

¹H NMR LOW FIELD RELAXOMETRY OF POROUS SYSTEMS

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Abstract

The ¹H Nuclear Magnetic Resonance Relaxometry has been used for studying properties of various porous materials. T₁ and T₂ relaxation times in such systems are influenced by the molecule confinement and T₁/T₂ ratio can reflect an interaction strength between an adsorbate molecules and an adsorbent surface. In this paper 1D relaxation times distributions and 2D T₁-T₂ maps from NMR measurements at magnetic field of 0.05 T are shown. Two mesoporous silica materials: MCM-41 and SBA-15 are studied at different water saturation states. Signals from hydroxyl groups, water confined in pores and bulk water are distinguished. Higher T₁/T₂ is measured for SBA-15 than for MCM-41 and the increase of T₁/T₂ ratio for the samples with lower amount of water is observed. Relaxation parameters for other porous systems such as exemplary geological samples in different saturation states and for biological samples are also compared.

Keywords: Low field NMR, MCM-41, SBA-15, porous materials, T₁/T₂ ratio

1. INTRODUCTION

The ¹H Nuclear Magnetic Resonance Relaxometry has been applied to characterize various porous materials. Among them mesoporous silica gels, zeolites, cements, biological samples and rock samples can be mentioned [1-6]. The main concept of these measurements is based on the differences in relaxation times for molecules confined in porous spaces in comparison to bulk liquid. Relaxation times for molecules situated close to a pore surface are shorter due to the interactions with a solid surface. In the case of fast diffusion all protons can interact with the surface within the time of the experiment and measured relaxation time depends on the fraction of bulk molecules f_b and those near the surface, f_s as follows:

$$\frac{1}{T_i} = \frac{f_b}{T_{i,b}} + \frac{f_s}{T_{i,s}},$$

where T_{i,b} and T_{i,s} are spin-lattice (T₁) or spin-spin (T₂) relaxation times of these two fractions.

The aim of this work was to characterize pure silica mesoporous materials, MCM-41 and SBA-15, at low magnetic field and using short echo time for wider range of saturation states than in earlier report [2]. T₁/T₂ ratio of log-mean values from 1D distributions for the samples with different water content are compared. 2D T₁-T₂ maps for chosen saturation states are shown. Additionally values of T₁/T₂ ratio from different water environments at exemplary geological and biological samples are discussed.

2. MATERIALS AND METHODS

Pure mesoporous silica materials, MCM-41 and SBA-15, were obtained from Sigma Aldrich and ACS Material, respectively. 0.9902 mg of MCM-41 and 1.0003 mg of SBA were weighted with the analytical balance (Radwag) with the accuracy of ± 0.1 mg. Mean diameters specified by the manufacturers ranged from 2.1 to 2.7 for MCM-41 and 7 - 10 nm for SBA-15. The samples were put into glass containers and filled with 6.97 and 8.86 g of demineralized water, respectively, they were dried in vacuum conditions at 80 °C for at least 0.5 h at several repetitive steps. The amount of water in the samples was monitored after each step of drying. Hence, filling factor $f = V_{H_2O}/(V_{intra}+V_{inter})$ was calculated, equal to the amount of the water in the sample to the total pores volume. Total pores volume was treated as a sum of volume of mesopores within silica particles (V_{intra})

and porous spaces between particles (V_{inter}). Additionally, ratio of water volume to total mesopores volume ($f_{meso}=V_{H2O}/V_{intra}$) was also estimated.

Shale sample was measured at dried (200 °C) and saturated state. Drying and saturation process was obtained in vacuum conditions for 12 h.

For preparing yeast cells sample fresh baker's yeasts were obtained commercially (Lallemand). 1.4 g of fresh yeasts was suspended in 14.1 g of demineralized water to obtain yeasts:water mass ratio of 1:10 and the sample was measured in a glass container.

NMR measurements were conducted on a Magritek Rock Core Analyzer at a magnetic field of 0.05 T and echo time of 60 μ s. T_1 Inversion Recovery (IR) and T_2 Carr-Purcell-Meiboom-Gill (CPMG) sequences were used. To obtain 1D T_1 and T_2 distributions Lawson&Hanson algorithm was applied. 2D T_1 - T_2 experiments were also registered for chosen steps and calculated using FISTA algorithm [8].

