Study of polymer networks using paramagnetic probes

Vanadyl in chemically cross-linked polyacrylamide gels

Gary C. Rex* and Shulamith Schlick†
Department of Chemistry, University of Detroit, Detroit, MI 48221-9987, USA
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Electron spin resonance (e.s.r.) spectra of the vanadyl probe $VO(H_2O)_5^{2+}$ in chemically cross-linked polyacrylamide (PAA) gels with pore diameters of 7–58 Å were used to analyse the changes in gel structure as a function of temperature and solvent composition. The PAA networks were swollen by water and acetone/water mixtures containing 0.1–0.6 volume fraction of acetone. Spectroscopic evidence has been obtained that indicates the absence of bulk water in all the networks studied. Depending upon experimental conditions, bimodal distributions of pore sizes have been detected for all networks. The appearance of this distribution is triggered by lowering the gel temperature in networks swollen by water; alternatively, the bimodal distribution appears for a homogeneous gel at a constant temperature, by adding acetone to the swelling fluid. Unlike the ionic gels, the transition from a homogeneous PAA gel to a gel having a bimodal distribution of pore sizes is gradual as a function of temperature in water swollen gels, and of the acetone content in gels swollen by the solvent mixtures. The microviscosity in the pores appears to depend on the free volume in the pores; this is evident from the Fujita-Dolittle plots in PAA swollen by water, at three different temperatures.

(Keywords: polyacrylamide gels; paramagnetic probes; electron spin resonance; correlation time)

INTRODUCTION

The collapse of charged PAA gels has been studied extensively by Tanaka *et al.*[1–3] as a function of solvent composition, pH and ionic concentration, by light scattering, and by measuring changes in the gel volume. The volume of gels at a given temperature and external pressure is a result of three internal forces: polymer-polymer interactions; network elasticity; and ionic interactions. The gel collapse was interpreted as a phase transition that occurs as a result of the interaction between these forces. Such transitions have also been obtained in neutral PAA networks swollen by a solvent mixture composed of a solvent and a non-solvent for the gel, or by temperature variations in a given solvent.

The objectives of our studies of PAA networks is to detect and quantify changes in the properties of water in various gels due to the proximity of the network, and to deduce the local microscopic structure in PAA gels prepared by chemical cross-linking and γ-irradiation[4–7]. We have also studied reversible PAA gels obtained from the linear polymer[6]. Our approach is based on incorporating a paramagnetic guest as a probe in the gel, and measuring the e.s.r. spectrum. Information on the structure and dynamics can be deduced from an analysis of the spectra. The binding of Cu^{2+} in the various gels was deduced from e.s.r. spectra at X-band (9.3 GHz) and at S-band (2.4 GHz), in the temperature range 100–300 K. We found that the amount of 'bulk' water in PAA with pore size in the range 7–58 Å is negligible, but the properties of the water vary gradually, as a function of the distance to the network. In addition, we found that the pore distribution in the reversible gels is more homogeneous that in the chemically cross-linked gels.

This study was undertaken in order to obtain information on neutral PAA networks with different degrees of cross-linking, and swollen by various solvents and solvent mixtures. The approach used in this study is to follow the e.s.r. spectrum of a paramagnetic probe that is sensitive to the local viscosity of the medium and to the volume available for its rotational diffusion, at ambient temperature. We chose the vanadyl probe VO^{2+} in the form of the hydrated complex $VO(H_2O)_5^{2+}$. This probe has several advantages for the specific application to the PAA networks. First, its spin-lattice relaxation time T_1 is relatively long, thus allowing resolved e.s.r. spectra even at ambient temperature. Second, the isotropic e.s.r. spectrum consists of eight lines due to the hyperfine splitting of the ^{51}V nucleus (99.76% abundance, $I = 7/2$). As a result of dynamical averaging processes for the specific values of the g- and hyperfine tensors, these lines have different widths, which can be interpreted in terms of a correlation time τ_c. Third, it has been shown that the dynamics of the probe is sensitive to the size of the compartment in which the probe is located[8]. This means that structural information can be obtained by measuring e.s.r. spectra in gels of different pore size.

* Present address: Union Carbide Corporation, PO Box 8361, South Charleston, WV 25303, USA
† To whom correspondence should be addressed

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In this paper, we present an analysis of e.s.r. spectra of the complex $VO(H_2O)_5^{2+}$ in neutral PAA gels undergoing collapse due to variations of the temperature and of the composition of the swelling solvent (acetone/water mixtures).

EXPERIMENTAL

The PAA gels were prepared by free radical polymerization of acrylamide in the presence of *N,N*-methylenebis(acrylamide) (BIS), a tetrafunctional monomer, at 288 K in an argon atmosphere, with potassium persulphate and sodium bisulphite as initiators. The gels were allowed to stand overnight, granulated by forcing through a screen, washed three times over two days, and dried. Additional experimental details have been published previously[4,5].

Aqueous solutions of $VOSO_4 \cdot 2H_2O$ (reagent grade) were prepared with deoxygenated, doubly distilled water under nitrogen. Preliminary experiments with solutions in which oxygen was not rigorously excluded required higher concentrations of VO^{2+} for adequate signal intensity; a decrease in the signal over several days also indicated the sensitivity to oxygen.

