polymer	y	Π, dyn/cm
PEO	2.77 ± 0.05	0.3–3.5
PTHF	2.2 ± 0.1	0.2–3
PVAc	2.80 ± 0.05	0.3–3
PMA	2.65 ± 0.10	0.2–12
PMMA	8.6 ± 1.0	0.2–10
PtBMA	13 ± 1	0.4–10

Registry No. PEO, 25322-68-3; PTHF (copolymer), 24979-97-3; PTHF (SRU), 25190-06-1; PVAC, 9003-20-7; PMA, 9003-21-8; PMMA, 9011-14-7; PtBMA, 25189-00-8.

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The State of Hydrated Vanadyl Ions Adsorbed on a Perfluorinated Ionomer As Studied by ESR and ENDOR

Giacomo Martini,* M. Francesca Ottaviani, Luca Pedocchi, and Sandra Ristori

Department of Chemistry, University of Florence, 50121 Firenze, Italy.

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ABSTRACT: An ESR and ENDOR study has been made of VO^{2+} water solutions at different metal ion concentrations adsorbed on the perfluorinated ionomer Nafion in its acidic form. The ESR parameters and the temperature dependence of the line shape indicated that the vanadyl probe maintained its square pyramidal structure and a relatively high mobility even at low temperatures. A very small fraction of these ions aggregated as dimers with an intercationic distance of ≥3.5–3.7 Å. The VO–F distance, as obtained from ENDOR experiments, confirmed that the ions were prevalently located in the ionic clusters that are formed after swelling with water. The ESR results were also discussed in terms of the polymer structure and of the properties of adsorbed water.

Introduction

Perfluorinated polymers consist of an organic backbone and ionic groups and are widely used as ionomeric materials. The presence of metal ions in these compounds has a profound relevance for the use in many processes and devices in several applications in the fields of electrochemistry and catalysis.[1-3] Ionomer membranes used for their ion selectivity or ion separation properties have been widely studied with different techniques to characterize either the effect of incorporated metal ions or their morphology both in the presence and in the absence of metal ions.[4-9] Most of the experimental techniques used for the study of perfluorinated ionomers suggest that their properties are very sensitive to the amount of adsorbed water and can be roughly explained on the basis of a phase separation into polar and nonpolar regions.[10] This results in an aggregation of the charges into the polar region. Several geometries have been suggested for the water-containing polymer, the most accepted being the so-called cluster-network model[11] in which approximately spherical holes (ionic clusters, whose diameter depends on the equivalent weight and on the water content) are connected through short and narrow channels.[12,13]

The electron spin resonance spectroscopy of transition-metal ions or of nitroxide radicals has been used to investigate both ionic mobility inside the ionic clusters and the peculiar behavior of the adsorbed water.[14-17] Recently we reported the use of neutral and charged nitroxides as sensitive probes toward the polarity changes of water adsorbed on the perfluorosulfonated membrane Nafion.[18] From the ESR line shapes of these radicals in the ionomer under conditions of full hydration and after exchange with different alkali and alkali-earth metal ions, we deduced that the ionic clusters have widely distributed sizes.

While the present work was in progress, an analysis of the ESR line-width behavior of aqueous solutions of vanadyl ions adsorbed on Nafion membrane was published.[19] The correlation times for the motion of the hydrated vanadyl ion are analyzed as a function of water content. Barklie et al. also give an estimation of the cluster sizes,

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which are in the 3.1–3.9-Å range for membranes with a water mass gain of 0.38 after hydration. These values are well in-line with the size distribution observed with nitroxides.[18]

In this work, we discussed ESR and ENDOR experiments in which VO^{2+} ions were used as a probe for the motional properties of water adsorbed on Nafion. The localization and the formation of VO^{2+} aggregates were also analyzed.

Experimental Section

The perfluorosulfonated Nafion 117 ionomer, produced by E. I. du Pont de Nemours & Co., Wilmington, DE, and purchased from Aldrich Chemical Co., was used either as powder (mesh 35–60) or as membrane. The characteristics, as given by the manufacturer, were as follows: polymer consisting of sulfonic groups linked to a poly(tetrafluoroethylene) (PTFE) skeleton through short chains of perfluoropropylene ether:

$$-(CF_2CF_2)_nC(CF_2)FO(CF_2C(CF_3)FO)_mCF_2SO_3-$$

equivalent weight 1100, ionic form SO_3H.

