


Using a microheterogeneous model to assess the applicability of ion-exchange membranes in the process of reverse electro dialysis

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This article belongs to the regular issue.

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Abstract

This paper shows the possibility of using a microheterogeneous model to describe the properties of ion-exchange membranes and calculate the characteristics of a reverse electro dialyzer from the data obtained. We studied the properties of eight samples of heterogeneous cation exchange membranes (two samples of each type of membrane). The samples differed in the year of issue and storage conditions. It is shown that for heterogeneous ion-exchange membranes MK-40 and MA-41, the samples' properties can differ significantly. The counterions transport numbers calculated within the framework of the microheterogeneous model for Ralex membranes differ insignificantly. The counterion transport number in 1 mol/L sodium chloride solution is 0.96 for Ralex CM and 0.98 ± 0.01 for Ralex AMH. For the MK-40 membrane, the transport number in the same solution is 0.94 ± 0.04 , and for the MA-41 membrane, it is 0.85 ± 0.1 . The possibility of calculating the transport numbers and predicting the open-circuit voltage based on simple physicochemical measurements allows selecting the best membrane pairs for the reverse electro dialysis process. Comparison of the open-circuit potential value calculated using the obtained transfer numbers with experimental data showed that in the case of using Ralex membranes, the difference between the experimental and calculated values is 2%. The calculated value of the open circuit potential was 0.19 V/membrane pair or 1.69 V for the investigated reverse electro dialyzer with nine pair chambers.

Keywords

reverse electro dialysis
ion-exchange membrane
conductivity
diffusion permeability
microheterogeneous model

Received: 30.03.2021

Revised: 28.04.2021

Accepted: 30.04.2021

Available online: 30.04.2021

1. Introduction

Electro dialysis is an electromembrane process designed to remove ionic impurities from aqueous solutions. In electro dialysis, ion-exchange membranes of two types are used: cation-exchange membranes permeable only for cations and anion-exchange membranes permeable only for anions. When an electric current is applied to the electro dialysis apparatus, which consists of a plurality of alternating cation-exchange and anion-exchange membranes, migration of cations occurs through the cation-exchange membranes and the migration of anions through the anion-exchange membranes. During the operation of the electro dialyzer, the concentration of ionic components in one

chamber, called the desalination chamber, decreases, and in the other, called the concentration chamber, increases. The two membranes (cation exchange and anion exchange) and the desalination chamber and the concentration chamber are collectively called a membrane pair. The collection of all membrane pairs in an electro dialyzer is called a membrane stack.

Electro dialysis can be used in several industrial processes associated with the transfer of ions: desalination of aqueous solutions [1,2], electromembrane synthesis [3], concentration of salts and acids [4,5], processing solutions in the agro-food industry [6], processing highly concentrated effluents from installations for obtaining drinking water from the sea [7,8]. In the latter case, the generated

highly concentrated effluents can also be used as a source of “blue” electricity using a process called reverse electro-dialysis [9].

Reverse electro-dialysis is a process of generating electricity based on the utilization of energy released when two solutions with different concentrations are mixed. When using an ion-exchange membrane, which separates concentrated and dilute electrolyte solutions, due to the diffusion of a substance through the membrane, an ion flux (electric current) occurs. At the interfaces between a dilute solution/membrane and a membrane/concentrated solution, a potential difference occurs called the Donnan potential. The sum of the two potential drops at the left and right sides of the membrane is called the membrane potential (E_m). Its value is determined by the ratio of ions' activities in solutions to the right and left of the membrane. Since each of the two membranes (cation-exchange (CEM) and anion-exchange (AEM)) has its own membrane potential, the total potential drop on the membrane pair will be the sum of two membrane potentials:

$$E_{\text{RED}} = N(E_m^{\text{CEM}} + E_m^{\text{AEM}})$$

$$E_m^{\text{CEM}} = \alpha^{\text{CEM}} \frac{RT}{nF} \ln \frac{a_b^+}{a_d^+} = \frac{RT}{nF} \ln \frac{c_b^+ \gamma_b^+}{c_d^+ \gamma_d^+}, \quad (1)$$

$$E_m^{\text{AEM}} = \alpha^{\text{AEM}} \frac{RT}{nF} \ln \frac{a_b^-}{a_d^-} = \frac{RT}{nF} \ln \frac{c_b^- \gamma_b^-}{c_d^- \gamma_d^-}$$

where N is the number of membrane pairs; α is the permselectivity of ion-exchange membrane; c is the electrolyte concentration, mol/L; γ is the ion activity coefficient; lower indexes “ b ” and “ d ” denote high concentration solution (brine) and low concentration solution (diluate); n is the number of electrons; R , T , F are universal gas constant, absolute temperature, and Faraday constant.

In recent years, interest in reverse electro-dialysis has grown significantly, as evidenced by many reviews devoted to this topic. Tian *et al.* [10] considered the effect of the electrode material and the redox pair used, the most important operating parameters (solution pumping rate, concentration of brine and dilute solutions, membrane channel geometry, etc.) were considered by Mei and Tang [11], current achievements and existing problems are disclosed by Pawlowski *et al.* [12].

For the first time, the possibility of transforming the concentration gradient in natural conditions (for example, at the mouth of a river flowing into the sea) was shown by Pattle in 1954 [13]. The energy density obtained in work was 0.2 W/m² at 39 °C using a hydroelectric pile composed of alternate 47 CEMs and 47 AEMs.

Further development of the technology made it possible to increase the energy density. Nowadays, the average value of the energy density is 0.94 ± 0.4 W/m² when using a concentrated solution, either solution from solar ponds or effluents from desalination plants (data from review [14] were taken to calculate the average value).

