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Characterization of shales using T_1 – T_2 NMR maps

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ABSTRACT

Nuclear Magnetic Resonance (NMR) relaxation methods are key techniques for evaluating shales, from both cores and logging data. First, very small pore sizes, down to nano-meter length scales, can be detected and quantified if the NMR tool has the ability to measure relaxation times in the range [0.1–1 ms], and second the different proton populations (water, oil, gas, and kerogen) can be distinguished using 2D T_1 – T_2 maps. We use a NMR instrument working at a higher frequency (23 MHz) that yields a much higher sensitivity than standard plug-size benchtop apparatus. In this work, we show the position of each proton population in this map: hydroxyls from the clay ($T_2 < 0.1$ ms, $10 < T_1/T_2 < 100$), water ($T_1/T_2 \sim 2$), and in certain situations kerogen ($10 < T_1/T_2 < 100$). Methane can be clearly distinguished with $T_1/T_2 \sim 10$. One can use the T_1/T_2 contrast to separate the different contributions. As an additional characterization, deuterium tracer techniques are used to quantify the connectivity of the pore network system, providing a measure of tortuosity. Due to high diffusivity, the T_2 distribution is affected by diffusive pore coupling and therefore, pores smaller than about 800 nm are theoretically all gathered at a single relaxation time.

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1. Introduction

The characterization of gas shales remains a challenge and cannot be performed using conventional petrophysical techniques. Even for basic properties such as porosity and permeability, specialized protocols and instrumentation are required. Standard measurement of pore sizes as well as advanced microscopic techniques (e.g. Scanning Electronic Microscopy coupled with Focused Ion Beam) have shown the existence of very small pores down to the nanometer scale (Josh et al., 2012; Loucks et al., 2009). In this context, NMR relaxation techniques become appropriate because small quantity of water or gas can be detected in such small pore sizes. For example in smectites having sheet-like pores, it is possible with an appropriate NMR instrument to detect and quantify the interlayer water content even when the pore width is only one or two water layers thick (Fleury et al., 2013). In such model systems, simple 1D NMR measurement are sufficient. However, for complex porous media such as shales, standard T_2 relaxation time distributions provide limited information (Sigal and Odusina, 2011). Indeed, there is a potential overlapping of the signature of the different proton populations originating from water, oil or gas and organic matter. Multidimensional NMR techniques improve the separation of the different proton contributions (Washburn and Birdwell, 2013; Rylander et al., 2013;

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http://dx.doi.org/10.1016/j.petrol.2015.11.006 0920-4105/© 2015 Elsevier B.V. All rights reserved. Kausik et al., 2011). The first well known technique used in conventional hydrocarbon systems is to use the diffusion contrast between liquids and/or gas in a D– T_2 map (Hürlimann and Venkataramanan, 2002). However, in shales, it has various advantages and drawbacks (Kausik et al., 2011). Another method is to use the T_1/T_2 contrast originating from the different intra- and inter-molecular NMR interactions (Washburn and Birdwell, 2013; Daigle et al., 2014; Korb et al., 2014). Recently, this contrast (i.e. T_1 – T_2 maps) has been used in conjunction with geochemical data (Birdwell and Washburn, 2015). We develop this approach in the present work and propose to locate all proton populations in a T_1 – T_2 map at different saturation conditions

We first recall the NMR relaxation theory for different proton populations in the context of nano-porous media, for liquid, gas, and also for solids. The NMR instrument and the methane high pressure cell are then described. In order to identify the different signatures, we studied kerogen isolated from different shales, and shales in different saturation states. We finally propose a T_1 – T_2 fluid mapping based on our observations.

2. NMR theory

2.1. Relaxation of water in nanoporous media

For water in porous media, the dominant relaxation process is the result of interactions between the spins carried by molecules exploring the pore space by diffusion, and the electronic spins at



Fig. 1. Graphical representation of Eq. (1) with two surface relaxivities covering the range of usual values.

the solid surface (Korringa et al., 1962). These interactions are effective only close to the surface in a layer of thickness ε_S (< 0.5 nm) and are characterized by a decay time constant T_S (i.e. a spin carried by a molecule diffusing only at the solid surface will be characterized by the relaxation time T_S). Similarly, far from the surface, the intra- and inter-molecular interactions produce a much longer decay time constant T_B . In a pore, let us define two regions: a bulk volume with a volume fraction f_b , and a surface layer with a volume fraction f_s where $f_b+f_s=1$. Due to molecular diffusion, there is an exchange between the surface and bulk volumes with a typical exchange time τ_{ex} . In the so-called fast exchange regime (τ_{ex} «T) or fast diffusion regime, the measured relaxation rate 1/T is an average of the bulk and surface relaxation rates weighted by the volume fraction:

$$\frac{1}{T_2} = \frac{f_s}{T_{2s}} + \frac{f_B}{T_{2B}} \approx \frac{S_p}{V_p} \frac{\varepsilon_S}{T_{2s}} + \frac{1}{T_{2B}}$$
(1)

