BUTTERWORTH
HEINEMANN

Polymer Vol. 36 No. 6, pp. 1141–1146, 1995
Copyright © 1995 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0032-3861/95/$10.00+0.00

Effect of solvents on phase separation in perfluorinated ionomers, from electron spin resonance of VO^{2+} in swollen membranes and solutions

Hongwei Li and Shulamith Schlick*
Department of Chemistry, University of Detroit Mercy, Detroit, MI 48219-0900, USA
(Received 1 April 1994; revised 1 September 1994)

We present a study of perfluorinated ionomers with pendent chains terminated by sulfonic groups (Nafion), partially neutralized by paramagnetic VO^{2+} cations. Electron spin resonance (e.s.r.) spectra of VO^{2+} were measured in the temperature range 120–300 K in ionomer solutions and membranes swollen by water, methanol and ethanol, and compared with the spectra of VO^{2+} in the neat solvents. E.s.r. spectra for all systems in the entire temperature range were simulated, using the Brownian diffusion motional model. The rotational correlation time τ_c of the cation at 300 K in the membranes swollen by water, in ionomer solutions in water and in neat water are all similar, and suggest that the cation is located in large water 'pools'. This conclusion is in agreement with the expected phase separation of the ionomer into polar and non-polar domains that leads to a reverse micellar structure. For the alcohols, however, the e.s.r. spectra and corresponding τ_c values of the cation in the swollen membrane and in ionomer solutions are similar, but clearly different from those measured in the neat solvents; these results were explained by assuming that the alcohols penetrate into the perfluorinated regions, and form small solvent pools with a diameter <20 Å, where the motion of the cation is highly hindered.

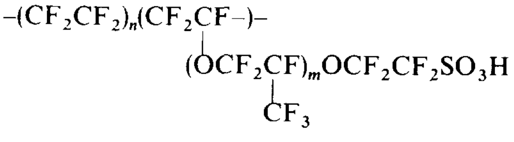
(Keywords: electron spin resonance; correlation time; perfluorinated ionomers)

INTRODUCTION

Perfluorinated ionomer chains terminated by sulfonic acid groups, such as Nafion (*Scheme 1*), are used on an industrial scale as ion-selective membranes in electrolytic processes, in fuel cells and in batteries[1]. Determination of the structure on the molecular level in dry membranes, in membranes swollen by solvents or in ionomer solutions is a great challenge, because of the amphiphilic nature of the polymer and the delicate balance of specific ionic and hydrophobic interactions within the polymer, and between the chains and the solvent. Studies of the membranes by small-angle scattering methods have suggested that in the presence of polar solvents (water, formamide, methanol, ethanol) the perfluorinated chains organize into a phase-separated morphology that consists of solvent pools surrounded by the organic chains; the sulfonic groups are at the interface between the polar and the non-polar domains[1,2]. This structure has been compared to the reverse micellar structure formed in the ternary system composed of a short-chain surfactant, water and an organic solvent as the 'oil'[3]. For the solutions, however, a rod-like micellar structure has been proposed from small-angle neutron and X-ray scattering (SANS and SAXS) of Nafion solutions in ethanol, water, formamide and *N*-methyl formamide (NMF)[4,5].

^{19}F n.m.r. studies of dry and swollen ionomers and of corresponding solutions in various solvents have provided additional structural and dynamic details[6,7]. The ^{19}F n.m.r. signal from the membranes swollen by water consists of a broad line typical of polymers in the solid state. The spectra for the membranes swollen by methanol and ethanol are more complex, and consist of a broad background signal and narrow signals at field positions corresponding to the chemical shifts of the different ^{19}F nuclei in the chain. In the corresponding solutions in the alcohols only narrow signals, typical of a true liquid, are detected, indicating chain mobility with a correlation time shorter than $\approx 10^{-4}$ s. Based on these results, we have suggested that the less polar solvents penetrate into the organic phase and plasticize the bulk polymer. Implied in this interpretation is the idea that the phase separation in the case of non-aqueous solvents is not as sharp as in the case of water-swollen or water-dissolved ionomer.

