Sorption Phenomena in Nafion Membranes

T. TAKAMATSU,* M. HASHIYAMA,† and A. EISENBERG, *Department of Chemistry, McGill University, Montreal, PQ, Canada H3A 2K6*

Synopsis

Sorption phenomena of water and aqueous salt solutions by a perfluorinated polymer containing sulfonic acid groups (Nafion) were investigated. The temperature and concentration dependencies of the sorption by the membranes in the acid and salt forms were studied. The apparent activation energies for the diffusion of water in the H-form membrane and in the K-salt form were obtained as 4.9 and ca. 13.0 kcal/mole, respectively. The sorption kinetics during the neutralization of the membranes were observed in several aqueous solutions. A maximum in the sorption curve during the neutralization process was found and explained as resulting from the differences in the diffusion coefficients of water and of the cations and from the different number of water molecules absorbed by a $SO_3^-H^+$ (acid) site and a neutralized site. The diffusion coefficients D of several cations (K^+, Cs^+, Ba^{2+}, and Ca^{2+}) were determined and found to be considerably smaller than that of water. For the various cations, log D was related linearly to q/a, where q is the cation charge and a is the separation between centers of charge of the cation and anion. The dependence of water sorption upon the degree of neutralization of the membrane was also studied at room temperature. It was observed that for membranes of a low degree of neutralization a secondary sorption process existed, while no such secondary sorption could be found for the pure acid or the highly neutralized membranes. This secondary sorption was attributed to a structural rearrangement in the polymer. The apparent diffusion coefficient of water and the number of water molecules absorbed at equilibrium by an ionic site, n_s, were obtained as a function of the degree of neutralization. The diffusion coefficient of water was dependent strongly on both the degree of neutralization and type of the salt, but no quantitative relation could be established. For all the salts studied in this paper, n_s was linearly related to the degree of neutralization, x, supporting the assumption that the value of n_s could be divided into those water molecules absorbed by an $SO_3^-H^+$ (acid) site, n_h, and those absorbed by a neutralized site, n_m. It was found that the value of $q \times n_m$ had a strong correlation with a characteristic constant of the cations since a plot of $q \times n_s$ versus log (q/r) yielded a straight line (r being the radius of the cation).

INTRODUCTION

The Nafion polymers are a recently developed family of materials which have found extensive use as separators in electrochemical applications.[1-9] They are based on a poly(tetrafluoroethylene) backbone and contain sulfonic acid groups at the end of short side chains based on the perfluoropropylene ether unit. The equivalent weight of the most common materials ranges from ca. 800 to 2000.

Until recently, most of the publications dealing with these materials centered on electrochemical aspects. In 1976, one study[10] appeared dealing with the steady-state diffusion of Na^+, Cs^+, and I^- from various solvents at room temperature. Another study[11] was devoted to a preliminary exploration of the viscoelastic and dielectric properties of the materials. More recently, one session of the Electrochemical Society Meeting (March 1977, Atlanta, GA) dealt with various features of the field, notably the supermolecular structure of the poly-

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* Present address: Institute for Physical and Chemical Research, Wako-Shi, Saitama, Japan.
† Present address: Toyo Rubber Industry Company, Japan.

mer,[12,13] as well as additional work on electrochemical and technological aspects.

Most of the previous studies led to the conclusion that the polymer is to some extent phase separated,[11–13] as are many other organic ionomers,[14,15] i.e., that the acid or salt groups (in the neutralized polymer) are aggregated. This aggregation process gives the material some most unusual properties, notably a very high glass transition temperature (ca. 100°C in the acid form, > 200°C for the salts), a very low modulus at T_g (ca. 10^8 dynes/cm^2, much lower than that of any other polymer at its T_g), a very high diffusion coefficient for water and some other solvents, as well as a high selectivity for ion transport.

In this laboratory the interest has centered primarily on the rheological or viscoelastic properties of these polymers. Before undertaking those studies, however, it was necessary to explore in some detail (although not exhaustively) several peripheral aspects, such as rates of neutralization, diffusion coefficients for various ions or solvent molecules as a function of temperature, as well as densities, expansion coefficients, etc., for the materials neutralized with various cations. The present paper is devoted to a preliminary study of the diffusion-related phenomena in these polymers for water molecules and ions other than sodium.

The method used in this work for the study of diffusion coefficients is based on the immersion of a dry membrane in the appropriate solvent or solution and the monitoring of the weight change as a function of time. The method has several shortcomings but is quite useful for preliminary explorations of the type reported here. Because of these shortcomings, the data reported here should not be taken as absolute; as a matter of fact, values of the diffusion coefficient D are referred to here as "apparent" diffusion coefficients.

Several equations are available for the calculation of D values from data of the type obtained in this work. In the case of sorption and desorption by a membrane, if the region within the surfaces of a plane sheet of thickness l is initially at a uniform concentration and the concentration at the surfaces is kept constant, the amount of diffusant, M_t, taken up by the sheet in a time t is given by[16,17]

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} \exp \frac{[-D(2m+1)^2\pi^2 t]}{l^2} \tag{1}$$

The uptake is considered to be a diffusion process controlled by a constant diffusion coefficient D, and M_∞ is the equilibrium sorption after infinite time.

The corresponding equation useful for short times is

$$(M_t/M_\infty) = 4 \left(\frac{Dt}{l^2}\right)^{1/2} \left(\frac{1}{\pi^{1/2}} + 2 \sum_{n=0}^{\infty} (-1)^n \, ierfc \, \frac{nl}{2(Dt)^{1/2}}\right) \tag{2}$$

where $ierfc \, X = (1/\pi^{1/2}) \exp(-X^2) - X \, erfc \, X$, $erfc \, X = 1 - erf \, X$, and $erf \, X$ = the error function.

In practice, sorption data may be analyzed by a method of successive approximations. If the value of (t/l^2) for which $M_t/M_\infty = 1/2$ is conveniently written as $(t/l^2)_{1/2}$, the diffusion coefficient D is given approximately as

$$D = \frac{0.04919}{(t/l^2)_{1/2}} \tag{3}$$

Thus, if the half-time of a sorption process is observed experimentally for a system in which the diffusion coefficient is constant, its value can be determined from eq. (3).

It is also possible to obtain the diffusion coefficient from the initial gradient of the sorption curve when M_t/M_∞ is plotted against the square root of time. Thus, in the early stage of sorption, for a constant diffusion coefficient D, we have from eq. (2)

$$\frac{M_t}{M_\infty} = \frac{4}{\pi^{1/2}} \frac{(Dt)^{1/2}}{l^2} \tag{4}$$

In many cases this plot yields a straight line as far as $M_t/M_\infty = 1/2$.

In another approximation of eq. (1), during the later stages of diffusion, in which only the first term in the series of eq. (1) is needed, one finds that a plot $\ln(M_\infty - M_t)$ against t approaches a straight line whose gradient is given by

$$\frac{d}{dt}[\ln(M_\infty - M_t)] = \frac{-D\pi^2}{l^2} \tag{5}$$

These equations will be used in the study reported here to calculate the apparent diffusion coefficients. If only one equation is used to calculate D, that equation will be mentioned in the text. If several equations are used, and there are differences among the results, these will be pointed out also.

Before concluding this introduction, it is worth noting that several papers at a recent symposium on ion-containing polymers (176th ACS Meeting, Sept. 1978, Miami Beach, FL) were devoted to the Nafions. These papers are pre-printed.[18–21] The papers include a structural model study,[18] an investigation of the morphology changes and transport phenomena in the material[19] an FTIR characterization as related to counterion association,[20] and a multinuclear FTNMR investigation.[21] Furthermore, a very recent paper is devoted to a ^{23}Na NMR study of ionic mobility and contact ion pairing in these materials.[22]

EXPERIMENTAL

Polymer samples in the acid form were kindly supplied by Dr. W. Grot of E. I. du Pont de Nemours & Company and by Dr. R. L. Dotson of Olin Corporation, in the form of sheets ca. 1.3 mm or ca. 0.26 mm thick, of equivalent weight of 1155 and 1200, respectively.

