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Ion mobility in Nafion-117 membranes

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Abstract

Transport phenomena in Nafion-117 perfluorosulphonic membranes have been studied by different techniques. Membrane electric conductivity has been measured under alternative current as a function of the equilibrating concentrations of MCl (M = Li, Na, K) and HCl solutions. Conductivities were found to increase for lithium and sodium membrane forms and decrease for the potassium form with an electrolyte concentration increase. The obtained data were compared with the results of diffusion permeability, ion-exchange kinetics, ^{7}Li and ^{35}Cl NMR measurements. In all cases permeability increased with electrolyte concentration growth. Diffusion coefficients and transport numbers for different counter- and co-ions were determined. The obtained data are discussed with the use of the two-phase membrane structure model. The selectivity of membrane sorption was found to increase with growth of cation radius.

Keywords: Diffusion; Nafion-117 membrane; Transport process; NMR

1. Introduction

Membrane materials are more and more used in a wide range of applications like substance separation processes, wastewater treatment, and fuel cell development [1–3]. Nafion membranes, uncross-linked, perfluorinated polymers containing a considerable number of functional HSO_3-groups, have attracted much attention. These membranes show high chemical stability at high temperatures [4]. There have been numerous works published on the characterization of transport processes in Nafion membranes [5–12]. Membrane conductivity is determined not only by the nature of the sorbed cation [8,9,11,12], but also by its concentration [9], membrane pretreatment [10] and hydration degree [8,10,11].

Real systems usually consist of membranes in contact with solutions containing different ions. Thus, transport phenomena can be influenced by

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several types of cations and anions. At the same time little research has focused on the relationship of various ion mobility in a matrix of perfluorinated membranes and their interaction, which plays an important role in ion transport. Cation mobility in compounds containing different mobile ions is often lower than their mobility in individual compounds (the so-called polyalkaline effect) [13]. Moreover, there is a noticeable concentration of co-ions in micro- and mesopores of a polymer matrix [3,14] that have an influence on transport properties.

The aim of this work was to study ion transport in Nafion-117 perfluorosulphonic membranes. Four experimental techniques were used: measurements of the membrane impedance, diffusion permeability, ^{7}Li and ^{35}Cl NMR, and ion-exchange kinetics investigation.

2. Experimental

Measurements were made using the Nafion-117 membrane, which is a homogeneous membrane produced by Dupont de Nemours (USA). Water content was determined as the water mass/dry sample mass ratio with the use of the gravimetric method (water was extracted at 105°C).

Membrane conductivity was measured by the mercury-contact technique in the frequency range from 10 Hz to 100 kHz [15,16]. Membranes were equilibrated with MCl (M = Li, Na, K) solutions at concentrations from 0 to 3 M or with solutions of 0.5 M MCl and HCl in the concentration range from 0 to 0.5 M. Diffusion permeability was analyzed in a cell of periodic service. The sorbed electrolyte was transferred through the membrane to a distilled water (or HCl solution) filled compartment. The electrolyte transfer rate was controlled by atom-absorption spectroscopy. Diffusion permeability (P) was calculated from the relation:

$$P = V \, l \, \Delta c \, / \, Sc \, \Delta t \tag{1}$$

where V is the chamber volume, l is the membrane thickness, S is the membrane area, and c is the concentration.

Potentiometric titration was performed with a Mettler Delta 340 pH millivoltmeter. Portions of a 0.1 M MOH solution were added step by step to the membrane in acid form contacted with 0.1 M and 1 M MCl solutions, and pH was measured every 3 s.

