$$O^{\bullet -} + O_2 \rightarrow O_3 + e$$

This electron reduces the π-cation radical to the nonradical oxoferryl porphyrin, which is fairly stable in low-temperature O_2 matrices. This mechanism accounts for the results shown in Figure 5A and 5B. Namely, the ν(FeO) of the π-cation radical (815 cm^{-1}) becomes weaker, whereas that of the nonradical oxoferryl porphyrin (853 cm^{-1}) becomes stronger as the irradiation time is increased. In contrast to the results presented above, formation of nonradical oxoferryl porphyrins in solution proceeds via a different route.[38]

$$\mathrm{Fe(II)(por)} \xrightarrow{O_2} \mathrm{Fe(Por)O_2} \xrightarrow{O_2} \mathrm{(por)Fe(III)OOFe(III)(por)} \rightarrow \mathrm{OFe(IV)(por)}$$

In solution at low temperature, Fe(II)(por) reacts with O_2 to form an oxygen adduct, which immediately converts to a more stable μ-peroxo-bridged species $[\mathrm{(por)Fe(III)}]_2O_2$. Its formation has been confirmed by the observation of the ν_s(Fe–O) at 574 cm^{-1} in toluene at ~190 K.[38] Such a dimer cannot be formed in an O_2 matrix since Fe(por)O_2 is surrounded by a large excess of O_2 molecules and frozen at 25 K. When the temperature of the solution is raised to ~220 K, the O–O bond of the peroxo dimer is cleaved homolytically and the nonradical oxoferryl porphyrin is formed without an intermediate species such as an oxoferryl porphyrin π-cation radical.

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Cation Solvation in Nafion/Cu^{2+} Swollen by Acetonitrile from Multifrequency ESR and Simulations

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Abstract: The gradual replacement of oxygen ligands around Cu^{2+} with nitrogen ligands in Nafion soaked with acetonitrile has been deduced from ESR spectra at L-, S-, C-, and X-bands and from computer simulations. Results suggest that after one cycle of drying and soaking of the membranes with acetonitrile, Cu^{2+} has two ^{14}N ligands in CH_3CN and *none* in CD_3CN. The isotope effect is assigned to the difference in the solvation energies of the sulfonic groups and of cations with deuteriated and protiated solvents and is similar to the recently published preferential solvation of Nafion salts by H_2O compared with D_2O. After two cycles of drying and soaking with the solvents, all four oxygen ligands in the equatorial plane of Cu^{2+} are replaced by nitrogen ligands. The components of the ^{14}N superhyperfine tensor have been deduced, taking into consideration the *apparent* tensor values calculated from the analysis of the splitting from parallel and perpendicular signals of ^{63}Cu. Multifrequency ESR spectra allow determination of all ESR parameters: Spectra at X-band are very important for deducing the **g**-tensor components; spectra at C-band are critical for the determination of the ratio $\delta g/\delta A$ of the distribution parameters due to strain; the greater resolution for the signals corresponding to $m_I = -^3/_2$ and $-^1/_2$ at C-band, to $m_I = -^3/_2$ at X-band, and to $m_I = -^1/_2$ at S-band is crucial for determining the many parameters involved in the simulation of experimental results. We emphasize the importance of ESR at frequencies *lower* than the usual X-band, for the analysis of disordered systems, in the presence of strain.

I. Introduction

The local environment of paramagnetic cations can be deduced from electron spin resonance (ESR) spectra, based on the **g** tensor and the hyperfine coupling constants of the central cation and on the line widths and line shapes of the signals. The interaction with magnetic ligands is sometimes detected as a line broadening and, in favorable cases, as resolved superhyperfine splittings (shf); this is the case for nitrogen ligands. Detection of shf is very important, because it reflects *directly* the number and symmetry of the ligands around the paramagnetic cation.

Most ESR spectra are taken at a frequency of about 9 GHz, because of convenient sample size and availability of spectrometer. Multifrequency ESR has proven beneficial for both the quality and quantity of information that can be obtained. The optimal frequencies are system dependent: Spectra at 35 GHz (Q-band) are used to increase the separation (in Gauss) when more than one species, differing in **g** values, are present. In recent years however it has become evident that microwave frequencies *lower* that 9 GHz are frequently the best choice, especially in disordered systems, where local structural inhomogeneities ("strain") lead to a distribution in the **g** and hyperfine tensors and cause considerable line broadening.[1]

A model that describes the line widths in the ESR spectra of Cu^{2+} complexes as a function of microwave frequency and m_I values has been suggested by Froncisz and Hyde.[2] The distribution widths of the parallel component of the **g** tensor and of the hyperfine tensor from the central cation, δg and δA, respectively, can be deduced from experimental spectra by using this dependence. For typical values of the distribution parameters, the model predicts increased resolution at lower frequencies; in particular the $m_I = -^1/_2$ signal is expected to be narrowest at a frequency of ≈2 GHz. This behavior has been verified in a number of biologically important Cu^{2+} complexes, where the advantage of multifrequency ESR has been convincingly demonstrated.[3,4]

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[†] On leave from the Institute of Applied Radiation Chemistry, Technical University of Lodz, Lodz, Poland.

