NMR relaxation dispersion of polar and non-polar molecules confined inside porous media with controlled amount of magnetic impurities

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Abstract

Natural or manufactured porous media (e.g. porous rocks, soils, concrete, catalytically active materials) may intrinsically contain heterogeneous and uncontrolled amounts of paramagnetic or ferromagnetic impurities inside their solid matrix which generate internal gradients [1]. The interpretation of NMR relaxometry data on such samples is cumbersome, and the control of magnetic impurities becomes an essential issue. That is why, in the present work, porous ceramics containing a controlled and increased amount of iron oxide as magnetic impurities are manufactured, and the dynamics of water (polar) and cyclohexane (nonpolar) molecules within the pore space is investigated. The porous ceramics were fabricated using the conventional method of preparation from powders which are first dry pressed and then subject to thermal treatment [2]. The mixing formula corresponds to a traditional ceramic, in particular: 60% kaolin, having the grain size between 63-80 µm, 30% feldspar and 10% quartz sand, with a grain size of 80-120 µm. The reason for choosing different grading is to obtain a better compaction, and thus to reduce the average pore size. Six samples with increasing concentration of Fe_2O_3 were prepared by adding 0, 2, 4, 6, 8 or 10g of Fe_2O_3 to 100g of mixed powder. In order to extract the pore size distribution of the produced samples they were examined both by scanning electron microscopy and the DDIF (Decay due to Diffusion in the Internal Fields) technique [1]. The magnetic characterization of the produced samples was done using a vibrating sample magnetometer indicating a linear dependence of the susceptibility constant with the iron oxide content. The solvents examined in this study were chosen in order to monitor the influence of the polarity on the surface relaxation process: earlier literature has shown that the polarity, via the average orientation and lifetime of a molecule near the surface, can be of fundamental importance for the relaxation dispersion [3]. The experimental relaxation dispersion curves could be compared with a two phase exchange model taking into account relaxation by interaction with paramagnetic centers on the surface of porous media [4, 5]. This comparison allowed us the conclusion that Fe_2O_3 clusters inside the porous matrix do not contribute to the relaxation in the frequency range of our experiments. It also allows the determination of the transverse diffusional correlation time at the liquid/solid interface. Moreover, a similar behavior in relaxation dispersion curves of water and cyclohexane filled samples could be observed, independently of the fact that water molecules are polar and cyclohexane molecules are nonpolar. On the other hand a longer correlation time was extracted in the case of water molecules as compared with cyclohexane. The results of this study will contribute to the interpretation of the experimental data obtained on natural or fabricated porous media with unknown magnetic properties.

References

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3. S. Stapf, R. Kimmich, J. Chem. Phys. 103 (1995), 2247-2250.
4. J. P. Korb, M. W. Hodges, and R. G. Bryant, Phys. Rev. E 56 (1997), 1934-1945.
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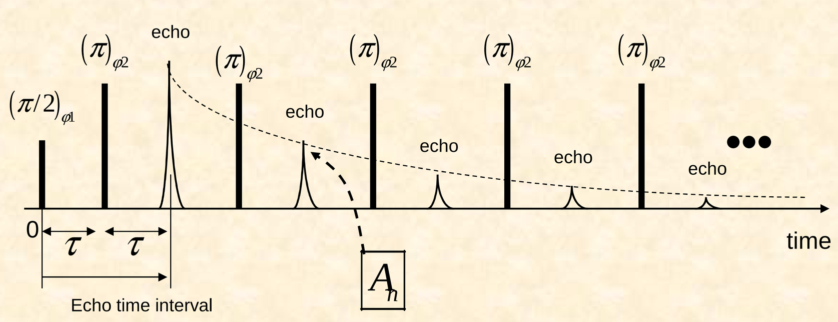
The NMR techniques

