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NMR evidence of $H_2^{17}O$ adsorbtion on silica pore surface

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Abstract

The paper try to explain the unusual behaviour of NMR relaxation between ^{16}O and ^{17}O water in pore volume of silica powder. The main benefits of NMR porosity with ^{17}O solution is: i) the determination of porous structure of silica powder become more easly using the ^{17}O water solution. ii) this behaviour can be explained by absorbtion of $H_2^{17}O$ on pore walls in silica powder.

1 Introduction

The new isotope separation techniques permit today to exploit the strange combination of isotope in physico-chemical experiments. Despite the lower abundance in nature, the ^{17}O is magnetic isotope of oxygen with large nuclear quadrupole moments and we exploit this magnetic properties in NMR experiments. The exploit of this specific properties allow us to obtain valuable information about pore structure and dinamics of spins in pore. The stage of adsorption at inner surfaces of solid porous materials (or at surfaces of other static or slowly moving objects such as fine particle agglomerates or globular macromolecules) become important for explain the referential molecular orientation relative to the local surface of molecules. The main consequence of adsorbtion of molecule is a little decaying component of the autocorrelation function of spin interactions. Once of molecule escape from adsorbate layer and departure from the immediate vicinity of the surface position the total correlation is loss. This results in give a strongly decaying components of correlation function, eight orders of magnitude more slowly than in the bulk liquid [1].

The consequence is the very important changes in spin-spin relaxation cummulate with insignificant changes in relaxation function arises from diffusion. This two components of relaxation function dominate the phases of water: diffusion dominate the bulk phase and relaxometry dominate the adsorbed molecules. The exchange between two phases complicate the explanation for shape of relaxation function. The simplest model is two-phase fast-exchange ($TPFE$). Presence of ^{17}O isotope in solution (with large quadrupolar interaction and large quadrupolar coupling constant, measured in [2]) modify the relaxation function and relative importance of each reservoir can change. The main reason to use ^{17}O isotope in this research is to see if the fluctuations of the spin interactions causing spin relaxation are linked with ^{17}O isotope state (adsorbed or not). The molecular fluctuations can be relate with the existence of a solid adsorbent in the form of pore walls or particle surfaces. Since the surfaces impose preferential orientations on adsorbed molecules, the time scale of molecular reorientations is determined by the total interaction period with the surface before the molecule escapes to the bulk-like phase. Thus, the interpulse

delay (the time between 180° pulse or reorientation pulse in pulse sequence) become an parameter usefull for time scale interaction with surface.

In the early paper we find the relative constance of spin spin relaxation rate in pore for sample wetted with 1% $H_2^{17}O$ solution. This behaviour is in contradiction with decreasing of spin spin relaxation rate ($R_2 = 1/T_2$) in function of interpulse delay t_0 of sample wetted only with $H_2^{16}O$. The decreasing of R_2 in pore volume of $H_2^{16}O$ sample is due to interaction of pore surface. The presence of ^{17}O nuclei in pore space avoid this dependence from interpulse delay t_0.This behaviour will be investigated in this works.

2 Experimental

Sample preparation

Our studies were carried out on wetted silica powder. First we carefully wetted the silica powder in Milli Q water and Milli Q water with 1% $H_2^{17}O$ and stabilised 24h in 25^0C thermostated chamber. All NMR measurements were performed after thermostated the samples at 25^0C for 2h in sample tube.

NMR measurements

The time domain NMR measurements were performed on a 40 MHz low-resolution pulse ^{1}H-NMR Spin Track spectrometer equipped with an audio filter bandwidth of 1 MHz and quadrature phase sensitive detector. NMR measurements were performed at constant temperature 25 ± 0.2^0C using the variable temperature unit. The standard TD-NMR (time domain) pulse sequences Carr-Purcell-Meiboom-Gill CPMG sequence [3],[4], were used to estimate the spin-spin relaxation time (T_2) values for protons in the sample. The repetition delay (RD) was set to 60 sec and the enhancement was 16 (256 scans). The total time for acquired of signal, corresponding to the various numbers of experimental points, is experimentally establish by total relaxation of protons in sample. The duration of these CPMG curves allows a correct characterization of the slow relaxing components (water protons and exchangeable –OH protons). We use various interpulse delay t_0(time interval between 90° pulse and 180° pulse in CPMG sequence; $100\mu s - 4000\mu s$) The points in the signal figured a decreasing exponential, curve that can be modeled using the equation 3 from [5] without external gradient g. Consequent on our previous work [6], regarding the stable reconstruction of T_2 distribution applied to NMR relaxation curve, we predict for all samples presented above, a multi-exponential distribution. The $T_{2,i}$, P_i values were calculated using this nonlinear regression program based on the Inverse Laplace transform algorithm, discussed earlier.