2.1. MCM-41 and SBA-15

On **Figure 1** 1D distributions for MCM-41 and SBA-15 are presented for different content of water: from overfilled ($f > 1$) to partially saturated systems ($f < 1$). T_1 and T_2 log-mean values are listed in **Table 1**. For the both samples the calculated log-mean values are shorter when the water content decreases. For overfilled samples signal from free water is also detected (except for step 1 in case of SBA-15, for which free water is distinguished on T_2 but not on T_1 distribution).

Table 1 Relaxation times and water content for MCM-41 and SBA-15

Step	Results for MCM-41				Results for SBA-15			
	m_{H2O} [g]	$V_{H2O}/(V_{intra}+V_{inter})$	T_1 log-mean [ms]	T_2 log-mean [ms]	m_{H2O} [g]	$V_{H2O}/(V_{intra}+V_{inter})$	T_1 log-mean [ms]	T_2 log-mean [ms]
1	6.97	1.73	160.3*	46.40*	8.86	1.41	2724.97	73.94*
2	5.59	1.39	161.2*	43.87*	5.76	0.92	2570.79	62.33
3	4.99	1.24	143.6*	41.70*	3.22	0.51	1857.96	32.60
4	3.89	0.97	128.2	28.97	2.64	0.42	1686.56	26.16
5	2.68	0.67	83.67	15.93	1.57	0.25	1310.34	15.28
6	1.77	0.44	61.56	10.30	0.71	0.11	689.22	6.85
7	1.06	0.26	35.93	5.55	0.55	0.088	663.24	6.19**
8	0.91	0.23	31.38	4.87	0.39	0.062	500.34	5.08**
9	0.81	0.20	25.58	3.90	0.19	0.030	333.13**	3.25**
10	0.65	0.16	24.74	3.52	0.08	0.013	204.908**	2.42**
11	0.510	0.13	21.35	3.12	0.014	0.0022	155.22**	2.21**
12	0.330	0.082	15.76	2.50**	0.007	0.0011	155.22**	1.70**
13	0.170	0.042	10.35**	1.43**				
14	0.052	0.013	3.18**	0.82**				

* - the signal from free water was not included into calculations;

** - T_1 and T_2 for the peak from water adsorbed on the pore surface (peak from OH groups, with $T_1 \sim 20$ -30 ms and $T_2 \sim 0.05$ ms) were not taken into account.

For the MCM-41 sample three first measurements are conducted on the overfilled system, for which free water is measured. Signal with relaxation times shorter than 1 s is related with the water confined in intra- and

extraparticle spaces. For T_2 distribution these 2 peaks are registered while for T_1 signal at 33.7 ms (for $f=1.73$) is also detected. In [2] origin of this peak was discussed as a signal from water adsorbed on the surfaces of mesoporous silica particles. Step 8 for $f_{\text{meso}}=0.94$ corresponds to the mesoporous silica with the mesopores almost completely filled with water and empty extraparticle spaces. For this measurement T_1 and T_2 log-mean values for mesoporous spaces are equal to 31.4 and 4.9 ms. For comparison, the interpolated T_1 of 25.6 and T_2 of 5.8 ms were reported in [2]. Estimation based on N_2 adsorption reported for the MCM-41 sample in our earlier study led to the conclusion that for f_{meso} close to 0.286 only one monolayer of water remains on mesopores, with the assumption that water evaporates radially from the center towards the pores walls [2]. Step 12 for MCM-41 may be therefore treated as the system with dominating surface water at T_1 of 13.7 and T_2 of 2.9 ms. Values of T_1 and T_2 for surface water, corresponding to the $f_{\text{meso}}=0.286$ were equal to 9 and 1.3 ms, respectively.

