Scientific Report

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

during the stage January-December 2014

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 2014:

Study of the molecule-surface interaction effects on the rotational dynamics of molecules confined inside model porous media without magnetic impurities

The associated activities:

A1. Measurement of the nuclear relaxation rates of polar and nonpolar molecules confined inside porous VitraPor as a function of temperature and frequency and the development of a theoretical model to describe the experimental data.

A2. Investigating the possibility of using dipolar correlation effect on the stimulated echo as a tool for extracting the correlation times at the porous media interface

A3. Determination of the relative role of intra and inter-molecular interactions in the nuclear relaxation by using deuterated molecules.

The **objective of the 2014 stage** was to study the effects of molecule-surface interaction on the rotational dynamics of molecules confined inside model porous media without containing magnetic impurities. This study was completed by conventional NMR relaxometry techniques (CPMG, Hahn echo) and by less known techniques such as the fast field cyclic (FFC) NMR relaxometry or via the dipolar correlation effect on the stimulated echo. In the following the main activities performed to achieve this objective will be schematically depicted and the main results will be discussed.

A1. Measurement of the nuclear relaxation rate of polar and nonpolar molecules confined inside porous VitraPor as a function of temperature and frequency and developing of a theoretical model to describe the experimental data

The nuclear relaxation rate (inverse relaxation time) of molecules confined in porous media provides information about their mobility and the nature of the pores wall [1]. In the previous stage of our project we showed that the effective transverse relaxation rate of molecules confined in porous
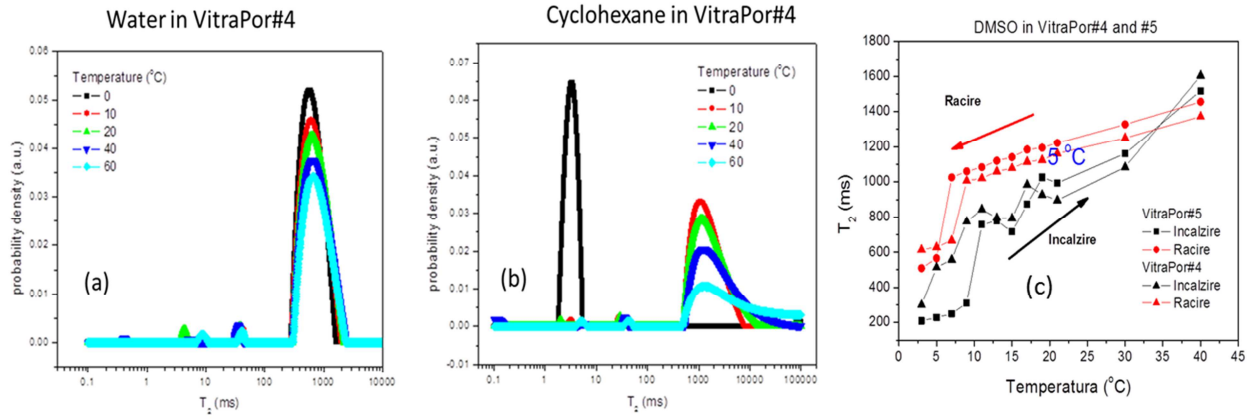
Fig.1. The relaxation time distribution of water (a) and cyclohexane (b) molecules in VitraPor#4 as a function of temperature. (c) The relaxation time of DMSO molecules confined inside two porous media as a function of temperature.

media measured via the CPMG NMR technique is described by a relation of the form [2]

$$\frac{1}{T_2} = \frac{1}{T_2^{bulk}} + \rho \frac{S}{V} + \frac{1}{3} D \gamma^2 g^2 \tau^2 \left[1 - 1.42 \frac{S}{V} \sqrt{D\tau} \right]. \tag{1}$$

