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Determination of the Distance between Paramagnetic Centers from Electron Spin Resonance Spectra at L, S, and X Bands. Copper(2+) in Nafion Ionomers

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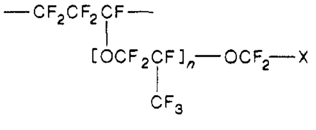
ABSTRACT: The distance between Cu^{2+} cations in perfluorinated membranes containing terminal SO_3^- groups has been deduced from an analysis of ESR spectra at L (1.25-GHz), S (2.36-GHz), and X (9.36-GHz) bands. The concentration of the cupric ion in the membranes is in the range 1-30% of the total amount needed to fully neutralize the pendant acid groups. At higher cation concentration, ESR spectra indicate the presence of regions containing *aggregated* ions. The distribution of the $g_\parallel$ and $A_\parallel$ (^{63}Cu) values makes an important contribution to the line widths of signals from *isolated ions*. The intercation distance d as a function of cation concentration was deduced as follows. First, the line widths of the $m_I = -^3/_2$ and $-^1/_2$ parallel transitions at S and X bands were used to estimate the residual width, the widths of the $g_\parallel$ and $A_\parallel$ distributions, and the correlation factor ϵ. Second, these values were finalized by simulating the experimental spectra in the entire cation concentration range at the three microwave frequencies. Third, the increase in the residual line width compared to that at the lowest cation concentration, $\delta(\Delta H)$, was used to calculate d, assuming a model for the relative positions of the cations. We suggest that determination of the distribution widths from ESR measurements at one frequency only, usually at X band, can introduce large errors in the values deduced for the residual widths and therefore also for the intercation distance. Choice of the correct parameters used for spectral simulations should be based on ESR spectra taken at *two* or more microwave frequencies. The intercation distances determined are less than those determined by assuming a homogeneous distribution of cations, thus reflecting the presence of the cations in the hydrophilic phase. Even at the highest cation concentration, we deduced $d > 10$ Å. This value is large enough to accommodate cupric ions fully hydrated by water molecules. This conclusion is in agreement with our recent suggestion that only in dimers, and perhaps in higher aggregates, are the cupric ions ligated to the sulfonic groups of the ionomers.

Introduction

Ionic polymers, or ionomers, are polymers consisting of an organic backbone and some ionic groups.[1,2] Most ionomers contain pendant acid groups that can be neutralized by addition of metal cations;[3-5] the amount of ionic groups is in most cases less than 10 mol %. Ionomers, some of which are used as ion selective or separation membranes, have been studied in order to assess the effect of incorporated ions on membrane morphology and to deduce the structure of the membrane containing various solvents and other guests.

The central question in ionomers research is the distribution of the ionic species. In small-angle X-ray scattering (SAXS) experiments, an extra peak is detected in ionomers containing various cations; this peak has been interpreted as an indication for the formation of ionic domains.[3,6-8] The value of the scattering vector corresponding to the maximum scattering has been used to deduce the size of the ionic domains. The exact interpretation of the scattering parameters is model dependent, as discussed in a recent paper by Yarusso and Cooper.[8] It is of great interest to deduce not only the size of the ionic domain but also the distribution of the ionic charges and the intercation distance.

Many of the present ideas on the structure of ionomeric membranes emerged from studies of perfluorinated ionomers made by Du Pont, which are used commercially as separation membranes in electrochemical cells.[6] These ionomers, known by their trade name of Nafion, have a Teflon backbone with pendant carboxylic or sulfonic groups attached to a perfluoro ether side chain. The acid groups can be neutralized to give various metal salts. Perfluorinated ionomers are very attractive for a variety of measurements because of their mechanical and thermal resistance as well as chemical stability in acids, bases, and oxidizing and reducing media.



Nafion
X = COOH or SO_3H

In recent years we have investigated Nafion membranes neutralized by paramagnetic cations, using electron spin resonance (ESR) and electron nuclear double-resonance (ENDOR) spectroscopy. The goal of our studies is to obtain information on the local environment and specific ligation of the ion as a function of water, or solvent, content, on the ionic mobility as a function of temperature and on the distribution of ionic species in the membranes. This type of information is necessary for an understanding of the ionic transport and selectivity properties of the membranes and the diffusion of gases and small molecules such as water in these media.

In a previous publication,[9] we reported an ESR study of Nafion-containing mixtures of paramagnetic Cu^{2+} and *diamagnetic* Zn^{2+} *as a function of temperature,* water content, and Cu^{2+} concentration in the cation mixture. In that study, we obtained direct spectroscopic evidence for location of the paramagnetic cation in two sites: Cu^{2+} ligated to water oxygens and to sulfonate groups of the polymer backbone in site I and only to water oxygens in site II. Cu^{2+} in site II was also observed to be ligated to both "mobile" and "bound" water. Cu^{2+}–Cu^{2+} pairs were observed at high Cu^{2+} concentrations and were identified by the appearance of the $\Delta m_s = 2$ spin-forbidden transition.

