

ABSOLUTE PORE SIZE DISTRIBUTIONS FROM NMR

G.H. Sørland^{1,3}, K. Djurhuus¹, J.R. Lien^{1,2}, and A. Skauge¹

¹Centre for Integrated Petroleum Research, University of Bergen, Norway

²Department of Physics and Technology, University of Bergen, Norway

³Anvendt Teknologi, Harstad, Norway

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ABSTRACT

NMR measurements on rock core plugs saturated with brine returns valuable information on the porous structure of the rock core. As one is monitoring a single fluid component, it is possible to extract information on the pore size distribution and thus monitor the degree of sorting of the porous rock. The basic assumption is that the mobility of the component confined in the porous rock is high enough to probe the pore space and that the surface relaxivity is fairly independent on the size of the pore to which the surface is connected. Then one may combine diffusion measurements at short observation times, to obtain a value of the surface to volume ratio (S/V), with a CPMG experiment to obtain an absolute pore size distribution instead of the standard T_2 distributions.

INTRODUCTION

Ever since Mitra et al. (1993) introduced the short observation time expansion of the observed diffusion coefficient, resolving the surface to volume ratio (S/V) from the surface relaxivity ρ , efforts have been made to measure the true surface to volume ratio in rock core plugs. The major obstacle has been the lack of a NMR spectrometer properly dedicated to this purpose, leading to loss of contribution from the smallest pores due to long values of the motional encoding/decoding intervals in the pulsed field gradient sequences, and therefore not achieving measuring points at short enough observation times for the square root of time expansion to be valid.

Here we present results on brine saturated rock cores using the Maran DRX 12 MHz spectrometer with a design optimized for diffusion measurements. The spectrometer comprises a set of gradient coils capable of delivering up to 225 Gauss/cm in applied magnetic field gradient strength. These are mounted on the magnetic pole shoes and not on the probe, in order to separate the sample from the coils. Thus we minimize the effect from knocking of the gradient coils when running the diffusion experiment. In addition we have modified the 13 interval Pulsed Field Gradient Stimulated Echo sequence such that we achieve eddy current dead times down to 400 μs without active shielding or pre-emphasis adjustment. Hence we are able to perform reliable diffusion measurements on brine saturated samples with motional encoding/decoding interval of as short as 1 ms and with shortest observation times of approximately 1.5 ms. When using the optimized experimental set up we are able to measure surface to volume ratios down to a few μm ,

where the extrapolation of the measured diffusion coefficient back to zero observation time yields the bulk diffusion of the brine well within $\pm 5\%$.

THEORY

By the means of various NMR measurement techniques it is possible to reveal information on the porous structure of a brine saturated rock core sample. Assuming that the brine is probing the pores within the porous rock, there is a simple relation between the measured T_2 distribution and the pore sizes

$$T_2 \approx \frac{V}{S\rho} \quad (1)$$

where ρ is the surface relaxivity, Brownstein and Tarr (1979). As the surface to volume ratio is coupled to the surface relaxivity, we must conduct an extra experiment to resolve their contribution. According to Mitra et al (1993) the root of the mean squared displacement at short observation times can be approximated as

$$\frac{D(t)}{D_0} \approx 1 - \frac{4}{9\sqrt{\pi}} \sqrt{D_0 t} \frac{S}{V} \quad (2)$$

$D(t)$ is the time dependent diffusion coefficient, D_0 is the unrestricted diffusion coefficient, in bulk fluid, and t is the observation time. Equation 2 is the first term of a perturbation expansion of the time-dependent diffusion coefficient. The implied approximation is valid at short observation times, i.e. when only a small amount of the fluid is probing the restrictions (pore walls). Then the deviation from bulk diffusion is dependent on the surface to volume ratio alone and not on the surface relaxivity. In a porous system one must assume that there is a large span in pore radii, i.e. one must expand Equations 1-2 to be valid for a heterogeneous system. If ξ_i is the volume fraction of the pores with relaxation time T_2^i corresponding to surface to volume ratio $(S/V)_i$, we may write

$$\sum_i \xi_i \frac{1}{T_2^i} = \sum_i \xi_i \rho^i \left(\frac{S}{V} \right)_i \approx \rho \sum_i \xi_i \left(\frac{S}{V} \right)_i = \rho \overline{\left(\frac{S}{V} \right)} \quad (3)$$

and

$$\sum_i \xi_i \frac{D_i}{D_0} \approx \sum_i \xi_i \left[1 - \frac{4}{9\sqrt{\pi}} \sqrt{D_0 t} \left(\frac{S}{V} \right)_i \right] = \left(1 - \frac{4}{9\sqrt{\pi}} \sqrt{D_0 t} \overline{\left(\frac{S}{V} \right)} \right) \quad (4)$$

