

A Sodium-23 Nuclear Magnetic Resonance Study of Ionic Mobility and Contact Ion Pairing in a Perfluorosulfonate Ionomer

Richard A. Komoroski* and Kenneth A. Mauritz

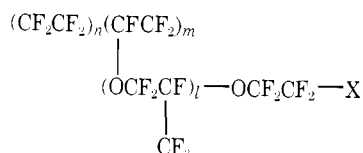
Contribution from the Diamond Shamrock Corporation.

T. R. Evans Research Center, Painesville, Ohio 44077. Received July 17, 1978

Abstract: Sodium-23 NMR at 26.46 MHz has been used to study cation binding in a perfluorosulfonate ion exchange resin (Nafion) as a function of water content and temperature. A large chemical shift change (~ 130 ppm) and line width increase are seen upon decreasing the water content from 30 to 1%. These effects are reversed with increasing temperature. The data can be interpreted in terms of a fast equilibrium between bound and unbound, but loosely associated, cations in the hydrophilic regions of the material. A larger fraction of cations is bound with decreasing water content and temperature. The large change in chemical shift points to the formation of contact ion pairs. The data suggest the presence of three or four water molecules in the first hydration sphere of the sodium ions. The ^{23}Na NMR behavior is consistent with a reversed micelle model of Nafion.

Introduction

Nafion¹ is a perfluorinated ion exchange resin with the structure



where X = SO₂F, SO₃H, SO₃Na, etc., and *l* is small. The material possesses exceptional chemical, thermal, and mechanical stability and can serve as an effective membrane separator in electrochemical cells.² Since the ion transport properties of a membrane separator are critical for its effective performance, an understanding of ionic mobility, at the molecular level, is essential. Very little data is available concerning the detailed microstructure of Nafion ionomers.

Alkali metal NMR is a sensitive probe of the immediate chemical environment and mobility of alkali metal ions in aqueous and nonaqueous solvents.³⁻⁵ Previous studies have revealed that ^{23}Na chemical shifts depend on the Lewis basicity of the solvent.^{3,6,7} With poor electron donors, the ^{23}Na resonance of a dissolved electrolyte occurs upfield of the same resonance in more basic solvents. Concentration-dependent ^{23}Na chemical shift changes, on the order of several ppm, have been observed for some sodium halide and thiocyanate solutions.^{3,7} These changes have been ascribed to the formation of contact ion pairs in these solutions.^{3,7}

We present here a ^{23}Na FT NMR study of Nafion-SO₃Na in the presence of water of swelling. Information concerning counterion binding, ionic solvation, and mobility is obtained using ^{23}Na chemical shifts and line widths. Evidence is presented for the formation of contact ion pairs between Na⁺ and the bound fluorosulfonate groups.

Experimental Section

Sodium-23 FT NMR spectra at 26.46 MHz were obtained on a Varian XL-100 spectrometer with Gyrocode Observe capability and ¹⁹F external lock. The following accumulation conditions were used: spectral width, 10 or 12 kHz; 8192 frequency domain points; 90° radio-frequency pulse width, 50 μs; pulse repetition rate, 0.1 s; 1K to 40K transients, depending on sample.

A commercial Nafion resin (du Pont) in powder form was converted from the potassium to the sodium form by treatment with a 3:2 H₂O/Me₂SO, 11.5% NaOH solution at 85 °C for approximately 4 h. The sample was then repeatedly washed with distilled water and dried overnight under vacuum at 80 °C. For the variable water content experiments, portions of the dried sample were quickly transferred

to capped 12-mm NMR tubes and then weighed. Measured amounts of H₂O were then added to the various samples to give predetermined percentages of H₂O. The sealed samples were vigorously mixed, warmed at 60 °C for several hours, and allowed to equilibrate overnight.

In an alternate method of preparation, weighed amounts of dried Nafion were saturated with H₂O in 12-mm NMR tubes and allowed to equilibrate. These samples were then allowed to dry to the appropriate weight in a vacuum oven at 60 °C. Reequilibration was allowed to take place overnight. Within experimental error, the same ^{23}Na chemical shifts and line widths were obtained using the two methods of sample preparation.