^{7}Li and ^{35}Cl NMR spectra were obtained on a Bruker MSL-300 spectrometer at 116.6 MHz [90° pulse (10.5 μs), recycling time 3 s, 8 scans] and 29.31 MHz [90° pulse (7.2 μs), recycling time 3 s, 400 scans], respectively. Samples were spun at 3–7 kHz at a magic angle. Chemical shifts were given relative to 0.1 M aqueous LiCl. ^{7}Li NMR-relaxation data were obtained using the T_1-Inversion Recovery Pulse Program. Spin relaxation times (T_1) were calculated from the relation:

$$I = I_0 [1 - 2 \exp(-t/T_1)] \tag{2}$$

The correlation frequency of lithium ions ($\nu_c = 1/\tau_c$, where τ_c is the correlation time) was calculated according to the known equation for quadrupole relaxation:

$$1/T_1 = 0.3 \, \pi^2 \, (2I + 3)/[I^2 \, (2I-1)] \, [1 + (\eta^2/3)]$$
$$(e^2 \, Qq/h)^2 \, [\tau_c \, /(1+\omega^2 \, \tau_c^2) + 4\tau_c/ \, (1+4\omega^2 \, \tau_c^2)] \tag{3}$$

where I is the spin, Q is the quadrupole moment of Li nuclei, η is the asymmetry parameter, q is the electrical field gradient, h is Planck's constant, and ω is the frequency used for spectra recording. Parameters e^2Qq/h and η were deduced from fitting wide-line NMR spectra.

3. Results and discussion

3.1. Conductivity

The conductive properties of membranes [14] are greatly influenced by the water content of the
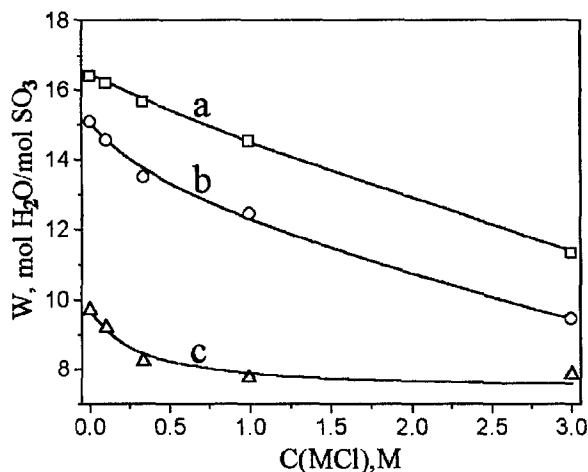
Fig. 1. Water content (mol H_2O/mol SO_3) in the Nafion-117 membrane equilibrated with LiCl (a), NaCl (b) and KCl (c) solutions of various concentrations.
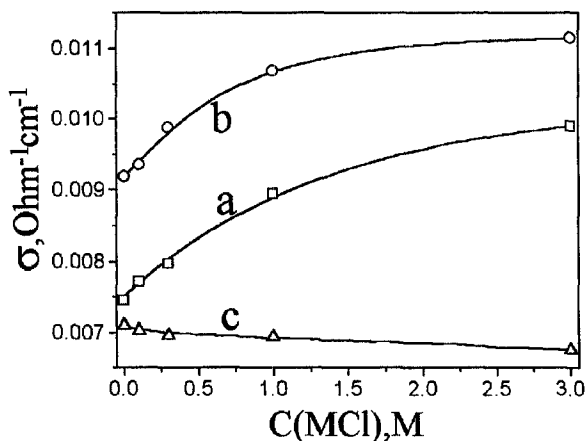

Fig. 2. Conductivity of the Nafion-117 membrane equilibrated with LiCl (a), NaCl (b) and KCl (c) solutions as a function of MCl concentration.

membrane, particularly when the membrane is in an acid form. For the salt forms of the Nafion-117 membrane, water content sequentially decreases with cation radius growth (Fig. 1), and it is much lower than for the acid form [8,10]. This dependence, first of all, is determined by a change in the hydration degree of cations in the membrane matrix. Water content decreases with increase in electrolyte concentration as well. This is determined by the well known effect of salting-out, the least pronounced in the case of large potassium ions (Fig. 1).

