

## Field cycling magnetic relaxation study of translational diffusion at surfaces of nanopores

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<sup>1</sup>H spin-lattice relaxation rates of several aprotic polar liquids on microporous chromatographic glass beads that have paramagnetic ion impurities are recorded over magnetic field strengths using a field-switched magnetic relaxation dispersion spectrometer. The data support quantitatively our theory of nuclear paramagnetic relaxation and give the translational diffusion at the surface of nanopores.

Les vitesses de relaxation spin-réseau du proton de différents liquides polaires aprotiques saturant des verres poreux calibrés ont été enregistrées en fonction des intensités de champ magnétique avec un spectromètre à cyclage de champ. Les courbes de dispersion observées s'accordent bien aux prévisions théoriques et permettent d'obtenir le coefficient de diffusion de translation à la surface des nanopores.

**Key-words :** Nuclear relaxation, field-cycling, pores, diffusion

### INTRODUCTION

The magnetic field dependence of the nuclear spin relaxation rate is a rich source of dynamical information in confined environments [1-3]. Varying the magnetic field changes the Larmor frequency, and thus, the fluctuations to which the nuclear spin relaxation is sensitive. Moreover, this method permits a more complete characterization of the dynamics than the usual measurements as a function of temperature at fixed magnetic field strength because many common solvent liquids have phase transitions that may alter significantly the character of the dynamics over the temperature range usually studied.

In the present study, we are interested in high surface area materials such as microporous chromatographic glass that contains contaminant surface

concentrations  $\sigma_S$  of paramagnetic centers S (iron) which may alter the nature of the relaxation significantly. In particular, these centers provide a large magnetic moment and local dipolar field in which the diffusing liquid proton spins I move. The effects of the electron magnetic moments are large and dominate unambiguously the proton spin-lattice relaxation,  $1/T_{1I}$ .

We present the magnetic field dependence of  $1/T_{1I}$  of polar but aprotic solvents in suspension of controlled pore chromatographic glass beads. We have proposed a theory [3] that treats the mobile liquid spins I diffusing in a surface restricted geometry and in the presence of the fixed magnetic dipolar fields of trace of paramagnetic impurities S on the glass surface. We obtained a theoretical expression for  $1/T_{1I}$ , valid at low frequency for the model considered :

$$\frac{1}{T_{1I}} = \frac{\pi}{15} \sigma_S (\gamma_I \gamma_S \hbar)^2 S(S+1) \frac{\tau_{\perp}}{d^2 \delta'^2} \left\{ 10 \ln \left[ \frac{d}{\delta'} + 1 \right] - 30.8 + \frac{1}{4} \left[ \begin{array}{l} 7 \ln(1 + \omega_S^{-2} \tau_{\perp}^{-2}) \\ + 3 \ln(1 + \omega_I^{-2} \tau_{\perp}^{-2}) \end{array} \right] \right\}, \quad (1)$$

Here  $\omega_S = 658.21 \omega_I$  and  $S=5/2$  for iron.  $\delta'$  is the distance of minimal approach between I and S, typically  $\delta'$  is comparable to the radius of the molecules  $\delta/2$ .  $\tau_{\perp}$  is the correlation time of I related to the translational diffusion coefficient  $\tau_{\perp} = \delta^2 / (4 D_{I\perp})$  parallel to the pore surface. We observe a bi-logarithmic magnetic field dependence of  $1/T_{1I}$ , over four orders of magnitude of the magnetic field, which is quantitatively consistent with Eq. (1). Our method thus provides a direct measurement of the translational diffusion  $D_{I\perp}$  of polar liquids in close proximity to the paramagnetic centers at the pore surface.

## EXPERIMENTAL AND DISCUSSION

Proton nuclear magnetic relaxation rates were measured using an instrument described in refs [2, 3]. This instrument switches current in a copper solenoid that is immersed in liquid nitrogen. Spins are polarized in a field corresponding to a  $^1\text{H}$  Larmor frequency of 30 MHz, then the field is switched to a field of interest for a variable relaxation period after which the field is switched to a  $^1\text{H}$  Larmor frequency of 7.25 MHz where the magnetization is detected by a Hahn spin echo. This field switching technique permits measurement of spin-lattice relaxation rates from 0.01 to 30 MHz with nearly constant signal-to-noise ratios. Controlled pore chromatographic glasses have mean pore diameters of 75Å and 159Å and specific area of 140 m<sup>2</sup>/g and 90.9 m<sup>2</sup>/g, respectively.