Samples and Drying Conditions

The procedure for the determination of the drying conditions for the H form and the alkali salts has been described elsewhere.[11] The same procedure was applied for the divalent and trivalent metal salts. The samples in the H form were dried at 150°C under vacuum for periods of 24 hr; samples treated that way are referred to as "dry" samples. For the salts it was found that the higher the valence of the cation, the higher the required drying temperature. In the present study the samples of univalent (alkali), divalent, and trivalent salts were dried under vacuum at 165, 170, and 180°C, respectively, for a period of ca. 24 hr.

For the preparation of the salts and of the partly neutralized samples, an H-form sample was immersed in an aqueous solution of the appropriate metal compound for periods of time which varied with the degree of neutralization required. This will be discussed more fully in the section dealing with diffusion phenomena. The degree of neutralization was calculated from the weight change after removal from the solution and thorough drying. The metal compounds used for neutralization in this study were LiOH, NaOH, NaCl, KOH, CsOH, CsCl, $Ca(OH)_2$, $CaCl_2$, $Ca(NO_3)_2$, $SrCl_2$, $Sr(NO_3)_2$, $BaCl_2$, $Ba(NO_3)_2$, $AlCl_3$, $FeCl_3$, and NH_4OH, all in aqueous solutions.

Sorption and Diffusion Measurements

The sorption process of water and of aqueous solutions in Nafion polymers was studied by measuring the weight change of the sample in water or in various solutions. First the weight of a sample, dried under the condition described before, was measured. Since thin samples absorbed moisture rapidly from the air, the sample weight was determined by extrapolating the value to zero time. Then the dry sample was immersed in pure water or an aqueous solution in a constant temperature bath. The samples were removed periodically from the solutions and the weight gain M_t (or sample weight W_t) was determined after the surfaces of the samples had been wiped off to remove excess water or solution. The same sample was then reimmersed in the same liquid for a period of time and the weight was remeasured. The procedure was repeated until there was no further weight gain. Total weight gain is referred to as the equilibrium sorption M_∞ (or corresponding sample weight W_∞).

The temperature dependence of the sorption or diffusion was studied for the H form and several alkali salt forms. The apparent diffusion coefficients for water and the corresponding apparent activation energies were determined for various membrane–solution systems. The diffusion process for various metal cations during the neutralization of the H-form membrane was also studied by measuring the amount of absorbed cations as a function of time by using the procedures described above.

The dependence of the sorption of water on the degree of neutralization was investigated using samples which had been partially neutralized by various cations. The diffusion coefficient and the number of water molecules at equilibrium per functional group were determined as a function of the degree of neutralization.

Nafion-H of $EW = 1155$ was used mainly for the experiments in which the temperature dependence was studied, while Nafion-H of $EW = 1200$ was used for other experiments. Although these samples are different both in their equivalent weight and their thickness, it was found that the differences in the sorption phenomena were very small or negligible for these two samples, probably because of the small difference in the equivalent weight. Therefore, no distinction between the two membranes will be made unless it is considered significant.

RESULTS

Sorption Phenomena in Nafion-H

Nafion-H in Water

Figure 1 shows a typical example of the relation between weight change (M_t/W_0) and storage time (t) when an H-form membrane $(EW = 1155)$ is immersed in distilled water at several temperatures; W_0 is the initial weight of the dry membrane and M_t $(= W_t - W_0)$ is the weight gain. It is clear that the rate of increase in M_t/W_0 and the equilibrium value of M_t/W_0 (denoted as M_∞/W_0) increase with rising temperature.

The apparent diffusion coefficients D for each temperature were initially obtained using eqs. (3) to (5). There were only relatively small differences between the three numbers; for example, for 20°C the D values were 1.6, 2.1, and 1.8×10^{-6}. The average values ($\pm 15\%$) for the different temperatures were 1.8 $\times 10^{-6}$, 2.9×10^{-6}, 5.1×10^{-6}, and 5.7×10^{-6} cm²/sec for 20, 41, 61, and 81°C, respectively. Since the difference of the values obtained by use of the various equations was quite small, the half-time method, eq. (3), was used for most of the remaining calculations.

The temperature dependence of the diffusion coefficient can be described by the Arrhenius equation:

$$D = D_0 \exp (-E_d/RT) \tag{6}$$

where D_0 is the preexponential factor, E_d is the activation energy for diffusion, R is the gas constant, and T is the absolute temperature. If $\log D$ is plotted as a function of $1/T$ and a straight line drawn through the points, the values of D_0 and E_d can be calculated from the slope and intercept.

Figure 2 shows a plot of log D versus $1/T$, along with the results for the Nafion salts which will be described later. The average values of D were used in this
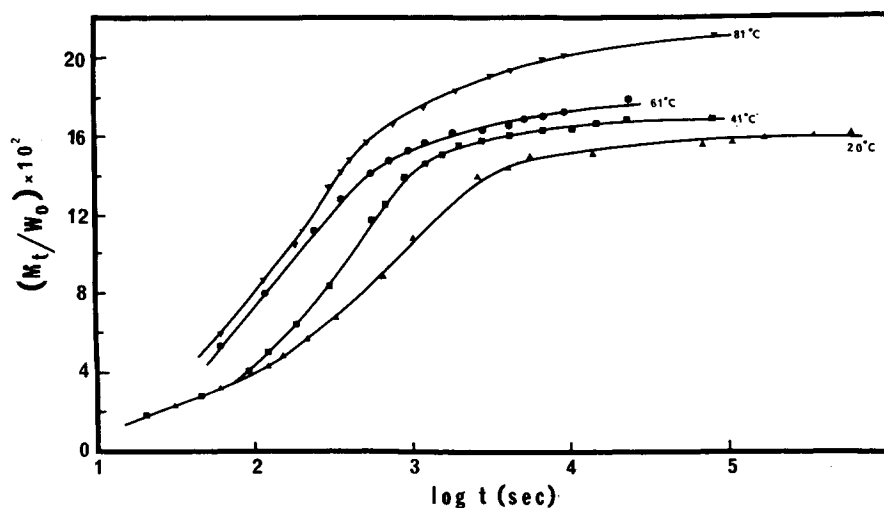

Fig. 1. Weight change M_t/W_0 vs. storage time t for an H-form membrane of $EW = 1155$ immersed in water at several temperatures.
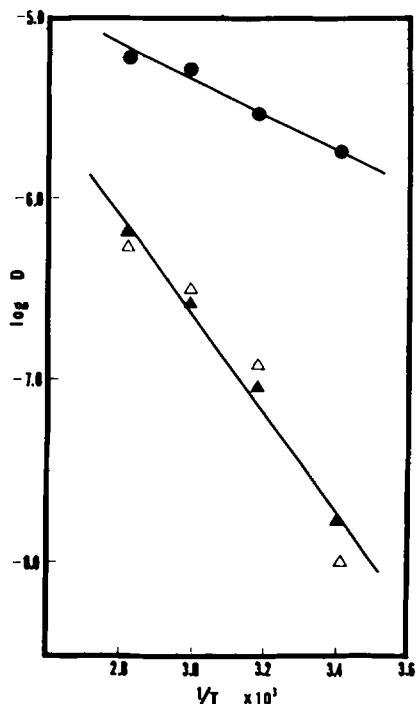
Fig. 2. Log D vs. $1/T$ for an H-form membrane of $EW = 1155$ immersed in water (●); and for K salts immersed in water (△) and in $1N$ KOH (▲).

plot, but use of the individual values did not produce any significant differences in E_d. The plot of log D versus $1/T$ yields a reasonably straight line for the acid, indicating that the diffusion of water in the Nafion-H membrane can be satisfactorily expressed by an equation of the Arrhenius type. The values of D_0 and E_d were calculated and are listed in Table I. The results for the salts will be described below.