•The CPMG technique



The echo train attenuation in heterogeneous samples

$$A_n = A_0 \int_0^\infty P(T_2) e^{-2n\tau \frac{1}{T_2}} dT_2$$

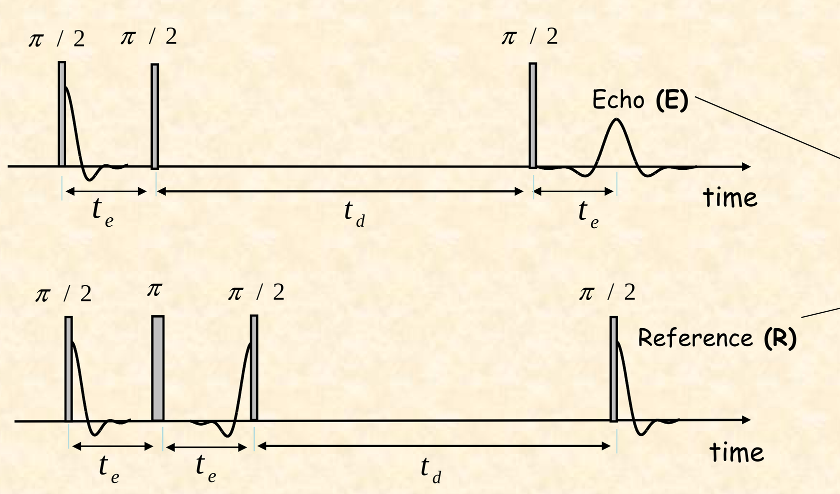
$P(T_2)$ = distribution function of the transverse relaxation time

The relaxation rate neglecting diffusion effects on CPMG echo train

$$\frac{1}{T_2} \approx \frac{1}{T_{2b}} + \rho\frac{S}{V} = \frac{1}{T_{2b}} + \rho\frac{3}{R}$$

$1/T_{2b}$ = bulk relaxation rate
ρ = the relaxivity constant
S/V = surface to volume ratio
R = pore radius

•The DDIF technique



The stimulated echo (E) intensity in a homogeneous sample

$$E(t_d) = \underbrace{a_0 e^{-t_d/\tau_0} e^{-t_d/T_{1b}}}_{\text{relaxation mode}} + \underbrace{\sum_{n=1}^{\infty} a_n e^{-t_d/\tau_n} e^{-t_d/T_{1b}}}_{\text{diffusion modes}}$$

$\tau_0 = \frac{d}{\rho}$ -for the slit pore model; T_{1b} = the bulk relaxtion time;

$\tau_n \approx \frac{d^2}{D\pi^2 n^2}$, $n = 1,2,3,\ldots$

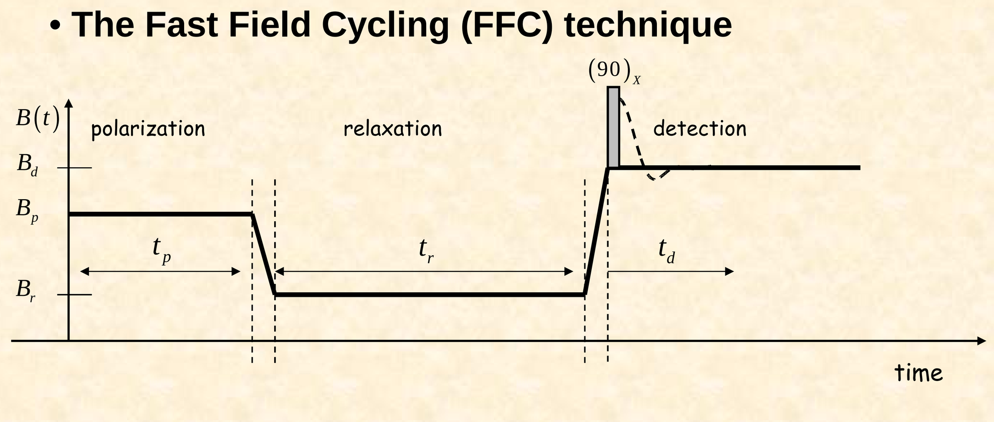
d = the pore size; ρ = the relaxivity; D = the diffusion coefficient;

$\gamma \Delta B_z^i t_e << 1$ -the limit of weak phase encoding

$$\Rightarrow E(t_d) \approx \underbrace{a_0 e^{-t_d/\tau_0} e^{-t_d/T_{1b}}}_{\text{relaxation mode}} + \underbrace{a_1 e^{-\frac{t_d}{\tau_1}} e^{-t_d/T_{1b}}}_{\text{diffusion mode}}$$

$\Rightarrow$ The pore size distribution can be obtained from the DDIF spectra = Inverse Laplace transform of $E(t_d)$ $\Rightarrow$ $d = \pi\sqrt{D\tau_1}$

