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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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used for neutralization of the membranes.[10,11]

The ionic peak has also been detected in small-angle neutron-scattering (SANS) studies of ionomers. In a comprehensive SANS study of Nafion swollen by H_2O and H_2O/D_2O mixtures,[10] it was concluded that the ionic peak is due mainly to the contrast between the scattering of the backbone and that of water; the ionic peak therefore represents the aggregation of solvent molecules.[10,11] This conclusion means that while the size of the solvent cluster can be deduced from these studies, the distribution of the cations and their local environment is still, to a large extent, an open question.

Solvent polarity and structure are expected to have a considerable effect on the morphology of bulk ionomers and of ionomer solutions. As of this date, however, only a limited number of studies have been reported on the subject. SANS has been used to study the properties of Nafion solutions in water and ethanol[12] and of sulfonated polystyrene (SPS) solutions in various solvents.[13,14] Viscosity measurements in various solvents and light scattering results on SPS have also been published.[15,16] Some electron spin resonance (ESR) studies of SPS neutralized by paramagnetic cations have been reported.[17] It seems that highly polar solvents such as dimethylformamide (DMF) ionize the sulfonic acid group and increase the hydrodynamic volume of the polymer chain, while in solvents of low polarity such as tetrahydrofuran (THF) the salt groups exist as ion pairs and induce aggregation of the chain and even gelation, due to dipole–dipole interaction, at high polymer concentrations.

SAXS measurements of SPS partially neutralized by Mn^{2+} ions and cast from polar and nonpolar solvents have also been collected,[18] and the temperature dependence of the SAXS peak from the cluster has been investigated.[19] It seems that in some nonpolar solvents such as THF the ionic peak disappears completely and reappears by heating to about 510 K. This effect has been assigned to an order–disorder transition.

The swelling behavior of perfluorinated ionomer membranes in a large number of solvents such as water, alcohols, and amines has been investigated in detail.[20] The results indicate that the sample treatment and history, the structure of the solvent, the nature of the cation used to neutralize the membrane, the degree of neutralization, and the temperature affect the amount of solvent uptake by the membrane. In addition, it was found that sulfonate and carboxylate membranes have different swelling properties.

We have used various electron magnetic resonance techniques such as continuous wave ESR and electron nuclear double resonance (ENDOR) in order to deduce the local geometry and the distribution of the ionic groups in perfluorinated ionomer membranes containing terminal sulfonic groups.[21-23] The paramagnetic ions used for the neutralization of the membranes are Cu^{2+} and Ti^{3+}. In most of our studies, so far, we have used water, as H_2O and D_2O, as the swelling solvent. Methanol was also used, for initial studies with Nafion containing Ti^{3+}, because of the greater stability of the cation in methanol, compared with water.

In previous studies, we have detected cation aggregation even in membranes that have been only partially neutralized by the cations.[22] The specific ligation of the cations is sensitive to the amount of solvent retained by the membrane, and this in turn depends on the degree of neutralization of the sulfonic groups. An important conclusion obtained from these studies is that both isolated *and* aggregated ions exist in a large concentration range of the paramagnetic cations. The intercation distance in the Cu^{2+} aggregates seems to be close to 5 Å; this value has been deduced from an analysis of the half-field forbidden transition for the Cu^{2+}–Cu^{2+} dimer, which is detected at a magnetic field of ca. 1650 G in Nafion swollen by water. Ti^{3+}–Ti^{3+} dimers have also been detected; the intercation distance in this dimer seems to be significantly larger than in the cupric ion dimer, about 7.5 Å.

In a recent study, we have deduced the intercation distance for isolated (nonclustered) ions in Nafion swollen by water and neutralized by Cu^{2+}, as a function of Cu^{2+} concentration.[24] This measurement is based on 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 dipolar interaction, which reflects the intercation distance. The intercation distance deduced is in agreement with that expected by assuming a random distribution of cations and pair interaction at a low degree of neutralization and is closer to that calculated for an cubic array of randomly distributed cations at higher concentrations.

The objective of this study is to investigate the effect of various solvents on the ionic distribution in Nafion neutralized by cupric ions. As described earlier, ionic clustering is usually deduced from SAXS and SANS measurements. The problem with these studies is that the ionic peak is sometimes not detected in SAXS studies in systems when ionic clustering is likely to take place, while SANS studies reflect mostly the solvent aggregation and not that of ions. ESR is a spectroscopic method suitable for a direct and specific study of cation aggregation. The line shapes of isolated cations, here defined for intercation distances larger than ca. 10 Å, are quite different from dimeric species or higher aggregates. The ESR method, a probe technique, is expected to be complimentary to the diffraction methods.

In this report we present multifrequency ESR studies of Cu^{2+} in Nafion, swollen by methanol, methanol/water mixtures, THF, and DMF. These solvents represent a wide range of polarities, as represented by the dielectric constants, and chemical structures. The results we obtained indicate significant differences in the aggregation of the cations and therefore in the membrane morphology, compared with those observed in Nafion swollen by water.[24]

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 treated as described in previous publications.[21-24] 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.

