to decrease the mean separation between the polymer chain ends.[17]

It is also interesting to note that 1 and 4 give nearly identical k_E values. This term should be sensitive only to the local interactions within the pyrene excimer. Its value might vary from solvent to solvent. It is reassuring that this value is not sensitive to the structure of the intervening chain.

We can conclude that the poly(bisphenol A–diethylene glycol carbonate) exhibits a classical behavior for its cyclization in dilute solution. Intramolecular excimer formation proved to be a very well-adapted and powerful technique for this study. We can thus expect that similar studies on closely related polymers could lead to a better understanding of the relationship between structure and chain dynamics.

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Dielectric Relaxation Studies of Ion Motions in Electrolyte-Containing Perfluorosulfonate Ionomers. 3. $ZnSO_4$ and $CaCl_2$ Systems

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ABSTRACT: The dielectric relaxation spectra of Nafion perfluorosulfonate membranes that were equilibrated in aqueous $ZnSO_4$ and $CaCl_2$ solutions were obtained as a function of electrolyte concentration and temperature over the frequency range 5 Hz to 13 MHz. A low-frequency conductivity peak, dormant at ambient temperature but activated slightly above, was observed for both incorporated electrolytes and attributed to a superposition of the enhancing effect of long-range ion migration throughout the membrane and the current-limiting effect of ionic space-charge capacitance in the near-electrode region. A single high-frequency peak, seen at all temperatures for all samples, was suggested to arise from a relaxation of interfacial polarization due to the diffusion-controlled accumulation and dissipation of mobile ionic charge at the hydrophilic cluster boundaries. The overall impedance behavior observed with increasing electrolyte concentration was rationalized in terms of a shifting equilibrium between dissociated ions and multipolar associations that acts to control ionic mobility. Finally, we have attempted to consolidate and refine our concepts of "interfacial polarization" and "dc conductivity" within the framework of the unique hydrophilic/hydrophobic phase separation presented by Nafion perfluorosulfonate materials.

Introduction

In recent correspondence Mauritz, Fu, and Yun have presented dielectric relaxation analyses of Nafion perfluorosulfonate membranes[1] that were equilibrated in aqueous NaOH and NaCl (referred to as part 1)[2] and CH_3COONa, KCl, and KI (referred to as part 2)[3] solutions at various temperatures over the frequency range 5 Hz to 13 MHz as a function of external solution concentration. In all cases, a temperature-activated absorption process was identified and suggested to arise from the relaxation of an interfacial polarization consisting of the diffusion-

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controlled accumulation and dissipation of mobile ionic charge at the boundaries of the hydrophilic cluster domains.

The observed variations of electrical conductivity (σ), storage and loss components of the complex dielectric constant (ϵ' and ϵ'', respectively), and the ac component of ϵ'' (ϵ''_{ac}) with frequency (f), temperature, external solution concentration, and ionic species type were interpreted within the framework of shifting hydration-mediated equilibria between ionic associations within cluster "microsolutions". Increasing the concentration or decreasing the temperature was viewed as suppressing ionic mobility due to increased association.

For $CH_3COO^-Na^+$-containing membranes we have noted the appearance of an additional distinctive σ vs f peak at low frequencies when the temperature was raised from 35 to 55 °C at a given ionic concentration (2.40 M, external).[3] The rise in σ to the maximum, with decreasing f, appears to be a dc conduction process that is also present to a considerably smaller degree at low temperatures but constantly enhanced in transition fashion within this temperature range.

On the other hand, the subsequent downturn of σ at the lowest tested frequencies was interpreted as arising from ionic polarization induced in the membrane/electrode near-interfacial region. In our view, diffuse layers of like-charged ions alternate with those of oppositely charged ions generating capacitance and a subsequent inhibition of conductance near the electrodes. This so-called "space-charge" region results from the competing processes of electromigration at low frequencies and ionic self-diffusion.

Our central investigative theme is the molecular level study of the structures and characteristic motions of ions and water molecules as incorporated within the clustered morphology[4] of perfluorinated ionomer membranes, particularly in the realm of high ion concentrations. Highly concentrated electrolytes are in fact more akin to molten salts containing small amounts of "dissolved" water than they are to being described by the celebrated Debye–Hückel model, valid up to around 0.01 M, or its later empirical modifications that sought to extend its applicability to concentrations just above the very dilute solution regime.[5] At the highest concentrations one envisions water molecules not as being free in the sense of bulk water but distributed among the more populous ions so that some ions will have complete and others incomplete hydration shells.[6] Electrostricted water molecules, especially about the cations, act to give an effectively lower charge density at the surface of the ion's impenetrable (hydrated) volume. This can be a critical factor in consideration of the short-range associations, e.g., outer sphere vs contact ion pairs, that are very important at high concentrations. The fact that electrolyte activity curves become strongly differentiated at high concentrations serves to illustrate this point.

