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An Investigation of Ionic Hydration Effects in Perfluorosulfonate Ionomers by Fourier Transform Infrared Spectroscopy

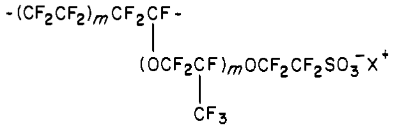
S. R. Lowry and K. A. Mauritz*

Contribution from the Diamond Shamrock Corporation, T. R. Evans Research Center, P.O. Box 348, Painesville, Ohio 44077. *Received March 26, 1979*

Abstract: FT IR spectroscopy has been utilized to monitor the effects of counterion type and degree of hydration upon the anionic sites of a perfluorosulfonate ion exchange resin (Nafion[1]). The location and width of the peak corresponding to the $-SO_3^-$ symmetric stretching mode ($\bar{\nu}_{SO_3^-}$) of the ionomer were measured as the degree of hydration and the counterion (Li^+, Na^+, K^+, Rb^+) were varied. The $\bar{\nu}_{SO_3^-}$ peak was observed to shift to higher frequency and broaden as the water content of the membrane decreased. The changes have been interpreted in terms of an increased interaction between the polyanion and counterion as the shielding water is removed. The magnitude of these effects is cation dependent, and the shift is largest for the Li^+ form of the membrane. Smaller shifts are observed in the membrane containing sodium and potassium ions, and no shift is observed in the rubidium-exchanged membrane. This cationic effect, and the fact that the peak does not shift until the water concentration is below about six molecules per ion exchange site, suggests that the shift is caused by short-range interactions, i.e., formation of contact ion pairs.

Introduction

Polymers with interesting physical and chemical properties have been developed by introducing ionic sites into perfluoroorganic polymer systems. Applications for these polymers as ionic separators have been found in the chemical industry. Nafion,[1] a perfluorinated ion exchange resin, has proven to be a particularly efficient membrane separator in chlor-alkali electrochemical cells.[2,3] The exceptional performance of these membranes derives from the chemical, mechanical, and thermal stabilities provided by a perfluorinated backbone as well as the ion-exchange properties supplied by the pendant sulfonate groups. In the salt form, Nafion has the "repeat" structure:



$$\begin{array}{l} -(CF_2CF_2)_mCF_2\overset{}{C}F- \\ \qquad\qquad\qquad | \\ \qquad\qquad (OCF_2CF)_mOCF_2CF_2SO_3^-X^+ \\ \qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\quad CF_3 \end{array}$$

where m is small and X^+ is an exchangeable cation. Although the performance of Nafion as an electrochemical separator is well documented, very little has been reported concerning the specific molecular architecture of this polymer other than the hydrophilic/hydrophobic phase separation consisting of ionic clusters embedded in a perfluorocarbon "matrix" and separated by about 50 Å. This morphological feature, depicted in Figure 1, is typical of ionomers in general and was discovered as the result of extensive electron microscopic and small angle X-ray studies.[4] A better understanding of polyion–water–counterion interactions within clusters in this system is essential for a rational understanding of the ion transport selectivity of these membranes.

Fourier transform infrared spectroscopy is a powerful technique for detecting small changes in the vibrational spectrum of a molecule.[5] Frequently, changes in the local environment of a specific functional group will cause a measurable change in the infrared spectrum of the molecule. In these cases, FT IR can provide a sensitive probe for evaluating the effects of variations in the local environment on particular functional groups in a complex molecule.

Because the sulfonate group is actively involved in the swelling, electrolyte uptake, ion exchange, and ion transport characteristics of the Nafion membrane, a careful study of the effect of hydration and counterion type, specifically on the symmetric vibration ($\bar{\nu}_{SO_3^-}$) of this functional group, seemed in order. In this work, FT IR has been utilized to monitor the $\bar{\nu}_{SO_3^-}$ vibrational mode as the counterion type and degree of hydration were varied. The results of this study provide evidence for strong cation-dependent interaction at low levels of hydration and very little cation effect in the fully hydrated membranes. Because this paper specifically addresses the phenomenon of side chain–counterion interactions, and the membrane internal hydration structure will be the subject of a later report, the particular behavior of H_2O bands will not be included in the present discussion.

Experimental Section

All the spectral data for this study were obtained from samples of perfluorosulfonic acid membrane material with an equivalent weight (EW) of 1100. The polymer was supplied as the potassium salt in a film 3–4 mils thick. Because of the thickness of the films, transmission spectroscopic techniques were not successful, and all spectra were obtained by attenuated total reflectance (ATR) spectroscopy.[6] ATR is a surface technique with a penetration depth of ~10 μm. While the assumption has been made that these spectra are representative of the entire film, the possibility of differences due to surface effects must always be considered. On the other hand, it might be argued that approximately 2000 morphological unit structures of 50-Å periodicity are sampled along a line penetrating 10 μm from the surface and that this large ensemble may conceivably offer a bulk representation of events occurring on a molecular scale.

