USING MULTIFREQUENCY NMR FOR PROBING WETTABILITY

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ABSTRACT

We present a new method for probing wettability of rock/oil/brine systems using multi-frequency NMR, *i.e.* nuclear magnetic relaxation dispersion (NMRD). Unlike conventional transverse relaxation studies, this approach gives a direct probe of the dynamical surface affinity of fluids, thus allowing the separation of wetting from non-wetting fluids through their typical NMRD features. To quantify these features we introduce a microscopic dynamical surface affinity index which measures the dynamical correlation (*i.e.* microscopic wettability) between a diffusive fluid and fixed paramagnetic relaxation sources at the pore surfaces.

For the first time we apply this technique to carbonate reservoir rocks of bimodal porosity saturated with oil (S_w=0%), brine (S_w=100%) and mixture of oil/brine (S_{wirr}). The measured NMRD features clearly discriminate the wetting behavior of the fluids in the pore system. We have interpreted these different NMRD profiles in a model of dynamical surface relaxation. We consider the two following situations: (i) for an aprotic liquid such as oil (dodecane), the affinity index varies between 1 (bulk *i.e.* non wetting case) and infinity (strong surface affinity *i.e.* wetting case). This index quantifies the degree of dynamical correlation with the paramagnetic impurities present at the pore surface. (ii) for a protic liquid such as brine, we define a similar index by comparing the time of residence of a proton in the ligand field of the paramagnetic ions to the electronic spin-lattice relaxation time (*i.e.* reflecting the presence of water close to the surface and thus a water-wetting behaviour). The experimental results obtained on carbonate core plugs of bimodal porosity saturated with an oil/brine mixture (S_{wirr}) have been processed using the proposed model and clearly reveal the pore size dependence of wettability.

INTRODUCTION

Wettability is the ability of a fluid to spread onto a solid surface in the presence of other immiscible fluids. It is relevant in fundamental interfacial phenomena underlying coating, bonding, adhesion and other related effects in porous media. For instance, the wettability of a rock/oil/brine system affects fluid saturation, capillary pressures, electrical properties and relative permeabilities[1-5]. Wettability of fluids in oil and gas reservoirs has a direct effect on efficiency of hydrocarbon recovery. In most cases massive water injection is performed to move oil toward the production zones, and if wettability variations occur the water has the tendency to flow in the water wet locations leaving oil in place in oil-wet locations. Due to its economical impact, control and monitoring of wettability *in situ* justify huge investments in core analysis for laboratory measurements.

Techniques able to map wettability in an oil field are still not developed. Measurements on cores require long and tedious preparation, and never reflect the actual state of wettability. Semi-empirical indices are used in the petroleum industry to describe core plug wettability: (i)Amott index[6] (from 1 for water wet rocks to -1 for oil wet cores) (ii) USBM[1] (*U.S. Bureau of Mines*) (varying from -∞ to +∞). Both Amott and USBM methods are accepted as a standard by the oil industry, however they do not completely compare in all cases[7]. A direct measurement of wettability between rocks oil and brine can be done in laboratory by Drop Shape Analysis (DSA) using pure flattened samples of non-porous rocks and oil and brine. However, porous rocks cannot be tested directly by DSA. Amott, USBM and DSA methods cannot be carried out in the well.

A more recently introduced NMR T_2 index[8-10] expresses the total surface of rock wetted by water minus the total surface of rock wetted by oil and divided by the total surface in contact with the fluid. This method uses the fact that a fluid surrounded by a wetting fluid shows a T_2 relaxation distribution of a bulk fluid, whereas a fluid in contact with the rock exhibits a shorter T_2 due to the confinement by the surface. This method has some limitations since it requires a measurement at complete water saturation and also requires the knowledge of the T_2 shape of the oil in bulk conditions. None of these techniques allow the local probing of interaction between the fluid and the rock-pore surface in a single non invasive measurement.

Here, we propose to use nuclear magnetic relaxation dispersion (NMRD)[11, 12] to probe the dynamical surface affinity of diphasic liquids as a measurement of wettability. This technique measures proton $1/T_1$ over a large range of applied magnetic fields. Unlike conventional transverse relaxation studies[8, 13], this approach is a direct probe of the dynamical surface affinity of fluids[14, 15]. We show that not only NMRD features allow to identify the wetting properties of carbonate rock saturated with both oil (dodecane) and water, but the NMRD features also provide a pore size information. To quantify these features we introduce a microscopic dynamical surface affinity index which measures the

dynamical correlation (*i.e.* the microscopic wettability) between the diffusive fluid and the fixed relaxation sources at the pore surfaces. For the first time, this technique is proposed to estimate the wetting properties of micro and macro porosities of carbonate rocks, which are known to hold about two thirds of the world's oil reserves[16].

