

DIFFUSION AND NUCLEAR RELAXATION OF SOLVENT IN A CROSSLINKED POLYMER

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1. Introduction

Nuclear proton relaxation has been recently used for the measurements of pore size distribution (1, 2) and permeability (3) in various fully or partially saturated inorganic porous media. These studies generally implies that the proton relaxation inside a pore is an average of bulk and surface contributions; this latter being dependent of the surface to volume ratio. As a consequence the pore size dispersity results in a distribution of spin-lattice relaxation rates which can be potentially extracted from the longitudinal magnetization decay (4).

In principle the proton relaxation may be used to the study of organic materials like polymer resins. (Fig. 1). This would be useful to give an insight of their possible structure. However this technique is not well suited owing to the difficulty to separate properly signals and relaxation due to the solvent and the polymer. This difficulty is not encountered in the ^{13}C or ^2H relaxation of small molecules diffusing in such matrices. But the relaxation of these nuclei is essentially intramolecular and governed by rotational motions which do not give any information on the structure of the matrix. A simple possibility is then to incorporate some paramagnetic probes in the matrix. In that case an intermolecular contribution to the relaxation occurs, which is dependent of the translational diffusion through the porous solid and thus provides information on the topology of the matrix.

Such systems can be obtained with a polymer whose the functional groups are able to give stable complexes with divalent or trivalent ions in order to form three dimensional crosslinked networks. This is the case of poly 4 vinyl pyridine (P4VP) whose copper II complexes have been subjected to several works dealing with its catalytic activity in redox reactions (5-7).

In this work, we have investigated the ^2H and ^{13}C relaxations of methanol and nitromethane adsorbed on P4VP crosslinked by paramagnetic VO^{2+} and Cu^{2+} ions as well as by diamagnetic Cd^{2+} ion. The latter samples being used to give an estimate of the contribution of relaxation mechanisms other than paramagnetic. As the samples crosslinked by VO^{2+} and Cu^{2+} yield nearly the same results, we report mainly the experiments with VO^{2+} . The choice of the two solvents has been motivated by their similar sizes and their very different behaviors towards divalent ions.

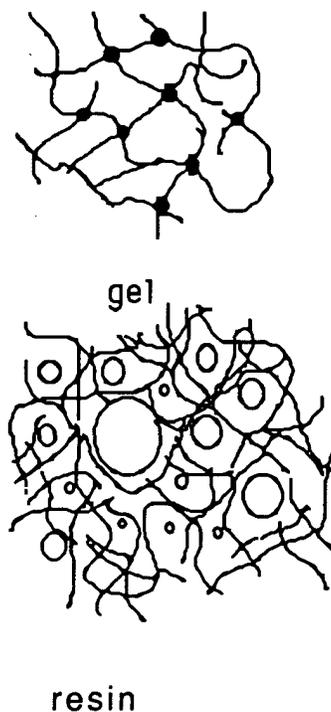


Fig.1 Schematic diagrams showing a crosslinked polymer in a gel phase and in a resin phase. In the resin the pores are materialized as circles of various radii.

2. Results

a) ESR and NMR experiments.

The P4VP - VO²⁺ complex is characterized by an ESR spectrum yielding $A_{\parallel} = 187$ G, $A_{\perp} = 68$ G and $g_{\parallel} = 1.945$, $g_{\perp} = 1.980$ for hyperfine coupling and g tensor, respectively (Fig. 2 (B),(C)). For the resin, the anisotropy of the hyperfine coupling remains virtually unchanged between 77 and 350K, showing that the motional correlation time of VO²⁺ is larger than 10⁻⁷s, even in presence of adsorbed solvent (Fig. 2(C)). One has probably a rigid network whose the nodes are the VO²⁺ ions, since the ¹³C NMR lines of the polymer are not observable (Fig. 3(A)) On the other hand, for the P4VP - VO²⁺ gel with an equivalent solvent content, one obtains the same spectrum (Fig. 2(B)), but a reduction of *ca.* 5% of the anisotropy of hyperfine coupling, which corresponds to a correlation time of reorientation of VO²⁺ of *ca.* 5 x 10⁻⁹s and the ¹³C NMR spectrum of the polymer is observed (Fig. 3(B)).