The increase in power density is achieved in various ways. Researchers pay special attention to the ion-exchange membranes used and their properties [14–16].

One of the key properties of membranes is their selectivity, i.e., cation-exchange membranes' ability to transfer only cations, and of anion-exchange membranes only anions. Considering the imperfect selectivity of ion-exchange membranes, the equation for the open-circuit voltage (OCV) of the reverse electro-dialyzer takes the form:

$$E^{\text{OCV}} = N \frac{RT}{nF} \ln \left(\frac{c_b \gamma_b^+}{c_d \gamma_d^+} \right) \left(\frac{T_{\text{CEM}}^+ - t^+}{1 - t^+} + \frac{T_{\text{CEM}}^- - t^-}{1 - t^-} \right), \quad (2)$$

where T_{CEM}^+ , T_{AEM}^- are the counterion transfer numbers in the cation- and anion-exchange membrane; t^+ , t^- are the counterion transfer numbers for a given membrane in solution.

The open circuit voltage is the driving force of the RED process and represents the sum of potential differences over each membrane [17].

The terms in the last parenthesis in Eq. (2) represent the selectivity of the cation-exchange and anion-exchange membranes (the first term in parentheses is α^{CEM} , and the second is α^{AEM}). The membranes' selectivity can be determined knowing the values of the counterion transport number in the membrane, for which the membrane potential method can be used [18]. However, the transport numbers determined by this method will be “apparent” since they do not consider the transfer of water molecules within the hydration shells of ions. To obtain the “true” value of the transport number, one can use the Skachard equation [19]. However, its use requires the water transport number's values, which are also difficult to determine experimentally.

One can calculate the “true” transport numbers across an ion-exchange membrane from the concentration dependences of electrical conductivity and diffusion permeability using the microheterogeneous model [20]. In view of the microheterogeneous model, the ion-exchange membrane is represented as a combination of two phases called “gel” and “intergel solution”. Integral properties of the membrane, such as electrical conductivity and diffusion permeability, are determined as the geometric mean of some electrotransport coefficients different for the gel and intergel phases.

The aim of this work is to test the possibility of using a microheterogeneous model and data on the concentration dependence of the transfer numbers of ions for various ion-exchange membranes to calculate the open-circuit potential and select the best membrane pair for carrying out the reverse electro-dialysis process.

2. Experimental

2.1. Membranes

The objects of the study were heterogeneous ion-exchange membranes MK-40, MA-41 (Shchekinoazot, Russia), and Ralex CM, Ralex AMH (Mega a.s., Czech Republic). Two samples of each membrane were studied representing membranes of different batches and years of production (named batch 1 and batch 2 later in the text).

The properties of membranes can change during storage because of material degradation due to UV radiation, exposure to atmospheric oxygen, changes in temperature and humidity. In addition, the batches of ion-exchange membranes themselves may differ in their properties, which depend on the conditions for obtaining each specific batch.

Table 1 shows the years of production of the tested membranes.

All studied heterogeneous membranes were produced by hot pressing (MK-40, MA-41) or rolling (Ralex CM, Ralex AMH) of the thermoplastic mixture consisting of the fine powder of the ion-exchanger and polyethylene, in the approximate ratio of 2:1. The ion-exchanger used in the production of membranes MK-40, MA-41, Ralex CM and Ralex AMH can be classified as polymer obtained by copolymerization of polystyrene with divinylbenzene. By type of the ionogenic groups, the membranes MK-40 and Ralex CM are strong-acid cation-exchange with sulfonic acid ionogenic groups, MA-41, Ralex AMH are strong-basic anion-exchange with quaternary ammonium bases.

Physicochemical properties of the membranes provided by the manufacturers are given in Table 2.

All membranes were subjected to the following pre-treatment procedure prior to the study:

- surface treatment with carbon tetrachloride for degreasing;
- soaking in ethanol for 6 hours to remove residues of monomers and oligomers from the ion-exchange resin;
- soaking of the membrane in excess volume (≈ 20 volumes of the membrane) of 1 M NaCl solution for 24 hours;
- washing of the obtained membranes with deionized water to a constant value of the electrical conductivity of the wash water.

The membranes prepared by this method were equilibrated with the working solution in which they were stored before the testing.

2.2. Study of the electrical conductivity

A mercury-contact method [22] was used for the study of the electrical conductivity of membranes. In this method, the membrane is placed between two mercury electrodes, so that a perfect adjoining of the electrode surface to the membrane is achieved. The internal resistance of mercury is insignificant in comparison with membrane resistance, which allows attributing the whole measured value to the membrane resistance only. The membranes were “air-dry”; thus, the formation of electrode/solution and solution/membrane non-ohmic boundaries is excluded. To obtain “air-dry” membranes the excess electrolyte solution was removed from the membrane surface prior to the measurement. Presence of the solution on the membrane surface may lead to an apparent low conductivity of the membrane as shown in [23].

A mercury-contact cell with a membrane was connected to the PARSTAT 4000 impedance meter (Fig. 1a). The connection was made using a two-electrode circuit.

The spectrum of the electrochemical impedance of the membrane (Fig. 1b) was recorded in the frequency range from 500 kHz to 10 Hz with a zero constant current component and an amplitude of the alternating current signal of 100 μ A.

