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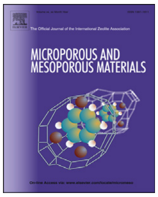

Characterization of pore geometry using correlations between magnetic field and internal gradient

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ABSTRACT

We have applied a novel multi-dimensional NMR experiment to characterize the pore geometry in liquid saturated porous systems with variation in material content and pore structure. Using the correlation between the internal gradient and the difference in magnetic susceptibility we have established a novel approach for determining the pore size distributions. The obtained pore size distributions correspond well with distributions obtained from measurements based on Decay due to Diffusion in the Internal Field, but seems to overestimate the size of pores larger than approximately 100 μm.

1. Introduction

In a liquid saturated porous system the rate constant of the Free Induction Decay (FID), T_2^*, is related to the line broadening, $\Delta\nu$, which is caused by the difference in magnetic susceptibility in the sample [1,2]

$$\frac{1}{\pi T_2^*} = \Delta\nu = \frac{\gamma}{2\pi} B_0 \Delta\chi_{app} \tag{1}$$

It is assumed that T_2^* is totally dominated by susceptibility differences. The apparent difference in magnetic susceptibility is given by $\Delta\chi_{app} = C\Delta\chi$, where C is a dimensionless constant that takes into account effects from large local variations in the internal magnetic field [2,3]. As a first order approximation the spatial variation of the internal magnetic field in a single pore is linear, and it scales with $B_0\Delta\chi_{app}$ and the size of the pore, a [4,5]

$$\nabla B_i \equiv G_0 \approx \frac{B_0 \Delta\chi_{app}}{a} \tag{2}$$

where G_0 is the internal gradient, which is assumed to be constant within the pore. However, simulations have shown that the internal gradients are stronger close to the liquid-solid interface compared to the middle of the pore [2,5–7].

The characteristic spatial properties of the internal magnetic field can be used to determine important properties of the porous structure. Sun and Dunn [8] presented a modified Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence with varying echo spacing, which enables determination of a correlation between the transverse relaxation time constant (T_2) and G_0. Another method is the Decay due to Diffusion in the Internal Field (DDIF) [9,10], where a distribution of pore sizes, a, can be determined based on higher order relaxation terms based on the theory of Brownstein and Tarr [11]. Both of these methods, the modified CPMG and DDIF, are based on relating the spatial variation in the magnetic field to the size of the pore. Using a different approach Mitchell [12] measured correlations between the longitudinal relaxation time constant (T_1) and $\Delta\chi_{app}$ in sand stones, and showed that a strong correlation indicated high degree of heterogeneity in mineralogy.

Recently [13] we presented a novel multi-dimensional NMR experiment that enabled us to measure correlations between $T_1 - \Delta\chi_{app}$, $G_0 - \Delta\chi_{app}$, $G_0 - T_1$, and $G_0 - a$ in one experiment. We showed that these correlations can be used to examine the heterogeneity of the porous system at different length scales. In the current paper we investigate the correlations that involves $\Delta\chi_{app}$ in

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more detail and in particular we demonstrate that the $G_0 - \Delta\chi_{app}$ correlation can be used as a novel approach to determine pore size distributions.

2. Experimental

2.1. Method

The multi-dimensional pulse sequence presented in Ref. [13] consist of a DDIF experiment followed by a modified CPMG sequence where the echo spacing (t_E) is varied [8] by varying the number of π-pulses, and finally the detection of the FID signal: $\pi/2 - t_e - \pi/2 - t_d - \pi/2 - t_e - nt_E - t_{FID}$. The corresponding reference pulse sequence necessary to subtract the contribution from T_1 - relaxation is: $\pi/2 - t_e - \pi - t_e - \pi/2 - t_d - \pi/2 - nt_E - t_{FID}$. By performing a series of experiments with varying values of t_d and t_E, while keeping the time intervals t_e and nt_E constant and detecting the FID signal, various correlations can be determined [13].

Our experiments are performed at relatively large values of $\Delta\chi_{app}B_0$ and the dynamics of water molecules in a spin echo experiment is most likely somewhere in between the fast diffusion (FD) or localization (LOC) regime [4]. To evaluate this dynamics Mitchell et al. [14,15] have suggested to express the diffusion exponent in CPMG data in a general form

$$\frac{M(nt_E)}{M(t_E = 0)} = e^{-bnt_E^k} \tag{3}$$

where b is a general decay constant due to diffusion in internal gradients and k describes a general echo time dependence of the diffusion exponent. For instance, in the FD regime $k = 3$ and $b = \frac{1}{12}D\gamma^2G_0^2$. By measuring CPMG decays with varying echo spacings and using the data collapse plot of Hurlimann [4], is then possible to find the optimal value of k that gives the most correct description of the data [14].