The magnetic field dependence of the proton spin-lattice relaxation rates for suspensions of these chromatographic glass beads are reported for fields corresponding to  $^1\text{H}$  Larmor frequencies from 0.01 MHz to 30 MHz over a range of temperature from 5°C to 45°C for acetone and acetonitrile (Fig. 1). A common feature of these data is that the relaxation rate is linear in the logarithm of the Larmor frequency in two regions of the magnetic field strength. This magnetic field dependence is unusual and not predicted by commonly used theories for molecular motions in liquids. The effects that derive from purely proton nuclear-nuclear interactions in such quasi two dimensional system [4] are too small to account for the relaxation rates observed in these samples. The relaxation must derive from stronger interactions that may be provided by trace paramagnetic centers in the glass preparations. The iron content of these samples, checked by EPR and analytical chemistry measurements, is 45 ppm and 36 ppm for the 75Å and 159Å pore glasses, respectively. This is sufficient to provide a dominant relaxation path for the proton spins. From the specific area of the glass and assuming that all the iron is at the pore surface, the surface density,  $\sigma_S$ , of paramagnetic centers is  $3.46 \cdot 10^{11} \text{ Fe cm}^{-2}$  for the 75Å glass and  $4.27 \cdot 10^{11} \text{ Fe cm}^{-2}$  for the 159 Å glass. The average distance between the paramagnetic centers is then on the order of  $1/\sqrt{\sigma_S}$  which is  $\sim 170\text{Å}$  for the 75Å glass and  $\sim 153\text{Å}$ , in 159Å glass samples. These figures provide an estimate of the range for the persistence length of the two dimensional character sensed by the magnetic relaxation of the proton spins induced by the paramagnetic center.

The slopes for the linear portions shown in Figs. (1) depend on solvent and temperature; however, the ratio of these slopes is indeed 10/3, which is consistent with and supports the theoretical result summarized by Eq. (1). The solid lines through the data in Figs. 1 were computed with Eq. (1) as best fits to the data using only  $\delta'$  and  $D_{\perp}$ , as adjustable parameters. Although we may adjust  $\delta'$ , its value is constrained by reasonable estimates for the sums of van der Waals radii modified in the case an hydrogen bonding is present with OH or FeOH groups at the pore surface. The fit to the theory is excellent over the range of magnetic fields studied.

The values of the transverse diffusion coefficients  $D_{\perp}$  obtained by this procedure are about an order of magnitude smaller than values for the bulk solvent. We observe an increase of  $D_{\perp}$  with the pore size,  $d$ , which is coherent with the release the effects of confinement. We found an approximately linear dependence of  $D_{\perp}$  on the reciprocal of molecular diameter  $1/\delta$ . This is consistent with Stokes law for the liquid dynamics in the confined spaces of the pores. Last, we verify that the surface constrained translational diffusion is a thermally activated process characterized by an activation energy about 2 to 3 kcal/mol.

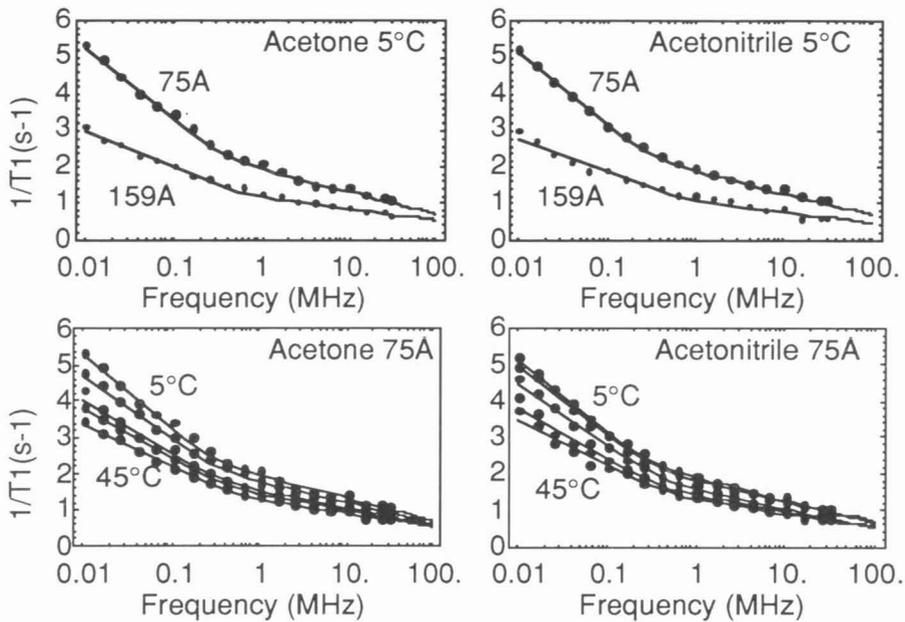


Fig. 1 Magnetic field dependencies of  $^1\text{H}$  spin-lattice relaxation rates of acetone and acetonitrile in a packed samples of calibrated porous glass beads of 75 and 159Å at 5°C (top), 5-45°C, 75Å (bottom). The continuous lines are the best fits to Eq. (1), as discussed in the text.

## CONCLUSION

Proton spin-lattice relaxation of different aprotic polar liquids in suspension of controlled nanopore chromatographic glass beads that have paramagnetic ion impurities have been reported between 0.01 and 30 MHz using a field-switched magnetic relaxation dispersion spectrometer. The unique properties of the magnetic field dependencies of these relaxation rates have allowed a direct measurement of the translational diffusion coefficients of these solvents at the surface of the pores.

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