diffusion-fundamentals.org

Probing individual saturations of crude-oil/brine/mud-filtrate mixtures confined in rocks

Lyès Benamsili[1,2], *Gérald Hamon*[1], *Jean-Pierre Korb*[2]

[1] TOTAL EP, CSTJF, Pau, France
[2] Physique de la Matière Condensée, Ecole Polytechnique-CNRS, 91128 Palaiseau, France

Corresponding author: Lyès Benamsili, E-Mail: lyes.benamsili@polytechnique.edu

Abstract

We propose a method that allows probing quantitatively the individual saturations of crude-oil/brine/mud-filtrate mixtures during imbibition-drainage experiments on a petroleum rock-system. The experiments have been also performed at different temperature and pressure conditions.

Keywords

D-T_2 experiment, rock, diffusion, relaxation, crude oil, petroleum

.1 Introduction

2D nuclear magnetic relaxation measurements are commonly used in well logging for the exploration part of oil recovery. For instance, the diffusion-transverse relaxation (*D*-T_2) correlation spectrum allows discrimination of brine and oil mixtures in pores [1]. However, there are still difficulties in data interpretation. The first difficulty is to probe quantitatively the individual saturations of each fluid in petroleum fluids mixtures. The second difficulty exists, for crude oil containing asphaltenes, in the interpretation of the anomalous relationship observed between the translational diffusion coefficient, *D*, and the transverse relaxation time, T_2 [2]. Here, we propose a new method allowing us to measure quantitatively the different saturations for various petroleum fluids mixtures in a rock-system. The rock samples and petroleum fluids have been properly characterized by standard petrophysical techniques (picnometry, gas flow in steady state conditions for absolute permeability, viscosimeter, SARA...). The *2D* NMR experiments have been realized at different *in situ* successive saturations in monophasic, diphasic and triphasic conditions. For proper measurement of the diffusion coefficients distributions, we used a pulsed field gradient spin–echo *PGSE* technique with bipolar pulsed gradients to reduce eddy currents and internal gradient effects [3, 4]. The final inverted *D*-T_2 spectrum has been obtained using our own inverse Laplace transform *(ILT)* program. The experiments of imbibition-drainage on a sandstone sample have been also performed at different temperature and pressure conditions.

.2 Systems and NMR methods

We use cylindrical sandstone rock samples 2” in length and 1.5” in diameter whose main characteristics have been measured with standard petrophysical techniques. The average porosity and

permeability are 22.75%, and 2.5 D, respectively. The rock contains less than 5% of clays, 0.13% of iron *(Fe)* and a few *ppm* of *Mn*. X-ray μCT shows that there is a homogeneous pore size distribution centered on 25 μm [5]. The petroleum fluids (brine/mud-filtrate/crude oil) are selected for their respective viscosities of 1, 2.5, and 25 cp at room temperature. The SARA analysis of the crude oil reveals a composition of saturates 40.3 %(wt), aromatics 44.0%(wt), resins 6.7%(wt) and asphaltenes 9.0%(wt), respectively. The brine is made with NaCl (45g/l) and $CaCl_2$ (5g/l). The oil based mud-filtrate has been synthesized in the laboratory.

We use the standard petroleum industry protocol to saturate an empty rock sample. The drainage/imbibition protocol is not different from the saturation protocol. However, the former depends on the fluids density to avoid gravity effects. First, we saturate the rock sample with a given fluid, then the drainage/imbibition procedure is performed and the volumes are measured during injection-recovery.

1D and *2D* NMR measurements have been made with an Oxford 2.5 MHz spectrometer. Data were processed using our own *1D* and *2D* inverse Laplace transform *(ILT). 1D* NMR (CPMG) measurements have been performed to probe T_2 on three similar samples saturated either with brine, crude oil or mud-filtrate, separately. The three T_2 distributions have their main peaks centered at 0.8s for brine, 0.45s for mud-filtrate and 0.05s for crude oil, respectively. The ratio $T_{2,peak,brine}/T_{2,peak,oil}\approx 16$ should facilitate an easy separation of brine and crude oil peaks in a mixture. However, we checked that this was not the case for a mixture of almost equal volume fractions of these two fluids. A supplementary dimension was thus necessary.

