^{14}N NMR Spectroscopy of Nitrate Co-ions in Ionomer Membranes

M. Rankothge, J. Hook, L. van Gorkom, and G. Moran*

School of Chemistry, University of New South Wales, Sydney, NSW 2052, Australia

Received March 12, 1996; Revised Manuscript Received April 18, 1997[⊗]

ABSTRACT: ^{14}N NMR spectroscopy has been used to observe the behavior of nitrate co-ions in cation-exchange membranes equilibrated with NH_4NO_3. The solubility of excess nitrate salts in Nafion membrane depends on the counterion used, increasing in the order $Li^+ < NH_4^+ < Na^+ < K^+ < Cs^+$ and $Na^+ < Mg^{2+} < Al^{3+}$. The ^{14}N quadrupolar splittings of the NH_4^+ and NO_3^- ions in Nafion are strongly dependent on the water content and on the macroscopic orientation of the membrane, with nitrate having the larger splitting in all samples. The immobilization of the ions in Nafion membrane was further investigated by measuring ^{14}N spin−lattice relaxation times. T_1 values are reduced by a factor of $\sim$10 for nitrate and 50−100 for ammonium ions in Nafion compared to aqueous solution.

1. Introduction

The ability of ionomer membranes to exclude co-ions is critical to their performance in electrodialysis and other applications. The strong permselectivity or so-called superselectivity exhibited at high electrolyte concentrations by perfluorosulfonate cation-exchange membranes such as Nafion has been extensively characterized,[1−7] and the transport properties of both cations and anions have been modeled theoretically by a number of groups.[4,5] It has been shown that while the solubility of excess electrolyte in Nafion can be high, the superselectivity relies on the slow rate of transport of the anions compared to the cations across the membrane.[1] This is the reverse of what is found for cation-exchange resins in which the anions diffuse faster and their rejection relies solely on Donnan exclusion. The superselective behavior of Nafion has been attributed to a high activation energy for the movement of anions through narrow channels connecting the hydrated ion cluster regions in the membrane.[4,5] Alternative paths for anion diffusion through interphase regions of low water content can be envisaged, but these might be expected to be unfavorable due to their high tortuosity. On the other hand, there is significant experimental evidence for separate diffusion pathways for anions and cations in Nafion, which implies a role for the interphase regions in anion transport.[1,3,6] In general, the mechanism of co-ion transport in ionomers has received relatively little attention compared to the extensive studies of cation binding in Nafion and related systems and has still to be fully elucidated.

We have previously found that ^{14}N NMR spectroscopy of NH_4^+ is a useful probe of counterion behavior in ionomer membranes.[8] In this work, we extend the use of ^{14}N NMR to the investigation of co-ions, specifically the uptake of NH_4NO_3 by Nafion perfluorosulfonate and Neosepta CMX poly(styrenesulfonate) cation-exchange membranes. There are two main reasons for our choice of the nitrate co-ion in this study. With NH_4NO_3 it is possible to observe both the counterions and co-ions simultaneously by ^{14}N NMR spectroscopy. Secondly, the rotational dynamics of both the NH_4^+ and NO_3^- ions in aqueous solution have been characterized in detail by ^{14}N[9−16] and ^{17}O NMR[13] and by Raman spectroscopy

for nitrate.[16−18] The concentration dependence of ^{14}N spin−lattice relaxation times has also been used to calculate ion pair association constants in a series of nitrate salts.[15] The use of NO_3^- as a probe anion for membranes or other ordered phases is not very common. Nitrate has been used as a model for bicarbonate in NMR studies of anion binding to the human anion-exchange protein AE1.[19] A recent study of NH_4NO_3 in lyotropic liquid crystals has direct relevance to the ionomer systems.[20] In that case, the quadrupolar splittings of NH_4^+ and NO_3^- and the ^{14}N spin−lattice relaxation times of the ions were used to characterize the interactions of these ions with the charged end groups of the liquid crystal molecules.

2. Experimental Section

Nafion 117 in sheet form (equivalent weight 1100, exchange capacity 0.91 mequiv g^{-1}) was purchased from Aldrich. The polystyrene-based membranes Neosepta CMX (exchange capacity 1.5−1.8 mequiv g^{-1}) and Neosepta AMX (exchange capacity 1.4−1.7 mequiv g^{-1}) were donated by Tokuyama Soda Co., Japan. Milli-Q deionized water was used in all experiments. Other reagents were analytical grade and used as received.

