

Theoretical and Experimental Investigation of Limiting Diffusion Current in the Systems with Modified Perfluorinated Membranes Containing Sulfonic Acid Groups

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Abstract—The limiting diffusion current density in electromembrane systems is theoretically estimated by using refined Pears equation and different model approaches for the calculating of the counter-ion transport number in the membrane and its diffusion permeability differential coefficient. To this purpose, experimental data on specific conductivity, diffusion and electroosmotic permeability, as well as the apparent transport numbers of counter-ions in perfluorinated sulfocationite MF-4SK membranes with different specific water content over wide range of sodium chloride solution concentrations are used. Special features of different approaches and models used in the evaluating of the membrane parameters necessary for calculating the electrodiffusion characteristics and the limiting diffusion current are analyzed. The possibility of adequate theoretical estimation of the limiting diffusion current for ion-exchange membranes modified by organic and inorganic dopants is shown. This allows predicting the effectiveness of membranes in electromembrane processes basing on relatively simple measurements of the transport characteristics of the modified ion-exchange membranes.

Keywords: perfluorinated sulfocationite membrane, limiting diffusion current density, conductivity, diffusion permeability, ion transport number, modification, modeling

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INTRODUCTION

Electromembrane technologies of the producing, isolating and concentrating of valuable components from solutions, natural waters, waste waters, and process waters of different purpose allow solving such problems as recovery of valuable substances and development of closed technology cycles. The limiting diffusion current in electromembrane systems is a key characteristic determining effectiveness of membrane application in electrodialysis because it allows determining optimal conditions for the process running with maximal effectiveness and minimal energy consumption. The using of ion-exchange membranes not only for desalinization but also for electrolyte solution concentration, as well as in chlorine–hydroxide electrolysis, requires estimating of the limiting diffusion current over wide range of the electrolyte solution concentrations [1–5]. Some information on this parameter can be obtained from polarization curves measured by the membrane voltammetry method [6–8]. However, it does not always happen that the

limiting diffusion current can be determined experimentally, the more so, over wide range of the electrolyte solution concentrations. By analyzing literature, we showed the concentration range in which current–voltage curves have been measured to be from 5×10^{-4} to 5×10^{-1} M; at that, concentrations from 2×10^{-2} to 1×10^{-1} M are most often used [9–19]. Therefore, there must be a way to give adequate theoretical estimate of this quantity in electromembrane system. This is the more important in the case of modified ion-exchange membranes because it allows predicting the degree of modifiers' effect on the effectiveness of the samples' usage in electromembrane processes.

Despite great interest to the studies of the ion-exchange membrane polarization behavior [20–23], including those modified with organic and inorganic components, the possibility of theoretical estimation of the current–voltage curve parameters with the taking into consideration of not only outer but also inner factors remains being not yet investigated in detail. The majority of papers are devoted to the studying of

phenomena occurring in overlimiting current regimes; at that, the effect of the membrane surface state on the concentration polarization conjugated effects and diffusion layer thickness is studied most thoroughly [24–30]. At the same time, the role of the membrane electrotransport characteristics and structural features is not yet elucidated. According to the Pierce formula, in the limiting current calculating from inner factors only the counter-ion transport number which characterizes the membrane selectivity is to be taken into consideration. Gnusin et al. [31] brought out clearly that the diffusion permeability of structure-nonuniform membranes affects the diffusion current as well.

In this work, we aimed at the studying of the possibility of the using of different model approaches for the calculating of the ion-exchange membrane electrodiffusion characteristics and adequate theoretical estimating of the limiting diffusion current.

THEORETICAL

To calculate the diffusion current density (i_{lim}), one can use the refined Pierce formula [31], which takes into consideration not only the solution concentration (C), the electrolyte diffusion coefficient (D), the diffusion layer thickness (δ), and the counter-ion transport number in membrane (t_i^*) and in the solution (t_i), but also the membrane permeability (P^*) and thickness (l):

$$i_{\text{lim}} = \frac{DCF}{(t_i^* - t_i)\delta} + \frac{P^*FC}{(t_i^* - t_i)l}. \quad (1)$$

Values of t_i and D required for the calculating of i_{lim} can be found in handbooks. Values of the counter-ion electromigration, or true, transport number t_i^* in membrane and the diffusion permeability differential coefficient P^* , which are immeasurable experimentally, can be calculated by different methods.

The counter-ion true transport number t_+^* in cation-exchange membrane can be calculated by three methods: by the Scachard equation, by using parameters of the extended three-wire model, and from the co- and counter-ion electrodiffusion coefficients. In the calculations by the Scachard equation [32]

$$t_+^* = t_{+\text{app}} + m_{\pm} M_w t_w, \quad (2)$$

one requires knowing experimental concentration dependences of the counter-ion apparent transport numbers ($t_{+\text{app}}$) and water transport numbers (t_w). In equation (2), M_w is the water molar mass, 18 g/mol; m_{\pm} is the solution average molality.

Another possibility of the membrane selectivity evaluation is the using of the extended three-wire model of the ion-exchange material conductivity. In terms of the model, it is possible to calculate fractions

of the current passing through different structural fragments of swollen membranes: successively through gel and solution, through gel alone, and through solution alone (the parameters a , b , and c , respectively) [33, 34]. Because the co-ion transfer which lowers the membrane selectivity can occur exclusively via the channel filled with equilibrium solution (the model parameter c), the counter-ion electromigration transport number can be calculated by the following equation [35]:

$$t_+^* = 1 - \frac{t_- c}{K_m}, \quad (3)$$

where $K_m = \frac{\kappa_m}{\kappa}$ is the membrane conductivity measured under alternating current (κ_m) and normalized to the conductivity (κ) of the solution of given concentration; t_- is the co-ion transport number in the solution. To calculate the true transport number with this method, one needs obtaining but the dependence of κ_m on the equilibrium solution concentration (C).

The third method of the counter-ion transport number calculations in the cation-exchange membranes involves the using of electrodiffusion coefficients for the counter- $L_+^*(C)$ and co-ions $L_-^*(C)$, which depend on the solution concentration:

$$t_+^*(C) = \frac{L_+^*(C)}{L_+^*(C) + L_-^*(C)}. \quad (4)$$

The electrodiffusion coefficients can be calculated by the following formulae [36]:

$$L_+^*(C) = \frac{\kappa_m^d(C)}{2F^2} \left[1 + \sqrt{1 - \frac{2P^*(C)CF^2}{RT\kappa_m^d(C)\pi_{\pm}}} \right], \quad (5)$$

$$L_-^*(C) = \frac{\kappa_m^d(C)}{2F^2} \left[1 - \sqrt{1 - \frac{2P^*(C)CF^2}{RT\kappa_m^d(C)\pi_{\pm}}} \right], \quad (6)$$

where κ_m^d is the membrane conductivity measured in direct current; F is the Faraday number; R is the universal gas constant; T is the temperature; π_{\pm} is the correction factor taking into consideration the solution nonideality:

$$\pi_{\pm} = 1 + \frac{d \ln \gamma_{\pm}}{d \ln C}. \quad (7)$$

The γ_{\pm} is the average coefficient of electrolyte activity in equation (7). To calculate the true transport number by this method, one requires the knowing of concentration dependences of the conductivity measured experimentally under alternating current and the integral coefficient of the membrane diffusion permeability.

