Determination of structural, selective, electrokinetic and percolation characteristics of ion-exchange membranes from conductive data

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Abstract

The structural, selective and electrokinetic characteristics and percolation parameters were determined for different ion-exchange polymer membranes from their conductivity data using the two-phase model of membrane conductivity and percolation theory. The two different combinations of micro-phases in IEM, used in the two-phase conductivity model and percolation theory are presented and discussed. Based on this two-phase model and concentration dependences of membrane conductivity, the structural membrane heterogeneity was determined for 14 commercial IEMs. The diffusion coefficient, molar conductivity of counter-ions and hydration capacity of the gel-phase were calculated and analyzed for cross-linked and linear ion-exchange polymers. The ion-exchange equilibrium constants for MK-40 were estimated from values of membrane conductivity at the iso-conductance point in individual electrolyte solutions and their mixtures. The percolation theory was used to describe the conductivity of different membrane compositions with various volume fraction of the conducting phase. The estimation of φ_{cr} and γ percolation parameters showed that the obtained values of critical index γ agree with the theory for investigated materials, and the value of the threshold parameter φ_{cr} depends on the preparation method and structural heterogeneity of a given composition.

Keywords: Ion-exchange membrane; Conductivity; Two-phase model; Percolation theory; Ion-exchange equilibrium constant; Diffusion coefficient

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1. Introduction

At the present time the application fields of ion-exchange membranes (IEMs) are getting larger. The IEMs are currently used in electro-dialysis processes, electrolysis synthesis modules, as structural elements for fuel cells, sensors, artificial organs. One of the most important properties of ion-exchange membranes is conductivity. The simplicity and rapidity of single measurement of the membrane resistance have promoted the use of conductivity values to verify various theoretical models and describe transport mechanisms in the membranes. The aim of this paper is to demonstrate the possibility of using IEM conductivity data to estimate microscopic structural parameters such as heterogeneity and hydration capacity, electro-kinetic characteristics of counter-ions, equilibrium ion-exchange constant and critical parameters of percolation transitions.

2. Objects

We investigated membrane conductivity in dependence on: (1) NaCl concentration for commercial membranes MK-40, CMV, AMV, CM-1,CM-2, CMX, CL-25T, Nafion-115, -117, -120, -125, -417, MF-4SC-101; (2) concentration of HCl, KCl, LiCl, and of LiCl:HCl, NaCl:HCl and KCl:HCl for MK-40; (3) conducting phase volume fraction for aromatic polyamides, ion-exchange granulates made of KUx2*8 and sulfocationic perfluorinated membranes.

3. Methods

The conductivity of the IEM was measured by mercury-contact methods using alternating current of high frequency (50–200 kHz) [1,2]. In measuring the membrane resistance, the AC frequency was chosen so that the phase angle, which characterizes the imaginary part of the impedance of the mercury/membrane/mercury was equal to zero.

4. Results and discussion

4.1. Model of ion-exchange membrane structure

To analyze IEM conductivity data two theoretical approaches were used: two-phase model of ion-exchange membrane conductivity and
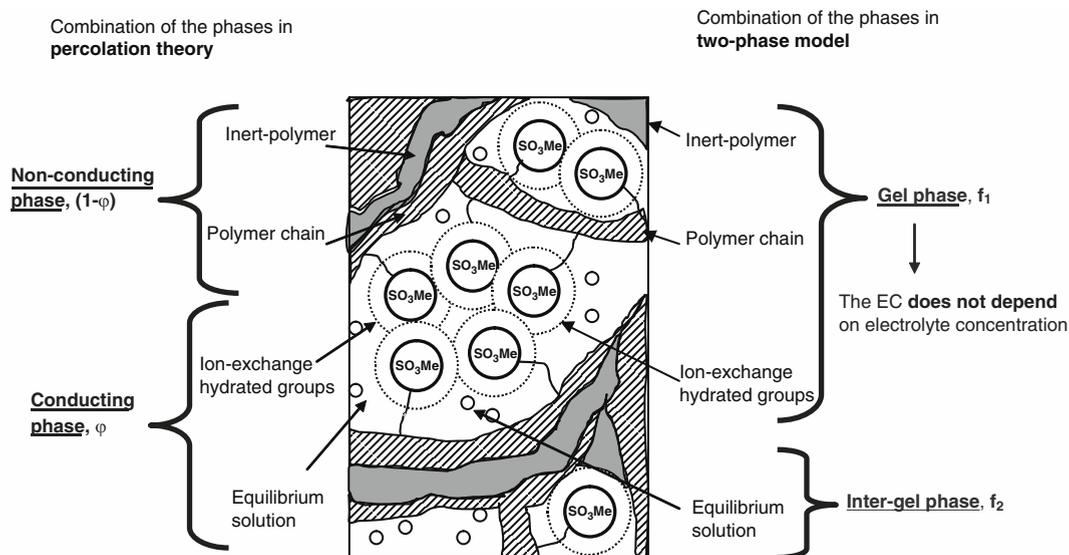