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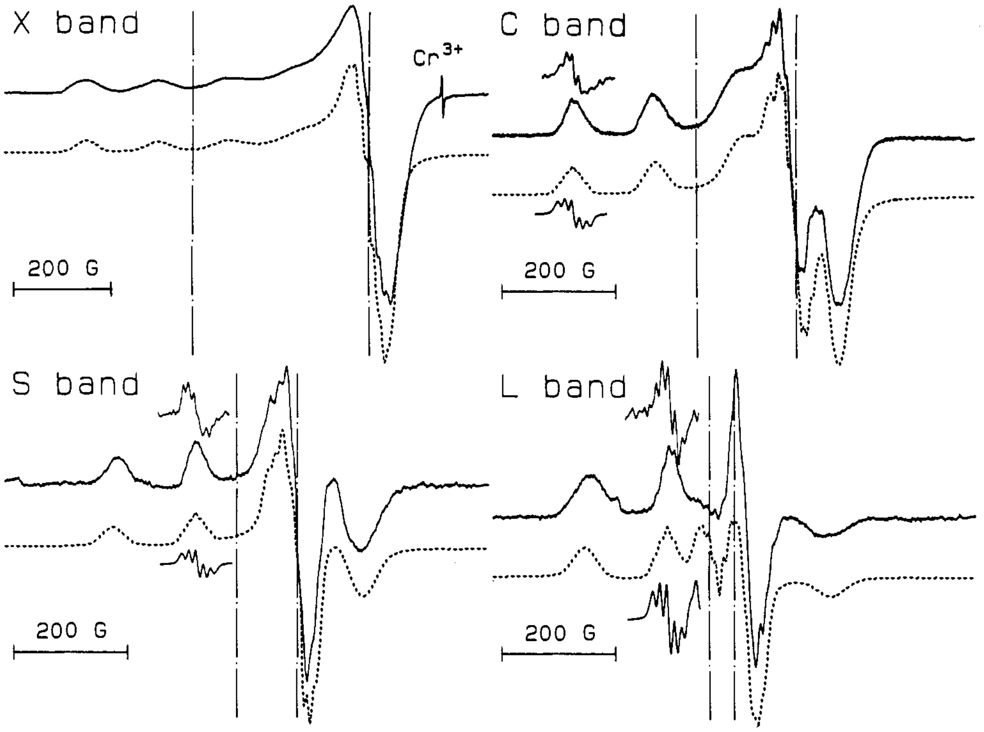


Figure 1. Experimental (—) and simulated (---) ESR spectra of Nafion/$^{63}Cu^{2+}$ (Cu^{2+} concentration 4%) soaked *once* by CH_3CN, at the X-band (9.36 GHz) and 110 K, and at the C-band (4.7 GHz), S-band (2.8 GHz), and L-band (1.2 GHz) at 123 K. Vertical lines (-·-) indicate the position of $g_\parallel$ (low field) and $g_\perp$ (high field). Experimental and calculated second derivatives for the parallel components $m_I = -{}^3/_2$ at C-band and $m_I = -{}^1/_2$ at S- and L-bands are given above and below the corresponding full spectra, respectively.

The model assumes no distribution for the perpendicular component.

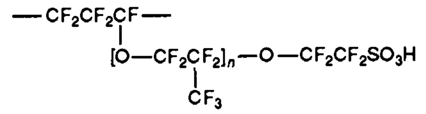
We have applied the multifrequency ESR method in two types of polymeric systems. In cross-linked polyacrylamide gels an analysis of ESR spectra of the cupric probe at *two* microwave frequencies has been used to determine the distribution parameters as a function of the gel pore size, and to quantify the gradual change in the water properties due to the proximity of the network.[5] In our studies of perfluorinated ionomers swollen by water, methanol, dimethylformamide, and tetrahydrofuran, spectra measured at *three* microwave frequencies have been analyzed, in order to extract and divide out the contribution of the **g** and hyperfine tensor distributions to the line width and to isolate the broadening associated with paramagnetic neighbors; thus the interaction distance was determined.[6-8] In all these systems the ligands were oxygens and, as expected, no shf was detected.

Recently[9] we reported the direct detection of ^{14}N shf from Cu^{2+} in Nafion membranes swollen by acetonitrile, as CH_3CN and CD_3CN (ANH and AND, respectively). The number of ^{14}N ligands around the cation in this system was suggested from ESR spectra taken at X-band, as a function of the specific conditions for sample preparation. The most surprising result from that study was the preferential solvation of the cation to oxygen ligands from the water remaining in the membranes after one cycle of drying the membranes to constant weight and soaking with acetonitrile. Only after an additional cycle of drying and soaking was it possible to detect an ESR spectrum that suggested four equatorial ^{14}N ligands around the cation.

In this study we present a detailed analysis of the process of cation solvation by ANH and AND in Nafion neutralized by Cu^{2+}, from ESR spectra at X-band and at three lower microwave frequencies, and from computer simulations.

II. Experimental Section

The Nafion 117 perfluorinated sulfonated membranes, with an equivalent weight of 1100 g/mol of SO_3H and a thickness of 0.13 mm, were obtained from DuPont. The formula is given below.



$$\text{—}CF_2CF_2CF\text{—} \quad [O\text{—}CF_2CF(CF_3)]_n\text{—}O\text{—}CF_2CF_2SO_3H$$

Nafion, $n = 1$

To prepare the Nafion salts, dried acidified membranes were neutralized with the stoichiometric amount of $CuSO_4$ containing ^{63}Cu (99.72% enrichment). The fraction of Cu^{2+} retained by the membrane as a function of the amount of cation available in the equilibrating solution has been determined by atomic absorption, as reported previously.[7] Some samples were prepared by neutralizing the membrane with a mixture of Cu^{2+} and Zn^{2+} (as $ZnSO_4$) cations.

The solvents, reagent grade ANH from Eastman Kodak and AND from Icon, were dried with molecular sieves (type 3A from Fisher) and kept in a glovebox. Samples were prepared as described,[9] with the exception that all manipulations were done under vacuum and in the glovebox, with no exposure to ambient conditions.