A similar behavior is observed in ESR experiments on the P4VP - Cu²⁺ either for resin and gel samples where $A_{\parallel} = 170$ G, $A_{\perp} = 15$ G and $g_{\parallel} = 2.260$, $g_{\perp} = 2.095$. However the spectrum of the gel is better resolved and shows a superhyperfine structure in one of the lines (Fig. 2(A)). This structure shows a 1.2.3.2.1 quintet of 13.5 G splitting indicating the hyperfine coupling of two equivalent nitrogens (Fig. 2(A)).

It is then concluded that, under our experimental conditions the crosslinking occurs by two pyridyl rings bound to a Cu²⁺. This cannot be concluded for the P4VP - VO²⁺ complex since the nitrogen hyperfine coupling is not resolved (8). However assuming that Cu²⁺, VO²⁺ and Cd²⁺ behave similarly, it appears that one monomer unit over 30 participates to the crosslinking for a standard concentration of 10²⁰ divalent ion /gr. of polymer.

b) Nuclear relaxation.

As pointed out above the ¹³C spectra of the P4VP - VO²⁺, P4VP - Cu²⁺, P4VP - Cd²⁺ gels swollen by alcohols or nitromethane show the lines of the solvent and of the polymer. The ¹³C longitudinal relaxation is monoexponential (Fig. 4(a)) and its frequency dependence shows that the segmental motions of the polymer as well as the rotational correlation time of the solvent is of the same order of magnitude than

the one of a solution of non crosslinked polymer of equivalent concentration.

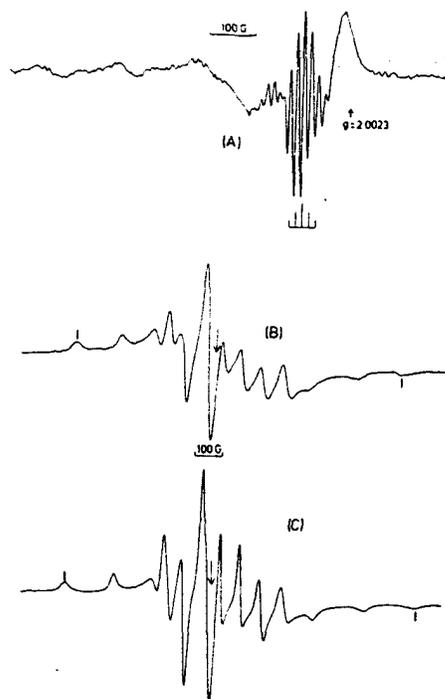


Fig.2. ESR spectra of P4VP crosslinked by paramagnetic ions. (A) second derivative of a P4VP-Cu²⁺ gel swollen by methanol; (B) First derivative of a P4VP-VO²⁺ gel swollen by ethanol; (C) Spectrum of a P4VP-VO²⁺ resin.

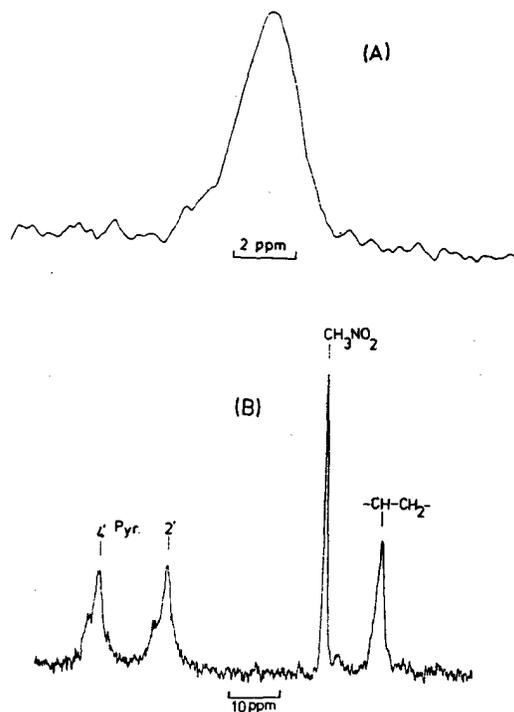


Fig.3 ¹³C NMR spectra of nitromethane (at 75.5 MHz) : (A) adsorbed on a P4VP-VO²⁺ resin.; (B) in a P4VP-Cu²⁺ gel swollen by nitromethane.

