

# Percolation Effects in Ion-Exchange Materials

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**Abstract**—The dependence of conductivity  $\kappa_m$  of homogeneous and heterogeneous ion-exchange materials on the volume fraction of a conducting hydrophilic phase  $f$  was studied. Approaches of the percolation theory were used to analyze the data obtained. Parameters appearing in the percolation equation  $\kappa_m = \kappa_0(f - f_{cr})^t$  were determined for the description of the conductivity behavior during water desorption from heterogeneous ion-exchange membranes, and in the preparation of various polymeric compositions from a conducting component distributed in the nonconducting medium. The obtained values of the critical exponent  $t$  agree with the theoretical value ( $t = 1.6 \pm 0.4$ ) for all the materials studied. The dependence of the percolation threshold  $f_{cr}$  on the structural organization of ion-exchange materials was determined.

## INTRODUCTION

As has shown in a number of studies [1–7], it is worthwhile to use the approaches of the percolation theory for the analysis of experimental data on the effective properties of compositions prepared from conducting and nonconducting materials. The basic ideas of this theory were formulated by Bredbent and Hammersly in 1957. Phenomena described by the percolation theory are characterized by a critical point (the percolation threshold) at the composition axis where some properties of a system change abruptly. The existence of the percolation threshold was shown to be a common phenomenon inherent in both regularly structured and disordered systems. As was shown in theoretical and experimental studies, the conductivity  $\kappa_m$  of compositions with various conductor–dielectric ratios in the vicinity of the percolation threshold is described by the equation

$$\kappa_m = \kappa_0(f - f_{cr})^t, \quad (1)$$

where  $\kappa_0$  is the coefficient whose order of magnitude is equal to the specific conductivity of the conducting material [8],  $f$  is the volume fraction of the conducting phase in a composition. The determination of the critical volume fraction of a conductor  $f_{cr}$  by numerical methods, mainly by the Monte Carlo method, showed that its value is determined by the size, shape, and the orientation of the dispersed particles of both phases [4, 7, 9, 10]. For three-dimensional systems, the critical volume fraction  $f_{cr}$  was found to be equal to  $0.15 \pm 0.03$ . At a pronounced asymmetry of the characteristic geometrical shapes of conducting and nonconducting regions, the jump in conductivity is observed at  $f_{cr}$  values exceeding the theoretical value, and, in some cases, the  $f_{cr}$  values can be equal to or higher than 0.5 for three-dimensional systems [7, 11]. The parameter  $t$  is called a critical exponent of conductivity or a universal

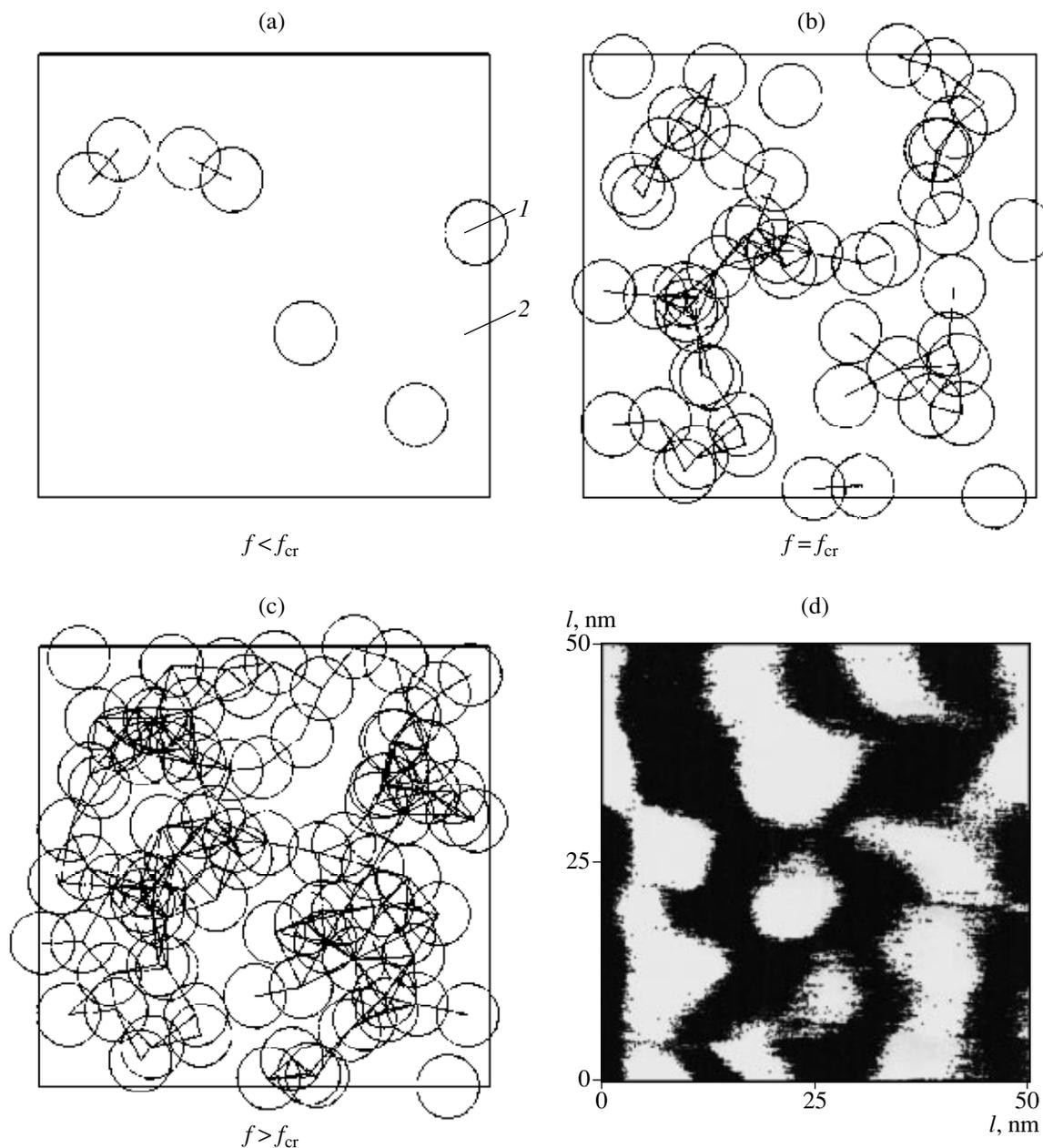
constant and depends on the space dimension. Using calculation models [7, 8, 12], it was shown that, for three-dimensional systems,  $t = 1.6 \pm 0.4$ .