In Nafion swollen by water and methanol and equilibrated by Cu^{2+} and Ti^{3+} paramagnetic ions, we have detected cation aggregation even in membranes that have been only partially neutralized by the cations.[10] The ligation of the cations at low concentrations, below 30% of the amount needed for full neutralization, has been studied in detail. An important conclusion obtained from this study is that both isolated *and* aggregated ions exist in a large concentration range of the paramagnetic cations. For

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the isolated ions, the intercation distance was estimated to be greater than ~10 Å; in ionic aggregates, this distance seems to be close to 5 Å. The dynamics of Ti^{3+} cations in Nafion swollen by methanol has been measured and simulated by using the Bloch equations.[11] In a recent ENDOR study, we have estimated the distance between the paramagnetic cation and the fluorine nuclei, from an analysis of the ^{19}F matrix ENDOR signal.[12]

In this report we present a measurement of the intercation distance for isolated (nonclustered) ions in Nafion neutralized by Cu^{2+} and swollen by water, as a function of Cu^{2+} concentration. This study is based on measurements of ESR spectra at three microwave frequencies: L (1.25-GHz), S (2.36-GHz), and X (9.36-GHz) bands. The basic approach is to divide out the contribution of a distribution in the $g_\parallel$ and $A_\parallel$ (^{63}Cu) values to the line width, in order to extract the contribution of the electron–electron dipole interaction, which reflects the intercation distance. This distance, deduced from experimental spectra, is then compared with the distance deduced on the basis of a homogeneous distribution of cations in the membrane.

Experimental Section

The Nafion 117 membrane, with an equivalent weight of 1100 g/mol of SO_3H and a thickness of 0.13 mm, was cleaned by soaking in 2-propanol, acidified in a 9 M H_2SO_4 solution, rinsed with deionized water, and dried to constant weight (24-h evacuation at ambient temperature and 3 h at 373 K, to a final dynamic pressure of 2×10^{-5} Torr). Nafion swollen by D_2O and equilibrated with Cu^{2+} enriched in the ^{63}Cu isotope was prepared, in order to obtain maximum resolution in all ESR spectra. ^{63}Cu (98%) as CuO was purchased from Oak Ridge National Laboratory and was reacted with stoichiometric amounts of D_2SO_4 in order to obtain $^{63}CuSO_4$ in D_2O. This solution was used for equilibration of the membranes. The pH of the solution containing the membrane varied from 2.2 to 2.5. Additional experimental details have been published.[9-12]

ESR spectra at the X band were measured with a Bruker 200D SRC spectrometer operating at 9.7 GHz, using 100-kHz modulation. Data acquisition and manipulation is based on an IBM PC, using the software EPRDAS (Mega Systems Solutions, Inc., Rochester, NY). Spectra were measured in the temperature range 100–300 K using the Bruker variable-temperature unit ER 4111 VT. Spectra at 77 K were taken in a liquid nitrogen Dewar inserted in the ESR cavity. The absolute value of the magnetic field was measured by using the Bruker ER 035 NMR gaussmeter. Calibration of g values was based on 2,2-diphenyl-1-picrylhydrazyl (DPPH) ($g = 2.0036$) and Cr^{3+} in MgO ($g = 1.9800$).

ESR spectra at the L band (1.25 GHz) and at the S band (2.36 GHz), at 123 K, were measured at the National Biomedical Center in Milwaukee, WI, using spectrometers equipped with loop-gap resonator cavities.[13]

Spectra were simulated by a Burroughs 6800 mainframe computer at the University of Detroit and plotted with an IBM PC and a Hewlett-Packard 7440A digital plotter.

In order to calculate the intercation distance based on a homogeneous distribution of cations, it is necessary to measure the water, copper, and sulfonic acid contents, as well as the density of the membranes.

The water content in Cu^{2+} containing Nafion was determined gravimetrically by weighing the difference between water-saturated membranes and membranes dried under vacuum to a constant weight and a pressure of 2×10^{-5} Torr. This treatment requires evacuation at ambient temperature for 24 h and heating under vacuum for 1–3 h at 373 K.[14]

For determination of the copper content, dry Nafion H membranes were soaked in a solution of $CuSO_4$ containing a theoretical amount of cupric ion, as calculated for partial equilibration of the sulfonic groups. After allowing ca. 3 days for equilibration, the membranes were washed with water (3 times) and maintained at 100% relative humidity. Finally the membranes were dried to constant weight, and the copper content was analyzed by atomic absorption (AA, by Galbraith Laboratories, Inc.). The relation between the available amount and that retained by Nafion and deduced from AA is presented in Figure 1.

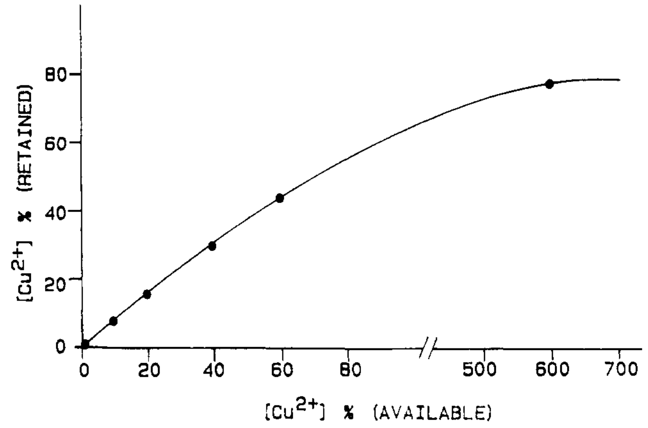

Figure 1. Concentration of the cupric ion in water-saturated Nafion (determined by atomic absorption) as a function of the amount available to the membrane (100% Cu^{2+} is the stoichiometric amount needed for full neutralization of the membrane).