Membrane conductivity has an ionic origin and is determined by the mobility and concentration of counterions in the membrane. An electronic component of conductivity is close to zero. Conductivity dependence on electrolyte concentration for the salt forms has a monotonic and nonlinear character (Fig. 2). The conductivity grows for the sodium and lithium forms, and decreases for the potassium form with an increase in MCl concentration. Such character of conductivity dependence and their ratio [$\sigma(Na^+)$ > $\sigma(Li^+)$ > $\sigma(K^+)$] is in good agreement with data of Lteif et al. [9]. In fact, the conductivity values

obtained slightly differ from [9] because of the difference in the membrane pre-treatment. The observed dependence of conductivity can be explained on the basis of the two-phase model of the membrane structure [3,14]. According to this model, the membrane consists of alternating sites of a gel phase and solution, which are contained in micropores. The composition of this solution is similar to the composition of an external electrolyte solution [3]. The overall membrane conductivity is determined by conductivity of its separate sites, their size and arrangement. The size of such hydrophilic clusters in Nafion-117 membranes depends on electrolyte concentration and is about 5 nm [14]. An increase of the external electrolyte concentration results in an increase in concentration of the solution in membrane pores and a gradual decrease in water content (Fig. 1). The first effect leads to a conductivity increase; the second one decreases it. The first effect (conductivity increase) predominates for the sodium and lithium forms of the Nafion-117 membrane. At the same time, a decrease in water content leads to the deceleration of conductivity growth at high electrolyte concen-

tration. A decrease in hydration degree is more critical for the potassium form, which has the lowest water content and the greatest cation size.

In general, membrane conductivity is given as the sum of products of mobile ions and their mobility. In the case of cation-exchange membranes, the concentration of cations in them is higher than that of anions. Thus, membrane conductivity, first of all, is controlled by diffusion of cations. Diffusion coefficients (D) calculated from conductivity with the use of the Nernst-Einstein equation are given in Table 1.

$$D = kT\sigma / [c \, (Ze)^2] \tag{4}$$

where k is the Boltzmann's constant, T is the absolute temperature, and c and Ze are the concentration of current-carrying species and their charge.

In a real experiment membranes can be in contact with solutions containing two or more types of cations. Therefore, a conductivity study of such systems is of great interest. The conductivity dependence for membranes equilibrated with 0.5 M MCl solution and HCl of various concentrations is shown in Fig. 3a–c. The overall conductivity of these systems can be expressed as the sum of conductivities of protons and alkali metal cations:

$$\sigma = \sigma(H^+) + \sigma(M^+) = c\,(H^+)\,\mu(H^+) + c(M^+)\,\mu(M^+)$$
$$= \bar{\sigma}\,(H^+) - c(M^+)\,[\mu(H^+) - \mu(M^+)] \tag{5}$$

where $\sigma(H^+)$, $c(H^+)$, $\mu(H^+)$, and $\sigma(M^+)$, $c(M^+)$, $\mu(M^+)$ are conductivity, concentration, mobility of protons and metal ions in a membrane with mixed cation composition, respectively, and $\bar{\sigma}(H^+)$ is the conductivity of the membrane in acid form. A combination of Eq. (5) and the relation $c_s = c(H^+) + c(M^+)$ between the overall concentration of counterions (c_s) and concentrations of protons and metal ions in a membrane (assuming that additional non-equivalent sorption is much
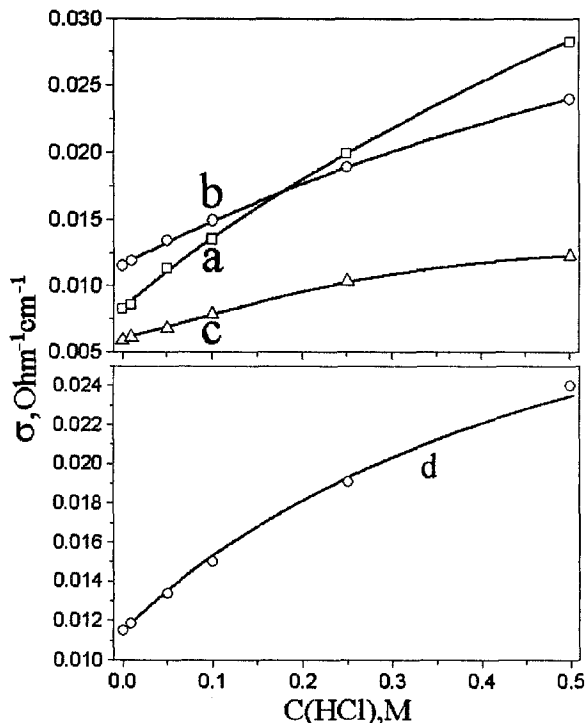

