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Dielectric Relaxation Studies of Ion Motions in Electrolyte-Containing Perfluorosulfonate Ionomers. 2. CH_3COONa, KCl, and KI Systems

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ABSTRACT: The dielectric response of hydrated $CH_3COO^-Na^+$-containing Nafion perfluorosulfonate membranes was determined over the frequency range 5 Hz to 13 MHz at various fixed temperatures as a function of the concentration of the external solution in which they were equilibrated. More limited results are also presented for aqueous KCl- and KI-containing films. As in our earlier studies of aqueous NaOH- and NaCl-imbibed membranes, the observed relaxation behavior is rationalized in terms of intra- and inter-cluster ion displacements. Specifically, a relaxation of interfacial polarization due to the accumulation and dissipation of mobile ionic charge at the cluster boundaries and a longer ranged cluster-to-cluster hopping are manifest. The dependence of dielectric response on ion concentration has been largely interpreted within the framework of a dynamic equilibrium between ionic associations within a hydrophilic/hydrophobic phase-separated morphology.

Introduction

Mauritz and Fu have recently reported a dielectric relaxation study of Nafion 117 perfluorosulfonate membranes[1] that were equilibrated in concentrated aqueous NaOH and NaCl solutions.[2] In that study, hereafter referred to as "part 1", the storage and loss components of the complex dielectric constants, ϵ' and ϵ'' respectively, were determined with an impedance analyzer over the frequency (f) range 5 Hz to 13 MHz as a function of external solution concentration and temperature in the range 22–55 °C.

While the dielectric responses of these electrolyte-imbibed systems were clearly dominated by long-range ion motions, an appropriate subtraction of the low-frequency dc component from the ϵ'' vs f curves uncovered a process which was suggested to consist of the relaxation of an interfacial polarization that arises from the accumulation and dissipation of mobile ionic charges at the boundaries of ca. 40-Å-diameter clusters, as depicted in Figure 1. This mechanistic assignment was motivated largely by the observance of very high values of ϵ' at the lowest frequencies; the inapplicability of the Onsager equation (which is based on the conventional molecular dipole orientation mechanism) to the experimental data and the prior knowledge of polymer microphase separation.[3] The shift of the relaxational time scale with temperature was seen to be Arrhenius-like with a well-defined activation energy at each fixed electrolyte concentration.

The overall depression of ϵ' and ϵ'' with increasing electrolyte concentration (at a given f and temperature T) was viewed as being reflective of an increasingly suppressed ionic mobility brought about by the progression of a greater relative population of electrically neutral ion pairs as well as sluggish higher order multipole structures that conceivably evolve with internal dehydration.

In short, the results of part 1 can be at least qualitatively understood in terms of the motions of hydrated mobile ions within the phase-separated morphology. More specifically, it appears that intra-cluster ion displacements might be distinguished from inter-cluster ion hopping events.

The investigation in part 1 was initially driven by our desire to better understand the characteristic motions of Na^+, OH^-, and Cl^- ions as well as H_2O molecules in these membranes in electrochemical cells designed for the important economical production of chlorine and caustic. Within a broader scientific context, however, we are now also interested in studying the physics of very concentrated electrolytes, finely dispersed as "microsolutions" that would

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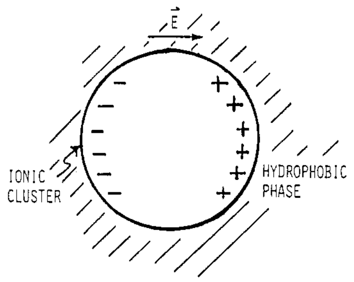

Figure 1. Interfacial polarization due to the separation and accumulation of mobile cations and anions at the cluster boundary along the direction of the external field $\vec{E}$. In a dynamic sense, the ionic cluster is viewed as an oscillating macrodipole.

necessarily possess a high surface-to-volume ratio as encapsulated in the clusters of ionomers such as the Nafion family of membranes. Toward this more general and fundamental goal, we have initiated dielectric relaxation analyses of these membranes as imbibed with other concentrated electrolytes having a variety of (mono, mono)-, (mono, di)-, (di, mono)-, and (di, di)-valent cation–anion combinations. This paper is a report of preliminary studies of (mono, mono)-valent couples.

