

Percolation Conductivity in Nafion Membranes

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Synopsis

This article deals with the method of determination of a threshold volume fraction of the conductive phase within perfluorosulfonic acid ionomer Nafion. Experiments have been performed with the commercial Nafion-120 and Nafion-427 membranes equilibrated with concentrated sodium chloride and sodium hydroxide solutions at 353 K. It has been stated that the insulator-to-conductor transition in membranes occurs at the critical volume fraction of the conductive phase (V_c) equal to 0.1. The same V_c has been estimated for a geometrical cluster-network model. Lower than the theoretical V_c for a classical dense-packed-hard-sphere model ($V_c = 0.15$), the volume fraction for the membranes is caused mainly by channels connecting the ionic clusters. The critical exponent t has been calculated for both membranes and found to be equal to 1.6 for Nafion-120 and 1.5 for Nafion-427. Both these constants correspond to those theoretically predicted for 3D systems. The ratios of sodium ion mobility in the internal membrane solution to its mobility in the equilibrating NaCl or NaOH solutions (\bar{u}_+/u_+) are below unity, and they are dependent on the nature and concentration of the electrolyte.

INTRODUCTION

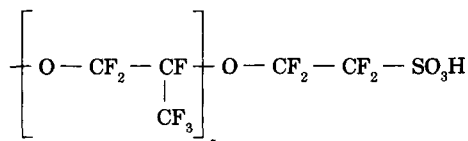
In ionomers the spontaneous internal microphase separation leads to the formation of clusters composed of ionic repeat units, surrounded by an inert polymer matrix. The electrical conductivity of the system with the conducting phase dispersed in a nonconducting medium is quite a general problem and it is characteristic for bi- and multicomponent mixtures, alloys, and block copolymers. The main problems in the study of these systems are: the relation between the conductivity and shape and mutual disposition of the conducting domains; the critical concentration of the dispersed phase which enables the conductance.

The perfluorosulfonic Nafion membranes exhibit ion clustered morphology.¹⁻³ These membranes have received considerable attention due to their exceptional chemical^{4,5} and physicochemical⁶⁻¹⁰ properties and transport behavior.¹¹⁻¹⁴ In our previous paper¹⁵ the results of electrolyte sorption and swelling of Nafion membranes in concentrated sodium chloride and sodium hydroxide solutions were presented. Proceeding further with the studies of Nafion membranes, we present now more data on their ionic conductivity and structure. The determinations of membrane conductivity have been carried out at ambient electrolyte concentrations and temperature close to those appearing in the chloralkali cells. The same conditions were also appropriate in order to determine the critical volume fraction of ionic clusters, according to the percolation theory.

EXPERIMENTAL

Materials

The membranes used in our studies were the commercially available Nafion-120 and Nafion-427 membranes. Both membranes are composed of the perfluoroethylene backbone and contain the acid side chains of the following composition¹⁶:



where $z = 1, 2, 3, \dots$

For these membranes the number of fixed charges, expressed in terms of equivalent weight (EW), i.e., the weight of ionic polymer which neutralizes one equivalent of base, is 1200. Nafion-427 is additionally reinforced with a Teflon cloth.

Prior to use, the membrane samples were submitted to a standard pre-treatment, i.e., they were boiled in distilled water for 3 h. Then, they were converted to their sodium form by soaking in sodium chloride solution (1 mol/dm³) for over 24 h with several changes of the solution, followed by washing with water. Before measuring the membrane conductivity, samples of known geometry were immersed in sodium chloride or sodium hydroxide solutions of appropriate concentration and temperature. After equilibration, the membranes were blotted with hard filter paper to remove surface moisture and their thickness was measured with a micrometer.