Preparation of NMR Samples. Nafion samples were pretreated by washing with 95% ethanol and then water. Nafion and Neosepta CMX were soaked in 1 M HCl to ensure complete protonation and finally washed again with water. Because of the possibility of batch-to-batch variations in the commercial polymers, experiments were carried out on membranes from the same batch, as far as possible. Pretreated Nafion samples were equilibrated several times in a large excess of the required nitrate salt solutions: NH_4NO_3, $LiNO_3$, $NaNO_3$, KNO_3, $CsNO_3$, $Mg(NO_3)_2$, or $Al(NO_3)_3$. Stretching experiments were carried out by passing strips of hydrated Nafion through a roller mill at room temperature and measuring the resulting elongation. Stretched membranes were then equilibrated with aqueous solutions of NH_4NO_3. Neosepta AMX (anion-exchange) and CMX (cation-exchange) samples, which are normally stored in 1 M NaCl, were washed well with water and then equilibrated as before with NH_4NO_3.

After ion exchange, excess solution was wiped from the surface of the membrane. The membrane was inserted into a 10 mm NMR tube and oriented so that the visible lines of strain were aligned either parallel or perpendicular to the magnetic field. This was achieved by rolling the membrane around a 5 mm NMR tube filled with D$_2$O, which was then placed inside the 10 mm tube.[8,21] In all cases the magnetic field lies in the plane of the membrane. In this cylindrical geometry, bulk susceptibility effects on the chemical shifts should be reduced.

* To whom correspondence is to be addressed. Fax: +61-2-9385 6141. E-mail: G.Moran@unsw.edu.au.

To carry out controlled humidity experiments, membranes soaked in 3.0 M NH₄NO₃ were wiped and dried for 4 days and then allowed to stand over 100% H_2O or saturated $MgCl_2$(aq) to provide atmospheres of 100% and 33% relative humidity, respectively. Variable temperature NMR spectra and relaxation time measurements were done at 100% relative humidity by putting 2−3 drops of water at the bottom of the 10 mm NMR tube.

NMR Spectroscopy. [14]N NMR spectra were recorded at 21.67 MHz on a Bruker ACP 300 NMR spectrometer using a 10 mm multinuclear probe. Free induction decays (FID) were acquired with a pulse width of 25 μs ($\pi/2$ pulse) and a spectral width of 20 kHz over 4K data points which gave an acquisition time of 0.102 s. A relaxation delay of 1.0 s was used. Generally, 2000−4000 scans gave spectra of sufficient quality, though samples giving weak signals were run overnight. Pulse breakthrough was eliminated in spectra by removing the first 2−8 data points of the FID. FID's were processed by zero filling to 8−16 K data points, line broadened and Fourier transformed. Chemical shifts, δ_N, are referenced externally to nitromethane, CH_3NO_2, in DMSO-d_6 (=0 ppm) and are not corrected for bulk susceptibility effects. T_1 data were obtained with the inversion recovery pulse sequence (180°−t−90°) and analyzed using Bruker software. Temperatures were controlled by a BVT-1000 temperature controller, were calibrated with methanol, and are accurate to ±1 deg.

Analysis of Nitrate Solutions. For quantitative analysis, the membrane was placed in a 10.0 mL calibrated sample tube, which was then made to the mark with deionized water. The excess nitrate salt was quantitatively washed from the membrane under these conditions. Solution concentrations of nitrate were in the range 4−1000 mg L⁻¹. Nitrate was determined using a Horiba C-141 compact nitrate ion-meter. For $Al(NO_3)_3$ solutions, where the cations can interfere with the electrode, UV spectrophotometry was used. Nitrate absorbances were measured at a wavelength of 302 nm, on a Varian Cary 5 spectrophotometer.

