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Nuclear Magnetic Resonance Studies of Time Dependent Diffusion in Partially Filled Pores

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1. Introduction

NMR microscopy of silica glasses with micrometer pores (Vitrapor#5; pores diameter d=1µm) partially filled with water or cyclohexane reveal heterogeneous distributions of the liquid on a length scale much longer than the pore dimension (Fig.1). This heterogeneity, which is not observed in MRI of saturated samples, is attributed to the spatial variation of the granular microstructure visible in electron micrographs. As a consequence of the inhomogeneous filling degree, the effective transverse relaxation time varies, which in turn leads to NMR imaging contrasts that are observed in Fig.1.

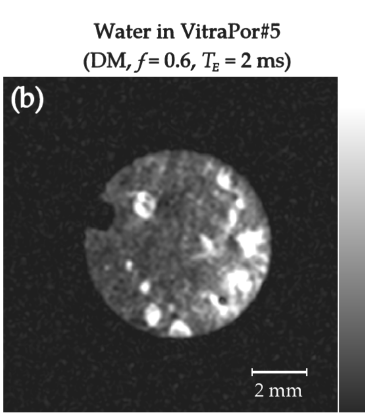

Fig.1: The NMR micrograph of a partially filled VitraPor#5 sample. The image was obtained with the aid of a two-dimensional slice selective sequence (2DFT; slice width 1 mm).

Since the spatial distribution of the transverse relaxation time prevents reliable measurements with the standard pulsed gradient stimulated echo technique (PGStE) [1], a combination of the fringe field stimulated echo method (FFStE) on the one hand and the magnetization grid rotating frame imaging technique (MAGROFI) on the other was employed for time dependent diffusion measurements [2].

Four decades of the diffusion time from 100 µs to 1 s can be covered using these techniques. The data were compared with Monte Carlo simulations of a model structure showing a qualitatively equivalent behavior in the common time window. The contribution of the vapor phase to the effective diffusion coefficient was thus monitored for different diffusion times.

2. Experimental results

The effective water diffusion coefficient was measured in VitraPor#5 for different filling degrees. The data are plotted in Fig. 2 for diffusion times between 100 µs and 1 s. As far as investigated in this study, the values decrease with increasing filling factor as a consequence of the decreasing vapor phase contribution [3]. The time dependence of the diffusion coefficient of water in partially filled porous glass also reflects the obstruction by the pore space tortuosity.

In order to perform reliable time dependent diffusion studies the fringe field stimulated echo (FFStE) technique for relatively short diffusion times (100 μs ÷ 10ms), and the magnetization grid rotating frame imaging (MAGROFI) variant for long diffusion times (10ms÷1s) was implemented [3]. The former is insensitive to internal gradients due to the large external field gradient employed (22 T/m in our investigations), the latter because of the use of gradients of the radio frequency amplitude, which are practically not affected by inhomogeneities of the magnetic susceptibility.

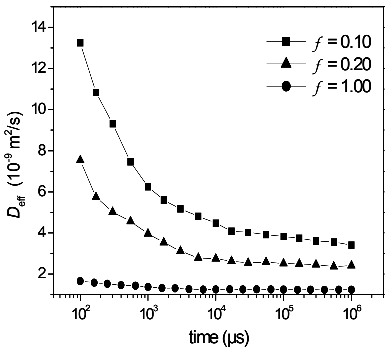

Fig.2. Effective (= overall average) diffusion coefficient versus diffusion time for different filling factors. The data were measured by a combination of FFStE and MAGROFI techniques.

3. Conclusion

It is often assumed that the correlation length of a porous medium is of the order of a few pore diameters. Here, it was possible to visualize microscopic heterogeneities in the structure of the VitraPor#5 sample partially filled with liquids. These images are an indication for much longer correlation lengths.

Another finding of our work is that the diffusion coefficients of liquids in partially filled porous glasses start close to their bulk values in the short time limit corresponding to a few molecular diffusion steps. When the root mean squared displacement approaches the mean pore size, a maximum is reached indicating a significant contribution of the vapor phase to the effective diffusion coefficient via exchange between the two phases (liquid and vapor). At longer diffusion times, the obstruction by the tortuosity of the pore space comes into play and the effective diffusion coefficient decays until a reduced effective value close to the bulk liquid value is reached.

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