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● *Contributed Paper*

TRANSLATIONAL DIFFUSION OF LIQUIDS AT SURFACE OF MICROPOROUS MATERIALS: NEW THEORETICAL ANALYSIS OF FIELD CYCLING MAGNETIC RELAXATION MEASUREMENTS

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[1]H spin-lattice relaxation rates of several aprotic polar liquids on calibrated microporous chromatographic glass beads that have paramagnetic ion impurities are recorded over magnetic field strengths using a field-switched magnetic relaxation dispersion spectrometer. The typical bilogarithmic magnetic field dependence of these rates supports quantitatively our theory of nuclear paramagnetic relaxation and gives the translational diffusion at the surface of nanopores. Our results demonstrate that magnetic relaxation dispersion at low magnetic field strengths in high surface area heterogeneous systems may be quantitatively understood in terms of the parameters of the spatial confinement and the local translational dynamics. © 1998 Elsevier Science Inc.

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INTRODUCTION

Nuclear magnetic relaxation methods offer a variety of opportunities for characterizing the molecular dynamics in confined environments.[1–2] Systems of interest are high surface area materials, including biological tissues, chromatographic supports, heterogeneous catalytic materials, and natural microporous materials, such as clay minerals and rocks.

The magnetic field dependence of the nuclear spin relaxation rate is a rich source of dynamical information.[3–5] 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 significantly alter the character of the dynamics over the temperature range usually studied.

We are interested in high surface area materials such as microporous chromatographic glass that contains contaminant surface concentrations σ_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, $1/T_{1I}$, at low magnetic field strengths.

In this paper we present a theoretical analysis of field cycling magnetic relaxation measurements appropriate to the case of a mobile liquid dipolar spin diffusing in a quasi two-dimensional porous system in the presence of rare paramagnetic impurities fixed at the surface of the pores.[5] This theory presents the magnetic field dependence of $1/T_{1I}$ of polar but aprotic solvents in suspension of controlled pore chromatographic glass beads.

The theory is tested at several temperatures using acetone, acetonitrile, dimethylformamide, and dimethylsulfoxide on microporous chromatographic glass beads that have paramagnetic ion impurities at the level of 40 ppm. [1]H spin-lattice relaxation rates are recorded over magnetic field strengths corresponding to [1]H Larmor frequencies between 0.01 and 30 MHz using a field-switched magnetic relaxation dispersion spectrometer. We observe a bilogarithmic magnetic field dependence

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of $1/T_{II}$, over four orders of magnitude of the magnetic field, which is quantitatively consistent with our theory. The diffusion constant for the proton-bearing molecule perpendicular to the normal of the pore surface is nearly a factor of 10 smaller than that in the bulk solvents. It is characterized by a small activation energy similar to those in the bulk solvent. 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.

THEORY OF HETERONUCLEAR DIPOLAR RELAXATION BY TRANSLATIONAL DIFFUSION OF FLUIDS IN A MODEL POROUS SYSTEM

We consider an ensemble of a large number of nuclear spins $I = \frac{1}{2}$ (protons) in a given fluid of uniform density that diffuse within an infinite layer of finite thickness, d, between two flat solid surfaces in the presence of a constant magnetic field, $\mathbf{B}_0$, oriented at the angle β from the normal axis, $\mathbf{n}$. We consider also the presence of a very small quantity of fixed paramagnetic species of spins, S, uniformly distributed on these surfaces with a surface density, σ_S. We restrict our calculation to the case of highly diluted paramagnetic species where the average distance between two S spins on the surface, $1/\sqrt{\sigma_S}$, is about or even larger than the pore size, d. This layered geometry simulates the simplest type of pore, the slit or channel pore, which is sufficient to account for the quasi two-dimensional characteristics implied by the observed logarithmic magnetic field dependence of the proton spin-lattice relaxation rates in the calibrated porous glass beads (see below).

Because the magnetic moment of the paramagnetic species is large ($\gamma_S = 658.21 \gamma_I$), there is no ambiguity about the relaxation mechanism of the diffusing proton spins, I, which is the intermolecular dipolar relaxation process induced by fixed spins, S, and modulated by the translational diffusion of the mobile spins, I, in close proximity to these surfaces. Basically, the nuclear spin-lattice relaxation rate of the diffusing spins, I, is given formally by the general expression $1/T_{II}$[6]:

$$\frac{1}{T_{II}} = \frac{2}{3}(\gamma_I \gamma_S \hbar)^2 S(S+1)\left[\frac{1}{3}J_L^{(0)}(\omega_I - \omega_S) + J_L^{(1)}(\omega_I) + 2J_L^{(2)}(\omega_I + \omega_S)\right], \quad (1)$$

where the spectral density, $J_L^{(m)}$, in the laboratory frame (L) of basis ($\mathbf{i_L}$, $\mathbf{j_L}$, $\mathbf{k_L} // \mathbf{B}_0$) is the exponential Fourier transform:

$$J_L^{(m)}(\omega) = \int_{-\infty}^{\infty} G_L^{(m)}(\tau)e^{i\omega\tau}\, d\tau, \quad (2a)$$

of the stationary pairwise dipolar correlation functions $G_L^{(m)}(\tau\{m \in (-2, +2)\})$ given by:

$$G_L^{(m)}(\tau) = \langle F_L^{(-m)}(t) F_L^{(-m)*}(t+\tau)\rangle. \quad (2b)$$