On the other hand in the crosslinked resin, the solvent relaxation is significantly faster in P4VP - VO²⁺ or P4VP - Cu²⁺ systems than in P4VP - Cd²⁺ and presents a non exponential behavior (Figs. 4 (b),(c)).

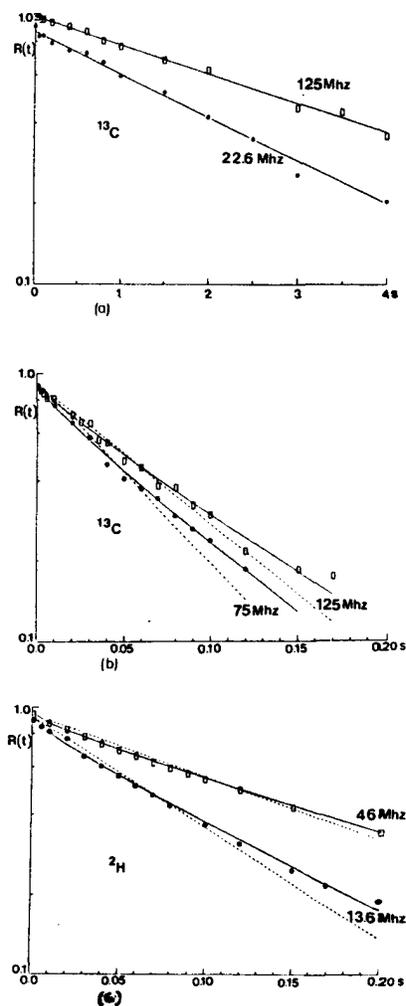


Fig. 4 (a) Semi logarithmic plots of ¹³C and ²H longitudinal magnetization decay $R(t)$ in methanol adsorbed on diamagnetic P4VP-Cd²⁺ sample (a) and on P4VP-VO²⁺ paramagnetic samples (b and c) both at two frequencies. In (a), $R(t)$ is fitted by a monoexponential function. In (b) and (c) the full lines are the best fits obtained with Eq. (1) while the dotted lines show the best fits obtained by monoexponential functions.

c) Scanning electron microscopy and X ray scattering

The examination of a sample of P4VP - Cu²⁺ by scanning electron microscopy has evidenced the existence of pores about 1 μ which remains virtually unchanged after a long duration in contact with a solvent. The small angle X ray scattering allows a determination of

the mean pore size about 200 Å. The reduction of the scattered intensity with adsorption of solvent confirms that the heterogeneities seen in the dry resin do not correspond to non crosslinked polymer domains but to void pores. We have therefore interpreted our relaxation data by a process of exchange between the solvent in contact with the polymer at the pore surface and the bulk solvent filling the pore.

4. Discussion

a) Longitudinal magnetization decay for a fractal distribution of quasi-disconnected spherical pores

In the interpretation of the relaxation experiments in saturated porous media it is commonly assumed that the fluid close to the surface of the pore relaxes much faster than the bulk fluid inside the pore. This could be due to the presence of paramagnetic impurities at the surface (9, 10), or to a fast two-dimensional diffusion of the fluid molecules which enhances drastically the number of reencounters in a finite two-dimensional domain (11). Other possibilities exist such as the hindered molecular motion close to the surface.