The membrane conductivity under direct current κ_m^d can be calculated by the formula [37]:

$$\kappa_m^d = \kappa_m t_+^f, \quad (8)$$

where f_2 is the solution volume fraction in swollen membrane; t_+ is the counter-ion transport number in the solution.

The membrane diffusion permeability differential coefficient can be calculated by two methods [38]. The first one is based on the using of the equation of constraints between the integral (P_m) and the differential (P^*) coefficients of the membrane diffusion permeability:

$$P^* = P_m \beta, \quad (9)$$

where $\beta = \frac{\log j}{\log C}$ is the slope of the bilogarithmic plot of the diffusion flux (j) vs. the concentration of the solution diffusing into water. In this case, it is necessary to have the experimentally measured concentration dependence of the diffusion flux, from which the parameter β can be found and the integral coefficient of the diffusion permeability calculated by the following formula:

$$P_m = \frac{j l}{C}, \quad (10)$$

where l is the membrane thickness; C is the concentration of the electrolyte solution diffusing into water.

Another method involves the calculating of P^* in terms of a two-phase microheterogeneous model of the membrane conductivity by the following equation [39]:

$$P^* = \left[f_1 (GC)^\alpha + f_2 D^\alpha \right]^{1/\alpha}, \quad (11)$$

where f_1 and f_2 is the volume fractions of the gel phase and intergel solution, respectively ($f_1 + f_2 = 1$); α is the parameter representing a character of the phases' relative arrangement, which varies from +1 to -1 for the parallel and series connection of the conducting phases, respectively; C is the equilibrium solution concentration; G is the complex parameter characterizing the gel phase diffusion properties: $G = k_D \bar{D}_- / \bar{Q}$, $\bar{Q} = Q / f_1$, Q , and \bar{Q} is the exchange capacity of the membrane and gel phase, respectively; k_D is the Donnan non-exchangeable sorption constant; \bar{D}_- , D is the diffusion coefficients of co-ion in the gel phase and of salt in the solution.

The making use of the equation requires the knowing of a set of the membrane's transport-structure parameters: f_1 (or f_2), α , and G , -which are at hand in literature for a number of the ion-exchange membranes [40-42]. The set of the membrane's transport-structure parameters also includes the membrane gel phase conductivity κ_{iso} , which opens way to the calculating of the concentration dependence of the membrane conductivity by the equation:

$$\kappa_m = \left[f_1 \kappa_{iso}^\alpha + f_2 \kappa^\alpha \right]^{1/\alpha}, \quad (12)$$

or:

$$\kappa_m = \kappa_{iso}^{f_1} \kappa^{f_2}. \quad (13)$$

Equation (13) is immediate from equation (12) when $\alpha \rightarrow 0$ [7, 43]. The obtained values of κ_m can be further processed in terms of the extended three-wire model and the membrane selectivity by the formula (3).

From the knowing of the set of the membrane's transport-structure parameters the membrane selectivity can be evaluated also by the formula (4), upon the calculating of electrodiffusion coefficients for the counter- $L_+^*(C)$ and co-ions $L_-(C)$ by equations (5) and (6), with the using of equations (11), (12), and (8) for the calculating of the P^* and κ_m^d .

In Fig. 1 we present the combination of different approaches to the calculating of the quantities t_+^* and P^* .

In the variant 1, both P^* and t_+^* are calculated in terms of the two-phase microheterogeneous model of the membrane conductivity, with the using of the membrane's transport-structure parameters. By contrast,

in the variant 2 the values of t_+^* are calculated with the using of the electrodiffusion coefficients found from the experimentally measured conductivity values. In the variant 3, both quantities P^* and t_+^* were calculated from experimental data on the concentration dependences of the conductivity and diffusion permeability. Variant 4 allows calculating the limiting current with the using of the P^* and κ_m , values found in terms of the two-phase microheterogeneous model of the mem-

brane conductivity; t_+^* , of the three-wire model. Variant 5 differs from the preceding one in the fact that the limiting current is calculated from the P^* value found from experimental data. By contrast, in variant 6 the P^* values are calculated in terms of the two-phase microheterogeneous model of the membrane conductivity, whereas the calculating of t_+^* in terms of the three-wire model makes use of the experimentally determined κ_m . Variant 7 allows calculating the limiting current by using values of P^* and κ_m , found from experimental data; t_+^* , in terms of the three-wire model. In variants 8 and 9, the quantity t_+^* is calculated by the Scachard equation, with the using of the experimentally obtained concentration dependences of the membrane's electroosmotic permeability and its potentiometric transport numbers, while the quantity P^* is calculated in terms of the two-phase microheterogeneous model of the membrane conductivity (variant 8) or from experimental data (variant 9). In this work, we used all above-described methods of theoretical evaluation of the quantities t_+^* and P^* required for the calculating of the limiting current by equation (1).

