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Microscopic Wettability of Carbonate Rocks: a Proton Field Cycling NMR Approach

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Abstract

Nuclear Magnetic Relaxation Dispersion (NMRD) is strongly sensitive to the microscopic wettability of oil and brine bearing carbonate rocks. Exploring a very large range of low frequency enables isolating the typical NMRD dispersion features, $1/T_{1\mathrm{Surf}}$, associated to the different processes of molecular surface dynamics. This allows a separation of the surface and bulk microdynamics of oil and water even for a biphasic saturation of petroleum rocks. Several surface dynamical parameters were determined and related to the concept of microscopic wettability of oil and water in porous media.

Keywords

Wettability, NMRD, carbonate, porosity, saturation, oil.

1. Introduction

Wettability of oil/water liquids mixtures measured in porous rocks is one of the most critical parameters for oil recovery with porosity, saturation and permeability. Roughly, wettability is the ability of a fluid to spread over or "wets" a solid surface. It influences saturation, pore distribution and flow of fluids in porous materials. Nowadays, wettability is mainly measured by macroscopic measurements such as contact angles and capillary pressure curves (Amott and USBM methods).

In this article, we qualitatively introduce the main concepts of microscopic wettability, interpreting the Nuclear Magnetic Relaxation Dispersion (NMRD) data of a liquid embedded in pores, and taking into account the dynamical and chemical properties at a microscopic level [1-3]. Quantitative results will be presented in the near future.

2. A new dimension in Nuclear Magnetic Relaxation: the frequency dependence of the Spin-lattice T_1 distribution

The magnetic field dependence of the longitudinal nuclear spin relaxation rate $1/T_1$ (NMRD) is a rich source of dynamical information. Varying the magnetic field changes the

Larmor frequency, and thus, the fluctuations to which the nuclear spin relaxation is sensitive. Furthermore, the magnetic field dependence of the spin-lattice relaxation rate, $1/T_1$, provides a good test of the theories that relate the measurement to the microdynamical behavior of the liquid. This is especially true in spatially confined systems where the effects of reduced dimensionality may force more frequent reencounters between spin-bearing bulk molecules and pore surface.

Fig. 1 below shows modifications of the observed distributions of T_1 in a carbonate rock fully saturated with aprotic dodecane where there is no chemical exchange between the dodecane protons and the functional groups on the pore surface of a carbonate rock when varying Larmor frequency f. Varying this frequency changes the lengthscale $\ell_D = \sqrt{6D/2\pi f}$ experiences by the diffusing molecules on the time scale of the NMR experiment. The narrowing of the T_1 distribution around 1 s at high frequency shows that the effective relaxing modes at large frequency are only due to the fast bulk motions. On the contrary, the broadening of the T_1 distribution at low frequency is due to the participation of the surface relaxing modes.

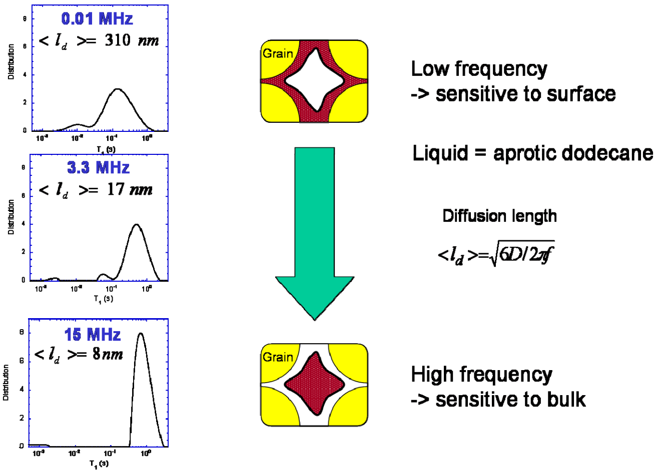

Fig. 1: Measured proton spin lattice relaxation T_1 distribution at different frequencies.

3. Direct probing of surface dynamics and wettability by proton field-cycling relaxometry $T_1(\omega_0)$

We consider the limit of fast-diffusion of liquid molecules (protic or aprotic) at the proximity of paramagnetic centers of a carbonate surface where the biphasic fast exchange model between surface and bulk molecules is valid. The presence of these ions is evidenced by Electron Spin Resonance experiments (Fig. 3b). The overall relaxation rate is then a linear combination of a bulk and a surface term: the former is the relaxation rate of the bulk $1/T_{1,\text{bulk}}$, the later is either due to, $1/T_{1,2D}(\omega_0)$, the relaxation rate of an aprotic molecule diffusing at the proximity of the surface (Fig. 2a) or $1/T_{1,\text{param}}(\omega_0)$, the relaxation rate of a protic molecule chemically bonded to a paramagnetic ion site (Fig. 2b).

$$\frac{1}{T_1(\omega_0)} = \frac{1}{T_{1,\text{bulk}}} + \frac{N_S}{N}\frac{1}{T_{1,2D}(\omega_0)} + \frac{N_{\text{param}}}{N}\frac{1}{T_{1,\text{param}}(\omega_0)} \quad . \tag{1}$$

Here N_S/N and N_{param}/N are the ratio of the number of aprotic (respectively protic) liquid molecules diffusing at the proximity of the surface (respectively bonded to the paramagnetic sink at the surface) over the number of bulk liquid molecules.

