

Electrotransport Characteristics of Polyaniline-Modified Cations-Exchange Membranes in Solutions of Sulfuric Acid and Nickel and Chromium Sulfates¹

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Received November 24, 2022; revised February 13, 2023; accepted February 20, 2023

Abstract—The electrotransport properties and the structure of polyaniline-modified sulfocationic membranes MK-40 and MF-4SK are studied in solutions of sulfuric acid and sulfates of nickel and chromium. The modification by polyaniline is performed in electro dialyzer. The decrease in conductivity and diffusion permeability of membranes after their modification with polyaniline is assessed in electrolyte solutions of different nature. The key effect of the counter-ion charge on the conductivity of original and modified membranes is confirmed. The unusual effect of the decrease in the MF-4SK/PANI membrane conductivity with an increase in the concentration of solutions containing multiply-charged cations is observed. The information acquired by porosimetry on the effect of multiply-charged ions on the structure of homogeneous and heterogeneous membranes is supplemented by calculations of the transport and structure parameters using the microheterogeneous model of ion-exchange membrane. Based on the analysis of parameters of current–voltage curves in solutions of nickel sulfate and sulfuric acid, the prospects of using the modified membranes in the electro dialysis of solutions containing sulfuric acid and multiply-charged ions are assessed.

Keywords: cation-exchange membrane, polyaniline, modification, multiply-charged ions, conductivity, diffusion permeability, current–voltage curve, structure

DOI: 10.1134/S102319352310004X

INTRODUCTION

The electro dialysis technologies appeared in the middle of the last century [1–3]. At present, the interest in these methods does not fade, as confirmed by a large number of publications in Russian and foreign journals. The analysis of the literature makes it possible to single out the main directions of the use of electro dialysis, namely, the cleaning of wastewater including water in the hybrid setups with reverse osmosis and filtration [3–6]; the extraction of precious or toxic substances from multicomponent mixtures, e.g., organic acids [7, 8], heavy metal ions [9], radioactive substances [10], various salts [11, 12], and their concentration aimed at the further use or utilization, and other applications.

The wide diversity of applications of electro dialysis determines the necessity of selecting ion-exchange membranes with the optimal set of properties to better suit the requirements imposed by a concrete technological process. However, the choice of ion-exchange membranes is limited to commercial brands, which

makes important the problem of imparting necessary properties to commercial materials by their modification. The various approaches to modifying ion-exchange membranes were analyzed in several publications [2, 13–15]. One of such methods of modifying membrane characteristics is the incorporation of organic or inorganic substances into the surface or bulk of the primary polymer material [16–18]. To separate the multiply-charged and singly-charged ions, a modifier layer with ionogenic groups oppositely charged as compared with the ion-exchange membrane is applied on its surface. This imparts to the membrane the ability to preferentially permeate singly-charged ions, blocking the multiply-charged ions [19–21].

Polyaniline (PANI) is a highly efficient modifying electroactive polymer due to its high conductivity, chemical and mechanical stability [22], and the high concentration of charged groups in the doped state. Furthermore, depending on synthetic conditions, the nature, and the concentration of the oxidant, the samples with nanosized PANI inclusions in the membrane bulk or in its surface layer can be obtained [23–25]. Several studies demonstrated the efficiency of using composites based on an ion-exchange membrane and

¹ Delivered at the 20th All-Russian Meeting “Electrochemistry of Organic Compounds” (EKhOS-2022), Novocheerkassk, October 18–22, 2022.

PANI in the electro-dialytic separation of singly-charged and multiply-charged ions, from solutions including acidic [26–32]; however, the working size of membranes gave no way of scaling these results for industrial electro-dialyzers. Moreover, it is also important to assess the efficiency of modifying membranes immediately in the electro-dialyzer based on the data on characteristics of membranes in solutions containing ions to be separated.

This is why, the goal of this work was to study the electrotransport and the structure of sulfocationic membranes modified by polyaniline immediately in the electro-dialyzer in solutions of nickel and chromium sulfates and sulfuric acid in order to assess the prospects of their use in the electromembrane separation of multiply-charged ions.

EXPERIMENTAL

We studied the cation-exchange membranes with sulfonic acid groups produced in Russia: heterogeneous membrane MK-40 (Shchekinazot, Shchekino) and perfluorinated membrane MF-4SK (Plastopolimer, St. Petersburg). The heterogeneous MK-40 membrane is the product of combining the ion-exchange resin KU-2 based on sulfonated polystyrene cross-linked by divinylbenzene, which is reinforced by a capron mesh. The perfluorinated membrane is a copolymer of tetrafluoroethylene and perfluorovinyl alcohol. Before modification and investigations, the heterogeneous membrane was subjected to the salt treatment and the perfluorinated membrane was subjected to the oxidation heat treatment by the standard procedure. Table 1 shows the main physicochemical characteristics of membranes (exchange capacity (Q), water content (W), and specific water content (n)) in their Na^+ form.

The chemical modification of cation-exchange membranes by PANI was carried out immediately in the electro-dialyzer which comprised 7 cation-exchange and 8 anion-exchange membranes. The modification involved using 10 L of 0.01 M aniline solution in 0.05 M sulfuric acid and 10 L of solution of 0.025 M sulfuric acid and 0.008 M ammonium persulfate, which circulated in the tracts of desalination and concentration, respectively. The PANI synthesis was carried out at different current densities: 10 min at 2 A/dm² to form PANI nuclei and 120 min at 1 A/dm²; the total time of polymerization was 130 min. After modification, the membranes were washed by 0.01 M sulfuric acid solution and then by distilled water.

The conductivity of membranes was determined based on their active resistance measured by the mercury-contact method [33]. The diffusion permeability was calculated based on the data on the diffusion flux that passed through the membrane surrounded by solution of certain concentration and distilled water.