Table I
Composition of Nafion-Cu^{2+}-H_2O Membranes

[Cu^{2+}], % retained	wt % H_2O (±1)	mol of H_2O/ mol of SO_3^-	mol of H_2O/ mol of Cu^{2+}	ρ (±0.05), g/cm^3
0	19.8	15		1.67
1	20.8	16	3500	1.69
8.3	18.7	14	350	1.73
16.2	18.7	14	179	1.77
30.5	17.6	13	88	1.75
44.9	15.5	11	51	1.80
78.6[a]	26.4	23	59	1.74

[a] This notation corresponds to samples equilibrated with Cu^{2+} after pretreatment of the membrane, *without evacuation of water to constant weight*. The membranes were equilibrated in a volume of 0.01 M Cu^{2+} solution containing 600% of the theoretical amount needed to fully equilibrate the sulfonic acid groups present in the membranes. The water content is affected by this type of treatment.

The sulfur content of some samples was also determined. The most important results are given in Table I.

The density of the membranes was determined by the buoyancy method, from measurements of the weight of the membrane in air and in hexane.[15,16]

All the results of this study are given in terms of the cupric ion retained by the membrane. This is considered advantageous for comparison with other studies of ionomers.

Results

ESR spectra were measured at the X band at 100 K and at the L and S bands at 123 K for a series of Nafion samples containing 1–80% Cu^{2+}, based on the stoichiometric amount needed for full equilibration of the membrane (two sulfonate groups per Cu^{2+} ion).

X-band ESR spectra of $^{63}Cu^{2+}$ in Nafion at 100 K and 100% relative humidity as function of the mole percent of copper ions as defined above are shown in Figure 2A.[10] The spectra are reproducible within the pH variation mentioned above. For low cation content, the spectral parameters indicate ligation of the Cu^{2+} ion to six water oxygens, site II.[9] For the higher cation contents, a strong signal appears, superimposed on the spectra from isolated ions, and is assigned to Cu^{2+} clusters. The increase in the line width of the signal from the parallel orientation with the cation concentration is shown in Figure 2B; the increase is attributed to magnetic dipole interaction between Cu^{2+} ions and can be used to determine the intercation distance. Dipole–dipole interaction is expected to contribute equally to all lines defined by an m_I value, whereas experimentally the lines of the parallel quartet have widely

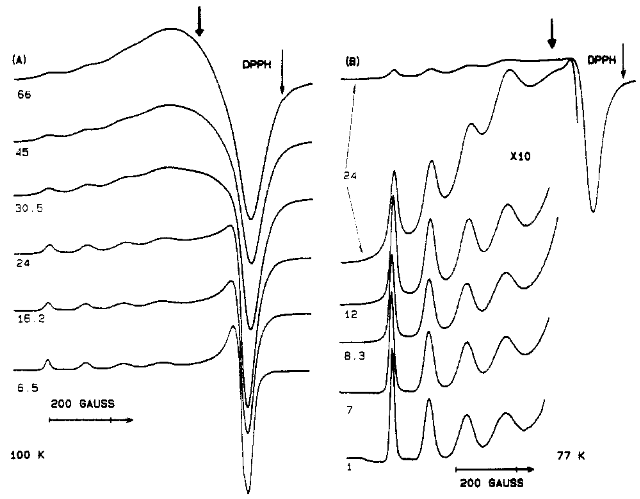

Figure 2. X-band ESR spectra of Nafion–^{63}Cu^{2+}–D$_2$O. (A) Indicated concentration of the cupric ion [Cu^{2+}] in water-saturated membranes, at 100 K. (B) Effect of increasing cation concentration [Cu^{2+}] on the line widths of the parallel component for the ^{63}Cu hyperfine tensor, at 77 K. The thick arrows indicate the approximate position of the cluster signal. (Adapted from ref 10. Copyright 1987 Royal Chemical Society.)

different amplitudes, most clearly seen at low Cu^{2+} concentrations. This means that the line widths cannot be used *directly* for intercation distance determination; first it is necessary to deduce the effect responsible for the unequal amplitudes of the four lines.

The variation of the line widths from the parallel component with m_I presented in Figure 2 has been observed before for Cu^{2+} in frozen glasses and treated phenomenologically,[17] assuming an explicit m_I dependence of the line width H or by generating a powder spectrum through superposition of spectra with different values of $g_\parallel$ and $A_\parallel$.[18-20]

A model proposed by Froncisz and Hyde[21] has satisfactorily explained both the m_I and the microwave frequency dependence of the line widths. The model is based on the assumption that small site fluctuations of molecular bonding parameters affect the range of values for $g_\parallel$ and $A_\parallel$. According to this model, the line widths measured in the parallel orientation have a contribution from the distribution parameters $\delta g_\parallel$ and $\delta A_\parallel$ and are frequency dependent. The line width at half-maximum intensity, $\Delta H_\parallel$, is composed of the residual width, $\Delta H_\parallel{}^{R}$, and a contribution from the distribution δH, as shown in eq 1.

$$(\Delta H_\parallel)^2 = (\Delta H_\parallel{}^{R})^2 + (\delta H)^2 \qquad (1)$$

