Structure and Dynamics of Micellar Aggregates in Aqueous Nafion Solutions Reported by Electron Spin Resonance and Fluorescence Probes

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ABSTRACT: Aqueous solutions of Nafion, an ionomer consisting of a perfluorinated backbone and pendant sulfonic groups, were studied by the electron spin resonance (ESR) spin probe method and by fluorescence spectroscopy. The spin probes used were 4-(*N*,*N*-dimethyl-*N*-alkyl)ammonium-2,2,6,6-tetramethylpiperidine-1-oxyl cations (CAT*n*) with *n*, the number of carbon atoms in the alkyl group of the probe, equal to 1 (CAT1), 8 (CAT8), and 16 (CAT16). The ESR spectra of the probes were analyzed in terms of line shapes as a reflection of the local dynamics and ^{14}N hyperfine splittings as indicators of the local polarity. The line shapes point to slower dynamics for the larger probes, CAT8 and CAT16, suggesting that these probes are located deeper inside the aggregates compared to CAT1. The high local polarity reflected in the magnetic parameters was explained by assuming water penetration into the aggregates. The local polarity was estimated from the intensity ratio, *R*, of the third to the first vibronic peaks ($R = I_{III}/I_I$) in the fluorescence spectrum of pyrene (P) as a probe; *R* is the *polarity index*. In the Nafion micelles $R = 0.64$, indicating a polar local environment, in accord with the ESR results. By comparison, *R* is 0.53 in water, 0.75 in methanol, and 1.91 in a perfluorinated oil. The fluorescence data also suggest that the upper limit of the critical micelle concentration, cmc, for Nafion is 0.01% w/w. The local viscosity was estimated to be 74 cP at ambient temperature from the fluorescence spectrum of 1,3-bis(1-pyrene)propane (P3P), based on a previously determined calibration curve of the intensity ratio of the excimer-to-monomer emissions, I_E/I_M, vs viscosity for 14 nonaqueous solvents of known viscosities.

Introduction

Ionomers are polymers containing a small fraction of ionic groups (usually ≤15% mol) located in the backbone, on pendant chains, or at chain ends. Because of the complex morphology of ionomers and their numerous applications as packaging materials, in fuel cells, and in electrochemical processes, great research efforts have been directed toward the elucidation of their structure and physicochemical properties.[1,2] Small-angle X-ray and neutron scattering have indicated a phase-separated morphology in bulk and solvent-swollen ionomers and self-assembling of the polymer chains into multichain micellar aggregates in the corresponding solutions in polar solvents.[3] Electron spin resonance (ESR) spectra of ionomer systems doped with paramagnetic probes have provided details on the local structure and dynamics.[4] Nuclear magnetic resonance (NMR) studies have been a source of information on the diffusion of cations and on the effect of temperature and solvents on the chain dynamics.[5]

Recently we have combined ESR spectroscopy of spin probes[6,7] and fluorescence measurements[8] for the study of poly(ethylene-*co*-methacrylic acid) (EMAA) ionomer membranes and corresponding aqueous solutions. Particularly informative were ESR spectra of the ionomer doped with *n*-doxylstearic acids or their methyl esters (*n*DSA or *n*DSE, respectively, where *n* denotes the position of doxyl ring relative to the stearic headgroup).[6] The ESR line shapes in the solutions and in membranes swollen by water are typical of slow-motional dynamics even at ambient temperature. This result was taken as clear evidence that the probes intercalate in the host micelles. The case of 10DSE was especially supportive of the intercalation concept, because this probe is insoluble in water and becomes soluble in the polymer solutions only because of the presence of chain aggregates. On the basis of the analysis of the ESR data, we proposed that the EMAA aggregates consist of three main regions: a hydrophobic core, an intermediate layer that contains both ionomer chains and some ions, and a hydrophilic region where most of the ions are located. Recently, we have examined aqueous solutions of EMAA doped with cationic nitroxide spin probes, 4-(*N*,*N*-dimethyl-*N*-alkyl)ammonium-2,2,6,6-tetramethylpiperidine-1-oxyl iodides (CAT*n*, Chart 1) with different alkyl groups: methyl (CAT1), octyl (CAT8), and hexadecyl (CAT16).[7] The results have indicated that most spin-probe molecules are bound to large intermolecular micelles; the alkyl chains of CAT8 and CAT16 penetrate into the interior of the aggregates and exhibit different dynamics, suggesting that the longer chain of CAT16 penetrates deeper, into the more viscous regions of the micelle, compared to CAT1.