Additional experimental details have been published.[5-10]

ESR spectra at X-band were measured with a Bruker 200D SRC spectrometer operating at 9.7 GHz (empty cavity at ambient temperature) and 100 kHz magnetic field modulation, interfaced with a data acquisition system based on an IBM PC/XT and the software EPRDAS (Mega Systems Solutions, Rochester, NY). Spectra were recorded at 110 K with use of the Bruker flow system; spectra at 77 K, taken in the finger dewar, were identical. We opted to work at the higher temperature, because of lower noise.

ESR spectra at 123 K, at C-band (4.7 GHz), at S-band (2.8 GHz), and at L-band (1.2 GHz) were measured at the National Biomedical Center in Milwaukee, WI, using spectrometers equipped with loop-gap resonators.[11] The data acquisition system is based on an IBM-PC/AT compatible computer using the VIKING software developed at the Center and written in FORTRAN.

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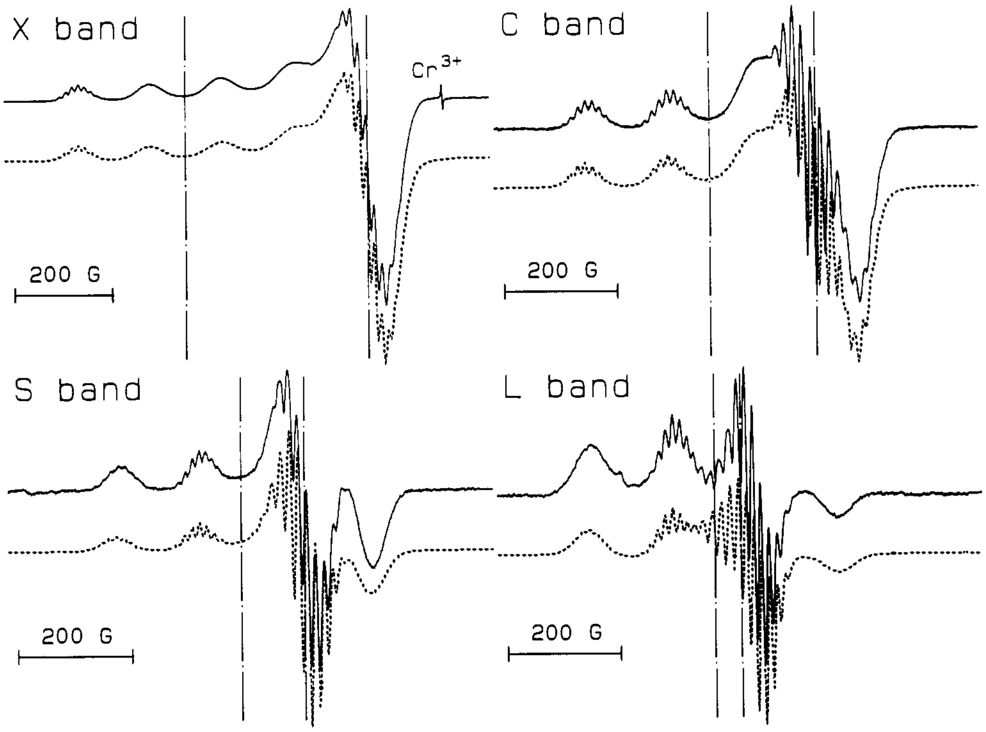

Figure 2. Experimental (—) and simulated (---) ESR spectra of Nafion/^{63}Cu^{2+} (Cu^{2+} concentration 4%) soaked *twice* by CH$_3$CN, at the X-band (9.36 GHz) and 110 K, and at the C-band (4.7 GHz), S-band (2.8 GHz), and L-band (1.2 GHz) at 123 K. Vertical lines (-•-) indicate the position of $g_{\parallel}$ (low field) and $g_{\perp}$ (high field).