3. Results and Discussion

[14]N NMR Spectra of NH₄NO₃ in Membranes. The proton-decoupled ^{14}N NMR spectrum of Nafion after soaking in 3.0 M NH₄NO₃ is shown in Figure 1. Since the commercial membrane is anisotropic,[8,21,22] with lines of strain clearly visible in the plane of the membrane, the NMR spectrum was measured in two orientations with respect to the magnetic field. A signal due to NO_3^- is readily detected at a chemical shift of −5.5 ppm in addition to the strong NH_4^+ peak at −363 ppm. The ^{14}N quadrupolar splitting of the NO_3^- peak is 0.22 kHz when the direction of anisotropy is parallel to the magnetic field, compared to 0.12 kHz for NH_4^+ (Table 1). For both ions, the quadrupolar splitting is reduced when the membrane is rotated so that the lines of strain are oriented perpendicularly in the magnetic field. The orientation dependence of the quadrupolar splitting clearly establishes that NO_3^- is located within the partially ordered membrane environment where the electric field gradient at nitrogen is not averaged to zero by molecular motion. A complete angular dependence study of the ^{14}N NMR spectrum of NH_4^+ in Nafion has previously been reported.[8] Bulk susceptibility effects on the ^{14}N chemical shifts, although expected to be small for both ions,[23] may contribute to some of the sample-to-sample variations observed. The [14]NH_4^+ chemical shift is relatively insensitive to lattice effects, while the [14]NO_3^- signal is known to shift upfield in strong acid solutions. The more negative chemical shifts for [14]NO_3^- in stretched membranes (Table 1) are reproducible and indicate a change in nitrate environment in the more oriented samples. When water is added to the membrane in the NMR tube, the excess NH₄NO₃ is immediately washed from the Nafion and two sharp
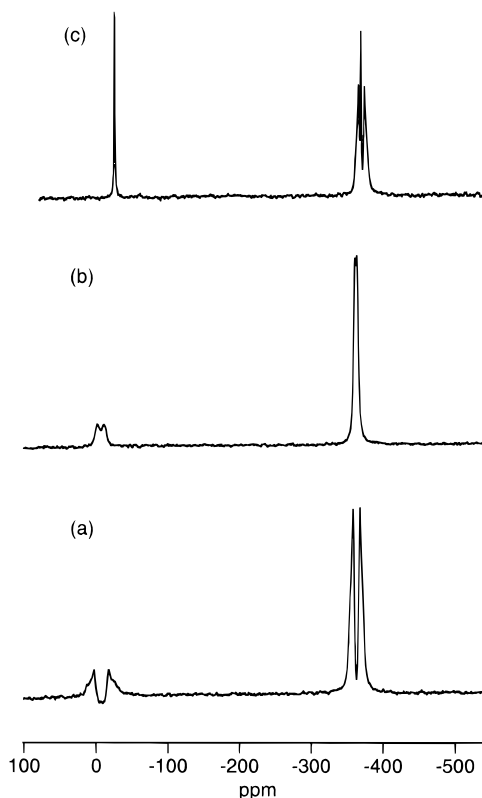
Figure 1. [14]N NMR spectrum of Nafion after equilibration with 3.0 M NH₄NO₃: (a) parallel orientation; (b) perpendicular orientation; (c) parallel orientation, after addition of water to the NMR tube.

Table 1. [14]N NMR of Nafion Equilibrated with 3.0 M NH₄NO₃(aq)

| orientation	chemical shift (ppm)		quadrupolar splitting (kHz)	
	NH_4^+	NO_3^-	NH_4^+	NO_3^-
parallel (as received)	−363	−5.5	0.12	0.22
parallel (stretched)	−363	−10.5	0.71	1.73
perpendicular (as received)	−364	−6.9	0.25	0.64
perpendicular (stretched)	−363	−9.6	0.22	0.65

singlets appear in the ^{14}N NMR spectrum corresponding to free aqueous NO_3^- and NH_4^+, the latter superimposed on the doublet due to the membrane-bound NH_4^+ ions, Figure 1c.

When Neosepta CMX, a poly(styrenesulfonate) cation-exchange membrane, was equilibrated in 3.0 M NH₄NO₃, the NO_3^- ion could not be detected in the ^{14}N NMR spectrum, Figure 2a. Only when water was added to the membrane to wash out any excess NH₄NO₃ was the presence of nitrate evident, Figure 2b. The ^{14}N NMR line width of NO_3^- in the less mobile environment[8] of the Neosepta membrane is too broad to be measured in the high-resolution probe used in these experiments. The analogous anion-exchange membrane, Neosepta AMX, showed similar characteristics. It was not possible to observe a ^{14}N NMR resonance due to NO_3^- for NH₄NO₃-exchanged Neosepta AMX under our experimental conditions, although the [14]NH_4^+ resonance could be seen. However, excess NH₄NO₃ could be shown to be present by adding water and observing the appearance of sharp [14]NH_4^+ and [14]NO_3^- signals in the NMR spectrum, as before.