The conclusions deduced from the ESR spectra in EMAA are in agreement with evidence obtained by fluorescence probe spectroscopy:[8] Pyrene (P) and 1,3-bis(1-pyrene)propane (P3P) fluorescence have been interpreted in terms of the local polarity and the local viscosity in the micelles. Both methods, ESR and fluorescence, supported the idea of an equilibrium between small "unimeric" aggregates and large multi-

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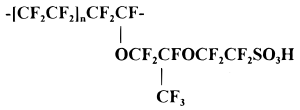
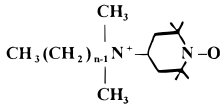
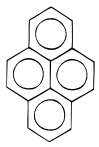
Chart 1. Nafion, Spin Probes, and Fluorescent Probes



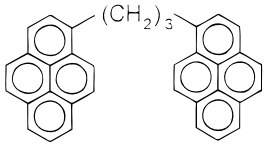
Nafion (in acid form)



CAT*n* (*n*=1, 8, 16)



Pyrene (P)



1,3-bis(1-pyrene) propane (P3P)

chain aggregates in aqueous solutions of the ionomer, and the critical micelle concentration (cmc) was deduced from the variation of the peak intensities in the fluorescence spectrum of P as a function of ionomer concentration.

Spin probe studies were also performed for Nafion, the ionomer consisting of a perfluorinated backbone and pendant chains terminated by sulfonic groups, doped with *n*DSA and *n*DSE spin probes.[4,9] As in EMAA, the ESR line shapes are typical of slow-motional dynamics, a clear evidence that the probes are located inside the ionomer micelles. The ^{14}N isotropic hyperfine splittings, a_N, which are indicators of the local polarity, were however close to the values in neat water. This paradox was explained by proposing that the probes "drag" part of their solvation shell into the hydrophobic environment, as suggested previously for the same probes in micellar solutions of ammonium perfluorooctanoate.[10] We will return to this issue in the Discussion.

The present study extends the ESR studies based on CAT*n* probes and fluorescence spectroscopy based on P and P3P to aqueous solutions of Nafion. The main objective was to deduce further details about the structure of, and dynamics in, the aggregates.[3,4,9] We note that the CAT1 probe in Nafion solutions in different solvents has been examined in the limited temperature range from the melting point of the solvent to 300 K.[11] The advantage of CAT*n* probes (with $n = 1$, 4, 8, 11, and 16) has been demonstrated recently in a nonionic polymeric surfactant, and the ESR spectra of the probes were used to determine the hydration profile in the isotropic and liquid crystalline phases and to clarify the mechanism of phase transitions.[12]

Experimental Section

Materials. Nafion solutions were prepared in an autoclave from the corresponding 117 Nafion membrane as the Li salt (90% neutralization of the acid groups in the ionomer) by dissolution in a water/ethanol 1:1 v/v mixture and were a gift from G. Gebel (CEA/Grenoble, France). The equivalent weight of the ionomer was 1100 in g of ionomer per mol of SO_3^-. The spin probes 4-(*N*,*N*-dimethyl-*N*-alkyl)ammonium-2,2,6,6-tetramethylpiperidine-1-oxyl iodides (CAT*n*) with $n = 1$, 8, and 16 were purchased from Molecular Probes, Eugene, OR, and used without further purification. Pyrene (P) from Aldrich was purified by column chromatography. 1,3-Bis(1-pyrene)propane (P3P) from Molecular Probes and a perfluoropolyether oil ("Fomblin") from Montedison USA Inc. were used as received. The ionomer and the probes are shown in Chart 1.

Sample Preparation. The soluble Nafion powder obtained by evaporation of the solvent mixture at ≈360 K was dissolved in ethanol to an ionomer concentration of 20% w/w; the ethanol solution was then dialyzed against excess water using Bio Design Dialysis tubing #D102. The dialysis was performed for 3 days, and the external solvent was exchanged seven times for pure water; the polymer content in the resulting aqueous solution was determined from the weight loss after drying to constant weight at 390 K. The appropriate amount of an aqueous LiOH solution was then added to ensure full neutralization of the sulfonic groups. This step was necessary in order to prevent the decomposition of the spin probes, which is accelerated by acids. The final Nafion concentration was ≈7% w/w. Less concentrated solutions were obtained by adding doubly distilled water and stirring overnight.