The D_2O in the membrane was exchanged by DMF (reagent grade, Sargent Welch), THF (chromatographic grade, Burdick & Jackson), CH_3OD (99% D enriched, Norell Chem. Co.), and D_2O/CH_3OD mixtures. To ensure a complete solvent exchange, the membrane equilibrated with the cation was dried to constant weight and saturated with the appropriate solvent for at least 5 h; this process was done 3 times. The exchange with D_2O/CH_3OD mixtures was carried out only once, after drying the neutralized Nafion to constant weight. Following swelling in the solvent, the membrane was dry blotted, transferred to 3-mm-i.d. quartz tubes, and maintained in an atmosphere saturated with the solvent for at least 3 days before ESR measurements.

Table I
Sample Analysis

sample	$[Cu^{2+}]$, % retained	solvent, % (by wt)	mol of solvent/ mol of SO_3^-	mol of solvent/ mol of Cu^{2+}	density, g cm^{-3}, ±0.05
Nafion–Cu^{2+}–H_2O	78.6	26.4 (22.3)	23 (17)	59 (46)	1.74
Nafion–Cu^{2+}–DMF	78.6	30.4 (29.6)	7 (7)	17 (17)	1.59
Nafion–Cu^{2+}–CH_3OH	78.6	21.5 (23.4)	10 (11)	25 (28)	1.59
Nafion–Cu^{2+}–THF	78.6	17.4 (19.0)	3 (4)	8 (9)	1.72
Nafion H–H_2O	0	30.9 (19.8)	27 (15)		1.67
Nafion H–DMF	0	53.1 (51.4)	28 (26)		1.46
Nafion H–CH_3OH	0	44.2 (43.2)	27 (26)		1.21
Nafion H–THF	0	16.7 (26.5)	3 (6)		1.73

A complete composition analysis of Nafion H and of Nafion saturated with Cu^{2+} and swollen by the various solvents was carried out. The solvent content was determined gravimetrically. The copper content was determined by atomic absorption (Galbraith Laboratories).[24] The most important results obtained from these analyses are summarized in Table I. The values in parentheses correspond to the solvent uptake after drying the Nafion to constant weight (24-h evacuation at ambient temperature and 3 h at 373 K, to a terminal dynamic pressure of 2×10^{-5} Torr). It seems that the membrane can be reversibly resolvated by methanol, THF, and DMF, but not by water. The densities of the membrane in the various solvents were determined by the buoyancy method[24] and are also given in Table I.

ESR spectra at the X band were measured with a Bruker 200D SRC spectrometer operating at 9.7 GHz (empty cavity at ambient temperature), 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 by 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 L and S bands, at 123 K, were measured at the National Biomedical Center in Milwaukee, WI, using spectrometers equipped with loop-gap resonator cavities.[25]

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

Results

In our studies of ionomers, we have determined the local environment of the cations from ESR spectra at low temperature (77–120 K), in membranes with a low degree of neutralization, typically less than 10%, because of increased spectral resolution. The dynamics of the ions is studied by varying the temperature, in the range 77–300 K. The aggregation process is reflected in the ESR line shapes of membranes fully equilibrated with the paramagnetic cations. As shown before,[24] this degree of equilibration means usually that 70–80% of the sulfonic groups are neutralized. In presenting the results, we will use "Cu^{2+} percent" to express the amount of cupric ions retained by the membranes in the neutralization step, compared to the stoichiometric amount needed to fully equilibrate the membrane. The relation between the amount retained by and the amount available to the membrane has been determined by atomic absorption.[24]

ESR spectra at L, S, and X bands, of Nafion containing 4.5% cupric ions and saturated with DMF and THF, are shown in Figures 1 and 2, respectively. ESR spectra at S and X bands for 1.5% copper content in Nafion swollen by CH_3OD and by a 50/50 (by volume) D_2O/CH_3OD mixture are shown in Figure 3. L- and S-band spectra were measured at 123 K. In the temperature range 77–123 K, no measurable variations in the spectra were detected; therefore, spectra at the three microwave frequencies, Figures 1–3, are directly comparable.

