

Comparative Study of Methods Used for the Determination of Electroconductivity of Ion-Exchange Membranes

L. V. Karpenko, O. A. Demina, G. A. Dvorkina, S. B. Parshikov, C. Larchet*,
B. Auclair*, and N. P. Berezina

Kuban State University, ul. Karla Libknekhta 9, Krasnodar, 350640 Russia

* *Laboratoire des Matériaux Echangeurs d'Ions, Université Paris XII, Avenue du Général de Gaulle, 94010 Creteil, France*

Received March 30, 2000

Abstract—The difference, differential-difference, and mercury-contact ac methods used for determining electroconductivity of ion-exchange membranes of various types in NaCl solutions are analyzed on the basis of the concentration dependence of their electroresistance. The sources of errors in the membrane electroresistivity measurements are analyzed. For each method, sodium chloride concentrations at which the error does not exceed 5% are determined.

The most perspective membranes for electromembrane technologies are selected by studying their main physicochemical properties. One of the most important characteristics of ion-exchange membranes is their electroconductivity (EC), determined from the resistance measurements. The concentration dependences of EC reflect structural features of the material [1–5]; in combination with the concentration dependences of diffusion properties, these provide basic information for calculating electric transport properties of membranes [3] and kinetic parameters of electromembrane processes [4]. A conductivity study in dilute electrolytes yields coordinates of isoconductivity points, which are necessary in some cases for testing the membranes and for modeling their properties with allowance made for their structural inhomogeneity [2, 6]. The specific resistance of membranes or their EC is included in catalogues of membrane manufacturers (as a rule, at a certain equilibrium solution concentration) alongside with the moisture contents and exchange capacities [7–9]. In [5, 10], resistance measurements, taken for different membranes while varying the equilibrium solution concentration, were employed for modeling properties and structure of membranes on the basis of an equivalent circuit in various concentration zones.

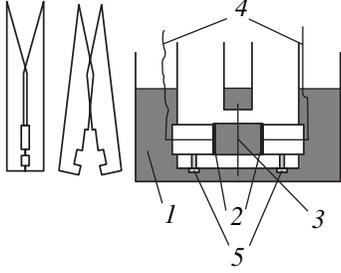
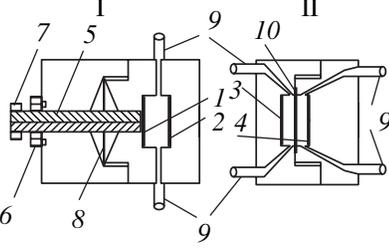
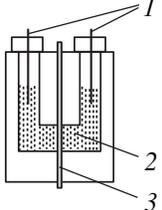
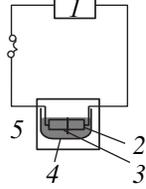
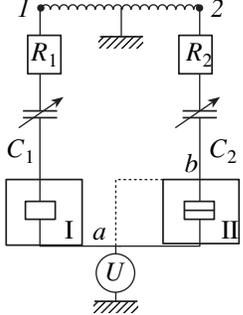
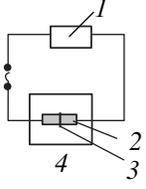
The diversity of the existing forms, cell designs, and measuring circuits for the determination of membranes' EC allows one to choose a procedure accounting for the investigation goal. However, at present, EC measurements for similar membrane type performed at various laboratories do not always yield comparable results. For example, a comparison of concentration dependences of EC for an AMX membrane in NaCl solutions measured with various methods in [11] and [12] shows that EC values differ by two times in a 0.1 M NaCl solution. The discrepancy can be due to

different techniques used for the sample preparation or the determination of the resistance of the membrane material (measuring electrodes, instruments, ac frequency ranges). At the same time, to test ion-exchange membranes and model the electric transfer in them, it is necessary to compare various methods used for measuring the concentration dependences of EC. To standardize conditions for measuring such dependences, we did perform a comparative analysis and determined working ranges of the differential-difference method (DDM), mercury-contact method (MCM, Russia), and difference method (DM), using a cell of the forceps type (France). The choice of these methods was determined by a Russian–French cooperation program. The first two techniques had been certified at the Physical Chemistry Department (PCD) of Cuban State University in the Ionit certifying laboratory.