Electron spin resonance (e.s.r.) studies of Cu^{2+} in membranes swollen by water, methanol and other



$$-(CF_2CF_2)_n(CF_2CF-)- \quad (OCF_2CF)_mOCF_2CF_2SO_3H \quad CF_3$$

Scheme 1 Nafion, acid form

---

* To whom correspondence should be addressed

solvents have established the unique properties of water as a solvent that promotes phase separation into polar and non-polar regions, leading to cation clustering in the polar regions[8-11]. No clustering has been detected in membranes swollen by methanol, tetrahydrofuran (THF) and dimethylformamide (DMF). E.s.r. studies of VO^{2+} as the paramagnetic cation in membranes swollen by water have strengthened the idea that the cation is in a water environment, and have suggested that the water pools in the swollen membrane have a diameter of 30–40 Å, somewhat smaller than that deduced from scattering data[12,13]. Electron nuclear double resonance (e.n.d.o.r.) has been applied to the study of Ti^{3+} in the ionomers swollen by water and methanol[14,15] and of VO^{2+} in membranes swollen by water[12]. Taken together, these studies have presented convincing evidence that the analysis of the e.s.r. spectra can provide important and detailed information on the degree of penetration of the swelling solvent in the membrane and on the extent of phase separation.

The first e.s.r. and e.n.d.o.r. study of Nafion solutions, using Cu^{2+} as the paramagnetic cation, has been reported recently[16]. In this study we have demonstrated that the cation is in an environment that consists of solvent molecules, and that the Cu–F distance is larger in solutions of the ionomer in water, compared to methanol solutions. More recently we have studied Nafion solutions by the e.s.r. nitroxide spin probe method and have obtained evidence for the formation of large aggregates consisting of perfluorinated chains in water and formamide solutions (in agreement with scattering studies), but not in ethanol and NMF solutions[17].

We present an e.s.r. study of VO^{2+} in Nafion solutions in water, methanol and ethanol and in membranes swollen by the same solvents. The results are compared with the spectra of the cation in the neat solvents. The objective of this study was to observe and quantify the dynamics of the cation on the time scale of the e.s.r. experiment, typically 10^{-8}–10^{-11} s for VO^{2+}. The ^{59}V nucleus ($I = 7/2$) gives a rich e.s.r. spectrum, and dynamic information can be extracted by spectral simulations. The long spin lattice relaxation time T_1 of the vanadyl cation is an advantage (compared to Cu^{2+}) because narrow e.s.r. signals are measured at ambient temperature; therefore the VO^{2+} results can be compared directly with the ^{19}F n.m.r. and spin probe e.s.r. results.

EXPERIMENTAL

The Nafion 117 perfluorinated sulfonated membranes with an equivalent weight of 1100 g polymer/mole of SO_3H and a thickness of 0.178 mm were obtained from DuPont. The membranes were acidified with 8 M nitric acid, dried to constant weight *in vacuo* and equilibrated with a solution of $VOSO_4 \cdot 2H_2O$ containing a cation amount corresponding to neutralization of 3% of the sulfonic groups. The membranes were then dried *in vacuo* to a pressure of 6.665×10^{-3} Pa, heated at 330 K for 1 h and soaked in 3 mm i.d. quartz e.s.r. sample tubes with the solvent for 72 h in a glove box. The ionomer as the lithium salt was solubilized in a 1/1 (v/v) water/ethanol mixture at 523 K in an autoclave[5]. A soluble powder was then obtained by evaporation of the solvent (at ~350 K) for 1 h and cryo-crushing. Because the powder is not soluble in water, the neutralization with VO^{2+} was done as for the membrane. Ionomer solutions (10% w/w) were prepared directly (for the alcohols) or by dialysis of an ethanol solution (for water). Solutions of VO^{2+} (as $VOSO_4$, 0.001 M) in the pure solvents were prepared in a glove box, and sealed after bubbling with nitrogen for 15–30 min. The ratio VO^{2+}/solvent was similar to that in the ionomer solutions. For measurement of VO^{2+} in neat water below freezing, 20% (v/v) glycerol was added, to prevent water crystallization[18]. The sorption of water and other solvents by Nafion membranes has been studied extensively[5,8,9,19,20]. For acid membranes dried to constant weight *in vacuo* at 373 K, the molar ratio of solvent/SO_3^- is 15 for water and 26 for methanol[8,9]; for ethanol the ratio is 17.1 (ref. 5).

E.s.r. spectra at X-band were measured with a Bruker 200D SRC spectrometer operating at 9.7 GHz and 100 kHz magnetic field modulation, interfaced with a data acquisition and manipulation system using the softwares EPRDAS (Mega Systems Solutions, Rochester, NY) and SpectraCalc (Galactic Industries Corporation, Salem, NH). Samples were cooled using the Bruker flow system 4111VT. The microwave frequency was measured with the HP 5342A frequency counter. Cr^{3+} in a single crystal of MgO was used as g marker ($g = 1.9796$). The swollen membranes were measured in quartz tubes, and the solutions in Pyrex capillaries. Typical spectra were measured with scan time 50 s, sweep width 1800 G, time constant 20 ms, microwave power 2 mW and 4k data points. The modulation amplitude was 4 G and 1 G for slow motional and motionally narrowed spectra, respectively.

