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Electron Spin Resonance Study of Water Finely Dispersed in Perfluorinated Polymers and of Their Micellar Solutions

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The electron spin resonance (ESR) spectroscopy of paramagentic probes (transition metal ions and nitroxide radicals) has been used for the characterization of some properties of perfluorinated compounds. This overview reports on the results obtained in the study of: a) the rheological properties of water finely dispersed into the porosities of the Nafion ionomer and of perfluoropolyethers (PFPE); in this investigation, neutral and charged small nitroxides were used, whose magnetic parameters and ESR lineshapes are extremely sensitive to the changes of local environments; with VO^{2+} as a probe, both dispersion and aggregation properties of the metal ion into Nafion skeleton have been analyzed; b) the aggregational properties of PFPE in water solution in the form of spherical and non-spherical micelles; large cationic and neutral nitroxides capable of interacting with the molecular assemblies or being trapped in their network allowed us to establish the optimum conditions for the use of spin probes for dynamic and structural studies in these systems and the limits of reliability of the ESR technique in micellar systems.

INTRODUCTION

Perfluorinated compounds are largely employed both as fine chemicals and as specialty products to be used in a variety of devices.[1] Particular attention has been dedicated to synthetic perfluorinated ionomers which contain a fluorocarbon polymer backbone with pendant ionic groups forming ionic clusters.[2,3] The best known compound of this class is the so-called Nafion[R] (Nafion is the trademark of E.I. duPont de Nemours and Co.), i.e. a polymeric material whose structural and dynamic characteristics have been deeply studied.[1,4-7] The structure of Nafion[R] consists of sulfonic groups connected to a polytetrafluoroethylene skeleton through short chains of perfluoropropylene ether:

$$-(CF_2CF_2)_n-CFO-(CF_2CFO)_m-CF_2CF_2-SO_3H$$
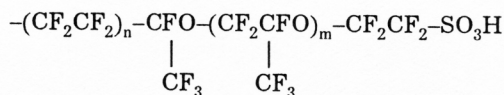
with m usually unity and n ranging between 5 and 11. The great technological importance of Nafion in electrochemical processes has prompted extensive studies by several spectroscopic and scattering methods[8] including differential scanning calorimetry (DSC), X-ray scattering,[9] small angle neutron scattering,[10] nuclear magnetic resonance,[11] and electron microscopy.[12] The thermodynamics of the Nafion membrane-based ion selective electrodes has been treated by Espenscheid et al.,[3] together with the use of Nafion coated electrodes for in vivo neurotransmitter.

The presence of metal ions in these compounds has a profound relevance to their use in both electrochemistry and catalysis.[2,3,13] The local structure of the metal ions has been analyzed by using, for instance, EXAFS,[14] IR,[15] Raman[16] and on the basis of the results from fluorescence and phosphorescence of organic chromophores interacting with the metal cations.[17,18] At a low solvent content, the properties of the ionomer are explained by assuming that a considerable aggregation occurs among the ionic groups to yield ionic clustering upon water adsorption. This structure arises due to equilibrium between electrostatic interactions and elastic forces of the polymer backbone. The ionic clusters contain sulfonic group, conterions, and hydration water as well as some of the fluorocarbon side chains.[4] The situation may, therefore, be pictured as a reverse micelle-like region with a water/fluorocarbon backbone interface, which minimizes both the hydrophobic interactions of water with the organic network and the electrostatic repulsions between neighboring sulfonic groups. Several theoretical models have been proposed in order to explain the experimental results.[19]

Other materials exhibiting some analogies with Nafion have been synthesized in the Montefluos S.p.a. laboratories (Spinetta Marengo and Bollate, Italy). These products, known as perfluoropolyethers (PFPE), have a high thermal, chemical and biological inertness and low hydrophilicity. They have been prepared with different chain lengths and branching with resultant higher conformational freedom than that of polycarbons.[20] Moreover, the presence of the $-CF_2-O-CF_2-$ethereal bridges in the PFPE structure allows the hydrophobic chains to be more flexible than those of simple perfluoroalcanoates. PFPE compounds are liquids over a broad range of temperature and molecular weights.

The surfactant properties of PFPE have been established; the occurrence of micellar aggregates and/or microemulsions is reported in the literature[21] with critical micellar concentration (cmc) of the order of 10^{-5} mol/L, well below the cmc's of the perfluorinated compounds.[22]

Since the first studies on the physico-chemical properties of perfluorinated polymers and on their technological applications, electron spin resonance spectroscopy (ESR) has been considered as a valid tool for the study of several features, viz.:

a) structure and dynamics of transition metal ions and organic radicals trapped as fluid solutions in the polymeric matrix, to clarify both the ionic mobility and the peculiar behavior of finely dispersed liquids, as well as peculiar electrochemical properties;[23-31]

b) properties of cross-linked products (in particular PFPE) studied in the form of spin-labeled adducts, to analyze the dynamics of the side chains and the pools formed after solvent swelling;[32]

c) the aggregation states in fluid solutions and the perturbations that can occur in PFPE surfactant systems when the spin probes are added in concentrations comparable to their *cmc*.[33,34].

In this paper, we give an overview of the work carried out in the last few years, mainly by ESR and ENDOR, in our laboratory, to provide further clarification of points a) and c), with particular emphasis on the study of the behavior of water finely dispersed in both Nafion and PFPE and to the micellar solutions of PFPE for which the spin probe technique revealed to be an accurate tool, when certain experimental conditions are fulfilled. Details on the experimental procedure and on the instrumentation used can be found in the quoted references.