The dry acidic ionomer (0.2 g) was soaked for 24 h at room temperature in 3 mL of $VOSO_4 \cdot 5H_2O$ (Aldrich Chemical Co.) solutions at 5×10^{-4}, 10^{-3}, 5×10^{-3}, and 10^{-2} M concentrations and then handled as previously reported.[18] Assuming that there was an almost (≥90%) complete vanadyl uptake[19] after soaking the charged polymer in each VO^{2+} solution, the $VO^{2+}/100SO_3^-$ ratios were as follows: VO^{2+} soln, 5×10^{-4}, 10^{-3}, 5×10^{-3}, 10^{-2} M; $VO^{2+}/100SO_3^-$, ≤0.8, ≤1.6, ≤8.0, ≤16.0. Assuming a 20% water adsorption after soaking for 24 h, as resulted from weight loss by heating (in good agreement with the literature[20]), the following approximate VO^{2+} molar concentrations in the Nafion porous frame were calculated: 3.7×10^{-2}, 7.5×10^{-2}, 3.7×10^{-1}, and 7.5×10^{-1} M, respectively.

The ESR and ENDOR spectra were registered with a Bruker spectrometer Model 200D operating in the X band equipped with an Aspect 2000 data handling system. Samples were introduced into quartz capillaries of i.d. ~2 mm for ESR and ~4 mm for ENDOR and immediately sealed. Temperature variations were reached by using the Bruker ST100/700 variable-temperature assembly. The 77 K spectra were registered with the aid of a liquid nitrogen cold finger. The 4.2 K spectra were obtained by using the continuous helium flow cryostat ESR (Oxford Instruments). The ENDOR spectra were obtained with the Bruker ENDOR attachment. Maximum power of the radio frequency unit was 100 W. In the ENDOR experiments nitrogen flow was used as a coolant.

Results and Discussion

Figure 1 shows the ESR spectra at different temperatures of Nafion powder containing ~$0.8VO^{2+}/100SO_3^-$. The same results were obtained by using membrane strips. As widely observed when water solutions of paramagnetic probes are adsorbed on porous supports,[21-24] the ESR line shape was typical of a probe undergoing progressive immobilization, without showing a true phase transition. The VO^{2+} ions showed partial mobility at temperatures well below the normal freezing point of water. For instance, the spectrum at T = 248 K is typical of a slow-motion condition,[25] with an approximate correlation time of ~10^{-9} s. This meant that water sorbed on Nafion did not crystallize and progressively turned to a glassy structure, as also previously observed with nitroxides.[18] The same experiments run on Nafion samples containing $VO^{2+}/100SO_3^-$ = 1.6 showed almost the same line shapes, whereas with higher vanadyl contents appreciable line overlapping occurred, thus indicating that spin–spin interactions such as dipole–dipole or Heisenberg spin exchange effects became effective (see below). These results agreed very well with those reported by Barklie et al.[19]

Figure 2 shows the experimental ESR spectrum at 77 K of the sample with $VO^{2+}/100SO_3^-$ = 1.6 as compared

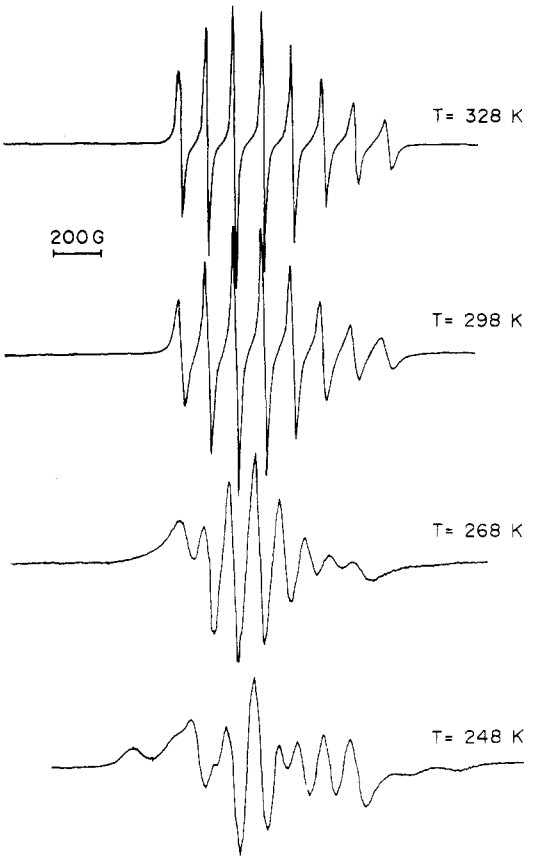

Figure 1. ESR spectra at different temperatures of VO^{2+} ions in water solution adsorbed on Nafion powder. $VO^{2+}/100SO_3^- \simeq 0.8$.

