

ESTIMATING SATURATIONS IN ORGANIC SHALES USING 2D NMR

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ABSTRACT

Tight organic shales are a challenge to the oil industry in several ways. An accurate petrophysical evaluation of these rocks includes porosity, permeability, hydrocarbon saturation and fracability. The evaluation of these petrophysical parameters has appeared more challenging in tight organic shales than in conventional reservoirs. In this paper, we describe a non destructive method allowing the measurement of hydrocarbon saturation based on two dimensional T_1 - T_2 NMR.

First, we give the experimental evidence of an NMR contrast between oil and water in organic shales. Contrary to the conventional reservoirs, the contrast between oil and water in shales is not based on diffusion, but on T_1/T_2 . Various imbibition tests with water/light oil/ D_2O were performed. These tests prove unambiguously that the oil and water NMR signals can be assigned unambiguously in 2D T_1 - T_2 NMR maps. They also prove that the high T_1/T_2 in organic pores is not due to bitumen (high viscosity), and that it can be achieved by light oil (isopar L). The high T_1/T_2 observed is only due to confinement in the organic pores. In order to understand how confinement only can lead to such a high T_1/T_2 , multi-frequency NMR dispersion (NMRD) experiments were performed. These experiments allow us to propose an interpretation that explains the unexpected dynamical behavior of the light oil in organic pore leading to high T_1/T_2 .

Hydrocarbon saturation in organic shales is commonly measured by Dean Stark, or retort method. Saturation is the ratio between a volume of fluid and a total pore volume. If thermal method may be good at estimating the volume of fluid produced, its major drawback is that it is destructive, therefore preventing the direct measurement of total pore volume. The total pore volume is then estimated by adding water, oil and gas volumes: this leads to an accumulation of errors in the estimation of hydrocarbon saturation in shales. The NMR method being non destructive, it allows performing a total porosity measurement afterwards; therefore providing a much more accurate saturation estimation. The porosity estimation being challenged for the thermal method, we compare water volumes measured by NMR and a thermal method for validating the NMR approach.

INTRODUCTION

Petrophysical properties including porosity, permeability, fracability and hydrocarbon saturation are crucial for hydrocarbon producibility and economic assessment in tight organic shales. Therefore, a technique to evaluate these petrophysical properties in tight organic shales has become more challenging. It has been demonstrated extensively that porosity measurement could have significant bias in these rocks [1-2]. Therefore, a proper experimental protocol is required to obtain usable data. The saturation is the ratio between fluids (water or hydrocarbon) volume and a total pore volume. Standard methods for evaluating water saturation are Dean Stark and retort fluid extraction. Dean Stark can be time consuming while the Retort method can be relatively fast. However, the hydrocarbon saturation estimated by retort method may be erroneous because the total pore volume is a summation of gas, water and oil volumes [3]. Nuclear magnetic resonance (NMR) is a non destructive method that is commonly used in the industry to provide the porosity. Advanced NMR techniques such as 2D D-T₂ maps are also commonly used to estimate saturations in conventional reservoirs. There is an effort to apply this technique in unconventional rocks [6] and they have shown the difficulty to measure diffusion coefficients in nanoporous materials. Recently, 2D T₁-T₂ NMR has been used by different authors to characterize the fluids contained in shale samples [5-9]. To summarize the finding of these different authors: (1) oil exhibits a high T₁/T₂, (2) water exhibits a low T₁/T₂, (3) bitumen is identified by Singer P.M. et al. [7] and Washburn K.E. et al [8] on their samples (Eagle Ford and Green River formation) and, (4) bitumen is not found in samples used by Korb J-P et al. [10].

Here, we use 2D T₁-T₂ NMR to estimate water and hydrocarbon saturation in tight organic shales. A contrast between water and oil signals in 2D T₁-T₂ maps is proved by spontaneous imbibitions test in cleaned and as received shales by various liquids, i.e. heavy water (D₂O), light oil (isopar L) and water (70 g/L NaCl). Moreover, dynamic behavior of light hydrocarbon confined in organic pore leading to high T₁/T₂ is proposed. This model is confirmed by multi-frequency NMR dispersion (NMRD) and 2D T₁-T₂ maps at 2.5 MHz and 23 MHz. We therefore propose a comprehensive approach, combining experiment and theory, allowing us to estimate accurately water and oil saturations by NMR. The saturation from 2D T₁-T₂ NMR is then compared to gravimetric method for the imbibitions test and by Thermo Gravimetric Analysis coupled to a mass spectrometer (TGA) for 15 shale samples (as received) from the Vaca Muerta formation in Argentina.

EXPERIMENTAL

Our samples were source rocks from the Vaca Muerta formation in Argentina. We worked with two different wells, shale A which comes from the oil window, and shale B which comes from the wet gas window.

