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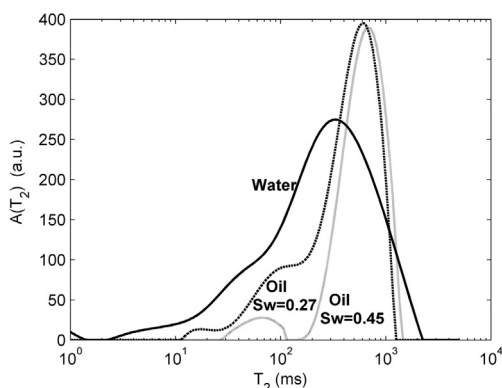
Measurement of interfacial area from NMR time dependent diffusion and relaxation measurements



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GRAPHICAL ABSTRACT



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ABSTRACT

The interfacial area between two immiscible phases in porous media is an important parameter for describing and predicting 2 phase flow. Although present in several models, experimental investigations are sparse due to the lack of appropriate measurement techniques. We propose two NMR techniques for the measurement of oil-water interfacial area: (i) a time dependent NMR diffusion technique applicable in static conditions, similar to those used for the measurement of the solid specific surface of a porous media, and (ii) a fast relaxation technique applicable in dynamic conditions while flowing, based on an interfacial relaxation mechanism induced by the inclusion of paramagnetic salts in the water phase. For dodecane relaxing on doped water, we found an oil interfacial relaxivity of $1.8 \mu\text{m/s}$, large enough to permit the measurement of specific interfacial surface as small as $1000 \text{ cm}^2/\text{cm}^3$. We demonstrate both NMR techniques in drainage followed by imbibition, in a model porous media with a narrow pore size distribution. While flowing, we observe that the interfacial area is larger in imbibition than in drainage, implying a different organization of the oil phase. In a carbonate sample with a wide pore size distribution, we evidence the gradual invasion of the smallest pores as the oil-water pressure difference is increased.

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1. Introduction

Taking into account the interfacial area may be a new way of understanding and predicting two-phase flow in porous media,

especially in the context of enhanced oil recovery where predicting the behavior of trapped phases is crucial. For example, capillary effects are intimately linked to interfacial phenomena from a thermo-dynamical point of view [1–3]. During forced displacement

of water by oil in a water-wet porous media, a fraction of the energy injected into the system is dissipated due to the multiple restrictions in the pore network system. The other fraction, reversible, is used to create an interfacial area between the two phases. These thermo-dynamical aspects have been considered as early as 1970 [1]; today, based on recent high resolution 3D tomography, it is estimated that about 40% of the energy is reversible [4,5].

Despite its importance, the interfacial area parameter has not been really studied due to measurement difficulties. For air-water systems in the context of hydrogeology, tracer techniques have been used successfully [6–11] but they require a flow of the tracer through the porous media; therefore, they can only measure the interfacial area of connected gas phases (and not trapped). In a more general way, recent progress in micro-tomography both in terms of resolution and acquisition speed [5,12] allows the determination of interfacial area [13–15].

We will first recall two NMR techniques that can be used for the measurement of solid and interfacial area: the time dependent diffusion and relaxation techniques. Then we first describe the results obtained on a reference material to show that the diffusion and gas adsorption techniques give similar values. Then we evidence and calibrate an interfacial relaxivity mechanism allowing the measurement of interfacial area from simple and fast NMR transverse T_2 relaxation. We use this new observation to determine the variation of interfacial area during flooding in an artificial porous media (Aerolith). Then, we describe qualitatively the distribution of the oil phase in a carbonate sample with a large pore size distribution.

2. Principles of surface area measurement

We explain below how surface area can be measured from NMR data. The first technique uses the reduction of diffusion coefficient due to the confinement, at diffusion length shorter than the length scale of the investigated porous structure. The second uses a measure of the magnetization decay to deduce the surface to volume of the investigated liquid phase.

2.1. Time dependent diffusion measurement

It is well known that the time dependent diffusion curve allows determining the total surface to total volume S_T/V_T of a fluid saturating a porous media. Indeed, in the presence of restrictions due to the solid, there is a decrease of the effective diffusivity $D(t)$ depending on the diffusion times that can be controlled experimentally. As shown by Mitra et al. [16], the normalized effective diffusivity $D_N(t)$ is linked to the total surface to volume S_T/V_T according to:

$$D_N(t) = \frac{D(t)}{D_m} = 1 - \frac{4}{9\sqrt{\pi}} \frac{S_T}{V_T} \sqrt{D_m t} + O(D_m t) \quad (1)$$