Experimental Section

Nafion sulfonate membranes having a nominal thickness of 0.007 in. and equivalent weight of 1100 ("Nafion 117") were kindly supplied by E. I. du Pont de Nemours & Co. Once as-received membranes were punched into circles to conform to the impedance test cell electrodes, they were equilibrated for 48 h at room temperature in selected electrolytes of sufficiently high concentrations to affect the total replacement of existing ions on the sulfonate groups with the cations of the selected electrolyte. Excess free electrolyte was then leached out of the films by soaking them in pure water for 24 h. Theoretically, water molecules will be driven from the pure external phase into the membrane ionic microphase under a considerable chemical potential gradient across the membrane/solution interface. Concurrently, owing to the opposite chemical potential gradient for the incorporated ions as well as resultant membrane swelling and enhanced ionic mobility due to greater hydration, all the internal coions and all the internal cations in excess of those required to neutralize the negative sulfonate groups will dialyze in charge-equivalent fashion from the membrane into the external water. This behavior is particularly expected to occur for the noncomplexing alkali cations especially when the water is refreshed during the ongoing dialysis, as it indeed was in our procedure. The expected resultant counterion/fixed-ion ratio of unity is quite characteristic of organic cross-linked polymeric ion exchangers prepared in this way, and we in fact have established its validity for Nafion sulfonate membranes that were equilibrated in dilute to highly concentrated aqueous NaOH and KOH solutions by mass uptake–titration. While we have not experimentally established that a cation/SO_3^- mole ratio of unity exists at this stage of membrane preconditioning for the systems in this work, there nonetheless is no compelling reason to expect otherwise anomalous behavior. In any case, this dialysis of electrolyte is a rational step that was identically performed on all membrane samples. As the final step consists of another electrolyte invasion, it is inconceivable that residual traces of unleached electrolyte would exert a profound effect on the subsequent dielectric measurements. Then, the membranes were vacuum dried at 120 °C for 2 days to remove the water. Owing to the fact that most properties of these materials are significantly affected by sample prehistory, all membranes were initialized in exactly the same fashion before adding the test electrolyte.

The membranes were then equilibrated in solutions of aqueous CH_3COONa, KCl, and KI over a range of concentrations at constant temperatures. These equilibrations of 2-day durations occurred at the constant temperatures at which the impedance measurements were subsequently taken. Finally, when the membranes were removed from the solutions, they were surface-blotted dry and then rapidly sandwiched between the parallel plates of the dielectric sample holder to minimize water loss or gain to or from the atmosphere. Infrared spectra of these samples indicated that the exchange of water with the atmosphere is not severe within the time between their transference from solution to sample holder. Furthermore, after the films are sandwiched between the plates, the membrane surface, less the edges, is rather well blocked to prevent water volatility.

The impedance analysis system used to investigate the dielectric relaxation of the membranes has already been described in part 1.[2]

Results and Discussion

Equilibrium Electrolyte Uptake and Ion Conductivity. Donnan theory[4] has been accepted, at least in a qualitative sense, as providing a sound rationale for the equilibrium partitioning of mobile ions across an ion-exchange membrane/electrolyte interface for dilute solutions. The final equations of this theory result from applying the conditions of electrical neutrality within each phase, equality of single-ion chemical potentials across the interface, complete ionization, and equivalent interdiffusion. In part 1,[2] however, we demonstrated that simple Donnan theory is quantitatively inadequate in modeling the equilibrium uptake of very concentrated aqueous NaOH solutions by Nafion sulfonate membranes even when the equations are modified to account for fixed ion aggregation and the swelling of clusters with imbibed electrolyte. Purely electrostatic energy stabilization of progressively larger associations of simple monovalent ions is expected to occur with increasing concentration. Multivalent ions can form more specific coordination complexes in solution. At high concentrations, a large fraction of the water molecules can be tightly structured about the ions with little H_2O–H_2O hydrogen bonding present. While the details of particular ionic–hydrate microstructures within the membranes in this study are presently unknown, we nonetheless expect the above general concepts to be valid, and they will be invoked to rationalize our results. To be sure, these phenomena would greatly complicate a standard Gibbs–Donnan treatment of electrolyte uptake. We plan to address this aspect in future experimentation by the analysis of out-leached electrolytes with specific ion probes and by infrared spectroscopic investigations along the lines of our earlier similar studies of these systems.[5,6]

In addition to inspecting the derived ϵ' and ϵ'' vs f curves as usual, it is instructive to consider the frequency response of the membrane conductivity (σ) of these systems, while expecting that the large charge carrier density will manifest itself in electrical phenomena characteristic of both long- and short-range ionic motions. For the purpose of allowing more direct comparison of our results to those of similar conductivity studies of other membrane systems, the measured conductances (G) were converted to specific conductivities by the familiar equation $\sigma = (l/A)G$ where l is the nominal membrane thickness (0.007 in. = 0.0178 cm) and A is the cross-sectional area of the flat circular electrodes of diameter 2.5 cm (4.91 cm^2). To be sure, the incorporation of ions and water by the membrane will produce l/A values that will not be strictly constant but will be a function of the chemical nature and concentration of electrolyte as well as temperature. However, the variance of l/A with the latter two quantities for these systems is monotonic rather than transitional and less profound than the variance of the quantity G.