We have begun to extend our work, originally involving alkali-metal cations, to other metal cation species within the Schwarzenbach classification according to their complex-forming characteristics, based on either mainly electrostatic or mainly covalent forces.[7] In this study, we present results for a divalent cation, Ca^{2+}, in aqueous $CaCl_2$ solutions over a broad concentration range. Purely electrostatic bonding is believed to dominate as its hydration number of ca. 7 suggests the absence of complex formation.[8] Also reported herein are results for another divalent cation, Zn^{2+}, in aqueous $ZnSO_4$ solutions. In contrast with the Ca^{2+} ion, Zn^{2+}–ligand interactions are considered as mainly covalent. On the other hand, it has been speculated that its association with the sulfate anion consists of an outer-sphere ion pair.[9]

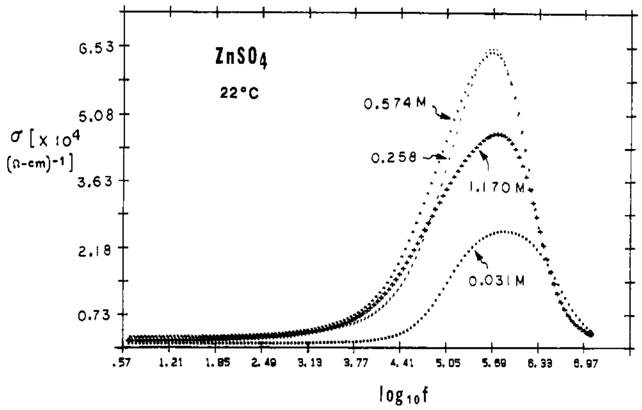

Figure 1. Conductivity (σ) vs frequency (f) for membranes equilibrated in aqueous $ZnSO_4$ solutions of indicated molarities at 22 °C.

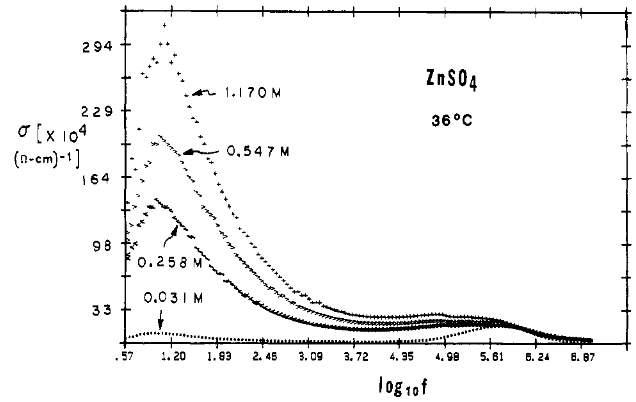

Figure 2. σ vs f for membranes equilibrated in aqueous $ZnSO_4$ solutions of indicated molarities at 36 °C.

These investigations are of considerable fundamental significance for several reasons. To begin with, little substantive progress has evolved in our basic understanding of the physics of concentrated electrolytes even in the bulk. Furthermore, the distinct hydrophilic/hydrophobic phase-separated morphology of perfluorosulfonate membranes presents an ordered matrix in which a sorbed electrolyte can be finely dispersed so as to generate a *high surface-to-volume ratio,* thus creating a unique microsolution environment with interesting structural/property possibilities.

Experimental Section

Nafion sulfonate membranes of 1100 equiv wt and 0.007-in. nominal thickness (Nafion 117) were supplied by E. I. du Pont de Nemours & Co. The standard membrane initialization procedure as well as the impedance analysis system used to determine the dielectric response of electrolyte-imbibed membranes has been adequately described in parts 1 and 2.

The membranes were equilibrated in solutions of aqueous $CaCl_2$ and $ZnSO_4$ over a range of concentrations at constant temperatures also at which the impedance measurements were taken (in the frequency range 5 Hz to 13 MHz).