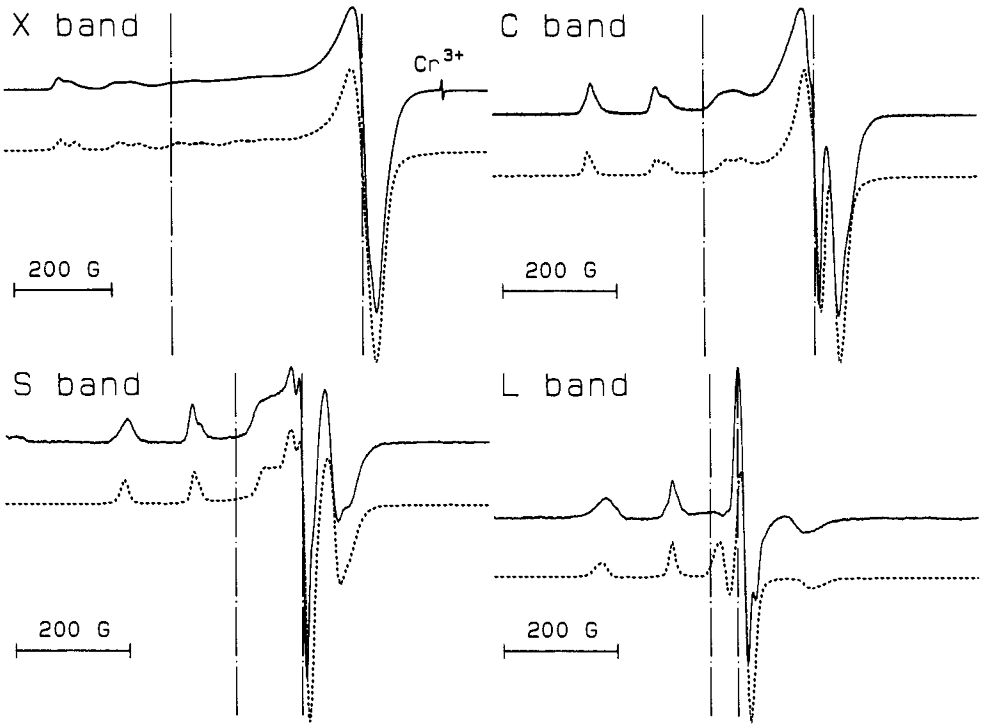

Figure 3. Experimental (—) and simulated (---) ESR spectra of Nafion/^{63}Cu^{2+} (Cu^{2+} concentration 4%) soaked *once* by CD$_3$CN, at the X-band (9.36 GHz) and 110 K, and at the C-band (4.7 GHz), S-band (2.8 GHz) and L-band (1.2 GHz) at 123 K. Vertical lines (-·-) indicate the $g_{\parallel}$ and $g_{\perp}$ values for site I, 2.3720 and 2.0830, respectively.

All spectra were recorded at a microwave power of 2 mw.

Spectra were simulated by an HP Vectra RS/20C computer equipped with a 386 processor, using programs developed in our laboratory and written in Turbo Pascal 5.0. For ease of comparison, all experimental and simulated spectra were transformed into the format used by EPR-DAS, using a Pascal program.

III. Results

1. ESR Spectra. The concentration of the cupric ions in Nafion is expressed in percent of the total amount required to fully neutralize the membranes, assuming two sulfonic groups per cation.

Typical ESR spectra at X-, C-, S-, and L-bands are presented in Figures 1–4. Spectra of Cu^{2+} (4%) in membranes that have been dried once to constant weight and soaked with dried ANH are shown in Figure 1. The values of $g_{\parallel}$ and $A_{\parallel}$ (^{63}Cu) are significantly different from those of Cu^{2+} in Nafion swollen by water. These changes are due to replacement of oxygen ligands by nitrogen ligands, as shown in the Peisach–Blumberg (PB)

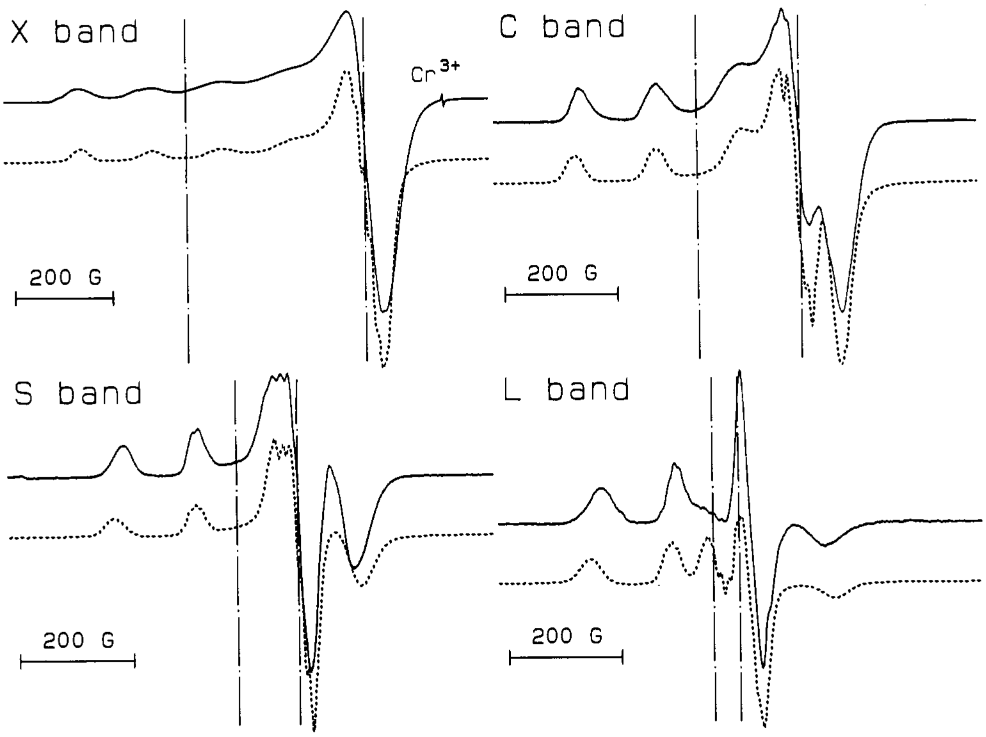

Figure 4. Experimental (—) and simulated (- - -) ESR spectra of Nafion/$^{63}Cu^{2+}$ (100% neutralization) soaked *once* by CH_3CN, at the X-band (9.36 GHz) and 110 K, and at the C-band (4.7 GHz), S-band (2.8 GHz), and L-band (1.2 GHz) at 123 K. Vertical lines (-••-) indicate the position of $g_\parallel$ (low field) and $g_\perp$ (high field).

diagrams.[12] Direct evidence for N-ligation is the broader lines in the parallel region, because of unresolved shf and the appearance of partially resolved lines in the perpendicular signals, clearly seen at X- and C-bands. Superhyperfine structure from nitrogen ligands is also seen in the second derivative of the parallel signals corresponding to $m_I = {}^3/_2$ at C-band and to $m_I = {}^1/_2$ at S- and L-bands (shown above the first derivative signals).

Spectra of Cu^{2+} (4%) in membranes that have been dried *twice* to constant weight and soaked with dried ANH are shown in Figure 2. Resolved splittings from ^{14}N are seen in the perpendicular region at all frequencies; even more significant is the improved resolution for the $m_I = -{}^1/_2$ parallel component at S- and L-bands and for the $m_I = -{}^3/_2, -{}^1/_2$, and ${}^3/_2$ parallel components at C-band. Indeed, the motivation for experiments at C-band was the expectation to improve the resolution at the *low* field edge of the parallel signal; the higher resolution at the *high* field edge ($m_I = {}^3/_2$ parallel signal) is an additional advantage.