The vanadyl probe was used for the study of PAA with various pore sizes, in the range 7–58 Å in diameter in water. The diameter of the pores in the gel was determined by correlating the swelling ratios (moles water/moles monomer) with gel filtration studies of the gel using model proteins[4,9]. The pore size was determined at 298 K for PAA swollen *by water*. The notation used in this study is PAA followed by the diameter of the pore in Å, for example PAA7, PAA10, PAA13, PAA17, PAA23, PAA32, PAA40 and PAA58. Networks PAA17 and PAA58 swollen by water/acetone mixtures containing a volume fraction of acetone in the range 0.1–0.6 were also studied.

Swelling of the gels to equilibrium was accomplished by weighing 0.1 g of the cross-linked gel into a 50 ml flask, sealing the flask with a septum, purging with nitrogen, and addition of the vanadyl solution in water or in the solvent mixture. The gels were then left in a desiccator for four days under nitrogen, and then transferred to 2 mm OD quartz tubes for e.s.r. measurements.

The absolute viscosity of the water/acetone mixtures containing 0.01 M of $VO(H_2O)_5^{2+}$ was determined at 278 K, 298 K and 318 K with a calibrated Cannon-Ubbelohde viscosimeter. E.s.r. spectra at X-band were measured with a Bruker 200D SRC spectrometer operating at 9.7 GHz (empty cavity at ambient temperature) with 100 kHz modulation. Spectra at 77 K were taken in a liquid nitrogen Dewar flask inserted in the e.s.r. cavity. Above this temperature the Bruker variable temperature ER 4111 VT was used. The absolute value of the magnetic field was measured using the Bruker ER 035 Gaussmeter. Calibration of g values was based on 2,2-diphenyl-1-picrylhydrazyl (DPPH, $g = 2.0036$). Spectra were simulated by a Burroughs 6800 mainframe computer at the University of Detroit or on a Kaypro PC, and plotted with an IBM PC and a Hewlett-Packard 7470 digital plotter.

RESULTS

In this section we will present the results obtained for PAA gels swollen by water and by water/acetone mixtures; the determination of the correlation times τ_c and of the microviscosity corresponding to isotropic e.s.r. spectra; and finally the simulation of spectra that consist of two superimposed components.

E.s.r. spectra of $VO(H_2O)_5^{2+}$ in PAA gels swollen by water

Spectra were taken in the temperature range 77–318 K in PAA gels with pore sizes from 7 to 58 Å, swollen by water. Above 270 K all spectra are isotropic, except for PAA7. At a constant temperature the line widths of the isotropic spectra for the probe are considerably larger than in bulk water; this effect is more pronounced in the gels with smaller pores. Below 255 K all spectra are 'rigid'. Selected results are presented in *Figures 1–3*.

The environment of the vanadyl complex in bulk water below freezing is different to that in the water-swollen gels, as seen by comparing spectra at 243 K, *Figure 1*. This effect is due to bulk water crystallization and aggregation of the $VO(H_2O)_5^{2+}$ molecules; the process is prevented in the gels, and the rigid spectrum is typical of the isolated probe molecules in a glass. A similar effect has been observed before for Cu^{2+} in PAA gels swollen by water[4–6]. The parameters measured at 77 K are: $g_\perp = 1.975$, $g_\parallel = 1.933$, $|A_\perp| = 69 \times 10^{-4}\ cm^{-1}$, $|A_\parallel| = 185 \times 10^{-4}\ cm^{-1}$. In line with data in the literature, the hyperfine splittings are considered negative[10].

In PAA7, a complex spectrum was detected in the temperature range 257–279 K, as seen in the data at