where D_m is the molecular diffusion of the liquid saturating the porous media. It means that initially only a small fraction of the diffusive molecules close to the pore walls are influenced by the solid. This relation is mostly independent of surface relaxation when surface relaxivity is low enough, which is the case for most porous media. When measuring the time dependent effective diffusivity at short times, one can in principle determine the ratio S_T/V_T . At long diffusion times, the molecules may travel over distances larger than one pore length and the diffusivity becomes independent of time. Then, the asymptotic value α of the effective diffusion coefficient depends essentially on the porosity Φ of the porous medium. In practice, the measurement of diffusivity at very short and very long diffusion times is not an easy task and the slope S_T/V_T is better estimated using all data at intermediate times. This requires an

interpolation function described below. Rewriting Eq. (1) using the one dimensional free diffusion length $L_D = \sqrt{2D\Delta}$, we obtain:

$$D_N(L_D) = 1 - C \frac{S_T}{V_T} L_D + O(L_D^2) \quad \text{and} \quad C = \frac{4}{9\sqrt{2\pi}} \cong 0.177 \quad (2)$$

With a given slope at $L_D = 0$ and a given asymptotic value α for $L_D \rightarrow \infty$, the general shape of D_N may be of the form:

$$D_N(L_D) = 1 - (1 - \alpha) \frac{f(L_D)}{1 - \alpha + f(L_D)} \quad (3)$$

where f is an arbitrary interpolating function following the conditions:

$$\frac{\partial f}{\partial L_D}(L_D = 0) = C \frac{S_T}{V_T} \quad \text{and} \quad f(L_D \rightarrow \infty) = \alpha \quad (4)$$

For example, the function f can be a polynomial of order 2:

$$f(L_D) = C \frac{L_D^2}{L_c^2} + \left(\frac{L_D}{L_c}\right)^2 \quad L_c = \frac{V_T}{S_T} \quad (5)$$

where L_c can be interpreted as a characteristic length scale of the distance between grains [17]. Introducing Eq. (5) in 3 yields:

$$D_N(L_D) = 1 - (1 - \alpha) \frac{C \frac{S_T}{V_T} L_D + \left(\frac{L_D}{L_c}\right)^2}{(1 - \alpha) + C \frac{S_T}{V_T} L_D + \left(\frac{L_D}{L_c}\right)^2} \quad (6)$$

The above function is an alternate way of fitting the diffusion curve compared to the Pade approximation proposed by Mitra et al. [16]. Here the objective is to extract more precisely the slope S_T/V_T at short time as in [18] rather than calculating it directly using the data points at short times as in [19] for example. Surface to volume can also be obtained using relaxation sequences sensitive to diffusion such as the CPMG sequence in the presence of a magnetic gradient [20]. We found however that such method could not be applied on the 20 or 23 MHz instrument used in the present experiment described in this paper due to well-known internal gradient issues [21]. We believe that a lower frequency such as 2 MHz can be appropriate.

The sequence for measuring diffusion coefficients is critical. We found that only sequences comprising bipolar gradients are adequate on our instrument made with permanent magnet [22]. In addition they also reduce the effects of internal gradients as mentioned above. The sequence shown in Fig. 1 gave satisfactory results, i.e. a stable value of diffusion coefficients is obtained on the entire range of diffusion times for a reference fluid such as dodecane. The gradient pulses are centered around the π pulse in order to better compensate for eddy currents. The time δ_1 can also be set to a large value without increasing too much the total time of the sequence when short diffusion times are needed. We calculated the echo attenuation as follows:

$$\ln \left[\frac{M(g, t)}{M(0, t)} \right] = -\gamma^2 D \left[g^2 \delta^2 \left(\Delta' + 2\tau - \frac{1}{3}\delta - \delta_2 \right) + \frac{4}{3} g_0^2 \tau^3 \right] \quad (7)$$

where g_0 is a constant gradient present during the entire sequence to mimic either internal gradient or imperfect gradient offset tuning. M is the measured magnetization, the time intervals are defined in Fig. 1, and the time $t = \Delta' + 2\tau - \delta/3 - \delta_2$. This result is in agreement with the more general calculation made in [23]. In addition, we used a 16 step phase cycling to remove potential spurious echoes [24]. The use of shaped gradients together with a pre-emphasis unit were also critical for the eddy current compensation. Typically, we used $\tau = 2$ ms, $\delta = 1.5$ ms, $\delta_2 = 0.2$ ms and g up to 150 G/cm for measuring water diffusivity. Therefore, the encoding time is 4 ms and the smallest accessible diffusion time t is about 10 ms.

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