Spectra of Cu^{2+} (4%) in membranes that have been dried once to constant weight and soaked with dried AND are shown in Figure 3. The reduced resolution for the $m_I = -{}^3/_2$ signal in the parallel region at the three lower frequencies, compared to X-band, is proof for the presence of cation sites differing in their $g_\parallel$ values, as suggested previously.[9] Drying the membranes and soaking with AND for the second time gives spectra that are almost identical with those given in Figure 2 and are not presented here.

Spectra of Cu^{2+} in membranes that have been fully neutralized, dried once to constant weight, and soaked with dried ANH are shown in Figure 4. Small differences are detected, compared to the results presented in Figure 1, which will be discussed in the next section. These membranes contain 78.6% of the amount calculated for fully neutralized membranes.[7]

ESR spectra at all microwave frequencies of Nafion neutralized by a cation mixture Cu^{2+} and Zn^{2+} (4 mol % Cu^{2+}) were also measured for membranes soaked once and twice by both ANH and AND. The spectra are very similar to those for the samples containing Cu^{2+} only (no zinc) and are not shown here.

2. Simulations. ESR spectra were simulated in an attempt to follow the process of replacement of the oxygen ligands from water and sulfonic groups by nitrogen ligands from acetonitrile. In calculating the spectra we assumed axial **g**, hyperfine, and superhyperfine tensors, with a common principal axes system. Line positions were calculated to second order for hyperfine and to first order for superhyperfine signals, and all ^{14}N ligands were considered identically bonded. The line shapes were a combination of Gaussian and Lorentzian components, chosen to obtain the best visual fit; the high-field rise into the base line in calculated spectra was particularly sensitive to the line shape chosen and was used as a criterion for the relative weights of the Gaussian and Lorentzian components. The high-field approximation was assumed at all microwave frequencies.

The full line width at half intensity of the parallel component $\Delta H_\parallel$ is composed of the residual width $\Delta H^R{}_\parallel$ and a contribution δH due to the distributions of $g_\parallel$ and $A_\parallel$, as shown below.

$$(\Delta H_\parallel)^2 = \left(\Delta H^R{}_\parallel\right)^2 + (\delta H)^2 \tag{1}$$

$$(\delta H)^2 = (m_I \delta A)^2 + \left(h\nu\delta g/g_\parallel{}^2\beta\right)^2 + \left(2\epsilon m_I h\nu/g_\parallel{}^2\beta\right)\delta g\delta A \tag{2}$$

In eq 2 β is the Bohr magneton, ν is the microwave frequency, and ϵ is a correlation factor between the distributions of $g_\parallel$ and $A_\parallel$. On the basis of previous simulations of Cu^{2+} centers ligated to oxygens only, we chose $\epsilon = 1$, meaning that the distributions are fully correlated, and all cations have the same $\delta g/\delta A$ ratio.[7,8] The last term in eq 2 can be positive or negative according to the value of m_I. This decreases the line broadening due to strain and is the origin of minima in the line width vs frequency curves.

No strain was introduced in the perpendicular component,[2] and an orientation dependent line width in the form given in eq 3 was used.

$$(\Delta H)^2 = (\Delta H_\parallel)^2 \cos^2\theta + (\Delta H_\perp)^2 \sin^2\theta \tag{3}$$

In calculating the intensity of ESR spectra a correction for the transition probability in a field-swept spectrum was introduced.[13]

To illustrate the importance and advantage of measuring multifrequency ESR spectra, we have plotted in Figure 5 the line

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Table I. Parameters Used To Simulate ESR Spectra at X-, C-, S-, and L-Bands for Cupric Ions in Nafion Membranes Swollen by Acetonitrile[a-c]

									X-band		C-band[d]		
system	$g_\parallel$	$g_\perp$	$A_\parallel(^{63}Cu)$	$A_\perp(^{63}Cu)$	$A_\parallel$(shf)	$A_\perp$(shf)	δg	δA	$\Delta H^R_\parallel$, G	$\Delta H^R_\perp$, G	$\Delta H^R_\parallel$, G	$\Delta H^R_\perp$, G	assignment and remarks
Cu(4%)/Nafion/ CH_3CN (soaked once)	2.3335	2.0720	0.0159	0.0011	0.0010	0.0013	0.0430	0.0024	13.0	20.0	13.0	17.0	2 N ligands
Cu(100%)/Nafion/ CH_3CN (soaked once)	2.3480	2.0794	0.0158	0.0011	0.0011	0.0012	0.0420	0.0024	13.0	20.0	13.0	17.0	1 N ligand (50%) 2 N ligands[e] (50%)
Cu(4%)/Nafion/ CH_3CN (soaked twice)	2.3472	2.0749	0.0160	0.0012	0.0015	0.0014	0.0190	0.0012	8.0	19.0	8.0	13.0	4 N ligands
Cu(4%)/Nafion/ CH_3CN (soaked once)	2.3720	2.0830	0.0146	0.0005			0.0300	0.0017	15.0	40.0	15.0	22.0	no N ligands[10]
	2.4100	2.0770	0.0137	0.0007			0.0300	0.0015	10.0	40.0	10.0	22.0	no N ligands[10]
Cu(4%)/Nafion/ CD_3CN (soaked twice)	2.3489	2.0749	0.0157	0.0012	0.0015	0.0014	0.0250	0.0016	5.0	18.0	5.0	12.0	4 N ligands

[a] For all simulations $\epsilon = 1$ was chosen (eq 2). [b] Principal components for the shf are calculated values, based on the *apparent* values used in simulations. [c] Values for the hyperfine and superhyperfine splittings are given in cm^{-1}. [d] Values at S- and L-bands are identical. [e] The parameters used to simulate species with one and with two nitrogen ligands are identical.