The question arises now about the homogeneity of the magnetization M_z in such disordered system. The behavior is dominated by a dimensionless parameter $E_s = \mu_s R_0 / D$ describing the efficiency of the surface relaxation process, μ_s characterizing the strength of the surface relaxation and D being the translational diffusion coefficient. μ_s is given as a product of the solvent-surface relaxation rate by the thickness of the solvent layer interacting with the surface. If $E_s \geq 1$ the surface relaxation process is dominant and it results an inhomogeneity of the magnetization close to the interface (diffusion-limited regime). If $E_s \ll 1$ the surface relaxation is finite but the diffusion process is sufficiently fast in one pore to relax homogeneously the bulk fluid in contact with the surface (complete averaging regime). Assuming that the surface relaxation, due to the spin-lattice relaxation rate T_{1s}^{-1} , is active over a thickness ϵ of the order of the molecular scale at proximity of the pore-grain interface, one has $E_s = \epsilon R_0 / (D T_{1s}) \ll 1$ for $\epsilon \sim 10 \text{ \AA}$, $R_0 \sim 1 \mu$, $D \sim 10^{-6} \text{ cm}^2/\text{s}$ and $T_{1s} \sim 10 \text{ ms}$ for the system considered in this work. In that case the magnetization is homogeneous in one pore and relaxes exponentially with a rate composed as a linear combination of bulk $1/T_{1b}$ and surface $1/T_{1s}$ spin-relaxation rates.

Following Mendelson (4), one modelizes the porous system (Fig.1) as a superposition of quasi disconnected categories of N^n ($n \in \{0, 1, \dots\}$) weakly connected spherical pores of radius $R_n = R_0/\alpha^n$ ($\alpha > 1$). Provided that $E_s \ll 1$ there is a uniform longitudinal magnetization M_{zn} in each pore with a spin-lattice relaxation rate composed as a linear combination of a bulk and surface contributions, this latter being scaled as the surface to volume ratio of such pore. For a fractal distribution of these categories of pores, one has $N \sim \alpha^{d_f}$ and the deviation $R(t)$ is given at short time by (4)

$$R(t) \approx e^{-t/T_{1b}} \left[1 - \Gamma(d_f - 2) \left(\frac{3 \epsilon t}{R_0 T_{1s}} \right)^{3-d_f} \right], \tag{1}$$

when $t \ll (R_0/3\epsilon) T_{1s}$, One then has a power law with a time exponent $3-d_f$ instead of $(3-d_f)/2$ of ref. (9). We have displayed in Fig. (5) the theoretical time decays of $R(t)$ for different fractal dimensions. One notes a drastic effect of this dimension on such decays, especially at very short time where the non exponential behavior is quite pronounced when $d_f \neq 2$.

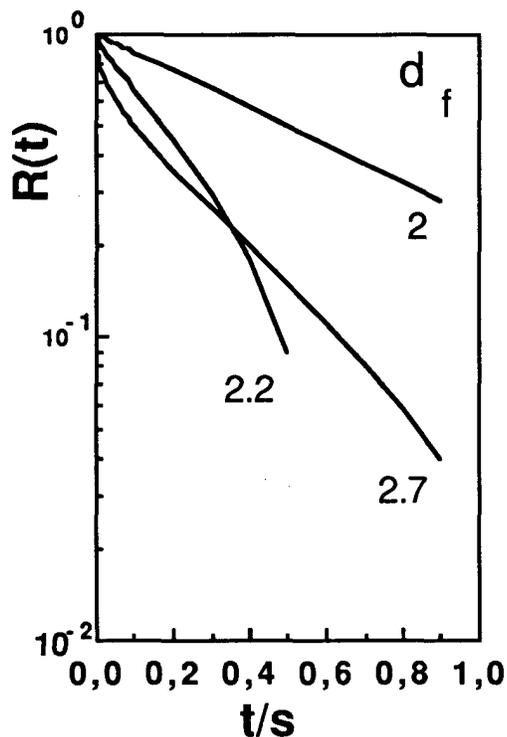


Fig. 5 Semilogarithmic plot of the

magnetization decay $R(t)$ given by Eq. (1) for different fractal dimensions; $(R_0/3\epsilon) T_{1s} = 0.33$

The self similarity assumed in this model can be deduced from the experiments described above. The small angle X ray scattering yields an estimate of the mean size of the pores ($\sim 200 \text{ \AA}$). The scanning electron microscopy yields an estimate of the biggest size of the pores ($\sim 1\mu$).