The quadrupolar splittings of both ions are strongly dependent on the water content of the membrane (Table 2). When a hydrated Nafion−NH₄NO₃ membrane was

Table 2. Spin−Lattice Relaxation Times (T_1) for NH_4^+ and NO_3^- in Nafion (Parallel Orientation) in NH_4NO_3(aq) and in Liquid Crystals (Data from Ref 20)

	T_1 (±2 ms), 295 K		quadrupolar splitting (kHz)	
sample	NH_4^+	NO_3^-	NH_4^+	NO_3^-
Nafion−3 M NH_4NO_3 (as received, 100% humidity)	25	17	0.10	0.25
Nafion−3 M NH_4NO_3 (stretched, 100% humidity)	16	7	0.71	1.73
Nafion−3 M NH_4NO_3 (as received, low humidity)	12	8	0.23	1.86
Nafion−1 M NH_4NO_3 (stretched, 100% humidity)	30	69	0.35	0.76
Nafion−NH_4^+ (in water)[8]	72		0.15	
3 M NH_4NO_3(aq)	1.3×10^3	89		
liquid crystals[20]				
$\quad C_{12}COO^-K^+/NH_4NO_3$		88	4.2×10^3	0.31
$\quad C_{10}NH_3^+Cl^-/NH_4NO_3$	1.03×10^3	n/a	1.2×10^3	46×10^3
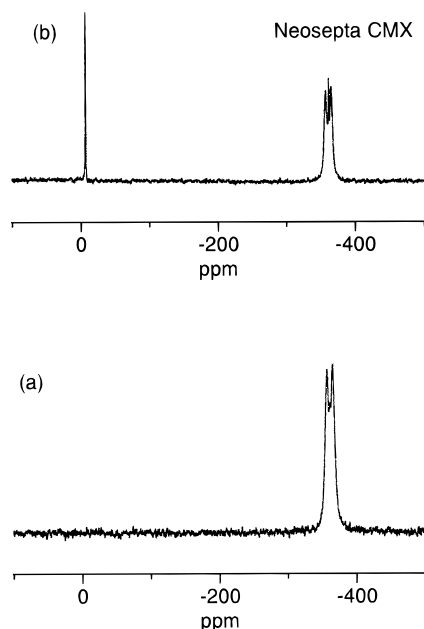
Figure 2. ^{14}N NMR spectrum of Neosepta CMX after equilibration with 3.0 M NH_4NO_3: (a) parallel orientation; (b) parallel orientation, after addition of water to the NMR tube.

allowed to stand for several days over a saturated $MgCl_2$ solution at 33% relative humidity, the $^{14}NH_4^+$ quadrupolar splitting increased from 0.23 to 1.1 kHz. Quadrupolar broadening of the $^{14}NO_3^-$ signals in these samples of lower water content led to line widths too large to be detected. When a second portion of the same sample was stored at 100% relative humidity, the $^{14}NH_4^+$ splitting gradually decreased from 0.23 to 0.11 kHz as a function of equilibration time. The corresponding nitrate splittings decreased from 1.9 to 0.24 kHz. Thus, reduced hydration of the membrane leads to increased ion−polymer interaction and larger quadrupolar splittings for both anions and cations. It is notable that this effect is much more pronounced for the nitrate co-ions than for the ammonium counterions.

Since the NH_4^+ ion is tetrahedral, the origin of the ^{14}N quadrupolar splittings must be an asymmetry in the ion or in its interactions with the lattice, which is not averaged to zero by rapid rotational motion. The angular dependence of the ^{14}N quadrupolar splittings in hydrated Nafion in its NH_4^+ form has been described previously,[8] and the principal axis of the electric field gradient was shown to correspond with the orientational anisotropy in the plane of the membrane. In order to characterize more fully the effects of this membrane anisotropy on the quadrupolar splittings of the $^{14}NO_3^-$ ion, Nafion samples were first stretched using a roller mill and then equilibrated in aqueous NH_4NO_3. Large increases in quadrupolar splittings were induced for

both NO_3^- and NH_4^+ (Table 1). The quadrupolar splitting for nitrate is consistently larger in all samples. The nitrate ion has an electric field gradient at nitrogen that leads to quadrupolar coupling constants of the order of 750 kHz in compounds such as $NaNO_3$.[24] The observation of residual quadrupolar splittings in the Nafion−NH_4NO_3 samples, which correlate with the direction of in-plane orientational anisotropy, indicates nonisotropic interaction of the ion with the polymer.

