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Dielectric Relaxation Studies of Ion Motions in Electrolyte-Containing Perfluorosulfonate Ionomers. 1. NaOH and NaCl Systems

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ABSTRACT: Nafion perfluorosulfonate membranes were equilibrated in concentrated aqueous NaOH and NaCl solutions, and the dielectric response of these electrolyte-imbibed materials was investigated with an impedance analyzer. The storage and loss components of the complex dielectric constants were determined over the frequency range 5 Hz to 13 MHz as a function of external solution concentration and temperature. The observed dielectric behavior, coupled with the knowledge of polymer microphase separation, strongly suggests a mechanism of the relaxation of an interfacial polarization that arises from the accumulation and dissipation of mobile ionic charge, between electric field reversals, at the boundaries of clusters along the direction of the external applied field. Also, there is a clear manifestation of long-range ion motion that might be attributed to intercluster migration in contrast with the shorter intracluster displacements conceivably involved in the interfacial polarization process. Furthermore, it appears that the equilibrium electrolyte uptake is characterized by an exclusion of OH$^-$ ions greater than that as predicted by simple Donnan theory even when fixed-anion aggregation is taken into account.

Introduction

Nafion[1] perfluorinated ionomers, acting mainly in the role of ion-permselective membranes, have received considerable attention over the past decade. The earliest reported investigations of structure and properties were largely driven by a competitive need to understand and control, from the standpoint of selective molecular transport, the characteristic motions of ions and water molecules within the hydration microstructure of these membranes in electrochemical cells designed for the economical production of chlorine and caustic.[2] Furthermore, the interplay between polymer microstructure, cation/anion transport selectivity, water transport, and the *electrolyte strength* of the highly concentrated salt and alkali hydroxide solutions with which these membranes interface was, and remains, an important industrial issue.

A distinguishing feature of these remarkable polymers is an underlying microstructural heterogeneity said to be characterized by ~30–50 Å wide hydrophilic *clusters*, containing fixed and free ions as well as water molecules, embedded in a hydrophobic fluorocarbon phase.[3] Fundamental models of the molecular energetics of cluster formation, and the swelling of clusters in Nafion membranes equilibrated in water, have been contributed by Hopfinger and Mauritz,[4] Hsu and Gierke,[5] and more recently Mauritz and Rogers.[6]

Regarding the hydrophobic fluorocarbon phase, the studies of Starkweather[7] indicate that the polymer chains therein are organized in a hexagonal bilayer configuration similar to the structure of poly(tetrafluoroethylene) at high temperatures.

Earlier infrared and nuclear magnetic resonance spectroscopic studies were performed by Lowry and Mauritz[8] and Komoroski and Mauritz[9a,b] on Nafion perfluorosulfonate membranes in the monovalent alkali cationic salt forms as a function of water content. These studies, by yielding important information relating to side chain–counterion interactions and internal water structure, provided an experimental foundation for a statistical mechanical four-state model of the dynamic equilibrium between bound and dissociated counterions, which, in turn, formed the backbone of a theory of membrane internal water activity[9b,c] which correctly predicted the general trend of membrane swelling with cation size.[10]

Later, Mauritz and Gray[11] determined that the electrolyte invasion of Nafion sulfonate membranes equilibrated in strong NaOH solutions is characterized by an OH$^-$/SO$_3^-$ mole ratio that is quite *invariant* over the large external concentration range: $7.5 \leqslant M \leqslant 17.9$, indicating that the progressive concentration of internal NaOH, with increasing external solution concentration, is essentially a dehydration process (Figure 1). This dehydration would deswell the polymer matrix causing an increase in the fixed charge (SO$_3^-$) density, which in turn resists further OH$^-$ uptake by an enhanced Donnan exclusion.

Mauritz and Gray also demonstrated how an FT-IR analysis of the O–H stretching region, for Nafion membranes equilibrated in NaOH and KOH solutions, can yield useful information that relates to (a) the underlying hydrated cluster morphology, (b) an anomalous OH$^-$ ion mobility due to proton transfer within hydrogen bonds, and (c) Na$^+$–OH$^-$ ion pairing within clusters as a function of external alkali hydroxide concentration.[11]

Nafion sulfonate membranes containing OH$^-$ ions and varying amounts of water were seen to generate infrared spectra displaying *continuous absorption*, that is, a diffuse background-like superposition that originates at the main OH peak maximum, for the H$_2$O molecule, and extends continuously to lower wavenumbers. The relative degree of continuous absorption was seen to be a characteristic function of the concentration of the external aqueous alkali hydroxide solution in which the membranes were equilibrated, for a given cation type and temperature. Recognizing that the fundamental molecular event giving rise to continuous absorption is the tunneling and/or activated transfer of protons in the H$_3$O$_2^-$ groups throughout the

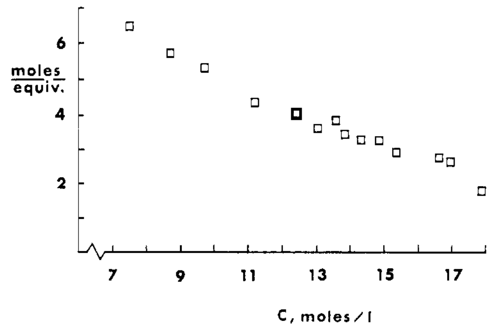
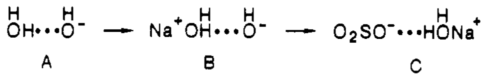


Figure 1. Average number of H_2O molecules per sulfonate group in 1100 EW Nafion films equilibrated in NaOH solutions of indicated molarities at room temperature. (Reprinted with permission from ref 11. Copyright 1983. American Chemical Society.)

internal hydrogen-bonded network, Mauritz and Gray deduced a simple progression of significant hydrogen bond configurations within the membrane structure

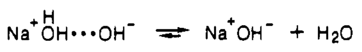


$$\underset{A}{\overset{H}{O}H\cdots\overset{H}{O}^-} \longrightarrow \underset{B}{Na^+\overset{H}{O}H\cdots\overset{H}{O}^-} \longrightarrow \underset{C}{O_2SO^-\cdots H\overset{H}{O}Na^+}$$

in order of increasing external NaOH concentration.

It should be understood that this proton transfer in hydrated OH^--containing membranes, as monitored by infrared spectroscopy, is indeed the same mechanism that accounts for the anomalously large electrical conductivities of simple aqueous alkali hydroxide solutions.[12,13] Clearly, the left-to-right motion of the protons in the hydrogen bonds of structures A and B above is equivalent to the translation of an OH^- ion from right-to-left. This transport mechanism is more efficient than that of simple electromigration or Fickean diffusion because the oxygen atoms are not required to move.