Extrapolation of the spectrum's linear section in the high-frequency area allows obtaining a value of the active (ohmic) membrane resistance (R) (Fig. 1b). The obtained value is converted into electrical conductivity according to the equation:

$$\kappa_m^{AC} = \frac{l}{RS} \quad (3)$$

The obtained value of electrical conductivity is called electrical conductivity in alternating current, it is related to electrical conductivity in direct current by the following relationship:

$$\kappa_m^{DC} = \kappa_m^{AC} t_+^2, \quad (4)$$

where κ_m^{AC} is the experimentally determined electrical

Table 1 Year of production of membranes studied

Membrane*	MK-40 1	MK-40 2	Ralex CM 1	Ralex CM 2	MA-41 1	MA-41 2	Ralex AMH 1	Ralex AMH 2
Year of production	2002	2015	2008	2017	2010	2015	2008	2017

* the number near the membrane name indicates the batch

Table 2 Physicochemical properties of the membranes studied

Membrane	Ralex CM	Ralex AMH	MK-40	MA-41
Functional groups	$-\text{SO}_3^-$	$-\text{N}^+(\text{CH}_3)_3$	$-\text{SO}_3^-$	$-\text{N}^+(\text{CH}_3)_3$
Ion-exchange resin	Lewatit S100	Lewatit M500	KU-2-8	AV-17-8
Inert binder	LDPE			
Reinforcing mesh	Ulester 32S		Nylon	
Ion-exchange capacity, mmol/g-wet	1.12	0.86	1.08	0.91
Water content, %	44	45	33	36
Wet thickness, μ m	720	750	540	530
Radii of the ion-exchanger on the membrane surface [21], μ m	1-14	-	2-26	-

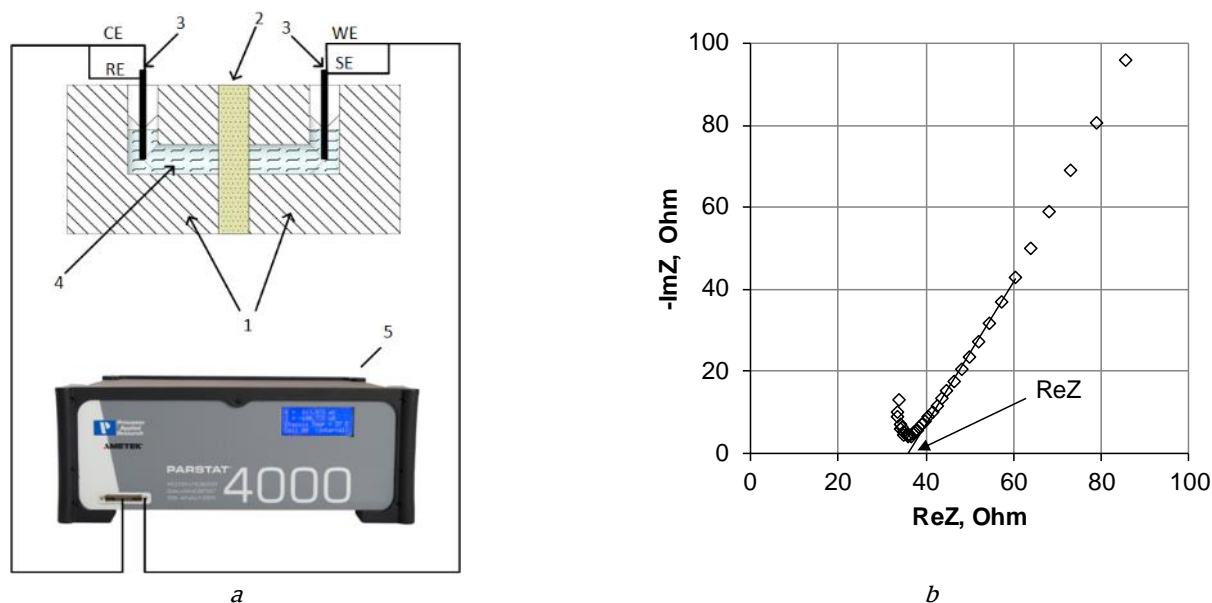


Fig. 1 The scheme of the mercury-contact cell (a) and a frequency spectrum example of the electrochemical impedance (b). 1 - mercury-contact cell, 2 - studied membrane, 3 - platinum electrodes, 4 - mercury, 5 - impedance meter.

conductivity of the membrane on alternating current, S/cm; t_+ is the counterion transport number in the solution; f_2 is the portion of intergel solution in the membrane [20].

2.3. Study of the diffusion permeability

A non-flow two-chamber cell was used for the study of the diffusion permeability. One half of the cell contained a salt solution, and the second half contained distilled water (Fig. 2). The half-cells were separated from each other by the studied membrane. A flow water jacket with constant temperature due to the thermostat was used outside the

non-flow semi-cells. The solutions in the non-flow cells were vigorously mixed using vertical mechanical mixers. This mixing is necessary to minimize the concentration polarization in the chamber and to eliminate the effect of the diffusion layer on the transport of ions through the membrane. It was experimentally determined that to remove the effect of concentration polarization on the parameters of diffusion transport through the membrane, a rotational mixers speed of 800 rpm is necessary. The resistance of distilled water was measured during the experiment at a frequency of 1/20 s using Pt/Pt electrodes connected to the E7-21 immittance meter.

Based on the calibration dependence of the solution concentration on its resistance, the initial experimental data were recalculated into the concentration change rate of time dc/dt . Based on the obtained data, it is possible to calculate the salt flow through the membrane (j_m) and the integral coefficient of diffusion permeability (P_m):

$$j_m = \frac{V dc}{S dt}, \tag{5}$$

$$P_m = \frac{j_m l}{c}. \tag{6}$$

2.4. Electromigration transport numbers of salt ions

Electromigration transport numbers of counter and co-ions can be calculated based on the data on the diffusion permeability and electrical conductivity of an ion-exchange membrane [20].