All spectra were obtained with a Nicolet 7199 Fourier transform infrared spectrometer. A total of 8192 data points were acquired for each interferogram and a 16 384-point transform was calculated utilizing the Happ–Genzel apodization function. Because of the low signal-to-noise ratios of the ATR experiment, 100 interferograms were coadded before the Fourier transform was performed. The time required to obtain 100 interferograms was about 2 min. As the films were pressed tightly in the ATR accessory, a fairly sealed system with little water loss was observed. All samples were run at 45° with a KRS-5 internal reflection crystal.

Membranes containing counterions other than potassium were produced by soaking samples of the original membrane overnight in concentrated hydroxide solutions of the respective cations, i.e., Li^+, Na^+, and Rb^+. All samples were then sufficiently leached in distilled water to remove excess caustic to obtain the Nafion salt.

Hydration effects were investigated by measuring the spectra of the membranes as a function of water loss. The water content of the membrane was determined by weighing the sample immediately after each

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[1] Registered trademark of E. I. du Pont de Nemours and Co. for its perfluorosulfonic acid products.

[2] W. G. F. Grot, G. E. Munn, and P. N. Walmsley, 141st National Meeting of the Electrochemical Society, Houston, Texas, May 1972.

[3] C. J. Hora and D. E. Maloney, 152nd National Meeting of The Electrochemical Society, Atlanta, Ga., Oct 1977.

[4] T. D. Gierke in ref 3.

[5] P. E. Griffiths, "Chemical Infrared Fourier Transform Spectroscopy", Wiley-Interscience, New York, 1975.

[6] N. J. Havrick, "Internal Reflection Spectroscopy", Wiley-Interscience, New York, 1967.

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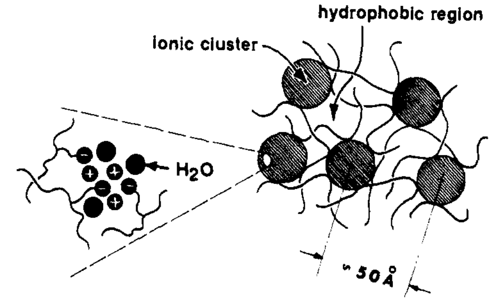

Figure 1. Microphase separation of Nafion into a hydrophobic fluorocarbon matrix and hydrophilic cluster regions.

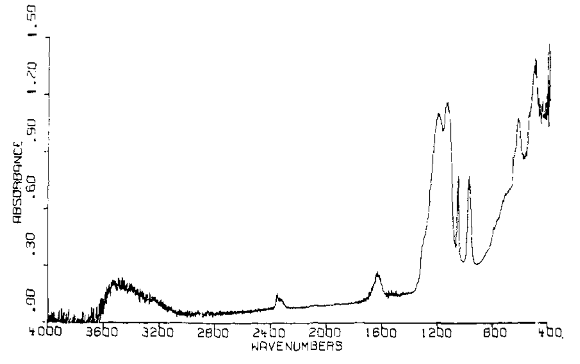

Figure 2. Infrared spectrum of the K^+ salt of Nafion, obtained by attenuated total reflectance.

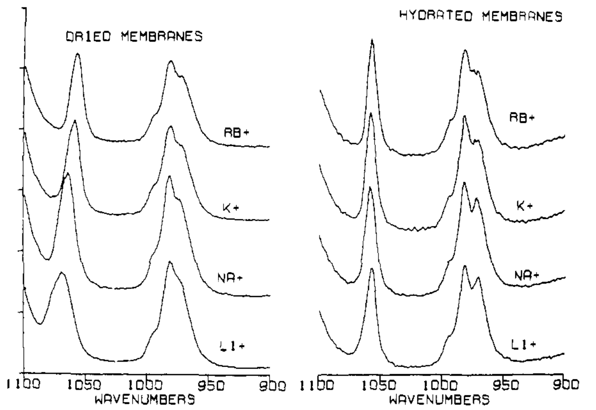

Figure 3. Infrared spectra of the $-SO_3^-$ symmetric stretch region from Nafion films in the Li^+, Na^+, K^+, and Rb^+ salt forms.

spectrum was obtained. Sample transference occurred within 0.5 min and procedural optimization resulted in good reproducibility. The initial degree of hydration was determined by boiling the films until a constant weight resulted. The final dry weight was obtained by drying the sample (to constant weight) in a vacuum oven at 105 °C for at least 12 h. Although residual water may remain in the films, the weights of these samples are defined as the dry weight.