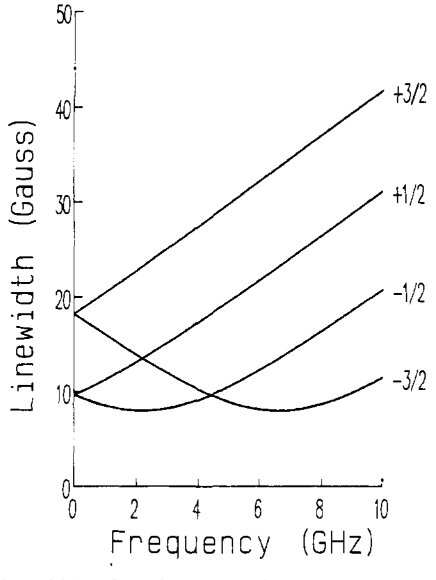

Figure 5. Line widths of the four parallel components ($\Delta H_\parallel$ in eq 3) as a function of the microwave frequency. The ESR parameters are those used to simulate the experimental spectra given in Figure 2, as listed in Table I.

width of the parallel component ($\Delta H_\parallel$) as a function of the microwave frequency for the four m_I values.[14] The line widths were calculated by using the parameters used to simulate the spectra given in Figure 2, the plots in Figure 5 are typical of all the samples studied. It is clear that for $m_I = -^1/_2$ the narrowest line can be detected at $\nu \approx 2$ GHz, and for $m_I = -^3/_2$ at $\nu = 6$–7 GHz.

The process of simulation was initiated by reading the approximate values of all parameters from the spectra. The **g**-tensor values were adjusted by fitting the spectra at X-band, which has the highest sensitivity to these changes. Next the shf pattern for the $m_I = -^3/_2$ and $-^1/_2$ parallel signals at C-band was used to adjust the ratio $\delta g/\delta A$, followed by variation of the δg and δA values in order to reproduce the experimental resolution of the parallel signals for $m_I = -^3/_2$ at X-band, $m_I = -^3/_2, -^1/_2$, and $^3/_2$ at C-band, and $m_I = -^3/_2$ and $-^1/_2$ at S-band.

For the final fit it was helpful to use Figure 6, which presents the calculated line widths at X-band and S-band as a function of δg for a fixed value of δA (10.9 G) and as a function of δA for a fixed value of δg (0.019). In both cases a fixed value of the residual line width, 8 G, was assumed. On the basis of Figures 5 and 6 it was possible to anticipate the effect of parameter variation on the data at the four microwave frequencies.[15]

Simulations were performed for one to four nitrogen ligands in each case and for multiple cation sites, as suggested by the spectra. The best parameters used in the simulations and the number and relative intensities of N-ligated complexes that were combined for the best fit are given in Table I.

The calculated spectra are presented in Figures 1–4, together with the experimental spectra. Some second derivatives of the calculated spectra are also given in Figure 1, to compare with experimental results. The agreement is very good for all spectra, with the possible exception of some data at L-band, most likely due to the breakdown of the high-field approximation. In general data at L-band have not contributed significantly to the choice of parameters used to simulate the spectra.

Examination of the parameters used in the simulations indicates that for four nitrogen ligands the widths of the $g_\parallel$ and $A_\parallel$ distributions are significantly lower than for the case of one and two such ligands. The values of δg are 0.019 and 0.025 (four ^{14}N ligands) for ANH and AND, respectively, compared to 0.043 (two ^{14}N ligands) for ANH; the corresponding values of δA are 10.9 and 14.3 G, compared with 22 G. This result suggests a more ordered and homogeneous system for Cu^{2+} fully ligated to nitrogen. In addition, we note that the $\Delta H^R_\perp$ values are larger at X-band than at the other frequencies, for instance 19 G vs 13 G in the case of four nitrogen ligands in Nafion/ANH, suggesting a small rhombic distortion of the g tensor, which is emphasized at X-band.

IV. Discussion

Solvation of Membrane by Acetonitrile. In our previous paper we suggested, from X-band ESR spectra only, ligation schemes for the various systems, based on the second derivative of the perpendicular component, where best resolution was observed.[9] Exact determination of the number of ^{14}N ligands was not possible, because the perpendicular component is complicated by forbidden transitions, extra lines derived from the powder line shapes, and a rhombic distortion. The advantage of basing our conclusions on the *parallel* component is that these complications are not expected. The disadvantage is that the effect of *strain* is important along the parallel component; this problem has been solved here by using multifrequency ESR.

In many systems the Peisach–Blumberg diagrams can be used to deduce the ligation scheme, because the number of ^{14}N ligands can be correlated with a decrease of the $g_\parallel$ value and an increase in the $A_\parallel$ value, compared with Cu^{2+} ligated to oxygen only. For four nitrogen ligands these diagrams predict $g_\parallel < 2.3$ and $A_\parallel > 0.0160$ cm^{-1}. Yet the ESR parameters read directly from the spectra presented here are outside the range predicted by the PB diagrams, suggesting that the PB predictions cannot be used in our system. This is probably due to a distortion from the square-planar symmetry considered in the PB diagrams, when the

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(14) Hyde, J. S.; Froncisz, W. *Annu. Rev. Biophys. Bioeng.* **1982**, *11*, 391.

(15) The program is available from the authors by request.