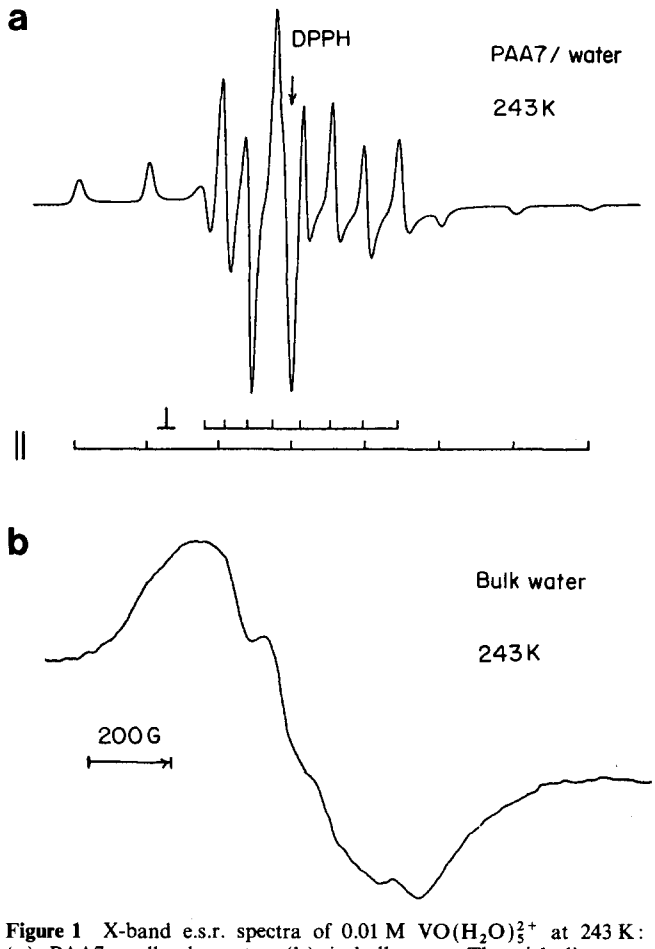

Figure 1 X-band e.s.r. spectra of 0.01 M $VO(H_2O)_5^{2+}$ at 243 K: (a), PAA7 swollen by water; (b), in bulk water. The stick diagrams corresponding to the parallel and perpendicular components are indicated in (a)

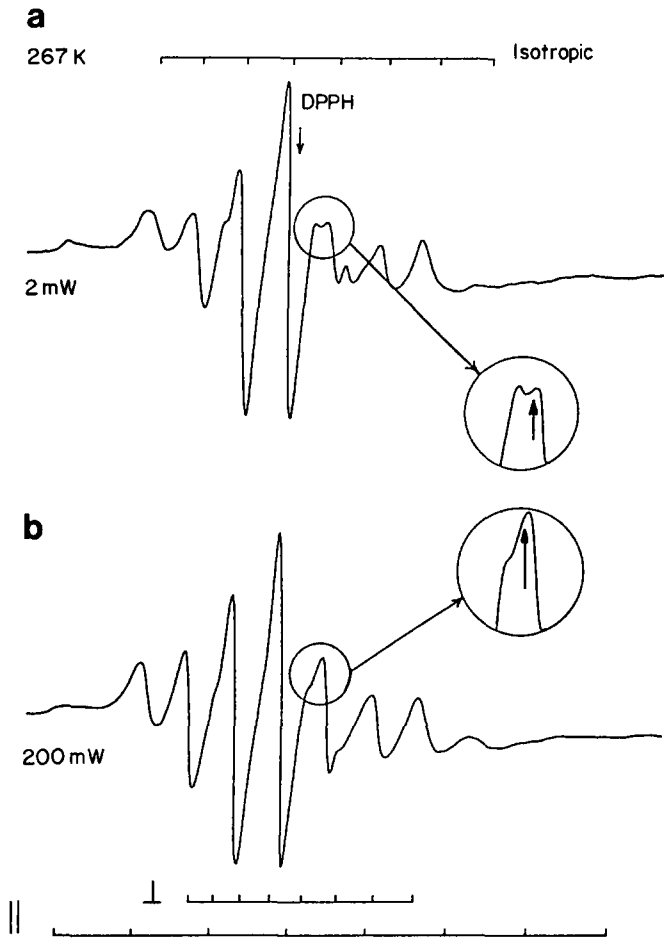

Figure 2 X-band e.s.r. spectra of $VO(H_2O)_5^{2+}$ in PAA7 at 267 K. The microwave power is 2 mW in (a) and 200 mW in (b). The signals circled correspond to isotropic and rigid components; the signal from the rigid component is indicated by the upward vertical arrow. Stick diagrams for the isotropic and rigid components are indicated at the top and bottom of the figure, respectively

267 K presented in *Figure 2*. We suggest that two components, differing in the rate of motional averaging, are present. An isotropic component is indicated by the upper stick diagram, while the parallel and perpendicular contributions of a 'slow' (or rigid) component are seen in the two lower stick diagrams. An alternative interpretation is that the spectrum is due to one species, undergoing partial averaging of the *g*- and hyperfine tensors. The correct interpretation was selected by measuring spectra at two microwave power levels, as seen in *Figure 2*. The two signals shown in the inset represent isotropic and anisotropic components; the relative intensities of the two signals change with the microwave power level, indicating different values for the spin-lattice relaxation time, and therefore different species.

At constant microwave power the relative amount of the 'slow' component increases with decreasing temperature, down to 257 K, where practically all the probe is in the slow motional regime. This can be seen from the spectra at 253 K, 267 K and 279 K, shown in *Figure 3*. Partitioning among slow and fast components has been detected in the gels with larger pores, at lower temperatures than those detected for PAA7.

E.s.r. spectra of $VO(H_2O)_5^{2+}$ in PAA gels swollen by water/acetone mixtures

The effect of the mixed solvent containing acetone fractions in the range 0.10–0.60 was studied in two polymer networks, PAA17 and PAA58, and in the bulk mixed solvent (as reference) at 278 K, 298 K and 318 K. Acetone is a non-solvent for PAA gels, therefore the amount of solvent retained by the network decreases as the acetone volume fraction increases[7]. The effect on the e.s.r. spectra from the probe is shown in *Figure 4* for PAA17, in water at 278 K. An isotropic spectrum is seen in *Figure 4a*, and a superposition of two components are shown in *Figures 4b* and *c*; the corresponding volume fractions of acetone are 0.20, 0.40 and 0.60.