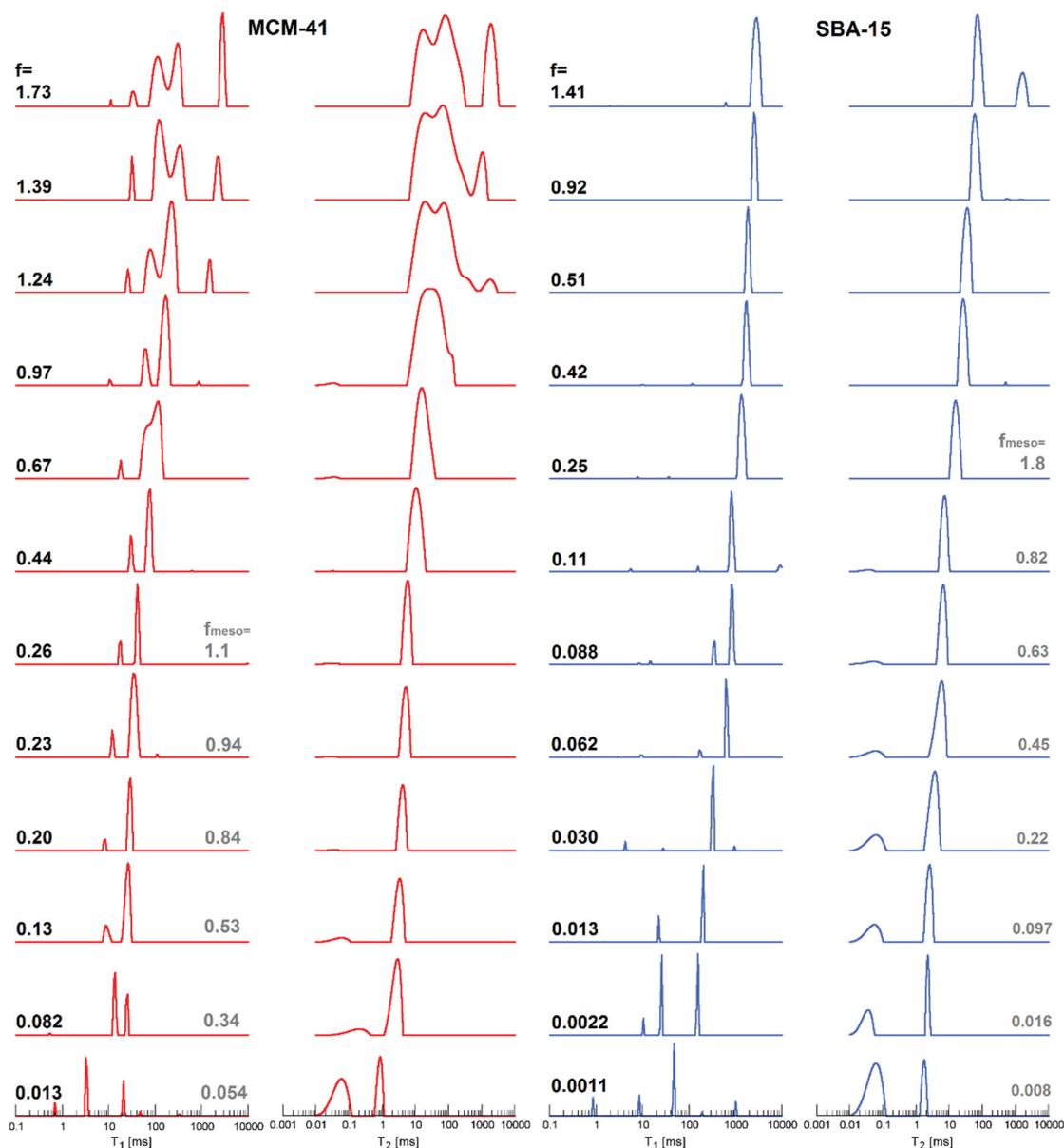


Figure 1 T_1 and T_2 relaxation times distributions for MCM-41 and SBA-15. Values of filling factors $f=V_{\text{H}_2\text{O}}/(V_{\text{intra}}+V_{\text{inter}})$ and $f_{\text{meso}}=V_{\text{H}_2\text{O}}/V_{\text{intra}}$ are shown. For f_{meso} close to 1 water fills only mesopores within particles, for f_{meso} close to 0.286 for MCM-41 and 0.184 for SBA water adsorbed on pores surface remains

For the SBA-15 sample free water is distinguished only on T_2 distribution for the first measurement with $f=1.41$. On T_1 distribution only one peak is observed. In comparison to MCM-41 for measurements 1 - 6 only one narrow peak from porous spaces is observed. Step 6 for $f_{\text{meso}}=0.82$ is the closest to the system with filled mesopores and empty extraparticle spaces with log-mean values: T_1 of 689.2 ms and T_2 of 6.9 ms. Interpolated T_1 and T_2 for SBA-15 in [2] were equal to 678.3 and 8.6 ms. For step 9 surface water dominates with a maximum at T_1 of 333 ms and T_2 of 3.65 ms. For $f_{\text{meso}}=0.184$ one monolayer of water remains. Relaxation times for surface water, corresponding to this filling factor were interpolated from the last four measurements and was equal to 296 and 3.0 ms for T_1 and T_2 , respectively.