SAMPLES AND METHODS

A. Samples

The rock samples used here are carbonate rocks from a Middle Eastern oil reservoir. They are intraclast skeletal ooid grainstone carbonates with 30% porosity and 700 mD permeability. A thin section observed by polarized microscopy (Figure 1) reveals the complex structure of this rock, formed by grains partially dissolved and coated by calcite cement. This rock is formed of medium to very coarse grains; those grains are oolites, coated grains, intraclasts, gastropods or forams. The macropososity, evidenced in blue in the thin section (Figure 1), has a pore size ranging from 2 mm to 50 µm. Microporosity however is not visible from thin section images, but the dual porosity of this rock is evidenced by the bimodal NMR T_1 distribution obtained after saturating this rock 100% with brine (Figure 2).
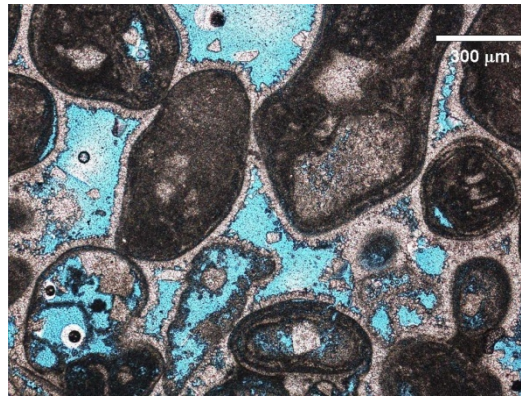

Figure 1 Thin rock section of the studied intraclast skeletal ooid grainstone of 30% porosity and 700 mD permeability as seen by polarized optical microscopy.
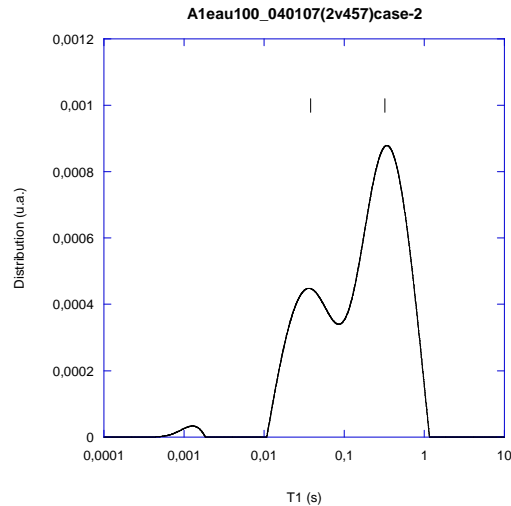
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Figure 2 T_1 **distribution of the rock saturated with water. The data is acquired at 2.5MHz. The distribution reflects the complex porosity distribution.**

This rock was sampled into cylindrical plugs of 8mm in diameter and 10mm in length. The sample size is restricted due to limitation in the bore diameter of the NMR system (maximum tube diameter is 10mm). The homogeneity of the rock at the plug scale allows comparing results from different plugs. Originally, the rock plugs are filled with native fluids, this is called "native state". They were cleaned using standard cleaning procedure in petrophysical laboratory, using toluene and methanol in a Soxhlet extractor to remove all the native fluids inside the rock (original crude oil and brine). Three rock plugs were then dried in an oven at 60°C during 48h and each of them prepared at a different saturation:

- 100% water saturation (S_w=100%): this plug was vacuumed and saturated with a 50kppm NaCl brine. The use of salty water prevents dissolution of the carbonate rock by fresh water.
- 100% dodecane saturation (S_w=0%): this plug was vacuumed and saturated with dodecane and said to be at 0% water saturation (S_w=0%).
- Irreducible water saturation S_{wirr}: this plug is first saturated 100% with water, and then dodecane is forced into the plug by high speed centrifugation. The density difference between dodecane and brine forces dodecane to replace brine in the pore space. This plug is said to be at irreducible water saturation (S_w=S_{wirr}).

B. Methods

The proton nuclear magnetic relaxation dispersion (NMRD) data were recorded using a fast field cycling FFC NMR spectrometer from *Stelar s.r.l., Mede, Italy*. We used a fast field cycling sequence to improve the signal to noise ratio, where spins are polarized at

15 MHz and the free-induction decays are recorded following a single 90° excitation pulse of 5.8 μs duration applied at 11 MHz. The temperature was fixed at 298K. The experiment was performed over a large range of proton Larmor frequencies (10 kHz - 20 MHz) in order to obtain the complete dispersion curve of $1/T_1$.