The salt CF₃SO₃Na was prepared by titrating CF₃SO₃H (Fisher Scientific) with 2 M NaOH to a phenolphthalein end point. The sample was dried at 80 °C overnight in a vacuum oven.

Resonance line widths at half-height were measured from expanded spectral plots. Chemical shifts were measured with respect to 0.1 M NaCl in a 3-mm o.d. concentric capillary. The direction of the shifts corresponded to the known field-offset relationship of the spectrometer and was confirmed by observing the position of NaI in pyridine relative to external aqueous NaCl.⁷

Results

In Table I are the ^{23}Na chemical shifts and resonance line widths at 26.46 MHz for Nafion-SO₃Na (1100 equivalent weight), as a function of water content and temperature. The ^{23}Na spectra at 30 °C as a function of water content are given in Figure 1. Only a single resonance arising from the resin is observed in each case. At large swelling (30% H₂O and above), the ^{23}Na line width is about one order of magnitude broader than is usually observed in concentrated aqueous electrolytes^{4,5} at comparable water-to-salt molar ratios. As the amount of water is decreased at constant temperature, the resonance increasingly broadens, reaching a value of 4 kHz at 1% H₂O. Concomitantly, the resonance shifts about 130 ppm upfield. The range of shifts seen here is substantially larger than is typical for the ^{23}Na resonance, even in the presence of organic solvents and under a variety of conditions.^{7,8} With increasing temperature at a given water concentration, both reduced line widths and chemical shift changes are seen.

In Table II are the ^{23}Na chemical shifts and line widths of the model salt CF₃SO₃Na as a function of concentration in aqueous solution. With increasing concentration, the ^{23}Na resonance broadens and shifts slightly upfield. Unfortunately, solubility limitations prevent the observation of larger chemical shift changes for this model salt.

Discussion

Nuclei with spin *I* greater than 1/2 (for ^{23}Na , *I* = 3/2) possess quadrupole moments which interact with electric field gradi-

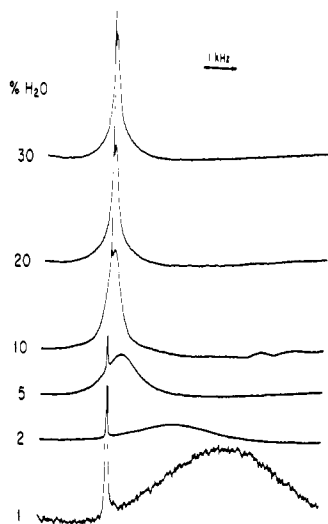


Figure 1. ^{23}Na FT NMR spectra of Nafion- SO_3Na (1100 equivalent weight) as a function of degree of swelling. The relatively narrow resonance arises from external 0.1 M aqueous NaCl used as a chemical shift standard. The spectra are plotted at different vertical gains. The "peaks" at high field in the 10% H_2O spectrum are artifacts.

ents at the nucleus produced by asymmetries in the electronic environment. Fluctuations in this interaction arising from translational or rotational diffusive motions in the liquid can provide an efficient mechanism of ^{23}Na nuclear spin relaxation. Equation 1 governs this relaxation,⁹ where T_2 is the spin-spin relaxation time, $\Delta\nu$ is the line width, eQ is the electric field gradient at the nucleus, eQ is the nuclear quadrupole moment, and $f(\tau_R, \tau_{ex})$ is some function of the correlation times, τ_R and τ_{ex} , for rotational motion and exchange of the ^{23}Na ions, respectively. An asymmetry parameter of zero is assumed in eq 1.

$$1/T_2 = \pi\Delta\nu = (1/10) (e^2qQ/\hbar)^2 f(\tau_R, \tau_{ex}) \quad (1)$$

Sodium-23 resonances in aqueous solutions of electrolytes are relatively narrow⁴ since the aqueous environment is, on the average, highly symmetric (small electric field gradients), with only minor distortions due to collisions with, or exchange of, solvent molecules. Binding of a sodium ion to a site on a polymer will produce a broadened resonance. This broadening can arise from two sources: production of substantial electric field gradients due to distortion of the sodium electronic environment upon binding, and decreased mobility due to the influence of the polymer (increased τ_R).