The sorption of electrolytes (\bar{S}) (mol sorbed electrolyte/mol—SO₃⁻ group) and the swelling (\bar{N}) (mol water/mol—SO₃⁻ group) were determined by the interpolation of experimental data presented in our previous paper.¹⁵

Membrane Conductivity Measurements

The conductivity was measured applying the A-C method using the equipment similar to the one elaborated previously¹⁷ in our laboratory. For the measurements a Meratronik Automatic C Bridge Type E315A was used. This bridge operates at the frequency of 1000 Hz with the automatic correction of capacitance. The measurements were carried out for membranes equilibrated with sodium chloride solution of the concentration 0.16–4.70 mol/dm³ and sodium hydroxide solution of the concentration 0.24–13.9 mol/dm³. All the measurements were performed at 353 K. The reproducibility of membrane conductivity determinations was 3–5%. The results are presented in Figure 1.

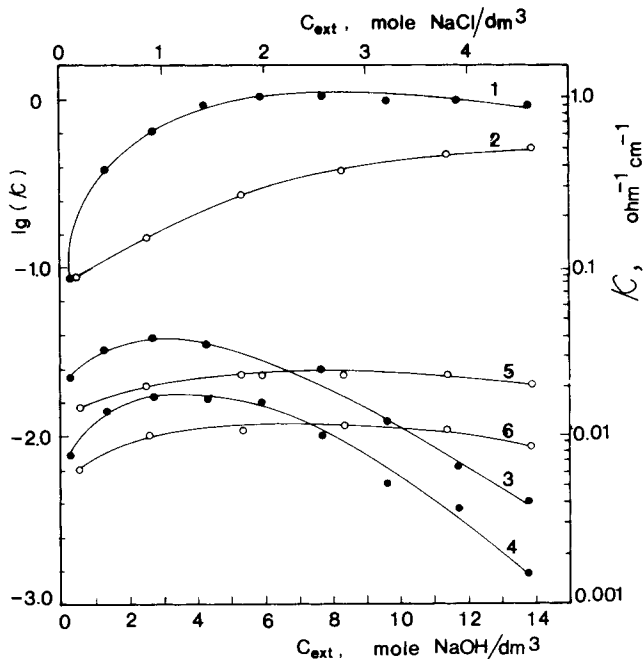


Fig. 1. Conductivity dependence on the concentration of an external electrolyte: NaOH solutions (1), NaCl solutions (2), Nafion-120 (3), and Nafion-427 (4) equilibrated with NaOH solutions; Nafion-120 (5) and Nafion-427 (6) equilibrated with NaCl solutions.

RESULTS AND DISCUSSION

The Conductivity of Nafion Membranes as the Two-Phase Systems

According to the theoretical considerations^{18,19} and experimental data,¹³ Nafion membranes represent a system composed of electrically conductive clusters dispersed in the continuous insulating phase of fluorocarbon polymer. Within the membrane equilibrated with an external electrolyte the clusters contain functional groups, water and an absorbed electrolyte. Water and ions in clusters form an internal solution of the total volume fraction V and specific conductivity κ_r . Both these quantities and spatial distribution of clusters are substantial for the properties of a membrane.

The relation between the membrane conductivity (κ_m), the conductivity and volume fraction of the internal solution (κ_r, V), and a set of parameters describing the spatial distribution and a shape of conductive domains (K) can be written in a general form:

$$\kappa_m = F(\kappa_r, V, K) \quad (1)$$

For the interpretation of the membrane structure and conductivity this equation should be solved. The function F can be derived from a number of different theories describing the conductivity of heterogeneous systems,

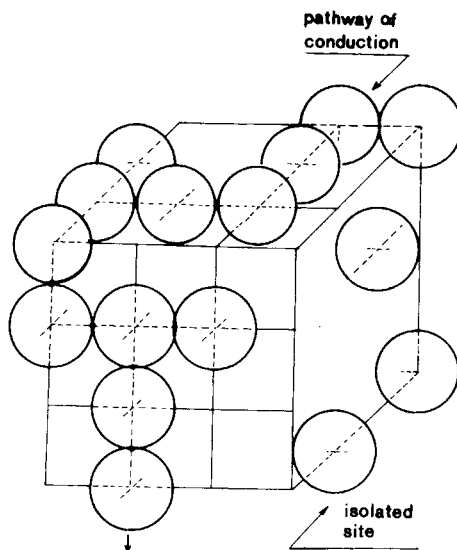


Fig. 2. A dense-packed-hard-sphere model; the spatial disposition of conductive spheres on the simple cubic (SC) lattice.