Equation (1) was used to describe the electrical properties of various composites: amorphous and crystalline semiconductors and alloys, as well as metal-filled polymers; i.e. the mixtures of conductor and dielectric [1–7]. In contrast to these compositions, ion-exchange materials operate in the hydrated form. In the course of material swelling in water or in electrolyte solution, the charge associates expand in dimensions and gradually coalesce with each other. The conductance changes abruptly after the attainment of the critical water content due to the formation of an infinite percolation cluster, which represents the connected system of hydrated fixed ion–counterion pairs. Figure 1a–1c<sup>1</sup> illustrate the formation of conducting channels at various  $f$ -to- $f_{cr}$  ratios. Figure 1d demonstrates the photomicrograph of the surface of a swollen Nafion 117 membrane taken using atomic force microscope operating in tapping mode [13].<sup>2</sup> The light regions of the photomicrograph depict the cluster zones of the membrane.

The dielectric–conductor transition is possible only for materials with the concentration of ionic groups providing for the formation of an infinite cluster and the appearance of a macroscopic charge flux in the course of hydration. Therefore, the percolation transition in ion-exchange materials can also be observed while studying conducting properties of swollen membranes on variations in the total amount of fixed ions in the matrix. Hence, we can specify two ways of the forma-

<sup>1</sup> The authors are grateful to Professor N. P. Gnusin and graduate V.V. Umnova for supplying the program, which was used to obtain computer images presented in Figs. 1a–1c.

<sup>2</sup> The photomicrograph was kindly provided by Dr. Vidal, Pier and Mary Curie University, Paris, France.



**Fig. 1.** (a–c) Computer images of the schematic formation of an infinite percolation cluster: (1, 2) are the conducting and nonconducting phases, respectively. (d) AFM-image of the surface of a swollen sample of a Nafion-117 membrane recorded in tapping mode [13]; the light regions are the clusters, and the dark regions is the polymeric skeleton.

tion of an infinite percolation cluster in ion-exchange materials.

(1) By varying the swelling degree of an ion-exchange material during controlled water sorption-desorption processes occurring upon the variations in the concentration of equilibrium electrolyte solution.

(2) By varying the total number of the hydrated fixed ion-counterion pairs at the stage of synthesis due to the change in one of the following factors: the degree of grafting of functional groups to a polymer, conductor-dielectric ratio in a polymeric composition, the

content of a cross-linking agent, and the alkali concentration during the hydrolysis of sulfonyl fluoride groups in perfluorinated membranes.

The effects of the formation of conducting channels in ion-exchange materials during their swelling in water or in electrolyte solution at a constant concentration of fixed ions in a sample we call the *first-kind percolation transitions*; in the case of variations in the number of the fixed ions in a polymer matrix during synthesis, these effects are called the *second-kind percolation transitions*.

Equation (1) was for the first time used to describe ionite conductivity as a function of the degree of the hydration of ionic groups (first-kind percolation transitions) in Nafion membranes [9]. Later, the percolation theory was used to describe the effects of swelling of Nafion 120 membranes in water or the effect of counterion charges on the electrical resistance of Nafion 117 membranes [14, 15]. Timashev et al. applied [16–20] the percolation theory to analyze the results of detailed study of water and ion transport in MF-4SK domestic perfluorinated sulfocationic membranes. These authors observed (using radioactive-tracer technique) abrupt changes in the self-diffusion coefficients of  $\text{Na}^+$  and  $\text{OH}^-$  ions depending on the concentration of NaOH solutions and water content in the membranes. They suggested a microscopic model of ion transport in the membrane matrix, which was used to derive the equation for the coefficient of ion self-diffusion expressing the threshold character of the experimental dependences [16, 20]. The studies of Nafion and MF-4SK perfluorinated sulfocationic membranes allowed to determine the key role of water content and cluster formation in the development of transport channels in ion-exchange materials [9, 14–21]. Recently, the percolation theory was shown to be applicable for the description of diffusion salt transport upon the variation in the composition of heterogeneous [22] and homogeneous [23] ion-exchange membranes.