Results and Discussion

Zn^{2+},SO_4^{2-}-Containing Membranes. The frequency responses of the membrane conductivity (σ) at 22, 36, and 52 °C are shown in Figures 1–3 for the four indicated external electrolyte concentrations. The pronounced conductivity peak initially increases and then decreases with increasing concentration in the same fashion as the peaks for the systems reported in parts 1 and 2. Furthermore, the peaks occur at roughly the same frequency

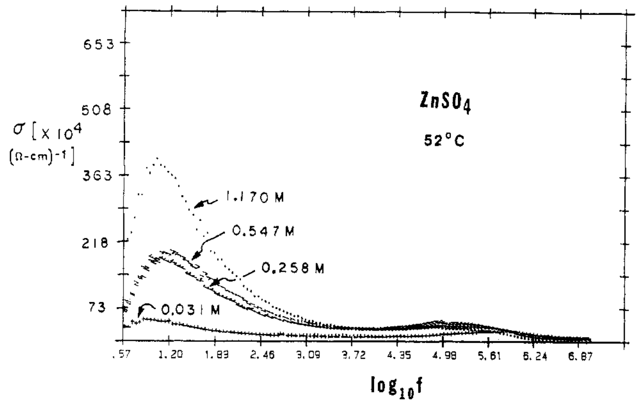

Figure 3. σ vs f for membranes equilibrated in aqueous $ZnSO_4$ solutions of indicated molarities at 52 °C.

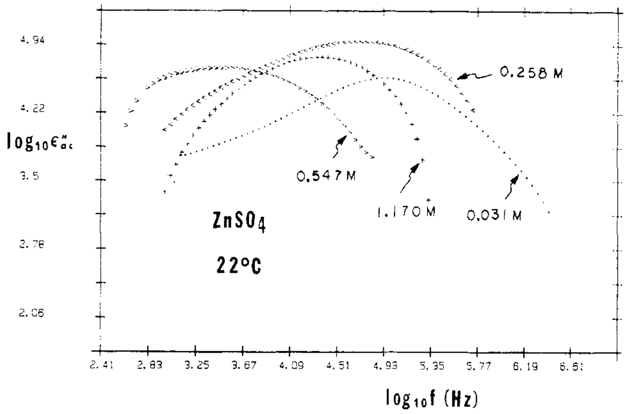

Figure 4. log ϵ''_{ac} vs f for membranes equilibrated in aqueous $ZnSO_4$ solutions of indicated molarities at 22 °C.

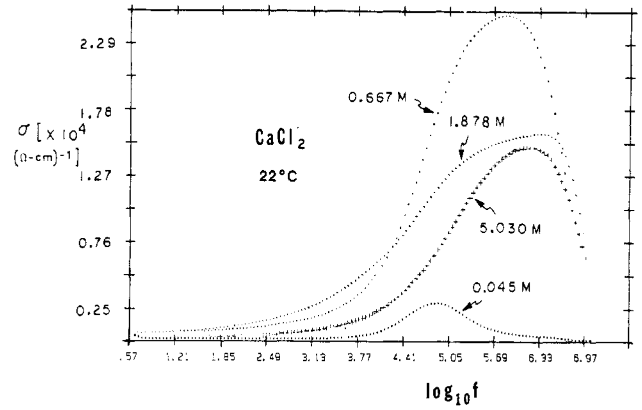

Figure 5. σ vs f for membranes equilibrated in aqueous $CaCl_2$ solutions of indicated molarities at 22 °C.

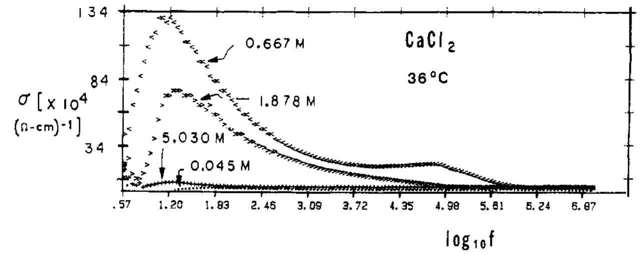

Figure 6. σ vs f for membranes equilibrated in aqueous $CaCl_2$ solutions of indicated molarities at 36 °C.

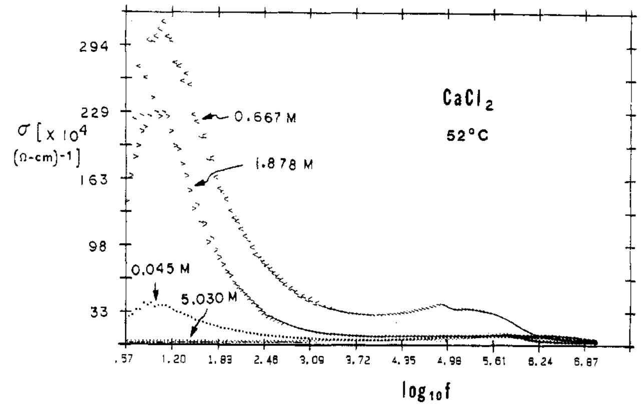

Figure 7. σ vs f for membranes equilibrated in aqueous $CaCl_2$ solutions of indicated molarities at 52 °C.

as those in our earlier work and do not appear to shift appreciably with concentration.