The stock solution of the spin probe in ethanol was divided into several vials, and the solvent was removed by evaporation with a stream of nitrogen; the resulting films were then dissolved in the ionomer solutions. To facilitate probe solubilization, the samples were sonicated for 20 min (Branson bath sonicator) and stirred with magnet bars at ≈313 K. The spin probe concentration was 0.5 mM, corresponding to a molar ratio $[SO_3^-]/[CATn] \approx 120$ and ≈18 in the 6.6% and 1% Nafion solutions, respectively. The solutions were prepared in a glovebox, in an oxygen-free atmosphere. The solvent and the original ionomer solution were bubbled with nitrogen for 20 min, and the nitrogen used for deaeration of the ionomer was presaturated with water. The ionomer solutions were transferred in the glovebox to capillaries made of disposable pipets and sealed with Parafilm. Finally, the tubes were flame-sealed prior to the ESR measurements.

The pyrene film prepared from a stock solution in ethanol was dissolved in the ionomer solutions, while P3P was introduced as a stock solution in dioxane (≈2% v/v dioxane added). The concentration of the fluorescent probes was 1×10^{-5} M. The samples were deaerated prior to measurements by bubbling with argon for 40 min at least.

ESR Spectroscopy. Spectra at X band were measured with a Bruker ECS106 spectrometer equipped with the ESP 3240 data system for acquisition and manipulation and with the ER4111VT variable temperature unit. The parameters used for data acquisition were as folows: magnetic field modulation, 100 kHz; microwave power, 2 mW; modulation amplitude, 0.5 or 1 G, depending on the line width and signal intensity; time constant, 20 ms; conversion time, 41 ms; number of points, 2048; number of scans, ≥10; temperature, 120−360 K. For low-temperature experiments the ionomer samples were quenched in liquid nitrogen, to ensure that the micellar structure is retained,[13] and transferred to the ESR cavity while at 120 K.

Fluorescence Measurements. Steady-state fluorescence spectra were recorded at ambient temperature (≈25 °C) with an Aminco-Bowman spectrofluorimeter and/or with the optical spectrometric multichannel analyzer (OSMA, Princeton Instruments) using excitations at $\lambda_{exc} = 337$ nm or $\lambda_{exc} = 345$ nm. Some spectra were recorded using the spectrofluorimeter LS50B Perkin-Elmer. Additional details have been published.[8]

Results

In this section we will describe the ESR spectra of the cationic probes measured as a function of temperature and ionomer concentration and the fluorescence spectra of P and P3P.

ESR Spectra of CAT*n* Spin Probes. X-band ESR spectra at 300 K of the probes in the Nafion solutions containing 6.6% w/w polymer are presented in Figure 1. A motionally averaged signal is observed for CAT1; the three lines are broader, however, than those ob-

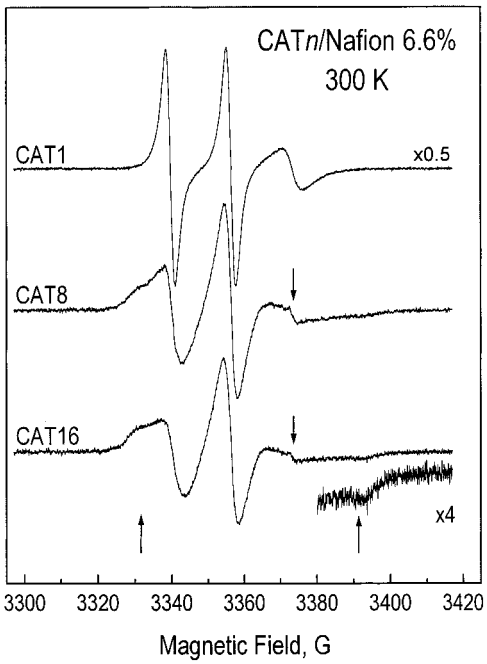


Figure 1. X-band ESR spectra of CAT*n* spin probes in aqueous Nafion solution (ionomer concentration 6.6% w/w) at 300 K. Modulation amplitude: 0.5 G. Spectra are normalized to the same integrated intensity and expanded or reduced vertically by the factor given on the right.

served for the probe in neat water,[7,14] indicating slower dynamics. The ^{14}N isotropic hyperfine splitting, a_N (half the separation of the two outermost lines), is 16.80 G, the same as in neat water at this temperature, indicating a polar environment; the experimental error is ±0.07 G. The amphiphilic spin probes, CAT8 and CAT16, exhibit slow-motional spectra; the maximum separation indicated by the upward arrows in Figure 1 is the same for CAT8 and CAT16, $2A_{zz}' = 60.5 \pm 1.0$ G. The weak isotropic component (≪1% of the total intensity), whose high-field lines are indicated by downward arrows in Figure 1, is assigned to spin probes on the micelle surface or associated with unimeric micelles and is too weak for detailed analysis. The pronounced changes of the ESR line shapes in the presence of Nafion compared to those observed in water are clearly due to association of the spin probes with the ionomer chains. The individual features for each probe result from the specific location in the ionomer aggregates.