The analysis of published data demonstrates that ion-exchange materials belong to percolation systems. The parameters of the equation of the percolation theory can be estimated to yield a valuable information on determining the range of conductance threshold, which reflects the appearance of a macroscopic flux of charge (conductance) or mass (diffusion permeability) in a heterogeneous polymer. In this connection, the goal of this work is to estimate and analyze the parameters of the equation of the percolation theory in order to describe the changes in the conductivity of ion-exchange materials under various formation conditions of hydrated channels for ion transport.

## RESULTS AND DISCUSSION

Swelling water of ion-exchange material ( $\nu$  is the volume fraction of water) is usually considered to be the conducting phase in the first-kind percolation transitions. A jump in the conductivity usually takes place at a certain critical value of water content  $\nu_{\text{cr}}$ .

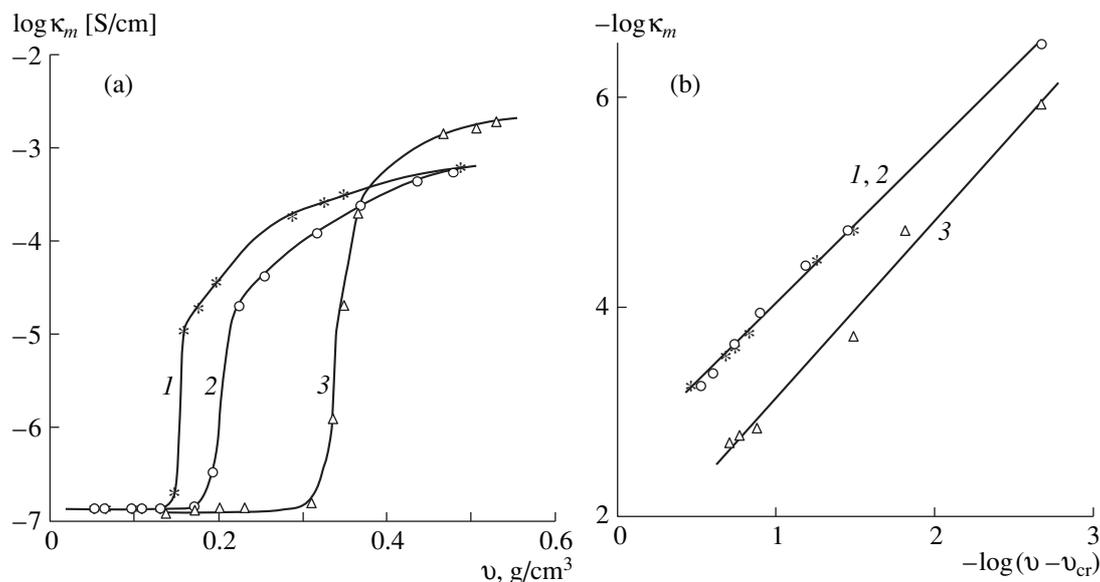
Figure 2 illustrates the measurement results of the conductivity of the commercial heterogeneous membranes MK-40, MA-41I, and MA-41 demonstrating the first-kind percolation transition from a swollen to a dry state. Water desorption from these membranes was studied by the conductometry combined with the measurements of membrane density and the recording of porosimetric curves [24]. However, the applicability of the percolation theory for the description of the dependences of membrane conductivity on water content

during this reverse process (desorption) has not yet been analyzed. Such a transition (conductor–dielectric) is of a considerable significance for the estimation of the electrochemical activity of heterogeneous membranes during electrodialysis, when the membranes are partially dehydrated under the action of various factors (current load, temperature drops, electrosorption of impurities, etc.). As is seen from Fig. 2a, an abrupt change in the conductivity is observed at definite values of water content  $\nu = \nu_{\text{cr}}$  for all membranes. The critical water content was estimated by means of  $\log \kappa_m - \nu$  dependences presented in Fig. 2a, which allowed us to calculate the  $(\nu - \nu_{\text{cr}})$  difference according to Eq. (1). The value of the exponent  $t$  of Eq. 1 was determined as the slope of the  $\log \kappa_m - \log(\nu - \nu_{\text{cr}})$  dependence (Fig. 2b); in this case, the  $\nu_{\text{cr}}$  values were also refined for each membrane. The linear dependences were processed by the standard procedures of the regression analysis [25]. The data processing and curve plotting were carried on IBM PC using Excel 5.0 standard programs. In the course of statistical processing, the  $\nu_{\text{cr}}$  values were adjusted so that the square of the correlation coefficient  $R^2$  characterizing the degree of the variable correlation was as close as possible to unity. The values of  $\nu_{\text{cr}}$ ,  $t$ , and  $R^2$  thus obtained are listed in Table 1. To confirm the data reliability, we verified the adequacy of the linear functions obtained by the Fisher criterion  $F$ . The observed  $F_{\text{obs}}$  and critical  $F_{\text{cr}}$  values of this criterion at the significance level  $q = 0.05$  are represented in Table 1. As is seen from this table, in all the cases  $F_{\text{obs}} > F_{\text{cr}}$ , thus indicating the significance of the linear functions describing the  $\log \kappa_m - \log(\nu - \nu_{\text{cr}})$  dependences. The criterion values suggest a good agreement between the selected model and the experimental data.