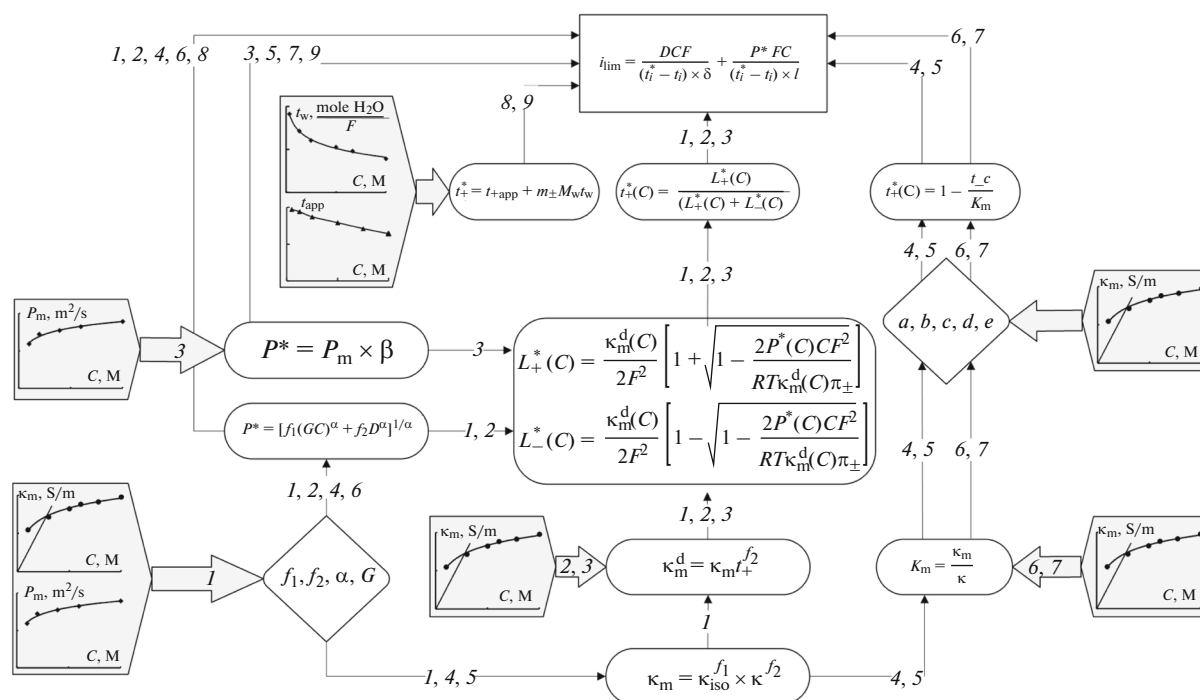


Fig. 1. Scheme of the limiting current density calculations with the using of different model approaches to the estimating of the counter-ion true transport number in membranes and its diffusion permeability differential coefficient (the numbers in the figure correspond to the calculation variants described in text).

EXPERIMENTAL

The objects of our study were perfluorinated sulfonation membranes MF-4SK with neighbor values of the dry-basis ion-exchange capacity (Q), yet, different water content (W , $\text{g}_{\text{H}_2\text{O}}/\text{g}_{\text{dry}}$) and, as a consequence, different specific water content; the latter is the averaged number of water moles per 1 mole of ionogenic groups (n , $\text{mol H}_2\text{O}/\text{mol}$). The choice of the samples is conditioned by the fact that the membrane's water content affects significantly its electrotransport characteristics. Membranes with different water content were obtained by the treating of a MF-4SK-1 initial sample with organic solvent that is miscible with water at temperatures exceeding the ionomer glass-transition temperature. For the given sample, the glass-transition temperature was 110°C . Ethylene glycol was the right solvent. The membrane's water content was controlled by the membrane treatment time: from 10 s to 3 min. The solvent was

removed by the membrane heating in deionized water at 100°C ; in so doing, we renewed the water three times. In Table 1 we give physico-chemical characteristics of the studied membranes, as well as characteristics of the MF-4SK-4 sample used in the experimental verifying of the theoretical calculations of i_{lim} .

The possibility of theoretical estimating of the limiting current was also verified for MF-4SK samples modified with organic and inorganic dopants (Table 2). An organic dopants were polyvinylbutyral (a hydrogel, that is able retaining water in the membrane structure) and sulfonated polysulphon, an ion-exchange resin ($Q = 2.00 \text{ mmol}/\text{g}_{\text{dry}}$). The membranes were manufactured by the cast coating, with the using of 10% (w/w) solution of the F-4SK co-polymer in dimethylformamide and 5% (w/w) sulfonated polysulphon and polyvinylbutyral aqueous solutions [44]. The polymers were combined by agitation of the corresponding solutions at the room temperature for 30 min. Then,

Table 1. Physico-chemical characteristics of the MF-4SK membranes in 0.1 M NaCl solution

Sample	l , μm	Q , $\text{mmol}/\text{g}_{\text{dry}}$	W , $\text{g}_{\text{H}_2\text{O}}/\text{g}_{\text{dry}}$	n , $\text{mol H}_2\text{O}/\text{mol}$
MF-4SK-1	210 ± 5	0.78	0.159	11.3
MF-4SK-2	230 ± 3	0.78	0.284	20.2
MF-4SK-3	270 ± 8	0.78	0.512	36.5
MF-4SK-4	310 ± 4	0.71	0.254	19.9

Table 2. Objects of the study

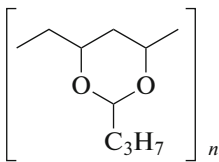
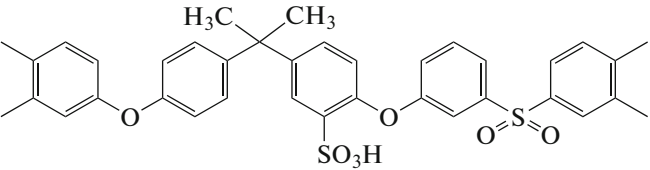
The MF-4SK perfluorinated membrane	$\left(\text{CF}_2-\text{CF}_2 \right)_n \text{CF}-\text{CF}_2-$ $\text{O} \left(\text{CF}_2-\underset{\text{CF}_3}{\text{CF}}-\text{O} \right)_m \text{CF}_2-\text{CF}_2-\text{SO}_3^-\text{H}^+$
Modifying additives	
Polyvinylbutyral	
Sulfonated polysulphon	
Zirconium hydrophosphate	$\text{Zr}(\text{HPO}_4)_2$

Table 3. Physico-chemical characteristics of initial and modified perfluorinated membranes

No.	Membrane	l , μm	Q , $\text{mmol}/\text{g}_{\text{dry}}$	W , $\text{g}_{\text{H}_2\text{O}}/\text{g}_{\text{dry}}$	n , $\text{mol H}_2\text{O}/\text{mol}$
Cast membranes					
1	MF-4SK	62 ± 3	0.98	0.311	17.6
2	MF-4SK/polyvinylbutyral	55 ± 3	0.93	0.360	21.5
3	MF-4SK/sulfonated polysulphon	65 ± 5	1.03	0.330	17.8
4	MF-4SK/zirconium hydrophosphate	61 ± 2	2.84	0.348	6.8
Extrusion membranes					
5	MF-4SK	85 ± 5	0.93	0.260	15.5
6	MF-4SK/zirconium hydrophosphate	105 ± 5	1.20	0.314	9.0

the obtained solution was filtered in vacuum through Capron filter, poured onto glass with a containment frame, and placed into thermostat for the solvent removal. The modifying additives amounted to 5% (w/w) in the membrane polymer.

The inorganic dopant was zirconium hydrophosphate, a mineral ion-exchanger. The zirconium-hydrophosphate-modified hybrid membranes were manufactured in the same way. In the first stage, an aqueous solution of zirconium oxychloride $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ was combined with a perfluorosulfonic acid F-4SK solution. Upon film formation, it was placed to phosphoric acid solution, to precipitate zirconium hydrophosphate $\text{Zr}(\text{HPO}_4)_2$. In the studied sample, the zirconium hydrophosphate additive came to 18% (w/w) in the membrane polymer.