Parts A, B, and C of Figure 2 present the temperature variation of the ESR spectra of CAT1, CAT8, and CAT16 in the Nafion solutions (6.6% w/w polymer). Rigid limit spectra are observed up to 200 K; the maximum line separation in these spectra (indicated by upward arrows) is $2A_{zz}$, the largest principal component of the ^{14}N hyperfine splitting tensor. The average values of $2A_{zz}$ in the temperature range 120−200 K are collected in Table 1, together with the corresponding data for the Nafion solution containing 1% w/w polymer (vide infra) and with earlier data for the EMAA solutions.[7] Above 200 K, the $2A_{zz}'$ values progressively decrease, indicating increasing mobility. At a given temperature $2A_{zz}'$ is lower for CAT1, indicating a higher mobility; for CAT8 and CAT16 the $2A_{zz}'$ values at a given temperature are close.

At and above 275 K the ESR spectrum of CAT1 consists of a three-line signal. The lines become narrower at higher temperatures, and the hyperfine splitting decreases. The temperature variation of $2a_N$ for the CAT1/Nafion system is plotted in Figure 3 and compared with the corresponding data for the EMAA solution containing 23% w/w ionomer and for neat water. In all cases the temperature dependence is essentially linear; the slopes of the linear best fits for

Table 1. Maximum Separation, $2A_{zz}$ (G), in the Rigid Limit ESR Spectra of CAT*n* Spin Probes in Nafion Solutions (Average Values for the Temperature Range 120−200 K, ±0.5 G) and in EMAA Solutions[7]

	Nafion		EMAA	
	1%	6.6%	1%	23%
CAT1		72.4		70.8
CAT8	75.1	73.2	72.3	70.7
CAT16	74.3	73.4	72.0	71.2

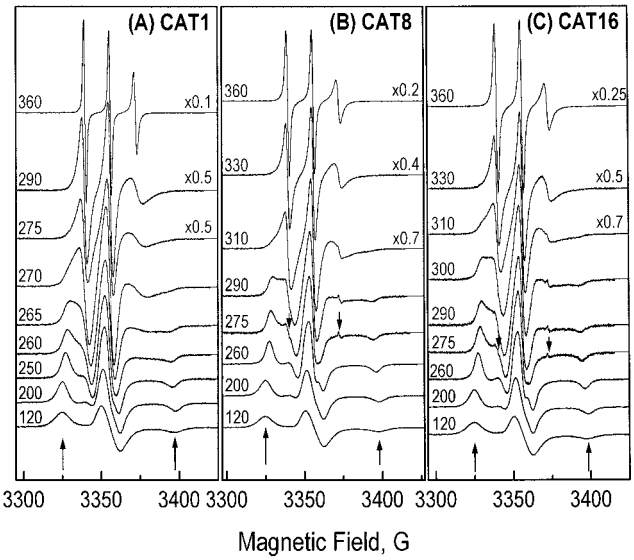


Figure 2. Temperature evolution of X-band ESR spectra of CAT1 (A), CAT8 (B), and CAT16 (C) in aqueous Nafion solution (ionomer concentration 6.6% w/w). Modulation amplitude: 1 G in the range 120−310 K and 0.5 G at higher temperatures. Spectra are normalized to the same integrated intensity; some spectra are reduced vertically by the factor given on the right. Upward arrows point to the extreme separation (at 120 K) for the probes. Downward arrows for CAT8 and CAT16 show the minor component that was not considered in the interpretation.