As is seen from Table 1, the experimental values of  $t$  and  $f_{\text{cr}}$  are consistent with the theoretical ones. An overestimated value of the threshold water content  $\nu_{\text{cr}}$  is observed for an MK-40 membrane. This can be associated with a higher hydration of sulfo groups ( $-\text{SO}_3^-$ ) as compared with amino groups ( $-\text{CH}_2-\text{N}^+(\text{CH}_3)_3$ ) of anionic membranes that can appear as a retardation of the percolation transition in the course of water desorption. It was disclosed [22] that the  $\nu_{\text{cr}}$  values calculated from conductivity and diffusion permeability measurements are higher for heterogeneous cationic ( $\nu_{\text{cr}} = 0.29$ ) than for anionic membrane ( $\nu_{\text{cr}} = 0.25$ ) prepared on the same chemical bases as MK-40 and MA-41 membranes.

The applicability of the percolation theory to the processes of water desorption from swollen membranes supplements the known ideas of the percolation transitions occurring during the water sorption by dry membranes (i.e., dielectric–conductor transitions) developed for perfluorinated membranes in [9, 14–16, 20, 21].

In order to study the second-kind percolation transitions, we used the data on conductivity ( $\kappa_m$ ) of various



**Fig. 2.** Variation in the specific conductivity of heterogeneous membranes during the water desorption as a function of water content: (a) in semilog coordinates; (b) in the  $\log \kappa_m - \log(v - v_{cr})$  coordinates; (1) MA-41; (2) MA-41I; (3) MK-40.

ion-exchange materials as a function of the conductor-dielectric ratio [26–30]. The data on chemical structure, composition, and preparation procedures for the studied polymeric composites are presented in Table 2. Hydrophilic and conducting properties of the samples of perfluorinated membranes (composition 1) were varied during their preparation at the stage of alkaline hydrolysis: the films 250–300  $\mu\text{m}$  thick made of a copolymer having the equivalent mass equals 1075 g/mol were hydrolyzed with sodium hydroxide solutions of various (concentrations from 1 to 8 M), thus producing samples with different hydrophilicity of the charged sites [26]. Note that the exchange capacity of MF-4SK samples per a unit mass of the dry material remains unchanged and equal to 0.93 mmol/g. All other compositions possess common property: they were prepared from a conducting highly swelling polymer and a non-conducting polymer, which will be called an inert polymer. The films of homogeneous membranes were prepared by copolymerization of conducting and nonconducting polymers. Compositions 2 and 3 were obtained from poly(arylenesulfamides) different in the chemical compositions and the lengths of the macromolecular chains, but having the same polyamide matrix. Their properties have been described in [27, 28, 31, 32]. The data of [29] were also used to compare conductivity of the membrane compositions. In [29], parameters of the

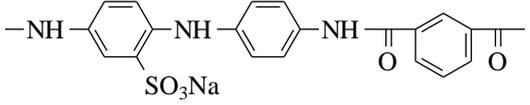
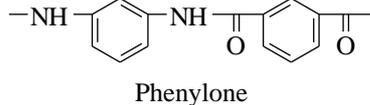
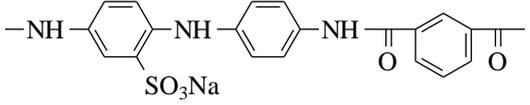
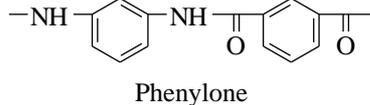
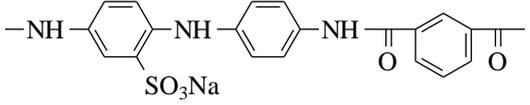
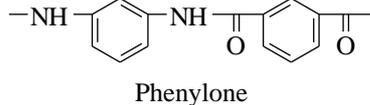
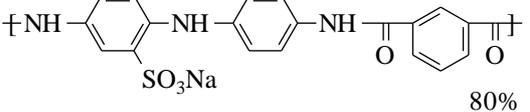
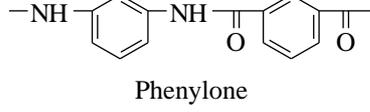
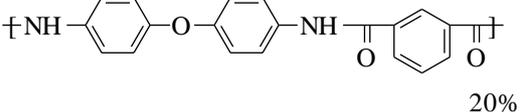
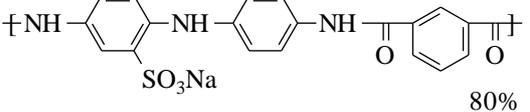
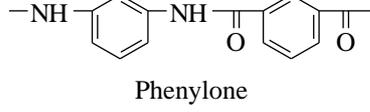
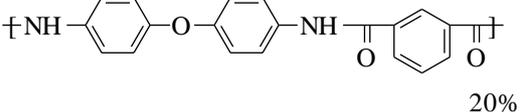
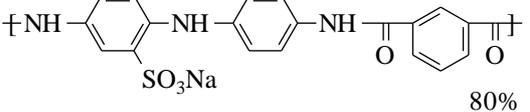
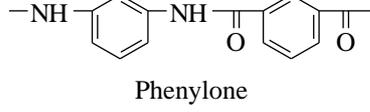
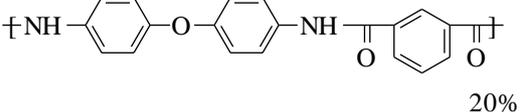
percolation theory were estimated, while studying conducting properties of homogeneous membranes with anisotropic structure prepared by grafting of poly(acrylic acid) on a thin polypropylene film. The content of poly(acrylic acid) varied by changes in the duration of grafting (composition 4). Heterogeneous compositions are represented by granulates (ion-exchange rods) (composition 5) prepared by the extrusion of heated resin and polyethylene mixed in various ratios [30].

