(9) Bessonov, M. I.; Koton, M. M.; Kudryavtsev, V. V.; Laius, L. A. *Polyimides—Thermally Stable Polymers*; Plenum Press: New York, 1987.
(10) Frechet, J. M. J.; Eichler, E.; Ito, H.; Willson, C. G. *Polymer* **1983**, *24*, 995. Ito, H.; Willson, C. G.; Frechet, J. M. J.; Farrall, M. J.; Eichler, E. *Macromolecules* **1983**, *16*, 510. Proceedings SPIE Conference, Santa Clara, 1987. Ito, H.; Willson, C. G.; Frechet, J. M. J. US Patent 4,491,628, 1985.
(11) Frechet, J. M. J.; Buchard, F.; Eichler, E.; Houlihan, F. M.; Izawa, T.; Kryozka, B.; Willson, C. G. *Polym. (Tokyo)* **1987**, *19*, 31.
(12) Pryde, C. A., *J. Polym. Sci., Part A: Polym. Chem.*, in press.
(13) Ueda, M.; Mochizuki, A.; Hiratsuka, I.; Oikawa, H. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 3291.
(14) Milevshaya, I. S.; Lukasheva, N. V.; Yel'yashevich, A. M. *Vysokomol. Soyed., Ser. A* **1979**, *A21*, 1302.

Dielectric Relaxation Studies of Ion Motions in Electrolyte-Containing Perfluorosulfonate Ionomers. 4. Long-Range Ion Transport

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ABSTRACT: Mauritz and co-workers have shown that the dielectric loss spectra in the low frequency (ω) region of Nafion sulfonate membranes incorporating aqueous electrolytes vary as ω^{-n} where $0 < n < 1$. A more detailed examination of n for selected systems reveals that this power is a distinct function of mobile ion type, ionic concentration, and system temperature. While we had earlier attributed this power law behavior, in general, to long-range, i.e., intercluster, ion motions, we have attempted herein to more carefully analyze this phenomenon in terms of (a) the related theories of processes that are fractal in space and time, (b) the theory of the dispersive transport of charge carriers in amorphous materials, and (c) the cluster theory of the anomalous low-frequency dielectric dispersion phenomenon. While all these models presently lack strong microstructural specificity, it is nonetheless felt that their refinement would allow for experimentally extracted values of n to be used as a rough qualitative index of morphological regularity or "texture" over an array of ionic clusters or as a quantitative measure of the degree of connectivity or tortuosity of the overall charge network.

Introduction

Mauritz et al. have recently communicated the results of detailed dielectric relaxation analyses of perfluorosulfonate membranes that were imbibed with a variety of aqueous electrolytes at various fixed temperatures over the frequency ($f = \omega/2\pi$) range 5 Hz to 13 MHz as a function of electrolyte concentration.[1-3] Our main goal throughout these studies has been a rationalization of the structures and characteristic motions of hydrated ions within the established clustered morphology of these ionomers, particularly in the realm of high ion concentrations. To be sure, there is a critical need to understand and control these motions from the standpoint of selective molecular transport across these membranes in the industrial arena of separations technology. On the other hand, from a fundamental scientific perspective, we are aware that little, at this time, is actually understood of the physics of concentrated electrolytes in the bulk, not to mention their being incorporated within a highly interactive ionomeric system possessing structural heterogeneity at the 50-Å level. The distinct hydrophilic/hydrophobic phase-separated morphology of perfluorosulfonate membranes offers an ordered matrix throughout which electrolytes can be finely dispersed so as to generate extraordinarily high surface-to-volume ratios for these sorbed solutions. Necessarily, a considerable fraction of the ions and water molecules incorporated within the approximately 40-Å diameter polar clusters must reside at the hydrophilic/hydrophobic interface and therefore experience fewer nearest-neighbor electrostatic interactions than ions and water molecules within the cluster interior.

In our view, the observed variances of the dielectric storage and loss factors, ϵ' and ϵ'', respectively, and conductivity over the frequency range at a given temperature are largely governed (a) at low electrolyte concentrations simply by an increasing number of ionic charges (assumed mostly dissociated) per unit volume and (b) at high electrolyte concentrations by a decrease in the mobility of these charges due to their progressive association in pairs, then triplets, quartets, etc., with increasing concentration within the cluster "microsolutions".

The ϵ'' versus ω spectra for membranes incorporating all of each of the electrolytes we have used are clearly dominated by dc conduction. Long-range ion motions are manifest on log ϵ'' versus log ω plots by a rather linearly decreasing segment at low frequencies as illustrated in the example of Figure 1, which is that of membranes containing Zn^{2+} and SO_4^{2-} ions at various concentrations at 36 °C.[3] We had earlier considered this dc contribution to be a somewhat uninteresting and bothersome obscuration that required routine mathematical subtraction from the spectra to uncover hidden relaxation peaks.