Schemes of the cells and measuring devices are presented in Table 1. As the EC measurements are performed at different ac frequencies, Table 1 provides frequency values for each method. In the difference methods, the real part of the membrane impedance is practically frequency-independent up to 20 kHz [13].

When determining EC of ion-exchange films by DM, the resistance of a cell with a membrane placed in equilibrium solution is determined together with that of the cell with similar solution and no membrane. The difference between these two measurements yields the membrane resistance, and does not include the electrode/solution transient interfaces. There is a large number of cell designs and circuits for measuring the membrane resistance by DM [14]. The forceps cell, used by Rhone-Poulenc for express tests of ion-exchange films, has been certified by the French Membrane Club as the basis for EC measurements in a standard 0.5 M NaCl solution. The cell was later improved at Laboratoire des Matériaux Echangeurs d'Ions

Table 1. Main characteristics of methods used for measuring CE of membranes

Characteristics	Measurement methods		
	difference method	differential-difference method	mercury-contact method
Cell design	 <p>1—vessel with equilibrium solution, 2—Pt/Pt electrodes, 3—membrane, 4—insulated conductors, 5—screws fixing position of electrodes 2</p>	 <p>1—4—Pt/Pt electrodes, 5—microscrew, 6—feed roll, 7—locknut, 8—inert elastic diaphragm, 9—nipples for solution supply, 10—membrane</p>	 <p>1—Pt electrodes, 2—mercury, 3—membrane</p>
Measuring circuit	 <p>1—ac bridge E7-13, 2—forceps cell, 3—membrane, 4—beaker with equilibrium solution, 5—air thermostat TSN-100</p>	 <p>1, 2—generator G3-34, R_1 and R_2 are resistance boxes MSR-60M, C_1 and C_2 are capacitor boxes R544, I and II are flow compartments with solution and with solution and membrane, respectively, U—oscilloscope C1-19B</p>	 <p>1—impedance meter VM-507, 2—mercury-contact cell, 3—membrane, 4—air thermostat TSN-100</p>
Frequency of ac	$\varphi = 1$ kHz	$\varphi = 5$ kHz	$\varphi = 50\text{--}200$ kHz

(LMEI), Université Paris XII [15, 16], and is now used for measuring concentration dependences for membranes of various types in electrolytes [5, 11]. The cell consists of two symmetrical pieces, contains a minimum of metallic parts, and permits changing the distance between measuring electrodes. The method allows one to monitor the establishment of equilibrium between a membrane and the outer electrolyte without separating phases and measure the resistance at several points over a membrane sheet without cutting it.

When using DM, including the forceps cell technique, the error of the membrane resistance measurement increases upon passing to dilute solutions [14, 17]. To determine coordinates of isoelectric points of heterogeneous electro dialysis membranes in the concentration range of equilibrium electrolytes, a DDM was developed at PCD (Table 1). For membranes featuring a resistivity of no less than 5–10 ohm cm^2 , isoelectric points occur in the concentration range 0.001 to 0.2 M, which determined the choice of the electric mea-

suring circuit and the cell design. The technique allows one to measure the electroresistivity of the same membrane while bringing it to equilibrium with solutions of variable concentration without taking the cell apart. However, the measurement circuit is very complicated; therefore, this method is not employed for testing series-produced membranes. This technique employs a flow-type two-compartment cell with four Pt/Pt electrodes of identical diameter and a bridge compensation measurement circuit (Table 1). In compartment I, one electrode is fixed and the other can be moved with a microscrew; in compartment II, both electrodes are fixed. Before measuring EC, the cell is balanced for a 0.01 M NaCl solution by selecting a position of the mobile electrode at which the resistivity of either compartment is identical. After the balancing, the sample under test is placed into compartment II and brought to equilibrium with the solution. The equilibrium is established and the resistivity measured with the technique described in detail in [18].