Spectra were simulated using the EPRR version 1.0 and EPRLF version 1.2 programs for rigid limit and slow motional simulations, respectively[21], using an HP Vectra RS/20C computer equipped with a 386 processor. For ease of comparison, experimental and simulated spectra were transformed into the format used by SpectraCalc.

RESULTS

E.s.r. spectra

Spectra of VO^{2+} were measured in the range 120–300 K in Nafion membranes swollen by water, methanol and ethanol, in Nafion solutions (10% w/w ionomer) in the same solvents, and in the neat solvents. Spectra at 300 K for the three solvents are presented in *Figure 1*. For water as solvent, all e.s.r. spectra of VO^{2+} are essentially the same, and consist of the typical octet of the cation, indicating a fast motional regime. The results obtained for the alcohols are different in two important ways. (1) The e.s.r. spectra for the ionomer membranes and ionomer solutions are similar, but quite different from those obtained for VO^{2+} in the neat solvents. (2) The spectra of VO^{2+} in the solutions and in the swollen membranes are typical of a slow motional regime. For ethanol as solvent, signals from the parallel and perpendicular components are clearly seen in the spectra of the membranes and of the corresponding ionomer solution; the extreme four signals of the parallel octet in the spectrum of the swollen membrane are indicated by arrows in *Figure 1*.

Representative e.s.r. spectra of VO^{2+} as a function of temperature, from the rigid limit at 120 K to the motionally narrowed signal at 300 K, are presented in