Also, we have noted that the σ vs f curves have more pronounced structure (i.e., sharper peaks) than that appearing on ϵ'' vs f curves for these highly conductive systems. This is due, in part, to the simple mathematical fact that the functionality of ϵ'' is proportional to that of σ times f^{-1}, producing smoother curves.

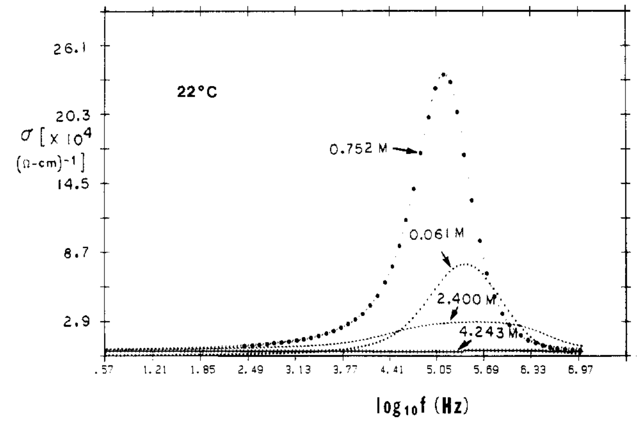

Figure 2. Electrolyte concentration dependence of the frequency (f) response of the conductivity (σ) of 1100 EW Nafion perfluorosulfonate membranes containing aqueous $CH_3COO^-Na^+$ at 22 °C.

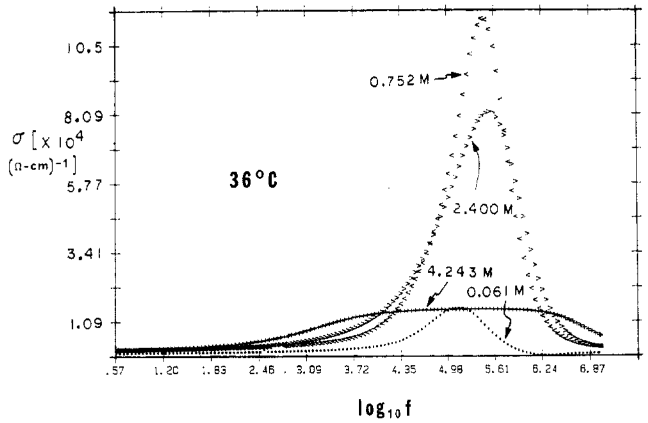

Figure 3. Same as Figure 2 but for 36 °C.

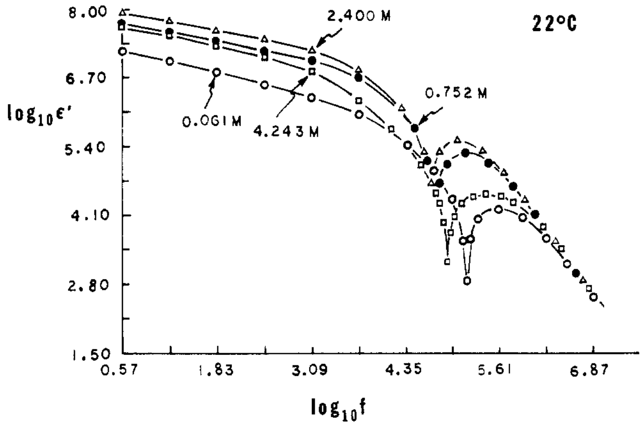

Figure 4. ϵ' vs f for membranes for various indicated $CH_3COO^-Na^+$ (external) concentrations at 22 °C.

