

# Percolation Transition in Heterogeneous Ion Exchange Membranes

V. ŠUMBEROVÁ,<sup>1</sup> M. BLEHA,<sup>1,\*</sup> and R. WODZKI<sup>2</sup>

<sup>1</sup>Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 Prague 6, Czechoslovakia, and

<sup>2</sup>Department of Physical Chemistry, Institute of Chemistry, Nicolaus Copernicus University, Torun, Poland

## SYNOPSIS

Electrical conductivity and permeability for NaCl and glucose of heterogeneous cation and anion exchange membranes was studied as a function of the type of ion exchanger and swelling water content. Using membrane composition and the character of data obtained, it was proved that the percolation theory is suitable for the interpretation of experimental results. It was found for both the cationic and anionic type of membranes that the "insulator to conductor" and "nonpermeable to permeable material" percolation transition proceeds at a critical water fraction approximately 0.25. The exponent  $\tau$  of the scaling equation is approximately 1.6, thus lying in the vicinity of the theoretical value for three-dimensional systems.

## INTRODUCTION

The number of membrane processes applications in many industrial branches, biological and medical technologies, and in tackling environmental problems has been sharply increasing during recent years. The preparation of membranes with improved and "tailor-made" properties becomes the main goal of research work in the membrane field. The condition for reaching this goal is a detailed knowledge of the mechanism of all processes included in the penetration of substances through the membrane. One of the most important questions connected with both basic and applied studies is the influence of membrane structure, i.e., detailed geometrical distribution of different components, on transport properties.

It was shown<sup>1-5</sup> that widely studied and applied ionomeric perfluorosulfonic membranes are capable of phase separation into an inverse micellar structure connected by narrow channels of aqueous microdomains. These are composed of more or less hydrated fixed groups, counterions, coions, and nonsolvating water molecules. The structure of heterogeneous ion exchange membranes prepared

by different technology did not draw so much interest as advanced Nafion membranes, yet in the swollen form it can be viewed as a dispersion of aqueous clusters scattered in the polymeric phase. The amount of aqueous microdomains is determined by the balance between the internal osmotic pressure in ion exchange material and the counteracting elasticity of the polymer matrix. In the membrane solution system it is related to the external electrolyte concentration, which affects the activity of water in the membrane internal solution. The distribution of aqueous domains is predetermined by the preparation method.

Membrane basic characteristics, such as electrical conductivity, are related to the probability of occurrence of contacts between aqueous microdomains forming conducting pathways. In the case of permeability of substances of different particle dimensions, the situation is more complicated because only conducting pathways of sufficient dimensions can contribute to the permeation flux of the studied substance. On the basis of membrane structure and character of conductance and permeation processes, the transport properties of membranes may be regarded as adequately described in terms of the percolation theory.

The purpose of this work is to determine experimentally the variation of membrane properties as a function of ion exchanger content, and conse-

\* To whom correspondence should be addressed.

quently water content, and to verify the suitability of the percolation theory for the interpretation of experimental data.

### Theoretical Background

In a wide variety of nonhomogeneous materials, whose components differ sharply in some material property—conductor–insulator composites being a well-known example of such material—a threshold dependence of one component content on the studied property was found. This means that a strong change of properties (the magnitudes often change by several orders) is observed in a very narrow composition range. An explanation of this threshold behavior was made possible by a new conceptual approach, i.e., the mathematical theory of percolation.<sup>6,7</sup> The theoretical bases were laid by Broadbent and Hammersley<sup>8,9</sup> and were first used in a description of heterogeneous material properties by Shante and Kirkpatrick.<sup>10</sup> Experimentally, this approach is based mainly on studies with metal powders; since the paper of Shante, electrical conductivity values, dielectric susceptibility, the Hall effect, optical permeability, magnetoresistance, and mechanical properties of various heterogeneous systems have been described.

In the membrane field the percolation theory was first used for perfluorinated membrane Nafion, whose electrical conductivity increases in a narrow range of swelling water content more than two hundred times.<sup>10–12</sup> In this case the application of percolation approach provided detailed information on the topology of cluster network that assists in the ion transfer. Using conductivity measurements, the threshold transition was also observed in other membranes, mostly in ion exchange ones.<sup>13–20</sup>

A similar phenomenon was found in the permeability of gases and small molecules,<sup>21,22</sup> and it was stated that the process has a percolation character.

