{H2O}^{OSM} = \frac{\varepsilon\cdot\zeta}{4\pi\mu}\cdot\frac{dE}{dx} = \frac{81\cdot 8{,}12\cdot 10^{-12}\cdot\zeta}{4\cdot 3{,}14\cdot 8{,}9\cdot 10^{-4}}\cdot\left(\frac{I}{\kappa\cdot\delta}\right) \;. \tag{4}$$

$\varepsilon = 81 \cdot 8{,}12 \cdot 10^{-12}$ - dielectric constant of water; ζ– zeta-potential, B; μ – dynamic viscosity of the electrolyte, Pa·s; $dE/dx = (I/(\kappa \cdot \delta)$- potential gradient in the electrolyte, V/cm; I– current, Ahm;κ-specific electrical conductivity of the electrolyte, ʊ*cm; δ– membrane thickness, cm.

The equation (4) is inconvenient for use in a mathematical model because it contains an inaccurate value of the zeta potential (ζ). In addition, the value of δ in the denominator means that as the membrane thickness increases, the electroosmotic flux must decrease. In reality, the rate of electroosmotic flux is a constant value that is proportional to the current and does not depend on the thickness of the membrane. Therefore, the mathematical model uses a more reliable and simpler equation, which includes only one unknown parameter k^{OSM}current values (mol/(Ahm·min) - the flow of $g_{H2O}{}^{OSM}$ at a current value of 1 A):

$$g_{H2O}^{OSM} = k^{OSM} \cdot I \square \qquad (5)$$

The water plays a unique role in all physicochemical processes that take place in the environment and especially in the biosphere [4], so in this study, the features of its movement through membranes, especially electroosmosis, are decisive. Electroosmotic water flow is an individual sensitive characteristic of membranes used in various technologies: on composite membranes in the purification of glycerol [5], in the purification by a combination of electrodialysis and ion exchange of electroplates from nickel [6] and etc. It can be assumed that even without the action of an electric field in the filtration process, the effects of water transfer due to osmotic phenomena (on organo-inorganic membranes [7]) may occur.

The summary mass flow of ions (g_{SUM})across the membrane of all components depends on the electrolysis conditions, so it is an unknown parameter to be determined.

Thus, the mathematical model of the process of electrolysis of NaOH solution is a system of 5 equations with specified values of the mode parameters (current, initial NaOH concentration, membrane thickness, initial conductivity parameters) and five unknown parameters. The mathematical model uses equations that approximate the concentration dependences of the electrolyte in the region C>> 0.02 mol/dm^3 parabolas of the 2nd and 3rd degree. One exponential equation was used to approximate nonlinear concentration dependences of electrical conductivity $\kappa = f(C)$in the region up to 1mol/dm^3:

$$\kappa = \kappa_0 + (\kappa_{MAX} - \kappa_0) \times \left[1 - exp\left(-\frac{C}{F_E} \right) \right] \quad , \qquad (6)$$

F_E is the characteristic parameter of the function $\kappa = f(C)$ at the points with the initial and maximum values of the concentration in the interval of the experiment duration of 30 minutes.

Formally, the mathematical model can be visualized in matrix form [Z] = [X]×[Y]

$$\begin{bmatrix} g_{OH}^{M} \\ g_{NaOH}^{D} \\ g_{H2O}^{R} \\ g_{H2O}^{OSM} \\ \kappa_0 \\ \kappa_{MAX} \\ F_E \end{bmatrix} = \begin{bmatrix} I \cdot \tau \cdot n^{+} / 26{,}8 \\ -D \cdot dC / dx \\ I \cdot \tau \cdot 0{,}871 \\ k^{OSM} \cdot I \\ 1 \\ 1 \\ 1 \end{bmatrix} \times \begin{bmatrix} g_{NaOH}^{M} \\ g_{H2O}^{R} \\ g_{NaOH}^{DIF} \\ g_{H2O}^{OSM} \\ g_{SUM} \end{bmatrix}$$

However, the matrix form of the mathematical model is inconvenient for practical use, because the third column has a structure that the number of elements and their physical content does not agree with the first two columns. Therefore, the main results of data processing of the experiment (column 3) were recorded in the form of table 1.

Table 1

Calculated unknown parameters of the experiment performed on the example of the membrane MF-4SKin the electrolyte NaOH (mol/min)

g_{NaOH}^{M}	g_{H2O}^{R}	g_{NaOH}^{DIF}	g_{H2O}^{OSM}	g_{SUM}
0,000274	0,008259	$-2{,}58\cdot10^{-8}$	0,004230	0,012763

Other conditions for which the experiment was performed are listed below in tables 2 and 3.

Processing of experimental data (tables 2 and 3) on the mathematical model was carried out by numerical iterative method. The numerical values of the unknowns were successively changed (Table 1) and the accuracy of the result was controlled by the least squares algorithm at each step. The procedure was performed until the values of the randomly selected unknowns thus did not coincide with the specified accuracy with their values obtained in the experiment (table 1).