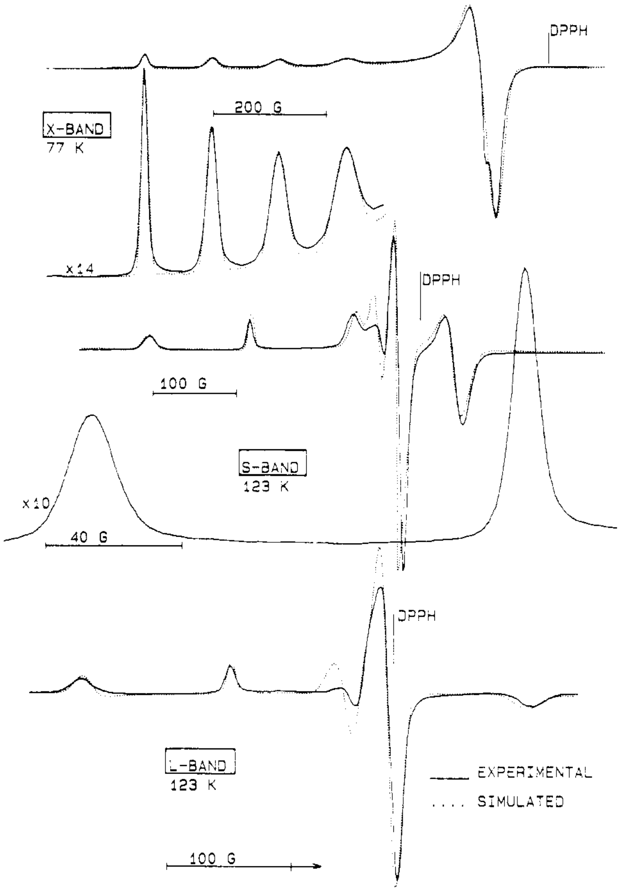

Figure 1. Experimental (—) and simulated (···) ESR spectra of Nafion–$^{63}Cu^{2+}$–DMF, for copper content of 4.5% and saturated in DMF, at the L band (1.25 GHz) and 123 K, at the S band (2.36 GHz) and 123 K, and at the X band (9.22 GHz) and 77 K. Enlarged spectra of the parallel signals are also shown: at the S band for the $m_I = -^3/_2$ and $-^1/_2$ transitions and at the X band for all four transitions.

X-band ESR spectra at 100 K of Cu^{2+} in cation-saturated Nafion (Cu^{2+} content 70%, I 3%), swollen by the various solvents and by D_2O/CH_3OD mixtures, are shown in Figure 4. The cluster signal, indicated in the spectrum corresponding to D_2O as solvent, is prominent only in D_2O/CH_3OD mixtures containing 80% or more water. S-band ESR spectra at 123 K of Cu^{2+}-saturated Nafion swollen by the same solvents are shown in Figure 5.

ESR spectra at X band as a function of temperature for Nafion swollen by D_2O, DMF, CH_3OD, and THF are given in Figure 6.

The increase in the line width of the signal from the parallel orientation with the cation concentration, seen by comparing the spectra in Figures 1–3 (for <5% Cu^{2+} in Nafion) with those in Figures 4 and 5 (for Cu^{2+}-saturated Nafion), is attributed to magnetic dipole interactions be-

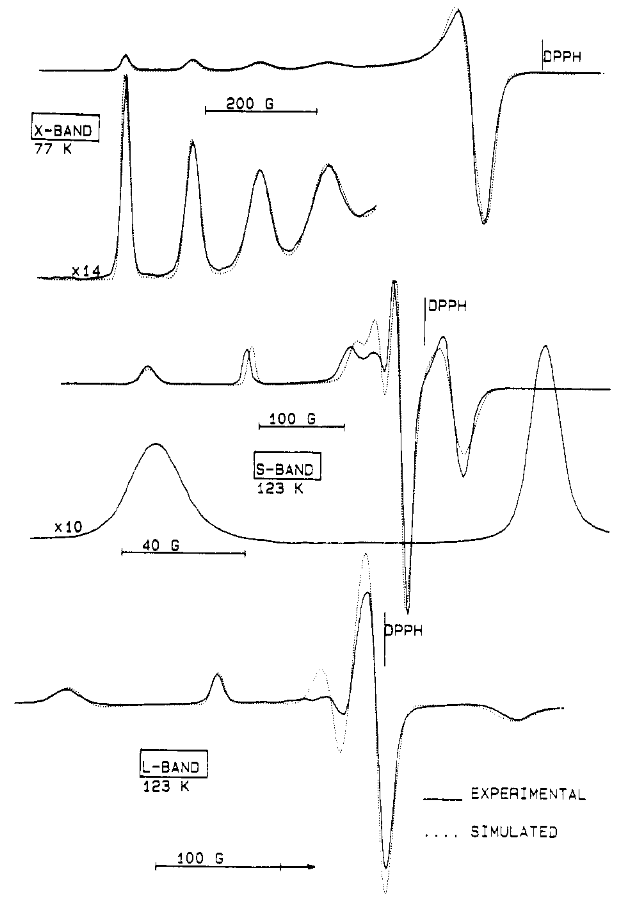

Figure 2. Experimental (—) and simulated (···) ESR spectra of Nafion-$^{63}Cu^{2+}$-THF saturated in THF and with 4.5% Cu^{2+} concentration, at the X band (9.22 GHz) and 77 K and at the S band (2.36 GHz) and L band (1.25 GHz) at 123 K. Enlarged spectra of the parallel signals are also shown: at the S band for the $m_I = -^3/_2$ and $-^1/_2$ transitions and at X band for all four transitions.