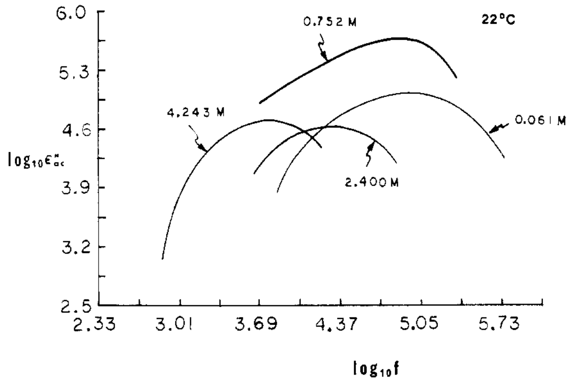

Figure 5. ϵ''_{ac} vs f for membranes for various indicated (external) aqueous $CH_3COO^-Na^+$ concentrations at 22 °C.

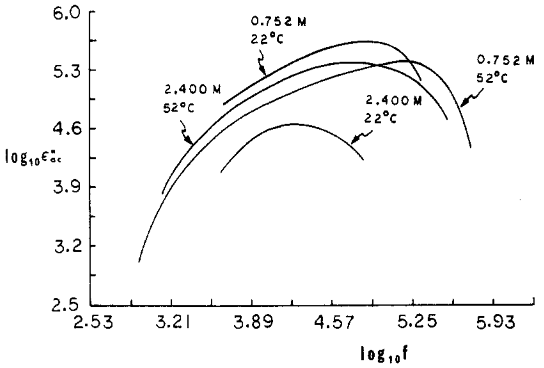

Figure 6. ϵ''_{ac} vs f for membranes at 22 and 52 °C and at (external) aqueous $CH_3COO^-Na^+$ concentrations of 0.752 and 2.400 M.

$CH_3COO^-Na^+$-Containing Membranes. Compared with the coions present in our work of part 1 (OH^-, Cl^-), the acetate anion is larger, organic (less hydrophilic), and less acidic. In general, a greater degree of counterion–coion binding and lower overall ionic mobility would be anticipated at a given concentration and temperature for membranes imbibed with this electrolyte. Inspection of tables of the conductivity vs concentration behavior of pure electrolytes reinforces this idea.[7]

The frequency response of σ at 22 and 36 °C for the four indicated electrolyte concentrations is shown in Figures 2 and 3. A distinctive conductivity peak is observed at all concentrations for both temperatures. Furthermore, at each temperature, the peak magnitude initially increases and then decreases with increasing concentration. We note that the peaks appear in approximately the same vicinity of the frequency scale as the absorption peaks for the NaOH- and NaCl-containing membranes.[2] The peak positions do not seem to shift in the same way with increasing concentration for the two temperatures, although the frequency variances are only within an order of magnitude.

The low frequency-limiting values of ϵ' are quite high as seen in Figure 4 (ca. 10^7–10^8 at 22 °C), also displayed by the systems of part 1. The curves in Figure 4 also exhibit an overall rise over the frequency range followed by depression with increasing concentration. It is seen that the drop of the σ curves occurs at a lower concentration than that for the drop of the ϵ' curves. An interesting feature of all the ϵ' vs f curves is the conspicuous dip followed by dielectric storage recovery in the vicinity of 10^5 Hz. In comparison with Figure 2, this phenomenon is observed to accompany the conductivity peak onset.

Having removed obscuring dc contributions for dielectric absorption spectra by using an earlier described procedure,[2] the resultant ϵ''_{ac} vs f curves for various electrolyte concentrations at 22 °C are displayed in Figure 5. The peak maxima shift to lower frequencies, that is, reflect longer relaxation times (1.4×10^{-6} to 2.5×10^{-5} s), with increasing concentration.

Figure 6 illustrates the shift of these peaks to higher frequencies as the temperature increases to 52 °C for membranes equilibrated in 0.752 and 2.400 M solutions. The relaxation times decrease from 1.8×10^{-6} to 8.0×10^{-7} s (0.752 M) and 7.1×10^{-6} to 2.2×10^{-6} s (2.400 M), where the activation energies are 7.9 and 10.9 kcal/mol, respectively.