These results can be compared qualitatively with those of Iida and Tracey,[20] who measured the ^{14}N NMR spectra of NO_3^- and NH_4^+ in lyotropic liquid crystals. In the decylammonium chloride system, the quadrupolar splitting of the NO_3^- counterion was 46 kHz compared to 1.2 kHz for the NH_4^+ co-ion. This trend was reversed in the potassium dodecanoate liquid crystal at pH 10, where the NO_3^- is now the noninteracting ion and its quadrupolar splitting drops to 0.31 kHz. The NH_4^+ ion splitting is raised to 4.2 kHz, though since the pH is 10, this must include a contribution from NH_3. In each case, the smaller splitting is associated with the unbound ion, though the nitrate signal is clearly much more sensitive to the orientational ordering. The fact that NO_3^- in partially ordered Nafion shows consistently larger splittings compared to the NH_4^+ counterion might suggest that the NO_3^- ion has a stronger interaction with the membrane than if it were only located in the center of hydrated pores away from the fixed charges on the polymer. It is possible that a significant fraction of the anions are located in the interphase regions of the membrane, which contain some water and a few fixed charges and where the anisotropic influence would be much greater. It has been suggested that such regions have a significant role in co-ion transport mechanisms.[1,3]

Concentration Effects. The molar ratio of NO_3^- to NH_4^+ in Nafion was first estimated by integrating the ^{14}N NMR signals and was found to increase approximately linearly from 0.13 to 0.27 as the concentration of the equilibrating solution was increased from 1.0 to 3.0 M NH_4NO_3. At these levels of NO_3^- uptake, the nitrate washed from the membrane can readily be analyzed with a nitrate ion-selective electrode. The solubility of NH_4NO_3 in Nafion was then measured quantitatively as a function of concentration in the range 0.10−3.0 M. The results (Figure 3) confirm the linear relationship between the excess of NH_4NO_3 taken up by the membrane and the external NH_4NO_3 concentration. Such linear correlations have been reported previously for NaCl and HCl[27] and indicate that the classical Donnan equation for co-ion exclusion is not obeyed. Neosepta CMX membrane takes up about half as much excess salt as Nafion under the same conditions. A comparison, using 0.5 M NH_4NO_3 to equilibrate the samples shows that the water content of Neosepta
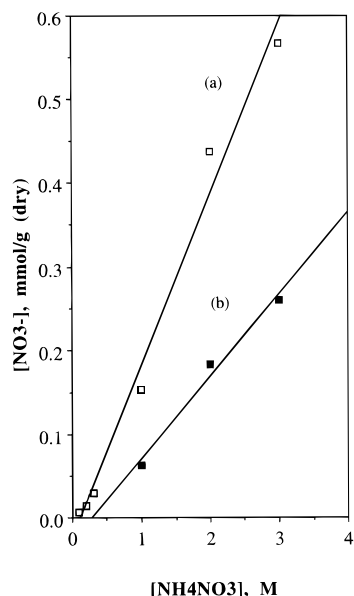
Figure 3. NO_3^- content of Nafion as a function of NH_4NO_3 concentration, for (a) as received and (b) stretched membrane ($\triangle l/l = 11\%$).

Table 3. Nitrate Uptake by Nafion as a Function of Counterion (Equilibration Solution Contained 1.0 M NO_3^- in All Cases)

| cation	$[NO_3^-]$, mmol g^{-1} (dry membrane)	NO_3^-/SO_3^-
NH_4^+	0.15	0.17
Li^+	0.11	0.12
Na^+	0.18	0.20
K^+	0.21	0.23
Cs^+	0.22	0.24
Mg^{2+}	0.21	0.23
Al^{3+}	0.24	0.26

(8.7% by weight) is also about half that of Nafion under the same conditions (19%).

There is a discrepancy beween the analytically determined nitrate content of the membrane and the peak integrations in the NMR spectrum, particularly for the high concentrations of NH_4NO_3. We have found batch-to-batch variations in the commercial Nafion membranes. However, we have observed that the NMR integration consistently underestimates the nitrate content of the membrane. It should be emphasized that the solution-state NMR experiment will not detect strongly immobilized ions whose quadrupolar relaxation is too fast. We have already seen the effect of this in the Neosepta membrane (Figure 2) where the nitrate ions were not observed.