Table 2. Membrane parameters

Membrane	Manufacturer	Thickness of membrane swelled in water (Na ⁺ form), mm	Surface resistivity in 0.1 M NaCl, ohm cm ²
MK-40	NIIPM NPO Plastmassy, Russia	0.502	8.0
MF-4SK-101	ONPO Plastpolymer, Russia	0.255	4.1
CMX	Tokuyama Soda, Japan	0.184	2.7
CM1		0.150	1.7
Carpion	Karpov Research Institute of Physical Chemistry	0.070	3.5

One of the contact methods of determining EC of ion-exchange membranes involves measuring the real part of the membrane impedance (R_m) between mercury electrodes at high ac frequencies (50–250 kHz). Using a high frequency for measuring the impedance allows one to considerably decrease contributions made by the resistance of mercury/membrane transition interfaces [19]. At ac frequencies of 1–10 kHz, which are usually used in DM, the error of the impedance measurement in a mercury-contact cell, which is caused by these contributions, can reach 100% [19] and diminish the real EC. In measuring the membrane resistance, the ac frequency was chosen so that the phase angle, which characterizes the imaginary part of the mercury/membrane/mercury system impedance was equal to zero. An essential distinctive feature of this method as compared to DM, is the possibility of measuring the resistance of both wet and dry samples at any temperatures, including those below the freezing point [20]. The method also permits studying EC of ion-exchange membranes in solutions of any nature and concentration, and also of membranes with salt deposits on the surface, whose formation is possible after a prolonged employment in an electro dialysis cell. However, the method employs a toxic metal, mercury.

Thus, the described methods are not free from intrinsic limitations and call for comparison when measuring the resistance at the same membrane sample.

To compare the methods, the EC measurements were performed on heterogeneous membrane MK-40 and homogeneous membranes CM1, CMX, and MF-4SK-101 in 0.001–3 M NaCl solutions. Parameters of materials are presented in Table 2. Membranes MK-40 and MF-4SK-101 were conditioned according to technique [21], after which they were kept in an Na⁺ form. Ion-exchange materials CM1 and CMX (Japan) were conditioned and transported into 0.5 M NaCl; then these membranes were immediately brought to equilibrium with the NaCl solution. The equilibrium establishment procedure is very important for obtaining reproducible results. According to studies, the equilibrium establishment time depends on the solution concentration, membrane type and size, and conditions of obtaining equilibrium (stagnant, shaking, solution circulation). The establishment of equilibrium between membranes and solution was thoroughly monitored by

conductimetry. The equilibrium was considered established if the solution resistance above the membranes was the same as the initial one. Depending on the solution concentration in stagnant conditions, membranes were balanced within 24 to 70 h. In studies by DDM, the membrane equilibrium with the outer solution established within one to two hours, as a result of continuous circulation of two liters of solution in the cell with the membrane.

The results of measuring the resistance of MF-4SK-101 by MCM were irreproducible, due to partial drying of these films when transferred from solution and fixed in the cell. A similar considerable influence of dehydration on conducting properties of sulfated polyaniline films, studied by MCM, was observed in [22]. To study the influence of partial drying of homogeneous membranes with MCM, we examined the dependence of the resistance of homogeneous membranes MF-4SK-101 and Carpio on the time interval between taking the sample out of equilibrium solution and bringing it in contact with mercury electrodes (Fig. 1). Usually this time was 20–25 s. During this time, the resistivity of MF-4SK-101 and Carpio membranes increased by,