The beginning of the percolation theory was linked with an effort to answer the following question (“site percolation problem”). Let us consider a medium composed of spherical particles of equal diameters of the conductor and insulator, randomly distributed in sites of a chosen lattice. What is the lowest probability of the site occupation by a conductor particle, at which with probability approaching unity in an infinite system the conducting particle has always a conductor neighbor so that these particles form a continuous network and the system as a whole behaves as a conductor?<sup>7</sup> It was shown, mainly by way of numerical calculations (Monte Carlo) but also using theoretical methods (group

renormalization) that such probability does exist. At this probability conductor particles are linked to form an “infinite cluster,” which allows the fluid to be transported (fluid may mean electrons, ions, or molecules) through the whole system length. The probability corresponds to the threshold or critical volume fraction of the conductor. By stepping over the threshold value, the percolation transition proceeds; this can be viewed as a special type of phase transition. The percolation transition was shown to be a very general phenomenon, relevant to lattice models on which most numerical calculation were done as well as to systems without an underlying regular structure. With increasing conductor content the growth of the infinite cluster is very quick because it absorbs clusters (areas with linked conductor particles) of smaller dimensions, which corresponds to a sharp increase in conductivity. However, further increase in the conductor content leads mainly to the formation of “dead ends” of the infinite cluster, which practically do not contribute to the conductivity of the system.

It was shown<sup>6</sup> that in the vicinity of the threshold and above it many properties can be described by a simple scaling equation, e.g., in the form for conductivity

$$b = b_0(v - v_k)^\tau \quad (1)$$

where  $b$  is the conductance of a heterogeneous material,  $b_0$  is the conductance of the conducting phase,  $v$  is the volume fraction of the conducting phase,  $v_k$  is the critical volume fraction, and  $\tau$  is the universal constant. Equations of this type can be applied to any percolation system irrespective of its chemical, structural, morphological, and other properties. Exponent  $\tau$  is considered to be universal constant dependent only on the dimensionality of the system and insensitive to the local conductive phase distribution. Its value is<sup>6</sup>  $1.6 \pm 0.2$  for site percolation in a three-dimensional system. Nevertheless, in many real mixtures  $\tau$  was reported<sup>23,24</sup> to vary in a relatively wide range from 1.5 to 3.

Scher and Zahlen<sup>25</sup> proposed the critical volume fraction of the conducting phase as a characteristic constant, dependent on particle shapes and the type of lattice. The significance of the scaling equation consists in the ability to separate the impact on the material structure [included in the term  $(v - v_k)^\tau$ ] from the impact on fluid transport (constant  $b_0$  reflects the specificity of interaction between medium and penetrating fluid). That means that it enables us to gain information on the membrane structure without detailed knowledge of material structure,

and thus without various assumptions whose validity is questionable. The greatest disadvantage of eq. (1) is that there is no possibility of an a priori determination of the margins of its validity.

## EXPERIMENTAL

### Membranes

Heterogeneous ion exchange membranes, prepared from ion exchange materials (derivatives of polystyrene crosslinked with divinylbenzene), blended with polyethylene were used. Test membranes were made<sup>26</sup> by the calandring and pressing technique from high-pressure polyethylene (Bralen FB 4, Slovnaft, Czechoslovakia), atactic polypropylene, and powdery ion exchangers based on styrene-divinylbenzene copolymers (see Table I). The range of ion exchanger content is as wide as mechanical properties of the membranes allowed (e.g., for cationic membranes it varied from 20 to 65 wt %). Basic characteristics of both cationic and anionic membranes are listed in Table I.

### Permeability of Membranes

The rate of transport of electrolyte (NaCl) or non-electrolyte (glucose) was studied in the system



The permeability cell consisting of two 50-mL chambers separated by a membrane with a working area of 3.14 cm<sup>2</sup> was used. The downstream chamber was filled with distilled water, the upstream one was

filled with a solution of known initial concentration (0.5 M for NaCl and 2 M for glucose). The solutions were intensively stirred in order to minimize the thickness of nonmoving surface films decreasing the measured value of permeability coefficient. The temperature of the system was held at 25 ± 0.1°C. The time dependence of solute concentration in the downstream chamber was measured using either a conductivity electrode in the case of NaCl or a refractometer in the case of glucose. The permeability coefficients  $P$  were calculated from the slope of the steady-state plot according to the equation

$$Q = cV = PA \left( \frac{C_0}{d} \right) \left( t - \frac{d^2}{6D} \right) \quad (2)$$

where  $Q$  is the total amount of the substance transported through the membrane during time  $t$ ,  $c$  is the concentration in the downstream chamber in time  $t$ ,  $C_0$  is the initial concentration in the upstream chamber,  $V$  is the volume of the downstream chamber,  $A$  is the membrane area,  $d$  the membrane thickness, and  $D$  the diffusion coefficient of substance in membrane.