Two attempts were made to determine D for absorption of water from the vapor phase at ca. 70% and ca. 100% relative humidity. Both runs yielded a value of D of $\sim 2 \times 10^{-8}$ cm²/sec at 23°C. Desorption from the wet membrane into air of 45% relative humidity yielded a value of D of $\sim 1.1 \times 10^{-7}$ cm²/sec. All these values were obtained from the half-time method, eq. (3).

TABLE I
Activation Energy and Preexponential Factor for Diffusion Process

Specimen	Solution	Activation energy E_d, kcal/mole	Preexponential factor D_0, cm²/sec
H form	water	4.9	8×10^{-3}
H form	$1N$ KOH	9.1[a]	2.8[a]
K salt (C $\sim$ 80%)	water	13.0	1.9×10^2
K salt (C $\sim$ 80%)	$1N$ KOH	13.0	1.6×10^2

[a] These values are highly approximate and are listed only for the sake of comparison.

Nafion-H in Alkali Solutions

The dependence of the sorption process on the type of univalent cation solution is shown in Figure 3 for $0.1N$ solutions at 22°C. It appears that at least for the smaller cations, the diffusion coefficient decreases with increasing ion size. The sorption curves for the LiOH and KOH solutions show a small maximum, which means that some of the absorbed material is desorbed at long times. It is also observed that the sorption curve for a $0.01N$ NH_4OH solution (not shown) gives a large maximum. This phenomenon will be described in detail later.

Figure 4 shows an example of the dependence of the sorption on the solution concentration. The experiments were carried out in CsOH solution at room temperature. It is obvious that the rate of sorption is strongly dependent on the concentration, and decreases with increasing ion concentration. It should be recalled that the sorption phenomenon in the alkali solutions is very much more complicated than that in pure water because several species are diffusing and the chemical potential and ionic strength vary as a function of concentration. This phenomenon may be understood better by studying the absorption of the cations as well as that of water quantitatively, as will be described more fully below.

The temperature dependence of the sorption in various alkali solutions was also studied. The general features of the sorption are the same as those in distilled water. The rate of sorption and the equilibrium sorption increase with rising temperature. Although in this type of sorption, the diffusion coefficient may not have a precise meaning because the total sorption process is a combination of sorption of water and cations, the apparent activation energy was calculated from the apparent diffusion coefficients and is given in Table I for the sake of comparison.
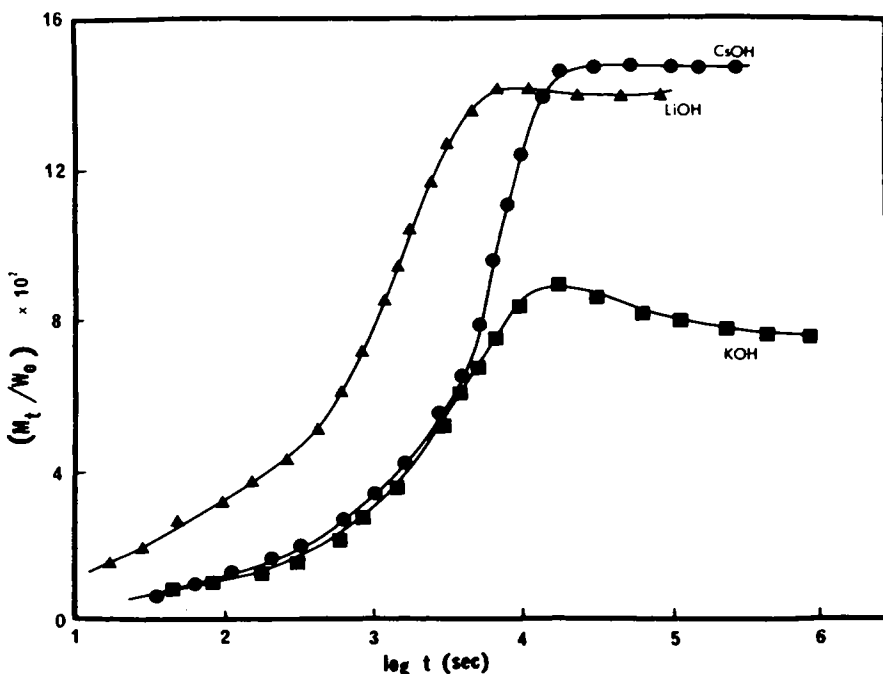

Fig. 3. Weight change M_t/W_0 vs. storage time t for H-form membranes of $EW = 1155$ immersed at room temperature in various $0.1N$ solutions: (●) CsOH; (■) KOH: (▲) LiOH.
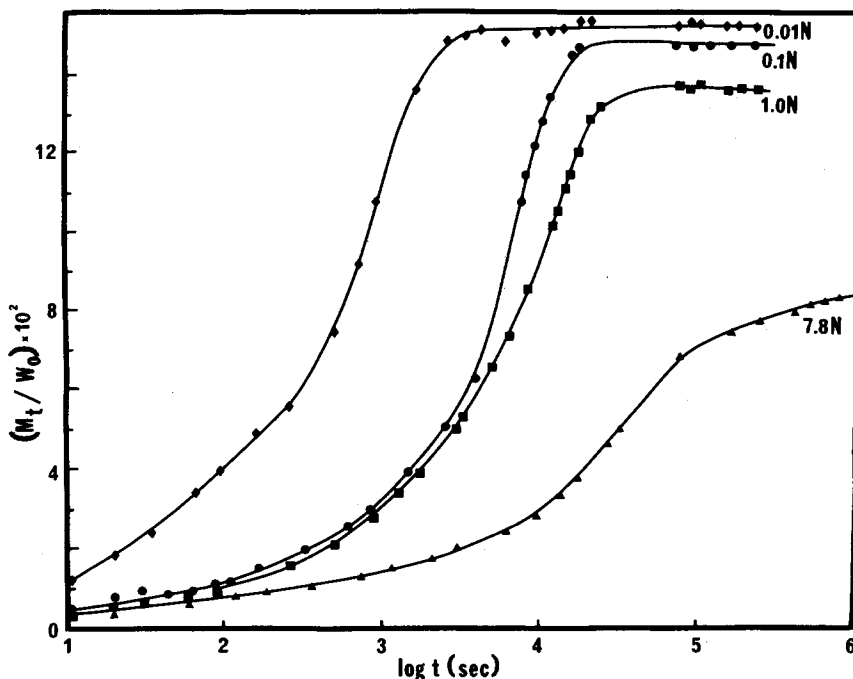
Fig. 4. M_t/W_0 vs. storage time for H-form membranes of $EW = 1155$ immersed in CsOH solutions of various concentrations at room temperature.

Nafion-H in Solutions of Divalent Cations

The sorption phenomena of Nafion acid in aqueous solutions of divalent metal compounds such as $CaCl_2$, $BaCl_2$, $SrCl_2$, $Ca(NO_3)_2$, $Ba(NO_3)_2$, $Sr(NO_3)_2$, and $Ca(OH)_2$ were also studied.   Typical examples of the sorption curves are shown in Figure 5, in which the experiments were carried out in $0.01N$ MCl_2 (M = Ca, Ba, or Sr) solutions at room temperature.   All sorption curves are essentially identical in the early stages but show some differences near equilibrium.   It is noteworthy that the sorption in a $M(NO_3)_2$ solution is identical to that in a MCl_2 solution, which indicates that these anions do not play any significant roles in the sorption process of the Nafion membrane.   There is no indication of a peak in the sorption curve as observed in LiOH, KOH, and NH_4OH solutions.

Absorption of Metal Cations

The observation of the maximum in the sorption curve of the H-form membrane in KOH, NaOH, or NH_4OH solution poses the question of why only these cations exhibit the phenomenon.   If the absorption behavior of the metal cations were known, it would be very helpful in answering this question.   Therefore, the diffusion of various metal cations during the neutralization was studied at room temperature by measuring the amount of absorbed metal cations as a function of time.   The solutions used here were $0.01N$ KOH, $0.01N$ CsOH, $0.05N$ $CaCl_2$, and $0.05N$ $Ba(NO_3)_2$ solutions.   The membrane was Nafion-H of $EW = 1200$.