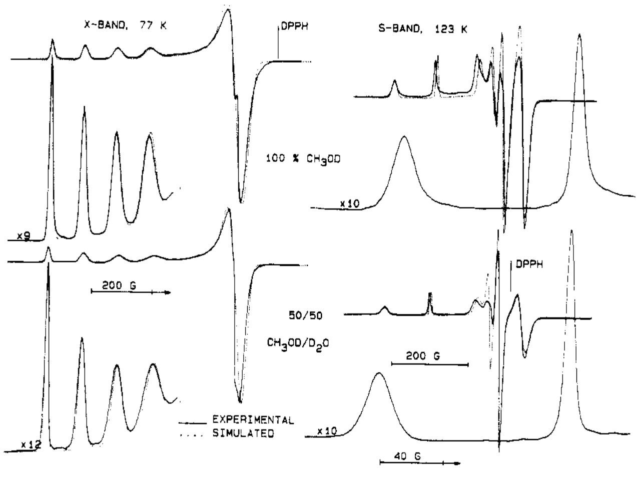

Figure 3. Experimental (—) and simulated (···) ESR spectra of Nafion-$^{63}Cu^{2+}$-swollen by two CH_3OD/D_2O mixtures (Cu^{2+} concentration 1.5%) at the X band (9.22 GHz) and 77 K and at the S band (2.36 GHz) and 123 K. Enlarged spectra of the parallel signals are also shown: at the S band for the $m_I = -^3/_2$ and $-^1/_2$ transitions and at the X band for all four transitions.

tween Cu^{2+} ions and can be used to determine the intercation distance in Nafion containing the high cation content. 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 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.

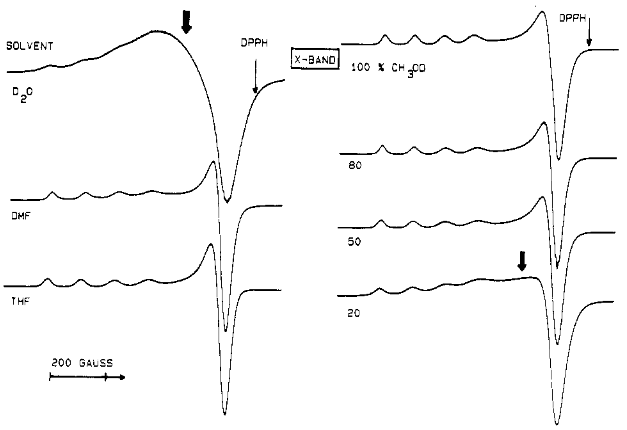

Figure 4. X-band (9.22-GHz) ESR spectra of Nafion-$^{63}Cu^{2+}$ at 77 K with 70% retained Cu^{2+} and saturated in D_2O, DMF, THF, and CH_3OD/D_2O mixtures as indicated. The thick arrows indicate the approximate position of the cluster signal.

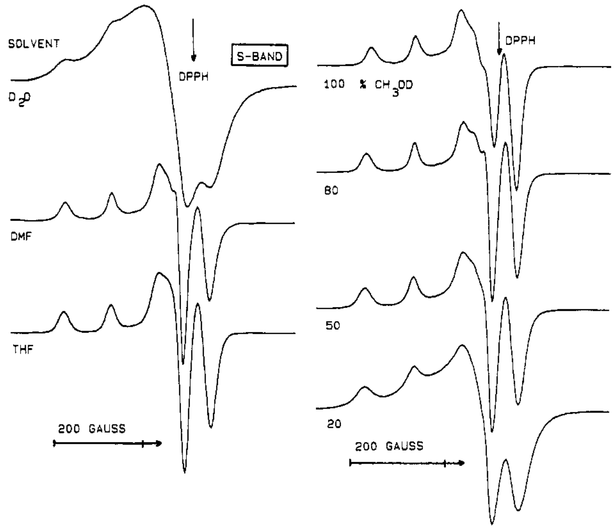

Figure 5. S-band (2.36-GHz) ESR spectra of Nafion-$^{63}Cu^{2+}$ at 77 K with 70% retained Cu^{2+} and saturated in DMF, THF, and CH_3OD/D_2O mixtures. The concentration of Cu^{2+} retained for the sample saturated in D_2O is 58%.

The variation of the line widths from the parallel component with m_I presented in Figures 1–5 has been observed before for Cu^{2+} in frozen glasses and treated phenomenologically, assuming an explicit m_I dependence of the line width ΔH or by generating a powder spectrum through superposition of spectra with different values of $g_\parallel$ and $A_\parallel$.[26–28]

A model proposed by Froncisz and Hyde[29] 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 can be described by the distribution parameters $\delta g_\parallel$ and $\delta A_\parallel$, which 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

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

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 position 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.[30] The dramatic changes between the spectra at low microwave frequency (L and S bands) and those taken at the X band indicate the effect of the microwave frequency on the line shapes and line widths.