On these samples we performed different types of measurements: NMR, mass balance and Thermo Gravimetric Analysis (TGA):

- 2D T_1 - T_2 maps were acquired at 2.5 MHz and 23 MHz on Oxford Instrument spectrometers with $TE = 200 \mu\text{s}$ and inversion recovery varying from 70 μs to 1 s in 200 values. The results were processed using an in-house 2D inverse Laplace transform. The temperature of the samples was $21 \pm 1 \text{ }^\circ\text{C}$. 2.5 MHz measurements were performed on cylindrical samples of 30 mm diameter by 50 mm height, while the samples for 23 MHz measurements were 10 mm in diameter by 15 mm height.
- Multi-frequency NMR dispersion (NMRD) was performed on a fast field cycling spectrometer from *Sterlar s.r.l., Mede, Italy*. The measurements were performed on samples of 9mm in diameter and 15mm height. At each frequency (varying from 10kHz to 35MHz), a full T_1 measurement is performed, and processed using an in-house 1D inverse Laplace transform.
- A TGA instrument (NETZSCH-STA 449) coupled with mass spectrometer (Aeolos-OMS 403 D) was used. Thermo gravimetric analysis (TGA) is an analytical technique used for accurately measuring mass changes as a function of increasing temperature, while the MS is used to analyze the produced gases. The 10 x 15 mm samples were placed in the TG furnace and heated under helium gas. The samples were heated from 25 $^\circ\text{C}$ to 315 $^\circ\text{C}$ at 5 $^\circ\text{C}/\text{min}$ heating rate and held at this temperature for 30 min. Final temperature of 315 $^\circ\text{C}$ was chosen after previous tests in order to evaporate all the water and the mobile oil, while minimizing the cracking of kerogen and the production of structural water. This temperature is consistent with retort method for total oil extraction [3-4]. The water molecule at mass 18 was monitored by mass spectrometer. An integrated area of water mass peak allows us quantifying the water mass. The oil mass was calculated by mass subtraction between total mass loss and water mass. Samples used for TGA were 10 mm in diameter by 15 mm.

SPONTANEOUS IMBIBITION TESTS: EVIDENCE OF AN NMR CONTRAST BETWEEN WATER AND OIL

Samples of 30 x 50 mm were used for imbibition tests. Firstly, shale A followed the following experimental procedure (detailed in Figure 1):

- As Received NMR measurement (Fig. 1a)
- Cleaning by chloroform for 4 days and iso-propanol for 4 days.
- Drying at 60 $^\circ\text{C}$ for 1 day.
- Spontaneous imbibition by water (70 g/L NaCl) (Fig. 1b and Fig. 2)
- Cleaning 4 days isopropanol and drying (60 $^\circ\text{C}$)
- Spontaneous imbibition by mineral oil (isopar L) (Fig. 1c and Fig. 2)

Figure 1 shows the 2D T_1 - T_2 maps for shale A: as received (a), cleaned and imbibed by water (b), and cleaned and imbibed by isopar L (c). In as received shale A (Fig. 1a), we noticed two separated signals. We have already shown [10] that the signal at low T_1 and T_2 was water and the other elongated signal with T_1/T_2 varying from 5 to 10 was oil. During imbibition by water, the signal at low T_1 and T_2 increased. On the contrary, during imbibition by isopar L, it was the signal with high T_1/T_2 that increased.

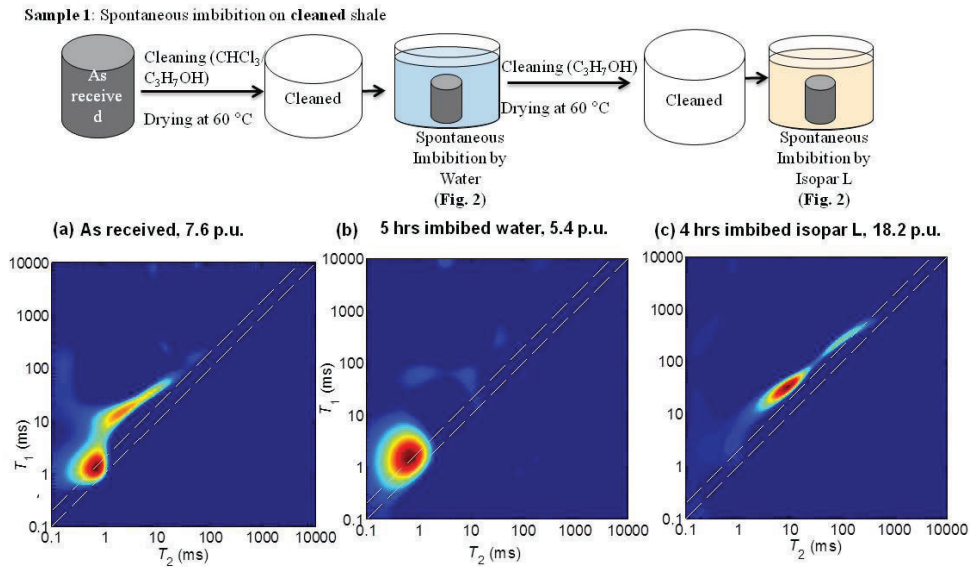


Fig. 1: 2D T_1 - T_2 2.5 MHz NMR for shale A: as received (a), cleaned/dried and imbibed by water (b) and cleaned/dried and imbibed by isopar L (c). The diagonal lines correspond to $T_1/T_2=1$ and $T_1/T_2=2$.