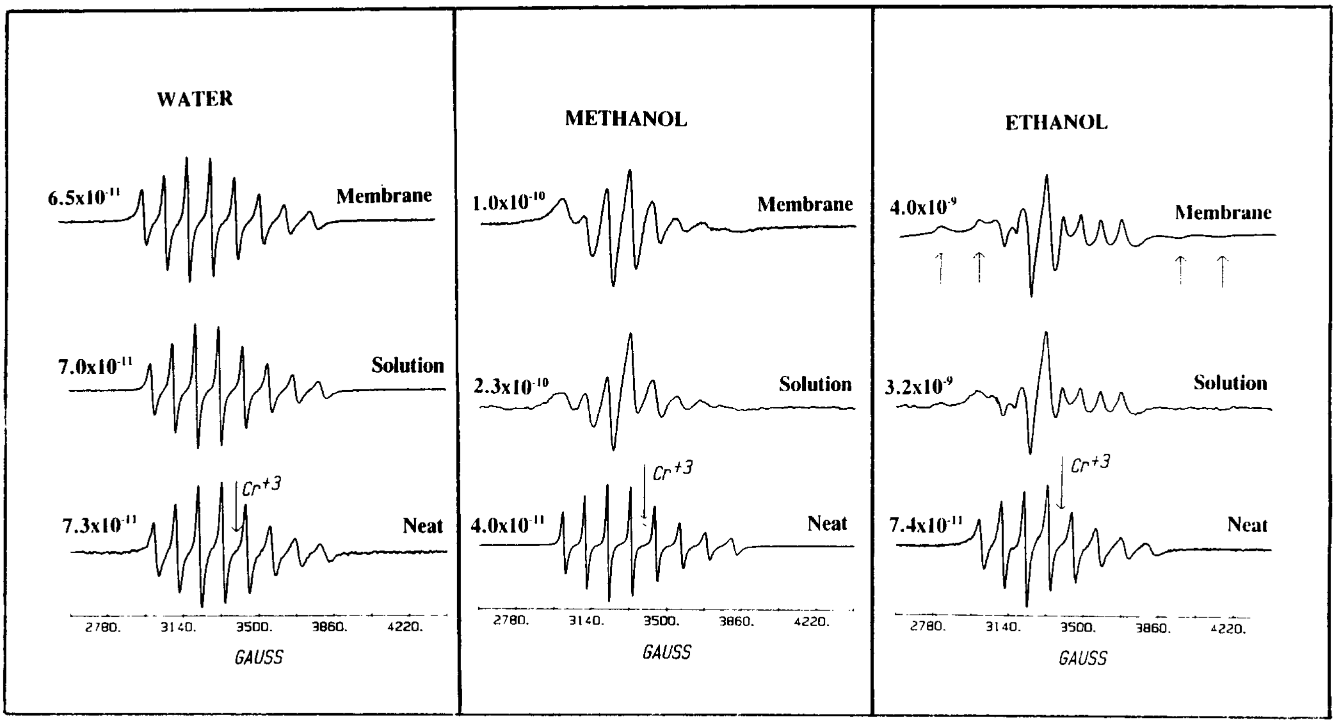


Figure 1 X-band e.s.r. spectra at 300 K of VO^{2+} in water, methanol and ethanol systems: in Nafion membranes swollen by the solvents, in the corresponding solutions of the ionomer, and in the neat solvents. The rotational correlation times τ_c (s rad^{-1}), deduced as described in the text, are also indicated. Arrows indicate the outermost parallel transitions for the membranes swollen by ethanol

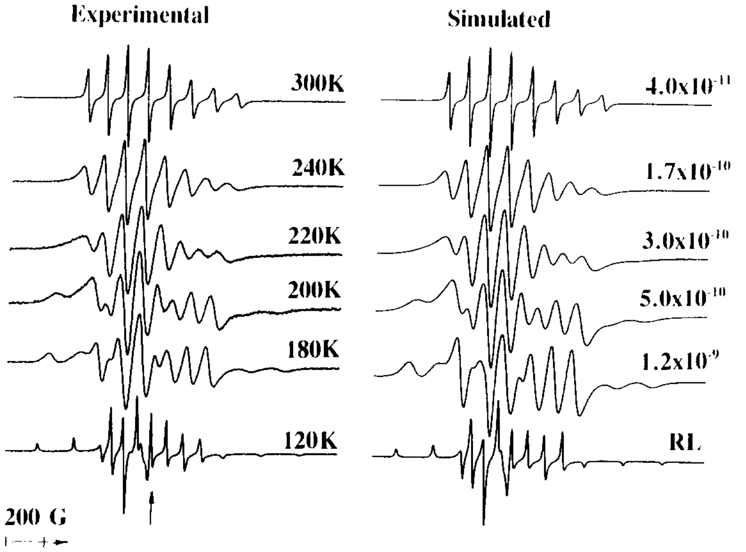


Figure 2 Experimental e.s.r. spectra of VO^{2+} in neat methanol as a function of temperature, and corresponding simulated spectra for the indicated rotational correlation times τ_c (in s rad^{-1}). The position of Cr^{3+}, the g standard, is indicated by the arrow, and the simulated spectrum in the rigid limit by RL

Figures 2 and *3*, for solutions of VO^{2+} in neat methanol and ethanol, respectively.

Simulations

A more quantitative picture of VO^{2+} dynamics was obtained by deducing the rotational correlation time τ_c in the entire temperature range for the three systems. Initially[22] we have estimated τ_c in the motionally narrowed limit ($\tau_c < 10^{-10}$ s rad^{-1}) from the heights and widths of the isotropic octet[23]; for longer correlation times ($10^{-10} < \tau_c < 10^{-7}$ s rad^{-1}), τ_c was calculated from the ratio of the extreme separation Δ (in G) at the given temperature, divided by the extreme separation in the rigid limit (at 120 K)[13,24].

In this study we deduce more accurate values of τ_c by simulating e.s.r. spectra in the entire temperature range using the stochastic Liouville method, for the Brownian isotropic diffusion model[21]. The simulations assume co-linear and axial hyperfine (from ^{59}V) and g tensors, and include non-secular terms and the nuclear Zeeman interaction. Lorentzian line shapes and different line widths for the parallel and perpendicular tensor components, $\Delta H_{\parallel}$ and $\Delta H_{\perp}$, respectively, were used. The principal values of the hyperfine and g tensors, deduced