### Electrical Conductivity Measurement<sup>27</sup>

A resistance cell similar to the permeability cell was used. The membrane previously equilibrated with 0.5 M NaCl solution, with an effective area of 0.78 cm<sup>2</sup> was placed between two stirred chambers. Both chambers were filled with a 0.5 M NaCl solution and after temperature stabilization the conductivity  $L_{m+r}$  was measured using Pt electrodes and a source of stabilized constant direct current. After removing

**Table I Basic Characteristics of Anionic and Cationic Membranes**

Membrane <sup>a</sup>	N Content (%)	Equil. Water <sup>b</sup> (g/g)	Membrane <sup>c</sup>	S Content (%)	Equil. water <sup>b</sup> (g/g)
A1	1.01	0.144	C1	2.73	0.091
A2	1.44	0.211	C2	3.14	0.224
A3	1.68	0.302	C3	5.10	0.326
A4	1.89	0.412	C4	6.24	0.453
A5	1.92	0.466	C5	7.07	0.479
A6	2.01	0.506	C6	7.14	0.493
A7	2.03	0.515	C7	7.80	0.515
A8	2.11	0.563	C8	8.43	0.642
A9	2.16	0.631	C9	9.00	0.672

<sup>a</sup> Prepared from the anion exchanger Varion AT-400 (Hungary).

<sup>b</sup> Per gram of dry membrane, at 25°C.

<sup>c</sup> Prepared from the cation exchanger Ostion KS-8 (Spolchemie, Czechoslovakia).

the membrane, the conductivity  $L_r$  of the system was measured. The conductivity was calculated according to the relation

$$L = \frac{d}{(1/L_{m+r} - 1/L_r)A} \quad (3)$$

## RESULTS AND DISCUSSION

The membranes possess heterogeneity of a dual character. It is caused by the topology and linkage of ion exchange resin particles inside the impermeable backbone in the first place, and also by the topology and shape of aqueous microdomains in these particles caused by nonrandom distribution of functional groups in the ion exchanger. The distribution of water microdomains is controlled by swelling rules of crosslinked polyelectrolytes and thus cannot be fully random. The heterogeneity of our membranes was proved by an equilibrium electrolyte partition study, which is the subject of the previous paper.<sup>26</sup> In respect to the shape of conducting aqueous microdomains, the best description is a system of strongly overlapping droplets of the "island" structure.

The conductivities of anionic membranes together with the permeability coefficients of NaCl and glucose in these membranes are summarized in Table II, and the dependence of the conductivity of cationic membranes on the internal water content is illustrated in Figure 1.

The equations of scaling type (1) were used in the description of the dependence of measured data on water content. In this connection interesting

questions arise, viz.: Are the constants  $v_k$  and  $\tau$  sufficiently universal for an accurate description of different properties, or should they be understood just as adjustable parameters, which differ for all types of data? Does the conductivity threshold coincide with the permeability one? Taking into account the idea of substance transport through water channels without any interaction with the surrounding medium, it is necessary to expect that species of larger diameter pass only through sufficiently wider branches of the network, and this fact should be reflected in the values of constants leading to larger  $v_k$  and smaller  $\tau$ . For this reason all types of data were analyzed, first independently and then simultaneously. The use of a nonlinear regression method in the determination of  $v_k$  and  $\tau$  was not without problems, and therefore the linearized dependence

$$\ln P = \ln P_0 + \tau \ln(v - v_k) \quad (4)$$

was used. For a series of  $v_k$  values a series of corresponding values of  $\tau$  was calculated by the least-squares method. The  $v_k$  value with the maximum correlation coefficient or the least-squares deviations between the experimental and calculated data was selected. All kinds of data (that is the conductivity and permeability coefficients of glucose and NaCl) were also treated simultaneously. In addition, the values of  $v_k$  were found, which by the least-squares method lead to the theoretical value 1.6 (Figs. 2 and 3). Calculated parameters are summarized in Table III.

