

Scientific report

on the implementation of the project **PN-II-IDEI 305/2011**

during the stage January-December 2015

The theme of the project:

The surface effect on the dynamics of molecules confined inside porous media with magnetic impurities

The objective of the stage 2015:

Study of the molecule-surface interaction effects on the rotational dynamics of molecules confined inside porous ceramics with magnetic impurities

The associated activities:

A1. Measurement of the relaxation rate of polar and nonpolar molecules confined inside porous ceramics as a function of temperature and frequency;

A2. Investigation of the relaxation dynamics in the vicinity of phase transition and the identification of the liquid and solid component;

The **objective of the 2015 stage** was to study the effects of molecule-surface interaction on the rotational dynamics of molecules confined inside model porous media containing magnetic impurities in a controlled manner. This study was completed both by the conventional NMR relaxometry technique also known as CPMG and by less known technique called fast field cyclic (FFC) NMR relaxometry. In the following the main activities performed to achieve this objective will be schematically depicted and the main results will be discussed. These two techniques allow measurements of the relaxation rates directly related to the rotational molecular dynamics. In the following the main results and activities during the stage 2015 will be shortly described.

A1. Measurement of the relaxation rate of polar and nonpolar molecules confined inside porous ceramics as a function of temperature and frequency;

The nuclear relaxation rate (inverse of the relaxation time) of molecules confined inside porous media provides information on molecule mobility, pore surface properties and magnetic impurities located on the surface of porous media [1,2]. In the previous stages of the present project we have demonstrated that the effective relaxation rate of confined molecules it is described by a formula as [2,3]

$$\frac{1}{T_i} = \frac{1}{T_i^{bulk}} + \rho_i \frac{S}{V_0} \frac{1}{f^k} + RD_i(D, g_{int}, f, \tau); \quad i = 1, 2. \quad (1)$$

In the above equation $1/T_i^{bulk}$ represents the longitudinal relaxation rate ($i=1$) or the transverse relaxation rate ($i=2$) under bulk conditions and is a function of temperature and the molecule properties. The coefficient ρ_i represents the surface relaxivity and is a function of the surface nature, the polar character of the confined molecules, the magnetic impurity content and the resonance frequency of the experiment (this can be probed in a FFC experiment). S/V is the surface to volume ratio, f the saturation degree of the pores and k an empiric constant characterizing the molecules distribution on the pore surface [4].

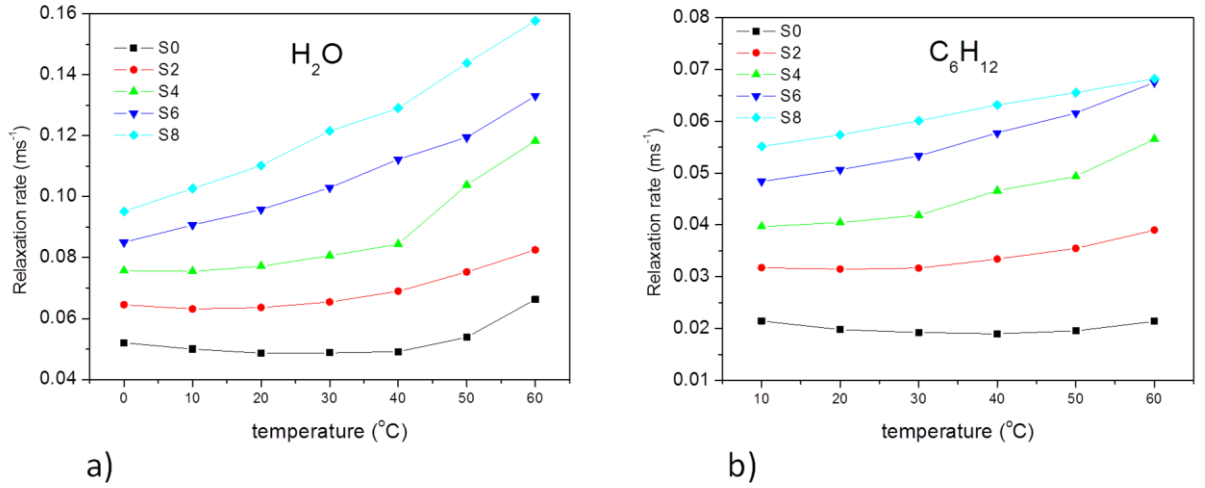


Fig.1. The transverse relaxation rates versus temperature in the case of porous ceramics S0-S8 saturated with water (a) or cyclohexane (b).