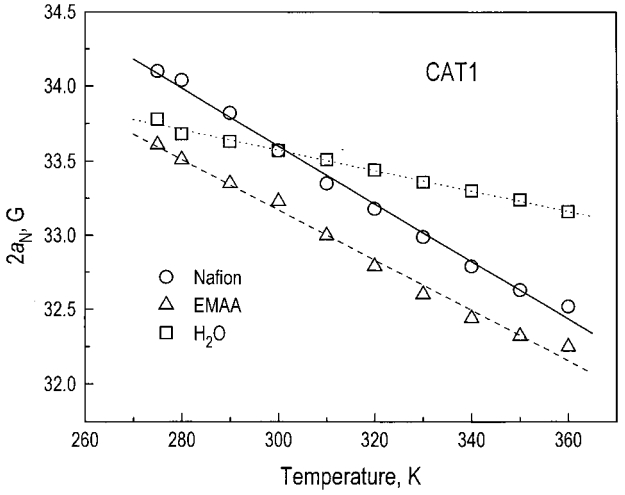


Figure 3. Hyperfine splitting, $2a_N$, vs temperature for CAT1 in aqueous Nafion solution (ionomer concentration 6.6% w/w), in aqueous EMAA solution (ionomer concentration 23% w/w), and in neat water.[7]

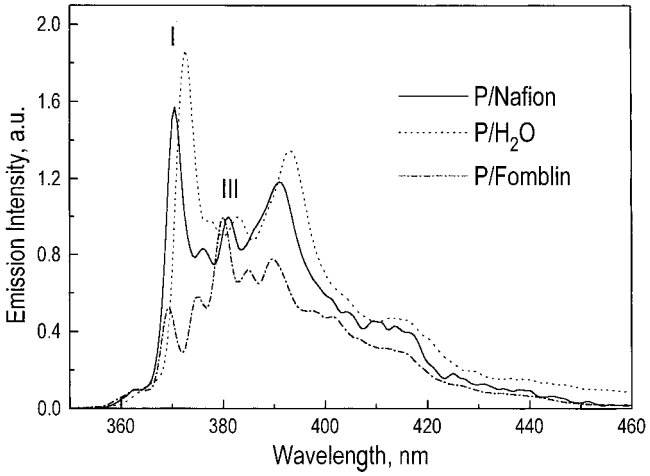


Figure 4. Fluorescence spectra of pyrene in aqueous Nafion solution (ionomer concentration 7% w/w), in neat water, and in the perfluorinated oil (Fomblin). In all spectra the intensity of the third maximum (III) was normalized to unity. The excitation wavelengths, λ_{exc}, were 332, 334, and 328 nm for Nafion, water, and Fomblin, respectively.

the two polymer systems are similar, but higher than the slope of the $2a_N$ vs temperature plot for CAT1 in neat water.

The weak isotropic component appears at 275 K, as shown by the downward arrows in Figure 2B,C; this minor component will not be discussed further. At 360 K the intensity ratio of the three signals in the spectra of CAT8 and CAT16 is similar to that for CAT1 at 300 K, but the lines are broader. Moreover, the lines at 360 K are broader for CAT16 compared to CAT8, suggesting that the dynamical processes take place with rates decreasing from CAT1 to CAT8 and to CAT16. At 360 K the ^{14}N hyperfine splittings are the same for CAT8 and CAT16: $a_N = 16.31$ G, within experimental error the same as the value of $a_N = 16.26$ G measured for CAT1 at this temperature.

The ESR spectra of the amphiphilic spin probes were also investigated in Nafion solutions containing 1% w/w ionomer. Qualitatively, similar spectra have been observed in the examined temperature range. There are, however, some quantitative differences: as seen in Table 1, the rigid limit separation is larger in the dilute solution and is within experimental accuracy the same for CAT8 and CAT16.

Fluorescence Spectra of P and P3P. The fluorescence spectrum of pyrene in the micellar Nafion solution is compared in Figure 4 with the spectra in water and in the perfluorinated oil, Fomblin. All spectra exhibit a well-resolved vibronic fine structure. The intensity ratio of the third to the first fluorescence maxima, I_{III}/I_I, is characteristic of the local polarity ("polarity index"):[15] The intensity of peak I, corresponding to the forbidden $S_0(v=0) \leftarrow S_1(v=0)$ transition, increases in more polar media, while that of peak III, corresponding to the allowed $S_0(v=1) \leftarrow S_1(v=0)$ transition, is almost unaffected. In the micellar solution of Nafion $I_{III}/I_I = 0.64 \pm 0.03$, a value intermediate between those determined for water (0.53) and for methanol (0.75),[15,16] indicating a polar environment for pyrene. This result is in contrast with the micellar EMAA solutions where $I_{III}/I_I = 1.52$, suggesting location of P in a region of low polarity.[7] Furthermore, the P/Nafion spectrum is shifted (by 2 nm) to shorter wavelengths compared to the P/H_2O spectrum. This effect was not observed in the EMAA system