Fig. 3. Conductivity of the Nafion-117 membrane equilibrated with solutions containing 0.5 M LiCl (a), NaCl (b), KCl (c) and HCl of various concentrations. Calculated conductivity of Nafion-117 membranes equilibrated with solutions containing 0.5 M NaCl and HCl of various concentrations (solid line) and experimental data points (open circles) (d).

less than the number of fixed sites) allows the estimation of the ratio $c(M^+)/c_s$:

$$c(M^+)/c_s = [\bar{\sigma}\,(H^+) - \sigma] / [\bar{\sigma}(H^+) - \bar{\sigma}(M^+)] \tag{6}$$

where $\bar{\sigma}(M^+)$ is the conductivity of the membrane in salt form. This is only a rough estimation because cation mobility can slightly vary with a change of membrane composition. The equilibrium constant (K_{eq}) for the M^+/H^+ ion-exchange process in the membrane can be expressed as:

$$K_{eq} = c(M^+)\,[H^+]/(c[H^+]\,[M^+]) \tag{7}$$

where $[H^+]$ and $[M^+]$ are the concentrations of

Table 1
Diffusion coefficients for some ions in Nafion-117 membranes

Techniques	Electrolyte solution	Ion	D, cm^2/s
Conductivity measurements	1N HCl	H$^+$	5.3×10^{-6}
	1N LiCl	Li$^+$	1.31×10^{-6}
	0.1N LiCl	Li$^+$	1.15×10^{-6}
	1N NaCl	Na$^+$	1.58×10^{-6}
	0.1N NaCl	Na$^+$	1.31×10^{-6}
	1N KCl	K$^+$	8.6×10^{-7}
	0.1N KCl	K$^+$	1.05×10^{-6}
	0.5N HCl + 0.5N LiCl	H$^+$ + Li$^+$	4.3×10^{-6}
	0.5N HCl + 0.5N NaCl	H$^+$ + Na$^+$	3.7×10^{-6}
	0.5N HCl + 0.5N KCl	H$^+$ + K$^+$	1.85×10^{-6}
Diffusion permeability	1N LiCl	Cl$^-$	4.9×10^{-8}
	0.1N LiCl	Cl$^-$	1.4×10^{-8}
	1N NaCl	Cl$^-$	5.5×10^{-8}
	0.1N NaCl	Cl$^-$	2.1×10^{-8}
	1N KCl	Cl$^-$	1.2×10^{-7}
	0.1N KCl	Cl$^-$	1.7×10^{-8}
	1N Li$_2$SO$_4$	SO$_4^{2-}$	4.6×10^{-9}
	1N NaNO$_3$	NO$_3^-$	6.6×10^{-8}
	1N Na$_2$SO$_4$	SO$_4^{2-}$	8.1×10^{-9}
	1N K$_2$SO$_4$	SO$_4^{2-}$	1.1×10^{-8}
	1N HCl and 1N LiCl	Li$^+$	1.3×10^{-6}
	1N HCl and 1N NaCl	Na$^+$	1.7×10^{-6}
	1N HCl and 1N KCl	K$^+$	1.5×10^{-6}
Ion exchange kinetics	0.03N HCl + 0.1N NaCl	Na$^+$	$(1.21 \pm 0.04)\times10^{-6}$
	0.03N HCl + 0.1N KCl	K$^+$	$(1.02 \pm 0.02)\times10^{-6}$

protons and metal ions in equilibrating solution. K_{eq}, estimated on the basis of data obtained with the help of the least-squares method, is equal to 0.57, 1.0 and 3.2 for lithium, sodium and potassium ions, respectively. Thus, the selectivity of membrane sorption increases with the growth of the cation radius.

