MEASURING WETTABILITY FROM BRINE T₂ DISTRIBUTIONS IN THE PRESENCE OF AN INERT MINERAL OIL

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ABSTRACT

NMR T_2 distributions obtained from saturated porous media are closely related to interactions between the liquids saturating the media and the pore surfaces of the media themselves. This would intuitively make NMR an ideal way of studying surface phenomena such as wettability. Here are presented two methods that use a relatively high-viscous mineral oil as the oil phase. We assume that the nuclear spins of the hydrogen atoms in the oil phase will interact with the pore walls only to a minor degree due to the low diffusivity of the oil. This assumption infers that the NMR T_2 distribution of such oil will remain constant and is independent of the porous medium. For a system satisfying this assumption it is possible to subtract a scaled version of a predetermined bulk oil signal from the signal consisting of both oil and water thus giving the water signal alone. A slightly different approach is to use the large difference in molecular mobility between water and the mineral oil to obtain the true oil distribution from the sample by use of pulsed field gradients to suppress the signal arising from water in the system. The resulting signal now originating from the oil phase alone can then be subtracted from the signal consisting of both oil and water thus again giving the water signal alone

Once one has access to the brine T_2 distribution for different brine saturations it is possible to gain information on the wettability of the system depending on the shape of the distributions. For example, brine that is wetting the surface will have significantly shorter T_2 compared to brine that is disconnected from the surface due to an oil film wetting the surface. In systems where large regions are oil wet, we may even see a bulk brine component of longer T_2 than the longest T_2 in brine saturated systems.

INTRODUCTION

The petroleum industry is frequently met with challenges relating to reservoir wettability. Traditional methods of wettability determination, including the Amott test (Amott, 1959) and the United States Bureau of Mines (USBM) test of wettability (Donaldson *et al.*,

1969) are relatively time consuming and generally based on displacement tests. There is also a question if these tests carry the same information, and if they are fit to differentiate between different generic types of wettability. Dixit *et al.*, 1998 showed that a combination of the Amott index (I_{AH}) and the USBM index (I_{USBM}) can differentiate samples of intermediate wettability into three distinct subdivisions. These were labelled as mixed-wet large (MWL), mixed-wet small (MWS) and fractional-wet (FW) pointing to whether the oil-wet surfaces are localized in the larger pores, the smaller pores or if the oil-wet pores are randomly distributed with respect to pore size.

Most reservoirs fall into the category of intermediate wet state and such reservoirs tend to show a maximum in oil recovery (Morrow, 1990; Skauge and Ottesen, 2002). Two different tests are needed to pinpoint the exact type of wettability and with the time consumption of the traditional methods involved, there is a need in the petroleum industry for other methods to characterize wettability. NMR relaxation measurements are generally an excellent non-invasive method that has proven most valuable in studies of petrophysical properties such as porosity and permeability of porous media both *in situ* and in the laboratory. The close connection between NMR T_2 distributions obtained from saturated porous media and the interactions between the liquids saturating the media and the pore surfaces of the media themselves would intuitively make NMR an ideal way of studying surface phenomena such as wettability. Another feature which makes NMR an interesting tool for reservoir wettability depiction is the possible methodology transfer to the use of NMR in borehole wire line logging and logging while drilling (LWD) tools, in contrast to the Amott and USBM tests which are confined to the laboratory.

Several authors have presented work on the subject of NMR and wettability, and different approaches and indices have been proposed. Early works dates back to results presented on unconsolidated sand packs by Brown and Fatt (1956). Guan *et al.* (2002) showed a linear relationship between both the difference and the ratio of the arithmetic mean relaxation times at S_{wi} and S_{or} and the corresponding Amott index of sandstone reservoir and outcrop samples. Fleury and Deflandre (2003) proposed a wettability index based on the idea that the wettability information of a porous sample is given by the fluid distribution in the sample. Their index corresponded well with the USBM index in the range [-0.3–1] for a series of reservoir sandstone and carbonate samples. Recently, Al Mahrooqi *et al.* (2004) presented a pore-scale modelling study resulting in a wettability index based on the logarithmic mean value of the T_2 distributions at irreducible water and residual oil saturations. The index was tested on several synthetic, outcrop and reservoir samples yielding good matches with the corresponding Amott index.