For the both samples the measurements with the residual amount of water signal allow to register a signal from hydroxyl groups with maximum of T_2 shorter or equal to 0.1 and T_1 in the range of 20-30 ms.

On **Figure 2** T_1 , T_2 and T_1/T_2 for log-mean values are presented. At each saturation state longer relaxation times and higher T_1/T_2 values are measured for the SBA-15 sample. Comparing these relations for the relaxation times, the difference is more pronounced for T_1 .

The parameter T_1/T_2 was proposed to be a direct and insensitive to pore geometry indicator of an adsorbate-adsorbent interaction strength. D'Agostino et al correlated it with the maximum energy of desorption for several oxide samples [4]. In ref. 3 and 7 it was used to distinguish a signal from different proton populations. Hence, higher T_1/T_2 values for SBA-15 indicates stronger interaction between water molecules and pores surface than for MCM-41. This observation was also confirmed in the earlier reports from NMR relaxometry [2] and spectroscopy studies [7]. For the both samples T_1/T_2 increases as the content of water decreases. For SBA-15 sample at low water saturation states a decrease of T_1/T_2 value is observed, however for this low amount of water higher uncertainty of T_1 and T_2 calculation using ILT algorithm can not be excluded.

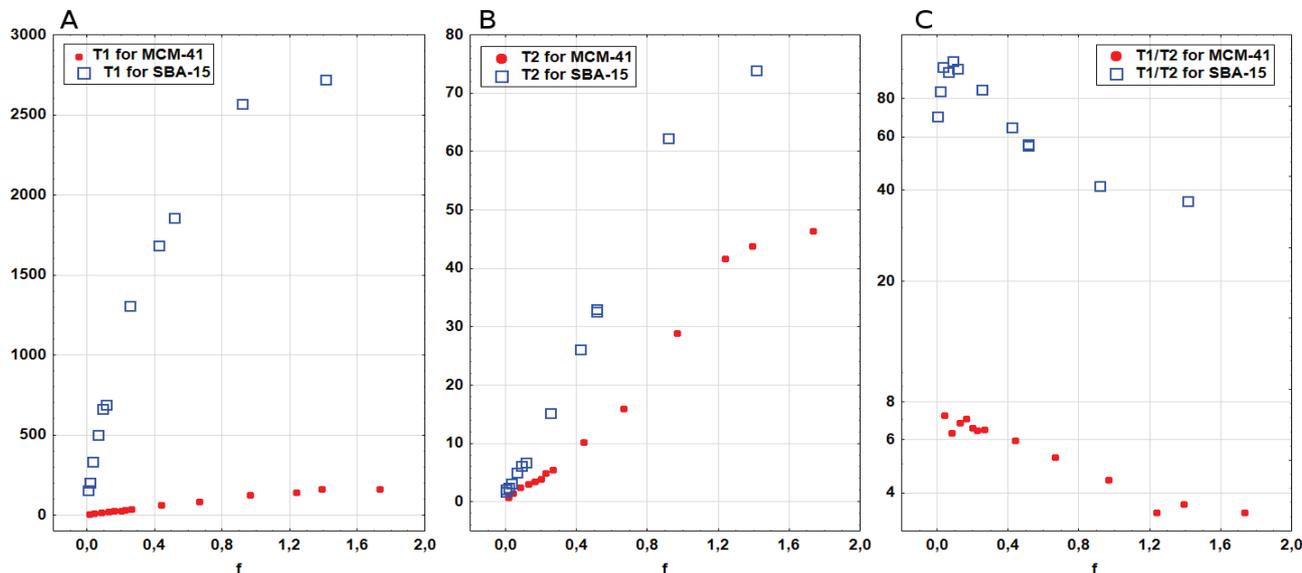


Figure 2 T_1 , T_2 and T_1/T_2 log-mean values for the MCM-41 and SBA-15 samples with different water content