In our previous reports we had argued that the high-frequency relaxation peaks extracted in this way were generated by the diffusion-controlled accumulation and dissipation of net ionic charge at the hydrophilic/hydrophobic phase boundaries along the direction of the applied electric field during a half-cycle of oscillation, during which time the field is unidirectional. As a perturbation, it is reasonable to expect that the oscillations of a single 40-Å scale macrodipole are electrically coupled to the oscillations of other cluster dipoles in the array, in particular to those adjacent to it. However, aside from such perturbations, this observed relaxation is considered to be a manifestation of the cooperative motions of hydrated ions on an *intracluster level.*

We have come to think of dc conduction within the context of these electrolyte-imbibed ionomers as involving

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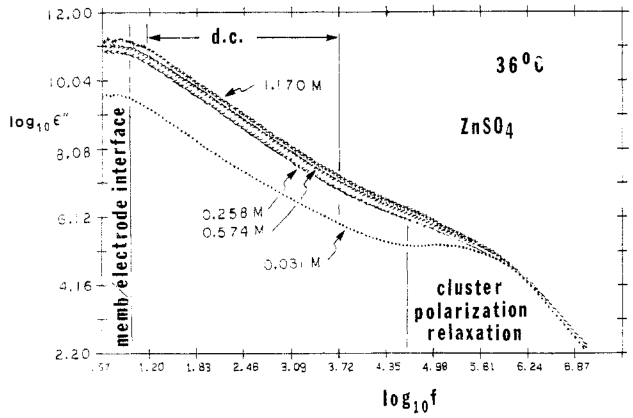

Figure 1. ϵ'' versus $f = \omega/2\pi$ for membranes equilibrated in aqueous $ZnSO_4$ solutions of indicated molarities at 36 °C.[3]

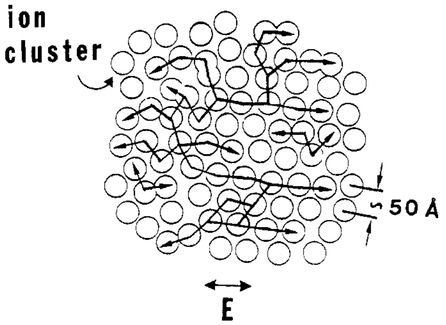

Figure 2. Long-range intercluster ion hopping along energetically favorable pathways that increase in sampled length with decreasing frequency of applied electric field.

long-range *intercluster* ion hopping, in contrast with the intracluster-confined ion dynamics giving rise to the relaxation of interfacial polarization mechanism outlined above. In short, mobile ions will be capable of executing increasingly greater net displacements during a half-cycle in a given electric field direction at increasingly lower applied frequencies, as illustrated in Figure 2. It is this process, in general, that is considered to account for the observed upswing in ϵ'' as $f \rightarrow 0$.

Specifically, the dc-dominated segments of the dielectric loss spectra were seen to be well-fitted by the relationship

$$\epsilon'' \approx A\omega^{-n} \tag{1}$$

where A is a constant and n exhibited considerable variance in the range $0 < n < 1$, depending on the type and concentration of sorbed electrolyte as well as on the system temperature.

We now believe that n is an important parameter that is intimately linked to the particular details of the biphasic morphology of these materials.

Aside from reference to specific underlying microstructures, the case of $n < 1$ is generally reflective of systems having random charge conducting paths across the sample dimensions that may or may not intersect each other.[4] The conducting elements, which in this case are hydrated ionic clusters, have a degree of interconnectivity, or coordination with nearest neighbor clusters, that is variable over the ensemble. Furthermore, dead ends, i.e., charge traps, are numerous on the conductivity grid. The degree of topological imperfection increases as n becomes smaller. A value of $n = {}^1/_2$ would suggest strong diffusion control and tortuous pathways. At the other extreme $n = 1$ corresponds to the ideal case wherein charge-conducting paths span the sample dimensions in direct fashion and drift is dominant.

The concepts and mathematical formalism of percolation theory[5] seem to be quite appropriate in formulating a future model of the conductivity of these ionomeric systems, at least with regard to intercluster topological and dimensional considerations. Hsu et al.[6] in fact performed a chemically and structurally nonspecific percolation theory analysis of aqueous NaOH-imbibed Nafion perfluorosulfonate membranes and identified an ionic insulator-to-conductor transition. This transition occurred at a threshold cluster volume fraction (0.10) that was lower than the value (0.15) corresponding to a completely random dispersion. It was therefore concluded that the pathways within the conducting grid were more extended than those within a random system. Clearly, the percolative properties of these heterogeneous systems, such as those issuing from the analysis of Hsu et al., are also the properties that largely influence the value of the parameter n. A in eq 1 will be proportional to the ionic dc conductivity, particularly in direct proportion for $n = 1$.[4] While n might be considered as mostly dependent upon topological-morphological, i.e. long-range, conditions, A is perceived as strongly reflecting the local chemical-structural environment experienced by individual migrating ions.