Fig. 1. Structure of ion-exchange membrane and grouping the phases in percolation theory (on the left) and two-phase membrane conductivity (on the right).

percolation theory. Fig. 1 shows the schematic structure of a heterogeneous ion-exchange membrane prepared from conducting and non-conducting polymers and swollen in an electrolyte solution. As can be seen from the figure, in the heterogeneous IEMs the following micro-phases (pseudo-phases) are considered: (1) inert polymer; (2) polymer chains of ion-exchange polymer; (3) hydrated ion-exchange groups, (4) absorbed electrolyte solution. In the figure we also show two different combinations of phases (on the left-hand side and right-hand side), which are used to describe (I) the concentration dependencies of IEM conductivity in the framework of the two-phase model of membrane conductivity and (II) IEM conductivity in dependence on conducting fraction in the framework of percolation theory.

4.2. Determination of membrane heterogeneity degree

In the framework of a two-phase model [3–5] the IEM is divided into two micro-phases: (1) gel-phase (joint phase of inert polymer and hydrated ion-exchange polymer consisting of polymer chains and hydrated ion-exchange groups) and (2) inter-gel spaces (or "free" solution) content absorbed electrolyte solution. The conductivity of gel-phase does not depend on equilibrium electrolyte concentration, but the conductivity of inter-gel spaces depends on it. The concentration dependencies of IEM conductivity is described by the following equation [5]:

$$\kappa_{\mathrm{m}}^{\alpha} = f_1 \cdot \bar{\kappa}^{\alpha} + f_2 \cdot \kappa^{\alpha} , \tag{1}$$

where $\bar{\kappa}$ is the conductivity of gel-phase, κ is the conductivity of equilibrium solution. f_1 and f_2 are the volume fractions of the phases. α reflects the reciprocal arrangement of the phases, $-1 \leq \alpha \leq +1$. At chaotic layout $\alpha \rightarrow 0$ and in the case Eq. (1) is rearranged in the expression:

$$\kappa_{\mathrm{m}} = \bar{\kappa}^{f_1} \cdot \kappa^{f_2} \tag{2}$$

Conductivity of gel-phase is determined as conductivity at the iso-conductance point, where conductivity of electrolyte solution is equal to gel-phase conductivity and membrane conductivity $\kappa_{\mathrm{m}} = \kappa = \bar{\kappa}$. According to this two-phase model the volume fraction of the inter-gel phase (f_2) is easily defined as the slope ratio from the bi-logarithmic dependence ($\lg\kappa_{\mathrm{m}}$–$\lg\kappa$):

$$f_2 = \mathrm{dlg}\, \kappa_{\mathrm{m}} / \mathrm{dlg}\, \kappa \tag{3}$$

The volume fraction of the gel-phase is equal to $f_1 = 1 - f_2$.

The method of the estimation of the volume fractions of the gel-phase and inter-gel spaces in IEMs has been widely used by co-workers of Kuban State University [6–10], where the model has been developed, as well as by other researchers [11–13] to characterize the IEM heterogeneity degree and to study IEM structure. In the work [14] a procedure was proposed for classification of ion-exchange membranes according to f_2: the membranes may be considered as homogeneous, if $0 < f_2 < 0.15$; and as heterogeneous, if $0.15 < f_2 < 0.25$; and porous, if $0.3 < f_2 < 0.45$.