FINELY DISPERSED WATER AND CATIONS

The electron spin resonance of paramagnetic probes (both nitroxides and transition metal ions) has been largely used to obtain information on the rheological properties of liquids dispersed in restricted spaces and on short- and long-range molecular interactions in these systems.[35,36] In particular, details on the interactions with support surfaces and spin-spin interactions have been obtained. Mainly the following nitroxides have been employed for the study of the rheological properties of dispersed liquids:
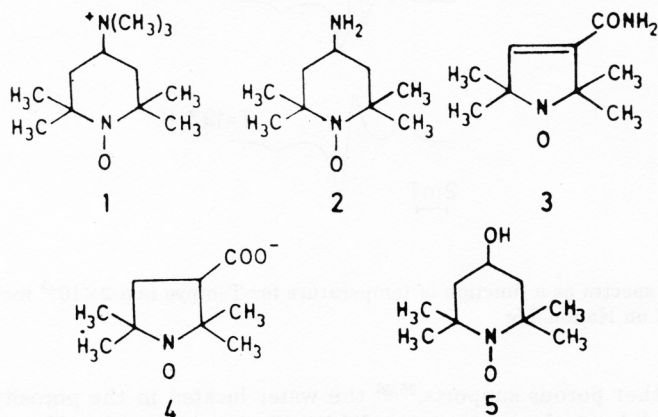
1: 4-trimethylammonium-2,2,6,6-tetramethylpiperidine-2-oxyl, iodide salt (Temp-TMA$^+$); 2: 4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl (Tempamine); 3: carboxyamido--2,2,5,5-tetramethylpyrroline-1-oxyl (Tempyo); 4: 2,2,5,5-tetramethylpyrrolidine-1-oxyl--3-carboxylate, sodium salt (Tempydo$^-$); 5: 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (Tempol).

Aqueous solutions of the nitroxides 1–4 have been used for the study of the physico-chemical status of water confined in the void spaces of Nafion membrane after ion exchange with Na$^+$, K$^+$, and Mg^{2+} (decomposition of the nitroxides occurred within a few minutes after the swelling of the membrane in its original acidic form).[31]

As an example, Figure 1 shows the temperature dependence of the EPR spectrum from Tempyo (3) in water solution adsorbed onto Mg-exchanged Nafion. In the analyzed range of temperature, the results indicated that the radicals moved at a continuously decreasing rate when temperature decreased. As previously observed in silica
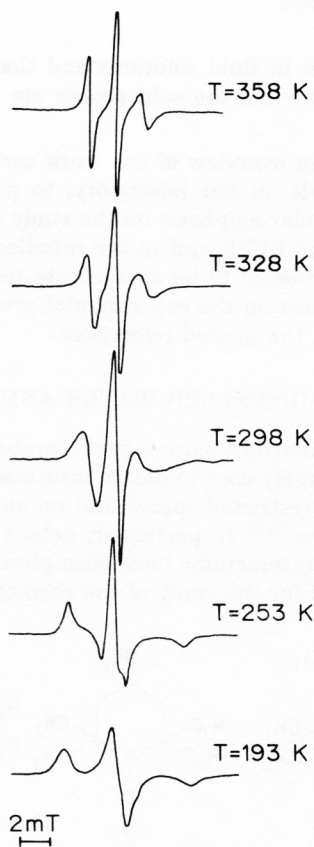
Figure 1. ESR spectra as a function of temperature for Tempyo in a 2×10^{-3} mol/L aqueous solution adsorbed on Nafion–Mg.

gels and in other porous supports,[35,36] the water located in the porosity of the polymeric matrix did not show any true solid-liquid phase transition. The lineshapes appreciably depended on the nature of the exchanged metal ion and, more markedly, on the type of nitroxide. In general, a relatively higher mobility was observed in Mg-Nafion than in K-Nafion or Na-Nafion. The same occurred with Tempamine and TempTMA$^+$, whereas the mobility was practically independent of the ion exchanged with Tempydo$^-$.

A clear dependence on the nature of the nitroxide radicals and of the exchanged metal ions was also observed for the hyperfine constant $<A_N>$, which is known to depend on the solvent polarity.[37] The measured $<A_N>$ are given in Table I. The $<A_N>$ changes observed as a function either of the probe or of the exchanged metal well agreed with the status of the water adsorbed on Nafion.[38] Two distinct forms of water have been suggested to be present in Nafion ionomers: a) hydrogen-bonded-water, with a decreased bond strength because of the partial exposure of the –OH groups to the cluster fluorocarbon chains; b) nonhydrogen-bonded water exposed to a fluorocarbon environment in intracavity regions. The data reported in Table I are indicative of

TABLE I

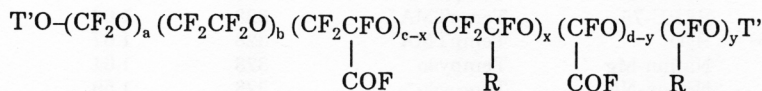^{14}N *Hyperfine coupling constants of nitroxide in water dispersed in perfluorinated compounds*

Compound	Nitroxide	T / K	$<A_N>$ / mT
Nafion-Mg	TempTMA$^+$	328	1.645
Nafion-Na	TempTMA$^+$	328	1.625
Nafion-K	TempTMA$^+$	328	1.62
PFPE-75	TempTMA$^+$	328	1.63
H$_2$O	TempTMA$^+$	328	1.67
Nafion-Mg	Tempydo$^-$	328	1.61
Nafion-Na	Tempydo$^-$	328	1.59
Nafion-K	Tempydo$^-$	328	1.59
H$_2$O	Tempydo$^-$	328	1.62
Nafion-Na	Tempol	328	1.645
Nafion-Na	Tempol	288	1.645
PFPE-75	Tempol	328	1.68
PFPE-75	Tempol	288	1.70
PFPE-65	Tempol	328	1.68
PFPE-65	Tempol	288	1.70
H$_2$O	Tempol	328	1.71
H$_2$O	Tempol	288	1.73

a decrease of the water polarity from Mg– to Na– and K-Nafion. The hydrophilic nature of the occupied sites seemed to directly depend on the hydration energies of the metal ions, whose trend is $Mg^{2+} >> Na^+ > K^+$.