With increasing NaOH concentration, either in "simple" free solutions or in ionomer cluster-encapsulated microsolutions, there exists an increasingly larger relative population of Na^+–OH^- ion pairs that are separated by a single H_2O molecule. Within this grouping B, the strong electric field of the Na^+ ion causes the proton to spend more time in the vicinity of the oxygen furthest from it, whereas in structure A, which predominates at lower concentrations, the proton is highly delocalized, being equally shared by both oxygens. With increasing concentration, as the hydrogen bond thus becomes less polarizable; i.e., as the proton becomes more localized on an ensemble-average basis, OH^- mobility decreases and electrically neutral Na^+OH^- contact ion pairs form:



$$Na^+\overset{H}{O}H\cdots OH^- \rightleftharpoons Na^+OH^- + H_2O$$

Ion pairing, of course, has long been implicated as a major factor contributing to the observed decrease in the equivalent conductivities (Λ) of simple electrolytes, with increasing concentration, although, in the case of aqueous alkali hydroxides, ion pair formation can be affected by the transfer of a proton away from a cation's water of hydration, as described above, in addition to the simple, electrostatically favorable, cation–anion juxtaposition that would occur in aqueous alkali halide solutions.

For reference, the conductivity ratio, Λ/Λ_0 (Λ_0 = infinite dilution limiting equivalent conductivity), for aqueous NaOH at 25 °C, is plotted as a function of solution molarity (C) in Figure 2.[14,15] Although Λ/Λ_0 is not, strictly speaking, the true degree of ionic dissociation of the solution, the "actual" values, obtained from a successive approximation approach,[16] will not be more than slightly larger. In any case, the gradual progression of ion pair association in free aqueous NaOH solutions is evident in Figure 2, and there is no reason to believe that the same qualitative behavior does not occur within NaOH-containing ionomer cluster microsolutions, although the severely limited volume of confinement, as well as the presence of fixed SO_3^- groups, certainly places the situation on a higher level of complexity, particularly at high microsolution concentrations. We also imagine that higher order ionic multipoles (e.g. triplets, electrically neutral quartets) must necessarily appear with increasing concentration.

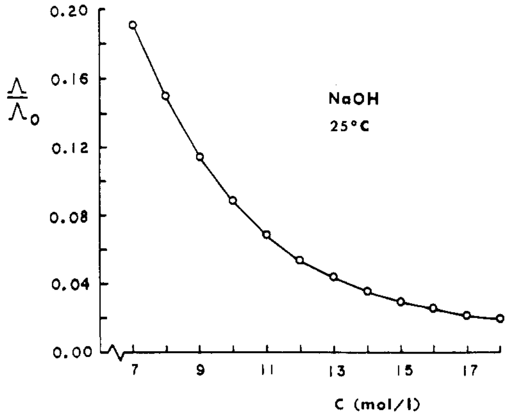


Figure 2. Ratio of equivalent conductivity of aqueous NaOH at molarity $C(\Lambda)$ to its infinite dilution limiting value (Λ_0) at 25 °C.[14,15]

Finally, as one proceeds to the highest concentrations, it was suggested that there becomes an increase in the tendency for proton transfer within the hydrogen bonds between SO_3^- groups and H_2O molecules owing to the perturbative effect of adjacent Na^+ ions on (increasing) OH bond polarization.

While the results of this earlier FT-IR study have contributed to an understanding of the mechanism of ionic conduction in OH^--containing perfluorosulfonate membranes on the most intimate molecular level, it is also important to investigate the manifestation of ion motions on a larger scale. It is quite relevant to be concerned with the nature of aggregate ionic motion over a finite cluster domain, subject to the constraint of severely reduced ionic mobility at the hydrophilic/hydrophobic interface.

It is quite natural to study the motions of charge carriers, within a heterophasic morphology, using dielectric relaxation/AC impedance methods. In addition to investigating molecular mechanisms relating to ion transport in membrane applications, these studies represent a contribution to a knowledge of the structure of, and interactions within, highly concentrated electrolytes as encapsulated in small volumes, i.e. microsolutions having a very large surface/volume aspect. Indeed, it is a point of fact that the physics of concentrated electrolytes, even in the bulk, is ill understood to date.

At least two dielectric relaxation studies of Nafion materials, namely, by Hodge and Eisenberg and Starkweather and Chang, have been reported. Comments on these prior studies, as they relate to our results, will be reserved for later in this manuscript.

In order to reduce confusion owing to the considerable number of symbols utilized, a Glossary is appended at the end of this text.

Experimental Procedure

Nafion sulfonate films nominally 0.007 in. thick, having an equivalent weight of 1100, were kindly supplied by E. I. Dupont de Nemours & Co. Prior to the dielectric testing, all samples were rendered to the dry Na^+ salt form by ion exchange in aqueous

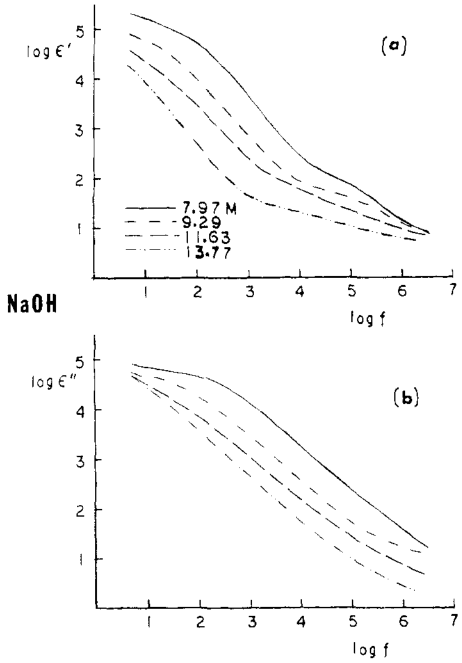


Figure 3. ε' and ε'' as a function of *f* at 22 °C for films equilibrated in NaOH solutions of indicated molarities.

NaOH, followed by leaching in pure water to remove excess Na^+ ions and OH^- ions, and finally vacuum-drying to constant weight.

Thus initialized, the samples were equilibrated in aqueous NaOH solutions having concentrations from 7.97 to 13.77 M at temperatures from 22 to 55 °C. The relative increase in weight as a function of electrolyte strength, equivalent weight, counterion type, and temperature was reported earlier for these materials.[10]

Also, for comparison, like-initialized samples were equilibrated in concentrated NaCl solutions over the same temperature range.

The experimental configuration used to investigate the dielectric response of the membranes is built around a microprocessor-controlled Hewlett-Packard 4192A impedance analyzer, capable of measurements in the frequency range *f* = 5 Hz to 13 MHz, with an HP85B data station. The sample cell is an in-house designed, accurately machined parallel-plate capacitor arrangement with a guard ring which can be immersed in an oil bath for controlled isothermal experiments. The real and imaginary parts of the complex dielectric constant, ε' and ε'', respectively, are derived from the measured values of the film capacitance and resistance in the usual fashion.[17]

Samples were always equilibrated and tested at the same temperature. Following equilibration, the film surfaces were gently blotted to remove excess electrolyte. It was determined that the membrane water contents did not change significantly between this step and that of securing the membrane between the electrodes.

Results and Discussion

NaOH-Containing Membranes. Parts a and b of Figure 3 illustrate the effect of external concentration on ε' and ε'' vs *f* curves at 22 °C. The general observations are as follows. ε' decreases with increasing *C* over the entire frequency range and attains rather high values in the low-frequency regime. ε'' also decreases with increasing *C* over the entire frequency range, and, for a given *C*, decreases rather monotonically with increasing *f* without the *apparent* display of absorption peaks.