When studying the percolation transitions in ion-exchange membranes with various content of inert component, the  $f$  value is calculated as the volume fraction of a charged polymer in the mixture with allowance for the swelling water [23, 29]. In some studies [22], only swelling water is considered to be the conducting phase. Different approaches to the estimation of the conductor volume fraction in membranes complicates the comparison of the parameters of Eq. (1) reported for various ion-exchange membranes. The jump in the membrane conductivity during the second-kind percolation transitions is caused by an increase in the total number of charged sites in a polymer matrix, which in turn changes the total polymer hydration capacity. Therefore, while estimating the fraction of the cluster phase, it is necessary to take into account both the fraction of water incorporated into the membrane

**Table 1.** The values of the critical percolation transition parameters during water desorption from heterogeneous membranes

Membrane type	$v_{cr}$	$t$	$R^2$	$F_{obs}$	$F_{cr}$
MA-41	0.144	$1.46 \pm 0.10$	0.9975	$1.56 \times 10^3$	$2.44 \times 10^{-6}$
MA-41I	0.190	$1.48 \pm 0.10$	0.9967	$1.49 \times 10^3$	$2.19 \times 10^{-7}$
MK-40	0.334	$1.66 \pm 0.27$	0.9863	$2.87 \times 10^2$	$7.11 \times 10^{-5}$