Our aim is to investigate if NMR can give supplementing information about the wetting state of core material compared to existing means of wettability determination. The brine phase T_2 distribution at different saturations has a large potential for wettability description as the pore surfaces are known to greatly affect the relaxation rate for water hydrogen atoms. One of the main concerns when applying NMR to multicomponent systems such as a porous medium saturated with oil and water is the separation of the

signals from the respective phases. Usually one is limited to the study of the combined signal from the two liquid phases as their characteristic T_2 values overlap. This makes interpretation difficult and ambiguous.

This paper presents two ways of utilizing the inertness of a heavy mineral oil towards diffusion and surface effects to remain with the water signal alone. The first approach uses results from preliminary measurements giving identical distributions for bulk mineral oil and a quartz sand model system saturated with the mineral oil. Measurements on real core samples saturated with brine and the mineral oil can then be undertaken, and the brine T_2 distribution can be extracted by subtracting the total NMR signal from the sample with the signal from the mineral oil alone scaled according to the oil saturation of the sample of interest

Another approach is to use the inert property of the mineral oil to subtract the true signal originating from the oil in the sample from the total signal. This is done by complementing the ordinary CPMG measurements with diffusion measurements and a combined CPMG-diffusion measurement.

PROCEDURES

Subtraction of Bulk Oil Signal

The first procedure is based on the assumption that the high-viscous nature of the mineral oil used makes the hydrogen spins of the oil phase interact with the pore walls only to a minor degree, and thus will not be influenced by surface properties such as magnetic susceptibility differences, internal gradients and wettability. The signal intensity of spinecho number i, $0 < i \le n$ where n is the number of echoes in a regular CPMG experiment (Carr and Purcell, 1954; Meiboom and Gill, 1958) of a sample containing both oil and water can be written as Equation 1 when assuming continuous exponential decay for both phases:

$$I(i\tau) = \int \rho(T_{2,o}) \exp\left(\frac{-2i\tau}{T_{2,o}}\right) dT_{2,o} + \int \rho(T_{2,w}) \exp\left(\frac{-2i\tau}{T_{2,w}}\right) dT_{2,w} + \varepsilon$$
(1)

Here $\rho(T_2)$ denotes the continuous distribution of T_2 values within the respective parts of the signal, 2τ is the inter-echo time and ε is the experimental noise. If the characteristic T_2 values of the different phases are of the same order of magnitude, it is practically impossible to separate the respective parts of the signal. By assuming that the oil phase is neglectable influenced by the porous medium and the other phases present, the first integral of Equation 1 can be determined separately on a bulk oil sample. The intensity of the oil part of the total CPMG signal is related to the oil saturation, and the bulk oil signal for subtraction must therefore be scaled accordingly. This is achieved by using a pulsed field gradient method to measure the oil saturation, which in short terms compares the NMR signal intensity with and without the use of pulsed field gradients assuming that the water signal will be sufficiently suppressed when gradients are applied. (Sorland *et al.*, 2004b; US Patent 6,946,837 B2, 2005) The resulting signal after the subtraction of the scaled bulk oil signal will then according to Equation 1 be given by Equation 2

$$I(i\tau) = \int \rho(T_{2,w}) \exp\left(\frac{-2i\tau}{T_{2,w}}\right) dT_{2,w} + \varepsilon_1$$
(2)

where ε_1 indicates that the noise might have changed in the process, $\varepsilon_1 \ge \varepsilon$. To avoid accumulation of noise the bulk oil signal is smoothed prior to scaling and subtraction to assure that the *S*/*N* of the *T*₂ attenuation of water is kept at the lowest possible level.