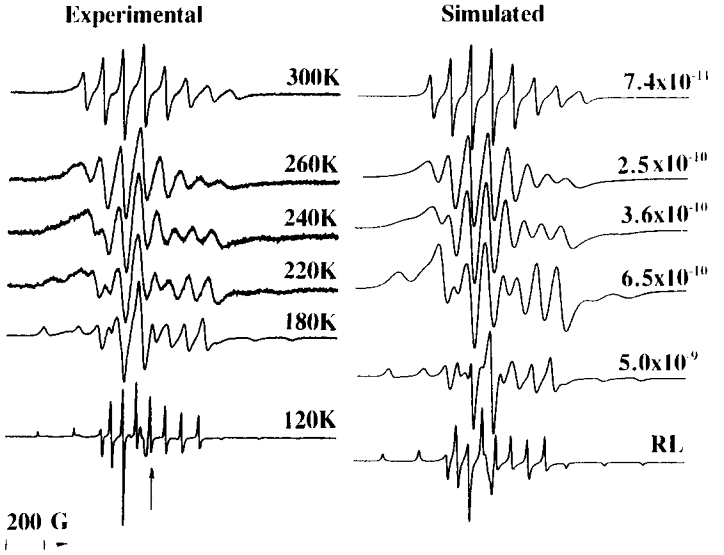


Figure 3 Experimental e.s.r. spectra of VO^{2+} in neat ethanol as a function of temperature, and corresponding simulated spectra for the indicated rotational correlation times τ_c (in $s\,rad^{-1}$). The position of Cr^{3+}, the g standard, is indicated by the arrow, and the simulated spectrum in the rigid limit by RL

Table 1 Parameters and line widths (G), used for the simulation of e.s.r. spectra of VO^{2+} in the different systems

System	$g_\parallel$	$g_\perp$	$A_\parallel$(G)	$A_\perp$(G)	$\Delta H_\parallel$(G)	$\Delta H_\perp$(G)
Water (S, M)[a]	1.934	1.979	202.5	76.1	6.0	8.0
Alcohols (S, M)[a]	1.922	1.966	199.0	74.5	7.5	7.8
Neat solvents	1.934	1.979	201.0	75.5	7.5[b] 5.0[c]	7.8[b] 3.0[c]

[a] S, ionomer solutions; M, swollen membranes. The g values are ±0.002, and the hyperfine values are ±1 G
[b] Line width for neat water
[c] Line width for the neat alcohols

from the simulation of the rigid limit spectra at 120 K, are given in *Table 1*, together with the line widths (peak-to-peak, in G). These line widths were assumed for the simulation of e.s.r. spectra in the entire temperature range; variation of the line widths within reasonable limits had no effect on the line shapes.

Simulated spectra for VO^{2+} in neat methanol and ethanol, respectively, are presented in *Figures 2* and *3*, and can be compared with the experimental spectra. The simulated spectra fit the experimental spectra for both solvents very well, in terms of line shapes and line positions. The fit between experimental and simulated VO^{2+} spectra in alcohol systems containing ionomer (solutions or membranes) is not as good as for the neat solvent, and the deduced values of τ_c reflect agreement in terms of the extreme separation and less in terms of detailed line shapes. The agreement for the water system was adequate in all three media (neat solvent, solution and membrane).

Rotational correlation times

The simulated spectra for the neat alcohol systems indicate a rotational correlation time τ_c in the range from the rigid limit (RL) to $\sim 10^{-11}\,s\,rad^{-1}$ (*Figures 2* and *3*). The e.s.r. spectra of VO^{2+} in neat water have been simulated from 240 K ($\tau_c = 1.4 \times 10^{-8}\,s\,rad^{-1}$ to 300 K ($\tau_c = 7.3 \times 10^{-11}\,s\,rad^{-1}$); the spectra change drastically between 240 and 260 K, and τ_c increases by two orders of magnitude in this range. (Drastic changes in e.s.r. spectra as a function of temperature occur when the spectral width (in s^{-1}) that is motionally averaged is comparable to the rate of motion $(2\pi\tau_c)^{-1}$. This condition depends on the spectral parameters of the paramagnetic centre (g- and hyperfine anisotropy), and is fulfilled usually in a narrow temperature range that is not always correlated to structural changes in the host. Above and below this narrowing temperature the e.s.r. spectra are not very sensitive to temperature variations.) The dynamic range for membranes swollen by water or water solutions is similar to that in neat water. In the case of the alcohols, however, the membranes and solutions have a limited dynamic range: minimum values of τ_c (at 300 K) are $2 \times 10^{-10}\,s\,rad^{-1}$ in methanol, and $4 \times 10^{-9}\,s\,rad^{-1}$ in ethanol.