Figs. 2 and 3 demonstrate the concentration dependencies of specific conductivity of IEM used in electro-dialysis (Fig. 2) and sulfo-cationic perfluorinated IEM used in membrane electrolysis and fuel cells (Fig. 3). The values of the structural parameter f_2 were estimated from the bi-logarithmic dependencies (Figs. 2(b) and 3(b)). The obtained values f_2, $\bar{\kappa}$, C_{iso} are presented in Table 1. As can be seen from the table the C_{iso} values for investigated membranes lie in interval 0.02–0.10 mol/L of NaCl, and $\bar{\kappa}$ −2.76–12.20 Ω^{-1} cm^{-1}. Now for CMV, AMV, CM-2, CM-1, CMX, CL-25T, Nafion-115, -117, -125, -417, MF-4-SC-101 $0 < f_2 < 0.15$ and therefore these membranes can be referred to homogeneous. The parameter f_2 for MK-40 and Nafion-120 is more then 0.15, and these membranes are referred to heterogeneous, although in view of the synthesis
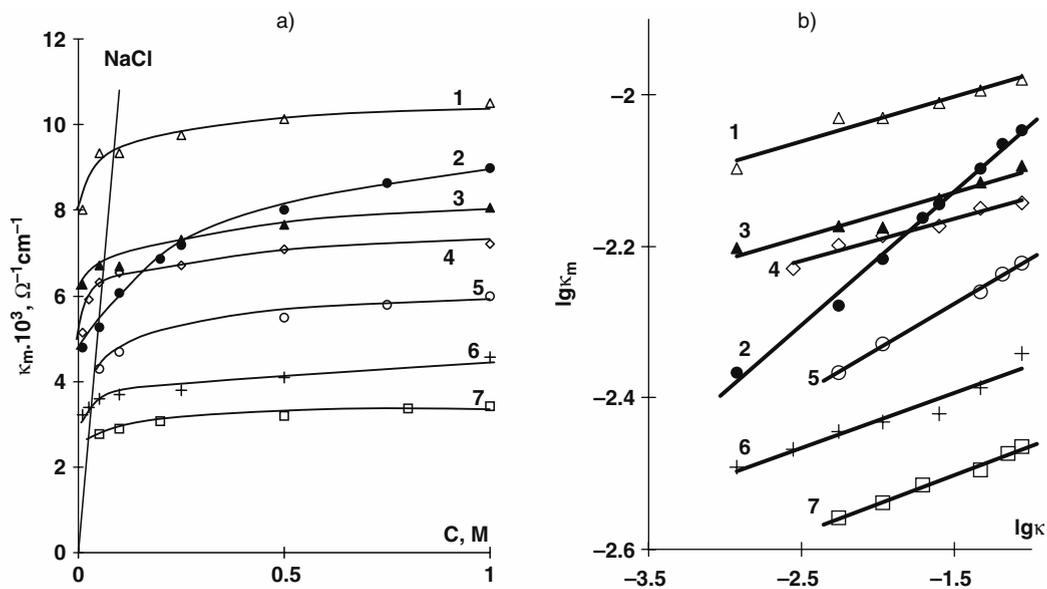
Fig. 2. Concentration dependencies of specific conductivity of ion-exchange membranes used in an electro-dialysis in (a) conventional and (b) bi-logarithmic coordinates: 1(Δ) CM-1, 2($\bullet$) MK-40, 3($\blacktriangle$) CMX, 4($\diamond$) CMV, 5($\circ$) CL-25T [15], 6(+) AMV, 7($\square$) CM-2 [16].
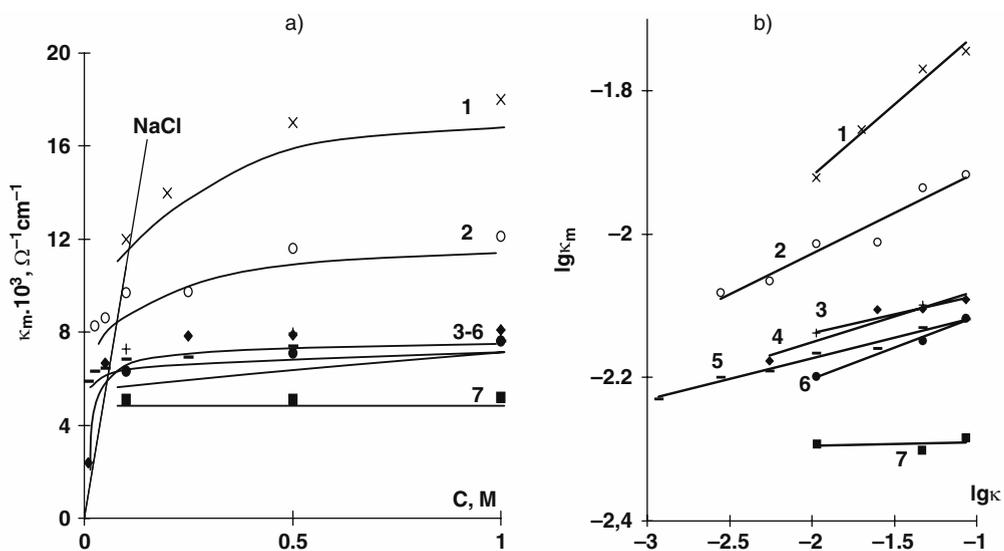