one of them being the percolation theory. The principles of this theory were formulated by Broadbent and Hammersley^{20,21} and later the theory was adapted by Shante and Kirkpatrick^{22,23} for the interpretation of the conductivity of two-phase systems and resistor lattices. An attempt to apply the percolation theory to the interpretation of the conductivity of ion-exchange membranes was reported by Hsu et al.²⁴

In order to solve the membrane conductivity problem with the percolation theory, an appropriate percolation model should be selected. The percolation can proceed through "sites" or through site connecting "bonds." Looking for a model for Nafion, as the first approximation, one may regard this polymer as a set of conductive spherical particles dispersed in a continuous medium and for such a model the site percolation theory can be applied. The model which corresponds to such a system is called a "dense-packed-hard-sphere" (DPHS) model, and it is this model that is presented as an example for a simple cubic (SC) lattice in Figure 2.

Near the conductor-to-insulator phase transition, the probability of conduction $P(X)$ of such systems satisfies the following relation very closely²³:

$$P(X) \propto (X - X_c)^\beta \quad (2)$$

where X and X_c are the concentration and the critical concentration of conductive sites and β is a universal constant. Scher and Zallen²⁵ stated that if conducting and insulating spheres of radii equal to one half of the nearest-neighbor distance are centered onto the nodes of various three-dimensional (3D) lattices, then the conductivity of the system may be expressed by

$$\kappa_m = \kappa_r (V - V_c)^t \quad (3)$$

where V is the volume fraction of a conductive phase, V_c the same volume at the conductivity threshold, and t a universal critical exponent. The same equation is adequate for the system composed of conducting spheres embedded in the continuous insulating medium. The corresponding volume fractions are defined as

$$V = f \cdot p \quad (4)$$

where f is a filling factor for the lattice and p is the probability of the occupation of each of the lattice nodes by a conductive site. The critical concentration and the critical volume appearing in eqs. (2) and (3) depend on the symmetry of a lattice or topological features of a conducting system whereas s and t are universal constants depending only on the spatial dimension of the system.

Determination of the Parameters V_c , t , and κ_r

Hsu et al.²⁴ reported the values of V_c , t , and κ_r determined on the ground of conductivity measured for Nafion membranes of equivalent weights from 1050 up to 1500, i.e., of different V . In their calculations they assumed κ_r invariant for the samples of different volume fractions of a conductive phase.

In our experiments we changed V in the membranes causing their shrinkage and deswelling in concentrated solutions of electrolytes. Consequently, the volume fraction of a conductive phase in the membranes at equilibrium with electrolytes of different concentrations were calculated as the sum of partial volumes of water, sodium counterions, and sorbed electrolyte. In the calculations it has been assumed that the partial molar volumes of NaCl and NaOH in membranes are the same as in aqueous electrolyte solutions of equal concentrations. The partial molar volumes V_{NaCl} were found through the interpolation of published data²⁶ whereas for NaOH they were computed using apparent molar volumes, according to Monk.²⁷ The partial molar volume of sodium counterions was assumed to be equal to that of sodium ions at infinite dilution, i.e., $-1.5 \text{ cm}^3/\text{mol}$.²⁷ The variations of V with the concentration of NaCl or NaOH as external electrolytes (C_{ext}) for both membranes can be seen in Figure 3.