Subtraction of True Oil Signal

A slightly different approach is to take advantage of the inert property of the mineral oil to subtract the true signal originating from the oil phase. First an ordinary CPMG experiment is run for which the attenuation is written in Equation 1. To find the true oil signal a combination of the pulsed field gradient (PFG) method (Stejskal and Tanner, 1965) with the CPMG experiment is used. The pulse sequence for such an experiment is shown in Figure 1, and the corresponding attenuation is given by Equation 3

$$I(i\tau) = \int \rho(T_{2,o}) \exp\left(\frac{-2i\tau}{T_{2,o}} + \gamma^2 \left(\frac{4g}{\pi}\right)^2 \delta^2 D_o(2\tau') \left(\frac{3}{2}\tau' - \frac{\delta}{8}\right) dT_{2,o} + \int \rho(T_{2,w}) \exp\left(\frac{-2i\tau}{T_{2,w}} + \gamma^2 \left(\frac{4g}{\pi}\right)^2 \delta^2 D_w(2\tau') \left(\frac{3}{2}\tau' - \frac{\delta}{8}\right) dT_{2,w} + \varepsilon$$
(3)

when using sinusoidal shaped gradients. Here γ is the gyromagnetic ratio, δ the gradient length, g the gradient strength, $2\tau'$ the time between echoes in the PFG part and D the diffusion coefficient of the respective phases. Running the experiment at sufficiently high gradient strength, the signal originating from the water phase will be suppressed such that only the signal from the oil phase remains. This is due to the large difference in molecular mobility between the water and the viscous mineral oil used as the oil phase. The signal can now be described by the components from the oil phase alone:

$$I(i\tau) = \int \rho\left(T_{2,o}\right) \exp\left(\frac{-2i\tau}{T_{2,o}} + \gamma^2 \left(\frac{4g}{\pi}\right)^2 \delta^2 D_o\left(2\tau'\right) \left(\frac{3}{2}\tau' - \frac{\delta}{8}\right)\right) dT_{2,o} + \varepsilon$$
(4)

It is then possible to run a series of PFG spin echo experiments with increasing gradient strength to determine the T_2 attenuation of the oil phase at zero gradient strength. This is done by interpolation of the points corresponding to gradient strengths where signal from the water phase is sufficiently suppressed to zero gradient strength.

The pulse sequence for this is shown in Figure 2. After interpolation the resulting attenuation can be described by Equation 5

$$I(i\tau) = \int \rho(T_{2,o}) \exp\left(\frac{-2i\tau}{T_{2,o}}\right) dT_{2,o} + \varepsilon$$
(5)

This procedure has previously been applied by Sorland et al. (2004a). It is here important to note that the start of the CPMG echo train is first after the PFG part of the sequence, at ~14 ms, meaning that information from T_2 components shorter than this is lost. As one is especially interested in the shorter components when studying surface phenomena such as wettability, because of the enhanced surface relaxation they reflect, it is critical to keep this information. To obtain the complete T_2 attenuation of oil alone an inverse Laplace transform is used on the interpolated data for zero gradient strength to provide a basis for calculation of points on the T_2 attenuation curve between t = 0 and the start of the echo train in the combined PFG-CPMG experiment. Here it is assumed that the oil phase does not have significant T_2 components shorter than 14 ms so that no signal from the oil phase is lost in the PFG part of the sequence. To assure that the intensity of oil at the first echo in the calculated part of the CPMG decay curve matches the intensity of oil in the real CPMG, the procedure described for bulk oil subtraction is used to calculate the oil phase contribution to the initial intensity. Following this procedure one remains with a complete T_2 attenuation curve for oil alone, which then can be subtracted from the total CPMG decay curve as described for bulk oil to ensure no compromising of the S/N ratio of the resulting T_2 attenuation for water alone. The result is a complete T_2 attenuation curve for water alone where all the information about shorter components is kept.

Experiments

Two sandstone samples, denoted as No. 3845 and No. 6227, were selected to the study. The samples were selected on the basis of earlier wettability studies, which according to the classification of Dixit *et al.* (1998) had characterized them as mixed-wet small and fractional-wet respectively. The study moreover proved the wettability of the samples to be quite robust, which also was a desirable property when selecting samples for this work. Synthetic brine was used as the water phase, and Marcol 82, delivered from Exxon Mobile was used as the oil phase. Bulk properties of the liquids used are given in Table 1.