Parts a and b of Figure 4 and parts a and b of Figure 5 display the effect of temperature on the ε' and ε'' vs *f* curves for films investigated at the lowest and highest concentrations, respectively. It is seen that, at both concentrations, both ε' and ε'' increase with increasing temperature at all frequencies. Again, no peaks are discernible on either of the ε'' vs *f* curves. The temperature splitting of the curves is greater at the higher concentration, and the highest concentration has the lowest ε' and ε'' over all *f* at all temperatures studied.

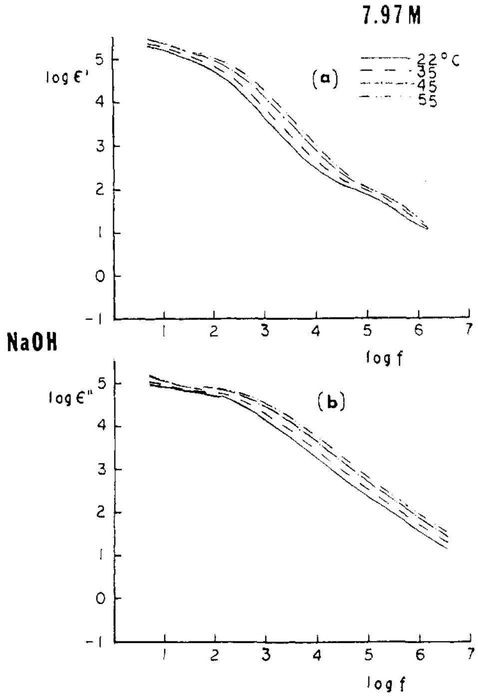


Figure 4. ε' and ε'' as a function of *f* for an external NaOH solution molarity of 7.97 M for films at the indicated constant temperatures.

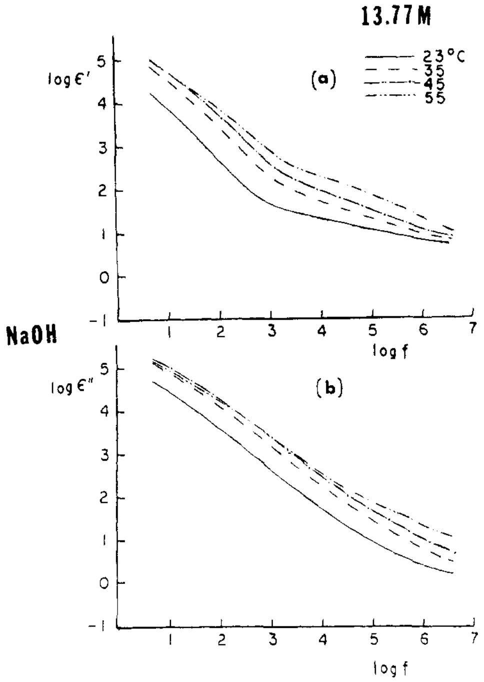


Figure 5. ε' and ε'' as a function of *f* for an external NaOH solution molarity of 13.77 M for films at the indicated constant temperatures.

First, consider the ε' vs *f* curves in relation to the Onsager equation[18] for dielectric dispersion, which is based upon the simple molecular dipole orientation mechanism

$$\mu^2 = \frac{9kT(\epsilon_0 - \epsilon_\infty)(2\epsilon_0 + \epsilon_\infty)}{4\pi S\epsilon_0(\epsilon_\infty + 2)^2} \qquad (1)$$

μ is the magnitude of the prominent orientable permanent molecular dipole in the system (e.g. a cation–anion bound pair), and S is its number per cm^3; i.e., $S = N_0\rho\omega/M$, where N_0 is Avogadro's number, ρ is the density of the polymer,

ω is the fraction, by weight, of the dipolar groups, and M is the molecular weight of this group. k is Boltzmann's constant, T is the absolute temperature, and ϵ_0 and ϵ_∞ are the low (static) and high (optical) frequency limiting values, respectively, of ϵ'. When reasonable values for these quantities are substituted in eq 1, it is seen that the value of the expression on the right is considerably greater than μ^2. As a point of reference, ion–counterion pairs (e.g. gaseous KCl, CsBr) typically have dipole moments of around 9–11 D. This comparison suggests that the conventional molecular dipole rotation relaxation mechanism is quite inadequate and that the huge dispersion ($\epsilon_0 - \epsilon_\infty$) producing this result may be due to larger scale *interfacial polarization* in a phase-separated system as indeed exists. It should be stated, however, that even "simple" polymers are too complex for their dielectric dispersion to be accurately modeled by eq 1,[19] but the analysis is common and appropriate in an order of magnitude sense in the search for relaxation mechanisms.

Considering pure electrical theory and using macroscopic continuum-based concepts, one might digress to view these ionomers as consisting of an isolated phase having a dielectric constant ϵ_2 and electrical conductivity σ_2 within a continuous phase with electrical parameters ϵ_1 and σ_1. The theory for the effective dielectric constants of dilute dispersions of spheres (volume fraction = $\phi \ll 1$) in constant electric fields was initiated some time ago by Maxwell[20] and later expanded by Wagner[21] to account for the dielectric response of these systems to alternating fields. This treatment has since been extended and refined to be applicable to higher values of ϕ (accounting for sphere–sphere interaction) as well as to shapes other than spheres and distributions of sorts of spheres (composition-wise) each having a different ϵ_2 and σ_2.

Within the specific context of electrolyte-imbibed clusters in a continuous perfluoro organic phase, $\epsilon_2 \gg \epsilon_1$ and $\sigma_2 \gg \sigma_1$. Then, on the basis of the simplest treatment, there should occur a dielectric absorption with a relaxation time roughly (in order-of-magnitude sense) equal to $\epsilon_2/(4\pi\sigma_2)$ (in cgs units). As the actual materials are equilibrated in electrolytes of increasingly greater concentration, the decreasing level of ionic hydration and subsequent ion pairing and multipolar association within the clusters would be expected to reduce the charge mobility and cause the relaxation time to increase. It was seen that this is in fact the case.

Another general theoretical result for such heterogeneous systems is that the overall, composite, dielectric constant is always greater than that of either phase taken separately.[22] The rationale for the particular system at hand is as follows. Because there are significant differences in the polarizabilities and charge mobilities across the hydrophilic/hydrophobic phase boundaries, there will occur the inevitable accumulation and dissipation of net charge at these interfaces along the direction of the applied electric field during each half-cycle of field oscillation (see Figure 6). It is then easy to visualize field-induced oscillating macrodipoles that are of a size of the order of cluster dimensions. This large-scale charge separation will clearly result in a rather large *induced* dipole moment per unit volume that is responsible for the observed high dielectric constants. It might be mentioned, in comparison, that simple polymers that are loaded with conducting inclusions at volume fractions below their insulator–conductor thresholds are also known to exhibit quite large dielectric constants at low frequencies.[23]

Dc Conductivity Component and Long-Range Ionic Motion. While the relaxation of interfacial polarization, as described, should give rise to characteristic absorption peaks, the actual ϵ'' vs f curves as plotted in straightforward fashion do not reveal their presence.