The zirconium-hydrophosphate-modified MF-4SK membrane was also prepared on the basis of an extru-

sion membrane. To this purpose, a MF-4SK membrane in its H^+ -form was exposed to water–ethanol solution, then, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ solution; afterwards, to phosphoric acid solution, to precipitate zirconium hydrophosphate. All samples were prepared in JSC Plastpolimer specially for their application in solid-state fuel cells and membrane-type electrolyzers. In Table 3 we present physico-chemical characteristics of the initial and modified perfluorinated membranes. The ion-exchange capacity of the MF-4SK/polyvinylbutyral and MF-4SK/sulfonated polysulphon samples were calculated on the basis of the membrane composition; that of the MF-4SK/zirconium hydrophosphate samples was determined experimentally by the alkali-titration of the H^+ -ions formed in the neutralization reaction.

To experimentally verify the theoretical calculations of the i_{lim} quantity, we measured current–voltage

Table 4. Transport–structure parameters of the MF-4SK membranes with different water content

Membrane	κ_{iso} , S/m	f_2	α	$G \times 10^{15}$, $\text{m}^5/(\text{mol s})$	β	c
MF-4SK-1	0.635	0.12	0.293	1.50	1.40	0.006
MF-4SK-2	0.933	0.13	0.283	8.38	1.51	0.003
MF-4SK-3	1.310	0.20	0.361	61.20	1.43	0.026

characteristics of the MF-4SK membrane over the sodium–chloride solution 0.01–0.1 M concentration range. The current–voltage characteristics were taken in a four-compartment cell [45] with two polarizing platinum electrodes allowing the current applying to the cell with the potential scanning rate of 1×10^{-4} A/s. The membrane potential was registered in real-time mode with the sampling interval 1 per second, by using silver/silver chloride reference electrodes lead to the ion-exchange membrane surface and connected to an Autolab PGSTAT302N potentiostat/galvanostat. Constant rate of the solution circulating in the cell (14 mL/min) was provided by a multichannel peristaltic pump. The limiting current value was determined by Newton method (the tangent method) using a Microsoft Excel program.

To determine the extended three-wire model parameters, we determined the ion-exchange membrane conductivity over wide range of the sodium–chloride solution concentrations: from 0.05 to 3 M. The membrane conductivity (κ_m , S/m) was calculated from the membrane impedance active component measured experimentally by mercury-contact method. The diffusion permeability integral coefficient P_m was determined in a two-compartment cell during the diffusion of sodium chloride solutions of different concentration through the membranes into water; the procedure was described in detail elsewhere [40]. The ion apparent transport numbers in the membranes were determined potentiometrically in the two-compartment cell under circulation of the solution whose concentration on the both sides of the membrane differed by a factor of 2. The membrane potential was measured using silver/silver chloride reference electrodes. The membrane electroosmotic permeability (required for the calculating of counter-ion true transport numbers in membranes by the Scachard equation) was measured by volumetric method in the two-compartment cell with polarizing equilibrium silver/silver chloride electrodes and horizontally arranged measuring capillaries [26]. The error in the determination of the electrotransport characteristics did not exceed 5%.

In the calculations, we used the sodium chloride solution characteristics taken from support literature: tabulated conductivity [46, 47], diffusion coefficients, mean activity coefficients [47, 48], and ion transport numbers [47] over wide range of the NaCl solution concentrations. In case of absence the characteristic for some concentration, the required value was deter-

mined on the basis of a polynomial describing the concentration dependence of the property. When calculating the activity coefficients and the correction factor π_{\pm} , taking into account the solution nonideality, we recalculated the molality given in the support literature to molar concentration, taking into consideration the sodium chloride solution density at 20°C [46].

THE RESULTS OF CALCULATIONS OF ELECTRODIFFUSION CHARACTERISTICS AND LIMITING CURRENT VALUES FOR PERFLUORINATED MEMBRANES WITH DIFFERENT WATER CONTENT

To evaluate the NaCl solution concentration range in which a correct estimating of the i_+^* and P^* values by the using of each calculation variant shown in Fig. 1 is possible, we used experimental data on the concentration dependences of conductivity, diffusion permeability, counter-ion and water transport numbers in perfluorinated membranes MF-4SK with different water content over wide NaCl solution concentration range. In Figs. 2a–2d the experimental data is shown by points connected with solid lines; results of calculations, by dashed lines. The membrane conductivity concentration dependences (Fig. 2a) were calculated by equation (13); the diffusion permeability differential coefficient (Fig. 2b), by equation (11); the ion true transport numbers (Fig. 2c), by the Scachard equation (2) with the using of experimental data on the water transport numbers (Fig. 2d).

The membrane's transport-structure parameters required for the P^* , κ_m , and t^* calculations with the using of the variants 1–9, found from the conductivity and diffusion permeability concentration dependences, are given in Table 4.

In the i_{lim}^* quantity calculations by different variants the δ was chosen equal to 2.5×10^{-4} m; it was found using the Pearce formula. At that, the i_{lim} value determined from the experimental current–voltage curve was also used.

The comparing of the theoretically calculated of the conductivity and the diffusion permeability integral coefficient with their experimental values allowed revealing the NaCl solution concentration range in which the i_+^* and P^* quantities can be correctly estimated by each calculation variant presented in Fig. 1. For example, the variant 1 with the using of the two-