With the increase of C_{ext} , however, not only the volume fraction V but also the conductivity of dispersed phase (κ_r) changes as a result of increased Donnan sorption. This made it impossible to calculate V_c and t by a simple approximation of experimental data with eq. (3). Therefore, the conductivity of an internal phase (κ_r) and its variation with C_{ext} , as well as constants V_c and t , were computed using the relations presented below. In derivations the Donnan-Kohlrausch equation was taken as a general relation describing both the sorption of an electrolyte and the conductivity. For the membrane equilibrated with 1:1 electrolyte its conductivity should be expressed as

$$\kappa_r = (\bar{M} + \bar{m})F\bar{u}_+ + \bar{m}F\bar{u}_- \quad (5)$$

where \bar{M} , \bar{m} , \bar{u}_+ , \bar{u}_- denote the concentrations of acid groups, the absorbed electrolyte, and the mobility of ions in the internal membrane solution.

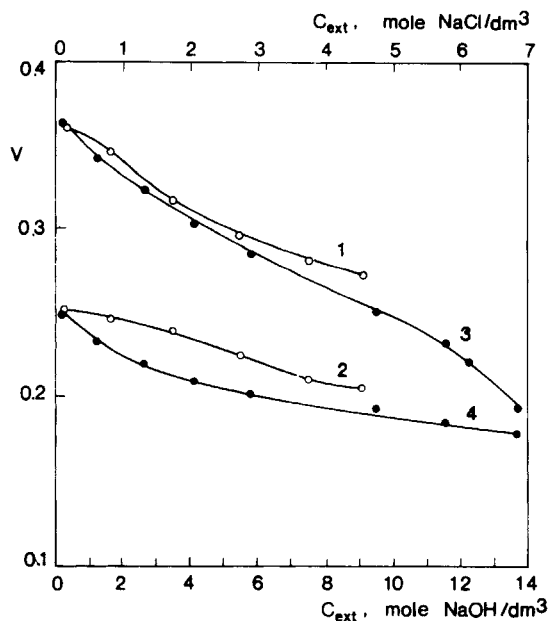


Fig. 3. Volume fraction of clusters dependence on the concentration of an external electrolyte: Nafion-120 (1) and Nafion-427 (2) equilibrated with NaCl solutions, Nafion-120 (3) and Nafion-427 (4) equilibrated with NaOH solutions.

Using eq. (5) the ratio of κ_r to the conductivity of the external solution κ_e may be written in the form:

$$\kappa_r/\kappa_e = [(\bar{M} + \bar{m})F\bar{u}_+ + \bar{m}F\bar{u}_-]/mF(u_+ + u_-) \quad (6)$$

Dividing the numerator and denominator of the right side of eq. (6) by \bar{M} , we get a new equation:

$$\kappa_r/\kappa_e = [(1 + \bar{S})\bar{u}_+ + \bar{S}\bar{u}_-]/X(u_+ + u_-) \quad (7)$$

in which

$$\bar{S} = \bar{m}/\bar{M} \quad \text{and} \quad X = m/\bar{M} \quad (8)$$

Introducing the expression for the transport number of counterions in membranes written in the form

$$\bar{t}_+ = (1 + \bar{S})\bar{u}_+ / [(1 + \bar{S})\bar{u}_+ + \bar{S}\bar{u}_-] \quad (9)$$

to eq. (7), we get another equation:

$$\kappa_r/\kappa_e = (1 + \bar{S})\bar{t}_+\bar{u}_+ / X\bar{t}_+u_+ \quad (10)$$

This relation can be already applied for the calculations of κ_r if \bar{t}_+ is known. It is possible, however, to eliminate \bar{t}_+ employing the Arnold and Swift²⁸

equation relating the counterion transport number in membrane to the sorption of an electrolyte (\bar{S}):

$$\bar{t}_+ = (1 + \bar{S})t_+ / (\bar{S} + t_+) \quad (11)$$

The validity of this equation for perfluorosulfonic membranes was verified earlier²⁹ comparing the counterion transport numbers calculated with eq. (11) with those determined from emf measurements.