As it has been asserted in previous literature,[35,39,40] calculation of the correlation times for the motion of the paramagnetic probe can further clarify the probe location and its dynamics as well as water diffusivity. This is usually done by the analysis of the ESR lineshape as a function of temperature on the basis of a well established calculation procedure.[41,42] However, the ESR spectra obtained from Nafion samples swollen with nitroxide aqueous solutions cannot be reproduced either by using a single isotropic correlation time or on the basis of an anisotropic motion with two different diffusion coefficients. This is a known situation in the ESR of synthetic polymers and it has been found with both spin labels and spin probes.[43-45] The observed lineshapes were reproduced with a reasonable approximation only by assuming a widespread range of correlation times. In a similar situation found in an amine-cured epoxy resin as a function of solvent plasticizer content,[43] a bimodal or broad monomodal distribution of correlation times for spin probes and spin labels have been suggested. This meant that the radicals occupied Nafion sites in which the dispersed water had different mobilities (diffusivities), although the activation energies calculated from Arrhenius plots were of the correct order of magnitude for the activation energies of the self-diffusion of water in aqueous solution (16.7–20.1 kJ mol^{-1}).[46] Differences in the surface/radius ratio of the cavities occupied by the radicals and differences in the structure of the water adsorbed into the various regions of the ionomer accounted for a distribution of correlation times. However, the above two explanations do not agree with the proposed network model for Nafion structure,[4,19] which suggests homogeneous ionic clusters. The ESR data strongly pointed to a distribution of the ionic cluster sizes. This result was later confirmed by Barklie et al.[26] in a study of the ESR

lineshape of aqueous solutions of VO^{2+} ions adsorbed into Nafion membranes. These authors estimate cluster sizes (after hydration corresponding to 38% water adsorption) in the range 31–39 Å, well in line with the size distribution calculated from the nitroxide ESR results.

On the basis of molecular analogies with the Nafion molecular skeleton and properties, a water pool formation has been assumed for the cross-linked polyethers:[32]

$$T'O-(CF_2O)_a\,(CF_2CF_2O)_b\,(CF_2CFO)_{c-x}\,(CF_2CFO)_x\,(CFO)_{d-y}\,(CFO)_yT'$$
$$\qquad\qquad\qquad\qquad\quad |\qquad\qquad |\qquad\quad |\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\; COF\qquad\; R\qquad\; COF\qquad R$$

where T' was CF_2COF or CF_2R and R the cross-linking site. The coefficients a–d were determined from ^{19}F-NMR to be:

$$a = 5.5 \qquad b = 6.9 \qquad c = 4.2 \qquad d = 0.45$$

Two differently cross-linked polymers were studied: PFPE-65 (equivalent weight = 750) and PFPE-75 (equivalent weight = 1040), with cross-linking degrees of 65% and 75%, respectively.

Average sizes of the water pools, depending on the cross-linking degree, have been suggested from the changes in the Heisenberg spin exchange frequencies of the corresponding spin labeled polymers:[32] the lower the degree of cross-linking, the smaller are the holes available for water adsorption. The status of water finely dispersed in PFPE has been also studied from the ESR lineshapes of nitroxides introduced into the polymer network as aqueous solutions. The positive TempTMA$^+$, as well as the neutral Tempol, have been used for this purpose. Figure 2 shows the ESR spectra of a 10^{-3} mol/L water solution of Tempol adsorbed onto PFPE-75, as a function of temperature down to T values near the glass transition temperature of PFPE-75 (T_g = 175 K). The signal was the typical absorption of radicals in the fast motion domain down to *ca.* 250 K, then it turned to the slow motion shape, which indicated no sudden crystallization of the intracavity water. This clearly reproduced the general trend of the ESR spectra of the nitroxide aqueous solutions adsorbed on Nafion,[31] as well as on various porous supports or confined to restricted spaces.[35] As reported for Nafion, the lineshape could not be exactly reproduced with a single set of radicals with the same isotropic diffusion coefficients and the above considerations apply to this situation as well. However, the fit was improved assuming anisotropic motion. For instance, Figure 3 compares the experimental spectrum of Tempol at 298 K with that calculated with Brownian diffusional coefficients $D_\perp$ = =1.76×10^8 s^{-1} and $D_{||}$ = 1.76×10^9 s^{-1}. Spectral shapes similar to those obtained with TempTMA$^+$ in the fast motional domain are usually observed for oriented systems and may be fitted on the basis of very anisotropic motion and order parameters[47-49] (see also the section on the aggregation properties of the perfluorocompounds). On the other hand, similar absorptions have been reported by Schlick and coworkers[50] in systems containing cross-linked polyurethane polymers and fitted by using a distribution of $<g>$ and $<A_N>$, which reflects the heterogeneity of the local environments. Thus, singly relaxing radicals could not explain the lineshape observed in PFPE polymers and the nitroxides sensed different motional regions, most of them in the fast-motion domain.

The bimodal-like distribution of the correlation times discussed by Brown and Sandreczki[43] well accounted for the observed superposition of a liquid-like and a slow-
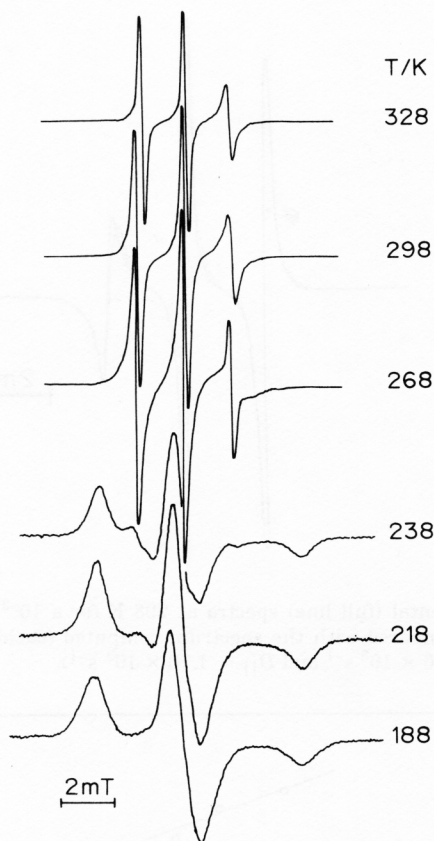
Figure 2. ESR spectra in the temperature range 188 to 328 K for Tempol aqueous solutions (10^{-3} mol/L) dispersed on PFPE-75.

motion signal observed at room temperature for both radicals and was interpreted by the occurrence of radicals localized in regions characterized by markedly different motional properties, namely radicals almost free to move in water pools and radicals strongly interacting with charged sites (the $-COO^-$ groups) of the polymer network.