The fractal dimensionalities of the percolation clusters (i.e., macroscopic contiguous clusters of ca. 40-Å diameter ionic clusters) throughout which long-range ion transport can occur are obviously linked to n in rather direct fashion.

Ngai et al. noted that for most solid materials, irrespective of chemical composition, nature of molecular bonding, or microstructural particulars, and for systems having either permanent dipoles or any kind of mobile charge carriers, the dielectric response is seldom Debye-like but rather follows the empirical relationship

$$\epsilon''(\omega) \propto \omega^{-m}, \qquad 0 < m < 1 \tag{2}$$

over many decades of frequency and Cole–Cole plots are monotonically increasing functions.[7,8] The slow process of diffusion within the fractal geometry of an inhomogeneous medium has been proposed as being important in explaining this universal dielectric response phenomenon.[9]

Theories of Charge Transport in Disordered Systems

Niklasson sketched a rough theory of how processes that are fractal in time, or those that occur on fractal structures as well as being fractal in time, can account for a power law dielectric response in the frequency domain.[10] A time fractal for the case at hand can be considered to be a hierarchy of bursts consisting of ions hopping between the closely spaced ionic clusters in Nafion ionomers, separated by a hierarchy of time gaps owing to a distribution of energetic barriers to intercluster ion hopping. Of course, one can also imagine inescapable ion traps to be present, but this aspect would seem to be more directly related to fractal structures than to fractal time. The time process might perhaps be modeled by a multitude of parallel sequences of bursts punctuated by so-called waiting times whose distribution in turn is a function of the energetic distribution of intercluster hopping.

We are particularly moved to review the general concepts of the Scher and Montroll theory of the dispersive transport of charge carriers (electrons, holes) in a variety of amorphous organic and inorganic semiconductors that are observed in transient photoconductivity experiments.[11] In this model, although an electric field-biased random walk occurs on an artificial lattice of equivalent sites that is coordinatively and dimensionally regular, structural disorder is accounted for by a broad distribution of intersite carrier hopping times. In real amorphous materials one imagines a dispersion in the distances between nearest-neighbor sites at and between which charge carriers can reside and hop. This morphological dispersion gives rise to a considerable variance in intersite potential energy barriers that, in turn, generates a profoundly broad range of intersite transition rates or hopping times. In short, the resultant distribution of hopping times varies as $\psi(t) \sim t^{-1-\alpha}$, $0 < \alpha < 1$ and the mean position of a propagating charge packet varies as t^{α}.

Niklasson[10] discussed a general stochastic time fractal of dimensionality D_t, with values between zero and unity, wherein the average number of hopping events accumulating up to time t is t^{D_t}. It was demonstrated that for long times or low frequencies the dielectric response for a process that is only fractal in time is characterized by a waiting time distribution that varies as t^{-1-D_t} and a dielectric loss permittivity that varies as ω^{-D_t}. The time fractal concept as applied to a rationalization of anomalous low-frequency dielectric dispersion (ALFD) in amorphous materials as discussed by Niklasson and the theory of dispersive charge transport in amorphous materials of Scher and Montroll are basically compatible and it would seem that D_t would essentially correspond to α in comparing respective forms of the waiting time distributions.

Consider now the issue of the direct incorporation of *structural* disorder or the superposition of a fractal time process on a defined fractal structure within a theoretical framework with a specific immediate goal of modeling the dielectric response of electrolyte-containing Nafion membranes or similar microphase-separated ionomeric, or hydrated, polymeric systems. Of course, the mathematical property of scale invariance cannot exist for these physical systems but a "fractal" structure can be considered on a dimensional scale considerably beyond the reported small-angle X-ray (intercluster) spacings of around 20–50 Å.[12] The broadness of but a single peak in the small-angle scattering region is reflective of disorder in the packing of ionic clusters.

Niklasson stresses that present theory aimed at combining spatial with temporal fractal processes needs refinement.