In the above equation $1/T_2^{bulk}$ is the bulk relaxation rate (depending on temperature), ρ the surface relaxivity (depends on the nature of the surface, nature of the confined molecules, temperature and frequency), D the self-diffusion coefficient of molecules (depends on temperature and molecules), g the effective value of the internal gradient (depends on pores dimension, magnetic impurity content, applied magnetic field), S/V the surface to volume ratio of the pores 2τ the echo time. In the case that two phases coexist in a porous medium (liquid and solid) they will be reflected in the distribution of relaxation rates that can be extracted from the numerical Laplace transform of the CPMG echo series of decreasing amplitude. Such distributions are typically shown in Figure 1 in the case of confined water in VitraPor#4 (1 µm pore diameter) at different temperatures as indicated in the figure.

A key issue that arises when studying a multiphase system is generated by the difference in susceptibility between its phases which finally translates through an internal gradient [3] and according to equation (1) produces an influence of the effective relaxation time measured. Therefore our investigations were always preceded by test measurements to highlight the role of internal gradients and set the intervals which will provide reliable results. In the case of the solid component of our system, the third term in equation (1) is not important but it becomes significant for the liquid phase (liquid layer which is unfrozen). The presence of the liquid layer on the surface of frozen samples is clearly demonstrated in the case of CYCLOHEXANE (apolar molecules with the melting point of the 6.47 ^{o}C) by the presence of the peak in the relaxation time distribution at a position of about 3 ms as illustrated in Figure 1b. This peak was not observed on confined water (Figure 1a) because the water inside the pores is still unfrozen at 0 ^{o}C. Similar distributions of relaxation times were seen on the sample filled with dimethyl sulfoxide (DMSO) which is composed of polar molecules as well and has a melting point of 19 ^{O}C.

To understand the mechanism of nuclear relaxation of molecules confined and to check if we can really assign the peak at 3 ms to the unfrozen layer we performed longitudinal relaxation time
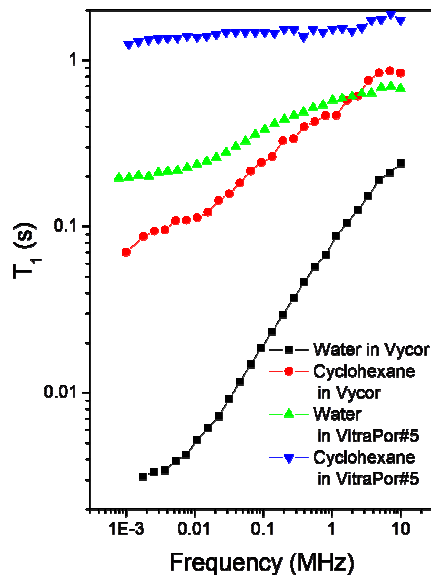
Fig.2. Frequency dependence of the relaxation times of water and cyclohexane molecules confined inside porous media Vycor and Vitrapor#5

measurements as a function of frequency on water and cyclohexane molecules confined inside the following porous media: VitraPor # 5 (1 μm pore size), VitraPor # 4 (pore size 10 μm) and the porous Vycor (4nm pore size). As can be seen from Fig. 2 in the case of VitraPor#5 sample the dispersion is smaller in the case of cyclohexane molecules (nonpolar) as compared with water molecules (polar) and the relaxation times are much longer than in the case of the same molecules confined inside Vycor. Since the pore size of Vycor sample is of the same order of magnitude as the size of the unfrozen layer it outcomes that the confinement plays a dominant role in reducing the nuclear relaxation time. The relaxation time shows a frequency dependence which is influenced by the polar character of molecules and thus confirms the interaction of molecules with the hydroxyl groups on the surface of the pores. The measurements were performed using the Fast Field Cycling NMR relaxometer (SmarTracer, Stellar SRL, Italy) acquired during the project which is unique in Romania.