For the diamagnetic sample, the ^{13}C longitudinal relaxation is monoexponential (Fig. 4a) and the single T_1 found is characteristic of a rotational diffusion process. On the contrary for the paramagnetic samples, we have used the Eq. (1) to fit our relaxation data (Figs. 4b,c) in the time domain required for its application, roughly $t < 1\text{s}$. The parameters d_f , T_{1b} , and $(R_0/3\epsilon) T_{1s}$ have been determined by least square minimization using the Simplex algorithm (12). The best fit of the magnetization decay, corresponding to a standard deviation smaller than 5% is achieved for $2.65 < d_f < 2.75$. This value of d_f can be compared qualitatively to the fractal dimension of the percolating cluster in a tridimensional system which is about 2.5. The quasi disconnection assumed in our model probably overestimates the surface contribution at short time. This fact together with the reproducibility in the determination of d_f using the relaxation of ^2H and ^{13}C in a wide frequency range, for two solvents of very different properties, seem a good criterion for the validity of the method outlined here.

b) Interpretation of the surface spin-lattice relaxation rates

In Fig. 6, we have plotted the frequency dependence of the surface contribution of the spin lattice relaxation rate $(3\epsilon/R_0) 1/T_{1s}$ for methanol and nitromethane in the temperature range 296-320K. Such temperature range was limited at one side by an excessive line broadening and at the other side by the desorption of solvents. Under these conditions, the uncertainties in the determination of T_{1b} and T_{1s} estimated to $\pm 10\%$ did not allow the observation of significant variations with temperature. Anyway a weak temperature dependence is expected for nuclear relaxation of adsorbed species (13). In consequence the computed frequency dependences of the surface and bulk relaxation rates have therefore been fitted on the means of experimental data in this temperature range.

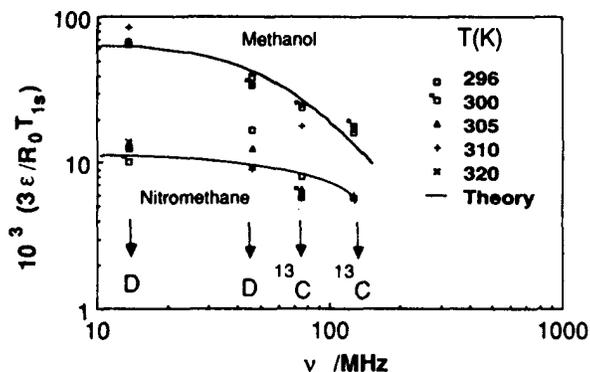


Fig. 6 : Logarithmic plot of $10^3 (3\epsilon/R_0) 1/T_{1s}$ (s^{-1}) for ^{13}C and 2H vs the frequency ν (MHz) for methanol and nitromethane at different temperatures. The value of T_s of the deuterons have been multiplied by $[\gamma(^2H) / \gamma(^{13}C)]^2 \sim 0.373$ to be normalized relatively to the one of ^{13}C . The solid line represents the theoretical result $(3\epsilon/R_0) 1/T_{1s} = 2.7 \cdot 10^7 \tau_e / (1 + \omega_I^2 \tau_e^2)$ [Eqs. (3), (4)] with $\tau_e \sim 2.5 \cdot 10^{-9}$ s.

In Fig. 6 the $(R_0/3\epsilon) T_{1s}$ of the deuterons have been multiplied by $[\gamma(^2H) / \gamma(^{13}C)]^2 \sim 0.373$ in order to be normalized relatively to that of ^{13}C . The choice of these two solvents has been motivated by their similar sizes and their very different behaviors towards divalent ions. The methanol is able to bind to M^{2+} whereas the nitromethane does not. It is then possible to make a discrimination between the inner and outer sphere contributions to the paramagnetic relaxation. For methanol, the relaxation rate at the surface of the pores is assumed as a weighted superposition of a rotational (bound) and translational (not bound) contributions; the former being due to the coordination of the solvent molecule to the paramagnetic ion M^{2+}

$$\frac{1}{T_{1s}} = f \left(\frac{1}{T_{1s}} \right)_{\text{bound}} + (1-f) \left(\frac{1}{T_{1s}} \right)_{\text{tr}} \quad (2)$$

where $f = [M^{2+}] / [CH_3OH]$ is the ion / solvent concentration ratio at the surface of the pores. In Fig. (6) a large frequency dependence and almost no temperature effect are observed for this solvent. For nitromethane, the first term of Eq. (2) does not exist and the surface

relaxation is restricted to the translational term. Here the frequency and temperature dependences are weak (dotted lines in Fig. 6). Assuming for $(1/T_{1s})_{\text{tr}}$ in methanol the value of $1/T_{1s}$ found for nitromethane, one notes that the first term in Eq. (2) dominates the relaxation in methanol at least by a factor 4, even if $f \ll (1-f)$. Two questions now remain about the value of f and the expression of $1/T_{1s}$.