For a 1:1 electrolyte, the counterion transport number (t_g^*) is defined as

$$t_g^* = \frac{L_g}{L_g + L_{co}}, \tag{7}$$

where L_g and L_{co} are the electrodiffusion coefficients of ion transport. Their values are found using the following relations:

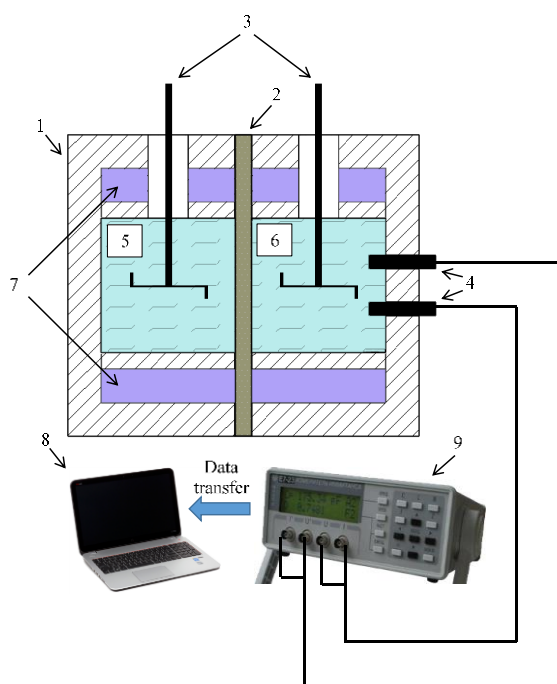


Fig. 2 Diffusion cell diagram. 1 - diffusion cell, 2 - studied membrane, 3 - mechanical mixers, 4 - platinum electrodes, 5 - semi-cell containing salt solution, 6 - semi-cell containing distilled water, 7 - water cooling jacket, 8 - computer, 9 - E7-21 immittance meter

$$L_g = \frac{\kappa_m^{DC}}{2F^2} \left(1 + \sqrt{1 - \frac{2F^2}{RT} \frac{P^*c}{\kappa_m^{DC} \pi_{\pm}}} \right), \quad (8)$$

$$L_{co} = \frac{\kappa_m^{DC}}{2F^2} \left(1 - \sqrt{1 - \frac{2F^2}{RT} \frac{P^*c}{\kappa_m^{DC} \pi_{\pm}}} \right),$$

where P^* is the differential diffusion permeability coefficient at concentration c , m^2/s , c is the concentration of the external solution, mol/m^3 ; π_{\pm} is the correction factor for the nonideality of the solution; F , R , T are the Faraday constant, the universal gas constant and the absolute temperature.

The differential diffusion permeability coefficient is calculated from the integral diffusion permeability coefficient (P_m):

$$P^* = P_m + c \frac{dP_m}{dc}. \quad (9)$$

The correction factor for the nonideality of the solution:

$$\pi_{\pm} = 1 + c \frac{d \ln \gamma_{\pm}}{dc}, \quad (10)$$

where γ_{\pm} is the average ionic activity ratio of the electrolyte.

3. Results and Discussion

3.1. Conductivity measurements

The results of measuring the electrical conductivity of ion-exchange membranes of two batches in a wide range of concentrations are shown in Fig. 3.

Within the microheterogeneous model, the conductivity of a heterogeneous ion-exchange membrane is the geometric mean of the conductivities of the phase of the ion-exchange material itself (the so-called “gel”) and the phase of an electrically neutral solution (also called intergel solution). The gel phase includes the polymer matrix of the ion exchanger, the condensed ion pairs counterion-fixed group, the solution inside the electric double layer, the reinforcing fabric, and the inert binder. The intergel

phase includes a solution that predominantly occupies macropores in the ion-exchange membrane phase. It is generally accepted that such a solution's physicochemical properties do not differ from the properties of an equilibrium external solution.

In view of the above, the conductivity of the membrane is expressed as follows:

$$\kappa_m = (f_1 \kappa_{iso}^{\alpha} + f_2 \kappa_s^{\alpha})^{1/\alpha}, \quad (11)$$

where f_1 and f_2 are the fractions of gel and intergel solutions and $f_1 + f_2 = 1$; κ_m , κ_{iso} and κ_s are the electrical conductivities of the membrane, gel and external solution, S/cm ; α is the characteristic parameter which describes the spatial distribution of conducting phases in the membrane ($\alpha = +1$ for parallel and $\alpha = -1$ for series-connected phases – in real samples the α parameter takes values in range 0.1-0.3).

In dilute solutions near the point of isoelectric conductivity (such a value of electrical conductivity when $\kappa_m = \kappa_s = \kappa_{iso}$), Eq. (11) is simplified:

$$\kappa_m = \kappa_{iso}^{f_1} \kappa_s^{f_2}. \quad (12)$$

It can be seen that the linearization of the equation in logarithmic coordinates $\lg \kappa_m = f(\lg \kappa_s)$. makes it possible to determine the value of the parameter f_2 .

The found values of the parameter f_2 and the coordinates of the isoelectric conductivity point for the membranes under study are given in Table 3.