To begin with, it is quite clear in general terms from the work of Hsu et al.[6] and Mauritz et al.,[1-3] the ionic diffusion studies of Yeager et al.,[13,14] and the overall fact of the high ionic conductivities of Nafion membranes that are equilibrated in an excess of concentrated aqueous electrolytes that ac ionic conduction at low frequencies must primarily occur on macroscopic, i.e., percolation, clusters. In any case, the theory for electrical conduction on a (single) *finite* fractal structure predicts a dielectric loss *peak* that occurs at a frequency, ω_ζ, corresponding to the correlation length,[15] ζ, of the fractal. Either side of the peak follows a power law dependence and Ngai et al.[7,8] have listed inorganic glasses, glassy polymers, and ferroelectrics as systems exhibiting this behavior. Our ϵ'' versus frequency plots for Nafion membranes incorporating a variety of ions at various concentrations and temperatures, however, do not display this behavior. Assuming the appropriateness of a fractal structure interpretation, the relative unimportance of finite clusters in ion transport is at least suggested in this case.

For a single *infinite* cluster the following relations are derived:[10]

$$\epsilon'' \sim \omega^{-D_t}, \qquad \omega < \omega_\zeta \tag{3}$$

$$\epsilon'' \sim \omega^{-D_{st}/2}, \qquad \omega > \omega_\zeta \tag{4}$$

D_{st} is a composite temporal–spatial fractal dimensionality defined in the following way. Let D be the structure fractal dimension and D_ω the dimension of a random walk on this fractal. Then for frequencies that sample net hopping displacements over which the structure appears fractal

$$D_{st} = 2D[D_\omega + D(1 - D_t)/D_t]^{-1} \tag{5}$$

Equations 3–5 provide a general fractal–theoretical rationale for the universal anomalous low-frequency dielectric dispersion phenomenon for the case of hopping charges as presented by Ngai et al.[7,8]

Of course, the added complication of having a *distribution of fractal cluster sizes* must be, and has to an extent been, considered.[10,16-21] While an a priori knowledge of such distributions for the ionomeric system at hand does not seem to be accessible, one might turn the problem around and utilize dielectric relaxation spectroscopy as a probe of morphological texture on this hierarchial level. Niklasson expresses the reasonable view that eq 3 and 4 are appropriate for a narrow cluster size distribution. Perhaps the two known levels of Nafion microstructural organization, i.e., the Teflon-like wide-angle X-ray-detectable cystallinity in the interionic cluster regions[22] as well as the small-angle X-ray-detectable intercluster semiorder might conspire to enforce a narrow distribution of fractal cluster size.

Owing to the fact that the dielectric losses for our electrolyte-containing membranes are dominated by dc conduction at low frequencies and the observation that a linear slope discontinuity as would appear at an $f_\zeta = \omega_\zeta/2\pi$ on log ϵ'' versus log f plots as in ALFD behavior is not present, we feel that our system is basically represented by the form of eq 3.

Dissado and Hill have advanced an interesting *cluster theory* of the ALFD phenomenon. While this model also lacks microstructural specificity, it provides an interpretation of experimental ALFD spectra in terms of ionic vibrational modes.[23,24] These workers appear to draw a distinction between "dc conduction", defined by strict $\epsilon'' \propto \omega^{-1}$ behavior and no dispersion of ϵ', and the ALFD response for $\omega < \omega_\zeta$. We feel that this partitioning in regard to real systems might be somewhat artificial and that above the charge percolation threshold there simply exists a dc continuum over the possible degrees of underlying charge pathway connectivity. In any case, the ϵ' versus ω curves for our electrolyte-containing Nafion membranes exhibit considerable dispersion but there is no question as to whether ions can be transported across macroscopic sample dimensions.

The Dissado–Hill theory considers charges residing within clusters having internal partial order. This local order within a disordered system will persist over a correlation length δ_c. The "clusters" of this model can be directly identified with the polar clusters within Nafion ionomers where $\delta_c \approx 40$ Å and "local order" could be taken to mean a quasi-ordering akin to that within molten salts containing small amounts of "dissolved water" as earlier discussed.[3] These domains continuously experience internal thermal fluctuations that are coupled to larger scale intercluster ion hopping events. Cooperative intracluster vibratory ion motions of amplitude $<\delta_c$ in a spatially uniform applied electric field give rise to a fluctuating polarization that extends over the entire cluster domain. In fact this proposed concept closely resembles the aforementioned high-frequency relaxation observed in our electrolyte-imbibed Nafion membranes, which was mechanistically assigned to the periodic accumulation and dissipation of net ionic charge at the boundaries of hydrated ionic clusters that generates oscillating, ca. 30–50-Å diameter, macrodipoles.[1-3] Intercluster hopping, i.e., excursions over distances $>\delta_c$, occurs when the motions of an ion in a given cluster become correlated with like motions within another adjacent cluster. These intercluster correlations are attributed to Coulombic interactions that are not explicitly represented in the theory. A spatially uniform fluctuation *within* a given cluster of interactively coupled charges causes a modification of the potential energy wells and therefore zero-point vibrational frequencies of each charge. If μ is the average single ion vibrational frequency in the *polarized* cluster state and $\bar{E}$ the average shift in frequency accompanying the fluctuation, then the quantity $q = \bar{E}/\mu$ is identified with the slope of the $\omega > \omega_\zeta$ line of the log ϵ'' versus log ω ALFD response. q, at least superficially, appears to be the counterpart of the frequency exponent $^1/_2D_{st}$ in Niklasson's fractal theory of the ALFD response. Decreasing values, say, of the index q would seem to reflect a progressive energetic inhibition of cooperative *intracluster* ionic displacements. q, therefore, is said to be a measure of degree of structural ordering within such cluster domains. At this point we need to call attention to the fact that this physical picture relates to a high dielectric loss region in which there is no relaxation *peak* whereas the high-frequency intracluster process seen in our work[1-3] is associated with a definite peak having an Arrhenius-like temperature dependence. While the Dissado–Hill process for $\omega > \omega_\zeta$ may be operative to a low degree in our membranes, it is clearly not dominant.