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; the set of parameters for each cupric ion content was deduced by comparison of calculated and experimental spectra. In most cases, the parameters from the least-squares program had to be varied slightly for obtaining the best visual agreement between experimental and calculated spectra. Simulations were based on an axial spin Hamiltonian, which specifically includes the line width dependence due to the distribution parameters and Gaussian line shapes.[21-24] An orientation-dependent line width was used, eq 3, with $\Delta H_{\perp} = \Delta H_{\perp}^{R}$.

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

In eq 3, θ is the angle between the magnetic field and the symmetry axis of the Cu complex.

Simulated spectra for Nafion with <5% Cu^{2+} content are shown in Figures 1–3, together with the experimental spectra at L, S, and X bands. We have not attempted to simulate ESR spectra of Nafion swollen by water or water/methanol mixtures containing 80% or more water, because in these samples the aggregate signal is dominating the spectra and the individual line widths cannot be deduced with reasonable accuracy.[24]

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. 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 set of parameters used for the simulated spectra given in Figures 1-5 seems to be, therefore, unique. The parameters used to simulate the spectra in Figures 1-5 are given in Tables II and III.

From Tables II and III, it can be observed that the residual widths of both the parallel and the perpendicular components increase with the copper concentration. The increase in line width, compared with that at the lowest cation concentration, where no such interaction is assumed, is due to magnetic dipole–dipole interaction. In principle, these increases can both be used for determination of the intercation distance. In practice, there are uncertainties in the simulation of the perpendicular component, due to the fact that the value of $A_{\perp}$ cannot be resolved. In addition, in the perpendicular region there are forbidden transitions and possibly a rhombic component of the hyperfine and/or g tensor. In such situations, the values of $g_{\perp}$, $A_{\perp}$, and $\Delta H_{\perp}$ are values that simulate well the spectral shape, but we do not exclude the possibility that these parameters are not unique. For these reasons, we prefer to use the increase in the line width of the parallel component for intercation distance determination.

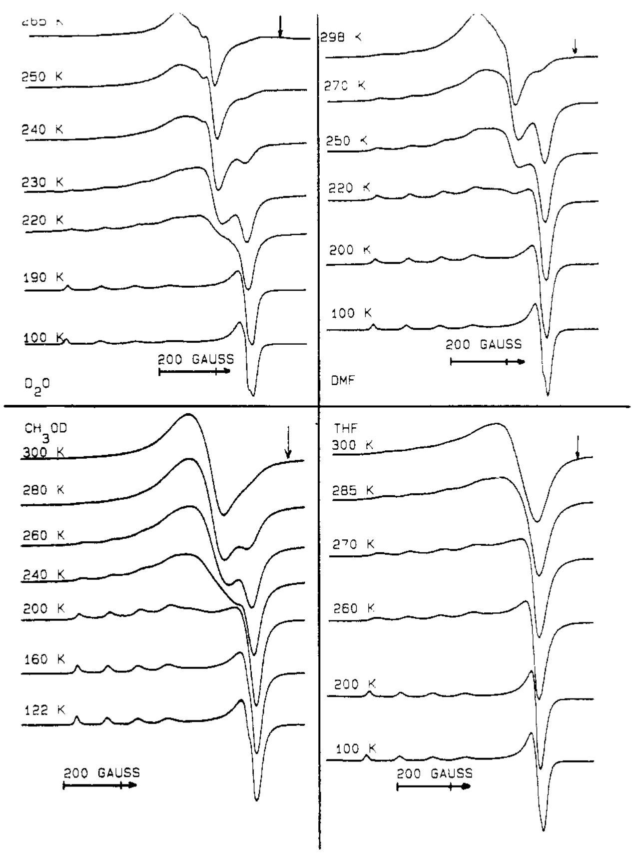

Figure 6. X-band ESR spectra of Nafion–$^{63}Cu^{2+}$, in the temperature range 100–300 K, saturated by D_2O, DMF, CH_3OD, and THF. Downward arrows mark the position of DPPH. The concentrations of Cu^{2+} in solvent-saturated membranes are as follows: D_2O, 1.5%; DMF and THF, 6.5%; CH_3OD, 4.5%.

The intercation 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 eq 4.[31]

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

If the isotropic g value for each solvent is used, a relation between the intercation distance, d (in angstroms), and the observed broadening is obtained. Using $g_{iso} = 2.185$ (for Cu^{2+} in Nafion/DMF), eq 4 can be rewritten as in eq 5; equivalent expressions can be deduced for the other solvents.

$$\delta(\Delta H) = 27168 d^{-3} \quad (5)$$

A similar expression holds if we assume a two-dimensional hexagonal array of cations, or a cubic octahedral array, except for a numerical factor of $6^{1/2}$. The results obtained from ESR data, based on pair interaction and also on a cubic array of cations, are given in Table IV. We have included in this table, for comparison, the results obtained in the preceding paper[24] for Nafion with 34% copper content swollen by water.