The large ^{23}Na line width of saturated Nafion- SO_3Na , relative to that seen for aqueous $\text{CF}_3\text{SO}_3\text{Na}$, is strong evidence for a significant interaction between the sodium ions and the polymer. Elementary electrostatics, as well as the parallel chemical shift changes seen for Nafion- SO_3Na and $\text{CF}_3\text{SO}_3\text{Na}$, dictate that cation binding occurs at the relatively fixed anionic sites.

The binding of sodium ions to Dowex 50 ion exchange resins has been studied previously using ^{23}Na NMR.^{10,11} Creekmore and Reilley¹¹ observed a ^{23}Na line width of 25 Hz for Dowex 50 with 2% cross-linking. This resonance is about twice as broad as that found for the monomeric analogue sodium *p*-toluenesulfonate. As the degree of cross-linking is increased to 12%, the resonance broadens beyond detection. This was attributed to an increase in the effective correlation time for ionic mobility of the sodium ions.¹¹ The ^{23}Na line width of saturated Nafion- SO_3Na is one order of magnitude broader than that of 2% cross-linked Dowex 50. This points to a substantial restriction of ionic mobility in the aqueous phase of Nafion, relative to that found for the porous Dowex 50.

Table I. ^{23}Na Chemical Shifts and Line Widths of Nafion- SO_3Na ^a as a Function of Water Content and Temperature

% H_2O ^b	T, °C	δ , ^c ppm	$\Delta\nu$, ^d Hz
satd	30	-2.2	220
satd	55		130
satd	92		100
30	30	-2.2 ± 0.1	230
20	30	-2.4 ± 0.1	260
10	30	-3.6 ± 0.3	460
5	30	-14.6 ± 1	1100
5	90	~ -4	600
2	30	-73 ± 4	2500
2	90	~ -34	1900
1	30	-130 ± 10	4000
1	90	~ -100	3000

^a The equivalent weight of the polymer, i.e., the weight of polymer in the acid form that will neutralize 1 equiv of base, is 1100. ^b As weight percent of dry polymer. ^c Relative to external 0.1 M NaCl, except for the values at 90 °C, which were measured using the value found for 30% H_2O . Positive chemical shifts are downfield. ^d Estimated accuracy $\pm 10\%$. Not corrected for field inhomogeneity or bulk susceptibility effects, which are estimated to be on the order of 5-10 Hz.

Table II. ^{23}Na Chemical Shifts and Line Widths of Aqueous $\text{CF}_3\text{SO}_3\text{Na}$ as a Function of Concentration

concn, M	approx $\text{H}_2\text{O}/\text{Na}$ molar ratio	δ , ^a ppm	$\Delta\nu$, Hz
0.1	540	0.0	
1.0	50	-0.7	16
4.5 ^b	8	-2.3	33

^a Relative to external 0.3 M NaCl. Positive shifts are downfield. Not corrected for bulk susceptibility effects, which are estimated to be on the order of 0.1 ppm. ^b This concentration of salt is close to that of a saturated solution.

The interaction of the sodium counterions with Nafion resin can be treated in terms of an equilibrium between ions bound, or strongly associated, with the polymer and relatively free ions in the aqueous phase. The decrease in the line widths with increasing temperature is indicative of fast exchange of ions between the bound and unbound states. In this situation, the observed line width and chemical shift are given by eq 2 and 3, respectively. Here, $\Delta\nu_{\text{obsd}}$ and δ_{obsd} are the observed line

$$\Delta\nu_{\text{obsd}} = P_f\Delta\nu_f + P_b\Delta\nu_b \quad (2)$$

$$\delta_{\text{obsd}} = P_f\delta_f + P_b\delta_b \quad (3)$$

width and chemical shift, respectively, at a given temperature and water content. The NMR parameters for the free (in the resin) and bound ions are designated by the subscripts f and b, respectively. The corresponding mole fractions of ions are given by P_f and P_b . These latter quantities are related such that $P_b = 1 - P_f$.