Samples were initially saturated with brine, drained to S_{wi} and waterflooded to reach S_{or} . NMR experiments were performed at each step. Prior to experiments samples were submerged in the dominating saturating fluid and preheated to the operating temperature to minimize fluid loss due to evaporation. Immediately before the experiments, the samples were taken out of the heat chamber and excess fluid removed before wrapping in plastic foil. All NMR experiments were performed on a 12 MHz Maran DRX rock-core analyzer from Resonance Instruments, with a gradient probe giving access to gradient strengths of up to 225 G/cm. The instrument was operating at 35 °C and ambient pressure. The resulting CPMG data were processed using Resonance Instruments Inverse Laplace software, the WinDXP which inverts the multiexponential attenuation data to a distribution of T_2 values.

RESULTS AND DISCUSSION

Subtraction of Bulk Oil Signal

Prior to the subtraction of the predetermined bulk oil signal, the stability of the signal was tested on a model system consisting of quartz sand saturated with the oil. The sand contains some magnetic impurities, and is known to have considerable internal gradients which should imply that the oil will be affected if there exists significant coupling to the surface. Figure 3 shows the T_2 distributions of the pure mineral oil and the saturated model system, and from the distributions it is clear that the oil signal is not significantly affected by the presence of a surrounding porous system, even if it is known to have considerable internal gradients.

For comparison, the pore size distributions in the form of T_2 distributions at 100% water saturation are first given in Figures 4 and 5 for the samples No. 3845 and No. 6227. The two distributions are quite similar in shape, with sample No. 6227 being shifted somewhat to the right indicating a larger pore structure or a less dominating surface relaxation than is the case for sample No. 3845. Figure 6 shows the resulting T_2 distribution for the brine phase only at S_{wi} and S_{or} for sample No. 3845. The distribution for sample No. 3845 at S_{wi} , which is characterized as a mixed-wet small core, shows a large peak at low T_2 values (7 ms), and a smaller peak at about 100 ms. To account for the different regions in the distribution, Figure 8 show a schematic view of the oil/water distribution at end-point saturations for different wettability regimes. The largest peak at lower T_2 values can then be attributed to the water filling the smallest pores which are entirely water saturated due to capillary effects, and the water residing between pore walls and the oil in the largest, water-wet pores as both these regions experience enhanced surface relaxation. The smaller peak at higher T_2 values could possibly be attributed to the water centred in the smaller, oil-wet pores.

As the water saturation increases one would expect the signal from the water centred in the smaller, oil-wet pores to increase somewhat in intensity though retaining its T_2 value. For the larger, water-wet pores one would both expect a marked increase in signal intensity as the majority of the water now would be found here, and a shift towards higher T_2 values as the surface to volume ratio of the water in contact with the pore walls decreases considerably. The curve for S_{or} in Figure 6 shows this behaviour to some extent. The peak at lowest T_2 values has a slight increase in intensity, and is also shifted slightly to the right. The majority of the signal now has a peak at about 200 ms, which clearly can be attributed to larger, water-filled water-wet pores. A bulk component for water in oil-wet pores can now not be observed. This can have two explanations. First, the signal might be hidden underneath the dominating peak from larger pores where water dominates. It is difficult to conclude more on that on the basis of the available data.

Another explanation could be that these oil-wet pores never have been reached in the water-flooding. An indication of this is the comparison with the T_2 distribution at 100% water saturation. There is no considerable shift towards higher T_2 values for the brine distributions with oil present as one would have expected if there existed a bulk component.

Figure 7 show the brine T_2 distributions at S_{wi} and S_{or} for sample No. 6227, a fractional wet core. Also here the smaller peak can be attributed to a signal arising from capillary bound water in the smallest pores, and water coating and close to surfaces in otherwise oil filled pores. The peak at higher T_2 values is of more interest. Compared to the distribution at 100 % water saturation as given in Figure 5 there is a marked shift to higher T_2 values, from 250 ms to 510 ms. This is most notable for the situation at S_{or} , where also the right cut-off values are significantly higher than for the water saturated case. Development of such a component is probably the result of water entering oil-wet pores, thereby filling the centre of the pores and thus acting more as a bulk fluid.

Subtraction of True Oil Signal

Although the preliminary experiments showed little sign of influence from the surroundings on the oil signal, there is still a question of the validity of the assumption of inertness in a true porous medium where the existence of oil-wet areas also may alter the distribution of the oil signal. Attempts where therefore made to subtract the true oil signal from the total signal of the sample, as described under Procedures.