Table 1. The main physicochemical characteristics of membranes MK-40 and MF-4SK

Membrane	Q , mmol/g _{sw}	W , %	n , mol H ₂ O/mol SO ₃ ⁻
MK-40	1.54 ± 0.04	37	13
MF-4SK	0.68 ± 0.04	20	16

The increase in the concentration in the chamber with water was controlled by conductometry [33].

The current–voltage curves (CVCs) of ion-exchange membranes were measured in a four-chamber flow-through cell by the procedure described in [34]. We used the galvanostatic mode of measurements at the direct current scanning rate of 1×10^{-4} A/s. The working solution circulated through the chambers at a constant rate of 14 mL/min. The CVCs were measured in solutions of sodium chloride, sulfuric acid, nickel sulfate with the concentration of 0.05 mol-equiv/L and also in a mixture of nickel sulfate and sulfuric acid with the concentration of each component of 0.025 mol-equiv/L, which in total gave 0.05 mol-equiv/L. To obtain reproducible results, no less than 3–5 CVCs were measured. As the CVC parameters, we considered the limiting current density (i_{lim}), the length of the limiting current plateau (Δ), the slopes of ohmic (dI/dE_{ohmic}) and overlimiting (dI/dE_{overlim}) CVC regions. For the original membranes, all values were determined by the tangent method in the Microsoft Excel program. i_{lim} of modified membranes was determined as the extremum point in the differential curve in coordinates dE/di vs. i , obtained by numerical differentiation using the Microsoft Excel program. The Student confidence interval was determined using the installed Microsoft Excel functions. The relative error was calculated as the ratio of the confidence interval to the average value of sought quantity. For i_{lim} , the error did not exceed 5% for original membranes and 10% for modified membranes. For the length of the limiting current plateau, the measurement error was about 10%, for slopes of CVC regions it did not exceed 15%.

The characteristics of membrane's structure were studied by the method of standard contact porosimetry by evaporating water from swelled samples under conditions of the capillary equilibrium between the studied samples and the standards with the known pore distribution over radii [35].

Before studying the electrotransport characteristics, the membranes were brought into equilibrium with solution of a given concentration. Before studying the membrane structure by the method of standard porosimetry, the membranes were converted into a certain ionic form and then washed with distilled water until the constant resistance of water above the membrane.

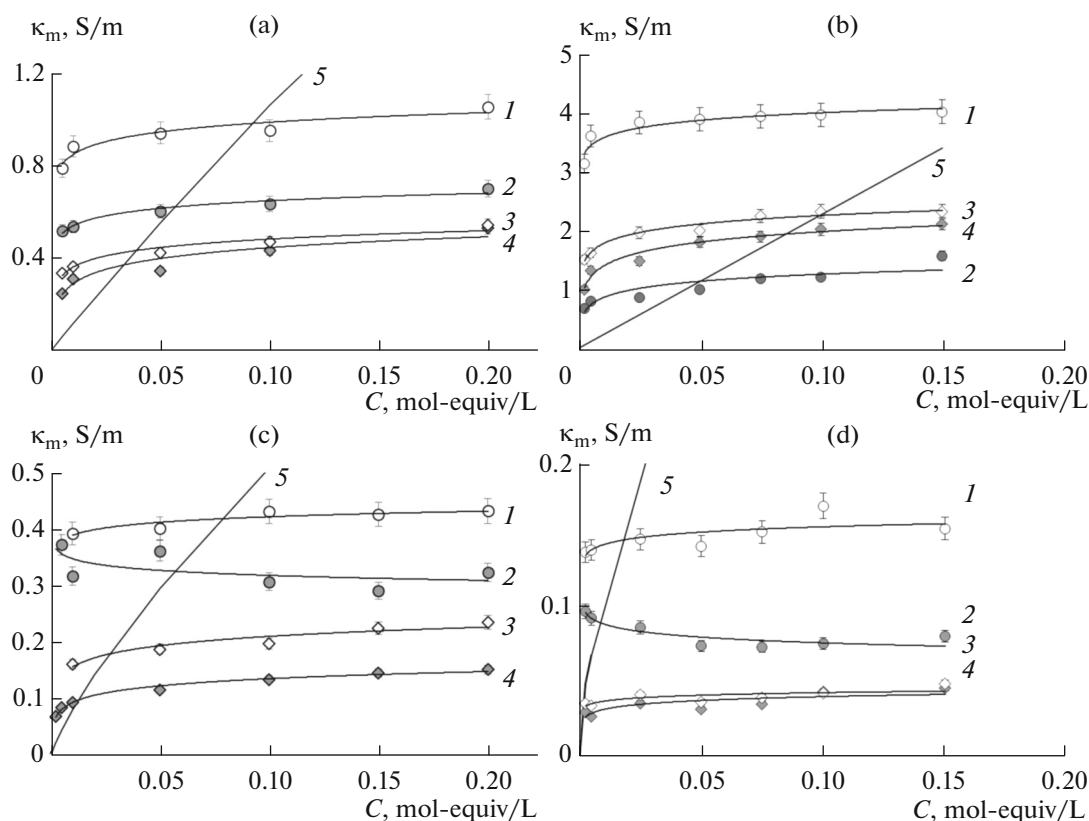


Fig. 1. Concentration dependences of the conductivity of membranes (1) MF-4SK, (2) MF-4SK/PANI, (3) MK-40, and (4) MK-40/PANI in solutions of (a) sodium chloride, (b) sulfuric acid, (c) nickel sulfate, (d) chromium sulfate; (5) equilibrium solution.