In Equation 3 we have assumed that the surface relaxivity is independent of the surface to volume ratio, and from Equation 4 we see that a fit of the diffusion coefficient as a function of short observation times t , yields a value for the average surface to volume ratio. This can be related to the average pore radius of the cavities.

One should note that in order to relate the surface to volume ratio from the diffusion experiment in Equation 3 to the surface to volume ratio from the relaxation time

experiment (Equation 1), the inter echo spacing of the two NMR experiments should be equal. The presence of position dependent strong internal magnetic field gradients will reduce the number of molecules probing the surface. As seen from the NMR experiment there will not be a constant distribution of nuclear spins within the cavities. To make use of Equations 1-2 the initial distribution of nuclear spins must therefore be equal. Otherwise they will probe apparently different pore structures. However, the presence of internal magnetic field gradients will not have an influence on the leading order term in the short observation time expansion. How long observation times Equation 2 will be valid at, will depend on such parameters as internal magnetic field gradient strength, surface relaxivity, and curvature of the surface. The short time expansion assumes piecewise smooth surfaces. When using the result from Equation 2 we are able to find the typical pore size, which according to Equation 1 should correlate to the typical T_2 value, i.e. the average $(1/T_2)$ value in the T_2 distribution. Knowing the average values for $(1/T_2)$ and surface to volume ratio, a value for the surface relaxivity ρ is thus found, and the T_2 distribution can be transformed into a normalized pore size distribution. The procedure is as follows:

- 1) (S/V) is found from fitting Equation 2 to a set of diffusion measurements at short observation times.
- 2) The value in 1) is the average (S/V) and can be correlated to the average $(1/T_2)$ found from a CPMG experiment. Equation 1 can then be written as

$$\overline{\frac{1}{T_2}} \approx \rho \left(\overline{\frac{S}{V}} \right)$$

hence we find the relaxivity ρ which is assumed to be pore size independent.

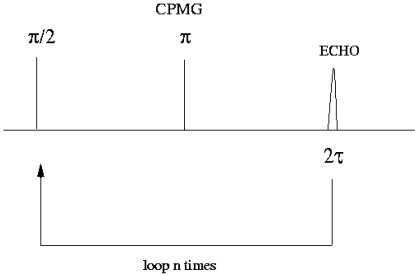
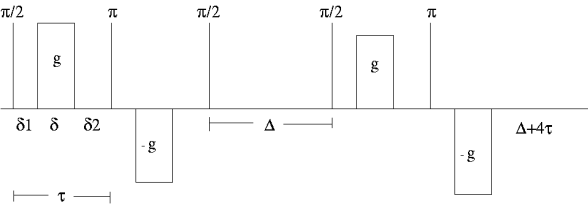
- 3) The value of ρ from 2) can then be used in Equation 1, thus resulting in a linear relation between T_2 and the volume to surface ratio, which is a measure of the pore size.
- 4) By multiplying the T_2 distribution by the relaxivity ρ found in 2), it becomes normalized to a pore size distribution in absolute length units.

EXPERIMENTAL

The method for determining pore size distributions were applied to two brine saturated sandstone core plugs using a 12 MHz Maran DRX from Oxford Instruments. The operating temperature was 35 °C and the bulk diffusion coefficient of the brine was $D_0=2.9 \times 10^{-9}$ m²/s. Due to finite rise time on the gradient amplifier the shortest duration of the applied gradient pulse was set to $\delta=0.6$ ms. The eddy current settling time was set to $\delta_1 + \delta_2 = 0.4$ ms, thus yielding an inter echo spacing of $\tau = 1$ ms. G_i is the internal magnetic field gradient while g is the applied magnetic field gradient. The pulse sequences used are summarised in Table 1. For comparison the pore size distribution was

also determined by the means of mercury intrusion measurements, Ritter and Drake (1945).