The width due to the distribution, δH, depends on the m_I value, on the microwave frequency, ν, and on the distribution parameters $\delta g_\parallel$ and $\delta A_\parallel$. In eq 2, β is the Bohr

$$(\delta H)^2 = (m_I \delta A_\parallel)^2 + \left(\frac{h\nu\delta g_\parallel}{g_\parallel{}^2\beta}\right)^2 + \frac{2\epsilon m_I h\nu}{g_\parallel{}^2\beta}\delta g_\parallel \delta A_\parallel \qquad (2)$$

magneton and ϵ is a parameter that indicates the extent of correlation between $\delta g_\parallel$ and $\delta A_\parallel$. If $\epsilon = 1$, these distributions are "perfectly correlated", in the sense that all ligated ions have the same ratio $\delta A_\parallel/\delta g_\parallel$. The last term in the expression for the line width, eq 2, depends on the microwave frequency and can be either positive or negative. For negative values of m_I, there is one value of m_I that, due to cancellation of terms in eq 2, results in the narrowest line observed.[22]

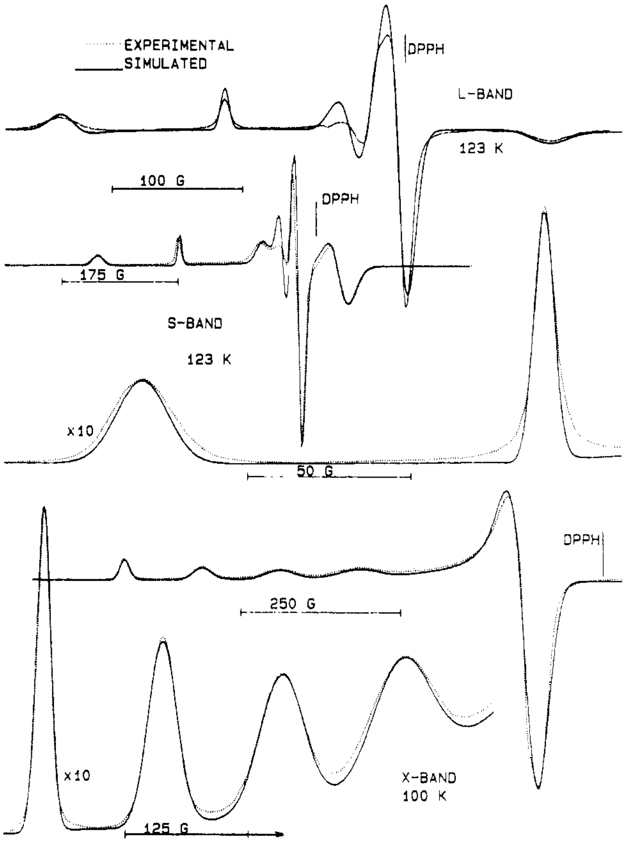

Figure 3. Simulated (—) and experimental (···), ESR spectra of Nafion–^{63}Cu^{2+}–D$_2$O (Cu^{2+} concentration 4.5%), at the L band (1.25 GHz) and 123 K, at the S band (2.36 GHz) and 123 K, and at the X band (9.36 GHz) and 100 K.

In Figure 3 ESR spectra of Cu^{2+} in Nafion saturated with D$_2$O at the L and S bands at 123 K and the X band at 100 K are shown; the sample contains 4.5 mol % cupric ions. S- and L-band spectra were measured at 123 K because of experimental convenience. Comparison with X-band spectra at 77 and 100 K is appropriate, because no change in the spectra has been detected in the temperature range 77–123 K. The dramatic changes between the spectra at low microwave frequency and those taken at the X band indicate the effect of the microwave frequency on the line shapes and line widths. The results obtained for a range of Cu^{2+} concentrations at the S band, 123 K, are shown in Figure 4.

The four parameters that determine the line width given in eq 1 and 2, $\delta A_\parallel$, $\delta g_\parallel$, $\Delta H_\parallel{}^{R}$, and ϵ, were first estimated from the experimental values of the line widths corresponding to $m_I = -{}^3/_2$ and $-{}^1/_2$ lines obtained from spectra at the S and X bands, using a least-squares fitting program. These values were used initially to simulate the experimental spectra at the two frequencies and varied so as to obtain the best fit; the set of parameters for each cupric ion content was deduced by comparison of spectra calculated using an axial spin Hamiltonian, which specifically includes the line width dependence on the distribution parameters and Gaussian line shapes, with experimental spectra. The only additional assumption made in the simulations is that the principal values of the g and A tensors are independent of the cation concentration; this assumption seems justified, because the positions of the lines do not change with changing cupric ion content. An orientation-dependent line width was used, eq 3, with $\Delta H_\perp = \Delta H_\perp{}^{R}$.

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

In eq 3 θ is the angle between the magnetic field and the symmetry axis ("parallel" direction) of the Cu complex.

Table II
Variation of Experimental Line Width ($\Delta H_{\parallel}$) at the X and S Band and Distribution Parameters ($\Delta H_{\parallel}^{R}$, $\delta g_{\parallel}$, ϵ) on Spectra Simulation of Nafion-$^{63}Cu^{2+}$-D_2O as a Function of Cu^{2+} Equilibration at 100 K^a

	ΔH for S band, G		ΔH for X band, G					
[Cu^{2+}], mol %	$m_I = -^3/_2$	$m_I = -^1/_2$	$m_I = -^3/_2$	$m_I = -^1/_2$	$\Delta H_{\parallel}^{R}$, G	$\delta g_{\parallel}$	$\delta A_{\parallel}$, G	ϵ
1	19.3	6.5	16.7	32.5	5.8	0.034	18.7	0.96
4.5	22.6	7.3	17.0	35.4	6.3	0.037	18.0	0.99
6.5	23.2	9.7	17.3	35.5	9.5	0.036	18.0	0.98
8.3	25.4	10.5	18.1	36.6	10.2	0.038	19.0	0.97
12.5	29.0	17.9	21.1	39.8	17.0	0.041	19.5	1.00
16.2	28.3	20.0	24.8	42.8	19.0	0.042	19.0	1.00
24.0	31.9	23.8	30.0	49.7	23.8	0.046	19.5	1.00
28.0	34.2	27.4	32.9	53.8	25.0	0.048	19.5	1.00
30.0	35.7	28.1	32.5	55.0	26.5	0.049	19.5	1.00
30.5	38.9	30.2	34.8	60.4	27.0	0.050	19.5	1.00

^{a}Using $g_{\parallel} = 2.416$, $g_{\perp} = 2.080$, $A_{\parallel} = 121$ G, and $A_{\perp} = 8$ G.