Expressing membrane conductivity through the mobility of cations and their concentration in an external solution, the overall conductivity of a membrane with a mixed cationic composition can be written as:

$$\sigma = \{K_{eq} [M^+]\, u(M^+) + [H^+]\, u(H^+)\} / \{K_{eq}[M^+]) + [H^+]\} \tag{8}$$

The calculated σ values slightly differ from the experimental (Fig. 3d). One reason for this is the

dependence of K_{eq} on composition and some decrease in mobility of one type of cation in the presence of another type of cation (polyalkaline effect) [13].

3.2. Diffusion permeability

In the case of the diffusion permeability study, the electrolyte was transferred through the membrane to another compartment filled with distilled water. The transfer of only counterions is impossible because it should be accompanied by charge diversity requiring essential energy consumption. Therefore, simultaneous transfer of alkali metal ions and anions should take place. Anions are characterized by a lower concentration in the membrane matrix and smaller mobility. Therefore, their transfer controls the rate of integral transfer and determines diffusion permeability values. Diffusion permeability for a binary electrolyte with single-charged ions is given by a well known relation [3]:

$$P = D_+ D_- / (D_+ + D_-) \qquad (9)$$

where D_+ and D_- are the diffusion coefficients of cations and anions through a membrane, respectively. In the case of cation-exchange membranes we can assume that $D_+ \gg D_-$; therefore, $P \approx D_-$. Anion diffusion coefficients found from this relation are listed in Table 1.

Fig. 4 shows the permeability dependence on electrolyte concentration. In all cases the permeability increases with electrolyte concentration growth. Diffusion permeability noticeably decreases with a decrease in alkali metal radius. It decreases by 1.5–2 times from lithium to potassium salts. The smaller anion mobility in the matrixes containing cations with a small radius can be determined by the tendency of ion pair formation and diminution of size of channels in which the transfer occurs. Diffusion coefficients also decrease about 3–6 times from chloride to sulphate solutions (Table 1).
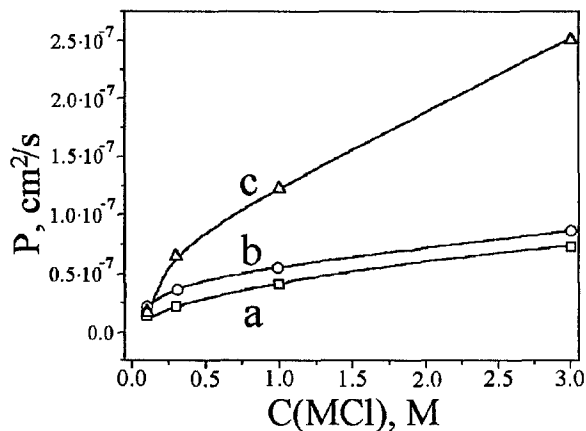

Fig. 4. Diffusion permeability of the Nafion-117 membrane equilibrated with LiCl (a), NaCl (b) and KCl (c) solutions as a function of MCl concentration.

Transport numbers for some ions in the Nafion-117 membrane were calculated using the diffusion coefficients obtained of cations and anions from the well known equation [3]:

$$t_i = Z_i^2 D_i / \Sigma (Z_j^2 D_j) \qquad (10)$$

where Z_i and D_i are the charge and diffusion coefficient of ions i. Calculated values of transport numbers are given in Table 2. t_- values strongly increase with the growth of cation radii and concentration of the electrolyte solution.