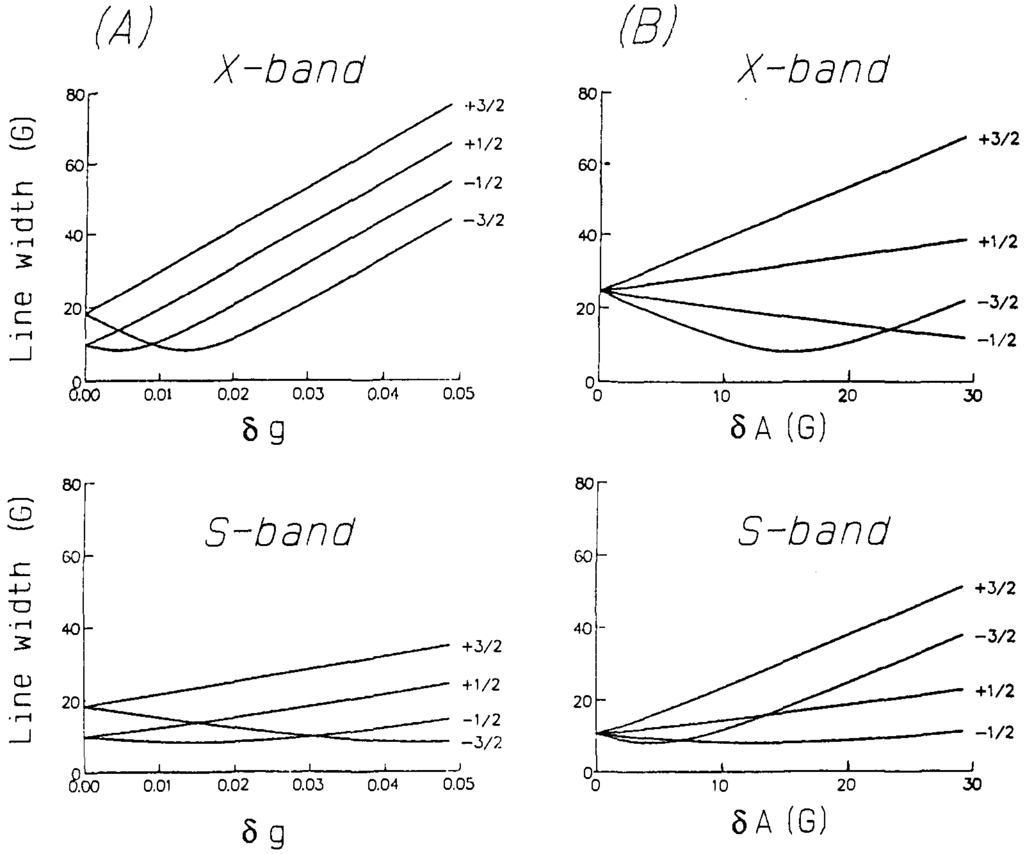

Figure 6. (A) Line widths of the parallel component as a function of δg, for δA = 10.9 G and $\Delta H^R_\parallel$ = 8 G at X-band and S-band. (B) Line widths of the parallel component as a function of δA, for δg = 0.019 and $\Delta H^R_\parallel$ = 8 G, at X-band and S-band. The other parameters are those used to simulate spectra given in Figure 2 and are listed in Table I.

ligands are nitrogens from ANH or AND.

As indicated in Table I, the results suggest one site for Cu^{2+} in Nafion exchanged once with ANH, with *two* ^{14}N ligands; the same number of N ligands has been detected for Nafion neutralized by a mixture of Cu^{2+} and Zn^{2+} cations (4% Cu^{2+}). In the case of Nafion fully neutralized by Cu^{2+}, we simulated the spectra by assuming two sites, with one and two nitrogen ligands, respectively, in an approximately 1:1 ratio, as indicated in Table I.

The simplest case to consider is that of Cu^{2+} in Nafion twice exchanged with the solvents (deuteriated or protiated), because of the high resolution obtained experimentally (Figure 2). Results of the multifrequency ESR spectra and of the simulations indicate four ^{14}N ligands.

Isotope Effect. For Nafion/Cu^{2+} (4%) exchanged once with AND we deduce *no* nitrogen ligands. This result means an isotope effect in the solvation of the membrane by AND and ANH, detected here for this solvent in Nafion for the first time. We found in the literature a report of an isotope effect in the solvation of both Nafion and Dowex ion-exchange membranes by water: H_2O is preferentially retained, compared with D_2O.[16,17] Moreover, the effect seems to depend on the type of cation in Nafion and is enhanced in acid Nafion compared with Nafion neutralized by Li^+ or Cs^+. The *direction* of the effect is similar to that reported here. We attribute the isotope effect to the different solvation of the sulfonic groups and of the cations in the membranes studied (H^+, Cu^{2+}, Zn^{2+}) by the protiated and deuteriated solvents. The small variations in the ligation scheme detected for Cu^{2+} in the membranes neutralized by the various cations is an indication that the solvation properties of the membrane depend on the presence of the sulfonic groups *and* on the specific cation. Preferential solvation in Nafion can be detected provided the membranes are treated with the solvent under rigorously identical conditions and on the same membrane.[18]

^{14}N Superhyperfine Splitting. Nitrogen ligands in the equatorial plane have a principal direction of the shf tensor along the Cu–N bond ($A_\parallel$(shf)). Because of the cylindrical symmetry of the **g** tensor, it is impossible to measure this nitrogen coupling constant directly from experimental spectra. For the magnetic field along $g_\parallel$ we detect an *apparent parallel* component ($A^{APP}{}_\parallel$(shf)) that is the *perpendicular* component of the shf tensor, or $A^{APP}{}_\parallel$(shf) = $A_\perp$ (shf). For the field direction perpendicular to $g_\parallel$ we expect splittings from both *parallel* and *perpendicular* shf tensor components.[19] The ^{14}N shf tensor has a dominant isotropic component[20] and therefore the net effect is a broadening of the signals in the perpendicular direction, and an apparent shf that represents an average: $A^{APP}{}_\perp$(shf) = 0.5 ($A_\parallel$(shf) + $A_\perp$(shf)). The *true* components of the shf tensor can then be calculated from the apparent values and are given in Table I. These values were used to simulate the experimental results.