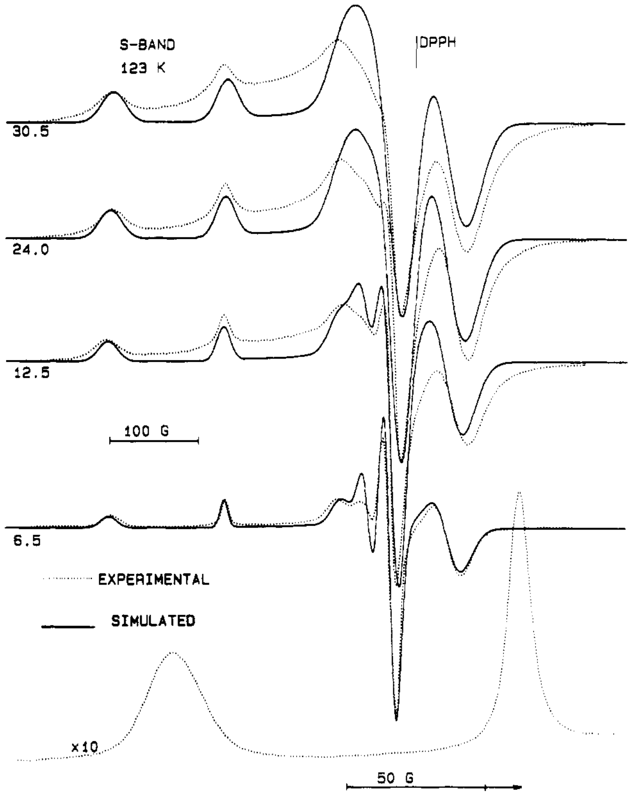

Figure 4. Simulated (—) and experimental (···) S-band ESR spectra of Nafion-$^{63}Cu^{2+}$-D_2O at 123 K, for the indicated concentration of cupric ion in water-saturated membranes.

The simulations for 1% Cu^{2+} content are shown in Figure 5, superimposed on the experimental spectra at the S band and X band, respectively. The agreement between the calculated and the experimental spectra is very good. Numerous simulations were performed in order to assess the effect of the various parameters in all simulated spectra. The results indicate that the simulated spectra are very sensitive to the choice of the distribution parameters and to the values of the residual widths $\Delta H_{\parallel}^{R}$ and $\Delta H_{\perp}^{R}$. The sets of parameters used for simulating spectra given in Figures 3–5 seem to be, therefore, unique.

For cation concentrations equal to or below 10%, excellent agreement of simulated and experimental spectra has been obtained, at both S and X bands. Above 10% content of cupric ions, the agreement is not so good, most likely due to the presence of the signal from cation aggregates, as seen in Figure 2A. The line widths of the two low-field lines in spectra at both frequencies are, however, the same in calculated and experimental spectra. This effect is clearly seen in Figure 6, where simulated spectra at the X band and two cupric ion contents are presented.

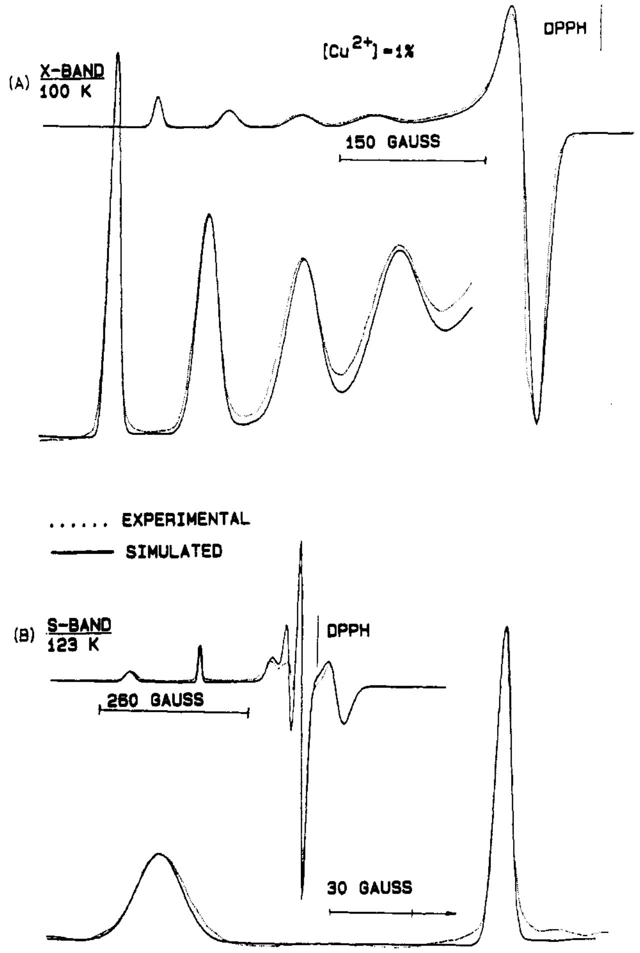

Figure 5. Simulated (—) and experimental (···) ESR spectra of Nafion-$^{63}Cu^{2+}$-D_2O (Cu^{2+} concentration 1%) saturated by D_2O. (A) X band, 100 K, $\nu = 9.376$ GHz. (B) S band, 123 K, $\nu = 2.359$ GHz.