Fig. 3. Concentration dependencies of specific conductivity of sulfo-perflourinated membranes used in fuel cells or in alkali electrolysis, (a) conventional and (b) bi-logarithmic coordinates: 1($\times$) Nafion120 [17], 2(O) Nafion117, 3(+) MF-4SK arm, 4($\blacklozenge$) Nafion 125 [18], 5(—) MF-4SK-101, 6($\bullet$) Nafion 417, 7($\blacksquare$) Nafion115.

Table 1
Physico-chemical and structural characteristics of the ion-exchange membranes

Membrane	W, g/g$_{dry}$, %	Q, mmol/g$_{dry}$	n_m, molH$_2$O/$-SO_3^-$	$\bar{\kappa} \cdot 10^3$, $\Omega^{-1} \cdot cm^{-1}$	C_{iso}, mol/L	f_2
IEM used in electrodialysis						
MK-40	50.30	2.53	11.05	5.27	0.050	0.18
CMV	37.09	2.3	8.98	6.25	0.060	0.06
AMV	–	–	–	3.50	0.030	0.07
CM-2	25.0–35.0	1.6–2.2	8.77	2.76	0.020	0.05
CM-1	37.5	2.15	9.70	9.19	0.085	0.05
CMX	27.5	1.65	9.25	6.72	0.063	0.06
CL-25T	25.0–35.0	1.5–1.8	10.10	4.30	0.040	0.14
Perfluornated sulfo-cationic IEM used in electrolysis and fuel cells						
Nafion 115	14.15	0.93	8.45	5.20	0.050	0.00
Nafion 117	18.95	0.93	11.32	9.10	0.085	0.10
Nafion 120	22.7	0.70	18.00	12.20	0.102	0.20
Nafion 125	12.9	0.81	7.00	6.70	0.065	0.07
Nafion 417	16.25	0.90	10.03	6.00	0.055	0.05
MF-4SC-101	15.63	0.86	10.10	6.40	0.060	0.05
MF-4SC –101 (reinf)	15.73	0.86	10.16	7.20	0.070	0.06

of sulfocationic perfluorinated membranes, Nafion-120 is a homogeneous polyelectrolyte.

4.3. Electro-kinetic characteristics of counter-ions

Electro-kinetic characteristics of counter-ions in membrane gel-phase can be estimated from membrane conductivity at the iso-conductance point: the diffusion coefficient using Nernst–Einstein equation, adapted for polyelectrolytes [19] (4) and molar conductivity by Eq. (5):

$$\bar{D} = \bar{\kappa} \cdot \frac{R \cdot T \cdot \bar{t}}{F^2 \cdot z} \cdot \frac{Q \cdot d_m}{f_1} \tag{4}$$

$$\bar{\lambda} = \bar{\kappa} / Q \tag{5}$$

4.4. Hydrate capacity of membrane gel-phase

Water molecule numbers combined with one ion-exchange group is determined from values of volume fraction of the inter-gel phase, water content and ion-exchange capacity by the expression [20]:

$$\bar{n} = \frac{1}{Q \cdot M_{H_2O}} \cdot \left(W - f_2 \cdot \frac{d_{H_2O}}{d_m} \right) \tag{6}$$

We estimated the gel-phase hydrate capacity, diffusion coefficient, molar conductivity of counter ion (Na$^+$) in the gel phase for cross-linked membranes MK-40, CM-1, CMX and for perfluorinated membrane MK-4SC-101 having a linear polymer matrix. As can be seen from Table 2 the electro-kinetic characteristics of the Na$^+$-ion increases for cross-linked membranes with increasing hydration capacity of the gel phase. In spite of MK-4SC-101 contents being 6.46 water molecules per ion-exchange group ($\bar{n} = 6.46$ molH$_2$O/$-SO_3$), this value is not much bigger than the one for MK-40 ($\bar{n} = 5.77$ molH$_2$O/$-SO_3$). Although $\bar{D}$, $\bar{\lambda}$ for