We have noted the appearance of a rather pronounced conductance peak at low frequencies when the temperature is raised to 55 °C, as seen in Figure 7. In fact, when the

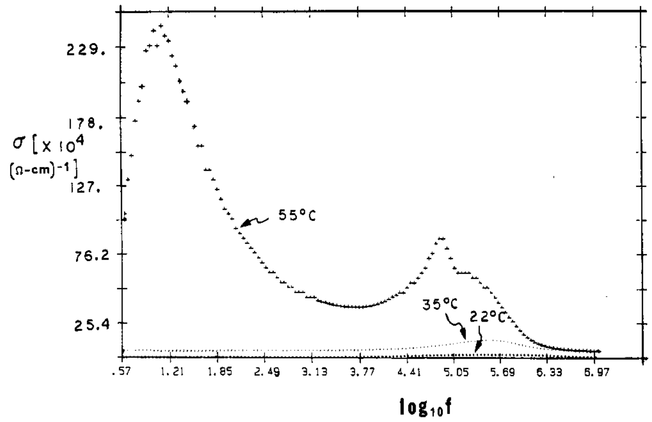

Figure 7. σ vs f for membranes equilibrated in 2.40 M aqueous $CH_3COO^-Na^+$ solutions at 22, 35, and 55 °C.

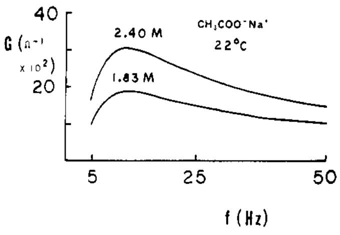

Figure 8. Conductance (G) vs f for membranes equilibrated in 2.40 and 1.83 M aqueous $CH_3COO^-Na^+$ solutions at 22 °C.

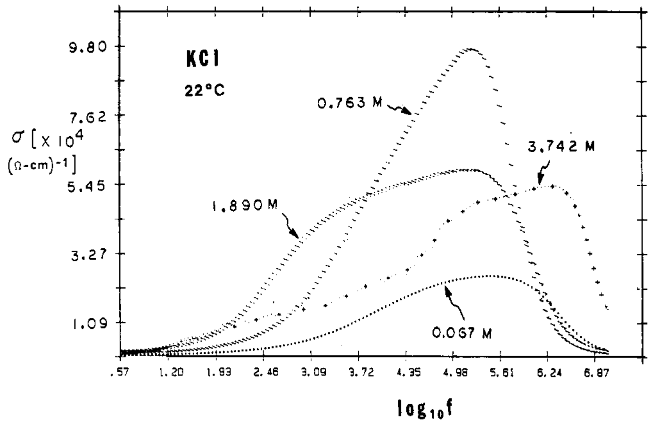

Figure 9. σ vs f for membranes equilibrated in aqueous K^+Cl^- solutions of indicated concentrations at 22 °C.

scales are expanded in the low-frequency region as in Figure 8, the curves also exhibit peaks (albeit considerably less-profound) that increase in magnitude with increasing concentration. Also the high-frequency feature now appears as a much stronger peak + shoulder combination.

K^+Cl^-- and K^+I^--Containing Membranes. For these salts we have generated the σ vs f curves at 22 °C for various concentrations as indicated in Figures 9 and 10. The conductivity peak height vs concentration trend is qualitatively the same as that for $CH_3COO^-Na^+$-containing membranes, that is, an increase followed by pronounced decrease. More specifically, it is readily seen that the peaks are distinctively broader for KCl-containing membranes than for KI-containing membranes. Furthermore, at comparable solution molarities, the KI peaks occur at higher frequencies than peaks for both the KCl- and CH_3COONa-imbibed films at 22 °C.

Ionic Relaxation Mechanism. Despite our present ignorance of the specific equilibrium distribution of mobile ions across the electrolyte/membrane interface, it is relevant and quite instructive to inspect the water content of the corresponding free solutions at their highest concentrations. To be sure, electrolyte encapsulation within small clusters and the presence of fixed anions do present nontrivial complications. Nonetheless, this is a logical starting point from which a concept of ionic associations in ionomeric clusters can evolve in orderly fashion.

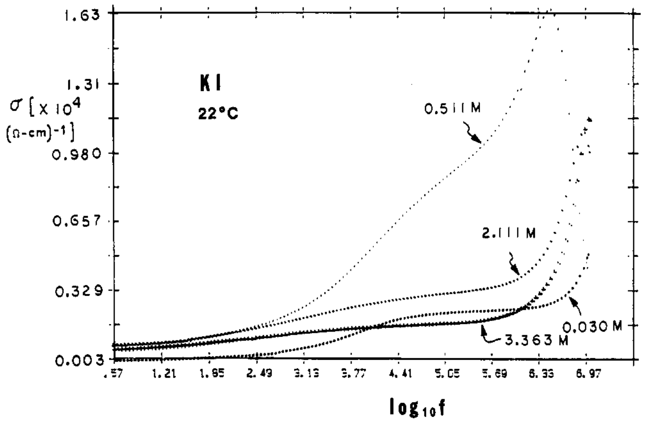

Figure 10. σ vs f for membranes equilibrated in aqueous K^+I^- solutions of indicated concentrations at 22 °C.