Some of the results are shown in Figure 6 for CsOH, in Figure 7 for KOH, and in Figure 8 for $CaCl_2$.   In each figure the total weight absorbed by the H-form membrane is given as curve 1.   Curve 2 is the amount of the metal cations ab-
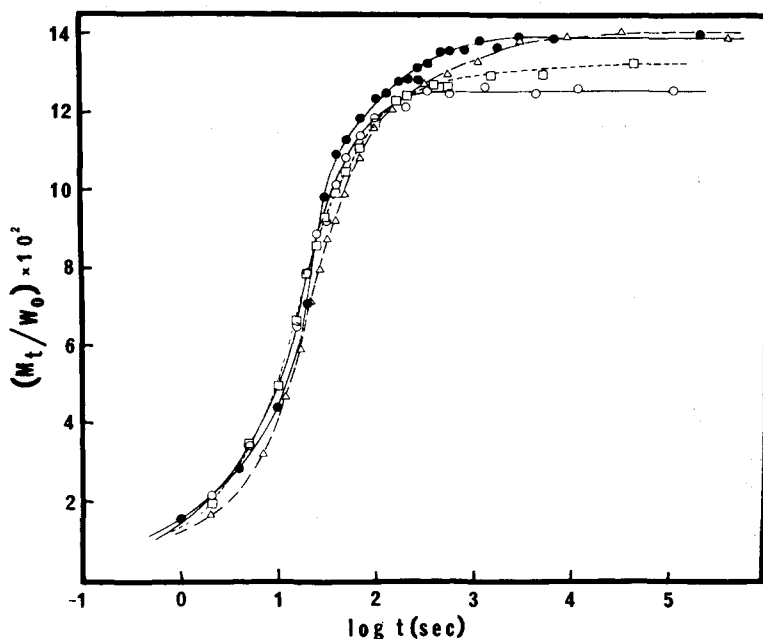
Fig. 5. M_t/W_0 vs. storage time for H-form membranes of $EW = 1200$ immersed in $0.01N$ MCl_2 solution at room temperature: (O) $CaCl_2$; (△) $BaCl_2$; (□) $SrCl_2$; (●) water.

sorbed by the membrane. Curve 3 is the value obtained by subtracting curve 2 from curve 1, which may be considered to be the amount of water absorbed during the neutralization process. The degree of neutralization is given in curve 4. As can be seen in all the figures, the curve for water absorption from solution (curve 3) is different from that for pure water (curve 5). This difference is obviously due to the presence of the metal cations in the solutions and also in the membrane at the later stages of the diffusion process. As shown in Figure 6 (for Cs neutralization), the water curve clearly shows a sharp maximum, while the total sorption does not have a peak. A similar water curve is observed in the sorption process in the KOH solution as given in Figure 7. The total sorption curve in the KOH solution, however, does have a maximum. In the sorption in $0.05N$ $CaCl_2$ it appears that neither the total sorption nor the water curve alone show any maximum, as shown in Figure 8. In the sorption in the $Ba(NO_3)_2$ solution a very small peak was observed in the water curve but no peak in the total sorption curve.

Sorption Phenomena in Nafion Salts

Completely neutralized membranes are very difficult to obtain for most of the salts. Among all the cations studied here, only Li^+ yielded close to complete neutralization, the best results for the others being in the range of $\alpha = 80-95\%$. Therefore, the results reported here were obtained on samples in that range of neutralization.
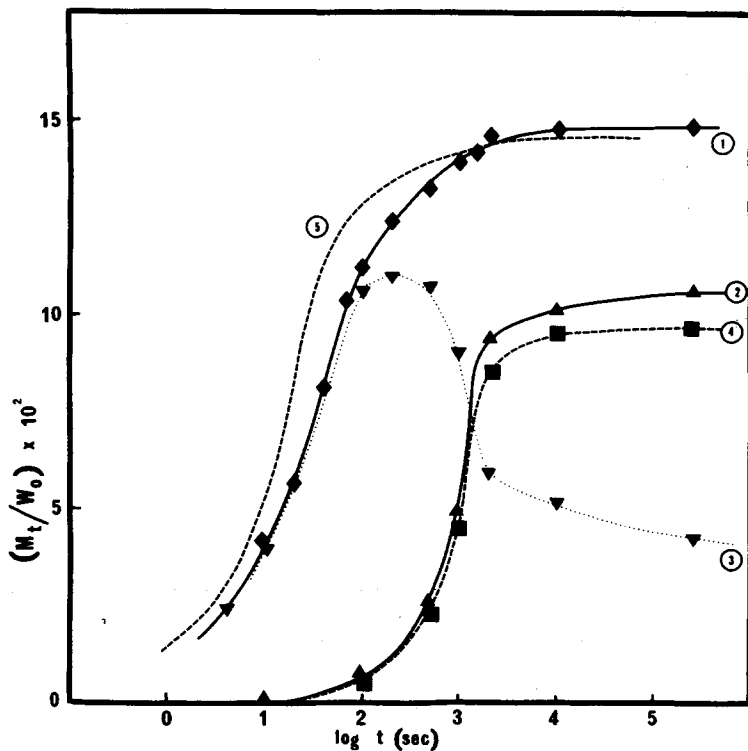
Fig. 6. Sorption (weight gain) of an H-form membrane during neutralization in $0.01N$ CsOH solution at 22°C: 1, total sorption; 2, cation sorption; 3, water sorption; 4, the degree of neutralization ($\times.10$); 5, sorption in pure water.

Nafion Salts in Water

Figure 9 shows the results for the K salt membrane ($\alpha \sim 80\%$) immersed in distilled water at several temperatures. The rate of increase in M_t/W_0 increases with rising temperature, and the value of M_∞/W_0 also increases with rising temperature. No maxima are observed, which is reasonable because the maximum in the sorption curve is a result of the competition between water molecules and cations and is thus not encountered with water molecules alone. The diffusion coefficient was calculated for each temperature and the activation energy was obtained from the plot of $\log D$ versus $1/T$, shown in Figure 2. The plot is clearly nonlinear, and the value of the activation energy is given in Table I strictly for the sake of comparison. Obviously, the low-temperature limit would yield a higher value of E_d, while the high-temperature range would yield a lower value than the average of 13 kcal.

Nafion Salts in Solutions

The sorption behavior of Nafion-K was studied in $1N$ KOH as a function of temperature; the results are shown in Figure 10. As observed in many other temperature dependence studies, the rate of increase in M_t/W_0 and the value of M_∞/W_0 increase with rising temperature. The activation energy calculated from the data of Figure 10 is listed in Table I.
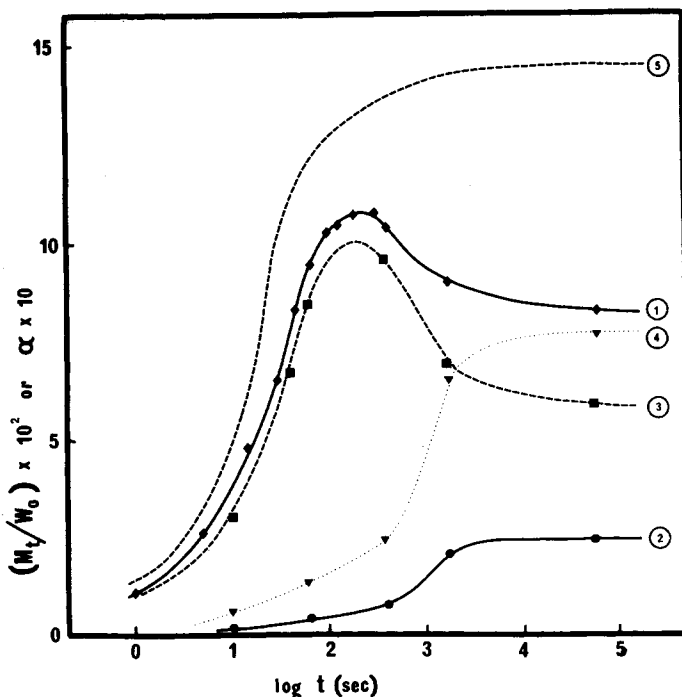
Fig. 7. Sorption (weight gain) during neutralization in 0.01N KOH solution at 22°C: 1, total sorption; 2, cation sorption; 3, water sorption; 4, the degree of neutralization ($\times.10$); 5, sorption in pure water.