.3 *2D* NMR measurements

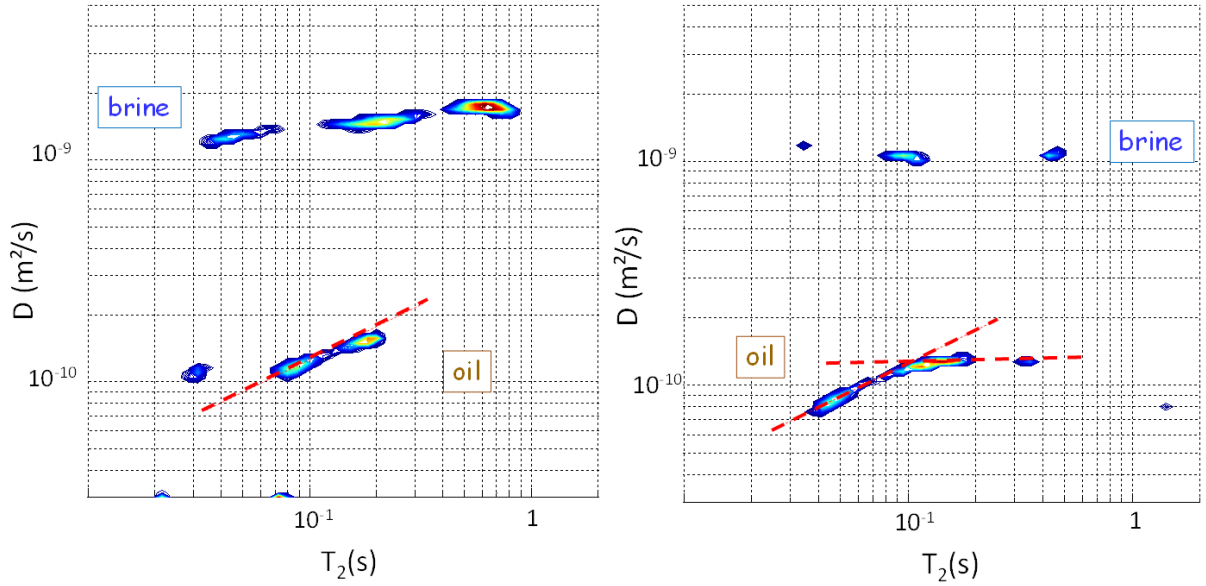
3.1 Confined brine/crude-oil mixture

We present in Figure 1 the D-T_2 correlation spectra obtained after *ILT* of a confined brine-crude-oil mixture ($SNR\geq 120$). In fact, these spectra correspond to two successive steps of a drainage process. The rock is initially 100% saturated with brine. Then, oil is progressively injected in steady state condition to reach a given saturation. We immediately notice that the brine and oil data are clearly separated on the basis of their individual diffusion coefficient values. We estimate the fluid saturations using these D-T_2 results by a localized integration procedure. For instance, in Figure 1a, we obtain a brine saturation of 59.4% with our NMR-method, 58.2% with the injected volumes and 54.8% with the recovered volumes. In Figure 1b, we obtain on the same system and some steps later, a brine saturation of 22.9% by using NMR-method, 22.6% with the injected volumes and 20.2% with the recovered volumes. The latter saturation state is characteristic of the water irreducible saturation state (S_{wi}). The small differences between these volumes, approximately 2-3 % (0.25-0.37cm^3), are due to errors during volume measurements in the experimental setting.

The anomalous relation, $D \propto \sqrt{T_2}$, shown in Figure 1a confirms previous results observed in crude oils containing asphaltenes [2]. However, an interesting and new result is shown in Figure 1b, where a levelling off of this relation for large T_2 is observed in the crude oil. This behaviour is generally observed in the wetting fluid phase. This is rather surprising for our rock sample, which is considered to be water-wet. We interpret this seemingly paradoxical behaviour by considering a surface diffusion process of small hydrocarbons (with long T_2) at the surface of asphaltene nanoaggregates. NMR dispersion data on crude oils with and without asphaltene confirm this interpretation [6].