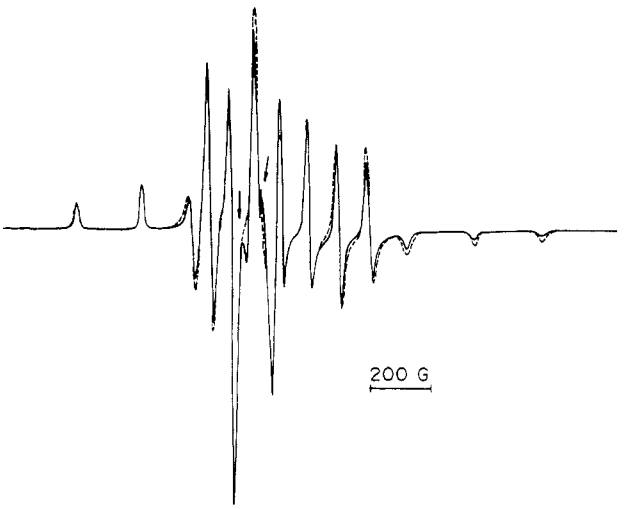

Figure 2. Experimental (77 K, full line) and computed (dashed line) ESR spectra of VO^{2+} ions in water solution adsorbed on Nafion. $VO^{2+}/100SO_3^- \simeq 1.6$.

with the computed one. The magnetic parameters used in the computation were $g_\parallel$ = 1.935, $g_\perp$ = 1.982, $A_\parallel$ = −0.0182 cm^{-1}, $A_\perp$ = −0.00698 cm^{-1}. These values are in good agreement with those previously published for VO^{2+} in aqueous solutions[26-29] or after adsorption on zeolites[26] and Nafion[19] and were deduced by using the procedure reported in ref 30. The powder spectrum computed with the above magnetic parameters fitted very well the experimental one, the only discrepancies being in the lack of the experimental transitions marked by arrows and usually attributed to $\Delta m_I = 1$ forbidden transitions.[30] This meant that the adsorbed species mainly responsible for the ESR signal was the same as in strongly acidic water solu-

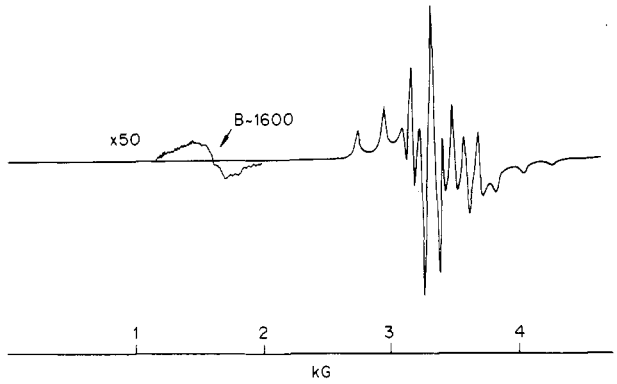

Figure 3. ESR absorptions of VO/Nafion at 4.2 K in the magnetic field range 0–5000 G.

tion,[28,29] that is, isolated, square pyramidal $VO(H_2O)_5^{2+}$, whose chemical and structural properties have been widely studied.[30]

In the 4.2 K spectrum (Figure 3), an additional signal appeared at $B \sim 1600$ G, whose features were typical of the so-called half-field transition usually observed for paramagnetic systems in a triplet state and attributed to the $\Delta m_s = 2$ forbidden transition.[31] This clearly indicated the presence of dimeric VO^{2+}–VO^{2+} species at 4.2 K.[32] The intensity of this signal decreased with increasing temperature, but it was again observed at temperatures as high as 70 K. The signal intensity also depended on the VO^{2+} content on Nafion since it was higher in $VO^{2+}/100SO_3^- = 16$ and practically undetectable when this ratio decreased to 1.6. A partial resolution of the hyperfine structure appeared in the half-field transition, but it was not possible to identify either the number of lines or the coupling constants.