Inserting eq. (11) into eq. (10), we get finally

$$\kappa_r / \kappa_e = (\bar{u}_+ / u_+)G \quad (12)$$

where

$$G = (t_+ + \bar{S}) / X \quad (13)$$

The calculations, while applying eq. (12), are possible (1) if the mobility ratio \bar{u}_+ / u_+ is known, (2) assuming $\bar{u}_+ = u_+$, or (3) trying to find this ratio through other data. As the ratio \bar{u}_+ / u_+ may vary with concentration, similarly as G , the left side of eq. (12) was replaced in the present work by the approximative function containing G as a variable:

$$\kappa_r / \kappa_e = f(G) \quad (14)$$

Taking for the preliminary analysis of κ_r the constants V_c and t from the paper published by Hsu,²⁴ we have established that the function $f(G)$ may be expressed as a polynomial. For the membranes equilibrated with NaCl solutions the linear relation is a sufficient approximation, i.e.,

$$f(G) = k_1 + k_2G \quad (15)$$

whereas for the membranes in contact with NaOH solutions the polynomial of the second order should be used:

$$f(G) = k_1 + k_2G + k_3G^2 \quad (16)$$

The corresponding curves can be seen in Figure 4. Going back to eqs. (15) and (16), we may now write the following approximating functions for the experimental quantities κ_m , κ_e and V :

$$\kappa_m / \kappa_e = (k_1 + k_2G)(V - V_c)^t \quad (17)$$

or

$$\kappa_m / \kappa_e = (k_1 + k_2G + k_3G^2)(V - V_c)^t \quad (18)$$

In these equations k_1 , k_2 , k_3 , V_c , and t are unknown constants whereas G and V are variables. According to the requirements of the theory and experiments, eqs. (17) and (18) can be applied if $\kappa_r \leq \kappa_e$. In practice it means

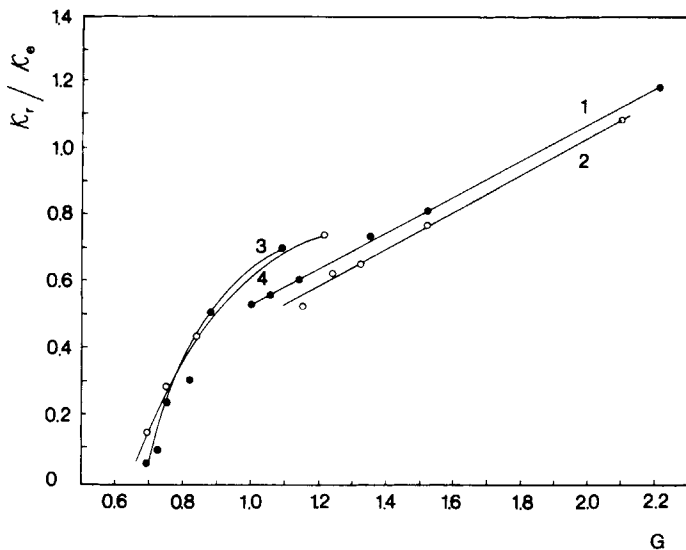


Fig. 4. Conductivity κ_r/κ_e dependence on G , with $t = 1.5$ and $V_c = 0.1$: Nafion-120 (1) and Nafion-427 (2) equilibrated with NaCl solutions, Nafion-120 (3) and Nafion-427 (4) equilibrated with NaOH solutions.

that these equations describe the conductivity of membranes equilibrated with the solutions of the conductivity above that of the isoconductance point, i.e., $\kappa_m = \kappa_e$.