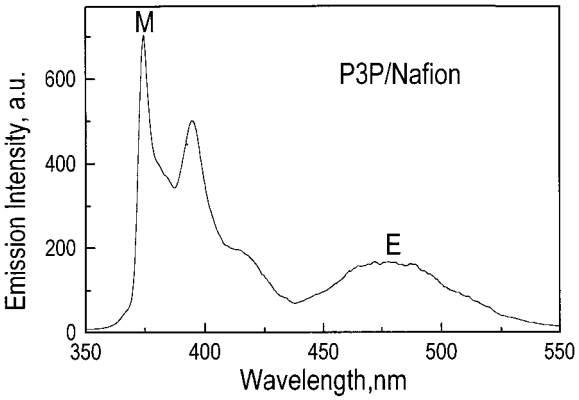


Figure 5. Fluorescence spectrum of P3P in aqueous Nafion solution (ionomer concentration 1.7% w/w) measured with $\lambda_{exc} = 332$ nm. M and E indicate maxima of the monomer and excimer emissions, respectively.

and seems to be due to the presence of fluorine atoms; it is even more pronounced for the P/Fomblin spectrum (shift of 3 nm with respect to water). In the oil $I_{III}/I_I = 1.91$, indicating as expected a nonpolar site. The blue shifts are also detectable in the absorption and the excitation spectra of pyrene in the two perfluorinated hosts; a similar effect has been mentioned by Blatt et al. for Nafion membranes swollen by water.[17] Moreover, the rate constant of exponential decay of excited pyrene in Nafion micelles is lower than in homogeneous solution in water, 3.5×10^6 s^{-1} vs 5.0×10^6 s^{-1}.

P3P is a microviscosity probe because it forms excimers on excitation, due to the presence of two pyrenyl moieties in the molecule; this process is more efficient in media of low viscosity. Figure 5 presents the fluorescence spectrum of P3P in the Nafion solution. The intensity ratio of the excimer (≈480 nm) to the monomer (374 nm) emission maxima, I_E/I_M, does not change with ionomer concentration in the range 0.8−7% w/w, and its average value is 0.235 ± 0.025. The intensity ratio corresponds to a microviscosity of 75 cP (±20%), based on a calibration curve obtained previously.[7] This value is lower than that deduced for EMAA (230 cP) but higher than the values in dodecyl- and hexadecyltrimethylammonium bromide micelles, which are 18 and 42 cP, respectively.

Discussion

In this section we will discuss the location of the spin probes and the effect of the ionic interactions on the location and will draw conclusions on the hydration of the micellar aggregates from both the ESR and the fluorescence results.

Location of Spin Probes and Fluorescent Probes. Only one spectral component was observed for each probe in the temperature range 120−360 K.[18] The motional rates decrease from CAT1 to CAT8 and to CAT16, but the motional mechanism seems to be the same for all probes; for instance, similar spectra are observed for CAT1 at 300 K and CAT8 and CAT16 at 360 K and for CAT1 at 265 K, CAT8 at 275 K, and CAT16 at 290 K. Moreover, the a_N values in the high-temperature limit, 360 K, are the same for all probes: 16.30 ± 0.07 G. The broader lines and slower dynamics for the probes compared to the spectra in neat water[14] are clearly a result of the probes association with large aggregates, as deduced for the doxyl probes for Nafion concentrations ≥5% w/w. For the CAT*n* probes, how-

ever, we observed only one component in solutions containing 1% w/w ionomer; at this low ionomer concentration probes associated with small ("unimeric") micelles were detected for 5DSA and 10DSA.[9]