The distance calculated from the ESR data can be compared with the intercation distance obtained assuming a cubic lattice and a homogeneous distribution of cations, based on the measured densities and membrane composition (data in Table I).

Table II
ESR Parameters Used To Simulate ESR Spectra of Nafion with Low Cu^{2+} Content[a]

solvent	$g_\parallel$	$g_\perp$	$A_\parallel$, G	$A_\perp$, G	$\Delta H_\perp$, G	$\Delta H_\parallel^R$, G	$\delta g_\parallel$	$\delta A_\parallel$, G	ϵ
D_2O	2.4169	2.0809	121.0	7.5	20.5	6.3	0.037	18.0	0.99
DMF	2.3997	2.0781	119.1	7.5	17.0	7.1	0.024	13.0	0.91
CH_3OD	2.4325	2.0872	107.6	10.5	23.0	6.0	0.025	11.0	0.91
THF	2.4173	2.0815	119.2	8.5	19.5	9.9	0.032	19.0	0.92
100% CH_3OD	2.4305	2.0872	110.3	10.5	23.0	6.2	0.025	12.0	0.92
90% CH_3OD	2.4260	2.0860	112.4	10.5	20.5	6.1	0.025	13.5	0.92
80% CH_3OD	2.4258	2.0845	113.6	10.5	19.0	5.9	0.028	16.5	0.94
50% CH_3OD	2.4215	2.0820	116.5	10.5	17.2	5.6	0.029	16.5	0.94
0% CH_3OD	2.4160	2.0809	121.0	8.0	19.0	5.8	0.034	18.7	0.96

[a] Methanol/water mixtures contain 1.5% Cu^{2+}. All other samples contain 4.5% Cu^{2+}.

Table III
ESR Parameters Used To Simulate ESR Spectra of Nafion with High Cu^{2+} Content[a]

solvent	$g_\parallel$	$g_\perp$	$A_\parallel$, G	$A_\perp$, G	$\Delta H_\perp$, G	$\Delta H_\parallel^R$, G	$\delta g_\parallel$	$\delta A_\parallel$, G	ϵ
DMF	2.3995	2.077	120.2	9.0	25.0	28.1	0.028	8.0	1.00
CH_3OD	2.4278	2.086	108.0	13.0	22.0	24.9	0.018	9.0	0.98
THF	2.4170	2.0795	122.1	11.0	22.5	32.6	0.022	18.6	0.98
100% CH_3OD	2.4278	0.086	108.0	13.0	22.0	24.9	0.018	9.0	0.98
80% CH_3OD[b]	2.4206	2.081	114.0	10.5	24.5	25.9	0.026	13.5	1.00
50% CH_3OD[b]	2.4179	2.0795	117.0	11.0	25.5	28.9	0.028	14.0	0.98
20% CH_3OD[b]	2.4139	2.077	121.3	11.0	28.0	37.4	0.031	15.0	1.00

[a] The amount of Cu^{2+} retained in all samples is 70%. [b] CH_3OD/D_2O mixtures.

Table IV
Intercation Distances

				d_{ESR}, Å		
solvent	dielectric constant	$\delta(\Delta H)$, G	g_{iso}	pairs	cubic lattice	d,[b] Å
H_2O	78.5	22.4	2.192	10.7[a]	14.4[a]	15.5
DMF	36.7	21.0	2.185	10.9	14.7	16.3
CH_3OD	32.7	18.9	2.202	11.3	15.2	15.7
THF	7.6	22.7	2.198	10.6	14.3	15.0

[a] These distances are read from Figure 8 of ref 24, for 30% Cu^{2+}. [b] Homogeneous distribution.

Discussion

The most striking result in this study is the absence of the signal from aggregated cations in DMF, THF, methanol, and methanol-rich methanol/water mixtures. It is logical to expect that the polarity of the solvent is an important factor in the distribution of the ionic charges in the systems studied. The fact that solvents with very different dielectric constants (DMF, 36.7; THF, 7.6; methanol, 32.7) have similar effects on the aggregation of cationic species indicates that the polarity, though important, is not the only factor that must be considered in rationalizing the results. The structure and size of the solvent molecules must be important factors.

Some insight into the solvation effects of each solvent can be obtained by inspection of the amount of solvent retained by the membranes in the acid form (Nafion H) and by completely neutralized membranes (saturated with Cu^{2+}), shown in Table I as the ratio of moles of solvent/moles of SO_3^-. For the nonpolar solvent THF, the amount of solvent retained is small, the above ratio is 3; it is significant that this ratio is the same in Nafion H *and* in Cu^{2+}-saturated Nafion. This result seems to indicate that the amount of THF does not depend on the presence of the ionic groups and is a function of the interaction with the polymer chains only. Due to solvation of the chains by THF, the distance between pendant ionic groups is larger and no cation aggregation can occur. Also there is no formation of large ionic domains in the solvent that would enable formation of aggregated cations.