• The Fast Field Cycling (FFC) technique

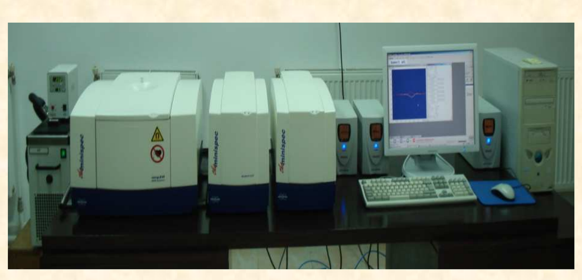


Signal attenuation versus relaxation interval

$A(t) = C_0 + A_0 e^{-t/T_1}$ - low relaxation fields

$A(t) = C_0 - A_0 e^{-t/T_1}$ - high relaxation fields

The NMR instruments



Bruker MINISPEC MQ20

-[1]H frequency: 20MHz
-max. gradient strength: 2T/m
-temp. range: -10÷100 °C

STELAR-Fast Field Cycling Relaxometer

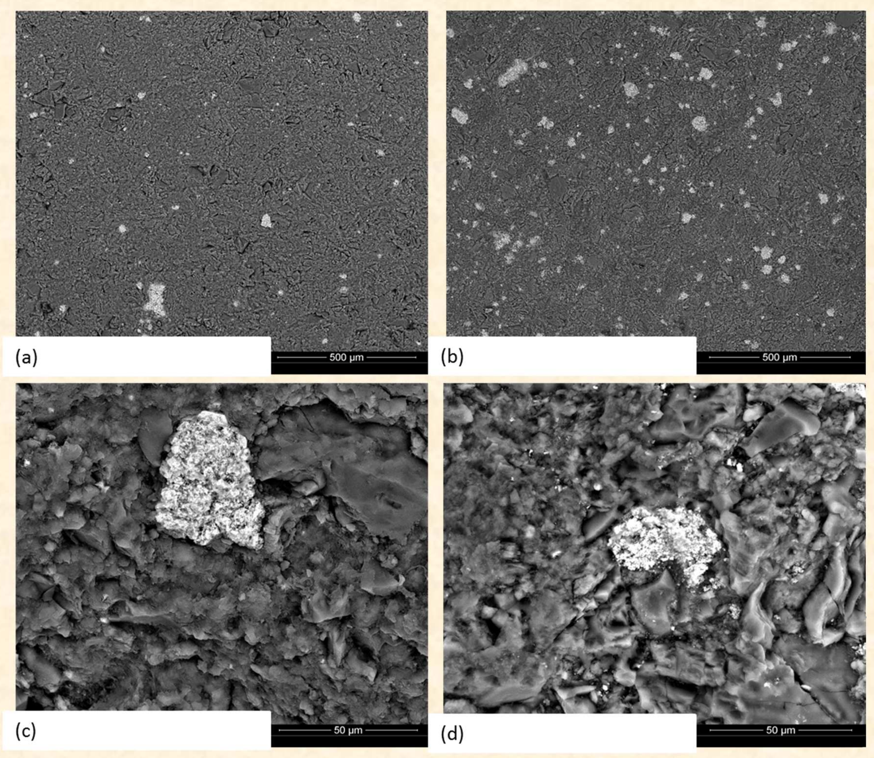
-[1]H frequency: 40- 0,01 MHz
-temp. range: -140÷140°C

The pore size distribution of porous ceramics with magnetic impurities

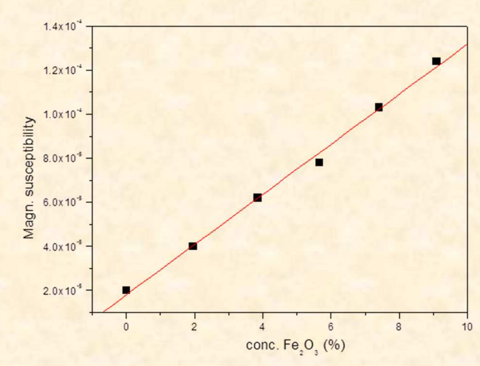
The samples

Six samples of porous ceramics with increased concentration of Fe_2O_3 were prepared by adding 0, 2, 4, 6, 8 or 10g of Fe_2O_3 to 100g of mixed powder. The samples are denoted S0, S2, S4, S6 S8 and S10 respectively. They reveal a linear increase of the susceptibility constant with the iron oxide content. The samples were examined by SEM. The white spots represent the Fe_2O_3 clusters. One can notice the higher concentration of magnetic impurities (white spots) in the case of sample S8 as compared with sample S2. The results were compared with those extracted from the DDIF experiment and CPMG relaxation time distribution revealing pore sizes in the range of 13µm.