Like in the Nafion membrane, $<A_N>$ values lower than in bulk water were obtained (see Table I). Figure 4 shows the temperature dependence of $<A_N>$ for Tempol and TempTMA$^+$ in PFPE-75 compared with that in unadsorbed water solution. This indicated a decreased water polarity; it again corresponded to partially non-hydrogen bonded water, which was exposed mainly to the hydrophobic fluorocarbon chains protruding into the water pool. The polarity change was, however, almost independent of the cross-linking degree and this was proved by either charged and uncharged nitroxides.

Analogous results on the motional properties of liquids adsorbed on perfluorinated ionomers have been also obtained by using transition metal ions as paramagnetic probes. In addition, the magnetic resonance of transition metal ions dispersed in the form
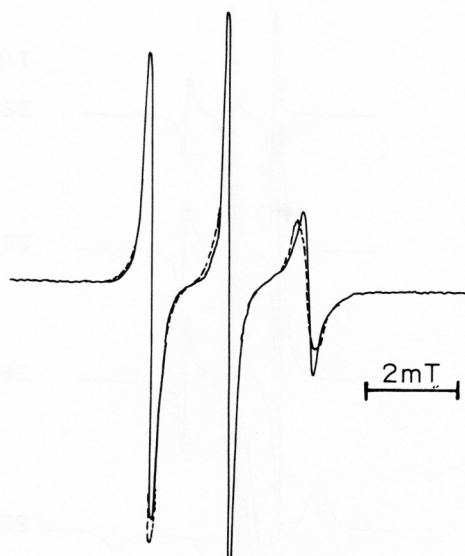
Figure 3. ESR experimental (full line) spectra at 298 K for a 10^{-3} mol/L aqueous solution dispersed on PFPE-75 compared with the spectrum computed (dashed line) for probes in anisotropic motion ($D_\perp = 1.76 \times 10^8$ s^{-1} and $D_{||} = 1.76 \times 10^9$ s^{-1}).
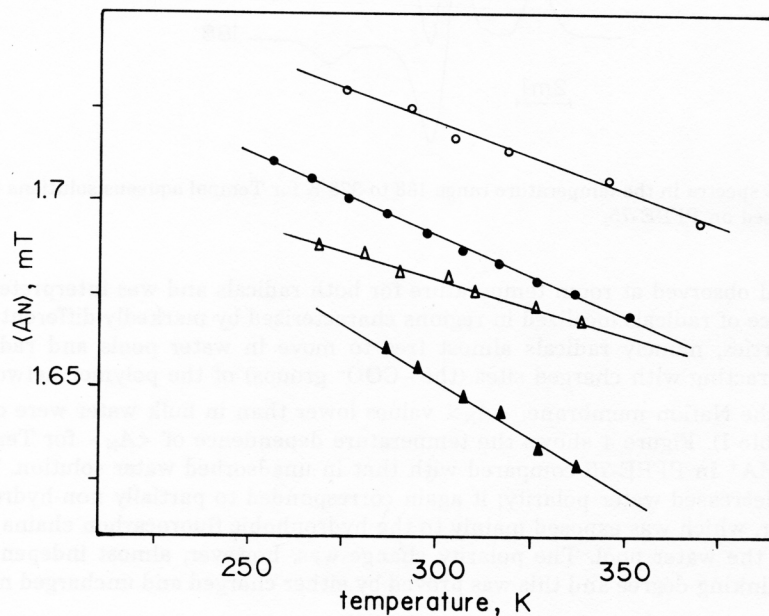

Figure 4. Behavior of $<A_N>$ against temperature for Tempol (circles) and TempTMA$^+$ (triangles) water solution adsorbed on PFPE-75. Open circles and open triangles give the $<A_N>$ values in unadsorbed water.

of liquid solutions (mainly water solution although other swelling solvents have been investigated)[23] exposed several problems of interest in the field of ionomers, *viz.* the local environment of the metal ion, the size of possible ionic aggregates and their intercation distances, the effect of the aggregation on the chain dimensions, the specific ligation of the ion as a function of the content of water or of other solvents. Many of these aspects need further experimentation. Among the ESR-active transition metal ions, Cu^{2+}, Mn^{2+}, VO^{2+}, and Ti^{3+} have been used.[23-27] These ions can be used in both Nafion membrane and powder in their acidic forms, thus complementing the results obtained from nitroxides. Water solutions of $VO(H_2O)_5^{2+}$, in particular, were the starting paramagnetic material for rheological investigation of the water dispersed in Nafion.[25,26] Figure 5 shows two spectra of VO^{2+} ions in water solution adsorbed on Nafion powder at temperatures above and below the usual freezing point of water, T_f. The experimental conditions were set to have a $VO^{2+}/100SO_3^- \approx 1.6$. In this case too, the paramagnetic probe revealed partial mobility of the intracluster liquid at $T < T_f$, whose structure progressively turned to a glassy structure. The same was observed at lower $VO^{2+}/100SO_3^-$ ratios, whereas at higher VO^{2+} concentrations spin-spin interactions occurred. In the absence of spin-spin effects, the calculation of the correlation times in the fast motional region was straightforward on the basis of the m_I dependence of the linewidth:[51]