We show here the transverse relaxation time T_2 but the equation is also valid for the longitudinal relaxation T_1 . The above equation yields the well-known dependence with the surface to volume ratio (Sp/Vp) of a single (closed) pore (Fig. 1). Note here that we neglect an additional gradient term. The strength of interactions with the solid is usually expressed as the surface relaxivity ρ_2 or relaxation velocity at the pore surface defined as ρ_2 $=\varepsilon_{\rm S}/T_{\rm 2S}$. Using typical values of surface relaxivities between 1 and 10 μ m/s, the relaxation time of water located in a sheet-like pore of thickness 1 nm for example (hence V/S=1 nm) will be in the range 0.1-1 ms. Such values are easily accessible to most commercial spectrometers and to some in-situ logging instruments. Therefore, NMR has the capability for detecting and quantifying the mass of water present in very small pores. However, there are two important issues. First, in nanopores, the measured relaxation time may not give an indication of the pore size (or thickness for a sheet) according to Eq. (1) because the length scale of the NMR interactions are comparable to the thickness (a few nanometer compared to ε_{s} ~0.5 nm). This is indeed the case in the interlayer space of smectites (Fleury et al., 2013) in which Eq. (1) has been found not to be valid. Second, the diffusive exchange between pores (Fleury and Soualem, 2009) may lead to a T_2 distribution that does not represent a pore size distribution (a distribution of V/S) but an average volume to an average surface ratio. We will discuss this effect further when presenting diffusion experiments. Note also that a consequence of the fast exchange model described above is that the measured relaxation time cannot be smaller than

 T_{2S} . Hence, if smaller values are detected, an another model must be used.

2.2. Relaxation of pseudo-solid material

Very short relaxation times (< 0.1 ms or less than T_{2S}) are produced by processes related to the mobility of protons. The theoretical framework is the so-called Bloembergen–Purcell– Pound (BPP) model (Abragam, 1961) relating the longitudinal and transverse relaxation times to the correlation time τ of the dipolar interactions:

$$\frac{1}{T_1} = 2C \left[\frac{2\tau}{1+\omega^2 \tau^2} + \frac{8\tau}{1+4\omega^2 \tau^2} \right]
\frac{1}{T_2} = C \left[6\tau + \frac{10\tau}{1+\omega^2 \tau^2} + \frac{4\tau}{1+4\omega^2 \tau^2} \right]$$
(2)

where ω is the Larmor frequency and *C* is a constant. A single value of correlation time τ is assumed here for simplicity. For fast isotropic molecular tumbling, as is the case in the above mentioned fast diffusion model, $\omega \tau \ll 1$ and $T_1/T_2 = 1$ (in fact, due to the heteronuclear dipole–dipole interactions with the electronic spins, we have $T_1/T_2 \sim 2$). When molecules are not mobile, the correlation time is several orders of magnitude larger, $\omega \tau \gg 1$, and the ratio $T_1/T_2 \sim \omega_2 \tau^2$ is much larger than 1 and depends on the Larmor frequency. For example for ice, $T_1 = 70$ s and $T_2 = 8 \,\mu$ s at 30 MHz (Weglarz, 1997). A large T_1/T_2 ratio is seen in many materials of interest for the petroleum industry: heavy oil, coal, and organic matter.

2.3. Relaxation of methane

For bulk methane in the gas phase (i.e. at temperature of interest here), the longitudinal and transverse relaxation mechanisms are dominated by spin rotation (Oosting and Trappeniers, 1971), in contrast with intra and intermolecular interaction occurring in simple liquids (or in liquid methane). T_1 and T_2 are still equal and governed by Eq. (2), but they increase with pressure and are in the range [500-5000 ms] for methane pressure between 25 and 200 bar. More interestingly in rock core materials (Straley, 1997) or for adsorbed gas in nanoporous material (Riehl, 1972) at low temperature (100 K), the T_1/T_2 ratio of methane increases considerably (~10 or more). This is due to anisotropic rotational motions at the surface, with the existence of two correlation times. T_1 will then be sensitive to the fast correlation time, while T_2 to the slow one. In a partially saturated porous media, relaxation of methane still occurs although weaker despite water wetting the surface (Straley, 1997).

3. Materials and NMR methods

3.1. NMR methods

The experiments have been carried out on a Maran Ultra proton spectrometer from Oxford Instruments with a proton Larmor frequency of 23.7 MHz. Standard free induction decay (FID) and transverse magnetization CPMG decay curves were measured. When needed, we used a modified CPMG sequence in which the inter-echo time is initially set at the lowest possible and then increased gradually up to 100 μ s or more in order to catch at the same time very short and very long relaxation times. 2D T_1 – T_2 maps were determined using an inversion recovery sequence followed by a CPMG sequence:

 $P_{180} - \tau_1 - P_{90} - (\tau - P_{180} - \text{echo} -)_n$

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