Nafion membranes take up less NH_4NO_3 after stretching, as seen in Figure 3. This may be due in part to the lower water content of the stretched membrane, which drops from 19% to 13% by weight for an elongation $\triangle l/l$ of 11%. It is likely that the morphology of the pores or ion clusters is affected by the stretching process. Evidence for pore elongation in partially oriented Nafion comes from small angle X-ray scattering experiments and measurement of anisotropic ionic conductivities.[22]

The solubility of a range of nitrate salts in Nafion was also measured (Table 3). Solubility increases monotonically with counterion charge in the series $Na^+ < Mg^{2+} < Al^{3+}$. For monovalent ions, the solubility increases in the order $Li^+ < NH_4^+ < Na^+ < K^+ < Cs^+$. Thus the extent of nitrate uptake correlates with the ion-exchange selectivities of these cations for a Nafion
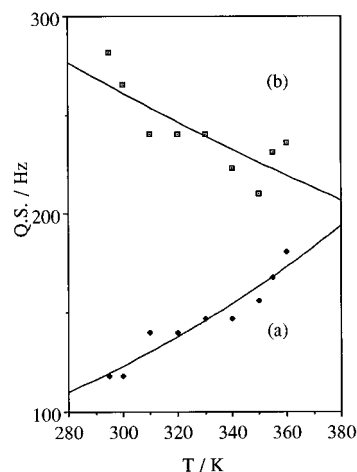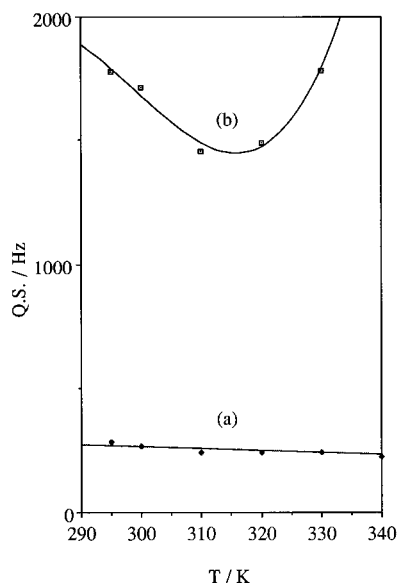

Figure 4. NH_4^+ (a) and NO_3^- (b) quadrupolar splittings as a function of temperature for Nafion-3 M NH_4NO_3 at 100% relative humidity.

membrane.[28] Nitrate is only weakly ion-pairing with NH_4^+ in water,[13,14] and even for ions such as Li^+, Mg^{2+}, and Al^{3+} the extent of ion pairing is not large. However, it is likely that within the membrane, ion-pairing interactions are more significant. This will be discussed further below.

Temperature Dependence. The temperature dependence of the NMR spectrum was monitored in the temperature range $295-360$ K for a Nafion membrane that had been soaked in 3 M NH_4NO_3 solution. In these experiments a few drops of water were added to the bottom of the 10 mm NMR tube to maintain the humidity of the sample. Figure 4 shows the change in the ^{14}N quadrupolar splitting of NO_3^- and NH_4^+ with temperature. The quadrupolar splitting of NO_3^- decreases gradually as the temperature is raised, reaching a minimum at 350 K and showing a slight increase again above this temperature. These changes associated with the NO_3^- ion are very similar to the behavior observed[21] in the ^2H NMR spectra of D_2O in Nafion. The more rapid molecular motion at higher temperatures should lead to decreased interaction of the NO_3^- ion with the membrane and hence smaller quadrupolar splittings. The slight increase at the end of the temperature range is probably due to some loss of water from the membrane. This is illustrated further by the temperature dependence for a drier sample (sample 3, Table 2), as shown in Figure 5. Here the effects are more pronounced, with a clear minimum in quadrupolar splitting observed at about 320 K.

In contrast, the quadrupolar splitting of NH_4^+ consistently increases with temperature. This trend is in agreement with our previous results[8] for Nafion$-NH_4^+$ immersed in water and is more difficult to explain. It cannot be attributed to changes in humidity or membrane orientation alone, because we have already seen that both of these effects should affect the NO_3^- quadrupolar splitting in the same direction. Analogous examples are scarce in the literature. An increase in quadrupolar splitting with temperature has been reported for $^{39}K^+$ in a potasssium oleate$-$water lamellar liquid crystal.[29] The authors proposed that a thermodynamically less stable, but more anisotropic, binding site was populated by K^+ ions on heating, leading to a net increase in quadrupolar splitting. However, it is difficult to see how such a model could apply to the $SO_3^- - NH_4^+$ situation where the ionic interactions are expected to be less directional in nature than those

Figure 5. Temperature dependence of NO_3^- quadrupolar splittings in Nafion for humidified (a) and dry (b) samples (note the change in scale from Figure 4).

between K^+ and carboxylate in the liquid crystal. A possible explanation is that at room temperature some NH_4^+ ions are located in domains of low mobility and are not in fast exchange with the bulk of the ions. Since only the mobile ions are observed under the solution-state NMR conditions, these ions would not contribute to the spectrum at low temperature. Thermal mobilization of these ions could then account for the observed increase in the net quadrupolar splitting. Further experiments are needed to test this hypothesis.