$$\Delta B = \alpha' + \alpha'' + \beta m_I + \gamma m_I^2$$

with the coefficients having the analytical expressions reported in the literature.[52] Figure 6 reports the Arrhenius plot of τ_c for VO^{2+} in pure and Nafion-dispersed water. The τ_c *vs.* T^{-1} slopes gave the activation energies of VO^{2+} in both systems. Table II compares the E_a values of nitroxides and VO^{2+} in Nafion isomers with the self-dif-
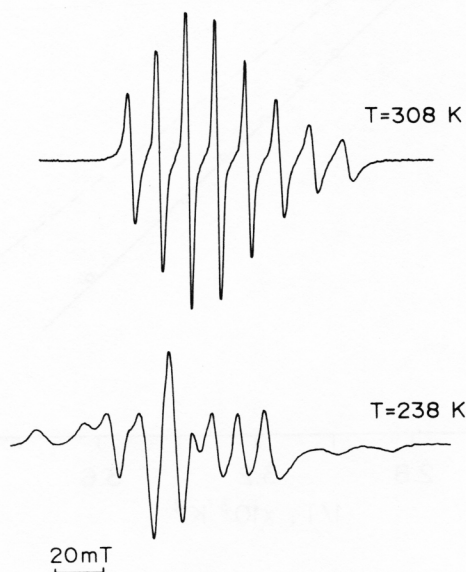

Figure 5. ESR spectra at 238 and 308 K of a 10^{-3} mol/L D_2O solution of VO^{2+} adsorbed on Nafion.

fusion E_a^s of H_2O in aqueous solutions. The reported values indicated that the interactions between positive probes (either metal ion or nitroxides) and negative surfaces of the polymer influenced the viscous process of self-diffusion, without, however, inner sphere coordination. The species responsible for the ESR absorptions was identified as the isolated, square-pyramidal $VO(H_2O)_5^{2+}$ with the usual C_{4v} symmetry. This was proved by the following observations: a) the ESR spectra at 77 K from VO^{2+} water solution adsorbed on Nafion powder and membrane were reproduced with the same magnetic parameters as for unadsorbed vanadyl solutions; b) the same reproducibility holds for ENDOR spectra at 100 K, which were very similar to those reported by van Willigen[53] in frozen aqueous solution and were, therefore, interpreted accordingly. A somewhat different situation is encountered with Cu^{2+} ions in Nafion salts swollen with acetonitrile.[23] The results indicate initial, preferential solvation of the cation with the remaining water molecules when the drying cycle of the system is not completed.

The ENDOR spectra in VO^{2+}/Nafion system gave an additional detail. From the calculated VO–F distance of 10–13 Å calculated from the relation between the electron
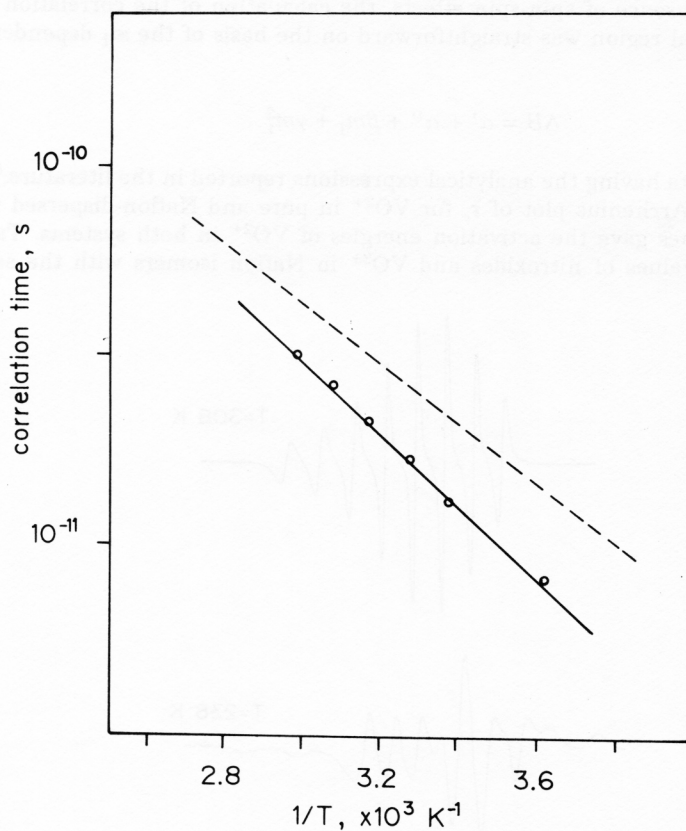

Figure 6. Correlation times *vs.* reciprocal temperature of the 10^{-3} mol/L solution in D_2O adsorbed on Nafion. Dashed line: τ_c *vs.* T^{-1} in unadsorbed water.

TABLE II

Activation energies for the viscous process, E_a, of nitroxides and VO^{2+} in Nafion ionomers, and for self-diffusion, E_a^s, of water in aqueous solutions

System	Activation Energy / kJ/mol
VO^{2+} – Nafion	$E_a = 14.7$
VO^{2+} – H_2O	$E_a = 17.6$
TempTMA$^+$ – Nafion–Na	$E_a = 14.7$
Tempamine – Nafion–Na	$E_a = 13.8$
Tempol – Nafion–Na	$E_a = 17.6$
Tempol – Nafion–Na	$E_a = 19.3$
H_2O self–diffusion	$E_a^s = 16.8–20.1$
H_2O – Nafion–Na	$E_a^s = 21.4$
H_2O – sulfonated exch. resins	$E_a^s = 20.1–212.8$

nuclear-dipolar interaction parameter, α_{ED}, and the distance of the paramagnetic center from the fluorine nuclei, r_F,[54] most of the VO^{2+} ions resulted located in the ionic clusters that are formed after swelling with water, being the mean diameter of the interconnecting channels *ca.* 10 Å. This calculation procedure has also been applied to Ti^{3+} ions.[55]

As observed in other cases of polymeric systems containing metal ions, including Nafion, the 4.2 K ESR spectrum of the VO^{2+}/Nafion system revealed the presence of dimeric species. This was shown by an additional signal appearing at ~160 mT, whose features were typical of the so-called half-field transition observed for triplet state paramagnets and attributed to the $\Delta m_s = 2$ forbidden transition. This observation paralleled those reported for dimeric species of Cu^{2+}, and Ti^{3+} in Nafion membranes.[24,27] A calculation procedure founded on the relationship between zero-field splitting and separations of the low- and high-field turning points allowed us to calculate the V–V distance in the dimeric species to be ≥ 3.5–3.7 Å. Values of ~5 Å are reported for Cu–Cu[24] and Ti–Ti[27] dimers.