The variation of τ_c with temperature for the three solvents is shown in *Figure 4*. The data indicate that in the entire temperature range the dynamics of the cation in ionomer solution and swollen membranes are similar; the small difference between the τ_c values in the ionomer solutions and the membranes is within experimental error, because the signal from the solutions is weaker and the error in the determination of τ_c greater. These results are quite different from the behaviour of the cation in the neat solvent, and the difference is larger in the case of ethanol, and larger for both solvents at lower temperatures. Two sets of activation energies for cation

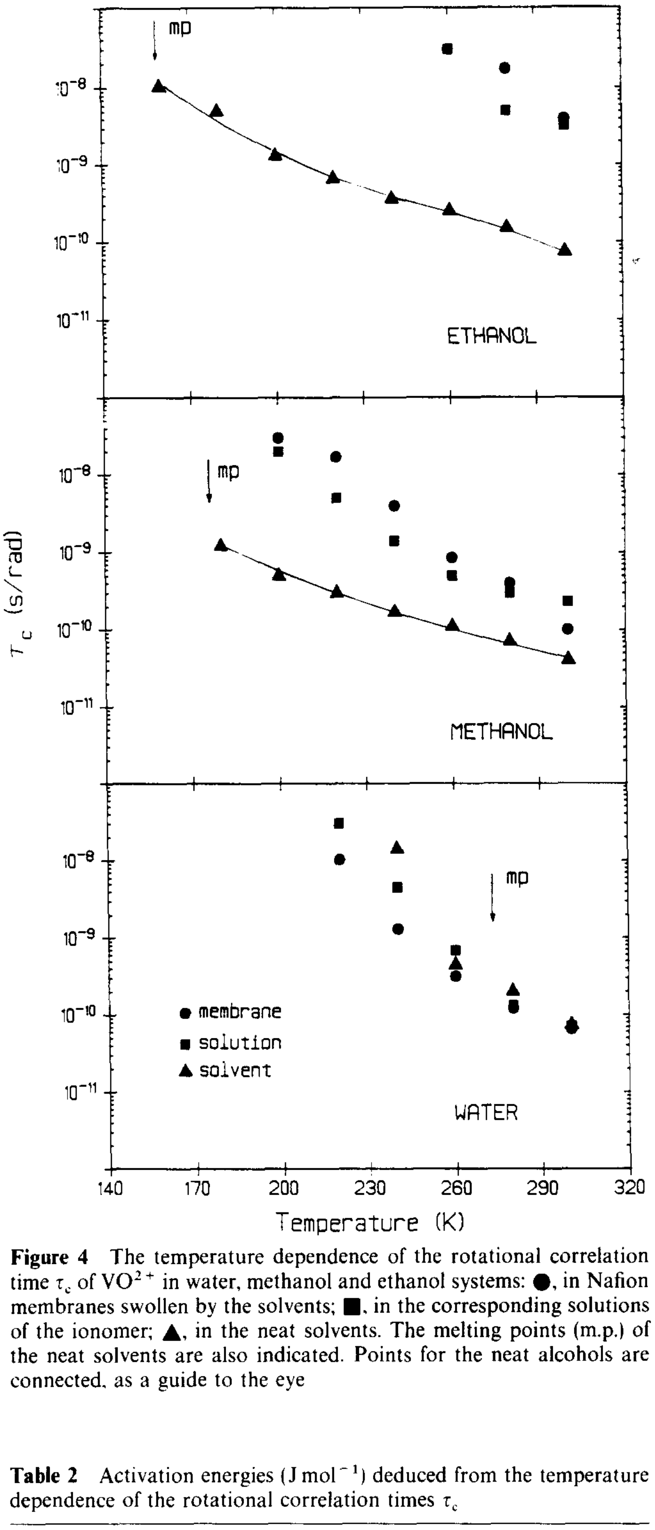


Figure 4 The temperature dependence of the rotational correlation time τ_c of VO^{2+} in water, methanol and ethanol systems: ●, in Nafion membranes swollen by the solvents; ■, in the corresponding solutions of the ionomer; ▲, in the neat solvents. The melting points (m.p.) of the neat solvents are also indicated. Points for the neat alcohols are connected, as a guide to the eye

Table 2 Activation energies (J mol^{-1}) deduced from the temperature dependence of the rotational correlation times τ_c

System	Neat solvent	Nafion solution	Swollen membrane
Water		40.1[a]	
Methanol	12.2	28.5[b]	
Ethanol	13.9	34.5[b]	

[a] Value for solvent, solution and membranes

[b] Data for solutions and membranes

dynamics have been deduced from Arrhenius plots of the data presented in *Figure 4*, one set for neat solvents, and a second set from all data for the corresponding membranes and solutions. In the case of water, however, τ_c values for membranes, solutions and neat solvent are similar, and one activation energy has been deduced from all experimental points. The results are given in *Table 2*.