Observing a shorter relaxation time for the unfrozen liquid layer on the surface of the pores can be justified by the fact that the relaxation is dominated by the re-orientation of molecules on the surface as a result of displacements in the liquid layer. This theoretical model known as RMTD model (reorientations mediated by translational displacements) is well documented in the literature and has been applied in our experiments as well [1, 4]. It is expected that this mechanism is also dominant in samples with magnetic impurities but this issue will be addressed in the next stage of the project. If it turns out to be true then our results will influence all interpretations to date of the nuclear relaxation measurements on cement based materials.

Another important observation of our studies is that the relaxation times measured during the heating process at a temperature lower than the temperature of the critical point are lower than those measured during the cooling process. The hysteresis behavior of the relaxation time (see Figure 1c) was observed only in molecules of DMSO (polar) and is particularly more significant with the smaller pore size. The observations can be explained on the basis of a different distribution of phases within pores during the heating process as compared with the cooling process. The hysteresis behavior is determined by blocking the transfer of the freezing front (cooling) if the pore necks are frozen. These effects were previously reported on porous samples with nanometer-sized pores [5].

A2. Investigating the possibility of using dipolar correlation effect on the stimulated echo as a tool for extracting the correlation times at the porous media interface

In some systems such as polymers or liquid crystals there is a non-averaged part of the dipolar coupling Hamiltonian between the nuclear spins. In this case we are discussing about dipolar correlations. The dipolar correlations effect manifests in a stimulated echo experiment if the system

under study undergoes slow molecular motions characterized by rotational correlation times in the range of milliseconds. These movements are outside the detectability range of any other NMR technique available and only the dipolar correlation effects can be used as a tool to investigate such slow molecular movements [1].

The experimental approach consists in monitoring the evolution of the stimulated echo appearing in the pulse sequence

$$(\pi/2)_x - \tau_1 - (\pi/2)_{-x} - \tau_2 - (\pi/2)_y - \tau_1 - \text{Stimulated echo},$$

as a function of the interval τ_1 and the comparison of the signal with that recorded in the pulse sequence (Hahn echo)

$$(\pi/2)_x - \tau_1 - (\pi/2)_{-x} - \tau_1 - \text{Hahn echo}.$$

The second pulse sequence was chosen in order to eliminate the role of transverse relaxation and to isolate the dipolar correlation contributions. To monitor the role of dipolar correlations on the stimulated echo attenuation it is performed a representation of the ratio between the amplitude of the stimulated echo (STE) and the amplitude of the Hahn echo (HE) versus τ_1 interval (blue squares in Fig.3). From this dependence it is possible in principle to extract the dipolar correlation time τ_C and the average dipolar coupling constant $\langle \Omega_d \rangle$. If a correlation function of an exponential form is considered, then the ratio of the two echo amplitudes is of the form [1]

$$\frac{A_{STE}}{A_{HE}} = \exp\left\{ -\frac{1}{4} \langle \delta\Omega_d^{\,2} \rangle P_1 \right\} \left[1 + \cos\left(\langle \Omega_d \rangle \tau_1 \right) \exp\left\{ -\frac{1}{4} \langle \delta\Omega_d^{\,2} \rangle P_2 \right\} \right] \tag{2}$$

Here the parameters P_1 and P_2 depend only on the correlation time τ_C and the evolution intervals τ_1 and τ_2 respectively. The fluctuating part of the dipolar coupling constant is represented by $\delta\Omega_d$ where $\langle \cdots \rangle$ denotes the ensemble average.
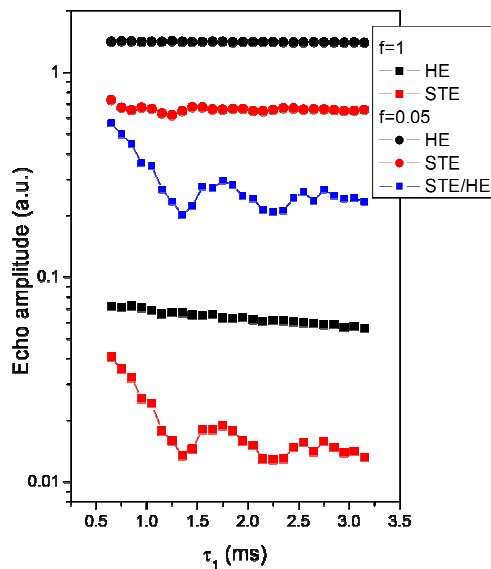

Fig. 3. The dipolar correlations effect on the stimulated echo decay versus the evolution interval τ_1.