Electron Spin Resonance (*ESR*) spectroscopy at room temperature was used to determine the nature and the quantity of paramagnetic impurities in our carbonate samples. On a dry sample, we observe the six-peak hyperfine structure centred on *g=2* characteristic of electronic spins *S=5/2* of paramagnetic Mn^{2+} ion in a single environment. This spectrum is a result of Mn^{2+} substituting for Ca^{2+} in a single site of trigonal symmetry having as its nearest neighbors six-carbonate ions in the carbonate crystal lattice. There exists a broadline underneath the Mn^{2+} ESR spectrum. This could be attributed to magnetic Fe^{3+} impurities.

RESULTS AND DISCUSSION

A. Monophasic saturation with dodecane, S_w=0% (aprotic liquid)

The NMRD data obtained in the case of a monophasic saturation of carbonate rocks with dodecane is shown on Figure 3. At each frequency, the peaks of the T_1 distribution are extracted. These peaks are named $T_{1\mu}$ for the micro-porosity and T_{1M} for the macro-porosity. We observe bi-logarithmic frequency dependences of the two relaxation rates $R_{1\mu}=1/T_{1\mu}$ (corresponding to the micro-porosity) and $R_{1M}=1/T_{1M}$ (corresponding to the macro-porosity). Owing to the constant value of the affinity ratio, $R_{1\mu}(\omega_I)=4\ R_{1M}(\omega_I)$, within all the frequency range studied, we successfully rescaled the NMRD data onto a single bi-logarithmic master curve (inset of Figure 3). This rescaling unambiguously proves the existence of a unique relaxation mechanism. In a previous paper[17] we proposed an interpretation and theoretical model for this relaxation mechanism: an intermolecular dipolar relaxation mechanism modulated by translational 2D diffusion of dodecane molecules, diffusing at the vicinity of paramagnetic impurities at the pore surface. This model introduces two correlation times:

- τ_m: the translational correlation time associated with individual molecular jumps in proximity to the surface.
- τ_s: the surface residence time which is limited by the molecular desorption. τ_s controls how long the proton species I and the manganese (Mn^{2+}) ion stay dynamically correlated. It depends on both the strength of the chemical bonds and the reoccurrence of first neighbor interactions induced by the fluid confinement in pores.
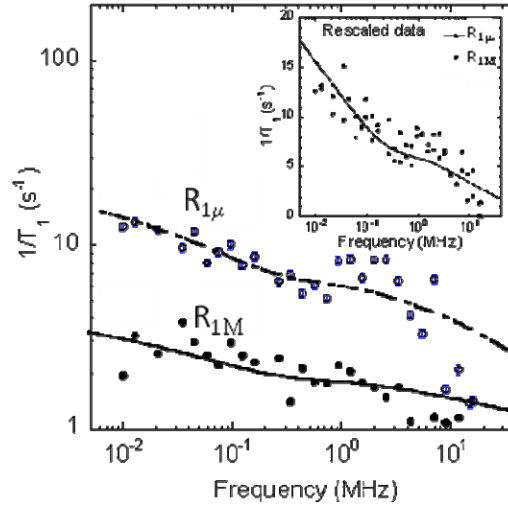
Figure 3 Measured NMRD of carbonate rock saturated with dodecane (S_w=0%). $R_{1\mu}$ and R_{1M} represent the relaxation rates corresponding to micro and macro porosities. The solid lines were obtained from Equation (1) leading to the surface dynamical affinity A=130. The inset shows rescaled data on a single master curve. The fit allowed extracting the following parameters: τ_m=1ns τ_s=130ns.

This model was used to fit the NMRD curves by the following equation:

$$\frac{1}{T_1(\omega_I)} = \frac{1}{T_{1bulk}} + \frac{N_{surface}}{N} \times \frac{\pi}{30} \langle \omega_d^2 \rangle \tau_m \left[3\ln\left(\frac{1+\omega_I^2\tau_m^2}{(\tau_m/\tau_s)^2 + \omega_I^2\tau_m^2} \right) + 7\ln\left(\frac{1+\omega_S^2\tau_m^2}{(\tau_m/\tau_s)^2 + \omega_S^2\tau_m^2} \right) \right] \quad (1)$$

where I refers to the nuclear spin, S refers to the paramagnetic spin, ω is the Larmor frequency, $\langle \omega_d^2 \rangle$ is the quadratic static dipole-dipole frequency and $N_{Surface}/N = \lambda S_P \rho_{liquid}$ is the ratio between the number of liquid molecules diffusing within the thin transient layer λ close to the pore surface and in the bulk (λ is of the order of a few molecular sizes[18]).