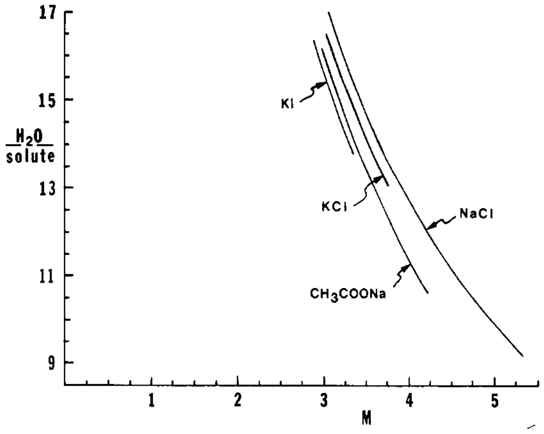

Figure 11. Average number of water molecules per cation–anion pair at high concentrations for various bulk electrolytes at 20 °C (derived from data in ref 7).

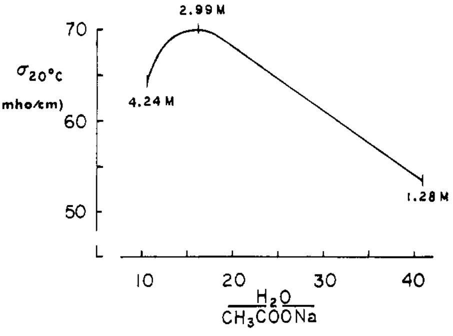

Figure 12. σ vs average number of water molecules per $CH_3COO^-Na^+$ ion pair for bulk solutions at 20 °C.

In Figure 11 are shown curves for the average number of water molecules per cation–anion pair for the (bulk) electrolytes used in this study, as derived from existing tables of their concentrative properties.[7] Obviously, with progressive concentration, there are increasingly fewer water molecules available to separate oppositely charged ions. Through the dilute regime, the ionic conductivity would be expected to monotonically rise as the number of charge carriers per unit volume increases. In general, the conductivity will reach a maximum and then decline with increasing concentration as the relative population of electrically neutral bound ion pairs grows to significance.[8]

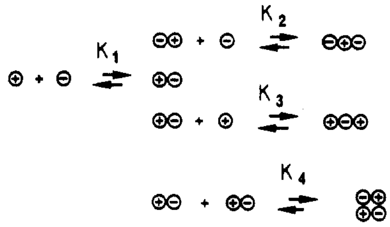

Figure 13. Schematic representation of the equilibrium between low order ionic associations in electrolytes where the K_i's are hypothetical equilibrium constants.

This in fact is the case for aqueous $CH_3COO^-Na^+$ as seen in Figure 12.[9] For conceptually equivalent concentrations of solutions, but now viewed as confined within 40-Å-diameter "containers", i.e., clusters, the space restrictions on ionic translational mobility might conceivably push the conductivity maximum to lower concentrations, although this is pure conjecture. Of course, the degree of side-chain-counterion binding will progressively increase as well. In some cases, a subsequent conductivity minimum will actually exist and this occasional phenomenon has been attributed to the evolution of charged triple ions, i.e., (+ − +),(− + −).[10] This conductance behavior is not exhibited by the (free) solutions of interest in this work, but it is nonetheless quite clear that quadrupoles and higher order multipoles must eventually evolve to prominence with decreasing water content as a prelude to saturation.[11,12]

The hydration-mediated dynamic equilibrium between low-order ionic associations is schematically represented in Figure 13. K_1, K_2, and K_3, ---, are hypothetical equilibrium constants that would necessarily be a function of solution concentration as well as temperature and ion species. While these constants retain their meaning at high concentrations, they are largely inaccessible from either theory or experiment.

We then transfer these general fundamental concepts to our view of cluster-encapsulated ionic microsolutions. The rise and fall of the conductivity peak maxima at given fixed temperatures with increasing concentration, as seen in Figures 2, 3, 9, and 10, is attributed to an increase, followed by decrease, in effective charge carrier density as the relative populations of bound ion pairs, and then quadrupoles as well as higher order multipolar associations, rise to significance within the cluster domains of the membranes.