The line widths and the distribution parameters used to stimulate all S-band and X-band spectra are given in Table II.

In Figure 7 we present the line widths corresponding to the four parallel transitions as a function of the microwave frequency, calculated for 4.5% cation content in the membranes, using the distribution parameters, and the residual widths from Table II. The experimental points are also indicated. The parameters used for calculating these curves predict accurately the slight increase in the line width of the $m_I = -^1/_2$ transition and the larger increase in the line width of the $m_I = -^3/_2$ transition at the L band, compared to those measured at the S band. It is

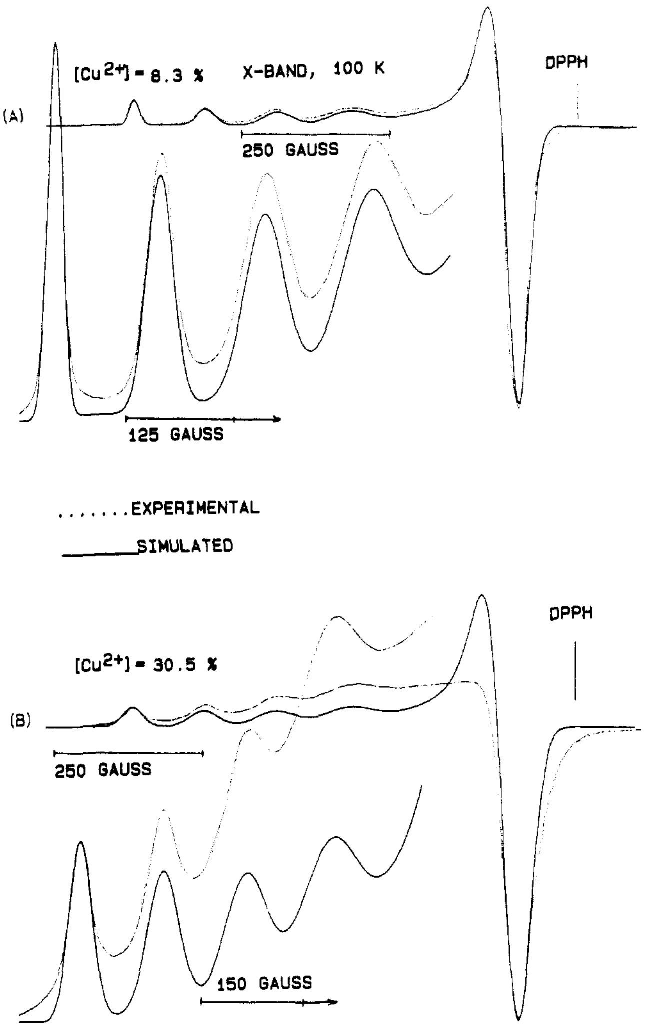

Figure 6. Simulated (—) and experimental (···) ESR spectra of Nafion-$^{63}Cu^{2+}$-D_2O. (A) Cu^{2+} concentration is 8.3%. (B) Cu^{2+} concentration is 30.5%. Nafion is D_2O saturated at 100% relative humidity.

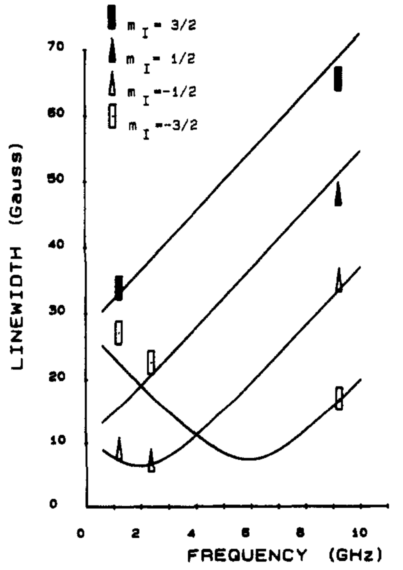

Figure 7. Variation of the line width from the four signals of the parallel transition as a function of the microwave frequency, for copper content of 4.5%. The solid lines are calculated from the values of $\Delta H_{\parallel}^{R}$, $\delta g_{\parallel}$, $\delta A_{\parallel}$, and ϵ given in Table II. Measured values at the S, L, and X bands are also indicated.

interesting to note that the line widths for positive m_I values, $^1/_2$ and $^3/_2$, increase with the microwave frequency; at the lower frequencies, however, it is difficult to measure these widths, because the signals are close to the perpendicular transition. For this reason, we have not included in Figure 7 a line width corresponding to $m_I = {}^3/_2$ at the S band.