Table 3 Values of coordinates of the point of isoelectric conductivity and transport-structural parameter f_2 for the studied ion-exchange membranes

Membrane*	f_2	κ_{iso} , mS/cm	c_{iso} , mol/L
MK-40 1	0.10	5.0	0.046
MK-40 2	0.12	6.0	0.056
Ralex CM 1	0.06	3.6	0.032
Ralex CM 2	0.03	4.0	0.037
MA-41 1	0.12	1.9	0.017
MA-41 2	0.14	2.8	0.025
Ralex AMH 1	0.04	4.3	0.039
Ralex AMH 2	0.07	4.6	0.042

* the number near the membrane name indicates the batch

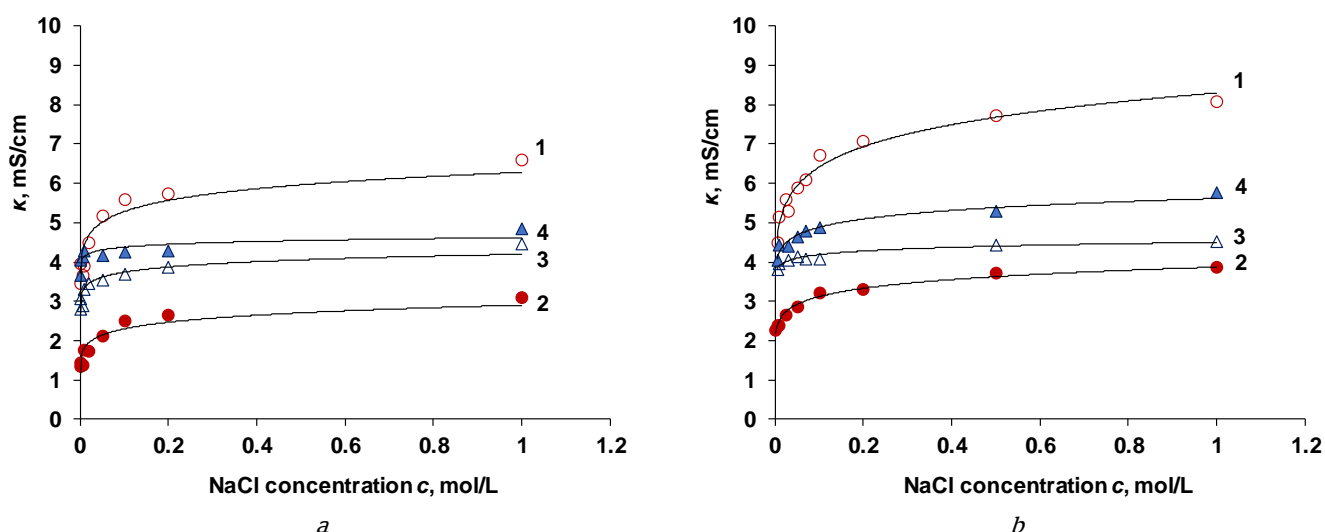


Fig. 3 Concentration dependence of the electrical conductivity of the ion-exchange membranes batch 1 (a) and batch 2 (b). Membranes: 1 – MK-40, 2 – MA-41, 3 – Ralex CM, 4 – Ralex AMH

It can be seen that for heterogeneous Ralex membranes, the value of the f_2 parameter is comparable to the value of this parameter for homogeneous membranes. Such values of this parameter were obtained in other works [24–26]. In [24], the authors suggested that such a value of the fraction of the intergel solution for these membranes is a consequence of the fact that the particles of the ion exchanger in these membranes are small enough and, at the same time, there are no macroscopic cavities inside the membrane, which electrically neutral solutions can occupy. These structural features of Ralex membranes were demonstrated by Akberova et al. [27] and Slouka et al. [28].

From the point of view of the influence on reverse electrodialysis, a large value of the parameter f_2 (characteristic of heterogeneous membranes MK-40, MA-41), on the one hand, provides high electrical conductivity. This difference is especially large in dilute solutions (Fig. 3). On the other hand, the electrically neutral solution in the membrane’s pores causes the decrease in selectivity.

Another factor that attracts attention is large scatter of electrical conductivity values among the samples under study (Fig. 3). According to Veerman, commercial membranes are not chemical compounds with unchanging properties; different lot numbers, years of production, and storage conditions can influence their properties [29].

3.2. Diffusion permeability

As already mentioned in the introduction, the membrane potential is significantly influenced by the selectivity of the membranes. Diffusion permeability is a value that characterizes the non-selective flux of electrolyte through an ion-exchange membrane.

The results of measuring the diffusion permeability of the studied ion-exchange membranes are shown in Fig. 4. The results obtained for diffusion permeability also differ

significantly for all studied membranes. For some samples, the results obtained when measuring the diffusion permeability correlate well with the results obtained when studying the electrical conductivity. For Ralex membranes, low values of the f_2 parameter are characteristic, which is reflected in the low dependence of the integral coefficient of diffusion permeability on the concentration of the external solution. At the same time, for the second batch, despite the same low value of the f_2 parameter, the diffusion permeability is comparable to the diffusion permeability of MK-40 and MA-41 membranes. Meanwhile, no such dependence was revealed for MK-40 and MA-41 membranes. Despite the different values of the integral coefficients of diffusion permeability obtained for different samples, the nature of the relationship between them does not change significantly.

To calculate the transport numbers according to Eq. (8), the differential (also sometimes called “local” [26]) diffusion permeability coefficient is used. In contrast to the experimentally determined integral coefficient of diffusion permeability, which is the average value over the entire thickness of the ion-exchange membrane, the differential coefficient corresponds to the diffusion permeability of a thin ion-exchange film in equilibrium with a “virtual solution” with a certain concentration c at a point in space x . To move from one coefficient to another, the following transformation is usually employed:

$$P^* = P_m + c \frac{dP_m}{dc} = P_m \beta_j, \tag{13}$$

where $\beta_j = d \lg j_m / d \lg c$ is the parameter which characterizes the concentration profile in the ion-exchange membrane [30] (linear at $\beta_j = 1$, convex at $\beta_j > 1$ or concave at $\beta_j < 1$).

The parameter values found on the basis of experimental data are shown in Table 4.