The graphs in Figures 2,3 - illustrate the dynamics of the time change of the electrolyte concentration with the initial value shown in table 2.

Table 2

Arbitrarily set process parameters in the cell at the beginning of the experiment. Membrane МФ-4СК, electrolyte –NaOH

I, Ahm	κ, ℧*cm	δ, *cm*	*C, mol/dm*^{3}
0,0091764	0,0017	0,02	0,0038

Table 3

Intermediate (calculated) process parameters in the electrolyzer

n+	F_E, *cm*	*W1*	*W2*
0,8	15	0,00002	125

***W1,W2 are parameters dimensionless for adjustment*

Visually, the degree of accuracy can be seen by reconciling the calculated (approximated) graphs with the experimental data in Figures 2 and 3.

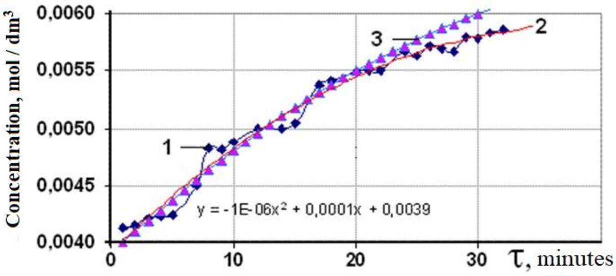

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Fig. 2. 1 –experiment, 2– approximation along the trend line (parabola of the 2nd order,), 3 – construction (according to the approximation formula) of the parabola at points with an interval of 1 minute

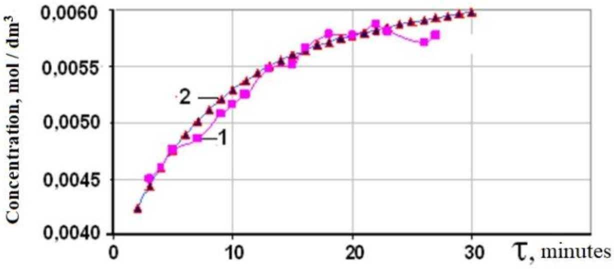

Fig. 3. 1- experimental data for the membrane MF-4SK in NaOH solution, 2 –approximation of the graph of the total mass flow of all components of g^{SUM} (equation 1÷ 5)

The common result of the experiment is the dependence $C=f(\tau)$ in the interval of 30 minutes. All other parameters (R, C_o…) are the primary intermediate data from which the final result is formed. In fig. 2 and 3 show the results of the experiment on the membrane МФ-4СКin NaOH solution with an initial concentration of 0,004 mol/dm^3.

Forms of graphs in Fig. 2 and 3 do not exactly coincide with each other, because only 5 unknown parameters are used in the calculations, shown in Table 1. If we introduce additional elements into the mathematical model, it would be possible to achieve greater consistency in the form of graphs. But this is not necessary, because for comparison only the qualitative similarity of the form of graphs in Figures 2 and 3, built on the same scale (here 0.006 mol / dm^3× 30 minutes) is important. This similarity is the basis for concluding that the values of the unknown parameters of the studied membrane (table 1) are determined correctly.

Modification of membranes in different ways [8] allows changing their individual properties in a wide range. This is the main purpose of the modification, and a mathematical model is only a convenient tool for identifying and analyzing these changes.

From table 1 you can see what role in the mass balance play for given conditions, the different mechanisms of transfer of components. In this case, the migratory and diffusion flows of NaOH have little effect on the total balance (0,000274 -2,58·10^{-8})/ 0,012763, which is about 2%. At the same time, the water flow rate in the reaction (0,008259) and the electroosmotic flux (0,004230) mol / minute are proportional to the total flow (0,012763) mol / minute.

Thus, choosing the desired conditions, the mathematical model shows the appropriate package of balance flows for comparative analysis.

Note that studies in NaCl solutions are possible only on membranes resistant to dissolved chlorine, even at low current densities. Heterogeneous membranes of the MK and MA-40 series satisfy this condition.

Also note that the function *C(τ)* represents the effect of changing the electrolyte concentration in the cathode chamber for a particular membrane (fig 4, eq.7).

$$n_2 = 1 - \frac{(C_\tau - C_0)}{C_\tau} \quad . \tag{7}$$

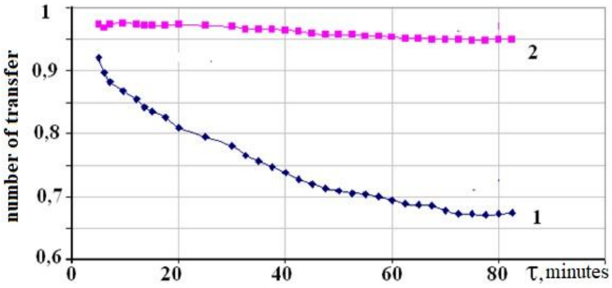

Fig.4. Time change of the anion transfer number calculated by equation 7. 1-primary experimental data, 2- calculation taking into account electroosmosis. NaCl electrolyte, MA-40 membrane.