By the same reasoning outlined in part 1,[2] we are motivated to assign the uncovered ϵ''_{ac} vs f peaks, seen in Figures 5 and 6, to the mechanism of relaxation of interfacial polarization wherein the derived relaxation times are indicative of the natural largely diffusion-controlled time scales required for the accumulation and dissipation of mobile ions near the hydrophilic/hydrophobic phase boundary. An increase in temperature enhances ionic mobility which would seem to account for the shift of the peaks of Figure 6 to higher frequencies, i.e., shorter relaxation times.

On the other hand, the shift to longer relaxation times with increasing electrolyte concentration, seen in Figure 5, is viewed in terms of a suppressed ionic mobility due to ionic association. This interpretation is quite consistent with the observation that the higher concentration has the highest activation energy.

ϵ', in essence, is a measure of charge polarization measured by capacitance. The rise in the curves of Figure 4 with increasing concentration can then be rationalized in terms of an increasing number of mobile ions available within clusters to participate in the interfacial polarization relaxation process. Eventually, however, the ionic mobility is decreased to the point where charge separation across cluster dimensions becomes increasingly inhibited and the ϵ' vs f curves respond by shifting downward. In general terms, the singular plunge in ϵ' in the vicinity of 10^5 might be thought of as a deterioration of a microscopic charge capacitive mechanism that appears when the time scale of the oscillating electric field becomes comparable to a characteristic time during which cooperative and reasonably large-scale ionic charge delocalization is sampled within the cluster domains at the onset of the conductivity peak.

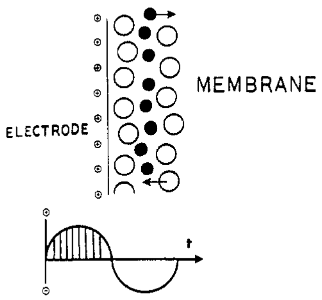

Figure 14. Ionic polarization induced at the membrane/electrode interface at low frequencies, giving rise to a depressed ionic conductance.

We now offer a rationale for the low-frequency conductivity peak seen at 55 °C in Figure 7. To be sure, additional impedance studies as well as temperature-dependent structural characterization are needed to construct a less-ambiguous understanding of this phenomenon. We will but briefly mention here that we have also observed this behavior with (+2, −1)- and (+2, −2)-valent salts, as this work will be reported in part 3 of this series of papers.

The rise in σ to the peak maximum with decreasing frequency appears to be a dc conduction process which is always present to some degree (although much smaller at lower temperatures as seen in Figure 8) but considerably activated somewhere between 35 and 55 °C. Direct current conductance, within the context of these membranes, can be thought of in general terms as involving longer ranged inter-cluster ion hopping in addition to ion electrodiffusional displacements within clusters.

On the other hand, we suspect that the ultimate downturn in conductance at the lowest sampled frequencies is a membrane/electrode interfacial effect as observed in other liquid and solid ion-containing systems.[13] In qualitative description, during a half-cycle of a *slow* electric field oscillation while the field is in the same direction, ionic polarization is induced in the near-interfacial region. Diffuse layers of like ions will alternate with those of oppositely charged ions, giving rise to a net nonzero charge near the blocking electrodes and an effective capacitance but reduced conductance in the region (see Figure 14). In this so-called "space charge" region, it is the competition between electromigration and diffusion that produces an excess charge near the electrode.

The apparent (i.e., measured) conductance, G_{app}, of a medium containing mobile ions at *low* frequencies can be written as the sum of a term representing the dc migration of ions and a term dealing with polarization near the electrode. It is assumed that there are no interfering polymer structural relaxations occurring at these frequencies. According to Johnson and Cole[13]

$$G_{app} = G' - (Z_0' \cos n\pi/2)\omega^{-n}G'^2 \tag{1}$$

where G' = ionic conductance in the bulk region, Z_0' = constant reflecting the magnitude of the impedance of the polarized electrode/medium interface, $\omega = 2\pi f$, and 0 <

$n < 1$ = a system-dependent but unspecified exponent.

While there is currently no theoretical basis for selecting a particular value of n in a given physical interfacial situation, it is nonetheless clear that the second term of eq 1 can account for the observed downturn of conductivity, at least qualitatively. From another perspective and given the validity our interpretation, one might think of fitting eq 1 to G (or σ) vs f curves, exhibiting this phenomenon in the interest of extracting Z_0' and n values to quantitatively assess the magnitude of this effect. It would then be very appropriate to investigate the magnitude of this effect for membranes as a function of thickness to ascertain whether this phenomenon is in fact interfacial rather than bulk in nature. Unfortunately, films of various thickness were unavailable to perform this critical test.