Results

Figure 2 shows the complete infrared spectrum of hydrated Nafion in the potassium form. The two bands which should provide the most information concerning the effects of environment on the ion-exchange properties of the membrane are the symmetric and asymmetric stretches of the sulfonate group.[7] Although both of these bands should provide useful data, the asymmetric stretch occurs in the spectral region dominated by the C-F vibrational modes and cannot be resolved. The symmetric stretch of the $-SO_3^-$ group occurs at ~1060 cm^{-1}. Shifts in the location of this band form the basis of the present study.

Figure 3 shows the spectral region around the 1060-cm^{-1} band for samples of Nafion containing various monovalent cations. Spectra are shown for both the fully hydrated and dried samples. While the spectra of the four hydrated membranes appear quite similar, significant differences can be detected in the spectra from the dried samples. Table I lists the peak maximum and peak width at half-height (pwhh) for the four samples. These data indicate that the degree of hydration, as well as counterion type, has a significant effect on both the vibrational frequency and bandwidth of the $-SO_3^-$ symmetric stretch.

Table I. Spectral Characteristics of the $-SO_3^-$ Symmetric Stretch

	hydrated		dry	
	$\bar{\nu}_{max}$, cm^{-1}	pwhh, cm^{-1}	$\bar{\nu}_{max}$, cm^{-1}	pwhh, cm^{-1}
Li^+	1058	10	1073	18
Na^+	1058	10	1064	14
K^+	1058	10	1059	13
Rb^+	1057	9	1057	11

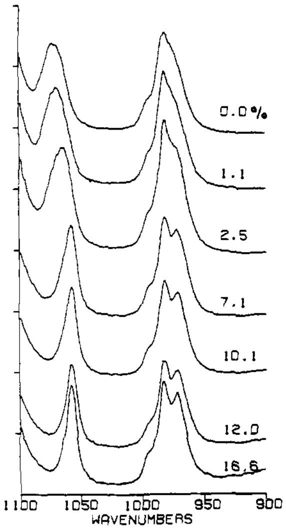

Figure 4. Spectra of Li^+-Nafion for various water contents expressed in weight percents.

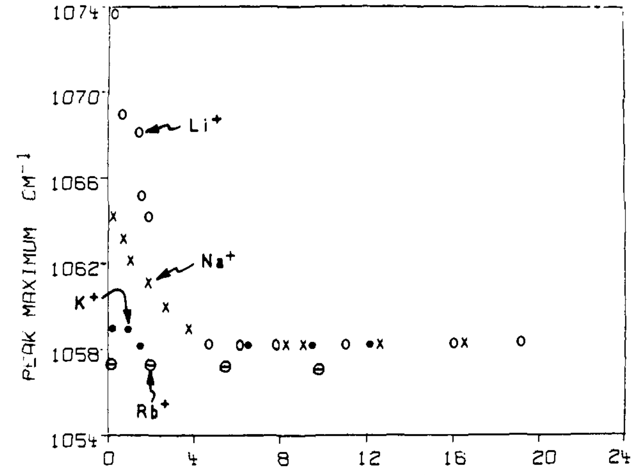

Figure 5. Plots of the $-SO_3^-$ symmetric stretch peak maxima as a function of the H_2O/SO_3^- mole ratio for the Rb^+, K^+, Na^+, and Li^+ salts of 1100 EW Nafion.

In order to better understand the relationship between degree of hydration and $\bar{\nu}_{SO_3^-}$, a series of spectra were acquired as each membrane was progressively dried. Figure 4 shows the results for the lithium sample. The $\bar{\nu}_{SO_3^-}$ peak appears to remain fairly constant until the water content falls below 7% by weight. At this point, the peak begins to shift to a higher frequency and broadens substantially. Figure 5 shows the plots of the peak maxima, for the various cationic forms, as a function of water

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[7] G. Zundel, "Hydration and Intermolecular Interaction", Academic Press, New York, 1969.

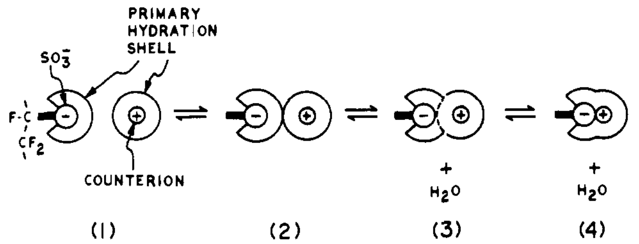

Figure 6. Four-state model of the hydration-mediated dissociation equilibrium between unbound and side chain associated counterions in Nafion membranes.

content. In this case, water content has been calculated as the average number of moles of H_2O present for each ion-exchange site. Three significant facts are revealed by these data. First, the magnitudes of the shifts of the $\bar{\nu}_{SO_3^-}$ peak decrease with increasing counterion radius. Second, the shifts begin at lower mole ratios for the heavier cations. Finally, no major shifts are observed in the spectra from the rubidium-exchanged membrane. In fact, careful examination of the data reveals that the $\bar{\nu}_{SO_3^-}$ band may actually decrease in frequency upon drying.