When the temperature is increased to 36 °C, these high-frequency peaks remain, but then a much stronger peak at low frequencies that monotonically increases in height with increasing concentration is activated. The same manifestation and ordering of the low-frequency peak magnitudes (now more intense overall) with concentration occur at 52 °C. This phenomenon was also observed for aqueous $CH_3COO^-Na^+$-containing membranes as reported in part 2.[3]

Once the obscuring dc contribution to the ϵ'' spectra is removed as described earlier,[2] the ϵ''_{ac} vs f curves at 22 °C appear as in Figure 4 for the various concentrations. As in our results for aqueous sodium acetate electrolyte, the peak maxima shift to lower frequencies with increasing concentration except for the highest concentration peak, which then shifts to the right.

Ca^{2+},Cl^--Containing Membranes. In Figure 5 are σ vs f curves for the four indicated electrolyte concentrations at 22 °C. As before, a high-frequency peak, with increasing then decreasing-in-magnitude behavior with increasing concentration is exhibited. In contrast with the zinc sulfate containing membranes, the peak positions here shift to a greater degree, however. It also seems that at 22 °C and at roughly the same external electrolyte molarity, the sodium acetate containing membranes have a greater high-frequency conductance (at the peak maxima) than the calcium chloride containing membranes.

Increasing the temperature of these systems to at least 35 °C again activates a low-frequency peak as seen in Figures 6 and 7. While the peak magnitude steadily increases with increasing temperature, it rises but then falls with increasing concentration, as opposed to the continuous rise observed for the low-frequency peak exhibited by the zinc sulfate containing membranes.

Conductivity of Concentrated Bulk $ZnSO_4$(aq) and $CaCl_2$(aq) Electrolytes and Concentration Dependence of Conductivity of Electrolyte-Imbibed Membranes. A plot of σ, at 20 °C, vs average number of H_2O molecules per $Zn^{2+}SO_4^{2-}$ ion pair for free solutions is seen in Figure 8.[10] At first sight, the monotonic increase in σ with decreasing water content does not suggest ionic association at high concentrations. σ, however, is a function of the number of charge carriers per unit volume as well as the mobility per charge carrier, and the first factor in this case is dominant over the second. However, if values of σ are converted to equivalent conductivities (Λ) at each concentration, it is then quite apparent that ionic association significantly develops with increasing concentration in the simple solutions, as seen in Figure 8.

Similarly, σ vs average number of water molecules per $Cl^-Ca^{2+}Cl^-$ ion triplet for free solutions at 20 °C is seen in Figure 9.[11] In this case, ionic association seems to be directly manifested by the downturn in σ at a ratio of slightly more than 20 $H_2O/CaCl_2$.

It appears, upon comparison of the Λ curves of Figures 8 and 9, that the overall mobility of ions in the $ZnSO_4$

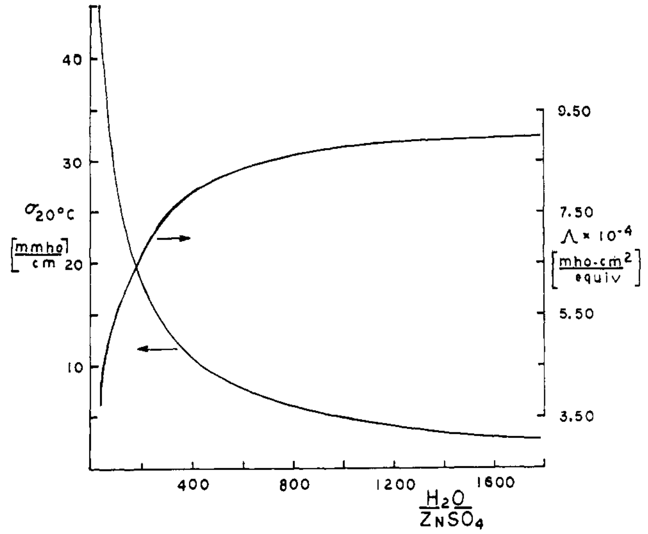

Figure 8. σ and Λ vs average number of H_2O molecules per $Zn^{2+}SO_4^{2-}$ ion pair for bulk solutions at 20 °C.[10]