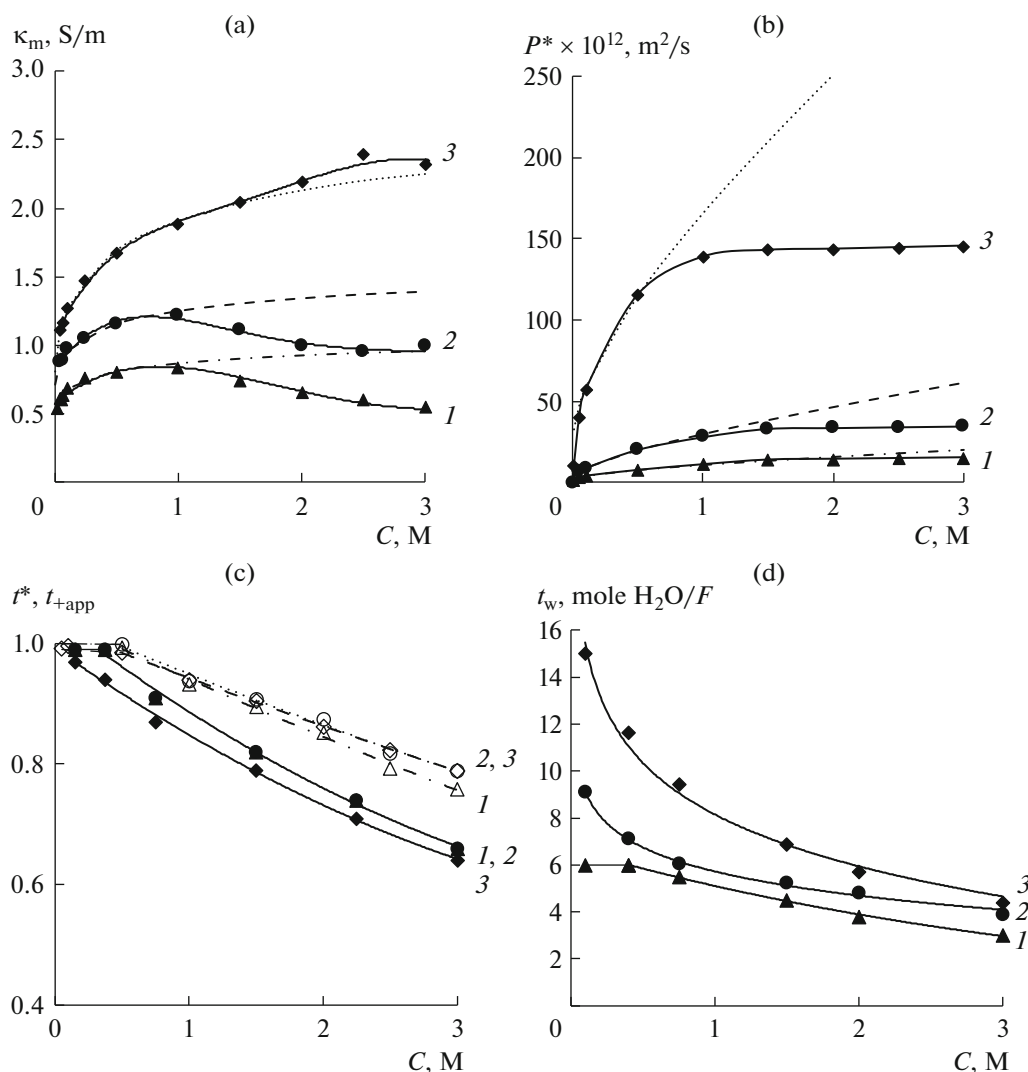


Fig. 2. Conductivity (a), diffusion permeability differential coefficient (b), counter-ion transport number (c), and water transport number (d) for perfluorinated membranes with different specific water content: (1) MF-4SK-1; (2) MF-4SK-2; (3) MF-4SK-3 in NaCl solutions. The experimental data is shown by points connected with solid lines; results of calculations, by dashed lines.

phase microheterogeneous model of the membrane conductivity can be realized only over the concentration range restricted for this particular model, that is, up to the concentration value corresponding to the conductivity maximal value in its concentration dependence, as shown in work [49]. These values equal 0.5 M for the MF-4SK-3 membrane; 1 M, for the rest of membranes with lower water content. The quantity i_{lim} can be calculated over the widest concentration range by using the calculation variants 7 and 9 (Table 5).

Statistical analysis of the obtained values of the limiting current density was carried out by using the Microsoft Excel built-in functions. In Table 5 we give the i_{lim} mean values from the data calculated by different methods. When three or more values were averaged, then, the standard deviation and the Student

confidence interval for the probability of 0.95 were determined. The error (Δ) in this case was calculated as the ratio of the confidence interval to the mean value. When the limiting current density was estimated in concentrated solutions with the using of two calculation variants, the error Δ was determined by the following formula:

$$\Delta = \frac{|i_{lim}^m - i_{lim}^n|}{\bar{i}_{lim}} \times 100\%, \quad (14)$$

where \bar{i}_{lim} is the average of the limiting current densities i_{lim}^m and i_{lim}^n , calculated by the variants m and n , respectively.

We see from Table 5 that the NaCl solution concentration range in which the i_{lim} value can be esti-

Table 5. Values of the limiting current density calculated by the averaging of all used variants and results of statistical treatment of the obtained data

C, M	$i_{lim}, A/m^2$			Numbers of realized variants of calculation			$\Delta, \%$		
	MF-4SK-1	MF-4SK-2	MF-4SK-3	MF-4SK-1	MF-4SK-2	MF-4SK-3	MF-4SK-1	MF-4SK-2	MF-4SK-3
0.05	48.09	48.13	49.68	1–9	1–9	1–9	0.2	0.1	0.2
0.1	93.99	94.06	98.22	1–9	1–9	1–9	0.3	0.1	0.5
0.5	470.52	471.13	536.85	1–9	1–9	1–9	0.8	0.9	3.9
1.0	971.72	979.1	1201.56	1–9	1–9	3, 5, 7, 9	1.8	2.9	2.8
1.5	1574.68	1524.78	2163.49	7, 9	7, 9	3, 5, 7, 9	7.4	11.5	0.6
2.0	2267.34	2137.71	2452.73	7, 9	7, 9	5, 7, 9	10.7	15.7	4.4
2.5	3146.68	2905.9	3291.16	7, 9	7, 9	7, 9	17.7	24.0	10.3
3.0	4072.77	3660.14	4218.29	7, 9	7, 9	7, 9	20.4	28.4	13.6

Table 6. Transport characteristics of MF-4SK membranes in 0.05 M NaCl solution

Sample	t_+^*			$P^* \times 10^{12}, m^2/s$		$i_{lim}, A/m^2$	
	(2)	(3)	equation (4)	(9)	(11)	average of 9 variants of calculations	experiment
MF-4SK-1	1.000	0.998	0.999	3.22	3.43	48.09 ± 0.09	–
MF-4SK-2	1.000	0.999	0.999	6.97	6.68	48.13 ± 0.03	–
MF-4SK-3	0.991	0.992	0.996	40.00	46.71	49.68 ± 0.12	–
MF-4SK-4	–	–	–	–	–	–	50.9 ± 1.7

mated with the error not exceeding 10% depends on the membrane's water content: for the MF-4SK-1 and MF-4SK-2 samples it expands to 1.5 M; for the MF-4SK-3 sample with higher water content value to 2.5 M. However, the i_{lim} value can be correctly estimated over the entire studied concentration range when only experimental data on concentration dependences of the apparent transport numbers for ions and water, as well as diffusion permeability, are used in the calculations (variants 7, 9).

The results on the P^* and t_+^* values calculated by different methods for membranes with different water content in 0.05 M NaCl solution are presented in Table 6. The table also gives averaged results of the i_{lim} quantity calculations carried out by equation (1) by each of the nine above-given variants (Fig. 1), as well as values of i_{lim} found from experimental current–voltage curves measured for the perfluorinated membranes that have close electrotransport characteristics.

The analysis of results given in Table 6 shows the calculated limiting current in dilute electrolytes to be practically independent of the membrane's electrotransport characteristics; it coincides with the value of i_{lim} found from the experiment.