To investigate the role of the surface to maintain a residual dipolar coupling of molecules we have performed experiments on water and cyclohexane confined inside the porous VitraPor # 5. The evolution of the Hahn echo and the stimulated echo was monitored for different saturation degrees between 100% (f = 1) and 5% (f = 0.05), i.e. until the detectability limit of the NMR instrument was reached. It was observed that for lower degrees of saturation (f <0.10) there are oscillations in the ratio of the two amplitudes (STE/HE) as is shown in Figure 3 (blue curve). On the other hand, in the sample saturated with liquid (represented by the circles in Fig. 3) the role of these correlations can be neglected. By comparing the experimental data with equation (2) could be extracted the correlation time of molecular motion on the surface and the residual dipolar coupling constant. No dipolar correlations effect was observed for samples filled with cyclohexane (nonpolar molecules) due to a weaker interaction with the surface hydroxyl groups. These observations are

consistent with those made on frozen samples showing the role of surface-induced ordering of the molecules confined.

A3. Determination of the relative role of intra and inter molecular interactions in the nuclear relaxation using deuterated molecules

As mentioned above, the nuclear relaxation is an important source of information on molecular dynamics. Nuclear relaxation phenomena are determined by the modulation of the dipolar interaction of the nuclear spins. This modulation of the dipolar interaction may be achieved by the relative rotation of the nuclear spins of the same molecule (intra-molecular mechanisms) or by the relative displacement of the spin of a tagged molecule with respect to the spin of another molecule (inter-molecular mechanism) or paramagnetic center. Under normal conditions the relative displacement
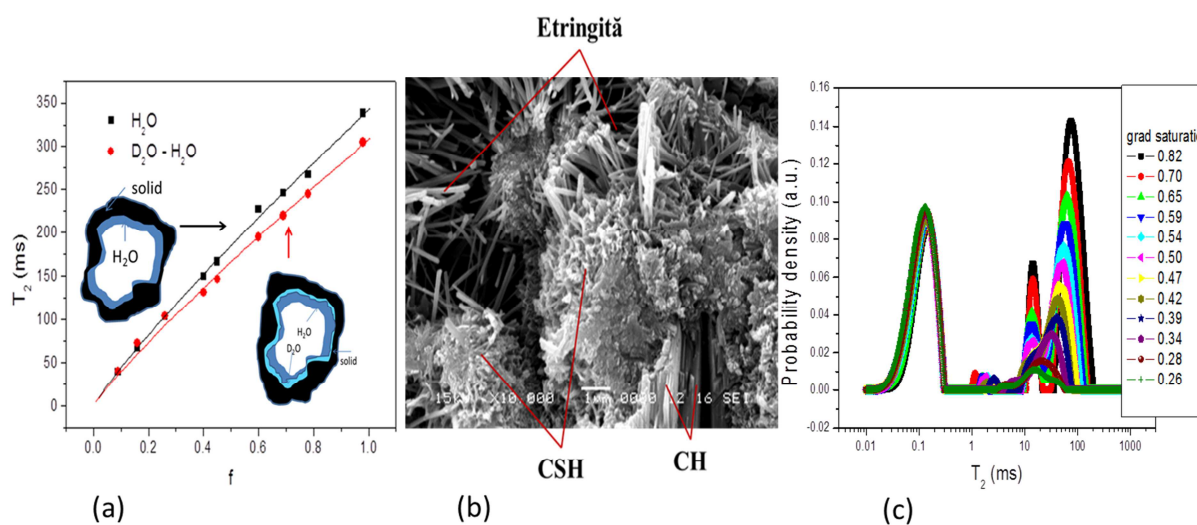
Fig.4. a) The dependence of the transverse relaxation time of H_2O molecules as a function of the filling factor in the case of a VitraPor#5 sample saturated with water (squares) as compared with the case where the sample is first immersed in D_2O and then filled with water (circles). b) The SEM image of a sample of cement paste after 28 days of hydration. c) The relaxation time of cyclohexane molecules at different degrees of saturation in a deuterated cement paste.