The life time of the methanol coupling is about 10^{-7} - 10^{-5} s and the correlation time τ_e corresponds to a reorientation of this molecule in the coordination sphere of the divalent ion. Such coordination takes place by the oxygen of the methanol. The distance M^{2+} -O is about 2 - 2.2 Å, the carbon and deuterons atoms are typically at 3.1 - 3.4 Å of the metallic ion. By neglecting the spectral densities dependence on the electron Larmor frequency, one has the following expression for the surface relaxation rate T_{1s}^{-1}

$$T_{1s}^{-1} = \frac{2}{5} S(S+1) \gamma_I^2 \gamma_S^2 \hbar^2 \langle r_{IS}^{-3} \rangle^2 J(\omega_I) \quad (3)$$

where $\gamma_I = 4107 \text{ rd s}^{-1} \text{ G}^{-1}$ (2H) or $6728 \text{ rd s}^{-1} \text{ G}^{-1}$ (^{13}C), $\gamma_S \sim 1.76 \cdot 10^7 \text{ rd s}^{-1} \text{ G}^{-1}$. Since the metal ion is fixed the spectral density associated to such rotation is

$$J(\omega_I) \approx (1 - S^2) \tau_e / (1 + \omega_I^2 \tau_e^2) \quad (4)$$

where S is the generalized order parameter defined by Lipari and Szabo (14). In case of an unhindered rotation of the methanol around the O- M^{2+} bonding S becomes $S = 1/2 \langle 3\cos^2\beta - 1 \rangle$, where $\beta \sim 23^\circ$ is the angle between r_{IS} and O- M^{2+} . A simple calculation shows that this parameter and $\langle r_{IS}^{-3} \rangle^2$ are almost equivalent for the two nuclei under consideration. In Eqs. [(3), (4)] the spin-lattice relaxation rate of the paramagnetic ion itself ($\sim 10^6 \text{ s}^{-1}$) given by the ESR has been neglected in comparison of the reorientation rate. The best Lorentzian fit of the frequency dependence of the experimental values of $[(3\epsilon/R_0) 1/T_{1s}]_{\text{exp}}$ (points for methanol in Fig. 6) gives a reorientation correlation time $\tau_e \sim 2.5 \cdot 10^{-9}$ s. Substituting into Eqs. [(3), (4)] $r_{IS} \sim 3.2 \text{ \AA}$ (for ^{13}C) and $S \sim 0.77$ yields, at 75MHz, for the bound surface spin-relaxation rate yields $(1/T_{1s})_{\text{bound}} \sim 1851 \text{ s}^{-1}$. With $f \sim 10^{-2}$, $3\epsilon \sim 15 \text{ \AA}$ and $R_0 \sim 1 \mu$ (from the

scanning electron microscopy), one then has $(3\epsilon/R_0) (1/T_{1s})_{\text{bound}} = 2.78 \text{ s}^{-1}$. For methanol at 75MHz and at 300K the observed value of $(3\epsilon/R_0) (1/T_{1s}) = 0.024 \text{ s}^{-1}$. Neglecting the translational part of Eq. (2), one then finds $f \sim 0.024 / 2.78 = 0.86 \cdot 10^{-2}$. All these calculations leads finally to the surface spin-relaxation times : $T_{1s} \sim 24 - 94 \text{ ms}$ for methanol and $125 - 250 \text{ ms}$ for nitromethane, in the frequency range studied.