RESULTS AND DISCUSSION

Electrotransport Characteristics

The electrotransport characteristics of original and modified membranes were studied in model solutions containing the main components used in hydrometallurgy, namely, sulfuric acid and sulfates of nickel and chromium. For a comparison, we also studied the membrane characteristics in a sodium chloride solution which is also used as a standard in studying the characteristics of ion-exchange materials. Figure 1 shows the concentration dependences of the conductivity of samples. As seen, in solutions of all electrolytes studied here, the conductivity of membrane MF-4SK was higher as compared with membrane MK-40. It is known that the conductivity of membranes is determined by the mobility of counter-ions which in aqueous solutions in the series of cations H^+ , Na^+ , $1/2Ni^{2+}$, $1/3Cr^{3+}$ is equal to 349.8, 50.28, 54.0, 67.0 $S\ cm^2\ mol^{-1}$, respectively [36]. At the same time, based on the results shown in Fig. 1, we can assume that the conductivity exerts the key effect on the charge of counter-ions in the series of salt forms of cation-exchange membranes studied here. This is associated with the decrease in the mobility of multiply-

charged cations in the membrane phase due to their interaction with several fixed ions.

Modifying by PANI decreased the conductivity of both membranes; moreover, this effect was more pronounced for the homogeneous membrane as compared with heterogeneous one. Thus, the conductivity of the homogeneous membrane MF-4SK/PANI in solutions of NaCl, $NiSO_4$, and $Cr_2(SO_4)_3$ decreased by a factor of 1.5–2, whereas for the heterogeneous membrane MK-40/PANI the decrease did not exceed 15%. This was associated with peculiarities of the PANI layer formation on the surface of homogeneous and heterogeneous membranes, which were observed in [37]: on the surface of MF-4SK/PANI the modifier formed a continuous layer, whereas the modification of MK-40 proceeded only in ion-exchange grains. Thus, a considerable part of the heterogeneous membrane surface remained unmodified. Due to formation of a dense modifier layer on the surface of the homogeneous membrane and the repulsion of multiply-charged cations from positively charged PANI in solutions of nickel and chromium sulfates, the descending concentration dependences of conductivity were observed for the MF-4SK/PANI membrane, which is untypical for ion-exchange membranes in dilute and moderately concentrated electrolyte solutions. This

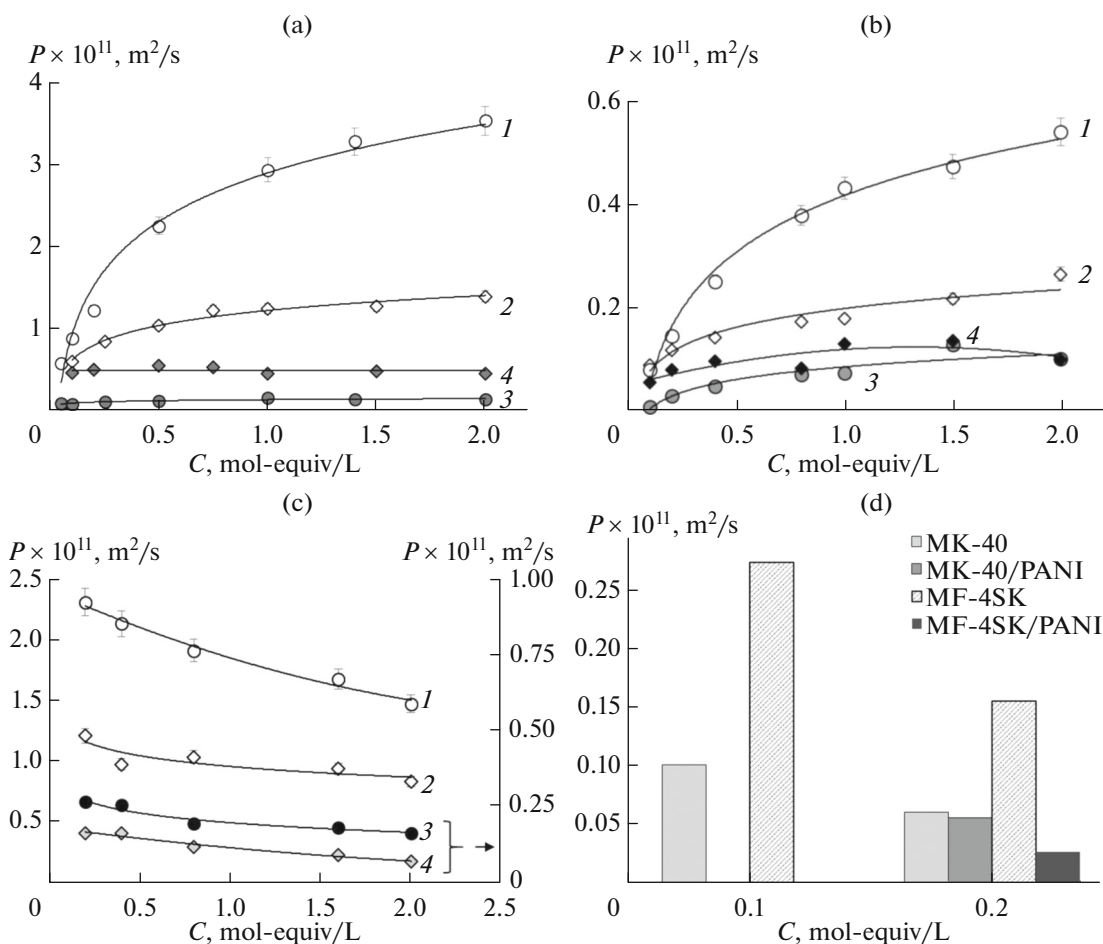


Fig. 2. Concentration dependences of the diffusion permeability of membranes (1) MF-4SK, (2) MF-4SK/PANI, (3) MK-40, and (4) MK-40/PANI in solutions of (a) sodium chloride, (b) sulfuric acid, (c) nickel sulfate, (d) chromium sulfate.

effect pointed to the good prospects of using these samples for separating solutions containing singly-charged and multiply-charged cations. It should be noted that the most pronounced 3–4-fold decrease in the conductivity was observed for the homogeneous membrane MF-4SK/PANI in sulfuric acid solution.