Table 1: A summary of the NMR pulse sequence applied on the brine saturated rock core plugs.

| NMR sequences | Corresponding attenuations / References |
|--|---|
|  | <p>The ordinary CPMG / Meiboom and Gill (1958)</p> $I = I_0 e^{-n \cdot \left[\frac{2\tau}{T_2} - \frac{2\tau^3}{3} \gamma^2 G_i^2 D \right]}$ <p><i>yields a T_2 distribution</i></p> |
|  | <p>The Pulsed Field Gradient Stimulated Echo / Cotts (1989)</p> $I = I_0 e^{-\frac{4\tau}{T_2} - \frac{\Delta}{T_1} - 4\gamma^2 g^2 D \delta^2 \left(\Delta + \frac{3}{2}\tau - \frac{\delta}{6} \right)}$ <p><i>yields the surface to volume ratio at short observation times</i></p> |

ABSOLUTE PORE SIZE DISTRIBUTIONS FROM NMR

As shown in the theoretical section we must conduct two NMR experiments to obtain a pore size distribution. Figure 1 shows the results from the short time diffusion experiment on two brine saturated sandstone core plugs where we vary the time between motional encoding and decoding, and thus varying the observation time t . According to Equation 2 this gives a linear attenuation, which yields the surface to volume ratio, S/V . From the two attenuations we see that the deviation from bulk diffusion is higher for plug A at equal observation times. As the first order deviation term is dependent on the bulk diffusion and the surface to volume ratio only, we may thus already conclude that plug A on average contains smaller pores than plug B. Even though their pore sizes differ significantly, the extrapolation back to zero observation time yields the bulk diffusion coefficient of water $D_0 = (2.9 \pm 0.1) \times 10^{-9} \text{ m}^2/\text{s}$. As shown in the work by Mitra et al (1993) a successful determination of the surface to volume ratio relies on the determination of the time dependent diffusion coefficient at observation times where the deviation from bulk diffusion is small. A test for whether we are within the limit of the short time approximation as given in Equation 2 is to extrapolate the diffusion coefficient $D(t)$ to zero observation time. If this deviates significantly from the true bulk diffusion coefficient of the brine, the short time expansion is not valid.

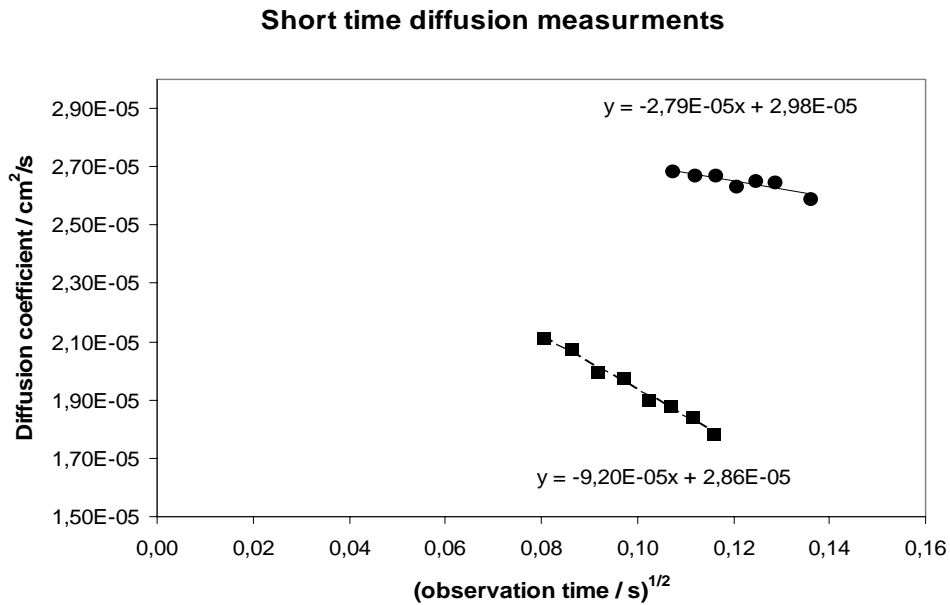


Figure 1: Diffusion measurements of two brine saturated sandstone core plugs at short observation times, Plug A (•) and plug B (▪).