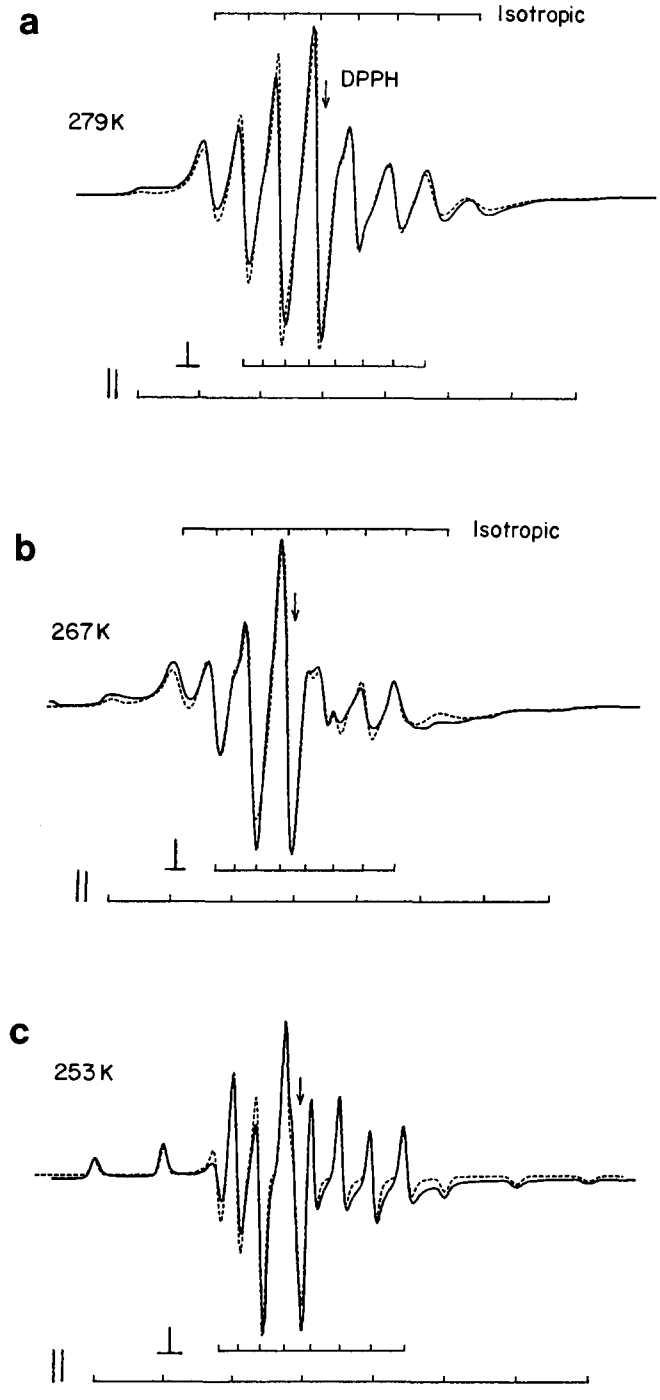

Figure 3 X-band e.s.r. spectra of $VO(H_2O)_5^{2+}$ in PAA7 swollen by water at the temperatures indicated (solid lines), and calculated spectra (broken lines), which are based on two components at 267 K and 279 K, and a rigid component only at 253 K, as seen in the corresponding stick diagrams

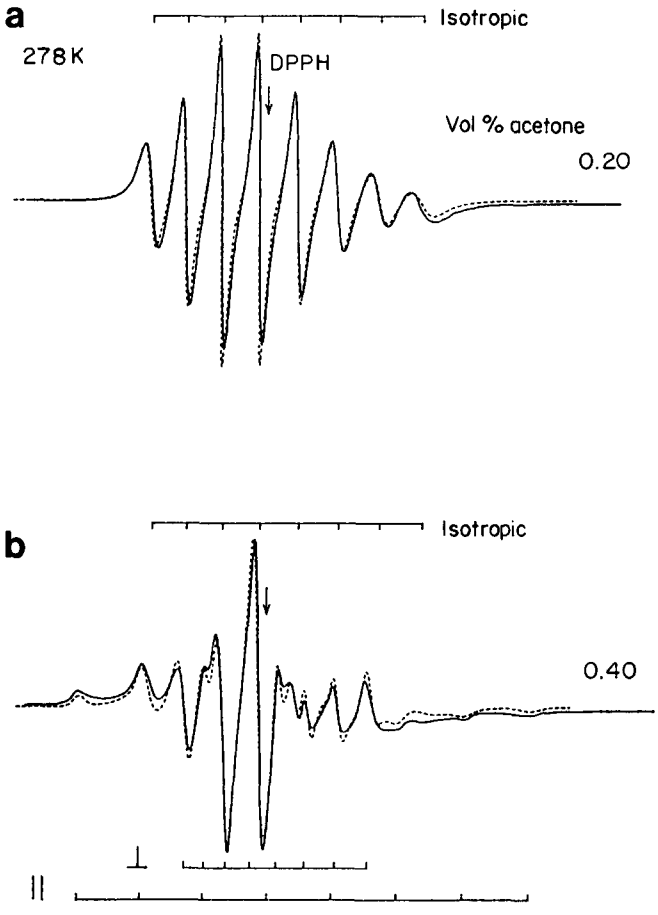

Figure 4 X-band e.s.r. spectra of $VO(H_2O)_5^{2+}$ in PAA17 swollen by the indicated acetone/water mixtures, at 278 K (solid lines), and calculated spectra (broken lines), based on two components in (b) and (c), and an isotropic component only in (a), as seen in the corresponding stick diagrams