The Structure of Nafion Membranes in Terms of the Percolation Theory

The calculations of the constants k , t and of a critical volume fraction V_c were performed with the Riad R-32 Computer, using the modified IBM Share Programme No. 1428. The constants, as determined from the best fit of eq. (17) to our experimental data, are presented in Table I. The values for V_c and t computed while applying eq. (18) for the membranes equilibrated with NaOH solutions are within the same range as for NaCl. These results are in agreement with those published by Hsu,²⁴ who found $V_c = 0.1$ and $t = 1.5 \pm 0.2$. Inconsiderable differences between V_c and t for Nafion-120 and Nafion-427 membranes reflect possibly an enhanced fraction of nonspherical conductive domains in Nafion-427. These domains appear as the cracks

TABLE I
The Critical Volume Fraction (V_c) and Critical Exponent t for Nafion-120 and 427 Membranes from the Conductivity Data

Parameter	Nafion-120	Nafion-427
V_c	0.10 ± 0.01	0.094 ± 0.015
t	1.61 ± 0.05	1.51 ± 0.08
k_1	-0.005	0.010
k_2	0.675	0.503

TABLE II
Critical Volume Fraction for a Dense-Packed-Hard-Sphere (DPHS) Model (Literature Data)
and Those Calculated for a Cluster-Network (CN) Model

Lattice	DPHS model (V_c^{DPHS})	CN model (V_c^{CN})	
		Nearest-neighbor correlation	Additional correlation
SC	0.163	0.112	0.094
BCC	0.169	0.115	0.097
FCC, HCP—	0.154	0.105	0.088
Diamond	0.146	0.100	0.084
RND	0.153	0.104	0.088

between the polymer and the reinforcing cloth and become easily filled with an electrolyte.

The t exponents are within the range predicted by theory²³ for site and bond percolation processes in the 3D systems (1.5 ± 0.2). The threshold volume fractions V_c are, however, much below those presented in Table II for a dense-packed-hard-sphere (DPHS) model on regular and random lattices. As the possible sources for discrepancies between the experimental and theoretical V_c , one may suggest (i) the distribution of the cluster sizes and the appearance of the "narrow-channels" between clusters³⁰ and (ii) the deformation of the cluster shape from spherical to rodlike one.¹³

The width of narrow channels and the smallest clusters is about 1.0 nm. They introduce an additional network structure to the system. With some simplifications, the entire system composed of clusters and channels may be imagined as that in Figure 5(a). In this figure the structure of Nafion is exemplified using SC lattice; however, the other lattices are also possible.

Considering the spatial distribution of clusters and channels in 3D space, the calculations were performed taking a cluster diameter and the size of channels as given by Hsu and Gierke.³¹ The mean number of bonds (narrow channels) between spherical domains (clusters) at the percolation threshold has been assumed as equal to 3. That number was predicted theoretically.³² According to the scheme presented in Figure 5(b), the critical volume fraction for a cluster-network (CN) model (V_c^{CN}) has been calculated with the relation:

$$V_c^{\text{CN}} = V_c^{\text{DPHS}} \cdot V_a/V_b \quad (19)$$

where V_a and V_b are the volumes of conductive units in CN and DPHS models, respectively [see Fig. 5(b)]. Additionally, we have calculated V_c^{CN} assuming the appearance of bonds longer than the narrow channels [see Fig. 5(c)]. The results of calculations are presented in Table II.

The experimentally determined volume fraction V_c for Nafion-120 membrane is in good agreement with that calculated for the cluster-network model (V_c^{CN}). For Nafion-427 membrane the results obtained assuming additional correlation are also appropriate. It has been mentioned above that