Table 2.
Electrokinetic characteristics of Na+-ion in gel-phase of cation-exchange membranes

Membrane	$d_m,$ $\dfrac{g}{cm^3}$	$\bar{n},$ $\dfrac{molH_2O}{-SO_3^-}$	$\bar{\lambda}$ $cm^2\Omega^{-1}mol^{-1}$	$\bar{D}\cdot10^7$ cm^2s^{-1}
MK-40	1.13	5.77	2.76	7.35
MF-4SC-101	1.67	6.46	5.14	13.69
CM-1	1.18	8.20	4.99	13.30
CMX	1.19	7.11	4.36	11.61

MK-4SC-101 is two times higher than the ones of MK-40. That can be explained with a difference in structure of the polymer matrix of the membranes: the counter-ions are transferred much easier in linear polymer structure of MK-4SC-101 than in cross-linked polymer matrix of MK-40. Moreover, the perfluorinated membrane contains oxygen atoms in the polymer chains, which build hydrogen connections with water molecules [21]. In that way perfluorinated membranes have better networked water molecules than MK-40 and it facilitates transport of the counter-ions along the hydrophobic polymer chains.

4.5. Determination of ion-exchange equilibrium constant

In the work [22] it was shown that an apparent ion-exchange equilibrium constant (IEEC) of two monovalent cations can be calculated from membrane electro-conductivity measured in individual electrolyte solutions and their mixtures. Two possible methods of determination of the IEEC were discussed and it was demonstrated that the IEECs determined conductometrically is in agreement with those determined by independent analytical methods. One of the methods is based on measuring the membrane specific conductivity at the iso-conductance point in individual electrolyte solutions and their mixture. In the case IEEC is estimated by the following relationship:

$$K=\left[\frac{\bar{\kappa}_H-\bar{\kappa}_\Sigma}{\bar{\kappa}_\Sigma-\bar{\kappa}_{Me}}\right]\cdot\left(\frac{1}{\alpha_{Me}}-1\right), \tag{7}$$

Table 3 demonstrates the electroconductivity values in iso-conductance point measured for MK-40 in LiCl, NaCl, KCl, HCl and equimolar mixtures of Li, Na, K chlorides with hydrochloric acid. As known the mobility of the alkali metal ions in the solution varies in the series $K^+>Na^+>Li^+$. The conductivity of gel-phase of the MK-40 in the respective ionic forms varies in the same order, which agrees with the data presented in [23]. For the mixed ionic form, the conductivity of gel-phase varied in a different order: $Li^+/H^+>K^+/H^+>Na^+/H^+$. This effect is due to a higher exchange sorption of H^+ from LiCl–HCl mixtures as compared with KCl–HCl and NaCl–HCl mixtures.

Table 3
Conductivity of the MK-40 in iso-conductance point, measured in individual solution and their equimolar mixtures

Electrolyte Solution	$\bar{\kappa}\times10^3,\ \Omega^{-1}cm^{-1}$
HCl	34.02 ± 0.28
LiCl	4.19 ± 0.07
NaCl	5.27 ± 0.09
KCl	8.25 ± 0.20
HCl–LiCl	19.95 ± 0.39
HCl–NaCl	14.00 ± 0.28
HCl–KCl	16.56 ± 0.28

Table 4
Ion-exchange equilibrium constants for MK-40 membrane determined by conductometrically and analytical methods

System	K (conduct)	K (analyt.)
Li^+/H^+	0.89 ± 0.03	0.86 ± 0.05
Na^+/H^+	2.30 ± 0.08	2.10 ± 0.05
K^+/H^+	2.01 ± 0.05	2.45 ± 0.12

Table 4 presents IEEC values calculated from the conductivity data presented in Table 3 and obtained independently by the analytical static method. As can be seen from Table 4 that the IEEC values estimated from conductivity measurements are close to those obtained independently by the analytical method.