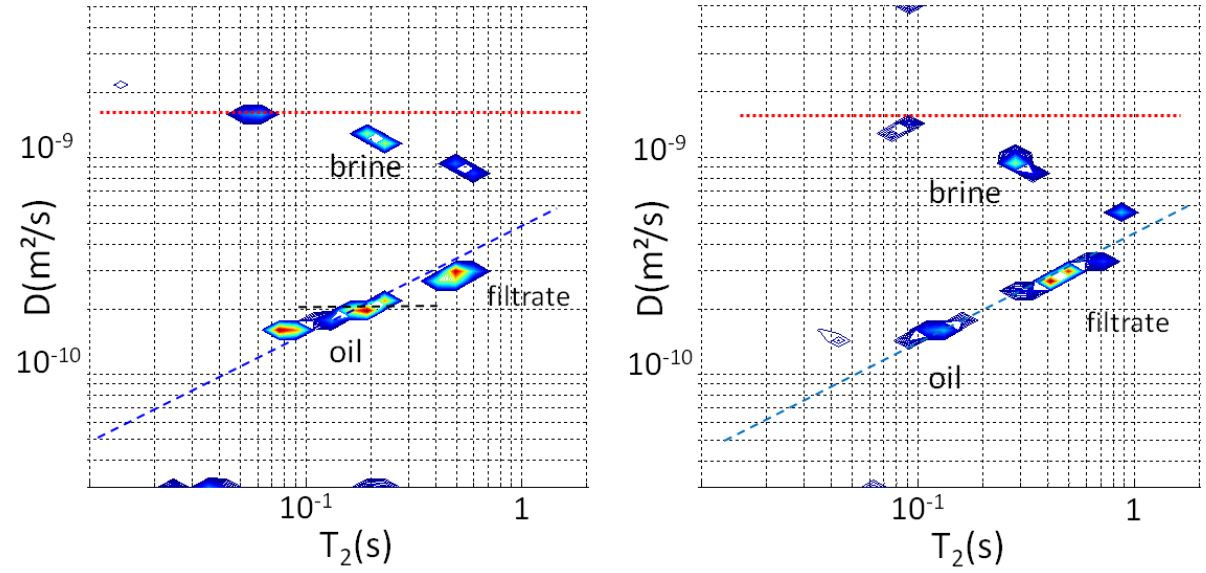
3.2 Confined brine/crude-oil/mud-filtrate mixture

We present in Figure 2 the D-T_2 correlation spectra obtained after *ILT* of a confined brine/crude-oil/mud-filtrate mixture at two successive steps of an imbibition process. The sample is initially in the final state of Figure 1b with a brine saturation of 22.9% and an oil saturation of 77.1%. Then oil-based filtrate is progressively injected in steady state condition. We notice that the brine, oil and filtrate data are clearly separated on the basis of their individual diffusion coefficient values. For instance, in Figure 2a, we still obtain a brine saturation of 22.7% with our NMR-method while we find 22.6% with the injected volumes. Similarly, oil saturation is 52.7% with NMR and 50.1% with the injected volume. The saturation of filtrate is 24.6% with NMR and 27.3% with injected volume. In Figure 2b, some steps later, we still obtain a brine saturation of 23.0% by using NMR-method. The oil saturation decreases to 17.2% and the filtrate saturation increases to 59.8%.



(a) *(b)*

Figure 1 *D-T_2 correlation spectra of brine-crude oil mixtures confined in sandstones pores at different steps of the drainage process. (a) Brine saturation of 59.4%, oil saturation of 40.6%. (b) Brine saturation of 22.9%, oil saturation of 77.1%.*



(a) *(b)*

Figure 2 *D-T_2 correlation spectra of crude oil/brine/mud filtrate mixtures confined in sandstones pores at two steps of imbibitions. (a) Saturations of brine (22.7%, S_{wi}), oil (52.7%) and mud-filtrate (24.6%); (b) Saturations of brine (22.9%, S_{wi}) oil (17.2%) and mud-filtrate (59.8%).*

.4 *D-T_2* correlation of confined crude oil at various temperatures and pressures

A set of *2D* NMR *D-T_2* measurements are performed on a sandstone sample saturated with crude oil varying the temperature and pressure (Figures 3a, b). The temperature values used are 20, 25, 30 and 40 degrees Celsius and pressure of 1 and 15 bars. After temperature is stabilized, the pressure is stabilized at a given value.

We note on Figure 3b the absence of an effect of pressure. On the contrary, there are systematic enhancements of D and T_2 values when temperature increases, which is expected for an activated process. We observe again the anomalous relation, $D \propto \sqrt{T_2}$ and the levelling off of this relation for

large T_2 (Figures 3a, b). The" high diffusivity" anomalies in Figure 3 at 30 and 40°C do not appear at lower temperatures. We verified that these small *2D* peaks are not due to *ILT* or experimental artefacts, but they are not clearly understood at the moment.