The formation of dimeric species in ionomers is not unusual. This is confirmed for instance by Mössbauer for Fe^{3+} in carboxylic and sulfonated perfluorinated ionomers.[33] ESR spectroscopy seems to be the most powerful tool for revealing ion pairs. This was successfully shown for Cu^{2+}–Cu^{2+} pairs in butadiene–methacrylic acid copolymers[34] or in Nafion membranes[15] and for Nafion membranes swollen with a methanol solution of Ti^{3+}.[16,35]

Several methods have been used to evaluate the distance between two unpaired electrons in dimeric species from triplet ESR powder spectra, either based on the value of the zero-field splitting parameters D and E as measured from the position of the low-field edge of the half-field transition[36-38] or from the low- and high-field turning points[39] or based on the peak height ratios and changes in the second moments of frozen glass spectra.[40] The temperature dependence of the line width is also used to estimate the values of the electron–electron distance.[41] Eaton et al.[42,43] report a perturbation calculation procedure based on the ratio of the intensities of $\Delta m_s = 2$ and $\Delta m_s = 1$ transitions that is shown to be dependent on the interelectron distance, r, and independent on the value of the exchange coupling constant, J. This procedure is used by Alonso-Amigo and Schlick[15] for the calculation of the Cu–Cu intercationic distance in the Cu^{2+} dimer containing Nafion. In the present case it was not possible to valuate the intensity of the $g \simeq 2$ peaks due to the $\Delta m_s = 1$ transitions of VO^{2+}–VO^{2+} triplet since they were completely buried under the very strong peaks due to the isolated vanadyl species. This prevented the calculation of the intercationic distance from the relative intensities.

However, the observed line shape in the region $g \simeq 2$ allowed evaluation of a lower limit for r from the expected zero-field splitting parameters. We did not observe Δm_s

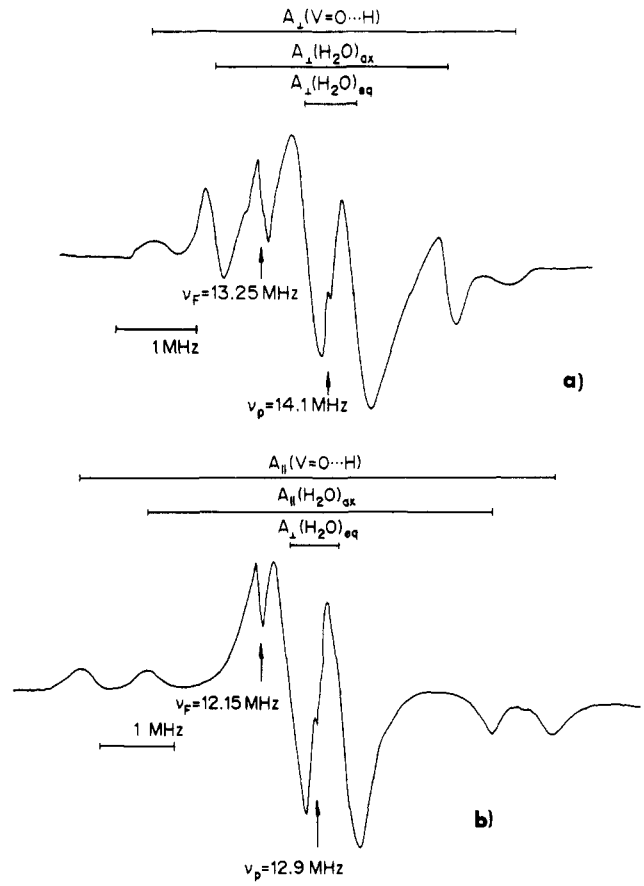

Figure 4. ENDOR spectra at 105 K of $VO(H_2O)_5^{2+}$ solution adsorbed on Nafion powder. The spectra in (a) and in (b) were obtained with field settings at the perpendicular $m_{I,\perp} = 3/2$ and at the parallel $m_{I,\parallel} = 5/2$ ESR transitions, respectively.