Measurement of τ_c

The calculation of the correlation time τ_c is based on measuring the amplitudes h_i and widths ΔH_i of the eight hyperfine lines in an isotropic spectrum, with the assumption of a Lorentzian line shape and no overlap contribution to the line width. An average line intensity I_i is deduced from equation (1), the corrected peak-to-peak width ΔH_i^c is calculated from equation (2) and fitted by a least squares program to a polynomial in m_I, as in equation (3).

$$I_i = (1/8)\sum h_i(\Delta H_i)^2 \quad (1)$$

$$\Delta H_i^c = (I_i/h_i)^{1/2} \quad (2)$$

$$\Delta H_i^c = A + Bm_I + Cm_I^2 + Dm_I^3 \quad (3)$$

In *Figure 5* we present some of the data fitted in this way, for bulk water and two PAA gels (PAA7 and PAA58) swollen by water. The coefficient A is not normally used to calculate τ_c, because it contains contributions from unresolved proton superhyperfine splittings and spin-rotation. The coefficient B can be used to calculate τ_c, but contains the modulation of both the g- and hyperfine tensors, and is rather sensitive to errors. Generally, the coefficient C is used, since it depends only on the hyperfine tensor values, which are more accurately known than those of the g-tensor. The value of τ_c was calculated using a least squares iterative program, as described in the literature[11].

The local microviscosity η was calculated from the τ_c values, using the modified Debye equation (4).

$$\tau_c = 4\pi r^3\eta/3kT \quad (4)$$

In order to check that the molecular motion is governed by the *macro*scopic viscosity, we have plotted (*Figure 6*) the τ_c values for water and the mixed solvents at 298 K, as a function of η/T, where η is the *measured* viscosity. Straight lines are obtained, and the radius r of the complex, calculated from the τ_c values at three temperatures, is 3.53 Å; this value is close to the value of 3.39 Å deduced for $VO(H_2O)_5^{2+}$ in 3 M HCl (ref. 11).

The coefficients A, B, C and D in equation (3), the τ_c values and the corresponding microviscosities in the gels

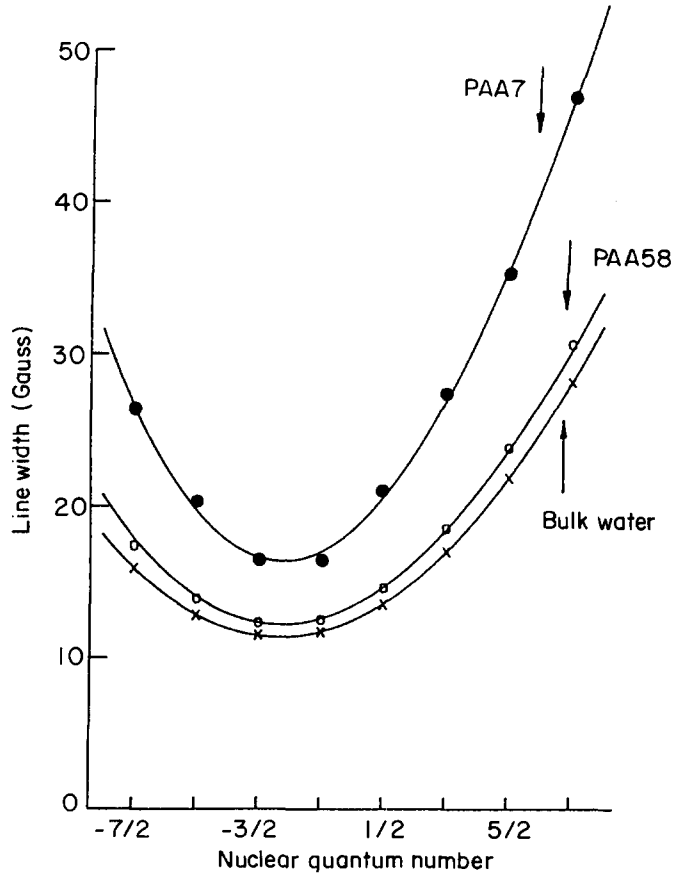

Figure 5 Experimental peak-to-peak line widths as a function of the m_I values for $VO(H_2O)_5^{2+}$ at 298 K in bulk water, PAA58 and PAA7. Curves fitted according to equation (3) are indicated