The RD_i term in the above in Eq. (1) takes into account the contribution of molecular diffusion in internal gradients effects on CPMG echo train attenuation. It is zero for the longitudinal relaxation rate ($i=1$) and different of zero in the case of transverse rate ($i=2$). In a CPMG-NMR, experiment for the determination of transverse relaxation time (or rate) which is mostly used in connection with porous media the term R_i is given as [3]:

$$R_i = \frac{1}{3} D \gamma^2 g_{int}^2 \tau^2 \left[1 - 1.42 \frac{S}{V} \sqrt{D\tau} \right] \quad \text{for } (i = 2). \quad (2)$$

D bulk diffusion coefficient of molecules (temperature dependent), g_{int} the effective value of the internal gradient (a function of pore dimension, magnetic impurity content and the main magnetic field B_0) and 2τ the echo time.

To understand how the temperature and the polarity influences the molecule interaction with the surface of porous ceramics with magnetic impurities which contain hydroxyl groups on the surface we performed both transverse relaxation measurements and longitudinal relaxation measurements. The investigated porous ceramic were produced and described in the previous stages of the present project and the corresponding publications [2,3,5]. These were denoted with S0, S2, S4, S6 and S8

respectively indicating the content of extra Fe_2O_3 introduced in the solid matrix of 0, 2, 4, 6 and 8% respectively. The investigated porous ceramics revealed pores with an averaged pore size of $13\mu\text{m}$ as determined via RMN techniques developed during the project. The same dimensions were confirmed by the recorded SEM images. The investigated molecules were both polar (water, ethanol) and nonpolar (cyclohexane, hexane). They were chosen on purpose to investigate the role of OH groups on the pores surface on the molecular dynamics.

To quantify the diffusion effects on transverse relaxation measurements using the CPMG technique, preliminary tests were performed using different echo times (0.08 ms, 0.1 ms, 0.2 ms). It was established that the echo time of $0.08\ \mu\text{s}$ provides reliable measurements when diffusion effects can be neglected.