For $\omega < \omega_\zeta$ vibrational modes of amplitude $>\delta_c$ are sampled. Charges will be transferred from one cluster to another with an energy requirement proportional to $\hbar\bar{E}$ and some clusters will acquire an instantaneous net charge subject to the condition that the entire cluster array remains electrically neutral. An hypothetical initial state consisting of an array of equal-sized, maximally polarized neutral clusters wherein each ion vibrates exactly in phase with the other ions in the same cluster is defined. Each cluster as a whole vibrates independently this way with a frequency η. A condition of zero intercluster strain within this superlattice construct is considered to be accomplished by increasing the intracluster strain from that existing in the actual average steady-state array. After $t = 0$, inevitable intercluster ion hopping that occurs subject to array-wide conservation of energy as well as electroneutrality acts to redistribute the stress that was initially localized within clusters. If $\hbar\bar{E}_c$ is the difference in the energy of an ion in the superlattice from that in the subsequent average array, then the index $p = \bar{E}_c/\eta$ is interpreted as a measure of the average range of effective ionic displacements that take place during the decay of the initial state. p is identified with the slope of the $\omega < \omega_\zeta$ line of the ALFD response. When p is large, i.e., close to unity, there is a broad distribution of cluster structures owing to significant exchanges of configurational entropy between them and the effective charge pathways are long and span a large number of clusters in the array. p corresponds to the frequency exponent D_t in Niklasson's theory.

On critical inspection and intercomparison, the above-outlined theory of the dispersive transport of charge carriers in amorphous materials and the fractal time theory as well as cluster theory of the ALFD phenomenon of disordered materials in the low-frequency regime are all reflective of essentially the same underlying transport mechanism but from somewhat different mathematical modeling perspectives. This author is also of the opinion that the general physical constructs embodied in these models are appropriate for use in the interpretation of the behavior of the measured low-frequency exponents that characterize long-range transport in Nafion membranes as a function of incorporated ionic species and their concentrations as well as temperature. To be sure, the aforementioned theories do not presently possess a level of mathematical refinement that provides quantitative interrelationships between the above variables for a specific polymer structure. At this stage, nonetheless, it is felt that this low-frequency exponent is, as stated by Dissado and Hill, a useful "coarse-grained index" of the regularity of structure in which the grain sizes and intergrain spacings vary over a range of nanometers for the case of electrolyte-imbibed Nafion ionomer membranes.

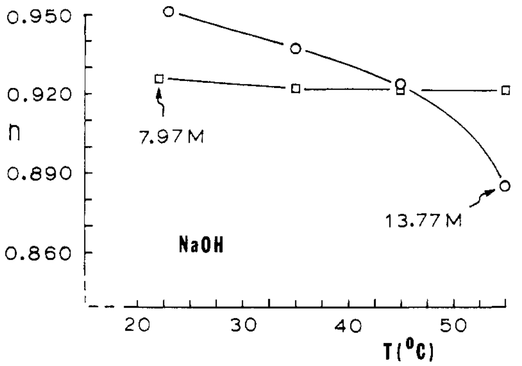

Figure 3. n versus temperature (T, °C) for membranes equilibrated in 7.97 and 13.77 M aqueous NaOH solutions.[1]

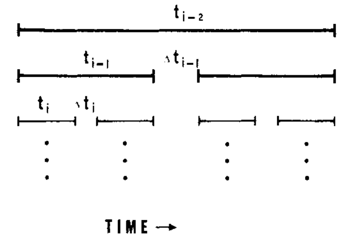

Figure 4. Hypothetical Cantor set defined in terms of the time spent by an ion in moving across (t_m) and between (Δt_m) polar clusters for fixed t_{m-1}/t_m and $\Delta t_m/t_m$ ratios.