can be neglected and the dominant relaxation mechanism is represented by the nuclear dipolar intra-molecular interactions (here we neglect the quadrupolar interactions). However, in physical systems containing paramagnetic impurities (ex. iron oxide III) the interaction of the electronic spin with the nuclear spin cannot be neglected anymore and the relaxation phenomena occurring here are dominated by paramagnetic centers. These phenomena have been already investigated in the previous stages of the present project. During the year 2014 we attempted to separate these two types of interactions using deuterated water. In addition, there were prepared several kinds of model samples that contain a negligible amount of magnetic impurities, thus enabling us to neglect their contributions.

To highlight the role of hydroxyl groups in influencing the molecular order and thus the nuclear relaxation mechanism (RMTD) the samples were prepared first by placing them in deuterated water which was adsorbed on the surface of the porous medium such as VitraPor # 5 and thus prevented in a certain degree the adsorption of water molecules introduced later. Analysis of the experimental

data (see Fig. 4a for an example) showed a decrease in the relaxation time for the case where the hydroxyl groups on the surface are first occupied with deuterated water. This dependence can be attributed to the rapid molecular exchange between adsorbed molecules (D_2O) and the pore volume molecules (H_2O) which leads to a canceling of the shielding effect of D_2O molecules. The same effect occurred in the case of cyclohexane molecules which were introduced in the porous sample after it was initially washed with deuterated water and then filled with cyclohexane.

Another porous medium model used in our investigations is the white cement paste (CEM II / A - L 52.5 N) prepared with deuterated water which has a negligible content of magnetic impurities (<0.5%). It is known that the cement paste has a complex porous structure and recent studies have shown that water in cement paste can occupy multiple locations: in capillary pores (1-10 µm), in the inter-pores of CSH (10- 50 nm) and in the intra-pores of CSH (2-4 nm) [6,7]. Between these systems might exist a molecular exchange process which can be however neglected under specific experimental conditions (short evolution times of the experiment). Therefore, the CPMG relaxation curves allow us to clearly identify these types of pores. In Fig. 4b the porous structure of a white cement paste hardened after 28 days of hydration is shown. It is noticed that the micrometric capillary pores have the same order of magnitude in size as in the case of samples VitraPor#4 and #5 used for comparison. In addition to the water components mentioned above may contribute to the NMR signal the solid hydration products that give relaxation times of tens of microseconds and may influence the relaxation rates of confined liquid molecules by the cross relaxation process [6].

To remove the contribution of the solid hydrates [6] to the relaxation rate of molecules confined inside the cement pores the cement paste samples were prepared with deuterated water. Thus, our instrument only detects molecules confined inside the pores, because the NMR experiments are carried out at the proton resonance frequency. By this approach it was possible to clearly identify three types of pores in the cement paste and monitor the evolution of their liquid contents according to the degree of saturation (denoted f). It is noticed that by emptying the sample it is eliminated first the liquid from the capillary pores and the inter-HSC pores and then the intra-lamellar liquid of the CSH pores. This is illustrated in the case of cyclohexane in Fig.4c and was for the first time revealed in our studies. The displacement of the peak corresponding to the cyclohexane in the capillary pores to lower values of the relaxation time is due to a higher influence of the surface with the partial saturation. Another category of investigations was to monitor the longitudinal relaxation rate as a function of the resonance frequency (relaxation dispersion curves) of cyclohexane molecules at different degrees of saturation. The measurements were performed by the FFC technique. It was observed a small dispersion which depends on the degree of saturation. This dispersion can be attributed to the RMTD relaxation process due to the fact that the magnetic impurities in our samples can be neglected.