The values of i_{lim} calculated over wide NaCl solution concentration range for the MF-4SK membranes with different water content are shown in Fig. 3. They were calculated by the procedure of variant 7 (Fig. 1), which is based on the using of values P^* and κ_m , found from the experiment and of value of t_+^* taken in terms of the three-wire model. In addition, Fig. 3 gives the values of limiting current taken from the experimental current–voltage curves for the MF-4SK-4 sample whose water content approaches that of the MF-4SK-2 sample (Table 1). The experimental dependence measurement range is limited to the equipment technical characteristics; it does not exceed 0.1 M under the experimental conditions. We see from the figure that over the concentration range from 0.01 to 0.1 M the experi-

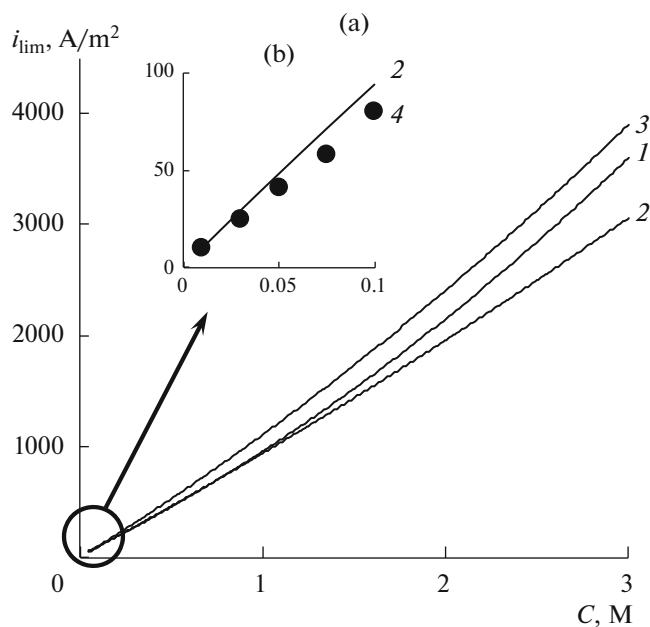


Fig. 3. Concentration dependences of limiting current density calculated theoretically by variant 7 (solid lines) (a) and found from experimental current–voltage curves (points) (b): (1) MF-4SK-1; (2) MF-4SK-2; (3) MF-4SK-3; (4) MF-4SK-4 (experimental data).

mentally measured and theoretically instead of thermodynamically calculated dependences are in good agreement. At that, the doubling of the membrane specific water content has no real impact on the i_{lim} value. However, the tripling of the characteristic leads to a significant increase in the i_{lim} value (Fig. 3, curve 3). It is likely that in the case of concentrated solutions the second summand in equation (1) contribution to the i_{lim} value becomes much more significant. Actually, this member (i_2) in equation (1) takes into consideration the contribution from the electrolyte reverse diffusion; it may be estimated by the formula:

$$\frac{P^*FC}{l(t_i^* - t_i)} \Big/ i_{lim} = \frac{i_2}{i_{lim}} \times 100\%. \quad (15)$$

We see from Fig. 4 that for the membrane with the highest water content the contribution is as large as 8%. Analysis of the obtained concentration dependences shows that the contribution of the second member in equation (1) grows with the increasing of the solution concentration up to 1.5 M; afterwards, it remains constant because the concentration dependence of the diffusion permeability coefficient has the same character (Fig. 2b).

Thus, the refined Pearce equation allows calculating the limiting diffusion current correctly over wide electrolyte solution concentration range. The using of this equation is an imperative for samples with the specific water content exceeding 20 mol H₂O/mol of

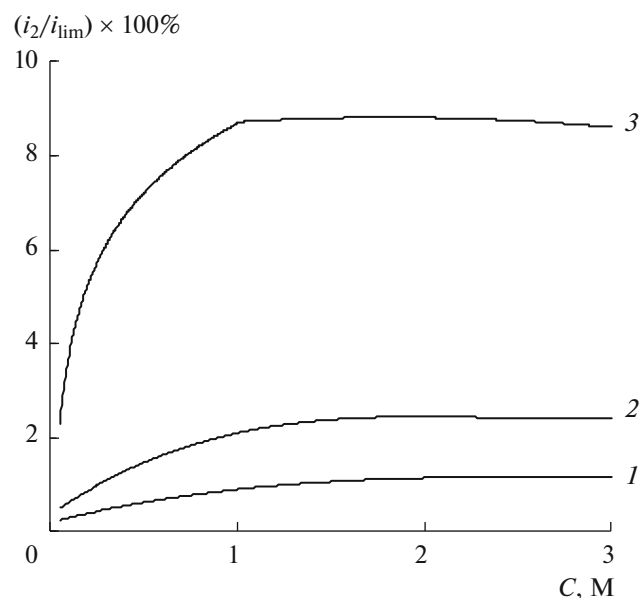


Fig. 4. The electrolyte reverse diffusion contribution to limiting current as a function of NaCl solution concentration for membranes with different specific water content: (1) MF-4SK-1; (2) MF-4SK-2; (3) MF-4SK-3.

functional groups because the electrolyte solution reverse diffusion by no means can be neglected.

RESULTS OF CALCULATIONS OF ELECTRODIFFUSION CHARACTERISTICS AND VALUES OF LIMITING CURRENT FOR MODIFIED PERFLUORINATED MEMBRANES

The above-described approach to the limiting current estimation for membranes with different water content was used in the calculations of this characteristic for perfluorinated membranes modified with polyvinylbutyral, sulfonated polysulphon, and zirconium hydrophosphate. To this purpose, the electrical conductivity and diffusion permeability of the above-listed samples in NaCl solutions of different concentration were measured. We see from Fig. 5a that the introducing of organic modifiers resulted in decrease of the conductivity over the entire range of studied concentrations. At that, the polyvinylbutyral-modified membrane demonstrates the most pronounced effect.