The diffusion permeability of membranes was studied in the aforementioned solutions and wide concentration intervals. Figure 2 shows the concentration dependences of integral coefficients of diffusion permeability. Insofar as the diffusion process was limited mainly by the transport of co-ions, the diffusion permeability of membranes in sodium chloride solution was higher as compared with sulfuric acid. In contrast to conductivity, the diffusion permeability in solutions of nickel and chromium sulfates decreased with the increase in electrolyte concentration both for original and modified membranes. As shown in [38], the descending concentration dependence of the diffusion permeability may be associated with different ratios between the diffusion coefficients of co-ions and counter-ions in the membrane. Furthermore, men-

tion should be made of the higher diffusion permeability of membranes in 0.1 mol-equiv/L solutions of nickel and chromium sulfates as compared with sulfuric acid and sodium chloride. This effect could be associated with the stronger coulomb interaction of multiply-charged counter-ions as compared with singly-charged cations, which made easier the transport of co-ion in the membrane. As a result of modification, the decrease in the diffusion permeability of membranes was more pronounced as compared with conductivity, namely, for MK-40 membrane it decreased by a factor of 1.5–2 in solutions of sodium chloride and sulfuric acid and 10-fold in solutions of nickel sulfate; for MF-4SK it decreased 5–10-fold in all solutions.

On the whole, as a result of modification by PANI, the changes in the conduction and diffusion properties of membranes in solutions of nickel and chromium sulfates agreed with the results obtained earlier in solutions of sodium chloride, hydrochloric and sulfuric acids [24, 26].

Table 2. Transport-structure parameters of membranes

Membrane	f_2	κ_{iso} , S/m	α	$G \times 10^{15}$, $\text{m}^5 \text{mol}^{-1} \text{s}^{-1}$
NaCl				
MK-40	0.13	0.43	0.35	1.77
MK-40/PANI	0.13	0.43	0.36	0.37
MF-4SK	0.05	0.95	0.58	28.4
MF-4SK/PANI	0.09	0.62	0.30	0.028
H_2SO_4				
MK-40	0.12	2.28	0.23	3.81
MK-40/PANI	0.15	1.97	0.11	0.090
MF-4SK	0.06	4.14	0.24	0.057
MF-4SK/PANI	0.16	1.06	0.19	0.012
NiSO_4				
MK-40	0.14	0.18	—	—
MK-40/PANI	0.19	0.10	—	—
MF-4SK	0.04	0.42	—	—
MF-4SK/PANI	—	0.32	—	—
$\text{Cr}_2(\text{SO}_4)_3$				
MK-40	0.09	0.034	—	—
MK-40/PANI	0.15	0.025	—	—
MF-4SK	0.04	0.15	—	—
MF-4SK/PANI	—	0.093	—	—

Transport-Structure Parameters

Based on the measured concentration dependences of conductivity and diffusion permeability, we calculated the transport-structure parameters for the membranes using the microheterogeneous model [33, 39], namely, the volume fractions of the conducting phases of gel (f_1) and internal equilibrium solution (f_2), the conductivity of the gel phase (κ_{iso}), the parameter reflecting the mutual arrangement of conducting phases (α), and the complex parameter characterizing the diffusion of co-ions in the membrane gel phase (G). Table 2 shows the model parameters. It should be noted that to calculate the model parameters using the microheterogeneous model, the concentration dependences of conductivity and diffusion permeability should be ascending. This is why the parameters α and G were not calculated for solutions of nickel and chromium sulfates.

As follows from Table 1, modifying both heterogeneous and homogeneous membranes with PANI increased the volume fraction of the internal equilibrium solution. At the same time, the conductivity of the membrane's gel phase decreased, as observed earlier for analogous samples [40]. This was associated with the decrease in the mobility of counter-ions in the gel due to the interaction of fixed groups in the sulfonation membrane with the positively charged sites

in PANI. This was also reflected in the values of parameter G , which decreased in certain cases by more than one order of magnitude. The observed decrease of the G value and also of the diffusion permeability as a whole, was probably associated with the decrease in mobility of counter-ion in the membrane phase due to their repulsion from the positively charged PANI sites. Insofar as the electrolyte transport depended on the diffusion coefficients of both counter and co-ions, the modification of membranes led to a decrease in the diffusion permeability of samples. Furthermore, the PANI chains synthesized inside the polymeric matrix can play the role of barriers to the electrolyte transport.

The parameter α lied in the interval 0.12–0.65 and slightly decreased as a result of modification, which corresponds to the increasing contribution in the series connection of conducting phases and agrees with the formation of the modifier layer on one of membrane's surfaces. Thus, the analysis of model parameters in solutions of sodium chloride and sulfuric acid made it possible to associate the changes in electrotransport properties with the regrouping of structure components in the homogeneous and heterogeneous membranes as a result of their modification with PANI. However, in solutions of nickel and chromium sulfates, the effect of PANI was observed only for conductivity of the gel phase.

Structure Characteristics

For studying the characteristics of the porous structure of membranes MF-4SK and MF-4SK/PANI, we used the method of standard contact porosimetry. Figures 3a and 3b show the integral and differential distributions of water over effective pore radii in membranes in the H^+ , Ni^{2+} , and Cr^{3+} forms.