Conclusions

In the reporting period the effect of molecule-surface interaction on the rotational dynamics of molecules confined inside model porous media without magnetic impurities was investigated. The aim of these investigations was to establish a behavior pattern of molecules which will be then compared with the results obtained porous media with magnetic impurities having similar size and similar properties of the pores surface. Our studies were based both on conventional NMR relaxometry techniques (Hahn echo, CPMG) and the Fast Field Cycling technique that allows observation of the nuclear spins at different frequencies. It was also investigated the possibility of

using dipolar correlation effect on the stimulated echo as a tool to study molecular dynamics at the pores surface. The samples under investigation were the commercial porous glasses VitraPor and Vycor, the cement paste prepared with deuterium and porous ceramics without magnetic impurities prepared in our laboratory. In our studies it was possible to separate different contributions to the relaxation phenomena which will help us in the interpretation of the experimental data on porous samples with magnetic impurities. The investigated molecules were water and cyclohexane as representatives of polar and nonpolar molecules respectively. They were chosen in order to quantify the role of the polarity on the molecular dynamics of molecules in the vicinity of pore surfaces containing hydroxyl.

Our findings were disseminated through publication of two articles in ISI journals or presented at international conferences among which one as invited speaker (see the list of publications below). Partial results obtained during the stage 2014 of the present project were included in the thesis of Pop Alexandra a member in the research team.

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Publications during the stage 2014

ISI classified journals

1. C. Badea, A. Pop, C. Mattea, S. Stapf and I. Ardelean, The Effect of Curing Temperature on Early Hydration of Gray Cement Via Fast Field Cycling-NMR Relaxometry, Appl. Magn. Reson. **45**, 1299-1309 (2014)
2. A. Pop and I. Ardelean, Monitoring the size evolution of capillary pores în cement paste during the early hydration via diffusion în internal gradients, Appl. Magn. Reson. 2014 (în press)

Conference presentations/invited seminars

1. I. Ardelean, Dynamics of molecules confined inside porous media as revealed by low field NMR, University of Debrecen, 10 Mach 2014 (invited speaker)
2. I. Ardelean, C. Badea, A. Pop, Monitoring the temperature effects on early stage cement hydration via low field NMR relaxometry, Ampere NMR School, 22-28 June 2014, Zakopane, Poland (invited speaker)
3. I. Ardelean, A. Pop, C. Badea, The influence of temperature and the superplasticizers on cement hydration via low field NMR relaxometry, Alpine NMR Workshop, 18-21 Sept. 2014, Bled, Slovenia (prezentare orala)
4. A. Pop, C. Badea, I. Ardelean, Influence of different admixtures on the strength of cementitious materials, Alpine NMR Workshop, 18-21 Sept. 2014, Bled, Slovenia (prezentare orala)
5. S. Boboia, M. Moldovan, I. Ardelean, The composition effects on mechanical properties, absorption and amount of residual monomers of dental flowable composites, Alpine NMR Workshop, 18-21 Sept. 2014, Bled, Slovenia (prezentare orala)
6. C. Badea, A. Pop, C. Mattea, S. Stapf, I. Ardelean, The temperature effects on cement hydration via Fast Field Cycling NMR relaxometry, 12th International Bologna Conference on

Magnetic Resonance în Porous Media (MRPM12), 9-13 February 2014, Wellington, New Zealand (poster prezentat de Prof. S. Stapf)

PhD thesis finalized during 2014
PhD student: eng. Pop Alexandra Daniela (member of the research team)
Thesis title: H*ydration study of the cement based materials via nuclear magnetic resonance relaxometry*
PhD supervisor: Prof.dr. Ioan Ardelean (project director)

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Prof.dr. Ioan Ardelean