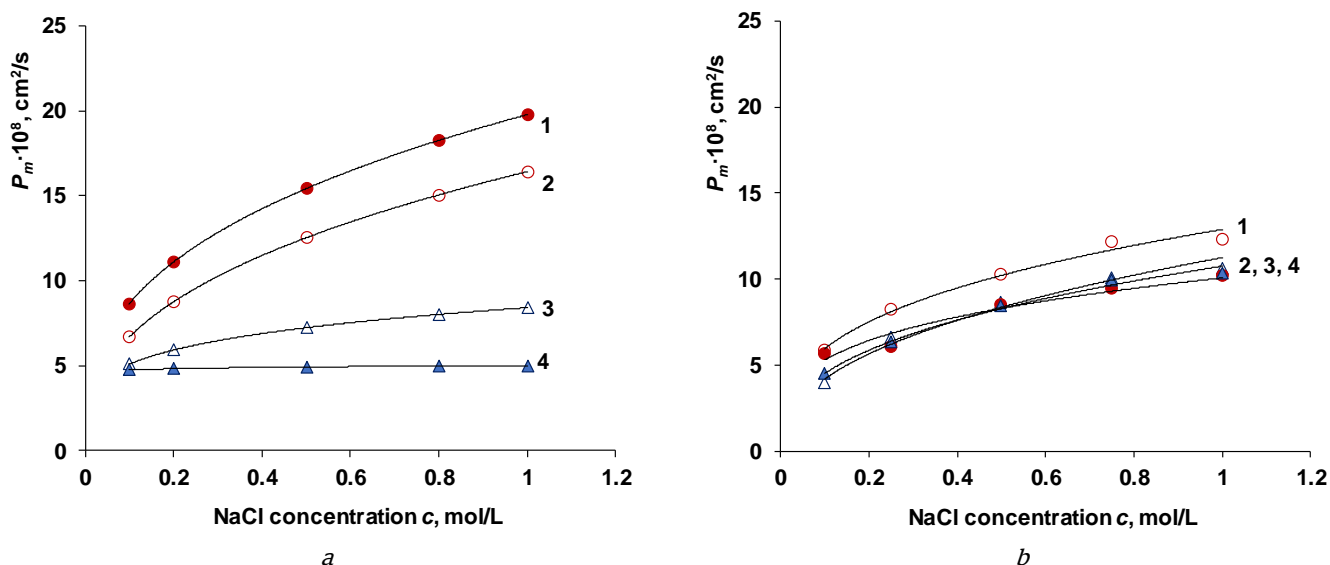


Fig. 4 Concentration dependence of the diffusion permeability of the ion-exchange membranes batch 1 (a) and batch 2 (b). Membranes: 1 – MK-40, 2 – MA-41, 3 – Ralex CM, 4 – Ralex AMH

Table 4 Parameter β_j values found for the studied ion-exchange membranes

Membrane	MK-40 1	MK-40 2	MA-41 1	MA-41 2	Ralex CM 1	Ralex CM 2	Ralex AMH 1	Ralex AMH 2
β_j	1.39	1.35	1.36	1.26	1.22	1.43	1.02	1.39

3.3. Transport numbers and OCV

According to the microheterogeneous model, the transport numbers are determined by the combined action of two factors – the electrical conductivity of the membrane (which is mainly determined by the counterion transport) and its diffusion permeability (which is determined by the co-ion transport). Moreover, both of these parameters depend on each other [30]. Thus, membranes with high diffusion permeability are characterized by high electrical conductivity in concentrated solutions. The counterion transfer number for membranes with higher diffusion permeability will be lower, since high diffusion permeability means more co-ions are present in the membrane phase. High electrical conductivity, especially in dilute solutions, is a very important characteristic for the reverse electro dialyzer process, since it allows to reduce the internal resistance losses of the electromembrane stack.

Counterion transport numbers were calculated using Eq. (7). The results are presented in Fig. 5.

It can be seen that for different samples of Ralex membranes, despite the detected differences in electrical conductivity and diffusion permeability, the transport numbers differ insignificantly, both for cation-exchange and

anion-exchange membranes. The maximum difference in concentrated (1 mol/L) solutions is negligible for Ralex CM and ± 0.01 for Ralex AMH.

For MK-40 and MA-41 membranes, the situation is drastically different. For MK-40 membrane, the difference in transfer numbers reaches ± 0.05 . The largest scatter was obtained for the MA-41 membrane, where, depending on the sample, the difference is ± 0.1 .

The low selectivity of the MK-40 and MA-41 membranes negatively affects the open circuit potential (OCV) and the power density of the reverse electro dialysis process. We used Eq. (2) and the results obtained to calculate the OCV. Let us assume that Black Sea water (brine solution) is used as working solution, the concentration of which in terms of sodium chloride is 20 g/L, and “river water” (dilute solution) with a concentration of 0.2–0.5 g/L NaCl. The number of membranes of each type is $N = 9$.

Table 5 shows the results of calculating the OCV for the “best” (denoted by “+”) and “worst” (denoted by “-”) membrane pairs among Ralex and MK-40 and MA-41 membranes.