General Relaxation Theory in the Pore Space

In the pore volume water move randomly, influenced by the pore wall structure, pore dimension, ionic charge in pore volume and temperature. All these parameters influence the transverse relaxation time [7]. If in pore can insert magnetic trap, like paramagnetic ions and other magnetic species adsorbite on the pore surface, the spin-spin relaxation time was influenced.

General theory can be summarize as: consider a spherical pore with a volume V and a surface S, completely filled with water where water molecules move randomly due to Brownian motion, characterized by the self-diffusion coefficient D_0. The transverse relaxation time for bulk water is $T_{2,bulk}$, which is on the order of few seconds give small contribution in eq.(1). This transverse relaxation time is largely decreased for molecules near the pore wall [8] to a value on the order of microseconds. Brownstein and Tarr [7]

calculated the resulting relaxation time T_2,meas for such a model system:

$$\frac{1}{T_2} = \frac{1}{T_{2,bulk}} + \frac{S}{V}\rho_{2,surf} \tag{1}$$

where $\rho_{2,surf}$ is the surface relaxivity. The nuclear magnetization $M(t)$ of a single pore, which reflects the contribution of that pore to the signal $S(t)$, is therefore described by:

$$M(t) = M_0 \exp\left(-\frac{t}{T_{2,bulk}} - \frac{t \cdot S}{V}\rho_{2,surf}\right) \tag{2}$$

If in the pore have a magnetic distribution, represented by the average gradient γ, the partial loss in the coherence of spins give a decreasing in the spin-spin relaxation function:

$$M(t) = M_0 \exp\left(-\frac{t}{T_{2,bulk}} - \frac{t \cdot D_0}{12}(\gamma g)^2 t_0^2\right) \tag{3}$$

where t_0 is the interpulse delay. The equations 1 is the simplest dependence of water magnetization in the pore from pore dimension (or structural length $l_S = V/S$). The equation 2 give the dependence of water magnetization on the magnetic gradient and self-diffusion coefficient. In this case other characteristic length can influence the general magnetisation: diffusion length $l_D = \sqrt{6D_0 t}$ and dephasing length $l_g = \sqrt[3]{\frac{D_0}{\gamma g}}$.

3 Discussions and Conclusions

In the early paper [9] we use a surface relaxivity $\rho_{2,surf} = (0.8 \pm 0.01) \times 10^{-5} m/s$ obtained from calibration method and we determine the mean pore sizes $a_c = 0.14\mu m$, $a_b = 1.1\mu m$ and $a_a = 4.60\mu m$ assuming the $V/S = a/3$ for spherical pore.

When we add ^{17}O, magnetic isotope of oxygen in water we obtain dependence of relaxation rate to the interpulse delay t_0 in the TPFE model:

$$R_2(t_0) = P\frac{35}{12}(2\pi J)^2 k_{ex}(1 - \frac{1}{t_0 k_{ex}}\tanh(t_0 k_{ex})) \tag{4}$$

where k_{ex} is the exchange rate between two water phases, P is population fraction of ^{17}O reservoir and J is the quadrupolar coupling constant between ^{17}O and ^{1}H (~93Hz). The total influence of magnetisation on the interpulse delay can be difficult to describe in the single equation because we do not knows the distribution in the pore of the magnetic species ^{17}O.

The relaxation of $H_2^{16}O$ and $H_2^{16}O$ give a triexponetial behavior. The most interesting aspect of this measurements is relative constance in function of interpulse delay of spin spin relaxation rate for sample wetted with $H_2^{17}O$. For the $H_2^{16}O$ sample, the decrease of spin spin relaxation rate $(1/T_2)$ in function of interpulse delay is probably due to interaction of surface pore with $H_2^{16}O$ reservoir. The presence of quadrupolar interaction of ^{17}O nuclei avoid this dependence from t_0. This behaviour can be explain by the two parameters: one is the very large k_{ex} parameter in equation 4 raised from very large amount of free protons H^+ in pore space and from quadrupolar interaction of surface with surroundings spins, and second is the unusual gradient γ in the pore given by the specific distribution of the ^{17}O nuclei.