As the amount of water or the temperature is reduced, a larger fraction of sodium ions is bound to the resin at a given instant. This causes the observed line width and chemical shift to approach the values for the totally bound species. In order to obtain the fraction of cations bound for a given water content and temperature, it is necessary to know the NMR parameters for the free and bound species under similar conditions. Estimates of δ_b and $\Delta\nu_b$ are not readily obtainable but are surely larger than those observed at 1% H_2O . Values for δ_f and $\Delta\nu_f$ can be extracted from the data for the model salt in Table II. Nafion- SO_3Na of 1100 equivalent weight absorbs about 35% H_2O at 30 °C. This corresponds to an electrolyte concentration in the aqueous phase of about 2.6 M, which yields values of -1.5 ppm and 24 Hz for δ_f and $\Delta\nu_f$, respectively. However,

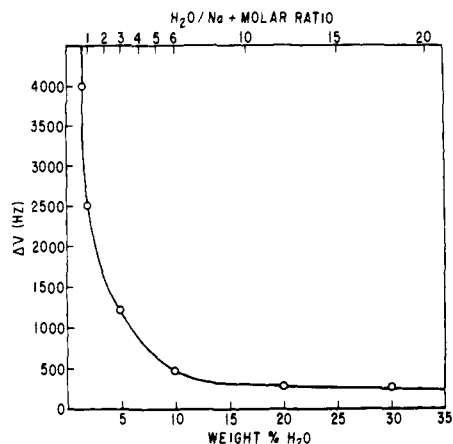


Figure 2. Plot of the ^{23}Na line width of Nafion- SO_3Na at 30 °C vs. water content and the $\text{H}_2\text{O}/\text{Na}$ molar ratio.

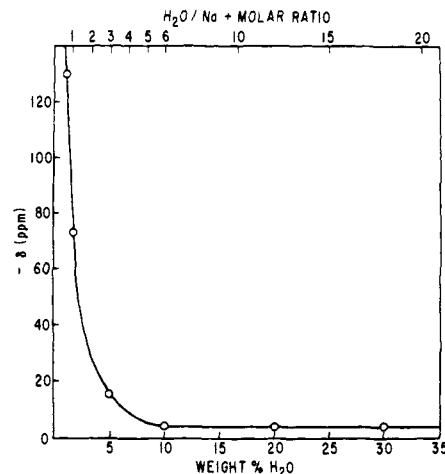


Figure 3. Plot of the ^{23}Na chemical shift of Nafion- SO_3Na vs. water content and the $\text{H}_2\text{O}/\text{Na}$ molar ratio.

since the line width of saturated Nafion is about ten times as large as that for the model, it does not appear to be valid to use line-width data for the model salt as an approximation of the unbound Na^+ line width in the resin. The mobility of an "unbound" ion in the aqueous phase of the resin is substantially less than that in a concentrated electrolyte solution. On the basis of the chemical shift data in Table I, less than 1% of the cations are bound in saturated Nafion. At 1% H_2O , a substantial fraction, probably greater than 50%, is bound. It must be kept in mind that, at very low water contents, the assumption of a fast equilibrium between bound and unbound states may no longer be valid.

In Figures 2 and 3 are plots of the line width and chemical shift, respectively, vs. water content and the $\text{H}_2\text{O}/\text{Na}$ molar ratio. The behavior of the two NMR parameters is quite similar. The largest changes begin to occur in the region of three to four water molecules per sodium ion. Since sodium chemical shifts are sensitive to only the immediate environment, this behavior suggests the presence of three or four water molecules in the first hydration sphere of Na^+ in Nafion- SO_3Na . Using ^1H NMR, Creekmore and Reilley¹¹ found hydration numbers in the range 2.8–3.5 for Dowex 50 cross-linked to various levels.