**Table 2.** Chemical structure, preparation methods, and characteristics of ion-exchange compositions

No.	Structural unit and preparation method	Exchange capacity ( $E$ , mmol/g), water content ( $W$ , wt %)	Reference				
1	$-(CF_2-CF_2)_x-(CF_2-CF)_y-$ $\begin{array}{c} \text{O} \\   \\ \text{CF}_2-\text{CF}-\text{O}-(CF_2)_2-\text{SO}_3\text{Na} \\   \\ \text{CF}_3 \end{array}$ <p>The structure was varied at the stage of alkaline hydrolysis: copolymer films 250–300 <math>\mu\text{m}</math> thick were hydrolyzed with NaOH solutions of different concentrations (from 1 to 8 M). The hydrolysis was carried out until the conversion of the sulfofluoride groups was completed</p>	$E = 0.78-0.82$ $W = 11.50-15.68$	[26]				
2	<table border="0" style="width: 100%;"> <tr> <td style="width: 50%; text-align: center;">           Conducting polymer   </td> <td style="width: 50%; text-align: center;">           Nonconducting polymer   </td> </tr> <tr> <td colspan="2" style="text-align: center;">Phenylone</td> </tr> </table> <p>The films were prepared by casting from DMFA solutions. Phenylone content varied from 0 to 70 mol %. The film thickness varied from 50 to 70 <math>\mu\text{m}</math></p>	Conducting polymer 	Nonconducting polymer 	Phenylone		$E = 0.90-1.55$ $W = 6.46-33.01$	[27]
Conducting polymer 	Nonconducting polymer 						
Phenylone							
3	<table border="0" style="width: 100%;"> <tr> <td style="width: 50%; text-align: center;">  <p>80%</p> </td> <td style="width: 50%; text-align: center;">  <p>Phenylone</p> </td> </tr> <tr> <td style="width: 50%; text-align: center;">  <p>20%</p> </td> <td style="width: 50%;"></td> </tr> </table> <p>Membrane films were prepared by casting from polymer solutions in DMFA. Phenylone content varied from 0 to 60 mol %. The films were from 50 to 70 <math>\mu\text{m}</math> thick</p>	 <p>80%</p>	 <p>Phenylone</p>	 <p>20%</p>		$E = 0.79-1.17$ $W = 16.91-33.15$	[28]
 <p>80%</p>	 <p>Phenylone</p>						
 <p>20%</p>							
4	<table border="0" style="width: 100%;"> <tr> <td style="width: 50%; text-align: center;">           Conducting polymer  <math display="block">-[-CH_2-\underset{\text{COOH}}{\text{CH}}-]_n-</math> <p>Poly(acrylic acid)</p> </td> <td style="width: 50%; text-align: center;">           Nonconducting polymer  <math display="block">[-CH_2-\underset{\text{CH}_3}{\text{CH}}-]_n</math> <p>Polypropylene</p> </td> </tr> </table> <p>The membranes were prepared by grafting of poly(acrylic acid) on a thin polypropylene film (<math>23 \pm 2 \mu\text{m}</math>). The amount of the grafted acid was varied from 20 to 80%</p>	Conducting polymer $-[-CH_2-\underset{\text{COOH}}{\text{CH}}-]_n-$ <p>Poly(acrylic acid)</p>	Nonconducting polymer $[-CH_2-\underset{\text{CH}_3}{\text{CH}}-]_n$ <p>Polypropylene</p>	$E = 1.30-1.86$ $W = 22.78-46.21$	[29]		
Conducting polymer $-[-CH_2-\underset{\text{COOH}}{\text{CH}}-]_n-$ <p>Poly(acrylic acid)</p>	Nonconducting polymer $[-CH_2-\underset{\text{CH}_3}{\text{CH}}-]_n$ <p>Polypropylene</p>						
5	<table border="0" style="width: 100%;"> <tr> <td style="width: 50%; text-align: center;"> <math display="block">\begin{array}{c} -\text{CH}-\text{CH}_2-\text{CH}-\text{CH}_2- \\   \quad \quad   \\ \text{C}_6\text{H}_4 \quad \text{C}_6\text{H}_4 \\   \quad \quad   \\ \text{SO}_3\text{H} \quad \text{CH}-\text{CH}_2-\text{CH}-\text{CH}_2- \\   \\ \text{C}_6\text{H}_4 \\   \\ \text{SO}_3\text{H} \end{array}</math> <p>KU-2 <math>\times</math> 8</p> </td> <td style="width: 50%; text-align: center;"> <math display="block">\text{-(CH}_2\text{-CH}_2\text{)}_n\text{-}</math> <p>Polyethylene</p> </td> </tr> </table> <p>The granulates were prepared by the extrusion of a ground KU-2 <math>\times</math> 8 ion-exchange resin and polyethylene at various weight ratios (from 48 to 76%). Diameters of the ion-exchange rods varied from 2 to 3 mm</p>	$\begin{array}{c} -\text{CH}-\text{CH}_2-\text{CH}-\text{CH}_2- \\   \quad \quad   \\ \text{C}_6\text{H}_4 \quad \text{C}_6\text{H}_4 \\   \quad \quad   \\ \text{SO}_3\text{H} \quad \text{CH}-\text{CH}_2-\text{CH}-\text{CH}_2- \\   \\ \text{C}_6\text{H}_4 \\   \\ \text{SO}_3\text{H} \end{array}$ <p>KU-2 <math>\times</math> 8</p>	$\text{-(CH}_2\text{-CH}_2\text{)}_n\text{-}$ <p>Polyethylene</p>	$E = 1.18-1.93$ $W = 29.08-50.00$	[30]		
$\begin{array}{c} -\text{CH}-\text{CH}_2-\text{CH}-\text{CH}_2- \\   \quad \quad   \\ \text{C}_6\text{H}_4 \quad \text{C}_6\text{H}_4 \\   \quad \quad   \\ \text{SO}_3\text{H} \quad \text{CH}-\text{CH}_2-\text{CH}-\text{CH}_2- \\   \\ \text{C}_6\text{H}_4 \\   \\ \text{SO}_3\text{H} \end{array}$ <p>KU-2 <math>\times</math> 8</p>	$\text{-(CH}_2\text{-CH}_2\text{)}_n\text{-}$ <p>Polyethylene</p>						

during its swelling and the fraction of the volume occupied by ion-exchange groups.

In this work, when studying the second-kind percolation transitions, the volume fraction of a conducting

phase was calculated with allowance for the following assumptions:

(a) all of swelling water of a polymeric composition is immobilized in ion-dipole fixed ion-counterion asso-

ciates, and the set of these associates forms a polycluster phase located between polymer chains;

(b) the inert phase consists of the polymer chains forming the structure skeleton and inclusions of a non-conducting thermoplast; e.g., polyethylene in the heterogeneous compositions.

The expression determining the volume fraction of a conducting phase in ion-exchange materials has the following form

$$f = \frac{V'}{V} = \frac{P' d}{d' P}, \quad (2)$$

where  $V$  and  $P$  are the total volume and weight of the ion-exchange material, respectively;  $V'$  and  $P'$  are the volume and weight of the conducting phase, respectively; and  $d'$  and  $d$  are the density of the conducting phase and the average density of the swollen material, respectively. Assuming that  $d' = d$ , we obtain

$$f = \frac{P'}{P}. \quad (3)$$

In terms of the accepted assumptions, Eq. (3) can be represented as

$$f = \frac{N(M + n_w M_w)}{P}, \quad (4)$$

where  $N$  is the total number of ionic groups (mole);  $M$  and  $M_w$  are the molar masses of ionic groups and water, respectively (g/mol); and  $n_w$  is the average number of water molecules per an ionic group.