Eq. (2b) describes the persistence of the second-order irreducible spherical spatial dipolar tensor, $F_L^{(m)}(t)$, between the magnetic moments associated with the spins I and S and modulated by the translational diffusion of spins I relative to the fixed spins S during a short time interval, τ. The notation $\langle\,\rangle$ stands for the ensemble average over all the positions of the spins I at times 0 and τ for a given density, σ_S/d, of spins S. All the detailed calculations of Eq. (2) have been reported previously.[6] Here we only discuss the resulting theoretical expression obtained for $1/T_{II}$, valid at low frequency for the model considered:

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

Here $\omega_S = 658.21\,\omega_I$ and $S = \frac{5}{2}$ for iron, d is the mean pore diameter, and δ' is the distance of minimal approach between I and S, typically δ' is comparable to the radius of the molecules $\delta/2$. $\tau_\perp = \delta^2/(4D_{I\perp})$ is the correlation time of I related to the translational diffusion coefficient $D_{I\perp}$ parallel to the pore surface. One sees from Eq. (3) that our theory predicts that the ^{1}H spin-lattice relaxation rate will be linear in two parts when plotted as a function of the logarithm of the magnetic field strength and the slopes of these distinct linear regions is in the ratio of 10/3 (Fig. 1a). Changing the translational diffusion coefficient $D_{I\perp}$ will affect also the aspect of the $1/T_{II}$ dispersion curves (Fig. 1a). The theory also predicts a typical pore size dependence ($\propto 1/d^2$) of $1/T_{II}$ (Fig. 1b).

EXPERIMENTAL AND DISCUSSION

Proton nuclear magnetic relaxation rates were measured using an instrument of the Redfield design[7] constructed partly in collaboration with Brown and Koenig.[8,9] This instrument switches current in a copper solenoid that is immersed in liquid nitrogen. Spins are polarized in a field corresponding to an ^{1}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 an ^{1}H Larmor frequency of 7.25 MHz
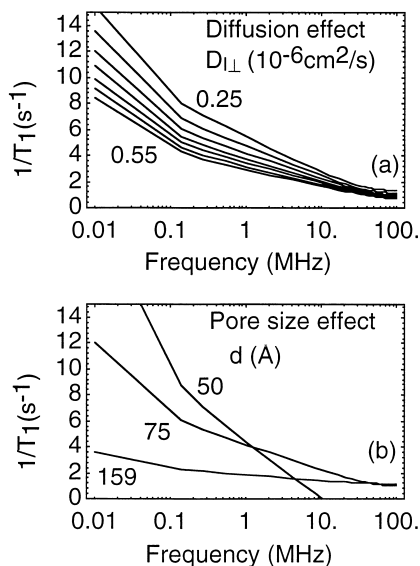
Fig. 1. Calculated variations of the magnetic field dependences of proton spin-lattice relaxation rates given by Eq. (3): (a) for pore size d = 75 Å, molecular size δ = 7 Å, δ' = 4.1 Å, and different values of the diffusion coefficient $D_{I\perp}$: (from top to bottom) 0.25×10^{-6} cm²/s (0.30, 0.35, 0.40, 0.45, 0.50) and 0.55×10^{-6} cm²/s; and (b) for $D_{I\perp}$ = 0.35×10^{-6} cm²/s, δ = 7 Å, δ' = 4.1 Å, and varying the pore size d (Å) as shown.
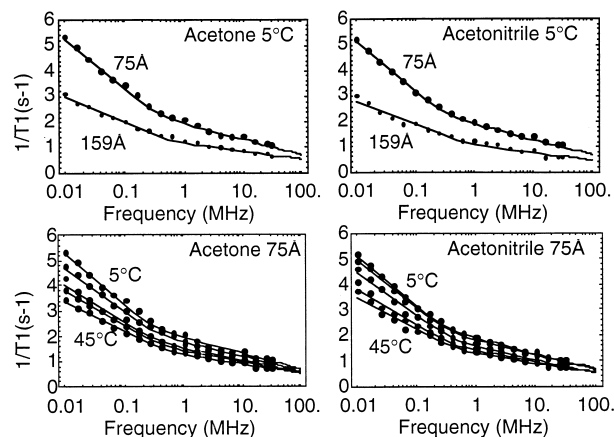