We see from Fig. 5 that the modifying with zirconium hydrophosphate increased the perfluorinated membranes' conductivity, irrespective of their preparation method, over the entire range of the studied sodium chloride equilibrium solution concentrations (Figs. 5a, 5c). The probable reason of the phenomenon is the larger ion-exchange capacity of the zirconium-hydrophosphate-modified samples as compared with the rest of the membranes. However, the

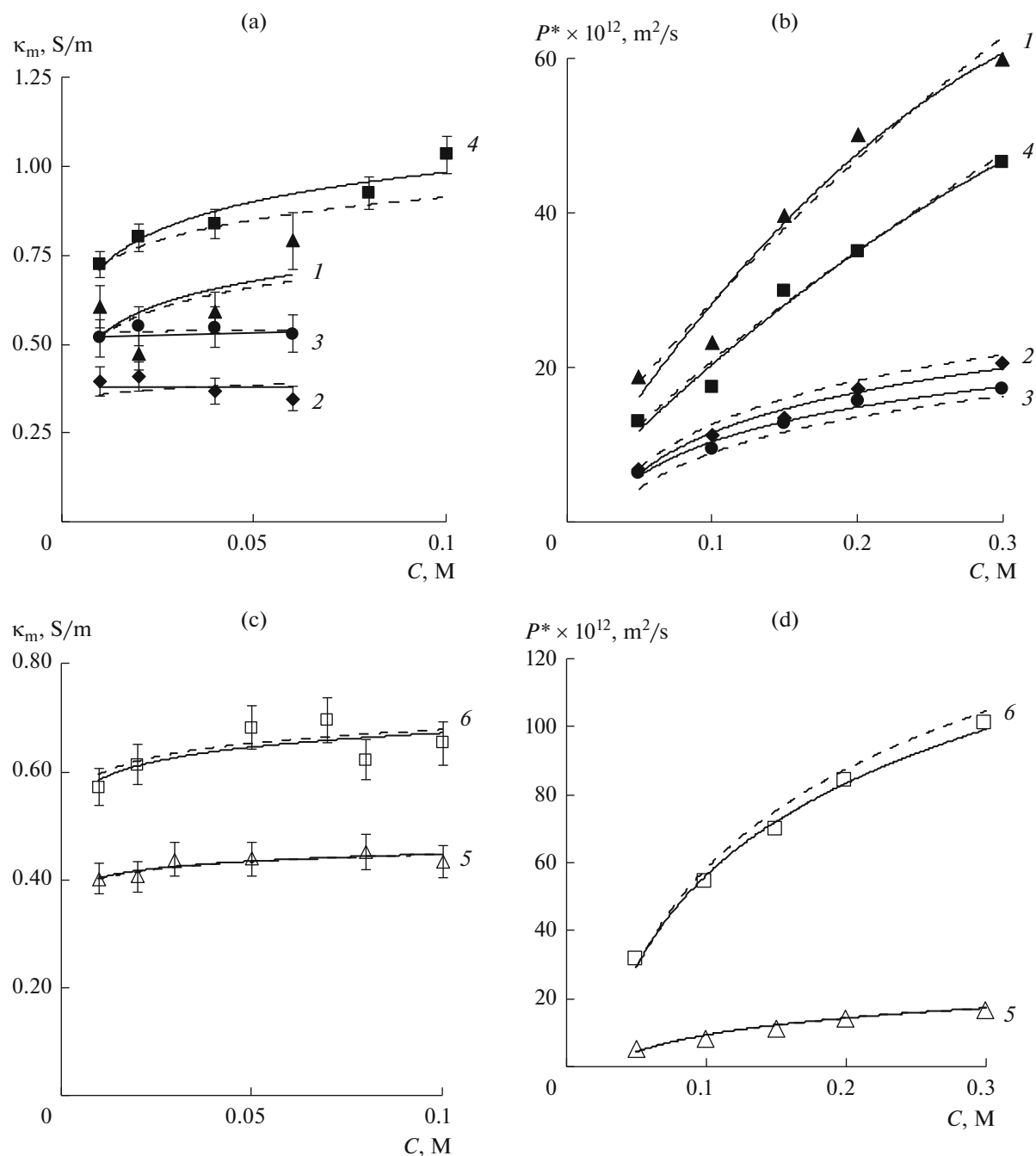


Fig. 5. Dependences of conductivity (a, c) and diffusion permeability differential coefficient (b, d) for initial and modified membranes on the NaCl solution concentration. Numbers by the curves correspond to the sample numbers in Table 3. The experimental data is shown by points connected with solid lines; results of calculations by equation (11) (b, d) and by equation (13) (a, c), by dashed lines.

modifying with zirconium hydrophosphate affects the diffusion permeability in a different way, depending on the method of the modifier introducing to the per-fluorinated membranes' matrix. In particular, the diffusion permeability coefficient of the sample prepared by casting is by a factor of 1.5 lower as compared with that of the initial membrane (Fig. 5b), whereas the modifying of extrusion membrane with the zirconium

hydrophosphate resulted in the increasing of the diffusion permeability over the entire range of studied concentrations (approximately, by a factor of six (Fig. 5d). In the case of the extrusion membrane, the zirconium-hydrophosphate precursor was introduced to ready-made film pre-exposed to ethanol for the expanding of the membrane structure [50, 51] and increasing of the added modifier amount. The con-

Table 7. Model parameters and electrodiffusion characteristics of modified membranes

Sample	f_2	κ_{iso} , S/m	α	$G \times 10^{15}$, $\text{m}^5/(\text{mol s})$	β	$P^* \times 10^{12}$, m^2/s	t^*
Cast membranes							
MF-4SK	0.16	0.686	0.16	90.8	1.70	18.6	0.997
MF-4SK/polyvinylbutyral	0.05	0.379	0.44	37.1	1.62	6.7	0.998
MF-4SK/sulfonated polysulphon	0.01	0.540	0.68	42.8	1.60	6.2	0.999
MF-4SK/zirconium hydrophosphate	0.11	0.897	0.19	85.0	1.70	12.9	0.998
Extrusion membranes							
MF-4SK	0.05	0.428	0.37	32.8	1.69	25.8	0.996
MF-4SK/zirconium hydrophosphate	0.06	0.660	0.55	252	1.66	156.7	0.975

Table 8. Limiting current density for membranes in 0.05 M NaCl solution and the electrolyte reverse diffusion contribution therein

No.	Membrane	i_{lim} , A/m ²		i_2 , A/m ²	$\frac{i_2}{i_{\text{lim}}}$, %
		experimental	calculated		
Cast membranes					
1	MF-4SK	43.7 ± 1.4	50.52	2.44	4.8
2	MF-4SK/polyvinylbutyral	44.1 ± 1.4	48.97	0.99	2.0
3	MF-4SK/sulfonated polysulphon	44.0 ± 0.5	48.68	0.76	1.6
4	MF-4SK/zirconium hydrophosphate	50.3 ± 1.2	49.68	1.72	3.5
Extrusion membranes					
5	MF-4SK	47.6 ± 1.9	50.59	2.48	4.9
7	MF-4SK/zirconium hydrophosphate	52.0 ± 1.2	57.71	7.82	13.5

comitant expanding of transport channels makes easier the electrolyte diffusion even after the zirconium hydrophosphate particles' formation in the membrane. In the casted membranes, the inorganic phase distribution in polymer is more uniform because the components were combined in solutions, precursor was added to the perfluorosulfonic acid, and then the film was poured. The obtained results are in good qualitative agreement with the data of work [52]. In this work the observed effects were explained by using a model in which the modifying additive inclusions to membrane clusters play the role of objections on the electrolyte diffusion paths.