We will rationalize the absence of CAT*n* probes associated with unimeric micelles in Nafion solutions by analyzing the ^{14}N hyperfine splittings: The a_N value for CAT1 at 300 K is identical to that in neat water, suggesting a polar environment; the a_N value at 275 K is even higher, 17.05 G (the water value is 16.95 G). We propose that the a_N increase in Nafion is due to the formation of an "ionic bond" between the cationic probe and the sulfonic groups,[11] in accord with the conclusions of a recent study of the effect of charge neutralization on a_N.[19] The concept of ionic bond must not be taken literally, only in the sense that interaction between the SO_3^- group of the polymer and the quaternary nitrogen in CAT1 leads to a reduced rate of rotational diffusion of the probe. As seen in Figure 3, a_N values of CAT1 in water, Nafion, and EMAA decrease as the temperature increases. The decrease of a_N with temperature in water is relatively small and has been related to the lowering of dielectric constant of the solvent.[7] Comparison of the a_N values for the two ionomer systems gives support to the idea of the ionic bond: The electrostatic interactions are stronger in Nafion micelles than in EMAA micelles, due to higher degree of ionization of the sulfonic groups in comparison with the carboxylic groups, and the net effect in the examined temperature range is the increase of a_N in Nafion compared to EMAA, as also seen in Figure 3. The larger slope for the ionomers compared to water is most likely due to the combined effects of solvent properties and ionic bond strength as a function of temperature.

We note, in parallel, the larger A_{zz} values for CAT1 in Nafion compared to EMAA (Table 1). Experimental data for CAT1 in neat water are not available, because phase separation occurs on freezing the aqueous solution of the probe; however, the ESR spectra at ambient temperatures have been simulated with $2A_{zz}$ values in the range 71.4−72.4 G.[20] The values for the three probes are larger in Nafion, and smaller in EMAA, than the range of values in water, again indicating the stronger guest−host electrostatic interactions in Nafion. Moreover, the a_N values determined from the ESR spectra of the probes at 360 K are 16.30 G in 6.6% Nafion solution vs 15.90 G for the slow-motional component of CAT8 and CAT16 in EMAA solution.[7] It is reasonable to assume that the CAT*n* probes prefer to associate with the multichain aggregates because the local density of the anionic (sulfonic or carboxylic) groups is higher, compared to that in unimeric micelles. The fluorescence emission of P shown in Figure 4 indicates a high local polarity, but also the presence of fluorine atoms in the site (from the blue shift).

Taken together, these results indicate that the piperidynyl ring of the CAT*n* spin probes is located close to the sulfonic headgroups of Nafion, while the alkyl substituents penetrate inside the aggregates due to the hydrophobic interactions with the ionomer chains, thus leading to slower dynamics for CAT16 and CAT8 compared to CAT1. The fluorescent probes also reside inside the aggregated chains (as indicated by the blue shift in the P spectra) in a region of high local polarity and lower viscosity compared to that in the hydrophobic core of EMAA micelles.

Hydration of the Multichain Aggregates. The slower dynamics of CAT8 and CAT16 (compared to CAT1) can be explained by the hydrophobic interactions of the alkyl groups inside the micellar aggregates. The A_{zz} value for the larger probes is, within experimental error, similar to that for CAT1 (Table 1), suggesting a hydrophilic environment of the nitroxide group. This behavior is partly due to ionic bond formation and partly a result of water penetration into the aggregates. The high-polarity index for P deduced from the fluorescence spectra provides strong support for the presence of water inside the aggregates. Moreover, the increase of the maximum separation, A_{zz}, in solutions containing only 1% w/w Nafion (Table 1) suggests that the amount of water in the micelles increases in the more dilute ionomer solutions. Additional support for this explanation has been presented recently, in a comparative study of pyrene fluorescence in fluorinated and protiated surfactants: a surprising finding was that the local polarity of pyrene (a hydrophobic probe) is *higher* in the fluorinated micelles, although the critical micelle concentration (cmc) of the fluorinated surfactant is lower.[21]

In the case of the *n*DSA probes in Nafion we proposed[9] that the nitroxide group *drags* some of its solvation water into the micelle. This is possible also in the case of the cationic probes. The results with pyrene, however, suggest that water is present inside the fluorinated micelles even if the probe is very hydrophobic and not solvated by water. The presence of water in the Nafion aggregates can also explain the previous results for pyrene fluorescence in Nafion membranes swollen by water, which also suggested a polar environment.[22]

We can now provide an answer to the important question: why do the doxyl probes and the cationic probes intercalate inside the aggregated protiated chains (EMAA) and report on a nonpolar site, while the same probes intercalate in the Nafion micelles but report a polar site? It seems that the answer lies in the hydrophobic interactions: the protiated probes prefer the water environment *inside* the micelles rather than the environment of the perfluorinated chains. The same protiated probes intercalate in hydrophobic regions of the aggregates in EMAA.