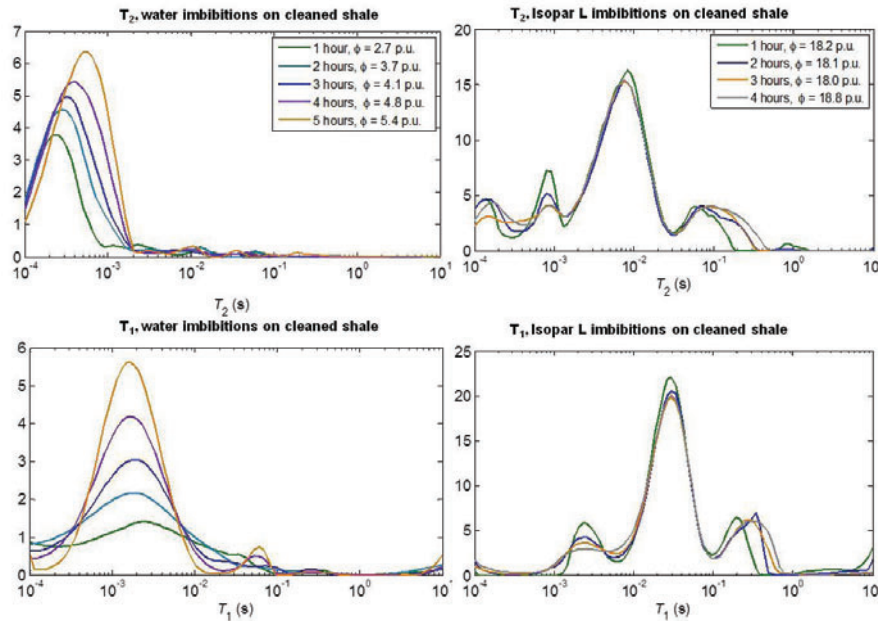


Fig.2: 2.5 MHz T_1 and T_2 projections of 2D T_1 - T_2 maps for cleaned shale A imbibed by water (Fig 1b) and isopar L (Fig 1c).

Figure 2 shows T_1 and T_2 projections of the 2D T_1 - T_2 maps obtained for shale A during spontaneous imbibitions by water (left) and isopar L (right). During imbibition by water, the T_2 distribution is shifted to longer T_2 s, while the T_1 distribution seems stable. Basically such a net difference can be explained by the basic relaxation features of T_2 and T_1 . Intrinsically, T_2 is dominated by the slow surface dynamical contributions driven by the dipolar fluctuations at zero Larmor frequency, while T_1 is only due to the much faster

volume dynamical contributions driven by the dipolar fluctuations at the Larmor frequency. T_2 is thus more sensitive than T_1 to the slow surface relaxation processes. Owing to the biphasic fast exchange conditions, the evolution of the T_2 distribution to longer T_2 s thus reveals the progressive enhancement of the volume contributions in the relaxation. On the contrary, the T_1 distribution which is less sensitive to the surface contributions mainly reveals the enhancement of the volume contributions with the imbibition processes.

One can wonder if these results from spontaneous imbibitions are affected by the partial saturation of the rock *i.e.* by the presence of gas in the sample. To answer that question we performed NMR T_1 - T_2 maps on another sample of shale A, and compared the results for as received and 100% saturated with water and isopar L (Fig. 3). Fluid saturations were performed by vacuuming the sample for 4 days, then saturating it with the fluid under 100 bars of pressure.

First, the as received NMR T_1 - T_2 map (Fig. 3a) of sample 2 is very similar to the one obtained for sample 1 (Fig. 1a). Second, when saturating the shale sample with 100% water (Fig 3b), we notice that water penetrates pores that were not penetrated under spontaneous imbibition, and exhibit an elongated NMR signal along the $T_1/T_2=1-2$. Third, when saturating the shale with 100% isopar L (Fig 3c), we notice that the NMR signature is very similar to the one obtained after spontaneous imbibition of isopar L (Fig 1c).

One can interpret that water spontaneously imbibe only in the mineral porosity, corresponding to the signal observed on Figure 1b (rounded signal at $T_1/T_2=1-2$). When water is forced into the organic porosity, it appears as an elongated signal at $T_1/T_2=1-2$ (Fig. 3b). For isopar L, it always exhibits an elongated signal at high T_1/T_2 .

