Unconsolidated Material Characteristics Obtained by PFGNMR using (two) different Probe Molecules

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Introduction

It is well known that NMR is able to probe the molecular dynamics of fluids confined in porous materials. This ranges from catalytic materials, such as zeolites and certain mesoporous materials, as well as geological materials like clay and sandstone and even biological materials such as wood and meat. The characteristic properties of pore confined molecules generally depend on:

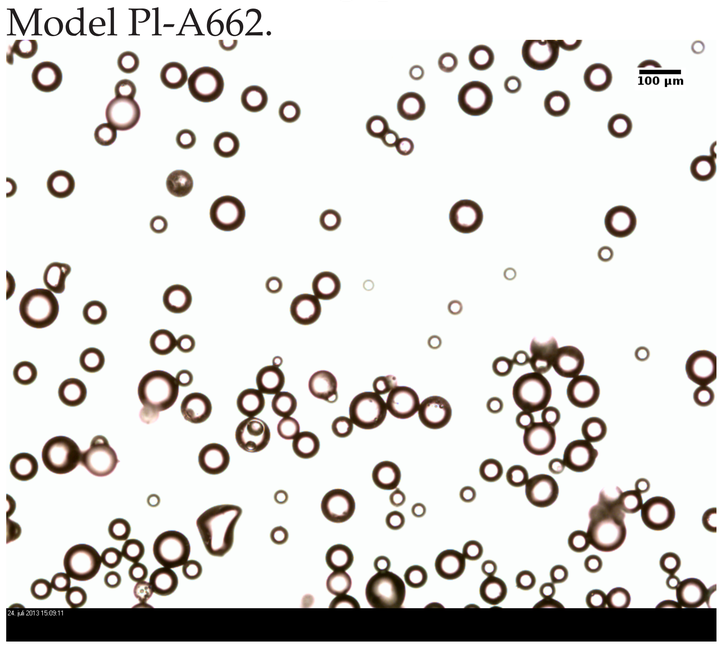
- Temperature, T, and pressure, p.
- Properties of the confined fluid, i.e. molecular dimensions and the fluid - fluid interactions.
- The properties of the porous matrix. The most profound parameters are the surface-to-volume ratio, S/V, the pore dimension (size) and the pore connectivity, or *tortuosity*, Γ.
- The interaction strength between the fluid and the matrix surface, ρ. This is usually referred to as the *surface relaxivity*.

References

[1] P. P. Mitra, P. N. Sen and L. M. Schwartz: *Short-time behavior of the diffusion coefficient as a geometrical probe of porous media. Physical Review B*, **47**, 8565-8574 (1993)
[2] S. D. Sentura and J. D. Robinson: *Nuclear spin-lattice relaxation of liquids confined in porous solids*. SPE, 10, 237-244 (1970).

Illustration

The bar equals 100 μm. The picture was taken using an Olympus BX51TF microscope with PixeLINK Megapixel FireWire Camera Model Pl-A662.



Theory and method

The effective self-diffusion coefficient $D(t_d)$ of a fluid confined within a porous material may be obtained by Pulsed Field Gradient Stimulated Echo (PGSTE) NMR using, for instance, a 13-intervall pulse sequence, where t_d represents the diffusion time. It is well known that the short-term behavior of $D(t_d)$ evolves according to equation 1 [1]:

$$D(t_d) = -\frac{4}{9\sqrt{\pi}} D_0^{3/2} \frac{S}{V} \sqrt{t_d} + D_0 \tag{1}$$

where D_0 is the short-time diffusion coefficient. The parameters D_0 and S/V are determined by fitting the measured echo intensities to equation 1. The *tortuosity factor* Γ, is defined as $\Gamma = D_0/D_\infty$ where D_∞ is the limiting diffusion as t_d becomes large and is a parameter describing the porous matrix (see figure in Results).
The remaining parameters presented in the introduction can then be estimated from equation 2;

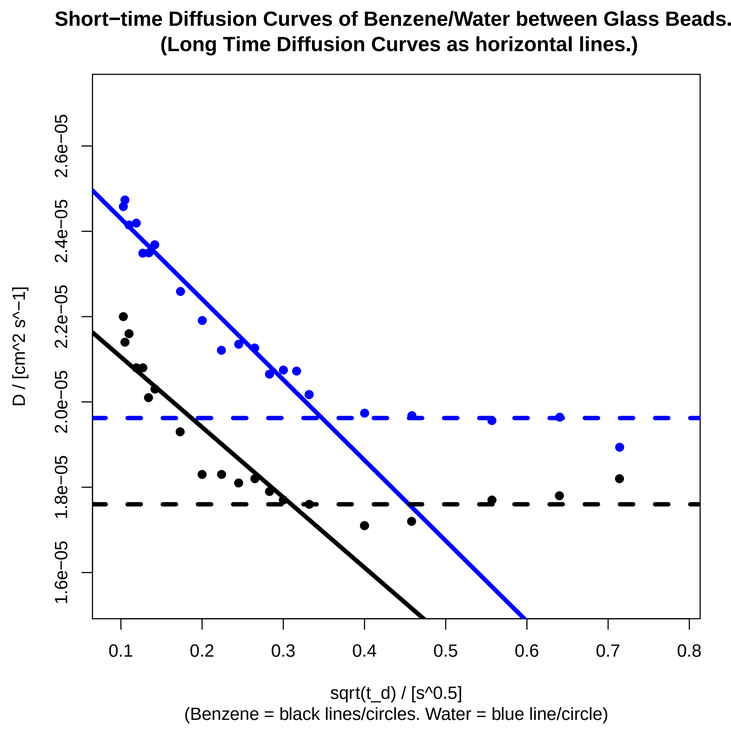
$$\frac{1}{T_{1c}} = \frac{1}{T_{1b}} + \rho \frac{S}{V} \tag{2}$$

where T_{1c} is the spin-lattice relaxation time for the fluid *confined* within the porous matrix and T_{1b} is the spin-lattice relaxation time for the *bulk* fluid [2]. These spin-lattice relaxation times are obtained from two separate Inversion Recovery-experiments, one on a bulk fluid/porous-matrix system and the other on the pure bulk fluid.

Results

All experiments were performed on a low field NMR Maran instrument operating at 20 MHz (proton frequency). The samples were prepared by mixing glass beads (see Illustration) and degassed liquid in an NMR tube which was filled with nitrogen gas and subsequently sealed (closed system). The samples were equilibrated at room temperature for at least one week before performing the NMR measurements at 35 $^\circ C$ (see figure). The derived parameters $S/V, \Gamma, \rho$ and R are summarized in table 1 where R represents a hypothetical spherical pore radius within the glass beads matrix as estimated from the relation: $S/V = 3/R$.
The plot shows the diffusion coefficient (D) vs. $\sqrt{t_d}$ for short and long t_d.

Parameter	Unit	Benzene	Water
S/V	cm^{-1}	$1.3 \cdot 10^3$	$1.1 \cdot 10^3$
Γ	$-$	1.5	1.5
ρ	cms^{-1}	4.9	5.4
R	μm	23	29



Conclusions

The pore characteristics ($S/V, \Gamma$ and R) of an unconsolidated porous matrix (the open network formed between glass beads) were derived from a combined use of NMR self-diffusion and spin-lattice relaxation time measurements on pore confined water and benzene, respectively. Within experimental error, these pore characteristics were found to be independent of the probe molecule (water/benzene) used. It should be noted that the method described by no means requires a high field instrument for this characterization.

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