The obtained experimental data on the concentration dependences of the modified membranes' conductivity and diffusion permeability were used in the calculations of transport-structure parameters (f_2 , κ_{iso} , α , G , and β) involved in the calculations of the membranes' electrodiffusion characteristics (P^* and t_+^*) required for the estimating of the limiting diffusion current. The electrodiffusion characteristics were calculated by using the variant 3 (Fig. 1). The found

model parameters and electrodiffusion characteristics are summarized in Table 7.

Values of i_{lim} calculated by equation (1) and the contribution of the electrolyte reverse diffusion to the limiting current (i_2/i_{lim}) calculated by equation (15) are given in Table 8. Our analysis of the results showed that in the membranes prepared by the cast method the i_{lim} values differ by 3–4% irrespective of the modifier nature. The practically identical i_{lim} values for these samples are due to their high selectivity and relatively small diffusion permeability; on this reason, the contribution of the electrolyte reverse diffusion to the limiting current does not exceed 5%. However, according to the calculations, the i_{lim} value for the zirconium-hydrophosphate modified extrusion membrane must increase by 14%, due to the significant increase in the sample's diffusion permeability.

To verify experimentally the adequacy of the theoretical calculation of the i_{lim} value for the modified membranes, we measured their current–voltage characteristics in 0.05 M NaCl solution (Fig. 6). We see from the figure that all samples of initial and modified

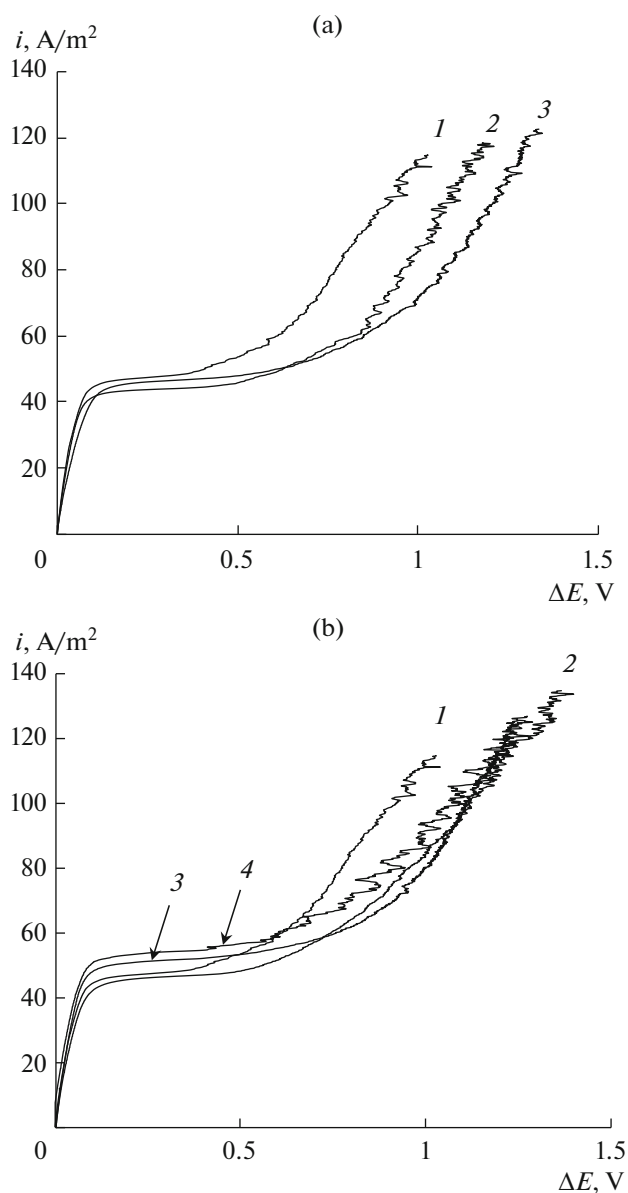


Fig. 6. Current–voltage curves taken in 0.05 M NaCl solutions for membranes modified with polymers (a) and zirconium hydrophosphate (b): (a) (1) MF-4SK_{ini}; (2) MF-4SK/polyvinylbutyral; (3) MF-4SK/sulfonated polysulphon; (b) (1) MF-4SK_{cast}; (2) MF-4SK/zirconium hydrophosphate_{cast}; (3) MF-4SK_{extrus}; (4) MF-4SK/zirconium hydrophosphate_{extrus}.

membranes show nearly the same slope of the Ohmic segment of the polarization curve because the membrane contribution to the electromembrane system full resistance is significantly less than that of the near-membrane diffusion layers in the solution. The limiting current densities derived from the measured current–voltage characteristics are given in Table 8. We see from the table that the membranes manufactured by casting have neighbor values of i_{lim} , whereas for the zirco-

nium-hydrophosphate-modified extrusion membrane the i_{lim} value increased by 9% which is in good agreement with the results of the theoretical calculations. The experimentally found increase of i_{lim} for the zirconium-hydrophosphate-modified cast membrane points to the necessity of further development of approaches to the theoretical estimation of limiting diffusion current in systems with modified membranes, as well as taking into consideration of additional factors introduced by the modifier presence.

CONCLUSIONS

Special aspects of different model approaches to the evaluation of membranes' electrodiffusion characteristics, required for the limiting diffusion current calculations, are analyzed. They include a two-phase microheterogeneous model of the membrane conductivity and a three-wire model of ion-exchange material. The limiting diffusion current density was calculated by the refined Pierce equation taking into consideration the membrane selectivity and the electrolyte reverse diffusion contribution. The counter-ion transport numbers in membrane and the differential coefficient of its diffusion permeability required for the limiting current estimation were determined from experimental data on the concentration dependences of the conductivity, diffusion permeability, the counter-ion and water transport numbers over wide range of the sodium chloride solution concentration. The range of the NaCl solution concentrations in which the theoretical calculation of the membranes' electrodiffusion characteristics is possible was revealed by example of the MF-4SK perfluorinated membranes with different specific water content. The concentration range in which the limiting current density can be correctly estimated was shown to depend on the applied model approach and the membrane's specific water content. The using of the refined Pierce equation is an imperative for samples whose specific water content exceeds 20 mol H₂O/mol of functional groups because in this case the electrolyte solution reverse diffusion by no means can be neglected.

The comparison of theoretically calculated limiting diffusion current density with that obtained from experimentally measured current–voltage curves showed the possibility of adequate theoretical estimating of this parameter for the MF-4SK perfluorinated membranes modified with organic and inorganic dopants. This allows using relatively simple measurements of the modified ion-exchange membrane transport characteristics for the predicting of the modifier effect not only on the transport properties but also on the limiting current under given conditions, hence, to predict the effectiveness of the using the membranes' modifications in electromembrane processes for the solving of particular practical problems.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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