As follows from the figures, the maximum water content decreased as proton is substituted by multicharged cations irrespective of their nature and charge. The most pronounced decrease in the maximum water content by 23% as compared with the H^+ form was observed for the membrane MF-4SK in the Cr^{3+} form. This relationship was explained by the decrease in the number of hydrophilic species, because a multiply-charged ion can enter into coulomb interaction simultaneously with two or three fixed groups in ion-exchange membrane. Moreover, this interaction favored the additional cross-linking in the polymeric matrix, which also decreased the degree of swelling of the membrane. Apparently, the second factor dominated, because the effect of the counter-ion nature was preferentially reflected in the porosimetric curve in the region of macropores with the effective radius larger than 1000 nm. The analogous dependences were also observed in the perfluorinated membrane after its modification with PANI (Fig. 3b).

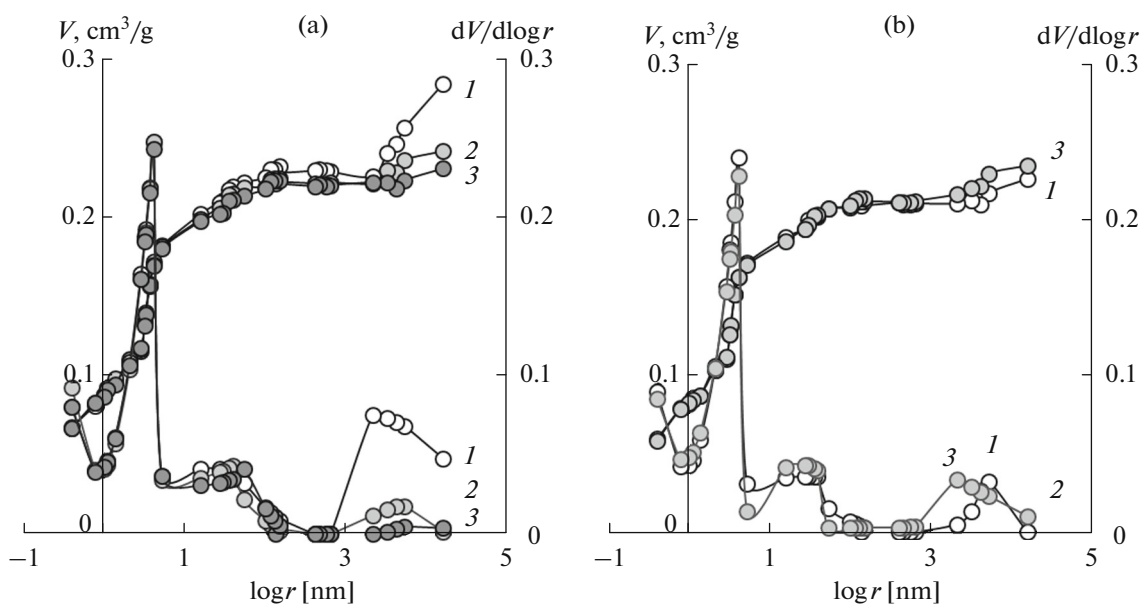


Fig. 3. Integral and differential curves of the water distribution over effective pore radii in membranes (a) MF-4SK and (b) MF-4SK/PANI in different forms: (1) H^+ ; (2) Ni^{2+} ; (3) Cr^{3+} .

Based on porosimetric curves, we calculated the maximum water content (V_0), the total internal specific surface (S), the distance between the fixed groups (L), the fraction of selective micro and mesopores (gel pores) in the total volume of membrane ($\frac{V_{\text{gel}}}{V_0}$), the volume fraction of macropores in the swelled membrane ($\frac{V_{\text{macro}}}{V_{\text{sw}}}$), the specific water content of the membrane (n) [41]. Table 3 shows the calculated structure characteristics for membranes MF-4SK and MF-4SK/PANI in different ionic forms.

As follows from Table 3, the nature of counter-ion had almost no effect on the characteristics of the membrane microstructure, viz., the specific internal surface, the distance between fixed groups, and the

interfacial charge density. However, when passing from the H^+ form to the Cr^{3+} form, the parameter $\frac{V_{\text{gel}}}{V_0}$ that characterizes the membrane selectivity increased by 25%. This is explained by the decrease in the volume of free water contained in macropores, which was also reflected by the value of parameter $\frac{V_{\text{macro}}}{V_{\text{sw}}}$. Modifying the MF-4SK membrane with polyaniline stabilized its structure as a result of which the changeover of the counter-ion H^+ for Ni^{2+} did not induce so large changes in the structure characteristics.

Current–Voltage Curves

The comparative studies of CVCs for original and modified membranes in solutions of different electro-

Table 3. Characteristics of the porous structure of MF-4SK membranes in different ionic forms

Membrane	Counter-ion	V_0 , cm^3/g	S , m^2/g	L , nm	$\frac{V_{\text{gel}}}{V_0}$	$\frac{V_{\text{macro}}}{V_{\text{sw}}}$	n , mol $\text{H}_2\text{O}/\text{mol SO}_3^-$
MF-4SK	H^+	0.33	255	0.68	0.63	0.13	20.2
	Ni^{2+}	0.26	254	0.68	0.78	0.07	16.1
	Cr^{3+}	0.26	252	0.68	0.79	0.07	15.6
MF-4SK/PANI	H^+	0.27	240	0.68	0.72	0.09	16.6
	Ni^{2+}	0.26	240	0.66	0.74	0.08	16.0