In order to check possible ligation of Cu^{2+} by THF, we tried to dissolve $CuSO_4$ in the solvent; the supernatant was checked for an ESR signal, but no signal was detected, even at very high spectrometer gain. This result indicates that we do not expect to find THF as a ligand of cupric ions in Nafion; most likely the cation is ligated to the sulfonic groups.

We must also comment that the amount of water is only slightly higher in Nafion H than in Cu^{2+}-saturated Nafion (the ratio mentioned above is 27 versus 23). We suggest that this result is due to the fact that water "sees" only the polar groups on the membrane and not the organic chain. This explanation is supported by the detection of the ionic peak in SAXS measurements in both Nafion H *and* neutralized membranes. Water and THF seem to have, therefore, quite contrasting behaviors. It is important to note that no ionic peak was detected in SAXS studies of the SPS films case from THF/water solution containing 90% THF,[18] again indicating the lack of solvent aggregation. Our studies thus indicate that the lack of nonpolar solvent (THF) aggregation also implies lack of cation aggregation.

The effect of DMF, methanol, and some methanol/water mixtures on the cation aggregation seems to be completely different from that of THF. First, there is a great difference in the amount of solvent retained by Nafion H, compared with Cu^{2+}-saturated Nafion: the relevant ratio mentioned above is 28 versus 7 for DMF and 27 versus 10 for methanol. We suggest that the lack of *cation* aggregation in these systems is due to the formation of polar domains that are too small to contain a larger number of cations *and their ligands*. This suggestion is supported by some of our still unpublished SAXS results.

In preliminary SAXS studies of Nafion H and Cu^{2+}-saturated Nafion solvated by water and by methanol, we have detected ionic peaks in all samples.[31] The size of the ionic domains, judged by the value of the scattering vector corresponding to maximum scattering intensity, is different from the two solvents. For water there is only a small difference in the scattering vector between Nafion H and neutralized Nafion, 0.161 versus 0.170 nm^{-1}. For methanol, the difference is much more pronounced, 0.130 versus

0.173, indicating much smaller ionic domains in Cu^{2+}-saturated Nafion solvated by methanol, compared with Nafion H/methanol. Methanol and DMF have similar dielectric constants (32.6 and 36.7, respectively), and we predict that solvent aggregation exists in both and that the ionic peak could be observed also in DMF. We are in the process of studying SAXS of Cu^{2+}-saturated Nafion containing DMF. The smaller ionic domains in Cu^{2+}-saturated Nafion solvated by methanol are in agreement with the methanol content measured gravimetrically and given in Table I. We suggest, therefore, *that solvent aggregation does not necessarily imply cation aggregation.*

In spite of the lack of signal from aggregated cations in Cu^{2+}-saturated Nafion swollen by the organic solvents, we have detected a weak signal corresponding to Cu^{2+}–Cu^{2+} dimers in all samples.[33] It seems that while massive cation aggregation is not taking place, formation of "multiplets" in the terminology used by Eisenberg[34] is detected.

Interestingly, the intercation distance deduced from ESR line width analysis (Table IV) is similar in all solvents and varies between 10.7 and 11.3 Å for pair interaction and between 14.3 and 15.2 Å for a cubic array of cations. This distance can be compared with that obtained by assuming an homogeneous distribution of the cations, which predicts an intercation distance of 15.0–16.3 Å. For small solvent domains and no cation aggregation, it is more logical to assume a *cubic array* for the cations, and therefore, it is very gratifying to find good agreement between ESR results for a cubic array and data obtained by assuming a homogeneous distribution of cations.

The intercation distance in Cu^{2+}-saturated Nafion swollen by the organic solvents is similar to that in Nafion swollen by water and containing 34% Cu^{2+}. This distance in water represents the intercation distance for nonaggregated cations.

The ESR spectra as a function of temperature for Nafion with low Cu^{2+} content (<10%) solvated by water and by the organic solvents (Figure 6) again indicates the difference between the polar solvents (water, methanol, and DMF) and THF. In all solvents, the averaging of the anisotropy occurs on increasing the temperature, and a signal centered on the g_{iso} value is detected; for D_2O and DMF, some splitting from the ^{63}Cu isotropic hyperfine interaction is also detected, at 265 and 298 K, respectively. At 280 K an anisotropic signal is also detected for the polar solvents, including water, which is not seen for THF. For Nafion solvated by water, we have assigned this signal to Cu^{2+} ligated by "bound" water or water that is close to the sulfonic groups and probably hydrogen bonded;[21] the isotropic signal was assigned to Cu^{2+} ligated by "free" water. This assignment was based on the fact that the isotropic signal disappears when the amount of water is reduced by partial evacuation of the sample. We have obtained a similar result when removing some of the DMF and methanol by evacuation: the intensity of the isotropic signal is reduced. These results suggest that "bound" and "free" DMF and methanol exist in Nafion, due to interactions with the polar groups on the polymer.