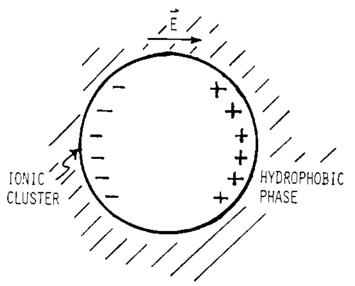


Figure 6. Simplified illustration of the accumulation of ionic charges at the hydrophilic/hydrophobic interface along the direction of the electric field due to the gradient of ionic mobility across the interface.

On the other hand, these curves exhibit an upward swing for $f \rightarrow 0$ which suggests the presence of dc conduction. In an equivalent circuit representation, a frequency-independent dc resistance is considered to be in parallel with a frequency-dependent ac resistance, in the usual way.[24] ϵ'' then becomes the sum of an ac term, ϵ''_{ac}, characterized by one or more absorption peaks, and a dc term, ϵ''_{dc}, which is simply inversely proportional to f.

Dc conduction, within the context of our system, refers to mobile ions being able to execute increasingly greater net displacements in the electric field direction during a half-cycle at increasingly lower frequencies. For the system reported in this work, a characteristic magnitude for ionic displacement between field reversals at a given low frequency is, of course, not within our knowledge, although a significant degree of intercluster migration, perhaps through connecting channels,[25] would seem inevitable.

If $\epsilon'' = \epsilon''_{\mathrm{ac}} + A/f$, where A is a constant that is directly proportional to long-range dc ion conductivity, then $\log(\epsilon'' - \epsilon''_{\mathrm{ac}}) = \log f^{-1} + \log A$ and A can be extracted from the vertical intercept of the extrapolated *linear* portion of a $\log \epsilon''$ vs $\log f^{-1}$ curve, assuming there are no interfering absorption peaks in the low-frequency regime (see Figure 7). Extracting A in this way allows for ϵ''_{dc} to be then split from ϵ'', revealing the underlying relaxation peak(s). We have tentatively ascribed the depression from linearity of these log–log plots at the lowest frequencies, as seen in Figure 7, to polarization at the membrane/electrode interface but choose to elaborate on this phenomenon in a subsequent paper in the interest of time and space.

This curve-decomposition procedure was performed, and the results for membranes equilibrated in 7.97 and 13.77 M NaOH are displayed in parts a and b of Figure 8 for various temperatures. Indeed, it is seen that there emerge well-defined absorption peaks that reasonably shift to higher frequencies with increasing temperature. At 7.97 M, the relaxation time ($(2\pi f_{\max})^{-1}$) corresponding to the average $f_{\max}$ for these temperatures is around 4×10^{-7} s. At 13.77 M, however, this number increases to around 5×10^{-6} s. At a given temperature, the relaxation time is seen to increase with increasing external (and, therefore, internal) NaOH concentration. For reference, these times are considerably longer than dielectric relaxation times characteristic of pure liquid water, or, say, even 1.0 M aqueous NaCl ($\sim 10^{-11}$ s), in the same temperature range.[26,27]

Plots of $\log f_{\max}$ vs T^{-1}, seen in parts a and b of Figure 9, are quite linear, with slopes that yield activation energies (E^*) of 3.49 (7.97 M) and 2.07 kcal/mol (13.77 M). The difference between these energies may perhaps not be significant. What is significant, however, is that the un-

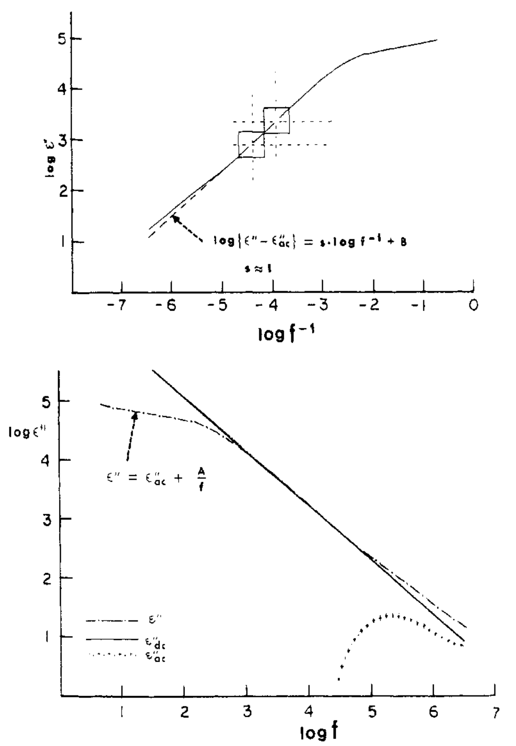


Figure 7. Isothermal log–log plots of ϵ'' vs f illustrating the subtraction of the dc loss component to yield an ac absorption peak.

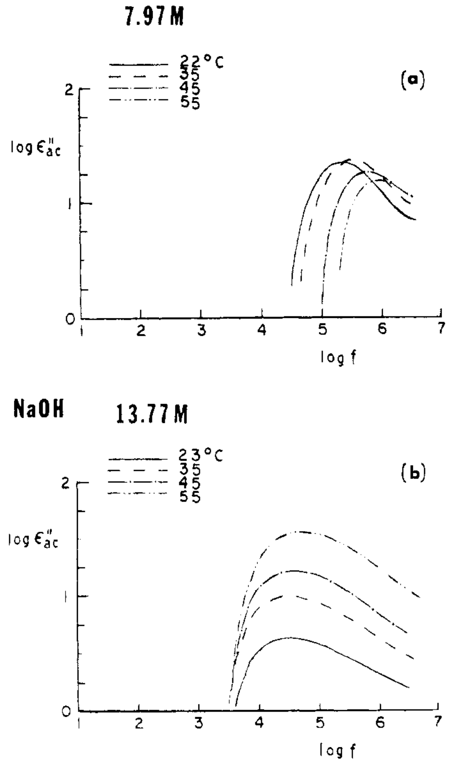


Figure 8. Ac absorption peaks for films equilibrated in 7.97 M (a) and 13.77 M (b) NaOH solutions at the indicated temperatures.

derlying relaxation mechanism appears to be temperature-activated in the traditional sense of absolute rate theory.[28]

NaCl-Containing Membranes. The dielectric relaxation spectra of identical Nafion sulfonate films, equilibrated in concentrated aqueous NaCl solutions, were obtained and analyzed in like fashion to test for possible significant departures from the previously discussed behavior of NaOH-containing films. It was thought that perhaps the anomalously high OH$^-$ ion mobility in the NaOH-imbibed systems[11] might affect a considerable difference in the dielectric response from that of films containing simpler halide co-ions. However, an inspection of the results seen in parts a and b of Figure 10 and Figures 11 and 12 for the example of 5.33 M indicates rather qualitatively similar behavior for membranes containing the two electrolytes. The aspects of a high ϵ' as $f \rightarrow 0$, a strong dc conductivity contribution, and general Arrhenius-like temperature effects seem to be common to both aqueous NaCl and NaOH systems. Furthermore, the re-