4.6. Percolation transitions in IEM

The percolation theory has been developed to analyze the effective properties of compositions prepared from conducting and non-conducting materials [24–27]. The electro-conductivity of compositions with various conductor–dielectric ratios in the vicinity of the percolation threshold is described by the equation:

$$\kappa_m = \sigma (\varphi - \varphi_{cr})^{\gamma} \tag{8}$$

where σ is the coefficient whose order of magnitude is equal to the specific conductivity of the conducting phase, φ is the volume fraction of the conducting phase, φ_{cr} is the critical volume fraction of this phase, at which the composition transform from non-conductor to conductor. The parameter γ is a critical exponent of conductivity. The theoretical values of the φ_{cr} and γ for three-dimensional system are equal corresponding to 0.15 ± 0.03, 1.6 ± 0.4.

For a mathematical description of the percolation transition in IEMs we use other grouping (combination) of the micro-phases in IEM (Fig. 1, left). The conducting phase of IEM consists of hydrated and absorbed electrolyte solution. In the work [28] we have proposed an expression to calculate the volume fraction of the conducting phase in ion-exchange materials:

$$\varphi = Q \cdot M + W \tag{9}$$

where Q is the ion-exchange capacity; W is the water content; M is the molar mass of ion-exchange group.

Fig. 4(a) shows the dependences of specific electro-conductivity of different polymer compo-
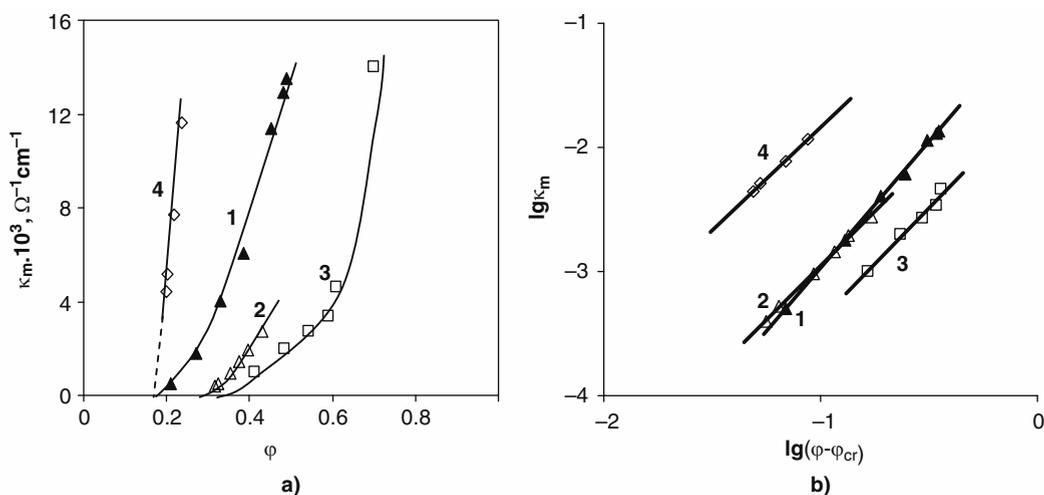

Fig. 4. (a) The dependences of the specific conductivity on the volume fraction of a con-ducting phase; (b) the $lg\kappa_m$ - $lg(\varphi - \varphi_{cr})$ dependences for the ion-exchange compositions presented in Table 5.The line numbers in the figure correspond to the composition numbers in Table 5.

Table 5
The values of the percolation transition critical parameters for various ion-exchange compositions

Number	Polymer composition	Parameters of percolation equation		
		φ_{cr}	γ	R^2
1	PA-1[a] with different content of poly-*m*-phenylene-iosphthalamide (Kevlar) [29]	0.140	2.04 ± 0.08	0.9988
2	PA-2[b] with different content of Kevlar	0.260	1.74 ± 0.09	0.9986
3	KU-2*8 ion-exchange resins with different content of polyethylene [30]	0.248	1.80 ± 0.47	0.9798
4	Perfluorinated sulfo-cationic membranes with different ion-exchange capacity and water content varied on a stage of alkaline hydrolysis with NaOH solutions with different concentration [31]	0.150	1.67 ± 0.19	0.9987

[a]PA-1 – poly(1-sulfo-5 amino-2[4-(3-carboxybenzamidyl)]phenylaminobenzene).
[b]PA-2 – poly [(1-sulfo-5 amino-2[4-(3-carboxybenzamidyl)]phenylaminobenzene)$_{80\%}$ (4-amino-4´-(3-carboxybenzamidyl)diphenylether)$_{20\%}$].

sitions on the volume fraction of conducting phase, φ, calculated using Eq. (9). As is seen from the figure, after reaching a specific value of $\varphi = \varphi_{cr}$ the conductivity increases exponentially with φ that corresponds to Eq. (8) of the percolation theory.