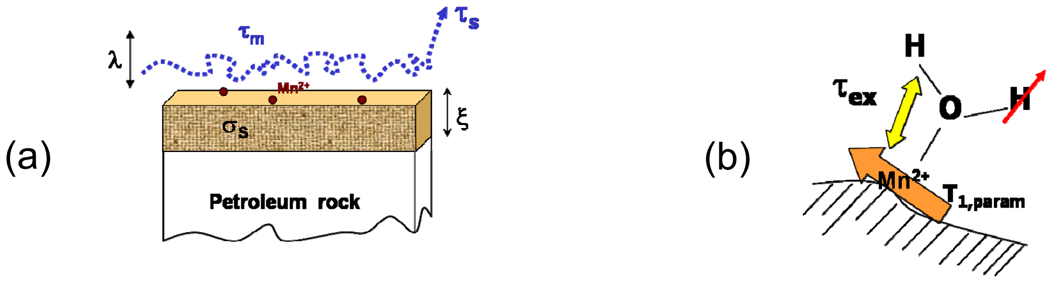

Fig. 2: (a) Schematic diagram representing the situation of an aprotic liquid (ex: alkane) diffusing at the solid-liquid interface by a 2D diffusion relaxation process. The dashed line is a schematic representation of the Brownian trajectory of aprotic liquid molecule at proximity of a carbonate pore surface near ion impurities. (b) Schematic diagram representing the situation of a protic liquid molecule (ex: water) chemically bound to a paramagnetic ion site (ex: Mn^{2+}) of a carbonate pore surface (orange and red arrows represent respectively the spins of Mn^{2+} and H). The relaxation process is a nuclear paramagnetic relaxation process.

In case of monophasic saturation, we qualitatively observe the dispersion curves shown in Fig. 3a below. For a carbonate rock filled with an aprotic solvent, we observe a constant relaxation rate value at low frequency and a peak at high frequency. For a carbonate rock filled with a protic solvent, we observe a slowly decreasing curve from low to high Larmor frequencies. This could be an interesting way to separate both contributions when oil and water are embedded in the same porous medium.

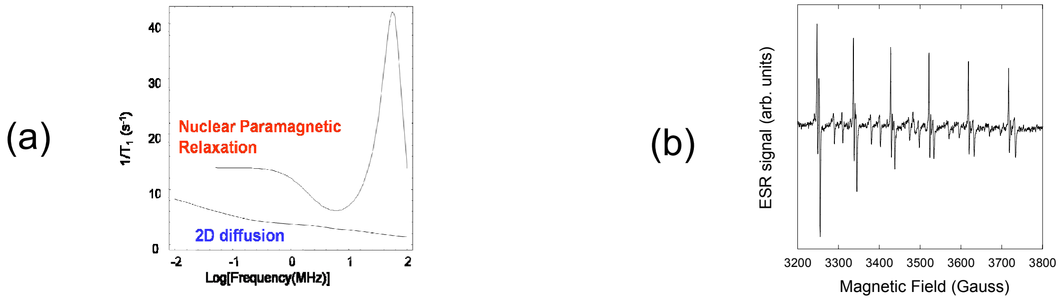

Fig. 3: (a) Typical examples of theoretical proton spin-lattice relaxation rates as function of the proton Larmor frequency for aprotic molecules following a 2D diffusion relaxation model and protic molecules following a Nuclear Paramagnetic Relaxation model on carbonate rock. (b) Electron spin resonance spectrum measured at room temperature on a carbonate rock. The six-peak hyperfine structure is typical of isolated Mn^{2+} paramagnetic ions (S=5/2) (see reference [4]).

4. Conclusion

A new approach aimed to better understanding microscopic wettability is proposed. Surface dynamical parameters allow us to describe the contributions of liquids embedded in petroleum rocks. Through this new parameters, a direct quantitative microscopic wettability can be evaluated which is more local than the so-called macroscopic wettability parameters (Contact Angles, Amott and USBM indexes). In the petroleum rocks, two limiting cases are encountered: a 2D diffusion model for aprotic liquids and/or Nuclear Paramagnetic relaxation for protic liquids bounded to paramagnetic sites at the pore surface.

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