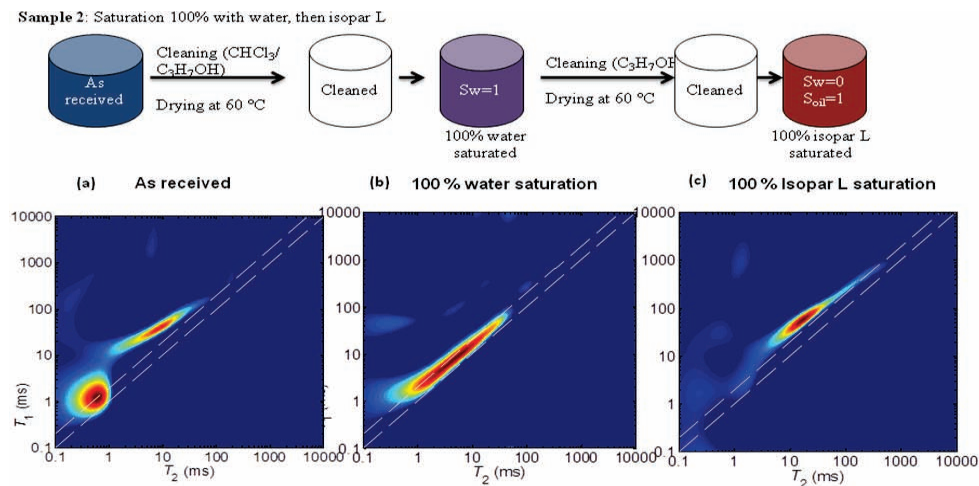


Fig.3 2D T_1 - T_2 2.5 MHz NMR for shale A: as received (a), 100 % water saturation (b) and 100 % isopar L saturation (c).

Additionally, we confirm the contrast between water and oil signal in 2D T_1 - T_2 maps by other imbibition tests: shale A (sample 3) was submitted to imbibition tests directly from the “as received” state. The 2D T_1 - T_2 maps for as received shale A imbibed by D_2O (for 9 hours) and by isopar L (for 8 hours) are presented in Figure 4. The 2D T_1 - T_2 map of the as received sample is very similar to the one presented in Figure 1a. In fact, most of our samples exhibit such 2D T_1 - T_2 contrast between oil and water in the as received state. The imbibition test by D_2O (D_2O has no NMR signal) shows that the signal of water at low T_1 and T_2 has disappeared. However, the resolution of the oil signal (elongated signal at high T_1/T_2) seems to be lost. After 9 hours of D_2O imbibitions, isopar L was then imbibed. During oil imbibition, it is clear that only the oil signal (elongated signal at high T_1/T_2) increased.

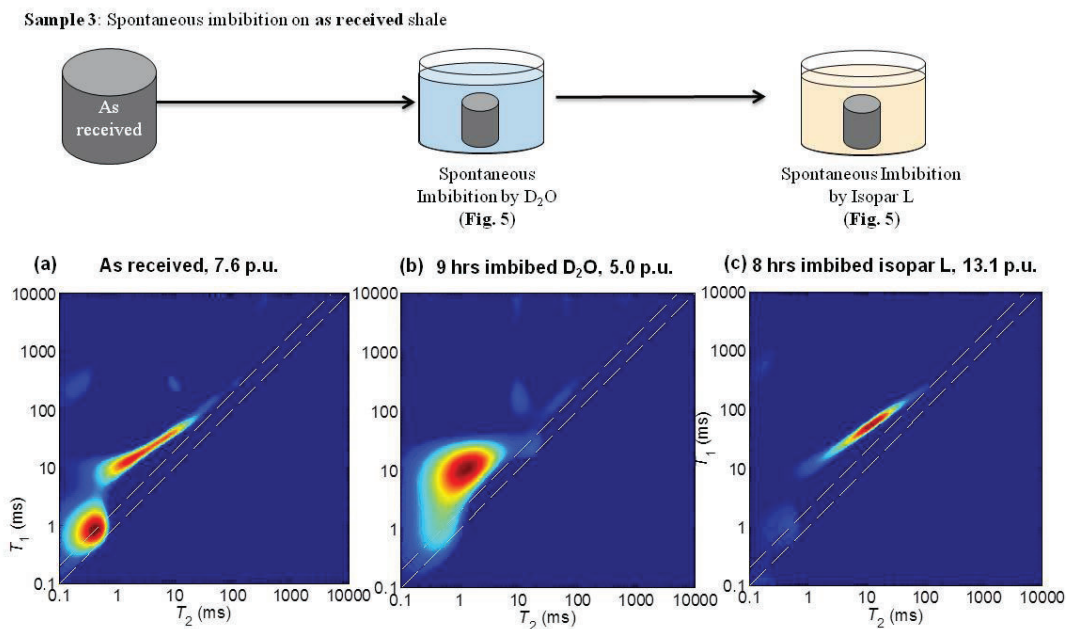


Fig. 4: 2D T_1 - T_2 2.5 MHz NMR for as received shale A (a) and imbibed by D_2O (b) and isopar L (c).