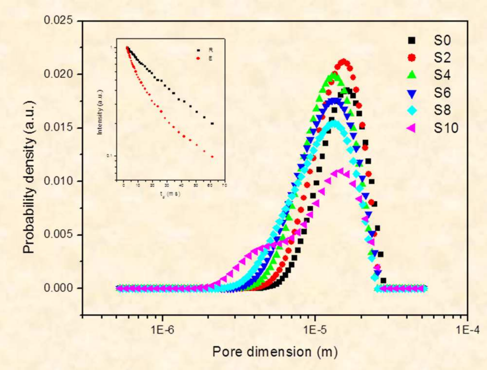
The SEM image of sample S2 (a,c) and S8 (b,d)



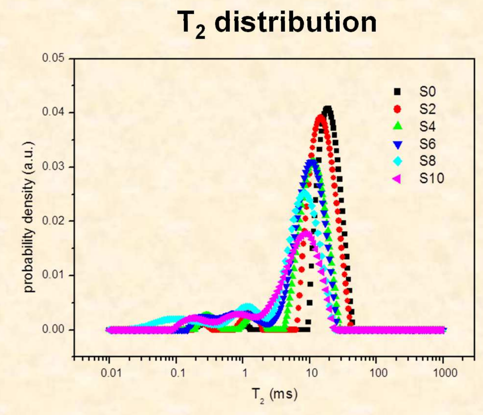
The magnetic susceptibility



The DDIF results

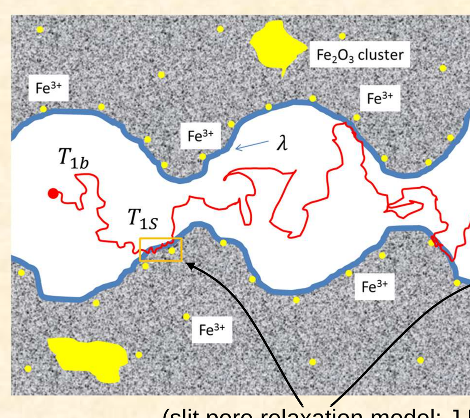


T_2 distribution



The relaxation dispersion curves

The two-phase fast exchange relaxation model



(slit pore relaxation model: J.P.Korb et al. PRE1997)

$$\frac{1}{T_1} = \frac{1}{T_{1b}} + \frac{\lambda S}{V}\frac{1}{T_1^{surf}} = \frac{1}{T_{1b}} + \frac{S}{V}\rho_{1S}$$

$\rho_{1S} = \lambda / T_1^{surf}$ - surface relaxivity

$$\frac{1}{T_1^{surf}} = \frac{\pi}{15}\sigma_S(\gamma_I\gamma_S\hbar)^2 S(S+1)\frac{\tau_\perp}{(2\lambda)^2\delta'^2}\left\{10\ln\left(\frac{2\lambda}{\delta'}+1\right) - 30.8 + \frac{1}{4}\left[7\ln\left(1+\omega_S^2\tau_\perp^2\right) + 3\ln\left(1+\omega_I^2\tau_\perp^2\right)\right]\right\}$$

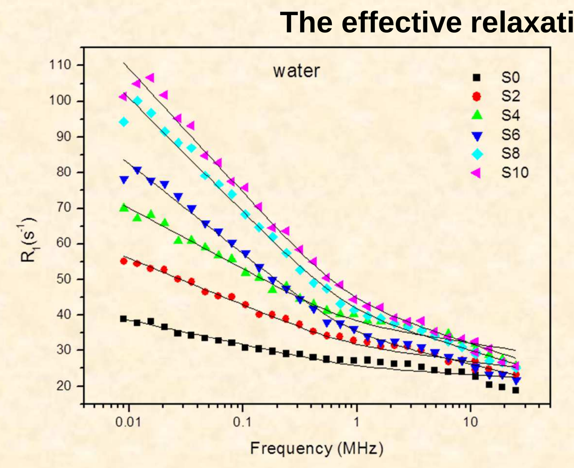
The effective relaxation rate

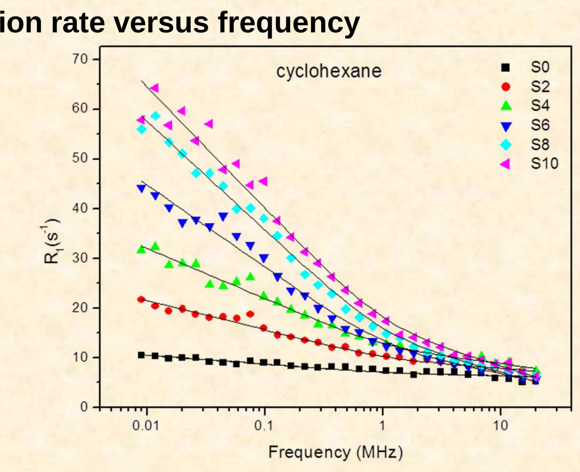
$$\frac{1}{T_1} = P_1 + P_2 \cdot \left[7\ln\left(1+\omega_S^{-2}\tau_\perp^{-2}\right) + 3\ln\left(1+\omega_I^{-2}\tau_\perp^{-2}\right)\right]$$