Inspection of the spectra given in Figure 2 indicates that the nitrogen splittings on a given parallel component, for instance for $m_I = -^3/_2$ at X- and C-bands, and for $m_I = -^1/_2$ at C- and S-bands, are *narrower* at the low-field edge of the component. This indicates a *distribution* of the shf, similar to that of the hyperfine splitting from ^{63}Cu. For simplicity we did not include this distribution in the simulations.

V. Conclusions

1. The gradual replacement of oxygen ligands around Cu^{2+} with nitrogen ligands in Nafion soaked with acetonitrile has been deduced from ESR spectra at four microwave frequencies and from computer simulations.

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2. Details on ligation are based mostly on an analysis of the *parallel* component of the ^{63}Cu hyperfine tensor, because of the higher resolution possible in multifrequency ESR spectra.

3. After one cycle of drying the membranes and soaking with acetonitrile two ^{14}N ligands around Cu^{2+} are deduced for CH_3CN and *none* for CD_3CN. The isotope effect is due to the difference in the solvation energies of the sulfonic groups and cations with deuteriated and protiated solvents.

4. The components of the superhyperfine tensor from ^{14}N have been deduced, taking into consideration the *apparent* tensor values determined along the parallel and perpendicular directions of the **g** tensor.

5. Ligation details are deduced from multifrequency ESR: spectra at X-band are very important for deducing the **g**-tensor components; spectra at C-band are critical for the determining the ratio of the distribution parameters due to strain, $\delta g/\delta A$; the enhanced resolution for the signals corresponding to $m_1 = -^3/_2$ and $-^1/_2$ at C-band, to $m_1 = -^3/_2$ at X-band, and to $m_1 = -^1/_2$ at S-band is crucial for determining the many parameters involved in the simulation of experimental results.

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Selective Two-Dimensional NMR Experiments for Topological Filtration of Fragments of Coupling Networks

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Abstract: In high-resolution NMR, a network of scalar-coupled spins can be broken down into fragments which encode information about the chemical shifts and couplings that are relevant to a cross-peak multiplet in a two-dimensional correlation ("COSY") experiment. Novel selective two-dimensional NMR correlation methods ("soft-COSY") are described which allow one to identify fragments on the basis of their topology. These new experiments allow one to "zoom in" on complicated cross-peak multiplets and include "passive spin filters" (PSFs), consisting of selective inversion pulses applied at the frequencies of passive coupling partners, i.e. spins that are not directly observed in the cross-peak multiplets under investigation. It is demonstrated how such PSFs can be inserted at various points in two-dimensional experiments and how such experiments can be characterized in terms of topology. The topology, couplings, and shifts of a fragment may be represented by a matrix **M**, while a selective experiment can be represented by a matrix **P**. Several degrees of matching of **M** and **P** can be distinguished. The techniques, which provide a novel method of discriminating and assigning spin systems, are demonstrated on a cyclopropane derivative and the cyclic undecapeptide cyclosporin.

Introduction

Two- and three-dimensional NMR experiments provide convenient methods for determining the parameters of a nuclear spin system, such as chemical shifts and scalar couplings among the protons and other nuclei in molecules dissolved in isotropic solution.[1,2] Traditionally, physical chemists tend to think of couplings and shifts as parameters of the "static" spin Hamiltonian (averaged over molecular motion), while organic chemists often prefer an interpretation which emphasizes the role of the chemical environment (substituent effects, etc.). With the development of multidimensional spectroscopy, a third formulation is beginning to emerge, which may help to bridge the gap. This description depicts the ensemble of spins and their mutual couplings by a *coupling network*. In such a graph, the spins (for example protons) are represented by *nodes* and the couplings by *edges*. A coupling network is a chromatic graph, since the nodes carry information about the chemical shifts (which might be represented by a frequency or "color", e.g. a shift expressed in ppm with respect to a standard) while the edges are labeled by the magnitude and sign of the couplings (also in units of frequency, usually in Hz). Strickly speaking, such a graph is nothing but a representation of the Hamiltonian and contains neither more nor less information than a table of shifts and couplings. The great advantage of a graph however lies in that it can be easily partitioned into subgraphs which we call *fragments*. A network with n scalar couplings can be split into n fragments. A fragment can be defined so as to contain all the information that is relevant to the frequency coordinates and fine structure of a cross-peak multiplet in a two-dimensional spectrum. Such a fragment F^{kl} consists of two active nodes A^k and A^l, plus all passive nodes P_i^{kl} coupled to the active nodes. We must distinguish *cyclic* passive nodes that are connected to both active nodes and *noncyclic* passive nodes which are coupled only to one active node. In earlier studies,[3,4] only the chemical shifts of the active nodes were considered relevant to the definition of a fragment, while in this paper the shifts of the passive nodes are also essential. On the other hand, while in earlier studies we had to consider the actual magnitudes of the couplings (and, in the case of cyclic passive nodes, also their relative signs) we are now primarily interested in the "topological" question of whether a coupling is observable or can be neglected.

There is a wide range of two-dimensional NMR experiments that may help to determine the parameters of a coupling network. Correlation spectroscopy ("COSY") and its many relatives, including variants such as multiple-quantum NMR, can be used for this purpose.[1,2,5-10] By and large, however, all of these

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