Spin−Lattice Relaxation. ^{14}N spin−lattice relaxation times (T_1) were measured for NH_4NO_3 in Nafion under three different conditions. The results are given in Table 2, which also contains solution-state and liquid crystal T_1 values for comparison. The spin−lattice relaxation mechanisms for both ions are entirely quadrupolar. The tetrahedral ammonium cation has zero electric field gradient at nitrogen, and in dilute aqueous solution the quadrupolar relaxation is due to the fluctuating electric field gradients caused by reorientation of the surrounding water dipoles. In concentrated electrolyte solutions or in the ionomer membrane environment, there will also be a contribution from an electric field gradient induced by ion-pairing interactions with NH_4^+. Reductions in T_1 values for NH_4^+ will therefore depend on a combination of these two factors, reduction in rotational mobility relative to the surrounding solvent and increased ion-pairing interactions. The T_1 values for the counterion NH_4^+ in the Nafion−NH_4NO_3 samples are some 50−100 times shorter than the T_1 for NH_4^+ in aqueous solution.

The corresponding changes in T_1 for the nitrate ion are still significant but are 1 order of magnitude less, consistent with its role as a co-ion having no ionic attractions to the polymer. The NO_3^- ion undergoes rapid but anisotropic reorientation in aqueous solution. The ^{14}N T_1 value is proportional to the rotational diffusion coefficient for end-over-end rotation, $D_\perp$, as well as the quadrupolar coupling constant. Nitrate quadrupolar coupling constants of up to 345 kHz[25] have been found in crystal lattices, and they are known to be strongly lattice dependent.[26] $D_\perp$ is sensitive to ion-pairing interactions, and the lowering of nitrate T_1 values as a function of electrolyte concentration in water

has been used by Nicholas and Wasylishen to compare the association of a range of cations with nitrate.[13] Using this criterion, ion-pairing between nitrate and ammonium ions in water was found to be particularly weak, though greater ion-pairing is expected in non-aqueous environments. This may affect the relaxation of NO_3^- ions located in interphase regions of the membrane having low water content. There will also be a contribution to T_1 from the electric field gradient caused by the anisotropic environment of the partially oriented polymer.

Spin−lattice relaxation measurements allow comparison of the degree of immobilization of the ions in the membrane under different conditions due to decreased rotational mobility and increased ion-pairing interactions. However, the mobility probed by these experiments relates to local rotational motion of the ions on a picosecond time scale and does not necessarily correlate with macroscopic rates of ion diffusion, particularly in heterogeneous ionomer membranes. To obtain mobility information that is more directly related to the bulk transport of ions, it will be necessary to carry out pulsed field gradient NMR experiments to measure self-diffusion coefficients directly.[30−33] Such experiments are currently being undertaken.

4. Conclusions

^{14}N NMR spectroscopy can be used to observe the uptake of nitrate co-ions in a Nafion membrane. Nitrate cannot be detected directly in the more rigid Neosepta CMX and AMX membranes, but the excess NH_4NO_3 washed from the membranes can be observed on adding water to the samples in the NMR tube. The $^{14}NO_3^-$ quadrupolar splitting in Nafion is larger than the $^{14}NH_4^+$ splitting in all samples. The $^{14}NO_3^-$ splitting is also more sensitive to membrane anisotropy (uniaxial stress in the plane of the membrane) than that of $^{14}NH_4^+$ and increases dramatically as the water content decreases. These results may indicate some co-ion occupancy of interphase regions and hence closer contact with the polymer chains.

Spin−lattice relaxation measurements show large reductions in T_1 for both ions in Nafion compared to aqueous solution, but the reduction is 1 order of magnitude greater for ammonium than for nitrate. The quadrupolar splittings and spin−lattice relaxation data obtained for nitrate in Nafion indicate relatively strong interactions of the co-ions with the membrane. The use of NH_4NO_3 as an NMR probe of membranes has the advantage that both the cations and the anions can be detected simultaneously in favorable cases.