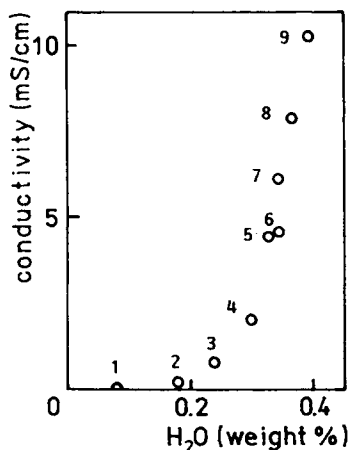
For anionic membranes all  $v_k$  and  $\tau$  values are in a surprisingly good agreement, and the calculated parameters  $v_k$  are within the limits of the theoretical value. In the case of cationic membranes the value

**Table II** Conductivity and Permeability Coefficients of Anionic Membranes

Membrane	Equil. Water (g/g) <sup>a</sup>	Conductivity (mS/cm)	$P(\text{NaCl}) \times 10^8$ (cm <sup>2</sup> /s) <sup>b</sup>	$P(\text{glucose}) \times 10^8$ (cm <sup>2</sup> /s) <sup>b</sup>
A1	0.126	$2.75 \times 10^{-4}$	0	0
A2	0.173	$3.5 \times 10^{-4}$	0	0
A3	0.232	0.495	1.32	0.61
A4	0.293	1.99	5.67	2.02
A5	0.318	4.72	8.40	3.79
A6	0.336	4.13	14.3	5.20
A7	0.340	5.51	16.9	6.01
A8	0.360	7.42	19.0	7.62
A9	0.385	10.07	25.6	9.60

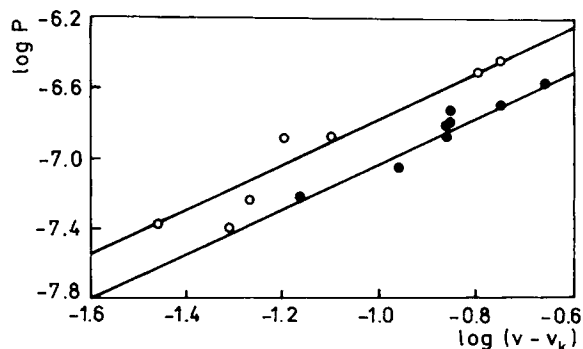
<sup>a</sup> Per gram of swollen membrane, at 25°C.

<sup>b</sup> Flux/concentration difference/thickness [see Eq. (2)].

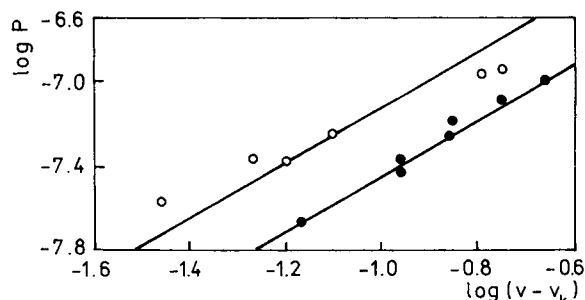


**Figure 1** Dependence of conductivity of cationic membranes C1-C9 on water content (wt %).

of  $v_k$  based on conductivity data differs by 5 absolute % from the permeability value. The value of exponent  $\tau$  is a little lower than predicted by theory and corresponds to the conductivity value of membranes with a conducting component distribution gradient.<sup>15</sup> An unambiguous solution to the above problem using the results obtained is questionable. Cationic membrane parameters would lead to conclusions slightly different from those obtained with the anionic membrane parameters, yet there is no apparent reason for this difference. When comparing the calculated parameters, it is necessary to note that the membranes in conductivity and permeability measurements are not identical as to their water content. In the case of conductivity measure-



**Figure 2** Logarithm of the permeability coefficient of NaCl plotted against the logarithm of water fraction in excess of the percolation threshold ( $v - v_k$ ) for cationic C3-C9 (○) and anionic A3-A9 (●) membranes. [The line represents the least-squares fit of data in eq. (4) for  $\tau = 1.6$ .]



**Figure 3** Logarithm of the permeability coefficient of glucose plotted against the logarithm of water fraction in excess of the percolation threshold ( $v - v_k$ ) for cationic C3-C9 (○) and anionic A3-A9 (●) membranes. [The line represents the least-squares fit of data in eq. (4) for  $\tau = 1.6$ .]

ments the membranes are equilibrated in a 0.5M NaCl solution, which causes deswelling of several percent of water compared with swelling in distilled water. During permeability measurements one membrane surface is in contact with the solution of substance, the other with distilled water and the concentration profile of NaCl and, consequently, that of water develop during the measurement.