Fig. 2. Magnetic field dependencies of ¹H spin-lattice relaxation rates of acetone and acetonitrile embedded in a packed samples of calibrated porous glass beads of pore sizes 75 and 159 Å, respectively, at 5°C (top) and varying the temperature (5, 15, 25, 35, and 45°C) at 75 Å (bottom). The continuous lines are the best fits to Eq. (3), as discussed in the text.

where the magnetization is detected by a Hahn spin echo. This field-switching technique permits measurement of spin-lattice relaxation rates from 0.01–30 MHz with nearly constant signal-to-noise ratios. Controlled pore chromatographic glasses have mean pore diameters of 75 and 159 Å and specific areas of 140 and 90.9 m²/g, respectively.

The magnetic field dependence of the proton spin-lattice relaxation rates for suspensions of 75 and 159 Å chromatographic glass beads are reported for fields corresponding to ¹H Larmor frequencies from 0.01–30 MHz over a range of temperature from 5–45°C for acetone and acetonitrile (Fig. 2). 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 is not predicted by commonly used theories for molecular motions in liquids. The effects that derive from purely proton nuclear-nuclear interactions in such a quasi two-dimensional system[1a] 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 contents of these samples, checked by electron spin resonance (ESR) and analytical chemistry measurements, are 45 and 36 ppm for the 75 and 159 Å pore glasses, respectively. This is sufficient to

provide a dominant relaxation path for the proton spins at low magnetic field strengths. From the specific area of the glass and if we assume that all the iron is at the pore surface, the surface density, σ_S, of paramagnetic centers is 3.46×10^{11} Fe cm⁻² for the 75 Å glass and 4.27×10^{11} 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 ~170 Å for the 75 Å glass and ~153 Å in 159 Å 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 Fig. 2, a and b, 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. (3). The solid lines through the data in Fig. 2 were computed with Eq. (3) as best fit to the data using only δ' and $D_{I\perp}$ as adjustable parameters. Although we may adjust δ', its value is constrained by reasonable estimates for the sums of van der Waals radii modified in the case where 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 $D_{I\perp}$ obtained by this procedure are about an order of magnitude smaller than the values for the bulk solvent. We observe an increase in $D_{I\perp}$ with the pore size, d, which is coherent with the diminution of the effects of confinement. We found an approximately linear dependence of $D_{I\perp}$ 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 2–3 kcal/mol.

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 verify the prediction of our theoretical model and allowed direct measurement of the translational diffusion coefficients of these solvents at the surface of the pores.

REFERENCES

1. Korb, J.-P.; Xu, S.; Jonas, J. Confined geometry effects on dipolar relaxation by translational dynamics in porous media. J. Chem. Phys. 98:2411; 1993.

1a. Korb, J.-P.; Delville, A.; Xu, Shu; Demeulenaere, G.; Costa, P.; Jonas, J. Relative role of surface interactions and topological effects in NMR of confined liquids. J. Chem. Phys. 101:7074; 1994.

2. Korb, J.-P.; Malier, L.; Cros, F.; Xu, Shu; Jonas, J. Surface dynamic of liquids in nanopores. Phys. Rev. Lett. 77:2312; 1996.

3. Stapf, S.; Kimmich, R. Molecular dynamics in confined monomolecular layers. A field-cycling nuclear magnetic resonance relaxometry study of liquids in porous glass. J. Chem. Phys. 103:2247; 1995.

4. Whaley-Hodges, M.; Lawrence, A.J.; Korb, J.-P.; Bryant, R.G. Magnetic cross-relaxation and chemical exchange between microporous solid and mobile liquid phases. Sol. State NMR 7:247; 1996.

5. Korb, J.-P.; Whaley-Hodges, M.; Bryant, R.G. Translational diffusion of liquids at surface of microporous materials: theoretical analysis of field-cycling magnetic relaxation measurements. Phys. Rev. E. 56:1934; 1997.

6. Abragam, A. The Principles of Nuclear Magnetism. Oxford: Clarendon Press; 1961.

7. Redfield, A.G.; Fite, W.; Bleich, H.E. Precision high speed current regulators for occasionally switched inductive loads. Rev. Sci. Instr. 39:710–715; 1968.

8. Hernandez, G.; Tweedle, M.F.; Brittain, H.; Bryant, R.G. Nuclear magnetic relaxation dispersion in protein solutions 1. Apotransferrin. Inorg. Chem. 29:985–988; 1990.

9. Koenig, S.H.; Schillinger, W.E. Nuclear magnetic relaxation in aqueous solutions of Gd(HEDTA) ion. J. Biol. Chem. 244:3283–3289; 1969.