A comparative inspection of Figures 2, 7, and 12 shows that the $CH_3COO^-Na^+ + H_2O$ bulk solution conductivities are roughly greater than the conductivities of $CH_3COO^-Na^+$-imbibed membranes by somewhat over an order of magnitude, although it is not exactly clear as to what particular concentration external to the membrane will produce a corresponding internal concentration equivalent to that of a given free solution. However, the activated conductivity seen at 55 °C (Figure 7) at low frequencies is in fact within an order of magnitude of the free solution conductivity.

We offer the following tentative rationalization of the appearance of the KI conductivity peaks at frequencies higher than the peaks for the membranes imbibed with either KCl or CH_3COONa solutions at comparable concentrations. First observe in Figure 8 that for a given molarity there is less relative water in the (free) KI solutions. Combine this information with the fact that the K^+ ion will hydrate less than the Na^+ ion and the I^- ion less than either Cl^- or CH_3COO^- ions; one is initially tempted to think that perhaps ion pairing and higher ionic associations should be most strongly promoted for this ion couple. On the other hand, while solvent separation of K^+I^- ion pairs is comparatively less effective, the larger ionic radii would also result in a lower electrostatic energy of binding that could shift the dynamic association ↔ dissociation equilibrium of ions to the right. Transferring this pure solution concept to the notions of cluster-encapsulated microsolutions and the diffusion-controlled relaxation of ionic polarization at cluster boundaries, we might then reason that the highly mobile (i.e., less H_2O interactive, less ionically bound) K^+ and I^- ions would manifest shorter intra-cluster motional relaxation times.

Conclusions

We have noted common features of the dielectric relaxation spectra of Nafion sulfonate membranes that contain aqueous NaOH, NaCl, KCl, KI, and CH_3COONa electrolytes. The most prominent of these features are the manifestation of a dc conductivity at lower frequencies that is reasonably attributed to inter-cluster (i.e., long-ranged) ion-hopping, and a high-frequency relaxation peak that is proposed to arise from diffusion-controlled ionic polarization across the entire dimensions of hydrophilic clusters. While the initial rise of the magnitude of the dielectric response, over the frequency range, with increasing electrolyte concentration is easily understood in terms of a growing mobile ionic charge carrier density, the ultimate drop in response magnitude at higher concentrations might be rationalized in terms of a progressively increasing degree of association of the mobile but less-hydrated ions.

Beyond these generalizations, however, significant differentiation exists between the dielectric responses of the various 1:1 electrolytes. The more broad aspect of the σ vs f peaks for the KCl-containing membranes, compared to the KI-containing membranes, may perhaps indicate a greater degree of microstructural heterogeneity within the former. Also, the higher frequency positions of the KI peaks, compared with the peaks of the KCl- and CH_3COONa-containing membranes at the same temperature and at comparable electrolyte concentrations, would seem to indicate a shorter time scale for the cooperative ionic diffusive motions that are implicated in the relaxation of interfacial polarization mechanism.

The strong low-frequency conductance peak for CH_3COONa-containing membranes that is activated at higher temperatures appears to arise from a competition between long-range ion conduction and an ionic polarization near the membrane/electrode interface that limits ion transport.

On the basis of the limited studies reported herein in addition to our earlier investigations,[2] we conclude that dielectric relaxation spectroscopy can be used to yield significant insight in the formation of structure–ion transport relationships in microphase-separated ionomer membranes in the sense of being capable of discriminating between intra- and inter-cluster ion motions. To be sure, these unique systems also represent fertile ground for the cultivation of a fundamental knowledge of the physics of highly concentrated electrolytes as they are finely dispersed throughout a polymer matrix so as to affect a high surface/volume ratio of this aqueous phase. In no small measure was our concept of the dynamic equilibrium between structures in an ensemble of ionic associations motivated by our awareness of past outstanding literature addressing the physics of concentrated *bulk* electrolytes. However, a more complete and specific molecular level of understanding must issue from the use of complementary microstructural probes such as Fourier transform infrared and solid-state multinuclei NMR spectroscopies, which we are currently using. Direct evidence of the nature and degree of ionic association as well as ionic hydration and hydrogen bonding and, importantly, interactions of electrolyte components with the hydrophilic and hydrophobic components of the polymer matrix are essential.

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Registry No. CH_3CO_2Na, 127-09-3; KI, 7681-11-0; KCl, 7447-40-7; Nafion 117, 66796-30-3.

References and Notes

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