In this paper we focus in more detail on one of the correlations obtained from the multi-dimensional pulse sequence. Using the reference experiment and keeping t_D short while varying values of t_E, the rate constant b can be correlated with T_2^*, giving the attenuation

$$M(t_E, t_{FID}) = \int\int P(b, T_2^*)e^{-bnt_E^k}e^{-\frac{t_{FID}}{T_2^*}}dbT_2^* \tag{4}$$

where P(b, T_2^*) is a 2D distribution function of b and T_2^*. It has been experimentally verified that a single exponential decay for the FID-signal is a good approximation for a single pore size [2].

Furthermore, assuming the FD regime the distribution involving internal gradients, $P(G_0, T_2^*)$, can be determined using $k = 3$ and $b = \frac{1}{12}D\gamma^2G_0^2$ according to Eq. (3). Finally, using Eq. (1) the T_2^*-axis can be rescaled to give the distributions $P(b, \Delta\chi_{app})$ or $P(G_0, \Delta\chi_{app})$.

Assuming that Eq. (2) is valid for the $P(\Delta\chi_{app}, G_0)$ distribution, one can determine the correlation between G_0 and $\Delta\chi_{app}$, and use this correlation to determine a pore size distribution. This is done using the following procedure on the obtained data: For each point in $p(G_0)$ the maximum value in $P(\Delta\chi_{app}, G_0)$ can be determined and the corresponding value of $\Delta\chi_{app}$ can be found. Thus, the G_0-axis can then be rescaled according to $a = \Delta\chi_{app}B_0/G_0$, giving an axis that describes range of pore sizes, a, and a corresponding distribution $p(a)$ can be obtained from $p(G_0)$.

2.2. Experimental details

All NMR experiments were performed at 25° C on a Bruker Avance 500 spectrometer ($B_0 = 11.7$ T), using a commercial probe from Bruker Biospin (DIFF30). Three different types of water-saturated random packed compact glass beads (Duke Scientific) were analyzed: Bead diameter of 30 μm (Soda lime glass); Bead diameter of 100 μm (Soda lime glass); Bead diameters with distribution between 5 and 50 μm (Borosilicate glass). The samples were prepared by adding water to 5 mm NMR-tubes first and then adding the glass beads. A sample of water-saturated Berea sandstone was also analysed. The Berea plug had a diameter of 3.5 mm and a length of 20 mm, and was wrapped in parafilm to prevent water evaporating during the experiments. The motivation for the choice of these samples is to study two different mono-disperse bead sizes of the same material but that will produce two different pore geometries when closely packed. Furthermore, the packings of 5–50 μm glass beads produces a sample where the solid material is the same, i.e. a uniform distribution of paramagnetic substances, but where the pore geometry is more complex. Finally, the Berea sandstone plug is a sample where the material content, and in particular paramagnetic substances, can vary in a non-uniform way, and where the pore geometry is very complex.

To determine the optimal value of k regular CPMG experiments with echo spacing varying between 0.1 and 30 ms were performed in all of the samples. The data was then plotted as a function of t_E^k, and the right condition for the data collapse was determined visually by varying k manually [15].

The encoding period t_e was 50 μs and t_d was varied logarithmically from 50 μs to 8 s in 32 steps for all four samples. The echo spacing, t_E was varied logarithmically between 0.1 and 20.4 ms by keeping the total echo time (nt_E) constant at 20.4 ms, with a corresponding variation of the number of π pulses from 204 to 1, in 32 steps. Notably, G_0^2 is not measured directly, but through DG_0^2, which can be normalized using the diffusion coefficient for water ($D_{H_2O} = 2.3 \times 10^{-5}$ cm^2/s at 25° C). In all the experiments the FID signal was acquired with a dwell time (dw) of 6.65 μs and with a total of 512 data points (td), so that $t_{FID} = td \cdot dw$. The obtained data were analyzed as 2D Fredholm integral equations using software [16] based on the Schlumberger algorithm [17].

3. Results and discussion

The optimal value of k was determined to be 2.00, 2.05, 1.95 and 1.70 for the 30 μm, 100 μm, 5–50 μm glass beads, and Berea sandstone sample, respectively [13]. Thus, as expected the dynamics of the molecules during the modified CPMG part of the sequence is in between the FD and LOC regimes. In the further analysis we chose to evaluate the obtained data according to the general decay constant, b, and the corresponding optimal value of k, but also assuming the FD regime ($k = 3$) where G_0 can be determined. We are then able to compare the plots based on b and G_0, evaluate the effect of not being in the FD regime, and thus carefully use the G_0 data to make physical interpretations of the obtained data.

Both the $P(a, b)$ and $P(a, G_0)$ plots presented in Ref. [13] showed a clear tendency of a stronger and more negative correlation between a and b (and G_0) when going from the more homogeneous pore geometry of the packings of mono-disperse glass beads, via the packings of multi-disperse glass beads, to the more heterogeneous pore structure of the Berea sandstone. Therefore, $P(a, b)$ or

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