Figure 5 shows T_1 and T_2 projections of the 2D T_1 - T_2 maps for as received shale A imbibed by D_2O and isopar L. It obviously shows a continuous decrease of the signal at low T_1 and T_2 when imbibed by D_2O . During D_2O imbibition, the peak of the T_2 distribution is slightly shifted to longer T_2 whereas the T_1 distribution remains centered on the same value. This was already observed in Figure 2 during H_2O imbibition. These different behaviors in the 1H T_2 and T_1 distributions have already been explained above on the basis of the origin of the 1H T_2 and T_1 relaxation processes. The progressive imbibition by the heavy water (with quadrupolar 2H nuclei) also explains the net decrease of the 1H T_1 and T_2 intensities.

Moreover, T_1 and T_2 projections for isopar L imbibitions present only an increase of oil signal at high T_1 and T_2 . The water signal at low T_1 and T_2 was stable.

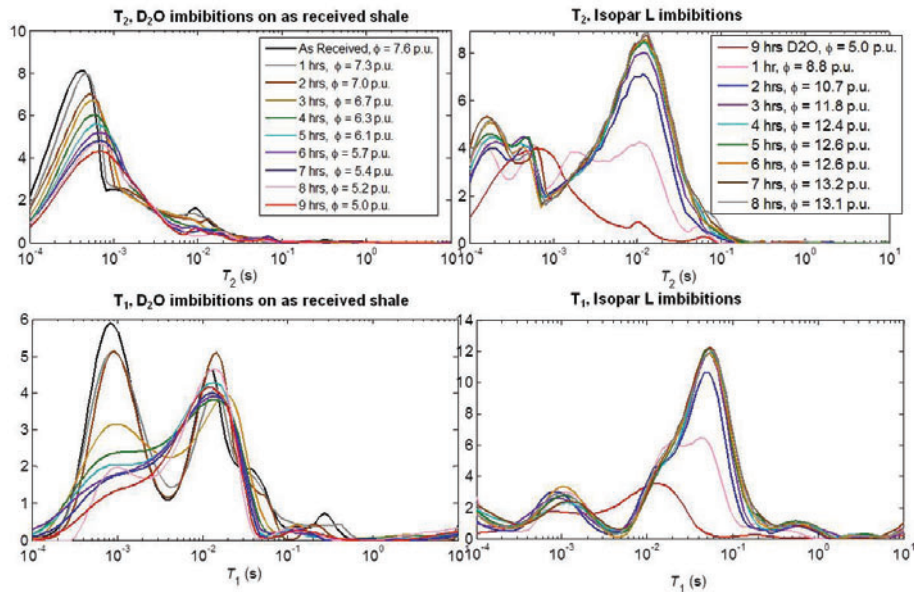


Fig. 5: 2.5 MHz T_1 and T_2 projections for as received shale A imbibed by D_2O (Fig 4b) and isopar L (Fig 4c).

Isopar L could imbibe very fast into both cleaned and as received shales. Particularly in the case of as received shale, an equivalent of 8.1 p.u. of isopar L imbibed the rock, and only air was expelled from the sample, no water was produced. This demonstrates that isopar L imbibed pores that were not accessible to water. This could be explained by a well connected network of strongly oil-wet organic pores.

Moreover, from isopar L (light oil) imbibitions test in cleaned shale A, we still observed a high T_1/T_2 for oil signal. Therefore, we proved that such a high T_1/T_2 is not due to bitumen (as reported in Green River formation [7]) but due to light oil confined in organic pore.

UNDERSTANDING THE NMR CONTRAST BETWEEN OIL AND WATER IN 2D T_1 - T_2 MAPS

Using NMR 2D T_1 - T_2 maps at 2.5 MHz, we have identified a contrast between water and oil. The water appears at short T_1 and T_2 with $T_1/T_2 \sim 1$, while oil exhibit a surprisingly high T_1/T_2 ratio. In order to understand why such a high T_1/T_2 ratio can be achieved with light oil like isopar L we performed multi-frequency NMR dispersion (NMRD).

At each frequency, a T_1 measurement is performed and the T_1 distribution is calculated. The T_1 distribution appears bimodal at all the frequencies. The peak corresponding to the water signal is identified by performing the same experiment on a 100% water saturated sample. A typical multi-frequency NMR dispersion plot is made by plotting the relaxation rates R_1 ($R_{1_oil} = 1/T_{1peak_oil}$ and $R_{1_water} = 1/T_{1peak_water}$).