Figures 9 and 10 show the brine T_2 distributions resulting from the subtraction of the true oil signal of the samples No. 3845 and No. 6227. The distributions show the same main features as for subtraction of the bulk oil signal in Figures 6 and 7, although some discrepancies are found. For sample No. 3845 (Figure 6), the major peak at S_{or} is shifted slightly to the right, closer to the peak found in the water saturated case (Figure 4) thus strengthening the hypothesis that there does not exist a bulk water component. The distributions for S_{wi} are changed in the same way, shifting the right peak to lower values thus indicating that assigning this peak to a bulk water component is probably a fallacy.

When comparing the distributions at S_{wi} for sample No. 6227 in Figures 7 and 10 there is much the same tendency as observed at S_{wi} for sample No. 3845. The right peak is shifted significantly to the left, indicating that there does not exist a bulk water component at this saturation. At S_{or} the situation is however different from the tendency seen for sample No. 3845. The major peak for sample No. 6227 has now shifted to higher values, hence strengthening the suggestion of a bulk water component in pores where oil is coating the surface. Summing up the distributions at both S_{wi} and S_{or} for sample No. 6227 there is evidence for the existence of both water and oil-wet areas.

Comparison of Procedures

Comparing the T_2 distributions arising from the two approaches it seems clear that the oil phase is not completely unaffected by the surroundings of the media it is in. The difference between the two methods is most notably seen for the right cut-off values in the distributions, especially for the fractional wet sample No. 6227. The difference is a result of the fundamental difference in assumptions made by the two methods. While subtracting a bulk signal assumes that there is virtually no influence from the porous system on the oil phase, subtraction of the true oil signal only assumes that there is sufficient mobility difference in the two phases to separate them with a pulsed field gradient experiment; there is insignificant loss of signal from the oil phase prior to the first measuring point in such an experiment.

CONCLUSIONS

Attempts to resolve the brine T_2 distribution from signals emerging from both oil and water has been made. Two similar, but yet distinctively different approaches have been used. In the first approach a predetermined, scaled bulk oil signal was subtracted from the total magnetization decay curve. The second approach utilized the true oil signal from the sample by measuring this with the water signal suppressed to subtract from the total magnetization decay curve. The major findings can be summarized as follows.

- Both procedures give the brine signal alone, and the resulting T_2 distributions show the same main features. There are though some discrepancies which can be attributed to the fundamental difference in assumptions between the two procedures.
- For the mixed-wet small case there is evidence of the majority of water residing in areas in contact with the pore surfaces, but there is little indication of the existence of a bulk water component from smaller, oil-filled pores.
- In the fractional wet case however, it is possible to distinguish between two regions corresponding to water in contact with the pore surfaces and a bulk water component.
- This study shows promising results, but to make reliable decisions based on the NMR data alone more statistics are needed in the form of a larger numbers of different cores. The method presented has though the possibility of distinguishing between different types of wettability as one is relieved from the ambiguity of overlapping signals from the oil and water phases.

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TABLES & FIGURES

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Table	1 1.10	uud n	roperfies
1 4010	1. LIQ	juiu p	roperties

Component	Dynamic viscosity (25 °C) mPas	Bulk T _{2, median} ms
Marcol82	20-25	136
Synthetic brine	0.89	3000

π/2

⊢τ-

g

δ1 δ δ2

g



Figure 1. The combined PFGSE-CPMG sequence



Figure 2. The 11-interval PFGSE sequence

g

g

4τ

Figure 3. Bulk oil T_2 distribution (\blacklozenge) and oil T_2 distribution from a saturated quartz sand model system (\circ).







Figure 6. Brine T_2 distribution after subtraction of bulk oil signal for sample No. 3845 at $S_{wi}(\blacklozenge)$ and $S_{or}(\circ)$



Figure 5. T_2 distribution for sample No. 6227 at $S_w = 1$



Figure 7. Brine T_2 distribution after subtraction of bulk oil signal for sample No. 6227 at $S_{wi}(\blacklozenge)$ and $S_{or}(\circ)$



Figure 8. Schematic view of the o/w distribution at end-point saturations



Figure 9. Brine T_2 distribution after subtraction of the true oil signal for sample No. 3845 at $S_{wi}(\blacklozenge)$ and $S_{or}(\circ)$