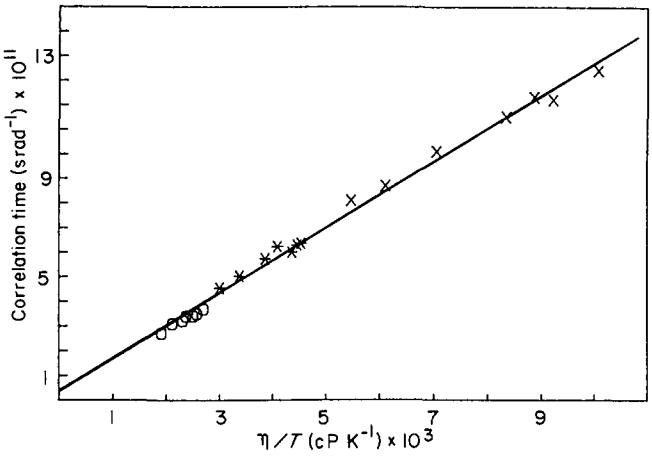

Figure 6 Plot of the correlation time τ_c for the bulk solvents (water and six acetone/water mixtures) as a function of η/T, where η is the measured viscosity: ×, at 278 K; *, at 298 K; ○, at 318 K

swollen by water and by the solvent mixture have been calculated[7]. A value of 3.53 Å for r was used in these calculations. The literature value for the absolute viscosity of water correlates well with the value calculated from the Debye equation at the three temperatures. In addition, the τ_c-derived microviscosities for the acetone/water mixtures compare favourably with the values obtained by direct measurement of the viscosity at the appropriate temperature. In *Figure 7*, we present three isothermic plots at 278 K, 298 K and 318 K of the microviscosity of water inside the gel as a function of pore size of the gel. An accelerated increase in the value of η is detected in a diameter of 15 Å. The viscosity of bulk water at these temperatures corresponds to a pore size of $\approx$80 Å.

Computer simulation of overlapping e.s.r. spectra from $VO(H_2O)_5^{2+}$

Some of the spectra shown in *Figures 2–4* consist of overlapping isotropic ('fast') and anisotropic ('slow') components. The input for the simulation of the isotropic component consists of the widths of the eight hyperfine lines and the values of g_{iso} and A_{iso}. The e.s.r. spectrum of the slow component was approximated in a phenomenological way by assuming the $g_{\|}$, $A_{\|}$, $g_{\perp}$ and $A_{\perp}$ values to be intermediate between the isotropic and rigid limit values at 77 K. The degree of anisotropy increases as the values of Δg ($\Delta g = g_{\perp} - g_{\|}$) and of ΔA ($\Delta A = A_{\perp} - A_{\|}$) approach the rigid lattice values of $\Delta g = 0.042$ and $|\Delta A| = 130$ G. The peak-to-peak widths $\Delta H_{\|}$ and $\Delta H_{\perp}$, suggested by examination of the experimental results, were fitted into equations (5) and (6), which have been used to describe the m_I dependence of the line widths in solids[12]. The procedure was repeated until a good agreement with the experimental results was obtained.

$$\Delta H_{\|} = (A_{\|} + B_{\|}m_I + C_{\|}m_I^2 + D_{\|}m_I^3)^{1/2} \quad (5)$$

$$\Delta H_{\perp} = (A_{\perp} + B_{\perp}m_I + C_{\perp}m_I^2 + D_{\perp}m_I^3)^{1/2} \quad (6)$$

The parameters used for the simulations were tested extensively. The appearance of the simulated spectra is very sensitive to the line widths of the individual lines; this analytical approach resulted in very good agreement with the observed spectra. Simulated spectra (superimposed on the experimental spectra) are shown in *Figures 3* and *4*, for the gels swollen by water and by the solvent mixture, respectively. It is important to note that the line-widths used to simulate the spectrum of the slow component in a composite spectrum are larger than those used to simulate the rigid limit component at 77 K, a result which seems reasonable for slow tumbling. All the parameters used for the simulated spectra have been published previously[7]. The line widths for the isotropic component in the case of a bimodal distribution of pore sizes were used to calculate a correlation time τ_c and the corresponding microviscosity.

DISCUSSION

Properties of water in the gels

The vanadyl ions in the PAA networks studied are hydrated by 'bound' water only. This is clear from the spectra shown in *Figure 1*, which indicate that crystallizable water is absent in PAA gels. Assuming as a first approximation that the pores are spherical and that the effective diameter of a water molecule is 3 Å (ref. 13), we can roughly estimate that the number of water layers in the pores studied ranges from one (in swollen PAA7) to ten (in PAA58). The absence of bulk water in these networks suggests that the effect of the polymer is felt through ten water layers. This conclusion contradicts previous results that indicate strong modification of the water structure only in the first two to three surface layers[14], and probably not beyond six layers[13]. This contradiction can be rationalized as follows. In order to visualize the distribution of water in the various layers, we have plotted the cumulative fraction of water in the first six layers as a function of pore diameter (*Figure 8*). The number of layers in the largest pores is ten, but the fraction of water molecules in the first six layers is 0.94, indicating that the increase in pore diameter does not increase proportionately the number of molecules distant to the network. The conclusion is that even if the probe is hydrated by the distant water, the number of these probe molecules is not large enough to contribute significantly to the total signal intensity observed. The line widths of the probe in the largest pores given in *Figure 5* are only slightly higher than the line widths in bulk water; this difference is beyond experimental error, and leads to different τ_c values, as shown in *Figure 7*.