Temperature Dependence of Equilibrium Sorption

The number of water molecules absorbed at equilibrium by the polymer is dependent on the temperature. Figure 11 shows some of the results obtained in the studies described above. In general, the number of water molecules absorbed per sulfonic group increases with increasing temperature. The result for Nafion-H membrane in water is similar to that obtained by Grot et al.[2] For the salt from membranes, the samples in the appropriate solutions absorb less water than those in pure water. The same tendency has been reported for the sodium salt form[9] and has been interpreted theoretically.[13]

Sorption Phenomena in Partially Neutralized Nafion

Sorption of Water

Water sorption kinetics of Nafion salts (Nafion-K, -Cs, -Ca, and -Ba) were studied at room temperature using samples of different degrees of neutralization. In Figure 12 the results are shown for the Cs salts and in Figure 13, for the Ba salts. For all the salts, it is found that as the degree of neutralization increases, the amount of water absorbed by the membrane decreases and that, furthermore, the rate of water absorption slows down. Another phenomenon which should be noted is that for the samples with a low to intermediate degree of neutralization (ca. 10–60%) there is a secondary absorption process which appears to start at around $t = \sim 10^3$–10^4 sec. This is seen very clearly for the 25% and 50%
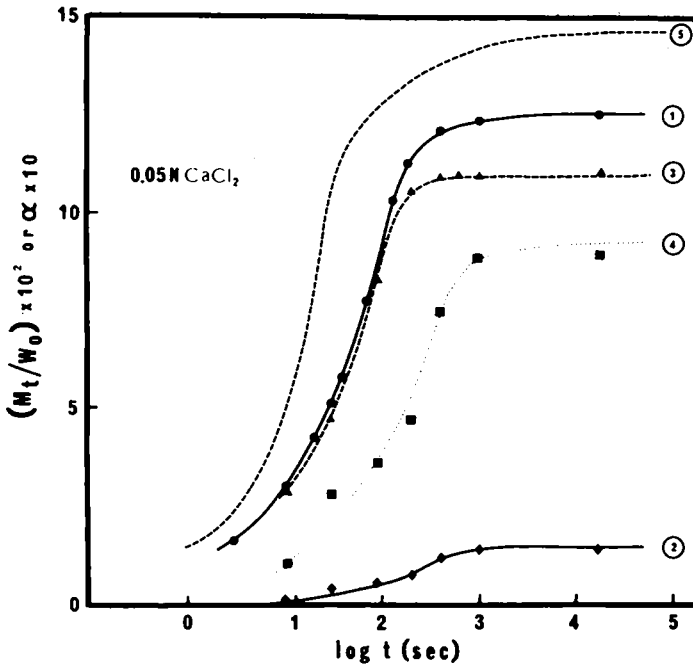
Fig. 8. Sorption (weight gain) during neutralization in $0.05N$ $CaCl_2$ solution at 22°C: 1, total sorption; 2, cation sorption; 3, water sorption; 4, the degree of neutralization ($\times.10$); 5, sorption in pure water.

neutralized samples in the plots of M_t/W_0 versus time (shown in Fig. 12), although it does not show up in a plot of M_t/M_∞ versus $t^{1/2}$, the more conventional way of plotting the data (shown in Fig. 14). The latter, as a matter of fact, shows excellent linearity at least up to ca. 50% neutralization. Thus, at lower neutralizations the sorption phenomena may be Fickian, while at higher neutral-
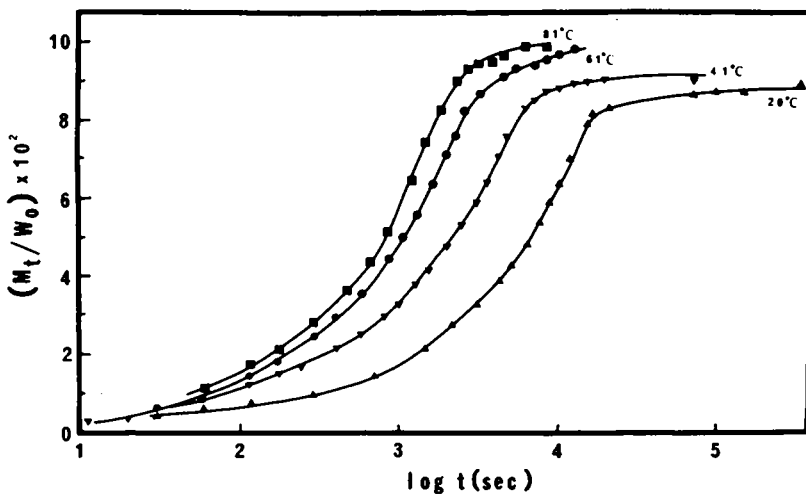

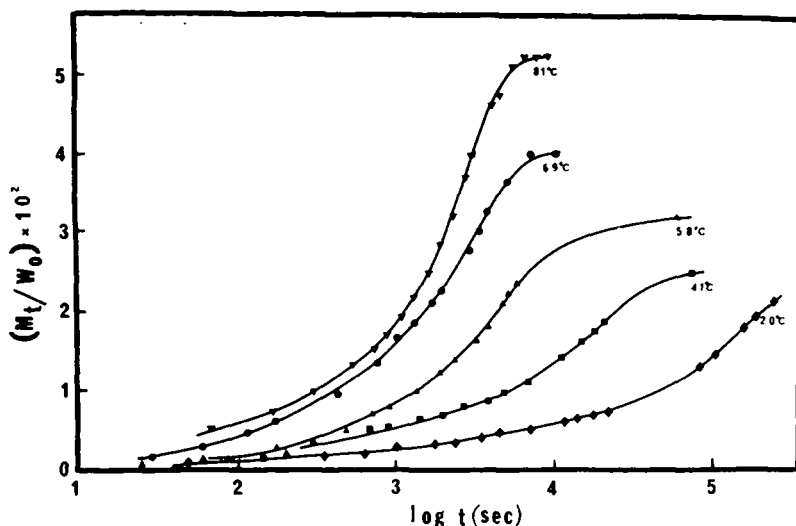Fig. 9. M_t/W_0 vs. storage time for K-salt membranes immersed in water at several temperatures.

Fig. 10. M_t/W_0 vs. storage time for K-salt membranes immersed in $1N$ KOH solution at several temperatures.

izations they probably are non-Fickian. Of course, as described by Fujita,[23] further studies such as desorption and thickness dependence are probably needed to conclude whether or not these sorption phenomena of the samples with zero or low degree of neutralization are indeed Fickian.