References and Notes

(1) Yeager, H. L. In *Structure and Properties of Ionomer Membranes*; Pineri, M., Eisenberg, A., Eds.; NATO ASI; D. Reidel: Dordrecht, The Netherlands, 1986.
(2) Eisenberg, A., Yeager, H. L., Eds. *Perfluorinated Ionomer Membranes*; ACS Symposium Series 180; American Chemical Society; Washington, DC, 1982.
(3) Herrera, A.; Yeager, H. L. *J. Electrochem. Soc.* **1987**, *134*, 2446.
(4) Hsu W. Y.; Gierke, T. D. *J. Membr. Sci.* **1983**, *13*, 307.
(5) Capeci, S. W.; Pintauro P. N.; Bennion, D. N. *J. Electrochem. Soc.* **1989**, *136*, 2876.
(6) Yeager, M. A. F.; Yeager, H. L. *Polym. Mater. Sci. Eng.* **1993**, *69*, 342.

(7) Lindheimer, A.; Molenat, J.; Gavache, C. *J. Electroanal. Chem.* **1987**, *216*, 71.

(8) Haryadi, M.; Rankothge, M.; Hook, J.; Van Gorkom, L.; Moran, G. *Magn. Reson. Chem.* **1994**, *32*, 446.

(9) Perrin, C. L.; Gipe, R. K. *Science* **1987**, *238*, 1393.

(10) Perrin, C. L.; Gipe, R. K. *J. Am. Chem. Soc.* **1986**, *108*, 1088.

(11) Brown, R. J. C. *J. Mol. Struct.* **1995**, *345*, 77.

(12) Nicholas, A. M.; Wasylishen, R. E. *J. Phys. Chem.* **1985**, *89*, 5446.

(13) Nicholas, A. M. de P.; Wasylishen, R. E. *Can. J. Chem.* **1987**, *65*, 951.

(14) Nicholas, A. M. de P.; Wasylishen, R. E. *Can. J. Chem.* **1986**, *64*, 1839.

(15) Owens, G.; Guariloff, P.; Steel, B. J.; Kurucsev, T. *Aust. J. Chem.* **1995**, *48*, 207.

(16) Laaksonen, A.; Kovacs, H. Can. *J. Chem.* **1994**, *72*, 2278.

(17) James, D. W. *Prog. Inorg. Chem.* **1985**, *33*, 353.

(18) Adachi, A.; Kiyoyama, H.; Nakahara, M.; Masuda, Y.; Yamatera, H.; Shimizu, A.; Taniguchi, Y. *J. Chem. Phys.* **1989**, *90*, 392.

(19) Galanter, W. L.; Labotka, R. *Biochim. Biophys. Acta* **1991**, *1079*, 146.

(20) Iida, M.; Tracey, A. S. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 3451.

(21) Rankothge, M.; Haryadi; Moran, G.; Hook, J.; Van Gorkom, L. *Solid State Ionics* **1994**, *67*, 241.

(22) Cable, K. M.; Mauritz, K. A.; Moore, R. B. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1994**, *35* (1), 421.

(23) Witanowski, M.; Stefaniak, L.; Webb, G. A. *Annu. Rep. NMR Spectrosc.* **1993**, *25*, 30.

(24) Gourdji, M.; Guibe, L.; Peneau, A. *J. Phys.* **1974**, *35*, 497.

(25) Wolff, E. K.; Griffin, R. G.; Watson, C. *J. Chem. Phys.* **1977**, *66*, 5433.

(26) Santos, R. A.; Tang, P.; Chien, W. J.; Kwan, S.; Harbison, G. S. *J. Phys. Chem.* **1990**, *94*, 2717.

(27) Pourcelly, G.; Lindheimer, A.; Gavache, C. *J. Electroanal. Chem.* **1989**, *259*, 113.

(28) Yeager, H. L.; Steck, A. *Anal. Chem.* **1979**, *51*, 862.

(29) Boden, N.; Jones, S. A. *Isr. J. Chem.* **1983**, *23*, 356.

(30) Soderman, O.; Stilbs, P. *Prog. NMR Spectrosc.* **1994**, *26*, 445.

(31) Lindblom, G. and Oradd, G. *Prog. NMR Spectrosc.* **1994**, *26*, 483.

(32) Stilbs, P. *Prog. NMR Spectrosc.* **1987**, *19*, 1.

(33) Zawodzinski, T. A., Jr.; Neeman, M.; Laurel, L. O. *J. Phys. Chem.* **1991**, *95*, 6040.

MA960375Y