Experimental Results and Discussion

In this section values of n extracted from selected experimental studies of membranes as a function of temperature and electrolyte concentration are presented.[1,3] We will attempt to interpret these limited results within the concepts of the theories outlined above.

First, consider Figure 3 in which n is plotted against temperature for 1100 equiv wt Nafion sulfonate membranes that were equilibrated in 7.97 and 13.77 M aqueous NaOH solutions. All values of n, except for that on the 13.77 M curve at 55 °C, are rather high, generally indicative of a well-connected ionic conductance grid.

In terms of the Scher–Montroll theory, one might infer that there is a rather narrow distribution of intercluster hopping times.

The Cantor set[25] has been invoked as a simple model of a fractal time process operative in dielectric relaxation.[10,26,27] Three iterations of equal waiting–hopping time intervals within such a well-defined discrete chronological hierarchy are illustrated in Figure 4. $\{\cdots < t_{m+1} < t_m < t_{m-1} < \cdots\}$ could be considered as an ordered sequence of average ionic residence times in polar clusters under a condition of directional transport. The t_m's should not refer to the average total time spent by one particular charge in traversing cluster dimensions but rather to the shortest average time interval between the arrival of a new ion and the departure of another for a given hopping "mode" indexed by m. Δt_m then would be the actual time of transit for the mth mode between clusters. The fractal dimensionality for this set, assumed homogeneous, is

$$D_t = \frac{\ln \dfrac{(t_{i-1}/t_i) + (\Delta t_i/t_i)}{1 + (\Delta t_i/t_i)}}{\ln (t_{i-1}/t_i)} \qquad (6)$$

Of course, the ion-hopping mechanism within real clustered ionomers would not be expected to possess either time or spatial scale invariance and *mode coupling*, at least between adjacent levels, should be and has in fact been considered.[28] By definition, the ratio $\Delta t_i/t_i$ will be constant over all levels of a homogeneous Cantor set. This temperature-dependent quantity will be a function of the energetic barriers encountered in ion migration through and between adjacent clusters. Additionally, the specific shape of the cluster-to-cluster potential energy profile will determine entropic contributions to a free energy of activation as well as kinetic jump frequencies. In general terms, $\Delta t_i/t_i$ is ultimately a reflection of the average intercluster structure. t_{i-1}/t_i, on the other hand, would seem to mirror the *distribution* of structure on this scale. Unfortunately, a given D_t value, such as one extracted from experimental dielectric relaxation studies, does not determine a unique t_{i-1}/t_i, $\Delta t_i/t_i$ pair but corresponds to a family of pairs.

According to the Dissado–Hill theory, long unobstructed charge pathways should pervade the system depicted in Figure 3.

Within the interpretive framework of each of the above models, the experimental results plotted in Figure 3 imply a rather good underlying morphological regularity or homogeneous texture over arrays of clusters that are considerable in spatial extent. More specifically, the level behavior of the 7.97 M curve would suggest an insensitivity of charge pathway organization to temperature at this concentration, whereas at 13.77 M the very regular drop in n with increasing temperature suggests progressively more tortuous ionic pathways. We had earlier discussed the role of ionic associations in affecting ionic mobility within and therefore the dielectric response of these membranes.[1-3] Expecting the degree of ionic association to be considerably greater at 13.77 M than at 7.97 M, a greater sensitivity of dielectric response to temperature for the 13.77 M sample would seem reasonable, but with an upward trend. To be sure, these curves must realistically be considered to result from a complex interplay between incorporated hydrated ions and the supporting polymer matrix microstructures. Perhaps then, within this more general view, we might consider that while increased ionic mobility will be promoted on a local level by increased temperature, a greater degree of structural disorder might also be imparted throughout the polymer matrix within which the ions are forced to migrate. In this way, n would be forced closer to the value $^1/_2$, which is associated with random charge pathways.

Our earlier infrared spectroscopic analyses of aqueous Na^+OH^--containing Nafion sulfonate membranes indicated an anomalously high OH^- ion mobility, which was attributed to the rapid transfer of protons within the hydrogen bonds of $H_3O_2^-$ groupings.[29] This proton-transfer mechanism, which involves tunneling at least in part, results in ion hopping with a considerably lower energetic requirement than that associated with the unit displacement of hydrated halide ions. Therefore, significant differences between the n versus temperature characteristics of aqueous Na^+Cl^--containing membranes and the curves in Figure 3 might not seem unreasonable since the dielectric response of these systems is strongly linked to ionic mobility mechanisms. Selected data for this system for membranes equilibrated in 4.00 and 5.33 M solutions are displayed in Figure 5. Save for the ubiquitous lowest-temperature point on the 5.33 M curve, n increases with increasing temperature for both concentrations, in contrast with the downward trend for Na^+OH^--containing membranes seen in Figure 3. Aside from the "anomalous" point, the 5.33 M curve lies below the 4.00 M curve.