AGGREGATION PROPERTIES OF PERFLUORINATED COMPOUNDS

Perfluorinated compounds with suitable molecular skeleton have been shown to act as surfactant materials. When bearing a fluorocarbon chain equal or longer than C_6, they are known to form micelles in aqueous solution.[22,56-59] Also the PFPE compounds, with general formula:
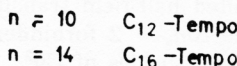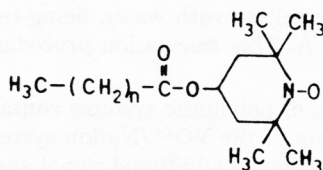
$$F_3C-(\;OCF_2CF\;)_n-OCF_2COO^-$$
$$|$$
$$CF_3$$
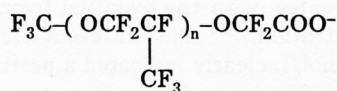
give aggregates in water solution and a critical micellar concentration (*cmc*) of 3×10^{-5} mol/L has been reported[21] for the ammonium salt of PFPE of equivalent weight 706 (from surface tension and conductivity measurements).

ESR spectroscopy of stable organic radicals gives details on the structural and dynamics features of micelles because of its time scale of the order of ns.[60] Indeed, the time events occurring in these auto-assembled molecular aggregates are mainly determined by the residence time of the surfactant molecule in the micelle itself. ESR pro-

bes have been, therefore, used just as fluorescence and NMR probes: they are usually small or bulky nitroxide derivatives, stable organic radicals, such as viologen derivatives, duroquinone, naphthoquinone, *etc.*, and the results obtained from ESR spectroscopy must be considered reliable only when the probe does not introduce strong perturbations in the micellar solution. This has been verified in many cases, such as, for instance, in the study of motional properties and of micellization kinetics of alkylsulfates.[61,62]

Some features of the aggregation properties of PFPE (*EW* = 706), in the form of ammonium salt, have been therefore studied in fluid aqueous solution by the ESR lineshape of differently charged and bulky nitroxides, namely the small, cationic TempTMA⁺ nitroxide, able to appreciably interact with the micelle surface from the aqueous phase, the large, cationic 4-(dimethyl-dodecyl)-ammonium-2,2,6,6-tetramethyl-piperidine-1-oxyl, iodide salt (CAT-12), also able to interact, and the large, neutral alkanoyl-derivatives of Tempol:

$$H_3C-(CH_2)_n-\overset{O}{\overset{\|}{C}}-O-\quad\text{(piperidine-1-oxyl ring with }H_3C\text{ }CH_3\text{ substituents, }N-O)$$

n = 10 C_{12} –Tempo
n = 14 C_{16} –Tempo

which penetrates into the micelle network as a true surfactant molecule. In fact, the latter two nitroxides themselves give micellar solution which *cmc* = 1.6×10^{-6} mol/L and 4.7×10^{-7} mol/L (respectively). Figure 7 reports the variation of the surface tension values with PFPE concentration in the absence (full line) and in the presence (dashed line) of a 10^{-4} mol/L CAT-12. The nitroxide concentration in these experiments was lower than the CAT-12 *cmc* (7.1×10^{-3} mol/L).[63] The two discontinuity points of the surface tension represented the *cmc* of PFPE in water solution (3×10^{-5} mol/L) and a change in the micellar shape from spherical to non-spherical aggregates (2×10^{-4} mol/L). Two discontinuities in the surface tension and conductivity values occurred in other cases of perfluorinated surfactants and were interpreted in terms of structural rearrangements of the aggregates, with the eventual formation of anisotropic phases at higher surfactant concentration.[57,64] The different trends of the surface tension values at [PFPE] < 5×10^{-5} mol/L clearly indicated a perturbation due to the addition of the large CAT-12 nitroxide. The perturbation was strong enough to modify the *cmc* of PFPE. This was promptly verified by the ESR spectra. Figure 8 compares the EPR spectra of 10^{-4} mol/L CAT-12 in water (spectrum a) with those of the same CAT-12 concentration in the presence of PFPE concentrations below the first discontinuity (spectrum b), near and well above the second discontinuity (spectra c and d), respectively). Spectra a and b were practically superimposable and they were the typical three-line absorptions of a nitroxide in solution with almost completely averaged magnetic anisotropies. The experimental spectra were simulated by using the procedure given by Schneider and Freed.[42] The best fit was given by $\tau_c = 6 \times 10^{-11}$ s, as expected
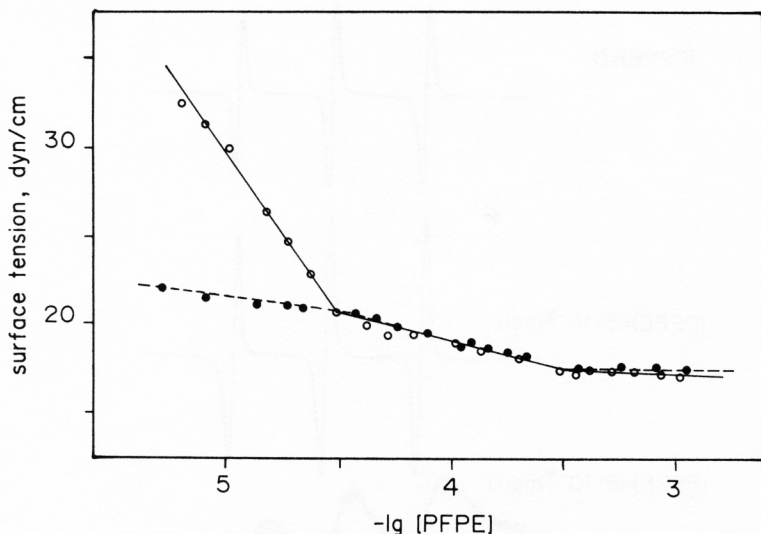
Figure 7. Variation of the surface tension as a function of PFPE concentration in the absence (full line) and in the presence of 10^{-4} mol/L CAT-12.