2.2. T_1/T_2 ratio for exemplary geological samples

On **Figure 3A** and B T_1 - T_2 map for dried and saturated state for shale sample is presented. For saturated sample peaks with T_1/T_2 close to 1 and T_2 of 13.6 and 111 ms represents bimodal pores distribution, while signal with shorter T_2 of 0.4 ms and slightly higher $T_1/T_2 \sim 1.8$ more restricted water fraction. For dried sample this signal is characterized by higher T_1/T_2 ratio equal to 10.4. For this sample signal from water adsorbed on the pore surfaces is also affected by the hydroxyl groups, which is visible as the peak elongation towards longer T_1 relaxation times [3,6].

2.3. T_1/T_2 ratio for yeast cell samples

On T_1 - T_2 map for yeast cells sample (**Figure 3C**) two peaks are measured: dominating signal with T_2 at 720 ms and $T_1/T_2 \sim 1.1$ and lower signal with T_2 of 40 ms and T_1/T_2 close to 4.5. This two peaks correspond to different water environments within the yeast sample. As for other porous systems the signal from the free water is located near $T_1/T_2 \sim 1$, while the signal from the restricted water has higher T_1/T_2 values. In the case of cell samples signal of confined water originates from intercellular spaces.

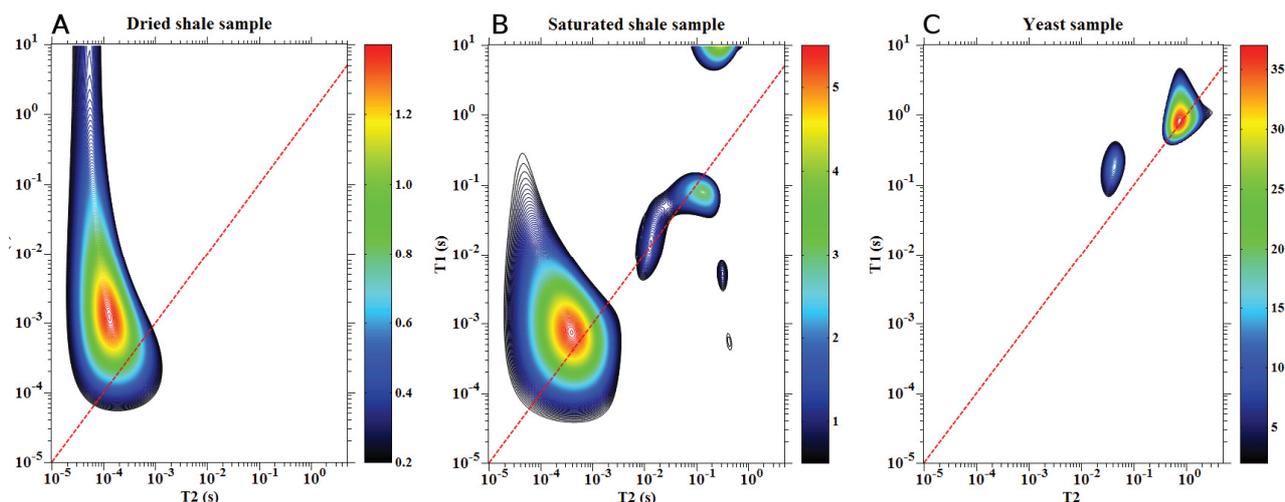


Figure 3 T_1 - T_2 maps for A) dried and B) saturated shale sample, C) yeast cells sample

3. CONCLUSION

In the presented studies pure mesoporous silica materials, MCM-41 and SBA-15, were characterized from overfilled to partially saturated states. Changes of T_1 and T_2 distributions are shown and particular peaks are interpreted as originating from different fractions: free water, restricted water in pore spaces and surface water. Signal from hydroxyl groups is also measured for the sample with the residual amount of water.

Higher T_1/T_2 of log-mean values are registered for SBA-15 than for MCM-41 and generally the increase of T_1/T_2 ratio for the samples with lower amount of water is observed. T_1/T_2 ratio for other porous systems such as exemplary geological samples in different saturation states and for biological sample are also compared. For these samples signal from bulk water is characterized by $T_1/T_2 \sim 1$, while for the water in restriction higher values are registered.

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