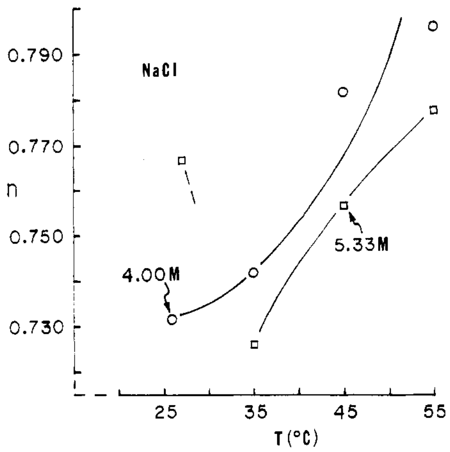

Figure 5. n versus temperature (T, °C) for membranes equilibrated in 4.00 and 5.33 M aqueous NaCl solutions.[1]

It might be deduced, from the range of n values exhibited by these two systems and given the above theoretical interpretations, that the conductive pathways within the Cl^--containing membranes are not as highly interconnected as those in the OH^--containing membranes and that the distribution of cluster-to-cluster hopping times is broader in the Cl^--containing system.

The increase in n with increasing temperature might in this case be simply accounted for by an increase in overall hydration as well as an enhancement of ionic mobility that overrides any possible decrease in polymer structural order caused by thermal agitation. This logic might be based on the view that the fundamental proton tunneling event in hydrogen bonds is said to be quite insensitive to temperature,[29] whereas simple ionic dissociation equilibria are strongly temperature dependent.[30] However, this logic becomes complicated by the consideration of dynamic rotational and translational motion within $H_3O_2^-$ groupings or larger clusterings of water molecules having a defect proton.

With the exception of the anomalous point of the 5.33 M plot in Figure 5, the depression of the points with increased ionic concentration might be attributed to a decrease in membrane hydration and suppression of charge mobility due to enhanced ionic association. The net effect of increased concentration, in terms of the aforementioned transport models, would be to broaden the distribution of ion hopping–waiting times or to increase ionic pathway tortuosity.

Now, consider n versus concentration of aqueous $ZnSO_4$ solutions, in which 1100 equiv wt Nafion sulfonate membranes were equilibrated at 22 °C, extracted from our dielectric relaxation studies of this system.[3] The results are displayed in Figure 6. First, in contrast with both the aqueous Na^+Cl^-- and Na^+OH^--containing systems previously described, all values of n on the graph are quite low. The condition that $n < 0.5$ in fact indicates that charge-transport pathways are more tortuous than if they were entirely random. We might also infer that there is a broad distribution of local structure on the dimensional scale at which the fundamental ionic hopping events take place.

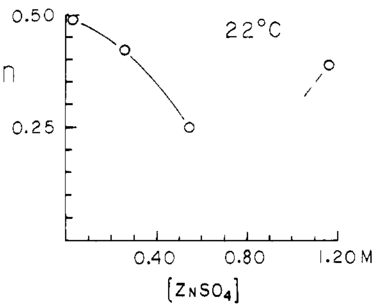

Figure 6. n versus concentration of aqueous $ZnSO_4$ solutions in which membranes were equilibrated at 22 °C.

It is straightforward logic that the more hydrated membranes that would exist at lower ionic concentrations would possess a greater degree of cluster connectivity as well as ionic mobility and would therefore display higher values of n. While this rationale might account for the observed downturn of n with increasing concentration, we presently find the upturn of the point at the highest concentration to be less explicable. However, it is rather interesting to take note of the behavior of the corresponding high-frequency relaxation peak over these concentrations in Figure 4 of ref 3. The relaxation peak shifts to a lower frequency upon increased concentration, except that the shift at the highest concentration is to a lower frequency. Recall that this peak was viewed as arising from strictly *intra*cluster ion motions. This observation would then tend to indicate a strong correlation between long- and short-range ion motions at least for this system.

General Conclusions

Aside from obvious and significant variance in counterion–co-ion species, ionic concentration, and temperature, the ϵ'' versus ω characteristics of Nafion sulfonate membranes that were equilibrated in a number of aqueous electrolytes all appear rather similar. The two general universal features are (1) a monotonically decreasing low-frequency response with distinctive inverse power law behavior attributed to long-range, i.e., intercluster, ion hopping and (2) a somewhat obscured high-frequency peak that is suggested to arise from the relaxation of hydrophilic/hydrophobic interfacial polarization, which is essentially an intracluster event.