In the case of electrolytes transferred through the membrane to the acid filled compartment, the charge balance can be reached not only by a parallel diffusion of cations and anions, but also mostly by a mutual diffusion of protons and alkali metal ions. The diffusion coefficients decrease in the series $D(H^+) > D(M^+) \gg D(Cl^-)$, and the contribution of anion diffusion can be neglected. In this case the diffusion permeability can be given as:

$$P(M/H) = D(H^+) D(M^+)/[D(H^+) \\ + D(M^+)] \gg D(M^+) \qquad (11)$$

Calculated diffusion coefficients $[D(M^+)]$ are

Table 2
Transport numbers of some ions in Nafion-117 membranes

Electrolyte solution	t_+	t_-
1N LiCl	0.965	0.035
0.1N LiCl	0.988	0.012
1N NaCl	0.967	0.033
0.1N NaCl	0.984	0.016
1N KCl	0.888	0.112
0.1N KCl	0.984	0.016
1N Li$_2$SO$_4$	0.993	0.007
1N NaNO$_3$	0.961	0.039
1N Na$_2$SO$_4$	0.990	0.010
1N K$_2$SO$_4$	0.977	0.023

rather similar to those obtained from conductivity data (Table 1).

3.3. ^7Li and ^{35}Cl NMR spectroscopy

The ^{7}Li NMR spectrum at room temperature for the lithium form of the Nafion-117 membrane exhibits only one narrow line with nuclear quadrupole satellites (Fig. 5a). Its chemical shift almost coincides with that for a 1 M aqueous LiCl solution. Thus, it demonstrates that the character of cation environment in a membrane is similar to that in a water solution, and the rate of ion exchange between gel phase and solution contained in micropores is high enough. The correlation frequency found from NMR relaxation data is equal to 2.5×10^{11} s^{-1} for membranes equilibrated with distilled water and is equal to 3.1×10^{11} s^{-1} for membranes equilibrated with 1 M LiCl. The diffusion coefficient can be estimated from NMR data by use of the well known equation [17]:

$$D = a^2\, v_c\, /6 \tag{12}$$

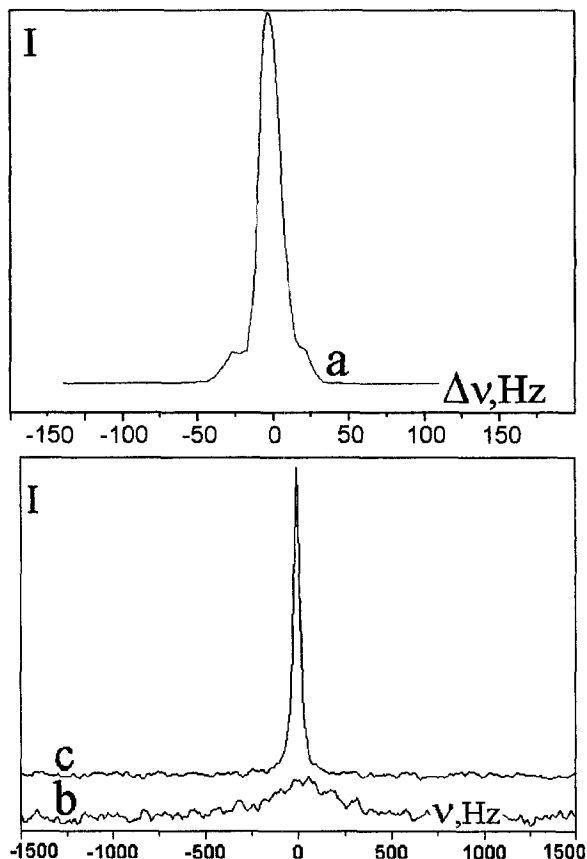where the jump length, a, is given as the distance

Fig. 5. ^{7}Li MAS NMR spectrum of a Nafion-117 membrane equilibrated with 1 M LiCl solution (a). ^{35}Cl MAS NMR spectrum of a Nafion-117 membrane equilibrated with 1 M LiCl solution (b). ^{35}Cl MAS NMR spectrum of 1 M LiCl solution (c).

between the centers of adjacent tetrahedra of oxygen atoms of water molecules (1.5 Å) (lithium ions are located in their centers). The diffusion coefficient for lithium ions calculated on the basis of this equation is equal to 1.1×10^{-5} cm^2/s.