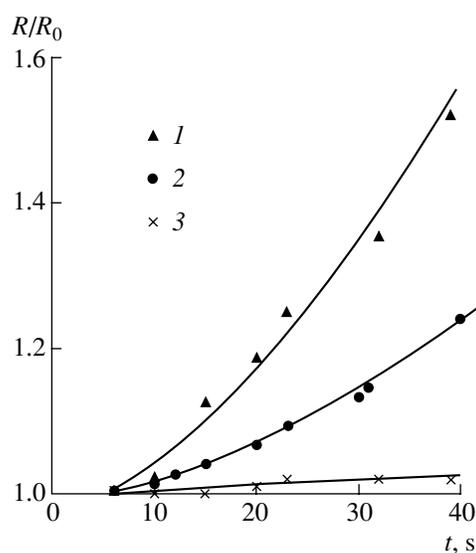


Fig. 1. Relative change in membrane resistivity vs. drying time: (1) Carpio, (2) MF-4SK-101, and (3) CM1.

Table 3. Equations for EC, s_r , and Θ

Methods	
DM, in forceps cell	MCM and DDM
$\kappa_m = \frac{l}{(\bar{R}_{s+m} - \bar{R}_s)B}$	$\kappa_m = \frac{l}{R_m B}$
$s_r = \sqrt{\left(\frac{S(l)}{l}\right)^2 + \frac{S^2_{(R_{s+m})} + S^2_{(\bar{R}_s)}}{(\bar{R}_{s+m} - \bar{R}_s)^2}}$	$s_r = \sqrt{\left(\frac{S(l)}{l}\right)^2 + \left(\frac{S_{(R_m)}}{R_m}\right)^2}$
$\Theta = \sqrt{\frac{\Delta^2_{(R_{s+m})} + \Delta^2_{(R_s)}}{(\bar{R}_{s+m} - \bar{R}_s)^2} + \left(\frac{\Delta(l)}{l}\right)^2 + \left(\frac{\Delta(B)}{B}\right)^2}$	$\Theta = \sqrt{(\theta_{(R_m)})^2 + \left(\frac{\Delta(l)}{l}\right)^2 + \left(\frac{\Delta(B)}{B}\right)^2}$

Note: \bar{R}_{s+m} and \bar{R}_s are average values of resistance of the cell containing solution and membrane and the cell containing solution, respectively; \bar{R}_m is the average resistance of membrane.

respectively, 10–20 and 30–40% (Fig. 1). These differences are due to different energy states of water in these films, which affects dehydration times. The resistance of membranes in the cell in contact with mercury electrodes remained virtually intact for 15–30 min. Thus, the time interval between taking a sample out of solution and performing measurements in a cell, which should be observed for obtaining reproducible results for rapidly drying membranes by MCM, should not exceed 6–8 s. A study of similar dependence for CM1 and CMX membranes showed that these were immune to such a rapid dehydration in air: within 30 s the resistance of the samples increased by no more than 2%.

When studying concentration dependences of EC of membranes by MCM and DM in a forceps cell, the resistance of each sample was measured no less than 10–12 times in isothermal conditions at 25°C. The root-mean-square deviation $S(x_z)$ of the average arithmetic variable was determined with the equation

$$S(\bar{x}_z) = \zeta S(\bar{x}_z) \sqrt{\frac{\sum_{i=1}^n (x_{zi} - \bar{x}_z)^2}{n(n-1)}}, \quad (1)$$

where \bar{x}_z and x_{zi} are the average and actual values of the measured variable, respectively; n is the total number of measurements; ζ is a correlation factor, introduced because of nonlinearity of deriving the square root, which depends on n [23]. Relative values of the residual systematic error of measuring devices (Θ), root-mean-square deviation (s_r), and confidence limits of determining the membranes' EC (κ_m) were estimated in accordance with the recommended treatment of results of indirect measurements [23, 24]. The working surface area of membranes (B) was assumed to be equal to the surface area of measuring electrodes, which is a constant for a given cell type. The resultant equations for Θ