Neutralization Dependence of Diffusion Coefficients

As described before, one should be careful in interpreting the diffusion coefficients of water in Nafion salts because the sorption behavior of highly neutralized samples is indeed anomalous. It may however be useful if it is taken as a semiquantitative measure for the rate of absorption of water. The apparent diffusion coefficients of water at room temperature were obtained as a function
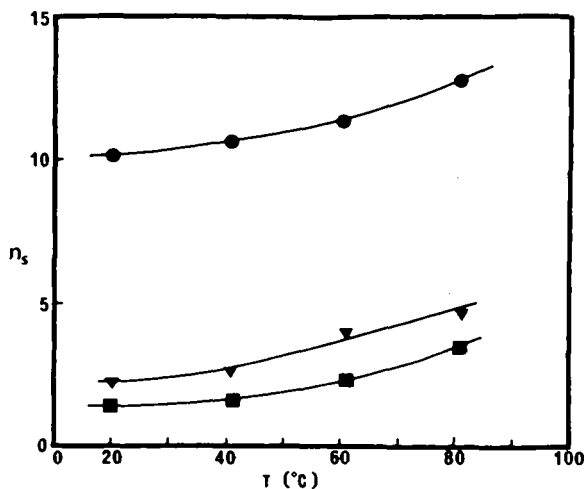

Fig. 11. Temperature dependence of n_s for an H-form membrane in water (●), for K salt in water (▼), and for K salt in $1N$ KOH (■).
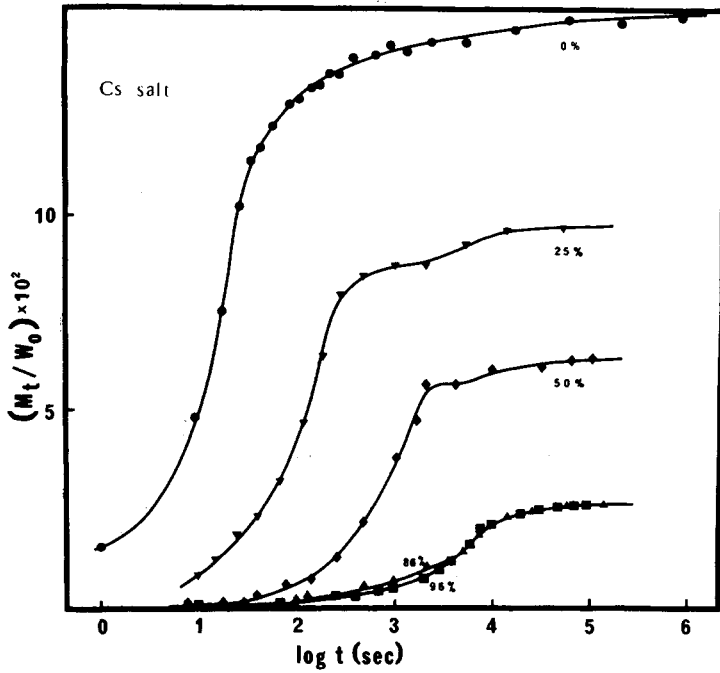
Fig. 12. M_t/W_0 vs. storage time for partially neutralized Cs salts immersed in water at 22°C.

of the degree of neutralization, α, and are given in Figure 15. The values were calculated using the half-time method.
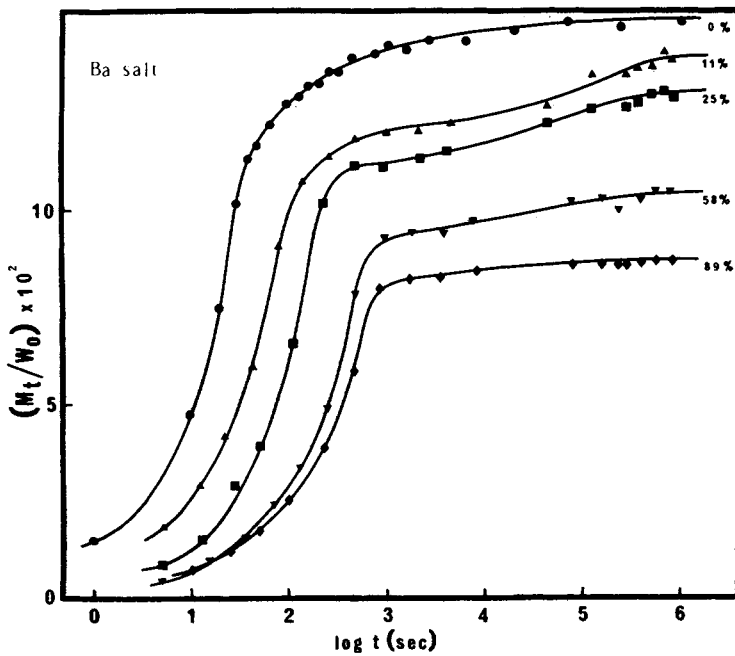

Fig. 13. M_t/W_0 vs. storage time for partially neutralized Ba salts immersed in water at 22°C.
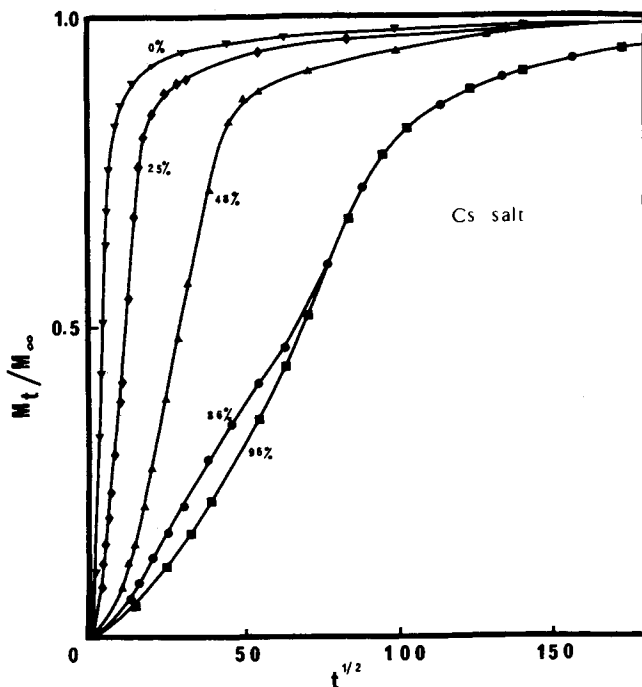
Fig. 14. M_t/W_∞ vs. $t^{1/2}$ for partially neutralized Cs salts immersed in water at 22°C.

Water Absorption at Equilibrium

It seems reasonable to assume that the total water absorbed by the Nafion membrane may be divided into two contributions, one due to $SO_3^-H^+$ sites and another due to $SO_3^-M^+$ sites. This may be described by the following equation:

$$n_s = (1 - \alpha)n_h + \alpha n_m$$
$$= (n_h - n_m)(1 - \alpha) + n_m \tag{7}$$

where n_s, n_h, and n_m are the average number of water molecules absorbed by a sulfonate site, by a $SO_3^-H^+$ pair, and by an $SO_3^-M^+$ pair, respectively, and α is the degree of neutralization. Equation (7) indicates that a plot of n_s versus $(1 - \alpha)$ should produce a straight line with the values of n_m and n_h obtainable from the zero intercept and the slope of the line, respectively.

To examine this possibility, the total water absorbed by K, Cs, Ca, Sr, and Ba salts at equilibrium at room temperature was measured as a function of the degree of neutralization. The samples were immersed in water for more than ten days to obtain equilibrium. The water molecules absorbed by an ionic site were then calculated from the amount of water absorbed by each sample. In Figure 16, n_s is plotted versus $(1 - \alpha)$. Results of less extensive experiments for Al and Fe salts are also given. From Figure 16 it is obvious that for all salts examined here the plot of n_s versus $(1 - \alpha)$ is quite linear. This suggests that the assumption made above is reasonably good, at least at equilibrium.

From the last figure, n_h and n_m may be calculated using eq. (7); the results are given in Table II. The values were determined by the least-squares method. It is seen that the values of n_m for the K and Cs salts are extremely small com-
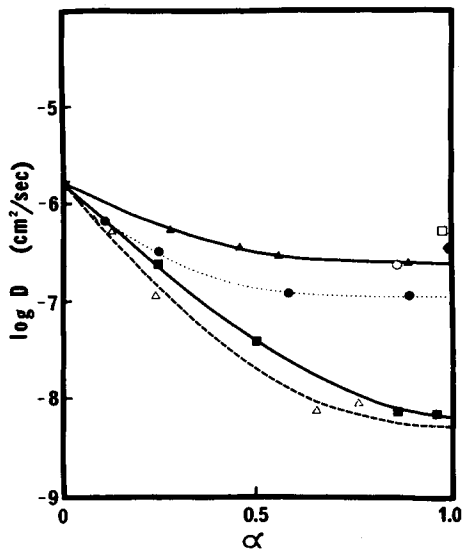
Fig. 15. Diffusion coefficient of water at room temperature in various salt-form membranes as a function of the degree of neutralization: (▼) acid; (♦) Li; (△) K; (■) Cs; (▲) Ca; (●) Ba; (□) Al; (○) Fe.