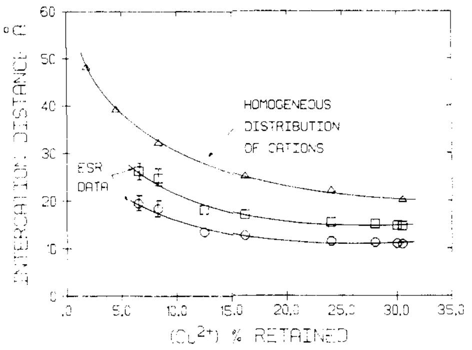

Figure 8. Variation of the intercation distance with concentration of the cupric ion in water-saturated Nafion. The upper limit for the intercation distance, obtained from ESR data, is calculated assuming a hexagonal array or a cubic octahedral arrangement of the ions; the lower limit is based on two interacting cations. The distance calculated by assuming a homogeneous distribution of the cations is also indicated.

From Table II it can be observed that the residual widths of the parallel and perpendicular components increase with the copper concentration. The increase in line width, compared with that at the lowest cation concentrtion where no such interaction is assumed, is due to magnetic dipole–dipole interaction. The interaction distance, d, can be calculated by observing that for two interacting paramagnetic cations the dipolar contribution, $\delta(\Delta H)$, to the line width for Gaussian lines is given by the equation[23]

$$\delta(\Delta H) = 2[(3/5)g^2\beta^2 S(S+1)]^{1/2} d^{-3} \tag{4}$$

If the isotropic g value of 2.192 is used, we obtain the relation between the intercation distance, d (in angstroms) and the observed broadening (in gauss):

$$\delta(\Delta H) = 27255 d^{-3} \tag{5}$$

A similar expression holds for a linear array of cations, except for a numerical factor of $2^{1/2}$. For a two-dimensional hexagonal array of cations, or a cubic octahedral array, the numerical factor is $6^{1/2}$. Calculated distances for pair interactions and for a cubic octahedral array lead to a range of calculated values for d, as a function of the cupric ion content, and are plotted in Figure 8. The range of values calculated by this approach is between these two limits.

Discussion

The distribution of cupric ions in Nafion as a function of cation concentration has been studied by Vasquez et al.[24] The method used is based on comparing ESR spectra of Cu^{2+} in Nafion with those obtained from reference frozen aqueous solutions of Cu^{2+}. It was mentioned that the results are difficult to interpret when ESR spectra of the cation in ionomers reveal two (or more) different local concentrations.

The intercation distance can, in principle, be deduced from the line width increase with concentration of the perpendicular component of ESR spectra. This method has been used to obtain Cu^{2+}–Cu^{2+} distances in cell wall polyuronides as a function of cation concentration.[24] In the simulation of the perpendicular component, there are uncertainties, due to the fact that the value of $A_\perp$ cannot be resolved and accurately measured. In addition, in the perpendicular region, there are sometimes forbidden transitions and possibly a rhombic component of the hyperfine and/or of the g tensor. In such situations, $g_\perp$ and

$A_\perp$ values that simulate the transition can be found, but we do not exclude the possibility that these parameters are not unique. We therefore prefer to deduce intercation distances by an analysis of the parallel transition.

In a previous study, we simulated the X-band ESR spectrum from a sample containing 1% Cu^{2+} in Nafion swollen by D_2O, based on the line widths of the four parallel transitions at this frequency. Good agreement with experimental spectra was obtained (as shown in Figure 3 of ref 10), although the values of the line widths for the $m_I = {}^1/_2$ and ${}^3/_2$ transitions could be read only with an error of several gauss. The uniqueness of the parameters used to simulate the above spectrum seemed to be satisfactory for ranges of the parameters in the vicinity of the values suggested by a multilinear regression procedure. For determination of *d*, however, we opted for additional, S-band measurements. Comparison of $\delta g_\parallel$, $\delta A_\parallel$, $\Delta H_\parallel{}^R$, and ϵ values from the X band alone with those given in Table II indicates small differences only in the values of $\delta g_\parallel$ and $\delta A_\parallel$ but a large difference in the value of the residual width, 11 G versus 5.8 G. Because we base the calculation of *d* on the values of the residual widths, we were very careful with the choice of the parameters. Considering the S-band results, in addition to X-band results, for an initial estimate of the parameters used for the simulations, we specifically introduced the condition that the residual widths be smaller than the line width of the $m_I = -{}^1/_2$ transition at the S band, which is the narrowest we observed, as seen in Figure 7. This limitation proved very important for directing us to the simulations we consider successful and to the results presented in Table II. We also noticed that additional errors can be introduced if the normal mixture of Cu isotopes is used to obtain ESR spectra.

Effects of a distribution of *g* and *A* tensors have been reported in several papers and attributed to variation in the bonding parameters of the paramagnetic center due to variations in the local environments, or "*g*–*A* strain".[26-31] In some cases, the effect has been theoretically estimated,[29-31] while in others the experimental spectra have been simulated on the basis of X-band data alone.[27,28] In view of the above comments, we believe that these simulations, although they seem to be in agreement with experiments, are obtained with parameters that might not be unique.

The intercation distance can be calculated by assuming a homogeneous distribution of cupric ions, from the membrane composition and its density, as given in Table I. The results for a simple cubic lattice are given in Figure 8, together with the results of the ESR measurements.

At 4.5% cation content, the value deduced for *d* is not very accurate, because it is based on a very small increase in the value of $\Delta H_\parallel{}^R$, compared with the value at 1% cation content, where we assume no contribution from the dipolar contribution to the line width (6.3 G compared with 5.8 G, Table II).