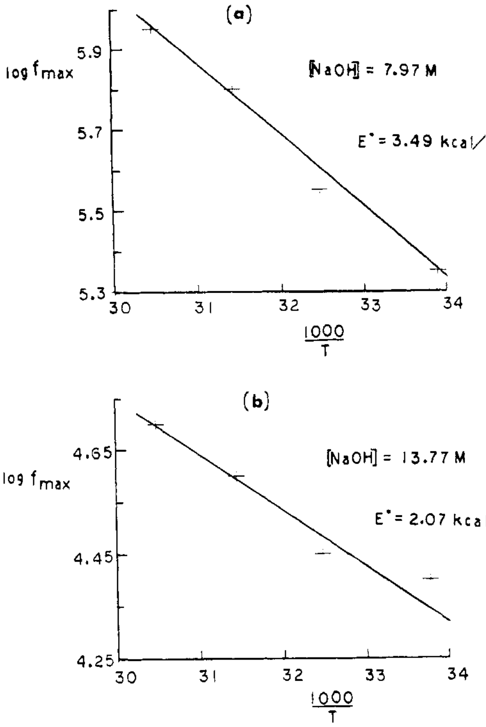


Figure 9. Plots of log f_{max} vs T^{-1} (K^{-1}) for films equilibrated in 7.97 M (a) and 13.77 M (b) NaOH solutions.

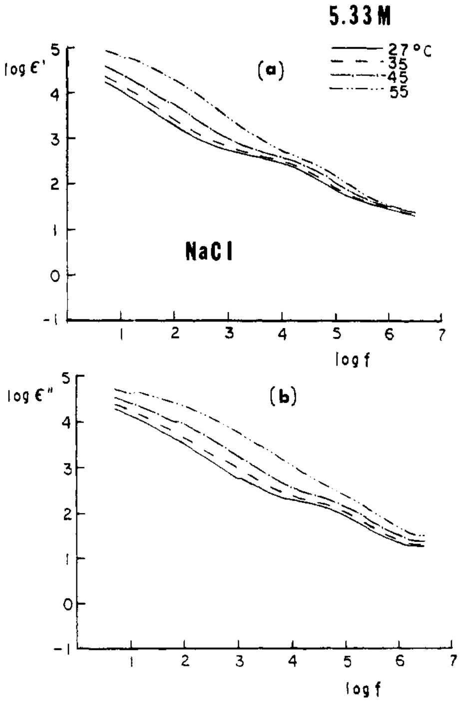


Figure 10. ϵ' and ϵ'' as a function of f for an external NaCl solution molarity of 5.33 M for films at the indicated constant temperatures.

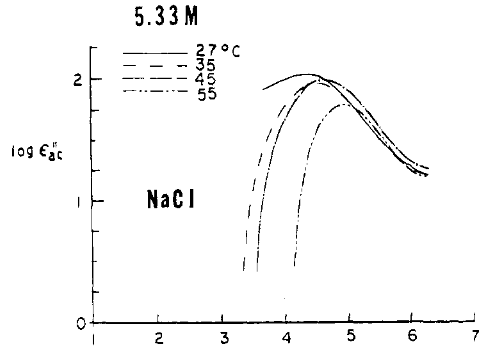


Figure 11. Ac absorption peaks for films equilibrated in 5.33 M NaCl solutions at the indicated temperatures.

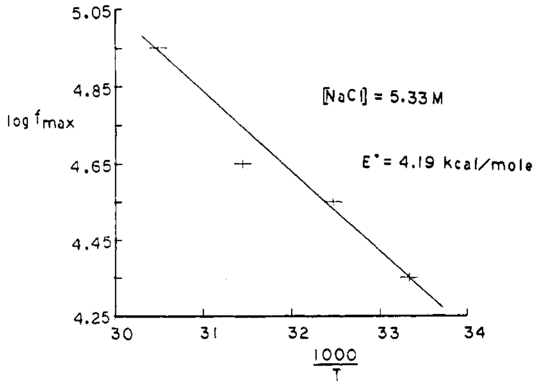


Figure 12. Plot of log f_{max} vs T^{-1} (K^{-1}) for films equilibrated in 5.33 M NaCl solutions.

laxation times and activation energies are not so radically different as to suggest different relaxation mechanisms.

Temperature and Concentration Effects. The general dominant mechanisms suggested as generating the observed dielectric relaxation behavior are (a) the relaxation of interfacial polarization due, in the main, to mobile ions arising from the underlying cluster morphology and (b) a dc conductivity, i.e. long-range, irreversible ion displacement. Consider a qualitative rationalization of the influence of temperature and concentration in terms of these concepts.

First, the decrease in ϵ' with increasing concentration (at a given f and T) can be viewed as being caused by an increasingly suppressed ionic mobility owing to the enhancement of the pairing of ions as well as the formation of sluggish higher order ionic multipoles as fewer water molecules are available to solvent-separate the ions. As pointed out earlier,[11] the uptake of aqueous NaOH by Nafion membranes in this concentration regime is basically a dehydration process. The ensuing difficulty of ion displacement at the hydrophilic/hydrophobic phase boundaries would understandably diminish the extent of interfacial polarization resulting in a depression of the observed ϵ'.

Likewise, the depression of ϵ'' with increasing concentration can be rationalized as a dampening of the overwhelming dc loss component by the formation of more electrically neutral ion pairs as well as larger sluggish ionic multipoles. As a long-range effect, perhaps one might also consider this electromigration to be made more difficult in an increasingly more "viscous" cluster microsolution.

The enhancement of both ϵ' and ϵ'' with increased temperature can be viewed as a promotion of ionic mobility in the usual way, in terms of either shifting the bound ↔ unbound equilibrium of ion pairs toward dissociation and/or diminishing the local "viscosity" within cluster microsolutions. These concepts are also consistent with the observation that temperature differentiation is more profound the higher the concentration.

The increase in relaxation times at a given temperature with increasing concentration can also be explained in terms of this progressive ionic interactive-retardation effect.

While the relaxation times for this system are much too long to correspond to those for liquid water, as pointed out earlier, the value for membranes soaked in 13.77 M NaOH (5×10^{-6} s) is but an order-of-magnitude lower than that of ice (e.g. 6×10^{-5} s at −11 °C). Water can, in fact, exist in icelike structure above its normal freezing temperature under a condition of sufficiently high pressure. Before one is tempted to invoke the compressive stress resulting from the deformation of the polymer matrix attending electrolyte invasion as playing this role, consider that the de facto very low water molecule/ion ratio would very obviously preclude the existence of an extensively hydrogen-bonded structure as in ice. Furthermore, the derived activation energies are even too low to reflect the breaking of a single hydrogen bond (~5 kcal/mol) and much less, in fact, than that for ice (~13 kcal/mol).

Equilibrium Distribution of Na^+ and OH^- Ions across the Membrane/Electrolyte Interface. As the ionic conductivity of an electrolyte-imbibed membrane is directly proportional to the number of effective charge carriers per unit volume, for each ionic species, as well as their intrinsic ionic mobilities, a knowledge of the manner in which the electrolyte concentration in the cluster microsolutions is related to the external bulk concentration is useful in the interpretation of the dielectric relaxation results. In this discussion, we adopt the view of a cluster as providing a microencapsulation for electrolyte wherein *all* sorbed solution resides in the cluster phase.