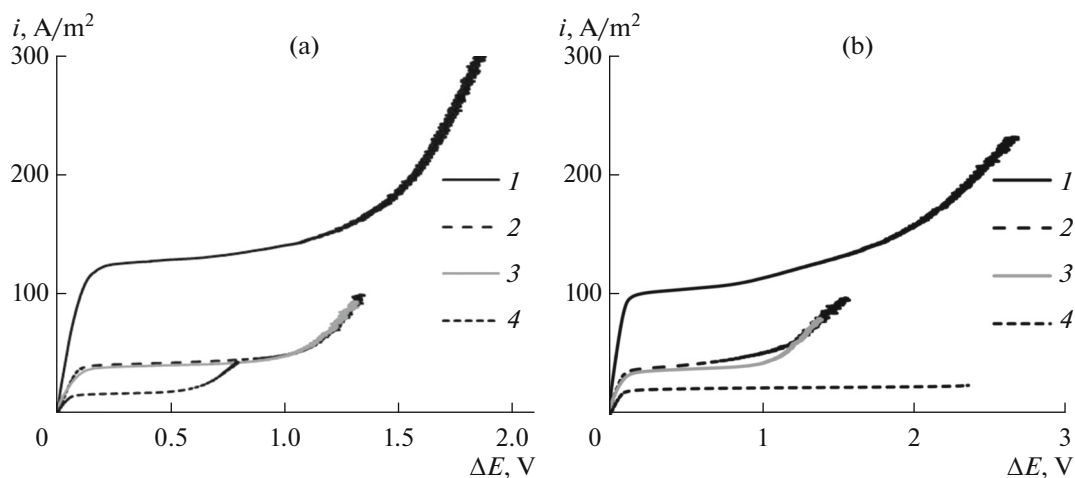


Fig. 4. CVCs of original membranes (a) MF-4SK, (b) MK-40 in solutions of different electrolytes: (1) 0.025 M H₂SO₄; (2) 0.0125 M H₂SO₄ + 0.0125 M NiSO₄; (3) 0.05 M NaCl; (4) 0.025 M NiSO₄.

lytes made it possible to single out the effect of the modifier on the electrochemical behavior of the electromembrane system in the underlimiting and overlimiting working modes. Traditionally, the electro dialysis uses the underlimiting mode, because the increase in the current above the limiting value leads to the development of conjugated effects of concentration polarization. The most considerable of the latter effects are the electroconvection and the water splitting [42]. The electroconvection makes it possible to increase the overlimiting mass transfer, being thus a positive effect, whereas the water splitting induces the pH variations in the near-membrane solution layer so that electric current is consumed in the transfer of hydrogen ions and hydroxide anions, which decreases the current efficiency in target ions and increases the energy consumption. Moreover, if the solution contains cations capable of forming poorly soluble hydroxides, the appearance of OH⁻ ions in the near-membrane layer leads to their deposition on the membrane, which increases the electric resistance and blocks the surface for the ion transfer. These factors also increase the consumed energy and decrease the efficiency of electro dialysis.

According to the Pears equation, i_{lim} depends on the concentration (C , M), the diffusion coefficient of electrolyte in solution (D , m²/s), the difference between transport numbers of counter-ions in the membrane (t_i^*) and in the solution (t_i), and the diffusion layer thickness on the permeate side of membrane (δ , m):

$$i_{lim} = \frac{DCF}{(t_i^* - t_i)\delta},$$

where F is the Faraday constant. Furthermore, the membrane surface state also has a substantial effect on

the quantity i_{lim} and the development of electroconvection [43–46]. Thus, the development of geometrical or electric microheterogeneities on the surface can intensify the electroconvection and change the limiting current density [47, 48].

Figure 4 shows CVCs of the original membranes MK-40 and MF-4SK in solutions under study. The i_{lim} value was somewhat higher for MF-4SK as compared with MK-40 in the sulfuric acid solution and approximately the same in all the other solutions except for nickel sulfate. The lower i_{lim} values for the heterogeneous membrane in sulfuric acid solution were associated with the lower fraction of the conducting surface as compared with the homogeneous membrane, which led to the higher concentration polarization at the same current and, correspondingly, to the earlier onset of the limiting state [49]. In the nickel sulfate solution, i_{lim} of membrane MK-40 was higher by a factor 1.6 as compared with MF-4SK. Moreover, for both membranes the highest i_{lim} was observed in sulfuric acid solution, which was associated with the highest values of the diffusion coefficient of electrolyte and the transport number of H⁺ counter-ions in solution. The lowest i_{lim} values for both membranes were observed in the nickel sulfate solution, in agreement also with the minimum value of diffusion coefficient in this solution (Table 4). The value of i_{lim} in the solution containing a mixture of sulfuric acid and nickel sulfate was between the corresponding values in individual solutions of H₂SO₄ and NiSO₄. However, i_{lim} in the mixture was substantially lower than in sulfuric acid for both membranes (by a factor of 2.7 for MK-40 and 3-fold for MF-4SK). Moreover, the i_{lim} value in the mixed solution was only 70% of its value in the nickel sulfate solution for the heterogeneous membrane, whereas for MF-4SK it was lower by a factor 2.8. These results agreed with the data obtained in [50]

Table 4. The limiting current density of original membranes MK-40 and MF-4SK in various solutions and the properties of solutions

Solution	$D \times 10^9, \text{m}^2/\text{s}$ [37]	$t_+ [37]$	$i_{\text{lim}}, \text{A}/\text{m}^2$		Δ, V	
			MK-40	MF-4SK	MK-40	MF-4SK
H ₂ SO ₄	2.61*	0.839	100 ± 9	120 ± 10	1.7 ± 0.2	1.3 ± 0.15
NiSO ₄	0.86	0.404**	22.2 ± 0.4	14 ± 2	—	0.59 ± 0.07
H ₂ SO ₄ + NiSO ₄	—	—	37 ± 2	39 ± 1	1.14 ± 0.04	1.02 ± 0.02
NaCl	1.61	0.387	37.2 ± 0.4	40 ± 2	1.07 ± 0.03	0.90 ± 0.04

* Diffusion coefficients of sulfuric acid and nickel sulfate were calculated as the geometrical mean of diffusion coefficients of the corresponding ions with due regard to their charge.