and s_r are given in Table 3. Absolute values of the measurement error for variables $\Delta(x_z)$ were determined by the instrument accuracy ratings. The relative error (in %) of the resistance measurement by an MSR-60M resistance box was determined in accordance with the instrument rating:

$$\theta(R_x) = \left(0.02 + 0.02 \frac{m}{R_x}\right), \quad (2)$$

where m is the number of the box decades and R_x is the value of the make-position resistance, in ohms. In the forceps cell, resistances were measured with an E7-13 ac bridge, at 1 kHz. The relative error of the measuring device (in %) was determined according to the device rating with the equation

$$\theta(R_x) = \left[\omega + 0.2 \left(\left|\frac{R_k}{R_x}\right| - 1\right)\right], \quad (3)$$

where ω is 0.5 or 0.4%, depending on the nominal scale value; R_k is the value of the nominal resistance limit; and R_x is the measured value. The value of the relative measurement error of the membrane resistances in a mercury-contact cell was determined as the ratio between half the scale division of a VM-507 impedance meter and the measured resistance. The maximum relative error of resistance determination was 5%.

The thickness of the samples was measured by a micrometer of the MK type with an accuracy rating of two.

A statistic treatment of experimental data showed that the resulting error of determining the membranes' EC by MCM never exceeded five to six percent in the entire concentration range of equilibrium solutions. For a detailed analysis of the resistance measurement error by DM, the estimated relative values of standard deviation and residual systematic error are presented in Table 4

Table 4. Membrane resistivities measured by DM in forceps cell

Solution		Membrane											
		CM1			CMX			MF-4SK-101			MK-40		
c_{NaCl} , M	R_s , ohm	R_m , ohm	$s_r(R_m)$	$\theta(R_m)$									
0.01	147.46	2.04	0.151	1.578	2.79	0.106	1.175	4.11	0.073	0.791	12.8	0.072	0.283
0.02	–	–	–	–	–	–	–	–	–	–	12.32	0.013	0.266
0.05	47.82	1.63	0.026	0.259	2.79	0.016	0.151	4.24	0.010	0.100	9.47	0.011	0.051
0.10	27.96	1.65	0.044	0.221	2.74	0.032	0.134	4.48	0.014	0.082	7.98	0.007	0.049
0.25	12.42	1.28	0.029	0.251	2.35	0.013	0.137	4.07	0.010	0.080	7.01	0.005	0.047
0.50	6.93	1.21	0.004	0.050	2.21	0.003	0.028	3.71	0.001	0.036	6.53	0.004	0.035
0.75	6.55	1.28	0.002	0.046	2.40	0.003	0.026	3.63	0.001	0.062	5.94	0.006	0.038
1.00	5.19	1.24	0.003	0.039	2.35	0.004	0.024	3.56	0.003	0.017	4.97	0.003	0.012
2.00	2.80	1.21	0.003	0.035	2.15	0.001	0.021	3.33	0.003	0.014	4.04	0.009	0.012
3.00	2.18	1.21	0.003	0.033	2.04	0.003	0.021	3.19	0.002	0.014	3.55	0.013	0.013

for measurements of R_m in the forceps cell for all the concentrations of the equilibrium NaCl solution. As seen, for thin homogeneous membranes, even in 0.1–0.25 M solutions, the error exceeds 20%, and in centimolar solutions, the measurements make no sense at all. Hence, we doubt that the concentration dependences, measured by authors of [11] for some Japanese anion-exchange membranes in 0.001–0.1 M NaF and NaNO₃ solutions in a forceps cell, can be applied for estimating structural parameters within a microheterogeneous model. Parameters of MA-40 measured in [11] are at variance with the data of [25, 26] obtained by DDM and MCM. The resistance values with an error of no more than 5%, measured in a forceps cell with an E7-13 bridge, were obtained for MK-40 at $0.05 \leq c_{\text{NaCl}} \leq 3$ M, and for CM1, CMX, and MF-4SK-101, at $0.5 \leq c_{\text{NaCl}} \leq 3$ M. A relationship for estimating the accuracy of a sample resistance measurement follows from the equation