Consider the initial state of a membrane as before to be that of the totally dry Na^+ form and containing no excess Na^+ ions nor OH^- ions.

It was earlier shown that, upon equilibration in simple electrolytes including NaOH solutions, the resultant fractional volume increase is twice the fractional mass increase.[10] This is an empirical relationship that is applicable in the membrane equivalent weight range $1000 \leq EW \leq 1400$ and in the external solution molarity range $0 \leq M \leq 14$. Then, if a is the fractional weight increase and ρ_0 the dry membrane density, the solution-equilibrated (wet) density can be written as $\rho = \rho_0(a + 1)/(2a + 1)$. If, in the wet state, the SO_3^- groups were homogeneously distributed throughout the membrane, their density would be $\bar{R} = 1000\rho/\mathrm{EW}$ (equiv/1000 cm^3). However, with these sites segregated into clusters, the effective larger local concentration should be considered. Specifically, if ϕ is the fraction of the total volume at equilibrium, occupied by the cluster phase, then the average concentration of SO_3^- groups *within clusters* is given by

$$R = \frac{1000\rho_0(a + 1)}{\phi(2a + 1)\mathrm{EW}} > \bar{R} \tag{2}$$

The following is a rationale for estimating ϕ.

First, call α the cluster-phase volume fraction in the *dry, electrolyte-free*, Na^+-salt form ($\alpha < \phi$) and assume that all SO_3^- groups reside in clusters. Then, if ν_0 is the total volume of the dry (initial) cluster phase and ν' is the total volume of the hydrophobic phase in the sample

$$\alpha = \nu_0/(\nu_0 + \nu') \tag{3}$$

Assume, also, that the polymeric repeat units are packed reasonably efficiently in this dry initial state. Such an

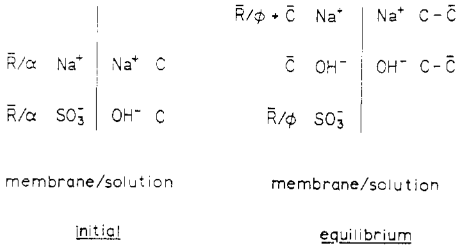


Figure 13. Initial and equilibrium distribution of mobile Na^+ and OH^- ions across the membrane/solution interface. During equilibration from the dry Na^+ form the cluster volume fraction changes from α to ϕ. The concentrations are considered on a per solution volume basis. Electroneutrality is obeyed in every phase and, in the simple model, ions cross the interface as single units and not as neutral or charged ionic associations.

efficient-packing concept is also a critical element of Dreyfus' model for multiplet clustering in dry conventional ionomers.[29] α can then be sensibly estimated as the ratio of the sum of the hard-sphere volumes of all the atoms constituting an "ionic fragment" to the sum of the volumes of all the atoms in an entire Nafion polymer repeat unit (i.e. unit whose molecular weight = EW). The ionic fragment was chosen to be $OCF_2CF_2SO_3^-Na^+$. The rationale for this assignment, as well as the straightforward method for computing α, was discussed in an earlier publication.[6] For EW = 1100, $\alpha = 0.20$.

In the electrolyte-equilibrated state, let the total volume of the ionic phase increase to ν and assume that the volume of the hydrophobic fluorocarbon phase in unchanged. Then

$$\phi = \nu/(\nu + \nu') \tag{4}$$

A rationale for constant ν' for Nafion-like materials was also presented earlier,[6] but the assumption that results in mathematical simplification clearly needs to be tested.

After algebraic manipulation of eq 3 and 4, while utilizing the fact that the fractional increase in the total volume $\simeq 2a$, the following simple equation for ϕ is obtained:

$$\phi = (2a + \alpha)/(2a + 1) \tag{5}$$

While it is quite obvious that the envisioned "cluster microsolutions" or even the free, but highly concentrated, external NaOH solutions are too complex to be considered ideal from the standpoint of dilute solution theory, it is nonetheless an interesting exercise to compare the experimental electrolyte uptake of these ionomers with that as predicted by classical Donnan equilibrium theory[30] that is corrected for fixed-ion clustering and attendant swelling. If the usual assumptions of complete ionization, external and internal (cluster) solution electroneutrality, and solute (or individual ion) activity coefficients of unity etc. are made, the equilibrium distribution of ions across the membrane/solution interface, depicted in Figure 13, according to the condition of a free energy balance for the diffusible Na^+ and OH^- ions is given by eq 6 wherein C

$$\bar{C} = C^2/(R + 2C) \tag{6}$$

is the *initial* external concentration (molarity) and $\bar{C}$ is the *equilibrium internal clustered* concentration. To be sure, the interrelated assumptions relating to ionization and activity coefficients, and other conceivable omissions, can be challenged.

Nafion samples, equilibrated in caustic solutions at ambient temperature over the range of concentrations as described in the Experimental Procedure, were also carefully titrated to yield the NaOH weight percents of the total weight uptakes, which were then converted to their corresponding molarities, i.e. $\bar{C}$, by using a standard solution concentration conversion table.[31] It is, of course, implicit in this conversion to molarity units that any determined NaOH weight percent will correspond to the same molarity regardless of whether the solution is in the bulk state or as encapsulated within cluster domains. Gierke et al. have estimated that there can be over a thousand H_2O molecules incorporated in a cluster within Nafion sulfonate samples equilibrated in *pure* water.[3] To be sure, electrolyte-equilibrated samples will contain fewer H_2O molecules but more counterions plus coions, and the total weight uptake will be less than samples containing pure water. The issue of whether an electrolyte will retain an identity as a "solution" in the traditional sense upon being finely dispersed into a large number of ~40 Å-diameter, high surface/volume clusters containing fixed anions is clearly an important one. On the other hand, spectroscopic evidence indicates a significant degree of hydrogen bonding as well as considerable ionic and water mobility commensurate with a liquid solution (albeit highly concentrated) state as well as aqueous phase segregation. Furthermore, if the mechanism of relaxation of interfacial polarization due to ion displacement within clusters is in fact real, then the relatively high observed values of $f_{\max}$ would suggest reasonably high ionic mobility.

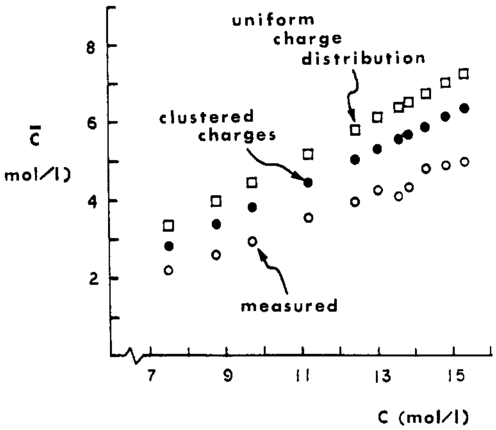


Figure 14. Equilibrium internal ($\bar{C}$) vs initial external (C) electrolyte concentrations for 1100 EW Nafion sulfonate membranes equilibrated at room temperature. Comparison of actual electrolyte uptake with that as calculated via Donnan theory assuming both uniform and clustered ion exchange site distributions.