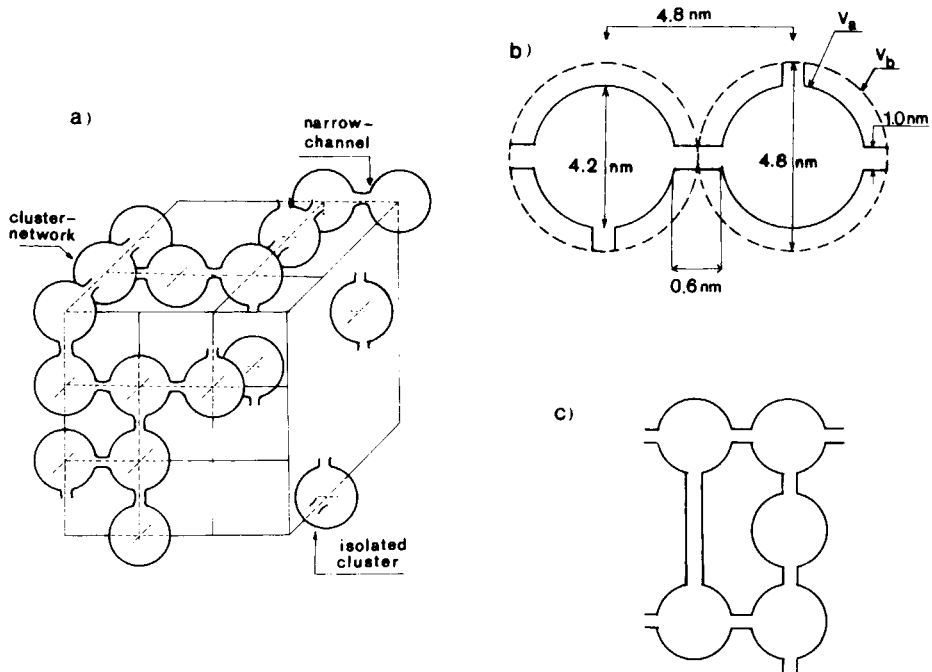


Fig. 5. A cluster-network model for Nafion membrane in Na^+ form: (a) the structure of cluster network in 3D space (SC lattice); (b) scheme and dimensions of cluster and channel (according to Ref. 31); (c) a model with additional correlation.

an additional correlation in this membrane may be caused by cracks filled with an electrolyte. The comparison of V_c computed from the experimental data and that estimated on the base of a geometrical model for the cluster-network structure does not allow us to determine a kind of a lattice on which clusters are disposed. The confidence limit for V_c from experimental data (see Table I) is of the range above the difference in the theoretical V_c^{CN} for different lattices. One can postulate only that this lattice is not a purely random type.

Cation Mobility in Nafion Membranes

The mobility ratio of sodium ions in the internal membrane phase and external electrolyte \bar{u}_+/u_+ has been calculated applying eq. (12). The results presented in Table III correspond with the concentration range of an electrolyte within which the condition $\kappa_r/\kappa_e \leq 1$ is fulfilled, as is required by the theory. These results show that the mobility ratio \bar{u}_+/u_+ does not change significantly at equilibrium with NaCl solutions of the concentration range 1.8–4.6 mol/dm³, and for both membranes it is within 0.7–0.6. Instead, for the membranes equilibrated with NaOH solutions of the concentration range 1.3–13.8 mol/dm³ this ratio is between 0.8 and 0.1, and it decreases when the concentration of the solution increases.

As in the calculations performed according to percolation theory, the differences in tortuosity factors are eliminated by introducing the factor

TABLE III
 Conductivity κ_s/κ_c and Mobility u_+/u_+ Ratios for Nafion-120 and 427 Membranes

Electrolyte	Electrolyte concentration (mol/dm ³)	G [eq. (13)]		Conductivity ratio κ_s/κ_c		Cation mobility ratio u_+/u_+	
		120	427	120	427	120	427
NaCl	1.8	2.02	1.26	1.00	0.73	0.70	0.58
	2.8	1.43	1.07	0.82	0.64	0.66	0.60
	3.8	1.24	0.97	0.80	0.62	0.70	0.63
	4.6	1.06	0.91	0.67	0.47	0.64	0.52
NaOH	1.3	1.10	1.23	0.85	0.72	0.78	0.59
	4.2	0.85	0.74	0.45	0.45	0.53	0.62
	9.6	0.78	0.76	0.26	0.19	0.34	0.25
	13.8	0.74	0.70	0.15	0.07	0.20	0.10

$(V - V_c)'$; the ratios $\bar{u}_+/u_+ < 1$ mean that in the membranes additional forces depress the cation mobility. A similar conclusion has been formulated by other authors,³³ who found the ratio \bar{u}_+/u_+ varying between 0.8 and 0.5, i.e., close to our results.

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