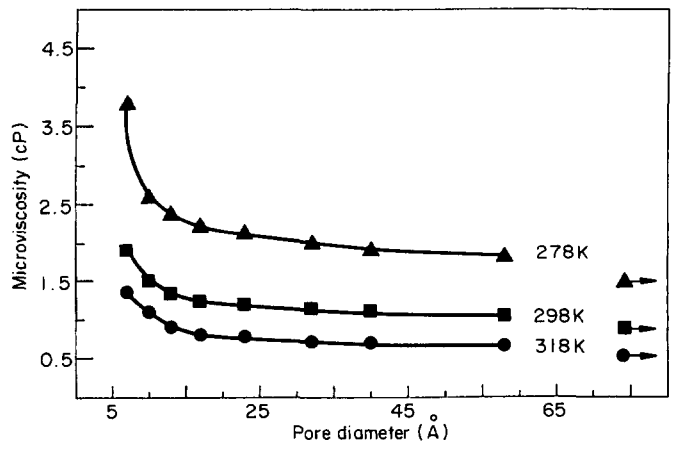

Figure 7 Plot of the microviscosity of water in the swollen gels (deduced from τ_c values) *versus* the pore diameter of PAA gels, at three temperatures. Data for bulk water are indicated by the horizontal arrows

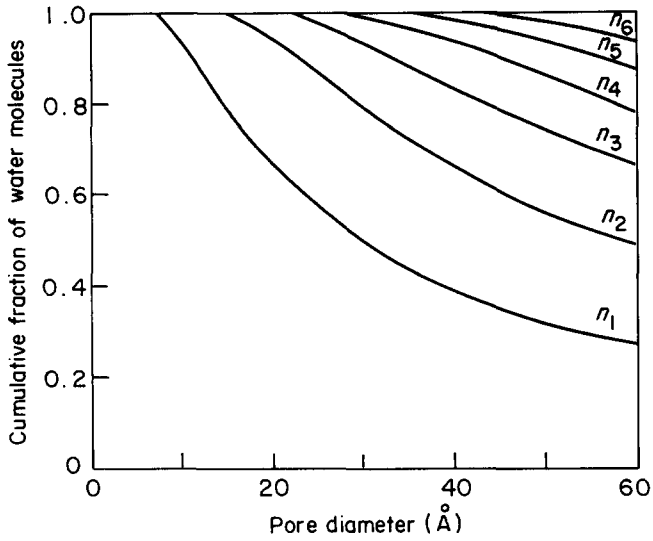

Figure 8 Cumulative fraction of water molecules $n_j = \sum n_i$, where n_i is the fraction of water molecules in the ith layer, as a function of pore diameter of the gels

Two component spectra in PAA gels

The observation of fast and slow components for the paramagnetic probe in the smallest pores, PAA7 swollen by water, *Figure 2*, is direct spectroscopic evidence for a bimodal distribution of pores in this gel in the temperature range 257–278 K. Two types of gel, with different polymer network densities, exist side by side under the same swelling and temperature conditions. The relative amount of each network can be varied in a very simple way, by variation in the temperature, as seen in *Figure 9a*. The microviscosity corresponding to the isotropic component is also shown in *Figure 9a*. Two components have been detected in all the networks studied, at lower temperatures compared with those detected for PAA7.

For gels swollen by a water/acetone mixture the transition to a bimodal site distribution has also been observed. The amount of each network depends on the acetone concentration, as seen for PAA17 at 278 K in *Figure 9b*, which also gives the microviscosity. For PAA17 the acetone volume fractions needed for the detection of a bimodal distribution of pores at 278 K, 298 K and 318 K are 0.3, 0.4 and 0.4, respectively. The corresponding acetone volume fractions for PAA58 are 0.4, 0.5 and 0.5 (all values ± 0.04).

PAA gels and free volume

The increase in τ_c with decreasing pore size can be translated into an increase in the microviscosity η of the medium. Changes in η are frequently related to changes in the free volume, using the Fujita-Dolittle equation given below[15–17].

$$1/\ln(\tau_c/\tau_r) = -(f_0^2/B\beta)(1/(v_1 - v_1^0)) - f_0/B \quad (7)$$

In equation (7): τ_c and τ_r are the correlation times for tumbling in the gel swollen by a given solvent and a reference state, respectively; B is the Dolittle equation parameter; β is a proportionality constant; f_0 is the free volume of the reference state; v_1 and v_1^0 are the solvent volume fractions in the swollen gel and the reference state. The reference state was taken to be bulk water, since the major component in these gels is water (this is true even in the smallest gels, which contain the smallest percentage of water). The density of water was assumed to be 1.0 g ml^{-1} at the three temperatures studied; the weight fraction and the volume fraction are therefore the same. The value of v_1, the solvent volume fraction in each gel, can be calculated gravimetrically. The Fujita-Dolittle plots for data at 278 K, 298 K and 318 K, shown in *Figure 10*, are linear, indicating that τ_c is sensitive to the free volume available to the paramagnetic probe in the gel pores. All plots have positive intercepts, while negative values are expected from equation (7); this indicates a constant error, most likely in the determination of τ_c values.