This is one order of magnitude higher than the diffusion coefficient calculated from conductivity (Table 1). Note that, with concentration growth, the conductivity of the lithium form increased faster than the correlation frequency found from NMR data. This was determined by the fact that NMR relaxation data characterize only the rate of

a local cation environment change while conductivity is mainly controlled by cation transfer in membrane channels. v_c calculated from NMR data is mostly determined by the jump frequency of lithium ions located in membrane micropores. The composition of solution in membrane micropores is close to that of the external solution. Thus, the diffusion coefficient for lithium ions in Nafion-117 membranes calculated from NMR data is almost equal to the diffusion coefficient for lithium ions in an external solution [18].

The ^{35}Cl NMR spectrum at room temperature for the lithium form of the Nafion-117 membrane also exhibits only one narrow line (Fig. 5b). It is broader than that for the LiCl water solution (Fig. 5c). The chloride-ion concentration in the membrane equilibrated with 1 M LiCl solution was estimated with the use of ^{35}Cl NMR data. It is equal to 0.12 mmol/cm^3 and is almost 15 times less than the concentration of cations in the membrane. A comparison of concentrations obtained of chloride and lithium ions with their diffusion coefficients shows that their mobility values are close. Moreover, obtained Cl$^-$ concentration was two times less than that found by Jones et al. [14] for a Nafion-117 equilibrated with 1 M NaCl solution. The lower concentration of chloride ions in the membrane equilibrated with LiCl solution can be another reason for the lower diffusion permeability value than in the case of the sodium chloride solution.

3.4. Ion-exchange kinetics

Cation diffusion coefficients were also estimated on the basis of H$^+$/M$^+$ ion-exchange kinetics data. Diffusion coefficients were determined using the equation proposed by Boyd and co-workers [19]. In the case when transfer occurs through the plate, this equation is given as:

$$F = 1 - 8/\pi^2 \sum 1/(2n-1)^2 \exp\left[-(2n-1)^2 \pi^2 Dt/h^2\right] \quad (13)$$

where F is the fractional attainment of equilibrium, t is time, and h is the thickness of the membrane. The series in Eq. (13) converges rather quickly for high exchange degrees.

The values obtained for diffusion coefficients are given in Table 1. The diffusion processes in a membrane proceed at a very high rate and are close to the limit of this method. Therefore, a few experimental data points related to the last stages of ion exchange are applicable for calculation (when a degree of proton substitution in a membrane is high enough). In general, in the case of interdiffusion, diffusion coefficient values are determined by the diffusion coefficient of less mobile (in comparison with protons) alkali metal cations. Nevertheless, they are noticeably above the values determined from conductivity data. Thus, the presence of protons leads to a rise in alkali metal cation mobility. Some contribution to cation mobility growth can be made by defect formation processes, which intensively proceed in a membrane after alkali addition [20].

4. Conclusions

Ion mobility and transport numbers in Nafion membranes depend strongly on the nature and composition of equilibrating solutions. Counterion and co-ion mobility in the membrane is highly affected by the presence of other electrolytes. A comparison of the data obtained by different techniques has given an estimate for diffusion coefficients for different ions in Nafion-117 membranes. Transport numbers of anions in the salt forms of the Nafion-117 membrane increase with the growth of radius of corresponding cations and with an increase in the equilibrating electrolyte concentration.

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