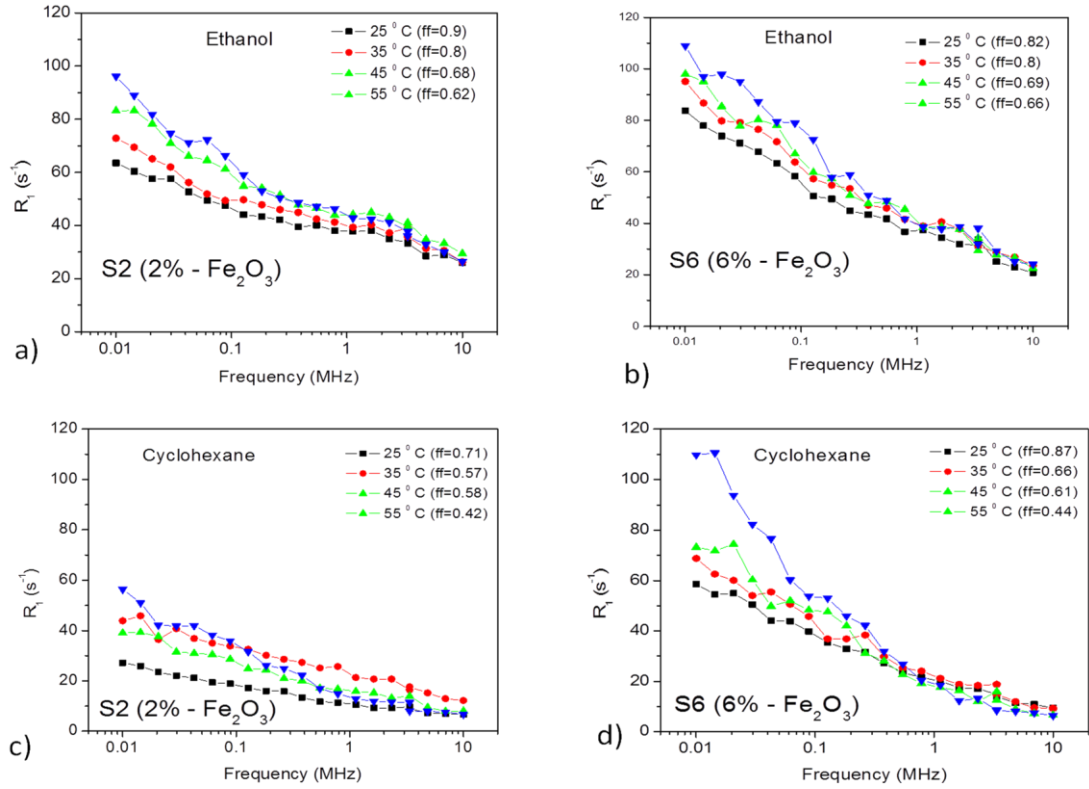


Fig.2. Frequency dependence of the relaxation rate of ethanol (polar) and cyclohexane (nonpolar) molecules confined inside porous ceramics S2 (a,c) and S6 (b,d). A similar dependence was recorded for the other samples (S0, S4, S8).

The relaxation rates extracted from these measurements in the case of samples S0-S8 are indicated in Figure.1 in the case of samples saturated with water (polar) and cyclohexane (nonpolar). One can observe an increase of the relaxation rates with temperature both in the case of water (polar) and cyclohexane (nonpolar) molecules. This increase cannot be attributed to the increase in the rotational correlation time τ_{CR} because it should follow an Arrhenius type law [6],

$$\tau_{CR} = \tau_{C0} e^{\frac{E_a}{K_B T}} \quad (3)$$

i.e., decreases with the rising of temperature. In Eq. (3) τ_{C0} is a constant depending on molecular geometry, E_a the activation energy of the rotational motion, K_B is Boltzmann's constant and T the

absolute temperature. We conclude that the increase of the relaxation rate with the temperature must have different cause related to the magnetic impurity content on the surface of porous ceramics. This conclusion is supported by the fact that an enhanced dependence on temperature was observed in the case of porous ceramics with higher magnetic impurity content.

An increase with the temperature was also observed in the case of longitudinal relaxation rates recorded as a function of the resonance frequency, as shown in Fig.2. The investigation approach relied on the Fast Field Cycling (FFC) technique [7] performed with recently acquired Stelar SmarTracer FFC instrument. The dispersion curves have indicated a frequency dependence of the relaxation rates in the frequency interval 10kHz-10MHz both in the case of ethanol (a, b) and cyclohexane (c, d) molecules. This frequency dependence proves the dominant character of the relaxation mechanism of molecules confined inside porous ceramics with magnetic impurities: modulation of dipolar inter-molecular interactions [8].

Fitting of the data in Fig.2 with a formula that accounts for the paramagnetic relaxation centers on the surface [8] indicates a small dependence of the transverse diffusional correlation time with the temperature in the interval 0.75ns to 0.82 ns. This increase, even if predicted according Eq. (3), is not high enough to explain the increase of the observed relaxation rates. It is rather the partial saturation effect that dominates the increase of the relaxation rate, according with Eq. (1). To support this conclusion, relaxation measurements were performed at different saturation degrees and constant temperature (25 °C). These measurements confirmed the dependence observed in Fig. 2.