$$\theta(R_m) = \frac{\sqrt{\Delta^2(R_{s+m}) + \Delta^2(R_s)}}{R_m}, \quad (4)$$

for the residual systematic error of R_m measurement; and, at $\Delta(R_{s+m}) \approx \Delta(R_s)$,

$$\theta(R_m) = \frac{1.41\Delta(R_s)}{R_m}. \quad (5)$$

For the error of the membrane resistance measurement not to exceed 5%, i.e. $\theta(R_m) \leq 0.05$, it follows from (5) that

$$R_m \geq 28\Delta(R_s). \quad (6)$$

Relationship (6) is true for the above concentration ranges of NaCl solutions both for MK-40 and for homogeneous membranes. With an increase in the solution resistance, the absolute error of its measurement $\Delta(R_s)$, determined by the instrument rating, also

increases, and ratio (5) decreases. As follows from (5), the concentration range can be extended by using an instrument of a higher accuracy rating and also when measuring membranes with a higher resistance.

Figure 2 illustrates results of studying the concentration dependences of EC by three methods and indicates NaCl concentration ranges (shaded areas), where the resulting EC determination error by DDM and MCM does not exceed 5%. As seen in Figs. 2a–2d, the resulting error intrinsic to MCM depends neither on the membrane type nor on the equilibrium solution concentration. The values of EC, determined by DM in a forceps cell coincide, within the confidence limits, with those measured by MCM. Figures 2c and 2d present results of measuring EC for MK-40 [16] and CM1 [5] by DM in a forceps cell performed at LMEI, which within 4 to 5% coincide with EC values obtained here. The values obtained by DDM for MK-40 at $0.001 \leq c_{\text{NaCl}} \leq 0.2$ M coincide with those obtained by MCM in the entire range, and at $0.05 \leq c_{\text{NaCl}} \leq 0.2$ M are comparable with the values of κ_m obtained by DM in a forceps cell. We failed to obtain reproducible values of CE for CM1, CMX, and MF-4SK-101, as the resistance of these membranes is lower than that of MK-40.

Thus, we compared concentration dependences of EC of ion-exchange membranes measured by three methods in 0.001–3 M NaCl solutions. It follows that the measurements of the resistances by DM are limited by a number of factors, such as the balance between resistances of the sample and solution at equilibrium with it, and by the accuracy rating of the measurement device. The accuracy of EC determined by MCM is independent of the equilibrium solution concentration and the membrane type; however, when measuring thin homogeneous films, it is necessary to prevent the membrane from drying in the process of moving the sample from solution into the cell. An analysis of errors allowed us to find concentration ranges for each