** The transport number of Ni²⁺ ions calculated as the ratio of the limiting equivalent conductivity of Ni²⁺ to the sum of limiting equivalent conductivity of ions Ni²⁺ and SO₄²⁻.

on the determination of the Nikolsky constant based on the concentration dependences of the conductivity in individual and mixed electrolyte solutions containing two types of counter-ions and a common co-ion. Similar to the case of i_{lim} in CVCs, the conductivity in the mixed solution was closer to that in the solution containing two-charged counter-ions. These facts confirmed the well-known concept on the preferential sorption of two-charged counter-ions as compared with singly charged ions and also on the relationship between the equilibrium (Nikolsky constant) and transport (conductivity, CVCs) properties of membranes.

The length of the limiting current plateau was approximately the same for both membranes, decreasing in the row: sulfuric acid, mixture of sulfuric acid and nickel sulfate, sodium chloride. We failed to determine this characteristic in sulfuric acid solution for membrane MK-40 due to the formation of a deposit on its surface which led to the absence of the overlimiting state in CVCs. For the membrane MF-4SK, the limiting current plateau was the shortest in the nickel sulfate solution (Table 4). It is interesting that CVCs in solutions of sodium chloride and the mixture of sulfuric acid and nickel sulfate coincided almost completely. Presumably, this was associated with the close properties of solutions; however, this requires additional tests. On the whole, our results well agreed with the concept that the properties of solutions and membranes can affect the CVC parameters.

In [40] it was shown that CVCs can be used as test signals for assessing the permselectivity with respect to singly and multiply-charged ions. In the cases of the pronounced CVC asymmetry of a modified membrane, i.e., the substantial difference in i_{lim} and the length of limiting plateau at different film orientations with respect to the ion flow, this can point to the presence of permselectivity. This is why, the CVCs of membranes MF-4SK/PANI and MK-40/PANI were measured in solutions of different electrolytes at dif-

ferent orientation to the flow of counter-ions. Figure 5 shows these results.

The appearance of the PANI layer had no effect on the CVC parameters of the heterogeneous membrane and its i_{lim} values remained unchanged within the experimental error for different orientations with respect to the counter-ion flow for both membrane MK-40/PANI and the original membrane MK-40. Similar to the case of original membrane MK-40, we failed to observe the transition to the overlimiting state in CVCs for the modified membrane in nickel sulfate solutions. However, a certain asymmetry was observed as regards the plateau length depending on orientation of membrane MK-4SK/PANI with respect to the counter-ion flow. The latter effect was the most pronounced in the solution of nickel sulfate and sulfuric acid: the quantity Δ was higher by a factor of 1.5 for the orientation with the unmodified side to the counter-ion flow. In the sulfuric acid solution, the effect of asymmetry decreased to 30% and almost disappeared in the sodium chloride solution. The shortening of the limiting current plateau with the increase in the electro-membrane system conductivity determined from the slope of the overlimiting CVC region pointed to the earlier development of electroconvection, which could be associated with homogenization of the surface of the heterogeneous membrane by the PANI layer and the decrease in its electric heterogeneity as compared with the original membrane. A possible reason can be the increase in the membrane surface hydrophilicity because PANI is more hydrophilic as compared with the original membrane MK-40 and the contact angle is 72° for MK-40 [51] and 65° for PANI [52]. However, both these assumptions require additional studies. Thus, the heterogeneous membranes modified with PANI may show promise in the electro-dialysis of solutions containing acids.

As expected, the more interesting effects were observed in CVCs of the PANI-modified homogeneous membrane (Fig. 5). The most unexpected effect was the insignificant asymmetry of CVC parameters