A2. Investigation of the relaxation dynamics in the vicinity of phase transition and the identification of the liquid and solid component

It is well known that for liquids confined inside nanometer sized pores a shift of the freezing point to smaller values arises. This shift satisfies the Gibbs-Thomson formula [9]

$$\Delta T = \frac{K}{d} \quad (4)$$

where K is a constant depending on the liquid nature and d is the pore size. In the case of our test liquids the constant K has a value of 104 nm/K in the case of cyclohexane and 42 nm/K in the case of water [9]. That is why in our NMR cryoporometry studies we prefer to use the cyclohexane as test molecules. Note however that, due to the relatively small value of the K constant, the displacement of the freezing point in the case of molecules confined in the micrometer sized pores can be neglected. That is why the shift effect is not visible in our experiments on samples S2-S8. It should be however visible in the case of cement based materials, the ultimate goal of our investigations to be done in the last stage of the project. In spite of the discussion above, the investigations on samples S0-S8 are still important because they allow us calibrating of the technique and setting up of the experimental parameters.

During the 2015 stage of the present project we performed temperature dependent experiments above and below the freezing temperature of cyclohexane (6.47°C). The samples under investigation were the porous ceramics S0-S8. They were filled with cyclohexane and then progressively cooled. The CPMG echo trains were recorded at different temperatures allowing us extraction of the relaxation time distributions, as shown in Fig. 3 for the samples S2 (2% Fe_2O_3) and S6 (6% Fe_2O_3). One can observe below the freezing temperature (6.47°C) the presence of a peak at 4.5 ms corresponding to the plastic cyclohexane.