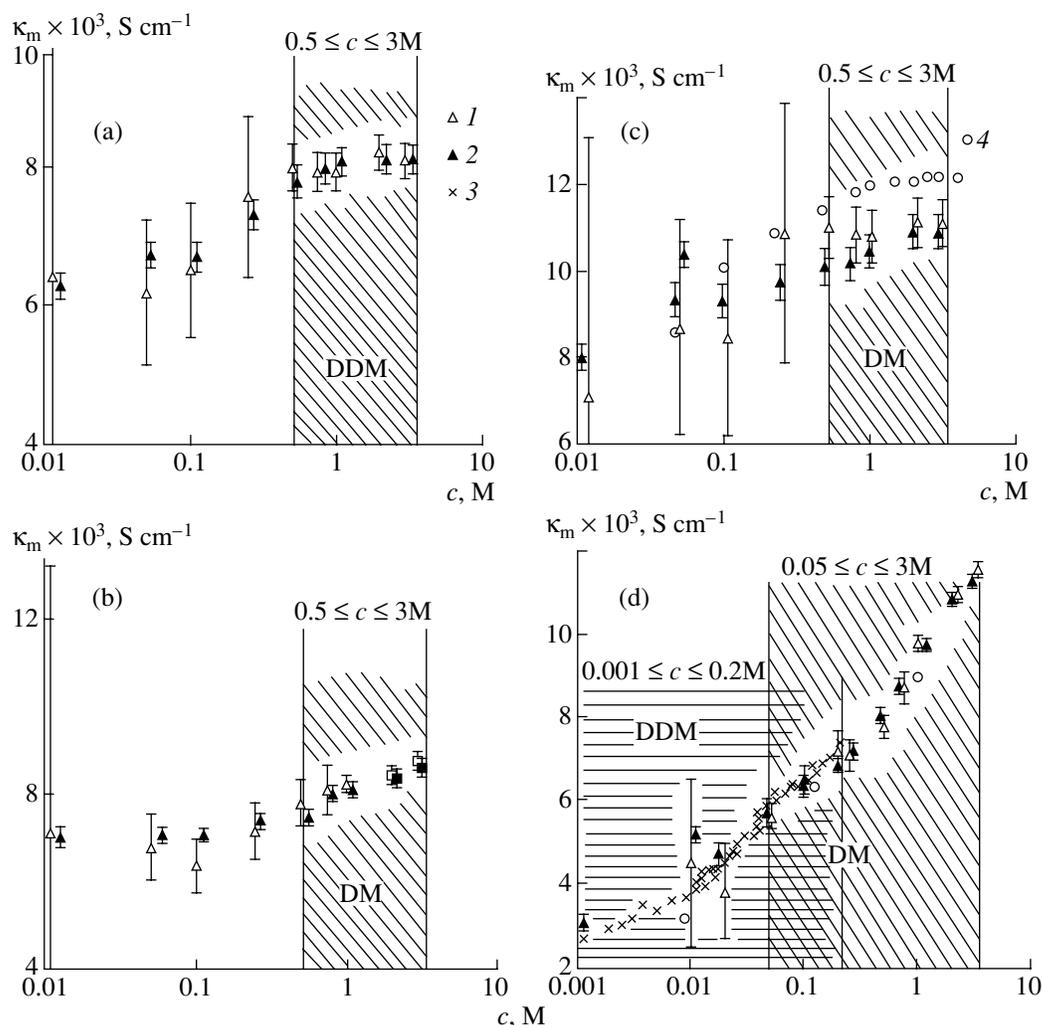


Fig. 2. Concentration dependences of EC for (a) CMX, (b) MF-4SK-101, (c) CM1, and (d) MK-40 membranes in NaCl solution, measured by (1) DM in forceps cell, (2) MCM, and (3) DDM; (4) measurements performed at LMEI; other measurements performed at Ionit laboratory; error of measurements performed by DDM did not exceed 2%; error of measurements performed by DM at LMEI did not exceed 1%.

method, where the error of the measured resistance does not exceed 5%.

ACKNOWLEDGMENTS

The authors acknowledge S.V. Timofeev (ONPO Plastpolymer) for donating membranes MF-4SK-101; Prof. T. Sata, for CM1 and CMX; and N.V. Kiseleva (Cuban State University) for discussing methodological part of the work.

This work was supported by the Russian Foundation for Basic Research, project nos. 00-03-96026 and 00-03-96028, and the Krasnodar Territory Administration.