It is interesting to note that the isotropic signal in water is detected at ca. 190 K, significantly below the melting point of bulk water. We suggest that even the free water is affected by the polar groups of the polymer and leads to the formation of a glass and not of crystalline ice.

Finally, we will mention that in a study of Cu^{2+} solvated by water in the pores of silica gel the presence of bulk water was detected only in pores larger than about 60 Å in diameter.[35] This dimension is similar to the size of the water clusters in Nafion, deduced by SAXS.[6-9]

At this point we can ask a most relevant question: Why do we detect solvent aggregation in SAXS studies (in Cu^{2+}-saturated Nafion swollen by methanol, for instance) while no *cation* aggregation is detected in ESR studies? We suggest that the *size* of the ionic domain formed by the solvent determines to what extent ionic aggregation occurs. A ligated Cu^{2+} ion is expected to have a diameter of no less than 10 Å when ligated octahedrally to methanol. In this respect, we might mention that we detected by ENDOR a distance of 4.3 Å between Ti^{3+} and the methyl protons in Nafion,[23] and this cation has an ionic radius comparable to that of Cu^{2+} (0.76 Å versus 0.72 Å). If the ionic domains in Nafion/methanol are of the order of 20–30 Å, not many cations can be crowded in this space; the situation is different in Nafion/water, where the ionic domain is much larger. This suggestion is supported by the observation of a smaller amount of *dimeric* cation species in all organic solvents studied.

Conclusions

We presented an ESR study of Cu^{2+} in Nafion perfluorinated membranes swollen by water, methanol, water/methanol mixtures, dimethylformamide (DMF), and tetrahydrofuran (THF). ESR spectra were obtained in the temperature range 77–300 K, at three microwave frequencies: L (1.25-GHz), S (2.36-GHz) and X (9.36-GHz) bands. The most important conclusions are as follows:

1. No spectroscopic evidence for cation aggregation has been detected in Cu^{2+}-saturated Nafion membranes swollen by DMF, THF, methanol, and methanol/water mixtures containing more than 20% methanol by volume. This result is in marked contrast with the ionic peak detected by small-angle X-ray scattering (SAXS) in Cu^{2+}-saturated Nafion membranes swollen by methanol (to be published).
2. The intercation distance, *d*, between the nonaggregated cupric solvents is deduced by analyzing the increase in the line width of ESR spectra, compared with the line width at the lowest cation concentration.
3. We emphasize that an accurate value of *d* can be obtained on the basis of ESR 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.
4. In Nafion saturated with Cu^{2+} and swollen by the organic solvents, the values of *d* are in agreement with those calculated assuming an homogeneous distribution of the cations arranged in a cubic array and are similar to those deduced for isolated cations in Nafion swollen by water, in which only ca. 30% of the sulfonic groups are neutralized by Cu^{2+}.
5. The absence of cation aggregation in Cu^{2+}-saturated Nafion membranes swollen by DMF, THF, methanol, and methanol/water mixtures containing more than 20% methanol by volume might be due to the formation of smaller ionic domains in the polar organic solvents (DMF, methanol), compared with water.
6. No evidence for the formation of ionic domains in THF is detected.

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Registry No. DMF, 68-12-2; THF, 109-99-9; Nafion 117, 66796-30-3; Cu^{2+}, 15158-11-9; CH_3OH, 67-56-1; H_2O, 7732-18-5.

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Crystallography of Highly Substituted Galactomannans: Fenugreek and Lucerne Gums

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ABSTRACT: Wide-angle X-ray fiber diffraction methods have been used to study the crystal structure of two highly substituted galactomannans, fenugreek and lucerne gums. Both hydrated polysaccharides crystallize on orthorhombic lattices with a = 9.12 Å, b = 33.35 Å, and c = 10.35 Å (for fenugreek gum) and a = 8.98 Å, b = 33.32 Å, and c = 10.34 Å (for lucerne gum). In each case, the density is consistent with four chains passing through the unit cell and the probable space group symmetry is $P2_12_12$. The results for the a and c parameters are essentially the same as those derived from less highly substituted galactomannans such as guar, tara, or carob, while the b dimension is slightly larger. Under vacuum, the b dimension contracts with little concomitant change in either a or c. This suggests that the same fundamental crystal structure applies to these gums as to the less substituted but commercially important guar and carob species.

Introduction

Galactomannans are neutral, polysaccharide gums which find widespread application as materials of commerce in applications ranging from enhanced oil recovery,[1-4] paper sizing, textile,[5] and food[6] industries and are derived from the seed endosperm of various *Leguminosae*. In the seed, the polysaccharides serve the dual function of protecting the embryo from desiccation[7] and providing a source of nutrient.[8] These biogums have linear core poly((1→4)-β-D-mannan) main chains with varying degrees (DS) of α-D-galactosyl substituents attached at the C6 primary hydroxyl groups as shown in Figure 1. Polysaccharides obtained from different species differ largely in the abundance and, possibly, the distribution of D-galactose substituents.[9] The gums obtained from fenugreek (*Tri-*

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