σ_S - surface density of paramagnetic centers
$\tau_\perp = \delta^2/4D_\perp$ - transverse diffusional correlation time
$D_\perp$ - transverse diffusion coefficient; δ - the molecules size;
δ' - the distance of minimum approach between I and S spins;
$\omega_S = 658.21\,\omega_I$

Experimental results and the comparison with the theory

The effective relaxation rate versus frequency





Note: in the fitting approach the transverse diffusional correlation times were kept constant

$\tau_\perp^{water} = 0.32\,\text{ns}$

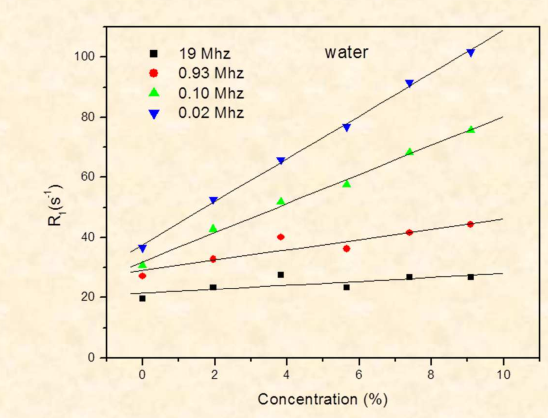
$\tau_\perp^{cyclo} = 0.24\,\text{ns}$

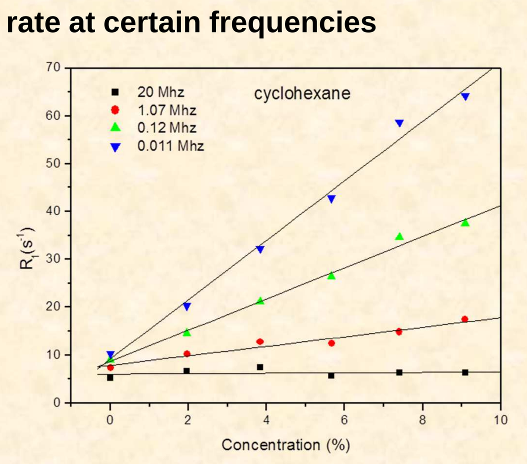
$\Downarrow$

$D_\perp^{water} = 0.7 \cdot 10^{-10}\ \text{m}^2/s$

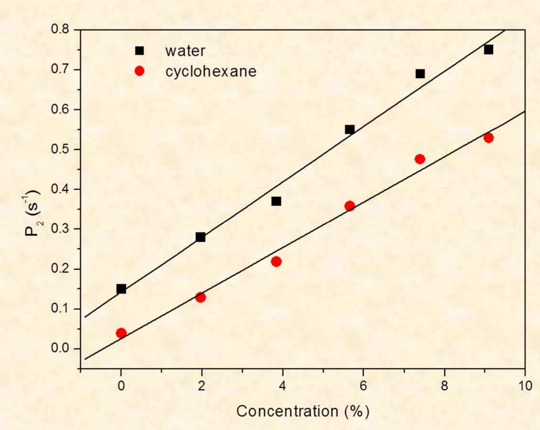
$D_\perp^{cyclo} = 3.7 \cdot 10^{-10}\ \text{m}^2/s$

The effective relaxation rate at certain frequencies





P2 versus Fe_2O_3 content



Conclusions

- A linear growth of the relaxation rate with the increase in iron oxide (III) concentration in the preparation approach was observed;
- The relaxation dispersion curves can be fitted well with a two phase exchange model taking into account relaxation by interaction with paramagnetic centers on the surface;
- A similar behavior in relaxation dispersion curves of water and cyclohexane filled samples can be observed, independently of the polar character;
- Fe_2O_3 clusters inside the porous matrix do not contribute to the relaxation in the frequency range of our experiments;
- The presence of paramagnetic centers does not influence the transverse diffusional correlation times.

Acknowledgements

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