During the experiment, all changes in the state of the system accumulate in the solution. Therefore, the numbers of transfer calculated by eq. (7), which gives the value of the resultas a constant, always decreases overtime (fig. 4, eq. 8).

$$n_1 = 1 - \frac{(C_0 - C_\tau)\cdot V_\tau}{((It)/26{,}8)} \quad ,$$

$$n_2 = 1 - \frac{(C_\tau - C_0)}{C_\tau} \quad . \tag{8}$$

The powerful factor is the electroosmosis of water from the chamber (-) to the chamber (+). The rate of electroosmotic water transfer was found on the MA-40 membrane by the value of the change in the volume V of the chambers (-) and (+).

In general, formula (7) does not take into account the volume of the chambers and is unsuitable for taking into account the transfer of water by electroosmosis. But due to the fact that the water transfer effect still exists (regardless of the formula), a formal approach was used to take it into account. According to the results of the experiment, 6 cm^3 were transferred in 90 minutes with a constant current drop from 18 to 3 mA, and the charge lasted only 0,012 Ahm· h. Hence the electroosmotic effect can be estimated as:

$$\vartheta=0{,}006\ \mathrm{dm}^3 / 0{,}012\ \mathrm{Ahm}\cdot \mathrm{h}= 0{,}5\ \text{дм}^3/ \mathrm{Ahm}\cdot \mathrm{h}.$$

It is clear that the obtained number ϑ is random, because in each measurement it strongly depends on the specific conditions of the experiment, such as the history of membrane swelling, as well as parameters that change continuously during the experiment (electrolyte concentration, current, instantaneous values of effective electrolyte diffusion coefficient, and etc.). Equation 9 was formed on the basis of the data of the exact experiment with the MA-40 membrane.

$$V= \quad Vo-\vartheta*(I\cdot\tau) \qquad (9)$$

This is generally a formal expression for the volume of the cathode chamber at some point in time τ, where $(I\cdot\tau)$ is a continuously increasing amount of missed charge.

Equation (9) was used to calculate the number of anion transfer across the MA-40 membrane (Fig. 4). From the result it can be seen that the consideration of electroosmosis gives a significant refinement of the calculation. The calculated average value of the number of chloride ion transfer increased from 0.76 to 0.96. But some slight slope (Figure 2) still exists. This means that in the process of electrolysis with the MA-40 membrane, the action of unknown factors not taken into account by the mathematical model is observed.

CONCLUSIONS. A mathematical model of processes in a two-chamber electrolyzer reactor for electrolysis of solutions of pure one-component electrolytes NaOH and NaCl has been created. The mathematical model contains a system of mass balance equations with five unknown parameters to be determined and reflect the dynamics of changes in instantaneous values of unknown mass flows of components.

Experimental studies of the transfer processes of system components (mass balance) in a two-chamber electrolyzer with platinum-plated titanium electrodes have illustrated the high accuracy and reproducibility of the results of measuring the transfer numbers in ion exchange membranes.

The complete correspondence between the experimental data and the result of their mathematical modeling is shown.

Data processing of a simple experiment in a two-chamber electrolyzer with the use of a mathematical model makes it possible to accurately determine the properties of membranes. It is a convenient tool for studying and comparing water-soluble ion exchangers in order to optimize their technologies.

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МАТЕМАТИЧНА МОДЕЛЬ ДИНАМІКИ ДВОКАМЕРНОГО ЕЛЕКТРОЛІЗЕРА ДЛЯ ВИВЧЕННЯ ВЛАСТИВОСТЕЙ ІОНООБМІННИХ МЕМБРАН НА ОСНОВІ ПРОТОННИХ ІОННИХ РІДИН

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Сформульовано математичну модель процесів масообміну в процесі електролізу однокомпонентних розчинів простих сильних електролітів NaOH та NaCl у двокамерному електрохімічному реакторі з сітчастими електродами на основі платинованого титану. Виконано експериментальне моделювання процесів. Електроліз здійснюється за умов безперервного точного контролю стану системи (концентрації NaOH та об′єму розчину в камерах). Систему електролізу призначено для встановлення балансу потоків перенесення компонентів через мембрану, властивості якої вивчають, і визначенням 5 невідомих параметрів математичного моделювання процесу. Математична модель є системою рівнянь, до якої входять невідоме число перенесення протиіону у мембрані, коефіцієнт дифузії електроліту, константа електроосмотичного потоку та емпіричні параметри апроксимуючих виразів.

Ключові слова: електроліз, математична модель, іонообмінна мембрана, число перенесення, електроосмос, дифузія.

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