Equation (4) can be simplified taking into account the definition of the material ion-exchange capacity ( $E$ , mol/g):

$$f = E(M + n_w M_w). \quad (5)$$

After the substitution of the expression  $n_w = \frac{W}{EM_w}$  (where  $W$  is the mass fraction of water in the swollen material) into Eq. (5), we obtain the equation for the calculation of the volume fraction of the conducting phase:

$$f = EM + W. \quad (6)$$

As follows from Eq. (6), we need data on the ion exchange capacity and the water content of the investigated membranes in order to calculate the  $f$  values.

We had at our disposal data of measuring the exchange capacity  $E$ , water content  $W$ , and conductivity  $\kappa_m$  at 25°C as a function of the ratio between conducting and inert components for all materials presented in Table 2. Prior to the measurements of  $\kappa_m$ , the samples of compositions 1–3 were equilibrated with a 0.1 M NaCl solution. Electrical resistance of the samples of composition 4 was measured in a 0.1 M KOH solution by the difference method. In spite of some experimental differences in measuring conductivity by the difference and the mercury-contact methods, the

analysis of data on the samples presented in the table showed that the results for the same salt form of the membranes (at  $t = 25^\circ\text{C}$ ) agree with each other within 7–10% [33].

The dependence of the conductivity of ionite rods based on a KU-2 × 8 resin on the concentration of an equilibrium NaCl solution was studied by the amperometric method [30]. An increase in the conductivity with an external solution concentration was observed in [30]. This resulted from a rise in the number of the current carriers in the ionite, mainly in the phase of the intergel solution and in the microstructure defects due to the Donnan sorption of an electrolyte. This effect is less typical of homogeneous membranes [28, 34]. In order to maximally eliminate the effect of a sorbed electrolyte on the resulting conductivity, we used the values of conductivity of the ion-exchange rods in a 0.01 M NaCl solution.

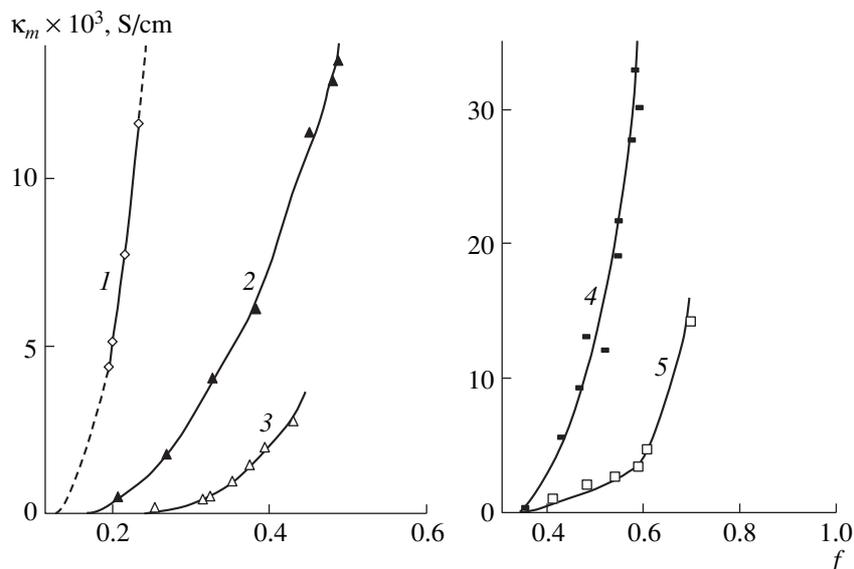
The dependences of the effective conductivity of the studied compositions on the fraction  $f$  of the conducting phase calculated by Eq. (6) are shown in Fig. 3. As is seen from this figure, after reaching specific value of  $f = f_{cr}$ , the effective conductivity increases exponentially with  $f$  that corresponds to Eq. (1) of the percolation theory. Note that, in the case of the first-kind percolation transitions,  $\kappa_m$  of heterogeneous membranes increases by several orders of magnitude in quite a narrow range of water content. The dependence of the conductivity on the fraction of the conducting phase (the second-kind percolation transitions) shows that this change in  $\kappa_m$  is not so abrupt in the studied composition range.

The values of  $f_{cr}$  and  $t$  were estimated based on the  $\log \kappa_m - \log(f - f_{cr})$  dependence. The linear functions obtained are demonstrated in Fig 4. The values of  $f_{cr}$  and  $t$ , as well as the squares of the correlation coefficients  $R^2$  and the values of Fisher criteria  $F$  for the significance level  $q = 0.05$  are listed in Table 3.