It is necessary to account for, in at least a qualitative manner, both the magnitude and direction of the shift change seen upon going to low water content. As water molecules are replaced by SO_3 groups in the neighborhood of the Na^+ ion, this nucleus experiences an increased shielding. Since the $-\text{CF}_2\text{SO}_3^-$ moieties of Nafion are weakly basic and poor electron donors, the upfield shifts are consistent with previous observations.^{6,7}

The magnitude of this shielding increase, most of which occurs in the region of low water content, is quite surprising in view of the typical chemical shift range (about ± 15 ppm from aqueous NaCl) of sodium.^{6–8} The 130-ppm difference observed between 30 and 1% H_2O is over twice the 60-ppm difference observed between the sodium cation and sodium anion, the latter existing in a cryptand complex in solution.¹² The shift difference between Na^+ and Na^- refers to the solvated species, whereas in Nafion at low water content, there is an insufficient quantity of water present for full hydration of the cations.

The large shift changes seen at low water content are strong evidence for the formation of contact ion pairs. The amount of water present at these levels is not sufficient to effectively provide for solvent-separated ion pairs. This behavior also explains why only relatively small shift changes are seen in both aqueous and nonaqueous electrolyte solutions as a function of

concentration. At the concentrations of electrolyte normally obtainable, the overwhelming majority of ions are solvent-separated, with only a small fraction of ions existing as contact ion pairs. It is also true that the chemical nature of the Nafion system (i.e., perfluorosulfonate) might be expected to yield larger cationic shift changes compared to other anionic types under similar conditions.

It should be pointed out that little can be learned concerning the detailed geometry of the ion pairs in Nafion from the data presented here. The electronic distribution around the sodium cation, due to the neighboring SO_3 group(s), is almost certainly highly anisotropic. No evidence for this can be seen in the spectra in Figure 1, most probably due to the rapid averaging between free and bound states that gives rise to the equilibrium spectra.

Behavior similar to that in Figures 2 and 3 has been seen for the ^{23}Na line width in the reversed micellar systems, sodium diisooctyl sulfosuccinate/water/heptane,¹³ and caprylic acid/sodium caprylate/water.¹⁴ Small-angle X-ray scattering studies¹⁵ suggest that swollen Nafion exists as a biphasic structure, consisting of hydrated ionic clusters embedded in the surrounding fluorocarbon phase. Such a structure resembles a reversed micelle. The ^{23}Na NMR results obtained here provide support for this picture of the structure of Nafion.

Acknowledgment. We thank Mr. N. J. Baldwin, of the Major Analytical Instrument Facility at Case Western Reserve University, for help in obtaining the ^{23}Na NMR spectra.

References and Notes

- (1) Nafion is a registered trademark of the du Pont Corp.
- (2) W. G. F. Grot, G. E. Munn, and P. N. Walmsley, 141st Electrochemical Society Meeting, Houston, Texas, May 1972.
- (3) A. I. Popov, *Pure Appl. Chem.*, **41**, 275 (1975).
- (4) G. J. Templeman and A. L. Van Geet, *J. Am. Chem. Soc.*, **94**, 5578 (1972).
- (5) G. J. Templeman, Ph.D. Thesis, State University of New York at Buffalo, 1970.
- (6) E. G. Bloor and R. G. Kidd, *Can. J. Chem.*, **46**, 3425 (1968).
- (7) M. S. Greenberg, R. L. Bodner, and A. I. Popov, *J. Phys. Chem.*, **77**, 2449 (1973).
- (8) J. P. Kintzinger and J. M. Lehn, *J. Am. Chem. Soc.*, **96**, 3313 (1974).
- (9) A. Abragam, "The Principles of Nuclear Magnetism", Clarendon Press, Oxford, 1961; A. G. Marshall, *J. Chem. Phys.*, **52**, 2527 (1970).
- (10) O. Jardetzky and J. E. Wertz, *J. Am. Chem. Soc.*, **82**, 318 (1960).
- (11) R. W. Creekmore and C. N. Reilley, *Anal. Chem.*, **42**, 570 (1970).
- (12) J. L. Dye, C. W. Andrews, and J. M. Ceraso, *J. Phys. Chem.*, **79**, 3076 (1975).
- (13) M. Wong, J. K. Thomas, and T. Nowak, *J. Am. Chem. Soc.*, **99**, 4730 (1977).
- (14) B. Lindman and P. Ekwall, *Kolloid Z. Z. Polym.*, **234**, 1115 (1969).
- (15) S. C. Yeo and A. Eisenberg, *J. Appl. Polym. Sci.*, **21**, 875 (1977).