for radicals under fast motional conditions. Marked changes both in the motion domain and in the $<A_N>$ values occurred when CAT-12 sensed non-spherical micelles (spectra c and d). Values of $\tau_c = 10^{-9}$ s and $<A_N> = 16.23$ G (with respect to 16.85 G of the same radical in pure water) gave the best fit. This result indicated a decreased mobility of the aggregate and a lower polarity sensed by the radical. CAT-12 was definitely inserted in a molecular medium different from the purely aqueous environment or from ionic aggregates held mainly by ionic interactions. When the PFPE/CAT-12 systems were investigated at PFPE concentrations between the two surface tension discontinuities, both spin-spin effects and superposition of signals arising from probes in different environments complicated the overall lineshape. Figure 9 shows the ESR absorption for CAT-12 in the 10^{-4}–5×10^{-5} mol/L concentration range. The three line signal was superimposed to a broad, unstructured signal, whose intensity increased by increasing [PFPE], then began to be resolved with a decreasing width. Such signals were simulated on the basis of the Bloch equations, modified in order to include the Heisenberg spin exchange frequencies. The exchange frequencies used in the spectral simulation decreased from 35 MHz to 10 MHz with the increase of [PFPE], thus indicating an increase in the mean distance amidst probes. All of the above ESR results were clearly a proof of the formation of mixed micelles between the perfluorinated surfactant and cationic nitroxides. This, of course, limited strongly the use of ESR as an experimental technique for the study of micellar systems when probe and surfactant are at comparable concentrations and give mixed micelles, as it happened in the present case. Only at [PFPE] well above the second surface tension discontinuity and at radical concentration significantly lower than that of the surfactant, the probe introduced negligible perturbations and the ESR method could be considered reliable.

No conclusive evidence of mixed perfluorcarbon/nitroxide micelles was reached on the basis of the ESR signals when the neutral, long chain nitroxides C_{12}- and C_{16}-Tem-
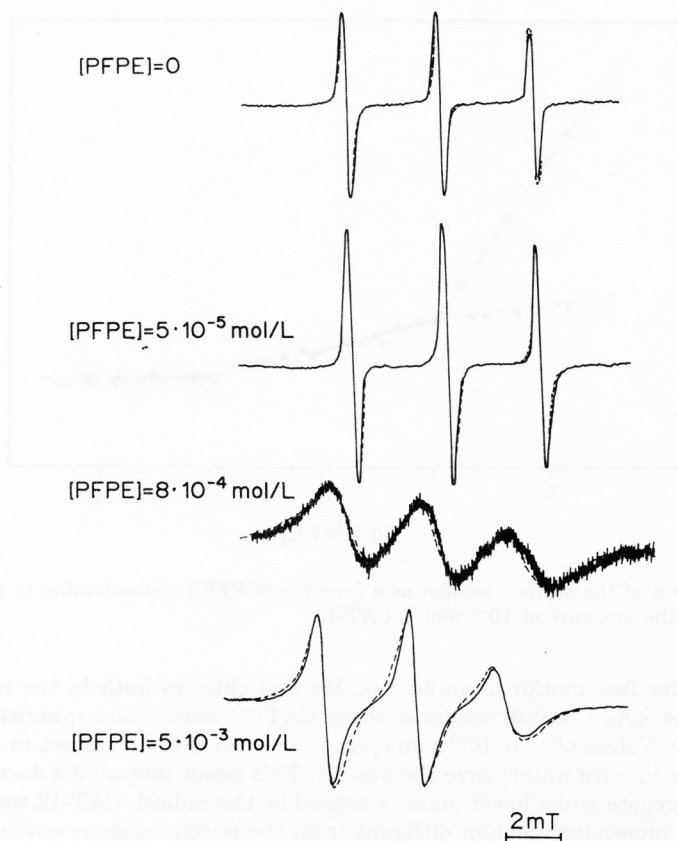
Figure 8. Experimental (full lines) and computed (dashed lines) ESR spectra of CAT-12 (10^{-4} mol/L) in PFPE solutions at different PFPE concentrations.

po were used. Up to the PFPE concentration corresponding to the second surface tension discontinuity, the ESR absorptions from these radicals were indeed dominated by the single, exchange-narrowed absorption due to either C_{12}- or C_{16}-Tempo micelles in a slow chemical exchange with their monomer in the bulk solution, which gave a weak three-line signal superimposed on the exchange-narrowed signal. Above $4-5\times10^{-4}$ mol/L PFPE, the absorptions turned into a relatively narrow triplet with $<A_N>$ values very similar to those observed for the same radicals in sodium dodecyl and sodium hexadecyl sulfate, respectively.[62] The motional properties were very close to those of CAT-12 in the same PFPE micelles and the same $\tau_c = 10^{-9}$ s was used for spectral computation. Both nitroxides resulted, therefore, inserted in the PFPE micelles showing a similar structure and mobility as CAT-12. In summary, C_{12}- and C_{16}-Tempo did not chemically interact with PFPE monomer and with spherical micelles, and they were progressively inserted as a very diluted impurity into the non-spherical micelles at [PFPE] > 2×10^{-4} mol/L. This behavior was in agreement with the mutual phobicity of hydrocarbons and fluorocarbons suggested by Mukerjee and Mysels,[65] who explain
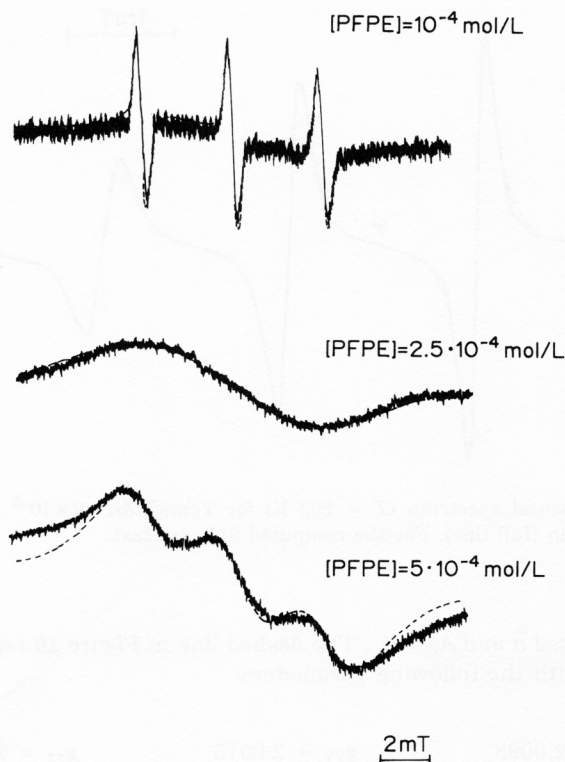
Figure 9. Experimental (full lines) and computed (dashed lines) spectra of CAT-12 in PFPE solutions with [PFPE]/[CAT-12] ratios 1÷5.