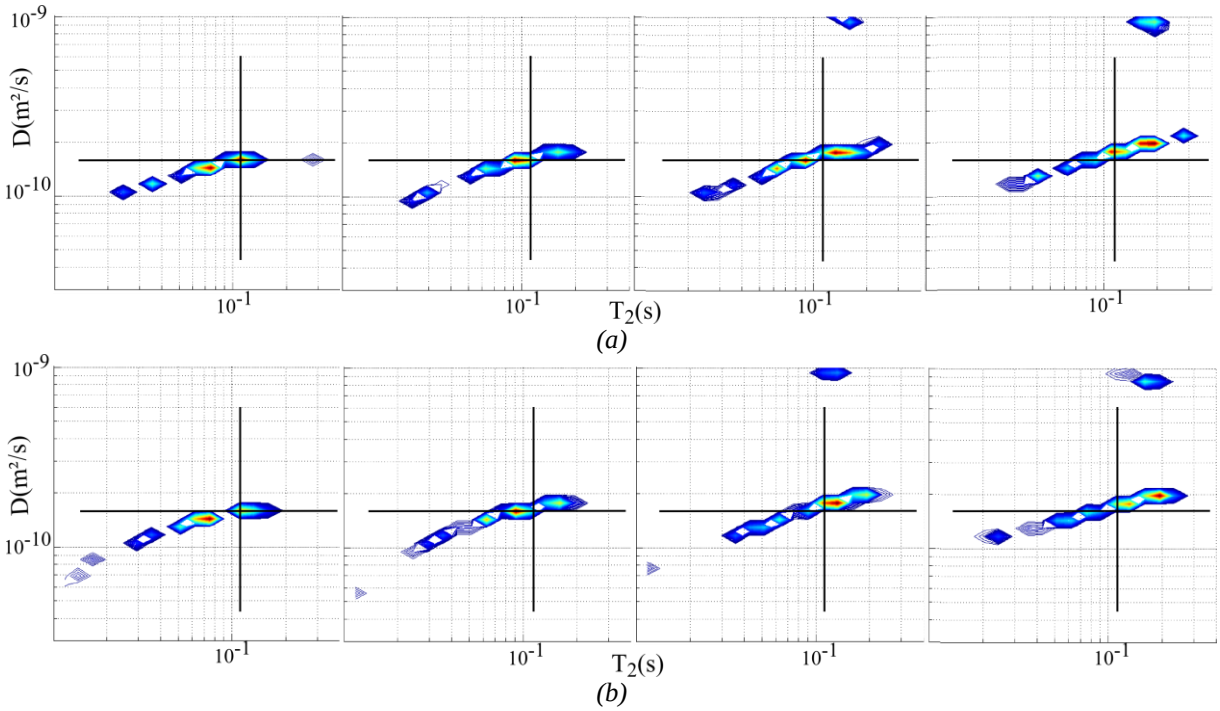


Figure 3 *D-T_2 correlation spectra of crude oil confined in sandstones at different temperature (20°, 25°,30°, 40°) and two pressures 1bar(a) and 15 bars(b). The continuous lines allow seeing the temperature effects.*

.5 Conclusion

We proposed *1D* and *2D* NMR methods allowing quantitative measurements of individual saturations for various petroleum fluids mixtures embedded in a rock-system at various temperature and pressure. The *D-T_2* experiments have been performed at different *in situ* saturations (monophasic, diphasic or triphasic). We succeeded in probing quantitatively the individual saturations of the fluids mixtures, during imbibition-drainage experiments in this rock-system. We observed the anomalous relationship, $D \propto \sqrt{T_2}$, and a levelling off of this relation for large T_2 in the bulk and confined crude oil. These observations persist at different temperature and pressure.

6. References

[1] M. D. Hürlimann and L. Venkataramanan, J. Magn. Reson. **157**, 31-42 (2002).
[2] A. R. Mutina, M. D. Hürlimann, J. Phys. Chem. A**112**, 3291-3301 (2008).
[3] W.S. Price, Concepts in Magnetic Resonance **10**, 197-237 (1998).
[4] P.T. Callaghan, *Translational dynamics and magnetic resonance*, (Oxford University Press 2011).
[5] I. Bondino, R. Nguyen, G. Hamon, P.A. Ormehaug, A. Skauge, S. Jouenne, paper SCA2011-18.
[6] A. Louis Joseph, L. Benamsili, J.-P. Korb, Microporous and Mesoporous Materials (submitted).