Owing to the possible rescaling of NMRD data shown in the inset of Fig. 3, the difference of a factor 4 between the NMRD of $R_{1\mu}$ and R_{1M} is solely a result of the prefactors in Equation (1), namely the specific surface area S_p associated to the different pore sizes.

We introduce a microscopic dynamic surface correlation parameter $A=\tau_s/\tau_m$ (affinity index) in lieu of the more traditional and loosely defined macroscopic wettability indices. The index A represents roughly the average number of diffusing steps of spins I in the vicinity of fixed paramagnetic sites S during the time scale of a NMRD measurement. The larger this index, the more numerous the 2D reencounters are and therefore the more correlated the I-S spins. As such, A reveals the affinity of the fluid to the pore surface, i.e., the microscopic wettability.

B. Monophasic saturation with brine, S_w=100% (protic liquid)

The NMRD data obtained in fully brine-saturated carbonate rocks is shown on Figure 4. Here again, we observe two relaxation rates $R_{1\mu}$ and R_{1M}. Owing to the constant value of the affinity ratio, $R_{1\mu}(\omega_I) \sim 8\ R_{1M}(\omega_I)$, within all the frequency range studied, we successfully rescaled the NMRD data in the inset of Figure 4.

The relaxation process at the origin of these NMRD data is the nuclear paramagnetic relaxation of water molecule bonded on the ligand field of the metallic paramagnetic ion at the pore surfaces. In this case, the frequency dependence of T_1 is the sum of two Lorentzian spectral densities at nuclear ω_I and electronic ω_s Larmor frequencies [19, 20]:

$$\frac{1}{T_1(\omega_I)} = \frac{1}{T_{1,bulk}} + \frac{N_{param}}{N} \times \frac{2}{15} \omega_{d,IS}^2 T_{1,elec}(\omega_S)\left[3/\left[1 + \omega_I^2 T_{1,elec}^2(\omega_S)\right] + 7/\left[1 + \omega_S^2 T_{1,elec}^2(\omega_S)\right]\right] \quad (2)$$

Where $\omega_{d,IS}^2$ is the quadratic dipole-dipole frequency, $T_{1,elec}(\omega_S)$ is the electronic relaxation time and where $N_{param}/N = \left(\lambda S_P \rho_{liquid}\right)\delta^2 \sigma_S f << N_S/N$ is the ratio between the number of liquid molecules bonded to the paramagnetic sites at the surface and in the bulk (δ=0.3 nm is the mean molecular size of water and f is a geometrical factor that takes into account the increase of accessibility of water to the paramagnetic relaxation sink on the very convoluted surface of carbonate rocks).

In this case, there is no need to define a wettabiltiy index: water is wetting the rock. In fact, for a given water molecule to be trapped in the ligand field of a paramagnetic ion at the rock surface, this molecule has to have access to the rock surface *i.e.* water has to wet the rock surface.
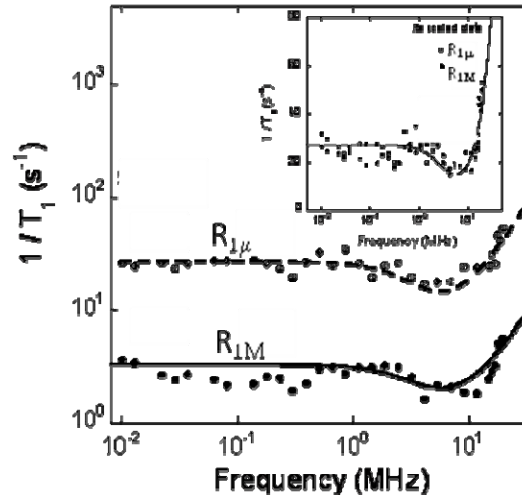

Figure 4 Measured NMRD of carbonate rock saturated with 50kppm NaCl brine (S_w=100%). $R_{1\mu}$ and R_{1M} represent the relaxation rates corresponding to micro and macro porosities. The solid lines were obtained from Equation (2). The inset shows rescaled data on a single master curve.

C. Diphasic saturation with dodecane and brine, S_{wirr} (aprotic and protic liquids)

The NMRD data obtained in the case of a diphasic mixture saturating the carbonate rocks with both dodecane and brine is shown on Figure 5. The relaxation rates of the mixture (large full dots) are compared with the rates $R_{1\mu}$ and R_{1M} (small empty dots) obtained with monophasic saturations of dodecane (S_w=0%, data taken from Figure 3) and water (S_w=100%, data taken from Figure 4), respectively. Here, R_{1M} has the typical NMRD signature of dodecane in large pores (Figure 3), whereas $R_{1\mu}$ exhibits the typical NMRD signature of brine in small pores (Figure 4).