$= 1$ triplet peaks outside the $g_\parallel$ and $g_\perp$ components of the isolated VO^{2+} paramagnets even after several spectral accumulations. This meant that the separations of the high- and low-field turning points, $D_\perp$ and $D_\parallel$, were lower than 500 and 1400 G, respectively. Assuming that the zero-field splitting parameter, D, was only due to dipole–dipole interaction with no contribution from anisotropic exchange, the use of the equation[44]

$$D = D_\perp g_\perp \beta = (D_\parallel/2) g_\parallel \beta \quad (1)$$

gave

$$D \leq 9.6 \times 10^{-18}\text{–}1.2 \times 10^{-17} \text{ (in ergs)} \quad (2)$$

and

$$r^3 \geq -(2g_\parallel^2 + g_\perp^2)\beta^2/2D \quad (3)$$

$$r \geq 3.5\text{–}3.7 \text{ Å}$$

The ENDOR spectra at 100 K confirmed the large predominance of square pyramidal $VO(H_2O)_5^{2+}$ after adsorption of vanadyl solutions on Nafion powder or membrane. The ENDOR absorptions shown in parts a and b of Figure 4 were obtained by setting the magnetic field at the perpendicular $m_{I,\perp} = +3/2$ and at the parallel $m_{I,\parallel} = +5/2$ ESR transitions, respectively. Almost equivalent ENDOR spectra were also recorded for field settings at other ESR peaks, namely $m_{I,\perp} = -1/2$ and $-3/2$ (spectrum 4a) and $m_{I,\parallel} = +7/2$ (spectrum 4b), the main differences being in the free proton frequencies, ν_P, and in the relative intensities of the peaks. The spectra shown in Figure 4 were very similar to those reported by Van Willigen for $VO(H_2O)_5^{2+}$ in frozen aqueous solutions[45] and were therefore interpreted accordingly. The experimental values

Table I
Proton Hyperfine Components (in MHz) of $VO(H_2O)_5^{2+}$ in Nafion Membrane from ENDOR Measurements at 105 K

	A_x	A_y	A_z	ref
H_2O equat.	−0.6	−0.6		this work
	ca. −1.0	ca. −1.0	∼17	45
	−0.6	−0.6	10.6	28
H_2O axial	−3.0	−3.0	4.9	this work
	−3.3	−3.3	5.2	45
	−3.27	−3.27	7.26	28
V=O···H	−4.6	−4.6	6.4	this work
	−4.6	−4.6	6.6	45

of the proton hyperfine splitting constants (phfsc) are reported in Table I and were in a good agreement, within the limit of the experimental error, with those obtained by Van Willigen[45] and those calculated by Albanese and Chasteen.[28]

It is interesting that the ENDOR spectra did not show a "matrix" proton signal, which is, on the contrary, the dominant feature of the ENDOR spectra of $VO(H_2O)_5^{2+}$ frozen aqueous solution.[45] The localization of the VO^{2+} complex in Nafion ionic clusters with consequent interactions with surface negative groups might shield the paramagnetic probe from solvent molecules, thus preventing the appearance of a matrix proton ENDOR signal. The same explanation is given by Van Willigen and Chandrashekar[46] for VO^{2+} aqueous solution adsorbed on Y zeolite.

In addition to the proton signals, a narrow line was observed at a frequency lower (0.8 MHz) than ν_P. This signal was typically due to fluorine nuclei from the fluorocarbon backbone, as further proved by the strong intensity increase of this peak with respect to the proton lines in experiments in which D_2O was used instead of H_2O as a solvent. Fluorine matrix ENDOR signals were observed for the first time in Nafion membrane swollen with deuteriated methanol solutions of Ti^{3+} by Schlick et al.[47]