Discussion

The results described above clearly demonstrate that the symmetric stretching vibrational mode of the sulfonate group in Nafion ionomers is affected by changes in its local chemical environment. The major cause of this is an induced polarization of the S–O dipole by the strong electrostatic field of adjacent counterions. In turn, the magnitude of this polarization understandably depends on the bare cationic radius. The smaller lithium ion has both a stronger electrostatic field at contact and a larger hydration sphere than the larger cations. This results in a major shift of the $\bar{\nu}_{SO_3^-}$ peak to a higher frequency upon ion-pair formation. Because of the weaker electrostatic field, at contact, of the larger cations, the polarization of the S–O dipole is less, and the corresponding frequency shift is much smaller. In fact, the electrostatic field of rubidium is so weak that, even upon SO_3^-–Rb^+ "contact" at low hydration levels, the $\bar{\nu}_{SO_3^-}$ frequency remains unchanged.

The pronounced *broadening* of the $\bar{\nu}_{SO_3^-}$ peak, upon drying, might also be caused by polarization within the sulfonate group. This may result from a gradual change in the dipole relaxation as water molecules are removed from the system. However, the spectral data suggest that the $\bar{\nu}_{SO_3^-}$ peak may shift in discrete steps.[8,9] This can be rationalized by considering the broadened peak to be a composite of several nonresolved peaks, arising from the multistage association–dissociation equilibrium between bound and unbound cations. A four-state model of ionic-hydrate association, similar to that as proposed for simple electrolyte solutions by Eigen et al., is depicted in Figure 6.[10,11] The states can be classified as (1) completely dissociated hydrated ion pairs, (2) ion pairs at the contact of undisturbed primary hydration shells, and (3) outer- and (4) inner-sphere complexes. Within this framework, in the fully hydrated membrane, the peak corresponding to the first state would dominate. As water is removed, the peaks corresponding to the higher states will become more important until, finally, too few water molecules remain to provide shielding between the two ions. At this stage, the relative population of contact ion pairs is large with a correspondingly strong interaction between the sulfonate group and cation. The onset of this state is, of course, dependent upon the hydration number and hydration energetics of the cation (as well as membrane-bound anion). For the Na^+ and Li^+ membranes, the shift begins when the water concentration falls below three to five molecules per sulfonate group. In the K^+ membrane, the water must fall below two molecules per side chain before a detectable shift is observed in the $\bar{\nu}_{SO_3^-}$ peak. As stated previously, no shift was observed for the Rb^+ sample.

The results reported here agree well with data reported for other sulfonate ionomers,[12,13] and provide the same interpretation resulting from NMR investigations of the identical system, also obtained in this laboratory.[14] In particular, the line width and chemical shift of the single observed resonance in the ^{23}Na NMR spectra increase with decreasing water content in such a way that the onset of the changes occurs at a membrane water content identical with that corresponding to the onset of the $\bar{\nu}_{SO_3^-}$ shift in the infrared. Agreement with the ^{23}Na NMR study is particularly gratifying because of the complementarity of the two techniques. While the infrared experiments monitor the effects of the local environment on the sulfonate anion, the ^{23}Na NMR study monitors the cationic environment and mobility. These results suggest that contact ion pairs do exist in the Nafion polymer at low levels of hydration, and that the dynamic equilibrium shifts to greater dissociation with increasing water content. Finally, a statistical mechanical model, based on the four states of ionic-hydrate associations, depicted in Figure 6, has been formulated for the side chain–counterion dissociation equilibrium in ionomers.[15] The relative populations of these states have been determined from Boltzmann statistics utilizing solvation and interionic energy formulations. The calculated shift in the spectrum of states is entirely consistent with the conceptual model arising from spectroscopic interpretation.

In summary, three major facts were obtained from this experiment. First, at high degrees of hydration, the symmetric stretch of the sulfonate group is relatively independent of both water concentration and counterion type. Second, the degree of hydration at which the frequency begins to shift depends on the counterion and is related to the hydration number and hydration energy of the specific cation, as well as sulfonate hydration. Finally, the magnitude of the frequency shift also depends on the cationic size in a way that is easily rationalized in terms of sulfonate–cation interactions in contact ion pairs.

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