These results thus reveal a clear identification of the nature of the liquids saturating the dual porosity of carbonate rock: water fills and wets the small pores, dodecane is located in the macro-porosity but is not or weakly wetting. Because we saturated the cores with water first, it is indeed expected that water preferably fills the small pores and dodecane the large ones. However, in a general case of native states samples where there is no a priori knowledge of preferred wettability the proposed methodology would allow to identify the wetting fluid for each pore type.

At each frequency, a T_1 distribution is obtained, integrating this distribution gives a water saturation. The water saturation obtained from each measurement is shown on Figure 6 for the corresponding frequencies. Due to signal to noise constraints in the NMR system, the resulting saturation is scattered. It is important to notice that no systematic bias is observed and that a mean water saturation can be derived from all the measurements (at different frequencies): S_{wirr}=20%.
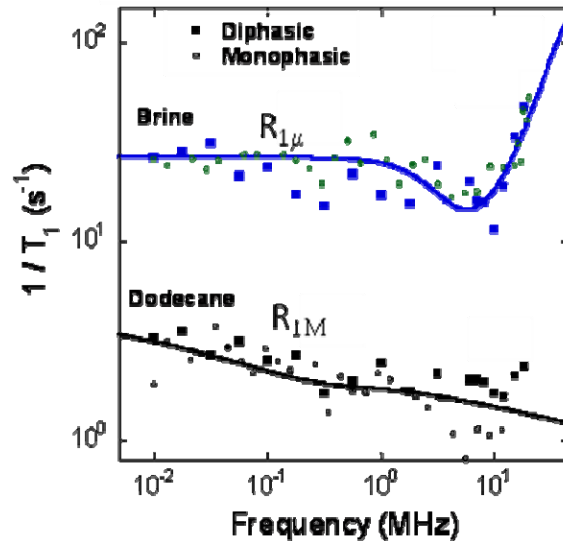
Figure 5 Measured NMRD of carbonate rock saturated with both dodecane and 50 kppm NaCl brine (S_{wirr} in large full dots). The data for water in micro-porosity and dodecane in macro-porosity (from monophasic saturation) is plotted in small empty dots. The black solid line was obtained from Equations (1) for dodecane, leading to the surface dynamical affinity A=130. The blue solid line was obtained from Equation (2) for water.
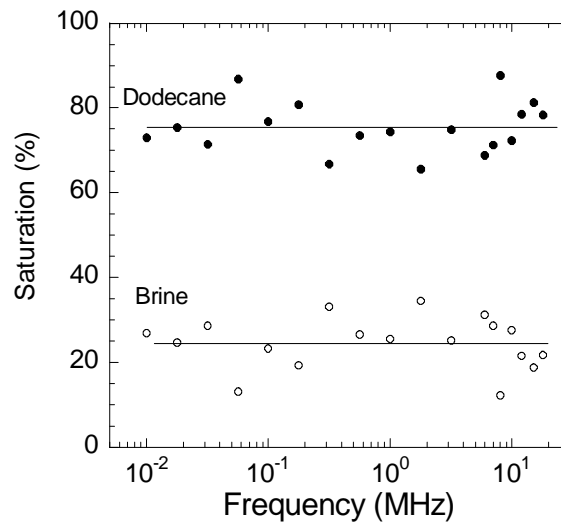

Figure 6 Saturation (%) of brine obtained by integration of the bimodal distribution at each frequency.

CONCLUSION

We present a new *in situ* method for estimating wettability of oil and brine at the pore surfaces of rocks. It is based on nuclear magnetic relaxation dispersion (NMRD): the measurement of proton spin-lattice relaxation rates as a function of magnetic field strength or nuclear Larmor frequency. We introduce a microscopic dynamical surface

affinity index which measures the dynamical correlation (*i.e.* the microscopic wettability) between the diffusive fluid and the fixed relaxation sources at the pore surfaces. Future work will include real crude oils, for which the NMR dispersion also carries information about the dynamics of the macromolecules.

This method has been applied to carbonate rocks representing about two thirds of the world's oil known reserves. The results obtained on carbonates of bimodal porosity saturated with an oil/brine mixture allow estimating the saturation and wettability of each pore type (micro vs macro porosity).

ACKNOWLEDGEMENTS

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