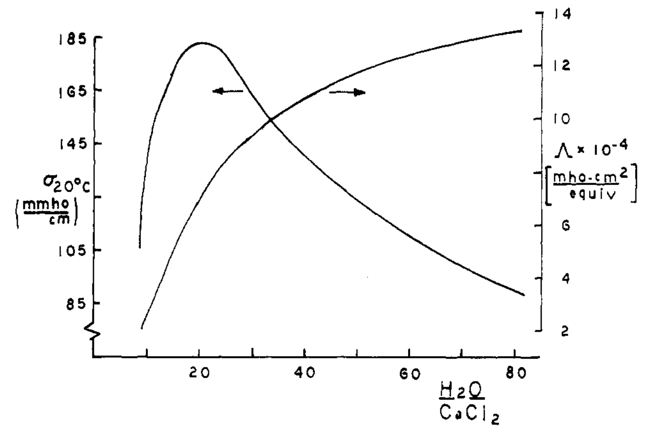

Figure 9. σ and Λ vs average number of H_2O molecules per $Cl^-Ca^{+2}Cl^-$ ion triplet for bulk solutions at 20 °C.[11]

system is lower than that of ions in the $CaCl_2$ system at a given H_2O/solute ratio. This would seem reasonable in considering that a large relative population of charged $Ca^{2+}Cl^-$ ion pairs would exist in solution as a prelude to the formation of a significant fraction of electrically neutral $Cl^-Ca^{+2}Cl^-$ ionic triplets with increasing solute concentration, as discussed in part 2 of this work.[3] On the other hand, electrically neutral divalent ion pairs would evolve directly from dissociated Zn^{2+} and SO_4^{2-} ions, and mobility suppression would subsequently occur at a comparatively lower concentration for the $ZnSO_4$ system.

To be sure, the ionic mobility vs concentration behavior of free electrolytes will be modified when they are dispersed throughout the polar domains within the membranes. Nonetheless, it is reasonable to expect that the above-discussed trends in the evolution of ionic association with increasing concentration will at least provide a starting point in the qualitative rationalization of the conductance behavior of electrolyte-imbibed membranes.

Unfortunately, however, the mobility of a given ionic species—defined as its net drift velocity per unit applied electric field strength—within the membranes cannot be split off from the measured overall conductivities because the in situ charge-carrier densities and ion-transport numbers within these heterogeneous materials are presently unknown.

A comparison of Figures 1 and 8 reveals that at around 21 °C the conductivities (at the high-frequency peak maxima) of Zn^{2+}-, SO_4^{2-}-, H_2O-imbibed membranes are about 2 orders of magnitude smaller than those of the free electrolyte at high concentrations. However, the conductivities associated with the low-frequency peaks that appear at 36 and 52 °C (Figures 2 and 3, respectively) are of the same order of magnitude as those of the concentrated free solutions at 20 °C.

In comparing Figures 5 and 9 it can be seen that at around 21 °C the conductivities (at the high-frequency peak maxima) of Ca^{2+}-, Cl^--, H_2O-imbibed membranes are about 3 orders of magnitude smaller than those of the free electrolyte at high concentrations. On the other hand, the conductivities associated with the low-frequency peaks that appear at 36 and 52 °C (Figures 6 and 7, respectively) are smaller by only about an order of magnitude than those of the free solutions at 20 °C.

It is of significant note that while the bulk $CaCl_2$ aqueous solutions are considerably more conductive on an equivalent concentration basis than the bulk $ZnSO_4$ aqueous solutions, all membranes imbibed with either of these electrolytes did not exhibit conductivities that vary with each other by more than an order of magnitude in either the respective high- or low-frequency peak regions over the range of concentrations at a given temperature. Of course, it is impossible to quantitatively compare Zn^{2+}, SO_4^{2-}-, and H_2O-containing with Ca^{2+}, Cl^-, and H_2O-containing membranes on an equivalent electrolyte concentration basis as *internal* concentrations have not been determined as yet, but the general fact of membrane conductivities that are not highly differentiated is nonetheless quite evident in the comparison of Figures 1, 2, and 3 with Figures 5, 6, and 7, respectively. Actually, on closer inspection it is seen that the order is reversed with the Zn^{2+},SO_4^{2-}-containing membranes being a bit more conductive than the Ca^{2+},-Cl^--containing membranes at a given temperature.