The multi-frequency NMR dispersion obtained on an as received sample of shale A (Figure 6) clearly shows a very different frequency behavior for oil and water: we observe a very strong frequency dependence of the relaxation of the oil (red squares) compared to the one for the water (blue circles). We have proposed theoretical models [10] for oil (red dash line) and water (blue solid line) allowing us to fit the experimental data. The details of the theory are not the purpose of this article and are explained in details in ref [10].

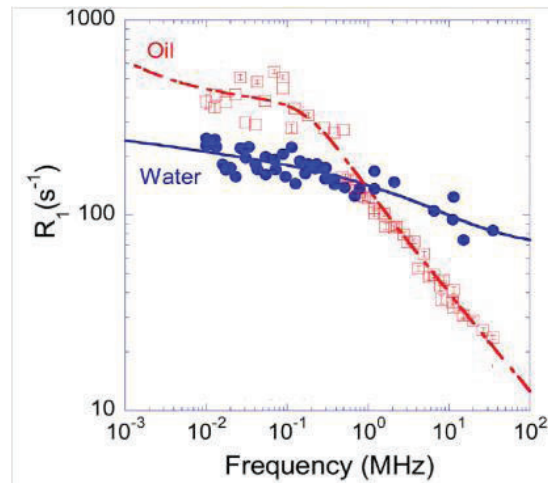


Fig. 6: Multi-frequency NMR dispersion plot showing the relaxation rates $R_1=1/T_1$ as a function of the Larmor frequency for as received shale A. (Figure taken from [10]).

We have applied our relaxation theory for T_1 and T_2 relaxation for the two different cases. We found a constant value of $T_1/T_2 \sim 1.36$ for water. While we found T_1/T_2 for oil varies with frequency. According to this theory, we display in Figure 7 the evolution of the ratio T_{1oil}/T_{2oil} with frequency, showing that the T_1/T_2 ratio for oil is expected to increase linearly with the square root of the frequency.

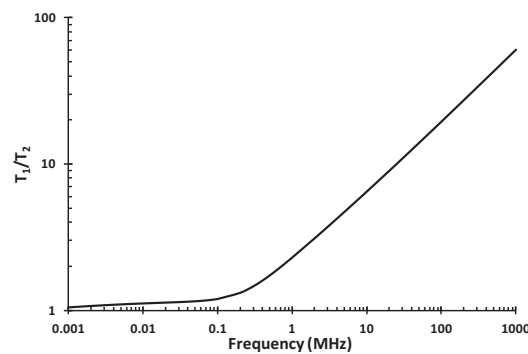


Fig. 7: T_{1oil}/T_{2oil} versus frequency, showing that the T_1/T_2 for oil is expected to increase with frequency.

Since the oil-water contrast we observed in the previous section is based on the T_1/T_2 ratio, this suggests that this contrast should increase with frequency. This led us to investigate higher frequencies and to perform NMR measurements at 23MHz.

Figure 8 shows 2D T_1 - T_2 maps obtained at 2.5 MHz and 23 MHz for cleaned shale A imbibed by isopar L and as received shale B. We observe that the T_1/T_2 ratio for oil (isopar L) obtained at 2.5 MHz is around 4 to 5. On the other hand the T_1/T_2 ratio for oil obtained at 23 MHz is the order of 10. The theoretical predictions T_1/T_2 for oil (Figure 7) are in excellent agreement with the experimental values found: $T_1/T_2(\text{oil}@2.5\text{MHz})\sim 4-5$ while $T_1/T_2(\text{oil}@23\text{MHz})\sim 10$.

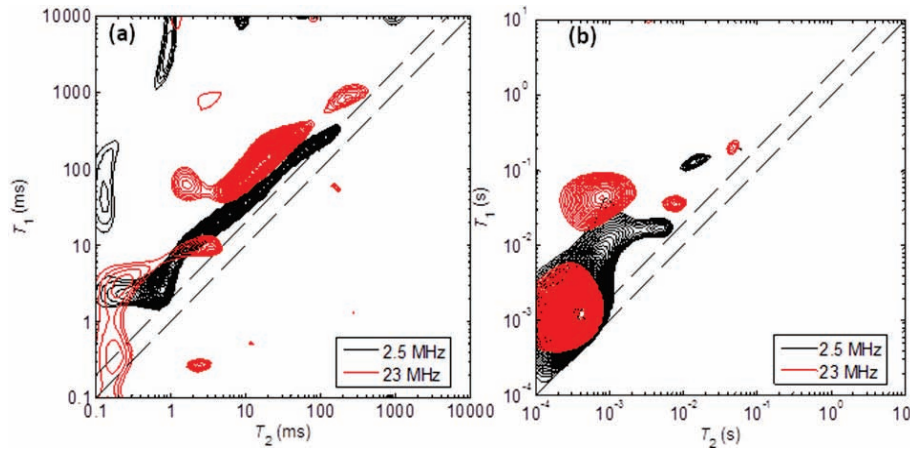


Fig.8: 2D T_1 - T_2 2.5 MHz and 23 MHz NMR for cleaned shale A imbibed by isopar L (a) and as received shale B (b).