Cmc in Nafion Solutions. For the EMAA solution, we determined the critical micelle concentration (cmc = 0.02% w/w) from the plot of the polarity index vs ionomer concentration: below the cmc the polarity index sharply decreases.[8] For the Nafion system a reliable estimate of the cmc is not possible because the difference in the polarity index between the micellar solution and neat water is very small. It is important to note, however, that the fluorescence spectrum of pyrene does not change, within the experimental uncertainty, in the concentration range from 0.025−7% Nafion. We did observe a slight decrease of the polarity index in the Nafion solution containing 0.01% w/w ionomer ($I_{III}/I_I = 0.59$); at this concentration the fluorescence and the excitation spectra are red-shifted, as seen in Figure 6. This finding suggests that at this low Nafion concentration there are fewer perfluorinated chains in the neighborhood of the probe, due to the collapse of the multichain aggregates or to partition of the probe between the micelles and the bulk aqueous phase.[23] In view of these results it is reasonable to take 0.01% w/w as the *upper limit* for the cmc of Nafion in aqueous solutions.

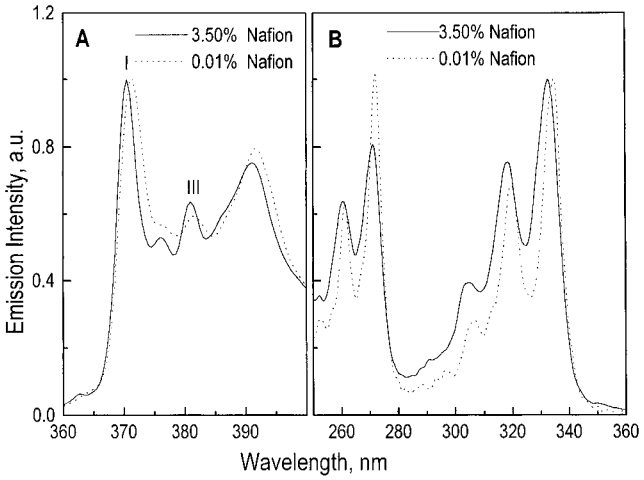


Figure 6. Effect of ionomer concentration on the fluorescence (A) and excitation (B) spectra of pyrene. For better visualization of the spectral shift only the 360−400 nm range is shown in (A). In (B) emission was recorded at $\lambda_{em} = 370$ nm for different excitation wavelengths.

Finally, we note that the slight changes in the appearance of spectra for CAT8 and CAT16 depending on the thermal treatment (for instance the spectrum at 300 K for CAT16 in Figures 1 and 2C) could be due to a redistribution of micellar sizes as a function of temperature.[18] Kinetic effects in polymer systems that consist of micelles have been detected recently,[24,25] and in our study of EMAA ionomers, we observed a time dependence over ≈2 days of the viscosity after dilution of the EMAA solution containing 23% w/w ionomer.[26]

Conclusions

Analysis of the ESR spectra of cationic nitroxide spin probes CAT*n* in terms of the ^{14}N hyperfine splittings (a_N and A_{zz}) and line shapes indicated the formation of an ionic bond between the sulfonic group of the ionomer and the positively charged probes. Because of this bond, the experimentally measured a_N values at temperatures below 300 K and the A_{zz} values (from the rigid limit spectra) are higher in the presence of Nafion than in neat water. The ionic bond between the probes and the sulfonic groups of Nafion is stronger than with the carboxylic groups of poly(ethylene-*co*-methacrylic acid) (EMAA, neutralized with K^+) ionomer. The larger probes, CAT8 and CAT16, are deeper inside the chain aggregates, but the high local polarity reflected in the magnetic parameters can be explained by water penetration inside the aggregates. It is clear that, for protiated probes inside perfluorinated micellar aggregates, the dynamics is a more reliable indicator of probe location than a_N.

The intensity ratio of the third to the first vibronic bands, I_{III}/I_I, in the fluorescence spectrum of pyrene in aqueous solutions of Nafion indicated a high polarity at the probe site and provided support for the idea that water penetrates into the polymer aggregates. This major conclusion is in agreement with the spin probe results. The microviscosity at the probe site, 75 cP, was determined from the intensity ratio of the excimer to the monomer fluorescence in the spectrum of 1,3-bis(1-pyrene)propane (P3P) as the probe, based on a previous calibration curve with solvents of known viscosity. The upper limit of the cmc for Nafion chains, 0.01% w/w, was estimated from the slight decrease of the ratio I_{III}/I_I and the spectral shifts in the fluorescence spectra of P at this concentration.

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