Now consider the electrolyte concentration dependence of the conductivity peaks. At 22 °C the trend of the increasing followed by decreasing conductivity in the high-frequency peak region, common to both electrolytes, might again be interpreted as being governed initially by (a) an increasing number of charge carriers per unit volume in the membrane with increasing concentration, followed by (b) a decrease in ionic mobility due to the evolution of ionic association at higher internal concentrations.

At the higher temperatures, the strictly monotonic increase in conductivity with increasing concentration in the region of the dominant low-frequency peak for Zn^{2+}-, SO_4^{2-}-, and H_2O-containing membranes is not suggestive of a strong influence of ionic association. Recall, first, that this peak, in our opinion, is not thought of as representing a single process but is viewed as a necessarily complex superposition of a near-electrode ionic polarization mechanism and a dc ionic conductance. In general, however, we might expect ionic association to be more tenuous and therefore ions to be more mobile at higher temperatures.

While the steady decrease in f_{max} with increasing concentration for the first three sequential ϵ''_{ac} peaks, seen in Figure 4, might be rationalized in terms of a progressive ionic association that slows down intracluster diffusion, the sudden shift to shorter relaxation times at the highest Zn^{2+},SO_4^{2-} concentration is presently inexplicable.

By contrast, the rise followed by decline of conductivity with increasing concentration seen in the low-frequency peak region of Ca^{2+}-, Cl^--, and H_2O-containing membranes at the higher temperatures does suggest the onset of ionic association.

Assignment of Molecular Relaxation Processes. Figure 10 contains plots of ϵ'' vs f for membranes con-

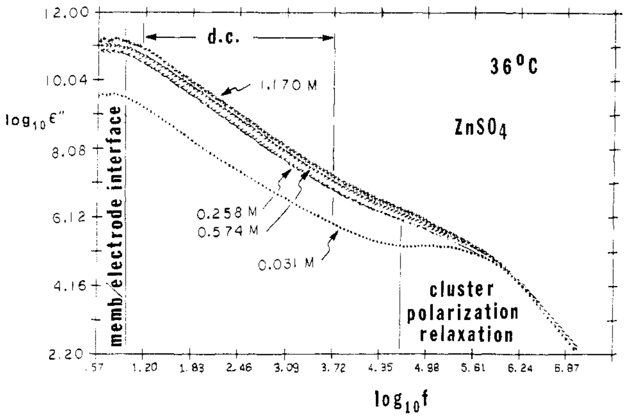

Figure 10. ϵ'' vs f for membranes equilibrated in aqueous $ZnSO_4$ solutions of indicated molarities at 36 °C.

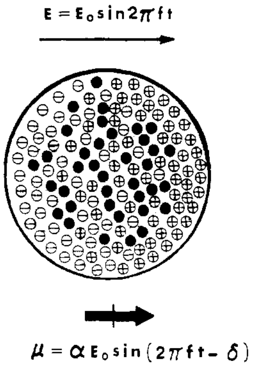

Figure 11. Induced polarization of an ionic cluster by an electric field of magnitude E varying sinusoidally in time t. α is the cluster polarizability and δ the phase lag of the induced dipole moment μ behind E.

taining Zn^{2+} and SO_4^{2-} ions and H_2O molecules of various concentrations at 36 °C. Over the frequency domain we have indicated regions in which we feel the following processes are manifest: (1) ionic polarization in the membrane/electrode near-interfacial region; (2) dc, or long-range ion conductivity; (3) relaxation of ionic polarization across the dimensions of single ionic clusters, in the order of increasing frequency.

With regard to process 1, the downturn of σ and ϵ'' with decreasing the frequency to the lowest tested values was similarly noted for the systems in part 2 of our work. As this mechanism, which we also suggest as being operative in the systems reported herein, has already been adequately discussed, we will refer the reader to this earlier paper for details.[3]

In the following section we will examine processes 2 and 3 more closely.