REFERENCES

1. Gnusin, N.P., Demina, O.A., Berezina, N.P., and Meshechkov, A.I., *Elektrokhimiya*, 1988, vol. 24, p. 364.
2. Gnusin, N.P. and Berezina, N.P., *Zh. Fiz. Khim.*, 1995, vol. 69, p. 2129.
3. Gnusin, N.P., Kononenko, N.A., and Parshikov, S.B., *Elektrokhimiya*, 1994, vol. 30, p. 35.
4. Gnusin, N.P., *Elektrokhimiya*, 1996, vol. 32, p. 420.
5. Belaid, N.N., Ngom, B., Dammak, L., *et al.*, *Eur. Polym. J.*, 1999, vol. 35, p. 879.
6. Gnusin, N.P., Berezina, N.P., Demina, O.A., and Kononenko, N.A., *Elektrokhimiya*, 1996, vol. 32, p. 173.
7. *Ionitovye membrany, granulyaty, poroshki: Katalog (Ion-Exchange Membranes, Granulated Substances, and Powders: A Catalogue)*, Moscow: NIITEKhim, 1977.
8. *Neosepta: Ion-Exchange Membranes*, Tokuyama Soda, 1989.
9. *Selemion: Ion-Exchange Membranes*, Tokyo: Asahi Glass, 1984.
10. Larchet, C., Kitari, T., and Auclair, B., *Elektrokhimiya*, 1996, vol. 32, p. 219.

11. Elattar, A., Elmidaoui, A., Pismenskaia, N., *et al.*, *J. Membr. Sci.*, 1998, vol. 143, p. 249.
12. Neubrand, W. and Eigenberger, G., Abstracts of Papers, *Third Int. Symp. Euromembrane'97*, Univ. Twente (The Netherlands), 1997, p. 194.
13. Bobreshova, O.V., Kulintsov, P.I., Murugova, T.N., *et al.*, *Teor. Prakt. Sorbtsionnykh Protseessov*, 1983, vol. 16, p. 79.
14. Zabolotskii, V.I., Dvorkina, G.A., and Gnusin, N.P., *Izv. Sev.-Kavk. Nauchn. Tsentra Vyssh. Shk., Ser. Estestv. Nauki*, 1987, vol. 57, p. 64.
15. Belaid, N.N., Dammak, L., Ngom, B., *et al.*, *Eur. Polym. J.*, 1998, vol. 34, p. 564.
16. Parchikov, S., *These de Doctorat de l'Universite Paris Val De Merne (Paris XII)*, 1998.
17. Shaposhnik, V.A., *Kinetika elektrodializa* (The Electrolysis Kinetics), Voronezh: Voronezh. Gos. Univ., 1989.
18. Dvorkina, G.A., Meshechkov, A.I., Gnusin, N.P., and Zabolotskii, V.I., *Elektrokhimiya*, 1984, vol. 20, p. 85.
19. Meshechkov, A.I., Demina, O.A., and Gnusin, N.P., *Elektrokhimiya*, 1987, vol. 23, p. 1452.
20. Zabolotskii, V.I., Berezina, N.P., Kononenko, N.A., *et al.*, *Zh. Prikl. Khim.*, 1997, vol. 70, p. 1619.
21. Saldadze, K.M., Pashkov, A.B., and Titov, V.S., *Ionoobmennyye vysokomolekulyarnyye soedineniya* (High-Molecular Ion-Exchange Compounds), Moscow: Goskhimizdat, 1960.
22. Doriomedoff, M., Hautire-Cristofin i, F., Surville, R., *et al.*, *J. Chem. Phys.*, 1971, vol. 68, p. 1056.
23. Selivanov, M.N., Fridman, A.E., and Kudryashova, Zh.F., *Kachestvo izmerenii: Metrologicheskaya spravochnaya kniga* (Quality of Measurements: A Metrological Reference Book), Leningrad: Lenizdat, 1987.
24. *Kharakteristiki pogreshnosti rezul'tatov kolichestvennogo analiza: Algoritmy otsenivaniya* (Algorithms for Estimating Errors of Quantitative Analyses), MI 2336-95, Yekaterinburg, 1995.
25. Zabolotsky, V.I., Dyomina, O.A., Berezina, N.P., *et al.*, in *Proc. Int. Conf. on Membrane Science and Technology (ICMST'98)*, China, Beijing, 1998, p. 218.
26. Dvorkina, G.A., *Cand. Sci. (Chem.) Dissertation*, Krasnodar: Kuban State Univ., 1988.