High T_1/T_2 is usually attributed to the presence of bitumen. In this case we prove that a signal with very high T_1/T_2 ratio can be obtained only by putting light oil (isopar L) inside a nanoporous system. On the other hand, the high T_1/T_2 ratio observed on as received samples (Fig. 1a) completely disappeared after cleaning with chloroform (Fig. 1b). While the definition of what is called “bitumen” is still highly debated [11], this confirms that the high T_1/T_2 ratio comes from a fluid that is soluble in chloroform. While previous authors observed bitumen at high T_1/T_2 ratio[7] we demonstrate that in our case, high T_1/T_2 ratio is only due to light oil in a high confinement. We also show that after cleaning and imbibing with isopar L (Fig. 1c) the signal at low T_1 and T_2 has disappeared; this proves that our samples do not contain bitumen as described in [7].

In other words:

- The T_1/T_2 for water is almost constant with frequency.
- The T_1/T_2 for oil varies strongly with frequency.
- Therefore, the higher the frequency the stronger the contrast between oil and water in 2D T_1 - T_2 maps.

We thus recommend using 23 MHz NMR 2D T_1 - T_2 data in order to measure the quantity of water and oil contained in a given sample. The next section aims at comparing water and oil volumes obtained by NMR and other techniques (mass balance and TGA).

COMPARISON OF WATER AND OIL VOLUMES BETWEEN NMR AND OTHER TECHNIQUES

Several imbibition tests have been performed on shale A samples and were reported in the previous section. For two imbibition test (water imbibition from Fig. 2 and isopar L imbibition from Fig. 5), the amount of fluid imbibed was monitored using NMR and also by weighing the sample (mass balance). In Figure 9, we compared the water and isopar L imbibed volume calculated from 2D T_1 - T_2 2.5 MHz NMR with mass balance. Water and oil volumes obtained from 2D T_1 - T_2 maps have been calculated by integrating the NMR signal attributed to each fluid in the 2D T_1 - T_2 map. The excellent agreement between NMR and mass balance measured volumes for both water and oil shows that 2D T_1 - T_2 NMR could be an accurate technique to estimate volumes of fluids confined in porous media.

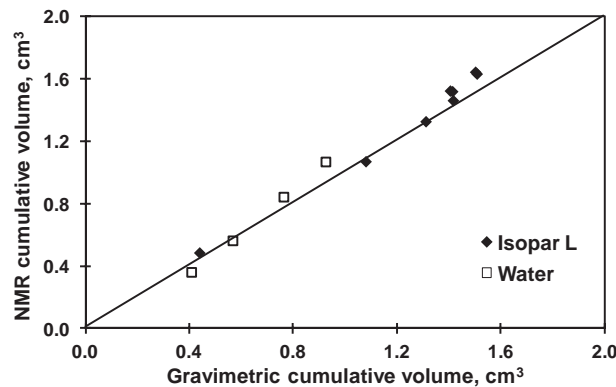


Fig. 9: Cross plot of water and isopar L volumes obtained from gravimetric and 2D T_1 - T_2 NMR methods.

The performance of the NMR approach was tested versus TGA on a set of as received samples from a different well (shale B). The water and oil volume of 15 as received samples from shale B obtained from 2D T_1 - T_2 23 MHz NMR were compared with TGA. The 2D T_1 - T_2 maps at 23 MHz acquired before and after TGA measurement are shown in Figure 10. Before TGA (Fig. 10a) the 2D T_1 - T_2 map is characteristic of a shale sample containing water (low T_1/T_2) and oil (high T_1/T_2). After TGA (Fig. 10b) the measured NMR porosity is less than 1 p.u., meaning that water and oil were almost totally lost after TGA analysis. This could confirm that high T_1/T_2 in our samples is not due to bitumen because boiling point of bitumen is higher than 315 °C [12].

Since TGA measures the mass loss, the density of water and oil is needed in order to convert the mass to volume unit. We used the following values for the density: 1.05 g/cm³ for water (70 kppm NaCl brine) and 0.85 g/cm³ for oil (light crude oil). The cross plot between volumes calculated from TGA and 2D T_1 - T_2 NMR is presented in Figure 11a. The water, oil and total volumes obtained from 2D T_1 - T_2 NMR and TGA are in very good agreement. In order to estimate saturations, one needs to measure porosity. TGA being a destructive measurement, we had to measure porosity on a set of twin samples. 15 twin samples were saturated by 100 % water to measure total porosity. Then, water

and oil saturation were estimated by dividing fluid volume with total pore volume. We present the water and oil saturation for 15 as received shales in Figure 11b.