Relaxation of Interfacial Polarization Mechanism. As in our previous analyses of electrolyte-imbibed Nafion membranes,[2,3] we argue that a mechanism of the relaxation of large-scale ionic polarization across the dimensions of polar clusters (~40 Å) is operative in the systems reported herein. This conclusion is motivated by the very high low-frequency-limiting values of ϵ', the inapplicability of the Onsager equation which is based on the process of the orientation of permanent molecular dipoles, and the a priori knowledge of microstructural heterogeneity, in the main. Our view, roughly depicted in Figure 11, is that of the accumulation and dissipation of net ionic charge at the hydrophilic/hydrophobic phase boundaries along the direction of the applied electric field ($E = E_0 \sin 2\pi ft$) during a half-cycle of oscillation during which time the field is in the same direction. The natural time scale for the cooperative motions of ions confined in this way, i.e., relaxation time, would be largely a function of an intracluster diffusion coefficient and the actual cluster dimensions, in addition to the specific ionic composition and degree of hydration in these domains. In effect, one might define a cluster polarizability = α and consider the cluster to be an oscillating macrodipole of induced moment $\mu = \alpha E_0 \sin(2\pi ft - \delta)$. δ, the lag in phase of the induced dipole behind the applied field, and α are strongly controlled by electrodiffusion within the clusters.

It should be pointed out that $\tan \delta$ is closely related but not equal to the overall dielectric loss tangent for an array of such closely spaced polarizable clusters owing to the complication of electrical interactions between the induced macrodipoles and resultant electrical cooperative effects within the array.

The often invoked theory of Wagner[12] is questionable as a model for this system. First, the equations therein apply to a *dilute* dispersion of conducting spheres. However, the dimensions of the conducting inclusions in Nafion ionomers are not considerably less than the intercluster spacing. The close spacing introduces the above-mentioned nontrivial complication posed by the mutual interaction between clusters arising from their polarization fields. This interaction, in addition to generating a mathematically intractable situation, introduces a correlation in cluster polarization that would influence macroscopic dielectric relaxation times.

Another problem with the Wagner theory and its subsequent modifications, although perhaps not as severe, is that it is formulated in terms of macroscopic-continuum concepts, whereas molecular granularity is clearly discernible at the known ultrastructural level of polar clusters.

Nonetheless, a more exact and complete theory of the dielectric relaxation of a concentrated dispersion of spheres having volume fraction ϕ, volume conductivity σ_2, and dielectric constant ϵ_2, throughout a continuous but nonconducting phase of dielectric constant ϵ_1, might still be worthy of evaluation as a model for the observed behavior. σ_2, ϵ_2, and ϵ_1 would necessarily have to be assigned appropriate values that have meaning on the level of nanometer distances.

Also of concern is the rather high surface/volume ratio presented by ion-containing clusters having diameters on the order of only 40 Å. Realistically, a considerable fraction of the mobile ions within such an aggregate must reside at its surface. Therefore, the concept of a pure *volume* conductivity, σ_2, as primarily controlling the relaxation is rendered less meaningful.

As we feel that the high-frequency peak observed in our dielectric relaxation studies is reflective of diffusion-controlled *intra*cluster motions, we need to provide at least a rough estimate as to whether a significant number of diffusive ion jumps can in fact be executed within the time frame of the observed relaxation. In other words, we need to be concerned with whether diffusion of this sort is actually fast enough to allow the cluster-incorporated ions to sample random (albeit confined) motions between the applied electric field reversals.

For most common concentrated aqueous electrolytes, the coefficients of mutual diffusion (i.e., referring to total solute rather than single ion), D_m, are slightly greater than 10^{-5} cm^2/s.[13] Assume now that the cluster microsolutions at least qualitatively resemble concentrated electrolytes. We could write $D_m = \delta^2/(K\Delta t)$, where δ is a sort of stoichiometric average of the characteristic jump distances of cation and anion and Δt is the average effective ionic jump time. K would be 6 in an isotropic bulk solution but in cluster-encapsulated solutions diffusive motions can be expected to be more restrictive, and a smaller value (but greater than 2) representing lower diffusion dimensionality might be more appropriate. If we let 10^{-8} cm $< \delta < 10^{-7}$ cm, as is reasonable, then $(\Delta t)^{-1}$, the effective number of diffusive jumps per second, is 10^{11}–10^{12}. Then, it is clear that the ions do in fact have sufficient time to execute appreciable electrodiffusive displacements during a half-cycle of applied electric field oscillation at $f = f_{\max}$.

Beyond the fact that D_m values for most bulk aqueous electrolytes are quite close together within the same order of magnitude, regardless of ionic size, valency, or chemical species, it is also significant that, with increasing concentration, D_m will decrease to a minimum and then increase with a rather mild downturn exhibited in some cases close to solution saturation. Interestingly, the ultimate D_m downturn of $CaCl_2$ solutions is quite pronounced. Although the specific nature of short-range ionic–hydrate structuring in even these free solutions is ill-understood to date, a progression of ionic associations of increasingly greater complexity with increasing concentration as discussed in part 2[3], is clearly implicated.