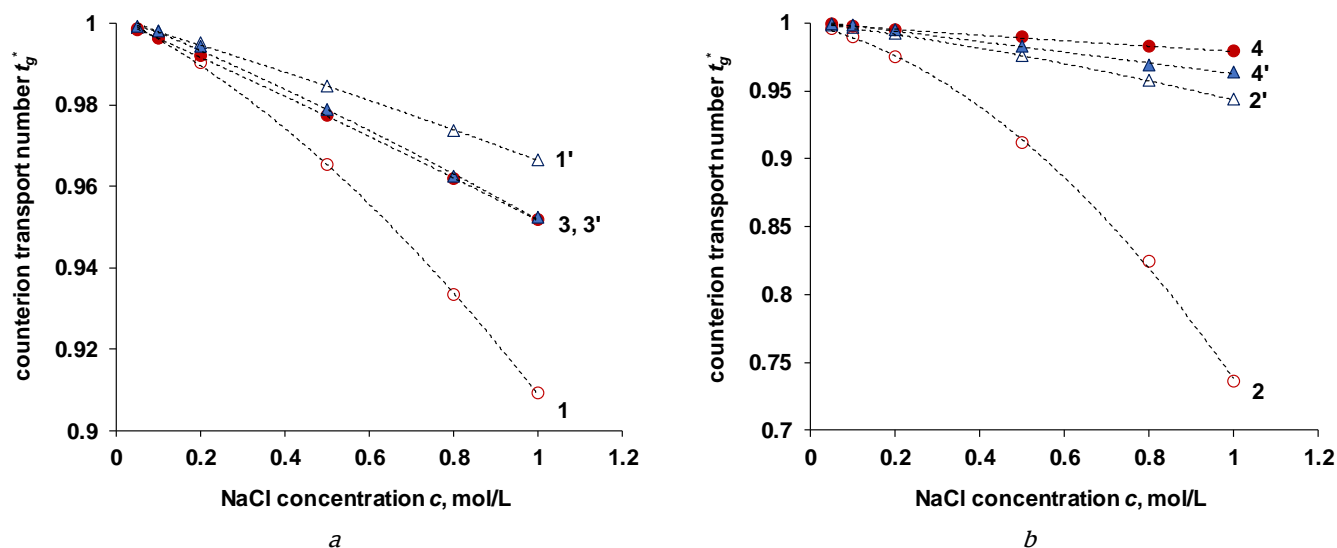


Fig. 5 Concentration dependence of the counterion transport number for cation-exchange (a) and anion-exchange (b) membranes. Batch 1 (a) and batch 2 (b). Membranes: 1, 1' – MK-40, 2, 2' – MA-41, 3, 3' – Ralex CM, 4, 4' – Ralex AMH. Membranes from batch 1 (1, 2, 3, 4) and membranes from batch 2 (1', 2', 3', 4').

Table 5 The magnitude of the open circuit potential for various membrane pairs investigated in this work

Membrane pair	MK-40 (batch 2) MA-41 (batch 2)	MK-40 (batch 1) MA-41 (batch 1)	Ralex CM (batch 1) Ralex AMH (batch 1)	Ralex CM (batch 1) Ralex AMH (batch 2)	Ideal selectivity**	Experimental***
OCV, V	1.65	1.56	1.66	1.65	1.70	1.69
Quality*	+	-	+	-	n/a	n/a

* “+” sign means the best possible membrane pair, a “-” sign means the worst possible membrane pair

** calculated using Eq. (2) with $T_{CEM}^+ = T_{AEM}^- = 1$

*** experimental value obtained for membrane pair Ralex CM/Ralex AMH

As one can see from Table 5, the “best” pair MK-40 (batch 2)/MA-41 (batch 2) shows results comparable to Ralex membranes. However, in the case of the “worst” set of characteristics, the OCV potential is significantly lower both for all studied membranes and for the case of “ideal selectivity”. Among the Ralex membranes, there is no significant difference between the “best” and “worst” results. In addition, the experimental results obtained exceed those calculated for a given membrane pair, which may be because nine cation-exchange and nine anion-exchange membranes are used in the electro dialyzer; thus, the obtained characteristics are averaged over the properties of these membranes.

4. Conclusions

This work shows the possibility of using a microheterogeneous model for describing the properties of ion-exchange membranes and calculating the characteristics of a reverse electro dialyzer using the data obtained. We studied the properties of eight samples of heterogeneous cation-exchange membranes (two samples of each type of membrane). The samples differed in the year of issue and storage conditions. It has been shown that for heterogeneous ion-exchange membranes MK-40 and MA-41, the properties of the samples can differ significantly. Both the electrical conductivity (higher for batch 2) and diffusion permeability (lower for batch 2) differ, which ultimately leads to a wide scatter of the obtained values of the transfer numbers of counterions. For Ralex membranes, such significant differences were not observed between different samples, with the exception of the extremely low diffusion permeability of the Ralex AMH membrane (batch 1).

The possibility of calculating the transfer numbers and predicting the open-circuit potential on this basis will allow in the future selecting the best membrane pairs for the reverse electro dialysis process based on measuring their physicochemical characteristics. The data obtained from these measurements on the electrical conductivity of ion-exchange membranes can also be used to calculate the ohmic components of the internal resistance of the electro dialyzer. The latter characteristic, in turn, will allow calculating not only the open circuit potential, but also the theoretical power.

Acknowledgements

The research was carried out with the financial support of the Kuban science Foundation in the framework of the scientific project № IFR-20.1/110.