Alternatively, the differences between conductivity ( $v_k = 0.239$ ) and permeability ( $v_k = 0.29$ ) data for cationic membranes can be explained by taking into account the properties of the internal electrolyte of membranes. It is well known that the electrolyte is sorbed into microdomains characterized by a low concentration of functional groups, and these zones may form the prevailing conducting pathways. Simultaneously, a significant part of aqueous microdomains characterized by a high concentration of functional groups remains inaccessible to an external electrolyte. This produces some excluded (toward effective conduction) volume that raises  $v_k$  in comparison with the value predicted by the theory. Naturally, this idea is correct only if the specific conductivity and permeability of "pure internal solution" is much lower than those of microdomains filled additionally with NaCl. This effect should be more visible for permeability data where diffusing ions are characterized by fixed charged groups and the selective zones described above do not take part in permeability processes. This explanation should hold also for anionic membranes, where, however, estimated  $v_k$  values agreed with each other. This reasoning would lead to a conclusion that the content of nonselective microdomains in cationic membranes is higher than in anionic ones. The Glueckauf's heterogeneity factors found in a previous

**Table III Critical Volume Fraction  $v_k$  and Exponent  $\tau$  Calculated According to the Eq. (4)**

Membrane	Data	$v_k$	$\tau$	Correlation Coefficient	$v_k$ ( $\tau = 1.6$ )
Anionic A3-A9	Conductivity	0.255	1.33	0.974	0.236
	$P(\text{NaCl})$	0.25	1.35	0.961	0.236
	$P(\text{glucose})$	0.25	1.30	0.992	0.239
	All data	0.255	1.32	—	0.240
Cationic C3-C9	Conductivity	0.239	1.66	0.951	0.238
	$P(\text{NaCl})$	0.29	1.20	0.941	0.275
	$P(\text{glucose})$	0.29	1.20	0.995	0.239
	All data	0.25	1.22	—	0.240

study<sup>26</sup> really confirm the above hypothesis, but a question remains whether the difference in heterogeneity factors ( $z = 0.90$  and  $0.77$ ) is sufficient to explain the differences in the  $v_k$  values.

In the same way the agreement of  $v_k$  values for electrolyte and nonelectrolyte permeability data can be explained because the solubility of saccharides in aqueous microdomains containing a higher than average concentration of charged groups is strongly limited.<sup>28</sup>

To confirm or exclude the preceding ideas, it would be useful to study the permeability of other substances, which is the goal of our forthcoming study, and to carry out investigations using electrolytes (or nonelectrolytes) of various concentrations.

The  $v_k$  value characterizing the membrane structure can be compared with values found in the literature obtained by simulation calculations for dif-

ferent models. In this way it is possible to estimate indirectly what the distribution of membrane domains can be.

The values of  $v_k$  parameters in Table III have the meaning of weight fractions. On the other hand, however, the percolation probability is related to volume fractions. The transformation of weight to volume fractions in a system of several components must be accompanied by simplifying assumptions. As the densities of all membranes in this study are not far from unity, it can be assumed that the weight and volume fractions are close. The  $v_k$  values from the literature are given in Table IV. For the Nafion membranes two different values of critical volume fractions were reported:  $v_k = 0.1$  (Refs. 11, 12) and  $v_k = 0.26$  (Ref. 19). The membranes prepared from 10–30  $\mu\text{m}$  particles of an ion exchanger material obtained by grinding cannot correspond to models of spherical particles. The values ( $v_k = 0.25 - 0.29$ ) found in this study lie in a range where according to Kirkpatrick<sup>6</sup> all the threshold concentrations of real compacted mixtures should fall. They are comparable with model values for nonspherical particles or models where conducting particles agglomerate to larger units. Both these symptoms can be attributes of heterogeneous membranes.

**Table IV Critical Volume Fraction  $v_k$  Values of Various Models**

Model	$v_k$	Reference
Spherical particles, whose diameters are $\frac{1}{2}$ of the distance between particles in a regular lattice (densely packed hard spheres)	0.15	12
Identical spherical particles (permitted to overlap) randomly distributed in space	0.29	6
	0.089	29
Nonspherical particles, both phases have similar form	0.07	30
	0.25	6
Conducting particles tend to flocculate several domains	0.27	31

## CONCLUSIONS

The percolation theory has been found useful for an interpretation of conductivity and permeability data of heterogeneous membranes. The critical water content lies in the typical range, while exponents of the scaling equation calculated by the least-squares method are slightly lower than the theoretical values

for site percolation. The results indicate that the relation of values of two quantities remains approximately constant in the range of validity of the scaling equation. This could enable us to make rough predictions of another quantity of interest in this range, using only 1–2 known experimental values of this quantity.

The estimated critical fractions for both types of membranes indicate that there is no random distribution of aqueous microdomains. This could be connected with the technology of membrane production.

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Received December 3, 1991

Accepted December 6, 1991