The ESR line-width behavior as a function of temperature allowed us to get further information on the chemical and physical status of water adsorbed on Nafion ionomers. It has been suggested[48] that two distinct forms of water exist within Nafion: (a) non-hydrogen-bonded water, mainly exposed to the hydrophobic fluorocarbon residues and localized in the intercavity regions; and (b) hydrogen-bonded water with a reduced H-bond strength because of the exposure of the OH groups to fluorocarbons chains that penetrate the ionic clusters. Nitroxide spin probes allow revelation of the decrease of the water polarity as a function of the exchanged metal ions and valuation of the activation energies for the viscous process.[18] More information could be obtained from the analysis of the temperature dependence of the correlation times for the motion of isolated VO^{2+} in Nafion-adsorbed water. The τ dependence on the water content in the Nafion ionomer containing vanadyl ions has been analyzed by Barklie et al.[19] They find an exponential dependence on the water mass gain, Δm,

$$\tau = 5 \times 10^{-11} \exp(0.15/\Delta m) \quad (\text{in s·rad}^{-1}) \qquad (4)$$

for $\Delta m \geq 0.1$. With $\Delta m < 0.1$, the inner sphere interactions with SO_3^- groups complicate the spectrum since there is an increasing degree of immobilization. This has been also observed in our samples under conditions of water depletion. By flowing nitrogen gas on fully hydrated VO–Nafion membrane strips inside the ESR resonance cavity, the starting liquidlike signal was converted quite rapidly (1–2 h) into a signal attributable to partially immobilized species. Simple soaking in water for a few minutes restored the initial signal.

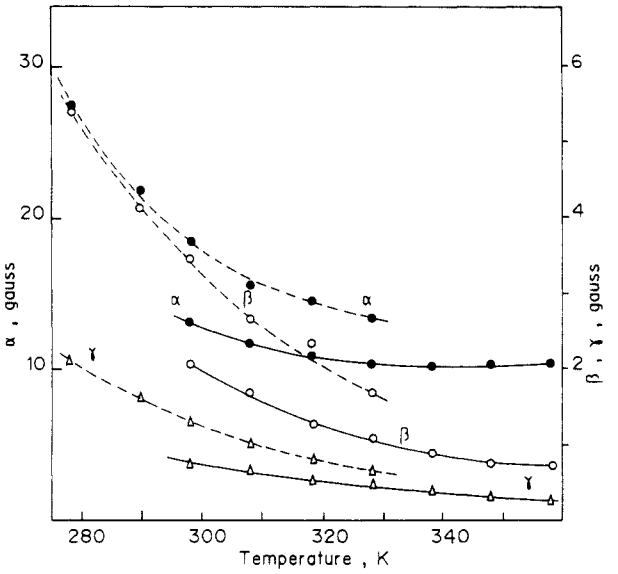

Figure 5. Variations of α, β, and γ coefficients as a function of temperature for $VO(H_2O)_5^{2+}$ in Nafion-adsorbed water (dashed lines, $VO^{2+}/100SO_3^- \simeq 1.6$) and in bulk water ($[VO^{2+}] = 10^{-2}$ mol/L).

The analysis of the ESR spectra at different temperatures (Figure 1) was carried out by fitting the well-known m_I dependence of the line width:[49,50]

$$B = \alpha + \beta m_I + \gamma m_I^2 + \delta m_I^3 \qquad (5)$$

where $\alpha = \alpha' + \alpha''$, with α' being the sum of the spin rotational term[51]

$$\alpha_{SR} = [(\Delta g_\parallel)^2 + 2(\Delta g_\perp)^2]/9\tau_R \qquad (6)$$

(τ_R is the Debye–Stokes–Einstein rotational correlation time, $\tau_R = 4\pi a^3/3kT$) and other terms not strictly due to motion such as unresolved superhyperfine structure, dipole–dipole, or spin exchange interactions. α'', β, γ, and δ are coefficients that include the magnetic anisotropies **A** and **g** and spectral densities ($[1/(1 + n\omega_0^2\tau_c^2)]$ where τ_c, the correlation time for the modulation of the anisotropies, may or may not correspond to τ_R). The analytical expression for these coefficients are reported in several papers and reviews.[49–53]