A more detailed examination of the first general spectral feature reveals that the frequency exponent itself exhibits very interesting correlations with both electrolyte composition and temperature. In this work we have attempted to rationalize the observed trends of n in terms of existing transport theories that are rather related to each other in physical concepts and that appear to be generally applicable to a polymeric system that (1) contains mobile hydrated ions that have a strong energetic preference for residence in nanometer-sized clusters in the equilibrium state and (2) has these clusters dispersed in a spatial array with significant geometric irregularity. To be sure, neither the theory of dispersive charge transport in amorphous materials nor either of the fractal or cluster theories of the ALFD phenomenon in disordered systems can discriminate between chemical structures, as yet. On the other hand, it is quite clear that these models do provide a rough but legitimate interpretive framework within which n is viewed as either a qualitative index of morphological texture or as a quantitative measure of ion conductive network tortuosity.

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Registry No. Nafion 117, 66796-30-3; $ZnSO_4$, 7733-02-0; NaOH, 1310-73-2; NaCl, 7647-14-5.

References and Notes

(1) Mauritz, K. A.; Fu, R.-M. *Macromolecules* **1988**, *21*, 1324.
(2) Mauritz, K. A.; Yun, H. *Macromolecules* **1988**, *21*, 2738.
(3) Mauritz, K. A.; Yun, H. *Macromolecules* **1989**, *22*, 220.
(4) Hasted, J. B. *Aqueous Dielectrics*; Chapman and Hall: London, 1973; p 133.
(5) Zallen, R. *The Physics of Amorphous Solids*; John Wiley & Sons: New York, 1983.
(6) Hsu, W. Y.; Barkley, J. R.; Meakin, P. *Macromolecules* **1980**, *13*, 198.
(7) Ngai, K. L.; Jonscher, A. K.; White, C. T. *Nature* **1979**, *277*, 185.
(8) Ngai, K. L.; White, C. T. *Phys. Rev. B* **1979**, *20*(6), 2475.
(9) Nigmatullin, R. R. *Phys. Stat. Sol.* (*b*) **1986**, *133*, 425.
(10) Niklasson, G. A. *J. Appl. Phys.* **1987**, *62*(7), 1987.
(11) Scher, H.; Montroll, E. W. *Phys. Rev. B.* **1975**, *12*(6), 2455.
(12) Gierke, T. D.; Munn, G. E.; Wilson, F. C. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 1687.
(13) Yeager, H. L.; Kipling, B.; Dotson, R. L. *J. Electrochem. Soc.* **1980**, *127*, 303.
(14) Yeager, H. L.; Steck, A. *J. Electrochem. Soc.* **1981**, *128*, 1880.
(15) See, for a precise definition of correlation length, ζ, for example: de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell: Ithaca, NY, 1979; p 139. ζ is essentially the root-mean-square cluster (in this case referring to a cluster of contiguous ionic clusters) size at the percolation threshold.
(16) Stauffer, D. *Introduction to Percolation Theory*; Taylor and Francis: London, 1985.
(17) Stauffer, D. *Phys. Rep.* **1979**, *54*, 1.
(18) Gefen, Y.; Aharony, A.; *Alexander*, S. *Phys. Rev. Lett.* **1983**, *50*, 77.
(19) Bunde, A.; Coniglio, A.; Hong, D. C.; Stanley, H. E. *J. Phys. A* **1985**, *18*, 137.
(20) Hong, D. C.; Stanley, H. E.; *Coniglio*, A.; Bunde, A. *Phys. Rev. B* **1986**, *33*, 4564.
(21) Hui, P. M.; Stroud, D. *Phys. Rev. B* **1985**, *32*, 7728.
(22) Starkweather, H. W., Jr. *Macromolecules* **1982**, *15*, 320.
(23) Dissado, L. A.; Hill, R. M. *Proc. R. Soc. London* **1983**, *A390*, 131.
(24) Dissado, L. A.; Hill, R. M. *J. Chem. Soc., Faraday Trans. 2* **1984**, *80*, 291.
(25) Mandelbrot, B. B. *The Fractal Geometry of Nature*; Freeman: New York, 1983.
(26) Shlesinger, M. F.; Hughes, B. D. *Physica* **1981**, *109A*, 597.
(27) Shlesinger, M. F. *J. Stat. Phys.* **1984**, *36*, 639.
(28) Hong, C.; Xiang, W.; Fang, J.-x. *J. Phys. C: Solid State Phys.* **1986**, *19*, L499.
(29) Mauritz, K. A.; Gray, C. L. *Macromolecules* **1983**, *16*, 1279.
(30) Komoroski, R. A.; Mauritz, K. A. *ACS Symp. Ser.* **1982**, *No. 180*, 113.