DISCUSSION

In this section we will discuss the effect of the solvents on the dynamics of the VO^{2+} cation, and will compare the e.s.r. results with ^{19}F n.m.r. studies.

The results for water as solvent indicate that there is no significant difference in the environment of the cation in pure water and in the solutions and swollen membranes. The picture that emerges is that of the completely dissociated $SO_3^- - VO^{2+}$ ion pair, and solvation of the cation by water. For the swollen membranes, these conclusions are in agreement with previous e.s.r. results obtained for Cu^{2+} and VO^{2+}, which have provided strong evidence for phase separation into polar and non-ionic domains, and formation of large water pools of diameter 30–50 Å (refs 8, 12, 13); these pools are large compared to the diameter (<6 Å) of the fully hydrated cation $VO(H_2O)_5^{2+}$ (ref. 18). In ionomer solutions the results can be explained by assuming regions of high polymer density side-by-side with solvent clusters; SANS studies that suggest the formation of micellar rods[4,5], and recent spin probe e.s.r. results that support the idea of chain aggregation[17], are in agreement with this picture.

The situation in the case of the alcohols as solvents is different. The higher values of the correlation times τ_c for both the membranes and the solutions at a given temperature compared with the neat solvent, and the similarity of these values in the membranes and in the ionomer solutions, suggest that cation dynamics is profoundly affected by the polymer chains. It might be argued that the $SO_3^- - VO^{2+}$ ion pair is not dissociated in the alcohol systems. E.s.r. results of Cu^{2+} in methanol solutions of the ionomer, however, suggest a solvent environment[16]. In addition, the τ_c values for the neat solvents are similar (*Figure 1*) and suggest that the $VOSO_4$ salt is completely dissociated in all three solvents. The dissociation of the $SO_4^- - VO^{2+}$ ion pair is not expected to be different from that of the $SO_3^- - VO^{2+}$ ion pair. The difference in the dynamics of VO^{2+} in water and the alcohols must therefore be in the size of the solvent pool felt by the cations. We propose that the alcohols penetrate into, and plasticize, the membranes. The solvent pools formed in this process are small (<20 Å) and motional averaging of the e.s.r. parameters is prevented[17,18]. Ethanol is more effective as a plasticizer than methanol, penetrates deeper into the polymer chains and forms smaller solvent clusters. The τ_c values suggest that the situation in the polymer solutions is similar, although the solvent content is larger.

Support of this picture is also provided by examining the viscosities of the neat solvents, together with the τ_c values. At 298 K the viscosities for ethanol, methanol and water are 1.08×10^{-3}, 5.47×10^{-4} and 8.90×10^{-4} Pa s, respectively[25]. The τ_c values (*Figure 1*) are in the same order; the viscosity and τ_c ratios are similar, 1:0.51:0.82 and 1:0.54:0.99, respectively, as required by theory. The τ_c ratios in the ionomer solutions and the membranes are 1:0.07:0.02 and 1:0.03:0.016, indicating a different environment. The difference between VO^{2+} in neat alcohols compared to alcohols containing the ionomer is also reflected in the significant difference in the activation energies for motion presented in *Table 2*. In addition, the poorer agreement between simulated and experimental spectra in the case of VO^{2+} for the alcohol systems containing the ionomer also suggests a different environment, where the motional model is different.

Previous ^{19}F n.m.r. results have indicated[6], for the ionomer solutions in methanol and ethanol, a motional correlation time for the polymer backbone and pendent groups shorter than $\sim 1 \times 10^{-4}$ s at 300 K, and the correlation time is shorter in ethanol, compared to methanol. The present results suggest that the correlation time for VO^{2+} is $\sim 3 \times 10^{-10}$ s rad^{-1} and $\sim 3 \times 10^{-9}$ s rad^{-1} for the polymer in methanol and ethanol, respectively, in an inverse order compared to n.m.r. The conclusion is that a better plasticizer (ethanol) allows faster motion of the polymer chains, but also forms smaller solvent clusters where the cation motion is more hindered.

CONCLUSIONS

E.s.r. spectra of VO^{2+} in membranes swollen by water, methanol and ethanol and in the corresponding solutions are compared with the spectra of the cations in the neat solvents.

The correlation time τ_c of the cation in membranes swollen by water, in ionomer solutions in water and in neat water are all similar, suggesting formation of large water pools around the cations, and aggregation of the polymeric material into micellar structures. For a given alcohol, however, the e.s.r. spectra of the label in the swollen membrane and in solution are very similar, and clearly different from those measured in the neat solvents. These results suggest the penetration of the alcohols into the membranes and the formation of small solvent clusters where the motion of the cation is highly hindered.