the reduced tendency of these two classes of materials in terms of very limited mutual solubility of the micelles of the corresponding surfactants.

In line with the above results were also the ESR data obtained wit the small positive TempTMA$^+$.[33] This is known to give details on the mobility and polarity of the water layers in the immediate environment of the micelle surface.[61] With this radical too, the only significant ESR data were obtained when [PFPE] $> 2 \times 10^{-4}$ mol/L. Below this value, the same ESR spectrum as in the bulk water was obtained, thus indicating that TempTMA$^+$ was unable to give details on the PFPE micelles formed at concentrations $< 2 \times 10^{-4}$ mol/L. Complex spectra were observed up to [PFPE] $\sim 10^{-3}$ mol/L. Above this surfactant concentration, the observed spectrum (Figure 10) had the typical features of nitroxides in partially oriented systems such as liquid-crystals or lipid bilayers with a very anisotropic probe motion.[41] For the computation of this absorption, we had to take into account for a microscopic order existing in the system, with the faster rotating axis of the nitroxide almost parallel to the fluorocarbon chain.[66] The microscopic order needed to be defined through an order parameter, identical to that used in describing liquid crystals:

$$S = 1/2(\overline{a_z^2} \cdots -1) \approx (A_{\parallel}{}' - A_{\perp}{}')/(A_z - A_x)$$

Figure 10. Experimental spectrum (T = 293 K) for TempTMA$^+$ 2×10^{-5} mol/L in a 2×10^{-3} mol/L PFPE solution (full line). For the computed line, see text.

with a time averaged $\overline{a}$ and $A_x \approx A_y$. The dashed line in Figure 10 represents the spectrum calculated with the following parameters:

$$g_{xx} = 2.0098 \qquad g_{yy} = 2.0075 \qquad g_{zz} = 2.0037$$
$$A_{xx} = A_{yy} = 6.8 \text{ G} \qquad A_{zz} = 35.9 \text{ G}$$
$$A_{xx}' = A_{yy}' = 11.62 \text{ G} \qquad A_{zz}' = 26.17 \text{ G}$$
$$S = 0.5 \qquad T_{2,0} = 1.5 \text{ G} \qquad N = 50 \qquad <\tau_c> = 1.5 \times 10^{-10} \text{ s}$$

where $T_{2,0}$ is the residual linewidth, and N is the ratio between the anisotropic coefficients. The reasonable fit suggested that partially ordered aggregates were formed.

The occurrence of partially ordered structures in water dispersion of perfluoropolyethers is, at the moment, an open question. Preliminary runs carried out with small angle neutron scattering (PAXE spectrometer, Saclay[67] showed that regularly packed lamellar bilayers existed at least from 1% to 75% volume fraction of PFPE (EW 706) in water, the lower limit corresponding to a molar concentration of $\approx 2 \times 10^{-2}$ mol/L. In the range of concentration 2×10^{-2}–10^{-3} mol/L problems in the interpretation of the scattering data came from the intrinsic instability of the binary system since a partial demixing was often encountered. It seemed, however, that SANS data for solution of PFPE $\approx 10^{-2}$ mol/L could be fitted assuming discoid micelles.

Finally, ESR experiments with doxyl nitroxides with the paramagnetic moiety located at different positions of the hydrocarbon chain seem to be encouraging enough to push our attention towards this problem.

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SAŽETAK

Elektro spin rezonancijska studija fino dispergirane vode u perfluoriranim polimerima i studija njihovih micelarnih otopina

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Spektroskopija elektronske spinske rezonancije (ESR) paramagnetnih spinskih oznaka (ioni prijelaznih metala i radikali nitroksida) bila je iskorištena za karakterizaciju nekih svojstava perfluoriranih spojeva. Dan je pregled rezultata postignutih u istraživanjima a) reoloških svojstava vode fino dispergirane u porozitetima Nafion-ionomera i perfluoropoliestera (PFPE) gdje su korišteni neutralni i mali nabijeni nitroksidi čiji su magnetski parametri i ESR-konture ekstremno osjetljivi na promjene lokalnih okolnosti, a analizirana su i disperzijska i agregacijska svojstva metalnih iona u Nafionskom skeletu s VO^{2+} kao spinskom oznakom; b) agregacijska svojstva PFPE u vodenim otopinama u formi sfernih i nesfernih micela; veliki kationski i neutralni nitroksidi sposobni da reagiraju s molekulskim nakupinama ili da budu uklopljeni u njihovu mrežu omogućili su da se uspostave optimalni uvjeti za upotrebu spinskih oznaka za dinamičke i strukturne studije u tim sustavima, te granice pouzdanosti ESR tehnike u micelarnim sistemima.