Figure 5 reports the α, β, and γ values as a function of temperature for VO^{2+} either in Nafion-adsorbed water or in bulk water solution. The γ values were used for the calculation of τ_c.[54] Figure 6 shows the dependence of log τ_c on the reciprocal temperature. From the slopes of log τ_c, an activation energy, ΔE_a, of 3.5 kcal/mol was calculated for the VO^{2+} motion in water adsorbed on Nafion, to be compared with 4.2 kcal/mol for the same ion in bulk water. We recently found[18] that positive nitroxides ($(TempT-MA)^+$ and protonated Tempamine) in water solutions adsorbed on Nafion membrane exchanged with alkali metal ions have almost the same activation energies (3.5 and 3.3 kcal/mol, respectively) as VO^{2+} ions, whereas neutral and negative nitroxides have ΔE_a values (4.2–4.6 kcal/mol) of the same order of magnitude as the self-diffusion activation energies of water in aqueous solutions (4.0–4.8 kcal/mol) and only slightly lower than the self-diffusion activation energies of water in Na–Nafion (5.1 kcal/mol)[55] or in water-swollen sulfonated ion-exchange resins (4.8–5.2 kcal/mol).[56] This meant that the interactions between positively charged probes, either VO^{2+} or nitroxides, and negative surfaces of the polymer, even if they did not lead to true inner sphere coordination, appreciably influenced the viscous process of self-diffusion.

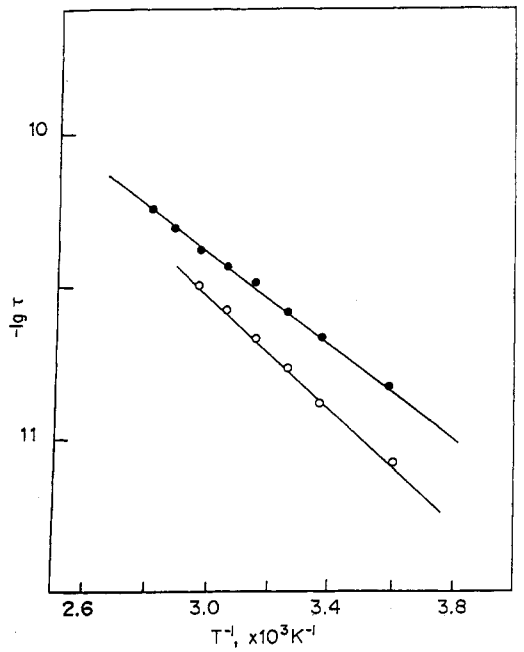

Figure 6. Variation of log τ as a function of reciprocal temperature of vanadyl ions in water adsorbed onto Nafion (full points, $VO^{2+}/100SO_3^- \simeq 0.8$) and in bulk water (open points, $[VO^{2+}] = 10^{-2}$ mol/L).

Vasquez et al.[57] have established water separation during cooling of polymeric cation-exchange membranes containing Cu^{2+} ions by comparison of the corresponding ESR spectra with those of frozen solutions of Cu^{2+} salts of reference concentrations. The linear dependence of log τ on $1/T$ (Figure 6) observed in our systems indicated that no microphase separation took place, as previously established with nitroxides as spin probes.[18]

The knowledge of the correlation times allowed evaluation of both the spin-rotational contribution to α, α_{SR}, on the basis of $\tau_R = \tau_c$ and evaluation of the residual line width due to nonmotional terms. The latter contribution was small (1–2 G) in samples containing $VO^{2+}/100SO_3^- \leq 1.6$, whereas it became dominant in samples with high vanadyl content. This broadening was mainly due to spin–spin effects, namely, dipole–dipole interactions and Heisenberg spin exchange. The temperature dependence was used as a criterion for establishing the dominant effect. The observed residual line width invariantly increased in the range 280–350 K with an almost linear trend and a slope increase that depended on the vanadyl concentration. This might agree with spin exchange, since dipole–dipole broadening depends on η/T.[58,59] However, two opposite dependences of spin exchange on T and η are predicted,[49,59] depending on the value of α:

$$\alpha = J'\tau_2([S(S+1)/3])^{1/2} \quad (7)$$

where J' is the effective exchange integral

$$J' = J([S(S+1)/3])^{1/2} \quad (8)$$

and τ_2 is the characteristic time during which the two probes are very near.[60] When $\alpha^2 \gg 1$, the exchange line broadening is given by

$$T_{2E}^{-1} = \nu_E = 1/\tau_1 \quad (9)$$

with ν_E, the exchange frequency, and τ_1, the time between paramagnet collisions,[60]

$$\tau_1 = 750\eta/RTM \quad (10)$$

where η is the viscosity and M the probe concentration. Although the viscosity dependence on the temperature of the intrapolymer water was not available, thus preventing exact calculation to be carried out, the almost linear increase of ΔB_{res} with temperature and its increase with the concentration strongly suggested that eq 9 and 10 might hold. This gave further proof for the high mobility of VO^{2+} ions in the water adsorbed on Nafion and for their location in a water pool, which had properties not largely different from those of bulk water, that is, water sorbed in the large ionic clusters.