TABLE II
Values of n_h and n_m for Various Salts ($T = 22°C$)

Salt	N_h	n_m
K	9.7	0.2
Cs	9.3	0.9
Ca	10.0	7.0
Sr	9.7[a]	6.0[b]
Ba	9.8	5.4
Al	9.7[a]	9.9[b]
Fe	9.7[a]	9.8[b]
$\bar{n}_h$	9.7	

[a] This value is assumed to be equal to $\bar{n}_h$.
[b] This value is obtained assuming $n_h = 9.7$.

pared with those for other salts. It appears that for divalent metal salts the smaller the ion, the more water is absorbed.

DISCUSSION

Nafion-H in Water

The temperature dependence for the diffusion of water in the Nafion-H membrane is very normal. The activation energy is only 4.9 kcal/mole, nearly equal to the result reported by Yeo and Eisenberg[11] (4.8 kcal/mole) and close to that found for many ion exchange resins and to that for self-diffusion of water (4.4 kcal/mole).

The difference in the apparent diffusion coefficient of water from liquid water and from the vapor is most probably due to the much lower concentration of
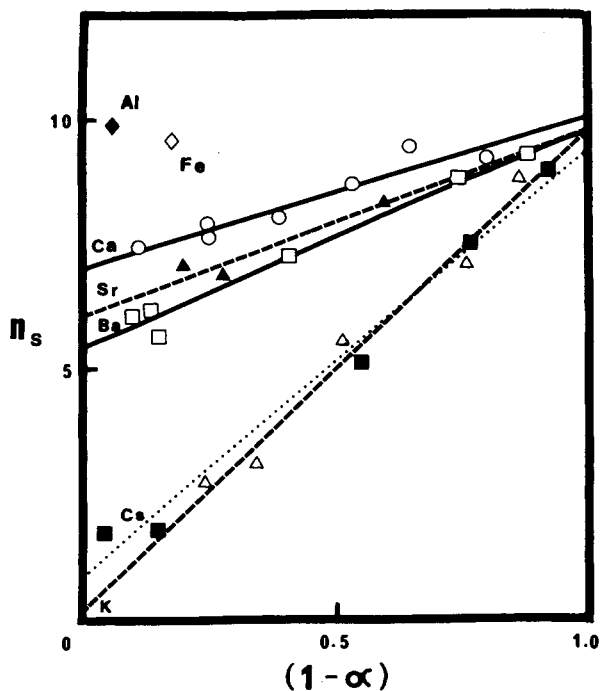
Fig. 16. Number of water molecules per ionic site vs. $(1 - \alpha)$, where α is the degree of neutralization: ($\triangle$) K; ($\blacksquare$) Cs; ($\circ$) Ca; ($\blacktriangle$) Sr; ($\square$) Ba; ($\blacklozenge$) Al; ($\lozenge$) Fe.

water in the vapor ($\simeq 3 \times 10^{-5}$ g/cm^3) than in the liquid. The concentration of water in the water-saturated sample is ca. 0.25 g/cm^3. Therefore, it seems reasonable that the apparent diffusion coefficient upon the desorption from the wet membrane into air is between the two values for absorption from liquid water and from the vapor.

Nafion Salts in Water

It should be stressed that in view of the occasional nonlinearity of the log D versus $1/T$ plot, the activation energies calculated here are only approximations. The nonlinearity is not unusual for membranes. It is conceivable that it is due to a change of the structure of the polymer with temperature, but this is highly speculative.

The average activation energy in the K salt form of Nafion (13.0 kcal/mole) is higher than that in the H form, and the diffusion coefficient of water is much smaller than that in the H form. A possible reason for this is that $SO_3^-K^+$ is much less hydrophilic than $SO_3^-H^+$, as reflected in the differences between n_m and n_h shown in Table II. Another reason may be due to the fact that the polymer chains in the salts are more tightly packed than those in the H form, because of the stronger interaction of the chains, which possibly leads to a change of the structure. This latter effect is demonstrated by the drastic increase of the glass transition temperature of the material upon the introduction of the metal ions. For instance, the T_g of the alkali salts is about 220°C,[11] and that of the Ba salt is even higher, while the T_g of the H-form membrane is only ca. 105°C.[11]

Generally, for normal polymers it has been observed[24] that for materials above T_g the diffusion is Fickian, while for materials below T_g the diffusion is non-Fickian. The fact that the sorption in the acid form or in samples of a low degree of neutralization appears to be Fickian may indicate that the segmental mobility of the chains is sufficiently high. For the samples with a high degree of neutralization, the sorption clearly becomes non-Fickian or anomalous, indicating again that mobility of the molecular segment is restricted more strongly, probably due to the very strong interaction between the chains. (For Nafion-Ca and Nafion-Ba this tendency appears to be weak, but it undoubtedly exists.)

As mentioned before, for the partially neutralized samples with a low degree of neutralization (ca. 10–60%) there is a secondary absorption process. In the plot of M_t/M_∞ versus $t^{1/2}$ it is hard to recognize the secondary absorption. This is one of the reasons why most of the data are presented as M_t/M_0 versus log t.

The mechanism for the secondary absorption is not clear, but it is most probably associated with some kind of structural rearrangement. It is interesting that for the sorption by the H-form membranes this secondary process appears to be absent for all practical purposes, which indicates that the presence of the metal cations and the resultant strong interactions may be related to this phenomenon. For the samples with a high degree of neutralization no such secondary absorption process can be seen. The reason for this is probably due to the fact that, even if a structural rearrangement occurs, the water sorption by those samples is very slow, giving the structure enough time to rearrange while the absorption of water is taking place. Alternately, it may be due to the possibility that the secondary absorption region in those samples occurs after very long times, beyond the experimental period of the present study.

One possible mechanism for the structural reorganization may be due to the possibility that the partly neutralized membranes are heterogeneous (salt form on the outside and acid form on the inside) and that ion migration takes place with a reasonable rate constant only after a certain amount of water has been taken up. Several previous investigations have encountered secondary absorption processes,[24,25] which have been ascribed to structural reorganizations taking place only after a certain amount of solvent had been absorbed.[26]

As suggested before[11] from rheological and small-angle x-ray scattering studies and from subsequent theoretical investigations,[12,13] Nafion has a supermolecular structure in which ions are clustered. Clustering was observed for both the dry Nafion-H and the dry Nafion-Cs.[11] Wilson et al.[27] and Marx et al.[28] have reported that the character of the small-angle x-ray scattering peak for the sodium salt of an ethylene–methacrylic acid copolymer was affected by the presence of water. Saturation with water destroyed the small angle peak. However, this is not the case for the Nafion-H membrane. It was reported[12] that ionic clustering did indeed exist in Nafion-H membranes swollen with water and that the average separation of the hydrated clusters is about 50 Å. This dimension is larger than that reported[11] for the dry Nafion-H membrame (28 Å) if the angle at which the peak is observed can be correlated with distances. Thus, upon saturation with water the ion cluster may be inflated with water and may be changed into a looser aggregate. However, it may be reasonable to consider that the time required for the salt clusters to become saturated with water is much greater than that for the acid clusters, because of the difference of the strength of interaction.

From Figures 15 and 16 it appears that the diffusion coefficients of water in the salt-form membranes and the number of water molecules absorbed by them are very closely related and that they both increase with increasing charge and with decreasing size of the cation. To study the quantitative correlation between the amount of water absorbed and the characteristic parameters of the cation, the number of water molecules absorbed per cation was plotted against log (q/r), where q is the cation charge (here simply taken as +1, +2, or +3) and r is the ionic radius.[27] The result is shown in Figure 17. The relation is reasonably well fitted (except for Cs^+) by the empirical equation

$$q \times n_m = 32.5 \times \log (q/r) + 5.0 \tag{8}$$

whre $q \times n_m$ is equal to the number of water molecules per metal sulfonate group containing one metal ion. It is worth noting that in the salts of ethylene–acrylic acid copolymers the K salt absorbs more water than the Na salt, which in turn absorbs more water than the Ca salt. This result is completely opposite to the result for Nafion. The reason is unknown at this time.