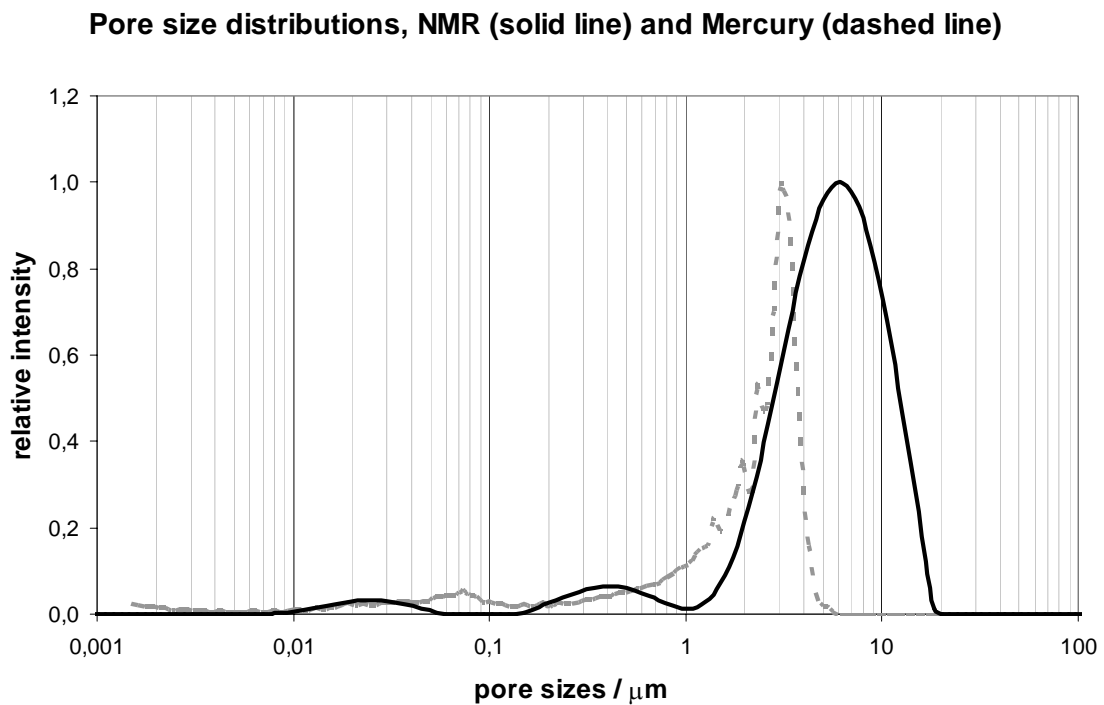


Figure 2: Pore size distributions of plug A from the NMR method (solid line) and from Mercury intrusion (dashed line).

To get a pore size distribution similar to the one obtained by mercury intrusion measurements we perform an ordinary T_2 relaxation time experiment followed by a one dimensional Inverse Laplace Transform (ILT) on the real time attenuation. From the ILT data we find the average of $(1/T_2)$ and may then calculate the surface relaxivity in accordance with Equation 5. Substitution of the surface relaxivity then transforms the ILT into a pore size distribution shown in Figure 2 for plug A, where V/S has been multiplied with 2 to get cylindrical pores and thus comparable to the mercury intrusion technique. When comparing the pore size distribution arising from the two methods we find the determined mean pore size to be larger from the NMR measurements than from mercury intrusion measurements. While the distribution curve from mercury intrusion is fairly constant, i.e. a narrow peak with a left shoulder, the pore size distribution from the NMR measurements varies more in shape from plug to plug. The average pore radius is $6.0 \mu\text{m}$ from the NMR measurements and $2.0 \mu\text{m}$ from the Mercury intrusion. The somewhat higher average radius and broader distribution from NMR can be explained as a result of fundamental differences in the measuring techniques: The mercury intrusion technique tends to underestimate the larger cavities within the rock and leaving a narrow distribution of pore sizes. In the NMR experiments we are monitoring molecules that are probing different cavities throughout the NMR measurement, resulting in a response depending on the size of the individual cavities. Thus we believe the NMR techniques to be more sensitive to variation in pore size distributions within the rock core as compared to the mercury intrusion technique.

CONCLUSION

We have shown that the NMR technique yields a method for absolute determination of pore size distributions on a limited number of rock core plugs.

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