c) Interpretation of the bulk spin-lattice relaxation rates

In Fig. 7, we have plotted the frequency dependence of the bulk contribution of the spin lattice relaxation rate $1/T_{1b}$ of ^{13}C and ^2H at different temperatures and for two different solvents (methanol and nitromethane). The time T_{1b} of the deuterons have been multiplied by $[\gamma(^2\text{H}) / \gamma(^{13}\text{C})]^2 \sim 0.373$ to be normalized relatively to the T_{1b} of ^{13}C . Spurious variations of $\pm 14\%$ (methanol) and $\pm 5.5\%$ (nitromethane) have been observed for $1/T_{1b}$ in the 296-300K range. The temperature dependence of $1/T_{1b}$ is therefore small and within the limits of experimental uncertainties. Such a behavior seems characteristic of the intermolecular contribution to the relaxation of adsorbed species (13). For both solvents, a frequency dependence of $1/T_{1b}$ has been observed more pronounced for nitromethane where this relaxation rate is an order of magnitude smaller than for methanol. These observations can be explained by a process of translational diffusion of solvent molecules relaxed by a random distribution of paramagnetic probes at the surface of the pores. The radii of the biggest pores are so large that the restricted diffusion effects do not occur. As a first approximation, one can apply the expression of $1/T_{1b}$ for the case of dipolar interactions between a nuclear spin I and a uniform density N_s of electronic spins $S=1/2$, modulated by translational diffusion :

$$T_{1b}^{-1} \cong \frac{6\pi}{5} N_s \gamma_I^2 \gamma_S^2 \hbar^2 \tau_t < \Delta_{IS} >^3 I(\omega_I) \quad (5)$$

where the spectral density $I(\omega)$ is given by (15)

$$I(u) = u^{-5} \left\{ u^2 - 2 + e^{-u} \left[(u^2 + 4u + 2) \cos u + (u^2 - 2) \sin u \right] \right\} \quad (6)$$

with $u = (2\omega_I \tau_t)^{1/2}$, τ_t being the translational correlation time, here equal to $= \Delta_{IS}^2 / D_I$ since the spins S are immobilized, and Δ_{IS} the distance of minimal approach between I and S. Owing to the small variations of $1/T_{1b}$ with temperature, global fits of the relaxation rates as functions of the Larmor frequencies have been performed, taking Δ_{IS} and τ_t (or D_I) as adjustable parameters in Eqs. [(5), (6)]. Figure 7 shows that the frequency dependence of $1/T_{1b}$ is consistent with this expression. Fitting the results at each temperature yields $\Delta_{IS} = 4.3 \pm 0.5 \text{ \AA}$, $8.0 \times 10^{-7} < D_I < 1.1 \times 10^{-6} \text{ cm}^2/\text{s}$ for methanol and $\Delta_{IS} = 9.5 \pm 0.9 \text{ \AA}$, $6.4 \times 10^{-7} < D_I < 1.15 \times 10^{-6} \text{ cm}^2/\text{s}$ for nitromethane. The diffusion coefficients of the solvents are then of the order of $10^{-6} \text{ cm}^2/\text{s}$. They are smaller by a factor 2-3 than in the gels of same composition and by one order of magnitude than in pure solvents (e.g. $3 \times 10^{-5} \text{ cm}^2/\text{s}$ for methanol at 300K (16)). The translational correlation times are $(2.1 \pm 0.7) \times 10^{-9} \text{ s}$ for methanol and $(1.2 \pm 0.4) \times 10^{-8} \text{ s}$ for nitromethane.