The values of φ_{cr} and γ were estimated based on $\lg \kappa_m - \lg(\varphi - \varphi_{cr})$ whose linear functions are demonstrated in Fig. 4(b). The values of φ_{cr} and γ, as well the squares of the correlation coefficient R^2 are listed in Table 5. As seen in the table, R^2 values are close to unity, thus conforming the adequacy of the percolation theory suggested for the description of electro-conductivity of the studies ion-exchange compositions. As seen in Table 5, the obtained values of the parameter γ from the experimental data agree with the theoretical one. The critical volume fraction of conducting phase φ_{cr} are close to the theoretical value of this parameter ($\varphi_{cr} = 0.15 \pm 0.03$) for the membrane compositions 1 and 4. The values of φ_{cr} for the compositions 2 and 3 exceed 0.15 that is associated with structural features and the preparation method of these samples. The polyamide membranes 2 content less (approximately twofold) sulfo-groups in the poly(aryleneamide) matrix

than the compositions 1. That causes a considerable decrease in the measured conductivity values. In this case, the percolation transition begins at a higher content of a charged component in a composition.

The composition 3 is ion-exchange granulates made of ion-exchange resin KU-2*8 and polyethylene. The presence of the polyethylene in the polymer composition causes structural defects, which occupy 9–20% of the total volume [30]. These defects are situated between polyethylene chains and contain a certain part of absorbed water. This part of water is taken into account while estimating the fraction φ of the conducting phase, but it does not take part in the formation of the percolation channel. Therefore, the critical volume fraction φ_{cr} of the composition 3 is somewhat higher than the theoretical one.

5. Conclusion

Using conductometry method and theoretical approaches of two-phase model of membrane conductivity we have investigated the degree of heterogeneity of 14 commercial ion-exchange membranes. The hydration capacity, and diffusion

coefficient and molar conductivity of the gel-phase were estimated and compared for membranes MK-40, CM-1, CMX, MF-4SC. It was shown that diffusion coefficient and molar conductivity of counter ions in the membrane gel-phase depends on hydration capacity of the gel-phase as well as on the structure of polymer matrix and degree of networking water.

The apparent ion-exchange equilibrium constants of K^+/H^+, Na^+/H^+, Li^+/H^+ for membrane MK-40 were calculated from the values of membrane conductivity at the iso-conductance point in individual electrolyte solutions and their mixtures. The ion-exchange constants determined conductometrically are in agreement with those determined by independent analytical method.

The conductivity of different membrane compositions with various volume fraction of conducting phase were described using percolation theory. The estimation of φ_{cr} and γ percolation parameters showed that the obtained values of critical index γ agree with the theory for the investigated materials, and the value of the threshold parameter φ_{cr} depends on the preparation method.

Nomenclature

κ_m	membrane conductivity
κ	conductivity of equilibrium solution and inter-gel phase in membrane
$\bar{\kappa}$	conductivity of membrane gel-phase
f_1, f_2	volume fraction of the gel-phase and inter-gel phase corresponding
α	parameter characterizing the spatial arrangement of membrane phases
C_{iso}	equilibrium electrolyte solution concentration at the iso-conductance point
$\bar{D}$	diffusion coefficient of counter ion in membrane gel-phase
$\bar{t}$	counter-ion transport number in membrane gel-phase
R	gas constant
T	temperature
Q	ion-exchange capacity of membrane
d_m	membrane density
F	Faraday constant
$\bar{\lambda}$	molar conductivity of counter ion in membrane gel-phase
$\bar{n}$	hydrate capacity of gel-phase, number of water molecules per one ion-exchange group
d_{H_2O}, M_{H_2O}	water density and water molar mass
K	ion-exchange equilibrium constant
$\bar{\kappa}_H, \bar{\kappa}_{Me}, \bar{\kappa}_\Sigma$	specific conductivity at iso-conductance point for membrane in H^+-, Me^+- and hetero-ionic forms corresponding

Greek symbols

α_{Me}	equivalent fraction of metal ion in equilibrium electrolyte mixture
φ	volume fraction of the conducting phase
φ_{cr}	critical volume fraction of conducting phase
γ	critical exponent of conductivity

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