References

1. Strathmann H. Electrodialysis, a mature technology with a multitude of new applications. *Desalination*. 2010;264:268–88.
2. Bazinet L, Geoffroy TR. Electrodialytic processes: Market overview, membrane phenomena, recent developments and sustainable strategies. *Membranes (Basel)*. 2020;10:1–72.
3. Pärnamäe R, Mareev S, Nikonenko V, Melnikov S, Sheldeshov N, Zabolotskii V, et al. Bipolar membranes: A review on principles, latest developments, and applications. *J Memb Sci*. 2020;617:118538.
4. Melnikov SS, Mugtamov OA, Zabolotsky VI. Study of electro dialysis concentration process of inorganic acids and salts for the two-stage conversion of salts into acids utilizing bipolar electro dialysis. *Sep Purif Technol*. 2020;235:116198.
5. Loza SA, Smyshlyaev NA, Korzhov AN, Romanyuk NA. Electro dialysis concentration of sulfuric acid. *Chimica Techno Acta*. 2021;8:20218106.
6. Bazinet L, Lamarche F, Ippersiel D. Bipolar-membrane electro dialysis: Applications of electro dialysis in the food industry. *Trends Food Sci Technol*. 1998;9:107–13.
7. Oren Y, Korngold E, Daltrophe N, Messalem R, Volkman Y, Aronov L, et al. Pilot studies on high recovery BWRO-EDR for near zero liquid discharge approach. *Desalination*. 2010;261:321–30.
8. Ahmed FE, Hashaikeh R, Hilal N. Hybrid technologies: The future of energy efficient desalination – A review. *Desalination*. 2020;495:114659.
9. Zhao D, Lee LY, Ong SL, Chowdhury P, Siah KB, Ng HY. Electro dialysis reversal for industrial reverse osmosis brine treatment. *Sep Purif Technol*. 2019;213:339–47.
10. Tian H, Wang Y, Pei Y, Crittenden JC. Unique applications and improvements of reverse electro dialysis: A review and outlook. *Appl Energy*. 2020;262:114482.
11. Mei Y, Tang CY. Recent developments and future perspectives of reverse electro dialysis technology: A review. *Desalination*. 2018;425:156–74.
12. Pawlowski S, Huertas RM, Galinha CF, Crespo JG, Velizarov S. On operation of reverse electro dialysis (RED) and membrane capacitive deionisation (MCDI) with natural saline streams: A critical review. *Desalination*. 2020;476:114183.
13. Pattle RE. Production of Electric Power by mixing Fresh and Salt Water in the Hydroelectric Pile. *Nature*. 1954;174:660–660.
14. Hong JG, Zhang B, Glabman S, Uzal N, Dou X, Zhang H, et al. Potential ion exchange membranes and system performance in reverse electro dialysis for power generation: A review. *J Memb Sci*. 2015;486:71–88.
15. Dugótecki P, Nymeijer K, Metz S, Wessling M. Current status of ion exchange membranes for power generation from salinity gradients. *J Memb Sci*. 2008;319:214–22.
16. Ran J, Wu L, He Y, Yang Z, Wang Y, Jiang C, et al. Ion exchange membranes: New developments and applications. *J Memb Sci*. 2017;522:267–91.
17. Pawlowski S, Crespo J, Velizarov S. Sustainable Power Generation from Salinity Gradient Energy by Reverse Electro dialysis. In: Ribeiro AB, editor. *Electrokinetics Across Disciplines and Continents*. 2016. page 57–80.
18. Geise GM, Cassady HJ, Paul DR, Logan BE, Hickner MA. Specific ion effects on membrane potential and the permselectivity of ion exchange membranes. *Phys Chem Chem Phys*. 2014;16:21673–81.
19. Larchet C, Dammak L, Auclair B, Parchikov S, Nikonenko V. A simplified procedure for ion-exchange membrane characterization. *New J Chem*. 2004;28:1260–7.
20. Zabolotsky VI, Nikonenko VV. Effect of structural membrane inhomogeneity on transport properties. *J Memb Sci*. 1993;79:181–98.
21. Akberova EM, Vasil’eva VI, Zabolotsky VI, Novak L. Effect of the sulfocation-exchanger dispersity on the surface morphology, microrelief of heterogeneous membranes and development of electro convection in intense current modes. *J Memb Sci*. 2018;566:317–28.
22. Karpenko L V, Demina OA, Dvorkina GA, Parshikov SB, Larchet C, Auclair B, et al. Comparative Study of Methods Used

- for the Determination of Electroconductivity of Ion-Exchange Membranes. *Russ J Electrochem.* 2001;37:287-93.
23. Kamcev J, Sujanani R, Jang E-S, Yan N, Moe N, Paul DR, et al. Salt concentration dependence of ionic conductivity in ion exchange membranes. *J Memb Sci.* 2017;547:123-33.
 24. Melnikov S, Loza S, Sharafan M, Zabolotskiy V. Electrodialysis treatment of secondary steam condensate obtained during production of ammonium nitrate. Technical and economic analysis. *Sep Purif Technol.* 2016;157:179-91.
 25. Sarapulova V, Butylskii D, Titorova V, Wang Y, Xu T, Zhang Y, et al. Transport and electrochemical characteristics of CJMCED homogeneous cation exchange membranes in sodium chloride, calcium chloride, and sodium sulfate solutions. *Membranes (Basel).* 2020;10:1-23.
 26. Sarapulova V, Pismenskaya N, Titorova V, Sharafan M, Wang Y, Xu T, et al. Transport characteristics of CJMAEDTM homogeneous anion exchange membranes in sodium chloride and sodium sulfate solutions. *Int J Mol Sci.* 2021;22:1-24.
 27. Akberova EM, Vasil'eva VI, Zabolotsky VI, Novak L. A study of ralex membrane morphology by SEM. *Membranes (Basel).* 2019;9:11-8.
 28. Svoboda M, Beneš J, Vobecká L, Slouka Z. Swelling induced structural changes of a heterogeneous cation-exchange membrane analyzed by micro-computed tomography. *J Memb Sci.* 2017;525:195-201.
 29. Veerman J. The effect of the NaCl bulk concentration on the resistance of ion exchange membranes-measuring and modeling. *Energies.* 2020;13.
 30. Berezina NP, Kononenko NA, Dyomina OA, Gnusin NP. Characterization of ion-exchange membrane materials: properties vs structure. *Adv Colloid Interface Sci.* 2008;139:3-28.