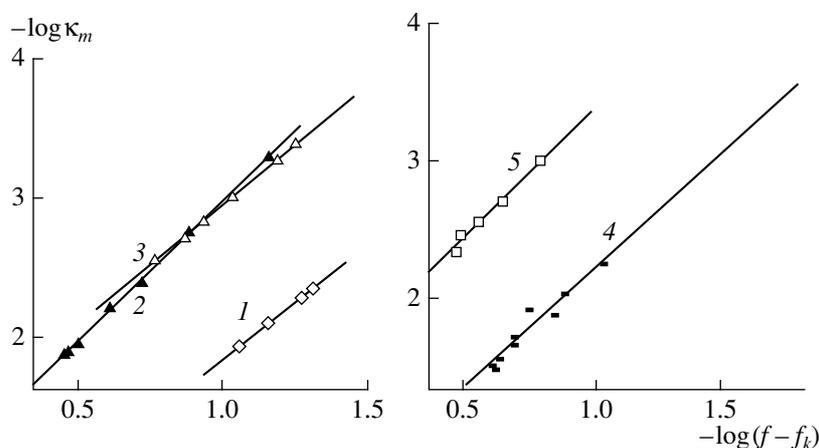
As seen in the table,  $R^2$  values are close to unity, and the observed values of Fisher criterion  $F_{obs}$  are by several orders of magnitude higher than the critical value for all the polymeric materials, thus conforming the adequacy of the model suggested for the description of the effective conductivity of the studied ion-exchange compositions.

As seen in Table 3, the experimental values of the parameter  $t$  agree with the theoretical one. The critical volume fractions of conducting phases  $f_{cr}$  are close to the theoretical value of this parameter ( $f_{cr} = 0.15 \pm 0.03$ ) for the compositions 1 and 2 (Table 2).

The values of  $f_{cr}$  for the membrane compositions 3–5 exceed 0.15 that is associated with the structural features and the preparation method of these samples. The Kaspion membranes (No. 3) differed from the composition 2 in the smaller (approximately twofold) amount of sulfogroups in the poly(aryleneamide) matrix that causes a considerable decrease in the measured con-



**Fig. 3.** The dependences of the specific conductivity of the ion-exchange compositions presented in Table 2 on the fraction of a conducting phase. The line numbers in the figure correspond to the composition numbers in Table 2.



**Fig. 4.** The  $\log \kappa_m - \log(f - f_{cr})$  dependences for the ion-exchange materials presented in Table 2.

ductivity values. In this case, the percolation transition begins at a higher content of a charged component in a composition. This can be explained by the effect of geometrical factors on the formation of a hydrated channel.

The quantitative agreement of the  $f_{cr}$  values for heterogeneous composition 5 and composition 3, on the one hand, indicates the formalism of the percolation theory; but, on the other hand, it reflects the shift of percolation transition associated with the presence of poly-

**Table 3.** The values of the percolation transition critical parameters for various ion-exchange compositions

Composition*	$f_{cr}$	$t$	$R^2$	$F_{obs}$	$F_{cr}$
1	0.150	$1.67 \pm 0.19$	0.9987	$1.52 \times 10^3$	$6.57 \times 10^{-4}$
2	0.140	$2.04 \pm 0.08$	0.9988	$4.02 \times 10^3$	$1.85 \times 10^{-8}$
3	0.260	$1.74 \pm 0.09$	0.9986	$2.94 \times 10^3$	$6.92 \times 10^{-7}$
4	0.331	$1.67 \pm 0.15$	0.9882	$6.68 \times 10^2$	$5.37 \times 10^{-9}$
5	0.248	$1.80 \pm 0.47$	0.9798	$1.46 \times 10^2$	$1.22 \times 10^{-3}$

\* The composition numbers correspond to those in Table 2.

ethylene domains in granulates. Structural defects found in granulate materials occupy from 9 to 20% of the total volume [30]. They contain a part of sorbed water, which is taken into account while estimating the fraction  $f$  of the conducting phase, but which does not take part in the transport processes. The heterogeneity of these materials decelerates the formation of percolation channel, thus affecting  $f_{cr}$  values. Such an approach to the  $f_{cr}$  values allow us to better understand the significant deviation of this parameter from the theory for anisotropic membranes made of composition 4. The deviation of  $f_{cr}$  experimental values for the membranes made of composition 4 from the theoretical one have been explained by the nonuniform distribution of the ion-exchange component in a polypropylene film [29]. The maximal retardation of the percolation transition in the studied membranes can be explained by their lamellar structure, which also hinders the formation of a conducting channel in a material.

### CONCLUSION

The dependence of the conductivity of heterogeneous and homogeneous ion-exchange materials on the volume fraction of a conducting hydrophilic phase was studied. The methods of the percolation theory were used to analyze the data obtained. The parameters of the percolation equation were determined for the case of a decrease in the material conductivity during water desorption from heterogeneous membranes with constant concentration of fixed charges (the first-kind percolation transitions). It was shown that the methods of the percolation theory are applicable also for the description of the conducting properties of ion-exchange membranes with the variations in the number of fixed charges on a polymer matrix in the course of the material preparation from conducting and nonconducting components (the second-kind percolation transitions).

Estimation of  $f_{cr}$  and  $t$  percolation parameters showed that the obtained values of critical index  $t$  agree with the theory ( $t = 1.6 \pm 0.4$ ) for all the materials, and the value of the threshold parameter  $f_{cr}$  varies over the 0.15–0.35 range depending on the structural type and preparation method of a material.

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