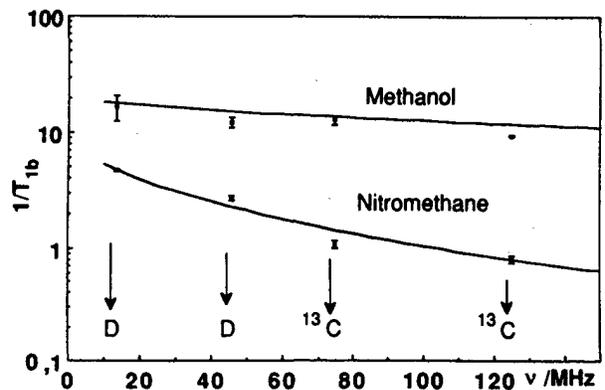


Fig. 7 : Semi-logarithmic plot of $1/T_{1b}$ (s^{-1}) for ^{13}C and ^2H vs the frequency ν (MHz) for different temperatures for methanol and nitromethane adsorbed on the P4VP-VO $^{2+}$ resin. The value of T_{1b}^{-1} of the deuterons have been multiplied by $[\gamma(^{13}\text{C}) / \gamma(^2\text{H})]^2$ for comparison with ^{13}C . The filled squares represent the average relaxation rates over the 296-320K and the vertical bars indicate the dispersion of the data obtained in this range. The solid lines correspond to the best fits obtained with Eqs. [(5), (6a)].

Considering only the molecular radii of methanol (2.5 Å) and nitromethane (2.8 Å), the large difference between the Δ_{1S} found for the solvents is quite unexpected. However, Δ_{1S} depends also on the polarity and size of the ligands in the first coordination sphere of the metal ion and on the symmetry of the complex formed. This is the possible origin of the difference reported above. The metal ion is indeed complexed by CH_3OH and not by CH_3NO_2 so that the molecular structure surrounding the metal ion is not the same for the two solvents.

5. Conclusion

We have investigated the longitudinal ^2H and ^{13}C relaxations of methanol and nitromethane adsorbed on poly 4 vinyl pyridine (P4VP) crosslinked by paramagnetic VO^{2+} and Cu^{2+} ions as well as by diamagnetic Cd^{2+} ion. We have proceeded to other measurements to obtain structural information on the matrix. The analysis of the superhyperfine ESR structure on the P4VP - Cu^{2+} has shown that the crosslinking involves two pyridyl rings. The anisotropy of the hyperfine coupling remains virtually unchanged between 77 and 350K, showing a rigid network (resin) whose the nodes are the paramagnetic ions. The scanning electron microscopy has evidenced the existence of pores about 1μ which remains virtually unchanged after a long duration in contact with a solvent. The small angle X ray scattering has allowed a determination of the mean pore size about 200Å. The reduction of the scattered intensity with adsorption of solvent has confirmed that the heterogeneities seen in the dry resin do not correspond to non crosslinked polymer but to void pores. We have applied the theory of Mendelson (4) to interpret the non exponential nuclear magnetization decay $R(t)$ by a superposition of exponential decays associated to a fractal distribution of quasi disconnected categories of spherical pores. We have considered the case of a fast exchange between the surface and the bulk fluids leading to a single spin-lattice relaxation rate as a linear combination of a bulk $1/T_{1b}$ and surface $1/T_{1s}$ contributions in each category of pore. The power law found in this theory for the short time approximation of $R(t)$ has allowed a possible determination of the fractal dimension d_f of the surface. The best fit of $R(t)$ has been achieved for $2.65 < d_f < 2.75$. The choice of the two solvents (methanol and nitromethane) has been motivated by their

similar sizes and their very different behaviors towards divalent ions. This makes possible the discrimination between the inner and outer sphere contributions to the paramagnetic relaxation.

The large frequency dependence of $1/T_{1s}$ and the small temperature effect observed for methanol have been explained by a reorientation of the adsorbed molecule in the coordination sphere of the paramagnetic ion. The comparison of a theoretical expression and the experimental data for different temperatures has led to a correlation time of 2.5×10^{-9} s for this reorientation. The frequency dependence of $1/T_{1b}$ of ^{13}C and ^2H at different temperatures and for two different solvents (methanol and nitromethane) can be explained by a process of translational diffusion of the solvent molecules relaxed by a random distribution of paramagnetic probes at the surface of the pores. The comparison of the experimental values of $1/T_{1b}$ with a theoretical expression has led to the values of the correlation time of translational diffusion $\tau_t \sim (2.1 \pm 0.7) \times 10^{-9}$ s for methanol and $(1.2 \pm 0.4) \times 10^{-8}$ s for nitromethane, giving a translational diffusion coefficient $D_t \sim 10^{-6}$ cm²/s two or three times smaller than in the gel of same composition and one order of magnitude smaller than in the pure solvent.

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