Long-Range Ion Conductance. The $\epsilon'' \propto f^{-n}$ behavior in general is indicative of a system having random conducting paths interspersed throughout its volume with varying degrees of connectivity of the conducting elements.[14] For very conductive situations wherein charge carriers have numerous pathways along which they can traverse the macroscopic dimensions of the sample, n can approach unity as an upper limit. For the system at hand, "long-range" connotes intercluster ion hopping as opposed to the intracluster ion dynamics involved in the relaxation of interfacial polarization process discussed in the previous section.

n, as described earlier, is the slope of the linear best-fit ($\log \epsilon'' \cong \log \epsilon''_{dc} = -n \log f +$ vertical intercept) to this dc-dominated segment of the $\log \epsilon''$ vs $\log f$ curve that is routinely extracted in the process of splitting ϵ''_{dc} from ϵ'' over the range of f in the search for hidden relaxation peaks.[2] At this time we will merely say that derived values of n varied considerably in the range $0 < n < 1$, depending on electrolyte type and concentration and temperature.

We are now beginning to realize that n may well be an important parameter that is intimately linked to the long-range aspects of this heterogeneous microstructure. In particular, we believe that the concept of the fractal dimensionality of percolating clusters (i.e., clusters of conductively connected ion clusters) is quite appropriate in providing the physical significance of n.

We will reserve an organized and detailed examination of this aspect for part 4 of this series, which is currently in preparation.

Summary and General Conclusions

We have seen that the dielectric relaxation spectra of membranes equilibrated in aqueous $ZnSO_4$ solutions share a number of features with the spectra of Ca^{2+}-, Cl^--, and H_2O-sorbed systems as well as with the spectra of earlier studied membranes containing various electrolytes.[2,3] The high-frequency conductivity peak and its electrolyte concentration dependence have been interpreted in terms of diffusion-controlled *intra*cluster ionic motions and the restrictions on these motions posed by ionic association at low levels of hydration. dc conductivity is considerable at lower frequencies and is viewed, within the framework of known microstructural heterogeneity at the 50-Å level, as reflecting long-range *inter*cluster ion hopping along a network of continuous but imperfectly interconnected pathways of a fractal nature. The low-frequency "peak" observed is actually believed to be generated by a downturn of the dc effect by the formation of a current-limiting ionic space-charge region near the electrodes.

While these characteristics of the impedance response are common to the two systems studied in this work, there are also differences worthy of mention. For one, it was suggested in the Introduction that unique properties might be imparted to electrolytes as they are finely dispersed into microsolutions throughout the phase-separated perfluorosulfonate matrix, as compared with the properties of the corresponding simpler bulk electrolytes. We have noted that despite the fact that bulk aqueous $CaCl_2$ solutions are considerably more conductive than bulk aqueous $ZnSO_4$ solutions, Nafion sulfonate membranes containing either of these electrolytes do not profoundly differ in conductivity among each other. In fact, the actual ordering according to conductivity is reversed.

Although a realistic, comprehensive, molecular-based mathematical model that links together the aspects of the dynamics of long- and short-ranged ion motions, ionic hydration and association, and polymer structural particulars within a heterophasic morphology, to name but a few, is not at hand, we believe that our studies have provided a measure of conceptual guidance in the formulation of such a model.

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Registry No. Nafion 117, 66796-30-3; $CaCl_2$, 10043-52-4; $ZnSO_4$, 7733-02-0.

References and Notes

(1) Nafion is a registered trademark of E. I. du Pont de Nemours & Co.

(2) Mauritz, K. A.; Fu, R.-M. *Macromolecules* **1988**, *21*, 1324.

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(6) Braunstein, J. In *Ionic Interactions*; Petrucci, S., Ed.; Academic: New York, 1971; Vol. I, p 182.

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(8) Based on isopiestic measurements on concentrated solutions at 25 °C (ref 5, p 138). To be sure, numerous hydration numbers have been reported for given ions (Marcus, Y. *Ion Solvation*; Wiley: Chichester, 1985) depending on the method of determination. Hydration numbers cited in this work are relevant in being equilibrium parameters at high electrolyte concentrations. Actually a fraction, although small, of this number is associated with the larger anion.

(9) Petrucci, S., in ref 6, p 148.

(10) The graph of Figure 8 was constructed from data in *CRC Handbook of Chemistry and Physics*, 62nd ed.; Weast, R. C., Ed.; CRC: Boca Raton, FL, 1981, p D-247.

(11) Reference 10, p D-204.

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