As can be seen from the linearity of the plots in Figure 16, the number of water molecules absorbed per ionic site of a certain type is independent of whether another type of site may be present in the membrane. This is demonstrated by the fact that the average value of n_h is 9.7 water molecules per SO_3H group, which is in good agreement with the experimental values of 9.3 to 10.0 obtained from the amounts of water absorbed by pure H-form membranes. The number of water molecules per neutralized site for Al and Fe salts is considerably larger than those for the uni- or divalent cations and almost equal to that for the H-form membranes.

Nafion-H in Solutions

The phenomena observed during the neutralization, notably the appearance of a peak, can be understood, at least qualitatively, from very simple considerations. The total weight absorbed by the membrane is the sum of the weights
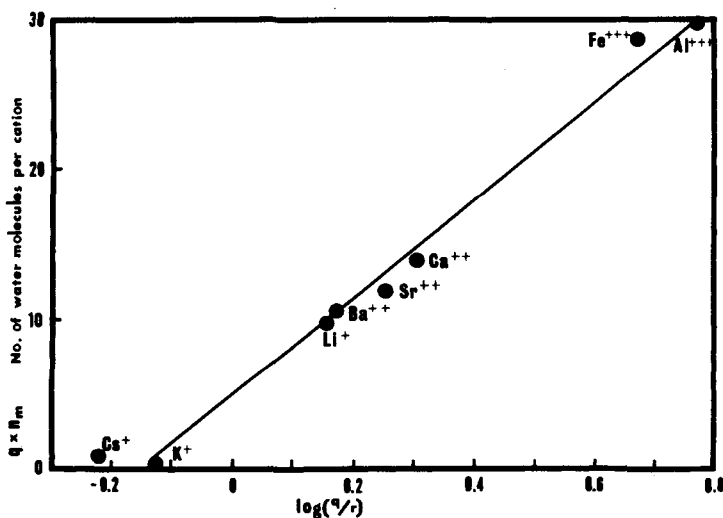

Fig. 17. $q \times n_m$ vs. log (q/r) at room temperature for various cations.

of both cations and water. Water may be considered to be absorbed by both $SO_3^-H^+$ and $SO_3^-M^+$ (or $SO_3^-M_{1/2}^{2+}$) sites. The total weight change is given by the expression

> total weight change = (water absorbed by $SO_3^-H^+$ sites) + (water absorbed by $SO_3^-M^+$ sites) + (weight change due to the conversion from H^+ to M^+)

or

$$W_{\text{total}} = \frac{K_1}{N_0} Z_h(t)\, n_h(t) + \frac{K_1}{N_0} Z_m(t)\, n_m(t) + \frac{K_2}{N_0} Z_m(t) \tag{9}$$

where $Z_h(t)$ and $Z_m(t)$ are the number of $SO_3^-H^+$ and $SO_3^-M^+$ sites at time t, respectively; $n_h(t)$ and $n_m(t)$ are the average numbers of water molecules absorbed by a $SO_3^-H^+$ and a $SO_3^-M^+$ (or $SO_3^-M_{1/2}^{2+}$) sites at time t, respectively; and N_0 is Avogadro's number; finally, K_1 and K_2 are constants related to the molecular weight ($K_1 = 18$ and K_2 is the difference in equivalent weight between the cation and hydrogen). For a given specimen, the value of $Z_h(t) + Z_m(t)$ should be constant assuming no degradation or decomposition; $Z_m(t)$ is directly related to the diffusion of metal cations into the membrane.

In the sorption in the CsOH solution in Figure 6 the diffusion of Cs^+ is very slow compared with that of water. The quantitative aspects will be discussed later. At the early stage of the sorption, only water molecules are absorbed because the diffusion coefficient of water is considerably larger than that of Cs^+. In this particular experiment, the cesium absorption parallels that of the water, but with a time delay of ca. two orders of magnitude. Until the cesium concentration reaches significant levels, the amount of water absorbed from solution (curve 3) parallels the curve of absorption from pure water, the difference being probably due to the difference in the activity of the water in the two cases. However, as the $SO_3^-H^+$ sites are replaced by $SO_3^-Cs^+$ sites, the number of water molecules which can exist in the membrane decreases because, at equilibrium, a $SO_3^-Cs^+$ site can accommodate much less water than a $SO_3^-H^+$ site; this is seen from Table II. Water molecules, once absorbed, must therefore move out of the membrane as the concentration of Cs^+ in the membrane increases. Consequently, the net value of the first and second term on the right-hand side of eq. (9), which represents the water curve, decreases after a certain time. However, since the atomic weight of Cs^+ is considerably higher than that of water (132.9 vs. 18), the weight gain due to the third term is sufficiently large to compensate for the loss of water. Thus, the total sorption curve in the CsOH solution does not show a maximum as observed in the KOH solution in which the atomic weight of K^+ (39.1) is not sufficiently large to overcome the loss of water.

This explanation can also be applied to the sorption in $0.05N$ $CaCl_2$ solution

TABLE III
Diffusion Coefficients of Cations ($T = 22°C$)

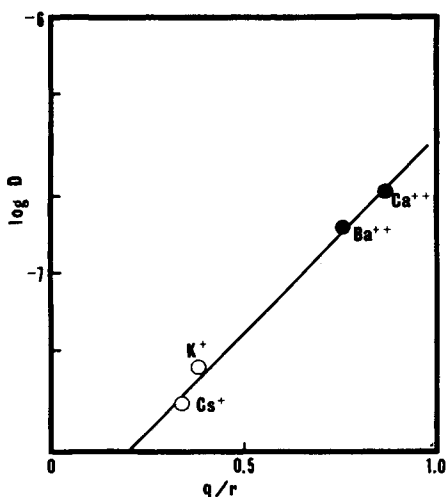| Cation	Solution	D, cm²/sec
K^+	$0.01N$ KOH	4.3×10^{-8}
Cs^+	$0.01N$ CsOH	3.1×10^{-8}
Ca^{2+}	$0.05N$ CaCl$_2$	2.1×10^{-7}
Ba^{2+}	$0.05N$ Ba(NO$_3$)$_2$	1.5×10^{-7}

Fig. 18. The diffusion coefficients of cations at room temperature vs. q/a.

in Figure 8; however, in this case there are some quantitative differences. As shown in Table II, a $SO_3^-Ca_{1/2}^{2+}$ can absorb much more water at equilibrium than a $SO_3^-Cs^+$ or a $SO_3^-K^+$ site, the number being fairly close to the value for $SO_3^-H^+$. Furthermore, the diffusion coefficient of Ca^{2+} is much larger than that of Cs^+ or K^+. These two factors acting together result in the absence of maxima for either the total weight or the water curves. Similar experiments were carried out in $0.05N$ $Ba(NO_3)_2$ solutions, and, at least qualitatively, they could be explained in the same manner as described before.

Diffusion coefficients of the metal cations K^+, Cs^+, Ca^{2+}, and Ba^{2+} may be calculated from the data presented before. Their values were obtained by the half-time method and are given in Table III. It is obvious that the diffusion coefficients for the metal cations are much smaller than that for water. There is a reasonably good correlation between the diffusion coefficients of the metal cations and the values of q/a. This relation is shown in Figure 18. Lopez et al.[10] have reported that the diffusion coefficients of Na^+ and Cs^+ in Nafion membranes are 1×10^{-6} and 1×10^{-7} cm²/sec, as measured by the tracer method. Their value for Cs^+ is much higher than that obtained here. One possible reason for this difference is the fact that in their experiment the solvent (water)-equilibrated membrane was used, which makes the diffusion of the cations much easier, while in the studies reported here a dry membrane was immersed into the solution.

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