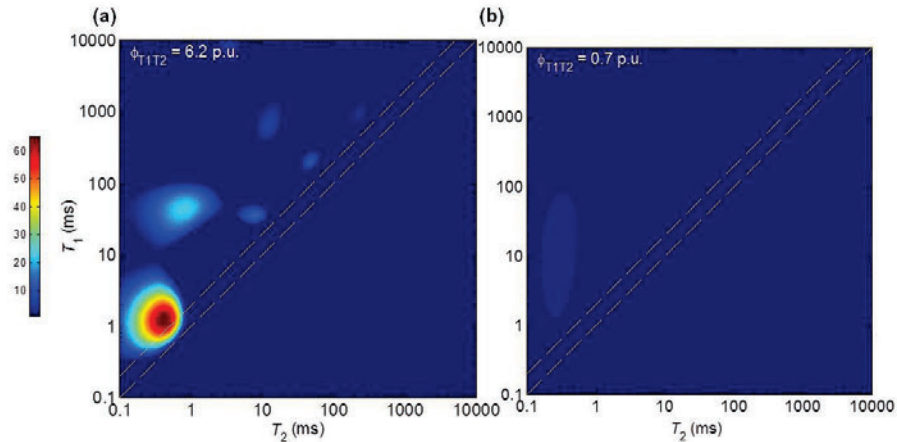


Fig. 10: 2D T_1 - T_2 maps at 23 MHz for as received shale B before (a) and after (b) TGA analysis.

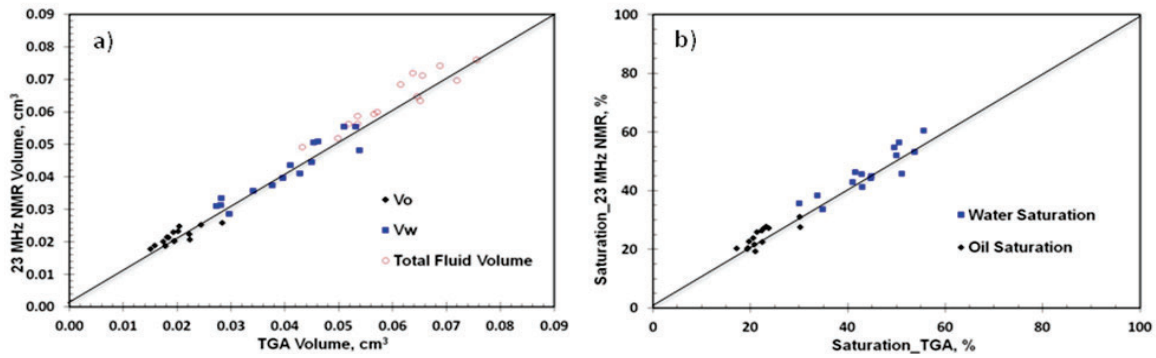


Fig. 11: Comparison of the results obtained by TGA and 23MHz NMR: a) volumes and b) saturations.

CONCLUSION

We proposed the 2D T_1 - T_2 NMR technique as a non destructive technique to estimate the water and oil saturation in tight organic shales. We interpreted the contrast between water and oil in 2D T_1 - T_2 maps on the basis of excellent agreement between experimental and theoretical arguments (multi-frequency NMR dispersion). According to our theory of NMRD in shales, oil and water are undergoing completely different dynamics, leading to a high T_1/T_2 ratio for oil, and a low T_1/T_2 ratio for water. We also showed in our samples that such a high T_1/T_2 ratio is not due to bitumen but comes from light oil (isopar L) confined in organic pore. The T_1/T_2 ratio of oil depends on the frequency whereas T_1/T_2 of water is invariant with frequency. Therefore, using 23 MHz NMR water and oil signals could be easily separated in 2D T_1 - T_2 maps. The water and oil volumes obtained from 2D T_1 - T_2 maps were compared with Thermo Gravimetric Analysis. The fluid volumes obtained from both techniques are in excellent agreement. Furthermore, the volume of

imbibed isopar L from 2D T_1 - T_2 maps is also correlated well with gravimetric method (mass balance). The water and oil saturation is calculated by dividing water or oil volume with total pore volume. Because NMR is a non destructive method, the total pore volume could be directly determined after 2D T_1 - T_2 maps acquisition. In our case, because the thermal method is destructive, the total pore volume was determined by T_2 measurement of 100 % water saturated twin samples. If NMR only was performed, one could even measure saturation and porosity (NMR acquisitions on as received and 100% water saturated sample) on the same sample. This would be a strong advantage compared to commonly used thermal methods (retort). Therefore, our proposed technique could give more accurate determination of water and oil saturation in tight organic shales.

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