Previous ^{19}F n.m.r. results have indicated, for the ionomer solutions in methanol and ethanol, a shorter correlation time of the polymer in ethanol, compared with methanol. The present results suggest that a better plasticizer (ethanol), which allows faster motion of the polymer chains, also forms smaller solvent clusters where the cation motion is more hindered.

ACKNOWLEDGEMENTS

This study was supported by the Polymer Program of the National Science Foundation through grants DMR-8718947 and DMR-9224972 and by the NATO Collaborative Research Programme grant CRG 901093 (US–France). We are grateful to J. H. Freed and D. Budil for their help with the simulations, and to Jan Pilar for numerous helpful discussions. We thank the DuPont company for donating the perfluorinated ionomers, and G. Gebel and P. Aldebert for preparing the soluble Nafion powder.

REFERENCES

1 Eisenberg, A. and Yeager, H. D. (Eds) 'Perfluorinated Ionomer Membranes', American Chemical Society, Washington DC, 1982

2 Pineri, M. and Eisenberg, A. (Eds) 'Structure and Properties of Ionomers', NATO ASI Series, Reidel, Dordrecht, 1987

3 Lossia, S. A., Flore, S. G., Nimmala, S., Li, H. and Schlick, S. *J. Phys. Chem.* 1992, **96**, 6071

4 Aldebert, P., Dreyfus, B., Gebel, G., Nakamura, N., Pineri, M. and Volino, F. *J. Phys. France* 1988, **49**, 2101

5 Gebel, G. PhD Thesis, Université Joseph Fourier, 1989

6 Schlick, S., Gebel, G., Pineri, M. and Volino, F. *Macromolecules* 1991, **24**, 3517

7 Avalos, J., Gebel, G., Pineri, M., Schlick, S. and Volino, F. *Am. Chem. Soc. Div. Polym. Chem. Polym. Prepr.* 1993, **34**, 448

8 Schlick, S. and Alonso-Amigo, M. G. *Macromolecules* 1989, **22**, 2634

9 Alonso-Amigo, M. G. and Schlick, S. *Macromolecules* 1989, **22**, 2628

10 Bednarek, J. and Schlick, S. *J. Am. Chem. Soc.* 1990, **112**, 5019

11 Bednarek, J. and Schlick, S. *J. Am. Chem. Soc.* 1991, **113**, 3303

12 Martini, G., Ottaviani, M. F., Pedocchi, L. and Ristori, S. *Macromolecules* 1989, **22**, 1743

13 Barklie, R. C., Girard, O. and Braddel, O. *J. Phys. Chem.* 1988, **92**, 1371

14 Schlick, S., Sjoqvist, L. and Lund, A. *Macromolecules* 1988, **21**, 535

15 Schlick, S., Myers, B. E., Sjoqvist, L. and Lund, A. *Z. Naturforsch.* 1992, **47a**, 702

16 Schlick, S., Gebel, G., Pineri, M., Rius, G. and Volino, F. *Colloids Surf. A: Physicochem. Eng. Aspects* 1993, **78**, 181

17 Szajdzinska-Pietek, E., Schlick, S. and Plonka, A. *Langmuir* 1994, **10**, 1011 and 2188

18 Rex, G. C. PhD Dissertation, Department of Chemistry, University of Detroit, 1989

19 Yeo, R. S. *Polymer* 1980, **21**, 432

20 Yeo, R. S. in 'Perfluorinated Ionomer Membranes' (Eds A. Eisenberg and H. D. Yeager), American Chemical Society, Washington DC, 1982, Ch. 5

21 Schneider, D. J. and Freed, J. H. in 'Biological Magnetic Resonance. Spin Labelling' (Eds L. J. Berliner and J. Reuben), Plenum, New York, 1989, Vol. 8, Ch. 1

22 Li, H. and Schlick, S. *Am. Chem. Soc. Div. Polym. Chem. Polym. Prepr.* 1993, **34**, 446

23 Rex, G. C. and Schlick, S. *Polymer* 1992, **33**, 2036

24 Bruno, G. V., Harrington, J. K. and Freed, J. H. *J. Phys. Chem.* 1977, **81**, 1111

25 'Handbook of Chemistry and Physics', 71st edn, CRC Press, Boca Raton, FL, 1990–1991