In the Fig 1 we shows the difference between $R_2(t_0)$ of $H_2^{17}O$ and $R_2(t_0)$ of $H_2^{16}O$ in function of diffusion length. These linear dependence shows that adding ^{17}O in water

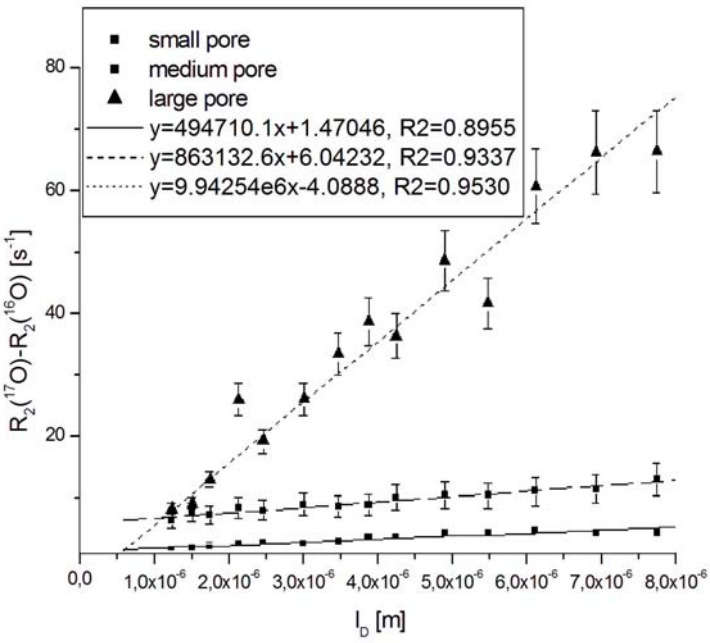

Figure 1: The difference in relaxation rate of pore filled with $H_2^{17}O$ and $H_2^{16}O$ as function of diffusion length.

perturbe the relaxation rate and dependence on the diffusion dissapear. These is linked by the supplementary relaxation induced by ^{17}O in the unusual manner. On the other hand, if ^{17}O remain free in water solution, the dependence on the interpulse delay is described by the equation 4, and presence of higher H^+ concentration in pore space (k_{ex} become very large) do not explain the nondependence of relaxation rate on the interpulse delay. The small dimension of pore is cover many times because diffusion length is much greater relative to pore dimension. Because of linear dependence, the hypothesis is raised: in this case is that relaxation difference depend on magnetic trap that produce an magnetic gradient at pore surface.

In Fig 2 we represent the slope of linear dependence extracted from Fig 1 in function of squared pore dimension. The very good linear dependence from Fig. 2 shows that surface of pore (proportional with squared pore dimension) influence directly the magnetic rate added at relaxation function.

The main conclusion is that $H_2^{17}O$ water molecule is adsorbed at pore surface and form the magnetic screen for protons. The adsorbtion of $H_2^{17}O$ at silica pore surface is related to the chiral state of silica microcristals [10] and chiral state of ^{17}O water.

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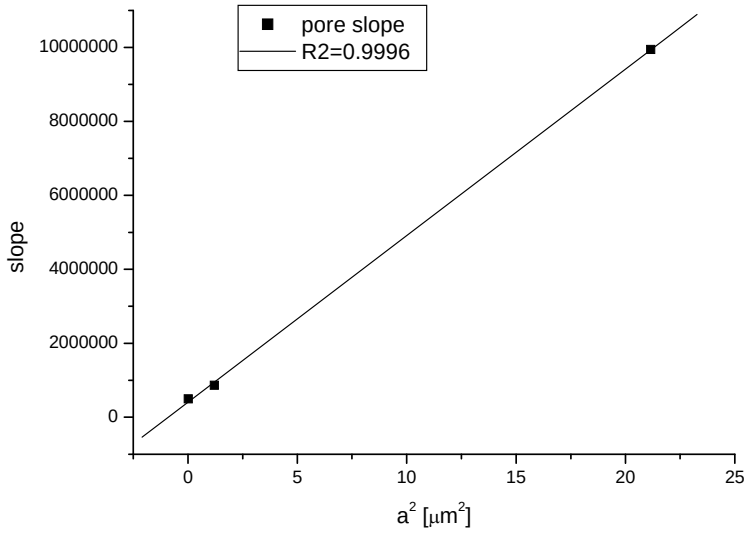

Figure 2: The linear dependence of pore slope from Fig. 1 as function of squared pore dimension.

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