The ENDOR spectra, on the other hand, allowed evaluation of the closest distance between the paramagnetic center and the fluorine nuclei, r_F. Schlick et al.,[47] in their ENDOR work on Nafion-containing Ti^{3+} ions, use the relation between the electron nuclear–dipolar interaction parameter α_{ED}, and r_F:[61]

$$\alpha_{ED} = g_e\beta_e g_n\beta_n/2r_F^3 \quad (11)$$

If we express α_{ED} in terms of the peak-to-peak line width of the matrix derivative signal, $\Delta B = 0.13$ MHz, and of the nuclear spin-packet line width, as evaluated from NMR experiments,[62,63] $T_{2F}^{-1} = 0.1$–0.067 MHz, the use of the relation

$$\alpha_{ED} = [\Delta B - T_{2F}^{-1}]/2 \quad (12)$$

gave $r_F = 10$–13 Å for the VO^{2+}–F distance. This was additional evidence for the localization of most of the VO^{2+} ions in the ionic clusters of the Nafion structure. No ENDOR proof was found for the presence of large amounts of VO^{2+} in the interconnecting channels whose mean diameters are valued[11] to be ~ 10 Å.

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Registry No. Nafion 117, 66796-30-3; VO^{2+}, 20644-97-7.

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^{13}C NMR Signal Assignment of Styrene/Butadiene Copolymer

Hisaya Sato,* Toraichi Ishikawa, Kenji Takebayashi, and Yasuyuki Tanaka

Department of Material Systems Engineering, Faculty of Technology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184, Japan. *Received April 25, 1988; Revised Manuscript Received August 17, 1988*

ABSTRACT: ^{13}C NMR signals of styrene/butadiene copolymer (SBR) were analyzed using low molecular weight model compounds corresponding to styrene/1,4-butadiene and styrene/1,2-butadiene structures together with partially deuterated copolymer. Aliphatic carbon signals were assigned in terms of diad or triad sequences of the styrene unit and three isomeric butadiene units: cis-1,4; trans-1,4; and 1,2. Signal splittings due to the tacticity and cotacticity of 1,2-butadiene and styrene units were also assigned. Head-to-tail arrangements were confirmed for 1,2-butadiene and styrene units in SBR prepared with free-radical initiators.

Introduction

Styrene/butadiene copolymer (SBR) has a complicated sequence structure that comprises units of styrene and cis-1,4, trans-1,4, and 1,2 units of butadiene. Thus, in order to analyze the structure of SBR, it is necessary to determine the sequence distribution of these four units and the configurational sequence of 1,2-butadiene and styrene units.

^{13}C NMR spectroscopy has been applied to the determination of the microstructure of SBR.[1-4] Aided by ^{13}C NMR studies of polybutadiene and polystyrene, Katritzky et al. assigned signals of aliphatic carbons in terms of diad sequences.[1] However, it was found that in polybutadiene some aliphatic carbons in the sequences containing more than two 1,2 units showed split signals reflecting diad or higher stereochemical configurations.[5,6] Recently it was suggested that assignment of most of the signals due to 1,2 units should take into account the triad sequence of the isomeric units.[6] Therefore, the signals of SBR should also be assigned by considering signal splittings due to the stereosequences of 1,2-butadiene and styrene units and by considering triad or higher sequences of the four units. Katritzky et al.[2] also determined the diad population of the four units in SBR including 1,4-butadiene units, i.e., trans–trans, trans–cis, cis–trans, and cis–cis diads, using aliphatic carbon signals. However, it seems impossible to determine the diad populations of 1,4-butadiene units because the methylene signal in the trans–trans sequence appears at the same chemical shift as that in the trans–cis sequence. In addition, the cis–cis and cis–trans sequences cannot be distinguished by aliphatic carbon signals even in polybutadiene.[6,7]

Segre et al.[3,4] assigned the ^{13}C NMR of SBR in terms of triad sequences of the four units by using the shift factors determined for each monomeric unit. However, their method predicts no signal splittings due to the tacticity and cotacticity of 1,2-butadiene and styrene units; consequently, they assigned these signal splittings by as-

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