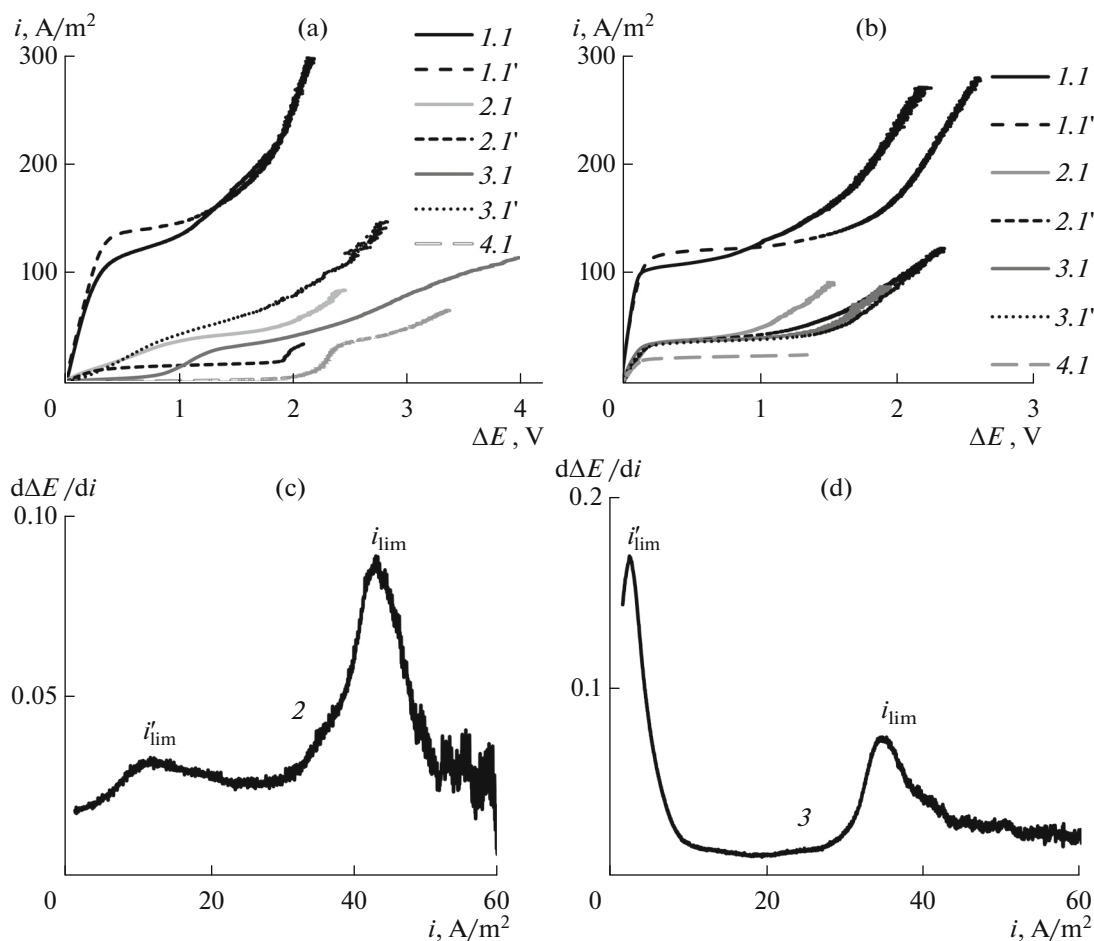


Fig. 5. (a, b) Integral and (c, d) differential CVCs of modified membranes (a, c, d) MF-4SK/PANI and (b) MK-40/PANI in solutions of different electrolytes: (1) 0.025 M H₂SO₄; (2) 0.0125 M H₂SO₄ + 0.0125 M NiSO₄; (3) 0.05 M NaCl; (4) 0.025 M NiSO₄. Orientation of membrane by its modified and unmodified sides with respect to electrolyte solution is indicated by symbols *I* and *I'* placed after the number, respectively.

for membrane MF-4SK/PANI and the absence of the pseudolimiting current in CVCs for its orientation with the modified surface to the cationic flow in sulfuric acid solution. Moreover, all CVC parameters in both orientations of the membrane turned out to be invariant within the experimental error also after the long-term storage of the modified membrane and at their repeated determination. This points, first of all to the reproducibility of this effect and its nonrandom character and, secondly, to the stability of properties of this material. Thus, the i_{lim} value and the length of the limiting current plateau were higher by 20 and 70%, respectively, for the orientation with the unmodified side to the counter-ion flow as compared with the opposite orientation. Such insignificant deviations in the CVC parameters of modified membranes were observed earlier; however, the total absence of the pseudolimiting current was observed only in sodium hydroxide solutions, which may be associated with complete deprotonation of PANI [53]. In this case, the asymmetry of CVCs of the modified membrane com-

pletely disappeared and the CVC parameters became equal to the corresponding parameters of the original membrane. However, it is evident that this explanation cannot be true for the sulfuric acid solution.

In the nickel sulfate solution, we failed to measure CVCs for the MF-4SK/PANI membrane due to the active deposition which, in the very first measurements, led to a considerable increase in the voltage drop on the membrane and the strong deformation of the CVC form. Furthermore, in the sodium chloride solution and the mixed solution of nickel sulfate and sulfuric acid, we observed both the characteristic asymmetry of CVC parameters and the pseudolimiting current which appeared as the first extremum in the low voltage drop region of the differential CVC (Figs. 5c and 5d). Such a form of CVC may point to the presence of permselectivity with respect to singly charge ions, similar to that observed in [40] in solution containing potassium chloride and hydrochloric acid.

CONCLUSIONS

The electrotransport and structure characteristics of sulfocationic membranes MK-40 and MF-4SK before and after their modification with polyaniline are studied. It is shown that the interaction of multiply-charged counter-ions with several fixed ions decreases their mobility in the membrane but makes easier the transport of co-ions. Hence, as the charge of counter-ion increases, the conductivity of the membrane decreases and its diffusion permeability increases. As a result of formation of a dense layer of positively charged modifier on the surface of the homogeneous membrane, the concentration dependence of its conductivity in solutions containing multiply-charged cations is descending.

Studying the structure of membrane MF-4SK in its forms with different counter-ions by the method of standard contact porosimetry shows that the transition from its H^+ form to Cr^{3+} form is accompanied by the 25% decrease in the free water volume. However, after its modification with PANI the membrane structure is stabilized and the substitution of the counter-ion Ni^{2+} for H^+ induces no substantial changes on the structure characteristics.

It is found that modifying heterogeneous and homogeneous membranes with PANI has different effect on their current–voltage curves. Thus, for heterogeneous membranes, the earlier onset of the over-limiting state is observed, which is associated with the development of electroconvection due to the decrease in the electric heterogeneity of the surface as a result of the appearance of PANI on the surface. The increase in the conductivity of the electromembrane system containing the modified MK-40 membrane as compared with the original membrane points to good prospects for such materials in electro dialysis of solutions containing acids.

Modifying the homogeneous membrane induces substantial changes in the form of CVC leading to the appearance of asymmetry depending on the membrane orientation with respect to the counter-ion flow. The effects are the most pronounced in the sodium chloride solution and the mixed solution of sulfuric acid and nickel sulfate. The observed changes in the CVC parameters may point to the appearance of permselectivity with respect to singly charged ions as compared with multiply-charged ions, which allows using MF-4SK/PANI membranes for electro dialytic separation of singly and multiply-charged ions.

FUNDING

This study was supported by the Ministry of Science and Higher Education of the Russian Federation (project FZEN-0022).

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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Translated by T. Safonova