Internal ($\bar{C}$) vs external (C) electrolyte concentration is plotted in Figure 14 for experimental data and also from values derived from eq (6) for both assumed uniform and clustered charge distributions. While the trends of the experimental and hypothetical curves are much alike, it is nonetheless evident that even an allowance for clustering does not produce a Donnan exclusion as good as that which is actually measured when the solutions are expressed on a per *solution volume* basis.

This discrepancy might be rationalized by analyzing the degree of validity of the previously mentioned assumptions dealing with ionization, ionic activity coefficients, nature of internal solution structure, etc., although insufficient quantitative information is presently available for a meaningful analysis.

On the other hand, if the assumptions are in fact reasonable to the point where the difference between the two lower curves in Figure 14 is significant at least in a qualitative sense, a recent theoretical analysis of local dielectric polarization effects in perfluorinated ionomers by Hsu[32] might be relevant. In this theory, owing to the considerable difference between the dielectric constants of the cluster and fluorocarbon phases, both positive and negative mobile ions in clusters when approaching the interface will induce a charge distribution at the interface (or, equivalently, create an "image charge" of *like sign* on the hydrophobic side of the interface) that is always repulsive. Hence, the electrolyte exclusion would be even more effective than that as based on Donnan equilibrium. One must be aware, however, that this analysis is based upon the theory of macroscopic dielectrics and its applicability on this molecular heterogeneous structural level should be questioned.

Conclusions

From this preliminary investigation we conclude that the results of dielectric relaxation studies of electrolyte-containing perfluorinated ionomers can be reasonably understood in terms of the motions of mobile ions in a phase-separated system. In particular, it appears that intracluster ion displacements might be distinguished from intercluster ion hopping. By this analysis, the temperature and concentration dependencies of the ion-motional time scales, as well as the energies required to activate these motions, are accessible. As these ionic relaxations would be sensitive to and therefore highly modulated by this unique heterogeneous polymer microstructure, one might consider the outcome of these studies to significantly contribute to the characterization database that will be critical in guiding the formulation and evaluation of ion transport mechanisms in these membranes.

We will now review previous dielectric relaxation studies of Nafion in comparison with the results of our investigation.

Hodge and Eisenberg[34] determined the dielectric and mechanical relaxations of Nafion SO_2F precursor films. As these materials were dry and ion-free, the spectra were solely reflective of the base polymer and considerations based on hydrophilic/hydrophobic phase separation were nonexistent. In short, four relaxations were observed in isochronal measurements in the temperature range of −196 to +80 °C. In order of increasing temperature, the motional assignments were (γ, −190 °C) SO_2F group rotation or wagging (β, −100 to −20 °C), which can, in turn, be resolved into two components at low frequencies that are thought to arise from backbone and other side-chain motions, and (α) a broad glass transition.

The dielectric constants of these largely hydrophobic films were only around 2, exhibited a very small dispersion, and the loss peaks were of low intensity over the investigated temperature range. Thus, in comparison with our hydrolyzed, electrolyte-containing films, it is obvious that the relaxations observed for the SO_2F form are overwhelmed by ionic effects.

Later, Starkweather and Chang[35] noted that the dielectric behavior of Nafion sulfonate films in the Na^+ form incorporating various degrees of water was, as in our case, dominated by conduction. It should be mentioned that these studies were performed at temperatures that were low (−72 to −39 °C) compared to ours. When the dc contribution to ϵ'' was split off, a relaxation peak, assigned to the glass transition of the aqueous domains, appeared. The peak position increased from 1×10^4 to 5×10^4 Hz as the temperature increased from −72 to −62 °C for samples saturated with water. This concept of an aqueous phase glass transition below the freezing point of water was also supported by the results of dynamic mechanical and proton NMR experiments performed by Starkweather and Chang.

In comparing our results with those of the above study, bear in mind that our samples contained excess, supposedly mobile, counterions, an equivalent number of co-ions, and little water, whereas the polar phase of the above-cited samples would have contained a rather copious amount of water, no excess electrolyte, and, at most, a small relative population of dissociated counterions at these low temperatures. We would also question the wisdom of extensive quantitative comparison with the studies of Starkweather and Chang owing not only to significant differences in experimental temperature ranges but also to differences in instrumentation and perhaps sample preparation.

Yeo and Eisenberg reported dielectric relaxation studies of Nafion SO_3H and $SO_3^-K^+$ form membranes as a function of water content in the temperature range −190 to ca. 150 °C (40 Hz to 10 kHz).[36] For the acid form above around a 2.1 H_2O/SO_3H mole ratio, there appeared a major peak with a higher temperature minor peak in isochronal tan δ vs temperature spectra, such that both peaks drastically shifted to lower temperatures with increasing water contents up to a mole ratio of 15. On the other hand, interestingly, the activation energies of both peaks were quite insensitive to water content (average: 26 kcal/mol, major; 16 kcal/mol, minor). Two similar peaks that shift with water content in qualitatively similar fashion were seen for the K^+ form, although no activation energies were reported for this case. Curiously, dc conduction was not mentioned, either as being present at all or, if so, having been accounted for in the display of spectra. Starkweather and Chang[35] in combining NMR, mechanical, and dielectric relaxation data for water-saturated membranes extracted activation energies of 17, 40, and 25 kcal/mol for the H^+, Na^+, and K^+ forms, respectively, in reasonable comparison with the values of Yeo and Eisenberg. While the relaxations noted in these two studies have been ascribed to the making–breaking of a glassy microstructure, the relaxations observed in our experiments are activated by energies of an order of magnitude lower. For this as well as earlier stated reasons we restate our postulate that the relaxation we are monitoring is rather related to the easier affected displacement of mobile ions in water-poor clusters in which a glassy aqueous structure would seem quite improbable.

Scibona, Fabiani, and Scuppa,[37] for Nafion 1200EW sulfonate membranes in aqueous NaOH, KOH, and LiOH solutions, determined the apparent potentiometric transport numbers, by emf measurements, of the cations (25 °C) as well as the dc membrane resistances at various current densities (18–280 mA/cm^2 at 25, 50, and 80 °C) as a function of external electrolyte concentration. The authors' interpretation of their results in the high concentration regime (i.e. reduced ionic mobility owing to Na^+–OH^- ion pairing) is in rather close harmony with our view as per the results of our experiments. Scibona et al. derived energies of activation for ionic conduction, in the temperature range 25–80 °C from their resistance measurements. When their activation energies at the two highest concentrations are coplotted in Figure 15 with those we have reported in our studies (Figure 9) and tentatively ascribed to an *intracluster* relaxation involving mobile ions, it is very interesting to see that the composite data could be described as a distinct linear decrease with increasing concentration. While caution should obviously be exercised in interpreting these limited data, it is tempting to conjecture a common molecular mechanism owing to the smoothness of fit. Specifically, this close comparison, as well as the implications of our earlier infrared spectroscopic studies of OH^--containing membranes[11] and realistic considerations of cluster connective