CONCLUSIONS

1. E.s.r. spectra of the vanadyl probe $VO(H_2O)_5^{2+}$ in chemically cross-linked PAA gels of diameters 7–58 Å were used to analyse the changes in gel structure as a function of temperature and solvent composition.
2. The PAA networks were swollen by water and by acetone/water mixtures containing 0.1–0.6 volume fraction of acetone.
3. Strong spectroscopic evidence has been obtained that indicates the absence of bulk water in all the networks studied. The number of water layers in the largest pores is about ten. However, a simple calculation shows that most of the water (>90%) is in the first six layers. Therefore we expect to observe the most signals from the probe in the first six layers.
4. A bimodal distribution of networks has been detected for all networks. The appearance of this distribution

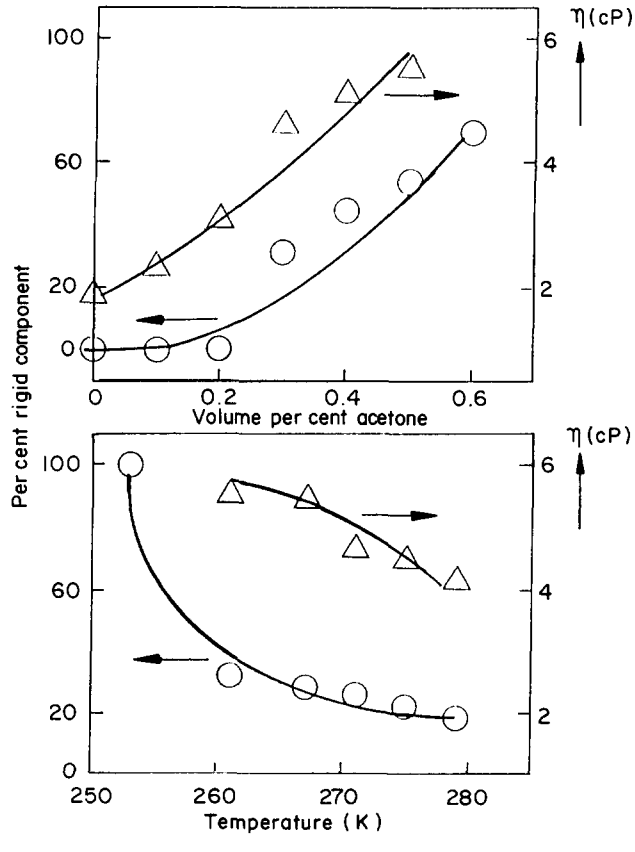

Figure 9 The relative amount of rigid component for PAA17 gels as a function of: (a) solvent composition; and (b), temperature. The microviscosities corresponding to the isotropic component (calculated from τ_c values) are also indicated

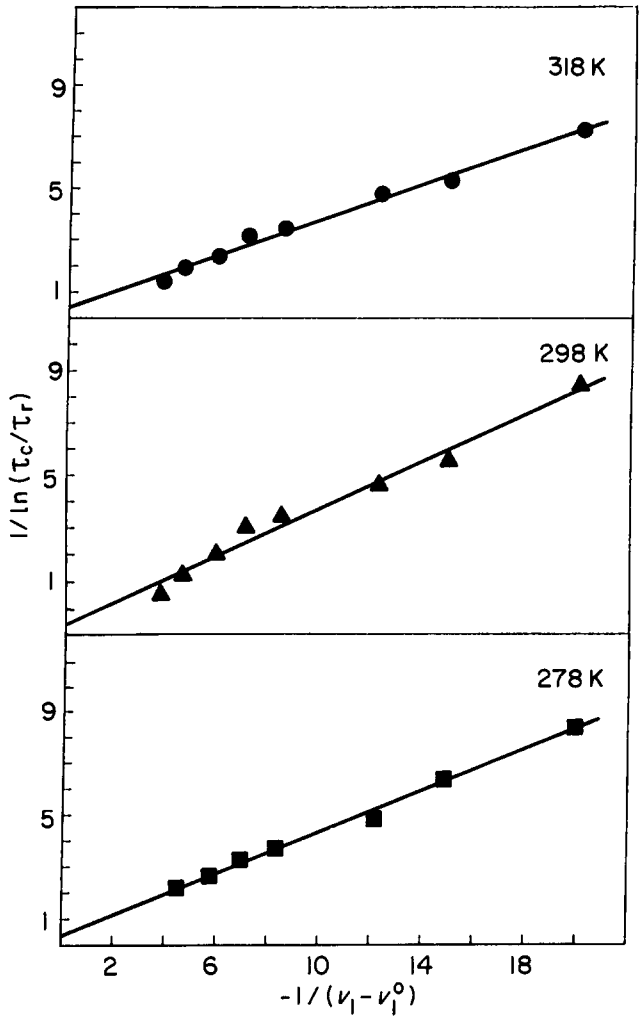

Figure 10 Fujita-Dolittle plots for the PAA gels swollen by water, at the temperatures indicated

is triggered by lowering the gel temperature in networks swollen by water; alternatively, the bimodal distribution appears for a gel at a constant temperature by adding acetone to the swelling fluid.

5. Unlike the ionic gels, the transition from a homogeneous PAA gel to a bimodal distribution of pore sizes is gradual as a function of temperature in water swollen gels, and as a function of the acetone content in gels swollen by the mixed solvent.
6. The microviscosity in the pores appears to depend on the free volume in the pores; this is evident by applying the Fujita-Dolittle equation in PAA swollen by water, at three different temperatures.

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