At higher cation concentrations, the values of *d* calculated from the line width analysis are accurate enough and can be compared with those deduced by assuming a homogeneous distribution of cations. The values deduced from ESR data are significantly lower, clearly indicating ionic clustering. The largest departure from the homogeneous distribution is detected around 10–15% cation content. At higher concentrations, the difference is not so pronounced. This effect might be explained by considering that part of the ions are clustered as dimers, as found in our recent studies of Cu^{2+} and Ti^{3+} in Nafion.[32] We suggested that the dimers are located at the periphery of the hydrophilic domains. The distance between the dimers and the single ions could be larger than 15 Å; therefore, the interaction and the line broadening are not as large as those derived in the event that all cations are isolated. The shortest distance deduced from the ESR experiments is ca. 10 Å. With a Cu–O distance of 2.4 Å, this intercation distance is large enough to accommodate fully hydrated cupric ions. This conclusion is in agreement with our earlier suggestion that isolated cupric ions are ligated to oxygens from the water and not to the sulfonic groups from the network.[9,32]

Conclusions

1. ESR spectra of Cu^{2+} in Nafion perfluorinated membranes indicate the presence of isolated and aggregated cations in a wide range of cation concentrations, compared with the total amount needed to fully neutralize the membranes.
2. The increase in the line width of ESR spectra, compared to that at the lowest cation concentration, is analyzed and used to deduce the distance, *d*, between the isolated cations as a function of cation concentration. In this study, the determination of *d* is based on experimental ESR spectra at L (1.25-GHz), S (2.36-GHz) and X (9.36-GHz) bands and spectra simulations.
3. An accurate value of *d* can be obtained from spectra at two microwave frequencies *at least*. This is necessary in order to evaluate and divide out the contribution of a distribution in the ESR parameters to the measured line widths in the parallel orientation. Values of *d* based on the perpendicular ESR signal are not always reliable.
4. Large differences in the intercation distances thus determined and values calculated for a homogeneous cation distribution are observed and are due to ion clustering in the hydrophilic regions of the ionomer.
5. The intercation distances deduced for the isolated ions are large enough (>10 Å) to accommodate cupric ions fully hydrated by water molecules. This result is in agreement with our previous suggestion that only in dimers, and perhaps in higher aggregates, are the cupric ions ligated to the sulfonic groups of the ionomers.

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Registry No. Nafion 117, 66796-30-3; Cu^{2+}, 15158-11-9.

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Local Environment and Clustering of Cations in Ionomers. Electron Spin Resonance of Copper(2+) in Nafion Swollen by Water, Methanol, Dimethylformamide, and Tetrahydrofuran

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ABSTRACT: The distribution of cupric ions in perfluorinated membranes containing terminal SO_3H groups and saturated with methanol, methanol/water mixtures, dimethylformamide (DMF), and tetrahydrofuran (THF) has been studied, based on ESR spectra at L (1.25-GHz), S (2.36-GHz), and X (9.36-GHz) bands. The mobility of the cations is studied in all solvents in the temperature range 77–300 K. In Cu^{2+}-saturated membranes swollen by DMF, THF, methanol, and methanol/water mixtures containing more than 20% methanol by volume, there is no spectroscopic indication for the presence of aggregated cations. This result is in marked contrast with the results obtained for membranes swollen by water or by methanol/water mixtures with low (<20% by volume) methanol content. We suggest that the absence of aggregation might be due to smaller ionic domains in the polar organic solvents (DMF, methanol), compared with water. No ionic domains seem to be formed in Nafion swollen by THF. The intercation distance d in Cu^{2+}-saturated membranes swollen by the organic solvents has been determined by measuring the line widths of the parallel signal at *three* microwave frequencies and by spectral simulations. This procedure allows determination of the increase in the residual line width in cation-saturated Nafion compared to that at the low (<10%) cation concentration; this increase is related directly to the intercation distance. In Nafion saturated with Cu^{2+} and swollen by the organic solvents, this distance is in agreement with that calculated by assuming a homogeneous distribution of the cations arranged in a cubic array and is similar to that in Nafion swollen by water, in which only 34% of the sulfonic groups has been neutralized by Cu^{2+}.

Introduction

Phase separation into hydrophilic and organic regions in ionomers is due to the presence of pendant ionic groups and to preferential solvation of these groups by water and other polar solvents.[1-4] The most convincing proof for the formation of polar regions has been obtained in small-angle X-ray scattering (SAXS) measurements.[5] The additional scattering peak detected in ionomers, compared to polymers that do not contain terminal polar groups, is called the ionic peak. In the perfluorinated ionomers known as Nafion and in other ionomers, this peak appears only when the polymer has been swollen by a polar solvent. Most SAXS studies have been performed with water as the solvent. The ionic peak has been detected in Nafion neutralized by various metal cations and containing terminal sulfonic and carboxylic groups.[6-8] It is interesting to note that the ionic peak is detected also in the acid form of Nafion (not neutralized) with terminal sulfonic groups, but not in carboxylic acid terminated membranes.[8] This result has been related to the smaller amount of water retained in the carboxylated membranes.

The quantitative interpretation of the SAXS results in terms of polar domain size and structure depends on the model assumed[9] and is still a question of debate. For this study it is important to mention that in Nafion neutralized by Na^+ the ionic peak is detected only in the presence of water. It has been suggested that the reason for the absence of the ionic peak in dry Nafion/Na^+ is due to a fortuitous cancellation of electron densities. In support of this hypothesis is the appearance of the ionic peak in dry Nafion when heavier cations such as Ag^+ and Cs^+ are

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