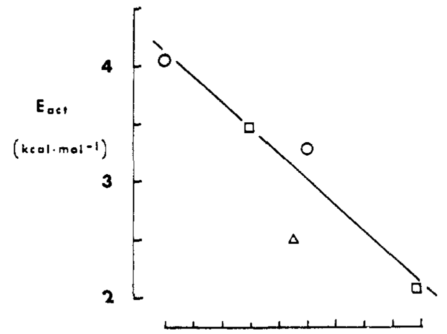


Figure 15. Coplot of activation energies for the dc membrane conduction (○) (Scibona et al.[37]), dielectric relaxation (□) (this work), and Na^+ ion self-diffusion (△)[39] in Nafion membranes equilibrated in aqueous NaOH solutions at high concentrations.

structure,[38] has caused us to favor the view that ion transport in perfluorosulfonate ionomers is largely controlled by molecular events *within the cluster microstructure* rather than by the energetics at play in ionic transit between clusters. A suggested rationale for the gradual decrease in activation energy with increasing concentration consists of the progressive breaking of the structure of hydrogen-bonded water. To be sure, a considerable fraction of the total water content of these membranes must be tightly bound around ions at these high concentrations. While this is reasonable, our infrared studies also unquestionably indicate that a considerable number of hydrogen bonds persist even at these low water levels.[11] Interestingly, the data of Figure 15 will back-extrapolate to the dilute regime to energies that are but slightly higher than those required to break a single H_2O–H_2O hydrogen bond.

Yeager et al. have performed very organized and definitive studies of the self-diffusivities of cations and anions in perfluorinated ionomer membranes by a radioactive tracer technique.[39–41] Emerging from these studies, and in consideration of the present structural database, is their hypothetical concept of different diffusive pathways for different ionic species. In addition to distinctive hydrophobic and hydrophilic regions, there will exist diffuse, less ordered, interfacial regions conceivably rich in perfluoroalkyl ether moieties. Yeager states that it is reasonable to expect membrane-incorporated ions to partition between the very hydrophilic cores of the clusters and the less hydrophilic interfacial regions. Thus, for example, Na^+ or Li^+ ions, having strong hydrative tendencies, would energetically favor the core whereas a Cs^+ ion, having a considerably larger radius and lower charge density, might be more energetically comfortable in the interface. In part 2 of this series, we will report on the conductivity vs frequency and temperature response of Nafion ionomers that contain concentrated electrolytes having a number of cation/anion combinations. We feel that Yeager's concept of the interface is quite relevant in the discussion of our proposed mechanism of the relaxation of interfacial polarization. In fact, the kinetics of the accumulation and dissipation of mobile ionic charge at the interface along the electric field direction during a half-cycle of oscillation will in strong measure be governed by the gradient of ion permeation (diffusivity and solubility) across that interface.

Yeager et al. determined an energy of activation for Na^+ self-diffusion in Nafion 1150 EW sulfonate membranes in 9.5 M NaOH of 2.5 kcal·mol.⁻¹ This value is in the vicinity of the activation energies seen in Figure 15. Perhaps the reason as to why this value is specifically lower than the interpolated value at 9.5 M is that Yeager's experiments were performed at higher temperatures (60–90 °C) at which the overall polymer ionic hydration microstructure is in a more dynamic state that facilitates the motions of ions. Furthermore, while the motions of the Na^+ and OH^- ions are necessarily coupled, the studies of Yeager et al. focus on Na^+ ion behavior, whereas the energies represented in Figure 15 contain a contribution from OH^- ion mobility as well.

Rubenstein, Rishpon, and Gottesfeld[42] performed an ac impedance study of electrochemical processes at Nafion-coated electrodes, namely, the system Pt/Nafion,$Ru(bpy)_3^{3+/2+}$. While this system is somewhat different from ours, it is interesting to see that a model that assumes two parallel uncoupled diffusion pathways with diffusion coefficients differing by an order of magnitude is consistent with the experimental results. In turn, an underlying three-domain morphology, as discussed by Yeager, was suggested to account for the two diffusional routes.

In short, we feel that our results are reflective of both the long- and short-range motions of mobile ions as modulated by a phase-separated polymer morphology. Accepting this premise, it is then natural to transfer the concepts developed in this work to the realm of selective steady-state ion transport, at least at current densities that are not excessive. These experiments have also been performed with Nafion sulfonate films incorporating a variety of other electrolytes and the results will issue in a subsequent publication. Indeed, the detailed physics of concentrated electrolytes, even in the simpler bulk state, is ill-understood at the present time. Studies such as ours, accompanied by structural probes, provide the additional opportunity to investigate concentrated electrolytes, finely dispersed as "microsolutions", having a high surface-to-volume ratio, as encapsulated in ionic clusters.

Glossary

Λ	equivalent conductivity of electrolyte (Λ_0 = infinite dilution limiting value)
C	molarity of external (bulk) electrolyte prior to membrane equilibration
$\bar{C}$	molarity of membrane-incorporated (clustered) electrolyte at equilibrium
$\bar{R}$	average (bulk) concentration of ion exchange groups in electrolyte-containing membranes (mol/1000 cm^3)
R	effective concentration of ion exchange groups within clusters of electrolyte-containing membranes (mol/1000 cm^3)
α	volume fraction of hydrophilic domains in dry, electrolyte-free membranes
ϕ	volume fraction of hydrophilic domains in electrolyte-equilibrated membranes
ν'	total volume of membrane hydrophobic phase (arbitrary units)
ν_0	total volume of cluster phase in dry, electrolyte-free membranes (arbitrary units)
ν	total volume of cluster phase in electrolyte-equilibrated membranes (arbitrary units)
a	membrane fractional weight increase with equilibration in electrolyte
EW	membrane equivalent weight (g/charge equivalent)
ρ_0	dry, electrolyte-free membrane bulk density (g/cm^3)
ρ	electrolyte-equilibrated membrane bulk density (g/cm^3)
f	frequency of applied electric field (Hz)
ϵ', ϵ''	real and imaginary components, respectively, of the complex dielectric constants ($\epsilon' - i\epsilon''$) of membranes
ϵ_0, ϵ_∞	zero and infinite frequency limits, respectively, of ϵ'
ϵ''_{ac}	dielectric loss factor associated with the periodic, short-ranged displacement of ionic charge ap-

	pearing as alternating current on a macroscopic level
f_{max}	frequencies corresponding to maxima in ϵ''_{ac} vs f plots
ϵ''_{dc}	dielectric loss factor associated with the irreversible long-range displacement of mobile ions appearing as direct current on a macroscopic level ($\epsilon'' = \epsilon''_{ac} + \epsilon''_{dc}$)
ϵ_1, ϵ_2	dielectric constants of continuous hydrophobic and isolated hydrophilic membrane phases, respectively
σ_1, σ_2	electrical conductivities of continuous and isolated membrane phases, respectively
E^*	energy required to activate relaxation of ionic interfacial polarization in electrolyte-containing membranes (kcal/mol)
E_{act}	activation energy, in general (kcal/mol)
μ	dipole moment of selected single molecule or molecular fragment (D)
S	number density of selected dipole (cm^{-3})
ω	weight fraction of selected dipole
M	molecular weight of selected dipole (g)
N_0	Avogadro's number
k	Boltzmann's constant (1.38×10^{-23} J·molecule^{-1}·K^{-1})
T	absolute temperature (K)

Registry No. Nafion, 39464-59-0; NaOH, 1310-73-2; NaCl, 7647-14-5.

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