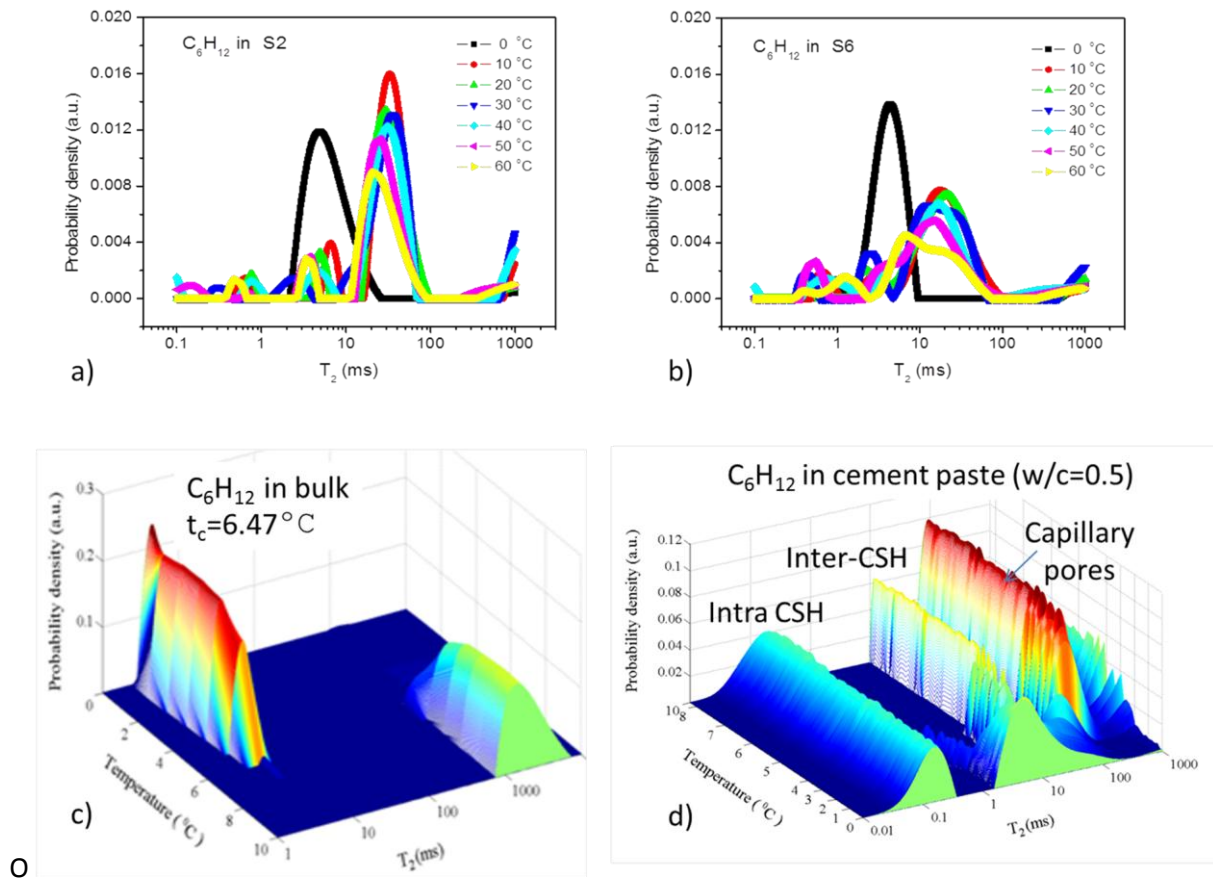


Fig.3 Relaxation time distributions of cyclohexane molecules confined inside sample S2 (a) and S6 (b) versus temperature. One can observe the presence of a plastic phase below the solidification temperature ($t_c=6.47^{\circ}\text{C}$). c) The transition from the liquid phase to the plastic phase in the case of pure cyclohexane. d) Relaxation time distribution versus temperature in the case of cyclohexane confined inside cement paste ($w/c=0.5$)

The position of this peak is similar with that obtained under the bulk conditions (Fig.3c) and is independent on the magnetic impurity content (compare Fig.3a and b). It is however observed a small shift of the peak maximum to higher values by rising the temperature. This dependence is opposite with that observed in the case of liquid component of cyclohexane under confinement conditions. It is also observed a dependence of the peak maximum corresponding to the liquid component by increasing the magnetic impurity content in accordance with the theory [8] and our the previous observations.

The fact that the relaxation time of the plastic component of cyclohexane is not influenced by the magnetic impurity content is important in NMR cryoporometric applications on cement paste. It is

the goal of the next stage of our research project to undergo such investigations by using cyclohexane as test substance. It is worth noting that only water was used up to now in the literature [10] but with the disadvantage of smaller K coefficients and consequently smaller sensibility [9]. Figure 3d shows a first example of such cryoporometric application on cement paste prepared with a water-to-cement (w/c) ratio of 0.5. One can clearly observe the different types of pores (Intra CSH, inter CSH and capillary pores) [11] and the cyclohexane evolution inside these pores with the temperature.

Conclusions

In the reporting period were studied the effects of the surface-molecule interaction on the dynamics of rotation of molecules confined inside porous ceramics containing controlled amounts of magnetic impurities. The aim of these investigations was to identify a behavior pattern for the molecules in porous media with controlled amount of magnetic impurities that can be compared to the results of natural porous media having similar pore sizes and surfaces with similar properties. Our studies were based both on conventional relaxometry techniques as CPMG and the Fast Field Cycling technique, allowing the observation of the nuclear spin at different frequencies. The main advantages of FFC technique in comparison with the classical relaxometry at a unique frequency are its sensitivity to a broader spectrum of molecular motions and that is not influenced by internal diffusion gradients. The FFC drawback compared with CPMG technique at a certain frequency is the lower signal/noise ratio and consequently the longer duration of the experiments (up to 20 hours in the case of our samples).

The investigations have revealed an increased relaxation rate by increasing the temperature despite of the drop in the rotational correlation time. This increase can be attributed to partial desaturation of samples at high temperatures and thus to an increased role of the surface of interchange contributing to the relaxation phenomena. The experiments performed around liquid-solid phase transition allowed us the identification of the plastic component of cyclohexane with a very small dependence on temperature and no dependence on magnetic impurity. This observation will be very useful in the final stage of the project when cement based materials naturally contained magnetic impurities will be studied.

Our findings were disseminated through the publication of two ISI articles, one article as ISI proceedings or have been presented at international conferences as indicated in the list of publications.

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